ABSTRACT

DONG, RUI. Towards Novel Energy Solutions - an Electronic/Atomistic Simulation Approach. (Under the direction of Jerry Bernholc.)

This thesis focuses on computer modeling and multi-scale simulations of new materials that can potentially be used in novel energy applications, i.e., the dye molecules in dye-sensitized-solar-cells and polymers for the capacitive energy storage. The aim is to understand physical properties of existing materials and then to find ways to improve them.

Using density functional theory (DFT) simulations, we study three newly synthesized Ru(II) polypyridyl complexes with electron-donor ancillary ligands. Absorption spectra of the three dyes are successfully reproduced by explicitly including the effect of solution. We find that the electron-donor ancillary ligands significantly enhance population of electronic states involved in photon-induced excitations. It results in significantly better light harvesting in the visible and the near-infrared regions than the reference dye N3. Furthermore, we find the chemical manipulation of ancillary ligands decreases the ionization potential. It improves the energy alignment with the redox potentials of the electrolyte. Our results demonstrate that the three novel dyes are better organic materials for energy applications.

We study two types of polymeric materials for capacitive energy storage, the polyvinylidene (PVDF) copolymer systems and the aromatic polyurea linear dielectrics. Phase diagrams of polyvinylidene fluoride (PVDF) and its copolymers with hexafluoropropylene (HFP) and bromotrifluoroethylene (BTFE) are investigated via first-principles simulations. The previously found non-polar to polar phase transition also exists in these two copolymers. By tuning defect concentration to higher value (25%), we find that higher energy density is obtained in P(VDF-BTFE) copolymer, particularly in the low electric field regime than in P(VDF-CTFE). The transition pathways connecting the polar and non-polar phases are also calculated for the two copolymers. The energy barriers are found to be similar for different species and concentrations, at about 70 meV per carbon atom.

Three members in the polyurea family are investigated, using a multi-scale simulation combining DFT and classic molecular dynamics (MD). The atomic geometries of aromatic the new high energy density linear dielectric polyurea (APU), meta-aromatic polyurea (mAPU) and para-aramid (PA) polymers are obtained in crystal-like ordered structures. All polymer energetically prefer anti-parallel arrangement of dipole moments, which leads to dielectric phases. We find that mAPU easily forms disordered structures with misaligned chains, and these disordered structures have significantly larger dielectric constants. The enhancement is due to stronger dipole motion induced by increased free volume and low frequency phonons induced by random geometries. We also find that large degree of entanglement leads to lower dielectric
constant because it reduces the number of effective dipoles in the material. The findings offer a new pathway to making polymer materials with high permittivities.
Towards Novel Energy Solutions - an Electronic/Atomistic Simulation Approach

by

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DEDICATION

To my family.
BIOGRAPHY

Rui Dong was born in Jinan, Shandong, P.R.China. He graduated from Shandong Experimental High School in 2002, received his B.S. from Nanjing University in 2009. He came to NC State University for Ph.D studies in 2009.
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Chapter 1

INTRODUCTION

Nowadays, everyone agrees that fossil fuel resources are depleting. The current reserves of oil will last 40 years, coal and gas will last 200 and 70 years, respectively [1]. In addition, the use of fossil fuels causes severe environmental issues, and some of them are irreversible. The job of seeking renewable, clean and efficient energy sources is thus urgent. Common types of alternative energy include solar, wind, tide and geothermal energy. Among them, solar energy has the largest potential of 2.3 PW/year, compared to the total 0.9 PW of coal. Sun has been providing energy for all creatures on earth since the beginning of life. Now, scientists and engineers are working on directly and efficiently converting the solar energy to easy-to-use form, such as electricity and heat.

A solar cell is an electric device which converts the energy in sunlight into electricity by the photovoltaic effect. Common types of solar cells are crystalline silicon solar cell, thin film solar cell, multi-junction solar cell and dye-sensitized solar cell (DSSC). Among them, DSSC attracts much industrial and academic interest, despite its relatively low energy conversion efficiency. One outstanding aspect of DSSCs is that they are much less expensive. Even with low efficiency, the price-performance ratio is quite competitive comparing to a traditional solid-state solar cell. DSSCs are semi-flexible, semi-transparent and very easy to process. A mixture of dye molecules and an oxide semiconductor (TiO$_2$) are the key parts of DSSCs, a photon is absorbed by the dye and excites one electron from an occupied molecular state to a virtual level. After that, the excited electron is injected to the conduction band of a semiconductor. The electron goes into the TiO$_2$ network and then through an outer circuit to the counter electrode, where the solution of I$^-$/I$_3^-$ donates one electron back to the dye to complete the circle.

A good dye sensitizer should have the following desired properties. First, it should have a fairly strong absorption spectrum that matches the solar emission (an upper threshold of 920 nm). Second, the dye must have an anchoring group to allow for a favorable attachment to the oxide surface. Most importantly, there must be a proper alignment of energy levels
of all components, \textit{i.e.}, the LUMO of the dye should be higher than the conduction band of TiO$_2$ to allow for injection, and the redox potential of the electrolyte should be higher than the dye HOMO for electron regeneration. The injection is controlled both by band alignment and anchoring group/oxide-surface coupling. The last requirement is stability of the dyes for about $10^8$ turnover circles (about 20 years). Many experimental and computational works have been devoted to improve the performance of DSSC [2, 3, 4, 5, 6]. Recently, Dr. El-Shafei and co-workers [7] have synthesized and tested several novel dyes, which have stronger absorbing strengths over the full solar emission spectrum than the state-of-art dye N3 [8], and the novel dyes have better energy alignment to reduce loss. In part of my work, I want to understand the physical reasons for the enhanced properties in the novel dyes.

After obtaining energy from the renewable energy sources, the next challenge is its green, efficient and user-friendly application in our daily lives. The plug-in hybrid and full electric vehicles are one good example. Comparing to traditional petroleum-powered vehicles, electric-powered cars have much simpler structures, low noise and smaller operating costs. However, until recently, the endurance of electric cars was far from acceptable. Improvement of the energy storage system is very important to the progress of electric cars.

The usual means of storing electrical energy are batteries and capacitors. Batteries typically have energy density of $10^2$-$10^3$ Wh/kg. However, they release energy very slowly at only 50-300 W/kg. On the other hand, capacitors have high power density, 200-1000 times larger than batteries [9]. However, the energy density of capacitors is low. The high power density in capacitive energy storage is suitable for electric cars, but one has to seek a solution for higher energy density. Beyond electric vehicles, capacitors with ultra-high energy density can be used in many fields such as integrated circuits, medical devices and energy burst devices. There are mainly two types of materials used in the capacitors, ceramics and polymers. Ceramics have high dielectric constants, but low breakdown fields. Polymer dielectrics have very high breakdown strength, and they remain insulators even at breakdown. Most importantly, polymers are cheap and easy to process compared to ceramics. Bi-axially oriented polypropylene (BOPP) is the state-of-art polymer in capacitors. Its energy density is about 4 J/cm$^3$ [10].

In 2006, polyvinylidene fluoride (PVDF) copolymer with 9% chlorotrifluoroethylene (CTFE) was found to have ultrahigh energy density more than 18 J/cm$^3$ [11]. Since then, many efforts have been devoted to finding new PVDF-based dielectrics and tuning them to maximum performance [12, 13, 14]. Evidence shows that there is a non-polar to polar phase transition, which is responsible for the ultrahigh energy storage in the PVDF-CTFE copolymer [15]. Two phases are involved in the transition, the non-polar $\alpha$ phase and the polar $\beta$ phase. In PVDF copolymers with low concentration of CTFE, the ground state is the $\alpha$ phase. However, the polar $\beta$ phase is stabilized at high electric field, which leads to a phase transition. In this transition, the electric displacement $\mathbf{D}$ increases non-linearly, which leads to the ultra-high energy
density. In part of this work, we investigate PVDF-bromotrifluoroethylene (BTPE) and PVDF-hexafluoropropylene (HFP) copolymers to further understand the phase transition mechanism and to find more candidates for capacitive energy storage.

One disadvantage of PVDF-based copolymers is high loss. There is strong correlation between PVDF units with large permanent dipole moments, which leads to a remanent polarization and loss. Furthermore, PVDF-based devices cannot be operated at temperatures higher than 125 °C. An alternative type of polymeric material for capacitive energy storage is the aromatic polyurea/polythiourea linear dielectric family. The polymers in this family also contain functional groups with large build-in dipole moments. In linear dielectrics, permittivity is very important since the energy density at a given electric field is solely determined by it. In part of my work we investigate several members of the aromatic polyurea family, obtaining dielectric constants from simulations, and seeking a method to enhance the dielectric properties.

To achieve the goals described above, we use computer modeling and multi-scale simulation techniques to investigate materials that can be potentially used in novel energy applications. Density functional theory (DFT) is one of the most widely used quantum mechanical approaches for electronic structure simulations. It has been successful in predicting and understanding properties of a large range of materials, from molecules to polymers and crystals. Classical molecular dynamics (MD) is able to carry out simulation of a system with up to $10^6$ atoms. It has also been proved to be a very useful tool.

The rest of the thesis is organized as follows: Chapter 2 outlines the simulation techniques used in this thesis, the DFT framework and MD approach. Chapter 3 investigates the newly synthesized dyes for solar energy conversion. Chapter 4 studies the ultra-high energy density in PVDF-BTPE and PVDF-HFP copolymers. Chapter 5 investigates the a few members of the aromatic polyurea linear dielectric family for capacitive energy storage.
Chapter 2

Methodology

2.1 Density functional theory

In order to exactly solve a system containing \( N \) interacting particles, one needs to solve the many particle wave function \( \Psi(\mathbf{r}_1, ..., \mathbf{r}_N) \) that satisfies the stationary many-body Schrödinger equation:

\[
\hat{H} \Psi = [\hat{T} + \hat{U} + \hat{V}] \Psi = \left[ -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \nabla_i^2 + \sum_{i<j}^{N} U(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i=1}^{N} V(\mathbf{r}_i) \right] \Psi,
\] (2.1)

where \( \hat{T} \) is the kinetic energy, \( \hat{U} \) is the interaction energy between electrons and \( \hat{V} \) is the potential energy under an external potential. This formalism is exact and universal. However, in most cases solving the full Schrödinger equation is impossible. Many methods with various levels of accuracy and complexity have been invented to approximate the exact solution. One usual approach is to use single particle wave function to form a Slater determinant [16], which includes relatively simple Hartree-Fock method [17] and the very complicated and expansive configuration interaction (CI) [18] and coupled clusters (CC) method [19]. A different approach is density functional theory (DFT). It uses the spatial particle density

\[
n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle = \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)|^2 d^3r_2...d^3r_N
\] (2.2)

instead of the 3N-variables wave function \( \Psi \). DFT treats the total energy as a functional of electron density. Basically, DFT is a ground state theory. Once the ground state particle density is obtained, the external potential and all properties of system can be calculated. In most cases, researchers are interested in using DFT to solve the electronic structure and calculate the properties that depend on electronic structure of atomic systems. DFT has achieved a
lot of success in describing materials ranging from clusters of atoms, molecules, and simple crystals to complex extended system such as interfaces and polymeric systems. Moreover, DFT is computationally cheap. It has become a very important tool in condensed matter physics. Many review papers on DFT have been published in the past, and more detailed information can be found in references [20, 21, 22, 23, 24, 25].

2.1.1 The Hohenberg-Kohn theorem

The Hohenberg-Kohn theorem [26] proves DFT to be an exact theory for the ground state. It states that:

1. For a system of interacting particles in an external potential \( V_{\text{ext}}(r) \), the potential \( V_{\text{ext}}(r) \) is determined uniquely, except for a constant, by the ground state particle density, and

2. A universal functional for the energy \( E[n] \) in terms of the density \( n(r) \) can be defined, valid for any external potential \( V_{\text{ext}}(r) \). For any particular \( V_{\text{ext}}(r) \), the exact ground state energy of the system is the global minimum of this functional, and the density that minimizes the functional is the exact ground state density \( n_0(r) \).

Theorem (1) can be easily proved by contradiction. Assume there are two external potential \( V(r) \) and \( V'(r) \) that have the same non-degenerate ground state particle density \( n(r) \), but different wave function \( \Psi(r) \) and \( \Psi'(r) \). The Hamiltonians are \( H(r) \) and \( H'(r) \) respectively. By the definition of the ground state,

\[
E = \langle \Psi | H | \Psi \rangle < \langle \Psi' | H' | \Psi' \rangle = \langle \Psi' | H' - H | \Psi' \rangle = E' - \int d^3r (V'(r) - V(r)) n(r).
\]

Then we have \( E < E' + \int d^3r (V(r) - V'(r)) n(r) \). We can apply the same procedure to \( H' \), and get \( E < E' + \int d^3r (V'(r) - V(r)) n(r) \). By adding the two inequalities we get a contradiction.

The proof of theorem (2) is also straightforward. In any particular particle system, the Hamiltonian contains the kinetic part, the interaction part and the external potential. Once the interaction between particles is known, a universal functional can be constructed. The energy driven by the external potential can be expressed as \( \int d^3r V(r) n(r) \). Considering a particle density \( n'(r) \) different from the ground state particle density \( n(r) \), it leads to a definitely different wave function \( \Psi' \neq \Psi \) in the ground state case \( E' = \langle \Psi' | H | \Psi' \rangle > \langle \Psi | H | \Psi \rangle = E \).

The Hohenberg-Kohn theorem proves that one can exactly solve an interacting particle system by solving for the electron density. However, practically it does not solve the problem, because no one knows the exact form of the functional.
2.1.2 The Kohn-Sham ansatz

The ansatz of Kohn and Sham [27] makes a dramatic step towards a simplified solution. The ansatz assumes that the original interacting system can be represented by a non-interacting system, and the two systems have the same ground state particle density. In principle, the Kohn-Sham ansatz is still exact if one can find the exact auxiliary non-interacting system. Instead of using the functional form,

\[ E[n] = T[n] + V[n] + U[n], \]  
(2.4)

the Kohn-Sham approach [27] uses the following energy functional of an electron system,

\[ E_{KS}[n] = T_s[n] + E_H + V_{ext}[n] + E_{xc}[n]. \]  
(2.5)

In the auxiliary non-interacting system, the wave functions can be represented as single particle orbitals, where the density is calculated as

\[ n(r) = \sum_{i=1}^{N} \int d^3r \phi_i(r), \]  
(2.6)

and \( T_s \) is the single particle kinetic energy.

\[ E_H[n] = \int d^3r d^3r' \frac{n(r)n(r')}{|r-r'|}, \]  
(2.7)

is the so-called Hartree term, which is the energy of electron charge density acting on itself. \( V_{ext}[n] = \int V_{ext}(r)n(r)d^3r \) is the external potential energy. The last term \( E_{xc}[n] \) takes care of the remaining electron-electron interaction and the difference in the many-body and single particle kinetic energies. It is called the exchange-correlation energy. In practice, approximations are introduced in this term. At present, there are various types of exchange-correlation functionals, from the most simple local density approximation (LDA) and generalized gradient approximation (GGA), to very complicated non-local functionals (meta-GGA [28], vdW [29, 30], EXX [31] and SIC [25]). Two types of widely used functional, namely LDA and GGA, will be briefly introduced in the next section.

