ABSTRACT

LIN, HAISHENG. Multifunctional Heterometallic–Oxide and –Oxyfluoride Hybrid Solids. (Under the direction of Prof. Paul A. Maggard.)

Heterometallic-oxide and oxyfluoride/organics are hybrids containing both organic ligands and inorganic metal-oxide/oxyfluoride components. These interesting types of materials are beginning to receive widespread attention because of their potential to express, within the same material, both the robustness and physical properties of inorganic components in conjunction with the versatility and chemical flexibility of organic ligands. My research efforts within this area have focused on the synthesis and design of new heterometallic hybrids which possess varied novel structures, and new investigations of their optical and photocatalytic properties.

Metal oxide systems were selected that contain an early transition-metal (i.e. V, Nb, Mo, W, Re) with a d⁰ electron configuration and a late transition-metal (i.e. Ag, Cu) with a d¹⁰ electron configuration. Organic ligands used in the reactions were chosen to possess different charges and sizes, and that would preferentially coordinate to the late transition metals that form part of the metal-oxide. The target of my work has been to investigate the hydrothermal syntheses of novel heterometallic hybrids and to explore the use of organic ligands in modifying and controlling the formation of resultant structures of metal oxides. The first section covers a new series of Ag/Cu-containing heterometallic-oxides/organics, with 0-1D, 2D layer, 3D pillar-layered or multi-fold interpenetrating structures through molecular-level interactions, and that have led to new insights regarding the
range of optical bandgap absorption in compounds with $d^0/d^{10}$ transition metals. The latter aspect is analyzed with regard to its use in designing future photocatalytic materials. The syntheses, properties, and potential applications of these new materials are presented and analyzed herein, and especially, for the first known series of photocatalytically active silver-vanadate hybrids evaluated. The second section is focused on the synthesis and probing of the structures of new heterometallic-oxyfluoride/organics containing symmetric and/or asymmetric early transition metal (V, Nb, Mo, W) oxyfluorides anions. Their optical properties were studied as a function of small molecule absorptions. An understanding of the structure-properties relationships is used for further design and synthesis new visible-light photocatalytic materials.
Multifunctional Heterometallic–Oxide and –Oxyfluoride Hybrid Solids

by
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Chair of Advisory Committee
DEDICATION

This work is dedicated to my parents and my wife, Yan Zou. Thank you for your love, support and encouragement.
BIOGRAPHY

The author was born in Putian, Fujian, China in 1981. In July 1999, he graduated from Putian HuaQiao Middle School and then attended University of Science & Technology of China (USTC) in Hefei. In the summer 2002, he joined the National Lab of Physical Sciences in Microscale and worked with Professor Yi Xie. His research was focused on the syntheses of Cu and CuS nanomaterials by using polymer framework templates and micro-emulsion. After five years studying in USTC, he received his bachelor degree in chemistry in 2004 and then was admitted to Department of Chemistry in North Carolina State University for the graduate study. Since the spring of 2005, he joined the Dr. Paul A. Maggard research group and has worked on multifunctional heterometallic hybrid materials for potential uses as visible-light photocatalysts.
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The graduate experience I found at NCSU has been one of the most positive experiences of my life. While Raleigh is a beautiful place to live, it is the community of people which makes this place so special. Thank you all for becoming part of my life.

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CHAPTER 1
INTRODUCTION

Overview

Oxides form the essential components of many different technological materials, owing to the large variety of possible compositions and structures and which couple to an even wider range of chemical and physical properties.\textsuperscript{1-3} For instance, their electronic properties range vastly from metallic (e.g., RuO\textsubscript{2}, ReO\textsubscript{3}, LaNiO\textsubscript{3})\textsuperscript{4,5} to insulating behavior (e.g. BaTiO\textsubscript{3}),\textsuperscript{6} and in addition, can show a sensitive dependence to changes of temperature, pressure, or composition (e.g. V\textsubscript{2}O\textsubscript{3}, La\textsubscript{1-x}Sr\textsubscript{x}VO\textsubscript{3})\textsuperscript{4,7}. A prime example is high temperature superconductivity, such as in YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-x},\textsuperscript{8} which is the basis of applications involving high-field magnets or in power transmission and has attracted worldwide interest in related transition-metal oxides. Metal oxides are also the primary components of many naturally-occurring minerals and zeolites, as well as man-made porous materials, and these have been utilized in chemical processes such as ion exchange, gas absorption and separation, and catalytic reactions. For example, the selective oxidation of propene to acrylonitrile by Bi\textsubscript{2}Mo\textsubscript{2}O\textsubscript{9}, or anion exchange by Mg\textsubscript{6}Al\textsubscript{2}(OH)\textsubscript{16}CO\textsubscript{3}4H\textsubscript{2}O\textsuperscript{9,10}. Of relevance herein, is the recent and significant growth in research on photocatalytic metal-oxides such as TiO\textsubscript{2},\textsuperscript{11} NaTaO\textsubscript{3},\textsuperscript{12} ZnO,\textsuperscript{13} and Fe\textsubscript{2}O\textsubscript{3},\textsuperscript{14} which function by using absorbed light to drive oxidation and reduction reactions at their surface. Examples include the production of hydrogen from water or the purification wastewater streams. \textit{However, despite the major impacts of metal}
oxides in many different technologies and research areas, their syntheses are often limited by the lack of any chemical control over their structures and bonding, and hence, the resultant physical properties.\textsuperscript{15-19}

Metal-oxide/organic compounds are hybrid materials containing both organic ligands and inorganic metal-oxide components and have received increasing interest for reaching a potentially finer molecular-level structural control as well as their potential new multifunctional types of materials.\textsuperscript{15} A variety of new hybrid structures can be manifested from the simple ‘building blocks’ of a metal-oxide, owing to the versatility and chemical flexibility of organic ligands that can attach to them. This synthetic approach of using metal-oxide ‘building blocks’ has helped to probe the underlying theories describing their structure-property relationships, and as well, enables a rational synthetic approach to target specific new structures. Recent examples include numerous types of metal-oxide/organic vanadates, molybdates, and phosphates, which exist in a variety forms that make them potentially useful in many different fields, such as in catalysis, gas absorption, electrical conductivity, magnetism and optical absorption.\textsuperscript{20} Some specific examples from the Maggard group include the previously reported microporous Cu\textsubscript{2}pz\textsubscript{c}\textsubscript{2}(H\textsubscript{2}O)ReO\textsubscript{4} (pz=pyrazine-2-carboxylate),\textsuperscript{16} the reduced vanadates M(pyz)V\textsubscript{4}O\textsubscript{10} (M=Co, Ni, Zn) (pyz=pyrazine)\textsuperscript{17} with low-dimensional conductivity and the formation of spin gap, and the pillared M(pzc)\textsubscript{2}(H\textsubscript{2}O)AgReO\textsubscript{4} (M = Cu, Ni, Co)\textsuperscript{18} series with access to open metal sites. In these examples, the organic ligands function in a variety of roles in the formation of the structures. These roles can typically be: 1) charge-compensating cations, 2) coordination to the heterometal sites to serve as linking bridges between metal-oxide clusters or layers, and 3)
effecting the local coordination environment of the metal ions. Thus, metal-oxide/organic hybrids provide an excellent gateway to understanding the properties of metal-oxide via the molecular-level interactions of their structures with organic ligands.

The most common strategy that is reported for the synthetic discovery of new hybrid materials is the selection of specific organic ligands and metal-oxoanions for use as structure-directing components, and that result in the formation of new structures and multifunctional properties. However, the synthesis of heterometallic oxides/organics with the desired framework architectures and resultant functionalities remains a challenging obstacle because of the chemical flexibility of organic ligands and the great variety of ways for ‘building blocks’ to assemble from solutions. Even with the identification of the ‘building blocks’ there still exists a substantial challenge in predicting their structures and properties within most chemical systems.

As hybrids containing rhenium and the late transition metals Ag$^+$ and Cu$^+$ did not previously exist, the initial research efforts in the Maggard group was conducted in order to develop the structural principles of their formation. For example, for the Ag$^+/\text{ReO}_4^-/L$ system, it was found that ‘AgReO$_4$’ layers could easily be obtained under hydrothermal conditions and coordinated to linear bridging metal-coordinated ligands to generate pillared structures, as in $M(\text{pz}c)_2(\text{H}_2\text{O})\text{AgReO}_4$ ($M = \text{Co, Ni}$) and $\text{Cu}(\text{pz}c)_2\text{AgReO}_4$,$^{18}$ where the water could be removed in the former at low temperatures to generate coordinatively-unsaturated metal sites. In the former, significantly tilted metal-organic pillars have resulted in the first known example of chirality in pillared solids. Thus, a series of new related compounds emerged that reflect not only the presence of a specific inorganic ‘building block’ in solution, but also a
growing ability to control the expression of the structures of new hybrids using the length, geometry, and coordination preferences of the organic ligand.

Thus, my research efforts involve the hydrothermal synthesis and investigation of new heterometallic-oxides/organics, and focus on attaining a deeper understanding of the interactions between each oxide/organic component in order to discover ways to design and control their formation as well as for targeting specific physical properties. Limited synthetic advances in preparing new modifications of a structure lead to severe restrictions in being able to modify, and therefore study, its properties in any way. One particular property that receives special attention herein is visible-light absorption and its use in driven photocatalytic reactions. The underlying idea is to better enable the study of the photocatalytic activity of metal-oxides by a new molecular-level structural control by using the versatility and chemical flexibility of organic ligands. However, this lofty goal first requires the development of a better understanding of how to target the formation of different metal-oxide/organic structures. Therefore, in this dissertation work, the study of a series of new types of hybrids, involving d⁰/d₁⁰ transition metals, help lead to a better understanding of how to control their structures and therefore to reach a deeper understanding of their properties, such as optical absorption and photocatalysis. The major efforts of work involve the following three areas:

1) Investigating hydrothermal conditions for the preparation of new heterometallic oxides/organics in the systems: (Cu⁺ or Ag⁺)/ReO₄⁻/L, (Cu⁺ or Ag⁺)/VₓOᵧ/n⁻/L, and their hybrid oxyfluoride analogues.
2) Analyzing the resultant structures for identifying the formation principles, i.e. what should be considered the ‘building blocks’ and under what hydrothermal conditions are they found.

3) New measurements of their optical bandgap sizes and photocatalytic activities, and calculation of their electronic structure, in order to understand and form new structure-property relationships.

The hydrothermal synthetic method, while more well developed for the synthesis of zeolites and related porous materials, has recently been utilized for the synthesis of a wide variety of metal-oxide/organic hybrids as it provides the conditions for which both metal-oxides and organics are reactive and interact without decomposition of the organic species. Further, hydrothermal conditions speed the diffusion processes in solution that result in the growth of high-quality single crystals, which can be characterized X-ray diffraction analysis. Thus, my research into new crystalline metal-oxides/organics has utilized low-temperature hydrothermal reactions in the temperature range of 120–260°C and under autogenous pressure in sealed reaction vessels. These reactions typically contain aqueous solutions of the metal-cations/oxides together with the appropriate ligands, and then exploit the self-assembly processes of soluble ‘building block’ precursors in solution. The equilibria of hydrothermal reactions are known to change with pH, time and temperature, resulting in changes in the expression of, for example, the overall network dimensionality or the formation of different metal-oxide building blocks (i.e. clusters, chains, layers). Thus, adjusting the reaction conditions (as well as geometry and size of ligand) provides a powerful
form of structural control. Though, quantitative predictions of reaction products still generally remain out of reach, the new structures described herein can lead to a new understanding that results in a higher success rate in the rational design of future hybrids.

Experimental Techniques

Hydrothermal reactions. Each reaction was performed by adding a stoichiometric amount of the metal cations and organic ligands into an FEP Teflon pouch. The pouch was heat sealed and placed inside a 125 mL Teflon-lined stainless steel reaction vessel that was backfilled with ~ 42 mL deionized H$_2$O before closing. Then the reaction vessel was put into a Mechanical Convection Oven with a heating program. Heating times and molar ratios are given in each chapter.

Single crystal X-ray crystallographic structure determination. Single crystals of each compound were selected for data collection on a Bruker SMART APEX CCD diffractometer or an Enraf-Nonius CAD4-MACH diffractometer using graphite-monochromatized Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å) at 173-293 K. Single-crystal data sets were collected and analyzed using associated software analysis packages. Some separate packages used for refinement and data manipulation included the SAINT program$^{24}$ used for the data reduction and SHELXL or SIR92 program,$^{25}$ with hydrogen atoms introduced at idealized positions and allowed to ride on parent carbon atoms. Details of the data collection and analysis may be found in the experimental sections of each of the chapter.

Powder X-ray diffraction (PXRD). Ambient PXRD data on the powder samples of new compounds were collected on an Inel XRG 3000 diffractometer (Cu K$\alpha$ radiation, $\lambda = 1.5406$
Å). The powder diffraction pattern was scanned over the angular range $2\theta = 0-106^\circ$ with a step size of 0.02°. The theoretical powder patterns were calculated and output from their cif files using the program MERCURY.²⁶

**Thermogravimetric analyses (TGA).** A weighed sample of each compound was loaded onto Pt pans, equilibrated and tarred at room temperature, and heated at a rate of 1, 5, or 10 °C min⁻¹ to 500-700 °C under flowing nitrogen gas (40 mL/min) on a TA Instruments TGA Q50, and the data plotted as the % starting weight versus temperature (°C).

**Optical absorption.** The UV-Vis diffuse reflectance spectra (DRS) were measured on a Cary 300 spectrophotometer or Shimadzu UV-3600 UV-Vis-NIR spectrophotometer equipped with an integrating sphere. ~50 mg of powder of each sample was mounted onto a fused-silica holder and placed along the external window. Pressed BaSO₄ powder was used as a reference and the data were plotted as the remission function $F(R_\infty) = (1-R_\infty)^2/(2R_\infty)$, where $R_\infty$ is diffuse reflectance based on the Kubelka–Monk theory of diffuse reflectance.²⁷

**X-ray Photoelectron Spectroscopy (XPS).** The XPS spectra of each sample were recorded on a RIBER LAS-3000 spectrometer using Mg KR monochromatized radiation ($h\nu = 1253.6$ eV). The base pressure of the sample chamber was approximately $1 \times 10^{-7}$ Torr. The diameter of the X-ray spot was set at 2-3 mm, and the sample sizes were ~1 cm². The binding energies of the valence band structures were calibrated by setting the O 1s core-level main peaks to 531.2 eV.

**Electronic band structure calculations.** Extended Hückel calculations were carried out within the tight-binding approximation using the CAESAR2 program²⁸ for the full structures at an array of $k$-points spread over the irreducible wedge. The atomic coordinates and lattice
dimensions were taken from the respective single crystal structures. The molecular orbitals were calculated using local structure fragments and analyzed and plotted using the associated SAMOA package and sub-programs.\textsuperscript{29}

**Photocatalytic reactions.** Methylene Blue (MB) was used as a model organic pollutant to evaluate the activities of the hybrid photocatalytic solids. The photocatalytic activity of each sample for the decomposition of MB was measured by suspending a weighed amount (150 mg) of the powdered samples in an aqueous solution of MB (6.0 mg/L, 50 mL) in an \sim 60\ mL cylindrical vessel. This mixture was stirred continuously under ultraviolet ($\lambda < 400$ nm) or visible-light ($\lambda < 400$ nm) irradiation from a 400 W high-pressure Xe arc lamp (focused through a shutter window), which was equipped with a heat filter to remove infrared radiation and with cutoff filters to select for the desired wavelength ranges. The reactions were stopped at 15-20 min intervals to determine the concentrations of aqueous MB solutions by UV−VIS spectroscopy (HP 8453 or Shimadzu UV-3600) at $\lambda = 655$ nm.

**Dissertation Organization**

This dissertation has been organized in the form of papers either formerly published or in a potentially publishable format. The results of Chapters 2-6 have been published with the citation listed at the beginning of each chapter, while Chapters 7-11 fall in the latter category. Also the thesis has been divided into four parts, to better delineate between the different metal-oxide systems. Parts 1 and 2 are focused on the Ag-Re and Cu-Re hybrids respectively, while Part 3 explains the vanadate hybrids and the last part concerns the related metal-oxyfluoride hybrids.
References


Chemistry 1993, 72(2), 183.


PART 1. SILVER(I)-RHENATE(VII) HYBRIDS
CHAPTER 2
SYNTHESIS AND PROPERTIES OF PYRAZINE-PILLARED AgReO$_4$
AND Ag$_3$Mo$_2$O$_4$F$_7$ LAYERED PHASES

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**Abstract**

The new pyrazine-pillared solids, AgReO$_4$(C$_4$H$_4$N$_2$)$_3$ (I) and Ag$_3$Mo$_2$O$_4$F$_7$(C$_4$H$_4$N$_2$)$_3$
(C$_4$H$_4$N$_2$ = pyrazine, pyz) (II), were synthesized by hydrothermal methods at 150 °C and
characterized using single crystal X-ray diffraction (I—P2$_1$/c, No.14, Z = 4, $a = 7.2238(6)$ Å, $b = 7.4940(7)$ Å, $c = 15.451(1)$ Å, $\beta = 92.296(4)^{\circ}$; II—P2$/n$, No.13, Z = 2, $a = 7.6465(9)$ Å, $b = 7.1888(5)$ Å, $c = 19.142(2)$ Å, $\beta = 100.284(8)^{\circ}$), thermogravimetric analysis, UV-Vis
diffuse reflectance, and photoluminescence measurements. Individual Ag(pyz) chains in I
are bonded to three perrhenate ReO$_4$– tetrahedra per layer, while each layer in II contains sets
of three edge-shared Ag(pyz) chains (π – π stacked) that are edge-shared to four Mo$_2$O$_4$F$_7^{3-}$
dimers. A relatively small interlayer spacing results from the short length of the pyrazine
pillars, and which can be removed at just slightly above their preparation temperature, at
>150–175 °C, to produce crystalline AgReO$_4$ for I, and Ag$_3$MoO$_4$ and an unidentified
product for II. Both pillared solids exhibit strong orange-yellow photoemission, at 575 nm for I and 560 nm for II, arising from electronic excitations across (charge transfer) band gaps of 2.91 and 2.76 eV in each, respectively. Their structures and properties are analyzed with respect to parent ‘organic free’ silver perrhenate and molybdate solids which manifest similar photoemissions, as well as to the calculated electronic band structures.

**Introduction**

Synthetic routes to new solids with layered structures is often desired in order to probe the structural or physical property effects of intercalating or deintercalating guest molecules between the interlamellar regions. Envisioned or existing applications include rechargeable batteries, catalysts, separations, ion exchange, and gas absorption, to name a few—for reviews of the intercalation chemistry of layered solids;¹ for a few selected examples of recent research articles.² Pillared layered structures in the mixed metal-oxide/organic systems, for example, are constructed through the use of organic ligands that bridge (or pillar) across the metal sites within separated metal oxide layers, predisposing the structure towards guest intercalation within the gallery or pillared areas. Chemical systems which feature layered pillared structures include many types of phosphonates³, sulfates⁴, and molybdates⁵ as well as heterometallic solids that incorporate additional transition metals for preferentially bonding to the bridging organic ligands.⁵⁷ The late transition-metal cations can be of a wide variety (e.g. Cu²⁺, Ni²⁺, Co²⁺, Fe²⁺) and are incorporated into the layer via coordination to the intralayer anions (PO₄³⁻, MoO₄²⁻, etc.). Thus, a significant diversity of layered pillared solids is possible by using a variety of transition metals and/or pillaring ligands, with some
recent examples including \([\text{Cu}(4,4’\text{-bipyridine})_{0.5}\text{MoO}_3]\) \(1.5\text{H}_2\text{O}\), \([\text{Cu}(\text{tripyridyltriazine})_2\text{-MoO}_4]\), \([\text{Co}_3(\text{pyrazine})(\text{HPO}_4)_2\text{F}_2]\), and \([\text{Cu}(4,4’\text{-dipyridylamine})\text{VO}_3]\). In these examples, the metal-oxide layer and the bridging organic ligand are formally neutral, but the removal of these pillaring molecules at relatively low temperatures has usually not been investigated.

The utilization of Ag-containing oxide layers within the context of organic-pillared solids remains relatively unexplored. Among Ag-containing heterometallic oxides, potential applications include carbon monoxide oxidation (AgCoO\(_2\)/Co\(_3\)O\(_4\), Ag\(_2\)O/\(\gamma\)-Mn\(_2\)O\(_3\) composites, \(\sigma\)-AgFeO\(_2\)), oxidative dehydrogenation of propane (AgMoO\(_4\)PO\(_4\)), as well as other oxidative reactions. Synthesis of pillared heterometallic-organic/oxides containing silver would hold promise for studying catalytic reactions whereby the guest molecules (such as CO) could be incorporated within the micropores. Or alternatively, heterometallic-organic/oxides that are pillared by easily removable ligands could potentially serve as useful precursors to new condensed oxides, with the resultant structure deriving from the condensation of the purely inorganic layers. In our group, prior research efforts on pillared solids have demonstrated that the parent AgReO\(_4\) solid can be pillared by metal-coordinated bridges, e.g. in \(\text{M(pzc)}_2(\text{H}_2\text{O})_2\) (\(\text{M} = \text{Co, Ni}; \text{pzc} = \text{pyrazine-2-carboxylate}\)) to give \(\text{M(pzc)}_2(\text{H}_2\text{O})_2\text{AgReO}_4\) or in \(\text{Cu(pzc)}_2\) to give the chiral \(\text{Cu(pzc)}_2\text{AgReO}_4\). In these examples, the neutral water ligands that are coordinated to the axial sites of the M(pzc)2 pillar can be reversibly removed without the loss of the structure crystallinity to generate coordinatively unsaturated metal sites, while the chelating pyrazine-2-carboxylate ligand is removed at higher temperatures (>300 °C) and can effect changes in the layer composition.
owing to its charge. These three reported structures can be viewed as derived from the AgReO$_4$(pyz) (pyz = pyrazine) structure, reported herein, whereby the pyrazine ligand has been substituted for with metal-coordinated pillars, i.e. M(pzc)$_2$(H$_2$O)$_2$. Thus, the syntheses of pyrazine-pillared structures can be used to help forecast future structures and compositions based on the substitutions of different organic pillars, such as for Ag$_3$Mo$_2$O$_4$F$_7$(pyz)$_3$ described below.

Presented herein is the synthesis, structure and physical properties of two new pyrazine-pillared structures, AgReO$_4$(C$_4$H$_4$N$_2$) (I) and Ag$_3$Mo$_2$O$_4$F$_7$(C$_4$H$_4$N$_2$)$_3$ (C$_4$H$_4$N$_2$ = pyrazine, pyz) (II), which have been characterized for ligand loss during thermogravimetric analysis, and also for their optical properties including photoluminescence and UV-Vis diffuse reflectance. The optical properties are analyzed with respect to the calculated electronic band structure and also to that exhibited by previously reported inorganic counterparts.

**Experimental Procedure and Characterizations**

Caution: Hydrofluoric acid is toxic and corrosive!

*Materials*: Ag$_2$O (99%, Aldrich), MoO$_3$ (99.9995%+, Alfa Aesar), Re$_2$O$_7$ (99.9%+, Alfa Aesar), pyrazine (99+, Aldrich), HCl (aq., 37.4% Fisher) and HF (aq., 49% Aldrich) were used as received. Reagent amounts of deionized water were also used in the synthesis.

*Synthesis*: The synthesis of AgReO$_4$(pyz) (I) was performed by adding 2.09×10$^{-1}$ g (4.32×10$^{-4}$ mol) of Re$_2$O$_7$, 1.00×10$^{-1}$ g (4.32×10$^{-4}$ mol) of Ag$_2$O, 6.91×10$^{-2}$ g (8.63×10$^{-4}$ mol) of pyrazine, and 6.22×10$^{-1}$ g (3.45×10$^{-2}$ mol) of H$_2$O to an FEP Teflon pouch. The pouch was heat sealed and placed inside a 125 mL Teflon-lined stainless steel
reaction vessel that was backfilled with ~42 mL deionized H₂O before closing. The reaction vessel was heated to 150 °C for 24 hours inside a convection oven and slowly cooled to room temperature at 6 °C/h. Colorless bar-shaped crystals were recovered by filtration in ~85% yield based on silver. Large (mm-sized) octahedral AgReO₄ crystals also formed as a side product. Hydrothermal reactions at lower temperatures (e.g. 120 °C) did not result in higher yield or purity of the product. However, AgReO₄(pyz) could be synthesized in high purity from a hydrothermal reaction of AgReO₄ and pyrazine at 150 °C for 24 h, resulting in only large transparent crystals of I. The crystals were extracted manually from the latter for subsequent physical property measurements.

The synthesis of Ag₃Mo₂O₇F₇(pyz)₃ (II) was performed analogous to the procedures above, by reacting 2.41×10⁻¹ g (1.67×10⁻³ mol) of MoO₃, 5.82×10⁻¹ g (2.51×10⁻³ mol) of Ag₂O, 6.71×10⁻² g (8.38×10⁻⁴ mol) of pyrazine, 5.94×10⁻¹ g (1.68×10⁻² mol) of 49% aqueous HF and 1.56×10⁻² g (6.28×10⁻⁴ mol) of concentrated HCl in an FEP teflon pouch that was placed inside a 125 mL Teflon-lined stainless steel reaction vessel and 1/3 backfilled with deionized H₂O. HCl is necessary to grow high-purity crystals, although the chloride ion itself does not go into the structure. The reaction vessel was heated to 150 °C for 24 hours inside a convection oven and slowly cooled to room temperature at 6 °C/h. Yellow needle-and tubular-shaped crystals were recovered by filtration in ~75% yield based on silver.

Crystallographic structure determination: Several bar-shaped and transparent crystals of AgReO₄(pyz) were examined under an optical microscope equipped with cross polarizers, and were mounted for data collection on a Bruker CCD diffractometer operating at 110 K. The unit cell obtained was monoclinic with \( a = 7.2238(6) \, \text{Å}, b = 7.4940(7) \, \text{Å}, c = 15.451(1) \)
Å, and $\beta = 92.296(4)^\circ$. One-half sphere of reflections $(\pm h, k, l)$ was collected and processed with SAINTPLUS$^{17}$ to $2\theta = 72.85^\circ$ to give 47921 reflections, of which 3825 were unique and observed $(F > 1\sigma_F)$. The structure was solved and refined using SHELXTL$^{18}$ in the monoclinic space group $P2_1/c$ (No.14) and checked for additional symmetry elements using the program PLATON$^{19}$. Hydrogen atoms on the pyrazine molecules were refined in idealized positions at a C–H distance of 0.96 Å. Final anisotropic structure refinement converged at $R_1/wR_2 = 0.039/0.050$ ($R_{ave} = 0.033$), with a data : variable ratio of ~35:1. The highest residual electron density peak was 1.47 e Å$^{-3}$.

Yellow-colored needle crystals of $\text{Ag}_3\text{Mo}_2\text{O}_4\text{F}_7(\text{pyz})_3$ were characterized according to similar procedures as outlined above, with the procedure modifications described below. A single crystal was selected and fixed on a glass fiber using epoxy and centered on an Enraf-Nonius CAD4-MACH diffractometer operating at 148 K. The unit cell was determined by a fit of 25 well-centered reflections in the range of $34^\circ < 2\theta < 36^\circ$, and was measured to be monoclinic with $a = 7.6465(9)$ Å, $b = 7.1888(5)$ Å, $c = 19.142(2)$ Å, and $\beta = 100.284(8)^\circ$. Two octants of data were collected $(\pm h, + k, + l)$ twice (i.e. a redundant data set), to give a total of 3630 reflections of which 1777 were unique and observed $(F > 1\sigma_F)$. Three standard reflections were measured every 80 min of X-ray exposure time to monitor and correct for crystal decomposition. Data reduction utilized routines from the NRCVAX suite of programs,$^{20}$ and the structure was solved using SIR92$^{21}$ in the monoclinic space group $P2/n$ (No. 13). Final anisotropic structure refinement converged at $R_1/wR_2 = 0.025/0.037$ ($R_{ave} = 0.040$) with a data : variable ratio of ~11:1. The highest residual electron density peak was
1.16 e Å$^{-3}$ (and −1.30 eÅ$^{-3}$).

Some data collection and refinement parameters for both solids, as well as selected atomic coordinates and isotropic-equivalent displacement parameters are listed in Tables 2.1–2.3. Interatomic contacts for selected bonds in both solids are given in Table 2.4. Included in the supporting information is a complete list of data collection, refinement and anisotropic displacement parameters and all near neighbor interatomic distances.

**Optical property measurements:** ~50 mg of powder of each sample was mounted onto a fused-silica holder and placed along the external window of an integrating sphere inside a Cary 300 spectrophotometer to measure the UV-Vis diffuse reflectance spectra (DRS). Pressed polytetrafluoroethylene powder was used as a reference and the data were plotted as the remission function $F(R_\infty) = (1 - R_\infty)^2/(2R_\infty)$, where $R$ is diffuse reflectance based on the Kubelka–Monk theory of diffuse reflectance. Emission and excitation spectra were measured with an ISS PC-1 fluorometer equipped with a Xenon arc lamp using front face detection geometry to orient the sample face at an angle of 22.51 with respect to the incident beam. A low band-pass UG-11 filter was placed after the excitation monochromator. Excitation spectra were corrected by a rhodamine-B quantum counter and emission spectra were corrected with respect to a standard quinine sulfate solution and a NIST spectrum.

**Thermogravimetric analyses:** Weighed samples of 31.79 of I and 32.81 mg of II were loaded onto Pt pans, equilibrated and tarred at room temperature, and heated at a rate of 1 °C/min for I or 0.5 °C/min for II to 400 °C under flowing nitrogen on a TA Instruments TGA Q50, and the data plotted as the % starting weight versus temperature (°C).

**Electronic band structure calculations:** Extended Hückel calculations were carried out
within the tight-binding approximation using the CAESAR2 program\textsuperscript{22} for the full structures of I and II at 960 k-points spread over the irreducible wedge. The double zeta basis sets were selected for the atomic orbital parameters, and the atomic coordinates and lattice dimensions were taken from the respective single crystal structures.

Results and Discussion

Structural Descriptions. \(\text{AgReO}_4\text{pyz} (I)\): Colorless crystals of I are comprised of neutral AgReO\(_4\) layers that are bridged via pyrazine ligands to the Ag sites in each layer, as shown in Figure 2.1. The single symmetry-unique layer stacks directly above and below, down the \(a\)-axis, to generate the full 3D structure. The shortest interlayer spacing is set by the length of the pyrazine ligand at 2.78 Å, while the ReO\(_4\) tetrahedra, which line the spaces between the Ag(pyz) pillars, are separated at a distance of 4.61 Å (O1–O2) across the individual layers (marked). Each ReO\(_4\) tetrahedron bonds via three O vertices to three different Ag\(^+\) in the layer (Ag–O of 2.603(3)–2.686(5) Å), with the fourth vertex either above or below the layer, as shown in Figure 2.2. The symmetry-unique atoms and distances are labeled in Figure 2.1 and listed in Table 2.4. Each Ag\(^+\) is bonded to the three oxide groups from the three separate ReO\(_4\) tetrahedra as well as to the nitrogen groups on two pyrazine ligands above and below each layer, at 2.229(3) Å and 2.238(3) Å for Ag1–N1 and –N2, respectively, similar to that in related silver-pyrimidine networks\textsuperscript{23}.

Related but nondistorted AgReO\(_4\) layers can be found in the [110] planes of the ‘organic-free’ AgReO\(_4\) crystal structure,\textsuperscript{24} with however a different rotational arrangement of all of the ReO\(_4\) tetrahedra. Roughly, the arrangement of cations and anions within the AgReO\(_4\)
layer of both solids has each Ag\(^+\) surrounded by four ReO\(_4^-\) groups (though with the fourth separated at a larger distance in I), and with each ReO\(_4^-\) group similarly bordered by four Ag\(^+\) cations, as shown in Figure 2.3. Thus, the layers of I can be viewed as sections of the [110] planes in AgReO\(_4\) that have been cleaved and pillared by bridging pyrazine ligands. However, fairly narrow ellipsoidal areas are formed as a result of the structural changes in each layer in I, as shown Figure 2.1, that are approximately 3 Å × 12 Å (from O3 to O3 or O4–Ag1 and O2–O2). The thermal displacement parameters of Ag do not indicate any preferential displacements into this area.

\(\text{Ag}_3\text{Mo}_2\text{O}_4\text{F}_7\text{(pyz)}_3\) (II): Yellow-needle synthesized crystals of II show that they are comprised of neutral Ag\(_3\)Mo\(_2\)O\(_4\)F\(_7\) layers that are bridged via pyrazine ligands that bond to Ag sites in each layer, as illustrated in Figure 2.4. The pyrazine-pillared molybdate layers stack directly above and below to generate the full 3D structure. The shortest interlayer spacing is set by the length of the pyrazine ligand at 2.78 Å, while Mo\(_2\)O\(_4\)F\(_7\)^{3–}\) dimers border the ‘open’ areas between the layers, together with the sets of three edge-shared Ag(pyz) chains, and are separated at a shortest distance of 3.69 Å (F2–F4) across the layers. Only the fluoride atoms of Mo\(_2\)O\(_4\)F\(_7\)^{3–}\) project between the layers, while the oxide groups bond to Ag\(^+\) in the plane of the layers.

Structural views normal to the individual layers of II are shown in Figure 2.5 with the symmetry-unique atoms labeled, and distances listed in Table 2.4. The Mo\(_2\)O\(_4\)F\(_7\)^{3–}\) dimer is the first known example of a vertex-shared octahedral dimer among oxyfluoride molybdates, although evidence for the formation of vertex-shared tetrahedra in Mo\(_2\)O\(_2\)F\(_9\)^{2–}\) in solution and W\(_2\)O\(_4\)F\(_7\)^{3–}\) in Cs\(_3\)[W\(_2\)O\(_4\)F\(_7\)] were both reported some time ago\(^{25,26}\). The Mo\(_2\)O\(_4\)F\(_7\)^{3–}\) dimer can
be viewed as a condensation of two \( \text{MoO}_2\text{F}_4^{2-} \) octahedral via an F vertex, with the Mo atoms displaced towards the two nearest cis-O groups. The Mo–O and –F distances are regular and fall within the expected ranges,\(^{27}\) with two short cis-O distances of 1.705(3) Å and 1.749(2) Å (Mo–O1 and Mo–O2) and four longer F distances of 1.904(2)–2.1552(8)Å (Mo–F4 to Mo–F1). Each \( \text{Mo}_2\text{O}_4\text{F}_7^{3-} \) dimer bonds via the four O vertices to Ag\(^+\) in the plane of the layer (Ag1–O1 and –O2 of 2.765(3) Å and 2.557(3) Å; Ag2–O2 of 2.733(2) Å, ×2), and also via two F atoms to the Ag\(^+\) sites (Ag1–F3 of 2.560(2) Å and Ag2–F3 of 2.718(2) Å, ×2). As a result, sets of edge-shared rows of three Ag\(^+\) each share O/F vertices to two sets of molybdate dimers, with one vertex missing on Ag1. Each Ag is additionally coordinated to pyrazine ligands both above and below (Ag1–N1 and –N2 at 2.207(3) Å and 2.201(3) Å; Ag2–N3 2.207(4) Å and 2.203(4) Å) that bridges to adjacent layers.

Between the layers the pyrazine groups arrange face-to-face at a \( \pi-\pi \) stacking distance of ~3.5 Å, which is within the ranges of \( \pi-\pi \) interaction distances reported previously.\(^{28,29}\) The close \( \pi-\pi \) interactions are formed as a result of the sets of three edge-shared Ag\(^+\) cations in II, whereas close \( \pi-\pi \) interactions and near neighbor Ag\(^+\) cations are both absent in I. The arrangement of cations and anions within each layer has a NaCl-type repeating pattern, with each set of three Ag\(^+\) cations surrounded by four \( \text{Mo}_2\text{O}_4\text{F}_7^{3-} \) dimers, and conversely each \( \text{Mo}_2\text{O}_4\text{F}_7^{3-} \) is surrounded by four sets of three Ag\(^+\) cations.

\textit{Thermogravimetric Analysis (TGA):} The thermal stability of I and II were investigated by heating each sample to 400 °C under flowing N\(_2\). Shown in Figure 2.6, the TGA of I displayed a weight-loss step of 17% extending from 150 to 175 °C that corresponded to the loss of pyrazine ligands (theoretical weight loss—18%). The silvery-white product formed
from heating I was determined to be crystalline AgReO$_4$ by powder X-ray diffraction. Further weight loss or change in structure up to 400 °C was not observed. The TGA of II up to 400 °C showed a single weight-loss step of 33% extending from ~150 to 200 °C, corresponding to a weight loss 8% greater than that expected by the loss of pyrazine alone (theoretical weight loss—25%). A powder X-ray diffraction of the deep red product obtained from the TGA analysis corresponded to Ag$_2$MoO$_4$ as well as containing some unidentified peaks. The origin of the additional weight loss is undetermined, but it would correspond to a loss of half of the original O/F atoms. The low temperatures for ligand removal (150 °C) shows these pyrazine-pillared phases hold promise as useful low temperature precursors to condensed oxides, as shown for AgReO$_4$ and Ag$_2$MoO$_4$ here.

*Optical Properties and Electronic Structure Calculations:* As both solids are two-dimensional versions of insulating/semiconducting metal oxides, the optical band gaps and photoluminescent properties were measured to analyze the resultant effects of pillaring and reduced dimensionality. The UV-Vis DRS of I (AgReO$_4$(pyz)) is plotted in Figure 2.7, and exhibits an optical absorption edge in the near ultraviolet with an estimated optical band gap of 2.91 eV. In the case of ‘organic-free’ AgReO$_4$, this excitation reportedly arises from a metal-to-metal charge transfer from Ag$^+$ to Re$^{7+}$ (i.e. Ag$^+$Re$^{VII}$ $\rightarrow$ Ag$^{III}$Re$^V$) at a relatively blue-shifted energy of 3.7 eV, but which decreases with increasing pressure at a rate of ~80 meV GPa$^{-1}$. Significantly, this MMCT in AgReO$_4$ also results in an orange photoluminescence at 580 nm owing to the photo emissive triplet state on silver. This photoluminescence is also expressed here in the pillared structure of I at a slightly different wavelength of 575 nm, shown in Figure 2.8. However, the Ag$^+$ cations in I have farther
spaced ReO$_4$ neighbors (and different orientations) than in the simpler AgReO$_4$, and are also coordinated covalently to the pyrazine ligands. To probe the nature of this electronic transition in AgReO$_4$(pyz), electronic structure calculations were performed and the densities of states (DOS) plotted in Figure 2.9. The partial DOS have been projected out for each element type, and show a predominance of states arising from Re (unfilled) and Ag (filled) both above and below the band gap, as found in AgReO$_4$ as expected for a metal-to-metal charge transfer. However, owing to the addition of pyrazine to the structure, additional states arising from the ligand (C and N) are located at just below and also ~0.8 eV above the Fermi level, and allows the possibility of photoemissive excited states arising from a ligand charge transfer instead. The ~0.8 eV smaller band gap in the pyrazine-pillared structure, though with an energetically similar photoluminescence as AgReO$_4$, could suggest a different electronic origin.

The UV-Vis DRS of II (Ag$_3$Mo$_2$O$_4$F$_7$(pyz)$_3$), plotted in Figure 2.7, exhibits an optical absorption edge in the visible region with an estimated optical band gap of 2.76 eV. The smaller visible-region band gap of II is confirmed by its yellow color, compared to crystals of I which are transparent and colorless. This lowest-energy optical absorption arises in ‘organic-free’ molybdates from a ligand-to-metal charge transfer (LMCT) between O$^{2-}$ and Mo$^{6+}$, to yield short-lived (transient) Mo$^{5+}$ and O$^-$ sites. The energy of this transition is typically ~2.81 eV for related molybdates and which is close to that for II here. Shown in Figure 2.8, a strong photoluminescent emission was also observed for II at $\lambda = 580$ nm with a maximum excitation at $\lambda = 380$ nm. Photoluminescence of a related oxyfluoromolybdate, CdMoO$_3$F$_2$, arises from the same type of LMCT and occurs at $\lambda = 660$ nm, which is
significantly red-shifted compared to II. In order to investigate the type of lowest-energy electronic transition in Ag$_3$Mo$_2$O$_4$F$_7$(pyz)$_3$, electronic structure calculations were performed and the DOS plotted in Figure 2.9. In analogy to that for I, the partial DOS have been projected out for each element type, and show the predominant number of states both above and below the Fermi level arise from filled Ag (higher energies) and O (lower energies)-based states and empty Mo-based states. These results suggest an MMCT transition (i.e. Ag$^{I}$Mo$^{VI}$ → Ag$^{II}$Mo$^{IV}$), similar to that in AgReO$_4$(pyz), is lower in energy and likely favored over the higher energy LMCT transition. Thus, it is expected that both I and II exhibit nearly energetically similar photoemissions (560 vs. 575 nm) arising from the photoemissive excited states on silver in both cases. However, a small amount of additional states arise from the pyrazine ligands (C and N) at just below and above the Fermi level that could also act as excited-state ($\pi^*$) acceptors, such as found similarly in the DOS for I. The effect of the pyrazine pillars in the electronic structures of I and II is the introduction of additional pyrazine-based states near the Fermi level, and suggests a similar origin of their photoluminescence that is related but different to that found in AgReO$_4$.

