ABSTRACT

KIM, BOHYUNG. Molecular Engineered Sensitizers Containing Heterocyclic Spacers in a D-π-A System and their Use in DSSCs. (Under the direction of Dr. Harold S. Freeman and Dr. Xiangwu Zhang.)

Dye sensitized solar cells (DSSCs) are of great interest because their construction involves low cost components and they are relatively simple, affording them the potential to compete with fossil fuel-based electrical generation, a non-renewable process. While a variety of dyes have been considered for DSSCs, the performance of DSSCs based on metal-free organic dyes has not exceeded that of solar cells based on Ru-complexed dyes. However, the former types remain of interest as sensitizers for DSSCs due to advantages that include a high absorption coefficient resulting from intramolecular π-π* transitions, simple synthesis, color tuning, structural modification for desired physical and photochemical properties, and their economy.

In the present study, molecular engineering aimed at unveiling structure-performance relationship in DSSCs was performed, where spacer and donor in a D-π-A system were methodologically modified. As a starting point, modeling methods involving Gaussian 03 were used to identify: 1) thermodynamically favorable electron injection into the conduction band edge of TiO₂ and 2) electronic energies and densities at homo and lumo levels. These studies led to 10 novel donor-acceptor systems connected by heterocyclic linkers, in which diphenylamine and carbazole units were used as a donor groups in D-π-A systems.

Results from modeled vertical electronic transitions and electronic levels were supported by experimental absorption maxima (~ 400 – 520 nm) and reduction potentials (< -0.5 V vs NHE). Photovoltaic performances of DSSCs based on two groups of novel dye sensitizers were evaluated under standard solar illumination (AM 1.5G) and analyzed in view of spectral properties and kinetics. The best performance was achieved with dye D1 having a thiophene spacer and diphenylamine donor, which gave an efficiency of 3.5 % (J_sc = 8.19 mA·cm⁻², V_oc = 0.618 V, ff = 0.697). On the other hand, dyes D3 and D8 having an N-methyl
pyrrole spacer gave the longest lifetime of electrons generated in TiO₂ and voltage parameters which corresponded to that of N719 (0.74 mV). **Series 2** gave lower dye loads on the TiO₂ surface in DSSCs, which could not compensate for the low current densities despite its better solar spectral coverage, resulting in lower efficiency compared to Series 1.

As a result of studies on the effect of additives on photovoltaic performance of DSSCs, the addition of DCA enhanced photovoltaic performance by increasing current densities, while TBP gave a \( V_{oc} \) gain at the expense of decreased current density, consequently producing low efficiency.
Molecular Engineered Sensitizers Containing Heterocyclic Spacers
in a D-π-A System and their Use in DSSCs

by
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DEDICATION

This dissertation is dedicated to my parents and my beloved sister and brother, for steady encouragement and moral support during my study in the USA.

It is especially dedicated to my mother.
BIOGRAPHY

Bohyung Kim was born on the 25th of October 1977 in Korea. She received two master's degrees from the Seoul National University, Seoul, Korea, the first in Clothing and Textiles and the second in Material Science and Engineering. She also worked as a research fellow at the OLED (Organic Light Emitting Diodes) Center in Seoul, Korea. As a further step towards the doctorate degree, she entered the Fiber and Polymer Science program at North Carolina State University in August 2007.
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LIST of ABBREVIATIONS

AM: air mass
CCA: charge control agent
CDCA: chenodeoxycholic acid
COSY: correlation spectroscopy
CTL: charge transporting layer
CTM: charge transporting material
CRT: cathode ray tube
DCA: deoxycholic acid
DSSC: dye sensitized solar cell
E_{cb}: conduction band edge of TiO_{2}
EIS: electrochemical impedance spectroscopy
ETM: electron transporting material
FF: fill factor
HMBC: heteronuclear multiple-bond correlation spectroscopy
HSQC: heteronuclear single-quantum correlation spectroscopy
HTM: hole transporting material
IPCE: incident monochromatic photon to current conversion efficiency
J_{sc}: short circuit current
PDP: plasma display panel
PDT: photodynamic therapy
RGB: red green blue
SMOLED: small molecule organic light emitting diode
TBP: 4-tert-butylpyridine
THF: tetrahydrofuran
V_{oc}: open circuit voltage
Chapter 1. Colors induced by physico-optical phenomena

1.1. Nature of light

Light can be considered as photons which have the characteristics of not only particles but also waves. Based on the wave-particle duality of light, the energy of a photon (photoelectron) is given by:

\[ E = h\nu = \frac{hc}{\lambda} \]

where \( \nu \) is the frequency of radiation, \( h \) is Planck’s constant, \( c \) is the velocity of light, and \( \lambda \) is wavelength of light. Also, light can be treated as an electromagnetic wave, that is a wave of wavelength \( \lambda \) with an electrical and magnetic field, for some aspects of the way in which light behaves. Fig. 1.1 represents a part of a light wave traveling along \( X \) with a velocity \( v \).

![Fig. 1.1. Illustration of light travelling along x–axis.](image)
This wave is described by following equation:

\[ y = a_0 \sin \left( \frac{2\pi}{\lambda}(x+vt) \right) \]

Here, \( y \) is the magnitude of electric field vector at position \( x \) and time \( t \) and \( a_0 \) is the amplitude of light. In terms of the frequency of the vibration of wave, this equation is also represented by:

\[ y = a_0 \sin \left( \frac{2\pi}{\lambda}(x+\lambda vt) \right) \]

Further simplification can be achieved using the wave number (\( k \), units of \( m^{-1} \)) and angular frequency (\( \omega \), units of \( s^{-1} \)). With these substitutions, the wave equation is given by:

\[ y = a_0 \sin (kx + \omega t) \]

Fig. 1.2 shows the electromagnetic spectrum. The light of the black shaded region is visually perceived, which corresponds to the light energy for color generation. In other words, perception of different wavelengths in the visible spectrum gives rise to color. On the other hand, light of shorter wavelengths (e.g. ultraviolet light) or longer wavelengths (e.g. infrared energy) can be used for laser optics or electronic devices.
1.2. Interaction of light with matter

If we consider incoming light through a transparent bulk matter, light can interact with a transparent material in several ways. Fig. 1.3 presents the possible diverse routes of the light when passing through a partly transparent material.

![Fig. 1.3. Interaction of light with a block of partly transparent material.](image)

According to the law of energy conservation, incoming light can be expressed by following summation of the each component.

\[ I_0 = I_r + I_s + I_a + I_t \]

Among divided components of incoming light, some of absorbed light can be re-emitted as heat or fluorescence. For a high quality optical material, the intensity of incident light is often expressed in a following way, since absorbed and scattered components passing through it are small.

\[ I_0 = I_r + I_t \]

Scattering, which occurs in materials such as opal glasses having scattering centers, gives a material a non-transparent appearance. On the other hand, color generation is a result of
absorption centers which are often found in dye molecules, transition metals, or small metal particles. The amount of absorption can be expressed by the Beer-Lambert law:

\[ \log \left( \frac{I}{I_0} \right) = -\varepsilon \, c \, l \]

where \( I \) is the intensity after passing through a material with travel length of \( l \), \( I_0 \) is intensity of incident light, \( \varepsilon \) is the molar absorption coefficient (extinction coefficient, units of L·mol\(^{-1}\)·cm\(^{-1}\) or mol\(^{-1}\)·cm\(^{2}\)), and \( c \) is the concentration of absorbing species in a material. Here, the product of \( \varepsilon \, c \, l \) corresponds to absorbance (sometimes optical density; \( A \)) and the ratio of \( I/I_0 \) is transmittance. Thus, the equation can be written as:

\[ \log T = -A \]

This Beer-Lambert law is widely used in spectroscopy (e.g. determination of the concentration of known materials).

1.3. Color generation from materials, atoms, or electrons

Organic molecules also interact with light in a similar manner to bulk matter, which involves optical phenomena such as selective absorption, emission, reflection, scattering, and deflection. All of these phenomena are accompanied by excitation of electrons, which is in turn responsible for color generation. Although most causes of colors are related to excitation, color can also be produced by rotations or vibrations of atoms (or molecules) caused by the relatively low energy of light.

Fig. 1.4 shows the Jablonski diagram\(^{3a}\) to help us understand the principles of color generation induced by excitation. Light absorption by ground state molecules causes transitions to excited singlet states. Transitions from ground state directly to the triplet state are strictly forbidden by selection rules. Electrons at higher energy states can dissipate energy through a non-radiative or internal conversion process. Thus they reach the lowest vibration state and the energy can be emitted in a form of heat or fluorescence in which the emitted
light has a smaller energy than the absorbed light.

Fluorescence occurs only between singlet states allowed by selection rules and corresponds to a rapid process (~ < 10\(^{-8}\) s). However, an internal conversion process is very short (~ 10\(^{-12}\) s). Although transitions between singlet and triplet are spin-forbidden by selection rules, transitions designated as intersystem crossings also occur at a slow rate (typically, 0.1 s) under certain conditions. The resulting excited state is in turn moved to the lowest vibration state by loss of energy caused by internal collisions. Again, there is no allowed transition for the fast dissipation of energy since there is no lower-lying triplet state. Therefore, phosphorescence is produced by transitions from triplet to singlet states with emissions lasting minutes or even longer. This phenomenon is relatively rare in organic compounds.

![Jablonski diagram](image)

**Fig. 1.4.** Jablonski diagram showing absorption (A), fluorescence (F), phosphorescence (P), internal conversion (IC), and intersystem crossing (ISC) processes.

If light energy corresponding to each transition routes is in the visible region of electromagnetic radiation (Fig. 1.2), color is perceived by the human eye.

The cause of colors can be classified based on the types of materials (e.g. metals,
organic materials, gases, etc.) or optical phenomena (absorption, fluorescence, phosphorescence, etc.). Table 1.1 shows the causes of colors classified by Nassau\textsuperscript{2}. Among these 15 causes of colors, some key optical phenomena will be described in this section. These important features will be connected to chapter 2, which involves the manipulation of light-induced optical phenomena for high-technology applications.

\textbf{Table 1.1.} Examples of the 15 causes of color.\textsuperscript{2}

\begin{tabular}{l}
\hline
\textbf{Vibrations and simple excitations} \\
1. Incandescence: flames, lamps, carbon arc, light \\
2. Gas excitations: vapor lamps, lightening, auroras, some lasers \\
3. Vibrations and rotations: water, ice, iodine, blue gas flames \\
\hline
\textbf{Transition involving ligand field effects} \\
4. Transition metal compounds: turquoise, many pigments, some fluorescence, lasers, and phosphors \\
5. Transition metal impurities: ruby, emerald, red iron ore, some fluorescence and lasers. \\
\hline
\textbf{Transition between molecular orbitals} \\
6. Organic compounds: most dyes, most biological colorations, some fluorescence and lasers \\
7. Charge transfer: blue sapphire, magnetite, lapis lazuli, many pigments \\
\hline
\textbf{Transitions involving energy bands} \\
8. Metals: copper, silver, gold, iron, brass, “ruby” glass \\
9. Pure semiconductors: silicon, galena, cinnabar, diamond \\
10. Doped or activated semiconductors: blue and yellow diamond, light-emitting diodes, some lasers and phosphors \\
11. Color centers: amethyst, smoky quartz, desert “amethyst” glass, some fluorescence and lasers \\
\hline
\textbf{Geometrical and physical optics} \\
12. Dispersive refraction, polarization, etc.: rainbow, halos, sun dogs, green flash of sun, “fire” in gemstones \\
13. Scattering: blue sky, red sunset, blue moon, moonstone, Raman scattering, blue eyes and some other biological colors \\
14. Interference: oil slick on water, soap bubbles, coating on camera lenses, some biological colors \\
15. Diffraction: aureole, glory, diffraction gratings, opal, some biological colors, most liquid crystals \\
\hline
\end{tabular}
1.3.1. Colors from simple light absorption

Colors of materials arising from light absorption indicate that the some of the incident rays are attenuated more than the others. A typical example of color production by absorption involves color filters. Regarding the red color filter (Fig. 1.5), it only passes the red light component of incident white light after absorbing green and blue light. As a result, the color perceived by the human eye is red.

![Diagram of light absorption](image)

**Fig. 1.5.** Red color filter (left), transmittance spectrum of a red color filter (right).

If a material absorbs visible light over a small region, the perceived color corresponds to the complementary color, which is the non-absorbed component of incident light. Table 1.2 shows the relationships between color absorbed and color perceived (complementary color).

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Color absorbed</th>
<th>Complementary color (color seen)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400-435</td>
<td>Violet</td>
<td>Greenish yellow</td>
</tr>
<tr>
<td>435-480</td>
<td>Blue</td>
<td>Yellow</td>
</tr>
<tr>
<td>480-490</td>
<td>Greenish-blue</td>
<td>Orange</td>
</tr>
<tr>
<td>490-500</td>
<td>Bluish-green</td>
<td>Red</td>
</tr>
<tr>
<td>500-560</td>
<td>Green</td>
<td>Magenta (Purple)</td>
</tr>
<tr>
<td>560-580</td>
<td>Yellowish-green</td>
<td>Violet</td>
</tr>
<tr>
<td>580-595</td>
<td>Yellow</td>
<td>Blue</td>
</tr>
<tr>
<td>595-605</td>
<td>Orange</td>
<td>Greenish-blue</td>
</tr>
<tr>
<td>605-700</td>
<td>Red</td>
<td>Cyan (Bluish-green)</td>
</tr>
</tbody>
</table>
There are two color mixing systems which are based on either additive primary colors or subtractive primary colors. Additive color mixing occurs when two or more differently colored light components combine and almost a full range of colors can be produced by mixing only three primary (R, G, and B) colors. Examples of colors when two or more additive primary colors mixed in equal proportions are:

- Red + Green = Yellow
- Green + Blue = Cyan
- Blue + Red = Magenta
- Red + Green + Blue = White

Based on this principle, combination of yellow and blue beams gives white light since the yellow is composed of red and green components of light and the resultant combination of R, G, and B produces white light. Additive coloration is applied to a color television or display devices by combination of light beams, where the three different small dots (R, G, and B component) are switched on or off to produce a range of colors.

On the other hand, the mixing of subtractive primary colors (cyan, magenta, and yellow) can be used to produce a full range of colors of dyes or pigments for the use in color printers or photography. The combination of yellow and blue dyes give a green color unlike the result of mixing of additive colors, since the yellow dye absorbs blue and the blue dye absorbs red, resulting in the reflection of green light.

1.3.2. Colors by luminescence

There are various types of luminescence depending on the types of energy employed. Some important features of luminescence (Table 1.3) will be described in the next subsections.
Table 1.3. Various types of luminescence.²

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incandescence</td>
<td>Thermally produced blackbody or near-blackbody radiation</td>
</tr>
<tr>
<td>Luminescence</td>
<td>All non-thermal light production</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>Rapid luminescence</td>
</tr>
<tr>
<td>Phosphorescence</td>
<td>Persistent fluorescence, specifically from a triplet state</td>
</tr>
<tr>
<td>Photoluminescence</td>
<td>Fluorescence induced by visible light or UV</td>
</tr>
<tr>
<td>Resonance radiation</td>
<td>Immediate re-irradiation of same wavelength</td>
</tr>
<tr>
<td>Cathodoluminescence</td>
<td>Fluorescence induced by cathode rays</td>
</tr>
<tr>
<td>Radioluminescence</td>
<td>Fluorescence induced by energetic radiation or particles</td>
</tr>
<tr>
<td>Thermoluminescence</td>
<td>Luminescence produced by raising the temperature</td>
</tr>
<tr>
<td>Candoluminescence</td>
<td>Non-blackbody radiation from a flame</td>
</tr>
<tr>
<td>Electroluminescence</td>
<td>Luminescence induced by an electric field or current</td>
</tr>
<tr>
<td>Galvanoluminescence</td>
<td>Luminescence produced by mechanical disturbance</td>
</tr>
<tr>
<td>Triboluminescence</td>
<td>Luminescence produced by mechanical disturbance</td>
</tr>
<tr>
<td>Sonoluminescence</td>
<td>Luminescence from sound waves passing through a liquid</td>
</tr>
<tr>
<td>Crystalloluminescence</td>
<td>Luminescence produced during crystallization</td>
</tr>
<tr>
<td>Lyoluminescence</td>
<td>Luminescence from dissolving a substance</td>
</tr>
<tr>
<td>Chemiluminescence</td>
<td>Luminescence derived from chemical energy</td>
</tr>
<tr>
<td>Bioluminescence</td>
<td>Chemiluminescence produced by a biological mechanism</td>
</tr>
<tr>
<td>Lasing</td>
<td>Any form of coherent luminescence</td>
</tr>
</tbody>
</table>

1.3.2.1. Thermally produced luminescence

- Incandescence

Incandescence is an emission of light by a hot body which is differentiated from the radiation of a cold body. The hot body can changes its colors depending on the temperature. Increasing temperature results in vibrations of the atoms or molecules making up the object and promotes them to higher energy levels. At the same time, atoms or molecules that already absorb energy emits energy as they fall back to lower energy states. Thus, as the temperature increases color changes from red and yellow to blue-white, which correspond to the order of increasing energy.

The emission curves (Fig. 1.6) dependent upon the temperature of the blackbody were theoretically predicted by Max Planck in 1901. The following equation was derived to
describe the energy density, $\rho(\lambda)d\lambda$, as a function of wavelength ($\lambda$) of a blackbody at temperature (T):

$$\rho(\lambda)d\lambda = \frac{2\pihc^2d\lambda}{\lambda^5\left[e^{\frac{hc}{\lambda kT}}-1\right]}$$

where $h$ is Planck’s constant ($6.626 \times 10^{-34}$Js), $c$ is the speed of light ($2.998 \times 10^8$ms$^{-1}$), $\lambda$ is a wavelength (m), $k$ is Boltzmann’s constant ($1.380 \times 10^{-23}$JK$^{-1}$), and $T$ is a temperature (K) of blackbody.

**Fig. 1.6.** Radiation curves for blackbodies at 700, 1700, 5700°C (bold line). Also shown is the curve for sunlight as perceived at the earth’s surface and the sensitivity curve of the eye.$^2$

Common examples of incandescent objects would be the sun, candle flame, tungsten lamp, or other light bulbs. The sun, which is the importance source of energy on Earth, has a solar spectrum similar to an emission curve of a blackbody at temperature 5700 °C (~ 6000 K). Considering that daylight is perceived as white by humans, the human eye should have evolved to be most sensitive to the yellow-green light which is the most abundant on Earth.
1.3.2.2. Non-thermally produced luminescence

- **Electroluminescence**

  Electroluminescence refers to the emission of light from a material by the application of, for instance, an electric current or electric field. Typical example of electroluminescence would be light production by gas discharge or light emission by means of charge injection (e.g. light emitting diode). In devices such as a neon sign, vapor discharge lamp, and plasma display panel, typically, a tube with electrodes is filled with a noble gas with additional materials like sodium or mercury. Under the application of high electrical field, electrons emitted from the cathode are accelerated across the gas and collide with gas molecules thus bringing them to higher energy states, which in turn induces the formation of ionized gases or excited atoms. Electroluminescence is a result of releasing photon of excited ions and atoms as they fall to lower energy states. In the case of vapor discharge lamps, initial discharge formed by inert gas plays a role in heating up the tube and vaporizing sodium or mercury atom. Resultant vaporized atoms at the higher energy states emit photons as just outlined. Table 1.4 shows the luminescence colors produced by the inert gas. On the other hand, electroluminescence in a light emitting diode is the result of recombination of holes and electrons in a material following charge injection from the electrode (chapter 2).

Table 1.4. The luminescence colors produced by inert gases.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium</td>
<td>Yellow</td>
</tr>
<tr>
<td>Neon</td>
<td>Pink-red</td>
</tr>
<tr>
<td>Neon + Argon</td>
<td>Red</td>
</tr>
<tr>
<td>Argon</td>
<td>Pale blue</td>
</tr>
<tr>
<td>Argon + Mercury</td>
<td>Blue</td>
</tr>
<tr>
<td>Krypton</td>
<td>Lavender</td>
</tr>
<tr>
<td>Xenon</td>
<td>Blue</td>
</tr>
</tbody>
</table>
Photoluminescence (Fluorescence)

Photoluminescence refers to the process in which ultraviolet light close to the visible region is converted into visible light. The most common example is fluorescent lamps which are widely used for interior lighting today. These types of lamps employing phosphors operate in the same way as vapor discharge lamps except additional contributions from phosphors. As shown in Fig. 1.7, electrons emitted from the cathode collide with mercury atoms. Subsequent excitation of mercury vapor results in the bulk of emission of ultraviolet light corresponding to 254 nm as well as some contributions in the visible region. Phosphor, which is coated inside the fluorescent tube, is used to convert the ultraviolet light to visible light. Although the light produced by a fluorescent lamp looks white, the light tone can be different depending on the fluorescent material employed. For example, Sb$^{3+}$ ions in the host matrix, Ca$_5$F(PO$_4$)$_3$ give a rather cooler color due to blue light emission, while Mn$^{2+}$ provides a warmer tone induced by orange-red emission (Fig. 1.8)\textsuperscript{5a}. On the other hand, elements in the lanthanoid series produce sharp emission spectra compared to broad emission bands of 3d transition metals. This phenomenon is attributed to the orbitals involved in the electron transitions producing the light.

![Fig. 1.7. Operating process of fluorescent lamps.](image-url)
Fig. 1.8. Emission spectra of fluorescent lamps\textsuperscript{5a} (right; calcium halo phosphate lamp, left; tricolor lamp).

- **Phosphorescence (Delayed fluorescence)**

  Phosphorescence is a delayed emission (or delayed fluorescence) of light from a triplet state as shown in Fig. 1.4. This re-emission of absorbed light has a low intensity since it is associated with a forbidden transition. Also, as this forbidden transition is kinetically unfavorable, phosphorescent materials have a slower decay, from milliseconds up to days. In other words, the absorbed energy can be thought of as trapped in a reservoir from which it slowly leaks. An example of phosphorescent material is glow-in-the-dark material, which emit the light over a long time, unlike the swift reactions shown in the fluorescent lamps.

1.3.2.3. Coherent luminescence

Nowadays, lasers have become ubiquitous as they are used as pointers, at check-out counters in stores, in surgery, and in optical devices. The laser is an acronym for Light Amplification by Stimulated Emission of Radiation. There are differences in the nature of light from normal light and laser beams. Normal light is described as being incoherent and unpolarized. As shown in Fig. 1.9, light from incandescent lamp is emitted in short bursts lasting $10^{-8}$ s and each short burst is in phase and linearly polarized. However, since both phase and polarization change from burst to burst in a random fashion, the produced light is a stream of unpolarized light with different energies.
Light from the laser is a coherent beam and emitted in a same direction. In 1917, two types of emission processes (Fig. 1.10) were suggested by Einstein. One is spontaneous emission in which light is emitted in a random direction as the excited atom loses energy in random fashion. The other type of emission is stimulated emission, where an atom in the excited state loses energy by interacting with a photon of exactly the same energy before spontaneous emission occurs.

In order to produce laser action (stimulated emission), an inverted population by way of optical pumping is required, from which a higher population of atoms occupies higher energy states rather than lower energy states. Fig. 1.11 shows how to generate a coherent set of laser beams. Since the first ruby laser, solid-state lasers, gas lasers, semiconductor diode laser, and dye lasers have been invented. In the case of dye lasers, laser output can be tuned over a wide range of wavelengths. Broad emission bands are the result of the characteristics of dye molecules which have vibrational and rotational energy states for each electronic energy state. A selective laser output from this broad emission can be achieved by use of a
diffraction grating. Table 1.5 shows laser output of some dye lasers.

![Fig. 1. 11. Laser action in a cavity bounded by reflecting mirrors, (black dot; metastable excited units, a; spontaneous emission, b; stimulated emission occurring at an angle to the length of the cavity, c; spontaneous emission directed along the length of the cavity, d; additional stimulated emission).]

**Table 1.5. Laser outputs of some typical laser dyes.**

<table>
<thead>
<tr>
<th>Dye</th>
<th>Structure</th>
<th>Typical solvent</th>
<th>Lasing wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxazine 9</td>
<td>1-1</td>
<td>Ethanol</td>
<td>644-709</td>
</tr>
<tr>
<td>Rhodamine B</td>
<td>1-2</td>
<td>Water-HFIP&lt;sup&gt;a&lt;/sup&gt;</td>
<td>580-655</td>
</tr>
<tr>
<td>Rhodamine 6G</td>
<td>1-3</td>
<td>Water-HFIP&lt;sup&gt;a&lt;/sup&gt;</td>
<td>450-605</td>
</tr>
<tr>
<td>Coumarin 9</td>
<td>1-4</td>
<td>Acidic ethanol</td>
<td>415-530</td>
</tr>
<tr>
<td>Sodium salicylate</td>
<td>1-5</td>
<td>Ethanol</td>
<td>395-418</td>
</tr>
</tbody>
</table>

<sup>a</sup>Hexafluoroisopropanol
Chapter 2. Applications of colorants for high-technology

This chapter describes the utilization of colorants for high technology applications, which recognizes a reduced emphasis on traditional textile applications. As shown in Fig. 2.1, dyes or pigments can be used in a variety of industries by a proper manipulation of light. An overview of some non-textile applications of colorants will be discussed in the sections below.