To minimize the Kohn-Sham energy functional, one can derive a variational equation. The functional derivative of Eq. 2.5 gives

\[ 0 = \frac{\delta E[n]}{\delta n} = \frac{\delta T_s[n]}{\delta n} + \frac{\delta V_{ext}[n]}{\delta n} + \frac{\delta E_H[n]}{\delta n} + \frac{\delta E_{XC}[n]}{\delta n} = \frac{\delta T_s[n]}{\delta n} + v_{ext}(r) + v_H(r) + v_{XC}(r). \]  
(2.8)
The Hamiltonian of the non-interacting system can be written as

$$H_{KS} \phi = T_s \phi + v_{KS}(r) \phi,$$  \hspace{1cm} (2.9)

with

$$v_{KS}(r) = v_{\text{ext}}(r) + v_H(r) + v_{XC}(r).$$  \hspace{1cm} (2.10)

Eq. 2.9 can be solved in a self-consistent manner using an iterative method. An initial guess of the electron density is made at the beginning and used to construct auxiliary potential $v_{KS}$. The obtained $v_{KS}$ is used in Eq. 2.9 to calculate new orbitals, therefore the new charge density can be calculated. This procedure is repeated until the electron charge density converges.

The Kohn-Sham ansatz significantly reduces the computational cost, which also makes DFT the most popular method to calculate electronic structure.

### 2.1.3 Exchange-correlation functional

LDA [27] is the simplest exchange-correlation functional. It assumes that the exchange-correlation energy depends on local electron density only, and it can be split into two parts.

$$E_{XC}^{LDA}[n(r)] = E_X[n(r)] + E_C[n(r)] = \int n(r)(\epsilon_X + \epsilon_C)d^3r.$$  \hspace{1cm} (2.11)

The most commonly used LDA is derived from homogeneous electron gas, where the exchange energy is in an analytical format,

$$\epsilon_X = -\frac{3e^2}{4\pi}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}n^{\frac{2}{3}}.$$  \hspace{1cm} (2.12)

The correlation energy is not known exactly. It can be obtained from quantum Monte Carlo calculation and fitted to a chosen analytical expression [32, 33, 34, 35]. Intuitively, one expects the LDA will work successfully for systems close to a homogeneous electron gas, such as a simple metal. However, it works very well for a wide variety of systems. Nevertheless, it makes significant errors, for example in binding energies of molecules.

Unlike LDA, the GGA exchange-correlation energy also depends on the gradient of charge density,

$$E_{XC}^{GGA}[n(r)] = E_{X}^{GGA}[n(r), \nabla(r)].$$  \hspace{1cm} (2.13)

Many forms of GGA have been proposed. Popular examples are BLYP (Becke-Lee-Yang-Parr) [36, 37] in chemistry and PBE (PerdewBurkeErnzerhof) [38] in physics. It is also common to improve the performance of GGA by tuning in part of the exact exchange term

$$E_{EXX} = \frac{e^2}{2} \sum_{ij} \int \phi_i^*(r)\phi_j^*(r')\phi_i(r)\phi_j(r)d^3rd^3r'.$$  \hspace{1cm} (2.14)
Popular examples are B3LYP [39] and PBE0 [40].

LDA and various GGA functional successfully predict the properties of many materials. However, they usually fail in materials with strong electron correlation.

2.1.4 Density functional perturbation theory

DFT calculates the total energy and many observables as functionals of electron density. When it comes to a quantity related to the derivative of the total energy or the charge density, one can always use a finite difference method. One example is the interatomic force constant \( C_{R_iR_j} = \frac{\partial^2 E}{\partial R_i \partial R_j} \). An alternative approach is the density functional perturbation theory (DFPT), which provides an easy and systematic way to calculate the response to a perturbation potential. Baroni, Giannozzi and Testa first proposed the idea of DFPT using linear response [41], then applied their method to calculations of lattice dynamics. Gonze developed a different method based on the variational principle [42, 43, 44].

Let us consider a Kohn-Sham system with the one-electron Hamiltonian in the form of Eq. 2.9. A small potential \( v'_{\text{ext}} \) is added to the system can be considered as a perturbation. Using the first order perturbation theory, we obtain the following equation

\[
(H_{KS}^0 + \varepsilon^0) \phi' = -(v'_{KS} - \varepsilon') \phi^0
\]  

(2.15)

\( v'_{KS} \) is the first order correction of the self-consistent potential. It contains the perturbing external potential, perturbed Hartree potential and the exchange-correlation potential

\[
v'_{KS} = v'_{\text{ext}} + v'_{\text{Hartree}} + v'_{XC}.
\]  

(2.16)

The first order correction to the orbitals is written

\[
\phi_n = \sum_{n \neq m} \frac{\langle \phi_m | v'_{KS} | \phi_n \rangle}{\varepsilon_n - \varepsilon_m} \phi_m
\]  

(2.17)

The first order perturbed electron density is

\[
n'(r) = 2 \sum \langle \phi^0((r)) | \phi'(r) \rangle + 2 \sum \langle \phi'(r) | \phi^0((r)) \rangle
\]  

(2.18)

These equations can be solved self-consistently similarly as in the DFT case. \( n'(r) \) goes into Eq. 2.16 in the Hartree and exchange-correlation terms. DFPT in a metallic system should be modified since the occupation numbers near the Fermi energy may change upon a perturbation. Details can be found in Gironcoli’s work [45].

When the perturbation is a homogeneous electric field, it is not straightforward to use the
above approach in a periodic system. The potential of a homogeneous electric field \( V'_{\text{ext}} = -E \cdot r \) diverges in an infinite system, and is not compatible with periodic boundary conditions. The operator \( r \) also is ill-defined in a periodic system. However, Eq. 2.17 shows that only the off-diagonal matrix elements matter [46]. These off-diagonal elements of a matrix representation of \( r \) are well-defined.

In insulators, the charge density response to an external electric field results in a induced polarization
\[
P_\alpha = -\frac{e}{\Omega_0} \int r_\alpha n'(r) d^3 r.
\] (2.19)
The permittivity in real material is a 3x3 matrix. It follows the relation
\[
D_\alpha = E_\alpha + 4\pi P_\alpha = \sum_\beta \epsilon_{\alpha\beta} E_\beta
\] (2.20)
and
\[
\epsilon_{\alpha\beta} = \delta_{\alpha\beta} + \frac{4\pi P_\alpha}{E_\beta}
\] (2.21)

By plugging Eq. 2.17, Eq. 2.18, and using Eq. 2.19, we obtain
\[
\epsilon_{\alpha\beta}^\infty = \delta_{\alpha\beta} - \frac{16\pi e}{\Omega_0 E_\beta} \sum_n \sum_{m \neq n} \frac{\langle \phi_n [H_{KS}, r_\alpha] | \phi_m \rangle}{\epsilon_n - \epsilon_m} \langle \phi_m | \phi'_n \rangle.
\] (2.22)
Physically, the dielectric displacement should be fixed in a calculation, because it is related to the applied field. However, it is more convenient to fix \( E \) in practical calculations. The procedure above only calculates the permittivity at very high frequencies, because there is only the contribution of electron wave functions. To calculate the low-frequency permittivity, the ionic contribution must be included. Having the dynamical matrix at \( \Gamma \) point, the frequency-dependent permittivity is calculated as
\[
\epsilon_{\alpha\beta}(\omega) = \epsilon_{\alpha\beta}^\infty + \frac{4\pi}{\Omega_0} \sum_{ij} \sum_{\alpha'\beta'} Z_{\alpha\alpha\alpha'}^i [\tilde{C}(q = 0) - M \omega_j^{-1}]_{\alpha'\beta'j} Z_{\beta\beta'\beta'}^j,
\] (2.23)
where \( Z^* \) is the Born effective charge, \( \tilde{C}(q = 0) \) is the dynamical matrix. We can define a quantity "mode-oscillator strength tensor" as
\[
S_{m,\alpha\beta} = \left( \sum_{i\alpha'} Z_{i,\alpha\alpha'}^* U_{m,0=i\alpha'} \right) \cdot \left( \sum_{j\beta'} Z_{j,\beta\beta'}^* U_{m,0=j\beta'} \right)
\] (2.24)
where \( U_{m,0} \) the normalized eigenvector of the mode \( m \). With help of Eq. 2.24, Eq. 2.23 is
simplified to
\[ \epsilon_{\alpha\beta}(\omega) = \epsilon_{\alpha\beta}^\infty + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha\beta}}{\omega^2_m - \omega^2} \]  
(2.25)
The static dielectric constant is
\[ \epsilon_{\alpha\beta}^0 = \epsilon_{\alpha\beta}^\infty + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha\beta}}{\omega^2_m}. \]

### 2.1.5 Time dependent density functional theory

The time-dependent Schrödinger equation of the Kohn-Sham auxiliary system [47] can be written as
\[ i \frac{\partial \phi(r,t)}{\partial t} = \hat{H}_{KS}(t) \phi(r,t) = (\hat{T} + v_{ext}(r,t) + v_{HXC}(r,t))\phi(r,t), \]  
(2.26)
where \( v_{ext} \) is the external potential and \( v_{HXC} \) is the Hatree plus exchange-correlation potential.

We assume that the external potential can be split into a time-independent part \( v_{ext}^0(r) \) and a time-dependent part \( v_{ext}'(r,t) \), with \( v_{ext}' \) being small enough. If the \( v_{HXC} \) term can be treated similarly, we can use the first order perturbation theorem to rewrite Eq. 2.26 as
\[ i \frac{\partial \phi'(r,t)}{\partial t} = (\hat{H}_{KS}^0 - \epsilon^0)\phi'(r,t) + (v_{ext}'(r,t) + v_{HXC}'(r,t))\phi^0(r), \]  
(2.27)
where \( \phi^0(r) = \phi(r,0) \) is the ground-state orbital of the time-independent (unperturbed) Hamiltonian, \( \hat{H}_{KS}^0 \phi^0(r) = \epsilon^0 \phi^0(r) \).

\( \phi'(r,t) = e^{\epsilon^0 t} \phi(r,t) - \phi^0(r) \) is called the orbital response function.

Eq. 2.26 can be written in terms of a quantum Liouville equation,
\[ i \frac{d\rho(t)}{dt} = [\hat{H}_{KS}(t), \rho(t)], \]  
(2.28)
where "[ ]" is a commutator. \( \rho(r',t) = \sum_i \phi_i^*(r',t)\phi_i(r,t) \) is the reduced one-electron Kohn-Sham density matrix.

Using first order perturbation theory in a similar manner as in Eq. 2.27, the quantum Liouville equation can be cast into
\[ i \frac{d\rho'(t)}{dt} = [\hat{H}_{KS}^0(t), \rho'(t)] + [v_{HXC}'(t), \rho^0(t)] + [v_{ext}'(t), \rho^0(t)]. \]  
(2.29)
Consider a Liouvillian super operator \( \mathcal{L} \) acting on the charge density matrix \( \rho' \),
\[ \mathcal{L} \cdot \rho' = [\hat{H}_{KS}^0(t), \rho'(t)] + [v_{HXC}'(t), \rho^0(t)]. \]  
(2.30)
Eq. 2.29 can then be written as
\[ i \frac{d\rho'(t)}{dt} = \mathcal{L} \cdot \rho' + [v_{ext}'(t), \rho^0(t)]. \]  
(2.31)
By Fourier transforming Eq. 2.31 to the frequency space, one obtains

\[(\omega - \mathcal{L}) \cdot \tilde{\rho}'(\omega) = \tilde{v}_{ext}(\omega), \tilde{\rho}^0]. \quad (2.32)\]

While the above formalism is general, a particularly important application is the absorption spectrum, in which case the perturbation is an homogeneous electric field. The potential of an electric field is \(v_{ext}(\omega) = -E(\omega, r) \cdot r\). The Dipole moment induced by an electric field is

\[d_i(\omega) = \sum_j \alpha_{ij}(\omega) E_j(\omega), \quad (2.33)\]

where \(\alpha_{ij}\) is the dynamical polarizability matrix. In the perturbative approach described before, the expectation value of an one-electron operator can be expressed as the trace of its product with the one-electron density matrix. Therefore, the expectation value of the dipole moment is

\[d(\omega) = Tr(\tilde{r}\tilde{\rho}'(\omega)). \quad (2.34)\]

Comparing Eq. 2.33 and Eq. 2.34, and using Eq. 2.32, one obtains the polarizability matrix

\[\alpha_{ij} = -Tr(\hat{r}_i(\omega - \mathcal{L})^{-1} \cdot [\hat{r}_j, \hat{\rho}^0]). \quad (2.35)\]

Finally, the absorption intensity \(I(\omega)\) is calculated as the imaginary part of the spherically averaged \(\alpha_{ij}\) multiplied by \(\omega\),

\[I(\omega) \propto \frac{1}{3} Im(\alpha_{11} + \alpha_{22} + \alpha_{33})\omega. \quad (2.36)\]

### 2.1.6 Modern theory of polarization (optional)

Electrical polarization induced by an external field has been discussed in section 2.1.4. In this section, we will briefly introduce how to calculate the polarization induced by a geometrical change in the frame work of DFT. In atomic systems, the polarization is defined as

\[\mathbf{P} = \frac{e}{\Omega} \left( \sum_i Z_i \mathbf{R}_i - \int n(\mathbf{r}) d^3 \mathbf{r} \right). \quad (2.37)\]

However, Eq. 2.37 can only be used in a finite system. In fact, in a periodic system, the polarization is ill-defined. In Eq. 2.37, we face the same problem as in section 2.1.4, that is the operator \(\mathbf{r}\) cannot be represented in a periodic system. The difficulty has not been solved until Vanderbilt proposed a quantum mechanic approach in 1993 [48]. He assumes that the polarization change is induced by a perturbation in the self-consistent Kohn-Sham potential (not an electric field),
which is parametrized with a variable $\lambda$ ranging from 0 to 1. We also assume the change in $\lambda$ is adiabatic. The derivative of polarization with respect to $\lambda$ is

$$\frac{\partial P_\alpha}{\partial \lambda} = -\frac{2ie\hbar}{N\Omega_0me} \sum_k \sum_i \sum_j \text{occ} \text{ empty} \langle \phi^\lambda_{ik} | \hat{p}_\alpha | \phi^\lambda_{jk} \rangle \langle \phi^\lambda_{ik} | \frac{\partial V_{KS}}{\partial \lambda} | \phi^\lambda_{jk} \rangle (\varepsilon^\lambda_{ik} - \varepsilon^\lambda_{jk})^2 + \text{c.c.} \quad (2.38)$$