Conclusions

As part of research efforts to uncover new layered solids, two new pillared hybrid structures containing Ag(pyz) chains were synthesized under hydrothermal conditions, AgReO$_4$(pyz) and Ag$_3$Mo$_2$O$_4$F$_7$(pyz)$_3$. The pyrazine-bridged layers in AgReO$_4$(pyz) are analogous to the [110] planes of layers in the simpler AgReO$_4$ compound, with a different orientation of the ReO$_4$ tetrahedra. The octahedral Mo$_2$O$_4$F$_7^{3-}$ dimers in Ag$_3$Mo$_2$O$_4$F$_7$(pyz)$_3$
share vertices with sets of three edge-shared Ag(pyz)\(^+\) chains that form \(\pi-\pi\) stacked pillars. In both the pyrazine pillars are removed at temperatures slightly higher than the preparation temperature, with a full loss of ligand that results in crystalline AgReO\(_4\) for \textbf{I} and Ag\(_2\)MoO\(_4\) and an unidentified product for \textbf{II}. Both pyrazine-pillared solids exhibit photoluminescence likely arising in both from a charge transfer excitation (MMCT or LMCT) and photoemission that is analogous to that reported for AgReO\(_4\). The synthesis of future pillared structures that are microporous and photoluminescent would hold promise for small molecule detection as well as for probing the fundamental chemical origins of the optical properties of the layers.

Supporting information available: Powder X-ray diffraction data for post-TGA products for \textbf{I} and \textbf{II}. Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 252350 & 252351. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

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References


Table 2.1
Selected Crystal and Refinement Data for AgReO$_4$(pyz) (I) and Ag$_3$Mo$_2$O$_4$F$_7$(pyz)$_3$ (II).

<table>
<thead>
<tr>
<th>Compound</th>
<th>I</th>
<th>II</th>
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<tbody>
<tr>
<td>Fw</td>
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<td>952.72</td>
</tr>
<tr>
<td>Space group, Z</td>
<td>$P2_1/c$ (No. 14), 4</td>
<td>$P2/n$ (No. 13), 2</td>
</tr>
<tr>
<td>$T$ (K)</td>
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<td>148</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>7.2238(6)</td>
<td>7.6465(9)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>7.4940(7)</td>
<td>7.1888(5)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>15.451(1)</td>
<td>19.142(2)</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>92.296(4)</td>
<td>100.284(8)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>835.8(1)</td>
<td>1035.3(2)</td>
</tr>
<tr>
<td>$\mu$ (MoKα) (mm$^{-1}$)</td>
<td>16.79</td>
<td>4.05</td>
</tr>
<tr>
<td>$d_{calc}$, (g cm$^{-3}$)</td>
<td>3.48</td>
<td>3.06</td>
</tr>
<tr>
<td>Reflections (total), $R_{int}$</td>
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<td>3630</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>3815/0/109</td>
<td>1777/0/157</td>
</tr>
<tr>
<td>Final $R_1$, $wR_2^{a}[I&gt;2\sigma(I)]$</td>
<td>0.039, 0.050</td>
<td>0.025, 0.037</td>
</tr>
</tbody>
</table>

$^a R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|; wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}, w=\sigma_F^{-2}$.

Table 2.2
Selected Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å$^2$) for AgReO$_4$(pyz) (I).

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<thead>
<tr>
<th>Atom</th>
<th>Wyckoff letter</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U(eq)^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re</td>
<td>4e</td>
<td>0.47856(2)</td>
<td>0.84442(2)</td>
<td>0.61992(1)</td>
<td>0.02696(9)</td>
</tr>
<tr>
<td>Ag</td>
<td>4e</td>
<td>0.47852(4)</td>
<td>0.63526(5)</td>
<td>0.36809(2)</td>
<td>0.0266(1)</td>
</tr>
<tr>
<td>O1</td>
<td>4e</td>
<td>0.2537(6)</td>
<td>0.9190(7)</td>
<td>0.6169(3)</td>
<td>0.060(3)</td>
</tr>
<tr>
<td>O2</td>
<td>4e</td>
<td>0.6247(7)</td>
<td>0.0228(6)</td>
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<tr>
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<td>4e</td>
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<td>0.7066(5)</td>
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</tr>
<tr>
<td>O4</td>
<td>4e</td>
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<tr>
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<td>0.6082(5)</td>
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<tr>
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Table 2.2 Continued

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<td>C3</td>
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<td>0.8896(6)</td>
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\(^a\) \(U(eq)\) is defined as one-third of the trace of the orthogonalized \(U_{ij}\) tensor.

Table 2.3
Selected Atomic Coordinates and Equivalent Isotropic Displacement Parameters (\(\text{Å}^2\)) for \(\text{Ag}_3\text{Mo}_2\text{O}_4\text{F}_7\text{(pyz)}_3\) (II).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff letter</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(U(eq)^a)</th>
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<td>Ag1</td>
<td>4g</td>
<td>0.82352(3)</td>
<td>0.44824(4)</td>
<td>0.43178(1)</td>
<td>0.0126(2)</td>
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<tr>
<td>Ag2</td>
<td>2f</td>
<td>0.75</td>
<td>0.50221(5)</td>
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<td>0.0130(2)</td>
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<tr>
<td>Mo</td>
<td>4g</td>
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<td>0.51726(4)</td>
<td>0.63963(2)</td>
<td>0.0105(2)</td>
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<tr>
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<td>2f</td>
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<td>0.5959(4)</td>
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<td>0.013(1)</td>
</tr>
<tr>
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<td>4g</td>
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<td>0.7825(3)</td>
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<td>0.017(1)</td>
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<tr>
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<tr>
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Table 2.4
Selected Interatomic Distances (Å) in AgReO$_4$(pyz) (I) and Ag$_3$Mo$_2$O$_4$F$_7$(pyz)$_3$ (II)

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<td>2.229(3) Re</td>
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<td>2.238(3) O2</td>
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<td>II</td>
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<tr>
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<td>N1</td>
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<td>2.207(3) Mo</td>
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<td></td>
<td>2.201(3) O2</td>
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<td>2.765(3) F1</td>
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<td>O2</td>
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<td>2.557(3) F2</td>
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<td>F3</td>
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<td>2.560(2) F3</td>
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<td>F3</td>
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**Figure 2.1.** A [010] polyhedral view of the I structure with the unit cell outlined. Red polyhedrons are Ag-centered coordination and blue are ReO$_4$.

**Figure 2.2.** Structural views of a single AgReO$_4$ layer in I, drew using (A) metal-centered polyhedra and (B) 80% probability thermal ellipsoids. Symmetry unique atoms are labeled in B, where red ellipses are O, blue are N, yellow are Re, and purple are Ag.

**Figure 2.3.** Structural views of similar layer fragments of AgReO$_4$ and AgReO$_4$(pyz) (I), (A) [110] planes of AgReO$_4$ and (B) ‘AgReO$_4$’ layer of I.
Figure 2.4. An ~[010] edge-on view of the pyrazine-bridged layers in II. Both the unit cell and the shortest interlayer F–F distance are marked. Red polyhedra are Ag-centered, blue are Mo-centered and yellow are pyrazine molecules.

Figure 2.5. Structural views of a single $\text{Ag}_3\text{Mo}_2\text{O}_4\text{F}_7$ layer in II, drew using (A) metal-centered polyhedra and (B) 80% probability thermal ellipsoids. Symmetry unique atoms are labeled in B.
**Figure 2.6.** Thermogravimetric curves for I, AgReO$_4$(pyz), and II, Ag$_3$Mo$_2$O$_4$F$_7$(pyz)$_3$, with the value at each temperature calculated as percent of the original weight.

**Figure 2.7.** A plot of UV-Vis diffuse reflectance spectra, F(R) vs. photon energy (eV), for AgReO$_4$(pyz) (I) and Ag$_3$Mo$_2$O$_4$F$_7$(pyz)$_3$ (II).
Figure 2.8. Electronic excitation (left curve) and emission (right curve) spectra of AgReO$_4$(pyz) (I) and Ag$_5$Mo$_2$O$_4$F$_7$(pyz)$_3$ (II).
Figure 2.9. Calculated electronic densities of states (DOS) for AgReO₄(pyz) (1) and Ag₃Mo₂O₄F₇(pyz)₃ (2), with projections of partial densities of states for each element.
CHAPTER 3
LIGAND-BASED MODIFICATION OF THE STRUCTURES AND OPTICAL PROPERTIES OF NEW SILVER(I)-RHENATE(VII)
HYBRID OXIDES/ORGANICS

A paper accepted by Inorganic Chemistry


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Abstract

A new series of silver(I)-rhenate(VII) hybrids was systematically prepared under hydrothermal conditions from eight different N-donor organic ligands (isonicotinate = inca, pyrazine-2-carboxylate = pzc, 1,2,4-triazole = tro, pyridazine = pda, 4,4’-bipyridine = bpy, 1,2-bis(4-pyridyl)-ethane = dpa, 2,3-bis(2-pyridyl)pyrazine = bpp, and tetra-2-pyridinylpyrazine = tpp) and their resulting structures and optical properties were investigated. The reactions targeted a 1:1 molar ratio of Ag:Re, and new hybrid solids were prepared with the compositions Ag(bpp)ReO$_4$ (1), Ag(tpp)ReO$_4$·H$_2$O (2), Ag(Hinca)$_2$ReO$_4$·H$_2$O (3), Ag(tro)ReO$_4$ (4), Ag(pda)ReO$_4$·½H$_2$O (5), Ag(Hpzc)ReO$_4$ (6), Ag$_2$(Hpzc)(pz)(H$_2$O)ReO$_4$ (7), Ag(bpy)ReO$_4$ (8) and Ag(dpa)$_2$ReO$_4$ (9). Hybrid solids 1, 2 and 3 each exhibit low-dimensional structures, consisting of [Ag$_2$(bpp)$_4$]$^{2+}$ and
[Ag$_2$(Hinca)$_4$]$^{2+}$ dimers in 1 and 3, respectively, and [Ag(tpp)]$_n^{n+}$ chains in 2. Hybrid solids 4 and 5 contain a [Ag(tro)]$^+$ chain and a [Ag$_3$(pda)$_3$]$^{3+}$ cyclic trimer, respectively, that are both ReO$_4$-bridged into layered structures. Both 6 and 8 consist of ligand-pillared ‘AgReO$_4$’ layers, while 7 is a Re-deficient analogue of 6 that contains ligand-pillared [Ag$_2$(H$_2$O)ReO$_4$]$^+$ layers where H$_2$O replaces the missing ReO$_4^-$ anion. The hybrid networks of 8 and 9 are interpenetrating, owing to the length of the bpy and dpa ligands, and consist of bpy-pillared ‘AgReO$_4$’ layers and ReO$_4$-filled [Ag(dpa)$_2$]$^+$ diamond-type networks that are two-fold and six-fold interpenetrating, respectively. Their optical properties and thermal stabilities were investigated using UV-Vis transmittance, X-ray photoelectron spectroscopy, and thermogravimetric analysis. The measured properties were analyzed with respect to the varying structural modifications. The Ag–ReO$_4$ network dimensionalities, Ag coordination environments, and the ligand lengths and geometries are found to play important roles in the absorption coefficients, bandgap sizes, and whether the structure collapses softly to give condensed AgReO$_4$, respectively.

**Introduction**

The optical properties of heterometallic oxides that include both an early and a late transition metal have attracted growing interest owing to their relatively small bandgap sizes and potential uses in efficiently harvesting solar energy. In particular, metal-oxides containing a d$^{10}$ electron configuration (e.g., Cu$^+$, Ag$^+$) in combination with a d$^0$ transition-metal cation (e.g., Re$^{7+}$, W$^{6+}$, Nb$^{5+}$) have recently been investigated for their optical properties and for use as photocatalytic materials. Owing to a Metal-to-Metal Charge
Transfer (MMCT) excitation between the electron-donating $d^{10}$ and electron-accepting $d^0$ configurations, the bandgap sizes of these solids occur ~0.5 – 1.5 eV lower than that of the alkali-metal analogues which have only a $d^0$ metal cation (e.g., AgNbO$_3$ versus NaNbO$_3$).

For example, AgNbO$_3$,$^{2a}$ Ag$_2$MoO$_4$,$^{2b}$ AgVO$_3$ and Ag$_3$VO$_4$,$^{2c}$ exhibit band-edge absorption in the visible part of the spectrum and have been investigated for use as visible-light photocatalysts for the production of H$_2$/O$_2$ from water under visible light. However, their synthetic preparation has proceeded primarily by conventional solid-state methods. There is therefore a severely restricted ability to investigate new structural or particle modifications in order to more deeply understand and tune their optical properties.

Solution-based hydrothermal synthetic techniques have enabled the incorporation of varying N-donor ligands as flexible structural components within metal-oxide frameworks, i.e., as metal-oxide/organic hybrid solids.$^7$ This synthetic approach has yielded an immense structural diversity and a growing ability to tune physical properties expressed in metal oxides.$^{8-14}$ The ligands function in a variety of roles to direct the structural arrangement, including as 1) charge-compensating cations, 2) bridging or terminating ligands coordinated to the metal sites, and 3) altering the local coordination environments. Thus, these methods can be used to alter a metal-oxide network and can serve as a gateway to more deeply probing the properties of heterometallic oxides. However, even with the identification of the ‘building blocks’ in solution, there still exists substantial challenges in predicting their structures and resultant properties owing to the numerous possible arrangements of three-dimensional structures. While many relatively small advances have been reported, it is rare
when a large and diverse set of ligands is utilized to unravel the effects of synthetic conditions, coordination preferences, and ligand geometries.\textsuperscript{15}

Our current research efforts have significantly expanded the known structural diversity of hybrid solids containing a combination of d\textsuperscript{0} with d\textsuperscript{10} transition metals,\textsuperscript{16-22} and which we have used to modify their bandgap sizes and photocatalytic reactivities. Recent research shows that, for example, ‘MReO\textsubscript{4}’ (M = Ag\textsuperscript{+} or Cu\textsuperscript{+}) layers derived from parent MReO\textsubscript{4} phases can be pillared by bridging or metal-coordinated ligands, leading to new hybrid metal-oxide/organic structures including M(pyz)ReO\textsubscript{4} (M = Cu, Ag),\textsuperscript{16,17} Cu(pzc)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}ReO\textsubscript{4},\textsuperscript{18} M(pzc)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}AgReO\textsubscript{4} (M = Co, Ni),\textsuperscript{19} and Cu(pzc)\textsubscript{2}AgReO\textsubscript{4}.\textsuperscript{20} The latter two examples can reversibly absorb interlayer water and consist of a chiral network, respectively. Hybrid solids in these systems can also undergo subsequent ligand-mediated structural transformations, such as for Cu(bpy)ReO\textsubscript{4} and Cu(bpy)\textsubscript{2}ReO\textsubscript{4}·\textfrac{1}{2}H\textsubscript{2}O,\textsuperscript{21} and that are accompanied by a significant modulation of their bandgap sizes. Further, some of the first reported to exhibit photocatalytic activity were recently found in the related hybrid vanadates [Ag(L)]\textsubscript{4}V\textsubscript{4}O\textsubscript{12}·xH\textsubscript{2}O (L = bpy, x = 2; L = dpa, x = 4) and Ag\textsubscript{4}(pzc)\textsubscript{2}V\textsubscript{2}O\textsubscript{6}.\textsuperscript{22} However, these investigations have been primarily based on only two or three different ligands.

Herein, a diverse and systematic investigation of Ag(I)–Re(VII) hybrid structures (at a Ag:Re molar ratio of 1:1) was carried out using a series of eight different ligands, shown in Scheme 3.1, with varying lengths and geometric arrangement of N-donor atoms. The underlying emphasis is to more deeply probe the structural origins of their charge-transfer absorptions, modulation of bandgap sizes, as well as optical absorption coefficients. The hybrids were characterized structurally via X-ray diffraction, and their properties investigated
using UV-Vis transmittance, X-ray photoelectron spectroscopy, and thermogravimetric analysis. The nine new hybrids were analyzed for the effect of the ligand on both their structures and properties, and that revealed the roles of the Ag coordination environments, Ag – ReO₄ network dimensionalities, and ligand lengths and geometries.

**Experimental Section**

**General Procedures.** All starting materials were purchased commercially and used without further purification. Hydrothermal conditions were used to synthesize each hybrid solid, which involved heat sealing the starting materials and solvent inside an FEP Teflon pouch (3”×4”). A reagent amount of de-ionized water was used as the solvent in each of the reactions. The pouch was then placed inside a 125 ml Teflon-lined stainless steel reaction vessel that was backfilled with ~40 ml (~33%) of de-ionized water before closing. After holding the reaction at a fixed temperature (120°C for 3 days for hybrids 1-7 and 9; 140°C for 3 days for 8), it was then slowly cooled to room temperature at a rate of 6 °C/h. The resulting products were filtered, washed with de-ionized water, and dried and weighed in air. The phase purity of each hybrid was >95% according to powder X-ray diffraction data (see Supporting Information, Figure 3.S1).

**Synthesis of Ag(bpp)₂ReO₄ (1), Ag(tpp)ReO₄·H₂O (2), Ag(Hinca)₂ReO₄·H₂O (3), Ag(tro)ReO₄ (4), Ag(pda)ReO₄½H₂O (5), Ag(Hpzc)ReO₄ (6), Ag₂(Hpzc)(pzc)(H₂O)ReO₄ (7), Ag(bpy)ReO₄ (8), and Ag(dpa)₂ReO₄ (9).** 1 was prepared from a reaction of bpp (= 2,3-bis(2-pyridyl)pyrazine) (93.7 mg, 0.40 mmol), Ag₂O (23.2 mg, 0.10 mmol), Re₂O₇ (48.4 mg, 0.10 mmol) and H₂O (0.4 g, 22.2 mmol) as colorless block crystals in ~30% yield based
on Ag. 

2 was prepared from a mixture of tpp (tetra-2-pyridinylpyrazine) (77.6 mg, 0.20 mmol), Ag$_2$O (23.2 mg, 0.10 mmol), Re$_2$O$_7$ (48.4 mg, 0.10 mmol) and H$_2$O (0.4 g, 22.2 mmol) as yellow bar-shaped crystals in ~98% yield based on Ag. 

3 was prepared from a reaction of Hinca (isonicotinic acid) (24.6 mg, 0.20 mmol), Ag$_2$O (11.6 mg, 0.05 mmol), Re$_2$O$_7$ (24.2 mg, 0.10 mmol) and H$_2$O (0.2 g, 11.1 mmol) as colorless bar-shaped crystals in ~64% yield based on Ag. 

4 was synthesized from a reaction of tro (1,2,4-triazole) (13.4 mg, 0.20 mmol), Ag$_2$O (23.2 mg, 0.10 mmol), Re$_2$O$_7$ (96.8 mg, 0.20 mmol) and H$_2$O (0.4 g, 22.2 mmol) as colorless block crystals in ~76% yield based on Ag. 

5 was prepared from a mixture of pda (pyridazine) (16.0 mg, 0.20 mmol), Ag$_2$O (23.2 mg, 0.10 mmol), Re$_2$O$_7$ (48.4 mg, 0.10 mmol) and H$_2$O (0.4 g, 22.2 mmol) as colorless plate-shaped crystals in ~78% yield based on Ag. 

6 was synthesized from a reaction of Hpzc (24.8 mg, 0.20 mmol), Ag$_2$O (23.2 mg, 0.10 mmol), Re$_2$O$_7$ (48.4 mg, 0.10 mmol) and H$_2$O (0.05 g, 2.80 mmol) as colorless bar-shaped crystals in ~84% yield based on Ag. 

7 was prepared from a mixture of Hpzc (pyrazine-2-carboxylic acid) (59.5 mg, 0.48 mmol), Ag$_2$O (55.7 mg, 0.24 mmol), Re$_2$O$_7$ (58.1 mg, 0.12 mmol) and H$_2$O (0.2 g, 11.1 mmol) as colorless bar-shaped crystals were in ~80% yield based on Ag. 

8 was prepared from a mixture of bpy (4,4'-bipyridine) (31.2 mg, 0.20 mmol), Ag$_2$O (23.2 mg, 0.10 mmol), Re$_2$O$_7$ (96.8 mg, 0.20 mmol) and H$_2$O (0.72 g, 40.0 mmol) as colorless prism crystals in ~68% yield based on Ag. 

9 was prepared from a mixture of dpa (1, 2-bis(4-pyridyl)-ethane) (73.6 mg, 0.20 mmol), Ag$_2$O (23.2 mg, 0.10 mmol), Re$_2$O$_7$ (48.4 mg, 0.10 mmol) and H$_2$O (0.3 g, 16.7 mmol) as colorless bar-shaped crystals in ~70% based on Ag.
Crystallographic Structure Determination of 1–9. Suitable single crystals of 1–9 were selected and mounted on a nylon loop with a small amount of NVH immersion oil. All X-ray measurements were made on a Bruker-Nonius X8 Apex2 CCD diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073Å). The frame integration was performed using the SAINT program. The resulting raw data were scaled and corrected for absorption using a multi-scan averaging of symmetry-equivalent data via the SADABS program. Each structure was solved by direct methods and refined by full-matrix least-squares fitting on F² using SHELX-97. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on the organic ligands were introduced at idealized positions and were allowed to ride on the parent carbon atoms. Details of the crystal parameters, data collections and structure refinements for all hybrid solids are summarized in Table 3.1. Selected interatomic distances and angles are listed in Table 3.2. Further refinement details are provided in the Supporting Information.

Optical Properties. Transmittance spectra for pressed pellets of each powdered sample were measured in a wavelength range of 200–800nm at room temperature on a UV-VIS spectrophotometer (UV-3600, Shimadzu). In order to account for the regular reflection losses at the boundary surfaces in the transmittance measurements, each compound was measured twice with two different pellet thicknesses, as detailed previously. Resultant absorption spectra were calculated using the Lambert Law (1) and evaluated as α (cm⁻¹) vs. wavelength (nm):

\[ \alpha = \frac{1}{\Delta x} \left( \log(1/R_2) - \log(1/R_1) \right) \]  (1)
where $\alpha$ is the absorption coefficient in cm$^{-1}$; $\Delta x = x_2 - x_1$, where $x_1$ and $x_2$ are the thicknesses of the two sample pellets.

**X-ray Photoelectron Spectroscopy (XPS).** The valence-band XPS spectra were recorded on a RIBER LAS-3000 spectrometer using Mg K\(\alpha\) monochromatized radiation ($h\nu = 1253.6$ eV). The base pressure of the analysis chamber was $\sim 1 \times 10^{-7}$ Torr. Sample sizes were $\sim 1$ cm square and the diameter of the X-ray spot was set at 2-3 mm. The binding energies of the valence-band electronic structures were calibrated by fixing the $C\ 1s$ core-level peak at 284.8 eV for each sample.

**Thermogravimetric Analyses (TGA).** The thermal stability and decomposition of the hybrids were measured on a TA Instruments TGA Q50 under flowing nitrogen gas and heating to 500 °C at a programmed rate of 5 °C/min. Weighed amounts ($\sim 20$ mg) of each hybrid solid were loaded onto Pt pans, equilibrated and tarred at room temperature, and the data plotted as the starting weight (%) versus temperature (°C). Post-TGA residuals were characterized by powder X-ray diffraction in transmission mode on an Inel XRG 3000 diffractometer fitted with a CPS 120 position sensitive detector and using Cu K$\alpha_1$ radiation from a sealed tube X-ray source.

**Results and Discussion**

The structures and properties of Ag(I)-Re(VII) hybrid solids have been systematically investigated by varying the geometry and local coordination sites of the organic ligands, shown in Scheme 3.1. The resultant hybrid structures are described within separate sections below, and range from 0D (molecules), to 1D (chains), to 2D (layered), and also to
interpenetrating 3D (pillar-layered or diamondoid) networks. A listing of all near-neighbor interatomic distances can be found in Table 3.2 for each of the hybrid structures of 1 – 9. All symmetry-unique atoms are labeled on at least one representative figure of each structure, a consistent coloring scheme is used, and all hydrogen bonds are drawn as dashed lines. Topological analyses were carried out using TOPOS\textsuperscript{27} for structures consisting of extended two- or three-dimensional coordination networks (cutoff distance of \SI{\sim}{3.0\ang}) and described herein using recently proposed conventional notations.\textsuperscript{28}

i) Monodentate and Multidentate Bridging Ligands Yielding the 0D and 1D Structures of 1, 2, and 3.

\textbf{Ag(bpp)}\textsubscript{2}ReO\textsubscript{4} (1; bpp = 2,3-bis(2-pyridyl)pyrazine). The single crystal X-ray characterization of 1 reveals a molecular (0D) structure that is comprised of [Ag\textsubscript{2}(bpp)\textsubscript{4}]\textsuperscript{2+} dimers that are interconnected via hydrogen bonding to the ReO\textsubscript{4}\textsuperscript{-} anions, i.e. C–H⋯O at \SI{2.463(5)–2.501(5)}{\ang} down the \textit{a}-axis, as shown in Figure 3.1. There is only one symmetry-unique Ag site that is coordinated by five nitrogen atoms (Ag–N at \SI{2.345(5) – 2.438(5)}{\ang}) in a distorted square-pyramidal geometry, twice by two different bpp ligands and once by a single bpp ligand. Two of the bpp ligands bridge between the two Ag atoms, while the other two bpp ligands are terminating on each Ag, with one of the nitrogen atoms remaining uncoordinated. Each [Ag\textsubscript{2}(bpp)\textsubscript{4}]\textsuperscript{2+} dimer is hydrogen bonded to four neighboring tetrahedral ReO\textsubscript{4}\textsuperscript{-} anions. The ReO\textsubscript{4}\textsuperscript{-} tetrahedra are nearly regular with Re–O distances of 1.690(5)–1.724(5) Å, with a narrow range of O–Re–O angles from \SI{106.9^o–111.3^o}. Two oxygen atoms of each ReO\textsubscript{4}\textsuperscript{-} are hydrogen-bonded to two neighboring [Ag\textsubscript{2}(bpp)\textsubscript{4}]\textsuperscript{2+} dimers. Thus
while the structure of 1 is considered to be molecular based upon the bpp ligand coordination, the weaker hydrogen-bonding interactions lead to some layer-like structural connectivity.

**Ag(tpp)ReO$_4$H$_2$O (2, tpp = tetra-2-pyridinylpyrazine).** The yellow needle-like crystals of 2 consist of $[\text{Ag(tpp)}]_n^{n+}$ chains that are oriented down the $a$-axis, as illustrated in Figure 3.2. The $[\text{Ag(tpp)}]_n^{n+}$ chains are constructed from a single symmetry-unique Ag atom that is coordinated in a distorted square-pyramidal geometry by five nitrogen atoms from three different tpp ligands, at Ag – N distances ranging from 2.393(3) – 2.469(3)Å. Each tpp ligand chelates via three nitrogen atoms to Ag, with two other nitrogen atoms bridging to the neighboring Ag sites to form the extended chain. By contrast, previously reported M(I)/tpp (M = Ag, Cu) cationic chains contain three distinct M coordination sites, while the $[\text{Ag(tpp)}]_n^{n+}$ chain in 2 consists of just one. The structure of 2 also contains tetrahedral ReO$_4^-$ anions and H$_2$O molecules that are linked via hydrogen bonds (O1w – H1w … O3, O1w – H2w … O4 at 2.053(3)Å and 2.505(3)Å, respectively) to form a collinear chain. The two chains, $[\text{Ag(tpp)}]_n^{n+}$ and $[\text{(ReO}_4^-)(\text{H}_2\text{O})]_n$, are hydrogen bonded to each other via the oxygen atoms of ReO$_4$/H$_2$O and the hydrogen atoms of the tpp ligands at ~2.32 – 2.48Å. Thus, while the Ag coordination geometry is similar to that in 1 with the bpp ligand, the addition of two pyridine groups on the tpp ligand affords the extended bridging coordination in the chains of 2.

**Ag(Hinca)$_2$ReO$_4$H$_2$O (3; inca = isonicotinate).** Shown in Figure 3.3, the structure of 3 contains dimeric ‘$\text{Ag}_2(\text{inca})_4(\text{ReO}_4)_2$’ molecular species that are linked to each other via hydrogen bonding interactions. Each Ag atom is coordinated in a slight-distorted seesaw geometry, which is formed by two oxygen atoms (Ag1 – O6 at 2.826(3)Å and 2.894(3)Å),
from ReO$_4^-$ and two nitrogen atoms (Ag1 – N1, – N2 at 2.111(3)Å, 2.117(3)Å, respectively) from two Hinca ligands. The axial N1 – Ag1 – N2 bond angle is nearly linear, at ~173.0°, as expected for a seesaw geometry. The carboxylate group of the inca ligand remains uncoordinated to any Ag atoms and must instead be protonated for charge balancing, i.e., as Hinca. However, the ReO$_4^-$ anion functions in a bridging role, leading to a relatively close Ag1 – Ag1 dimer at 3.4811(7)Å. Within the bc-plane, shown in Figure 3.3B, neighboring Hinca ligands are oriented face-to-face (~3.75Å, π – π interaction) with hydrogen bonding between the carboxylate groups (O – H … O at 2.012(3)Å and 2.091(3)Å). The ReO$_4^-$ anions and uncoordinated water molecules form hydrogen-bonded [(ReO$_4^-$)(H$_2$O)$_n$] zigzag chains (O1w – H … O7, … O8 at 1.992(2) Å, 2.038(3) Å, respectively) down the a-axis. The distances and angles for ReO$_4^-$ are closely similar to 1 and 2, with Re – O distances of ~1.710(4) – 1.723(4)Å and O – Re – O angles of ~107.3 – 111.3°. However, the terminating rather than bridging role of the Hinca ligand results in a molecular structure of ‘Ag$_2$(inca)$_4$(ReO$_4$)$_2$’ dimeric species that are hydrogen bonded to each other and to water.

ii) Ligands with Neighboring N-Donor Groups Yielding the 2D Structures of 4 and 5.

Ag(tro)ReO$_4$ (4; tro = 1,2,4-triazole). The structure of 4 consists of corrugated [Ag(tro)ReO$_4$]$_n$ layers comprised of [Ag(tro)]$_n^{m+}$ zigzag chains that are crosslinked by ReO$_4^-$ anions that coordinate to the Ag sites, as shown in Figure 3.4. The [Ag(tro)]$_n^{m+}$ zigzag chain consists of two symmetry-unique Ag atoms that alternate down the b-axis and are coordinated in a distorted seesaw geometry via the nitrogen atoms of two bridging tro ligands each at Ag – N distances of 2.140(4) – 2.155(4)Å and to two ReO$_4^-$ anions each at Ag – O...
distances of 2.625(4) – 2.773(4)Å. The tro ligands coordinate to the axial sites with a N – Ag – N of ~170° and form the backbone of the $[\text{Ag(tro)}]_n^{\text{n+}}$ zigzag chain. Alternatively, a corrugated ‘AgReO$_4$’ chain can also be described that is oriented down the $a$-axis and which is crosslinked by the tro ligands. The distorted ReO$_4^-$ tetrahedra exhibit bond angles and distances consistent with the structures previously described above. A topological analysis of the layer structure of 4 shows that it is classified as a 2,4-c net with 2 nodes (Ag and Re atoms) and the Schlafli symbol \{6;8;10\}{6}. This layer structure has resulted from the greater number of bridging ReO$_4^-$ anions that serve to crosslink the Ag atoms within a single layer, as compared to the non-bridging ReO$_4^-$ anions in 1 and 2 that result from the chelating and more sterically-crowded tpp and bpp ligands.

**Ag(pda)ReO$_4$·$\frac{1}{2}$H$_2$O (5; pda = pyridazine).** The hybrid solid 5 exhibits a layered structure consisting of $[\text{Ag(pda)ReO}_4]_n$ layers stacked down the $a$-axis, as shown in Figure 3.5. This layer is constructed from a remarkable trigonal-planar cluster of three Ag atoms, i.e., a $[\text{Ag}_3(\text{pda})_3]^{3+}$ cyclic trimer in Figure 3.5A, that features a slightly distorted $[\text{Ag}_3\text{N}_6]$ core with N – Ag – N bond angles between ~170.0° – 173.9°. This $[\text{Ag}_3(\text{pda})_3]^{3+}$ trimer is unusual but structurally similar to that reported for pyrazolate-bridged Cu$^1$/Ag$^1$ molecular species,$^{30}$ and here represents the first such structural motif synthesized in a hybrid solid. Each $[\text{Ag}_3(\text{pda})_3]^{3+}$ cluster is also coordinated to seven bridging ReO$_4^-$ anions that extend the structure in the $bc$-plane to form the $[\text{Ag(pda)ReO}_4]_n$ layer. A topological analysis of this layer indicates it is a new 2,4,5,6,7-c net with 6 nodes (Ag and Re atoms) and the Schlafli symbol \{3$^3$;4$^4$;5$^2$\}{3$^4$;4$^4$;5$^2$}{3$^5$;4$^3$;5$^2$;6$^2$;7$^2$;8}{3$^5$;4$^3$;5$^2$;6$^2$;7$^2$;8}{3$^7$;4$^5$;6$^2$;7$^2$;8}{4}. 

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Including both the N-donor and anionic ReO$_4^-$ ligands, the [Ag$_3$(pda)$_3$]$^{3+}$ cluster contains three different Ag coordination geometries, a seesaw (Ag1), a distorted square-pyramidal (Ag2), and a distorted octahedral (Ag3) coordination environment. Each Ag is coordinated to two N atoms on the pda ligands at distances ranging from 2.177(9) – 2.283(9)Å, with the differences in coordination geometries owing to the asymmetric arrangement of the ReO$_4^-$ ligands. The Ag1 site is bonded to two oxygen atoms on two ReO$_4^-$ tetrahedra (Ag1 – O6, – O11 at 2.690(9)Å and 2.802(9)Å, respectively), to give the seesaw coordination geometry. The distorted square-pyramidal geometry of Ag2 is completed by three oxygen atoms from three ReO$_4^-$ anions (Ag2 – O2, – O5, – O9, at 2.747(9)Å, 2.616(9)Å, and 2.492(11)Å, respectively). The Ag3 site is bonded to four oxygen atoms from ReO$_4^-$ anions (Ag3 – O1, – O6, – O8, – O9, at 2.579(8)Å, 2.681(9)Å, 2.598(8)Å, and 2.527(12)Å, respectively) and that occupy the equatorial sites of the distorted-octahedral coordination geometry. There are three symmetry-unique ReO$_4^-$ tetrahedra, two of which (Re1 and Re3) are bridging between the Ag atoms on two different [Ag$_3$(pda)$_3$]$^{3+}$ clusters, while the other (Re2) is bridging between three neighboring [Ag$_3$(pda)$_3$]$^{3+}$ clusters, shown in Figure 3.5A. Analogous to that described above for 4, the layered structure of 5 has resulted from the bridging ReO$_4^-$ anions that serve to crosslink the [Ag$_3$(pda)$_3$]$^{3+}$ cyclic trimers, as compared to the lower-dimensional structures of 1 – 3 with more ligand-crowded Ag sites and non-bridging ReO$_4^-$ anions.
iii) Small Asymmetric Bridging Ligands Leading to the Pillar-Layered Structures of 6 and 7.

Ag(Hpzc)ReO$_4$ (6; pzc = pyrazine-2-carboxylate). The structure of 6 is comprised of neutral ‘AgReO$_4$’ layers that are cross-linked by Hpzc ligands, shown in Figure 3.6, with a shortest interlayer distance of ~2.79 Å. A single symmetry-unique ‘AgReO$_4$’ layer stacks down the c-axis to generate the full three-dimensional structure in the monoclinic space group $P2_1/n$. Within the layer, there is a single symmetry-unique Ag site that has a distorted-octahedral coordination geometry, with the equatorial positions occupied by one carboxylate group (Ag1 – O2 at 2.573(3) Å) and three bridging ReO$_4$ anions (Ag1 – O3, – O4, – O5, at 2.648(3) Å, 2.842(3) Å, and 2.552(3) Å, respectively). The axial positions are bonded by two nitrogen groups from pzc ligands above and below the layer (Ag1 – N1, – N2, at 2.284(2) Å and 2.249(2) Å, respectively), completing the octahedral environment. Each tetrahedral ReO$_4$ bridges between three different Ag atoms, with the fourth oxygen vertex located alternately above or below the layer, shown in Figure 3.6A. A topological analysis of 6 shows that it is classified as a 3,5-c net with 2 nodes (Ag and Re atoms) and the Schlafli symbol $\{6^3\} \{6^9; 8\}$.

Each Hpzc ligand chelates to a single Ag atom via the carboxylate and nitrogen groups, and also bridges to a neighboring Ag atom through its opposing nitrogen atom to form the [Ag(Hpzc)]$^+$ chains oriented down the c-axis. The Hpzc ligands in a single chain are all oriented in the same direction, while the ligand orientations of neighboring chains are reversed to cancel any net dipole moment, as required for space group $P2_1/n$. While the carbonyl end (C = O at ~1.21 Å) of the carboxylate group preferentially coordinates to the Ag
atom, the alcoholic end (C – OH at ~1.32Å) remains protonated and uncoordinated. These carboxylate distances are consistent with those of the Hinca ligand of 3 (C = O, C – OH at ~1.22Å and ~1.34Å, respectively), that is uncoordinated and protonated as well. Thus, while the terminating Hinca ligand in 3 yields a molecular-type structure, the introduction of a para nitrogen group in the Hpzc ligand of 6 results in ligand-bridged ‘AgReO$_4$’ layers. Similar pillared ‘AgReO$_4$’ layers are also found in Ag(pyz)ReO$_4$,$^{17}$ showing that the opposing nitrogen atoms on the ligand (sans the carboxylate functionality) are key to forming this type of hybrid structure.

Ag$_2$(Hpzc)(pz)(H$_2$O)ReO$_4$ (7; pzc = pyrazine-2-carboxylate). The structure of 7 is the only one of the nine hybrids described herein to crystallize in a non-centrosymmetric space group, Pca$_2_1$. Further, it is the only one with a Ag:Re molar ratio of 2:1 rather than 1:1, as for the other hybrids. Shown in Figure 3.7, the hybrid structure of 7 is comprised of asymmetric [Ag$_2$(H$_2$O)ReO$_4$]$^+$ layers that are stacked down the c-axis with pzc/Hpzc ligands bridging between the Ag atoms in each layer, in analogy with the structural role of the Hpzc ligands in 6. These layers consist of two symmetry–unique Ag sites, distorted square-pyramidal (Ag1) and distorted trigonal-bipyramidal (Ag2) coordination environments that alternate down the [Ag$_2$(pz)(Hpzc)]$^+$ chains. Each Ag1 atom is chelated by two nitrogen atoms and two oxygen atoms from two pzc ligands above and below (Ag1 – N1, – N3 at 2.253(3)Å and 2.277(2)Å; Ag1 – O1, – O3 at 2.537(2)Å and 2.492(2) Å, respectively), and is also coordinated to one terminal oxygen atom from the ReO$_4$$^-$$^-$ anion (Ag1 – O7 at 2.785(2)Å). Similarly, Ag2 is coordinated to two pzc ligands through the opposing nitrogen atoms (Ag2 – N2, – N4 at 2.229(3)Å and 2.240(3) Å, respectively) and to two ReO$_4$$^-$$^-$ anions via its oxygen
atoms (Ag2 – O6, – O8 at 2.397(2)Å and 2.878(2)Å, respectively). Additionally, Ag2 is equatorially-bonded to one H2O molecule (Ag2 – O5 at 2.608(2)Å) that hydrogen bonds to neighboring carboxylate groups (O5 – H…O at ~2.1 Å) shown as dashed lines in Figure 3.7.

A topological analysis shows that the [Ag2(H2O)ReO4]⁺ layer in 7 is a new topology with a 3,4-c net with 3 nodes (two Ag and one Re atom) and the Schläfli symbol \{6;8^2\}\{6^2;8^4\}\{6^2;8\}. As before for 6, each tetrahedral ReO4⁻ anion bridges between three different Ag sites in 7, with the fourth oxygen vertex located between the layers in a polar arrangement, shown in Figure 3.7B. Thus, an undulating [Ag2ReO4]⁺ layer is formed in 7 that is structurally similar to 6, but that is Re-deficient owing to the 2:1 (versus 1:1) Ag:Re molar ratio. Further, the layer structure has been able to compensate for this deficiency by incorporating a coordinated water molecule on the same position as the missing ReO4⁻ anion.

iv) Longer Bridging Ligands Yielding the Interpenetrating Structures of 8 and 9.

Ag(bpy)ReO4 (8; bpy = 4,4'-bipyridine). The structure of 8 is a three-dimensional pillar-layered framework that is two-fold self-interpenetrating, as illustrated in Figure 3.8 for both a single layer (A) and multiple layers (B). The network is comprised of a single symmetry-unique ‘AgReO4’ layer that consist of alternating tetrahedral ReO4⁻ anions and Ag-centered trigonal bipyramids that are arranged into 6₃ hexagonal nets that are pillared via the bridging bpy ligands. A topological analysis indicates that the interpenetrating framework of 8 represents a three-dimensional hms topology (class IIa) with 3,5-connectivity and a 2-nodal (Re, Ag) net, with the Schläfli symbol \{6^3\}\{6^8;8\}. The hybrid network of 8 is iso-structural to that recently reported for Cu(bpy)ReO4,²¹ with the replacement of Cu⁺ for Ag⁺, and thus is described here only briefly.
Within each layer, each ReO$_4^-$ anion bridges via its O vertices to three different Ag$^+$ in the layer (Ag – O of 2.869(2) – 3.002(2)Å), with the fourth vertex oriented either above or below the layer, as found similarly in the silver-rhenate layers of 6 and 7. The coordination environment of Ag consists of three O atoms from three different ReO$_4^-$ as well as two N atoms from two pyrazine ligands located above and below each layer (2.141(2)Å and 2.132(2)Å for Ag1 – N1 and – N2, respectively). The layer-to-layer distance is determined by the length of the bpy ligand at ~7.08Å, and which allows for intervening layers that interpenetrate through the hexagonal faces of the ‘AgReO$_4$’ net via the bpy ligands. Thus, the bridging role of the bpy ligand in 8 results in a pillared structure similar to that of 6 and 7 (sans the carboxylate group), but the longer ligand length significantly expands the interlayer spacing and results in the two-fold interpenetration of the pillared network.