![Fig. 2.1. Uses of colorants in the high-technology industry.](image)

2.1. Displays

The technology of display devices have changed through past centuries. Since the advent of the cathode ray tube (CRT) in the early stage of the display industry, LCD (liquid crystal display) for laptop computers, PDP (plasma display panel), and LED (light emitting diode) have been developed. The CRT, which uses bulky and heavy evacuated glass envelopes, has been replaced by a PDP or LED (in the case of large area displays).
2.1.1. CRT and PDP

CRT and PDP utilize phosphors to produce visible colors. CRT\textsuperscript{5a} is a form of cathodoluminescence in which an electron beam generated from the cathode is accelerated by electrostatic or electromagnetic means under vacuum (Fig. 2.2). The resultant electron impacts the phosphors coated on the surface of the glass vessel excites the phosphors, resulting in emission of visible light. In the case of color television, three R, G, and B electron guns (source of electrons) are used with R, G, and B phosphors comprising a pixel as well. In order for each electron beam to excite its own R, G or B, a metal shadow mask or aperture grill is placed between the guns and phosphors. In the case of a shadow mask composed of tiny holes serving a group of RGB phosphors (typically, triangular shaped arrangement), the spacing of holes, the spacing of the phosphors, the placement of the gun are appropriately arranged for the lightening of a desired phosphor. In other words, all three electron beams pass through the same holes in the mask but the approaching angle is different for each gun. Thus, each electron gun (red gun) only illuminates the correct phosphor (red phosphor) without hitting the wrong phosphors. Additive color mixing of emitted light from RGB phosphors produces full color. Table 2.1 shows phosphors used for color TV.

![Fig. 2.2. Schematic representation of cathode ray tube.\textsuperscript{5b}](image_url)
Table 2.1. Phosphors for color TV.

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>Emission color</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS:Cu, Au⁺, Al</td>
<td>Green</td>
</tr>
<tr>
<td>ZnS: Cu</td>
<td>Green</td>
</tr>
<tr>
<td>ZnS: Ag⁺</td>
<td>Blue</td>
</tr>
<tr>
<td>Y₂O₃:Eu³⁺</td>
<td>Red</td>
</tr>
<tr>
<td>Y₂O₂S: Eu³⁺</td>
<td>Red</td>
</tr>
</tbody>
</table>

PDP employs ionized gas (plasma) to excite phosphors. Fig. 2.3 shows a schematic structure of the PDP cell. The noble gas is placed between two plates of glass comprising tiny cells which are also equipped with electrodes on the top and bottom. R, G, and B phosphors comprising one pixel are coated on the back of the cell. The voltage difference between the electrodes on the front and back side causes the gas to form plasma, thus emitting ultraviolet light. The subsequent excitation of the same phosphors as in CRT produces visible light. Although PDPs have attracted significant attention as the promising thin flat panel color display for wide screen applications, they have some operating challenges such as emission of infrared light and the orange light during the plasma discharge. Therefore, optical filters are required to compensate these operating challenges in PDPs. Among optical filters, the CCF (color compensating film) is fabricated with organic dyes having a sharp absorption around 590 nm. This imparts high picture quality to the PDPs by the selective absorption of undesirable light induced by red phosphor (593 nm) and neon gas (585 nm) of PDPs⁶⁻⁷. Fig. 2.4 shows some examples of dyes used in CCFs⁸.
2.1.2. Electroluminescence devices

As already described in chapter 1, electroluminescence (EL) is luminescence induced by an electric field or current. EL devices can be categorized as follows: 1) conventional semiconductor light emitting diodes fabricated by p-n junction of semiconductor materials, 2)
inorganic ELs based on the phosphors (typically group II-VI elements, e.g. ZnS/Mn), and 3) OLEDs (organic light emitting diodes) based on low molecular weight molecules (SMOLED) or conjugate polymers (PLED). Fig 2.5 shows the structures of three different types of EL devices. Among these EL devices, OLEDs have advantages such as easy tuning of molecular properties, low voltage operation, and economical process, compared to the conventional semiconductor ELs. Since a 1987 report involving a green EL that uses Alq₃, many studies have been conducted in an effort to replace conventional LC (liquid crystal) displays or light sources (e.g. the use of while light OLED for the backlighting in LCD). Although OLEDs can be used for high resolution applications by employing an active matrix (AMOLED), expensive processing cost has limited a production of large area display.

![Schematic structures of electroluminescence devices.](image)

(Left; semiconductor LED, middle; inorganic LED, right; low molecular based OLED).

At the heart of a low molecular weight OLED is an HTL (hole transporting layer), followed by a relatively thin EML (emissive layer), and ETL (electron transporting layer). Fig. 2.6 illustrates the energy diagram of SMOLED. By applying voltage, a current of electrons flows from the anode to cathode resulting in the formation of electrons and holes at the EML and HTL, respectively. The electrostatic forces cause these carries to diffuse and combine at the EML, inducing the emission of light (or heat) by rapid relaxation of exciton. The internal quantum efficiency of the OLED device is determined by the ratio of the emitted photons to the number of injected electrons.
Indium tin oxide is generally used as an anode due to the high work function, which promotes injection of holes in the HTL. Metals such as Al are typically employed as a cathode. In the case of HTL, aromatic amines having high hole mobility are used and this also requires molecular properties such as high lumo level, high thermal stability, formation of stable cation radicals. Fig. 2.7 illustrates the diversity of hole transporting materials. On the other hand, EML, which has electron withdrawing character, is composed of emissive metal complexes (e.g. Alq) or host materials doped with fluorescent molecules (e.g. perylene or coumarin). The advantage of host electron transporting materials doped with emitting materials is their ability to produce a wide range of colors for one host HTL materials. Fig. 2.8 and Fig. 2.9 show examples of the molecular structures of electron transporting materials and dopants used for OLEDs. Additionally, Table 2.2 shows emission colors of OLEDs, when employing an ETM made up of host material with dopant.
Fig. 2. 7. Chemical structures of hole transporting materials, (Upper; aromatic amine based HTM, middle; starburst aromatic amine based HTM, bottom; spirofuorene amine based HTM).
Fig. 2. 8. Chemical structures of electron transporting materials, (upper-left; emissive metal complex based ETM, upper-right; emissive distyrylarylene based ETM, bottom; nonemissive ETMs).

Fig. 2. 9. Molecular structures of dopants used in OLEDs.
Table 2.2. Host/dopant based RGB organic luminescent materials.

<table>
<thead>
<tr>
<th>ETM/host</th>
<th>Dopant</th>
<th>Emission color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alq₃</td>
<td>DCJTB</td>
<td>Red</td>
</tr>
<tr>
<td>Alq₃</td>
<td>MeQA</td>
<td>Green</td>
</tr>
<tr>
<td>Alq₃</td>
<td>Coumarin 6</td>
<td>Green</td>
</tr>
<tr>
<td>Beq</td>
<td>QA</td>
<td>Green</td>
</tr>
<tr>
<td>BAlq₂</td>
<td>Perylene</td>
<td>Blue</td>
</tr>
<tr>
<td>DPVBi</td>
<td>None</td>
<td>Blue</td>
</tr>
</tbody>
</table>

2.2. Optical data storage

There are several types of optical storage media, such as CD-ROM (compact disc read-only memory), WORM (write once read many), CD-RW (compact disc rewritable), DVD (digital versatile disc rewritable). Typically, dye has been utilized as a recording material for the types of write once or read only optical data storage systems while phase changeable or gyrotropic material is used as a recording medium for the CD-RW, DVD-RW, and DVD-RAM (random access memory). As shown in Fig. 2.10, the principle of the optical data storage based on the thermal mode is as follows: 1) laser light (~1 μ in diameter) in the near infrared region is focused on the optical disc composed of a thin uniform film (1 ~ 0.1 μ) of a near infrared absorber laid down on a reflecting substrate. 2) Where the laser beam hits the disc, a shallow pit or phase change is formed. The laser beam, which induces heat by converting the absorbing energy of the recording medium, is of sufficient energy to cause changes in the recording medium. 3) These changes (e.g. pits) can constitute the recorded data. 4) In order to read the recorded data, a low intensity laser is used, so that the energy of the laser beam is not enough to cause any changes in the recording medium. Detecting of the recorded disc is followed by recording the difference in reflectance between the non-recorded (unexposed) and recorded regions.
In the case of dye used as a recording medium, it should meet following criteria: 1) proper absorption of the laser radiation (absorption in the wavelength of 775 ~ 830 nm for WORM and CD-R, absorption in the wavelength of 630 ~ 650 nm for DVD-R), 2) Easy to process thin and uniform films, 3) appropriate melting point of 100 ~ 200 ºC, 4) Good durability to light, heat, oxidation, and humidity, and 5) high reflectivity of the resultant films. Phthalocyanines are commercially used dyes for CD-R or WORM, due to their good durability and spectroscopic properties. On the other hand, carbocyanines with light stabilizers can be applied to a DVD-R because of its requirement of absorptions at shorter wavelengths. Fig. 2.11 shows representative dyes used in WORM, CD-R, and DVD-R.
Recent developments in photoactive materials make them suitable for high capacity digital optical memories. In the photonic devices based on photon-mode recording, all processes including reading, writing, and erasing are controlled by light energy\textsuperscript{14} which can induce change in the physical properties of recording media such as transmittance, reflectance, polarization, or fluorescence. Compared to most erasable and rewritable media based on the heat-mode recording in current (e.g. the phase change or magneto-optic materials), photon-mode recording has the potential advantage of higher-density data storage on pico or femto scale. One of the approaches to data storage in photomode recording is to use the characteristics of interconversion between the two distinct isomeric states when stimulated by two different wavelengths of the light. Therefore, a diversity of photochromic materials\textsuperscript{15} (Fig. 2.12) such as spiropyrans, spiroxazines, diarylethenes, fulgides are candidates for switching materials. As shown in Fig. 2.13, molecular switching by light stimulus is based on ring opening and ring closure\textsuperscript{5a}. Color changes from colorless to colored (or vice versa) depending on the types of photochromic materials. As requirements of switching materials for use in optical memories, it is reported they should have 1) thermal stability and fatigue resistance to irreversible photo and thermal induced transformations between two forms (closed/opened), 2) high speed and efficiency of photochromic transformation, 3) non-destructive readout which does not induce interconversion between the two different forms, and 4) compatibility with polymer matrix. Among these factors, thermal stability and non-destructive readout are key issues to consider for long-term
information storage\textsuperscript{5a, 12a}.

Fig. 2. 12. The chemical structures of representative photochromic materials.
2.3. Reprographics

Reprography, which is the reproduction of graphics by thermal, mechanical, or electrical means, is an area of imaging science. As shown in Fig. 2.14, although there is a wide diversity of reprographic technologies\textsuperscript{12a}, more familiar and important reprographic technologies such as ink-jet printing, photocopying, and laser/LED printing will be focused in this section.
2.3.1. **Electrophotography**

Electrophotography is a non-impact electrostatic printing process which includes photocopy (xerography) and laser/LED printing. For photocopy and laser/LED printing, the printing mechanisms are similar except they use a different light source (e.g. 780 nm laser radiation in the case of laser printing). Fig. 2.15 illustrates the electrophotographic process for photocopying and laser printing. This process contains 6 steps: 1) charging of photoconductor → 2) production of latent image by expose to light → 3) development of visible image by using oppositely charged toner to that of photoconductor → 4) Transfer of the toner image to the substrate → 5) fixation → 6) cleaning to make ready for next use.
For color copying requiring a four-pass process (Fig. 2.16), RGB color filters are used as well as a photoconductor sensitive to the entire visible light region. Production of a colored image by color laser copier is achieved by the use of CCDs (charge-coupled device). Light reflected from the original image is converted to the R, G, and B components by an array of CCDs. CCDs play a role in converting light into the digitalized signal, which is then sent to the copier unit, thus making the semiconductor laser write the digitized data on the photoconductor. By three-pass writing for each R, G, and B component of the image followed by the each contact of CMY toners, full color can be produced. This laser copying process has advantages such as the use of photoconductor sensitive to laser output of 780 nm and easy electronic manipulation compared to conventional color copying. Among the key components of photocopying and laser/LED printing, photoconductor and colorants will be reviewed in the subsequent sections.
Fig. 2. 16. Process for full-color photocopying.\textsuperscript{12a}

- **Photoconductor\textsuperscript{5a, 12a, 16}**

Requirements for photoconductor materials can vary with the type of copier. In the case of color copiers, the ideal photoconductor should have panchromatic absorption, but the dyes having maximum absorption around 550 nm are typically employed. Laser and LED printers (or copier) require the photoconductor sensitive to, typically the 780 nm and 630 \textendash; 660 nm regions, respectively. Most photoconductors currently in use are based on the organic photoconductor (OPC) instead of inorganic photoconductor (e.g. selenium), due to the broad range of spectral sensitivity.

Fig. 2.17 shows the typical arrangement (double layers) of commercial OPCs. The photoconducting mechanism of OPCs is as follows: corona discharge induces the negative charge build-up on the top of CTL. Subsequent light irradiation causes the CGL to generate carriers. Negative charges on the CTL on the point of light contact are discharged by the hole hopping through the CTL, thus rendering the photoconductor latent image (Fig. 2.17). Fig. 2.18 shows representative charge generating materials (CGMs) and charge transporting materials.
Fig. 2.17. Mechanism of photoconduction in organic photoconductor, (right; latent image after irradiation, CTL; charge transporting layer, CGL; Charge- generating layer, T; charge transporting material).\textsuperscript{12a}

Fig. 2.18. The chemical structures of CGM and CTM for photocopiers, (CGM; charge generating material, CTM; charge transporting material).
• **Colorants**

Colorants are the one of the components of the toner which is composed of resin (90%), pigment (8%), and charge control agent (2%). This component can be utilized for both CCAs and the color production. The CCAs play a significant role in imparting an adequate electrostatic charge level. The correct level of triboelectric charge, which is generated by the friction between resin, CCA, and carriers, is important for the production of high quality images. The triboelectric charge on the toner can be positive or negative, depending on the resin and carrier used. The charge on the toner is determined by the photoconductor and the process discussed in section 2.3.1. Although colored CCAs can be used for the black toner, non-colored CCAs are preferred for the toner of the color copier, which are intended not to interfere with bright CMY colorants. Fig. 2.19 shows representative CCAs.

The colorants in a toner can be either dyes or pigments. However, pigments are commercially favored because of their stability to light and heat. Typical colorants used for the production of colored images are shown in Fig. 2.20.

![Fig. 2.19. Some examples of charge control agents (CCAs).](image-url)
2.3.2. Ink-jet printing

Ink-jet printing is a widely used technology in the small office or home. In ink-jet printing, the image is produced by firing a jet of ink onto a substrate. According to the method of supplying ink, ink-jet printing is divided into continuous ink-jet and drop on demand (DOD) ink-jet. Ejection of the ink from the nozzle head can be achieved by a thermal or mechanical (e.g. piezoelectric crystal) process. Fig 2.21 shows the types of ink-jet printing methods.

Fig. 2.20. Examples of colorants used in electrophotography.
In continuous ink-jet printing (Fig. 2.22), ink is ejected in the form of continuous stream of ink droplets through a fine nozzle and passes through a charging electrode where the charges are selectively imparted on the ink droplets based on the digitized image data. These selectively charged ink droplets pass by a high-voltage deflection plate where they are sent to the substrate and uncharged droplets go back to the ink reservoir by way of a gutter drain (for raster method).

DOD, which is generally the system used in home or office printers, only ejects the ink droplets on a substrate which a dot is required. In DOD ink-jet printers, the printer head can be either thermal jet (or bubble jet) or piezo. As shown in Fig. 2.23, in the thermal/bubble jet, the bubbles in the ink formed by heating cause a build-up of pressure on the nozzle, resulting in the ejection of the ink. For the piezo head, the pressure formed by applying an electric signal on the piezoelectric crystal induces the ejection of the ink onto the substrate.
Concerning ink-jet inks, there are three types: aqueous, solvent, and hot-melt. Among these inks, DOD prefers aqueous inks while solvent inks are generally adopted for the continuous ink-jet printer (e.g. used for industrial labeling). Each ink has inherent disadvantages. For example, water based aqueous inks are susceptible to microorganisms and cause corrosion especially when certain impurities are present in the ink. Solvent inks have a potential disadvantage of flammability.

In the case of colorants (dye or pigments) for the ink-jet printer, choice of colorants depends on the types of the printer, as mentioned before. Whether they are water soluble dyes or pigments, they should meet the requirements shown in Table 2.3.
Table 2.3. Required properties of ink-jet colorants.\textsuperscript{12a}

<table>
<thead>
<tr>
<th>Property</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>cyan/magenta/yellow/black</td>
</tr>
<tr>
<td>Color strength</td>
<td>high</td>
</tr>
<tr>
<td>Solubility</td>
<td>5 - 20 %</td>
</tr>
<tr>
<td>Insolubles</td>
<td>&lt; 0.5 (\mu)m</td>
</tr>
<tr>
<td>Electrolyte/metals (ppm)</td>
<td>low Cl\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}, Ca\textsuperscript{2+} levels</td>
</tr>
<tr>
<td>Fastness</td>
<td>light, water, smear</td>
</tr>
<tr>
<td>Shade</td>
<td>same on different paper; print definition</td>
</tr>
<tr>
<td>Toxicology</td>
<td>Ames negative</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>no kogation\textsuperscript{a}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The buildup of insoluble deposits on the heating element

Water soluble dyes provide a good color gamut and bright shades, and are environmentally benign compared to the solvent based inks. In an effort to increase wet fastness, a breakthrough by the ICI and Hewlett-Packard Inc\textsuperscript{17} was made. The concept is to use dyes having different solubilities according to variations in pH. Alkaline pH is used to give high dye solubility in the ink and low solubility arises under acidic conditions, thus resulting in increased substantivity on papers. Fig. 2.24 illustrates how to accomplish the formation of the wet fast dye on a paper\textsuperscript{12a}. In the case of pigments, despite their good wet/light fastness, they have a tendency to clog the inkjet nozzle due to their particle size. Therefore, pigments having a particle size less than 0.02 \(\mu\)m have been developed by using dispersants\textsuperscript{5a}. Fig. 2.25 and Fig 2.26 show examples of subtractive trichromats and black colorants for ink-jet printing.

\textbf{Fig. 2. 24.} Concept for the differential solubility of ink-jet dyes.\textsuperscript{12a}
Fig. 2. 25. Black and yellow colorants used in ink-jet inks.
Fig. 2. 26. Magenta and cyan colorants used in the ink-jet inks.
2.4. Biomedical technology

2.3.1. PDT (photodynamic therapy)

PDT is a light-assisted treatment of cancerous cells, certain skin disorders, or viral infections. In PDT, two benign components, a photo-sensitizer (typically a dye) and light source, are required\(^\text{18}\). Selective uptake of photosensitizer into the diseased tissue and controlled laser light transmission characterize the PDT process.

Unlike the behavior of typical organic molecules described in the chapter 1, photosensitizers for PDT generally have a relatively stable excited singlet state and in turn induce ISC (intersystem crossing). The excited triplet state generated by ISC induces photodynamic action with adjacent molecules. The plausible pathway of photodynamic action is shown in Fig. 2.27.

![Fig. 2.27. Two main pathways of photodynamic action by photosensitizers, \(^{1}\text{S}_0\); ground state of sensitizer, \(^{1}\text{S}^*\); excited singlet state of sensitizer, \(^{3}\text{S}^*\); excited triplet state of sensitzers, ISC; intersystem crossing).\(^{47b}\)](image)

The type 1 pathway is the direct reaction of the excited triplet state of sensitizers (\(^{3}\text{S}^*\)) with adjacent molecules (e.g. hydrogen extraction or electron transfer), resulting in the formation of a radical species. The resultant radical can produce hydroperoxides by interaction with \(^3\text{O}_2\) which initiates oxidation. The type 2 pathway involves direct energy transfer from \(^{3}\text{S}^*\) to \(^3\text{O}_2\), inducing the formation of singlet oxygen (\(^1\text{O}_2\)). Between these two pathways, the PDT
mechanism has been known to follow the type 2 process in which $^{1}\text{O}_2$ functions as a cytotoxic agent\textsuperscript{5a}.

Photosensitizers for PDT should meet the following criteria: 1) efficient $^{1}\text{O}_2$ production, 2) absorption in the therapeutic region where absorption by biological tissues is minimal (preferred above 650 nm but not above 830 nm), 3) absorption at longer wavelengths in the case of tumors requiring high depth of light penetration\textsuperscript{19}, and 4) low toxicity and minimal side effects. For efficient ISC, it is known that incorporation of a heavy atom into the chromophoric moiety increases the rate of ISC\textsuperscript{20}.

Since the development of the first photosensitizer photofrin\textsuperscript{21} (Fig. 2.28), which is a clinically used PDT agent, a considerable level of effort have been expended to develop more efficient PDT agents\textsuperscript{22}. Fig. 2.29 shows examples of PDT agents arising from those efforts.

![Figure 2.28](image-url)  
**Fig. 2.28.** Characteristics of Photofrin as a PDT agent.
Fig. 2.29. Second generation photosensitizers developed for PDT treatment.
Part II. Solar Cells

Chapter 1. General background and research plan

Environmental concerns and depletion of fossil fuels have triggered a global search for renewable energies. Among the possible alternatives to fossil fuels, solar energy has attracted significant attention as a clean and renewable option. The average solar energy reaching Earth is 1367 W/m² per second. If we consider energy losses due to absorption, refraction, and reflection, the potentially useful level reaching Earth is 800~1000 W, which corresponds to a total energy of 795,000 x 10¹² kWh per year. This energy level is 10,000 times larger than the total consumed energy (82.83 x 10¹² kWh) by the whole world. In other words, covering even 0.1% of Earth with 10% efficiency would meet the world’s energy needs.

The solar cell (photovoltaic cell) is a device for converting light energy into electric power and can be made from various types of materials, depending on the structures of the cell. Solar cells can be divided into inorganic based solar cells and organic solar cells. Inorganic solar cells, employing materials such as crystalline silicon, amorphous silicon, or other semiconductor compound, have held a dominant market share for decades. Among the semiconductor materials for solar cells, GaAs provides the highest efficiency up to ~40%. On the other hand, silicon based solar cells have dominated most of the solar cell market. They give maximum efficiencies of 28%, 20%, 12% in the case of crystalline, polycrystalline, amorphous silicon, respectively. However, the price of silicon is increasing every year, since it is also an essential component in the fabrication of semiconductor devices.

The dominance of inorganic materials in the photovoltaic field is now being challenged by the emergence of dye sensitized solar cells (DSSCs), since Grätzel and co-workers made a breakthrough. The prototype DSSCs, which are based on the Ru-poly-pyridyl-complex type sensitizers, have shown solar to electrical power conversion efficiency
of up to ~11%, making them close to amorphous silicon solar cells. Also, since DSSCs can be made at very low cost (one-fourth that of classical silicon solar cells), they have attracted considerable interest as alternatives to classical solid-state p-n junction devices. Ruthenium complexes have i) broad MLCT (metal to ligand charge transfer) absorption bands from the UV to visible region, which is advantageous for light harvesting, ii) chemically stable excited state and oxidized form for long-term use. However, key drawbacks of Ru complex based DSSCs are high cost of a limited supply of Ru and difficult dye purification which limit their practical use of DSSCs.