The change in polarization can be calculated,

$$\Delta P = \int_0^1 \frac{\partial P}{\partial \lambda} d\lambda. \quad (2.39)$$

If we introduce a set of periodic Bloch functions compatible with the cell, $u^\lambda_{ik}$, and use the reciprocal representation of the Hamiltonian, Eq. 2.39 can be cast into

$$\frac{\partial P_\alpha}{\partial \lambda} = -\frac{ie}{4\pi^2} \sum_i \int_{BZ} d^3k d^3\lambda \sum_{\text{occ}} \langle \partial u^\lambda_{ik} | \frac{\partial u^\lambda_{ik}}{\partial \lambda} \rangle \langle \partial u^\lambda_{ik} | \frac{\partial u^\lambda_{ik}}{\partial \lambda} \rangle \quad (2.40)$$

Integrating Eq. 2.40 by part, we obtain the polarization at any $\lambda$ as

$$P_\alpha^\lambda = -\frac{ie}{4\pi^2} \sum_i \int_{BZ} d^3k \langle u^\lambda_{ik} | \frac{\partial}{\partial k_\alpha} | u^\lambda_{ik} \rangle \quad (2.41)$$

Eq. 2.41 is closely related to the Berry phase of band $i$ [49, 50]. The physical meaning of Eq. 2.41 will be more obvious if we change the Bloch functions to Wannier functions.

$$P_\alpha^\lambda = \frac{2e}{\Omega_0} \sum_i \int d^3r (|W^\lambda_i(r)|^2 r_\alpha) \quad (2.42)$$

with

$$u^\lambda_{ik}(r) = \frac{1}{\sqrt{N}} \sum_R e^{-ik \cdot (r - R)} W^\lambda_i(r - R) \quad (2.43)$$

If we integrate Eq. 2.40 along a path that forms a closed loop, the change of polarization is not 0, instead we have $\Delta P = \oint d\lambda \frac{\partial P}{\partial \lambda} = \frac{e}{\Omega_0} \mathbf{R}$. It means, we can only determine the polarization to an arbitrary factor of $\frac{e}{\Omega_0} \mathbf{R}$. However, it is not a problem because in most cases, we are interested in a polarization change $|\Delta P| \ll \frac{e}{\Omega_0} R_{\text{min}}$, where $R_{\text{min}}$ is the smallest lattice vector component.

### 2.2 Molecular dynamics with reactive force field

Molecular dynamics (MD) is a simulation process in which the classical equations of motion (Newton’s equations)

$$m\ddot{\mathbf{r}}(t) = \mathbf{F}(\mathbf{r}(t)) = -\nabla V(\mathbf{r}(t)) \quad (2.44)$$
are solved numerically with a given time step $\delta t$. The dynamical effects are very important in study of phase transitions or chemical reactions. In biochemistry and biophysics, MD can be used to determine the structure of proteins and macromolecules. Because the potential energy surface of a macromolecule can be very complicated, the global minimum may not be accessible by optimization. In physics, MD can be used to simulate atomic-level phenomena, such as thin film growth and ion implantation. Also, MD allows one to investigate the effects of temperature directly.

Forces in Eq. 2.44 can be calculated in quantum mechanics, for example by DFT. Born-Oppenheimer approximation \cite{51} assumes the motion of atomic nuclei and electrons can be separated, because the electrons move much faster than the nuclei. One can thus assume that the electron wave function responds instantaneously to the motion of nuclei, and at any time the electrons are in ground state. Thus, the forces can be calculated by DFT at each time step, and the system is updated accordingly. However, DFT typically deals with systems containing hundreds of atoms. Proteins typically contain $10^3 \sim 10^4$ atoms, as do polymers. One has to create classical inter atomic potentials, which depend on the atomic positions analytically, to carry out simulation for huge systems.

Thermodynamical ensembles can be simulated in MD to calculate the corresponding physical quantities. The ergodic hypothesis assumes that all accessible microstates are equally probable over a long period of time. In principle, the phase space can thus be sampled by substituting the time average for the ensemble average

$$\langle A \rangle = \lim_{N \to \infty} \frac{1}{N} \sum_{i} A(t_i).$$

The numerical integration of Newton’s equations leads to cumulative errors that can not be eliminated entirely. However, by using appropriate algorithms and parameters, the error can be controlled to a sufficient level.

### 2.2.1 Verlet Algorithm

To numerically solve Eq. 2.44, the most naive integrator is the so-called Euler algorithm. One uses the Taylor expansion of $r(t)$ truncated at the second order,

$$r(t + \delta t) = r(t) + \dot{r}(t)\delta t + \frac{\ddot{r}(t)}{2}\delta t^2.$$  

However, the local error at each time step is $\sim O(\delta t)$. The Euler algorithm is not time-reversible and it leads to large energy drift. By modifying the Euler algorithm a little, we get the most
widely used Verlet algorithm [52]. Considering the Taylor expansion Eq. 2.46 at \( t - \delta t \) and \( t + \delta t \)

\[
\begin{align*}
\mathbf{r}(t - \delta t) &= \mathbf{r}(t) - \dot{\mathbf{r}}(t)\delta t + \frac{\ddot{\mathbf{r}}(t)}{2}\delta t^2 \\
\mathbf{r}(t + \delta t) &= \mathbf{r}(t) + \dot{\mathbf{r}}(t)\delta t + \frac{\ddot{\mathbf{r}}(t)}{2}\delta t^2
\end{align*}
\]

(2.47)

From the two equations we get the trajectory at \( t + \delta t \) as

\[
\mathbf{r}(t + \delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \delta t) + \ddot{\mathbf{r}}(t)\delta t^2.
\]

(2.48)

The velocity at \( t \) is

\[
\dot{\mathbf{r}}(t) = \frac{\mathbf{r}(t + \delta t) - \mathbf{r}(t - \delta t)}{2\delta t}
\]

(2.49)

The local error of Eq. 2.48 is \( \sim O(\delta t^4) \). There are several integration algorithms that are equivalent to the Verlet integration, such as "leap frog" algorithm [53]. Beeman algorithm [54] also has local error \( \sim O(\delta t^4) \). It gives the same trajectories as the Verlet scheme, but yields a better estimation of the velocities.

Sometimes, higher-order integration algorithms are needed to allow for larger time step or obtain higher accuracy for a given time step. An example is the so-called predictor-corrector algorithm. Higher-order methods requires more storage and often are irreversible. For most MD simulations, the Verlet scheme is best choice.

2.2.2 OPLS force field

In the OPLS force field [55], the total energy has the following form

\[
E_{\text{total}} = \sum_{\text{bonds}} K_r (r - r_{eq})^2 + \sum_{\text{angles}} K_\theta (\theta - \theta_{eq})^2 +
\]

\[
\sum_{\text{torsions}} \left( \frac{V_1}{2}(1 + \cos(\phi + f_1)) + \frac{V_2}{2}(1 - \cos(2\phi + f_2)) + \frac{V_3}{2}(1 + \cos(3\phi + f_3)) + \right) +
\]

\[
\sum_{\text{non-bonded}} \left( \frac{q_i q_j e^2}{r_{ij}} + 4\epsilon_{ij} \left( \frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^6}{r_{ij}^6} \right) \right) f_{ij}
\]

(2.50)

The first term in Eq. 2.50 counts the energy of bond stretching. It assumes that the two bonded atoms are connected by a spring, and \( K_r \) is the strength. More sophisticated formulations of the bond energy can be used to increase accuracy. For example, one can add the higher order terms \( K_r^{(3)} (r - r_{eq})^3 \) and \( K_r^{(4)} (r - r_{eq})^4 \). Or one use the Morse potential \( D_r (1 - e^{-a(r-r_{eq})})^2 \).

The second summation in Eq. 2.50 stands for the energy of bond angles, and it also uses the harmonic form. The third term is for the energy of dihedral angles that involve three consecutive
bonds. The last term is the non-bonded interaction, i.e., the electrostatic energy and the van der Waals energy. It includes the interactions between atoms separated by three or more bonds. The coefficient is 0.5 if atom $i$ and $j$ are the first and last atoms of a dihedral angle, otherwise $f_{ij} = 1$.

The OPLS force field is among the cheapest full atom potentials for organic compounds. In this work, we mainly use it for preliminary simulations and tests.

### 2.2.3 Reactive force field

In this work, we are interested in simulating the dielectric response of polymeric materials. When atoms are subject to an electric field, their charges change. Thus, it is very important to have an inter-atomic potential which is able to capture the variation of charge.

A force field called "reaxFF" was introduced by van Duin and co-workers in 2001 [56], which is able to simulate a chemical reaction. The total energy in reaxFF has the following form

$$E_{\text{total}} = (E_{\text{bond}} + E_{\text{over}} + E_{\text{under}}) + (E_{\text{val}} + E_{\text{pen}}) + E_{\text{tors}} + E_{\text{conj}} + E_{\text{non-bond}}. \quad (2.51)$$

The key quantity in reaxFF is the bond order $BO_{ij}$, which allows for continuous bond formation/breaking. $BO_{ij}$ determines the whether the two atoms $i$ and $j$ are bonded and what type of bond it is. It is first calculated from the inter-atomic distance,

$$BO'_{ij} = \exp(p_1 \left( \frac{r_{ij}}{r_0} \right)^{p_2}) + \exp(p_3 \left( \frac{r_{ij}}{r_0} \right)^{p_4}) + \exp(p_5 \left( \frac{r_{ij}}{r_0} \right)^{p_6}), \quad (2.52)$$

where $p_1 - p_6$ are predetermined constants. Then, the degree of deviation of a single atom is calculated as

$$\Delta_i = \sum_j BO'_{ij} - Val_i, \quad (2.53)$$

where $Val_i$ is valency of atom $i$ (Val=4 for carbon). At last, $BO'_{ij}$ is corrected

$$BO_{ij} = BO'_{ij} \cdot f_1(\Delta_i, BO'_{ij}) \cdot f_4(\Delta_i, BO'_{ij}) \cdot f_4(\Delta_j, BO'_{ij}) \quad (2.54)$$

where $f_1$ and $f_4$ are complicated functions and will not be given here. Once we have the bond order, the bond energy in Eq. 2.51 is given by

$$E_{\text{bond}} = -D_e BO_{ij} \cdot \exp(p(1 - BO'_{ij})). \quad (2.55)$$

Even with correction, the bond order exceeds the valency in some cases, and $\Delta_i$ may be smaller than 0. $E_{\text{over}}$ and $E_{\text{under}}$ are the energy penalty terms that deal with over- and under- coordination. $E_{\text{val}}$ and $E_{\text{pen}}$ terms account for the energy of bond angles. $E_{\text{conj}}$ is designed to describe
contribution of conjugation effects in aromatic systems. They all have dependence on the bond order $BO$, $BO'$ and $\Delta$. $E_{\text{non-bond}}$ is the van der Waals and Coulomb interaction energy. All atomic charges are calculated according to the electron equilibration method (EEM) [57, 58]. More details can be found in the original paper by van Duin et al [56].
Chapter 3

Optical Enhancement in Heteroleptic Ru(II) Polypyridyl Complexes Using Electron-Donor Ancillary Ligands

Organic dyes are a viable alternative to silicon for energy conversion. Using simulations from first-principles, we show that chemical manipulation is a powerful tool for tuning the optical absorption spectra of a special class of dyes in a way that is convenient for exploitation in dyesensitized solar cells. Specifically, we have carried out density functional theory calculations on three Ru(II) polypyridyl complexes with electron-donor ancillary ligands. These complexes were recently developed to study how different electron-donor ancillary ligands affect the photophysical and electrochemical properties of these dyes for light harvesting and photon-to-electron conversion efficiency. We found that the electron-donor ancillary ligands significantly enhance the light harvesting in the visible and the near-infrared regions relative to the reference dye N3. Furthermore, we detected a decrease in the ionization potential, which improves the energy alignment with the redox potentials of the electrolyte. These findings demonstrated that better organic materials for energy applications were developed.

3.1 INTRODUCTION

Dye-sensitized solar cells (DSSCs) have been intensively investigated in both academia and industry in recent years for their potential of low cost and high efficiency [2, 3, 4, 5, 6]. A percolating mixture of a molecular dye and a metal-oxide semiconductor nanoparticle (e.g.,
TiO$_2$, ZnO) is the key optical part of DSSCs, where photons are absorbed by the dye and the excited electrons are injected into the conduction band of the semiconductor and collected at the external leads. An ionic electrolyte, typically I$^-$/I$_3^-$, donates electrons back to the dye to complete the cycle.

Figure 3.1: Optimized structures in vacuo of the four investigated dyes. Color code: C=cyan, H=white, O=red, N=blue, Ru=green, S=yellow.

We investigate in this work novel dye sensitizers (Figure 3.1). A good dye sensitizer should have the following properties [59]: (1) strong absorption over the entire visible and near-IR (NIR) range, in the challenging search for panchromatic dyes [60, 61, 62, 63]; (2) the presence of an anchoring group to favor the attachment to the oxide surface and the proper band alignment of all components, i.e., the LUMO of the dye should be higher than the conduction band of the semiconductor host substrate (e.g., TiO$_2$) to allow for thermodynamically favorable electron injection, and the redox potential of the electrolyte should be higher than the HOMO of the dye for effective dye regeneration (hole replenishment). The last requirement ensures optimal performance over $\sim 10^8$ turnover cycles (about 20 years). A scheme of the alignment of our target dyes is illustrated in Figure 3.2.

The N3 dye [bis(2,2'-bipyridine-4,4'-dicarboxylate)-Ru(II)], labeled as 1 in this work, satisfies all such requirements and has become a benchmark since it was introduced in 1993 [8]. Its strong
absorptivity is due to a metal-to-ligand charge transfer (MLCT) transition, in which an electron is transferred from the \( t_{2g} \) orbital of the Ru(II) center to the \( \pi^* \) orbital of a polypyridyl ligand. This mechanism enhances charge separation and reduces electron-hole recombination. However, the high ionization potential of N3 (0.85 V vs saturated calomel electrode, SCE), generates a potential drop with respect to the redox level of the \( \Gamma^-/\Gamma^-_3 \) couple used in the electrolyte (0.15 V vs SCE), which in turn makes the dye regeneration process consume 0.7 eV without increasing the open-circuit voltage, \( V_{OC} \), that is instead dictated by the Fermi level of the electrodes. This is the main loss factor in this type of DSSCs. Finally, N3 has only a moderate extinction coefficient and relatively weak absorption at long wavelengths.