**Ag(dpa)$_2$ReO$_4$ (9; dpa = 1,2-bis(4-pyridyl)-ethane).** Shown in Figure 3.9, use of the slightly longer and more flexible dpa ligand in 9 results in a three-dimensional [Ag(dpa)$_2$]$^+$ diamond-type network that is six-fold interpenetrating. The structure represents a three-dimensional *dia* topology (class Ia for six-fold interpenetration) with a 4c-net that is uninodal with the Schläfli symbol {6}$^6$. The overall structure is highly symmetric and contains only one symmetry-unique Ag and Re atom. The [Ag(dpa)$_2$]$^+$ network is constructed from tetrahedrally-coordinated Ag via the N donors of four dpa ligands (Ag – N at 2.316(9)Å), Figure 3.9A. The open channels (dimensions of ~6.1Å × ~6.1Å from N1 to N1’) are filled by five other symmetry-related nets as well as the ReO$_4^-$ anionic guests. This network type is relatively common, and has been found for Cu(bpy)$_2$ReO$_4$·½H$_2$O and for several other metal-organic frameworks.$^{21,31,32}$ However, the tetrahedral ReO$_4^-$ anions in 9 are not involved in
bridging between the Ag sites, which is their typical role in all other silver(I)-rhenate(VII) hybrids reported herein. The charge-balancing ReO$_4^-$ anions have a much narrower range of tetrahedral Re – O distances (1.701(1)Å) and O – Re – O angles (109.2 – 109.7°). Thus, use of the longer dpa ligand (versus bpy or pzc in 6 and 8) results in the only hybrid herein with tetrahedrally-coordinated Ag atoms, as compared to the more typical trigonal bipyramidal or seesaw coordination geometries. The absence of ReO$_4^-$ from the Ag coordination environment prevents the formation of any extended Ag – ReO$_4$ connectivity, as found for hybrids 4 – 8.

**Optical Properties.** Measurements of the optical absorption coefficients and bandgap sizes were carried out in order to investigate the changes arising from the new structural modifications (e.g., coordination environment, network dimensionality, etc.) of the Ag(I)-Re(VII) hybrids. The absorption coefficient, $\alpha$ (cm$^{-1}$), determines the rate of light absorption in a solid as a function of depth (at $\alpha^{-1}$ the intensity drops to ~36% of its starting intensity). It is one of the most critical but underexplored parameters of semiconductor materials for efficiently capturing solar energy for conversion into fuels and/or electricity; for example, a low $\alpha$ leads to light being poorly absorbed in a material.$^{33}$ Generally, semiconductors exhibit a sharp edge in their absorption coefficient spectra, since light which has energy below the band gap does not have sufficient energy to excite an electron across the band gap. Thus, $\alpha$ depends on both the solid and on the wavelength of light. As studied previously in AgReO$_4$ and AgReO$_4$(pyz),$^{17,34,35}$ the Ag(I)-Re(VII) hybrids are promising candidates for light absorption at relatively low visible-light energies owing to a Metal-to-Metal Charge Transfer (MMCT) excitation between the electron-donating d$^{10}$ (Ag) and electron-accepting d$^0$ (Re).
configurations. Thus, an investigation of their optical properties was conducted herein to probe how the atomic-level structure alters their light-absorption characteristics.

Measurements of $\alpha$ of hybrid solids 1 – 9 were taken on UV-VIS spectrophotometer using transmittance methods in the range of 200 – 800 nm, and the resultant spectra are plotted as $\alpha$ (cm$^{-1}$) versus wavelength (nm) in Figure 3.10A. These spectra include data for the previously reported pillar-layered structure of AgReO$_4$(pyz) (10, pyz = pyrazine) and the ligand-free AgReO$_4$ (11) for comparison. The measured values of $\alpha$ for these hybrids all fall within one of two different groups, which either exhibit larger bandgap sizes and higher absorption coefficients (3, 4, 5, 8, 9 and 11) or smaller bandgap sizes in the visible range with lower absorption coefficients (1, 2, 6, 7 and 10). A steep onset of absorption occurs at ~350 nm for the first group and at ~450 nm for the second group. Previous theoretical and experimental studies on Ag(I)-Re(VII) solids have shown that the band-edge absorption occurring at around 340 nm in AgReO$_4$ can be assigned to a MMCT transition ($\text{Ag}^{\text{I}} \rightarrow \text{Re}^{\text{VII}}$).$^{34-36}$ Further, the shift of the absorption edge by ~0.8 eV to lower energies is consistent with a Ligand-to-Metal Charge Transfer (LMCT) excitation, as was investigated previously in AgReO$_4$(pyz) and AgReO$_4$.$^{17}$ Thus, the steep rise in absorption in the first group owes to a MMCT transition, while that of the second group to a LMCT transition.

The optical bandgap size for each of the hybrid solids can be calculated from the respective wavelength-dependent absorption coefficient spectrum. Electronic transition probabilities are given by the following equation (2) when the energy of the photon exceeds the bandgap energy: $(\alpha \hbar \nu)^n \propto (\hbar \nu - E_g)$ \quad (2)$^{37}$
where $\alpha$ is the absorption coefficient (cm$^{-1}$), $h\nu$ is the photon energy (eV), $E_g$ is the band gap energy (eV), and $n = 2$ when the transition is direct, and $n = \frac{1}{2}$ when the transition is indirect. Bandgap sizes ($E_g$) can be estimated from the linear portion of the plots of $(\alpha h\nu)^n$ vs. $h\nu$ when extrapolating to zero. The plots of $(\alpha h\nu)^2$ vs. $h\nu$, shown in Figure 3.10B, yield bandgap sizes that are consistent with the observed colors and also suggest that each of the lowest energy excitations are direct. The calculated bandgap sizes for each compound are 2.89 eV (1), 2.60 eV (2), 3.70 eV (3), 3.75 eV (4), 3.30 eV (5), 2.90 eV (6), 2.96 eV (7), 3.71 eV (8), 3.46 eV (9), 2.91 eV (10; AgReO$_4$(pyz)) and 3.68 eV (11; AgReO$_4$). Hybrid solids in the group with the higher values of $\alpha$ show a range of bandgap sizes from ~3.30 – 3.75 eV, while those in the second group with lower values of $\alpha$ show a range of bandgap sizes from ~2.60 – 2.96 eV. For hybrids in the former group, i.e., 3, 4, 5, 8, 9, 11 assigned to a MMCT excitation, there is a close correlation of $\alpha$ with the Ag–ReO$_4$ network dimensionality but not with the bandgap size. For example, as $\alpha$ decreases in the order of 11 > 8 > 4 > 5 > 3 > 9, the network dimensionality of Ag–ReO$_4$ (minus the ligand) decreases from 3D condensed (11) to 2D layers (8, 4, 5) to 0D molecular (3) and to no connectivity (9). The ligands have a predominant role in altering the Ag–ReO$_4$ network dimensionality, and thus, the absorption coefficients that are dependent on the electronic transition probabilities.

**X-ray Photoelectron Spectroscopy (XPS).** Electronic structure calculations on Ag(I)/Cu(I)-Rhenate(VII) hybrids have shown previously that the conduction band is comprised primarily of unfilled Re 5d orbitals, while the valence band originates from mixture of Ag 4d, O 2p, and N 2p orbitals. As described above, the ReO$_4^-$ anions in hybrid
structures 1 – 9 exhibit nearly identical tetrahedral coordination geometries, while the coordination environments and connectivities of the Ag sites vary substantially as a result of the different ligands. Thus, while the valence bands are expected to exhibit a larger variation in energies, the conduction bands are more fixed at similar energy levels.

The XPS results show that the valence band energies of the hybrids, shown in Figure 3.11, closely correlate with the changes in their bandgap energies ($E_g$) (central peak positions arranged from smallest to largest $E_g$: 2, 3.85 eV; 1, 4.40 eV; 10, 4.45 eV; 6, 4.50 eV; 7, 4.52 eV; 5, 4.80 eV; 9, 4.95 eV; 11, 5.10 eV; 3, 5.18 eV; 8, 5.20 eV; 4, 5.45 eV). For example, the highest valence band energy was measured for 2 which has the lowest $E_g$ of 2.60eV, followed by 1, 10, 6, and 7 with the next highest $E_g$ sizes that range from ~2.89 – 2.96eV. The next lowest set of valence band energies for 5, 9, 11, 8, 3 and 4 also closely follows the same trend towards increasing $E_g$ from ~3.30 – 3.75eV. Owing to the nature of the bandgap transition, i.e., LMCT for the first five hybrids and MMCT for the next six, the valence band is comprised primarily of the Ag d-orbitals in the latter and the ligand-based $\pi$-orbitals in the former. Obviously, there is significant orbital mixing between the Ag 4d and ligand $\pi$-orbitals and a gradual progression of their mixture in the valence band, and both are significant factors in determining the resultant $E_g$ of the hybrids.

The hybrid network dimensionality (e.g., clusters, chains) and local coordination environments should effect the bandgap sizes, such as via the strength of the d-orbital-to-ligand interactions or in the band broadening for extended versus molecular networks. Described above, the local Ag coordination environments vary quite significantly among the hybrids 1 – 9, and are dependent on the N-donor positions, the presence of carboxylate
groups, and the geometry and size of the ligand. These include a distorted seesaw \{AgN_2O_2\} coordination geometry in 3 and 4, a distorted \{AgN_4\} tetrahedral geometry in 9, a distorted \{AgN_2O_4\} octahedral geometry in 6, and distorted \{AgN_5\} or \{AgN_2O_3\} square pyramidal or trigonal bipyramidal coordination geometries in 1, 2, 7, 8 and 10. The structure of 5 contains Ag-centered seesaw, octahedral and square-pyramidal coordination geometries. The greater d-orbital interactions of the distorted square-pyramidal/trigonal-bipyramidal and octahedral coordination geometries in 1, 2, 6, 7 and 10 raise the filled Ag 4d^{10} orbitals to higher energies and results in their relatively smaller bandgap sizes. By comparison, the tetrahedral and seesaw coordination geometries of 3, 4, 9, and 11 result in weaker d-orbital interactions, a lower-energy valence band, and increased bandgap sizes. By contrast, no trends were found between the Ag–ReO_4 network dimensionality and the bandgap sizes, owing to the relatively much weaker interaction between the Re 5d-orbitals and the Ag- or ligand-based orbitals.

**Thermogravimetric Analysis (TGA).** Many hybrid metal-oxides/organics exhibit high thermal stabilities, can be thermally converted to new or known condensed phases after removal of the ligand, and reversibly absorb water or other small molecules. The TGA results for hybrid solids 1 – 9 are shown in Figure 3.12. The post-TGA products were characterized using Powder X-ray Diffraction (PXRD) and these results provided in the Supporting Information (Figure 3.S2). The TGA results can be separated into two groups, one group (1, 2, 8, and 9) that decomposes into Ag(s) and other amorphous solids, and another group that decomposes to yield the condensed AgReO_4 (4, 5, 6, and 7) or the ReO_2 (3) phase.
In the first group, the strongly chelating bpp and tpp ligands in 1 and 2 produce two of the most thermally stable hybrid structures at temperatures of up to ~300 – 350°C. Further, heating to ~500°C results in a weight change corresponding to only a partial loss of the ligands (~20.2%, calcd. 56.7% for 1; ~21.8%, calcd. 50.8% for 2), although the lattice H₂O in 2 is easily removed at ~100 °C (~2.3%, calcd. 2.4%). Both post-TGA residuals contain a similar mixture of Ag(s) and an amorphous material. The same residual products were found for 8 and 9 as well, with the bridging bpy and dpa ligands. In 8, removal of the bpy ligand begins at ~300 °C and extends to ~480 °C, while the removal of the dpa ligand in 9 extends from ~150 to ~480 °C. The thermal stability of 9, which is lower than any of the other hybrids, is because of the absence of any close Ag – ReO₄ interactions. Thus, all of the larger and chelating ligands (bpp, tpp, bpy and dpa) inhibited the soft collapse of the metal-oxide framework, and instead yielded Ag(s) and amorphous products rather than crystalline AgReO₄.

In the second group, the thermal decomposition of hybrids 5, 6, and 7 lead to the low temperature loss of their respective pda and pzc ligands at ~200 – 250°C and the formation of condensed AgReO₄. Interestingly, while this transformation occurs in a single weight-loss step for 5 and 6, the weight loss of 7 exhibits four distinct steps. On heating 7 to ~500 °C, an ~2.4% weight loss of coordinated water from 120 – 160 °C (calcd. 2.5%) occurs, followed by an ~16.7% weight loss at ~160 – 240 °C that corresponds to the removal of one pzc ligand per formula (calcd. 16.9%), and lastly followed by another ~16.8% weight loss of the remaining pzc ligand at ~280 – 300 °C, and resulting in the formation of AgReO₄ and Ag. The intermediate products are unknown and have not yet been structurally characterized.
The fourth and last weight loss for 7 at $>400$ °C is due to the decomposition of AgReO$_4$. The post-TGA products of 4 were also determined to be a mixture of AgReO$_4$ and Ag, with the loss of tro ligands from $\sim$220 – 360 °C ($\sim$16.9%, calcd. 16.2%). Lastly, the decomposition of 3 exhibits two weight-loss steps of $\sim$41% extending from 180 °C to 500 °C, and that corresponds to the loss of both lattice water and inca ligands (calcd. 42.5%), yielding a mixture of Ag and ReO$_2$. Thus, all of the shorter ligands (tro, pda, and pzc) resulted in a soft collapse of the hybrid structures to give AgReO$_4$ in the products.

**Conclusions**

A series of nine new silver(I)-rhenate(VII) oxide/organic hybrids was synthesized. The use of large multidentate chelating ligands resulted in the molecular and chain-like structures of Ag(bpp)ReO$_4$ and Ag(tpp)ReO$_4$·H$_2$O with limited Ag–ReO$_4$ connectivity. Conversely, shorter bridging ligands yielded the layered and pillared-types of hybrid structures of Ag(tro)ReO$_4$, Ag(pda)ReO$_4$·½H$_2$O, Ag(Hpzc)ReO$_4$, and Ag$_2$(Hpzc)(pzc)(H$_2$O)ReO$_4$, respectively, each with a two-dimensional Ag–ReO$_4$ connectivity. Lastly, the interpenetrating networks of Ag(bpy)ReO$_4$ and Ag(dpa)$_2$ReO$_4$ are found with the longest bridging ligands. Measured bandgap sizes show that the hybrid solids fall into two groups, and exhibit either larger bandgap sizes of $\sim$3.30 – 3.75eV owing to MMCT excitations, or smaller bandgap sizes of $\sim$2.60 – 2.96eV from LMCT excitations. For the hybrid group with the larger bandgap sizes and MMCT, the absorption coefficients are relatively larger and closely correlate with the Ag–ReO$_4$ network dimensionality. The XPS spectra reveal that the bandgap sizes are primarily determined by changes in the valence band
energies that are a function of the Ag coordination geometries and d-orbital energies. TGA results reveal the highest possible thermal stability of ~300°C for Ag(bpp)ReO₄, Ag(tpp)ReO₄·H₂O, and Ag(bpy)ReO₄, while for the smaller ligands in Ag(tro)ReO₄, Ag(pda)ReO₄·½H₂O, and Ag(Hpzc)ReO₄ there is a lower-temperature structural collapse to yield condensed AgReO₄. In summary, the nature of the coordinating ligand plays a critical role in directing the structure of each hybrid, and therefore can be of great utility in tuning their optical properties in the future design of new materials for solar-energy conversion.

**Acknowledgments**

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**Supporting Information Available**

Crystallographic data for 1 – 9 in CIF format, tables of atomic coordinates and equivalent isotropic displacement for each compound, powder X-ray diffraction results for all prepared compounds including for the as-synthesized hybrids and post-TGA residuals. These materials are available free of charge via the Internet at [http://pubs.acs.org](http://pubs.acs.org).
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Scheme 3.1. The series of selected N–donor organic ligands used in the synthesis of new silver(I)–rhenate(VII) hybrid solids and their different coordination modes to Ag.
Table 3.1. Single Crystal Data and Structure Refinement Details for Hybrid Solids 1 – 9.

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<td>296(2)</td>
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$^aR_1 = \Sigma (|F_o| - |F_c|) / \Sigma |F_o|$; wR2 = [$\Sigma w(F_o^2 - F_c^2)^2 / (\Sigma F_o^2)^2$]$^{1/2}$; w=$\sigma_F^{-2}$.
### Table 3.2. Selected Interatomic Distances (Å) in Hybrid Solids 1–9.

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Ag(bpp)$_2$ReO$_4$ (1)

| Ag1    | N1     | 2.469(2)     | Re1    | O1     | 1.705(2)     |
| N2     | 2.408(2) | O2       | 1.709(3) | |
| N4     | 2.468(2) | O3       | 1.712(3) | |
| N5     | 2.393(2) | O4       | 1.712(3) | |
| N6     | 2.409(3) | O1w–H⋯O3  | 2.053(3) | |
|        |        | O1w–H⋯O4  | 2.505(3) | |

Ag(tpp)ReO$_4$·H$_2$O(2)

| Ag1    | O6     | 2.826(3)     | Re1    | O5     | 1.710(4)     |
| N2     | 2.894(3) | O6       | 1.723(4) | |
| N1     | 2.111(3) | O7       | 1.710(4) | |
| N2     | 2.117(3) | O8       | 1.721(3) | |
| O1w–H⋯O7 | 1.992(3) | O2–H⋯O3  | 2.012(3) | |
| O1w–H⋯O8 | 2.038(3) | O4–H⋯O1  | 2.091(3) | |

Ag(Hinca)$_2$ReO$_4$·H$_2$O (3)

| Ag1    | O1     | 2.625(4)     | Re1    | O1     | 1.720(3)     |
| O3     | 2.690(4) | O2       | 1.712(3) | |
| N1     | 2.146(4) | O3       | 1.723(3) | |
| N4     | 2.155(4) | O4       | 1.737(3) | |
| Ag2    | O5     | 2.773(4)     | Re2    | O5     | 1.730(3)     |
| O8     | 2.707(4) | O6       | 1.720(3) | |
| N2     | 2.146(4) | O7       | 1.719(3) | |
| N5     | 2.140(4) | O8       | 1.738(3) | |
| N6–H⋯O6 | 2.045(4) | N3–H⋯O4  | 1.921(4) | |

Ag(tro)ReO$_4$ (4)

| Ag1    | O6     | 2.690(9)     | Re1    | O1     | 1.715(7)     |
| O11    | 2.802(9) | O2       | 1.721(8) | |
| N2     | 2.179(9) | O3       | 1.718(9) | |
| N3     | 2.177(9) | O4       | 1.718(9) | |
Table 3.2 Continued

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Figure 3.1. Structural view of 1, Ag(bpp)$_2$ReO$_4$, with hydrogen bonds drawn as dashed lines and symmetry-unique atom types labeled. Hydrogen atoms are omitted for clarity.

Figure 3.2. Structural view of 2, Ag(tpp)ReO$_4$·H$_2$O, showing the extended [Ag(tpp)$_n$]$^{n+}$ and [(ReO$_4$)$^-$(H$_2$O)]$_n$ chains aligned down the $a$-axis direction. Hydrogen bonds are drawn as dashed lines with labeled bond distances.
Figure 3.3 Local (A) and extended (B) structural views of 3, [Ag(Hinca)$_2$ReO$_4$·H$_2$O], with all symmetry-unique atoms and hydrogen bonding interactions labeled. The polyhedral view in (B) is aligned down the $a$-axis, with red polyhedra = Ag-centered and blue polyhedra = ReO$_4$. 
Figure 3.4. (A) Structural view of a single layer in Ag(tro)ReO$_4$ (4) with the symmetry-unique atom types labeled, and (B) an ~[010] polyhedral view of the layers stacked down the $c$ axis; Red polyhedra = Ag-centered and blue polyhedra = ReO$_4$.

Figure 3.5. (A) Structural view of a single layer in Ag(pda)ReO$_4$·½H$_2$O (5), showing six trigonal-planar $[\text{Ag}_3(\text{pda})_3]^{3+}$ clusters bridged by ReO$_4^-$ anions; (B) An ~[010] polyhedral view of two of these layers stacked in 5 with interlayer hydrogen bonds drawn as dashed lines; Red polyhedra = Ag-centered and blue polyhedra = ReO$_4$. 
Figure 3.6. Structural views of Ag(Hpzc)ReO$_4$ (6), showing the (A) ‘AgReO$_4$’ layer with atom types labeled, and (B) an ~[100] polyhedral view. Red polyhedra = Ag-centered and blue polyhedra = ReO$_4$.

Figure 3.7. Structural views of Ag$_2$(Hpzc)(pzc)(H$_2$O)ReO$_4$ (7), showing the (A) [Ag$_2$(H$_2$O)ReO$_4$]$_n$ layer with atom types labeled, and (B) an ~[010] polyhedral view with hydrogen bonds as dashed lines; red polyhedra = Ag-centered and blue polyhedra = ReO$_4$. 
Figure 3.8. (A) A single ‘AgReO₄’ layer of Ag(bpy)ReO₄ (8) with 6³ hexagonal nets and all symmetry-unique atom types labeled, and (B) ~[010] polyhedral view of its interpenetrating structure; Red polyhedra = Ag-centered and blue polyhedra = ReO₄.

Figure 3.9. (A) Simplified view of a single diamond-type Ag(dpa)₂⁺ network, upper, and the six-fold interpenetration of the same diamond-type net in Ag(dpa)₂ReO₄ (9), lower. Each node represents a Ag atom. (B) An ~[100] polyhedral view of 9, with red polyhedra = Ag-centered tetrahedra and blue polyhedra = ReO₄.
Figure 3.10. (A) A plot of the optical absorption coefficients, $\alpha$ (cm$^{-1}$) versus wavelength (nm), and (B) a plot of $(\alpha \nu)^2$ vs. $\nu$ for hybrids 1–9, 10 (AgReO$_4$(pyz)), and 11 (AgReO$_4$).
Figure 3.11. XPS valence-band spectra of hybrids 1–9, 10 (AgReO₄(pyz)) and 11 (AgReO₄), ordered according to decreasing binding energies.
Figure 3.12. Thermogravimetric analyses (TGA) of hybrids 1–9, plotted as weight (%) versus temperature (°C).
Supporting Information

Ligand-Based Modification of the Structures and Optical Properties of New Silver(I)-Rhenate(VII) Hybrid Oxide/Organic Solids

Haisheng Lin, Xiaomeng Wu and Paul A. Maggard

Figure 3.S1. Powder X-ray diffraction patterns for compounds 1–9, simulated (bottom) and as-synthesized (top).
Figure 3.S2. Powder X-ray diffraction patterns for the TGA residuals of compounds 1–9 and the simulated patterns of pure-phase ReO₂, Ag and AgReO₄.
Figure 3.S3. The XPS spectra of C 1s of compound 1–10.
PART 2. COPPER(I)-RHENATE(VII) HYBRIDS
CHAPTER 4

COPPER(I)-RHENATE HYBRIDS: SYNTHESIS, STRUCTURES AND OPTICAL PROPERTIES

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Abstract

The new copper(I) rhenates, CuReO$_4$(pyz) (I) and Cu$_3$ReO$_4$($q6c$)$_2$ (II) (pyz = pyrazine; $q6c$ = quinoline-6-carboxylate), were synthesized by hydrothermal methods at 140-150 °C, and their structures determined via single-crystal X-ray diffraction (I, $P2_1/n$, No. 14, Z = 4, $a = 7.972(1)$ Å, $b = 11.928(2)$ Å, $c = 8.430(1)$ Å, $\beta = 102.161(2)^\circ$; II, $P2_1$, No. 4, Z = 2, $a = 8.253(2)$ Å, $b = 6.841(2)$ Å, $c = 18.256(6)$ Å, $\beta = 101.37(2)^\circ$) and characterized by thermogravimetric analyses and UV-vis diffuse reflectance. The structure of I contains ‘CuReO$_4$’ layers that are pillared through bridging pyrazine ligands via the Cu sites, while the structure of II is polar and contains chains of ‘Cu$_2$ReO$_4$’ that are condensed into layers by coordination to linear ‘Cu($q6c$)$_2$’ bridges between the chains. In contrast to air-sensitive CuReO$_4$, both hybrid analogues are stable in air owing to a stabilization of the Cu$^+$ oxidation state by N-donating ligands, but decompose upon heating with the removal of the organic
ligands, which for I yields crystalline CuReO$_4$. UV-vis diffuse reflectance measurements and electronic structure calculations on all three copper perrhenates, I, II, and CuReO$_4$, show that each exhibits an optical band gap of $\sim$2.1-2.2 eV, with conduction and valence band levels that are primarily derived from the Re d$^0$ and Cu d$^{10}$ orbitals, respectively, and mixed with O p-orbital contributions. In contrast to the silver rhenates, which have relatively lower energy Ag d$^{10}$ orbitals, the inclusion of the organic ligands into the structures has only a very minor effect ($\sim$0.1 eV) on the band gap size. The optical absorptions, in combination with the air-stable open-framework layered structures, illustrate that heterometallic Cu$^{1+}$/Re$^{7+}$ oxides can be promising candidates for investigating in visible-light photocatalytic reactions.

**Introduction**

Growing investigations into the chemical compatibility and structural synergy between metal-oxide and organic species during hydrothermal reactions have led to many new strategies for targeting highly functionalized metal-oxide/organic solids. For example, the selective coordination of an organic ligand, in combination with both an early and late transition metal, can be utilized to achieve new types of layered structures, such as in the multilayered M(pyz)V$_4$O$_{10}$ (M = Co, Ni, Zn; pyz = pyrazine)$^1$ or in the pillared M(pzc)$_2$(H$_2$O)$_x$AgReO$_4$ (M = Cu, Ni, Co; pzc = pyrazine-2-carboxylate) series and related solids.$^2-6$ Another recently emerging area is the use of heterometallic solids in photocatalyst systems, wherein a solid-state compound absorbs light and uses it to catalytically drive reactions at its surfaces for the production of hydrogen and oxygen from water, for example.

Current metal-oxide photocatalysts, such as TiO$_2$ or NaTaO$_3$, absorb only ultraviolet
light, owing to their large band gaps. However, the incorporation of both an early and late transition metal can result in a decreased band gap size and the absorption of lower-energy visible light. Recent reported examples include \( \text{Ag}_3\text{VO}_4 \), \( \text{Ag}_2\text{MoO}_4 \), and \( \text{AgTaO}_3 \) where each contains both a late (Ag\(^{+}\)) and early (V\(^{5+}\), Mo\(^{6+}\), Ta\(^{5+}\)) transition metal. These absorb visible light owing to an \(-0.5\) eV decrease of their band gap sizes, relative to the alkali metal versions, that arises from the Ag 4d\(^{10}\) orbitals mixing into and raising the valence band energies. As an initial step to expand this chemistry to more diverse metal-oxide/organic formats, we have described in chapter 2 and 3 on the syntheses and optical properties of \( \text{AgReO}_4\)(L) (L = organic ligands) and \( \text{Ag}_3\text{Mo}_2\text{O}_4\text{F}_7\)(pyz)_3, which exhibit decreased band gap sizes compared to the inorganic versions. Further, these types of metal-oxide/organics can reversibly absorb water, e.g., \( \text{M}(\text{pzc})_2(\text{H}_2\text{O})\text{AgReO}_4 \) (M = Co, Ni), and/or be thermally converted to the inorganic version, e.g., \( \text{AgReO}_4 \), by heating to remove the organic components.

However, despite the rising interest in heterometallics for visible-light band gap absorption, there are little to no previous investigations of heterometallic-oxide photocatalysts containing Cu\(^+\) (d\(^{10}\)), even though the substitution of Cu\(^+\) for Ag\(^+\) should be expected (from ionization energies; 20.29 vs 21.48 eV, respectively) to shift their optical absorption even more strongly into the visible region. Typical solid state synthetic approaches have provided a relatively limited number of compounds and structural diversity in which to investigate the properties of Cu\(^+\)/(early transition metal) oxide systems, including, for example, \( \text{CuNb}_2\text{O}_8 \) and \( \text{CuNbO}_3 \), \( \text{Cu}_2\text{WO}_4 \), and \( \text{CuReO}_4 \) within the respective Cu\(^7\)/Nb\(^{5+}\), Cu\(^7\)/W\(^{6+}\), Cu\(^7\)/Re\(^{7+}\) systems. Further, the \( \text{CuReO}_4 \) compound decomposes in air to
Cu\(^{II}\)(ReO\(_4\))\(_2\):4H\(_2\)O, Cu\(_2\)O, and Cu(s). Hydrothermal synthesis of metal-oxide/organic analogues of these solids has the potential to dramatically expand this area of chemistry, such as we have demonstrated for the AgReO\(_4\)-based solids in chapter 2 and 3, and can also enable new investigations into the effects of open metal sites and microporosity,\(^4\) chirality,\(^2\) and organic functionality on their optical properties and photocatalytic behavior. Previously, our group has reported on two previous copper-rhenate hybrids, [Cu\(_2\)(pzc)\(_2\)(H\(_2\)O)\(_2\)ReO\(_4\)] and [Cu(pzc)(H\(_2\)O)ReO\(_4\)]\(_2\)H\(_2\)O,\(^\text{16}\) both of which contain Cu\(^{2+}\), as opposed to only Cu\(^{+}\) ions, and their optical properties and electronic structures were not investigated.

Discussed in this chapter are the hydrothermal syntheses of two new Cu\(^{+}\)-rhenate hybrid structures, CuReO\(_4\)(pyz) (I) and Cu\(_3\)ReO\(_4\)(q6c)\(_2\) (II) (pyz = pyrazine; q6c = quinoline-6-carboxylate) and that contain pyrazine-pillared ‘CuReO\(_4\)’ layers in I and chains of ‘Cu\(_2\)ReO\(_4\)’ that are connected into layers via ‘Cu(q6c)\(_2\)’ bridges in II. The latter hybrid is analyzed with respect to several interesting structural features, including a polar symmetry group from alignment of the ReO\(_4\) tetrahedra, and a triangular arrangement of three Cu\(^{+}\) ions with a short Cu-Cu distance. The optical properties of the copper-rhenate hybrids are analyzed with respect to their calculated electronic structures and to the isoelectronic silver-rhenate hybrid systems in order to discern the origin of their smaller band gap sizes and to evaluate their potential in photocatalytic reaction systems.

**Experimental Section**

**Materials.** Cu\(_2\)O (99% metal basis, Alfa Aesar), Re\(_2\)O\(_7\) (99.9+%, Alfa Aesar), pyrazine (99+%, Aldrich), and quinoline-6-carboxylic acid (98%, Alfa Aesar) were used as received. A reagent amount of deionized water was also used in each of the reactions, as well as used
for the backfill into the hydrothermal reaction vessel.

**Synthesis of CuReO_4(pyz) (I).** The synthesis was performed by adding weighed amounts of pyrazine (35.2 mg, 0.44 mmol), Cu_2O (31.5 mg, 0.22 mmol), Re_2O_7 (106.6 mg, 0.22 mmol), and H_2O (0.32 g, 17.6 mmol), at a 1:1:1:40 (pyz/Cu/Re/H_2O) molar ratio, into a 3”× 4” FEP Teflon pouch that was subsequently heat sealed. Next, the pouch was placed inside a 125 mL Teflon-lined stainless steel reaction vessel that was backfilled with ~40 mL of deionized water before closing. The reaction vessel was placed inside a convection oven and heated to 150 °C for 3 days, followed by slow cooling to room temperature at a rate of 6 °C h\(^{-1}\). Faster cooling rates result in smaller and lower-quality crystals. After cooling, the products were immediately filtered and gave orange-colored brick shaped crystals in high purity and in ~75% yield based on Cu.

**Synthesis of Cu_3ReO_4(q6c)_2 (II).** Weighed amounts of quinoline-6-carboxylic acid (34.6 mg, 0.20 mmol), Cu_2O (43.2 mg, 0.30 mmol), Re_2O_7 (96.8 mg, 0.20 mmol), and H_2O (0.27 g, 15 mmol), in a 1:3:2:75 (q6c/Cu/Re/H_2O) molar ratio, were mixed and heat sealed inside a 3”× 4” FEP Teflon pouch. Next, the pouch was loaded into Teflon-lined stainless steel reaction, as before, and heated inside a convection oven to 140 °C for 24 h, and then slow cooled to room temperature at a rate of 6 °C h\(^{-1}\). Brown block-shaped crystals were obtained as the primary product after filtering, with a few big gray-green tabular powders as a side product. The large brown crystals were easily manually separated and weighed to give a yield of ~36% based on Cu. The low yields likely result from the oxidation of Cu (green side products) and/or the decomposition of the organic ligand. The manually extracted crystals were also used in subsequent physical property measurements.
**Structure Determination.** An orange single crystal of dimensions 0.10 mm × 0.11 mm × 0.42 mm for I was selected for data collection on a Bruker-Nonius CCD diffractometer operating at a temperature of 193 K and using graphite-monochromatized Mo Kα1 radiation (λ = 0.71073 Å). The unit cell parameters were determined with the Bruker SMART program using all observed reflections within a range of 7.92° < 2θ < 60.92°, which totaled 5984 reflections, of which 1699 were unique and observed (F > 1σF). The unit cell was determined to be monoclinic with a = 7.972(1) Å, b = 11.928(2) Å, c = 8.430(1) Å, and β = 102.161(2)°. The data reduction was performed using the SAINT program, and an absorption correction was applied using the SADABS program. The structure was solved in the monoclinic space group P21/n (No.14) and refined using SHELXTL-97. Hydrogen atoms on the pyrazine rings were refined in idealized positions at a C–H distance of 0.95 Å. The final anisotropic structure refinement converged at R1/wR2 = 0.056/0.152, with a data/variable ratio of ~15:1. A secondary extinction coefficient was also included in the final cycles of refinement.

A brown single crystal of II was mounted for data collection on a Bruker SMART APEX CCD diffractometer as before. The unit cell parameters were determined using all observed reflections in the range of 4.56° < 2θ < 57.68°, which totaled 9465 reflections, of which 4614 were unique and observed (F > 1σF). The unit cell was determined to be monoclinic with a = 8.253(2) Å, b = 6.841(2) Å, c = 18.256(6) Å, and β = 101.37(2)°. The structure was solved and refined using SHELXTL-97 in the monoclinic space group P21 (No. 4), and the resultant structure solution was checked for additional symmetry elements.
using the program PLATON. Hydrogen atoms on the quinoline-6-carboxylic ligands were refined to ride on idealized positions around the carbon atoms in the ring. The Flack parameter refined to 0.633(8) and is indicative of racemic twinning which can occur in acentric single crystals. The final anisotropic structure refinement converged at $R_1/wR_2 = 0.0301/0.0798$, at a data/variable ratio of ~15:1.

Selected data collection and X-ray refinement parameters are listed in Table 4.1 for each of the respective structures of I and II. The atomic coordinates and isotropic-equivalent displacement parameters for each are given in Tables 4.2 and 4.3. The closest interatomic distances and bond angles are listed in Tables 4.4 and 4.5.

**Thermogravimetric Analyses.** Weighed samples of 24.86 mg of I and 5.08 mg of II were loaded onto Pt pans, equilibrated and tared at room temperature, and heated at a rate of 5 °C min$^{-1}$ for I and 1 °C min$^{-1}$ for II to 400 °C under flowing nitrogen on a TA Instruments TGA Q50.

**Optical Property Characterization.** The UV-vis diffuse reflectance spectra were measured on a Cary 300 spectrophotometer equipped with an integrating sphere. Approximately 50 mg of powder of each sample was mounted onto a fused-silica holder and placed along the external window. A pressed polytetrafluoro ethylene powder was used as a reference, and the data were plotted as the remission function $F(R_\infty) = (1 - R_\infty)^2/(2R_\infty)$, where $R$ is diffuse reflectance based on the Kubelka-Monk theory of diffuse reflectance.

**Electronic Band Structure Calculations.** Extended Hückel electronic structure calculations were carried out within the tight binding approximation using the CAESAR2 program, using the full structures of I and II at 960 $k$-points spread over the irreducible
wedge. The internal double-ζ basis sets were selected for the atomic orbital parameters, and the atomic coordinates and lattice dimensions were imported from their respective crystal structures. Molecular orbital pictures were calculated using local structural fragments and analyzed and plotted using the associated SAMOA program and subroutines.²³

Results and Discussion.

Structures. The structure of I, CuReO₄(py), is comprised of ‘CuReO₄’ layers that are cross-linked by pyrazine ligands and separated at a shortest interlayer distance of ~2.78 Å, shown in Figure 4.1(left). The ‘CuReO₄’ sheets thereby stack into a three-dimensional pillared-layered structure via bonding of the pyrazine ligands to the Cu⁺ ions in separate layers. Selected interatomic distances and angles are listed in Tables 4.4 and 4.5, and a structural view perpendicular to a single layer is drawn in Figure 4.1(right). Each Cu⁺ is approximately five coordinate, shown in Figure 4.1, with two Cu–N (1.929(5) and 1.940(5) Å) and one short and two long Cu–O (2.164(6), 2.582(6), and 2.688(6) Å) bonds in a highly distorted trigonal-bipyramidal coordination geometry, e.g., CuN₂O₃. The axial sites are occupied by the oxygen groups from two different ReO₄ tetrahedra, while the equatorial positions are coordinated by one oxygen group from ReO₄ and two nitrogen groups from the pyrazine ligands located above and below the layer. Each ReO₄ tetrahedron serves as a bridge between two Cu⁺ sites within the layer and dimerizes the Cu⁺ polyhedra through a single shared edge to give local Cu₂(pyz)₄(ReO₄)₄ units. The Cu1–Cu1 dimer is at 3.6587(4) Å. The ReO₄ tetrahedron is relatively regular, with Re–O distances that span 1.702(7)–1.754(6) Å and O–Re–O bond angles of 108.7(4)–111.3(4)°, as known for previous structures containing the perrhenate anion.²⁻⁴
Heterometallic rhenates/organics often exhibit similar local structural fragments as compared with condensed (non-organic) rhenates, and which help reveal the recurring bonding patterns that assemble from solution. For example, described in chapter 2, AgReO$_4$(pyz) is constructed from layers that share a strong structural similarity to layers in the condensed AgReO$_4$, and which are also present in the M(pzc)$_2$(H$_2$O)$_x$AgReO$_4$ (M = Co, Ni, Cu) series. By contrast, the isoelectronic ‘CuReO$_4$’ layers in I are dissimilar to any local structural fragments of the recently reported and chiral CuReO$_4$. The CuReO$_4$ solid is constructed from helical chains of tetrahedrally coordinated Cu and Re, e.g., MO$_4$, and that condense via corner-sharing into 4-, 6-, 8-, and 10-membered rings. In I, the local Cu environments are far from tetrahedral, as additional bonding interactions to the pyrazine ligands lead to a higher overall coordination number but a lower dimensionality of the oxide network. Also, edge-shared dimer motifs arise from a different bridging mode of the ReO$_4$ groups. These structural differences likely suppress the interconversion of the two solids at low temperatures (see below) but which is possible between AgReO$_4$ and AgReO$_4$(pyz).

The dark-brown crystals of II, Cu$_3$ReO$_4$(q6c)$_2$, exhibit a unique layer structure comprised of undulating [Cu$_3$ReO$_4$(q6c)$_2$]$_{\infty}$ layers that stack with an offset of 1/2(a + c), shown in Figure 4.2(A). The shortest interlayer bonding interactions are the C−H⋯O hydrogen bonds and the Cu−Cu near neighbors, labeled with solid and dashed lines in Figure 4.3. Selected interatomic distances and angles are given in Tables 4.4 and 4.5, respectively. The bonding arrangement within an individual [Cu$_3$ReO$_4$(q6c)$_2$]$_{\infty}$ layers, shown in Figure 5.2, includes chains of ‘Cu$_2$ReO$_4$’ that are interconnected into layers via the bridging carboxylate groups of ‘Cu(q6c)$_2$’ units. Thus, there are two types of Cu coordination environments. One
type occurs in the ‘Cu$_2$ReO$_4$’ chains (Cu1 and Cu2) as Cu–Cu dimers that are edge-bridged by two carboxylate groups at Cu–O distances of 1.893(5)–1.919(4) Å, and coordinated by two ReO$_4$ groups at Cu–O distances of 2.206(4) and 2.251(4) Å. The dimer also exhibits a very short Cu–Cu distance of 2.531(1) Å, an interesting feature that has been found previously in other similar Cu$^+$–Cu$^+$ carboxylate bridged dimers. The existence of Cu$^+$–Cu$^+$ (d$^{10}$–d$^{10}$) bonding interactions, or ‘cuprophilicity’, for distances as short as ~2.45 Å in Cu$_2$(hpp)$_2$ is highly controversial despite investigations into several known cases. The second type of Cu coordination environment, Cu3, occurs in the bridging ‘Cu(q6c)$_2$’ units, where Cu is coordinated in a nearly linear fashion by two nitrogen groups from the two quinoline-6-carboxylate ligands at Cu–N distances of 1.893(5) Å and 1.897(5) Å with a N1-Cu3-N2 angle of 177.9(2)°. The next closest neighbors to Cu3 are at a much farther distance and are in the adjacent layer to the dimerized Cu atoms at ~3.09–3.10 Å and to ligand oxide groups at >3.15 Å.