Recently, metal-free organic dyes such as coumarin\textsuperscript{26}, indoline\textsuperscript{27}, oligoene\textsuperscript{28}, merocyanine\textsuperscript{29}, and cyanine dyes\textsuperscript{30} have been developed as sensitizers for DSSCs, with efficiency in the range of 5 - 9%. The low efficiencies of currently available organic dyes arise from short photoelectron lifetimes, dye aggregation leading to intermolecular electron transfer, insufficient pore filling\textsuperscript{31}, narrow absorption bands, and instability during the reduction process. Although the performances of DSSCs containing metal-free organic dyes have not exceeded those on Ru-based dyes, the former types remain of interest as sensitizers for DSSCs due to their practical advantages that include i) high absorption coefficients ($\varepsilon_{\text{max}}$ values) resulting from intramolecular $\pi$-$\pi^*$ transition, 2) simple synthesis, color tuning, and structural modification for desired physical and photochemical properties, and 3) their economy. Considerable efforts are in progress to make organic dyes more practical sensitizers for DSSCs. These efforts include: i) increasing the conjugation length of dye structures to get a more red-shifted absorption spectrum, which provides higher light harvesting\textsuperscript{26b, 28a-28b, 32, 36b}, ii) structural control for efficient charge separation\textsuperscript{30c, 33} (e.g., push-pull structure, non-planar geometry), iii) tuning the homo and lumo energy levels of dyes for thermodynamically favorable electron transfer\textsuperscript{26b, 34}, iv) control of aggregation to prevent intermolecular electron transfer\textsuperscript{29, 35} (e.g., introduction of alkyl groups as a side chain unit or substrate control), v) introduction of alkyl group to obtain longer electron lifetime\textsuperscript{36}, and vi) modification of metal oxide substrate (e.g., use of ZnO instead of TiO$_2$\textsuperscript{37}, thickness control, introduction of scattering layer, fabrication of highly ordered TiO$_2$ nanotube\textsuperscript{38} or nanofibrous TiO$_2$\textsuperscript{39}).
1.1. Operating principles

Based on the types of materials employed, solar cells can be classified into inorganic solar cells using silicon or other type semiconductors, organic photovoltaics (OPVs) based on donor and acceptor groups and dye sensitized solar cells utilizing dye adsorbed on the surface of a mesoporous semiconductor oxide. Depending on the cell structure, they can also be categorized as semiconductor p-n junction or photo electrochemical solar cells.

Fig. 1.1 shows schematic diagrams and operating principles for each type of solar cell. The structure of inorganic solar cells depicts the p-n junction type. External light energy absorbed by these solar cells induces excitation of electrons from the valence band to the conduction band of the p-type semiconductor, resulting in the formation of carriers. The electron then migrates toward the n-type semiconductor through the junction by the built-in electric field formed between the p-n junction, thus generating a current through the circuit.

OPVs are composed of electron donors and electron acceptors. Since the electron acceptor of OPVs corresponds to an n-type semiconductor as in the inorganic solar cells, a photovoltaic effect is caused by the formation of a hole-electron pair. Migration of the hole and electron is similar to that in inorganic solar cells. Exciton induced by irradiation is formed within the diffusion length of the junction and then separated, resulting in the generation of photocurrent. However, the short diffusion length of the exciton (~10 nm) is an issue, as this limits the layer thickness of organic materials, causing low efficiencies.40

![Fig. 1-1. Operating principles and energy diagrams based on the different types of solar cells, (left; inorganic solar cells, middle; organic photovoltaics, right; DSSCs).](image)
At the heart of DSSCs is a wide band gap mesoporous oxide (typically, TiO$_2$), to which a molecular sensitizer is anchored. Unlike the semiconductor p-n junction, this system utilizes the principles of photosynthesis. Under illumination, electrons and holes are formed within dye molecules and electrons are then injected into the conduction band of the semiconductor metal oxide. Migration of electrons through the surface of the oxide and to the transparent electrode generates photocurrent through the external circuit. Electrolyte, which is usually composed of an iodide/triiodide redox couple, causes regeneration of the oxidized dye by electron donation and triiodide is converted to iodide at the counter electrode connected to the external circuit.

1.2. Dye sensitized solar cells

1.2.1. Key components

The typical DSSCs are composed of five or six components: 1) dye sensitizer, 2) mesoporous semiconductor oxide, 3) electrolyte (liquid redox couple or hole transporting material), 4) anode, 5) counter electrode, and 6) additives.

1.2.1.1. Dye sensitizers

Organic sensitizers for DSSCs include metal-complexes and metal-free organic sensitizers. In the case of metal-complex sensitizers, optical transitions arise from the metal-to-ligand charge transfer (MLCT) character, where excitations from the metal to the p* orbital of the carboxylated ligand impart efficient electron injection to the conduction band of the metal oxide. In spite of low extinction coefficients for the MLCT (typically, $\epsilon_{\text{max}} \leq 20,000$), high efficiencies of these types of sensitizers are attributable to favorable kinetics of electron transfer, stable oxidized state, and broad absorptions from the visible to the NIR region.

First developed in 1991, cis-dithiocyanato bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) (coded as N3) has attracted much attention due to a low cost compared to inorganic sensitizers and high photon-to-current conversion efficiency.
Development of promising metal-complex sensitizers has also involved Ru-bipyridyl complexes. Fig 1.2 shows the chemical structures of the N3, black dye, and N719 which have an efficiency of 10%, 10.4%, 11.18%, respectively, under standard solar illumination (AM 1.5)\textsuperscript{41–43}.

![Chemical structures of N3, black dye, and N719](image)

**Fig. 1-2.** Chemical structures of N3, black dye, and N719 used in DSSCs.

Increased panchromatic absorption was achieved with black dye compared to N3. N719 gave the highest voltage ($V_{oc}$: 846 mV), which is achieved by the employment of two tetrabutyl ammonium ions instead of the four protons of N3. The second generation sensitizers (e.g. Z-907, K-19) were developed in an attempt to increase thermal stability (Fig. 1.3)\textsuperscript{44}. However, since most of the second generation sensitizers had somewhat low molar extinction coefficients, third generation sensitizers were aimed at increasing spectral response by tuning the $\pi$-conjugation length\textsuperscript{45}. HRS-1 showed enhanced efficiency ($\eta= 9.5\%$) over N719 ($\eta = 8.9\%$) under the same test conditions.
On the other hand, the limited supply of Ru for use in sensitizers has triggered the search for metal-free organic sensitizers due to economy and easy color tuning. Unlike metal-complex sensitizers (absorption by MLCT), $\pi-\pi^*$ transitions of pure organic sensitizers are responsible for high extinction coefficients. They have relatively sharp absorption bands as well, thus they have both advantages and disadvantages to give high light harvesting. For efficient organic sensitizers, there are several issues to be considered with regard to stability and kinetics as well as spectral response. Since Arakawa and coworkers reported metal-free sensitizer NKX-2311($\eta = 5.2\%$) in 2001, coumarin, indoline, oligoene, merocyanine, and cyanine dyes have been developed in attempt to obtain efficient sensitizers for DSSCs. Among the organic sensitizers obtained so far, D149, TA-St-CA, and D205 afforded efficiencies of 9.0 %, 9.1 %, 9.5 %, respectively (Fig. 1.4).
A lot of effort has been devoted to systematically investigating structure-property relationships, in order to efficiently control spectral response and obtain desired physical and photochemical properties.\textsuperscript{26b, 28a-28b, 29, 30c, 32-36} A detailed review of the literature of recent developments in organic sensitizers for DSSCs shows that the associated dyes have the following types of features\textsuperscript{47}.

- Push-pull structure
- Broad spectral response
- Proper electronic energies (Homo; Highest Occupied Molecular Orbital, Lumo; Lowest Occupied Molecular Orbital)
- Controlled aggregation and recombination

Fig. 1.5 shows a schematic representation of the push-pull structure (coded as D-spacer-A) of organic sensitizers for efficient charge separation, where the molecular skeleton is mainly composed of three parts: i) one or two donating groups, ii) oligothiophene, polyene, or other conjugated bridges to tune spectral response, iii) electron acceptor having anchoring group to fix the sensitizers on the surface of a semiconductor metal oxide.

The lumo of the dye should be located above the conduction band edge of the metal oxide (typically TiO\textsubscript{2}) for thermodynamically favorable electron injection, whereas the homo of the dye should lie below the energy level of the redox couple to reduce oxidized state (Fig. 1.6). On the basis of this fundamental strategy, dyes can be engineered to minimize charge recombination and aggregation.

**Fig. 1-5.** Schematic representation for organic sensitizers for DSSCs.
Concerning recombination, electrons on the semiconductor oxide can be returned to the oxidized dye molecules or electrolyte instead of being transported electrons towards the anode. Therefore, the positive charge induced after photo excitation should be located on the donor group, which is as far from the TiO$_2$ surface as possible. Also, structural variations in the bridging group or introduction of alkyl side chains have been studied to investigate recombination kinetics, with the aid of ultrafast optics or electrochemical techniques. Dye aggregation on the surface of metal oxide induces electron self-quenching instead of electron injection into the semiconductor metal oxide, resulting in low efficiency. Introduction of long alkyl chains help prevent aggregate formation.

1.2.1.2. Semiconductor metal oxide

Nano-size semiconductor crystalline oxides with a wide bad gap (diameter of 15 - 20 nm) can be used as an electrode to absorb dye molecules. Regarding metal oxides for DSSCs, controlling factors include size, morphology, crystallinity, and surface state. However, the main factor to consider is the energy value of the conduction band, which should be located below the lumo energy of the dye. Fig. 1.7 shows band edges of various semiconductor materials. Among these potential candidates, TiO$_2$ has been shown to give the highest efficiency for DSSCs. TiO$_2$ exists in three different forms in nature: anatase, rutile, and brookite. According to SEM images of typical nanocrystalline TiO$_2$ films (Fig. 1.8), anatase
TiO$_2$ film has a compact packing of spherical types of particles with an average particle size of 20 nm (diameter), whereas rutile TiO$_2$ has a somewhat loosely packed morphology with rod-like particles having a diameter of 20 nm and length of ~ 80 nm. This difference in morphology has an effect on photo-induced current-voltage characteristics. In this regard, anatase TiO$_2$ is more efficient, generating more current and much faster electron diffusion through the surface of TiO$_2$. This means that anatase TiO$_2$, with its higher surface area, gives high adsorption of dye particles and high photovoltaic performance.

Fig. 1-7. Band edge positions of several semiconductors in contact with aqueous electrolyte at pH 1.$^{24a, 25b}$
Although TiO$_2$ has been a frequently used material, modification such as introduction of a core-shell structure$^{52}$ or some other semiconducting oxide$^{53}$ has been attempted, to effectively control surface state or morphology. To be specific, significantly enhanced efficiency in DSSCs has been achieved by engineering a porous conducting material with a very high surface area$^{25d, 54}$. Results of a recent study showed that there is an inversely proportional relationship between porosity (P) and diffusion coefficient (D) ($D \propto |P - 0.76|^{0.82}$)$^{55}$. In an effort to achieve surface modification of the porous metal oxide substrate, ultra-high surface area porous TiO$_2$ nanofibers instead of conventional TiO$_2$ particles were used as an electrode in DSSCs. The required nanofibers are prepared by electrospinning (Fig. 1.9), a technology that has gained attention due to its ability to generate nanofibers with well-defined topologies at relatively low cost$^{56a-c}$. Through the careful control of processing parameters, electrospun nanofiber substrates can be produced that have a wide range of porosity values, from nearly nonporous films, to very porous and delicate fibrous structures$^{57}$. 

**Fig. 1-8.** Surface (top) and cross sectional (bottom) SEM images of a rutile (left) and an anatase (right) film coated on conducting glass.$^{51}$
Fig. 1-9. Schematic representation of the electrospinning process.

1.2.1.3. Electrolyte

Fig.1.10 shows the equations representing a cycle of photocurrent generation upon light absorption by DSSCs.

\[
\begin{align*}
\text{S} | \text{SC} + h\nu & \rightarrow S^* | \text{SC} \quad \text{(I) light absorption of sensitizer} \\
S^* | \text{SC} & \rightarrow S^+ | \text{SC} + e^- (\text{SC}) \quad \text{(II) electron injection} \\
2S^+ + 3I^- & \rightarrow 2S + I_3^- \quad \text{(III) regeneration of oxidized dye sensitizer} \\
I_3^- + 2e^- (\text{CE}) & \rightarrow 3I^- \quad \text{(IV) reduction of triiodide}
\end{align*}
\]

Fig. 1-10. A cycle of photocurrent generation in DSSCs following light absorption, (S; sensitizer, SC; semiconductor, CE: counter electrode).

Electrolyte is required for the regeneration of oxidized dye sensitizer (step III). Based on the type of medium, DSSCs can be divided into liquid type, quasi-solid and solid-state DSSCs. In the case of liquid type DSSCs, high efficiency can be achieved due to the fast regeneration of oxidized dyes. A frequently employed liquid electrolyte is composed of iodide/triiodide...
redox couple, where I regenerates oxidized dye sensitizers and the resultant oxidized species are reduced by electron transfer from the counter electrode. In an effort to increase the performance of DSSCs, different types of redox couple have been considered. Fig. 1.11 shows the effects of redox couple of cations\textsuperscript{58} on the performance of DSSCs. With increasing cation size, a higher voltage was achieved, but resulting in lowering photocurrent. Fitzmaurice et al.\textsuperscript{59} and Lindquist et al.\textsuperscript{58-b} explained the relationship between cation size and photovoltage with reference to change in interfacial energetics.

Fig. 1-11. Influence of redox couple cations on current-voltage characteristic of DSSCs, measured under 19.5mW/cm\textsuperscript{2}\textsuperscript{58-b}.

Nanoporous TiO\textsubscript{2} has electron-accumulated surface on which cations absorb (or intercalate into TiO\textsubscript{2} lattice) for charge compensation, resulting in a potential drop through Helmholtz layer. As a result, changes in E\textsubscript{cb} (conduction band edge of TiO\textsubscript{2}) can be induced depending on cation type. Compared to a smaller cation that affects charge compensation by both absorption and intercalation, a larger cation only absorbs on the TiO\textsubscript{2} surface resulting in relatively negative shift of E\textsubscript{cb}\textsuperscript{60} and consequent increased Voc. However, a negative shift in E\textsubscript{cb} reduces the driving force for electron injection from S* (excited dye) to TiO\textsubscript{2} giving a lower photocurrent density.
Fig. 1-12. Chemical structures of HTMs for solid-state DSSCs.

In addition to the study of different types of redox couples mentioned above, additives such as TBP (4-tert-butylpyridine) and GuCN (guanidium thiocyanate) are known to affect \( V_{oc} \) by controlling of \( E_{cb} \) or (and) recombination, via a surface passivation effect. TBP tends to interact with Ti(IV) sites from which charge transfer from TiO\(_2\) into electrolyte is significantly reduced, resulting in enhancement of \( V_{oc} \). MBI (1-methylbenzimidazole) as an additive has been reported to have similar effects to TBP. In this case, Santiago and co-workers investigated the effects of electrolyte in the view of transport and recombination. As a result, enhancement of \( V_{oc} \), fill factor, and efficiency by introducing MBI was interpreted as a shifting of \( E_{cb} \) upward and suppression of recombination, which was supported by impedance spectroscopy.

The various liquid based electrolytes have disadvantages such as leakage or evaporation in the case of poor sealing of the cell. Solvent evaporation or leakage can be significantly reduced in the quasi-solid or solid-type DSSCs. However, both types of DSSCs usually render low performance caused by mass-transfer limitations on the photocurrent (quasi-solid case) and by the inferior pore filling of porous TiO\(_2\) film (solid-type). Although solid-state DSSCs have lower efficiencies than liquid-type DSSCs, they have gained much attention due to their high stability for a long-term use. Fig. 1.12 shows examples of hole transporting materials (HTMs) for solid-state DSSCs that have been developed since OMeTAD (2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenyl-amine)9,9′-spirobifluorene) was reported in 1998.
1.2.1.4. Effect of coadsorbate

As will be shown in section 1.2.3, recombination of photo-generated electrons at the TiO$_2$/dye/electrolyte interface is a major efficiency-limiting factor for DSSCs. As an approach to reducing charge recombination, coadsorbate is sometimes employed on TiO$_2$ surface. It has been reported to be effective for breaking up $\pi$-stacked dye aggregates $^{54-b, 47-a, 65-a}$, resulting in enhancement of $J_{sc}^{27-c}$ by increased electron injection yield and sometimes $V_{oc}$ gain as well$^{66}$. Representative coadsorbates are cholic acid derivatives DCA and CDCA (Fig. 1.13).

![Chemical structure of DCA (left) and CDCA (right).](image)

In a study of coumarin based$^{67}$, it was found that both DCA and DCNa increase $J_{sc}$ and $V_{oc}$. This additive functions as a spacer between dye aggregates, which reduces $\pi-\pi$ stacking and charge recombination, contributing to increased photocurrent. A notable achievement is the identification of intrinsic factors affecting $V_{oc}$ enhancement. In this type work, size and acidic character of cations affected $V_{oc}$, with DCNa more beneficial for $E_{cb}$ movement, while DCA was more effective for suppressing charge recombination. Therefore, $V_{oc}$ gain obtained by suppression of recombination can be counteracted, depending on $E_{cb}$ movement, leading to $V_{oc}$ loss caused by proton exchange of CDA (or CDCA) on the TiO$_2$ surface.$^{68}$ In other studies, DPA (1-decylphosphonic acid)$^{44-b}$, HDMA $^{65-b}$ were reported to be less effective in breaking up organic dye aggregates than DCA because of their linear structure. Concerning the concentration of coadsorbate, excess amounts offset the usual effect of increased IPCE...
(incident photon-to current conversion efficiency), which is due to the adsorbed dye loss, resulting in decreased $J_{sc}$.\textsuperscript{68-b}

### 1.2.2. Photovoltaic performance

Solar energy-to-electricity conversion efficiency ($\eta$) is usually calculated under standard illumination conditions (AM 1.5). AM (Air Mass) can be used to describe the solar spectrum and irradiance level and is related to travel distance through the atmosphere. Based on the angle of inclination the sun makes from the zenith to the horizontal, AM can be defined as $1/\cos\theta$. Under no atmospheric attenuation of solar radiation (region outside the Earth’s atmosphere), it is described as AM 0, which has the spectrum close to black body radiation and irradiance energy of 1365W/m$^2$. As shown in Fig. 1.14, the irradiance energy of this solar energy is attenuated upon passing through the atmosphere. Therefore, AM1.5 corresponds to the irradiance of 844W/m$^2$ ($\theta = 48.19^\circ$). However, standard global AM1.5 for the measurement of photovoltaic performance is normalized to 1000W/m$^2$ and is determined by the solar spectral irradiance for a 37$^\circ$ tilted sea level.

![Concept of AM (left) and solar spectra based on the AMs (right).][1]

Under standard solar energy conditions, the overall conversion efficiency is described by following equation:
where \( I_{sc} \) is short circuit current, \( V_{oc} \) is open circuit voltage, \( P_{output} \) is output power, \( P_{input} \) is input power, and FF is fill factor. The photocurrent of the cell is determined by the photocurrent efficiency (IPCE), which is defined as a percentage of the number of electrons produced by light in the external circuit divided by the number of photons absorbed (eq. 2).

\[
\text{IPCE}(\lambda) = \frac{LHE(\lambda) \Phi_{inj} \Phi_c}{1240 \, I_{sc}(\mu A cm^{-2})/ \lambda (nm) \, P_{input} (W m^{-2})}
\]  

(eq. 2)

where the light harvesting efficiency (LHE) depends on the spectral properties of the dye sensitizer. Factors such as recombination, excited state redox potential, and lifetime can have an effect on charge injection efficiency (\( \Phi_{inj} \)) and charge collection efficiency (\( \Phi_c \)), depending on the structure and morphology of the TiO\(_2\) layer.

The \( V_{oc} \) in DSSCs is the absolute difference between the standard reduction potential of redox coupling, \( V_{red} \), and the fermi level, \( V_f \) (-0.5 V vs NHE) of the TiO\(_2\) electrode\(^{71}\). However, voltage can also be affected by charge recombination. Therefore, open-circuit voltage, in terms of recombination kinetics of the injected electrons, can be described by eq. 3.\(^{41,72}\)

\[
V_{oc} = \left( \frac{KT}{e} \right) \ln \left( \frac{I_{inj}}{n_{cb} K_{et} I_3} \right)
\]  

(eq. 3)

where \( I_{inj} \) is the flux of charge from the injection, \( n_{cb} \) is the concentration of electrons on the TiO\(_2\) surface, and \( K_{et} \) is the recombination rate constant of injected electrons by \( I_3^- \) in the electrolyte.

**1.2.3. Kinetics**

Detailed investigation of the kinetics of electrons generated in DSSCs plays an important role of understanding structure-performance relationships. Fig. 1.15 shows the major kinetic processes that take place in DSSCs.
Fig. 1-15. Schematic representation of kinetic processes during the operation of DSSCs, (solid arrows: forward reactions by photo-excitation, dashed arrows: possible back reactions).

Forward reactions (Fig. 1.15, solid arrows) by photo-excitation of dye include light absorption of dye ($K_1$), electron injection ($K_2$), regeneration of oxidized dye by redox shuttle ($K_3$), and transportation of generated electrons ($K_4$). These reactions compete with back reactions (dashed arrows) which limit the efficiency of DSSCs. The major back reactions are relaxation of excited dye ($B_1$), back electron transfers of generated electrons with oxidized dye ($B_2$), and oxidized electrolyte ($B_3$).

Among reactions at each interface, charge dynamics surrounding TiO$_2$ are the most important routes that determine cell efficiency. A lot of work has been conducted to find kinetics information about each physical step in a time scale$^{26-c, 73}$. To be specific, DSSCs employing ruthenium complex as a sensitizer are reported to have i) electron injection time of $<$1 ps ~ 100 ps, ii) excited state life times on a nanosecond scale, iii) regeneration of oxidized dye within a 0.1 - 10 $\mu$s scale, iv) back transfer of electrons from photo-induced electron to oxidized dye on a time scale of 100 $\mu$s or $<$ ms. By comparison, previous research on metal-free organic sensitizers led to injection yields near unity (i.e. electron injection time of $<$ 100 ~ 200 fs and emission lifetimes on a ns scale)$^{28-b, 74}$. Fast recombination components were identified as efficiency-limiting reason.

Compared to ruthenium complexes, studies on the charge dynamics of organic sensitizers have been conducted mostly on high efficiency dyes such as coumarin and D5.
Therefore, it is likely that extensive research on the kinetics of different types of sensitizers, where different time scale values at each interface can be extracted, will lead to the development of high performance DSSCs.

Several authors have reported kinetics in DSSCs using experimental methods such as pump-probe transient absorption spectroscopy, femtosecond stimulated raman spectroscopy, TPC (transient photocurrent) and TPV (transient photovoltage) measurements, simultaneous transient absorption and transient electrical measurements, TCSPC (time correlated single photon counting), electrochemical impedance spectroscopy. Depending on the analytical methodology employed, time scale values obtained were still comparable but were not always consistent on the same DSSCs. Therefore, the optimization of analytical methods is an on-going investigation in the area of DSSCs.

Among the well-known methods for studying kinetics, impedance spectroscopy is the one of the powerful tools used to understand charge dynamics, interfacial properties, or material properties in DSSCs. Impedance in DSSCs is effectively expressed by the equivalent circuit developed by Kern, Bisquert, or Adachi’s group. Fig. 1.16 shows the typically adopted equivalent circuit for DSSCs.

![Equivalent Circuit for DSSCs](image)

**Fig. 1-16.** (a) Simple equivalent circuit in a solar cell. (b) Representative impedance circuit model for a dye solar cell.

Here, each equivalent component has following meaning.

- \( R_s (\Omega \text{ m}^2) \): sheet resistance for the transport resistance of TCO
• $R_{TCO}$ (Ω m$^2$) and $C_{TCO}$ (F m$^2$) : contact resistance and capacitance at the interface between TCO and TiO$_2$ layer
• $R_{su}$ (Ω m$^2$) and $C_{su}$ (F m$^2$) : charge transfer resistance at TCO/electrolyte interface and double layer capacitance at the TCO/TiO$_2$/electrolyte interface
• $R_{CE}$ (Ω m$^2$) and $C_{CE}$ (F m$^2$) : charge transfer resistance and double layer capacitance at counter electrode/electrolyte interface
• $Z_d$ (Ω m$^2$) : mass transport impedance at the counter electrode
• $R_T$ (= $r_T$ L, unit: Ω m$^2$) : total transport resistance in TiO$_2$ film, where L is film thickness
• $R_r$ (= $r_r$ /L, unit: Ω m$^2$) : charge transfer resistance at TiO$_2$/electrolyte interface
• $C_\mu$ (= $c_\mu$ L unit: F m$^2$) : total chemical capacitance which means the change of electron density as a function of Fermi level

Note that $r_T$, $r_r$, and $c_\mu$ are not dependent on film thickness but are related to material properties. Total impedance is the sum of the contribution of $Z_0$, $Z_1$, $Z_2$, and $Z_3$, where $Z_0$ is contact impedance, $Z_1$ is complex impedance which takes place in TiO$_2$/electrolyte interface, $Z_2$ is Warburg impedance describing diffusion of electrolyte, and $Z_3$ is impedance at the counter electrode/electrolyte interface. The resultant impedance spectra can be shown as arcs in the plot of the real part of $Z'(\omega)$ versus the imaginary part of $Z''(\omega)$ as a function of frequency. As a result, parameters obtained by fitting of data using the equivalent circuit model are useful for interpreting electron transfer dynamics in DSSCs.