To improve the efficiency of DSSCs one can rely on chemical modifications that implement two conditions: (1) an upward energy shift of the HOMO of the dye while maintaining at least 0.3 eV of energy difference between the HOMO of the sensitizer and the redox potential of the electrolyte; (2) a maximization of the light harvesting. The latter requires an increase of the extinction coefficient of the MLCT band and an extension of the absorption toward longer wavelengths. Various attempts to improve the light absorption of organic dyes have been reported [64, 65], pointing out the limitations of simple shifts of the electronic levels and the need for other factors (e.g., modulation of the electrolyte redox potential). Recently, El-Shafei and co-workers [7] have synthesized and tested novel Ru-based dyes, by replacing the carboxyl groups in one bipyridine of N3 with electron-donor ancillary ligands to form a stilbazole antenna.
(these are labeled as 2-4 in this work, see Figure 3.1). Experimental data showed that these novel dyes are red-shifted and have stronger molar extinction coefficient over the visible range of the solar spectrum extending into the NIR region, with a lower ionization potential \(i.e.,\) upshift of the HOMO level and a reduced HOMO-LUMO energy gap, while conserving the correct band alignment. Furthermore, one of the dyes outperforms N3 by 44\% in molar absorptivity and 14.6\% in the total solar-to-electric conversion efficiency under experimental conditions optimized for N3. These encouraging results stimulated us to study the modified Ru-based dyes using first-principle calculations, to investigate the atomistic nature of these improvements and understand at the molecular level the origin of the underlying mechanisms.

3.2 METHODS AND MATERIALS

Our calculations were carried out in the framework of density functional theory (DFT) as implemented in the Quantum Espresso (QE) package [66]. We used a plane-wave basis set with a kinetic energy (charge density) cutoff of 25 (250) Ry, ultrasoft pseudopotentials [67] and the PBE [68] exchange-correlation functional. The Brillouin zone of the reciprocal lattice was sampled at the Γ point. We used periodic supercells where at least 10 Å of vacuum or solvent separated neighboring periodic replicas. Atomic coordinates were relaxed until all force components were smaller than 0.05 eV/Å.

The absorption spectra were calculated with the turboTDDFT code [69], which is based on a Lanczos approach to the linearized quantum Liouville equation [70, 71]. This method allows for the calculation of extended portions of the optical spectrum in systems comprising several hundred atoms, such as our large dyes in explicit solvent (up to ~750 atoms and ~2100 electrons). The simulation of the color was obtained following the tristimulus colorimetry theory [72], which provides the red (R), green (G), and blue (B) representation of the perceived color, starting from the knowledge of an illuminant source, the retina matching functions and the absorption spectrum. The retina matching functions exist in reference databases, while the optical absorption spectrum was taken from the TDDFT calculations [73].

We considered four different dyes, illustrated in Figure 3.1. One is the well-known Ruthenium polypyridyl sensitizer N3, whose dideprotonated form is commonly referred to as N719 [74]. Dyes 2-4 are the ones recently synthesized by El-Shafeis group[7] by attaching an ancillary ligand (Ar) to one of the two bipyridyls (bpy). Dyes 2 and 3 were molecularly engineered to furnish a stilbazole with alkoxy groups (auxochromes) in one of two forms, cyclic or acyclic. Dye 4 was synthesized by using carbazole-based ancillary ligands. Stilbazole and carbazole chemistry were used because they have strong two-photon absorption cross-section and form a highly conjugated system with auxochrome character, which should increase the intensity of the MLCT bands. The ancillary ligands were introduced in position para with respect to
the COOH anchor group in order to facilitate a stronger electron coupling and hence a strong electron injection into the conduction band.

We performed DFT/TDDFT calculations both in vacuo and in solution. We used water and DMSO as explicit solvents for 1, while DMSO was chosen all for the other dyes, although experiments are performed in a DMF solution. Here we chose a compromise between accuracy and feasibility: DMSO has properties similar to DMF, both being organic aprotic polar solvents with relatively similar dielectric constants, dipole moment, and refractive index; yet, the smaller number of atoms in DMSO gives a net reduction of the computational cost. Water has different characteristics (highly polar protic solvent), and it was used as a benchmark with published data on 1, and to confirm negative solvatochromic behavior as a function of the solvent polarity [74].

Our explicit solvation model included hundreds of solvent molecules wrapping the dye within the supercell to create a polarizing environment. The initial configurations of the explicit solvent were prepared by classical molecular dynamics (MD) simulations to ensure a reasonable equilibrated environment and then relaxed in DFT after adding the solutes.

We assessed our method against NWChem [75] calculations that allow for implicit solvent treatment (COSMO [76] model) and the use of hybrid B3LYP [77] functionals.

3.3 STRUCTURAL AND ELECTRONIC PROPERTIES

The bond lengths between the central Ru atom and the surrounding ligands are listed in Table 3.1. In dye 1, all of the bond lengths are exactly the same as previously reported from PW91 calculations [78], while angles are slightly different. The geometry of the isothiocyanate does not substantially change by planting different antenna ligands to one bipyridine. The N-C and S-C bond lengths in the NCS units vary by less than 1% both in vacuo and in solvent and the two isothiocyanate groups are almost at right angles. The Ru- N distances undergo variations by less than 1%, both relative to the Ar-bpy and to the bpy-COOH groups.

The solvent effect on the bond lengths is contained within a maximum of 1%. Only the O-H bond length in the COOH groups of 1 in explicit water increases significantly (by about 10%) upon solvent addition (not reported in Table 3.1). This is due to an artificially prepared H-bonding configuration at the COOH groups. The solvent effect is more pronounced in the angles: in 3 and 4 the methyls in the stilbazole are no longer in the same plane, as it is the case in vacuo.

The novel dyes and 1 are overall quite similar in their structure. The electron donor and the bpy of stilbazoles moiety are basically in the same plane and no distortion can be observed. The central Ru atom and the six surrounding N atoms form a quasi-octahedral configuration, which is a common characteristic of 3-4. In working DSSCs, the COOH-bpy unit serves as anchoring
Table 3.1: Geometry Parameters of Sensitizers 1-4

<table>
<thead>
<tr>
<th></th>
<th>environment</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-NCS</td>
<td>vacuum</td>
<td>2.049</td>
<td>2.051 (+0.1%)</td>
<td>2.052 (+0.1%)</td>
<td>2.051 (+0.1%)</td>
</tr>
<tr>
<td></td>
<td>DMSO</td>
<td>2.075</td>
<td>2.067 (-0.4%)</td>
<td>2.073 (-0.1%)</td>
<td>2.072 (-0.1%)</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>2.077</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru-bpy(COOH)</td>
<td>vacuum</td>
<td>2.075</td>
<td>2.061 (-0.7%)</td>
<td>2.060 (-0.7%)</td>
<td>2.063 (-0.6%)</td>
</tr>
<tr>
<td></td>
<td>DMSO</td>
<td>2.079</td>
<td>2.070 (-0.4%)</td>
<td>2.074 (-0.2%)</td>
<td>2.075 (-0.2%)</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>2.083</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru-bpy(Ar)</td>
<td>vacuum</td>
<td>2.075</td>
<td>2.088 (+0.6%)</td>
<td>2.089 (+0.7%)</td>
<td>2.091 (+0.8%)</td>
</tr>
<tr>
<td></td>
<td>DMSO</td>
<td>2.079</td>
<td>2.086 (+0.3%)</td>
<td>2.067 (0.6%)</td>
<td>2.088 (+0.4%)</td>
</tr>
<tr>
<td></td>
<td>water</td>
<td>2.083</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*aThe percentage variations of the bond lengths for 2-4 in vacuo and DMSO are indicated relative to 1 in vacuo and DMSO. The structural parameters in explicit solution are reported from the optimized configurations with supercells with 485, 797, 755, and 793 atoms for 1-4. Errors smaller than 0.001 Å and 0.1% are not indicated.

The percentage variations of the bond lengths for 2-4 in vacuo and DMSO are indicated relative to 1 in vacuo and DMSO. The structural parameters in explicit solution are reported from the optimized configurations with supercells with 485, 797, 755, and 793 atoms for 1-4. Errors smaller than 0.001 Å and 0.1% are not indicated.

The electronic structure of 1 has been characterized by other authors at different accuracy levels [78, 79, 80, 81]. In particular, De Angelis and co-workers [78, 74] characterized the frontier molecular levels of 1 in good agreement with experiments and classified them into four groups (three occupied and one unoccupied) according to the correspondence with the absorption bands. Here, we use both experimental results and previous simulations for dye 1 as benchmarks to test the validity of our approach and keep the same classification for consistency.

Our results for the electronic density of states (DOS) of the four dyes in vacuo are presented in Figure 3.3, where the highest occupied orbital (HOMO) of 1 is set as the origin of the energy scale. The alignment between the various curves allows us to comment on the energy shifts due to different ancillary ligands. The fundamental DFT HOMO-LUMO gaps are reported in Table 3.2.

The first group of occupied orbitals (labeled occ1) of 1, between 0 and -0.3 eV, contains four energy levels, which are mainly NCS $\pi$ and $t_{2g}$ Ru d orbitals. The HOMO-1 and HOMO-2 are semidegenerate and give a double-intensity peak. The HOMO-3 is a pure NCS level (N and S p-like contribution). Between -1.4 and -1.7 eV we find another group (occ2) of three levels that have a NCS-Ru nature: Ru shows d character and the electrons of NCS are in C-S $\pi$ bonding. Between -2.6 and -2.7 eV there is a third group (occ3) composed of six electronic levels, having a bpy $\pi$ bonding character.
Table 3.2: Calculated Gaps and HOMO’s

<table>
<thead>
<tr>
<th>HOMO-LUMO gap(^a)</th>
<th>PBE gas phase (QE)</th>
<th>PBE explicit solution (QE)</th>
<th>B3LYP implicit solution (NWCHEM)</th>
<th>B3LYP implicit solution HOMO (NWCHEM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.52</td>
<td>1.22</td>
<td>2.42</td>
<td>-5.66 (-5.76)</td>
</tr>
<tr>
<td>2</td>
<td>0.54</td>
<td>1.05</td>
<td>2.32</td>
<td>-5.49 (-5.53)</td>
</tr>
<tr>
<td>3</td>
<td>0.55</td>
<td>0.98</td>
<td>2.30</td>
<td>-5.46 (-5.52)</td>
</tr>
<tr>
<td>4</td>
<td>0.56</td>
<td>1.01</td>
<td>2.28</td>
<td>-5.43 (-5.50)</td>
</tr>
</tbody>
</table>

\(^a\)HOMO-LUMO gaps (values in eV) of dyes 1-4, calculated by DFT with different functionals, in vacuo and in DMSO solution. HOMO energies are evaluated in implicit DMSO solvent (COSMO). Values in parentheses are experimental measurements [7].

The calculated DFT energy gap between the HOMO and the lowest occupied molecular orbital (LUMO) is 0.52 eV: this small value is affected by both the environmental setup and the exchange-correlation functional (e.g., we show later that the B3LYP functional, which contains a part of exact exchange, yields a larger HOMO-LUMO gap for 1 in the gas phase).

In the lowest unoccupied part of the spectrum (unocc1), we find six electronic energy levels with a bpy \(\pi^*\) bonding nature, which favor electron injection into the semiconductor. The nature of the gas-phase orbitals has been inferred by analyzing the projected DOS and the individual wave functions. These observations are in good agreement with previous works [74].

In Figure 3.3 we also present the DOS of the novel dyes in vacuo (each curve is labeled with the code of the dye). The DOS curves of 2-4 reflect the same character as 1. However, we find significant differences: essentially, the novel dyes have more electrons to distribute in the same energy range (from substituted antenna ligand). This results in new peaks in the DOS and an increase in the width of the groups accompanied by energy shifts.

The HOMOs of 2-4 are very close to each other, between 0.095 and 0.105 eV above the HOMO of 1, with 4 being intermediate between 2 and 3. The HOMO-LUMO gap is 0.54-0.56 for 2-4, practically identical to the value of 1.

To understand the differences arising in the electronic structure because of the presence of the larger ligands, we choose to focus first on the character of the electronic states in 4. Representative states for each identified group are shown in Figure 3.4. The first occupied MO group (occ1) contains four states as in 1, with a slightly larger splitting between HOMO-1 and HOMO-2 (0.05 eV) relative to 1 due to further breaking of symmetry. Both states maintain the same Ru \(t_{2g}\) and NCS \(\pi\) character of the pristine dye 1. The second group occ2 has seven levels instead of the three in 1; these lie between -1.0 and -1.7 eV, with a 0.7 eV spread. The occ2 group in 4 has less Ru-d/NCS character than in 1, while it has contribution from the carbazole...
antenna (absent in 1). HOMO-4 and HOMO-5 have $\pi$ bonding character on one of the two carbazole-bpy moieties. They are followed, at lower energies in the same group, by three Ru-d/C-S $\pi$ orbitals, and then two combined Ru-d/carbazole-$\pi$ orbitals. The third occupied MO group lies between -2.1 and -3.0 eV, with spread of 0.9 eV. This third occupied group, occ3, contains eight bpy (antenna) $\pi$ bonding electronic states plus two electronic states of the two carboxyl groups (one for each group).

The first unoccupied group, unocc1, contains six virtual states as in 1 but with different character: LUMO+1, LUMO+3, and LUMO+5 are $\pi^*$ orbitals located on the Ar-bpy, LUMO, LUMO+2, and LUMO+4 are $\pi^*$ orbitals located on dc-bpy; the latter are responsible for the coupling to the semiconductor. Dyes 2 and 3 have very similar electronic states as 4. The occ1 group contains four states with the same nature as in 1 and 4, the degeneracy between HOMO-1 and HOMO-2 is removed as in 4. The occ2 group in 2 is between -1.03 and -1.56 eV, with width of $\sim$0.5 eV and significant contribution from stilbazole. The occ3 group in 2 includes eight bpy $\pi$ orbitals between -2.1 and -2.9 eV. The occ2 group in 3 has seven levels with mixed Ru-NCS stilbazole orbitals, between -0.7 and -1.5 eV. The occ3 group in 3 contains six bpy-$\pi$ orbitals in a width of 0.45 eV between -2.25 and -2.7 eV. Both 2 and 3 have a clear gap below occ3. Above the fundamental gap, unocc1 in 2 and 3 is also similar to 4: it contains six levels, half of them located on dc-bpy and the other half located on Ar-bpy.

In general, we find that the insertion of large antenna ligands into the molecular structure
induces an enrichment of the occupied electronic density of states in the proximity of the fundamental gap. This population enhancement produces an abundance of starting states for allowed optical transitions. The four dyes have identical characters in the first occupied and unoccupied groups of orbitals. Furthermore, for all analyzed dyes the symmetries of the frontier orbitals are coherent with MTLC $d\rightarrow\pi^*$ transitions. The second group of occupied orbitals gains a significant contribution from the ligand Ar in 2-4, while it is due to purely Ru-NCS orbitals in 1. Thus, we expect that in the novel dyes the second optical absorption band may have at least a partial contribution from $\pi/d\rightarrow\pi^*$ transitions, at odds with 1 where the second absorption band is due to $d\rightarrow\pi^*$ transitions solely. We will return on this point in the next Section.