Shown in Figure 4.2, the tetrahedral ReO$_4$ groups are aligned in a polar fashion down the $b$-axis on one side of the [Cu$_3$ReO$_4$(q6c)$_2$]$_\infty$ layers and have nearly regular geometries with Re–O distances of 1.721(4)–1.735(4) Å and O–Re–O angles of 108.1–111.7°. Two of the O vertices are bonded to Cu1 and Cu2 within the ‘Cu$_2$ReO$_4$’ chains, while the other two O vertices form C–H···O hydrogen bonds to the carboxylate groups of the ligands in the adjacent layer. The C···O and H···O distances in the hydrogen bonds ($d_{C\cdot\cdotO} = 3.169, 3.188$ Å; $d_{H\cdot\cdotO} = 2.315, 2.351$ Å) are slightly shorter than the average distances (3.540, 2.553 Å) of reported C–H···O hydrogen bonds.
Thermal Properties. The thermal stability and the removal of organic ligands from I and II were investigated by heating each sample under flowing N₂ gas. It is notable that both solids are stable in air, while the ‘organic-free’ CuReO₄ is unstable in air and slowly decomposes to Cu(II)(ReO₄)₂·4H₂O, Cu₂O, and Cu(s).¹⁵ The equilibrium governing the relative stability of Cu⁺/Cu²⁺ oxidation states is known to depend on the types of ligands involved, with softer ligands (more covalent; CN⁻, I⁻) stabilizing Cu⁺ and harder ligands (more ionic; ClO₄⁻) showing a greater affinity for Cu²⁺.²⁸ Thus, the additional covalent bonding provided by the softer N-donating ligands helps to more strongly stabilize the Cu⁺ oxidation state and keeps the hybrid compounds from decomposing in air. Thermogravimetric analysis (TGA), plotted in Figure 4.3, indicates that upon heating the organic ligands are removed/decomposed beginning at temperatures of ~190 °C for I and ~290 °C for II. The higher decomposition temperature of II likely owes to the presence of more strongly bonded carboxylate groups, see for example AgReO₄(pyz) vs M(pzC)₂(H₂O)₂AgReO₄.³⁴ The TGA of I also exhibits two weight-loss steps, one of 9.4% between 190 and 275 °C, and another of 9.6% between 275 and 400 °C. The total weight loss of 19% matches well with that expected from the removal of all pyrazine ligands (theoretical weight loss = 20%). The powder X-ray diffraction (PXRD) of the orange-colored residue from the first weight-loss step indicates an unidentified crystalline structure. The PXRD data of the final brown residue after the second weight loss was confirmed to be CuReO₄, with some additional small diffraction peaks owing to Cu(II)(ReO₄)₂ because of exposure of the product to air for a short time. The TGA of II revealed a single weight loss step of ~35% by 400 °C, indicating only an incomplete removal of the ligands (theoretical weight loss = 44%), and which continues slowly at higher
temperatures. The final residue was an amorphous black material that was not characterized.

**Optical Properties and Electronic Structure Calculations.** Heterometallic oxides that contain both a late (Ag\(^{+}\)) and early (V\(^{5+}\), Ta\(^{5+}\), Mo\(^{6+}\)) transition metal, with d\(^{10}\) and d\(^{0}\) electron configurations respectively, have been investigated for their absorption of visible light (\(E_g \approx 2.2\)–3.0 eV) and ability to drive photocatalytic reactions.\(^9\)–\(^11\) In order to analyze the influence of Cu\(^{+}\) on the optical absorption energies, the UV-vis diffuse reflectance spectra of \(\text{I}\) and \(\text{II}\) were measured, shown in Figure 4.4. Both exhibited a strong optical absorption in the visible region, with optical band gaps of \(~2.23\) and \(~2.20\) eV for \(\text{I}\) and \(\text{II}\), respectively, as calculated from the onset of their absorption edges. These band gap sizes are significantly smaller than in AgReO\(_4\) (3.7 eV) or AgReO\(_4\)(pyz) (2.9 eV),\(^3\) arising from the replacement of lower-energy d orbitals of Ag\(^{+}\) for the higher-energy d orbitals of Cu\(^{+}\). Thus, a much larger fraction of visible-light is absorbed by these Cu\(^{+}\)-containing heterometallic oxides.

The electronic structures of \(\text{I}\) and \(\text{II}\) were calculated on the basis of the Extended Hückel approach, both in order to evaluate the atomic-orbital contributions to the valence and conduction bands and to analyze the factors that influence the sizes of their optical band gaps. Contour maps of the electron density of the calculated HOMO and LUMO for local structure fragments of \(\text{I, II,}\) and CuReO\(_4\) are shown in Figure 4.5. Also, shown in Figure 4.6 are the total densities of states (DOS) overlaid with the projected partial densities of states (PDOS) for each element. In all three structures, the lowest unoccupied orbitals in the conduction band were confirmed to derive from the Re 5d and O 2p orbitals, as seen in the PDOS in Figure 4.6 and in the local orbital pictures in Figure 4.5. The highest occupied orbitals of all three are fairly similar and are formed mainly from the Cu 3d, N 2p, and O 2p orbitals.
However, the band gap of II is calculated to be slightly smaller than that of I and contains no contributions from the N 2p orbitals in its highest-energy valence band levels. Thus, the optical excitation from the valence to the conduction band can be viewed as a metal-to-metal charge transfer between Cu\(^{+}(d^{10})\) and Re\(^{7+}(d^{0})\), with moderate contributions from the ligand-based orbitals.

As the measured optical band gaps for I and II are a relatively constant ~2.2 eV, the contribution and effect of the overall structures and organic ligands to the relevant valence and conduction band levels appear minimal (≤ 0.1eV). Diffuse reflectance spectra taken on the TGA residuals after removal of 50% of the pyrazine ligands in I, i.e., CuReO\(_4\)(pyz)\(_{0.5}\), and after the complete removal of the ligand to give crystalline CuReO\(_4\), gave optical band gaps of 2.20 and 2.10 eV, respectively. This trend confirms the band gap size is effected only slightly by the removal of pyrazine, causing it to decrease slightly. By comparison, the loss of pyrazine ligands from AgReO\(_4\)(pyz) to give AgReO\(_4\) causes a dramatic increase in the band gap from 2.91 to 3.71 eV.\(^7\) This arises because the pyrazine orbitals mix into the valence bands at energies higher than the Ag 4d\(^{10}\) electrons. For I, however, the pyrazine orbitals are lower in energy than the Cu 3d orbitals which comprise the valence band, and therefore the ligand orbitals have a smaller effect on the magnitude of the band gap size.

The positions of the conduction and valence bands, with respect to relevant redox couples, are also of significant importance in photocatalytic reactions. Band gap trends in these and related heterometallic oxides suggest that Re and Cu d orbitals straddle the redox potentials for the oxidation and reduction of water, and will be discussed below. Initial photocatalysis testing of these solids, however, including the oxidation of methanol or the reduction of Ag\(^{+}\)
over their surfaces, does not show any detectable activity. Kinetic factors likely begin to play a more dominant role for smaller band gap sizes and thus requires a closer analysis of the local coordination sites, as well as the potential mechanisms of electron transfer. However, the optical properties and electronic structures of these solids illustrate the high potential for Cu\(^{+}\)-containing heterometallics for the discovery of active photocatalysts with smaller visible-light band gaps.

**Conclusions**

New copper(I) rhenate hybrids, CuReO\(_4\)(pyz) (I) and Cu\(_3\)ReO\(_4\)(q6c)\(_2\) (II), have been synthesized hydrothermally and feature ‘CuReO\(_4\)’ layers and ‘Cu\(_2\)ReO\(_4\)’ chains, respectively, and that are bridged by pyrazine and ‘Cu(q6c)\(_2\)’ units into 3D and 2D structures. The structure of II has a polar symmetry group from the alignment of ReO\(_4\) between the layers and also contains a short Cu-Cu distance from bonding to the bridging carboxylate groups on the ligands. Both hybrids are stable in air but decompose upon heating with the removal of the organic ligands, which for I yields crystalline CuReO\(_4\). Both exhibit relatively low-energy optical band gaps of \(\sim 2.2\) eV, compared to \(\sim 2.9\) eV for that of AgReO\(_4\)(pyz), that arise from the higher-energy d orbitals of Cu\(^{+}\) compared to Ag\(^{+}\). Electronic structure calculations confirm the valence and conduction bands derive primarily from the Cu d\(^{10}\) and Re d\(^0\) orbitals, respectively. Further synthetic studies are in progress in the heterometallic Cu\(^{7+}\)/Re\(^{7+}\) system in order to better probe the effects of local structure on the optical band gaps and potential photocatalysis mechanisms.
Acknowledgment

P.M. acknowledges support from the Beckman Foundation as a Beckman Young Investigator and from the American Chemical Society Petroleum Research Fund (40963-G10).

Supporting Information Available

Crystallographic data in CIF format, and the PXRD and UV-vis diffuse reflectance of the TGA residues of I and II. This material is available free of charge via the Internet at http://pubs.acs.org.

References


Table 4.1: Selected Crystal and Refinement Data for CuReO₄(py2)(I) and Cu₃ReO₄(q6c)₂(II).

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<td>0.0301,0.0798</td>
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\(^a\)R₁ = \(\sum|F_o| - |F_c|/\sum|F_o|\), \(wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2}\) \(^1/2\), w = \(σ_F^{-2}\)
Table 4.2 Selected Atomic Coordinates and Equivalent Isotopic Displacement Parameters (Å²) for CuReO₄(py) (I).

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<thead>
<tr>
<th>Atom</th>
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<th>z</th>
<th>U(eq)b</th>
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</thead>
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a All atoms are located on a 4e Wyckoff site. b U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 4.3 Selected Atomic Coordinates and Equivalent Isotopic Displacement Parameters (Å²) for Cu₃ReO₄(q6c)₂ (II).

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*a All atoms are located on a 4e Wyckoff site. b U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.
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<th>Distance(Å)</th>
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Table 4.5 Selected Interatomic angles (deg) in I and II.

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Figure 4.1. Left: ~[010] polyhedral view of the CuReO$_4$(pyrazine) (I) structure with the unit cell outlined. Right: structure of a single ‘CuReO$_4$’ layer with selected atoms labeled. Red polyhedra = Cu-centered coordination environments, blue polyhedra = ReO$_4$. All H atoms are omitted for clarity.

Figure 4.2. (A) Structural view down the metal-oxide/organic layers of Cu$_3$ReO$_4$(q6c)$_2$ (II); The dashed lines mark the shortest Cu–Cu and C–H…O hydrogen bond distances between layers. (B) ~[010] structural view drawn perpendicular to a single layer of II with the shortest Cu–Cu distance and symmetry unique atom types labeled.
Figure 4.3. Thermogravimetric analysis (TGA) of I and II, plotted as weight (%) versus temperature (°C).

Figure 4.4. UV-vis diffuse reflectance spectra of I and II, plotted as a function of the photon energy in eV.
Figure 4.5. Electron density contour maps of the calculated LUMO and HOMO of local structural fragments in CuReO₄(py2) (I), Cu₃ReO₄(q6c)₂ (II), and CuReO₄.
Figure 4.6. Calculated total and projected densities-of-states for CuReO$_4$(pyz) (I), Cu$_3$ReO$_4$(q6c)$_2$ (II), and CuReO$_4$. 
Supporting Information
Copper(I)-Rhenate Hybrids: Syntheses, Structures and Optical Properties
Haisheng Lin and Paul A. Maggard

Figure 4.S1. A plot of UV-vis diffuse reflectance spectra, F(R) vs. photon energy, (a) the residual of the first step TGA of II, (b) the residual CuReO₄ of the final TGA of II.

Figure 4.S2. Powder X-ray diffraction patterns for (a) CuReO₄ (theoretical), (b) TGA residue after second weight loss step from I, (c) TGA residue after first weight loss step from I, and (d) freshly prepared CuReO₄(pyz).
CHAPTER 5
LIGAND-MEDIATED INTERCONVERSION OF MULTIPLY-INTERPENETRATING FRAMEWORKS IN Cu/I/Re/VII-OXIDE HYBRIDS

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Abstract

Two new copper(I)-rhenate(VII) hybrid solids, Cu(bpy)ReO$_4$ (I) and Cu(bpy)$_2$ReO$_4$·0.5H$_2$O (II) (bpy = 4,4’-bipyridine), with 2-fold and 4-fold interpenetrating networks, respectively, were prepared from hydrothermal reactions, and their structures characterized by single-crystal X-ray diffraction [I, *Pbca* (No. 61), Z = 8, $a$ = 10.8513(3) Å, $b$ = 12.9419(4) Å, $c$ = 15.6976(5) Å; II, *P-1* (No. 2), Z = 2, $a$ = 11.8190(4) Å, $b$ = 12.6741(4) Å, $c$ = 13.7585(5) Å, $\alpha$ = 85.8653(13)$^\circ$, $\beta$ = 81.6197(13)$^\circ$, $\gamma$ = 84.0945(11)$^\circ$]. The structure of I contains $6^3$ nets of neutral CuReO$_4$ layers that are pillared via bpy ligands on the Cu sites {$CuO_3N_2$} to yield a 2-fold interpenetrating pillared-layered network. Conversely, the structure of II consists of a 4-fold interpenetrating diamond-type network with tetrahedral {$CuN_4$} coordination nodes that are bridged by bpy ligands, with both H$_2$O and ReO$_4$ within...
the pores. A surprising reversible structural interconversion between these two interpenetrating structures is possible via the insertion and removal of a single bpy ligand and 1/2H$_2$O per copper atom. The structural interconversion is accompanied by a change in color from yellow to red for I and II, respectively. Measured UV-vis diffuse reflectance spectra exhibit a significant red-shift in the absorption edge of ~0.3 eV, with the optical bandgap size decreasing from ~2.5 eV to ~2.2 eV for I and II, respectively. X-ray photoelectron spectra and electronic structure calculations indicate that the valence band derived from the Cu 3d and N 2p orbitals in II are pushed higher in energy compared to those in I because of the coordination of the additional bpy ligand. There is a much smaller change in the energy of the conduction band that is derived from the Re 5d orbitals. These results demonstrate that the ligand-mediated structural transformations of (d$^0$/d$^{10}$)-hybrid solids represent a new and convenient low-temperature approach to modulate their optical bandgap sizes toward the visible wavelengths for use with solar energy.

**Introduction**

Synthetic strategies that aim at the formation of specific solid-state structures have been intensely pursued and aided by the assimilation of the rich diversity and versatility of organic ligands into inorganic metal-oxides, chalcogenides and other chemical systems.\(^1\) The growing family of metal-oxide/organic hybrids includes many members that have been explored for potential applications in areas such as small-molecule absorption, ion-exchange, conductivity, magnetism and catalysis.\(^2,3\) As described above, the synthetic strategies to target new hybrid solids typically emphasize the use of the local metal-coordination
geometry, as well as the geometry and size of the ligand, to help control the structure type that forms.\textsuperscript{4,5} For example, our group has utilized hydrothermal synthetic techniques to extend this to heterometallic-oxide/organic hybrids, such as reported in the layered rhenates $\text{M(pzc)}_2(\text{H}_2\text{O})_x\text{AgReO}_4$ ($\text{M} = \text{Co, Ni, Cu; pzc = pyrazine-2-carboxylate}$)\textsuperscript{6,7} and $\text{MReO}_4(\text{pyz})$ ($\text{M} = \text{Ag, Cu; pyz = pyrazine}$),\textsuperscript{8,9} and also in the layered vanadates $[\text{Ag(L)}]_4\text{V}_4\text{O}_{12+x}\text{H}_2\text{O}$ (L = 4,4′-bipyridine or 1,2-bis(4-pyridyl)-ethane).\textsuperscript{10} The latter vanadates were the first known hybrid solids to have been found to exhibit photocatalytic activity under visible-light irradiation (chapter 4). Thus, in this chapter, the research work into hybrid solids primarily aims at the ligand-mediated control over the structures of metal oxides, and thus which can serve as a tool for understanding the relationship between hybrid structures and their bandgap sizes and photocatalytic activity.

Currently, an emerging route to obtain small visible-light bandgaps (i.e., $\sim1.5 - 3.0\text{eV}$) is based on incorporating mixed $d^0$ and $d^{10}$ transition-metal combinations within the hybrid solids, and which results in a higher energy valence band consisting of the $d^{10}$ transition metal and/or the ligand-based $\pi$ orbitals.\textsuperscript{10} For example, it has previously been shown in chapter 2 that the absorption edge of $\text{AgReO}_4$ (3.7 eV) is shifted to lower visible-light energies via incorporation of the pyz (= pyrazine) ligand into its structure, as observed in the pillared-structure $\text{Ag(pyz)ReO}_4$ (2.9 eV).\textsuperscript{8} However, much smaller visible-light bandgaps can be obtained by replacing $\text{Ag}^+$ with the $\text{Cu}^+$ in these heterometallic hybrid solids, owing to the relatively higher-energy $d$ orbitals of $\text{Cu}^+$. The $\text{Cu}_3\text{ReO}_4(q6c)_2$ ($\text{q6c} = \text{quinoline-6-carboxylate}$), $\text{Cu(pyz)ReO}_4$, and $\text{Cu(pyz)}_{0.5}\text{ReO}_4$ and $\text{CuReO}_4$ solids each exhibit an optical bandgap size within the narrow range of $\sim2.1–2.2\text{eV}$.\textsuperscript{9} In the $\text{Cu}^+$-containing examples, the
introduction of ligand-based π orbital has a negligible effect on the bandgap size because the higher energy Cu 3d-orbitals primarily form the valence band rather than the ligand-based orbitals. Thus, for CuⅠ/ReⅦ-oxide hybrids, there are no prior examples of using ligand-mediated tuning of the structure to influence the bandgap absorption energy.

The structural flexibility of many types of hybrid solids has enabled investigations into new low-temperature structural transformations arising from the removal or insertion of guest molecules and ligands. These structural transformations have been primarily limited to the guest-exchange abilities of the hybrid structure and to its expansion or collapse, such as in the reversible absorption/desorption of coordinated water molecules in the layered molybdate and rhenate frameworks in \([\text{M}_2(\text{pzc})_2(\text{H}_2\text{O})_x][\text{Mo}_5\text{O}_{16}]\) (M = Co, Ni; pzc = pyrazinecarboxylate) and \(\text{M}(\text{pyz})_2(\text{H}_2\text{O})_x\text{AgReO}_4\) (pyz = pyrazine). Crystal-to-crystal transformations of hybrid solids are also quite limited to small guest molecules (e.g. water and methanol). The structural conversion of a hybrid to a condensed metal-oxide is often possible, such as in the \(\text{MReO}_4(\text{pyz})\) (M = Ag, Cu) hybrids that exhibit layered structures containing ligands that are easily removed (irreversibly) to produce \(\text{MReO}_4\). However, the reversible insertion or removal of organic ligands within hybrid metal-oxide/organic solids is not well explored. By contrast, reversible structural transformations involving the insertion of organic ligands have been found for many solid-state coordination polymers, such as those involving a 1D \(\rightarrow\) 2D or 0D \(\rightarrow\) 2D structural transformations. Thus, we have investigated the use of the longer bridging ligand \(\text{bpy} (= 4,4'\text{-bipyridine})\) in the CuⅠ/ReⅦ-oxide system to prepare new hybrid structures and also investigated the ligand-mediated control over their structures and bandgap sizes.
Herein, in this chapter we investigated and described the hydrothermal syntheses of two new Cu$^1$/Re$^{VII}$-oxide hybrid solids, Cu(bpy)ReO$_4$ (I) and Cu(bpy)$_2$ReO$_4$.0.5H$_2$O (II), and the reversible structural interconversion between them via the insertion or removal of one bpy ligand and solvent water per formula. These hybrids illustrate a unique ligand-mediated structural transformation between multiply interpenetrating frameworks, from a pillared-layered structure that is two-fold interpenetrating in I to a diamond-type framework that is four-fold interpenetrating in II. The accompanying changes in their optical absorption edges are analyzed with respect to their atomic and electronic structures in order to understand the role of the bpy ligand on the structure and bandgap sizes.

**Experimental Section**

**Materials.** All starting materials were purchased commercially and used without further purification: Cu$_2$O (99% metal basis, Alfa Aesar), Cu(CN)$_2$ (99.9%, Alfa Aesar), Re$_2$O$_7$ (99.9+%, Alfa Aesar), and 4,4’-bipyridine (98%, Alfa Aesar). A reagent amount of deionized water was also used in the syntheses.

**Synthesis.** The initial synthesis of Cu(bpy)ReO$_4$ (I) was performed by adding 28.8 mg (0.20 mmol) of Cu$_2$O, 96.8 mg (0.20 mmol) of Re$_2$O$_7$, 62.4 mg (0.40 mmol) of bpy, and 0.40 g (22.2 mmol) of H$_2$O to a FEP Teflon pouch. The pouch was heat-sealed and placed inside a 45-mL Teflon-lined stainless steel reaction vessel which was backfilled with ~15 mL of deionized H$_2$O before closing. The reaction vessel was heated to 150 °C for 72 h inside a convection oven and slowly cooled to room temperature at 6 °C/h. Pale-yellow platelet crystals of I suitable for single-crystal X-ray diffraction were obtained in ~50% yield based
on Cu. However, the highest yields (~85%) and purities were found when reacting 23.1 mg (0.20 mmol) of Cu(CN)$_2$, 96.8 mg (0.20 mmol) of Re$_2$O$_7$, 31.2 mg (0.20 mmol) of bpy, and 0.40 g (22.2 mmol) of H$_2$O at 220 °C for 5 days.

The synthesis of Cu(bpy)$_2$ReO$_4$·0.5H$_2$O (II) was initially discovered by reacting the yellow product crystals of Cu(bpy)ReO$_4$ (II) with additional amounts of bpy ligand (1:1 ratio) in aqueous solution at 100–150 °C for 72 h (yield of ~90%), as shown in Scheme 5.1. The optimum synthetic procedures for the growth of larger red-block crystals of II were similar to that of II described above and using the same starting materials, with the exception of adjusting the Cu(CN)$_2$:bpy ratio to 1:2. The hydrothermal reaction was heated to 220 °C for 5 days with a yield ~95% based on Cu. Each hybrid solid was obtained in high purity (~100%) according to powder X-ray diffraction data and TGA results (see below).

**Crystallographic Structure Determination.** Single-crystal X-ray diffraction data for I and II were collected on a Bruker-Nonius X8 Apex2 CCD diffractometer at a temperature of 173 K using Mo Kα radiation (λ = 0.71073 Å). The samples were mounted on a nylon loop with a small amount of NVH immersion oil. The frame integrations were performed using SAINT program. The resulting raw data were scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using the SADABS program. Both structures were initially found by direct methods using the SIR92 program. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent carbon atoms. Next, the structural model was fit to the data using the full-matrix least-squares method based on F within the LSTSQ program from NRCVAX. The final structural
analyses and refinement details of I and II are summarized in Table 5.1. The interatomic distances and angles for nearest-neighbor atom pairs are listed in Table 5.2.

**Thermogravimetric Analyses (TGA).** Weighed amounts (~20 mg) of each compound were loaded onto Pt pans, equilibrated and tarred at room temperature on a TA Instrument TGA Q50, and the data plotted as the % starting weight versus temperature (°C). The samples were heated to 550 °C or 270 °C at a rate of 5 °C/min under flowing nitrogen gas (40 mL/min). Post-TGA residuals were characterized by powder X-ray diffraction in transmission mode on an Inel XRG 3000 diffractometer fitted with a CPS 120 position sensitive detector and using Cu Kα1 radiation from a sealed tube X-ray source.

**Optical Properties.** The UV-vis diffuse reflectance spectra of each powdered sample were measured on a Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer equipped with an integrating sphere. Roughly 10 mg of each sample was mounted onto a pressed BaSO₄ powder holder and placed along the external window. A pressed BaSO₄ powder was used as a reference, and the data were plotted as the remission function \( F(R_\infty) = (1-R_\infty)^2/(2R_\infty) \), where \( R \) is diffuse reflectance based on the Kubelka-Monk theory of diffuse reflectance.

**X-ray Photoelectron Spectroscopy (XPS).** The XPS spectra of I, II, CuReO₄, and CuReO₄(pyz) were recorded on a RIBER LAS-3000 spectrometer using Mg KR monochromatized radiation (\( h\nu = 1253.6 \) eV). The base pressure of the sample chamber was approximately 1 \( \times 10^{-7} \) Torr. The diameter of the X-ray spot was set at 2-3 mm, and the sample sizes were ~1 cm square. The binding energies of the valence band structures were calibrated by setting the O 1s core-level main peaks to 531.2 eV.
Results and Discussion

Structural Descriptions. Cu(bpy)ReO$_4$ (I). The structure of I, illustrated in Figure 5.1, generally consists of neutral 6$^3$-net layers of ‘CuReO$_4$’ that are bridged to neighboring layers via bpy (bpy = 4,4’-bipyridine) ligands that pillar between the Cu sites. These inorganic layers are comprised of corner-shared ReO$_4$ tetrahedra and {CuO$_3$N$_2$} trigonal bipyramids that alternate and are arranged into a 6$^3$ network, as shown in Figure 5.1B. Each ReO$_4$ tetrahedron is bonded to three different Cu$^+$ atoms in the layer via three O vertices (Cu–O distances of 2.812(4)–3.195(4) Å), with the fourth O vertex oriented either above or below the layer. Each Cu$^+$ atom is also surrounded by three oxide groups from the three separate ReO$_4$ tetrahedra, and also to the nitrogen groups on two bpy ligands oriented above and below each layer at a Cu–N distance of 1.888(5) Å. The symmetry-unique atoms are labeled in Figure 5.1B and the corresponding interatomic distances are tabulated in Table 5.2. All near-neighbor distances are within the same range as observed in other Cu/organic hybrid solids, except for ionic Cu–O distances (>2.8 Å) that are longer than typical covalent bond lengths for copper rhneates. In addition, the calculated bond valence sums ($\Sigma S_{ij}$) for Cu and Re, listed in Table 5.2, are consistent with +1 and +7 oxidation states for each, respectively.

The overall pillared-layered structure of I is roughly similar to that in Ag(bpy)ReO$_4$, with the exception that II has two separate frameworks that are interpenetrating, as shown in Figure 5.1 (C and D). The two interpenetrating frameworks are related by symmetry so that there is only one symmetry-unique layer that stacks down the $a$-axis to generate the full 3D structure. A structural analysis using TOPOS indicates that the interpenetrating framework of I represents a 3D $hms$ topology (class IIa) with (3,5)-connectivity and a 2-nodal (Re, Cu)
net, which is similar to that of silver coordination polymers with hms topology\textsuperscript{20.21}. The total Schl"afli symbol of this net is (6\textsuperscript{3})(6\textsuperscript{8}8), and the long vertex symbol with rings is [6\textsuperscript{6}6\textsuperscript{2}6\textsuperscript{2}6\textsuperscript{2}6\textsuperscript{2}6\textsuperscript{2}6\textsuperscript{2}6\textsuperscript{2}6\textsuperscript{2}6\textsuperscript{2}6\textsuperscript{2}6\textsuperscript{2}] [6\textsuperscript{3}6\textsuperscript{3}6\textsuperscript{3}].

The layer-to-layer distance is set by the length of the bpy ligand at 7.08Å. However, the two pillared-layered frameworks interpenetrate through every open hexagonal face of the 6\textsuperscript{3} ‘CuReO\textsubscript{4}’ net, such as shown for one face in Figure 5.1C. Thus, the layer-to-layer distance between the two interpenetrating nets is set by half the length of the bpy ligand at ~3.54 Å. No pores are present within or between the ‘CuReO\textsubscript{4}’ layers because of the 2-fold interpenetration of the frameworks.

**Cu(bpy)\textsubscript{2}ReO\textsubscript{4}·0.5H\textsubscript{2}O (II)**. The structure of II, shown in Figure 5.2, has a cubic diamond or adamantoid framework (Schl"afli symbol: dia 6\textsuperscript{6}, class IIIa for interpenetration) that is four-fold interpenetrating with perrhenate ReO\textsubscript{4}\textsuperscript{−} anions and uncoordinated water molecules filling the pores. These frameworks are constructed from two symmetry-unique Cu\textsuperscript{+} atoms that are each tetrahedrally coordinated by four bpy ligands, with Cu–N distances of 2.000(3) to 2.073(3) Å. There are four such independent [Cu(bpy)\textsubscript{2}]\textsuperscript{+} diamond-type networks that are interpenetrating, as shown in Figure 5.2B and C. The Cu⋯Cu distances from one framework to the next range from 11.11 to 11.20 Å, and which allows sufficient space for three other frameworks to interpenetrate. However, a notable feature is that the interpenetrating frameworks still leave sufficient pore space to accommodate isolated ReO\textsubscript{4}\textsuperscript{−} anions between the different networks. Each of the four independent diamond-type frameworks contains channels (shortest: ~4.7 × 6.0 Å\textsuperscript{2}) that are oriented parallel to the [001] direction of the four frameworks, shown in Figure 5.2A, and that are filled with ReO\textsubscript{4}\textsuperscript{−} counter-ions and H\textsubscript{2}O molecules. There are two symmetry-unique ReO\textsubscript{4}\textsuperscript{−} tetrahedra with...
Re–O distances ranging from 1.699(4)–1.731(4) Å, listed in Table 5.2. All interatomic distances are consistent with those in previously reported perrhenate hybrids. The calculated bond valence sums ($\Sigma S_{ij}$) for Cu and Re (Table 5.2) are consistent with +1 and +7 oxidation states, respectively.

The amount of bpy ligand used in the reaction has dramatic local and long-range structural consequences on each of the crystal structures. The structure of II is significantly dissimilar to that observed for I in which a twofold-interpenetrating $6^3$ net framework is formed. As the bpy-ligand stoichiometry is increased, the Cu$^+$ sites in II change from a distorted trigonal-bipyramidal $\{\text{CuO}_3\text{N}_2\}$ coordination geometry to a tetrahedral $\{\text{CuN}_4\}$ coordination geometry in I in which the coordinating perrhenate anions are displaced, as shown in Scheme 5.1. The result is a structural conversion of I, containing pillared layers of ‘CuReO$_4$’, to II that has Cu(bpy)$_2$$^+$ diamond networks but no extended inorganic layers. These two structures are related to those of [Cu(bpy)$_{1.5}$](NO$_3$)$_2$·1.25H$_2$O, [Cu(bpy)$_2$](NO$_3$)$_2$ and [Cu(bpy)$_2$](PF$_6$)$_2$. In the latter two structure, the higher bpy content results in four interpenetrating Cu(bpy)$_2$$^+$ diamond-like frameworks, while the former structure contains a trigonal $\{\text{CuN}_3\}$ coordination geometry with six interpenetrating networks. The results described herein indicate that the different structural preferences of these systems are primarily controlled through the bpy-ligand stoichiometry via the resultant changes in the coordination geometry of Cu$^+$.

**Ligand Mediated Interconversion Transformation.** Metal-oxide/organic hybrid solids serve to incorporate the broad structural diversity and functionality of organic ligands into metal oxides, thereby achieving new structural topologies and physical properties. However,
the ligand-mediated control over the metal-oxide structural features is nearly always investigated by reactions involving only the most basic inorganic reagents.\textsuperscript{6-11} Less well explored is the utilization of hybrid solids themselves as intermediates for subsequent reactions yielding more complex structures, such as by incorporating additional ligands in order to modify the chemical composition and structure. The relatively similar chemical compositions for I and II, as well as their open-framework structures, suggested they could be amenable to low-temperature transformation reactions.

The bulk crystalline samples of I and II were characterized by Powder X-Ray Diffraction (PXRD), as shown in Figure 5.3. PXRD data for the hydrothermally-prepared samples, Figure 5.3b and e, were both in excellent agreement with the calculated diffraction patterns from the single-crystal refinement data, Figure 5.3a and d. Next, the interconversion transformation of the yellow crystals of I into the reddish-colored crystals of II was achieved by reacting them with one equivalent of the bpy ligand in aqueous media at 100–150 °C for 1–3 days. A gradual but significant change of color was observed, shown in Scheme 5.1, that finally yielded orangish-red crystals that exhibited the PXRD patterns shown in Figure 5.3c. The PXRD data of this sample matched up very closely to that for the calculated and experimental patterns of II. These data demonstrate that the structure of I can be transformed into the structure of II via the insertion of one bpy ligand into its pillared layered structure and yielding the fourfold-interpenetrating diamond-type topology. The interconversion of multiply-interpenetrating frameworks is previously unknown in hybrid metal-oxide/organic systems, and there is only one such example known for coordination polymers.\textsuperscript{25}
Previous research has shown that ligand removal from hybrid solids can be carried out by heating them to relatively low temperatures of \(~100–300^\circ C\) (chapter 2–5). Most often, the resultant phases are found with the removal of all organic ligands from the structure, thereby generating a new or known condensed metal oxide. Very interestingly, the crystals of II can be converted back into I by heating them to 270 °C for 10–20 minutes, shown in Figure 5.3f. The result is the removal of only one-half of the coordinated bpy ligands (and all water molecules) per formula. The crystal color also changes from red to yellow in the process. These results are significant in that II did not fully collapse into a condensed oxide, but instead transformed to the lower twofold-interpenetrating framework of I.

Thermal Gravimetric Analysis (TGA) was used to follow the entire thermal decomposition pathway of both I and II by heating each sample to 550 °C under flowing N\(_2\) gas. The results of the TGA of I, shown in Figure 5.4, show that the structure is thermally stable to ligand loss at up to \(~300^\circ C\), and which is followed by a large weight loss of \(~44\%\) from \(~300^\circ C\) to 550 °C. This weight loss is significantly greater than that expected for the loss of bpy alone (calc. 33\%). However, previous research on layered vanadates has shown that ligand removal can sometimes proceed by oxidation of the ligand and reduction of the structure via the removal of oxygen.\(^{3e,26}\) A PXRD pattern of the black residue contained both Cu\(_2\)O and unknown rhenium-containing phases, indicating that the fully collapsed structure of I leads to the loss of all bpy ligands and partial loss of \(\sim\frac{3}{4}\) oxygen atoms per formula. By contrast, the TGA result for II showed three distinct weight-loss steps. The first weight loss of \(~1.5\%) occurred at \(~200^\circ C\) and corresponded to the loss of one-half of a water molecule per formula (calc. 1.4\%). The second weight-loss step of \(~23.8\%\) occurred between 200 °C
and 270 °C, and which matches with that expected from the removal of one bpy ligand per formula (calc. 24.6%). Further, the PXRD pattern of the yellow residue after the second weight-loss step was a close match with that of I, analogous to that discussed above when heating II to 270 °C. The data confirm that the loss of the water contained in the pores of II precedes the loss of the bpy ligand and the partial-condensation of the structure to give the yellow crystals of I. The last weight-loss step of ~36% between 300 °C and 550 °C shows the full collapse of the structure with the loss the other bpy ligand and a few oxygen atoms per formula, similar to that already described for I. However, as shown in Scheme 5.1, the reversible interconversion conversion between I and II, involving the insertion and removal one bpy ligand and one-half water molecule per formula, could be cycled back and forth numerous times. Accordingly, the reversible change in framework structures between I and II suggests that the interpenetrating Cu⁺/Re⁷⁺-oxide networks with bpy ligands are quite flexible and dynamic.

**Optical Properties and Electronic Structure Calculations.** Recent research has demonstrated that heterometallic hybrids containing transition metals with d⁰ and d¹⁰ electron configurations can exhibit small bandgap sizes with visible-light absorption that can be used to drive photocatalytic reactions.⁹,¹⁰ Thus, in the synthesis of both I and II the electronic configurations were targeted to be d⁰ for Re⁷⁺ and d¹⁰ for Cu⁺. UV-Vis diffuse reflectance spectra were taken of pure powdered samples of I and II in order to understand the influence of their different structures on their colors and bandgap absorption energies. Shown in Figure 5.5, the optical band gaps of I and II were estimated from the onsets of absorption edges to be ~2.5 eV and ~2.2 eV, respectively. These band gap sizes are significantly smaller than in
the related silver-containing versions of Ag(bpy)ReO₄ (3.5 eV) and Ag(pyrazine)ReO₄ (pyz = pyrazine, 2.9 eV), and which arises from the replacement of the lower-energy d orbitals of Ag⁺ for the higher-energy d orbitals of Cu⁺. However, the bandgap size of I is also ~0.3 eV larger than that of Cu(pyrazine)ReO₄ (2.2 eV). As has been described for the Ag(bpy)ReO₄ and Ag(pyrazine)ReO₄, hybrid solids containing pyrazine ligands typically have a smaller bandgap size owing to its higher energy π orbitals. By contrast, the bandgap size of II is smaller or nearly the same as that of Cu(pyrazine)ReO₄. Further, the XPS spectra of both I and II, shown in Figure 5.6, confirm that the valence orbitals in I are shifted to a higher binding energy by ~0.6 eV compared to that in II. The valence band energy of II is nearly the same as for the condensed CuReO₄, and slightly higher than Cu(pyrazine)ReO₄, and they all also share nearly the same bandgap sizes in the range of ~2.1–2.2 eV.

To understand how the change in bpy composition affects the bandgap size, the electronic structures of I and II were calculated within the Extended Hückel approach. Shown in Figure 5.7 is the calculated electronic Densities of States (DOS) for I and II, and which is overlaid with the partial DOS contribution from each constituent atom type. The electron density contour maps for the LUMO and HOMO of I and II are shown in Figure 5.8. In both structures, the lowest unoccupied orbitals (i.e., the bottom of the conduction band) were mainly formed by the Re 5d and O 2p orbitals (more minimally), as seen in the PDOS in Figure 5.7 and in the local orbital pictures in Figure 5.8. The highest occupied orbitals (i.e., the top of the valence band) consisted of only the Cu 3d and N 2p orbitals in both I and II. The O 2p orbitals were not found to contribute to the valence band of either structures owing to the ionic Cu–O interactions in I (at > 2.8 Å) and to the lack of any close Cu–O
distances in II. Therefore, the optical excitation from the valence to the conduction band in both structures can be viewed as mainly a metal-to-metal charge transfer between Cu$^+$ (3d$^{10}$) and Re$^{7+}$ (5d$^5$), with moderate contributions from the ligand-based orbitals in each case. Considering only the strongly interacting bpy ligand, as the amount of bpy increases from I to II, the Cu environment changes from a linear \{CuN$_2$\} to a tetrahedral \{CuN$_4$\} coordination geometry, respectively. As a result, the Cu d-orbitals in I are split into two sets, with $dz^2$ at the highest energies. In contrast, the d-orbital splitting in II is separated (ideally) into two sets, the $t_2$($d_{xy}$, $d_{yz}$, $d_{xz}$) and $e$ ($dx^2-y^2$, $dz^2$), with the former at the higher energies. Therefore the highest occupied crystal orbitals of I consist of mostly Cu $dz^2$ and N 2p orbitals, while the highest occupied crystal orbitals in II are primarily composed of the $d_{xy}/d_{xz}/d_{yz}$ set and the N 2p orbitals. Thus, the greater Cu-ligand orbital interactions of II result in its higher-energy crystal orbitals within the valence band and also in its greater band broadening compared to I. In II, the contribution of the bpy ligands (i.e., N 2p orbitals) to the valence band is therefore larger. The result of having two additional ligands is that the valence band, composed mainly of the Cu 3d orbitals, is pushed to higher energies in II, as shown in Figure 5.7. Therefore, the band gap of II has been decreased as a result of the additional bpy ligands. These results show that a similar approach in other hybrid solids, focusing on the orbital energies at the local metal-coordination sites, could potentially lead to the better rational design of both the structures and optical properties of photocatalytic solids for use with solar energy.
Conclusions

Two new copper(I)-rhenate(VII) hybrid solids, Cu(bpy)ReO$_4$ (I) and Cu(bpy)$_2$ReO$_4$·0.5H$_2$O (II) (bpy = 4,4’-bipyridine), with 3D 2-fold $hms$ (3,5) connected and four-fold $dia$ 6$^6$ interpenetrating networks respectively, could be prepared in hydrothermal reactions. An interconversion transformation was observed from I to II via the insertion one bpy ligand and one-half water molecule per formula in aqueous media at 150 °C. Conversely, the removal of a single bpy ligand and one-half water molecule per formula from II at 270 °C yielded the structure of I again. The optical bandgap sizes were ~2.5 eV for I and ~2.2 eV for II, both within the visible-light wavelengths. While both I and II contain nearly identical conduction and valence band contributions, from the Re 5d and Cu 3d orbitals respectively, the valence band of II is relatively more pushed up in energy owing to the two additional bpy ligands coordinated to Cu$^+$. These results demonstrate that hybrid structures are quite flexible and dynamic, and that tuning of the ligand stoichiometry and the coordination geometries at low temperatures is a promising approach for the rational design of new structures with interesting optical and photocatalytic properties.

Acknowledgments

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References


13. Bruker-Nonius, SAINT+ version 7.34A, 2006, Bruker-Nonius, Madison, WI 53711, USA


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$^a$R$_1 = \Sigma (|F_o| - |F_c|) / \Sigma |F_o|; \text{ wR}2 = [\Sigma (w(F_o^2 - F_c^2)^2) / (\Sigma (F_o^2)^2)]^{1/2}; \text{ w}=\sigma F^{-2}.$
Table 5.2. Selected Interatomic Distances (Å) and Bond Valence Sums\(^a\) in I and II.

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\(^a\) S_{ij} = \exp[(R_0-R_{ij})/B], B = 0.37; R_0 = 1.574 Å, 1.600 Å, 1.930 Å for Cu\(^I\)–N, Cu\(^I\)–O and Re\(^V\)–O, respectively.\(^18\)
Scheme 5.1. Synthesis of I (left) and II (right) and the interconversion of their multiply-interpenetrating frameworks via a modification of the local coordination environment around Cu as a function of the ligand stoichiometry. Ellipsoids are drawn at the 50% probability level and all H atoms on the ligands are omitted for clarity.
Figure 5.1. An ~[010] polyhedral view of I, Cu(bpy)ReO$_4$ (A), red polyhedra = Cu-centered trigonal bipyramids, blue polyhedra = ReO$_4$ tetrahedra; A single ‘CuReO$_4$’ layer (B) drawn with 80% probability thermal ellipsoids, with all symmetry-unique atom types labeled; Local structural view of I (C) showing the interpenetration of the two frameworks, Re = yellow spheres and Cu = blue spheres; Extended ball-and-stick drawing (D) of the two interpenetrating nets of I colored red and green, where each node represents a Cu or Re atom. All H atoms on the ligands are omitted for clarity.
Figure 5.2. An ~[001] polyhedral view of the structure of Cu(bpy)$_2$ReO$_4$·0.5H$_2$O (A), II, with red polyhedra = Cu-centered tetrahedra and blue polyhedra = ReO$_4$ tetrahedra; A single diamond-type Cu(bpy)$_2^+$ network in II (B), drawn in perspective (left) and as a simplified stick model (right); A schematic representation of the four interpenetrating networks (C) in II, where each node represents a Cu atom. All H atoms on the ligands are omitted for clarity.
Figure 5.3. The powder XRD patterns (a) calculated from the single-crystal X-ray data of II, (b) of the as-synthesized crystalline sample of II, (c) after the reaction of I and bpy in water at 150 °C for 72 h, (d) calculated from the single-crystal X-ray data of I, (e) of the as-synthesized crystalline sample of I, (f) after heating II to 270 °C for ~10–20 minutes under flowing N₂ gas.