### 1.2.4. Metal free organic dye sensitizers

Although many sensitizers for DSSCs have been reported, there remains a need to develop systematic structure-property relationships for DSSC dyes. This type of work would afford the chemist a way to efficiently design high performance sensitizers for DSSCs. The following examples are mainly focused on how to control spectral properties, aggregation, and charge recombination by structural modifications.
1.2.4.1. Variations involving donor units

Donor units can be engineered to control interface phenomena such as aggregation or charge recombination, which have a negative effect on the DSSC efficiency. They are structurally tuned to have targeted spectral properties (e.g. red-shifted absorption) and electronic energy levels. Table 1.1 shows the performance of dye sensitizers having different donor units. Ko and co-workers showed that a twisted non-planar geometry plays a significant role in the control of aggregation and high rates of charge separation.\textsuperscript{48c, 78-79} Dye \textsuperscript{2}, having a stable and bulky bis-dimethylfluoreneaniline group, afforded enhanced efficiency compared to the julolidine based dye \textsuperscript{1}.

Tian et al.\textsuperscript{81} reported the effects of an additional donor group, to give a D-D-\pi-A, on photovoltaic performance. Here, dye \textsuperscript{4}, which has a starburst triarylamine, gave higher efficiency as well as a red-shifted absorption spectrum compared to closely related dye \textsuperscript{3}. It seems that a more bulky amine unit renders increased open-circuit voltage by retarding recombination between TiO\textsubscript{2} and electrolyte or oxidized sensitizer.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Structure</th>
<th>J\textsubscript{sc} [mAcm\textsuperscript{-2}]</th>
<th>Voc [V]</th>
<th>FF</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Structure 1" /></td>
<td>6.26</td>
<td>0.61</td>
<td>0.64</td>
<td>2.47</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Structure 2" /></td>
<td>14</td>
<td>0.75</td>
<td>0.77</td>
<td>8.01</td>
</tr>
</tbody>
</table>

Table 1-1. Examples of dye sensitizers with variations in the donor unit.
Table 1-1. Continued

<table>
<thead>
<tr>
<th></th>
<th>Structure</th>
<th>$\pi$-conjugation path</th>
<th>$\pi$-conjugation unit</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>13.6</td>
<td>0.62</td>
<td>0.69</td>
</tr>
<tr>
<td>4</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>13.8</td>
<td>0.63</td>
<td>0.69</td>
</tr>
</tbody>
</table>

1.2.4.2. Variations in $\pi$-conjugation units

Tuning the conjugation unit has been achieved by introducing side chains into the $\pi$ conjugation system, typically on an oligoene or thiophene based $\pi$ bridging unit, or by modifying the conjugation path length. Dyes employed in these studies are shown in Table 1.2. Lin et al.\textsuperscript{82} showed that conjugation path length is an important factor in efficient charge separation. Although increased path length enhanced spectroscopic properties, dye having a high oxidation potential afforded the highest efficiency (e.g. dye 5). Similar results were reported by Arakawa and coworkers\textsuperscript{26b}. The highest photovoltaic performance was shown for the sensitizer having optimum chain length, since a too short chain length is not favorable for high light harvesting while a too long chain length has a negative effect on charge separation (e.g. dye 6). Koumura N. et al.\textsuperscript{36a} showed that the introduction of n-hexyl groups on the spacer results in a longer electron lifetime ($\tau$) as well as efficient packing of dyes on the TiO$_2$ surface, which helps retard charge recombination and gives high open-circuit voltage (e.g. dyes 7 vs 8). In the case of dye 9,\textsuperscript{33} which is intended to be a low band-gap sensitizer for the high light harvesting, it was reported that benzothiadiazole based sensitizers impart better performance due to its more effective pulling of electrons toward the anchoring group,
inducing higher extinction coefficient and good charge separation.

From the research of Yang et al.\textsuperscript{83}, the effects of a thiophene spacer on DSSC performance were reported. Changing the C=C double bond spacer in dye 10 to a thiophene based spacer (dyes 11, 12) induces a broader absorption spectrum on TiO\textsubscript{2} compared to that in solution, thus giving increased efficiency. Also, dye 13 having a rigid thienothiophene system afforded greater light harvesting properties than the flexible vinylene thiophene system in dye 14. The higher efficiency of dye 13 was attributed to the presence of a rigid spacer and the more negative excited state oxidation potential (E\textsubscript{ox}*)

Yang et al.\textsuperscript{84} also reported that a thienothiophene based sensitizer gave lower efficiency relative to that of a bithiophene based sensitizer. The somewhat lower open circuit voltage using dye 16 (vs dye 15) might be attributable to a stronger tendency for aggregation, which results in the unfavorable reverse electron transfer. Similar results were reported by Sun and co-workers\textsuperscript{32,85}, who found that dye 18 gave higher efficiency relative to that of the fused thiophene system in dye 17.

Recently, Yeh and co-workers\textsuperscript{86} designed a sensitizer containing a furan moiety. As a result of comparing the performance of dye 20 with 19, it was found that dye 20 had good spectral properties for large light harvesting and that dye 20 showed a relatively slow recombination lifetime.
Table 1-2. Examples of dye sensitzers having different π conjugation units.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Structure</th>
<th>Jsc [mA cm(^{-2})]</th>
<th>Voc [V]</th>
<th>FF</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td><img src="image" alt="Structure 5" /></td>
<td>12.47, 9.81</td>
<td>0.65, 0.61</td>
<td>0.65, 0.67</td>
<td>5.23, 3.35</td>
</tr>
<tr>
<td></td>
<td>Ar = 1-naphthyl</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td><img src="image" alt="Structure 6" /></td>
<td>15.2, 15.1</td>
<td>0.55, 0.47</td>
<td>0.52, 0.47</td>
<td>5.2, 3.5</td>
</tr>
<tr>
<td>7</td>
<td><img src="image" alt="Structure 7" /></td>
<td>10.8</td>
<td>0.63</td>
<td>0.71</td>
<td>4.8</td>
</tr>
<tr>
<td>8</td>
<td><img src="image" alt="Structure 8" /></td>
<td>11.1</td>
<td>0.71</td>
<td>0.71</td>
<td>5.6</td>
</tr>
<tr>
<td>9</td>
<td><img src="image" alt="Structure 9" /></td>
<td>8.35, 10.44</td>
<td>0.52, 0.54</td>
<td>0.67, 0.66</td>
<td>2.91, 3.77</td>
</tr>
<tr>
<td>10</td>
<td><img src="image" alt="Structure 10" /></td>
<td>14</td>
<td>0.60</td>
<td>0.71</td>
<td>6</td>
</tr>
</tbody>
</table>
Table 1-2. Continued

11

\[
\text{N} \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{2} \quad \text{H} \\
\text{H} \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{2} \quad \text{H} \\
14.7 \quad 0.67 \quad 0.73 \quad 7.2
\]

12

\[
\text{N} \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{2} \quad \text{H} \\
\text{H} \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{2} \quad \text{H} \\
14.3 \quad 0.73 \quad 0.74 \quad 7.7
\]

13

\[
\text{C}_2\text{H}_5 \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{2} \quad \text{H} \\
\text{C}_2\text{H}_5 \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{2} \quad \text{H} \\
15.23 \quad 0.56 \quad 0.73 \quad 6.23
\]

14

\[
\text{C}_2\text{H}_5 \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{2} \quad \text{H} \\
\text{C}_2\text{H}_5 \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{2} \quad \text{H} \\
10.64 \quad 0.52 \quad 0.70 \quad 3.87
\]

15

\[
\text{N} \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{2} \quad \text{H} \\
\text{H} \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{2} \quad \text{H} \\
15.3 \quad 0.63 \quad 0.73 \quad 7.00
\]

16

\[
\text{N} \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{2} \quad \text{H} \\
\text{H} \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{S} \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{2} \quad \text{H} \\
15.4 \quad 0.61 \quad 0.70 \quad 6.57
\]
1.2.4.3. Variations in anchoring groups

The two typical anchoring groups for DSSCs sensitizers are the cyanoacrylic acid and rhodanine containing unit, as illustrated in Table 1.3. Uchida et al.\textsuperscript{27a-b} investigated the photovoltaic performance of a series of sensitizers containing indoline based donor and rhodanine based anchoring group. As shown in Table 1.3, dyes 21 - 25 gave an efficiency of 5.5 % - 9.5 %. The incorporation of rhodanine into dye 21 to give dye 22 resulted in a bathochromic shift about 25 nm as well as increase of \(~10,000\) in the extinction coefficient, thus contributing to the increased efficiency. The introduction of 3 rhodanine units in dye 21 backbone caused a significant drop in open-circuit voltage due to a lowered $E_{ox}^{\ast}$. Dye 23 having two carboxyl groups to anchor the sensitizers onto the TiO$_2$ surface gave
lower efficiency, which might be caused by dimerization of dye molecules rather than strong interaction between dye and TiO$_2$. In the case of dyes 24$^{27d}$ and 25$^{27e}$, the highest efficiencies were obtained among these metal-free organic sensitizers.

Table 1-3. Some examples of dye sensitizers with variations on anchoring group.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Structure</th>
<th>Jsc [mAcm$^{-2}$]</th>
<th>Voc [V]</th>
<th>FF</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>17.76</td>
<td>0.604</td>
<td>0.57</td>
<td>6.1</td>
</tr>
<tr>
<td>22</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>18.75</td>
<td>0.645</td>
<td>0.538</td>
<td>6.51</td>
</tr>
<tr>
<td>23</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>17.50</td>
<td>0.584</td>
<td>0.538</td>
<td>5.5</td>
</tr>
</tbody>
</table>
1.3. Objective

Dye sensitized solar cells (DSSCs) are of great interest because their construction involves low cost components and are relatively simple, affording them the potential to compete with fossil fuel-based power generation, a non-renewable process. Efforts devoted to developing promising metal-free sensitizers have shown that structural modifications that impart the desired spectral properties can conflict with factors affecting the high efficiency of DSSCs. For example, extended conjugation gives the red-shifted absorption spectrum needed for good light harvesting but can also induce aggregation and/or positive shift in the lumo of the dye molecules. Therefore, a systematic study involving the design of DSSC dyes for enhanced efficiency was deemed of interest. Developing structure-performance relationships will broaden our understanding of the role of properties such as polarizability, electronic energies, geometry, and absorption spectra in achieving efficient DSSCs.

Taking into account the above literature review, the primary goals of this study were 1) the synthesis of molecular-engineered novel metal-free organic dyes as alternatives to
presently available metal-complex dyes and 2) investigation of intrinsic factors affecting performance through application of the resultant dyes in DSSCs.

1.3.1. Dye candidates
The initial consideration in the design of molecular structures for DSSCs involved the design of pronounced push-pull structures (donor-spacer-acceptor) for efficient charge separation. In the present case, structures without conventional C=C double bonds to achieve π conjugation were of interest. Based on this resultant backbone, introduction of a bulky strong electron donor was designed to control aggregation and give a red-shifted absorption spectrum. Fig. 1-16 and Fig. 1-17 show the two series of dye sensitizers that take these design features into consideration.

**Fig. 1-17.** Chemical structures of the group of DSSC dyes having variations in polarizability.
1.3.1.1. Variations in the polarizability of spacer unit

In the first series of target dyes (D1 - D5), different heterocyclic rings were employed as a linker unit for the D-spacer-A structure, to determine the effects of heterocyclic unit variation on DSSCs performance. This approach differs from the research of other groups, which emphasized modifications to donor or/and acceptor having C=C double bond systems as spacer units.

Despite the introduction of strong donors and/or strong acceptors for efficient charge separation, the widely employed C=C double bond as a spacer can limit DSSC efficiency by introducing negative effects such as self-quenching of generated electrons by cis-trans isomerization\(^{87}\) or aggregation\(^{88}\) as well. Recently, photovoltaic performance of furan-based sensitizer (vs thiophene-based sensitizer) was investigated in view of recombination kinetics and the furan-based dye showed a much slower recombination lifetime, resulting in a more efficient solar cell\(^{86}\). However, introduction of any other heterocyclic ring as a spacer and the effects of heterocyclic rings on polarizability, which is a measure of the push-pull properties for DSSCs, have not been reported.
Results of theoretical investigations involving the role of heteroaromatics in the design of efficient nonlinear optical molecules\textsuperscript{89} showed that the replacement of the benzene ring on the acceptor group with rings such as thiophene, furan, or pyrrole results in higher $\beta$-values (first-order hyperpolarizability). Therefore, target dyes were expected to provide viable new spacer units for DSSCs that overcome the limitations of current prototypes.

1.3.1.2. Variations in the donor unit

In second series of target dyes D6 – D10 (Fig. 1-17) variations in the donor unit were considered. The chosen donor unit is a bulky and star-shaped carbazole-based amine. One of the critical factors for high DSSC efficiency is related to interface engineering\textsuperscript{27a,46}. Most of the interface engineering for DSSCs has been conducted by modification of the metal oxide substrate, use of additives, or the control of dye aggregation. In this regard, aggregate formation on the TiO$_2$ electrode generally induces negative effects such as intermolecular electron transfer, a hypsochromic shift, or low LHE (light harvesting efficiency). Hagberg et al.\textsuperscript{49} reported the effects of alkoxy-substituted donor groups on controlling photovoltaic properties and showed that this structural feature plays an important role in controlling aggregation. Koumura. et al.\textsuperscript{36a} introduced long alkyl groups as a side chain, with the aim of producing longer electron lifetimes ($\tau$), which is a kinetic solution for the decrease in charge recombination.

Donor units are also utilized to tune the energy level and (or) spectral sensitivity and to prevent reverse electron transfer. In the proposed work, the structural differences between Series 1 (D1 – D5) and Series 2 (D6 – D10) were compared in view of aggregation phenomenon, electron lifetime ($\tau$), and spectral sensitivity, to investigate the effect of a bulky strong donor unit on photovoltaic properties of DSSCs.
Chapter 2. Experimental

2.1. Synthesis and Materials

All reagents were purchased from Sigma-Aldrich, TCI, or Fisher Scientific. All chemicals used in this study were of reagent-grade quality and solvents purchased from commercial suppliers were used without further purification. Moisture-sensitive reactions were performed under either nitrogen or argon gas. All reactions were followed by thin-layer chromatography (TLC) using Analtech silica gel GHLF. The N719 used for fabrication of reference solar cell was received as a gift from Dyesol and used without further purification.

2.1.1. Intermediates for indole formation

2.1.1.1. 2-Methyl-1-(thiophen-2-yl)propan-1-one (1a)

Thiophene (5g, 73.4 mmol) and isobutyric anhydride (13.5 g, 85.2 mmol) were placed in a flask under N\textsubscript{2} gas. To the rapidly stirred mixture at room temperature was added BF\textsubscript{3}·O(C\textsubscript{2}H\textsubscript{5})\textsubscript{2} (1.0 g, 7.3 mmol) all at once. The reaction mixture was then heated to 100 °C and stirred for 30 min. After cooling to room temperature, 50 ml of water was added to the reaction mixture followed by extraction with ether. The combined ether extracts were shaken with sat. NaHCO\textsubscript{3} to remove acid. The solvent was evaporated and the crude product was purified by column chromatography (ethyl acetate/hexane, 1/6, v/v) on silica gel to give a colorless oil. Yield: 100 %. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta = 7.65\) (dd, 1H, \(J = 3.9\) Hz, \(1.2\) Hz), \(7.56\) (dd, 1H, \(J = 4.6\) Hz, 0.9 Hz), \(7.06\) (dd, 1H, \(J = 4.9\) Hz, 3.7 Hz), \(3.32\) (sept, 1H, \(J = 6.9\) Hz), \(1.17\) (d, 6H, \(J = 6.9\) Hz).

2.1.1.2. 1-(Furan-2-yl)-2-methylpropan-1-one (2a)

Compound 2a was prepared using the same procedure as for 1a except furan was used in lieu of thiophene. The crude product collected after evaporation of solvent was purified by column chromatography (DCM (dichloromethane)/hexane, 2/1, v/v) on silica gel to produce a colorless oil. Yield: 54 %. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta = 7.52\) (dd, 1H, \(J = 1.7\) Hz).
Hz, 0.9 Hz), 7.13 (dd, 1H, J = 3.6 Hz, 0.9 Hz), 6.47 (dd, 1H, J = 3.6 Hz, 1.5 Hz), 3.27 (sept, 1H, J = 6.9 Hz), 1.15 (d, 6H, J = 6.9 Hz).

2.1.1.3. 2-Methyl-1-(thiazol-5-yl)propan-1-one (3a)
A solution of isobutyric chloride (0.68g, 12.7 mmol) in DCM (95 ml) was added to a stirred solution of 2-trimethyl silyl thiazole in DCM (62 ml) under N₂ gas. After stirring for 6 h at room temperature, reaction mixture was treated with sat. NaHCO₃ followed by stirring for 30 min. The reaction mixture was extracted with DCM and dried using anhydrous MgSO₄. The crude product was distilled to afford a colorless oil. Yield: 75 %, ¹H NMR (300 MHz, CDCl₃) δ = 7.95 (d, 1H, J = 3Hz), 7.60 (d, 1H, J = 3 Hz), 3.78 (sept, 1H, J = 6.9 Hz), 1.28 (d, 6H, J = 6.9 Hz)

2.1.1.4. 2-Methyl-1-(1-methyl-1H-pyrrol-2-yl)propan-1-one (4a)
To a solution of isobutyric anhydride in 1,2-dichloroethane (250 ml) was added BF₃·O(C₂H₅)₂ (19.25 g, 135.6 mmol) under N₂ gas and the reaction mixture was stirred for 10 min. N-methyl pyrrole (5 g, 61.6 mmol) was added portionwise and stirring was continued at room temperature for 4 h. The reaction mixture was quenched with cold water and extracted with DCM. Purification by column chromatography (ethyl acetate/hexane, 1/15, v/v) on silica gel produced a colorless oil. Yield: 42 %, ¹H NMR (500 MHz, CDCl₃) δ = 6.96 (dd, 1H, J = 4.25 Hz, 2.55 Hz), 6.79 (m, 1H), 6.11 (dd, 1H, J = 4 Hz, 2.50 Hz), 3.93 (d, 3H, J= 0.5 Hz), 3.31 (sept, 1H, J = 7.0 Hz), 1.17 (d, 6H, J= 6.9 Hz). ¹³C NMR (500 MHz, CDCl₃) δ = 200.3, 126.6, 125.1, 123.3, 109.8, 37.1, 36.8, 19.6.

2.1.1.5. 1-(4-Bromophenyl)-2-methylpropan-1-one (5a)
To a solution of iodobenzene (5 g, 24.5 mmol) and AlCl₃ (7.84 g, 58.8 mmol) was added dropwise isobutyric chloride (3.13 g, 29.4 mmol). The reaction mixture was stirred at 40 °C until evolution of HCl ceased. The reaction mixture was poured into ice water, extracted with ether, and the organic layer was washed with water. Purification of crude 5a
was carried out by column chromatography (toluene/hexane, 4/1, v/v) on silica gel to yield a colorless oil. Yield: 32 %, $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 7.76 (AA’BB’, 2H), 7.60 (AA’BB’, 2H), 3.42 (sept, 1H, J = 6.9 Hz), 1.14 (d, 6H, J = 6.9 Hz).

2.1.2. Synthesis of carbazole based amine unit

2.1.2.1. 9-(4-Methoxyphenyl)-9H-carbazole (I)

Anisole (9.1 g, 38.9 mmol), carbazole (5 g, 29.9 mmol), potassium carbonate (33.1 g, 239.2 mmol), copper powder (7.6 g, 119.6 mmol), and 18-crown-6 (0.74 g, 1.8 mmol) were added into flask under argon gas followed by adding o-dichlorobenzene (50 ml). The reaction mixture was stirred under reflux at 170 °C. After heating for 24 h, the solution was allowed to cool to room temperature before filtering copper and inorganic salts. The crude product was collected by evaporation of solvent and recrystallized from methanol to yield I as a white solid. Yield: 84 %, $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$ = 8.23 (d, 2H, J = 7.50 Hz), 7.53 - 7.50 (m, 2H), 7.44 - 7.39 (m, 2H), 7.29 - 7.20 (m, 6H), 3.87 (s, 3H).

2.1.2.2. 3-Bromo-9-(4-methoxyphenyl)-9H-carbazole (II)

To a stirred solution of I (0.8 g, 2.93 mmol) in tetrahydrofuran at 0 °C was added N-bromosuccinimide (0.36 g, 2.05 mmol) in small portions. The reaction mixture was then allowed to warm to room temperature and stir overnight. The solvent was evaporated and the residue was extracted with ether. Crude II was collected by solvent evaporation and recrystallized from hexane to produce a white solid. Yield: 67 %, $^1$H NMR (300 MHz DMSO-d$_6$) $\delta$ = 8.49 (d, 1H, J = 2.1 Hz), 8.29 (dd, 1H, J = 8.4 Hz, 0.9 Hz), 7.54 (dd, 1H, J = 8.7 Hz, 2.1 Hz), 7.51 (AA’BB’, 2H), 7.44 (td, 1H, J = 7.2 Hz, 1.2 Hz), 7.31 - 7.20 (m, 5H), 3.87 (s, 3H).

2.1.2.3. 9-(4-Methoxyphenyl)-3-nitro-9H-carbazole (III)

To a stirred solution of I (4.5 g, 16.46 mmol) in acetic acid (70 ml) was added urea nitrate (2.03 g, 16.4 mmol) and stirring continued at 70 °C. The precipitate formed by
addition of water was collected by filtration and dried. Pure III was obtained by recrystallization from acetic acid, resulting in a yellow solid. Yield: 89 %, $^1$H NMR (300 MHz, DMSO-d6) $\delta = 9.28$ (d, 1H, $J = 1.8$ Hz), $8.51$ (d, 1H, $J = 7.8$ Hz), $8.31$ (dd, 1H, $J = 9$ Hz, 2.1 Hz), $7.59 - 7.52$ (m, 3H), $7.42 - 7.23$ (m, 5H), $3.89$ (s, 3H).

2.1.2.4. 9-(4-Methoxyphenyl)-9H-carbazol-3-amine (IV)
Into an oven-dried 1-neck flask were placed III (0.4 g, 1.26 mmol), Sn(II) chloride dihydrate (2.83 g, 12.5 mmol), and ethanol (10 ml) and the reaction mixture was stirred under reflux for 48 h under N$_2$ gas flow. The reaction mixture was allowed to cool to room temperature followed by evaporation of solvent. NaOH (40%) solution was added to the reaction mixture while the residue cooled in an ice bath and stirred vigorously. The resulting solid was collected by filtration and extracted with toluene several times and the combined extracts were dried using anhydrous MgSO$_4$. Pure IV was obtained by recrystallization from toluene, resulting in an off-white solid. Yield: 75 %, $^1$H NMR (300 MHz, DMSO-d6) $\delta = 8.00$ (dd, 1H, $J = 7.8$ Hz, 0.6 Hz), $7.45$ (from AA’BB’, 2H), $7.31$ (td, $J = 7.35$ Hz, 0.9 Hz), $7.23 - 7.12$ (m, 4H), $7.04$ (d, 1H, $J = 8.4$ Hz), $6.77$ (dd, 1H, $J = 8.7$ Hz, 2.1 Hz), $4.85$ (s, 2H), $3.33$ (s, 3H).

2.1.2.5. 9-(4-Methoxyphenyl)-N-(9-(4-methoxyphenyl)-9H-carbazol-6-yl)-9H-carbazol-3-amine (V)
An oven-dried 1-neck flask containing a magnetic stirrer was evacuated and backfilled with argon gas. The flask was then charged with tris(dibenzylideneacetone)-dipalladium (0) (0.14g, 0.15 mmol), 2-dicyclohexylphosphino-2’,4’,6’-triisopropylbiphenyl (0.28 g, 0.59 mmol), sodium tert-butoxide (0.99 g, 0.33 mmol), II (2.6 g, 7.38 mmol), IV (2.13 g, 7.38 mmol) followed by addition of toluene (30 ml) using a syringe. The flask was sealed under a positive pressure of argon, using a Teflon screw cap, and heated at 80 °C for 24 h. The solution was cooled to room temperature and diluted by adding ethyl acetate. The mixture was filtered through Celite and the solvent was removed by evaporation. Purification of crude V by column chromatography (DCM/hexane, 3/1, v/v) on silica gel produced a pale
greenish yellow solid. Yield: 45 %, $^1$H NMR (300 MHz, DMSO-d6) δ = 8.11 (d, 2H, J = 7.8 Hz), 7.93 (s, 1H), 7.88 (d, 2H, J = 0.6 Hz), 7.52 (from AA’BB’, 4H), 7.37 (td, 2H, J = 7.50 Hz, 0.9 Hz), 7.28 - 7.16 (m, 12H), 3.87 (s, 6H).