Let us now discuss the modifications induced by a solution environment on the ground-state electronic structure of the dyes (see Figure 3.5). We immediately notice an increase of the HOMO-LUMO gap in solution relative to the gas phase (see also Table 3.2. Moreover, the DOS below the highest occupied group broadens and the second and third groups mix with each other. Let us focus again on 4 to describe the changes.

In 4 the DFT-PBE HOMO-LUMO gap increases from 0.54 to 1.01 eV. We find distinct peaks due to individual electronic energy levels around the HOMO, but overall the three highest occupied groups of levels are redistributed more continuously within $\sim$3 eV below the HOMO. The energy redistribution, as well as the change in peak intensity, is a manifestation of the dielectric coupling between DMSO and the sensitizer. A deeper analysis, not shown, reveals that in this energy range there is no orbital mixing between occupied states of DMSO and the sensitizer. However, the first three unoccupied states of DMSO fall in the forbidden gap of 4. Even though these solvent states (which would be impossible to detect using an implicit solvent model) do not modify the symmetry of the lowest virtual states of the dye (i.e., no
Figure 3.5: Electronic density of states of the dyes in DMSO solution (1 in water solution is explicitly indicated). The DOS in this figure has been computed by summing over all atomic projections excluding the H atoms and the solvent atoms. The alignment has been done on the lowest occupied orbital, which is an inert COOH orbital. The HOMO of 1 in water is set as the origin of the energy scale. Note that the curves in this plot are not aligned to those in vacuo, hence the shifts due to the solvent do not emerge from this kind of plotting. Solvent shifts are discussed in the Supporting Information.

direct hybridization), their presence might in principle modify the adsorption properties of the systems or give rise to exciton dark states that may act as nonradiative deexcitation traps.

The calculated HOMO-LUMO gaps of the molecules in explicit solvent with the PBE functional are 1.05 and 0.98 eV for 2 and 3, respectively. The behavior of the occupied orbitals is very similar to those in 4: there is an energy redistribution and an intensity change, with the first three groups spanning an energy range of 2.5 eV, and more significant dye-solvent orbital mixing at lower energies.

We have also performed calculations of the dyes in implicit solvent to eliminate the limit of a particular solvent configuration. The results show that the first four/five occupied orbitals are the same as in the gas phase for all dyes. This is in agreement with what was shown before for 1 in implicit solvent [71]. From Table 3.2 we observe that in a solvent environment the presence of antennas significantly reduces the HOMO-LUMO gap. This is different from the gas phase, where the effect of the antenna ligands appears to be negligible despite the enhancement in \(\pi\)-conjugation discussed above.

To inspect how the ionization potential (HOMO energy relative to the absolute vacuum level) of this class of dyes varies by varying the chemistry of the antennas, we have computed
Table 3.3: Absorption Peaks in Calculation

<table>
<thead>
<tr>
<th>RGB</th>
<th>band I&lt;sup&gt;a&lt;/sup&gt;</th>
<th>band II</th>
<th>band III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wavelength (nm)</td>
<td>wavelength (nm)</td>
<td>wavelength (nm)</td>
</tr>
<tr>
<td></td>
<td>vacuum solution&lt;sup&gt;c&lt;/sup&gt;</td>
<td>vacuum solution&lt;sup&gt;c&lt;/sup&gt;</td>
<td>vacuum solution&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>1</td>
<td>245/193/133</td>
<td>141/154/135</td>
<td>880</td>
</tr>
<tr>
<td>2</td>
<td>237/163/153</td>
<td>197/169/141</td>
<td>907</td>
</tr>
<tr>
<td>3</td>
<td>233/152/169</td>
<td>206/164/142</td>
<td>895</td>
</tr>
<tr>
<td>4</td>
<td>225/152/166</td>
<td>196/158/148</td>
<td>907</td>
</tr>
</tbody>
</table>

<sup>a</sup> Peaks in the absorption spectra of the investigated dyes. Values separated by a comma indicate distinct peaks in the same band, while values separated by a dash indicate a broad peak in the band.

<sup>b</sup> The RGB values were obtained after the procedure described by Malcioglu and co-workers [73].

<sup>c</sup> The values reported in this table are the results of our linear-response TDDFT calculations in explicit solvent.

the electronic structures of 2-4 in implicit DMSO solvent using NWChem with the hybrid B3LYP exchange correlation functional, which has been demonstrated to correct the well known deficiencies of DFT. The results are summarized in Table 3.2 and illustrated in Figure 3.2, where we show the variation in the alignment of the HOMO level with respect to the redox potential of $I^-/I_3^-$ and to the TiO$_2$ bandgap. In all cases, the correct staggered oxide-molecule-electrolyte band-alignment is maintained. The HOMOs of dyes 2-4 are shifted upward relative to dye 1, reducing the voltage drop by 0.17-0.23 eV. This is in excellent agreement with the experimental findings [7] (Table 3.2) and demonstrates the efficiency of the novel dyes in minimizing the mismatch between the $I^-/I_3^-$ redox level and the HOMO of the new dyes.

In summary, the use of these strong electron donor antennas reduces the HOMO-LUMO gap, which results in a red shift of all absorption peaks, and hence enhanced light harvesting efficiency in the red/NIR region. At the same time, the modification of the energy levels of the frontier orbitals confirms the upward shift of the HOMO while maintaining thermodynamically favorable dye regeneration because the energy gap between the HOMO of the dye and the redox potentials is still higher than 0.3 eV. Simultaneously, the LUMO still lays 0.1 eV above the conduction band edge of the semiconductor, which is a necessary thermodynamic condition for efficient photoelectron injection into the conduction band edge of TiO$_2$. 

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3.4 OPTICAL ABSORPTION SPECTRA

For all four sensitizers, the absorption spectra calculated by the Lanczos recursive method are plotted in Figure 3.6. The absorption maxima from our calculations are listed in Table 3.3. All spectra show a clear band pattern. Response charge densities and the color scheme are presented in Figure 3.7. The absorption spectrum of 1 is dominated by three bands in the visible range (namely I, II, and III, from lower to higher energy).

![Figure 3.6: Optical absorption spectra computed by linear-response TDDFT. Panels a-d illustrate the effect of the solvent separately for each dye. Panels e and f illustrate the comparison between the various dyes at fixed environmental conditions. The legends specify the conditions for each panel. The scales along the x and y axes are the same in all panels.](image)

The strong absorption in the visible is the necessary prerequisite for the light harvesting activity in DSSCs. The absorption bands were previously attributed to the electronic transi-
tions: \((d\rightarrow\pi^*)\), \((d\rightarrow\pi^*)\), and \((\pi\rightarrow\pi^*)\), from occupied groups 1, 2, and 3 (occ1, occ2, and occ3) to unoccupied group 1 (unocc1), respectively [78]. Here, we analyze the lowest energy peaks of 4 using a postprocessing Lanczos procedure that allows us to obtain the decomposition of the optical transitions in terms single–article electron-hole pair (as in a standard Casidas procedure), as well as to display the response charge, which describes the light-induced charge dipole distribution within the molecule.

The lowest energy band I at 907 nm has a net \(d\rightarrow\pi^*\) character and is mostly due to HOMO, HOMO-1, and HOMO-2 transitions to LUMO, as can be easily visualized by comparing single particle states of Figure 3.3 and the charge response of Figure 3.7(a). These transitions mostly involve the central Ru ions, the isothiocyanate and the carboxylate units as in 1. Transitions corresponding to bands II and III have a large contribution from Ar-bpy antenna. Band II has a much larger contribution from Ru-d states than band III, so the former can be classified as \((d\rightarrow\pi^*)\) transitions, while the latter are better described by \((\pi\rightarrow\pi^*)\) transitions, in agreement with the classification given for 1.

Figure 3.7: Color scheme and RGB codes for the four dyes in vacuo and in solution.

Figure 3.6(e) summarizes the results for the gas phase: all novel dyes manifest a stronger optical absorption, indicating the possibility of a better behavior for photon harvesting. 4 has the strongest absorption in all three bands; band I of dyes 2, 3 and 4 is red-shifted relative to dye 1, implying a better performance in the long wavelength region.

Figure 3.6(a)-(d) shows the solvent effect on the optical absorption spectra. In 1, we observe both a hypsochromic shift (blue-shift) and a hyperchromic effect (increase of intensity) in bands
I and II. The hyperchromic effect also characterizes band III, in good agreement with previous PW91 calculations for 1 [79]. In the case of 1 we also note a negative solvatochromic shift going from DMSO to water (i.e., increasing the polarity of the environment). This is a fingerprint of an enhancement of the transition dipole moments of the molecule in the exFd state with respect to the ground state due to the dipolar interaction with the external medium [82].

As in 1, band III of 4 is greatly enhanced in solution; it has a peak at 337 nm and a shoulder at 385 nm. Band II is blueshifted about 20 to 495 nm. Band I is now at 704 nm, redshifted with respect to the 680 nm of 1. This indicates that 4 has a potential for better performance in the long wavelength region. Compared to band II/III, band I is not as distinguishable; this band is formed by several weak maxima not very close to each other, forming an unstructured shoulder at 607 nm.

In 2 we identify optical features at 333 nm (band III), 488 nm and a small shoulder at 437 nm (band II), and 681 nm (band I). In 3, the high-energy band III overlaps with the UV peak, band II has two maxima at 430 and 494 nm and band I shows two small shoulders at 678 and 784 nm.

As discussed above, the lowest unoccupied states of DMSO lie in the pristine HOMO-LUMO gap of the dyes and this could affect the optical properties of the system. Thus, we studied the absorption spectrum of DMSO. The absorption edge of the solvent is around 270 nm, far away from the adsorption edge of the dyes. The lack of electronic superposition between molecular and DMSO states in the gap region prevents the formation of dark states that might be detrimental to the photocharge separation and for the efficiency of the DSSCs.

To visualize the different absorption properties of the dyes, we simulated the perceived colors corresponding to the molecules in the minimum energy geometry in vacuo and in solvent (Figure 3.7). In vacuo, for all dyes, bands I and III are transparent since they lie in the near-IR and UV range, respectively. Only band-II contributes to color, absorbing light in the range 460-510 nm, which corresponds to the blue-green band. Since the color is related to the transmitted (i.e., not absorbed) radiation and the spectra have a minimum in the frequency range corresponding to red (∼600 nm), the final colors of all dyes are reddish. The darker color of the three new dyes is mainly due to the higher absorption intensity with respect to 1. This is a compelling indication of the potential for enhanced light harvesting capabilities of the new moieties.

The effect of the solvent is 2-fold: the overall hypercromism is responsible for the darker colors of all dyes; the hypsochromism of band I, now absorbing in the red region, causes the shift of color toward green-brownish hues. Notably, the color representation of Figure 3.7(b) does not include vibronic effects due to temperature. The latter may enlarge and broaden the absorption spectra of the molecule in liquid solvents and thus their actual color [73].
3.5 CONCLUSIONS

Using calculations from first-principles within DFT/TDDFT we have demonstrated that chemical alterations are powerful tools to tailor the optoelectronic properties of DSSCs.

Our calculations show that the inclusion of conjugated ligands enriches the population of the occupied frontier molecular levels, reduces the ionization potential and the HOMO-LUMO gap: this helps to improve the performance of the sensitizer by reducing the hole-regeneration loss. Moreover, absorption spectra display: (i) a stronger absorption strength, due to enriched initial excitation states (i.e., larger light harvesting); (ii) absorption at red/NIR wavelengths due to the reduction of the intrinsic gap (i.e., panchromatic sensitizers). Among the four moieties, 4 is the most promising, in agreement with experiments.

Many past attempts to improve the photovoltaic efficiency of organic dyes by aligning the HOMO level to the electrolyte have been fruitless, because this adjustment acted negatively on charge regeneration. We have obtained here favorable results because of a fine-tuning: the particular modified chemical groups allowed us to raise the HOMO level by an amount that is useful to modify the optical absorption spectra, while leaving enough energy for regeneration. As a matter of fact, the total solar-to-electric conversion efficiency of dyes 2-4 are 10.32%, 7.25%, and 9.91%, respectively.
Chapter 4

First Principle Simulation of PVDF Copolymers for High Energy Storage: PVDF-HFP and PVDF-BTFE

Phase diagrams of polyvinylidene fluoride (PVDF) and its copolymers with hexafluoropropylene (HFP) and bromotrifluoroethylene (BTFE) are investigated via first-principles simulation, and compared to previously studied PVDF-chlorotrifluoroethylene (CTFE) data. The non-polar to polar phase transition also occurs in HFP and BTFE copolymers, and the results for P(VDF-HFP) show good agreement with existing experiments. For P(VDF-BTFE) copolymer, we predict that by tuning the BTFE concentration to a higher value (25%), higher energy density can be achieved, in particular in low electric field regime. The transition pathway connecting the polar and non-polar phases are also calculated for the two copolymers, and the energy barriers are found to be similar for the three copolymers and different concentrations.

4.1 INTRODUCTION

Materials with high energy density have important applications in hybrid vehicles, micro-actuators, capacitors and integrated circuits. Among these materials, dielectric polymers are at present used in high energy capacitors, because they have high break down strength, high stability and low cost. Bi-axially oriented polypropylene (BOPP) is used in the state-of-art energy dielectric film. However, its energy density is only 4 J/cm$^3$. In 2006, a polyvinylidene fluoride (PVDF) copolymer with 9% chlorotrifluoroethylene (CTFE) was found to have ultrahigh en-
ergy density more than 18 J/cm$^3$ [11], and later in 2009 PVDF with 4.5% hexafluoropropylene (HFP) was found to have similar performance. In these copolymer systems, the dielectric displacement $D$ increases non-linearly with the electric field $E$. The non-linear behavior is the reason for the ultrahigh energy density and late saturation of $D$ and high breakdown field are essential.

PVDF is well known and has been investigated for the past 20 years, but mainly because of its ferroelectricity and electromechanical properties. Its polymer chain has a large spontaneous polarization that originates from the charge distribution in the CF2-CH2 unit [83, 84, 85]. However, pure PVDF is not suitable for energy storage, because the strong coupling between its dipoles leads to a large remanent polarization and causes loss. Also, it has very low crystallinity. Studies show that mixing with comonomers such as trifluoroethylene (TrFE) or tetrafluoroethylene (TeFE) dramatically increases the crystallinity and reduces the coupling between dipoles [86]. Adding a large third monomer to form a terpolymer system [13] or irradiating to form chemical pinning [87] further reduces ferroelectric coupling between domains.

PPVDF copolymers exist in both non-polar and polar phases, a previous study in our group showed that a non-polar to polar phase transition in P(VDF-CTFE) polymers is responsible for the ultrahigh energy density [15]. P(VDF-CTFE) copolymer with CTFE concentration below 30% have a non-polar ground state. Since a polar phase has lower electric enthalpy in high enough field, a transition to the polar state will eventually happen. We assume the experimental sample consists of nano domains with different defect concentrations, which give the overall measured concentration (e.g. 9% of CTFE in Ref. [11]). As the field increases, different domains convert to polar as their critical field is reached. This is the reason for the non-linear increases in dielectric displacement and the ultrahigh energy density.