Figure 5.4. Thermogravimetric analysis (TGA) data of I and II plotted as weight (%) versus temperature (°C).
Figure 5.5. The UV–Vis diffuse reflectance spectra of I and II, plotted as F(R) vs. wavelength (nm).

Figure 5.6. XPS valence band spectra CuReO$_4$ (a), CuReO$_4$(pyz) (b), compound II (c), and compound I (d).
Figure 5.7. The calculated electronic Densities Of States (DOS) for I and II, with the partial DOS projected out for each atom type. The Fermi level ($E_f$) is labeled by the dashed line.

Cu(bpy)ReO$_4$ (I)  

Cu(bpy)$_2$ReO$_4$·0.5H$_2$O (II)

Figure 5.8. Electron-density contour maps of the LUMO and HOMO of I and II, calculated using the tight-binding method.
PART 3. M(I)-VANADATE(V) HYBRIDS (M = Ag, Cu)
CHAPTER 6
A NEW SERIES OF SILVER(I)-VANADATE (V) HYBRID SOLIDS:
SYNTHESES, STRUCTURES AND THEIR OPTICAL AND
PHOTOCATALYTIC PROPERTIES

A paper published in Inorganic Chemistry

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Abstract

Three new silver-vanadate hybrid solids, [Ag(bpy)]₄V₄O₁₂·2H₂O (I), [Ag(dpa)]₄-
V₄O₁₂·4H₂O (II), and Ag₄(pzc)₂V₂O₆ (III) (bpy = 4,4′-bipyridine, dpa = 1,2-bis(4-pyridyl)-
ethane, pzc = pyrazinecarboxylate), were synthesized by hydrothermal methods and
characterized using single crystal X-ray diffraction (I, P2₁/c, Z = 4, a = 11.375(2) Å, b =
14.281(4) Å, c = 13.598(3) Å, β = 91.46(1)°; II, P2₁/c, Z = 8, a = 13.5748(3) Å, b =
15.3372(4) Å, c = 14.1854(3) Å, β = 114.1410(9)°; III, P-1, Z = 2, a = 3.580(1) Å, b =
11.839(4) Å, c = 19.321(7) Å, a = 89.110(7)°, β = 87.719(9)°, γ = 86.243(8)°),
thermogravimetric analysis, and UV-vis diffuse reflectance. The structures of I and II are
constructed from neutral \{Ag₄V₄O₁₂\}_n layers of clusters that are pillared via the coordination
of organic ligands (bpy for I and dpa for II) to the Ag sites in each layer. Conversely, the
structure of III is composed of a three-dimensional \( \{ \text{Ag}_2(\text{pzc})^+ \}_n \) coordination network with channels containing \( \{ \text{VO}_3^- \}_n \) chains. The lattice water molecules can be removed upon heating to \( \geq 180 \, ^\circ\text{C} \) for I (reversibly) and to \( \geq 120 \, ^\circ\text{C} \) for II (irreversibly). All three decompose with the removal of organic ligands at higher temperatures of \( >200-300 \, ^\circ\text{C} \). Their optical bandgap sizes were measured to be 2.77 eV for I, 2.95 eV for II, and 2.45 eV for III, which decrease most notably as a result of the band widening for the more extended vanadate structure in III. All three hybrid solids are photocatalytically active for the decomposition of methylene blue under UV light (\( \lambda < 400 \, \text{nm} \); 1.01, 0.64, and 2.65 mg L\(^{-1}\) h\(^{-1}\) for I, II, and III, respectively), while only III exhibits a high activity under visible-light irradiation (\( \lambda > 400 \, \text{nm} \); 1.20 mg L\(^{-1}\) h\(^{-1}\)). These new hybrid solids are among the first reported to exhibit high photocatalytic activities under either ultraviolet or visible-light irradiation and have also been analyzed with respect to the effect of the different organic ligands on their atomic- and electronic-structures.

Introduction

Hybrid solids that combine both metal-oxide and organic ligand “building blocks” are a growing class of new materials that are beginning to receive widespread attention because of their potential to express, within the same compound, both the robustness and physical properties of metal oxides in conjunction with the versatility and chemical flexibility of organic ligands.\(^1\) This chemical synergy can yield new routes to a plethora of novel structures and properties with many potential applications, such as in those explored for absorbent, catalytic, and sensor-related properties.\(^2\) In addition, “retrosynthetic” analyses of
their structures have enabled new progress toward rational synthetic principles to aid in targeting specific structural features. Specific recent examples from our group include the layered rhenates $M_2(\text{pyzc})_2(H_2O)_x\text{ReO}_4$ ($M = \text{Co, Ni, Cu}$; pyzc = pyrazinecarboxylate), $M\text{ReO}_4(\text{pyz})$ ($M = \text{Ag, Cu}$; pyz = pyrazine), layered molybdate hybrids such as $[\text{M}_2(\text{pyzc})_2(H_2O)_x][\text{Mo}_5\text{O}_{16}]$ ($M = \text{Co, Ni}$), and the vanadate hybrids $M(\text{pyz})V_4\text{O}_{10}$ ($M = \text{Co, Ni, Zn}$) and $M(\text{bpy})V_4\text{O}_{10}$ ($M = \text{Ag, Cu}$). The structural flexibility of the latter hybrid solids, for example, has helped to probe the underlying theories of strongly correlated electrons and the magnetic properties of vanadate layers.

Our current research efforts continue to focus on the synthesis of new heterometallic-oxides/organics containing both early ($V^{5+}$, $\text{Mo}^{6+}$, $\text{Re}^{7+}$) and late ($\text{Cu}^+$, $\text{Ag}^+$) transition metals in combination with structure-directing organic ligands that will coordinate preferentially to the late transition metal sites. This selection of early/late transition metals is useful for probing the structural and electronic origins of the bandgap sizes of heterometallic oxides that arise from a Metal-to-Metal Charger Transfer (MMCT) between the $d^{10}$ (e.g., $\text{Ag}^+$) and $d^0$ (e.g., $V^{5+}$) electron configurations. Previous investigations, such as reported for $\text{AgMO}_3$ ($M = \text{V, Nb, Ta}$), have revealed that these MMCT transitions between $d^{10}/d^0$ electron configurations are the cause of their photocatalytic activities in the light-driven production of $\text{H}_2$ and/or $\text{O}_2$ in aqueous solutions. Further, these transitions can lead to the absorption of lower-energy visible light in metal-oxides owing to an $\sim1.5-0.5$ eV decrease in their band gap sizes, relative to the alkali metal versions, which arises from the Cu/Ag ($3d^{10}/4d^{10}$ orbitals) mixing into and raising the valence band energies. However, current photocatalytic investigations into solids with this type of electronic structure have been limited to only
condensed metal-oxides prepared by conventional solid-state methods.

Research into hybrid solids has served to significantly expand the structural diversity of heterometallic-oxides/organics that contain a combination of d⁰ with d¹⁰ transition metals, wherein a greater structural flexibility and control can be used to probe the origins of their optical and photocatalytic properties. For example, our group has demonstrated that “AgReO₄” layers of the parent AgReO₄ solid can be pillared by bridging organic or metal-coordinated ligands, leading to hybrid solids that exhibit microporosity or chirality in M(pzc)₂(H₂O)₂AgReO₄ and Cu(pzc)₂AgReO₄, respectively.⁴,⁶ In these examples, the water molecules that are coordinated to the axial sites of the M(pzc)₂ pillars can be reversibly removed to generate coordinatively-unsaturated metal sites without the loss of crystallinity. At higher temperatures (>300 °C) the organic ligands are typically liberated to yield either the parent phases or amorphous reduced materials. In another example, we have recently reported on the syntheses and optical properties of copper(I)-rhenate hybrids, CuReO₄(pyz) and Cu₃ReO₄(q6c)₂.⁸ These hybrid solids have much smaller optical bandgap sizes of ~2.2 eV and also yield the new CuReO₄ parent phase upon removal of the ligands. However, these new rhenate hybrids have not been found to exhibit high photocatalytic activities under the testing conditions investigated to date.

Described herein is the synthesis and characterization of the first known series of photocatalytically active silver-vanadate hybrids, [Ag(bpy)]₄V₄O₁₂·2H₂O (I), [Ag(dpa)]₄V₄O₁₂·4H₂O (II), and Ag₄(pzc)₂V₂O₆ (III). All three compounds are composed of silver-vanadate layered or network structures that are pillared at the silver sites by the coordinating organic ligands. Further, their atomic structures and optical properties are analyzed with
respect to their calculated electronic structures. These analyses are used to understand the
trends leading to smaller optical bandgap sizes, as well as their resulting photocatalytic
activities for the decomposition of methylene blue (MB) under both ultraviolet and visible
light.

**Experimental Section**

**Synthetic Approach.** Each hybrid solid was synthesized under hydrothermal conditions
by heat-sealing all reactants into an FEP Teflon pouch (3” × 4”). Starting materials included
Ag₂O (99+% metal basis, Alfa Aesar), NH₄VO₃ (purified grade, Fisher), 4,4′-bipyridine
(98%, Alfa Aesar, = bpy), 1,2-bis(4-pyridyl)-ethane (99%, Aldrich, = dpa) and pyrazine-2-
carboxylic acid (98%, Alfa Aesar, = pzc). A reagent amount of 3.0 M NH₃(aq) solution was
also added to the solvent in each of the reactions. The heat-sealed pouches were then placed
inside a 125 mL Teflon-lined stainless-steel reaction vessel which was backfilled with ~40
mL of deionized water before closing. After heating the reaction vessel to 105−150 °C for
1−3 days, it was slowly cooled to room temperature at 6 °C·h⁻¹. The products were then
filtered, washed with deionized water, and dried in air. The phase purities and crystallinities
of the compounds were checked by powder X-ray diffraction using an Inel XRG 3000
diffractometer (Cu Kα radiation, λ = 1.5406 Å), and these results are given in the Supporting
Information (Figure 6.S1).

**Synthesis of [Ag(bpy)]₄V₄O₁₂·2H₂O (I).** A stoichiometric mixture of 4,4′-bipyridine
(31.3 mg, 0.20 mmol), Ag₂O (23.2 mg, 0.10 mmol), NH₄VO₃ (23.4 mg, 0.20 mmol), and 3 M
NH₃(aq) (0.2 g, 10.2 mmol) was heat sealed into an FEP Teflon pouch. The reactants were
heated at 150 °C for 1−3 days inside a convection oven. The products were pale-yellow bar-shaped crystals. Yield: ~85% based on Ag.

**Synthesis of [Ag(dpa)]₄V₄O₁₂·4H₂O (II).** A stoichiometric amount of dpa (36.8 mg, 0.20 mmol), Ag₂O (23.2 mg, 0.10 mmol), NH₄VO₃ (23.4 mg, 0.20 mmol), and 3 M NH₃(aq) (0.4 g, 20.4 mmol) was loaded and heated inside the hydrothermal reaction vessel at 105 °C for 24 h within a convection oven. Pale yellow needle-like crystals were obtained. Yield: ~79% based on Ag.

**Synthesis of Ag₄(pzc)₂V₂O₆ (III).** This hybrid solid was similarly prepared by heating a stoichiometric mixture of Hpzc (24.8 mg, 0.20 mmol), Ag₂O (46.4 mg, 0.20 mmol), NH₄VO₃ (23.4 mg, 0.20 mmol), and 3 M NH₃(aq) (0.4 g, 20.4 mmol) at 150 °C for 3 days inside a convection oven. Gold-yellow needle crystals were obtained with a yield ~91% based on Ag.

**Crystallographic Structure Determination.** A bar-shaped crystal (0.32 × 0.10 × 0.02 mm) of I was mounted onto a glass fiber with a small amount of epoxy. All X-ray measurements were made on a Bruker-Nonius X8 Apex2 CCD diffractometer at 293 K. The unit cell dimensions were determined from a symmetry constrained fit of 8090 reflections with 5.70° < 2θ < 53.93°. The data collection strategy included both ω and φ scans that collected data up to 54.1° (2θ). The integration of frames was performed using the SAINT program. The resulting raw data were scaled and corrected for absorption using a multi-scan averaging of symmetry-equivalent data using the SADABS program. The structure was solved by direct methods using SIR92. The biphenyl hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent carbon atoms. The final
anisotropic structure refinement reached convergence, and the final structure refinement and atomic coordinate tables were created using the NRCVAX crystallographic program suite.\textsuperscript{18}

A single crystal of II was selected and mounted on a nylon loop with a small amount of NVH immersion oil. All X-ray measurements were made on a Bruker-Nonius X8 Apex2 diffractometer at a temperature of 110 K. The unit cell dimensions were determined from a symmetry constrained fit of 9896 reflections with $5.32^\circ < 2\theta < 66.12^\circ$. The data collection strategy included both $\omega$ and $\phi$ scans that collected data up to 66.32$^\circ$ ($2\theta$). The frame integration was performed using the SAINT program.\textsuperscript{15} The resulting raw data were scaled and absorption corrected using a multi-scan averaging of symmetry-equivalent data using SADABS.\textsuperscript{16} The structure was solved by direct methods using the SIR97 program.\textsuperscript{17} The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent atom. The final anisotropic structure refinement reached convergence, and the final structure refinement and atomic coordinate tables were taken from the NRCVAX crystallographic program suite.\textsuperscript{18}

A single crystal of III was mounted on a nylon loop for data collection on a Bruker SMART APEX CCD diffractometer at a temperature of 193 K. The unit cell parameters were determined using 4525 reflections in the range of $8.04 < 2\theta < 55.0$. The structure was solved and refined using SHELXTL-97 in the triclinic space group $P\bar{1}$.\textsuperscript{19} The hydrogen atoms on the pzr rings were refined in idealized positions at a C–H distance of 0.95Å.

Selected data collection and refinement parameters for all three crystals are listed in Table 6.1. The atomic coordinates and isotropic equivalent displacement parameters of I, II, and III are given in the Supporting Information in Tables 6.S1, 6.S2, and 6.S3, respectively.
Interatomic contacts for selected bonds and angles for all three structures are listed in Table 6.2.

**Thermogravimetric Analyses.** Weighed samples (23.4 mg of I, 17.4 mg of II, and 12.4 mg of III) of each compound were loaded onto Pt pans, equilibrated, and tarred at room temperature and heated at a rate of 1 to 5 °C/min to 600 °C under flowing nitrogen on a TA Instruments TGA Q50.

**Optical Bandgap Measurements.** The UV–vis diffuse reflectance spectra were measured on a Cary 300 spectrophotometer equipped with an integrating sphere. Approximately 50 mg of powder of each sample was mounted onto a fused-silica holder and placed along the external window of the integrating sphere. A pressed polytetrafluoroethylene powder was used as a reference, and the data were plotted as the remission function $F(R_\infty) = (1 - R_\infty)^2/(2R_\infty)$, where $R$ is the diffuse reflectance based on the Kubelka–Monk theory of diffuse reflectance.

**Electronic Band Structure Calculations.** Extended Hückel electronic structure calculations were carried out within the tight binding approximation using the CAESAR2 program, using the full structures at 960 $k$-points spread over the irreducible wedge. The internal double-$\zeta$ basis sets were selected for the atomic orbital parameters, and the atomic coordinates and lattice dimensions were imported from their respective crystal structures.

**Photocatalytic Reactions.** Methylene Blue (MB) is often used as model dye contaminant to evaluate the activity of photocatalysts in the purification of dye wastewater. It is reportedly very difficult to degrade this organic dye under visible light. Herein, MB was used as a model organic pollutant to evaluate the activities of the hybrid photocatalytic
solids. The photocatalytic activity of each sample for the decomposition of MB was measured by suspending a weighed amount (150 mg) of the powdered samples in an aqueous solution of MB (6.0 mg/L, 50 mL) in an ~60 mL cylindrical vessel. This mixture was stirred continuously under ultraviolet (\(\lambda < 400 \text{ nm}\)) or visible-light (\(\lambda < 400 \text{ nm}\)) irradiation from a 400 W high-pressure Xe arc lamp (focused through a shutter window), which was equipped with a heat filter to remove infrared radiation and with cutoff filters to select for the desired wavelength ranges. The reactions were stopped at 15 min intervals to determine the concentrations of aqueous MB solutions by UV−vis spectroscopy (HP 8453) at \(\lambda = 655 \text{ nm}\).

Results and Discussion

Structural Descriptions. The structures of \([\text{Ag(bpy)}]_4\text{V}_4\text{O}_{12}\cdot2\text{H}_2\text{O} \ (\text{I})\) and \([\text{Ag(dpa)}]_4\text{V}_4\text{O}_{12}\cdot4\text{H}_2\text{O} \ (\text{II})\) (bpy = 4,4′-bipyridine, dpa = 1,2-bis(4-pyridyl)-ethane) share many general structural similarities, as shown in Figure 6.1. In addition, both share the same space group (\(P2_1/c\)). Both \(\text{I}\) and \(\text{II}\) are composed of neutral \(\{\text{Ag}_4\text{V}_4\text{O}_{12}\}\_n\) layers of clusters that are pillared via coordination by the organic ligands (bpy for \(\text{I}\), dpa for \(\text{II}\)) to the Ag sites between layers, shown as the blue polyhedra in Figure 6.1. The heterometalllic \(\{\text{Ag}_4\text{V}_4\text{O}_{12}\}\_n\) layers consist of isolated \(\{\text{V}_4\text{O}_{12}\}\^{4-}\) tetramer rings that are linked together by eight nearest Ag\(^+\) cations per ring to yield the layer structures shown in Figure 6.2 (A and B). Each \(\{\text{V}_4\text{O}_{12}\}\^{4-}\) ring is constructed from four corner-shared VO\(_4\) tetrahedra with V−O bond distances within the expected ranges of 1.63−1.83Å, listed in Table 6.2.

In both \(\text{I}\) and \(\text{II}\), there are two symmetry-unique Ag sites, Ag1 and Ag2 in Figure 6.2 (A and B). In each layer, Ag1 is coordinated to two terminal oxygen atoms from separate
\{V_4O_{12}\}^{4-} \text{ rings at Ag–O distances of 2.739(3)Å and 2.674(4) Å for I and 2.699(2) Å and 2.689(2) Å for II. The Ag1 atoms are also bonded to two nitrogen groups from the organic ligands (bpy for I, dpa for II) from above and below each layer at ~2.17 Å, to complete a \{AgO_2N_2\} distorted square-planar coordination geometry. The Ag2 atoms in each structure coordinate to three terminal oxygen atoms from two separate \{V_4O_{12}\}^{4-} clusters, with a range of Ag–O distances of 2.751(3)–2.859(3)Å for I and 2.625(2)–2.641(2)Å for II. The Ag2 atoms are also bonded to two nitrogen groups from the respective organic ligands, both above and below each layer, to give a \{AgO_3N_2\} distorted trigonal-bipyramidal coordination geometry. For each structure, the coordination of the bridging organic ligands to the Ag sites results in extended 1D chains, that is, \{Ag(L)^+\}_n, along the [100] direction of the unit cells. The Ag1 and Ag2 atoms occur as relatively close pairs of dimers with Ag–Ag distances of 3.189(1) Å in I and 3.173(1) Å in II, shown in Figure 6.3. These pairs are a result of the face-to-face arrangement of the \{Ag1(L)^+\}_n and \{Ag2(L)^+\}_n chains, as expected for \pi-\pi stacking interactions of ligands that can help to stabilize the full three-dimensional network. One primary structural difference between I and II is found in the packing arrangement of the Ag–Ag dimer subunits. In the layers of I, infinite Ag1–O–Ag2 chains occur that are bridged via \{V_4O_{12}\}^{4-} rings. In II the Ag1/Ag2 polyhedra are also similarly edge-shared, but here their packing only yields isolated dimers that are more fully separated by the tetrameric \{V_4O_{12}\}^{4-} rings.

Another key aspect of I and II is that, although they share similar layered structures, they contain differing amounts of internal water molecules that can interact via hydrogen bonding. This difference is caused by the relatively shorter bpy bridging ligand for I that leads to a
shorter $a$-axis length (11.375(2) Å) and a smaller interlayer spacing that can accommodate only two water molecules per formula. In II, however, the longer dpa bridging ligand and $a$-axis length (13.5743(3) Å) yields larger interlayer galleries that can accommodate four water molecules per formula. As shown in Figure 6.3, each $\{V_4O_{12}\}^{4-}$ ring in I is hydrogen-bonded to two H$_2$O molecules both above and below at a distance of 2.208(3) Å (O1···H1w) and at an angle of 168.99(1)° (O1−H1w−O1w). In II, the four H$_2$O molecules are hydrogen-bonded into tetrameric clusters at distances of 2.037(1) Å (O1w···H2w) and 2.210(1) Å (O2w···H1w). Each tetrameric water cluster is further hydrogen-bonded to two terminal O2 groups and to two bridging O4 groups of the $\{V_4O_{12}\}^{4-}$ rings (both above and below) at distances of 1.836(1) Å (O2···H1w) and 2.256(1) Å (O4···H2w). Thus, the structure of II provides larger inter-gallery spaces owing to the longer dpa bridging ligands, and which represents a valuable strategy for increasing the absorption capacity of small molecules within the micropores of hybrid solids.²

The structure of Ag$_4$(pzc)$_2$V$_2$O$_6$ (III) (pzc = pyrazinecarboxylate) is dissimilar to that of I and II, and is composed of a three-dimensional $\{Ag_2(pzc)^+\}_n$ coordination network that contains $\{VO_3^-\}_n$ double chains within its open channels, as shown in Figure 6.4. The structure may also be roughly viewed as containing heterometallic $\{Ag_2VO_3\}_n^{n+}$ layers that are bridged to each other through the coordination of pzc ligands to the Ag sites in each layer. The structure is more condensed than in I or II owing to the shorter pzc ligands, and thus, there are no internal lattice water molecules. The local coordination geometries of all symmetry-unique silver and vanadium atoms in III are plotted in Figure 6.5. The metavanadate $\{VO_3^-\}_n$ chains are remarkably similar to that found in Ni(VO$_3$)$_2$·4H$_2$O$^{26}$ and
consist of square-pyramidal \((\text{VO}_3)\) polyhedra condensed via edge-sharing into zigzag chains that are aligned along the \(a\)-axis direction. In \(\text{III}\), these \(\{\text{VO}_3^-\}_n\) chains run parallel to the silver-oxide chains, shown in Figure 6.6. The \(\text{VO}_3\) polyhedra are highly distorted, with \(\text{V}–\text{O}\) distances \((1.63(1)–2.03(1) \, \text{Å}; \text{Table } 6.2)\) consistent with those in previously reported metavanadate chains. The calculated bond valence sums \((\sum S_{ij})^{21}\) for vanadium, also listed in Table 6.2, are consistent with a fully oxidized +5 oxidation state.

The silver-organic network consists of four crystallographically-independent Ag atoms, comprising \(\text{Ag}_1\), \(\text{Ag}_2\), and \(\text{Ag}_3\) with distorted square-pyramidal \(\{\text{AgNO}_4\}\) coordination geometries and \(\text{Ag}_4\) with a distorted tetrahedral \(\{\text{AgNO}_3\}\) coordination geometry. As shown in Figure 6.6, the coordination polyhedron of each Ag site is linked to others via corner- and edge-sharing to form infinite metavanadate chains along the \(a\)-axis direction. Specifically, the square pyramidal \(\text{Ag}_1\) polyhedra share edges with each other via the \(\text{O}1\) groups from the \(\text{pzc}\) ligands and form infinite double chains. Next, these infinite \(\text{Ag}_1\) double chains are condensed via corner-shared \(\text{O}8\) groups to the tetrahedral \(\text{Ag}_4\) chains that are also connected via the \(\text{O}8\) vertices. The other infinite chain containing \(\text{Ag}_2\) and \(\text{Ag}_3\) is, by contrast, formed from square-pyramidal double chains of \(\text{Ag}_2\) polyhedra. These chains are connected to edge-sharing square-pyramidal \(\text{Ag}_3\) dimers via two \(\text{O}5\) groups, and are in turn shared with a neighboring vanadate chain. These two silver-oxide chains (\(\text{Ag}_1/\text{Ag}_4\) and \(\text{Ag}_2/\text{Ag}_3\)) are bridged to each other through the multidentate \(\text{pzc}\) ligands to form the full three-dimensional network.

**Thermogravimetric Analyses and Reversible Water Absorption.** The thermal stabilities, decomposition pathways, and reversible water absorption (i.e., microporosity)
were probed in this series of three new vanadate hybrid solids. As an initial check of their full decomposition pathway, each sample was slowly heated to 600 °C under flowing N₂, and the changes in the structure and final products were characterized using Powder X-ray Diffraction (PXRD). The Thermogravimetric Analysis (TGA) of I exhibited a major weight loss of \( \approx 42\% \) from \( \approx 180–300 \) °C, corresponding to the loss of both the lattice water and the bipyridine ligands (calcd 43%), shown in Figure 6.7. A second minor weight-loss step of 7% was observed from 300–430 °C and likely corresponds to the reduction of Ag\(^+\) to Ag(s) and the loss of O\(_2\) (calcd 8% for one O\(_2\) per formula). The final black residue of I was determined by PXRD to be a mixture of Ag and VO\(_x\) (see supporting Information Figure 6.S2). The TGA result for II is similar to that of I, with a major weight loss corresponding to the removal of four lattice water molecules and dpa ligands by \(-300–350 \) °C (exp. 48%; calcd 49%), followed by the loss of about one O\(_2\) per formula (exp. 6%; calcd 7%). As before, the final black residue was found by PXRD to be a mixture of Ag and VO\(_x\). For III, the loss of the pzc ligand occurs within a broad temperature range between 300–500 °C (exp. 27%; calcd 28%). The compound also exhibits a higher thermal stability than either I or II. Typically, the presence of more strongly-bonded carboxylate ligands in the structure results in a greater thermal stability, such as reported in the comparison of the thermal stability of CuReO\(_4\)(pyz) versus Cu\(_3\)ReO\(_4\)(q6c) (described below in chapter 4).\(^8\)

For both \([\text{Ag(bpy)}]_4\text{V}_4\text{O}_{12}\cdot2\text{H}_2\text{O} \) (I) and \([\text{Ag(dpa)}]_4\text{V}_4\text{O}_{12}\cdot4\text{H}_2\text{O} \) (II), it is expected that the lattice water molecules located in the gallery spaces could be relatively easily removed without the concurrent loss of organic ligands or loss of sample crystallinity. After 6 h at 180 °C the crystalline powder of I can be completely dehydrated with the retention of a very
similar crystalline structure, as evidenced by the PXRD results that show a small shifting of the diffraction peak positions (see Supporting Information Figure 6.S3). This dehydrated powder can be completely rehydrated in an aqueous solution at 140 °C. An almost identical PXRD pattern as before the dehydration is obtained, demonstrating the integrity of the structure during both the dehydration and rehydration steps. By contrast, the complete dehydration of II can be achieved at only 100 °C after 6 h, but which induces an irreversible change in the structure and cannot be rehydrated under similar conditions as found for I.

**Optical Bandgap Sizes and Electronic Structures.** As we have reported previously,\(^8\) heterometallic oxides containing transition metals with both d\(^0\) and d\(^{10}\) electron configurations, such as MM'O\(_3\) (M = Cu, Ag; M' = V, Nb, Ta),\(^{13, 14}\) exhibit small optical bandgap sizes with the absorption of visible-light energies that can be used to drive photocatalytic reactions. The hybrid solids I, II, and III are related to these condensed heterometallic oxides but contain either two- or three-dimensional “Ag\(_x\)VO\(_3\)” layers. These layers can function as the light-absorbing structural components as well as serve as the potential sites for photocatalytic reactivity. The UV–vis diffuse reflectance of each was measured and is shown in Figure 6.8. The absorption edge of each sample fell within or near the visible range of wavelengths, with approximate optical bandgap sizes of 2.77 eV for I, 2.95 eV for II, and 2.45 eV for III. By comparison, in the case of “organic free” α-AgVO\(_3\) the optical bandgap edge occurs at ~2.5 eV owing to an electronic excitation from the Ag-4d/O-2p to the empty V-3d orbitals.\(^{13}\)

Calculations of the electronic structures of [Ag(bpy)]\(_4\)V\(_4\)O\(_{12}\)-2H\(_2\)O (I), [Ag(dpa)]\(_4\)V\(_4\)O\(_{12}\)-4H\(_2\)O (II), and Ag\(_4\)(pzc)\(_2\)V\(_2\)O\(_6\) (III) were performed to evaluate the atomic-
orbital contributions to the valence and conduction bands and to understand the structural factors that influence the sizes of their optical band gaps. Shown in Figure 6.9 is the calculated total Densities-Of-States (DOS), and overlaid is the partial DOS contributions from each constituent element of the solid. In all three hybrid solids the lowest unoccupied crystal orbitals of the conduction band were confirmed to derive from the V 3d orbitals, consistent with prior results reported for the condensed α-AgVO₃. Also, the highest occupied crystal orbitals of all three are closely similar and are formed primarily from contributions from the Ag 4d, N 2p, and O 2p orbitals. The same general trend in bandgap sizes is reproduced as found in the UV-vis DRS measurements, which decreases from II to I to III. This ordering of their bandgap sizes can be understood as a result of changes in both the local coordination geometries and the degree of the structural connectivity. The vanadate structures in I and II contain isolated tetrameric rings consisting of VO₄ tetrahedra, which lead to a relatively small amount of conduction band broadening and a larger bandgap size. The structures of α-AgVO₃ and III, by contrast, contain infinite edge-sharing chains of VO₅ polyhedra. This leads to relatively greater conduction band widening and the decreased bandgap size. In an analogous fashion, the valence bands are relatively wider in II and I compared to those in α-AgVO₃ and III. This is caused by going from the dimers of Ag(L)⁺ chains in I and II to the much larger clusters of extended chains in α-AgVO₃ and III. Thus, these results help to understand the effect of the “AgₓVO₃” structural connectivity upon the bandgap sizes, and which is governed by the choice of the size and coordination preference of the organic ligand.
**Photocatalytic Decomposition Reactions.** MB is commonly used as a representative of widespread organic dyes that contaminate textile effluents and that are very difficult to decompose in waste streams under visible-light irradiation.\textsuperscript{21-24} Herein, MB was used as a model organic dye to evaluate the photocatalytic activities of the three new hybrid solids toward the decomposition of organic pollutants. Owing to their different bandgap sizes, the photocatalytic reaction of $[\text{Ag(bpy)}]_4\text{V}_4\text{O}_{12}\cdot2\text{H}_2\text{O}$ (I) and $[\text{Ag(dpa)}]_4\text{V}_4\text{O}_{12}\cdot4\text{H}_2\text{O}$ (II) should take place under only ultraviolet light ($\lambda < 400$ nm), while $\text{Ag}_4(\text{pz}c)_2\text{V}_2\text{O}_6$ (III) should be active under both ultraviolet and visible-light ($\lambda > 400$ nm) irradiation. During the course of the photocatalytic reactions the stability of the hybrid solids was monitored using PXRD (see Supporting Information Figure 6.S4). The PXRD confirmed that the crystal structures of the hybrid solids were unaltered, and the powders remained stable under these testing conditions.

The photocatalytic reactions were performed as described in the Experimental Section. As shown in Figure 6.10, changes in the concentration of the aqueous MB solution were plotted versus irradiation time. As a control, simple photolysis experiments of the MB solution were also performed under the same conditions without the use of the hybrid solids. The results show that I, II, and III are all active for the decomposition of MB under UV light irradiation, with rates of 1.01, 0.64, and 2.65 mg L$^{-1}$ h$^{-1}$ respectively. During the first 30 min there is a faster rate of removal of MB from solution owing to its adsorption to the particle surfaces. This initial rate increases as expected with increasing amounts of solid sample used in the photocatalytic reaction. Thus, the first 30 min of the photocatalytic reaction was not included in the rate calculation. After 3 h of irradiation, approximately 70% and 65% of MB has been decomposed with the use of 150 mg of I and II, respectively. Neither sample is
active under visible-light irradiation. By contrast, the lower-energy bandgap of III enables the decomposition of 80% of the MB after only 3 h under only visible-light irradiation, Figure 6.10B, with a rate of 1.20 mg L$^{-1}$ h$^{-1}$. Shown in Figure 6.11 is the evolution of the MB absorption spectra versus time in the presence of 150 mg of III under visible light irradiation, which illustrates the decreasing concentration of MB over time. Notably, the photocatalytic rate of III under either ultraviolet or visible light is higher than either I or II. These results suggest that the more extended network of III, that is, the vanadate chains as well as the much larger clusters of Ag-oxide/organic chains, aids in the transport of excited holes/electrons to the surface to initiate the photocatalytic decomposition reaction with MB.

More generally, these results also show that more reactive hybrid photocatalysts can be achieved as a result of a better ability to tune the structural features and optical properties of heterometallic oxides with the use of suitable organic ligands.

**Conclusions**

A series of three new silver-vanadate hybrid solids, [Ag(bpy)]$_4$V$_4$O$_{12}$·2H$_2$O (I), [Ag(dpa)]$_4$V$_4$O$_{12}$·4H$_2$O (II), and Ag$_4$(pzc)$_2$V$_2$O$_6$ (III), has been synthesized via hydrothermal methods. All three hybrid solids are composed of silver-vanadate layers pillared by the organic ligands (bpy, dpa, and pzc) via coordination to the silver sites. The structures of I and II contain Ag(L)$^+$ (L = bpy, dpa) chains and tetrameric \{V$_4$O$_{12}$\}$^{4-}$ rings, while III is found to be constructed from two different extended \{Ag$_4$N$_4$O$_6$\} chains and also zigzag \{VO$_3$\}$\_n$ chains. The TGA analysis of each shows the removal of water, followed by ligands, at >180 °C for I, >120 °C for II, and at >300 °C for III. Further, hybrid I exhibits
microporosity with the reversible absorption of lattice water molecules at the low
temperatures of 140−180 °C. Their measured optical bandgap sizes decrease from II (2.95
eV) to I (2.77 eV) to α-AgVO₃ (2.5 eV) to III (2.45 eV), owing to the changes in the
extended network dimensionality. Photocatalytic studies have been used to demonstrate that
the new silver-vanadate hybrids can efficiently decompose MB. The photocatalytic activities
of I and II are limited to UV light owing to their large bandgap sizes, while III is active
under visible-light irradiation because of its smaller bandgap size. These results demonstrate
the significant utility of using organic ligands for control over the atomic- and electronic-
structures of heterometallic oxides to both understand and modify their photocatalytic
properties.

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Supporting Information Available

Crystallographic data for I, II, and III in CIF format, and powder X-ray diffraction
results for all prepared compounds including for the as-synthesized hybrids, for their TGA
residues, for the dehydrated/rehydrated analogues of I, and for all three samples during the photocatalytic reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table 6.1. Selected Single Crystal and Structure Refinement Details for compound I–III.

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\[ R_1 = \frac{\sum |F_o| - |F_c|)}{\sum |F_o|}; \ R_w = \left( \frac{\sum (w(F_o^2 - F_c^2))^2}{(\sum F_o^2)^2}\right)^{1/2}; \ w=\sigma_F^{-2}. \]

Table 6.2. Selected Interatomic Distances (Å) and Bond Valence Sums\(^a\) for I–III.

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\({}^a\) S_{ij} = \exp[\{(R_0 - R_{ij})/B\}], B = 0.37, and R_0 = 1.803 \text{ Å} for V. \textsuperscript{21}
Figure 6.1. ~[001] polyhedra view of the [Ag(bpy)]$_4$V$_4$O$_{12}$2H$_2$O (I) (left) and [Ag(dpa)]$_4$V$_4$O$_{12}$4H$_2$O (II) (right) structures with the unit cell outlined. Blue polyhedra = Ag-centered coordination environments, red polyhedra = VO$_4$, red spheres = O, yellow spheres = N, white spheres = C and light-blue = Ag. All H atoms are omitted for clarity.

Figure 6.2. Structural view of a single “AgVO$_3$” layer in I (A) and II (B), drawn using 80% probability thermal ellipsoids and with symmetry-unique atoms labeled.
Figure 6.3. Structural view of the $\{V_4O_{12}\}^{4+}$ rings and $\{Ag(L)^+\}_n$ chains of I (A) and II (B) with labels for hydrogen bonds and the shortest Ag1···Ag2 distances. All atom types are labeled.
Figure 6.4. Polyhedral structural view of Ag₄(pzc)₂V₂O₆ (III) down the [100] direction of the unit cell (outlined). Blue polyhedra = Ag-centered coordination environments, red polyhedra = VO₅, red spheres = O, yellow spheres = N, white spheres = C, and light-blue spheres = Ag. All H atoms are omitted for clarity.

Figure 6.5. Structural view of the local coordination environments of all atoms in III, with all atoms labeled and thermal ellipsoids drawn at an 80% probability level.
Figure 6.6. Structural views of the two different silver-oxide chains in III, containing Ag1/Ag4 (left) and Ag2/Ag3 (right), with selected atoms labeled.

Figure 6.7. Thermogravimetric analyses of I, II, and III, plotted as weight (%) versus temperature (°C).
**Figure 6.8.** UV-vis diffuse reflectance spectra of I, II, and III plotted as a function of the photon energy in eV and as a function of wavelength in nm (inset).

**Figure 6.9.** Calculated total and projected densities-of-states (DOS) for all three solids.
Figure 6.10. Photocatalytic decomposition of MB solutions (6.0 mg/L, 50 mL) using 150 mg of the three silver vanadates, either under UV (A; upper) or under visible-light (B; lower) irradiation for I (b), II (c), III (d). Photolysis of the ligand by itself is labeled (a).

Figure 6.11. Absorption spectra of a solution of MB (6.0 mg/L, 50 mL) during a photocatalytic test reaction using 150 mg of III under visible light irradiation.
### Supporting Information

A New Series of Silver-Vanadate Hybrid Solids: Syntheses, Structures and Their Optical and Photocatalytic Properties

Haisheng Lin and Paul A. Maggard

**Table 6.S1.** Selected Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å$^2$) for [Ag(bpy)]$_4$V$_4$O$_{12}$·2H$_2$O (I).

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<th>$z$</th>
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All atoms are located on a 4e Wyckoff site. \(^b\) \(U(\text{eq})\) is defined as one third of the trace of the orthogonalized \(U_{ij}\) tensor.

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Table 6.S2. Selected Atomic Coordinates and Equivalent Isotropic Displacement Parameters (\(\text{Å}^2\)) for [Ag(dpa)]\(_4\)\(V_4O_{12}\cdot4\text{H}_2\text{O}\) (II).

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*All atoms are located on a 4e Wyckoff site. "U(eq) is defined as one third of the trace of the orthogonalized U_ij tensor.*

Table 6.S3. Selected Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å²) for Ag₄(pzc)₂V₂O₆ (III).

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a All atoms are located on a 2i Wyckoff site. b $U$(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Figure 6.S1. Powder XRD patterns: (a) Simulated pattern of I; (b) Observed pattern of I; (c) Simulated pattern of II; (d) Observed pattern of II; (e) Simulated pattern of III; (f) Observed pattern of III.
Figure 6.S2. Powder XRD patterns of the black TGA residuals of all three compounds: (a) simulated pattern of Ag; (b), (c), (d) are observed patterns of I, II and III, respectively.

Figure 6.S3. Powder XRD patterns of the dehydrated and rehydrated sample of I: (a) simulated pattern of I; (b) Observed pattern of as-synthesized I; (c) Observed pattern of I after dehydration at 180 °C for 6 hours; (d) Observed pattern of I after re-hydration at 140 °C.
Figure 6.S4. Powder XRD patterns of each sample (I-III): simulated (bottom), as synthesized (middle) and after photocatalytic reaction (top).