2.1.3. Fisher indole cyclization

2.1.3.1. 5-Bromo-3,3-dimethyl-2-(thiophen-2-yl)-3H-indole (1b)

To a solution of 4-bromophenyl hydrazine hydrochloride (4.45 g, 19.9 mmol) and 1a (3.07g, 19.91 mmol) in ethanol was added p-toluenesulfonic acid monohydrate (1.89 g, 9.95 mmol). The reaction mixture was stirred at 100 °C until 1a was consumed as determined by TLC. The solution was diluted with ether followed by neutralization using aq. NaHCO₃ before extraction with ethyl acetate. The organic extracts were dried using anhydrous MgSO₄ and concentrated under vacuum. The crude obtained was purified by column chromatography (ethyl acetate/hexane, 1/20, v/v) on silica gel to yield a yellow-white solid. Yield: 40 %, $^1$H NMR (300 MHz, CDCl₃) δ = 7.61 (dd, 1H, J = 3.6 Hz, 0.9 Hz), 7.48 (dd, 1H, J = 4.95 Hz, 0.9 Hz), 7.47 - 7.41 (m, 2H), 7.38 (dd, 1H, J = 1.8 Hz, 0.6 Hz), 7.12 (dd, 1H, J = 5.2, 3.6 Hz), 1.51 (s, 6H).

2.1.3.2. 5-Bromo-2-(furan-2-yl)-3,3-dimethyl-3H-indole (2b)

Compound 2b was prepared using the procedure given for 1b, except that 2a was used in lieu of 1a. Crude 2b was collected after evaporation of solvent and purified by column chromatography (ethyl acetate/hexane, 1/15, v/v) on silica gel, to produce a pale yellow-white solid. Yield: 19 %, $^1$H NMR (300 MHz, CDCl₃) δ = 7.60 (dd, 1H, J = 1.6 Hz, 0.9 Hz), 7.47 - 7.41 (m, 2H), 7.38 (dd, 1H, J = 1.5 Hz, 0.6 Hz), 7.10 (dd, 1H, J = 3.6 Hz, 0.6 Hz), 6.54 (dd, 1H, J = 3.6 Hz, 1.8 Hz), 1.48 (s, 6H).

2.1.3.3. 5-Bromo-3,3-dimethyl-2-(thiazol-2-yl)-3H-indole (3b)

Compound 3b was prepared using the procedure given for 1b except that 3a was used in lieu of 1a. Crude 3b was collected after evaporation of solvent and purified by column
chromatography (ethyl acetate/hexane, 1/20, v/v) over silica gel to produce an off-white solid. Yield: 44 %, $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta = 8.17$ (d, 1H, J = 3 Hz), 8.05 (d, 1H, J = 3.3 Hz), 7.86 (d, 1H, J = 2.1 Hz), 7.63 (d, 1H, J = 8.4 Hz), 7.57 (dd, 1H, J = 8.4 Hz, 1.8 Hz), 1.60 (s, 6H).

2.1.3.4. 5-Bromo-3,3-dimethyl-2-(1-methyl-1H-pyrrol-2-yl)-3H-indole (4b)

Compound 4b was prepared using the procedure given for 1b except that 4a was used in lieu of 1a. Crude 4b collected after evaporation of solvent and purified by column chromatography (ethyl acetate/hexane, 1/2, v/v) over silica gel to produce a sticky brownish yellow semi-solid. Yield: 44 %, $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta = 7.65 \sim 7.62$ (m, 2H), 7.42 (dd, 1H, J = 8.1 Hz, 1.8 Hz), 7.34 (d, 1H, J = 8.1 Hz), 6.84 (dd, J = 1.8 Hz, 1.5 Hz), 6.65 (dd, 1H, J = 2.7 Hz, 1.8 Hz), 3.70 (s, 3H), 1.42 (s, 6H). $^1$H NMR (300 MHz, CDCl$_3$) $\delta = 7.41 \sim 7.38$ (m, 3H), 7.33 (dd, 1H, J = 2.0 Hz, 1.8 Hz), 6.78 (dd, 1H, J = 2.4 Hz, 1.8 Hz), 6.67 (dd, 1H, J = 2.6 Hz, 2.4 Hz), 3.73 (s, 3H), 1.49 (s, 6H).

2.1.3.5. 5-Bromo-2-(4-iodophenyl)-3,3-dimethyl-3H-indole (5b)

Compound 5b was prepared using the procedure given for 1b except that 5a was used in lieu of 1a. Crude 5b collected after evaporation of solvent and purified by column chromatography (ethyl acetate/hexane, 1/20, v/v) over silica gel to produce an off-white solid. Yield: 57 %, $^1$H NMR (500 MHz, DMSO-d$_6$) $\delta = 7.95$ (AA’BB’, 2H), 7.90 (AA’BB’, 2H), 7.81 (d, 1H, J = 1.5 Hz), 7.56 (d, 1H, J = 8.4 Hz), 7.53 (dd, 1H, J = 8.4 Hz, 2.0 Hz), 1.53 (s, 6H). $^{13}$C NMR (500 MHz, DMSO-d$_6$) $\delta = 182.30, 151.45, 150.30, 137.73, 131.44, 130.65, 130.05, 124.91, 122.22, 119.07, 98.73, 53.59, 23.64.

2.1.4. Iodization of 5-Bromo-3,3-dimethyl-2-(1-methyl-1H-pyrrol-2-yl)-3H-indole (4c)

Into a stirred solution of 4b (1.43 g, 4.75 mmol) in tetrahydrofuran (35 ml) was added, portionwise N-iodosuccinimide (1.28 g, 5.70 mmol). The reaction mixture was stirred 12 h and then poured into cold water before extraction with ethyl acetate. The organic extract was
concentrated under vacuum and the product purified by column chromatography (ethyl acetate/hexane, 1/5, v/v) on silica gel to yield a yellow solid. Yield: 22 %, \( \text{H} \text{NMR (300 MHz, DMSO-d6)} \delta = 7.67 \text{ (d, 1H, J = 1.8 Hz)}, 7.44 \text{ (dd, 1H, J = 8.1 Hz, 2.1 Hz)}, 7.39 \text{ (d, 1H, J = 7.8 Hz)}, 7.30 \text{ (d, 1H, J = 3.3 Hz)}, 6.79 \text{ (d, 1H, J = 3.0 Hz)}, 3.66 \text{ (s, 3H)}, 1.41 \text{ (s, 6H)}. \)

2.1.5. \textit{Pd-catalyzed C-N coupling under Buchwarl-Hartwig conditions}

2.1.5.1. 3,3-Dimethyl-N,N-diphenyl-2-(thiophen-2-yl)-3H-indol-5-amine (1c) and 9-(4-Methoxyphenyl)-N-(9-(4-methoxyphenyl)-9H-carbazol-6-yl)-N-(3,3-dimethyl-2-(thiophen-2-yl)-3H-indol-5-yl)-9H-carbazol-3-amine (6c)

An oven dried 1-neck flask containing a magnetic stirrer was evacuated and backfilled with argon gas. The flask was then charged with tris(dibenzylideneacetone) dipalladium(0) (0.06 g, 0.06 mmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (0.13 g, 0.26 mmol), sodium tert-butoxide (0.44 g, 4.57 mmol), 1b (1 g, 3.26 mmol), diphenylamine (0.66 g, 3.92 mmol) followed, by addition of 15 ml of toluene using syringe. The flask was sealed under a positive pressure of argon with a Teflon screw cap and stirred at 80 °C. The solution was cooled to room temperature and diluted by adding ethyl acetate. The diluted mixture was filtered through Celite and solvent was then evaporated. Purification by column chromatography (ethyl acetate/hexane, 1/6, v/v) on silica gel produced bright yellow solid 1c. Yield: 84 %, \( \text{H} \text{NMR (300 MHz, DMSO-d6)} \delta = 7.82 \text{ (dd, 1H, J = 4.0 Hz, 0.9 Hz)}, 7.79 \text{ (dd, 1H, J = 4.5 Hz, 0.9 Hz)}, 7.47 \text{ (d, 1H, J = 8.1 Hz)}, 7.32 - 7.27 \text{ (m, 4H)}, 7.24 - 7.21 \text{ (m, 2H)}, 7.04 - 6.99 \text{ (m, 6H)}, 6.92 \text{ (dd, 1H, J = 8.1 Hz, 2.4 Hz)}, 1.46 \text{ (s, 6H)}. \)

Compound 6c was produced by exactly same procedure except that V was used in lieu of diphenylamine. The organic extract collected from concentration in vacuum was purified by column chromatography (ethyl acetate/hexane, 1/2, v/v) on silica gel to yield a brownish yellow solid. Yield: 66 %, \( \text{H} \text{NMR (300 MHz, DMSO-d6)} \delta = 8.11 \text{ (d, 2H, J = 7.5 Hz)}, 8.05 \text{ (s, 2H)}, 7.72 - 7.70 \text{ (m, 2H)}, 7.52 \text{ (AA’BB’, 4H)}, 7.39 - 7.33 \text{ (m, 3H)}, 7.27 - 7.13 \text{ (m, 9H)}, 7.19 \text{ (AA’BB’, 4H)}, 7.10 \text{ (d, 1H, J = 1.8 Hz)}, 6.78 \text{ (dd, 1H, J = 8.1 Hz, 2.1 Hz)}, 3.84 \text{ (s, 6H)}, 1.40 \text{ (s, 6H)}. \)
2.1.5.2. 2-(Furan-2-yl)-3,3-dimethyl-N,N-diphenyl-3H-indol-5-amine (2c) and N-(2-(Furan-2-yl)-3,3-dimethyl-3H-indol-5-yl)-9-(4-methoxyphenyl)-N-(9-(4-methoxyphenyl)-9H-carbazol-6-yl)-9H-carbazol-3-amine (7c)

Compound 2c (or 7c) was prepared using the same procedure as for 1c (or 6c) except that 2b was used in lieu of 1b. The crude product collected after evaporation of solvent was purified by column chromatography (ethyl acetate/hexane, 1/4, v/v to yield 2c, ethyl acetate/hexane, 2/1, v/v to yield 7c) on silica gel. For 2c, a yellow solid, Yield: 87 %, \(^1H\) NMR (300 MHz, CDCl\(_3\)) \(\delta = 7.61\) (d, 1H, J = 1.8 Hz), 7.5 (dd, 1H, J = 8.4 Hz, 1.6 Hz), 7.26 ~ 6.97 (m, 13H), 6.57 (dd, 1H, J = 3.6 Hz, 1.8 Hz), 1.47 (s, 6H). For 7c, a brownish yellow solid, Yield: 80 %, \(^1H\) NMR (300 MHz, DMSO-d\(_6\)) \(\delta = 8.11 - 8.07\) (m, 4H), 7.92 (d, 1H, J = 1.2 Hz), 7.53 (AA’BB’, 4H), 7.41 ~ 7.35 (m, 3H), 7.28 - 7.14 (m, 14H), 6.81 (dd, 1H, J = 8.7 Hz, 2.4 Hz), 6.70 (dd, 1H, J = 3.6 Hz, 1.8 Hz), 1.36 (s, 6H).

2.1.5.3. 3,3-Dimethyl-N,N-diphenyl-2-(thiazol-2-yl)-3H-indol-5-amine (3c) and 9-(4-Methoxyphenyl)-N-(9-(4-methoxyphenyl)-9H-carbazol-6-yl)-N-(3,3-dimethyl-2-(thiazol-2-yl)-3H-indol-5-yl)-9H-carbazol-3-amine (8c)

Compound 3c (or 8c) was prepared using the same procedure as in 1c (or 6c) except the 3b was used in lieu of 1b. The crude product collected after evaporation of solvent was purified by column chromatography (ethyl acetate/hexane, 1/11, v/v to yield 3c, ethyl acetate/hexane, 1/2, v/v to yield 8c) on silica gel. For 3c, a brownish yellow solid, Yield: 28 %, \(^1H\) NMR (300 MHz, DMSO-d\(_6\)) \(\delta = 8.11\) (d, 1H, J = 3 Hz), 7.98 (d, 1H, J = 3.3 Hz), 7.57 (d, 1H, J = 8.1 Hz), 7.34 - 7.29 (m, 4H), 7.20 (d, 1H, J = 2.4 Hz), 7.08 - 7.03 (m, 6H), 6.94 (dd, 1H, J = 8.1 Hz, 2.1 Hz), 1.52 (s, 6H). For 8c, an orange solid, Yield: 39 %, \(^1H\) NMR (300 MHz, DMSO-d\(_6\)) \(\delta = 8.16 - 8.13\) (m, 4H), 8.07 (d, 1H, J = 3.3 Hz), 7.92 (d, 1H, J = 3.3 Hz), 7.54 (AA’BB’, 4H), 7.47 (d, 1H, J = 8.7 Hz), 7.40 (t, 2H, J = 7.8 Hz), 7.32 - 7.16 (m, 8H), 7.21 (AA’BB’, 4H), 7.09 (d, 1H, J = 2.1 Hz), 6.81 (dd, 1H, J = 8.4 Hz, 2.4 Hz), 3.87 (s, 6H), 1.48 (s, 6H).
2.1.5.4. 5-(5-(Diphenylamino)-3,3-dimethyl-3H-indol-2-yl)-1-methyl-1H-pyrrole-2-carbaldehyde (4e) and 5-(5-(9-(4-Methoxyphenyl)-N-(9-(4-methoxyphenyl)-9H-carbazol-6-yl)-9H-carbazol-3-amino)-3,3-dimethyl-3H-indol-2-yl)-1-methyl-1H-pyrrole-2-carbaldehyde (9e)

Compound 4e (or 9e) was prepared using the same procedure as for 1c (or 6c) except that 4d was used in lieu of 1b. The crude product collected after evaporation of solvent was purified by column chromatography on silica gel (ethyl acetate/hexane, 1/1.5, v/v) to yield 4e, ethyl acetate/hexane, 1/3, v/v) to yield 9e. For 4e, a brownish yellow solid, Yield: 80 %, $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta = 7.49$ (d, 1H, J = 8.1 Hz), 7.32 - 7.26 (m, 5H), 7.19 (d, 1H, J = 1.8 Hz), 7.04 - 6.99 (m, 6H), 6.93 (dd, 1H, J = 8.4 Hz, 2.1 Hz), 3.94 (s, 3H from N-methyl.), 1.42 (s, 6H). For 9e, a yellowish brown solid, Yield: 31 %, $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta = 10.42$ (s, 1H), 8.12 (d, 2H, J = 7.5 Hz), 8.06 (d, 2H, J = 1.5 Hz), 7.54 (AA’BB’, 4H), 7.41 - 7.36 (m, 3H), 7.29 - 7.12 (m, 9H), 7.21 (AA’BB’, 4H), 7.11 (d, 1H, J = 2.4 Hz), 6.81 (dd, 1H, J = 8.4 Hz, 2.1 Hz), 6.75 (d, 1H, J = 2.7 Hz), 3.87 (s, 6H), 1.37 (s, 6H).

2.1.5.5. 4-(5-(Diphenylamino)-3,3-dimethyl-3H-indol-2-yl)benzaldehyde (5d) and 4-(5-(9-(4-Methoxyphenyl)-N-(9-(4-methoxyphenyl)-9H-carbazol-6-yl)-9H-carbazol-3-amino)-3,3-dimethyl-3H-indol-2-yl)benzaldehyde (10d)

Compound 5d (or 10d) was prepared using the same procedure as for 1c (or 6c) except that 5c was used in lieu of 1b. The crude product collected after evaporation of solvent was purified by column chromatography on silica gel (ethyl acetate/hexane, 1/5, v/v) to yield 5d, (ethyl acetate/hexane, 1/2, v/v) to yield 10d. For 5d, a yellow-orange solid, Yield: 73 %, $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta = 8.35$ (d, 2H, J = 8.4 Hz), 8.09 (d, 2H, J = 8.4 Hz), 7.58 (d, 1H, J = 8.4 Hz), 7.34 - 7.29 (m, 4H), 7.23 (d, 1H, J = 2.1 Hz), 7.08 - 7.02 (m, 6H), 6.95 (dd, 1H, J = 8.1 Hz, 2.1 Hz), 1.51 (s, 6H). For 10d, red solid, Yield: 30 %, $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta = 10.07$ (s, 1H), 8.32 (d, 2H, J = 8.7 Hz), 8.15 - 8.12 (m, 4H), 8.00 (d, 2H, J = 8.4 Hz), 7.54 (AA’BB’, 4H), 7.48 (d, 1H, J = 8.4 Hz), 7.40 (t, 2H, J = 8.1 Hz), 7.31 - 7.16 (m, 12H), 7.12 (d, 1H, J = 2.1 Hz), 6.83 (dd, 1H, J = 8.4 Hz, 2.4 Hz), 3.87 (s, 6H), 1.46 (s 6H).
2.1.6. Formylation

2.1.6.1. 5-(5-(Diphenylamino)-3,3-dimethyl-3H-indol-2-yl)thiophene-2-carbaldehyde (1d) and 5-(5-(9-(4-Methoxyphenyl)-N-(9-(4-methoxyphenyl)-9H-carbazol-6-yl)-9H-carbazol-3-amino)-3,3-dimethyl-3H-indol-2-yl)thiophene-2-carbaldehyde (6d)

A solution of 1c (0.9 g, 2.28 mmol) in THF (90 ml) was cooled to -78 °C while the system was purged with N$_2$. n-BuLi (2.85 ml, 4.56 mmol) was added dropwise over 10 min and the reaction mixture was stirred at -78 °C for 1 h. The solution kept at -78 °C for a dropwise addition of dry N,N-dimethylformaldehyde (0.53 ml, 6.84 mmol). The reaction mixture was stirred for additional 1 h at -78 °C before allowing it warm to 0 °C. The solution was neutralized using 10 % HCl. The crude product obtained from extractions with dichloromethane was dried over anhydrous MgSO$_4$ and concentrated under vacuum. Purification was performed by column chromatography (ethyl acetate/hexane, 1/2, v/v) on silica gel to give an orange solid. Yield: 59 %, $^1$H NMR (300 MHz, DMSO-d6) $\delta$ = 9.98 (s, 1H), 8.09 (d, 1H, J = 3.9 Hz), 7.98 (d, 1H, J = 4.2 Hz), 7.55 (d, 1H, J = 8.7 Hz), 7.34 - 7.29 (m, 4H), 7.22 (d, 1H, J = 2.1 Hz), 7.08 - 7.02 (m, 6H), 6.92 (dd, 1H, J = 8.4 Hz, 2.1 Hz), 1.47 (s, 6H).

Likewise, compound 6d was produced from starting material 6c. The crude product collected from concentration under vacuum was purified by column chromatography (ethyl acetate/hexane, 1/2, v/v) on silica gel, to yield a violet-red solid. Yield: 80 %, $^1$H NMR (700 MHz, DMSO-d6) $\delta$ = 9.96 (s, 1H), 8.14 (d, 2H, J = 7.7 Hz, 0.7 Hz), 8.12 (dd, 2H, J = 2.1 Hz, 0.7 Hz), 8.03 (d, 1H, J = 4.2 Hz), 7.88 (d, 1H, J = 3.5 Hz), 7.54 (AA’BB’, 4H), 7.45 (d, 1H, J = 8.4 Hz), 7.40 (ddd, 2H, J = 8.8Hz, 6.8 Hz, 0.7 Hz), 7.33 - 7.21 (m, 8H), 7.21 (AA’BB’, 4H), 7.11 (d, 1H, J = 2.8 Hz), 6.81 (dd, 1H, J = 8.4 Hz, 2.1 Hz), 3.87 (s, 6H), 1.43 (s, 6H).

2.1.6.2. 5-(5-(Diphenylamino)-3,3-dimethyl-3H-indol-2-yl)furan-2-carbaldehyde (2d) and 5-(5-(9-(4-Methoxyphenyl)-N-(9-(4-methoxyphenyl)-9H-carbazol-6-yl)-9H-carbazol-3-amino)-3,3-dimethyl-3H-indol-2-yl)furan-2-carbaldehyde (7d)

Compound 2d and 7d were prepared using the same procedure as for 1d except that 2c (or 7c) was used as a starting material instead of 1c. The crude product obtained from
evaporation of solvent was purified by column chromatography on silica gel (ethyl acetate/hexane, 1/3, v/v) to yield 2d, (ethyl acetate/hexane, 1/1, v/v) to yield 7d. For 2d, an orange solid, Yield: 15 %, $^1$H NMR (300 MHz, DMSO-d6) δ = 9.73 (s, 1H), 7.70 (d, 1H, J = 3.9 Hz), 7.55 (d, 1H, J = 8.1 Hz), 7.50 (d, 1H, J = 3.6 Hz), 7.34 ~ 7.29 (m, 4H), 7.21 (d, 1H, J = 2.7 Hz), 7.08 - 7.02 (m, 6H), 6.94 (dd, 1H, J = 8.1 Hz, 2.4 Hz), 1.45 (s, 6H). For 7d, a violet–red solid, Yield: 13 %, $^1$H NMR (300 MHz, DMSO-d6) δ = 9.69 (s, 1H), 8.16 – 8.13 (m, 4H), 7.68 (d, 1H, J = 3.9 Hz), 7.54 (AA ’BB’, 4H), 7.47 – 7.16 (m, 16H), 7.10 (d, 1H, J = 2.1 Hz), 6.82 (dd, 1H, J = 8.7 Hz, 2.4 Hz), 3.87 (s, 6H), 1.41 (s, 6H).

2.1.6.3. 2-(5-(Diphenylamino)-3,3-dimethyl-3H-indol-2-yl)thiazole-5-carbaldehyde (3d) and 2-(5-(9-(4-Methoxyphenyl)-N-(9-(4-methoxyphenyl)-9H-carbazol-6-yl)-9H-carbazol-3-amino)-3,3-dimethyl-3H-indol-2-yl)thiazole-5-carbaldehyde (8d)

Compounds 3d and 8d were prepared using the same procedure as for 1d except that 3c (or 8c) was used as a starting material instead of 1c. The crude product obtained from evaporation of solvent was purified by column chromatography on silica gel (ethyl acetate/hexane, 1/6, v/v) to yield 3d, (ethyl acetate/hexane, 1/2.5, v/v) to yield 8d. For 3d, a reddish orange solid, Yield: 51 %, $^1$H NMR (300 MHz, DMSO-d6) δ = 10.12 (s, 1H), 8.89 (s, 1H), 7.64 (d, 1H, J = 8.4 Hz), 7.36 -7.31 (m, 4H), 7.19 (d, 1H, J = 1.8 Hz), 7.12 - 7.06 (m, 6H), 6.93 (dd, 1H, J = 8.1 Hz, 2.1 Hz), 1.53 (s, 6H). For 8d, a violet–red solid, Yield: 88 %, $^1$H NMR (300 MHz, DMSO-d6) δ = 10.10 (s, 1H), 8.85 (s, 1H), 8.17 ~ 8.15 (4H), 7.54 (AA ‘BB’, 4H), 7.56 - 7.17 (m, 13H), 7.42 (t, 2H, J = 8.4 Hz), 7.08 (d, 1H, J = 2.4 Hz), 6.81 (dd, 1H, J = 8.7 Hz, 2.4 Hz), 1.48 (s, 6H).

2.1.6.4. 5-(5-Bromo-3,3-dimethyl-3H-indol-2-yl)-1-methyl-1H-pyrrole-2-carbaldehyde (4d)

Compound 4d was produced using the same procedure as in 1d except 4c was used in lieu of 1c. The crude product obtained from evaporation of solvent was purified by column chromatography (ethyl acetate/hexane, 1/1.5, v/v) on silica gel, to yield a yellow solid. Yield:
2.1.6.5. 4-(5-Bromo-3,3-dimethyl-3H-indol-2-yl)benzaldehyde (5c)

Compound 5c was produced using the same procedure as for 1d except that 5b was used in lieu of 1c. The crude product obtained from evaporation of solvent was purified by column chromatography (ethyl acetate/hexane, 1/6, v/v) on silica gel, to yield a pale yellow solid. Yield: 41 %, 1H NMR (300 MHz, DMSO-d6) δ = 8.39 (d, 2H, J = 8.4 Hz), 8.05 (d, 2H, J = 8.1 Hz), 7.87 (d, 1H, J = 1.8 Hz), 7.62 (d, 1H, J = 8.4 Hz, 7.56 (dd, 1H, J = 8.1 Hz, J = 2.1 Hz), 1.58 (s, 6H).