To prove this transition is feasible, our group has also uncovered a two-step transition pathway connecting the polar and non-polar phases. This torsional and rotational pathway has an energy barrier of 100 meV/carbon atom in pure PVDF. The sample with 10% CTFE investigated in simulation has a barrier of 70 meV/Carbon, which makes the transition easier to be triggered by thermal fluctuation. The barrier is further reduced with electric field present, because all intermediate stages with polarization have lower enthalpies.

In the current work, we first investigate P(VDF-HFP) copolymers and reproduce of the experimental results, which supports the validity of our model. In the next step, we apply the same approach to PVDF-bromotrifluoroethylene (BTBE) copolymers with varying concentrations and find it to be a good candidate for high energy storage. The rest of this chapter is organized as following: Section 4.2 describes the methodology and calculations, Section 4.3 discusses various properties of P(VDF-HFP) and P(VDF-BTFE) copolymers, such as phase stability, dielectric properties, and energetic and transition pathways. Our conclusions are in Section 4.4.
4.2 COMPUTATIONAL DETAILS

All of our work is done within the frame of Density Functional Theory (DFT), as applied in plane wave package QuantumEspresso (QE) [66]. We use 50 and 600 Rydberg (Ry) cutoffs for wave functions and charge density, respectively. These values are much higher than in normal calculations using ultrasoft pseudopotentials [67]. Our convergence tests show that the potential energy surface of PVDF based polymers is extremely flat, and very high energy cutoffs are needed to converge the geometry. Reciprocal space sampling does not play as important a role in the convergence as the energy cutoff, 2x4x4 Monkhorst-Pack k-point grid [88] is chosen for the primitive $\alpha$-PVDF cell, and is modified accordingly for larger cells. Although weakly bonded, dipole-dipole interaction dominates the interchain binding in PVDF based polymers instead of the usual van der Waals interaction. We have also performed tests with the newly developed vdW-DF functional [30] and the DFT+D method [89]. These tests do not show systematic improvement over the simple PBE [68] runs. Therefore, PBE exchange-correlation functional is used throughout the current work.

Both the cell parameters and the atomic positions are relaxed via BFGS optimization method [90], until all force components are smaller than 0.01 eV/Å, and all stress components are smaller than 0.5 KBar. We chose such restrictive convergence criteria for the same reason the potential energy surface is extremely flat. Berry phase calculations [48] are then carried out for the optimized configurations to obtain the polarization.

4.3 RESULTS AND DISCUSSION

4.3.1 P(VDF-HFP)

PVDF exists in several possible crystalline phases [91] and three of them are involved in the non-polar to polar phase transition, see Figure 4.1. The $\alpha$ phase has the TGTG chain conformation in which dihedral angles of the carbon backbone alternate between 60 and 180. Each chain has a weak dipole moment indicated by arrows in Figure 4.1, but the antiparallel packing cancels the net polarization in cell. The $\gamma$ phase is formed by the same TGTG chains but with parallel packing. It has a moderate dipole moment per unit cell. In the $\beta$ phase the carbon chain has all dihedral angles equal to 180 and the dipoles are all aligned, so this phase has the strongest polarization among all the three studied in this work. All comonomers involved in this work are also shown in Figure 4.1. Experiments [13] show that the copolymer systems also exist in crystal phases with both TGTG and all-trans chains, but there are no specific measurement of structure.

For the pure PVDF and P(VDF-CTFE) with low CTFE concentration, the non-polar $\alpha$ phase has the lowest energy [15]. However, the polar $\beta$ phase is stabilized by large electric field
by lowering the electric enthalpy $H(E)$,

$$H(E) = U_{DFT} - \Omega \mathbf{P} \cdot \mathbf{E},$$

(4.1)

where $U_{DFT}$ is the DFT total energy, $\Omega$ is the volume, and $\mathbf{P}$ and $\mathbf{E}$ are polarization and electric field. Under a high enough electric field, the $\beta$ phase will have lower enthalpy than the $\alpha$ phase and a phase transition will happen. The critical field for the transition is

$$E_c = \frac{(U_\alpha - U_\beta)}{\Omega P},$$

(4.2)

We assume the experimental sample is not uniform, but consists of various nano-domains. Each domain has its own comonomer concentration and thus a corresponding value of the critical field. When $E$ reaches the critical value for one particular concentration, all domains with this concentration convert from the non-polar to the polar phase. Following Ref. [15] we assume a Gaussian broadening of the concentration, which leads to a wide range of critical fields. The sample is thus able to respond to a large range of electric fields. This is the reason for the nonlinear increase of dielectric displacement and very late saturation as the electric field is increased.

Both $\alpha$ and $\gamma$ phases have primitive unit cells containing 4 CF$_2$-CH$-$2 units (two chains).
These cells are larger than the primitive cell of the $\beta$ phase. For convenience, we use the same unit cell size for all phases. To get different comonomer concentration in PVDF copolymers, the primitive cell is multiplied along the direction of carbon backbone, and one VDF unit of each chain is replaced by comonomer. We place the comonomer units at the same place in the polymer backbone, because tests show that different doping models have comparable total energies. In this approach, only a few special values of concentration can be modeled, and the physical quantities for other concentrations are obtained by interpolation.

![Figure 4.2](image)

**Figure 4.2:** Phase equilibrium and dielectric properties of P(VDF-HFP) copolymers vs. concentration, with P(VDF-CTFE) data as benchmark. (a) Energy difference between $\alpha$ and $\beta$ phases (negative value means that the $\alpha$ phase is more stable). (b) Polarization. (c) Critical field of phase transition.

Zhang’s group [12] has shown that the P(VDF-HFP) 4.5% copolymer reaches the breakdown field of more than 700 MV/m and energy density of more than 25 J/cm$^3$. This sample has very similar energy density as P(VDF-CTFE) 9% [11]. P(VDF-HFP) is thus a good material to test the reliability of our model. Based on the methodology described above, we calculate the total energy of $\alpha$ and $\beta$ phases of P(VDF-HFP) copolymers with varying concentrations. The total energy difference $\Delta U_{\alpha-\beta}$ vs. concentration is plotted in Figure 4.2(a), with previously calculated data of P(VDF-CTFE) as a benchmark. $\Delta U$ determines the relative stability of the two phases. A negative value means that the $\alpha$ phase is more stable. The HFP comonomer unit is much larger than CTFE, so it leads to much greater change in geometry, resulting in a distinct energy difference curve. At low concentrations, $\Delta U$ increases sharply to zero at about 17% percent. The same turning point is at about 30% for P(VDF-CTFE). As a consequence, $|\Delta U|$ is much smaller for P(VDF-HFP) at the same concentration (when $\Delta U < 0$). Although the polar phase is more preferred in P(VDF-HFP) from the energy diagram, the physical pictures in both systems are the same and the phase transition mechanism is available in the appropriate concentration region. Limited by the computational resources, we use 10% concentration to...
mimic 9% copolymer sample, and 4.17% for 4.5%. In our simulations, the energy differences between the phases are close for the two cells with 10% CTFE and 4.17% HFP. Figure 4.2(b) shows the polarizations of the two copolymers, and they decrease as concentration increases for both systems. The reasons are twofold: (i) the defect unit has nearly zero dipole moment and higher defect concentration leads to larger fraction of non-polar units; (ii) a larger defect unit expands the cell and therefore reduces the polarization. P(VDF-HFP) has a significantly larger unit cell volume, and consequently a smaller polarization at the same concentration. The critical field $E_c$ is calculated using the Eq. 4.2 and is plotted in Figure 4.2(c). The 4.17% HFP and 10% CTFE cells also have very similar critical fields, i.e., they will be converted to polar phase at similar electric fields.

![Figure 4.3](image)

Figure 4.3: Demonstration of two step transition pathway connecting the non-polar $\alpha$ phase and the polar $\gamma$ and $\beta$ phases. The left panel shows the conversion to the $\gamma$ phase through a rotation of one chain. The right panel shows the distortion of the backbone in converting the $\gamma$ phase to the $\beta$ phases. $\phi$ is the dihedral angle and $\theta$ is the interchain angle, see text. Red arrows indicates the direction of the dipole moment. Black arrows show the geometrical evolution.

Our groups previous studies also discovered a transition pathway directly connecting the non-polar $\alpha$ phase and the polar $\beta$ phase. The pathway is schematically shown in Figure 4.3. Half of the dihedral angles in the carbon backbone are 180 and they do not change in transition. is defined to be value of the other half of dihedral angles. The interchain angle is defined according to the angle between the dipole moments of the two chains. For example, the $\alpha$ phase has $\phi=60$, $\theta=180$. In step one, one chain in the unit cell rotates, after which we get the $\gamma$ phase with $\phi=60$, $\theta=0$. Step two distorts the carbon backbone, leading to the $\beta$ phase with $\phi=180$, $\theta=0$. The energy differences between the phases are close for the two cells with 10% CTFE and 4.17% HFP. Figure 4.2(b) shows the polarizations of the two copolymers, and they decrease as concentration increases for both systems. The reasons are twofold: (i) the defect unit has nearly zero dipole moment and higher defect concentration leads to larger fraction of non-polar units; (ii) a larger defect unit expands the cell and therefore reduces the polarization. P(VDF-HFP) has a significantly larger unit cell volume, and consequently a smaller polarization at the same concentration. The critical field $E_c$ is calculated using the Eq. 4.2 and is plotted in Figure 4.2(c). The 4.17% HFP and 10% CTFE cells also have very similar critical fields, i.e., they will be converted to polar phase at similar electric fields.

![Figure 4.3](image)

Figure 4.3: Demonstration of two step transition pathway connecting the non-polar $\alpha$ phase and the polar $\gamma$ and $\beta$ phases. The left panel shows the conversion to the $\gamma$ phase through a rotation of one chain. The right panel shows the distortion of the backbone in converting the $\gamma$ phase to the $\beta$ phases. $\phi$ is the dihedral angle and $\theta$ is the interchain angle, see text. Red arrows indicates the direction of the dipole moment. Black arrows show the geometrical evolution.
\( \theta = 0 \). There are energy barriers for both steps and the barrier in the second step is dominant, see Figure 4.4. It is 100 meV/carbon in pure PVDF. However, 10\% admixture of CTFE reduces it to 70 meV/carbon. However, this transition still needs to be driven by thermal fluctuations. According to Eq. 4.1, the energies of entire path are reduced in electric field because there is a non-vanishing polarization except at the very beginning, for \( \alpha \) phase. To save computational resources, we use a rigid dipole approximation for all intermediate stages. We assume that the dipole moment of the VDF monomer is permanent, the different values of polarization along the pathway come from the orientation of VDF unit, and they can be calculated from interchain and dihedral angles. This approximation was previously tested and found to reproduce the Berry phase results [92]. The previous study shows the barrier of P(VDF-CTFE) 10\% is below 50 meV/carbon atom in the high field of 1000 MV/m [92].

![Figure 4.4: Energy along the transition pathway of P(VDF-HFP) 4.17\%, P(VDF-CTFE) 10\% as benchmark, from the \( \alpha \) phase to the \( \beta \) phase: (a) at zero field, (b) at 500 MV/m, (c) at 1000 MV/m. (d) Polarization along the path. The total energy of the \( \alpha \) phase is used as reference and is set to 0. The vertical dashed line divides the transition path into two parts. The angles are defined from \( \alpha \) to \( \gamma \) phase and from \( \gamma \) to \( \beta \) phase.](image)

The \( \alpha \) to \( \beta \) transition pathway of 4.17\% HFP is displayed in Figure 4.4, together with the benchmark results for 10\% CTFE. Panel 4(a)-(c) show the energy pathway in 0/500/1000 MV/m electric field, respectively, and panel 4(d) is the polarization along the path. The two compounds again have almost identical properties. Admixture of 4.17\% HFP also reduces the barrier to 70 meV/carbon atom without electric field, and 50 meV/carbon at very high 1000
MV/m. These results show that our model describes this system successfully.

4.3.2 P(VDF-BTFE)

As shown in the phase diagram of P(VDF-HFP) in Figure 4.2(a), only the concentration with non-polar ground state can be used in energy storage. Comparing to P(VDF-CTFE), P(VDF-HFP) actually has limitations, because of the narrow range of effective concentration. The reason to use HFP is that HFP is much larger than the VDF unit. It can expand the distance between PVDF chains and thus give more space for the chains to rotate. Following the same idea, the chlorine in CTFE can be substituted by Bromine. Bromine has similar chemical properties and a much larger volume.

Figure 4.5: Phase equilibrium and dielectric of P(VDF-BTFE) (red) and P(VDF-CTFE) (black) vs. comonomer concentration. (a) Energy difference between $\alpha$ and $\beta$ phases (negative value means that the $\alpha$ phase is more stable). (b) Polarization. (c) Critical field at phase transition.

P(VDF-BTFE) copolymers of varying concentration are studied following the same strategy, and phase equilibrium and dielectric properties are plotted in Figure 4.5 (with P(VDF-CTFE) as benchmark). In contrast to P(VDF-HFP), the energy difference curve of P(VDF-BTFE) is below P(VDF-CTFE). The flipping of relative stability of polar and non-polar phases occurs later. It indicates that we have a wider choice of comonomer concentration in P(VDF-BTFE), because copolymers whose non-polar phase stable at zero electric field have the potential to store energy through the phase transition mechanism. Having a larger bromine atom, the BTFE unit expands the volume of copolymer more than CTFE does. It thus makes the polarization slightly smaller than in P(VDF-CTFE) at the same concentration. With a larger energy difference and lower polarization, the calculated critical field is larger for P(VDF-BTFE) at the same concentration.
Figure 4.6: Energy density as a function of electric field of 10% and 25% P(VDF-BTFE) and 10% P(VDF-CTFE). The comonomer distribution is a Gaussian function with a broadening parameter \( \sigma = 8\% \), centered at values showed in the legend. When increasing the concentration from 10% to 25% of BTFE, the low-field performance surpasses the benchmark of 10% P(VDF-CTFE).