Figure 6.S5. Polyhedral structural views of the two different ‘Ag$_2$VO$_3$’ layers in III. The Ag1/Ag4 layer on the left and Ag2/Ag3 layer on the right, where blue polyhedra = Ag centered coordination environments and red polyhedra = VO$_5$. 
Figure 6.S6. Thermogravimetric analyses of I at a heating rate of 1°C/min, plotted as weight (%) versus temperature (°C).
Abstract

A new heterometallic-oxide hybrid, \([\text{Cu(dpa)}]_4\text{V}_6\text{O}_{17}\text{H}_2\text{O}\) (dpa = 1,2-bis(4-pyridyl)-ethane) (I), has been prepared using the hydrothermal method. Despite use of the longer and more flexible bridging-ligand dpa, I exhibits an un-interpenetrated 3D structure comprised of unique \([\text{V}_6\text{O}_{17}]^{4-}\) chains covalently bridged to eight \([\text{Cu(dpa)}]^+\) chains through the terminal oxygen atoms of VO$_4$ tetrahedra. Interestingly, each \([\text{V}_6\text{O}_{17}]^{4-}\) chain consists of cyclic \([\text{V}_4\text{O}_{12}]^{4-}\) and dimeric \([\text{V}_2\text{O}_7]^{2-}\) anions that share O vertices. The single lattice water molecule is located in the gallery spaces and can be exhibit reversibly water absorbed/desorbed, as found by TGA and powder X-ray diffraction data. The UV-Vis diffuse reflectance spectrum shows a relatively small visible-light bandgap size of \(\sim 2.0\) eV, that compared to related Ag(I)-vanadate(V) oxide/organic hybrid solids.
Introduction

The different types of metal-oxovanadate species that form in solution are strongly dependent upon the reaction conditions, such as the pH, temperature.\textsuperscript{1–6} Vanadium in its highest oxidation state tends to oligomerize readily to form various polynuclear oxyanions, for example, form ring, chain, and layer structures under different synthetic conditions. Generally, the vanadate species show a similar pattern of condensing via vertex- and edge-sharing oxygen atoms into cluster, chain, and network frameworks containing tetrahedral VO$_4$, tetragonal bipyramidal VO$_5$, and octahedral VO$_6$ polyhedra. Examples include the cluster species \{V$_4$O$_{12}$\},\textsuperscript{1} \{V$_{10}$O$_{28}$\},\textsuperscript{2} the chain species \{V$_2$O$_6$\},\textsuperscript{3} \{V$_4$O$_{12}$\},\textsuperscript{4} and the layered species \{V$_{12}$O$_{12}$\},\textsuperscript{5} and \{V$_6$O$_{17}$\}.\textsuperscript{6} These vanadate species are known to predominate at specific pH ranges, and which can be controlled during the hydrothermal reaction. Examples from our previous research show these vanadate clusters expressed in [Ag(bpy)$_4$]$_4$V$_4$O$_{12}$·2H$_2$O, [Ag(dpa)$_4$]$_4$V$_4$O$_{12}$·4H$_2$O, and the extended vanadate chains in Ag$_4$,(pzc)$_2$V$_2$O$_6$.$^{1b}$ In the first structure, the lattice water can be reversibly removed without the loss of the structure crystallinity to generate a porous framework. Also, these vanadates were the first known hybrid solids to have been found to exhibit photocatalytic activity under visible-light irradiation.

In hybrid solids, because the vanadate species bond to and charge balance the cationic Cu$^+$/Ag$^+$-organic networks, both therefore need to be structure- and charge-matched in order to form the desired heterometallic-oxide/organic structure. Our group has previously reported on this charge and structure matching approach in some recent vanadates,$^7$ and illustrates the fact that new structure-forming principles will be emerge from a structural
analysis of new hybrid solids. However, new hybrid structures will be difficult to predict in advance because of the lack of a better understanding of how these ‘building blocks’ assemble from solution. Prior research has revealed subtle changes in ligand geometry or donor group orientation can produce unanticipated structural consequences. Thus, presented in this chapter is the synthesis, structure and properties of a new hybrid vanadate structure, [Cu(dpa)]$_4$V$_6$O$_{17}$H$_2$O (I), which has been characterized for reversibly of water loss, and also for its visible-light band edge.

**Experimental Section**

**Materials.** All the starting materials for synthesis were purchased commercially and used without further purification, including Cu$_2$O (99% metal basis, Alfa Aesar), NH$_4$VO$_3$ (purified grade, Fisher), and 1,2-bis(4-pyridyl)-ethane (99%, Aldrich). A reagent amount of deionized water was also used in the syntheses.

**Synthesis.** The synthesis of [Cu(dpa)]$_4$V$_6$O$_{17}$H$_2$O (I) was performed by adding 18.0 mg (0.125 mmol) of Cu$_2$O, 44.0 mg (0.375 mmol) of NH$_4$VO$_3$, 46.0 mg (0.25 mmol) of dpa, and 0.40 g (22.2 mmol) of H$_2$O to an FEP Teflon pouch. The pouch was heat-sealed and placed inside a 45-mL Teflon-lined stainless steel reaction vessel which was backfilled with ~15 mL of deionized H$_2$O before closing. The reaction vessel was heated to 180 °C for 72 hours inside a convection oven and slowly cooled to room temperature at 6 °C/h. Brown-colored block-shaped crystals of I were obtained in ~92% yield based on Cu. The phase purities of I were >95% according to Powder X-ray diffraction data.
Crystallographic Structure Determination. A suitable single crystal was mounted on a nylon loop with a small amount of NVH immersion oil. All X-ray measurements were made on a Bruker-Nonius X8 Apex2 diffractometer at a temperature of 223 K. The unit cell dimensions were determined from a symmetry-constrained fit of 9080 reflections with $5.06^\circ < 2\theta < 55.38^\circ$. The data collection strategy utilized a number of $\omega$ and $\phi$ scans which collected data up to $57.34^\circ (2\theta)$. The frame integration was performed using SAINT+. The resulting raw data were scaled and absorption corrected using a multi-scan averaging of symmetry-equivalent data using SADABS. The structure was solved by direct methods using the SIR97 program. All non-hydrogen atoms were obtained from the initial E-map. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent carbon atoms. The structural model was fit to the data using full matrix least-squares based on F. The calculated structure factors included corrections for anomalous dispersion using the usual tabulation. The structure was refined using LSTSQ program from NRCVAX. Table 7.1 lists the selected data collection and refinement parameters for \( I \). The atomic coordinates and isotropic equivalent displacement parameters of \( I \) are given in the Table 7.2, and the interatomic contacts for selected bonds and angles are listed in Table 7.3.

Thermogravimetric Analyses (TGA). A weighed amount (~20 mg) of \( I \) was loaded onto a Pt pan, equilibrated and tarred at room temperature on a TA Instrument TGA Q50, and the data plotted as the % starting weight versus temperature (°C). The sample was heated to 600 °C at a rate of 5 °C/min under flowing N\(_2\) gas (40 mL/min). Post-TGA residuals were characterized by powder X-ray diffraction in transmission mode on an Inel XRG 3000 diffractometer fitted with a CPS 120 position-sensitive detector and using Cu K\(\alpha_1\) radiation.
from a sealed-tube X-ray source.

**Optical Properties.** The UV-vis diffuse reflectance spectrum of I was measured on a Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer equipped with an integrating sphere. Approximately 10 mg of powder was mounted onto a pressed BaSO₄ powder holder and placed along the external window. A pressed BaSO₄ powder was used as a reference, and the data were plotted as the remission function \( F(R_\infty) = (1-R_\infty)^2/(2R_\infty) \), where \( R \) is diffuse reflectance based on the Kubelka-Monk theory of diffuse reflectance.

**Results and Discussion**

**Structural Description.** The structure of I consists of an un-interpenetrated network constructed from the linking of \([\text{Cu(dpa)}]^+\)ₙ and \([\text{V}_6\text{O}_{17}^4^-]ₙ\) chains. As shown in Figure 7.1, there are two symmetry-unique Cu(I) atoms, both of which are coordinated to one oxygen atom from \([\text{V}_6\text{O}_{17}^4^-]ₙ\) chains and to two nitrogen atoms from the dpa ligands, completing a T-shaped coordination geometry. The Cu–O and Cu–N distances are similar (Cu–O = 2.20(1) Å; Cu–N = 1.91–1.93(1) Å) and fall within the typical ranges. The Cu(I) atoms bridge via two different but symmetry-equivalent dpa ligands, forming a nearly linear chain along the \( c \)-axis with N–Cu–N bond angles of 160.8(1)° and 162.8(1)°. Selected interatomic distances and angles are listed in Table 7.3, and the local coordination environments of each atom are shown in Figure 7.1. All three V atoms are coordinated to four oxygen atoms in a tetrahedral geometry. The V–O distances range from 1.600(2) to 1.834(2) Å, with O–V–O angles in the range of 107.1(1) – 112.1(1)°, and which are comparable to those in similar hybrids. Bond
Valence sum calculations are consistent with the oxidation states of Cu and V are +1 and +5, respectively, listed in Table 7.3.\textsuperscript{12}

\([\text{Cu(dpa)}]_4\text{V}_6\text{O}_{17}\text{H}_2\text{O} \text{ (I)}\) is a new member in the family of copper(I)-vanadium(V) oxide/organic hybrid solids. Other reported hybrids in this family are two-dimensional \text{Cu(dpa)VO}_3,\textsuperscript{13} the 2-fold interpenetrating framework \([\text{Cu(bipy)}]_4\text{V}_4\text{O}_{12}\text{2H}_2\text{O},\textsuperscript{14} and the self-catenated network \([\text{Cu}_4(\text{bpp})_4\text{V}_4\text{O}_{12}]\text{3H}_2\text{O}\textsuperscript{15} The structure of I is also related to other previously reported Ag(I)-vanadium(V) oxide/organic hybrids.\textsuperscript{1b} Within these known structures, the vanadate species are either \([\text{V}_4\text{O}_{12}]^4^-\) tetramer rings or \([\text{VO}_3^-]_n\) chains. By contrast, in I, the vanadate species exhibit a different building unit, a \([\text{V}_6\text{O}_{17}]^4^-\) chain that is built from bridging \(\text{V}_2\text{O}_7\) dimeric units and cyclic \(\text{V}_4\text{O}_{12}\) tetramers. As shown in Figure 7.1, the \([\text{V}_2\text{O}_7]^{4-}\) dimeric unit is comprised of two neighboring \(\text{V}(1)\text{O}_4\) groups via a corner-sharing \(\text{O}(2)\) atom, whereas two \(\text{V}(2)\text{O}_4\) and two \(\text{V}(3)\text{O}_4\) tetrahedra form the tetramer \(\text{V}_4\text{O}_{12}\) cluster rings via corner-sharing \(\text{O}(6)\) an \(\text{O}(7)\) atoms. A similar \([\text{V}_6\text{O}_{17}]^{4-}\) chain has been reported in \(\text{Co}_2(\text{phen})_4\text{V}_6\text{O}_{17}\) and \(\text{Cu}_2(\text{bipy})_2\text{V}_6\text{O}_{17}\textsuperscript{3b,16} This type of vanadate chain is distinct to those in \([\text{M}_4(2\text{-pzC})_4(\text{V}_6\text{O}_{17})]\text{xH}_2\text{O} \text{ (M = Co, Ni), in which the infinite \([\text{V}_6\text{O}_{17}]^{4-}\) chain double chain is bent to give perpendicularly-arranged 8-rings}.\textsuperscript{17} The TOPOS analysis\textsuperscript{18} indicates that the structure of I is a new topology, with the total Schlafli symbol \(\{12^3\}{4;12^2}\{8;12;14\}\{8^2;10\}. As shown in Figure 7.1, each \([\text{V}_6\text{O}_{17}]^{4-}\) chain in I is connected to eight parallel \([\text{Cu(dpa)}]^+\) chains to form a three-dimensional un-interpenetrating framework with open channels along the \(c\)-axis. The structure also contain
guest water molecules located inside the metal-oxide/organic tubes and that bond via hydrogen bond interactions to the vanadate chains (O1w−H−O5, 2.192(2) Å).

**Thermogravimetric Analysis and Reversibility of Water Desorption.** The thermal stability, decomposition pathways, and reversibility of water desorption (i.e., microporosity) were probed for I.\(^9\) As an initial check of its full decomposition pathway, each sample was slowly heated to 600 °C under flowing N\(_2\), and the changes in the structure and final products were characterized using Powder X-ray Diffraction (PXRD). Shown in Figure 7.2, I exhibited a small weight-loss step of \(\sim 1.3\%\) from \(\sim 50–250^\circ\mathrm{C}\), consistent with the loss of the lattice water (calcd 1.2\%). A second major weight-loss step of \(\sim 43.3\%\) was observed extending from 250 to 600°C and likely corresponds to the loss of the dpa ligand (calc. 45.9\%).

Similar to that for both [Ag(bpy)]\(_4\)V\(_4\)O\(_{12}\)-2H\(_2\)O and [Ag(dpa)]\(_4\)V\(_4\)O\(_{12}\)-4H\(_2\)O,\(^{1b}\) it is possible that the lattice water molecules located in the gallery spaces of I could be relatively easily removed without the concurrent loss of organic ligands or the loss of sample crystallinity. After 1 h at 150 °C the crystalline powder of I can be partially dehydrated with the retention of a very similar crystalline structure, and also completely dehydrated after 1 h at 250 °C with a color change from brownish to deep-orange, as shown by the PXRD patterns in Figure 7.3. The diffraction peaks show small shifting and also the emergence of some new peaks. Further, the dehydrated powder of I can be completely rehydrated in a hot aqueous solution at 80°C. An almost identical PXRD pattern as before the dehydration is obtained, demonstrating the integrity of the structure during both the dehydration and rehydration steps. Also, the water desorption and absorption step could be cycled numerous times.
**Optical Properties.** Heterometallic oxides that contain both a late (Ag\(^{+}\)) and early (V\(^{5+}\), Ta\(^{5+}\), Mo\(^{6+}\)) transition metal, with d\(^{10}\) and d\(^{0}\) electron configurations respectively, have been investigated for their absorption of visible light (\(E_{g} = 2.2 - 3.0\) eV) and ability to drive photocatalytic reactions. In order to analyze the influence of Cu\(^{+}\) on the optical absorption energies, the UV-vis diffuse reflectance spectrum of I was measured, shown in Figure 7.4. Hybrid I exhibited a strong optical absorption in the visible region, with an optical bandgap size of ~2.0 eV, as calculated from the onset of its absorption edge. The band gap size is significantly smaller than that of silver-vanadate hybrids (2.45–2.77 eV)\(^{20}\) and arises from the replacement of the lower-energy d orbitals of Ag\(^{+}\) for the higher-energy d orbitals of Cu\(^{+}\). Thus, a much larger fraction of visible-light is absorbed by Cu\(^{+}\)-containing heterometallic hybrids, and which illustrates the great potential for Cu\(^{+}\)-containing hybrids in the discovery of active photocatalysts with visible-light bandgap sizes.
Conclusions

A new Cu$^+$-containing hybrid $[\text{Cu(dpa)}]_4\text{V}_6\text{O}_{17}\text{H}_2\text{O}$ (I), has been synthesized and structurally characterized. Its structure consists of $[\text{V}_6\text{O}_{17}]^{4-}$ chains linked together by $[\text{Cu(dpa)}]^+$ chains into a 3D framework. There is one guest water molecule per formula located in the gallery spaces that can be reversibly desorption. The DRS results show a small bandgap size of $\sim$2.0eV, and which illustrates the great potential for Cu$^+$-containing hybrids in the discovery of active photocatalysts with visible-light bandgap sizes.

Acknowledgments

Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund (#46803-AC10), and the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy (DE-FG02-07ER15914) for support of this research, and also for assistance with the collection of single crystal X-ray data (P. Boyle).

References


18. Blatov, V.A.; TOPOS, A Multipurpose Crystallochemical Analysis with the Program Package, Samara State University, Russia, 2004.

Table 7.1. Selected Crystal Data and Structure Refinement Details of I.

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<td>Formula Weight (g/mol)</td>
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<td>$\mu$, (cm$^{-1}$)</td>
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<tr>
<td>Min &amp; Max peak heights ($e^/-\AA$)</td>
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\[
R_f = \frac{\Sigma |F_o - F_c|}{\Sigma F_o}, \quad R_w = \left[ \frac{\Sigma (w(F_o - F_c)^2)}{\Sigma F_o^2} \right]^{\frac{1}{2}}
\]

Table 7.2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\AA^2$) for I.

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Table 7.2 Continued

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*U(eq) is defined as one third of the trace of the orthogonalized \(U_{ij}\) tensor.*

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Table 7.3. Selected Bond Distances (Å), Angles (°) and Bond Valence Sums\(^a\) in I.

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</table>

\(^a\) \(S_{ij} = \exp\left[(R_0-R_{ij})/B]\right\), B = 0.37; \(R_0 = 1.574\ \text{Å}, 1.600\ \text{Å}, 1.803\ \text{Å}\) for Cu\(^{I}\)–N, Cu\(^{I}\)–O, and V\(^{V}\)–O respectively.\(^{12}\)
Figure 7.1. (A) (B) ~[001] and [010] polyhedral views of [Cu(dpa)]$_4$V$_6$O$_{17}$H$_2$O (I), yellow polyhedra = VO$_4$; (C) Structural view of connected [Cu(dpa)$^+$]$_n$ and [V$_6$O$_{17}$$^{4-}$]$_n$ chains with all symmetry-unique atom types labeled; the hydrogen bond (O1w−H1wa···O5, 2.192(2) Å) is labeled as a dashed line. All H atoms on the dpa rings are omitted for clarity.
Figure 7.2. Thermogravimetric analysis (TGA) curve of [Cu(dpa)]_4V_6O_{17}H_2O (I), plotted as weight (%) versus temperature (°C).

Figure 7.3. Powder XRD patterns of dehydration and rehydration of I: (a) Observed pattern of as-synthesized I; (b) Observed pattern after dehydration of I at 150 °C; (c) Observed pattern after dehydration of I at 250 °C; (d) Observed pattern after rehydration of I at 80 °C in an aqueous solution.
Figure 7.4. UV–vis diffuse reflectance spectrum (DRS) for $[\text{Cu(dpa)}]_4\text{V}_6\text{O}_{17}\text{H}_2\text{O}$ (I), plotted as $F(R)$ versus photon-energy (eV).
PART 4. RELATED METAL-OXYFLUORIDE HYBRIDS
CHAPTER 8
MICROPOROSITY, OPTICAL BANDGAP SIZES, AND
PHOTOCATALYTIC ACTIVITY OF M(I)-Nb(V) (M = Cu, Ag)
OXYFLUORIDE HYBRIDS

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Abstract
Using hydrothermal methods, a new series of five M(I)–Nb(V) oxyfluoride hybrid solids was prepared having the compositions [Cu(pyz)]$_2$NbOF$_5$ (1, pyz = pyrazine), Ag(pyz)NbOF$_4$ (2), M(bpy)NbOF$_4$·2H$_2$O (3, M = Cu; 4, M = Ag; bpy = 4,4’-bipyridine), and [Cu(dpe)]$_2$NbOF$_5$·8H$_2$O (5, dpe = 1,2-bis(4-pyridyl)-ethene). Each of the hybrid solids consist of layered structures with bridging ligands that coordinate via the Ag$^+$ or Cu$^+$ (i.e., M$^+$) sites in each layer. The structure of 1 is comprised of linear [Cu$_2$(pyz)$_2$$^{2+}$]$_n$ double chains that are cross-linked into double layers by partially O/F-disordered [NbOF$_5$$^{2-}$] octahedra. Hybrids 2 – 4 contain pyz- and bpy-pillared [MnbOF$_4$] layers, with the longer bpy ligand affording two interlayer water molecules per M$^+$ site. These [MnbOF$_4$] layers consist of ordered polar [NbOF$_4$]$^-$ chains that are bridged across the M$^+$ sites and that orient in alternating directions. The longest ligand in 5, dpe, results in a three-fold interpenetrating pillared network.
consisting of \([\text{Cu(dpe)}^+\])_n \text{ chains bridged by O/F-disordered [NbOF}_5^{2-}\text{ octahedra and accommodating four lattice water molecules per Cu}^+ \text{ site. Thermally-driven removal of water from 5 results in a loss of crystallinity, but which can be rapidly reversed by re-absorption of water. By contrast, the structures of 3 and 4 are retained with the removal of their water. Both show the reversible absorption of either two waters or one methanol molecule per M}^+ \text{ site. Measured optical bandgap sizes for the Ag-containing hybrids occur at ~3.13 eV and ~3.54 eV for 2 and 4, and for the Cu-containing hybrids at ~2.15 eV, ~2.71 eV, and ~2.30 eV for 1, 3, and 5, respectively. Dehydration of 3 and 4 results in a ~0.3 eV red-shift of their bandgap sizes. Hybrids 2 and 4 are also found to be the first metal-oxyfluorides active for the photocatalytic decomposition of methylene blue with rates of 1.83 and 1.37 mg L\(^{-1}\) h\(^{-1}\), respectively.}

**Introduction**

The field of hybrid solids has expanded rapidly owing to the rich structural diversity achieved through the use of organic ligands in controlling the structures of metal-oxide and –oxyfluoride frameworks. One of the most commonly reported strategies is the selection of specific inorganic ‘building blocks’ that are accessible in solution, such as metal-oxide clusters and layers, and that can modified and cross-linked via coordination to a wide possible array of bridging ligands. A range of important physical properties are found in metal oxides and that have been synthetic targets in many hybrids, including magnetism, ferroelectricity, microporosity, catalysis, as well as combinations thereof.\(^{1,5}\) However, currently a significant number of metal oxides are intensely investigated for their ability to
harness solar energy to drive photocatalytic reactions, while the properties and applications of hybrid solids in this area remain relatively unexplored.

Our current research efforts have focused on hybrid solids containing a combination of d⁰ (e.g., Re⁷⁺, V⁵⁺) and d¹⁰ (e.g., Cu⁺, Ag⁺) transition metals, in order to investigate the structural and electronic origins of their low-energy light absorption and photocatalytic activity. For example, several condensed metal-oxides, such as Ag₃VO₄,⁶ Ag₂MoO₄,⁷ and AgNbO₃,⁸ have been reported to exhibit photocatalytic activities at close to visible-light energies. Recently, we have synthetically targeted hybrid versions of these condensed metal oxides in order to probe new ligand-modified forms containing controllable [–O–M–O–M–]ₙ connectivities and dimensionalities. For example, ‘MₙReO₄’ or ‘MₙVO₃’ (M = Cu⁺ or Ag⁺; n = 1 or 2) layers can be pillared by bridging ligands and resulting in new hybrids such as M(pyz)ReO₄ (M = Cu, Ag),⁹,¹⁰ M(pzc)₂(H₂O)₂AgReO₄ (M = Co, Ni),¹¹ and Cu(pzc)₂AgReO₄.¹² Also, recently the Cu(bpy)ReO₄ and Cu(bpy)₂ReO₄·½H₂O hybrids have been shown to exhibit ligand-mediated structural transformations that result in a significant modulation of their bandgap sizes within visible-light energies.¹³ The first discovery of photocatalytic activity for hybrids was recently reported in the related vanadate hybrids [Ag(L)₄]V₂O₁₂·xH₂O and Ag₄(pzc)₂V₂O₆.¹⁴ However, while condensed niobium oxides represent some of the best known photocatalysts, the potential of Nb-containing hybrids remains entirely unexplored.

Niobium oxyfluorides have been investigated for their distorted Nb-centered octahedra that serve as convenient polar ‘building units’ that can lead to noncentrosymmetric structures and properties.¹⁵ The two commonly found [Nb(O/F)₆]ₙ⁻ octahedra include the O-bridged
[NbOF$_4$]$^-$ chain and isolated [NbOF$_5$]$^{2-}$ anions. The [NbOF$_4$]$^-$ chains are constructed from trans-[NbO$_2$F$_4$] octahedra, and have been found in MNbOF$_4$ (M = NH$_4^+$ or alkali metal)$^{16}$ but so far not for hybrids. These octahedra are bridged via the trans O atoms to give a chain with alternately shorter Nb = O and longer Nb – O bonds. By contrast, the individual [NbOF$_5$]$^{2-}$ anion has previously been reported in both inorganic solids and in hybrid solids. The distorted [NbOF$_5$]$^{2-}$ octahedra exhibits an out-of-center Nb atom that displaces towards the O ligand, forming a shorter Nb = O and longer trans Nb – F bond. Hydrothermal techniques have been used to prepare a number of hybrids containing [NbOF$_5$]$^{2-}$ octahedra that are usually O/F disordered and bridged by secondary metal cations.$^{15}$ However, none have been found as part of layered structures, and instead usually exhibit chain-type structures.

Presented herein are the syntheses and characterization of pillared-layer niobium-oxyfluoride hybrids, [Cu(pyz)$_2$]NbOF$_5$ (1), Ag(pyz)NbOF$_4$ (2), M(bpy)NbOF$_4$2H$_2$O (3, M =Cu; 4, M = Ag), and [Cu(dpe)$_2$]NbOF$_5$8H$_2$O (5), and that contain [NbOF$_5$]$^{2-}$ anions (1 and 6), as well as the first reported examples comprised of polar [NbOF$_4$]$^-$ chains (2, 3, and 4). These new hybrids have been investigated for their thermal stability, absorption/desorption of methanol and water from within the interlayer spaces, as well as their optical bandgap absorption and photocatalytic activity towards the decomposition of methylene blue.

**Experimental Section**

**General Procedures and Materials:** The syntheses of all hybrid compounds were performed using hydrothermal conditions. Starting materials included Ag$_2$O (99+%, Alfa Aesar), Cu$_2$O (99%, Alfa Aesar), Nb$_2$O$_5$ (99.5%, Alfa Aesar), pyrazine (99+%, Aldrich),
4,4’-bipyridine (98%, Alfa Aesar), and 1,2-bis(4-pyridyl)-ethene (99%, Aldrich). All reactants were heat sealed inside an FEP Teflon pouch (3”×4’’) that was placed inside an 125 ml Teflon-lined stainless steel reaction vessel and was backfilled with ~40 ml of deionized water before closing. All reactions were heated inside a convection oven at 150 °C for 1 – 3 days and slowly cooled to room temperature at ~6°Ch⁻¹. The products were recovered by filtration, washed with deionized water, and dried in air. The crystallinity and phase purity of each compound were confirmed by Powder X-ray Diffraction (PXRD) on an Inel XRG 3000 diffractometer (Cu Kα radiation; λ = 1.5406 Å), given in the Supporting Information. The PXRD patterns were scanned over the angular range 2θ = 0 – 106° with a step size of 0.02°.

**Synthesis of [Cu(pyz)]₂NbOF₅ (1), Ag(pyz)NbOF₄ (2), Cu(bpy)NbOF₄·2H₂O (3), Ag(bpy)NbOF₄·2H₂O (4), and [Cu(dpe)]₂NbOF₅·8H₂O (5).** The synthesis of 1 was performed by mixing 61.1 mg (0.23 mmol) of Nb₂O₅, 32.9 mg (0.23 mol) of Cu₂O, 36.8 mg (0.46 mmol) of pyrazine, 0.188 g (4.6 mmol) of 49% aqueous HF and 0.400 g (22.2 mmol) of deionized H₂O. Orange-red crystals were obtained in ~84% yield based on Cu. Compound 2 was synthesized by reacting 53.2 mg (0.20 mmol) of Nb₂O₅, 46.4 mg (0.20 mol) of Ag₂O, 32.0 mg (0.40 mmol) of pyrazine, 0.188 g (4.6 mmol) of 49% aqueous HF and 0.400 g (22.2 mmol) of deionized H₂O. Colorless-prism crystals were obtained in ~47% yield based on Ag. Compound 3 was prepared by reacting 61.1 mg (0.23 mmol) of Nb₂O₅, 32.9 mg (0.23 mmol) of Cu₂O, 71.8 mg (0.46 mmol) of bpy, 0.188 g (4.6 mmol) of 49% aqueous HF and 0.400 g (22.2 mmol) of deionized H₂O. Greenish-yellow bar crystals were recovered in ~66% yield based on Cu. The synthesis of 4 was performed by reacting 53.2
mg (0.20 mmol) of Nb₂O₅, 46.4 mg (0.20 mol) of Ag₂O, 63.7 mg (0.40 mmol) of bpy, 0.188 g (4.6 mmol) of 49% aqueous HF and 0.400 g (22.2 mmol) of deionized H₂O. Colorless prism-shaped crystals were recovered in ~70% yield based on Ag. Compound 5 was prepared by reacting 20.0 mg (0.075 mmol) of Nb₂O₅, 21.5 mg (0.15 mmol) of Cu₂O, 54.7 mg (0.30 mmol) of dpe, 0.188 g (4.6 mmol) of 49% aqueous HF and 0.400 g (22.2 mmol) of deionized H₂O. Orange plate-shaped crystals were obtained in ~70% yield based on Cu.

**Crystallographic Structure Determination of 1 – 5.** Suitable single crystals were selected and mounted on a nylon loop with a small amount of NVH immersion oil. All single-crystal X-ray measurements were made on a Bruker-Nonius X8 Apex2 CCD diffractometer at 296 K using Mo Kα radiation (λ = 0.71073 Å). The frame integrations were performed using the SAINT program. The resulting raw data were scaled and absorption corrected via a multi-scan averaging of symmetry-equivalent data using the SADABS program. Each structure was solved by direct methods and refined by full-matrix least-squares methods within the Bruker SHELXTL-97 program package. Anisotropic thermal displacement parameters of all non-hydrogen atoms were allowed to refine. The phenyl hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent carbon positions. The hydrogen atoms for water molecules were found in the residual electron density maps and constrained in the refinement at an O – H distance of 0.96Å. Further details of the data collections and structural refinements are summarized in Table 8.1. Selected interatomic distances and angles are listed in Table 8.2. Full details of the refinements can be found in the Supporting Information.
**Diffuse Reflectance Measurements.** UV-Vis diffuse reflectance spectra of all compounds were measured on a Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer equipped with an integrating sphere. Approximately 10 mg of powder of each sample was mounted onto a pressed BaSO$_4$ powder holder and placed along the external window. A pressed BaSO$_4$ powder was used as a reference, and the resulting data were plotted as the remission function $F(R_\infty) = (1-R_\infty)^2/(2R_\infty)$, where $R$ is the diffuse reflectance based on the Kubelka-Monk theory of diffuse reflectance.$^{20}$

**Thermogravimetric Analyses (TGA).** The thermal stability and decomposition of the hybrids were measured on a TA Instruments TGA Q50 under flowing nitrogen gas while heating to 650 °C at a programmed rate of 5 °C/min. Weighed amounts (~20 mg) of each compound were loaded onto Pt pans, equilibrated and tared at room temperature, and the data plotted as the starting weight (%) versus temperature (°C). Post-TGA residuals were characterized by PXRD (described above).

**Photocatalytic Reactions.** Methylene Blue (MB) was used a model dye contaminant in order to evaluate the photocatalytic activities of each sample in the purification of dye wastewater.$^{21}$ MB is reportedly difficult to degrade under visible light.$^{22-24}$ The photocatalytic activity of each sample for the decomposition of MB used previously described procedures.$^{14}$ The photocatalytic activity was measured by suspending a weighed amount (150 mg) of the powdered samples in an aqueous solution of MB (6.0 mg/L, 50 mL) in an ~60 mL cylindrical vessel. This mixture was stirred continuously under ultraviolet ($\lambda < 400$ nm) or visible-light ($\lambda < 400$ nm) irradiation using a 400 W high-pressure Xe arc lamp (focused through a shutter window). The Xe arc lamp was fitted with a water filter to
remove infrared radiation and with cutoff filters to select for the desired wavelength ranges. The reactions were paused at ~20 min intervals to determine the concentration of the aqueous MB solutions using a UV−Vis spectrophotometer at $\lambda = 655$ nm.

Results and Discussion

The structures, lattice water content, and optical properties of Ag(I)/Cu(I) niobium oxyfluoride hybrid solids have been systematically investigated using a series of linear bridging ligands, including pyz, bpy, and dpe. The hybrid structures of 1−5 are described within separate sections below according to the length of the bridging ligand. All symmetry-unique atoms are labeled on at least one representative figure of each structure. A listing of all near-neighbor interatomic distances can be found in Table 8.2 together with a Bond Valence Sum (BVS) analysis\textsuperscript{25} for each of the metal atoms. The BVS calculations of 1−5 indicate that all Ag and Cu sites have +1 oxidation states and that all Nb sites are in the +5 oxidation state, as expected.

i) Structures of 1 and 2 with Pyrazine.

$[\text{Cu(pyz)}]_2\text{NbOF}_5$ (1; pyz = pyrazine). The single-crystal characterization of 1 reveals a double-layer structure consisting of one symmetry-unique $[\text{Cu}_2(\text{pyz})_2^{2+}]_n$ double chain that is cross-linked into double layers by coordination to the $[\text{NbOF}_5]^{2−}$ octahedra, as shown in Figure 8.1. Each Cu$^{+}$ is coordinated to two fluoride ions from two neighboring $[\text{NbOF}_5]^{2−}$ octahedra, and to two nitrogen atoms on opposing pyrazine ligands above and below each chain, to form a distorted $\{\text{CuF}_2\text{N}_2\}$ sawhorse coordination geometry. Two Cu$^{+}$ sites share two common fluoride ions as a dimeric subunit, with a Cu − Cu distance of
These dimeric subunits form chains via coordination to the pyrazine ligands, which align face-to-face and run parallel to each other. Structurally similar dimeric subunits have been found in Cu(pyz)ReO$_4$ and [Ag(L)$_4$V$_4$O$_{12}$nH$_2$O (L = bpy, L = dpa)$_{9,14}$ and shows that π-π stacking interactions likely help to stabilize of the structure.

The single symmetry-unique [NbOF$_5$]$_2^-$ octahedron is nearly regular with the niobium site located on the inversion center, consistent with other known niobium oxyfluorides.$^{15}$ The Nb – F/O bond distances range from 1.903(3) to 1.931(3) Å. Bond-valence sum calculations (Table 8.2) indicate the disorder of O on the terminal F1 site (valence of 0.91) compared to the equatorial F(2) or F(3) sites (valences of 0.76 and 0.75, respectively). The O/F-disordered [NbOF$_5$]$_2^-$ octahedra and [Cu$_2$(pyz)$_2$$^{2+}$]$_n$ dimers link together via the corner-sharing F2, and form linear chains that run along the $b$ axis. Open spaces in the square net are relatively small at ~2.8 × ~4.8 Å$^2$ (Figure 8.1B), and which form between the cross-linked Cu – pyrazine and Cu – NbF$_4$(F/O)$_{2/2}$ chains.

$^{15}$

**Ag(pyz)NbOF$_4$ (2; pyz = pyrazine).** The structure of 2 is comprised of inorganic [AgNbOF$_4$] layers that are stacked and bridged via coordination of the pyz ligands to the Ag$^+$ sites in each layer, shown in Figure 8.2A. Each [AgNbOF$_4$] layer, shown in Figure 8.2B, consists of two types of homoatomic chains. One type consists of distorted {NbO$_{2/2}$F$_4$} octahedra that bridge via vertex-shared O atoms, while the other type is comprised of chains of edge-shared and distorted {AgN$_3$F$_{4/2}$} octahedra. These two chains are connected via two of the equatorial F atoms in {NbO$_{2/2}$F$_4$} to four different Ag$^+$ atoms within the layer. The layers are pillared via the pyrazine ligands, forming [Ag(pyz)]$_n$$^+$ chains with a face-to-face
orientation of the pyrazine ligands at ~3.9 Å for a relatively weak \( \pi - \pi \) interaction.\(^{26}\) The Ag – F and Ag – N distances are in the typical range, shown in Table 8.1.

Each niobium is in a slightly-distorted octahedral coordination geometry with four F atoms at the equatorial sites (Nb – F1, – F2, and – F3, at 1.89(1) Å, 1.90(1) Å and 1.93(1) Å, respectively), and two O atoms in a \textit{trans} orientation (Nb – O1 at 1.81(2) Å and 2.14(1) Å). As found in other [NbOF\(_4\)]\(^{-}\) layers, the shortest intra-octahedral bonds of ~1.8 Å correspond to Nb = O, the next largest of ~1.9 Å for Nb – F, and the longest of ~2.1 Å for Nb – O. However, this type of \{NbO\(_{2,2}F_{4}\}\} chain has previously only been observed in condensed MNbOF\(_4\),\(^{16}\) e.g., KNbOF\(_4\), (NH\(_4\))NbOF\(_4\) and Rb\(_5\)Nb\(_3\)OF\(_{18}\), with the first examples reported herein for hybrid solids. In (NH\(_4\))NbOF\(_4\) the Nb atom is shifted out of the basal plane for each of the octahedron by 0.323 Å, with adjacent chains aligned in opposite directions, as found in 2. Between neighboring [AgNbOF\(_4\)] layers the NbOF\(_4\)\(^{-}\) octahedra are separated by ~3.4 Å, to form relatively small open channels of ~3.4 Å \( \times \) ~5.4 Å as marked in Figure 8.2A.

ii) Structures of 3 and 4 with 4,4’-Bipyridine.

M(bpy)NbOF\(_4\)\(2\)H\(_2\)O (3, M = Cu; 4, M = Ag; bpy = 4,4’-bipyridine). Shown in Figure 8.3, the structures of 3 and 4 are similar and contain [MNbOF\(_4\)] layers, such as described above for 2, and that are pillared by the longer 4,4’-bipyridine ligand. Both 3 and 4 share comparable unit cell dimensions and sizes, and so are described together. However, the substitution of pyz for bpy results in significantly expanded interlayer spaces with open dimensions of ~6.0 \( \times \) ~7.0 Å in 3 and ~6.2 \( \times \) ~7.6 Å in 4, marked in Figure 8.3. The interlayer spaces are accessible and filled by two H\(_2\)O molecules per formula that hydrogen bonds to F atoms in the [MNbOF\(_4\)] layers (O1w\(\ldots\)F2, 2.86(6) Å in 3, and Ow\(\ldots\)F, 2.74(2) Å in
4). The two main structural differences between 3 and 4 are in the stacking and flatness of the [MNbOF₄] layers. In 3, the [CuNbOF₄] layers stack directly on top of each other with the bpy ligands oriented perpendicular to the layers, while for 4 the [AgNbOF₄] layers are shifted and the bpy ligands are slanted at an angle of ~80.9° (Figure 8.S2 in Supporting Information). Further, the [CuNbOF₄] layers in 3 are completely flat, while the [AgNbOF₄] layers in 4 are slightly undulated, as shown by the M–Nb–M’–Nb’ torsional angles in Table 8.2.

Shown in Figures 8.3C and 8.3D, each [MNbOF₄] layer in 3 and 4 consists of two types of homoatomic chains, as described above in 2. One type consists of a vertex-shared chain of distorted \{NbO₂₂F₄\} octahedra and the other a chain of edge-shared and distorted \{MN₂F₂/2\} octahedra. These two types of chains are connected via two of the equatorial F atoms in \{NbO₂₂F₄\} to four different M⁺ atoms within the layer. Each niobium atom is in a slightly distorted \{NbO₂₂F₄\} octahedral coordination geometry with four F atoms at equatorial sites within a narrow Nb – F distance range of 1.914(3) – 1.928(6)Å, and also to two axial O atoms. Bonding to the axial O atoms alternate between a shorter 1.725(7)Å and 1.728(9)Å for Nb = O, and a longer 2.107(7)Å and 2.082(9)Å for Nb – O, in 3 and 4 respectively. Within the chain, each Nb atom is shifted out of the basal plane of the octahedra by ~0.382Å in 3 and ~0.354Å in 4. These intra-octahedral distortions align down the chain in a polar fashion, with neighboring chains facing the opposite direction to cancel its dipole moment.

iii) Structure of 5 with 1,2-bis(4-pyridyl)-ethene.

[Cu(dpe)]₂NbOF₅·8H₂O (5, dpe = 1,2-bis(4-pyridyl)-ethene). The hybrid solid 5 exhibits a three-fold interpenetrating framework constructed from [Cu(dpe)⁺]ₙ chains that are
linked by \([\text{NbOF}_3]^2-\) octahedra, as illustrated in Figure 8.4A. Each Cu\(^+\) is coordinated to one F atom from \([\text{NbOF}_3]^2-\) and to two N atoms from separate dpe ligands, to give a local T-shaped \{CuN\(_2\)F\} coordination geometry. Each dpe ligand bridges between two Cu\(^+\) atoms to form a nearly linear \([\text{Cu(dpe)}]^+\)\(_n\) chain with a N – Cu – N bond angle of 166.0(1)\(^\circ\), respectively. The \([\text{Cu(dpe)}]^+\)\(_n\) chains are interconnected via coordination to the trans F atoms of the \([\text{NbOF}_3]^2-\) anions at positions alternately above and below each chain, shown in Figure 8.4B. However, the interlayer bridging between the \([\text{Cu(dpe)}]^+\)\(_n\) chains in 5 is not coplanar, and has a torsion angle of ~24\(^\circ\). This network is three-fold interpenetrating, shown in Figures 8.4C and 8.4D, with each exhibiting a stair-like framework similar to that known for \([\text{Ag(4,4'}-\text{bpy})\text{NO}_3]^{27}\). Despite the threefold interpenetration, the structure contains open channels with dimensions of ~4.8Å × 6.2Å, and that are filled by eight guest H\(_2\)O molecules per formula. All interatomic distances are otherwise within the typical ranges as reported for other metal-oxyfluoride hybrid structures containing chains or layers.\(^{28-30}\)

Within the framework, all \([\text{NbOF}_3]^2-\) octahedra are isolated from each other and exhibit a partial disorder over the O and F positions. Each Nb-centered octahedron is formed from four equatorial Nb - F distances of 1.941(11)Å (×2) and 1.969(10)Å (×2), and also to two axial Nb – O/F distances of 1.885(12)Å (×2). This last distance is intermediate between that typically found for Nb = O and the trans Nb – F distance (~1.73Å and ~2.10Å) as found in other niobium-oxyfluorides and in 1 above. Interestingly, the O/F disorder in the \([\text{NbOF}_3]^2-\) octahedra results the centrosymmetric space group \(Fddd\) rather than the polar space group \(Fdd2\) that would align its polar direction down the \(c\)-axis. Trial structural refinements in
Fdd2 did not result in alternately shorter Nb = O and longer Nb – F distances down the polar axis, and instead gave the intermediate distance expected for O/F disorder.