2.1.7. Knoevenagel reaction for formation of dye

2.1.7.1. (2E)-2-Cyano-3-(5-(5-(diphenylamino)-3,3-dimethyl-3H-indol-2-yl)thiophen-2-yl)acrylic acid (D1) and (2E)-2-Cyano-3-(5-(5-(4-methoxyphenyl)-N-(9-(4-methoxyphenyl)-9H-carbazol-6-yl)-9H-carbazol-3-amino)-3,3-dimethyl-3H-indol-2-yl)thiophen-2-yl)acrylic acid (D6)

To a solution of compound 1d (0.3 g, 0.70 mmol) and 2-cyanoacetic acid (0.07 g, 0.85 mmol) in acetonitrile (70 ml) was added a few drops of piperidine under N2 gas flow. The reaction mixture was then stirred under reflux at 80 °C. The precipitate formed during reaction was collected by filtration and dried. Pure D1 was obtained by column chromatography (dichloromethane/methanol, 12/1, v/v) on silica gel, to give a red solid. Yield: 87 %, 1H NMR (300 MHz, DMSO-d6) δ = 8.13 (s, 1H), 7.87 (d, 1H, J = 3.9 Hz), 7.76 (d, 1H, J = 3.6 Hz), 7.54 (d, 1H, J = 8.4 Hz), 7.33 - 7.28 (m, 4H), 7.21 (d, 1H, J = 2.1 Hz), 7.06 - 7.01 (m, 6H), 6.93 (dd, 1H, J = 8.2 Hz, 2.1 Hz), 1.47 (s, 6H). HRMS-ESI: calculated for C30H25N3O2S (M+H)/z 490.1584, Found: 490.1579. D6 was prepared using same procedure as for D1 to afford a reddish violet solid, using 6d instead of 1d as a starting material. The precipitate collected from filtration was purified by column chromatography.
(dichloromethane/methanol, 11/1, v/v) on silica gel. Yield: 24 %, $^1$H NMR (300 MHz, DMSO-d6) $\delta$ = 8.15 (d, 2H, J = 7.8 Hz), 8.107 (s, 2H), 8.105 (s, 1H), 7.79 (d, 1H, J = 3.9 Hz), 7.73 (d, 1H, J = 3.9 Hz), 7.55 (AA’BB’, 4H), 7.45 (d, 1H, J = 8.1 Hz), 7.40 (td, 2H, J = 8.1 Hz, J = 1.2 Hz), 7.31 - 7.16 (m, 12H), 7.12 (d, 1H, J = 1.8 Hz), 6.81 (dd, 1H, J = 8.4 Hz, 2.1 Hz), 3.87 (s, 6H), 1.43 (s, 6H).

HRMS-ESI: calculated for C$_{56}$H$_{41}$N$_5$O$_4$S (M+H)/z 880.2952, Found: 880.2940.

2.1.7.2. (2E)-2-Cyano-3-((5-(5-(diphenylamino)-3,3-dimethyl-3H-indol-2-yl)furan-2-yl)acrylic acid (D2) and (2E)-2-Cyano-3-((5-(9-(4-methoxyphenyl)-N-(9-(4-methoxyphenyl)-9H-carbazol-6-yl)-9H-carbazol-3-amino)-3,3-dimethyl-3H-indol-2-yl)furan-2-yl)acrylic acid (D7)

D2 and D7 were prepared using the same procedure as for D1 except that 2d (or 7d) was used as a starting material instead of 1d. Pure D2 and D7 were obtained by column chromatography (dichloromethane/methanol, 10/1, v/v to yield D2, dichloromethane/methanol, 10/1, v/v to yield D7) on silica gel. For D2, red solid, Yield: 29 %, $^1$H NMR (300 MHz, DMSO-d6) $\delta$ = 7.38 (s, 1H), 7.49 (d, 1H, J = 8.4 Hz), 7.46 (d, 1H, J = 3.6 Hz), 7.35 (d, 1H, J = 3.6 Hz), 7.33 - 7.28 (m, 4H), 7.18 (d, 1H, J = 2.1 Hz), 7.07 - 7.01 (m, 6H), 6.92 (dd, 1H, J = 8.1 Hz, 2.1 Hz), 1.52 (s, 6H). HRMS-ESI: calculated for C$_{30}$H$_{23}$N$_3$O$_3$ (M+H)/z 474.1812, Found: 474.1806. For D7, a dark red solid, Yield: 74 %, $^1$H NMR (300 MHz, DMSO-d6) $\delta$ = 8.14 (d, 2H, J = 7.8 Hz), 8.10 (s, 2H), 7.78 (s, 1H), 7.55 (AA’BB’, 4H), 7.41 - 7.37 (m, 3H), 7.31 - 7.16 (m, 14H), 7.08 (d, 1H, J = 2.4 Hz), 6.08 (dd, 1H, J = 8.08 (dd, 1H, J = 8.4 Hz, 2.1 Hz), 3.87 (s, 6H), 1.48 (s, 6H). HRMS-ESI: calculated for C$_{56}$H$_{41}$N$_5$O$_5$ (M+H)/z 864.3180, Found: 864.3138.
2.1.7.3. (2E)-2-Cyano-3-(2-(5-(diphenylamino)-3,3-dimethyl-3H-indol-2-yl)thiazol-5-y1)acrylic acid (D3) and (2E)-2-Cyano-3-(2-(5-(4-methoxyphenyl)-N-(9-(4-methoxyphenyl)-9H-carbazol-6-yl)-9H-carbazol-3-amino)-3,3-dimethyl-3H-indol-2-yl)thiazol-5-y1)acrylic acid (D8)

D3 and D8 were prepared using the same procedure as for D1 except that 3d (or 8d) was used as a starting material instead of 1d. The pure D3 and D8 were obtained by column chromatography (dichloromethane/methanol, 11/1, v/v) on silica gel, to yield D3, (dichloromethane/methanol, 11/1, v/v) to yield D8. For D3, dark red solid, Yield: 49 %, ¹H NMR (300 MHz, DMSO-d₆) δ = 8.55 (s, 1H), 8.18 (s, 1H), 7.62 (d, 1H, J = 8.4 Hz), 7.35 - 7.30 (m, 4H), 7.19 (d, 1H, J = 2.1 Hz), 7.09 - 7.04 (m, 6H), 6.95 (dd, 1H, J = 8.1 Hz, 2.1 Hz), 1.52 (s, 6H). HRMS-ESI: calculated for C₂₉H₂₂N₄O₂S (M+H)/z 491.1536, Found: 491.1531.

For D8, a reddish violet solid, Yield: 84 %, ¹H NMR (300 MHz, DMSO-d₆) δ = 8.51 (s, 1H from vinyl.), 8.19 - 8.15 (m, 5H), 7.56 - 7.51 (m, 5H), 7.42 - 7.17 (m, 14H), 7.08 (d, 1H, J = 2.4 Hz), 6.83 (dd, 1H, J = 8.4 Hz, 2.4 Hz), 3.87 (s, 6H), 1.48 (s, 6H). HRMS-ESI: calculated for C₅₅H₄₀N₆O₄S (M+H)/z 881.2905, Found: 881.2878.

2.1.7.4. (2E)-2-Cyano-3-(5-(5-(diphenylamino)-3,3-dimethyl-3H-indol-2-yl)-1-methyl-1H-pyrrol-2-yl)acrylic acid (D4) and (2E)-2-Cyano-3-(5-(5-(9-(4-methoxyphenyl)-N-(9-(4-methoxyphenyl)-9H-carbazol-6-yl)-9H-carbazol-3-amino)-3,3-dimethyl-3H-indol-2-yl)-1-methyl-1H-pyrrol-2-yl)acrylic acid (D9)

To a stirred solution of 4e (0.13 g, 0.31 mmol) and 2-cyanoacetic acid (0.05 g, 0.61 mmol) in ethanol (20 ml) was added NaOH (0.05 g, 1.22 mmol) under N₂ gas flow. The reaction mixture was then stirred under reflux at 80 °C. The mixture formed during reaction was filtered and product was dried. Pure D4 was obtained by column chromatography (dichloromethane/methanol, 10/1, v/v) on silica gel, to afford an orange-yellow solid. Yield: 34 %, ¹H NMR (300 MHz, DMSO-d₆) δ = 8.28 (s, 1H), 7.34 (d, 1H, J = 8.4 Hz), 7.30 - 7.25 (m, 4H), 7.18 (d, 1H, J = 2.7 Hz), 7.15 (d, 1H, J = 2.1 Hz), 7.02 - 6.97 (m, 6H), 6.90 (dd, 1H, J = 8.4 Hz, 2.4 Hz), 6.80 (d, 1H, J = 3.0 Hz), 1.40 (s, 6H). HRMS-ESI: calculated for C₃₁H₂₆N₄O₂ (M+H)/z 487.2129, Found: 487.2129.
D9 was produced by the same procedure as in D4 from which 9e was used as a starting material in lieu of 4e. The crude dye was purified by column chromatography (dichloromethane/methanol, 10/1, v/v) on silica gel, to yield a red brown solid. Yield: 53 %. $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$ = 8.11 - 8.07 (m, 4H), 7.92 (s, 1H), 7.53 (AA’BB’, 4H), 7.38 (ddd, 2H), 7.35 - 7.09 (m, 15H), 6.81 (dd, 1H, J = 8.4 Hz, 2.4 Hz), 6.70 (dd, 1H, J = 3.4 Hz, 1.5 Hz), 3.86 (s, 6H), 3.34 (s, 3H), 1.36 (s, 6H). HRMS-ESI: calculated for C$_{57}$H$_{44}$N$_6$O$_4$ (M+H)/z 877.3497, Found: 877.3485.

2.1.7.5. (2E)-2-Cyano-3-(4-(5-(diphenylamino)-3,3-dimethyl-3H-indol-2-yl)phenyl)acrylic acid (D5) and (2E)-2-Cyano-3-(4-(5-(9-(4-methoxyphenyl)-N-(9-(4-methoxyphenyl)-9H-carbazol-6-yl)-9H-carbazol-3- amino)-3,3-dimethyl-3H-indol-2-yl)phenyl)acrylic acid (D10)

D5 and D10 were prepared using the same procedure as for D4 except that 5d (or 10d) was used as a starting material instead of 4e. Pure D5 and D10 were obtained by column chromatography on silica gel (dichloromethane/methanol, 10/1, v/v) to yield D5, dichloromethane/methanol, 10/1, v/v) to yield D10). For D5, an orange solid, Yield: 36 %, $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$ = 8.25 (d, 2H, J = 8.4 Hz), 7.99 (d, 2H, J = 8.1 Hz), 8.00 (s, 1H), 7.56 (d, 1H, J = 8.1 Hz), 7.33 - 7.28 (m, 4H), 7.21 (d, 1H, J = 1.8 Hz), 7.06 - 7.02 (m, 6H), 6.94 (dd, 1H, J = 8.4 Hz, 2.1 Hz), 1.50 (s, 6H). HRMS-ESI: calculated for C$_{32}$H$_{25}$N$_3$O$_2$ (M+H)/z 484.2020, Found: 484.2017. For D10, a red solid, Yield: 36 %, $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$ = 8.21 (d, 2H, J = 9 Hz), 8.15 - 8.10 (m, 4H), 7.90 (d, 2H, J = 8.7 Hz), 7.96 (s, 1H), 7.54 (AA’BB’, 4H), 7.46 (d, 1H, J = 8.4 Hz), 7.39 (td, 2H, J = 8.1 Hz, 1.2 Hz), 7.31 - 7.16 (m, 12H), 7.11 (d, 1H, J = 2.1 Hz), 6.82 (dd, 1H, J = 8.7 Hz, 2.4 Hz), 3.87 (s, 6H), 1.46 (s, 6H). HRMS-ESI: calculated for C$_{58}$H$_{43}$N$_5$O$_4$ (M+H)/z 874.3388, Found: 874.3396.

2.2. Structure confirmation

$^1$H NMR spectra were recorded on a 300 MHz Bruker Advance spectrometer using DMSO-$d_6$ or CDCl$_3$ as a solvent. $^{13}$C NMR was measured on a 500 MHz Bruker Advance
spectrometer. 2-Dimensional NMR spectra including COSY, HSQC, and HMBC were recorded on a 500 MHz or 700 MHz Bruker Advance. HRMS (high resolution mass spectra) were obtained using electrospray ionization (ESI), in the positive mode, on an Agilent Technologies (Santa Clara, California) 6210 LC-TOF mass spectrometer.

2.3. Molecular modeling

DFT (density functional theory)\textsuperscript{90} calculations were conducted using Gaussian 03 software. Geometries were optimized using the B3LYP hybrid functional (Beck’s three-parameter functional and Lee-Yang-Parr functional) as an exchange-correlation functional\textsuperscript{91} and 3-21G(d) was used as the basis set. HOMO and LUMO orbitals were determined using optimized geometries. Transition energies were calculated using TDDFT (time-dependent density functional theory)\textsuperscript{92}. B3LYP and BHandH (designed by Becke with 50% of LSDA exchange)\textsuperscript{91-a} were implemented to study electronic transitions.

2.4. Fabrication of dye sensitized solar cell\textsuperscript{93}

To prepare a porous TiO\textsubscript{2} electrode, an FTO glass plate (F-doped SnO\textsubscript{2}, TEC-8, 8Ω, Pilkington, USA, 2.2 mm thick) was cleaned in a detergent solution using an ultrasonic bath, for 15 min, followed by rinsing with water and ethanol. Residual contaminants were removed by heating the cleaned FTO glass at 400 °C for 20 min. A layer of TiO\textsubscript{2} anatase nanoparticles (Ti-Nanoxide D/SP, Solaronix, Switzerland) was first coated on FTO glass using a doctor-blade method. After drying the film at 120 °C, a scattering layer of TiO\textsubscript{2} nanoparticles (Ti-Nanoxide R/SP, Solaronix, Switzerland) was deposited and then gradually heated in air at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and sintered at 500 °C for 15 min. The resulting thin film was composed of a 12 μm thick TiO\textsubscript{2} nanocrystalline layer and a 6 μm thick scattering layer. The nanoporous TiO\textsubscript{2} electrode was immersed into 0.3 mM dye solution in THF and kept at room temperature 24 h to give adsorption of dye onto the TiO\textsubscript{2} surface. Coadsorbate of 1 mM DCA (deoxycholic acid) was added.
A platinized electrode was prepared by placing a drop of H$_2$PtCl$_6$ solution (2 mg Pt in 1 mL ethanol) on punctured FTO and subsequent heating at 400 °C for 15 min. The dye loaded TiO$_2$ electrode and thermally platinized counter electrode were sealed together with a 60 μm hot-melt gasket (Suryln 1702, Dupont). After injecting electrolyte into cell by vacuum backfilling, the cell was again encapsulated using sealant (Suryln 1702, Dupont, 60 μm thick) and a cover glass. Two types of electrolytes were employed for performance measurement of the DSSCs, which were composed of 0.6 M DMPII (1,2-dimethyl-3-n-propylimidazolium iodide), 0.1 M LiI, 0.05M I$_2$ or 0.6 M DMPII (1,2-dimethyl-3-n-propylimidazolium iodide), 0.1 M LiI, 0.05M I$_2$, 0.5 M TBP (4-tert butyl pyridine) in anhydrous acetonitrile (anhyd. AN). An N719 dye mediated DSSC was fabricated as a reference cell for device measurements, where a 0.3 mM dye solution in ethanol was used and the electrolyte composition was 0.1 M LiI, 0.05M I$_2$ or 0.6 M DMPII (1,2-dimethyl-3-n-propylimidazolium iodide), 0.1 M LiI, 0.05M I$_2$, 0.5 M TBP (4-tert butyl pyridine) in anhyd. AN.

2.5. Characterizations

2.5.1. Spectroscopic analysis

UV-Vis spectra in solution and in dye-loaded TiO$_2$ film were recorded on a Varian Cary 300 UV-Vis spectrophotometer. Photoluminescence of dye solutions was recorded using a fluorometer (Fluorolog®-3, HORIBA, USA) equipped with a 450 W xenon lamp (FL-1039/40, HORIBA, USA). Concentration of dye solution for emission spectra was constrained to have absorbance of ~ 0.2. Fluorescence lifetime of each dye in THF was measured by a system using a TCSPC (time-correlated single photon counting) controller. LED (NanoLED-460, HORIBA) having a peak wavelength of 460 nm was used as an excitation source and Ludox® in distilled water was used as an internal reference. The instrument response was measured below 200 ns of time range. The decay curve obtained was fitted to multi-exponential function which is represented by $A + B_1\exp\left(-t/T_1\right) + B_2\exp\left(-t/T_2\right)$. In order to predict the amount of dye adsorbed on TiO$_2$ surface, dye on TiO$_2$ film dissolved in 0.1 M NaOH in THF-H$_2$O (v/v, 1:1) followed by measurement of UV-Vis spectra which
leads to calculation of adsorbed amount of dye using Beer-Lambert’s law. Thickness of dye loaded TiO$_2$ film for all characterizations was 6 μm.

2.5.2. Voltammetry and impedance measurement
The oxidation potential of dye adsorbed on TiO$_2$ films was measured using a three electrode electrochemical cell in acetonitrile containing 0.1 M TBAPF$_6$ (tetrabutylammonium hexafluorophosphate) at a scan rate of 100 mVs$^{-1}$. Dye coated TiO$_2$ film was used as a working electrode and Ag/Ag+ electrode and Pt wire were employed as a reference and counter electrode, respectively. The potential of the working electrode was calibrated with ferrocene as an internal reference. The impedance spectroscopy of the cell was recorded using an impedance analyzer connected to a potentiostat (reference 600™, Gamry instruments, USA) in a frequency range of 0.1 Hz - $10^5$ Hz at room temperature under dark condition. The applied forward bias was between - 0.65 V and AC amplitude was set to 10 mV.

2.6. Photovoltaic measurement
Photocurrent-voltage characteristics of DSSCs were measured using a Keithley 2400 source meter under illumination of AM 1.5 G solar light coming from solar simulator (SOL3A, Oriel) equipped with a 450 W xenon lamp (91160, Oriel). The incident light intensity was calibrated using a reference Si solar cell (Newport Oriel, 91150V) to set 1 Sun (1mW/cm$^2$). The current-voltage curve of the cell was obtained by applying external voltage bias and the measuring generated photocurrent. The measurement was fully controlled under Oriel IV Test Station software. A mask (0.30 cm$^2$) was covered on the testing cell during photocurrent and voltage measurement. Photo active area of cell was 0.5 X 0.4 cm.

IPCE (incident monochromatic photon to current conversion efficiency) experiments were carried out using a system (QEX10, PV Measurements, USA) equipped with a 75 W short arc xenon lamp (UXL-75XE, USHIO, Japan) as a light source connected to a monochrometer. Calibration of incident light was performed using a silicone photodiode
Monochromatic quantum efficiency was recorded at short circuit conditions under AC mode with white-light bias. Wavelength sampling interval was 10 nm. The beam size of monochromatic light illuminated on DSSCs was $0.1 \times 0.5$ cm and chopping speed of AC was set to 10 Hz.
Chapter 3. Results and Discussion

3.1. Synthesis and structure confirmation

3.1.1. Synthetic routes

Scheme 3.1 and Scheme 3.2 show pathways for the synthesis of dyes D1 - D10. Both series of dyes were prepared using the same synthetic approach and reaction intermediates, except an additional synthetic step was needed to make the carbazole-based amine unit in the synthesis of Series 2. In order to make the target carbazole-based amine unit V, carbazole and 4-iodoanisole were reacted under Ullman conditions. The resultant intermediate I was either brominated or aminated, through nitration, for the formation of II and IV, respectively. Subsequent C-N coupling of II with IV by the Buchwald-Hartwig reaction produced V. Intermediates 1a, 2a, 4a, 5a were synthesized by the reaction of each heterocyclic starting material with isobutyric chloride (or isobutyric anhydride) in the presence of Lewis acid. 2-Trimethylsilyl thiazole was used as a starting material to produce 3a.

Target dyes D1 - D3 and D6 – D8 were synthesized by the Knoevenagel reaction of formylated intermediates (1d - 3d) with cyanoacrylic acid. Compounds 1b - 3b were prepared from the 4-bromophenyl hydrazine and 2-isobutyryl substituted heterocyclic intermediates (1a, 2a, and 3a) by Fisher indole cyclization. Subsequent C-N coupling of 1b – 3b with diphenylamine (or V in the case of Series 2) under Buchwarld-Hartwig conditions produced intermediates 1c - 3c. In order to make formylated 1d - 3d, an organometallation method, involving n-BuLi followed by the addition of DMF, was used.

Target dyes D4 and D5 (or D9 and D10) were prepared using the same method employed for dyes D1, D2, and D3 (or D6, D7, and D8) except using iodinated intermediates (4c, 5b) in the formylation step. The use of these iodinated intermediates was aimed at the halogen-metal exchange step, since the α-proton of N-methyl pyrrole or para-proton of benzene is not acidic enough to undergo deprotonation by n-BuLi.
Scheme 3.1. Synthetic pathways for the intermediates for indole formation (upper) and carbazole-based amine unit employed for the Series 2 (bottom).
Scheme 3.2. Synthetic routes to dyes D1 - D10, where R’2NH refers to the carbazole based amine unit.
3.1.2. **2-Dimensional NMR analysis**

2-Dimensional NMR spectra was used to characterize the structural isomer of acylated N-methyl pyrrole (4a: 2-methyl-1-(1-methyl-1H-pyrrol-2-yl)propan-1-one). A related study involving pyrrole derivatives\(^{95}\) pointed out the formation of acylated products from both ortho and para position of pyrrole rings. Therefore, the desired structural isomer (4a) was needed to be confirmed to identify it from the possible structural isomer 2-methyl-1-(1-methyl-1H-pyrrol-3-yl)propan-1-one.

Fig 3.1 – 3.4 shows 2-D NMR spectra of target product 4a, where the chemical shifts of each proton and carbon are assigned via COSY and HSQC analysis. Eventually, long range coupling of H\(_d\) with both C\(_2\) and C\(_5\) (reference given numbers from inset of Fig. 3.1) was identified, confirming the desired structural isomer.

![COSY of 2-methyl-1-(1-methyl-1H-pyrrol-2-yl)propan-1-one (4a).](image)
**Fig. 3-2.** HSQC of 2-methyl-1-(1-methyl-1H-pyrrol-2-yl)propan-1-one (4a).

**Fig. 3-3.** HMBC of 2-methyl-1-(1-methyl-1H-pyrrol-2-yl)propan-1-one (4a).
3.2. Molecular modeling

3.2.1. Electronic properties

A key component of the design of D1 – D10 was prediction of the properties of dyes having these types of D-π-A systems. DFT calculations were used to predict electronic energies and physical properties including dipole moments and polarizabilities for dyes D1 - D10, the results of which are shown in Table 3.1 All dyes gave calculated lumo values above the conduction band edge of TiO$_2$ (-4.0 eV vs vacuum). Introduction of a carbazole-based amine unit in lieu of diphenylamine as the donor group resulted in more negative homo and lumo values compared to those from diphenylamine based dyes D1 - D5. This is consistent with previous research showing that strong electron donor causes a negative shift in homo and lumo$^{99}$. Comparing results for Series 2 with respect to Series 1, these shifts were
generally more pronounced for the homo than the lumo, resulting in a decreased energy gap between homo and lumo. Therefore, based on the calculated electronic properties, it is believed that the carbazole-based donor imparts a more electron rich nature to the donor side of these push-pull structures.

Concerning the effects of heterocyclic linkers on the energy of the lumo, the lumo energy decreased in the order of N-methyl pyrrole > furan > thiophene > thiazole for both series of dyes. Considering delocalization energies of heterocyclic ring of thiophene (29 kcal/mol), thiazole (25 kcal/mol), pyrrole (21 kcal/mol), and furan (16 kcal/mol) compared to benzene (36 kcal/mol), introduction of a simple five-membered heterocyclic linkers on the acceptor side of the push-pull structures is expected to impart not only a more negative shift in the energy of first excited state but also efficient charge transfer relative to the benzene spacer.

Despite the higher delocalization energy of pyrrole-based dyes relative to that of furan-base dyes, the more negative electronic energies of pyrrole-based dyes may be attributable to the reduced electron pulling ability of the molecule due to its electron-rich nature, thus increasing the electronic energy level. On the other hand, the lowest lumo of thiazole based dyes, which has 25kcal/mol of delocalization energy for the thiazole unit, may be responsible for the strong electron pulling effect of thiazole rings introduced in the acceptor side in D-π-A system.

Total dipole moments and polarizabilities were calculated as well as normal dipole moment at the axis where the carboxyl group of the molecule was aligned out of perpendicular to the TiO₂ surface. Generally, both normal dipole moments and polarizabilities were increased by introduction of a carbazole based amine unit. Compared to Series 1, Series 2 having big bulky strong amine unit was found to give a correlation between calculated dipole moments and aromatic delocalization energies of heterocyclic rings. Observed polarizabilities increased in the order of increased electron deficient nature. On the other hand, this dependence of physical properties on electronic nature (or delocalization energies) of heterocyclic rings was less significant in D-π-A system, which has a relatively less strong donor or/and more twisted structure present. That is, in the case of
Series 1, electronic interactions between donor and acceptor (heterocyclic rings) may be reduced and geometry plays an important role in determining physical properties such as dipole moment and polarizability.