To compare the relative performance of the two copolymer systems, we directly simulate the energy assuming that the distribution of concentration of domains is in the form of a Gaussian; \( n(x) \) is the function of concentration \( x \), \( \sigma \) is a broadening parameter, and \( C \) is the normalization factor.

\[
n(x) = C \cdot \exp\left(-\frac{(x - x_0)^2}{2\sigma^2}\right)
\]  

(4.3)

As the electric field increases from 0, we assume that when it reaches the critical field of a certain domain, this domain converts to the polar phase. The gained polarization is accumulated in the total dielectric displacement \( D \). After \( D \) vs. \( E \) relation is obtained, the energy density is calculated using

\[
\xi = \int_0^{D_{\text{max}}} E(D) dD.
\]

(4.4)

For the physical quantities \( \Delta U_{\alpha-\beta} \), \( P \) and \( E_c \), interpolation is used to get intermediate values between the DFT-simulated data points. The same broadening parameter \( \sigma = 8\% \) as in Ref. [15] is chosen for the P(VDF-BTFE) copolymer. The energy densities of 10% and 25% P(VDF-BTFE) are plotted in Figure 4.6, with 10% P(VDF-CTFE) as the benchmark. Of both copolymers have concentrations 10%, P(VDF-BTFE) stores less energy, because the P(VDF-BTFE) requires a larger critical field of transition to the polar phase, i.e., a larger effective onset field. After saturation at about 700 MV/m, the two copolymers have comparable energy densities. Unfortunately the high field performance is not very important. It is less practical and the ferroelectric loss and leakage current in high field will become significant. To achieve
better low field performance, the majority of the material needs to be tuned to have lower $E_c$. As shown in Figure 4.5(a), 25% P(VDF-BTFE) has $E_c$ around 300 MV/m. Therefore, it effectively improves energy storage in the low field regime and surpasses 10% P(VDF-CTFE), see Figure 4.6.

Figure 4.7: Energy along the transition pathway of P(VDF-BTFE), with that of 10% P(VDF-CTFE) shown as a benchmark. (a) At zero field. (b) At 500 MV/m. (c) At 1000 MV/m. The total energy of the $\alpha$ phase is used as reference and set to 0. (d) Polarization. The vertical dashed line divides the transition path into two parts, corresponding to the $\alpha$ to $\gamma$ and $\gamma$ to $\beta$ transitions, respectively. The angles are defined in Figure 4.3.

The calculated energies and polarizations for the same geometrical transition pathway are shown for 10% and 25% P(VDF-BTFE), and for 10% P(VDF-CTFE) in Figure 4.7. Interestingly, different concentration of P(VDF-BTFE) have similar barriers in zero electric field (including 33% BTFE not shown), which are around 70 meV/carbon atom and very close to the value of 10% P(VDF-CTFE). This result indicates that these copolymers have very similar dynamical properties. With polarization, energy barrier is reduced in electric field, and the reduction is determined by the value of polarization ($\Delta E = -\Omega P \cdot E$). The enthalpies of intermediate stages with larger polarization are reduced more. Therefore there is a crossover in the sense that a polymer with greater polarization will have lower a barrier at high field. For example, 10% P(VDF-CTFE) has a higher energy barrier than 25% P(VDF-BTFE) in 0 electric field, and lower barrier in 1000 MV/m, see Figure 4.7. However, this crossover happens occurs beyond 500 MV/m for 10% and 25% P(VDF-BTFE), which does not conflict with
our previous suggestion, that higher defect concentration has better low field performance for P(VDF-BTFE) copolymers.

4.4 CONCLUSION

In this chapter, we investigate phase equilibria and transition pathways of two PVDF-based copolymer systems P(VDF-BTFE) and P(VDF-HFP), via first-principles simulations. We find that the same non-polar to polar phase transition mechanism exists in both copolymers. 10% P(VDF-CTFE) and 4.17% P(VDF-HFP) behave almost identically in all calculated aspects. This result agrees with experiments done with 9% P(VDF-CTFE) and 4.5% P(VDF-HFP), which shows that these two copolymers have similar energy density curves. Our results confirm that our phase transition model is sufficient to capture the essence of high energy storage mechanism in this novel PVDF-based copolymer.

For P(VDF-BTFE) copolymers, our results show that it prefers non-polar phase to a larger extent than either P(VDF-CTFE) or P(VDF-HFP). It offers more freedom to choose the concentration of the copolymer. At the same concentration, it also has a larger critical field. We show that by tuning the concentration to 25%, the energy storage of 25% P(VDF-BTFE) is better than 10% P(VDF-CTFE) in the low field regime.
Chapter 5

Multi-Scale Simulation of Aromatic Polyurea and Polyamide for Capacitive Energy Storage

Materials for capacitive energy storage with high energy density and low loss are desired in many fields. We investigate several polymers with urea and amide functional groups through multi-scale simulations, using density functional theory and classical molecular dynamics. For aromatic polyurea (APU) and para-aramid (PA), we find several nearly energetically-degenerate ordered structures, while meta-aromatic polyurea (mAPU) tends to be rotationally disordered along the polymer chains. Simulated annealing of APU and PA structures result in the formation of hydrogen-bonded sheets, highlighting the importance of dipole-dipole interactions. In contrast, hydrogen bonding does not play a significant role in mAPU, hence the propensity to disorder. We find that the disordered structures with misaligned chains have significantly larger dielectric constants, due to significant increase in the free volume, which leads to easier reorientation of dipolar groups in the presence of an electric field. Large segment motion is still not allowed below the glass transition temperature, which explains the experimentally observed very low loss at high field and elevated temperature. However, the degree of disorder needs to be controlled, because highly entangled structures diminish the free dipoles and decrease permittivity. Among the considered materials, mAPU is the most promising dielectric for capacitive energy storage, but the concept of increasing permittivity while maintaining low loss through disorder-induced free volume increase is generally applicable and provides a new pathway for the design of high-performance dielectrics for capacitive energy storage.
5.1 INTRODUCTION

In the quest for quickly storing and releasing electrical energy, capacitors stand apart both by releasing energy 300-2000 times faster [9] than batteries and by being able to undergo $\sim 10^6$ charge-discharge cycles, in contrast to $\sim 10^3$ for batteries. However, the maximum density of energy stored in capacitors is much lower than that of batteries, hence the quest for better dielectric materials with much higher effective dielectric constant. Among candidate dielectrics, polymers are particularly attractive because of their high breakdown strength, gentle failure, i.e., remaining insulators even at breakdown, easy processability and light weight. However, the state-of-the-art commercial polymer for energy storage, biaxially oriented polypropylene (BOPP) has a dielectric constant of only 2.2 [10]. With the low permittivity, the energy density is only moderate at 4 J/cm$^3$. Although the loss in BOPP is very low (0.02%) at moderate electric fields [93], the conduction loss increases significantly at high field [94], and operating temperatures above 85 °C reduce the breakdown strength [95].

Both experimental and computational efforts have been devoted to finding new polymers with enhanced properties. One route is the ferroelectric copolymer/terpolymer system based on polyvinylidene fluoride (PVDF) [11, 15, 12, 92], which have dielectric constants of 10-50. In particular, polymers of VDF and defect co-polymers chlorotrifluoroethylene (CTFE) or hexafluoropropylene (HFP) have energy densities greater than 18 J/cm$^3$ [11, 12], far more than PVDF alone. Previous work in our group uncovered the reason for this enhancement: a reversible, non-polar to polar phase transition occurs as high electric field is applied and then released [15]. In PVDF with low copolymer concentration (<20%), the non-polar phase has the lowest energy, but the polar phase is preferred in high electric field. The electric displacement D increases non-linearly during the non-polar to polar phase transition, which leads to the ultra-high energy density. A geometrical transition pathway with low energy barrier that makes the transition thermally accessible was identified [92]. The role of the copolymers is both to lower the activation energies and to nanostructure the polymer into domains, enabling a gradual and smooth transformation. Other copolymers, such as tetrafluoroethylene (TeFE) [13], trifluoroethylene(TrFE) [14] and their combinations have been tested experimentally to maximize the dielectric performance. However, the PVDF-based systems are not suitable for working temperatures higher than 150 °C, and they exhibit unacceptably high losses due to remanent polarization. Recently, an alternative route to high performance dielectric polymers was discovered [96, 97, 98]: the aromatic polyurea/polythiourea family of polymers have permittivities of 4.2-5.6 in broad temperature and frequency ranges, and they have significantly lower losses at high field than BOPP. Polyureas have already been widely used in industry, in applications focusing on their great elasticity and strength. Moreover, aromatic polyureas have been reported to have sizable pyroelectric, piezoelectric and nonlinear optical properties.
more than a decade ago [99, 100, 101, 102, 103], suggesting their potential as capacitive dielectrics. All polymers in this family have functional groups with large dipole moments, i.e., urea, thiourea and amide, but they do not form a ferroelectric phase as PVDF-based materials do. This aspect eliminates a large potential factor for loss. The polyureas act thus as linear dielectric materials, in which the relation between the energy density $U$ and the applied electric field $E$ is simply $U = \frac{1}{2} \varepsilon_0 \varepsilon_r E^2$, where $\varepsilon_0$ is the vacuum permittivity, and $\varepsilon_r$ is the relative permittivity. Therefore, the relative permittivity $\varepsilon_r$ is the key to high energy density.

![Aromatic Polyurea (APU)](image1)

![meta Aromatic Polyurea (mAPU)](image2)

![para-Aramid (PA)](image3)

Figure 5.1: Schemes of polymers investigated here: aromatic polyurea, meta-aromatic polyurea, and para-aramid.

In this work, we study three members in the aromatic polyurea family, aromatic polyurea (APU) [97], meta-aromatic polyurea (mAPU) [98] and para-aramid (PA). Their chemical formulas are shown in Figure 5.1. We use multi-scale simulations, combining results from both density functional theory (DFT) and classical molecular dynamics (MD) to search for the relation between microscopic structures and the dielectric properties. Significantly, we find larger
dielectric constants in structures that either are disordered with partially misaligned chains or blended into nano domains. However, substantial entanglement has a negative effect on permittivity, due to a reduced number of large effective dipole groups. This indicates that the degree of disorder needs to be controlled. We attribute the enhancement of the dielectric response to disorder-induced increase in the specific volume, compared to ordered crystal-like structures. The larger free volume leads to easier re-orientation of the dipolar functional groups in response to an external field, and therefore to a larger permittivity. Our findings demonstrate a novel way to enhance the permittivities of linear dielectrics without introducing high loss.

The rest of this chapter is organized as follows: Section 5.2 describes the theoretical background and computational details, Section 5.3 presents the results and discussion, while Section 5.4 contains summary and conclusions.

5.2 Theory and computational details

5.2.1 Theoretical background

In this work we focus on calculation of $\varepsilon_r$, so we omit the subscript $r$ in the following. In general, permittivity is a complex and frequency-dependent quantity

$$\varepsilon(\omega) = \varepsilon_1(\omega) - i\varepsilon_2(\omega), \quad (5.1)$$

where $\varepsilon_1$ and $\varepsilon_2$ are real and $\varepsilon_2$ is the dielectric loss. In anisotropic materials, permittivity is a complex tensor that depends on the orientations of the field and the sample. The elements of the static permittivity tensor $\varepsilon_{\alpha\beta}(0)$ have both electronic and ionic contributions, which can be expressed as [104, 105, 106, 107, 108]

$$\varepsilon_{\alpha\beta}(0) - \varepsilon_{\alpha\beta}(\infty) = \frac{4\pi}{\Omega k_B T} M_{\alpha\beta}, \quad (5.2)$$

where $\alpha$ and $\beta$ stand for the three Cartesian directions, $\varepsilon_{\alpha\beta}(\infty)$ is the electronic dielectric constant, $\Omega$ is the volume of simulation supercell, $k_B$ is Boltzman constant, and $T$ is temperature. $M_{\alpha\beta}$ is the covariance of two dipole moment components,

$$M_{\alpha\beta} = \langle M_\alpha M_\beta \rangle - \langle M_\alpha \rangle \langle M_\beta \rangle. \quad (5.3)$$

In MD simulation with charged atoms, $M_\alpha = \sum_i q_i r_{i\alpha}$ is the dipole moment in $\alpha$-direction, $q_i$ is the charge and $r_{i\alpha}$ is the $\alpha$ coordinate of atom $i$. The summation is over all atoms in the simulation cell. The dipole moment $\mathbf{M}$ can be obtained from MD simulation in the canonical ensemble. The frequency dependent permittivity $\varepsilon_{\alpha\beta}(\omega)$ can then be extracted by Fourier-
transforming the cross-covariance of time-dependent dipole moments

\[ \varepsilon_{\alpha\beta}(\omega) = \varepsilon_{\alpha\beta}^0 - \frac{4\pi}{\Omega k_B T} i\omega \int_0^\infty e^{-i\omega t} \mathcal{M}_{\alpha\beta}(t), \]

(5.4)

where \( \mathcal{M}_{\alpha\beta}(t) = \langle M_\alpha(0) M_\beta(t) \rangle - \langle M_\alpha \rangle \langle M_\beta \rangle \). The imaginary part of \( \varepsilon_{\alpha\beta}(\omega) \) is the loss.

5.2.2 Computational details

The classical MD code LAMMPS [109] is used in this work, with force field REAXFF. We employ different force fields for urea-based polymers [110] and amide-based polymers [111]. The use of REAXFF is essential in our simulations, because it is able to capture the variation of atomic charges and thus results in a more realistic dielectric response, and charge variation affects the total dipole moment. Simulated annealing is used to obtain microscopic structures with the following schedule: 600 K equilibration of 1 ns in the \( NPT \) ensemble, cooling to 300 K at the rate of 25 K/100 ps, and equilibration time of 1 ns at 300 K in the \( NPT \) ensemble. Nosé-Hoover thermostat [112, 113] is used for temperature and pressure control with the target pressure set to 0. The time step is fixed at 0.5 fs throughout the MD simulation. Our simulation cell contains 8 independent polymer chains and each chain has 8 monomers. The chains extend periodically through the system. For different polymers, this simulation cell has 896 to 1024 atoms in total. In the final run of 1 ns at 300K, the dipole moment \( \mathbf{M} \) is sampled every 10 fs in the \( NVT \) ensemble.

In the DFT part of our simulation, the plane wave code Quantum Espresso [66] is employed. We choose ultrasoft [67] pseudopotentials with exchange-correlation functional PBE+D [68, 89]. Energy cutoffs of 35 and 420 Rydbergs are used for electron wave functions and electron charge density, respectively. To save the computational time in the DFT part, a smaller simulation cell with 2 infinite chains with 4 monomers each is used. After optimization, all force components are smaller than 0.01 eV/Å³, and the cell parameters are relaxed until all stress components are smaller than 0.5 KBar. The electronic permittivity tensor for the lowest energy structure is obtained from density functional perturbation theory (DFPT) [46].

5.2.3 Effects of cell size and interatomic potential

Based on the methodology described above, the ionic permittivity is calculated in two mAPU simulation cells, containing 8 and 64 monomers, respectively. Figure 5.2a shows the convergence of Eq. 5.2 vs. simulation time in the two cells. Figure 5.2b shows the thermal loss in the two cells at very low frequencies. The thermal loss at very low frequencies should be close to 0, because atomic motions have much higher frequencies. While the use of the 8-monomer cell results in high loss, the low frequency loss in the 64-monomer cell is very small. The
reason is that the geometry is artificially constrained in the small cell. Figure 5.3 compares
the atomic configurations in the two cells. The 64-monomer cell has a more realistic geometry.
The neighboring urea units are close to each other because the strong dipole-dipole interaction
lowers the total energy. On the other hand, the phenylene groups do not favor being in close
proximity to each other. Therefore, each phenylene group is in the middle of two phenylene
groups of the next chain. However, such configuration is not accessible in the small 8-monomer
cell. Because there are only two independent chains, chains 1 and 3 have to be identical. Due
to the more favorable packing, the 64-monomer unit cell has total energy 5.6 meV/atom lower
than the 8-monomer cell. Moreover, the average ionic permittivity of 64-monomer unit cell
is 0.8 higher than that of the small cell. These results show that a realistic geometry is very
important for calculating ionic dielectric properties.