**Thermogravimetric Analyses (TGA).** The thermal stabilities and structural collapse involving the loss of water and ligands were investigated for 1 – 5 by heating each sample to 650 °C under flowing N₂. The TGA results for the hybrid solids are shown in Figure 8.5. The hybrids containing pyrazine, 1 and 2, show thermal stability up until a single major weight-loss step beginning at ~250 – 275 °C, owing to the loss of pyrazine ligands as well as additional O or F atoms (43.6% and 33.1% for 1 and 2, respectively). Previous studies have shown that pyrazine may oxidize upon liberation from the hybrid, and accounts for the additional weight loss of O or F atoms from the hybrid solids and reduction of the post-TGA products. The small weight gain of ~2.7% at ~350 – 400 °C for 1 arises because of a re-oxidation of the products. The post-TGA products were analyzed by Powder X-ray Diffraction (PXRD) to contain CuNb₂O₆ and CuO for 1, and Ag and AgNbO₃ for 2 (see Supporting Information). Thus, while Ag has not been re-oxidized in 2, the formation of CuO must have occurred via the re-oxidation of Cu in the products. The TGA of 3 – 6 each exhibit multiple weight-loss steps owing to the removal of the incorporated lattice water and the ligands separately. Each hybrid loses all of its water content upon heating from ~50 – 100 °C, exhibiting a total weight loss that is consistent with their refined compositions (obsd.(calc.) H₂O content of 8.4%(8.2%), 7.3%(7.4%) and 16.2%(17.1%) for 3, 4, and 5, respectively). A second weight-loss step occurs beginning at ~300 – 350 °C for 3 – 5, and that corresponds to the complete loss of ligands and approximately two F or O atoms per formula (obsd.(calc.) of 42.8%(44.1%), 41.7%(40.1%) and 50.5%(50.3%) for 3, 4, and 5,
respectively). As before, the post-TGA products were analyzed by PXRD to contain a mixture of CuNb$_2$O$_6$ and CuO for 3 and 5, and a mixture of Ag and AgNbO$_3$ for 4. Thus, neglecting the loss of water, the thermal stability of the hybrid frameworks increased upon going from the shorter pyz ligand (in 1 and 2), to the longer bpy and dpe ligands (in 3 – 5), each with the same mixture of post-TGA products either for Cu (1, 3, and 5) or Ag (2 and 4).

**Desorption and Reabsorption of Water or Methanol.** Each hybrid solid 3, 4, and 5 crystallizes in a pillared-layered structure that exhibits cavities containing guest water molecules that can be removed at just ~ 50 – 100 °C without the concomitant loss of ligands. Thus, the desorption of guest water molecules, followed by the reabsorption of guest water or methanol molecules, was probed and the resulting products were characterized by TGA and PXRD analyses. After dehydration at 120 °C for 1h, hybrid solids 3 and 4 retain their crystalline structures, as shown in the PXRD of Figure 8.6, with a very small shift of the diffraction peaks to higher angles. Unfortunately, suitable single crystals of their dehydrated forms have not yet been found to make a more precise structure determination. By contrast, most all of the intense PXRD peaks for 5 disappear, shown in Figure 8.S4 in the Supporting Information.

Interestingly, the loss of guest water molecules was accompanied by a noticeable change in color from greenish-yellow to goldish-orange for 3 and from colorless to gray for 4. Further, when the dehydrated samples of 3 and 4 are exposed to either water or methanol solutions, within about one minute their colors quickly returned to the original greenish-yellow for 3 and colorless for 4. The PXRD patterns of 3 and 4 after exposure to methanol and water are shown in Figure 8.6, with each exhibiting the characteristic diffraction peaks
corresponding to their respective original crystal structures. A TGA analysis of these products, Figure 8.7, showed weight losses corresponding with the removal of two water molecules per formula (calc./obsd. of 7.1%(8.2%) in 3 and 7.3%(7.4%) in 4) and about one methanol molecule per formula (calc./obsd. of 6.9%(7.3%) in 3 and 6.4(6.6%) in 4). Further, both 3 and 4 can be cycled between the dehydrated and rehydrated forms, and between the methanol absorbed and desorbed forms with the same molar capacity each time. The relative ease of this small-molecule absorption likely owes to the favorable hydrogen bonding interactions to both water and methanol to the interlayer F atoms on the chains of \{\text{NbO}_2\text{F}_4\} octahedral, i.e., forming \text{OH}_2\text{⋯F} or \text{MeOH}\text{⋯F} hydrogen bonds.\(^{33}\)

A similar dehydration and rehydration of the three-fold interpenetrating structure of 5 was investigated, especially considering its greater water content. However, the low-temperature removal of its water content (120 °C for 1 – 3 h) is accompanied by the loss of the crystallinity of its structure, as shown by PXRD (Figure 8.S4 in the Supporting Information). Only a few very weak and broad diffraction peaks were observed that could not be assigned. Also, the crystal habit changed from transparent orange platelets to opaque blackish-orange platelets that exhibited a high amount of cracks. Interestingly, these dehydrated samples can be fully rehydrated by immersing in an aqueous solution for several hours. Their color returns to greenish-orange and the PXRD patterns are nearly identical to that for the originally-synthesized samples. Thus, the hybrid structure of 5 easily reforms at room temperature in an aqueous solution.

**Optical Properties.** Heterometallic hybrid solids containing transition metals combining a d\(^{10}\) (e.g., \text{Cu}^+, \text{Ag}^+) and a d\(^0\) (e.g., \text{Nb}^{5+}, \text{Mo}^{6+}, \text{Re}^{7+}) electron configuration have drawn
increasing attention owing to their potentially low-energy visible-light absorptions that arise from a Metal-to-Metal Charger Transfer (MMCT) transition.\textsuperscript{6-8,34} The series of M(I)-Nb oxyfluoride hybrids in 1 – 5 exhibits colors varying from colorless to orangish-red. Thus, solid-state diffuse reflectance spectra of each was measured in order to probe the influence of the choice of late transition-metal (Ag\textsuperscript{+} versus Cu\textsuperscript{+}), the bridging ligands, and the water content on their optical bandgap sizes.

Shown in Figure 8.8, the onset of the optical absorption edges for the Ag-containing hybrid solids, 2 and 4, occurred in the ultraviolet energy range with estimated bandgap sizes of \~3.13 eV and \~3.54 eV, respectively. By contrast, the absorption edges for the Cu-containing hybrids, 1, 3, and 5, were generally positioned in the lower-energy visible-light energies with estimated bandgap sizes of \~2.15 eV, \~2.71 eV, and \~2.30 eV respectively. The substitution of Cu\textsuperscript{+} for Ag\textsuperscript{+} is expected to shift the optical absorption strongly into the visible region owing to the replacement of lower-energy d orbitals of Ag\textsuperscript{+} for the higher-energy d orbitals of Cu\textsuperscript{+}, as we reported earlier.\textsuperscript{9} Thus, the bandgap sizes of the Cu-containing hybrids are \~1 – 1.2 eV smaller than their Ag-containing analogues, i.e. for pyrazine-based structures in 1 versus 2, or the bipyridine-based structures in 3 versus 4.

The ligand-free MNbO\textsubscript{3} solids (M = Ag\textsuperscript{+}, Cu\textsuperscript{+}) also show a similar trend in bandgap sizes, of \~2.9 eV for AgNbO\textsubscript{3} and \~2.1 eV for CuNbO\textsubscript{3}.\textsuperscript{8,35} Hybrid solids 1 and 2 with pyz ligands each exhibit closely-similar bandgap sizes to that of the ligand-free MNbO\textsubscript{3} solids, showing that the pyz-based orbitals must fall outside the bandgap region and also have little effect on the bandgap size. Also, as expected for an electronic transition primarily involving the two metal centers, i.e., a MMCT transition, the incorporation of F into the metal-oxide
structure has had little discernible effect on its bandgap size. However, substitution of the shorter pyz ligand for the longer bpy ligand in 3 and 4 results in an ~0.4 – 0.6 eV blue-shift of their optical absorption edges compared to 1 and 2, respectively. A red-shift of ~0.3 eV in the bandgap sizes of 3 and 4 can be achieved, shown in Figure 8.8, upon removing the guest water molecules in the framework. Post-dehydration, the bandgap size of 3 is decreased to ~2.39 eV, while that for 4 is decreased to ~3.24 eV. Thus, the incorporated water molecules in the structures of 3 and 4 play a significant factor in increasing their bandgap sizes compared to the pyz-based structures of 1 and 2. Hydrogen-bonding interactions to the water molecules must be responsible for the modification of the atomic and electronic structure of the \([\text{M(bpy)NbOF}_4]\), though a structural determination of their dehydrated forms has so far proven difficult. In contrast, the dpe-containing structure of 5 contains guest water molecules but exhibits a smaller bandgap size.

**Photocatalytic Decomposition Reactions.** A dye molecule that is often used to represent the common contaminates in textile effluents is Methylene Blue (MB). MB is typically difficult to decompose in wastewater streams,\textsuperscript{21-24} and thus was selected in order to investigate the photocatalytic activities of the new hybrid solids toward the decomposition of organic pollutants. Only three hybrid solids, all of them silver-vanadates, have been investigated for this reaction and found to be active.\textsuperscript{14} However, the activity of metal-oxyfluoride hybrids is entirely unexplored. Changes in the concentration of the aqueous MB solution were plotted versus irradiation time, as shown in Figure 8.9. The simple auto-photolysis of the MB solution, i.e., with no added hybrid solid, was used as a control and is shown to decrease in concentration very slightly. During the first 20 min there is a slightly
faster apparent rate owing to the adsorption of MB to the particle surfaces, and that was not included in the calculation of the rate. Further, this decrease in MB concentration owing to surface absorption increased with the amount of solid used.

Only the Ag-containing hybrids, 2 and 4, were found to be photocatalytically active for this reaction under ultraviolet light, with the corresponding rates of 1.83 and 1.37 mg L$^{-1}$ h$^{-1}$, respectively. Compared to the hybrid vanadates these rates fall within the same range,$^{14}$ with the higher rates for the more extended metal-oxide/-oxyfluoride networks. After 2 h of irradiation, approximately 65% and 45% of MB has been decomposed with the use of 150 mg of 2 and 4, respectively. However, the Cu-containing hybrids (1, 3, and 5), with lower-energy bandgap sizes, were not active either under visible or ultraviolet light. Owing to the different energies of the 3d$^{10}$ versus 4d$^{10}$ orbitals, the Cu-containing hybrids have higher-energy valence bands and a reduced oxidizing strength compared to the Ag-containing hybrids. Thus, the presence of Ag in the hybrid framework appears to be critical for photocatalytic activity towards the decomposition of MB or potentially other organic pollutants.

**Conclusions**

Three different bridging ligands, pyz, bpy, and dpe, were used to investigate the range of structure and property modifications possible by varying the ligand length in copper- and silver-niobate oxyfluoride structures. The structure of 1 contains layers of $[\text{Cu}_2(\text{pyz})_2^{2+}]_n$ double chains that are cross-linked into double layers by coordination to the disordered $[\text{NbF}_6(\text{F/O})_2]^{2-}$ anions. The structures of 2 – 4 all contain $[\text{MNbOF}_4]$ (M = Ag/Cu) layers
constructed from ordered polar [NbOF$_4$]$^-$ chains and that are pillared by either pyz or bpy ligands. Hybrid 6 has a three-fold interpenetrating framework consisting of [Cu(dpe)$^+$]$^n$ chains that are linked by coordination to disordered [NbOF$_5$]$_2^-$ anions. Each of the bridging ligands results in a layered or pillared structure that accommodates an increasing amount of intralayer water from 0 for pyz, to 2 for bpy, and to 8 for dpe. The guest water molecules of 3 and 4 can be removed at only ~120 °C without a loss of their crystallinities. Both can also re-absorb up to about two water molecules or one methanol molecule per formula at room temperature. The solids either exhibit bandgap sizes at ultraviolet energies for the Ag-containing hybrids or visible-light energies for the Cu-containing hybrids. Further, the Ag-containing hybrids are photocatalytically active for the decomposition of MB in aqueous solutions.

**Acknowledgments**

Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund (#46803-AC10) and the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy (DE-FG02-07ER15914) for support of this research, and also for assistance with the collection of single crystal X-ray data (P. Boyle).

**Supporting Information Available**

Crystallographic data for 1 – 5 in CIF format and powder X-ray diffraction results for all prepared compounds including for the as-synthesized hybrids, TGA residual products, and
de/rehydration of 5. These materials are available free of charge via the Internet at
http://pubs.acs.org.

References
18. Bruker-Nonius, SADABS version 2.1, 2004, Bruker-Nonius, Madison, WI 53711, USA
212


Table 8.1. Crystal Data and Structure Refinement Details for Compounds 1 – 5.

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₁ R₁ = Σ(|Fₒ - F_c|) / ΣFₒ; wR₂ = [Σ( w(Fₒ² - F_c²)² ) / (Σ(Fₒ²)²) ]½; w=σₒ².
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$[\text{Cu(dpe)}]_2\text{NbOF}_5\cdot8\text{H}_2\text{O}$, (5)

| Cu1 N1        | $\times2$ | 1.870(11) | N1 – Cu1 – N2 | 166.0(1) |
| F1            | 2.276(12) | N1 – Cu1 – F1 | 97.0(1) |
| $\sum S_{ij}$ | 1.00      |

| Nb1 F1/O      | $\times2$ | 1.885(12) | (F – Nb1 – F)$_{trans}$ | 180.0 |
| F2            | $\times2$ | 1.941(11) | (F – Nb1 – F)$_{ciss}$ | 90.0 |
| F3            | $\times2$ | 1.969(10) |
| $\sum S_{ij}$ | 4.71      |

$^a S_{ij} = \exp[(R_0 - R_{ij})/B]$, $B = 0.37$, $R_0 = 1.574$ Å for Cu$^1$ – N, $R_0 = 1.94$ Å for Cu$^1$ – F, $R_0 = 1.798$ Å for Ag$^1$ – N, $R_0 = 1.592$ Å for Ag$^1$ – F, $R_0 = 1.822$ Å for Nb$^v$ – F, and $R_0 = 1.911$ Å for Nb$^v$ – O.$^{31}$
Figure 8.1. (A) An −[100] polyhedra view of layer structure 1; red polyhedra are Cu-centered, blue are Nb-centered. (B) Structure view of 1 with the square nets ca. 2.8 × 4.8 Å², where white balls are C, blue are N, green are F, orange are Nb, and light-blue are Cu.
Figure 8.2. (A) An ~[010] Polyhedra view of structure 2 with open channels (~3.4 × 5.3 Å). Red polyhedra are Ag-centered, blue are Nb-centered and yellow are pyrazine molecules. (B) Structure view of a single AgNbOF$_4$ layer, where white balls are C, blue are N, green are F, orange are Nb, and pink are Ag. All H atoms are omitted for clarity.
Figure 8.3. Polyhedral views of structures 3 (A) and 4 (B) with open channels marked; Red polyhedra are Cu/Ag-centered and blue are Nb-centered. View of a single [MNB\textsubscript{OF}_{4}] layer in 3 (C) and 4 (D) with a symmetry-unique atom set labeled; White circles are C, blue are N, green are F, orange are Nb, pink are Ag, and light-blue are Cu. H atoms on bpy omitted for clarity.
Figure 8.4. Structural views of 5: (A) A [001] polyhedral view with H$_2$O in open channels, (B) the local coordination environments with the torsion angle between neighboring chains, (C) the local T-shaped Cu coordination geometry, and (D) the simplified view of the resulting network interpenetration. Blue octahedral are Nb-centered, white circles are C, blue are N, green are F, orange are Nb, and light-blue are Cu. All H atoms are omitted for clarity.
Figure 8.5. Thermogravimetric analysis (TGA) of 1 – 5 plotted as wt% via temperature (°C).

Figure 8.6. Powder X-ray diffraction patterns of 3 and 4: as synthesized (a) and (e), and after dehydration at 120 °C (b) and (f), and rehydration (c) and (g), and intercalation by methanol (d) and (h), respectively.
Figure 8.7. The thermogravimetric analysis (TGA) at 120 °C for 3 and 4 plotted as wt% versus time (min): (a) after intercalation of the dehydrated structures by H₂O; (b) methanol.
Figure 8.8. (A) UV–vis diffuse reflectance spectra (DRS) for 1 – 5. (B) Comparison of DRS of 3 and 4, (a) as-synthesized, (b) dehydrated structures.
Figure 8.9. Photocatalytic decomposition of MB solutions (6.0 mg/L, 50 mL) using 150 mg of 2(a) and 4(b) under UV light irradiation. Photolysis of the ligand by itself is labeled (c).
Supporting Information

Microporosity, Optical Bandgap Sizes, And Photocatalytic Activity Of M(I)-Nb(V) (M = Cu, Ag) Oxyfluoride Hybrids

Haisheng Lin and Paul A, Maggard

Figure 8.S1. Powder X-ray diffraction patterns of 1–5, as synthesized (top) and simulated (below).
Figure 8.S2. ~[100] and [010] polyhedra view of structure 3(A) and 4(B). Red polyhedra are Cu/Ag-centered, and blue are Nb-centered.
Figure 8.S2. Powder X-ray diffraction patterns of TGA residuals for 1−5 with the simulated patterns of Ag, AgNbO$_3$, CuO and CuNb$_2$O$_6$.

Figure 8.S3. Powder X-ray diffraction patterns of 5: as synthesized (a), and after dehydration at 120 °C (b), and rehydration (c).
CHAPTER 9

A NEW SERIES OF HETEROMETALLIC HYBRIDS CONTAINING M(L) (M = Cu, Ag; L = pyz, bpy) CHAINS AND EARLY TRANSITION METAL (Ti, V, Mo, W) OXYFLUORIDE ANIONS

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Abstract

Using hydrothermal reactions, a series of new heteromeric oxyfluoride/organic hybrid solids, Cu$_2$(pyz)$_3$TiF$_6$ (1), [Cu(pyz)]$_2$V$_3$O$_2$F$_{10}$ (2), [Cu(pyz)]$_2$MO$_2$F$_4$ (M = Mo, 3; M = W, 4), Cu(bpy)VOF$_4$·2H$_2$O (5), [Cu(bpy)]$_2$[Mo$_2$O$_4$F$_6$(H$_2$O)]·2H$_2$O (6), [Ag(bpy)]$_2$[V$_2$O$_3$F$_6$·(H$_2$O)]·2H$_2$O (7), and [Ag(bpy)]$_4$[Mo$_2$O$_4$F$_6$][Mo$_2$O$_4$F$_6$(H$_2$O)]·6H$_2$O (8), (pyz = pyrazine, bpy = 4,4’-bipyridine) were synthesized by combining early (Ti$^{4+}$, V$^{5+}$, Mo$^{6+}$, W$^{6+}$) and late (Cu$^+$, Ag$^+$) transition metals with the bridging ligands (pyz and bpy). The overall structures of these materials reflect the influences of the early transition metal oxyfluoride anions and the length of bridging organic ligands. The structure of 1 is a 3D pillar-layered framework comprised of neutral [Cu$_2$(pyz)TiF$_6$] layers pillared via pyz ligands. Hybrid 2 forms a 2D sheet structure with alternating polymeric [Cu(pyz)]$^+$ linear double chains and inorganic vanadium oxyfluoride [V$_3$O$_2$F$_{10}$]$^{2-}$ infinite chains, while isostructural 3 and 4 exhibit a
different 2D sheet framework consisting of one symmetry unique \([\text{Cu}_2\text{MO}_2\text{F}_4]\) infinite linear chain that has covalent Cu–pyz–Cu bridges to two neighboring chains. In contrast, using the longer length of bridging organic ligand bpy, the latter four structures of \(5\)–\(8\) with 2D layer and 3D pillared-layered frameworks consisted of nearly linear \(\text{M(bpy)}^+\) chains (\(\text{M = Cu, Ag}\)) and new asymmetric V/Mo oxyfluorides anions, including a \([\text{VOF}_4]^-\) chain in \(5\), two different clusters \([\text{Mo}_2\text{O}_4\text{F}_6]^{2-}\) and \([\text{Mo}_2\text{O}_4\text{F}_6(\text{H}_2\text{O})]^{2-}\) in \(6\) and \(8\), and \([\text{V}_2\text{O}_3\text{F}_6(\text{H}_2\text{O})]^{2-}\) in \(7\), respectively. UV-vis diffuse reflectance spectra exhibit red-shifted absorption bands, with estimated band gap sizes ranging from \(~3.2\) to \(~2.1\) eV depending on their structures and compositions. Thermogravimetric analyses (TGA) show that hybrids \(1\)–\(4\) exhibit one weight loss step of pyz ligands and partial F atoms per formula, while in \(5\), \(7\) and \(8\) the lattice waters were easily removed by heating to \(~90\) °C, and then followed by the removal of bpy ligands and partial F atoms to \(~400\) °C. However, \(6\) exhibited a robust and stable structure without any weight-loss by heating to \(~280\) °C under flowing \(\text{N}_2\) gas.

**Introduction**

The synthesis of heterometallic hybrids has been of growing contemporary interest in the field of solid-state chemistry, because of their abilities to express the functionality and flexibility of organic ligands within metal-oxide structures. The combination of inorganic components and organic ligands gives the potential for generating novel covalently networked materials with possible applications in catalysis, separations, magnetism and optics.\(^1\)-\(^4\) Thus, the ability of chemists to rationally design new solid-state architectures has become a particularly topical and important subject.\(^5\) As for heterometallic
oxyfluoride/organic hybrids, several recent groups recently outlined general principles for
crystal engineering of three dimensional coordination compounds, with several notable
two in the design of chiral and polar chains.6-10

One of our research interests in this field has been directed toward new 3D stable pillar-
layered and/or porous solids that predispose the structure toward guest intercalations within
the gallery or pillared areas and thus to probe the structural or physical property effects of the
intercalating or deintercalating guest molecules between the open areas. The strategy is to
introduce the (N, N)-bridging organic ligands linked via the late transition metal sites (e.g.
Ag, Cu) to form the metal-organic chains and to be pillars between the separated metal-oxide
layers. For example, we have recently extended this idea to the incorporation of Cu/Ag-
(N,N)-bridging organic ligands and niobium oxyfluoride systems, and which resulted in 3D
nonpolar and polar hybrid structures.11 Also, these structures are effected by the length of
organic ligands, and exhibit a red-shift of their optical absorption wavelength via
intercalating with small molecules.

Presented herein are the syntheses and structures of a new series of Ti, V, Mo and W-
based hybrids with late (Cu\(^{+}\), Ag\(^{+}\)) transition metals and the bridging ligands (pyrazine, 4, 4’-
bipyridine). There are Cu\(_2\)(pyz)\(_3\)TiF\(_6\) (1), [Cu(pyrazine)]\(_2\)V\(_5\)O\(_2\)F\(_{10}\) (2), [Cu(pyrazine)]\(_2\)MO\(_2\)F\(_4\) (M = Mo,
3; M = W, 4), Cu(bpy)VOF\(_4\)2H\(_2\)O (5), [Cu(bpy)]\(_2\)[Mo\(_2\)O\(_4\)F\(_6\)(H\(_2\)O)]2H\(_2\)O (6) [Ag(bpy)]\(_2\)-
[V\(_2\)O\(_3\)F\(_6\)(H\(_2\)O)]2H\(_2\)O (7), and [Ag(bpy)]\(_4\)[Mo\(_2\)O\(_4\)F\(_6\)][Mo\(_2\)O\(_4\)F\(_6\)(H\(_2\)O)]6H\(_2\)O (8). The
employed characterization methods include powder and single-crystal X-ray diffraction,
thermogravimetric analysis (TGA) and UV-vis diffuse reflectance.

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Experimental Section

General Procedures and Materials. All the compounds were synthesized under hydrothermal conditions by heat sealing all the starting materials into a FEP Teflon pouch (3’’×4’’). Then the pouch was placed inside a 125 mL Teflon-lined stainless steel reaction vessel which was backfilled with ~40 mL of deionized water before closing. Starting materials include Ag₂O (99+% metals basis, Alfa Aesar), Cu₂O (99% metals basis, Alfa Aesar), TiO₂ (99.9%, Alfa Aesar), V₂O₅ (99.99%, Alfa Aesar), MoO₃ (99.999%+, Alfa Aesar), WO₃ (99.8%, Alfa Aesar), HF (aqueous, 49% Aldrich), pyrazine (= pyz, 99+% Aldrich), pyrazine (= pyz, 99+% Aldrich), and 4,4’-bipyridine (= bpy, 98%, Alfa Aesar) were used without further purification. After reaction, it was slowly cooled to room temperature at 6 °C/h⁻¹, and then the products were filtered, washed with deionized water and dried in air. The phase purity and crystallinity of each compound were checked by powder XRD patterns using an Inel XRG 3000 diffractometer (Cu Kα radiation, λ = 1.5406 Å).

Synthesis. The synthesis of Cu₂(pyz)₃TiF₆ (1) was performed by adding 28.8 mg (0.20 mmol) of Cu₂O, 32.0 mg (0.40 mmol) of TiO₂, 32.0 mg (0.40 mmol) of pyrazine, 0.188 g (4.6 mmol) of 49% aqueous HF, and 0.40 g (22.2 mmol) of H₂O to an FEP Teflon pouch. The reaction vessel was heated to 150 °C for 24 h inside a convection oven. Red prism crystals of 1 were obtained in ~60% yield based on Cu. The synthetic procedures for [Cu(pyz)]₂V₃O₅F₁₀ (2), and [Cu(pyz)]₂MO₂F₄ (M = Mo, 3; M = W, 4) were similar to that of 1 with identical stoichiometric ratios of the starting materials, except for the use of V₂O₅, MoO₃ and WO₃ in place of TiO₂. The reaction of 2 was heated to 180 °C for 72 h, and pure orange prism crystalline samples of 2 were also obtained in ~60% yield. The reactions of 3
and 4 were 150 °C 24 h with pure red prism crystalline samples obtained in ~65% and ~50% yield for 3 and 4, respectively.

The synthesis of Cu(bpy)VOF$_4$·2H$_2$O (5) was performed by adding weighed amount of 37.9 mg (0.21 mmol) of V$_2$O$_5$, 30.0 mg (0.21 mmol) of Cu$_2$O, 65.0 mg (0.42 mmol) of 4,4'-bipyridine, 0.19 g (4.6 mmol) of 49% aqueous HF and 0.2 g (11.1 mmol) of deionized H$_2$O in an FEP Teflon pouch that was subsequently heat sealed. The reactants were heated at 180 °C for 3 days in a reaction vessel inside a convection oven. Dark-brown prism crystals were obtained by filtration ~22% yields based on Cu. The synthetic procedures for [Cu(bpy)$_2$][Mo$_2$O$_4$F$_6$(H$_2$O)]2H$_2$O (6), [Ag(bpy)$_2$][V$_2$O$_3$F$_6$(H$_2$O)]2.5H$_2$O (7), [Ag(bpy)$_4$][Mo$_2$O$_4$F$_6$][Mo$_2$O$_4$F$_6$(H$_2$O)]6H$_2$O (8) were similar to that of 5 with identical stoichiometric ratios of the starting materials, except for the use of MoO$_3$ in place of V$_2$O$_5$ and Ag$_2$O in place of Cu$_2$O. The reactants of 6 were heated at 180 °C for 5 days and orange block crystals were obtained by filtration in ~82% yield based on Cu. The reactants of 7 were heated at 180 °C for 24 hours with pale-yellow bar/prism crystals obtained in ~54% yield based on Ag. The colorless bar/platelet crystals of 8 were obtained in ~75% yield based on Ag by heating the reactants at 150 °C for 72 hours. The phase purities of 1–8 were >95% according to the powder X-ray diffraction data.

Crystallographic Structure Determination. X-ray single-crystal diffraction for compounds 1–8 were collected on a Bruker-Nonius X8 Apex2 CCD diffractometer at ambient temperature (296 K) using Mo Kα radiation (λ = 0.71073 Å). The frame integrations were performed using the SAINT program. The resulting raw data were scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using the
The structures of 1−8 were solved by direct methods using the SHELXS-97 program of the Bruker SHELXTL package and refined by the full-matrix least-squares methods with SHELXTL-97. The structural model was fit to the data using full matrix least-squares based on F. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent carbon atoms. Details for structural analysis and refinement are summarized in Table 9.1. Table 9.2 lists selected interatomic contacts and bond-valence-sums for each of structures.

**Optical Properties.** The UV-vis diffuse reflectance spectra of each powdered sample were measured on a Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer equipped with an integrating sphere. ~10 mg of powder of each sample was mounted onto a pressed BaSO₄ powder holder and placed along the external window. A pressed BaSO₄ powder was used as a reference, and the data were plotted as the remission function $F(R_\infty) = (1 - R_\infty)^2 / (2R_\infty)$, where $R$ is diffuse reflectance based on the Kubelka-Monk theory of diffuse reflectance.

**Thermogravimetric Analyses (TGA).** Weighed amounts (~20 mg) of each compound were loaded onto Pt pans, equilibrated and tarred at room temperature on a TA Instrument TGA Q50, and the data plotted as the % starting weight versus temperature (°C). The samples were heated to 600 °C at a rate of 5 °C/min under flowing nitrogen gas (40 mL/min).
Results and Discussion

Structural Descriptions. Cu$_2$(pyz)$_3$TiF$_6$ (1). The structure of 1, illustrated in Figure 9.1, generally consists of neutral [Cu$_2$(pyz)TiF$_6$] layers that are bridged via pyz ligands to the Cu sites in each layer. The single symmetry-unique [Cu$_2$(pyz)TiF$_6$] sheet stacks directly above and below, down the c-axis, to generate the full 3D pillar-layered structure, similar to the structure of M(pyz)ReO$_4$ (M = Cu, Ag)\cite{16,17} as shown in Figure 9.1A. Each [Cu$_2$(pyz)TiF$_6$] sheet is comprised of corner-shared [TiF$_6$]$^{2-}$ octahedra and {CuF$_2$N$_3$} trigonal bipyramids that alternate and are arranged in a $4^4$ network, as shown in Figure 9.1B. Interestingly, within each $4^4$ network, there is one extra pyz ligand cross-linked to two closest-neighbor Cu sites. The [TiF$_6$]$^{2-}$ octahedra are slightly-distorted with four symmetric equatorial distances Ti–F$_1$ at 1.868(1) Å and two shorter axial distances Ti–F$_2$ at 1.839(1) Å due to the Jahn-Teller distortion. Each TiF$_6$ octahedron is bonded to four different Cu$^+$ atoms in the layer via four equatorial F$_1$ atoms (Cu–F$_1$ at 2.636(2) Å), while each Cu$^+$ atom is also bridged by two F groups from the two separate TiF$_6$ octahedra, and also to the nitrogen groups on two bpy ligands oriented above and below each layer at a Cu–N distance of 1.888(5) Å. The symmetry-unique atoms are labeled in Figure 9.1B and the corresponding interatomic distances are tabulated in Table 9.2. In addition, the calculated bond valence sums ($\sum S_{ij}$)\cite{18} for Cu and Ti, listed in Table 9.2, are consistent with +1 and +4 oxidation states for each, respectively.

[Cu(pyz)]$_2$V$_3$O$_2$F$_{10}$ (2). As shown in Figure 9.2, the structure of 2 is a 2D layer framework consisted of two distinct chains, a [Cu(pyz)]$^+$ linear double chain and a vanadium oxyfluoride [V$_3$O$_2$F$_{10}$]$^{2-}$ chain. These chains are alternate and connected to each other.
through *cis*-O atoms of vanadium oxyfluoride octahedra, and are extended along the *a*-axis. Each Cu atom is coordinated in a slightly-distorted seesaw geometry, which is formed by two oxygen atoms (Cu1–O1 at 2.482(2) Å and 2.479(2) Å) from two [V(1)O2F4] octahedra and two nitrogen atoms (Cu1–N1, –N2 at 1.928(3) Å, 1.911(3) Å, respectively) from two pyz ligands. The axial N1–Cu1–N2 bond angle is nearly linear, at ~164.3°, as expected for a seesaw geometry. The [V3O2F10]2− chain contains two symmetry unique V atoms with octahedral geometry. Each V(1) is bonded to one *cis*-O with a shorter V1–O1 distance at 1.729(2) Å and three F atoms in the equatorial sites (V(1)–F1, –F1’, –F5 at 2.008(2) Å, 2.060(2) Å, 1.774(2) Å), and two more *trans*-F atoms (V1–F2, –F3 at 1.962(2) Å, 1.964(2) Å, respectively), to give an acentric distorted octahedra. The octahedra of V(2) is centrosymmetric with nearly regular V–F distances (V2–F2, –F3 and F4 at 1.958(2) Å, 1.938(2) Å, and 1.916(2) Å respectively). Two [V(1)OF5]3− octahedra are edge-sharing to two F(1) atoms and form a [V2O2F8]4− dimeric unit, which are further interconnected via corner-sharing F atoms with the centric [V(2)F6]2− octahedra to form a 1D vanadium oxyfluoride chain along the *a*-axis. The symmetry-unique atoms are labeled in Figure 9.2 and the corresponding interatomic distances are tabulated in Table 9.2. In addition, the calculated bond valence sums (Σ*S*~ij~)18 for Cu and V listed in Table 9.2, are consistent with +1 and +5 oxidation states for each, respectively.

[Cu(pyz)2MO2F4 (M = Mo, 3; M = W, 4). Hybrids 3 and 4 are isostructural with a different 2D sheet framework from that of 2, and both consist of one symmetry-unique [Cu2MO2F4] linear chain that has covalent Cu–pyz–Cu bridges to two neighboring chains, as
shown in Figure 9.3. Each Cu is coordinated by two F atoms from two isolated \([\text{MO}_2\text{F}_4]^{2-}\) octahedra and two nitrogen atoms from the pyrazine ligands above and below each chain, to complete a \(\{\text{CuO}_2\text{N}_2\}\) seesaw geometry (N–Cu–N = 163.2(1)°). The coordination of each Cu atom to two nitrogen atoms of bridging pyrazine ligands results in the extended 1D chains \(\{\text{Cu(pyz)}^+\}_n\) along the direction of [100]. The dimer subunit of two closest \(\{\text{Cu(pyz)}^+\}_n\) chains are face-to-face and face-sharing via two F atoms with a shortest Cu–Cu distance 3.2484(8) Å, which has been reported in \(\text{Cu(pyz)}\text{ReO}_4\) and in the analogous Ag dimer in \([\text{Ag(L)}]_4\text{V}_4\text{O}_{12}\cdot n\text{H}_2\text{O}\) (L = bpy, n = 2; L = dpa, n = 4), indicating some π–π stacking interactions help to stabilize the framework.

The \([\text{MO}_2\text{F}_4]^{2-}\) octahedra are centric, where each M is found on an inversion center, and similar to other known metal-oxyfluoride octahedra. All of the O/F atoms are disordered with M–F/O bonds ranging from 1.844(3) to 1.896(4) Å. The bond valence calculation results (listed in Table 9.2) indicate that the oxidation states of both Cu and M are +1 and +6, respectively. The \([\text{MO}_2\text{F}_4]^{2-}\) octahedra and \([\text{Cu}_2\text{O}_2\text{N}_2]\) dimer subunits link together via corner-sharing (O1), leading to the linear chains running along the [010] direction. The Cu–pyrazine–Cu and Cu–MO\(_2\)F\(_4\) chains are cross-linked via the Cu sites, and the framework exhibits 2D square nets of \(\sim 2.8 \times 4.6\) Å\(^2\) (located in Figure 9.3).

\(\text{Cu(bpy)}\text{VOF}_4\cdot 2\text{H}_2\text{O}\) (5). The structure of 5 is iso-structural to that of \(\text{M(bpy)}\text{NbOF}_4\cdot 2\text{H}_2\text{O}\) (M = Cu, Ag). As shown in Figure 9.4, its structure is comprised of neutral \([\text{CuVOF}_4]\) layers that are cross-linked by 4,4′-bipyridine ligands to Cu sites in each layer. Within each layer, each Cu atom has a distorted octahedral coordination geometry with four F atoms in the equatorial sites (Cu–F2 at 2.774(6) and 3.119(6) Å; –F3 at 2.983(3) and
3.034(6) Å, and two N atoms from bpy ligands above and below in the trans-positions (Cu–N1 at 1.902(5) Å). These edge-sharing Cu-centered octahedrons are bridged via cis-F atoms to form an infinite chain along the a-axis. Each vanadium atom has a slightly distorted octahedral coordination with four F atoms at the equatorial sites (V–F at 1.75–1.93 Å), and two oxygen atoms in the trans positions with V–O1 at 1.72(2) and 2.03(2) Å in 5. In contrast to the Cu-centered octahedral chains, the V oxyfluoride chains are constructed by the corner-sharing V-centered octahedra through trans-O atoms. Within the chain, each V atom is shifted from the base plane of the octahedron by ~0.31 Å in 5 in the same direction to form a polar chain. However, there is no net-dipole moment in the structure, as this shift in adjacent chains onsets in the opposite direction. Further, the arrangement of cations and anions within the [CuVOF₄] layer are the same as that in M(bpy)NbOF₄·2H₂O (M =Cu, Ag).⁵

Also, the bpy ligands in both structures arrange face-to-face at a π–π stacking distance of ~3.7 Å, exhibiting weak π–π interaction as a result of the chains of edge-shared Cu⁺ cations at a relatively close distance Cu–Cu of ~3.73 Å.

[Cu(bpy)]₂[Mo₂O₄F₆(H₂O)]·2H₂O (6). 6 exhibits a 2D sheet structure with [Cu(bpy)]ₙ and {Cu₂[Mo₂O₄F₆(H₂O)]}ₙ chains as shown in Figure 9.5. Two symmetry-unique Cu⁺ atoms are coordinated in a square planar geometry by two F atom from Mo₂O₄F₆(H₂O)²⁻-dimers (Cu–F, 2.705 and 2.825(5) Å), forming the double inorganic chains {Cu₂[Mo₂O₄F₆(H₂O)]}ₙ running down the a-axis. Each Cu is also bonded to two bpy ligands, with Cu–N distances of 1.855(5) and 1.879(5) Å, to form [Cu(bpy)]ₙ chain down the b-axis. The vertex-shared Mo₂O₄F₆(H₂O)²⁻ octahedral dimer can be viewed as a condensation of two acentric MoO₂F₄²⁻ octahedra via one F vertex. Also, the calculated bond valence sums
(ΣSij)\textsuperscript{18} for Cu and Mo in 6 listed in Table 9.2, are consistent with +1 and +6 oxidation states, respectively.

[Ag(bpy)]\textsubscript{2}[V\textsubscript{2}O\textsubscript{3}F\textsubscript{6}(H\textsubscript{2}O)]2H\textsubscript{2}O (7). Compound 7 is a 3D pillared-layer structure comprised of neutral Ag\textsubscript{2}V\textsubscript{2}O\textsubscript{3}F\textsubscript{6}(H\textsubscript{2}O) layers that are bridged via bpy ligands to the Ag sites in each layer, as shown in Figure 9.6. These inorganic layers are comprised of chains of vertex-shared V\textsubscript{2}O\textsubscript{3}F\textsubscript{6}(H\textsubscript{2}O)\textsuperscript{2–} and {AgOFN\textsubscript{2}} square planar polyhedra that are arranged into a 10\textsuperscript{3} rectangular network, as shown in Figure 9.6B. The V\textsubscript{2}O\textsubscript{3}F\textsubscript{6}(H\textsubscript{2}O)\textsuperscript{2–} dimer is the first known example of this polyhedral dimer, consisting of an acentric VOF\textsubscript{5}\textsuperscript{2–} octahedra and VO\textsubscript{2}F\textsubscript{2}(H\textsubscript{2}O)\textsuperscript{–} square bipyramid with one vertex-shared F atom. The V–O and V–F distances are regular and fall within the expected ranges, with V–O distances of 1.577(7) Å and 1.621(6) Å, V–O\textsubscript{w} distances of 2.075(9) Å, and longer V–F distances of 1.795–1.897(6) Å. Each V\textsubscript{2}O\textsubscript{3}F\textsubscript{6}(H\textsubscript{2}O)\textsuperscript{2–} dimer bonds via two O vertices from the VO\textsubscript{2}F\textsubscript{2}(H\textsubscript{2}O)\textsuperscript{–} unit to Ag\textsuperscript{+} in the plane of the layer (Ag1–O2 of 2.599(6) Å), and also via two equatorial F atoms from VOF\textsubscript{5}\textsuperscript{2–} to the Ag\textsuperscript{+} sites (Ag1–F3 of 2.871(6) Å). Each Ag atom is additionally coordinated to two bpy ligands both above and below (Ag–N1 and –N2 at 2.142(5) Å and 2.135(5) Å) that bridges to adjacent layers, forming a 3D pillared-layer framework with an open channel that accommodates two lattice water molecules. The calculated bond valence sums (ΣSij)\textsuperscript{18} for Ag and V, listed in Table 9.2, are consistent with +1 and +5 oxidation states for each, respectively.

[Ag(bpy)]\textsubscript{4}[Mo\textsubscript{2}O\textsubscript{4}F\textsubscript{6}][Mo\textsubscript{2}O\textsubscript{4}F\textsubscript{6}(H\textsubscript{2}O)]6H\textsubscript{2}O (8). The structure of 8 contains a 2D sheet comprised of two different chains, [Ag(bpy)\textsuperscript{+}]\textsubscript{n} and [Ag\textsubscript{4}[Mo\textsubscript{2}O\textsubscript{4}F\textsubscript{6}][Mo\textsubscript{2}O\textsubscript{4}F\textsubscript{6}(H\textsubscript{2}O)]]\textsubscript{n}, illustrated in Figure 9.7. Each of the atom types are labeled, and the corresponding bond
distances and angles can be found in Table 9.2. The structure of 8 is comprised of four symmetry-unique Ag$^+$ atoms with disordered square planar geometries that are coordinated to one F atom from a Mo$_2$O$_4$F$_6$(H$_2$O)$^{2-}$ dimer (Ag–F, 2.705 to 2.764(5) Å), and one oxygen atoms from a Mo$_2$O$_4$F$_6$$^{2-}$ dimer (Ag–O, 2.951 to 3.225(5) Å), to form the inorganic chains \{Ag$_4$[Mo$_2$O$_4$F$_6$][Mo$_2$O$_4$F$_6$(H$_2$O))]$_n$ running down the b-axis. Each Ag atom is also bonded to two bpy ligands, with Ag–N distances of 2.122(5) to 2.139(5) Å), to form the backbone of the [Ag(bpy)$^+$]$_n$ chain along the a-axis. Interestingly, within the structure of 8, there are two different acentric Mo-oxyfluoride dimer anions. The first is a edge-shared Mo$_2$O$_4$F$_6$$^{2-}$ octahedral dimer that can be viewed as condensation of two MoO$_2$F$_4$$^{2-}$ octahedra via two shared equatorial F vertices. The second is a vertex-shared Mo$_2$O$_4$F$_6$(H$_2$O)$^{2-}$ octahedral dimer that is a condensation of two MoO$_2$F$_4$$^{2-}$ octahedra via one F vertice, and which is similar to that in 6. The Mo–O and –F distances are regular and fall within the expected ranges. The Mo atoms within both dimer anions consist of two short O distances of 1.665(4) to 1.706(4) Å and four longer F distances of 1.889(4)–2.141(3) Å, and one longer distance of Mo–O(9)$_{\text{water}}$ 2.157(4) Å in Mo$_2$O$_4$F$_6$(H$_2$O)$^{2-}$. In addition, the calculated bond valence sums ($\Sigma S_{ij}$)$^{18}$ for Ag and Mo listed in Table 9.2 are consistent with +1 and +6 oxidation states, respectively.