Table 3-1. Calculated physical properties based on dye D1 – D10.

<table>
<thead>
<tr>
<th></th>
<th>( E_{\text{homo}} ) (eV)</th>
<th>( E_{\text{lumo}} ) (eV)</th>
<th>( \Delta(E_{\text{homo}} - E_{\text{lumo}}) )</th>
<th>( \mu ) (D)(^a)</th>
<th>( \mu_{\text{normal}} ) (D)(^b)</th>
<th>( \alpha ) (Bohr(^3))(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D1</td>
<td>-5.12</td>
<td>-2.78</td>
<td>2.34</td>
<td>8.62</td>
<td>-4.97</td>
<td>458.93</td>
</tr>
<tr>
<td>D2</td>
<td>-5.08</td>
<td>-2.66</td>
<td>2.42</td>
<td>8.02</td>
<td>-5.27</td>
<td>429.63</td>
</tr>
<tr>
<td>D3</td>
<td>-5.20</td>
<td>-2.99</td>
<td>2.21</td>
<td>7.24</td>
<td>-4.30</td>
<td>467.60</td>
</tr>
<tr>
<td>D4</td>
<td>-5.06</td>
<td>-2.45</td>
<td>2.61</td>
<td>7.76</td>
<td>-2.88</td>
<td>443.74</td>
</tr>
<tr>
<td>D5</td>
<td>-5.14</td>
<td>-2.70</td>
<td>2.44</td>
<td>8.84</td>
<td>-3.42</td>
<td>458.75</td>
</tr>
<tr>
<td>Series 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D6</td>
<td>-4.66</td>
<td>-2.62</td>
<td>2.04</td>
<td>7.86</td>
<td>-7.33</td>
<td>846.16</td>
</tr>
<tr>
<td>D7</td>
<td>-4.59</td>
<td>-2.60</td>
<td>1.99</td>
<td>4.71</td>
<td>-4.09</td>
<td>810.80</td>
</tr>
<tr>
<td>D8</td>
<td>-4.76</td>
<td>-2.78</td>
<td>1.98</td>
<td>7.77</td>
<td>-7.44</td>
<td>849.78</td>
</tr>
<tr>
<td>D9</td>
<td>-4.58</td>
<td>-2.29</td>
<td>2.29</td>
<td>4.88</td>
<td>-4.66</td>
<td>800.51</td>
</tr>
<tr>
<td>D10</td>
<td>-4.66</td>
<td>-2.54</td>
<td>2.13</td>
<td>9.09</td>
<td>-7.67</td>
<td>832.58</td>
</tr>
</tbody>
</table>

All values obtained were calculated using DFT- B3LYP as exchange-correlation functional and 3-21G\(^*\) as basis set. \(^a\)Total dipole moments; unit of Debye. \(^b\)Vertical dipole moment at the geometry of dyes where carboxyl group is vertically bound to the TiO\(_2\) surface; unit of Debye. \(^c\)Isotropic polarizability.

3.2.2. Electron density

Fig. 3.5 and Fig. 3.6 show calculated isodensity surface plots for dyes D1 – D5 and D6 – D10, respectively. The results showed that the homo-lumo excitation moved the electron distribution from the amine substituted indole moiety to the cyanoacrylic acid group. As a result, thermodynamically favorable electron injection as well as efficient charge separation was anticipated by photo-excitation of dyes in DSSCs.
Fig. 3-5. Calculated isodensity surface plots for dyes D1 – D5 (left: homo, right: lumo).
Fig. 3-6. Calculated isodensity surface plots for dyes D6 – D10 (left: homo, right: lumo).
3.2.3. Electronic transition

In order to get insight into electronic transition energies, the TDDFT (time dependent density functional theory) method was employed. The exchange correlation functional for optimized geometry was based on B3LYP for all cases and suggested that the optimized geometry based on B3LYP was similar to that of MP2 (second-order Møller-Plesset Theory) theory\textsuperscript{100} with reduced computational cost.\textsuperscript{74-b} As a starting process for TDDFT calculations, B3LYP and BHandH were used as exchange correlation functionals using optimized structures for Series 1. The resultant vertical transition energies were compared for further studies, which included solvent effects using the PCM (polarizable continuum model).\textsuperscript{101}

As shown in Table 3.2, results of TDDFT calculations implemented in vacuum were found to be dependent on the hybrid functional employed. The B3LYP hybrid functional resulted in overestimation of transition energies compared to the BHandH hybrid functional, which was much more evident for ICT transition (internal charge transfer) band. This overestimation based on B3LYP (having 20% of HF) is consistent with a previous report demonstrating that a fraction of HF (Hartree–Fock) exchange is had a significant effect on predicted $\lambda_{\text{max}}$.\textsuperscript{102} As a result, BHandH hybrid with increased fraction of HF (50%) was selected for further investigation of solvent effects since the expected $\lambda_{\text{max}}$ was much more close to the experimental values. (\textit{vide infra})

Regardless of methods used, there were two main transitions corresponding to absorption band in visible region and in the UV region around 300 nm. In the case of Series 1 dyes based on a diphenylamine donor, the $S_0 \rightarrow S_1$ transition was mainly responsible for homo to lumo transition whereas $S_0 \rightarrow S_2$ was mainly due to the homo-1 to lumo transition. Using D\textsuperscript{1} (Fig. 3.7) as an example of electron densities in homo, lumo, homo-1 level, $S_0 \rightarrow S_1$ was assigned to the ICT transition, while the $S_0 \rightarrow S_2$ transition was identified as a localized $\pi-\pi^*$ transition. Although Series 2 (Table 3.5, Fig. 3.8) showed somewhat different main configuration contributions for $S_0 \rightarrow S_2$ transition band with respect to Series 1, the $S_0 \rightarrow S_1$ transition is responsible for ICT from donor to acceptor side of the molecules.

As a final step for investigating TDDFT-PCM based electronic transitions, two different basis sets were adopted, namely 3-21G(d) and 6-31G(d). These results are listed in
column d) and e) in Table 3.2. Since the ICT band is crucial to light harvesting for converting photon energies to electricity in a DSSC system, computed results for only $S_0 \rightarrow S_1$ transitions are compared with experimental results. For small and expended basis set, small deviations below 0.2 V ($\leq 30$ nm) from experimental ICT absorption energies were observed except for D4. From these results, BHandH was determined to be a reasonable exchange correlation functional for screening process to predict absorption bands of organic dyes. This observation is well supported by calculated results from a D-$\pi$-A system having triphenyl amine donor.\textsuperscript{102}

Compared to measured wavelengths of maximum absorption, expended basis set 6-31G(d) provided better correlations between different types of dyes at the expense of slightly increased deviation from experimental values. Therefore, the BHandH hybrid functional for TDDFT seems to be a good candidate for predicting ICT bands with small deviations, whereas B3LYP can be used to determine relative trends among different types of molecules having a D-$\pi$-A system.

By the comparison of Series 2 respect to Series 1, they predicted more red-shifted $\lambda_{\text{max}}$ as well as higher oscillator strength under TDDFT-PCM-THF/3-21G(d). This might be related to their geometries where more reduced twisting angles between donor and conjugation unit were found. (e.g. Figure 3.9)

![Fig. 3-7. Isodensity surface plots of Homo, Lumo, and Homo-1 for D1 obtained using TDDFT-PCM-BHandH/3-21G(d).](image)
Fig. 3-8. Isodensity surface plots of Homo, Lumo, and Homo-1 for D₆ obtained using TDDFT-PCM-BHandH/3-21G(d).

Fig. 3-9. Representative examples of optimized geometries, (D₆; left, D₁; middle, D₃; right).
Table 3-2. Effects of exchange correlation functional and solvent
on electronic transition energies.

<table>
<thead>
<tr>
<th>Series 1</th>
<th></th>
<th></th>
<th></th>
<th>B3LYPa)</th>
<th>BHandHb)</th>
<th>BHandHc)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S₀ → S₁ b)</td>
<td>S₀ → S₂ c)</td>
<td>S₀ → S₁</td>
<td>S₀ → S₂</td>
<td>S₀ → S₁</td>
<td>S₀ → S₂</td>
</tr>
<tr>
<td>D1</td>
<td>624 (0.580)</td>
<td>402 (0.613)</td>
<td>446 (1.032)</td>
<td>322 (0.328)</td>
<td>470 (1.015)</td>
<td>333 (0.317)</td>
</tr>
<tr>
<td>D2</td>
<td>608 (0.547)</td>
<td>398 (0.589)</td>
<td>448 (0.851)</td>
<td>323 (0.300)</td>
<td>472 (0.833)</td>
<td>333 (0.277)</td>
</tr>
<tr>
<td>D3</td>
<td>643 (0.624)</td>
<td>405 (0.565)</td>
<td>448 (1.029)</td>
<td>318 (0.145)</td>
<td>474 (1.018)</td>
<td>326 (0.375)</td>
</tr>
<tr>
<td>D4</td>
<td>562 (0.580)</td>
<td>387 (0.786)</td>
<td>415 (1.067)</td>
<td>316 (0.214)</td>
<td>428 (1.152)</td>
<td>322 (0.217)</td>
</tr>
<tr>
<td>D5</td>
<td>598 (0.591)</td>
<td>378 (0.800)</td>
<td>404 (1.080)</td>
<td>296 (0.551)</td>
<td>433 (0.995)</td>
<td>307 (0.537)</td>
</tr>
</tbody>
</table>

Exp’t h) Series 1

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S₀ → S₁</td>
<td>S₀ → S₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D1</td>
<td>464</td>
<td>353</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>453</td>
<td>343</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D3</td>
<td>480</td>
<td>349</td>
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<tr>
<td>D4</td>
<td>395</td>
<td>307</td>
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</tr>
<tr>
<td>D5</td>
<td>435</td>
<td>311</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Series 1: BHandH a) calculated with a basis set of 3-21G(d). b) calculated with a basis set of 6-31G(d). c) PCM-THF with a basis set of 3-21G(d) d) PCM-THF with a basis set of 6-31G(d). e) unit of nm; oscillator strength in parenthesis. h) experimental results measured in THF dye solution.

Table 3-3. Calculated electronic transition energies for D6 – D10. a)

<table>
<thead>
<tr>
<th>Series 2</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S₀ → S₁ b)</td>
<td>S₀ → S₂ c)</td>
<td>S₀ → S₁</td>
<td>S₀ → S₂</td>
<td>S₀ → S₁</td>
<td>S₀ → S₂</td>
</tr>
<tr>
<td>D6</td>
<td>477 (1.091)</td>
<td>344 (0.391)</td>
<td>497 (1.206)</td>
<td>352 (0.383)</td>
<td>513</td>
<td>367</td>
</tr>
<tr>
<td>D7</td>
<td>485 (0.869)</td>
<td>347 (0.337)</td>
<td>493 (1.000)</td>
<td>351 (0.349)</td>
<td>491</td>
<td>~360</td>
</tr>
<tr>
<td>D8</td>
<td>486 (1.067)</td>
<td>343 (0.412)</td>
<td>512 (1.170)</td>
<td>354 (0.415)</td>
<td>532</td>
<td>366</td>
</tr>
<tr>
<td>D9</td>
<td>435 (1.118)</td>
<td>330 (0.296)</td>
<td>448 (1.245)</td>
<td>338 (0.296)</td>
<td>417</td>
<td>318</td>
</tr>
<tr>
<td>D10</td>
<td>437 (1.074)</td>
<td>317 (0.618)</td>
<td>450 (1.177)</td>
<td>323 (0.610)</td>
<td>477</td>
<td>318</td>
</tr>
</tbody>
</table>

Series 2: in Vacuum

a) calculated with a basis set of 3-21G(d). b), c) unit of nm; oscillator strength in parenthesis. d) experimental results measured in THF dye solution.
Table 3-4. Calculated electronic transition energies and oscillator strengths (f) for D1 – D5.\textsuperscript{a)}

<table>
<thead>
<tr>
<th>Transition state</th>
<th>Main Configurations</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>f</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>D1</strong></td>
<td>( S_0 \rightarrow S_1 )</td>
<td>H ( \rightarrow ) L (83 %)</td>
<td>466</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-1 ( \rightarrow ) L (6 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( S_0 \rightarrow S_2 )</td>
<td>H-1 ( \rightarrow ) L (76 %)</td>
<td>330</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H ( \rightarrow ) L (8 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( S_0 \rightarrow S_3 )</td>
<td>H ( \rightarrow ) L+2 (74 %)</td>
<td>289</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H ( \rightarrow ) L+3 (5 %)</td>
<td></td>
</tr>
<tr>
<td><strong>D2</strong></td>
<td>( S_0 \rightarrow S_1 )</td>
<td>H ( \rightarrow ) L (82 %)</td>
<td>464</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-1 ( \rightarrow ) L (6 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( S_0 \rightarrow S_2 )</td>
<td>H-1 ( \rightarrow ) L (77 %)</td>
<td>331</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H ( \rightarrow ) L (9 %)</td>
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</tr>
<tr>
<td></td>
<td>( S_0 \rightarrow S_3 )</td>
<td>H ( \rightarrow ) L+1 (80 %)</td>
<td>290</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-7 ( \rightarrow ) L (70 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-7 ( \rightarrow ) L+1 (15 %)</td>
<td></td>
</tr>
<tr>
<td><strong>D3</strong></td>
<td>( S_0 \rightarrow S_1 )</td>
<td>H ( \rightarrow ) L (85 %)</td>
<td>478</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-1 ( \rightarrow ) L (4 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( S_0 \rightarrow S_2 )</td>
<td>H-1 ( \rightarrow ) L (77 %)</td>
<td>328</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H ( \rightarrow ) L (6 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( S_0 \rightarrow S_3 )</td>
<td>H-7 ( \rightarrow ) L (70 %)</td>
<td>305</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-7 ( \rightarrow ) L+1 (15 %)</td>
<td></td>
</tr>
<tr>
<td><strong>D4</strong></td>
<td>( S_0 \rightarrow S_1 )</td>
<td>H ( \rightarrow ) L (77 %)</td>
<td>432</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-1 ( \rightarrow ) L (10 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( S_0 \rightarrow S_2 )</td>
<td>H-1 ( \rightarrow ) L (73 %)</td>
<td>325</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H ( \rightarrow ) L (10 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( S_0 \rightarrow S_3 )</td>
<td>H ( \rightarrow ) L+1 (74 %)</td>
<td>290</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H ( \rightarrow ) L (6 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-1 ( \rightarrow ) L+1 (5 %)</td>
<td></td>
</tr>
<tr>
<td><strong>D5</strong></td>
<td>( S_0 \rightarrow S_1 )</td>
<td>H ( \rightarrow ) L (83 %)</td>
<td>423</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-1 ( \rightarrow ) L (6 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H ( \rightarrow ) L+1 (5 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( S_0 \rightarrow S_2 )</td>
<td>H-1 ( \rightarrow ) L (73 %)</td>
<td>304</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H ( \rightarrow ) L (7 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-6 ( \rightarrow ) L (6 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( S_0 \rightarrow S_3 )</td>
<td>H ( \rightarrow ) L+1 (69 %)</td>
<td>283</td>
</tr>
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<td>H ( \rightarrow ) L+5 (7 %)</td>
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<tr>
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<td></td>
<td>H ( \rightarrow ) L (6 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H-8 ( \rightarrow ) L (6 %)</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a)} All values was predicted by TDDFT-PCM-BHandH/3-21G(d). H and L represents homo and lumo, respectively.
<table>
<thead>
<tr>
<th>Transition state</th>
<th>Main Configurations</th>
<th>$\lambda_{max}$ (nm)</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>D6</strong></td>
<td>$S_0 \rightarrow S_1$</td>
<td>$H \rightarrow L$ (82 %)</td>
<td>497</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H-2 \rightarrow L$ (6 %)</td>
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</tr>
<tr>
<td></td>
<td>$S_0 \rightarrow S_2$</td>
<td>$H-2 \rightarrow L$ (51 %)</td>
<td>352</td>
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<tr>
<td></td>
<td></td>
<td>$H \rightarrow L$ (12 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H-3 \rightarrow L$ (9%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_0 \rightarrow S_3$</td>
<td>$H-1 \rightarrow L$ (96%)</td>
<td>317</td>
</tr>
<tr>
<td><strong>D7</strong></td>
<td>$S_0 \rightarrow S_1$</td>
<td>$H \rightarrow L$ (81 %)</td>
<td>493</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H-2 \rightarrow L$ (7 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_0 \rightarrow S_2$</td>
<td>$H-2 \rightarrow L$ (55 %)</td>
<td>351</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H \rightarrow L$ (12 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H-4 \rightarrow L$ (8 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H-5 \rightarrow L$ (8 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_0 \rightarrow S_3$</td>
<td>$H-1 \rightarrow L$ (93%)</td>
<td>314</td>
</tr>
<tr>
<td><strong>D8</strong></td>
<td>$S_0 \rightarrow S_1$</td>
<td>$H \rightarrow L$ (83 %)</td>
<td>512</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H-2 \rightarrow L$ (5 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_0 \rightarrow S_2$</td>
<td>$H-2 \rightarrow L$ (53 %)</td>
<td>354</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H \rightarrow L$ (13 %)</td>
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<tr>
<td></td>
<td></td>
<td>$H \rightarrow L$ (11 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_0 \rightarrow S_3$</td>
<td>$H-1 \rightarrow L$ (96%)</td>
<td>331</td>
</tr>
<tr>
<td><strong>D9</strong></td>
<td>$S_0 \rightarrow S_1$</td>
<td>$H \rightarrow L$ (75 %)</td>
<td>448</td>
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<tr>
<td></td>
<td></td>
<td>$H-1 \rightarrow L$ (4 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_0 \rightarrow S_2$</td>
<td>$H-1 \rightarrow L$ (28 %)</td>
<td>338</td>
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<td></td>
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<td>$H-2 \rightarrow L$ (24 %)</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>$H \rightarrow L$ (16 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H-3 \rightarrow L$ (12 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_0 \rightarrow S_3$</td>
<td>$H \rightarrow L+2$ (82%)</td>
<td>306</td>
</tr>
<tr>
<td><strong>D10</strong></td>
<td>$S_0 \rightarrow S_1$</td>
<td>$H \rightarrow L$ (83 %)</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H-2 \rightarrow L$ (5 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_0 \rightarrow S_2$</td>
<td>$H-2 \rightarrow L$ (50 %)</td>
<td>323</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H \rightarrow L$ (12 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H \rightarrow L$ (11 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$H-7 \rightarrow L$ (8 %)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_0 \rightarrow S_3$</td>
<td>$H \rightarrow L+2$ (82%)</td>
<td>306</td>
</tr>
</tbody>
</table>

a) All values was predicted by TDDFT-PCM-BHandH/3-21G(d). H and L represents homo and lumo, respectively.
3.3. Spectroscopic studies

3.3.1. Optical properties

Spectroscopic properties in solution and on TiO$_2$ films, one of the key factors affecting the efficiency of DSSCs, were investigated and the results are listed in Table 3.6. Fig. 3.10 and Fig. 3.11 spectra indicate absorption and emission properties of dyes in solution state for Series 1 and Series 2, respectively. Compared to Series 1, Series 2 having a strong donor gave a bathochromic shift by an average of ~ 40 nm, which is the preferred absorption spectrum for efficient light harvesting of solar energy. These red-shifts by changing the donor from a diphenyl to carbazole based amine might be ascribed to more planar geometries and increased polarizabilities. The relatively plane geometries and higher polarizabilities of Series 2 with respect to Series 1 were supported by optimized geometries obtained from molecular modeling studies. Fig. 3.9 shows reduced dihedral angle of D6 with respect to D1, which imparts increased donating properties in a D-π-A system, resulting in increased light absorption.

All dyes exhibited more than two absorption bands, except for D4 with N-methyl pyrrole spacer, as shown in TDDFT studies (section 3.2). The first absorption band appeared below 350 nm and was assigned to a localized π-π* transitions, while the band in the visible region is responsible for the charge transfer transition. The ICT band has been reported to be dependent not only on the acceptor or/and donor strength of the molecules but also on solvents used. The localized π-π* band would be affected by modification of the conjugation path length. Provided that the nature of electron pushing (or pulling) of each heterocyclic ring toward acceptor side in D-π-A system is considered, more sensitive band shifts, more closer to charge transfer band. As can be seen in Table 3.6, the second absorption band shifts measured in THF/H$_2$O (v/v, 1/1) were evident for both series, with the first absorption band almost unchanged, supporting a charge transfer band. The observed solvatochromism probably stems from deprotonation of the carboxylic group, which reduces the electron pulling effect of the acceptor group.

In the case of absorption strength, thiazole based dyes D3 and D8 produced hyperchromism but D4 and D9 represented hypochromism. Substantially lower absorption
strength of dyes based on N-methyl pyrrole versus the other dyes is attributable to the deformation of planarity caused by steric hindrance between N-methyl pyrrole and neighboring groups, decreasing efficient electronic transitions. This sterically induced electronic crowding taken place near N-methyl pyrrole was consistent with optimized geometries obtained from molecular modeling (Fig. 3.9).

Introduction of different heterocyclic rings had significant effects on optical properties. Compared to benzene spacer based dyes (D5 and D10) with delocalization energy of 36 kcal/mol, introduction of five-membered heterocyclic rings having lower delocalization energies is expected to impart efficient charge transfer. However, N-methyl pyrrole based dyes (D4 and D9) showed most hypsochromic-shifted ICT band. In a related theoretical investigation involving heteroaromatic stilbenes, it was reported that both aromatic delocalization energy and electronic nature of heterocyclic rings influence the first hyperpolarizability as well as the first charge-transfer excited state in donor-spacer-acceptor molecules. Nonetheless, in the case of heterocyclic rings employed in the acceptor side of the molecule, electronic nature would have a much more pronounced effect on the ICT band. That is, electron rich character of N-methyl pyrrole reduces electron-withdrawing effects of the acceptor, resulting in a blue-shifted absorption spectrum.

A red-shift was observed in the order of furan < thiophene < thiazole, which is the exact order of increased electron-deficient nature of these residues. These trends in the optical properties caused by electronic effects were more pronounced following increasing donor strength (Series 2), demonstrating the electronic effects of heterocyclic rings. Likewise, absorption spectra correspond to the trends in the emission spectra, where D4 and D9 having the smallest charge transfer character showed the most blue-shifted emission and D3 and D10 having the most electronegativity spacer gave emissions at the longest wavelengths.

Absorption spectra of dye-loaded TiO2 films were characterized by somewhat different trends from those in solution state. Following adsorption of dyes on the TiO2 surface, there was 1) broadening of the absorption spectrum and 2) shift in absorption maxima to longer wavelength, depending on dye structure. The broadened spectra of dye-loaded TiO2 film are known to be caused by dye-dye or/and dye-TiO2 interactions.
the case of N-methyl pyrrole based dyes (D4 and D9) having an absorption maxima below 420 nm in solution, the absorption spectra of dye-load TiO2 films could not be resolved because of overlap of their absorption peaks with that of the TiO2 coated film which was used as a reference during measurements. However, the blue-shifted absorption spectrum for D4 in Series 1 (or D9 in Series 2) as well as its broadened characteristics on TiO2 film state is expected from absorption edges that are not related to the TiO2 reference film.

Shifts in absorption maxima of dye-loaded TiO2 film, either blue or red, have been reported and are viewed as evidence of dye aggregates on TiO2 film resulting from interactions between dye-TiO2 or/and between dyes.27-b, 28-b, 66-b, 106 As shown in Fig. 3.12 and Fig. 3.13, the organic dyes studied in this work behaved more like J-aggregates, based on spectral shifts toward longer wavelengths following adsorption of dyes on TiO2 film. It is interesting to note that benzene based D5 in Series 1 gave an unchanged λmax while furan based dyes D2 and D7 gave a relatively large shift in λmax. Also, Series 2 with respect to Series 1 exhibited less of a shift in absorption bands except for furan based dye (D2, D7). In general, smaller absorption shift moving from solution to film state has been interpreted as less tendency to form aggregates in film state.25-b, 107-a Therefore, a reduced shift in the absorption bands on films for Series 2 might be attributed to the bulky amine donor, leading to suppression of aggregate formation on the TiO2 surface. Although aggregation phenomena might be deduced from the λmax shifts, it is also believed that strong dye-TiO2 interactions could contribute to the red shifted spectra accompanied by decreasing lumo energies.107-b

In order to further investigate the aggregation phenomena of dyes on the film surface versus in THF solution, DCA was co-adsorbed with dyes on the TiO2 surface, as DCA is known to suppress dye aggregation on TiO2. The changes in λmax on going from solution to TiO2 film are listed Table 3.6. For all dyes, λmax values obtained by addition of DCA were closer to those obtained in THF solution, which could be interpreted as a result of suppression of dye aggregation on TiO2 films.
Table 3-6. Optical properties of D1 – D10.