Turning to electronic permittivities, the 8-monomer cell has $\varepsilon_{xx}(\infty)=3.09$, $\varepsilon_{yy}(\infty)=2.63$,
$\varepsilon_{zz}(\infty)=4.36$, and $\varepsilon_{\text{avg}}(\infty)=3.36$. The 64-monomer cell has $\varepsilon_{xx}(\infty)=2.66$, $\varepsilon_{yy}(\infty)=3.11$, $\varepsilon_{zz}(\infty)$
=4.45, and $\varepsilon_{\text{avg}}(\infty)=3.41$. The difference is smaller than 0.1. It indicates that the electronic
permittivity is not sensitive to the packing of polymer chains. Therefore, we use the small unit
cell to calculate electronic permittivities for the systems considered here.

![Figure 5.2: (a) The convergence of ionic permittivity, Eq. 5.2, vs. simulation time of 8-monomer
and 64-monomer mAPU cells. (b) The low frequency thermal loss in 8-monomer and 64-
monomer mAPU cells. A damping function $f(t) = \exp(-0.005t)$ is applied to the cros covariance
$M_{\alpha\beta}(t)$ in Eq. 5.4 to avoid finite time artifacts, such as negative loss.]

According to Eq. 5.2, dipole moment variation is the source of ionic permittivity. Therefore,
capturing the variation of atomic charge is essential in simulations. To demonstrate the effect of
varying charge, we performed tests in the ordered structures of APU and mAPU. The averaged
charges $\langle q_i \rangle$ of each atom are calculated in the $NVT$ ensemble during the sampling period. We
then use the average values $\langle q_i \rangle$ instead of $q_i(t)$ to calculate the dipole moment. The results are shown in Table 5.1. The ionic permittivity calculated using the fixed charges is one order of magnitude smaller than the one calculated with the varying charges. This is the reason we choose REAXFF, although it is much more expensive than a fixed-charge force field.

Figure 5.3: Local arrangement of dipole pairs and phenylene groups in 8-monomer and 64-monomer unit cells. The blue line indicates unit cell boundaries. (a) The top view of the 64-monomer unit cell. (b) The top view of the 8-monomer unit cell. (c) Zoomed-in partial view of the 64-monomer unit cell. The urea units form antiparallel pairs, while the phenylene groups misalign along the chains. (d) Zoomed-in partial view of the 8-monomer unit cell. The urea units form antiparallel pairs, but the phenylene groups are aligned because chains 1 and 3 are identical.

5.3 Results and Discussion

To search for possible ordered structures, four initial guesses of geometries are created, as displayed in Figure 5.4. Since all the polymers have dipolar functional groups, the dipole moments in chains can be arranged parallel or antiparallel. The chains can also be shifted along the $z$-axis to align two neighboring urea units or to alternate them. The four starting geometries are arranged with: a) parallel chains and aligned polar units; b) antiparallel chains and aligned polar units; c) parallel chains and alternating polar units; and d) antiparallel chains and alternating polar units.

After simulated annealing, several ordered crystal-like structures are found for these poly-
Figure 5.4: Starting geometries of ordered mAPU simulation cells. Color code: white - hydrogen, green - carbon, blue - nitrogen, red - oxygen. (a) Parallel-aligned dipoles. (b) Antiparallel-aligned dipoles. (c) Parallel-shifted dipoles. (d) Antiparallel shifted dipoles.

mers. We obtain four different ordered structures for APU, shown in Figure 5.5(a)-(d). The energy difference between the four structures is $\sim 20$ meV/atom in REAXFF and only $\sim 4$ meV/atom at the DFT level. The lowest energy structure has urea units with the anti-parallel arrangement. Interestingly, only one of the four starting mAPU geometries converges to an ordered crystal-like structure, which is shown in Figure 5.5(e). The other three converge to disordered structures, in which the chains are misaligned in the xy-plane, as shown in Figure 5.5(f)-(h). The disordered structures still have infinite polymer chains along the z-axis. There is no entanglement between the chains and the structures are still highly anisotropic. The three misaligned structures have total energies $\sim 20$ meV/atom higher than the ordered structure in REAXFF, similar to the energy variation between ordered APU structures. The four starting geometries of PA converge to two different ordered structures. The energy difference is $\sim 6$ meV/atom in REAXFF and $<1$ meV/atom at the DFT level. Uniquely among the polymers studied in this work, PA has dipolar amide linkers pointing in opposite directions in the same chain. Therefore, regardless of inter-chain arrangements, PA has an antiparallel structure and zero spontaneous polarization. We thus find that the lowest energy structures of APU, mAPU and PA all have zero spontaneous polarization, in agreement with experiments.

Table 5.1: Ionic permittivity of APU and mAPU calculated with varying and fixed charges. See text.

<table>
<thead>
<tr>
<th></th>
<th>$\varepsilon_{\text{avg}}(\text{ionic})$ in ordered structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>mAPU</td>
<td>APU</td>
</tr>
<tr>
<td>Varying charge</td>
<td>2.48</td>
</tr>
<tr>
<td>Fixed charge</td>
<td>0.35</td>
</tr>
</tbody>
</table>

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Many of the APU and PA ordered structures arrange into sheets. The dipolar functional groups form hydrogen bonds linking neighboring chains, and the linked chains form hydrogen-bonded sheets (H-sheets). H-sheets of APU and PA are shown in Figure 5.6. However, the only mAPU ordered structure does not have such nanostructure. Instead, the ureas form antiparallel dipole pairs as shown in Figure 5.3. Therefore, the interactions between nearby dipoles in mAPU are weaker than those in APU and PA. The tendency of mAPU to be disordered is facilitated by weaker interactions between the dipole units.

Figure 5.5: Front view of APU, (a)-(d), and mAPU, (e)-(h), supercells. The polymer chains are along the z axis. Colors represent different polymer chains. (a)-(e): ordered crystal-like structures, where polymer chains occupy sites on a lattice. (f)-(h): disordered structures with misaligned chains.

Figure 5.6: The hydrogen-bonded sheets in ordered structures of: (a) PA and (b) APU. Dashed lines indicate hydrogen bonds between dipolar groups.
The ionic and electronic contributions to the dielectric constants of the ordered structures, calculated according to the methodology described in Section 5.2, are listed in Table 5.2. For the polymers that have more than one ordered structure, the lowest energy one is selected. As mentioned in Section 5.2, the spherically averaged electronic permittivities are similar for all the studied structures of each polymer. It shows that the electronic permittivity does not depend on the packing and arrangement of individual chains. However, the ionic contributions strongly depend on atomic geometries. Moreover, we find that the misaligned disordered structures of mAPU have significantly larger ionic permittivities than the ordered one. The average ionic contribution and total dielectric constant of disordered mAPU structures are listed in Table 5.3. The reasons for enhancement are explained in Ref. [114]: The three misaligned structures have specific volumes ~12% larger than the ordered structure. In particular, dipole reorientation is facilitated by the larger free volume, enhancing permittivity. Suppression of periodicity also allows for lower frequency optical phonons, which enlarge the dielectric constant. However, the polymer chains are still closely packed and large segment motion, which would lead to high loss, is not feasible.

To confirm that the enhancement is induced by disorder, we study similar effects in APU and PA. For these two polymers, a disordered structure cannot be obtained from annealing. Therefore, we artificially create a mixture of the four starting geometries shown in Figure 5.4. To test the reliability of this procedure, we also use it to create a mixed structure of mAPU. The same simulated annealing procedure is applied to the mixtures before calculating the ionic permittivities.

The ionic and total permittivities of the blended structures are shown in Table 5.3. The test for the blended mAPU structure suggests that this approach is reasonable, because it leads to the same total energy and similar ionic permittivity as for the annealed single structures. A similar enhancement of ionic permittivities for the blended structures is also found in APU and PA, cf. Tables 5.2 and 5.3. These results unequivocally show that the enhancement in ionic permittivity is due to disorder, either thermally induced or through the formation of

| Table 5.2: Calculated electronic, ionic and total permittivities of APU, mAPU and PA. |
|-----------------------------------|---------|---------|---------|
|                                  | APU     | mAPU    | PA      |
| $\varepsilon_{xx}(\infty)$; $\varepsilon_{yy}(\infty)$; $\varepsilon_{zz}(\infty)$ | 2.93; 3.05; 4.10 | 3.09; 2.63; 4.36 | 2.49; 3.42; 5.49 |
| $\varepsilon_{avg}(\infty)$  | 3.36    | 3.36    | 3.8     |
| $\varepsilon_{avg}(ionic)$  | 1.96    | 2.48    | 1.12    |
| $\varepsilon_{avg}(0)$       | 5.32    | 5.84    | 4.92    |
| Exp.                           | $\sim$4.2 (Ref. [97]) | $\sim$5.6 (Ref. [98]) | |

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Table 5.3: Calculated electronic, ionic and total permittivities of APU, mAPU and PA.

<table>
<thead>
<tr>
<th></th>
<th>mAPU(annealed)</th>
<th>mAPU(mixed)</th>
<th>APU(mixed)</th>
<th>PA(mixed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_{avg}(ionic)$</td>
<td>3.86</td>
<td>4.17</td>
<td>2.9</td>
<td>4.1</td>
</tr>
<tr>
<td>$\varepsilon_{avg}(0)$</td>
<td>7.22</td>
<td>7.53</td>
<td>6.26</td>
<td>7.9</td>
</tr>
<tr>
<td>$\Delta E_{total}$ [meV/atom]</td>
<td>+20</td>
<td>+20</td>
<td>+8</td>
<td>+12</td>
</tr>
</tbody>
</table>

nano domains. This enhancement suggests a new way to increase the dielectric constant while avoiding high loss due to large segment motion.

The larger ionic permittivity in disordered structures motivated us to study a highly entangled model, which has an even larger degree of disorder. A simulation cell is prepared where a random coil consisting of a finite 100-monomer mAPU chain and its replicas fill the entire space. The same simulated annealing procedure is applied. After annealing, the highly entangled disordered structure has a similar specific volume as the misaligned disordered structures, but it is essentially isotropic. The annealed unit cell with a fully unwrapped chain is shown in Figure 5.7. However, the ionic permittivity of the highly entangled structure is just 2.2, compared to the 3.86 average of the misaligned structures.

In the misaligned structures, all polymer chains are still essentially straight and uniaxial. The urea units are all in the same configuration shown in Figure 5.8(a), which has the maximum dipole moment because the dipoles of the C=O bond and the two N-H bonds point in the same direction. However, the polymer chain in the highly entangled structure has many turning points. At the turning points, reorientation of bonds reduces the dipole moments of the urea units. Figure 5.8(b)-(d) show three urea configurations with reduced dipole moment. The dielectric responses of these dipole units are thus less effective. We conclude that a larger free volume and a disordered geometry are needed to enhance the ionic permittivity. At the same time, entanglement of the chains should be avoided to maintain the maximum number of effective dipolar units.

Comparing the results for the ordered (Table 5.2), misaligned (Table 5.3), and entangled structures to experimental values also listed in Table 5.2, we note that the theoretical values do not fully reproduce the experimental ones. There are several potential sources of errors. The electronic permittivities, calculated from first principles by DFT, are probably quite accurate. The ionic permittivities, calculated using the variable-charge REAXFF force field, are likely to be less precise. The variable-charge aspect, as shown in Table 5.1, is important, because the ionic permittivities calculated with the fixed-charge potential are unphysically small. However, the largest source of discrepancy between the theoretical and experimental results is likely due to differences in structures. The theoretical unit cells contain up to $\sim 1000$ atoms and are...
annealed for $\sim 1$ ns. The experimental polymer chains contain thousands of atoms each and the film deposition times are obviously far longer. Furthermore, the experimental structures may consist of different nano- and microdomains: ordered, misaligned, and entangled. Nevertheless, the simulations clearly reproduce the experimental trends in permittivity and the well-known tendency of para-aramid to form hydrogen-bonded sheets. The disorder-induced increase in permittivity, discovered through simulations, has also been confirmed experimentally [114].

Figure 5.7: Highly entangled structure of mAPU after simulated annealing. The blue box indicates the unit cell boundaries.

5.4 Summary and Conclusions

We have investigated the dielectric properties of different microscopic geometries of three urea/amide based aromatic polymers using multi-scale simulations: aromatic polyurea (APU), meta-aromatic polyurea (mAPU), and para-aramid (PA). In all three cases, the average elec-
tronic permittivity is largely independent of the detailed atomic arrangement of the chains. However, ionic permittivity is closely related to the microscopic geometry. A realistic geometry is thus very important for calculating the dielectric properties.

The ionic part of the dielectric constant has been calculated using molecular dynamics with the interatomic force-field potential REAXFF. In order to obtain reliable results for these highly dipolar polymers, it is essential to use variable-charge potentials.

Several starting geometries have been used to form polymer models to be optimized by simulated annealing. For APU and PA, simulated annealing resulted in various energetically-close ordered structures. Their calculated dielectric constants agree well with experimental data. For mAPU, we uncovered a strong propensity for disordered structures with misaligned chains, due to weaker dipole-dipole interaction. The misaligned structures have significantly higher ionic permittivities than an ordered mAPU structure. The main reason for the enhancement is the larger free volume introduced by the disorder, which enables greater reorientation of dipolar groups as the electric field is applied. Moreover, disorder allows for lower frequency phonons, which also increases the ionic permittivity. Our studies of blended APU and PA structures consisting of different nano-domains further confirm that the enhancement is due to disorder. One should stress that the above mechanism of enhancing the ionic permittivity by increasing the free volume does not lead to large segment motion. Therefore, it does not introduce high loss. However, we also find that in highly entangled mAPU structures, which have much greater disorder, the ionic permittivity is somewhat smaller than that of the ordered structure, although their specific volumes are similar to the misaligned structures. The lack of enhancement can be explained by the fact that entanglement leads to many turning points along the chains, and the urea units at the turning points have configurations with reduced dipole moments. These are less effective in responding to the electric field, hence a smaller dielectric constant. Our results thus suggests that entanglement of polymer chains should be reduced to a minimum, while still
introducing rotational disorder along the chains.

Our findings suggest a new path to optimization of polymer dielectrics that could lead to much enhanced dielectric materials. Among the three polymers that we have studied, mAPU is the best candidate for energy storage due to its large dipole density and easy formation of the disordered structure.
REFERENCES