**Optical Properties.** In heterometallic oxide solids containing a d$^{10}$ (e.g. Cu$^+$, Ag$^+$) and a d$^0$ (e.g. Ti$^{4+}$, V$^{5+}$, Mo$^{6+}$) electron configuration, metal-to-metal charge transfer (MMCT) transitions may occur at relatively low energies. These can cause an absorption at visible light energy. In order to analyze the influence of early transition metals on the optical

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absorption energies, diffuse reflectance spectra of as-synthesized powders of hybrids 1–8 are shown in Figure 9.8. The metal-oxyfluoride hybrids exhibit colors varying from orange to yellow to white. The band gaps estimated from the onsets of absorption edges were 2.21 eV, 2.09 eV, 2.08 eV, 2.10 eV, 2.07 eV, 2.22 eV, 2.81 eV and 3.20 eV, for hybrids 1–8, respectively. These bandgap sizes significantly decrease from 7 and 8 to to 1–6, owing to the replacement of the lower-energy d orbitals of Ag⁺ for the higher-energy d orbitals of Cu⁺. Further, as the measured optical band gaps for 1–6 are a relatively constant ~2.1-2.2 eV, the inclusion of the organic ligands (pyz, bpy) into the structures has only a very minor effect (<0.1 eV) on the bandgap size. However, these bandgap sizes slowly decrease from 1 to 4, arising from the replacement of higher-energy d orbitals of Ti⁴⁺ for the lower-energy d orbitals of V⁵⁺, Mo⁶⁺, and W⁶⁺, respectively.

Thermogravimetric Analysis (TGA). In order to probe the thermal stabilities of 1–8, the weight losses from H₂O and the removal of organic ligands were investigated by heating each sample to 600 °C under flowing nitrogen gas and the results were plotted as weight-percent versus temperature (°C), shown in Figure 9.9. For 1–4, each exhibits one weight loss step from the removal of pyz ligands and F atoms. The TGA trace of 1 showed a sharp weight loss drop of ~58% from 180 °C to 400 °C, corresponding to the removal of all pyz ligands and half of the F atoms per formula (calc. 56%). Hybrid 2 displays a broad weight loss of all pyz ligands and two F atoms per formula (29.9%, calc. 30%) from 200°C to 390°C. The structures of 3 and 4 both exhibit a similar weight loss of 41% and 29%, respectively, and that consistent with the loss of all pyz ligands and two F atoms for 3 (calc. 40%), and one F atom for 4 (calc. 31%). However, after the removal of pyz ligands and F atoms, all four
hybrids showed a small weight-gain, that is likely due to a reaction between the product and \( \text{N}_2 \) or \( \text{O}_2 \) gas at higher temperatures. The final black TGA residuals were still unidentified.

The TGA plots of 5, 7 and 8 exhibit two weight-loss steps owing to the removal of \( \text{H}_2\text{O} \), organic ligands and some of F atoms. In 5, the first weight loss step extends out to ~250 °C that corresponds to the removal of all \( \text{H}_2\text{O} \) in its structures (obsd. 8.4%, cald. 8.2%). A second weight loss step occurs from ~250 °C to 400 °C that corresponds to the loss of organic ligands and two F per formula (obsd. 42.8%, cald. 44.1%). Simiarly, 7 and 8 showed a 6.9% and 6.1% weight-loss before 100 °C, corresponding to the removal of all lattice water molecules (calc. 6.3% and 6.5%), respectively and a second weight-loss of 44.6% and 43.3% between 100 and 400 °C owing to the loss of the two bpy ligands and half of the F atoms per formula (calc. 43.1% and 44.3% for 7 and 8 respectively). By constrast, the TGA results for 6 demonstrate a higher thermal stability with a 43.0% weight loss between 280 and 450 °C that represents the removal of both lattice water and bpy ligands (clac. 42.4%). This is followed by a 2.4% weight-loss extending out to 600 °C owing to the loss one F per formula (calc. 2.2%).
Conclusions

In summary, a new series of heterometallic oxyfluoride/organic hybrids has been prepared using hydrothermal methods. Their structures varied from 3D pillar-layered to 2D sheet frameworks that feature some of the first examples of open framework structures containing either symmetric or asymmetric early transition metal (Mo, V) oxyfluoride species, including \([\text{V}_3\text{O}_2\text{F}_{10}]^{2-}\) and \([\text{VOF}_4]^-\) chains in 2 and 5 respectively, dimeric clusters \([\text{Mo}_2\text{O}_4\text{F}_6]^{2-}\) and \([\text{Mo}_2\text{O}_4\text{F}_6(\text{H}_2\text{O})]^{2-}\) in 6 and 8, and dimeric \([\text{V}_2\text{O}_3\text{F}_6(\text{H}_2\text{O})]^{2-}\) in 7. Further, the DRS results revealed the visible-light bandgap sizes, ~2.1-2.2 eV in 1–6 of the Cu-containing hybrids.

Acknowledgments

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References


18. Hormillosa, C. *Bond Valence Calculator*, version 2.0; McMaster University: Hamilton, Ontario, Canada, **1993**.

Table 9.1. Selected Crystal Data and Structure Refinement Details of hybrid 1–8.

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| N1    |       |       | 1.928(3) | F1'   |       |       | 2.060(2) |
| N2    |       |       | 1.911(3) | F2    |       | 1.962(2) |
| ∑S_{ij} |     |       | 0.97     | F3    |       |       | 1.964(2) |
| V2    | F2    | ×2    | 1.958(2) | F5    |       |       | 1.774(2) |
| F3    |       | ×2    | 1.938(2) |       |       |       | 4.44     |
| F4    |       | ×2    | 1.916(2) |       |       |       |          |
| ∑S_{ij} |     |       | 4.40     |       |       |       |          |

3

| Cu1   | O1    | ×2    | 2.285(2) | Mo1   | F1    | ×2    | 1.889(2) |
|       | N1    | ×2    | 1.926(2) |       | F2    | ×2    | 1.844(3) |
| ∑S_{ij} |     |       | 1.09     |       |       |       | 5.5      |

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| Cu1   | O1    | ×2    | 2.291(3) | W1    | F1    | ×2    | 1.883(4) |
|       | N1    | ×2    | 1.922(3) |       | F2    | ×2    | 1.863(4) |
| ∑S_{ij} |     |       | 1.09     |       |       |       | 5.8      |

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| F2'   |       |       | 2.744(6) | F2    |       |       | 1.915(9) |
| F3    |       |       | 3.034(6) | F3    |       |       | 1.754(2) |
| F3'   |       |       | 2.983(6) | O1    |       |       | 2.03(2)  |
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\[ S_{ij} = \exp\left(\frac{R_{ij} - R_0}{B}\right), \quad B = 0.37; \]
\[ R_0 = 1.574 \text{ Å, 1.390 Å, 1.600 Å for Cu}^{\text{I}}\text{–N, Cu}^{\text{I}}\text{–F and Cu}^{\text{I}}\text{–O, respectively; R}_0 = 1.798 \text{ Å, 1.592 Å, 1.842 Å for Ag}^{\text{I}}\text{–N, Ag}^{\text{I}}\text{–F, and Ag}^{\text{I}}\text{–O respectively; R}_0 = 1.682 \text{ Å, 1.803 Å for V}^{\text{V}}\text{–F, and V}^{\text{V}}\text{–O; R}_0 = 1.808 \text{ Å and 1.907 Å for Mo}^{\text{VI}}\text{–F and Mo}^{\text{VI}}\text{–O respectively; R}_0 = 1.836 \text{ Å and 1.917 Å for W}^{\text{VI}}\text{–F and W}^{\text{VI}}\text{–O respectively; and R}_0 = 1.718 \text{ Å for Ti}^{\text{IV}}\text{–F.} \]
Figure 9.1. (A) An ~[100] polyhedral view of Cu$_2$(pyz)$_3$TiF$_6$ (1), red polyhedra = Cu-centered coordination environments, blue polyhedra = TiF$_6$, yellow plane = pyz; (B) 80% probability thermal ellipsoids of one [Cu$_2$(pyz)TiF$_6$]$_n$ layer; All symmetry-unique atom types are labeled; All H atoms on the benzene rings are omitted for clarity.
Figure 9.2. Structural view of $[\text{Cu(pyz)}]_2\text{V}_3\text{O}_2\text{F}_{10} (2)$. All selected symmetry-unique atoms are labeled, where white balls are C, blue are N, green are F, orange are M, and light-blue are Cu.

Figure 9.3. Structural view of $[\text{Cu(pyz)}]_2\text{MO}_2\text{F}_4 (3, M = \text{Mo}; 4, M = \text{W})$ with the square nets marked at ca. $2.8 \times 4.6 \text{Å}^2$. All selected symmetry unique atoms are labeled, where white balls are C, blue are N, green are F, orange are M, and light-blue are Cu.
Figure 9.4. (A) An \( \sim(100) \) polyhedral view of the 3D pillared-layer structure of 5, where red polyhedra are Cu-centered, blue are V-centered; (B) 80% probability thermal ellipsoid plot of a single layer containing the asymmetric chains \([VOF_4]^-\) with selected symmetry unique atoms labeled.
Figure 9.5. (A) An (001) polyhedral view of the 2D sheet structure of 6, where red polyhedra are Cu-centered, blue are Mo-centered; (B) 80% probability thermal ellipsoid view of the chain containing the asymmetric [Mo$_2$O$_4$F$_6$(H$_2$O)$_3$]$^{2-}$ unit with selected symmetry-unique atoms labeled.
Figure 9.6. (A) An \((100)\) polyhedral view of the 3D pillared-layer structure of 7, where red polyhedra are Ag-centered, blue are V-centered; (B) 80% probability thermal ellipsoid view of a single layer containing the asymmetric \([V_2O_3F_6(H_2O)]^{2-}\) units with selected symmetry unique atoms labeled.
Figure 9.7. (A) An (001) polyhedral view of the 2D sheet structure of 8, where red polyhedra are Ag-centered, blue are Mo-centered; (B) 80% probability thermal ellipsoid view of the chain containing the asymmetric [Mo₂O₄F₆]²⁻ and [Mo₂O₄F₆(H₂O)]²⁻ units with selected symmetry-unique atoms labeled.
Figure 9.8. The UV–vis diffuse reflectance spectra (DRS) for 1–8, plotted as F(R) versus Wavelength (nm).

Figure 9.9. Thermogravimetric analysis (TGA) curves of hybrid 1–8, plotted as weight (%) versus temperature (°C).
CHAPTER 10

STRUCTURES OF NEW PILLARED-LAYER METAL-OXYFLUORIDE HYBRIDS AND THEIR PROPERTIES

A paper prepared for submission

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Abstract

Three new pillared-layer Ag$_2$[Cu(pzc)$_2$][MO$_x$F$_{6-x}$] (I, M = Mo, x = 2; II, M = W, x = 2; III, M = Nb, x = 1; pzc = pyrazine-2-carboxylic) hybrid solids were synthesized via hydrothermal reactions at 150 °C, and their structures were determined by single-crystal X-ray diffraction (P2$_1$/n, No. 14, Z = 2; $a = 7.2302(1)$, $7.2124(2)$, $7.2715(2)$ Å; $b = 7.9460(1)$, $7.9270(2)$, $7.98436(3)$ Å; and $c = 13.9173(2)$, $13.8959(4)$, $13.8226(5)$ Å, for I, II, and III, respectively). All three hybrids are isostructural and contain inorganic {Ag$_2$Cu[MO$_x$F$_{6-x}$]}$^{2+}$ layers consisting of two chains, {Ag$_2$O$_2$F$_2$}$_n$ and {Cu[MO$_x$F$_{6-x}$]}$_n$. All [MO$_x$F$_{6-x}$]$^{2-}$ octahedra are located on inversion centers with +5 and +6 oxidation states for Nb and Mo/W, respectively. UV-Vis diffuse reflectance measurements and electronic structure calculations on all three hybrids show that each exhibits an optical bandgap sizes of ~2.8 eV that arises from electron transitions between the M-derived conduction band and the Cu(II)-derived valence band. Magnetic susceptibility measurements show a temperature dependence and
Curie constant that is consistent with Cu\(^{2+}\) (d\(^9\)). Thermogravimetric analyses indicate that the hybrids are stable up to ~280 °C and followed by a single weight-loss step that extends to ~600 °C that corresponds to the loss of pzc ligands and some of O/F atoms.

**Introduction**

Recent synthetic investigations of metallic-oxide/organic hybrid solids have lead to many intriguing structures with interesting frameworks and topologies that hold promise for potential future applications, for example, same molecule absorption, electrical-conductivity, optical, catalytic and magnetic materials.\(^1\), \(^2\) These new type of hybrid structures can typically be described originating from the simple ‘building blocks’ of metal-oxides, and the versatility and chemical functionality of organic ligands that can attach to them, and resulting in extended topologies, such as polynuclear units (ranging from dimer, trimer to giant clusters), chains and layers.\(^3\), \(^4\) For example, the Maggard group has demonstrated that ‘M\(_n\)ReO\(_4\)’ (n = 1, 2; M = Ag, Cu)\(^5\)\(^-\)\(^7\) layers can serve as the building blocks coordinated to varied bridging organic ligands or metal-coordinated ligands.\(^8\)\(^-\)\(^10\) The investigation of new metal-oxide/organic hybrid frameworks provide a new gateway to probe the effects of organic ligands on the properties of metal-oxides via their molecular-level interactions.\(^3\)\(^-\)\(^10\)

The strategy here is to utilize a metal-containing building block constructed from pyrazinecarboxylate, because of its known ability to bridge metal sites into coordination polymers.\(^11\) Previous reports in the Maggard group have demonstrated that layers in the parent AgReO\(_4\) solid can be pillared by M(pzc)\(_2\)(H\(_2\)O)\(_2\) (M = Co, Ni; pzc = pyrazine-2-carboxylate) to give M(pzc)\(_2\)(H\(_2\)O)\(_2\)AgReO\(_4\),\(^9\) or by Cu(pzc)\(_2\) to give the chiral
Cu(pzc)$_2$AgReO$_4$. These structures can be viewed as derived from the simpler Ag(pyrazine)ReO$_4$ hybrid via the replacement of the short pyrazine with M(pzc)$_2$ pillars. Also, in these examples, the coordinated water ligands to the axial sites of the M(pzc)$_2$ pillar can be reversibly removed without the loss of the structure crystallinity to generate coordinatively-unsaturated metal sites. By analogy, we have found that [M NbOF$_4$] (M = Ag, Cu) oxyfluoride layers can be pillared by bridging organic ligand (e.g. 4,4’-bipyridine = bpy) to form 3D pillared-layer frameworks. Thus, new synthetic efforts focused on the design and synthesis of other new layered oxyfluorides with the use of M(pzc)$_2$ pillars instead of the bpy ligand.

Herein we present the synthesis and crystal structures of three new layered oxyfluoride hybrids, Ag$_2$[Cu(pzc)$_2$][MO$_{6-x}$F$_x$] (I, M = Mo, x = 2; II, M = W, x = 2; III, M = Nb, x = 1), that contain the [M–F–Cu–F–M] linear chains and [Ag$_2$O$_2$F$_2$] dimer chains that are pillared by pzc. The hybrids are characterized by powder and single-crystal X-ray diffraction, UV-vis diffuse reflectance, electronic structure calculations, magnetic properties and thermogravimetric analysis (TGA).
Experimental Section

Materials. All the starting materials for synthesis were purchased commercially and used without further purification, CuCl$_2$·2H$_2$O (99+, Alfa Aesar), NaOH (Fisher), MoO$_3$ (99.9%, Alfa Aesar), WO$_3$ (99.8%, Alfa Aesar), Nb$_2$O$_5$ (99.5% metals basis, Alfa Aesar), AgNO$_3$ (99.9+, Alfa Aesar), and pyrazine-2-carboxylic acid (98%, Alfa Aesar). A reagent amount of deionized water was also used in the syntheses.

Synthesis. The synthesis of Cu(pzc)$_2$·2H$_2$O has been reported before.$^{14}$ Hpzc (0.40 g, 3.22 mmol) was added to a solution of NaOH (0.13 g, 3.22 mmol) in 10 mL of water. The mixture was stirred at room temperature for several minutes. A clear light solution was obtained. CuCl$_2$·2H$_2$O (0.28 g, 1.61 mmol) was added slowly to the above solution, whereupon a blue precipitate formed immediately. The mixture was stirred at room temperature for additional ~10 min and then left overnight. Blue-colored prism-shaped crystals of Cu(pzc)$_2$·2H$_2$O were obtained in ~99% yield.

The synthesis of Ag$_2$[Cu(pzc)$_2$][MoO$_2$F$_4$] (I) was performed by adding 28.8 mg (0.20 mmol) of MoO$_3$, 68.0 mg (0.40 mmol) of AgNO$_3$, 69.6 mg (0.20 mmol) of Cu(pzc)$_2$·2H$_2$O, 0.20 g (5.0 mmol) of 49% aqueous HF and 0.40 g (22.2 mmol) of H$_2$O to an FEP Teflon pouch. The pouch was heat-sealed and placed inside a 125-mL Teflon-lined stainless steel reaction vessel which was backfilled with ~45 mL of deionized H$_2$O before closing. The reaction vessel was heated to 150 °C for 24 h inside a convection oven and slowly cooled to room temperature at 6 °C/h. Prism-shaped green-colored crystals of I were obtained in ~65% yield, and which typically intimately covered a fine yellow-gray amorphous powder in the Teflon bag. These fine yellow-gray powders can be removed by dispersing the green crystals
in ~30 mL of water and sonicating for ~20-30 seconds and then pouring the water off after allowing the solid products to settle for ~1-2 min. This sonication/separation process was repeated three times until a pure sample of I was obtained, as judged by PXRD and visually under a microscope. The synthetic procedures for Ag$_2$[Cu(pzc)$_2$][WO$_2$F$_4$] (II) and Ag$_2$[Cu(pzc)$_2$][NbOF$_3$] (III) were similar to that of I with identical stoichiometric ratios of the starting materials, except for the use of WO$_3$ or Nb$_2$O$_5$ in place of MoO$_3$. Pure samples of both II and III were also obtained using repeated sonication in ~75% and ~55% yield for II and III, respectively. The phase purities of each compound were >95% according to Powder X-ray diffraction data.

**Crystallographic Structure Determination.** Single-crystal X-ray diffraction for hybrids I–III were collected on a Bruker-Nonius X8 Apex2 CCD diffractometer at ambient temperature (296 K) using Mo Kα radiation (λ = 0.71073 Å). The frame integrations were performed using the SAINT program. The resulting raw data were scaled and absorption corrected using a multi-scan averaging of symmetry-equivalent data using the SADABS program. The structure of I was solved by direct methods using the SIR97, and the structures of II and III were solved by direct methods using the SHELXS-97 program of the Bruker SHELXTL package and refined by the full-matrix least-squares methods with SHELXTL-97. The structural model was fit to the data using full matrix least-squares based on F. All non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl hydrogen atoms were introduced at idealized positions and were allowed to ride on the parent carbon atoms. Details for structural analysis and refinement are summarized in Table 10.1. Table 10.2 lists selected the interatomic contacts for selected bonds in these structures.
**Optical Properties.** The UV-vis diffuse reflectance spectra of each sample were measured on a Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer equipped with an integrating sphere. ~10 mg of powder of each sample was mounted onto a pressed BaSO$_4$ powder holder and placed along the external window. A pressed BaSO$_4$ powder was used as a reference, and the data were plotted as the remission function $F(R_\infty) = (1-R_\infty)^2/(2R_\infty)$, where $R$ is diffuse reflectance based on the Kubelka-Monk theory of diffuse reflectance.

**Magnetic Properties.** Magnetic susceptibility measurements were taken using a Quantum Design MPMS XL SQUID magnetometer. The measurements were performed under both zero-field cooled (zfc) and field cooled (fc) conditions. In both cases the magnetization was measured in the temperature range of 2–300 K at an applied field of 1 kG.

**Thermogravimetric Analyses (TGA).** Weighed amounts (~20 mg) of each compound were loaded onto Pt pans, equilibrated and tarred at room temperature, and then heated at a rate of 5 °C/min to 600 °C under flowing nitrogen on a TA Instruments TGA Q50.
Results and Discussion

Structure Description. The three new layered hybrids Ag$_2$[Cu(pzc)$_2$][MO$_{6-x}$F$_x$] (I, M = Mo, x = 2; II, M = W, x = 2; III, M = Nb, x = 1), shown in Figure 10.1, are isostructural and comprised of inorganic {Ag$_2$Cu[MO$_x$F$_{6-x}$]}$_{2+}$ layers that are pillared via coordination of pzc ligands to both the Ag and Cu sites between the layers. Selected interatomic distances for each structure are given in Table 10.2. The single symmetry-unique layer stacks directly above and below, running down the c-axis, to generate the full 3D structure. The inorganic {Ag$_2$Cu[MO$_x$F$_{6-x}$]}$_{2+}$ layers, drawn in Figure 10.1B, consist of two alternate parallel chains, a {Ag$_2$O$_2$F$_2$}$_n$ dimer chain and a [M–F–Cu–F–M]$_n$ linear chain, that are linked to each other through pzc ligands and [MO$_x$F$_{6-x}$] octahedra. The para-nitrogens on each pzc ligand are bonded to Cu(1) in the upper layer and to Ag(1) in the lower layer. Hence, pzc serves as a pillar to support the inorganic layers. However, the pzc ligands are slanted with the respect layers at an angle of ~71.4° for I, ~70.9° for II and ~70.3° for III, respectively. This results in a shortest interlayer distance of only ~2.6 Å.

Each symmetry-unique Ag(1) site is coordinated to three F atoms (Ag–F = 2.54–2.81 Å) from two isolated [MO$_x$F$_{6-x}$] octahedra and two O atoms (Ag–O = 2.71–2.85 Å, III < I, II) from two separate {CuF$_2$N$_2$O$_2$} octahedra in the equatorial positions. The axial sites are coordinated to one N and O atoms (Ag–O = ~2.3 Å; Ag–N = 2.27–2.29 Å, I > II > III) from two pzc ligands above and below each layer. Further, each Ag polyhedron is edge-sharing through the O and F atoms to form a {Ag$_2$O$_2$F$_2$}$_n$ chain along the b-axis (Ag–Ag distances at ~3.8 Å and 4.4 Å). The Cu atoms hybrids I–III are coordinated in octahedral environments
{CuF$_2$N$_2$O$_2$}, with bonds to two cis-O atoms (Cu–O = 1.96–1.98 Å, ×2) and to two N atoms (Cu–N = 1.98–1.99 Å, ×2) on the pzc ligands, and to two apical F atoms on two [MO$_x$F$_{6-x}$] octahedra (Cu–F = 2.29–2.30 Å, ×2), shown in Figure 10.1C.

Octahedra [MO$_x$F$_{6-x}$] within hybrid I–III are are partially ordered. The M atoms are located on inversion sites with symmetric M–F/O distances (×2) ranging from 1.857 to 1.896 Å for I and II, and 1.922 to 1.930 Å for III. The calculated bond valence sums ($\Sigma S_{ij}$)$^{19}$ for Mo, W and Nb, listed in Table 11.2, are consistent with a fully oxidized +6, +6 and +5 oxidation states, respectively. Further, the calculations show that Ag and Cu have +1 and +2 oxidation states, respectively, which are consistent with the magnetic properties below. The [MO$_x$F$_{6-x}$]$^{2-}$ octahedra are bridged to {CuF$_2$N$_2$O$_2$} octahedra via corner-shared F atom to form the [M–F–Cu–F–M] linear chain, running down the b-axis, as shown in Figure 10.1B.

**Optical Properties and Electronic Structure Calculations.** As reported previously, heterometallic oxyfluoride hybrids based on Ag and Nb, such as Ag(bpy)NbOF$_4$ (bpy = 4,4’-bipyridine),$^{12}$ can absorb UV-light energies that can potentially be used to drive photocatalytic reactions. To probe the effect of a third transition metal, i.e. Cu(II), on the bandgaps of these hybrids, their optical properties and electronic structures were investigated. The UV-Vis diffuse reflectance spectra of hybrids I–III and Ag(bpy)NbOF$_4$ are shown in Figure 10.2 (left). All three new hybrids exhibit a strong absorption within the visible light wavelengths with optical bandgap sizes of ~2.8 eV for I–III, as calculated from the onset of their absorption edges. By comparison with the bandgap sizes of Ag(bpy)NbOF$_4$, the addition Cu(II) into the Ag-Nb oxyfluoride layers results in a decrease of the optical band
gaps by \(-0.5\) eV. Thus, a much larger fraction of visible-light can be absorbed by these Cu(II)-containing hybrids. The smaller absorption edge at \(\sim 2.0\) eV is assigned as the d-d transition of Cu(II).

Heterometallic oxides that contain both a late (Ag\(^{+}\)) and early (V\(^{5+}\), Mo\(^{6+}\), Ta\(^{5+}\)) transition metal, with \(d^{10}\) and \(d^{0}\) electron configurations respectively, have been investigated for their absorption of visible light \((E_g, \sim 2.2-3.0\) eV), owing to an \(-0.5\) eV decrease of their bandgap sizes, relative to the alkali metal versions, that arises from the Ag 4d\(^{10}\) orbitals mixing into and raising the valence band.\(^{20-22}\) However, it is critical to understand the origin of their valence and conduction bands and bandgap sizes. Therefore, the electronic structure calculations were performed using the tight-binding approach,\(^{23}\) and the total Densities-Of-States (DOS) and projected atomic contributions are drawn in Figure 10.3 (right). In all three hybrid solids the lowest unoccupied crystal orbitals of the conduction band were confirmed to derive from the Mo 3d, W 4d and Nb 3d orbitals for I, II and III, consistent with prior results reported for the condensed Ag(bpy)NbOF\(_4\). However, owing to the insertion of Cu(II) d-orbitals to the structure, additional filled orbitals within the valence band are located at just below the Fermi level. This allows the possibility of transitions arising from Cu 3d instead of Ag 4d/O 2p/ F 2p orbitals to the M d orbitals \((M = Mo, W, Nb)\).\(^{24}\) Therefore the \(-0.5\) eV smaller band gap in the Cu(II)-containing structure of III suggests a new higher-energy valence band is formed, as required for visible-light photocatalysts.

**Magnetic Properties.** The magnetic susceptibilities of hybrids I–III were measured from 2 to 300 K in the applied fields of 1 kG. The magnetic susceptibility data for I–III, as shown drawn in Figure 10.3, fit very well to the Curie–Weiss law\(^{25}\) in the full range of
2–300K. The results are collected in Table 10.3. The linear plot of $1/\chi$ versus $T$ reveals the paramagnetism, with a small positive Weiss constant ($\Theta = 1.62–1.77$ K), which suggests a very weak short range ferromagnetic interactions. The effective magnetic moments ($\mu_{\text{eff}} = 1.83–1.89$ BM for I–III) obtained from the Curie–Weiss plot, are consistent with a noninteracting and single spin center, consistent with one Cu(II) per formula unit.

**Thermogravimetric Analyses (TGA).** The thermal stabilities and weight losses of each hybrid were investigated by heating each sample to 600 °C under flowing N$_2$ gas. Shown in Figure 10.4, all three hybrids are stable up to ~280 °C without any weight loss. A single weight-loss step for each hybrid extends from ~280 °C to 600 °C, for a total of ~40.5% for I and III, and ~34.5% for II. These correspond to a weight loss that is 6.6% and 4.2% greater than that expected by the loss of pzP alone for I/III and II, respectively. The gray-black products obtained from the TGA analysis corresponded to Ag metal as well as some unidentified phases, as calculated by powder X-ray diffraction. The origin of the additional weight loss is undetermined, but it would correspond to a loss of half of the O/F atoms, such as has been described previously in a reaction with the ligand to give, for example, CO or CO$_2$.\(^5\)
Conclusions

Presented herein are the syntheses, structures and properties of three new pillared-layer hybrids obtained by the use of metal-coordinated ligands bridging ligand Cu(pzc)$_2$2H$_2$O. The interlayer insertion of Cu(II) results in a ~0.5 eV smaller bandgap sizes in III compared to Ag(bpy)NbOF$_4$, owing to a new higher-energy Cu 3d valence band. Thus, the absorption edge of each hybrid fell within the visible-light wavelength, as required for candidates for the visible-light photoscatalytic reactions with water.

Acknowledgements

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References


Table 10.1. Selected Crystal Data and Structure Refinement Details of I–III.

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*aR₁ = Σ(|F₀ - F_c|) / ΣF₀; wR² = [Σ(w(F₀² - F_c²)²) / (Σ(F₀²)²)]½; w=σ_F⁻².*
Table 10.2. Selected Interatomic Distances (Å) and Bond Valence Sums\(^a\) for I–III.

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\(^a\)\(S\(_{ij}\) = \exp[(R_0 - R_{ij})/B], \ B = 0.37; \ R_0 = 1.574 \text{ Å}, 1.594 \text{ Å}, 1.679 \text{ Å} \text{ for Cu}^{II}–\text{N}, \text{Cu}^{II}–\text{F} \text{ and Cu}^{II}–\text{O}, \text{ respectively}; \ R_0 = 1.798 \text{ Å}, 1.592 \text{ Å}, 1.842 \text{ Å} \text{ for Ag}^{I}–\text{N}, \text{Ag}^{I}–\text{F} \text{ and Ag}^{I}–\text{O}, \text{ respectively}; \ R_0 = 1.808 \text{ Å} \text{ and 1.907 Å} \text{ for Mo}^{VI}–\text{F} \text{ and Mo}^{VI}–\text{O} \text{ respectively}; \ R_0 = 1.836 \text{ Å} \text{ and 1.917 Å} \text{ for W}^{VI}–\text{F} \text{ and W}^{VI}–\text{O} \text{ respectively}; \ R_0 = 1.822 \text{ Å} \text{ and 1.911 Å} \text{ for Nb}^{V}–\text{F} \text{ and Nb}^{V}–\text{O} \text{ respectively.}^{19}\)
Figure 10.1. (A) An ~[100] polyhedral view of pillared-layer structures of I–III: red polyhedra = Ag-centered coordination environments, blue polyhedra = Cu-centered, and green polyhedra = M-center octahedra (I, M = Mo; II, M = W; III, M = Nb); (B) Single layer view of structures I–III in ab-plane; (C) ORTEP view with 80% probability thermal ellipsoids. Symmetry unique atoms are labeled in B and C. All H atoms on the pzc rings are omitted for clarity.
Figure 10.2. Left, UV–vis diffuse reflectance spectra (DRS) for I–III, plotted as F(R) versus photon-energy (eV); and right, the calculated densities of states for I–III.
Figure 10.3. Temperature dependences of $\chi$ and $\chi^{-1}$ for hybrids I, II and III.
Table 10.3. Fitting Parameters for the Magnetic Susceptibility According to the Curie–Weiss Model in the temperature range of 2–300 K for I–III.

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Figure 10.4. Thermogravimetric analysis (TGA) curves of compound I, II and III, plotted as weight (%) versus temperature (°C).
Supporting Information

Structures of New Pillared-Layer Metal-Oxyfluoride Hybrids and Their Properties

Haisheng Lin and Paul A. Maggard

**Figure 10.S1.** Powder XRD patterns for I–III for (a) simulated and (b) as-synthesized.

**Figure 10.S2.** Powder XRD patterns of TGA residuals at 600 °C for I–III.
CHAPTER 11

CONCLUSIONS

A recently emerging topic has been the use of hetero-metallic solid in photocatalyst systems, wherein the solid absorbs bandgap light and uses it to catalytically drive redox reactions at its surfaces for the production of hydrogen and oxygen from water, for example. Current metal-oxide photocatalysts, such as TiO$_2$ or NaTaO$_3$,\textsuperscript{1,2} absorb only ultraviolet light owing to their large band gaps. However, the inclusion of both an early and late transition metal results in a shifting of the band gap to lower-energy visible light. For example, the reported Ag$_3$VO$_4$, Ag$_2$MoO$_4$, and AgTaO$_3$,\textsuperscript{3-5} each containing both a late (Ag$^+$) and early (V$^{5+}$, Mo$^{6+}$, Ta$^{5+}$) transition metal, and absorb lower-energy light owing to a $\sim$0.5 eV decrease in their band gap sizes relative to the alkali metal versions. This arises from the interactions of the added higher-energy Ag 4d$^{10}$ orbitals with the valence band O p-orbitals, thereby raising the valence band in energy. However, the number of hetero-metallic oxides that can be synthesized by typical solid-state procedures in these systems has been very limited.

Herein, as an initial step to expanding this chemistry to more diverse metal-oxide/organic systems, the research work in this thesis has therefore focused on the syntheses and optical properties of new hetero-metallic-oxide/organic hybrids with a combination of d$^0$/d$^{10}$ electron configurations. The investigations have been demonstrated the developing ability to synthesize many new oxide/organic versions where the bandgap sizes can be studied and analyzed as compared to the inorganic versions. Among the possible research areas in photocatalysis, one of the main challenges for metal oxides has been to lower the
band gap to absorb lower-energy visible-light (~1.5 – 2.0eV; >50% of sunlight) while keeping the conduction band above the H₂/H₂O redox couple. In general, one should also avoid partly-filled d-orbital bands that could function as electron/hole recombination centers.

Thus, the approach to the photocatalysis research described in this dissertation began with the syntheses of specific new hybrid materials that could fulfill these band-energy requirements through the use of transition metals with d¹⁰ and d⁰ electron configurations and finding suitable coordinating organic ligands.

In general, the structures of the resulting hybrids ranged from 0D (molecules), to 1D (chains), to 2D (layers), and also to interpenetrating 3D (pillared-layer or diamondoid) networks, and that have been controlled by varying the length and local coordination sites of the organic ligands. For example, the use of large multidentate chelating ligands resulted in the molecular and chain-like structures of Ag(bpp)ReO₄ and Ag(tpp)ReO₄·H₂O with limited Ag–ReO₄ connectivity. Conversely, shorter bridging ligands yielded the layered and pillared-types of hybrid structures of Ag(tro)ReO₄, Ag(pda)ReO₄·½H₂O, Cu₃(q6c)₂ReO₄, M(pyz)ReO₄ (M = Cu, Ag), Ag(Hpzc)ReO₄, and Ag₂(Hpzc)(pzc)(H₂O)ReO₄, respectively, each with a two-dimensional M–ReO₄ connectivity. Lastly, the interpenetrating 3D networks of M(bpy)ReO₄, Cu(bpy)₂ReO₄·½H₂O and Ag(dpa)₂ReO₄ are found with the longest bridging ligands. Further, in the resultant hybrid networks, the vanadate, niobate, and molybdate oxide or oxyfluoride anions are also influenced by the organic ligands. For example, these include the typical centrosymmetric [NbOF₅]²⁻ in the layered structure of [Cu(pyz)]₂NbOF₅ using shorter bridging pyz ligand, the polar [NbOF₄]⁻ chains in the pillared-layer network of Cu(bpy)NbOF₄·2H₂O using the longer bridging bpy ligand, and also the interpenetrating
framework of $[\text{Cu(dpe)}]_2\text{NbOF}_5 \cdot 8\text{H}_2\text{O}$ resulting from the longer dpe ligand. The longer ligand lengths also expand the size of the void space which can accommodate more water molecules, e.g. no $\text{H}_2\text{O}$ in $[\text{Cu(pyz)}]_2\text{NbOF}_5$, two $\text{H}_2\text{O}$ per formula in $\text{Cu(bpy)}\text{NbOF}_4 \cdot 2\text{H}_2\text{O}$ and eight $\text{H}_2\text{O}$ per formula in $[\text{Cu(dpe)}]_2\text{NbOF}_5 \cdot 8\text{H}_2\text{O}$.

This research has also discovered how how changes in hybrid structures affect their band positions and optical bandgap sizes. By taking into account all of the measured bandgap sizes, and the optical absorption of each new hybrid, a generalized band-energy profile for heterometallic hybrids can be drawn in Scheme 11.1, and which predicts the positions of the valence and conduction bands with respect to the redox potentials for the oxidation and reduction of water. These band positions are highly approximate, and their precise positions will also depend on the coordination geometries of the transition metals and the widths of the bands. For example, the hybrid network dimensionality (e.g., clusters, chains) and local coordination environments will effect the bandgap sizes via the strength of the d-orbital-to-ligand interactions or in the band broadening of extended versus molecular networks. For example, in the Ag-Re hybrids, the greater d-orbital interactions of the distorted square-pyramidal/trigonal-bipyramidal and octahedral coordination geometries raise the filled Ag 4$d^{10}$ orbitals to higher energies and results in their relatively smaller bandgap sizes. By comparison, the tetrahedral and seesaw coordination geometries of Ag atoms result in weaker d-orbital interactions, a lower-energy valence band, and increased bandgap sizes. By contrast, no trends were found between the Ag–ReO$_4$ network dimensionality and the bandgap sizes, owing to the relatively much weaker interaction between the Re 5d-orbitals and the Ag- or ligand-based orbitals. For Ag-V hybrids, their optical bandgap sizes (2.77 eV for
[Ag(bpy)]_4V_4O_12·2H_2O, 2.95 eV for [Ag(dpa)]_4V_4O_12·4H_2O, and 2.45 eV for Ag_4(pzc)_2V_2O_6) decrease most notably as a result of the band widening for the more extended vanadate structure in Ag_4(pzc)_2V_2O_6. However, the inclusion of the organic ligands into the Cu(I)-containing hybrid structures has only a very minor effect (<0.1 eV) on the band gap size, owing to higher energy Cu 3d orbitals. This establishes a strong starting point to show that ideal systems for strong visible-light absorption and photocatalysis are the d^9/d^10 systems with Ag^+ or Cu^+ with V^{5+} or Re^{2+}.

New investigations into the optical properties of these hybrids show that the absorption coefficients (α) are correlated with the metal-oxide network dimensionality. The ligands play a significant role in altering the metal-oxide network dimensionality, and thus, the absorption coefficients that are dependent on the electronic transition probabilities. In Ag-Re hybrids, for example, α decreases in the order of decreasing network dimensionality of Ag–ReO_4 (minus the ligand), decreasing from 3D condensed to 2D layers to 0D molecular and to no connectivity.

Lastly, many hybrid metal-oxides/organics exhibit high thermal stabilities and/or can be thermally converted to new or known condensed phases after removal of the ligand, or reversibly absorb water or other small molecules. Chelating ligands always resulted in the highest possible thermal stability, such as for Ag(bpp)ReO_4, Ag(tpp)ReO_4·H_2O, and Ag_4(pzc)_2V_2O_6 (decomposing at >300 °C). Also, interpenetrating networks using longer ligands add thermal stability to the hybrid structures, i.e., in the 2-fold interpenetrating structures of M(bpy)ReO_4, and in the 3-fold interpenetrating stairlike structure of [Cu(dpe)]_2NbOF_5·8H_2O. Further, removal of all organic ligands of many hybrid structures
resulted in new or known condensed phases, such as in the conversion of M(pyz)ReO₄ to MReO₄ by heating to remove all pyz ligands. Also, a surprising reversible structural interconversion between the interpenetrating structures of Cu(bpy)ReO₄ and Cu(bpy)₂ReO₄·½H₂O was possible via the intercession and removal of a single bpy ligand and ½H₂O per copper atom. In summary, the nature of the coordinating ligand plays a critical role in directing the structure of each hybrid, and also in their thermal stabilities and structural interconversion.

Other requirements that should be considered to achieve an efficient photocatalyst include the separation of charge carriers (i.e. excited electrons and holes should not recombine rapidly), migration of the charge carriers to active sites, and interfacial electron transfer. From these considerations, it is anticipated that the most suitable structures will absorb light from a charge-transfer transition that separates the electrons and holes (i.e. d¹⁰ to d⁰ transition), and also has an extended pathway for charge carriers (i.e. extended chains, or layers), as well as has local metal coordination geometries that promote the interfacial charge transfer kinetics for the reduction and oxidation of water. While structures that satisfy the first two criteria can be envisioned, however, the types of structural features that lead to the latter are completely unknown in this area. For example, we have observed and investigated the photocatalytic activities of the Ag-V hybrids ([Ag(bpy)]₄V₄O₁₂·2H₂O, [Ag(dpa)]₄V₄O₁₂·4H₂O, and Ag₄(pzc)₂V₂O₆) and the Ag-Nb oxyfluoride hybrids for the degradation of MB solutions under UV and visible-light. However, other hybrids (i.e. Ag-Re or Cu(I)-containing hybrids) are not active under either UV or visible light irradiations. This presents the challenge of finding the types of Cu⁺/Ag⁺ coordination geometries that facilitate
the oxidation of water and also the types of rhenates/molybdates/vanadates that facilitate the reduction of water, and which should be the focus of much future research.

References

Scheme 11.1. A schematic illustration of the band-energy profile for heterometallic-oxides and their hybrids.