<table>
<thead>
<tr>
<th>Series 1</th>
<th>Exp’t. spectroscopic properties in solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max_soln}}$</td>
</tr>
<tr>
<td>D1</td>
<td>464, 353, 25,491, 17364, 621</td>
</tr>
<tr>
<td>D2</td>
<td>453, 343, 22,086, 18,433, 611</td>
</tr>
<tr>
<td>D3</td>
<td>480, 349, 25,931, 17,065, 642</td>
</tr>
<tr>
<td>D4</td>
<td>395, 307, 17,062, N/A, 576</td>
</tr>
<tr>
<td>D5</td>
<td>435, 311, 22,905, 31,955, 608</td>
</tr>
</tbody>
</table>

| Series 2 | $\lambda_{\text{max\_soln}}$ | $\varepsilon_{\text{max}}$ | $\lambda_{\text{emi\_soln}}$ | $\lambda_{\text{max\_soln}}$ | $\lambda_{\text{max\_film\_w/d}}$ |
|----------|------------------------------------------|
| D6       | 513, 367, 26,013, 25,165, 688 | 499, 365 | 519 | 514 |
| D7       | 491, 360, 25,673, 28,206, 662 | 483, 360 | 511 | 505 |
| D8       | 532, 366, 27,292, 23,220, 711 | 520, 365 | 539 | 531 |
| D9       | 417, 318, 19,567, 56,128, 606 | 414, 318 | N/A | N/A |
| D10      | 477, 318, 26,046, 59,237, 661 | 465, 316 | 480 | 477 |

a), b) Absorption was recorded in THF; unit of nm and $\text{M}^{-1}\text{cm}^{-1}$, respectively. c) Emission was measured in THF; unit of nm. d) Absorption was recorded in THF/Water (V/V, 1/1); unit of nm. e) maximum absorption wavelength of dye-loaded TiO$_2$ film. f) maximum absorption wavelength of dye-DCA loaded TiO$_2$ film.

Fig. 3-10. Absorption and emission spectra for Series 1 in THF solutions, (line: absorption, dashed line: emission).
**Fig. 3-11.** Absorption and emission spectra for **Series 2** in THF solutions, (line: absorption, dashed line: emission).

**Fig. 3-12.** Absorption spectra for **Series 1** in THF solutions and on TiO$_2$ films, (line: absorption, dashed line: emission).
Fig. 3-13. Absorption spectra for **Series 2** in THF solutions and on TiO$_2$ films, (line: absorption, dashed line: emission).

### 3.3.2. Adsorbed amount of dyes on TiO$_2$ films

In order to investigate the effects of dye amounts adsorbed on TiO$_2$ films, absorption curves (Fig. 3.14 and Fig. 3.15) were normalized by $\varepsilon_{\text{max}}$ at $\lambda_{\text{max}}$. As can be seen in Table 3.7, each dye adsorbed at different levels. However, two facts are evident: 1) the presence of a bulky group in **Series 2** reduced the amount of dye adsorbed on TiO$_2$ films compared to **Series 1** having dyes with smaller molecular size; 2) When co-adsorbed with DCA on TiO$_2$ film, the amount of absorbed dyes decreased in the range of 5 - 20 % versus the case without addition of DCA. From related research involving oligothiophene based dyes, it was pointed out that the increased amount of adsorbed dyes might be attributed to $\pi$-$\pi$ stacking interactions.$^{74}$ Nonetheless, relatively increased (or decreased) amount of different types of dyes on TiO$_2$ film might not be due to one factor but rather the result of a combination of factors, including molecular geometry or/and binding strength of dyes on the TiO$_2$ surface as well as intermolecular $\pi$-$\pi$ stacking.$^{108}$

If **Series 1** is taken into consideration, **D1, D2, D3** showed relatively increased amounts of dye adsorbate, while **D4, D5** produced relatively low dye adsorption on TiO$_2$. 

---

**Table 3.7**: Adsorbed amount of dyes on TiO$_2$ films.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Adsorbed amount of dye (molecules/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>12.3</td>
</tr>
<tr>
<td>D2</td>
<td>10.7</td>
</tr>
<tr>
<td>D3</td>
<td>8.9</td>
</tr>
<tr>
<td>D4</td>
<td>5.6</td>
</tr>
<tr>
<td>D5</td>
<td>4.2</td>
</tr>
</tbody>
</table>

---
Under the assumption that **Series 1** dyes have similar 3-dimensional geometries, only differences in the characteristics of hetero atoms could lead to differences in intermolecular interactions (e.g. S-S interaction, π-π stacking) as well as electronic coupling of dyes with 3d orbitals of the Ti atom of TiO₂ which in turn, affect the desorption process of adsorbed dyes. As potential evidence for the strength of electronic coupling, \( \mu_{\text{norml}} \) (normal dipole moment) was employed from modeling studies, since these values were calculated under the assumption that isolated dye molecules are aligned perpendicular to the TiO₂ surface.

Based on calculated \( \mu_{\text{norml}} \) values, dyes (e.g. **D1, D2, D3**; - 4.30 D - -5.27 D) having large \( \mu_{\text{norml}} \) gave higher dye amounts on TiO₂, while **D4, D5** (-2.88 D, -3.42 D, respectively) produced low adsorptions. However, it is still too early to make conclusions about the relationship between \( \mu_{\text{norml}} \) and observed dye adsorption levels, since **D1, D2, and D3**, with respect to **D5**, also showed greater shift in their absorption spectra on TiO₂ film, which could be evidence for presence of intermolecular interactions resulting in increased dye amounts on TiO₂. The dependence of dye adsorption levels on \( \mu_{\text{norml}} \) or/and intermolecular interactions became less significant following the introduction of a bulky amine group (**Series 2**). However, **D6, D8, D10** with high \( \mu_{\text{norml}} \) values still gave higher dye adsorption levels than **D7 and D9** with low \( \mu_{\text{norml}} \) values.
Table 3-7. Adsorbed amounts of dyes on TiO$_2$ films and DCA co-adsorbed on TiO$_2$ films.

<table>
<thead>
<tr>
<th>Series</th>
<th>Ads. amount$^a$</th>
<th>Ads. amount by DCA$^b$</th>
<th>Rel. ads. amount$^c$</th>
<th>Rel. ads. amount by DCA$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D1</td>
<td>1.16E-07</td>
<td>1.10E-07</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>D2</td>
<td>1.18E-07</td>
<td>1.00E-07</td>
<td>1.02</td>
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<tr>
<td></td>
<td>D3</td>
<td>1.10E-07</td>
<td>8.72E-08</td>
<td>0.95</td>
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<tr>
<td></td>
<td>D4</td>
<td>8.79E-08</td>
<td>6.86E-08</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>D5</td>
<td>9.73E-08</td>
<td>8.85E-08</td>
<td>0.84</td>
</tr>
</tbody>
</table>

$^a$ Adsorbed amount of dyes on TiO$_2$ film; unit of mol/cm$^2$. $^b$ Adsorbed amount of dyes on DCA/dye loaded TiO$_2$ film. $^c$, $^d$ Relative adsorbed amount with reference to D1, D6 in the case of Series 1, Series 2, respectively.

Fig. 3-14. Absorption spectra of dye-loaded TiO$_2$ film for Series 1, (line: dye loaded TiO$_2$ film, dashed line: DCA/dye loaded TiO$_2$ film).
3.3.3. Fluorescence lifetime measurements

As one of several methods used to obtain kinetic parameters involved in DSSCs, emission lifetimes were measured by means of time-resolved single photon counting (TCSPC). Table 3.8 indicates lifetimes with CHISQ values after fitting of decay curves (Fig. 3.16) to the exponential functions shown below.

\[ F(t) = A + B_1 e\left(-\frac{t}{\tau_1}\right) + B_2 e\left(-\frac{t}{\tau_2}\right) \]

Where \( B \) is light intensity and \( \tau \) is lifetime obtained. CHISQ values (Table 3.8) show the goodness of fit of decay curves for a given exponential function. For all cases, CHISQ values were close to 1 which could be used as an index to support good fitting of decay curves obtained. Among the two lifetimes shown in equation above, the lifetime with higher relative amplitude was taken as the lifetime at given species. As discussed in the introduction section,
electron injection process competes with relaxation process for photons absorbed by sensitizer during the operation of DSSCs. Therefore, short lifetimes measured are the reflection of the ease with which a photo-generated electron returns to the ground state instead of injecting electrons from dye into the TiO₂ surface.

As shown in Table 3.8, all time constants were in the range of nanosecond scale for Series 1. Considering pico or femto second scale of electron injection process for organic sensitizers in DSSCs, a relaxation process resulting from Series 1 will be much slower, with more than 10^3 order. On the other hand, Series 2 showed shorter lifetimes compared to Series 1. However, those orders in lifetime were still in the range of more than 10^2 larger with respect to injection process. Based on studies on emission decays, the electron relaxation route will not pose a challenge to the electron injection process for all sensitizers in DSSCs.

Table 3-8. Emission lifetimes of D1 - D10 in THF.

<table>
<thead>
<tr>
<th>Series 1</th>
<th>D1</th>
<th>D2</th>
<th>D3</th>
<th>D4</th>
<th>D5</th>
</tr>
</thead>
<tbody>
<tr>
<td>lifetime (ns)⁷⁺⁺ ¹</td>
<td>4.11</td>
<td>4.07</td>
<td>2.26</td>
<td>3.50</td>
<td>3.66</td>
</tr>
<tr>
<td>CHISQ⁷⁺⁺ ¹</td>
<td>1.06</td>
<td>1.13</td>
<td>1.10</td>
<td>1.15</td>
<td>1.13</td>
</tr>
<tr>
<td>Series 2</td>
<td>D6</td>
<td>D7</td>
<td>D8</td>
<td>D9</td>
<td>D10</td>
</tr>
<tr>
<td>lifetime (ns)</td>
<td>0.15</td>
<td>0.31</td>
<td>0.07</td>
<td>0.93</td>
<td>0.27</td>
</tr>
<tr>
<td>CHISQ</td>
<td>1.10</td>
<td>1.12</td>
<td>1.20</td>
<td>1.03</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Fig. 3-16. Emission decay curves for D1 – D10 in THF obtained by single photon counting methods.
3.4. Electrochemical studies

3.4.1. Redox properties

Redox properties of dye-loaded TiO$_2$ films are listed in Table 3.9. The first oxidation peak potentials are believed to involve oxidation of the arylamine moiety. Reduction potentials ($E_{\text{red}}$) of all dyes were higher than the energy of conduction band edge of TiO$_2$ (-0.5 V vs NHE). Also, $E_{\text{ox}}$ was lower in energy than redox electrolyte I/I$^{-}$ (0.42 V vs NHE). As a result, the driving force for both electron injection and regeneration of oxidized dyes was energetically secured during DSSC operation.

A strong electronic coupling between the arylamine group and the electron rich heterocyclic unit leads to much lower oxidation of the arylamine but this normally strong electronic interaction is reduced by increasing the donor strength in a D-π-A system. Taking the effects of different heterocyclic rings on the redox potential of the various dye molecules into consideration, the more electron-deficient the heterocyclic ring is, the more difficult to oxidize the dye. In the present study, homo and lumo energies decreased in the order of pyrrole > furan > thiophene > thiazole based dye. These results were consistent with data from molecular modeling studies and were consistent with other research which is related to the shift in the 1st excited state energy by introduction of a simple five-membered heterocyclic linkers in push-pull structures.$^{104}$

In the case of N-methyl pyrrole based dye D4, $E_{\text{ox}}$ could not be resolved from the experimental setup due to the overlapping peaks caused by a large background charging current. However, it is expected that D4 would show the highest oxidation energy of all dyes in the series, since pyrrole has the most electron rich character of the heterocyclic rings employed. Relative shifts in energetics arising from varying the heterocyclic units in push-pull structures turned out to be more sensitive to reduction potentials than oxidation potentials.

On the other hand, Series 2 having a stronger donor than in Series1 lowered the first oxidation potential of the aryl amine moiety. The second oxidation peaks observed at higher potential in Series 2 might be assigned to the oxidation of the electron donor which is part of a carbazole system.
Table 3.9. Redox properties of D1 - D10.

<table>
<thead>
<tr>
<th>Series 1</th>
<th>$E_{ox}$ (V) vs NHE</th>
<th>$E_{red}$ (V) vs NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>1.389</td>
<td>-0.920</td>
</tr>
<tr>
<td>D2</td>
<td>1.342</td>
<td>-1.020</td>
</tr>
<tr>
<td>D3</td>
<td>1.437</td>
<td>-0.793</td>
</tr>
<tr>
<td>D4</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>D5</td>
<td>1.369</td>
<td>-1.062</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Series 2</th>
<th>$E_{ox}$ (V) vs NHE</th>
<th>$E_{red}$ (V) vs NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>D6</td>
<td>1.079, 1.568</td>
<td>-0.988, -0.499</td>
</tr>
<tr>
<td>D7</td>
<td>1.048, 1.361</td>
<td>-1.094, -0.781</td>
</tr>
<tr>
<td>D8</td>
<td>1.175, 1.623</td>
<td>-0.902, -0.454</td>
</tr>
<tr>
<td>D9</td>
<td>0.864, N/A</td>
<td>-1.656, N/A</td>
</tr>
<tr>
<td>D10</td>
<td>1.094, 1.550</td>
<td>-1.108, -0.652</td>
</tr>
</tbody>
</table>

a) $E_{ox}$ (oxidation potential) b) $E_{red}$ (reduction potential)

3.4.2. Recombination kinetics

Investigation of recombination kinetics was performed using impedance spectroscopy (EIS) which will lead to enhance our understanding of kinetic parameters during the operation of DSSCS. Fig. 3.17 and Fig 3.18 show both Nyquist and bode phase plots for Series 1 and Series 2 based DSSCs, respectively. Electron lifetimes ($\tau$) extracted from EIS are listed in Table 3.10.

General trends among electron lifetimes were found when different heterocyclic rings and bulky donor groups were assembled in dye molecular structures. Upon comparing electron lifetimes among DSSCs fabricated without additives, it was found that Series 1 imparted longer lifetimes than dyes in Series 2 except for the thiazole based DSSCs. Higher dye loads on the TiO$_2$ electrode (13 - 23 % higher than for Series 2) or/and lower polarizabilities could be pointed out as reason for the higher lifetimes from Series1. As efficient surface blocking$^{109}$ or/and lower polarizabilities$^{110}$ have been considered as important factors for increasing lifetimes, Series 1 might take advantages of higher dye loads.
and lower polarizabilities resulting in decreased recombination between generated electrons and acceptor species in the electrolyte. However, taking thiazole based dye (D3 versus D8) into consideration, D8 showed slightly a higher electron lifetime (2.5 ms) than D3 (1.0 ms), which is contrary to the above points. Here, the dependence of electron lifetimes on dye loads and polarizabilities might be reduced and more dependent on how well positioned the dye is on TiO₂ surface to block access of acceptor species from electrolyte. This “efficient surface blocking” also looks become significant in the case of addition of DCA or TBP which could occupy TiO₂ sites and induce deformations in the 3-D generic geometries of dyes on TiO₂. For example, D4 based DSSCs containing TBP gave lowered electron lifetime (63.4 ms) than D9 based device (79.8 ms).

Regarding the different electron lifetimes obtained from the various heterocyclic units, the following outcomes were noted: 1) lifetimes increased in the order of DSSCs sensitized with D4 > D5 >> D1 > D2 > D3 dyes for Series 1. 2) Series 2 showed lifetimes in the same order as in Series 1 except that the furan (D7) based DSSCs recorded the lowest lifetime. The observed electron lifetimes followed the relative orders found in polarizabilities and electron-deficient nature of heterocyclic rings, provided DSSCs based on furan (D2, D7) are excluded from the comparisons. In other words, device based on electron-rich pyrrole based sensitizers (D4, D9) imparted the lowest polarizabilities and gave the highest lifetimes. The reverse was found for the thiazole based devices using D3, D8. The reasons for the somewhat lower lifetimes for D2 and D7 based devices are still in question, considering the relatively low polarizability and electron rich character. In this case, the question is how do these dyes efficiently block the TiO₂ surface? Despite possible limitations regarding investigation of the alignment of furan based sensitizers on the TiO₂ surface, the 3-D geometries might one of the major factors affecting lifetime. Note that carbazole substituted D7 exhibited the lowest lifetime in Series 2. Keeping the significant loss in dye loads by introducing of the bulky amine donor in D7 compared to D2 in mind, the poor surface coverage of dyes on TiO₂ also contributed to the decrease in electron lifetime of furan (D7) based device.
Additives such as DCA and TBP afforded changes of electron lifetimes found in devices assembled in the absence of these additives. As discussed in the introduction section, DCA has been used to suppress dye aggregation on TiO₂. Consequently, the surface blocking behavior of DCA on TiO₂ is expected to some extent. In practice, it was found that the lifetimes obtained by addition of DCA were an average of 1.5 times larger than in devices without DCA. In addition, TBP resulted in an increase in lifetimes of up to 8 times, depending on the sensitizer used. The observed changes in the lifetimes caused by the two additives were consistent with results from the dark current measurements, which are reported in a later section. All of these results support the published effects of TBP, which is known to be an effective additive for reducing recombination of generated electrons during DSSC operation.

In this study, reference dye N719 gave a lifetime of 101 ms and DSSCs sensitized with dyes having an N-methyl pyrrole spacer gave the same (or even higher) lifetime following the addition of both DCA and TBP. Specifically, device based on D4 and D9 gave lifetimes of 101 ms and 127 ms, respectively.

Table 3-10. Electron lifetimes of DSSCs sensitized with D1 – D10. a)

<table>
<thead>
<tr>
<th>Series</th>
<th>τ (ms)</th>
<th>Series</th>
<th>τ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>w/o additive</td>
<td>w/ DCA</td>
<td>w/ TBP</td>
</tr>
<tr>
<td>D1</td>
<td>8.0</td>
<td>10.1</td>
<td>25.2</td>
</tr>
<tr>
<td>D2</td>
<td>3.2</td>
<td>3.2</td>
<td>20.2</td>
</tr>
<tr>
<td>D3</td>
<td>1.0</td>
<td>2.5</td>
<td>5.0</td>
</tr>
<tr>
<td>D4</td>
<td>40.0</td>
<td>50.4</td>
<td>63.4</td>
</tr>
<tr>
<td>D5</td>
<td>15.9</td>
<td>15.9</td>
<td>40.0</td>
</tr>
<tr>
<td>N719</td>
<td>100.5</td>
<td>100.5</td>
<td>100.5</td>
</tr>
</tbody>
</table>

a) w/o, w/DCA, w/TBP indicates DSSCs fabricated without additives, with DCA, and with TBP, respectively.
Fig. 3-17. EIS results from **Series 1** based device.

(left; Nyquist plot, right; Bode phase plot. Top, 2nd, 3rd, bottom indicate the EIS result from DSSCs without additive, with DCA, with TBP, and with DCA/TBP, respectively.)

Fig. 3-18. EIS results from **Series 2** based device.
3.5. Current-voltage characteristic of DSSCs

3.5.1. Photovoltaic performance

The current-potential characteristics of DSSCs based on sensitizers D1 - D10 were obtained under simulated AM 1.5 G irradiation (100mW·cm\(^{-2}\)). The resulting photovoltaic parameters are listed in Table 3.11 and Table 3.12. The effects of additives on the photovoltaic performance of DSSCs were investigated as well. N719 was used in the reference cell, which exhibited an efficiency of 7.05 % where the short-circuit current, open-circuit voltage, and fill factor were 13.43 mA·cm\(^{-2}\), 0.74 mV, and 0.71, respectively.

Based on the current-potential characteristics of the devices sensitized with synthesized dyes, the thiophene based device gave the best performance, whereas it was generally observed that the DSSCs sensitized using thiazole based dyes showed low efficiency. Notably, devices based on Series 1 dyes afforded much better efficiencies than those based on Series 2 having a bulky carbazole amine unit. Considering the lower photovoltaic performance of DSSCs sensitized with Series 2 dyes, with respect to current density and voltage, it is considered that even better coverage of the visible spectrum and larger driving force for electron injection would not compensate for reduced dye loads or/and non-efficient surface blocking, resulting in reduce in current density. On the other hand, the decrease in voltage might stem from decreased lifetimes caused by higher polarizabilities and inefficient surface coverage of TiO\(_2\).

Taking the effects of Series 1 dyes on photovoltaic performances into consideration, current density of the devices increased in the order of sensitizer based on thiazole (5.06 mA·cm\(^{-2}\)) < N-methyl pyrrole (5.85 mA·cm\(^{-2}\)) < furan (6.40 mA·cm\(^{-2}\)) < benzene (6.89 mA·cm\(^{-2}\)) << thiophene (8.19 mA·cm\(^{-2}\)). Current density is a result of the product of LHE (light harvesting efficiency), electron injection, and electron collecting efficiency. Under the assumption of LHE as the unity for all sensitizers by considering molar extinction coefficient of Series 1 (17,000 – 25,931), a driving force, which is related to the electron injection efficiency\(^{111}\) increased in the order of N-methyl pyrrole, benzene > furan > thiophene > thiazole residues. However, this does not account for the observed order for short circuit currents, even considering the adsorbed amounts of dye on TiO\(_2\) surface which will result in
the order of N-methyl pyrrole > furan > benzene > thiophene > thiazole. Therefore, IPCE
curves (Fig. 3.19) were recorded to further explain the obtained current densities, since short
circuit current is a reflection of current density produced from incident photons at a given
wavelength. It is interesting to note that the maximum quantum efficiencies at a given $\lambda_{max}$
shown in the IPCE spectra did not follow the trends shown in current densities. To be
specific, the IPCE plateau increased in the order of benzene > thiophene > furan ~ N-methyl
pyrrole > thiazole based sensitizer. The resultant lower plateau could be due to reduced
electron transfer yield. Therefore, somewhat lower plateaus for devices based on N-methyl
pyrrole and furan, despite those high driving force for electron injection, is attributed to
aggregation behavior as discussed in Section 3.3. On the other hand, devices constructed
from the benzene based sensitizer having unchanged absorption spectrum on TiO$_2$ resulted in
the highest plateau. This finding further supports the suggestion that aggregation behavior
is one of the factors affecting increase (or reduce) IPCE plateaus. Nonetheless, the high
electron transfer yield of the D$_5$ based device did not give the highest current, due to the
relatively small coverage of visible spectrum compared to the D$_1$ based DSSC.

Regarding Series 2 based DSSCs, the highest current density was obtained by
sensitization using D$_6$ (5.35 mA·cm$^{-2}$) followed by D$_{10}$ (3.88 mA·cm$^{-2}$) ~ D$_9$ (3.86 mA·cm$^{-2}$)
> D$_8$ (3.82 mA·cm$^{-2}$) > D$_7$ (3.38 mA·cm$^{-2}$). Here, a small difference in the short circuit
currents of DSSCs was discovered depending on the sensitizers used. Based on similar dye
loads and reduced aggregation behavior of Series 2 compared to Series 1, it can be deduced
that the driving force becomes significant to determine photocurrent densities under
assumption of LHE as unity. This was evident from IPCE spectra (Fig. 3.21), where IPCE
plateaus for Series 2 based devices followed the order of N-methyl pyrrole > benzene ~
thiophene > furan > thiazole spacer. Again, the sensitizer (e.g. furan based sensitizer)
showing a relatively large shift in absorption spectra on TiO$_2$ film might cause a decrease in
electron transfer yield, which is responsible for lowering the IPCE plateau. As depicted in
Fig. 3.21, benzene or N-methyl pyrrole dye based devices still were not able to compete with
spectral coverage of thiophene based device. Also, slightly higher IPCE plateau obtained
from the furan based device did not exceed the broad spectral coverage of the thiazole based
device, resulting in a lower short circuit current for the D7 device compared to D8 device. Consequently, much larger driving force as well as aggregation behavior turned out to be crucial factors in increasing IPCE plateau considering the fact that N-methyl pyrrole or benzene based devices gave higher IPCE plateau for both dye Series.

Concerning voltage parameters measured, a correlation as found between the observed voltages and the electronic nature of sensitizers in DSSCs. For Series 1 and Series 2 based DSSCs, the measured voltages, in general, increased in the order of N-methyl pyrrole > benzene > thiophene > furan > thiazole based devices. As mentioned in Section 1.2.2, $V_{oc}$ (open circuit voltage) can be determined by the potential difference between conduction band edge of TiO$_2$ and the redox species in electrolyte with electron density in TiO$_2$ serving as a factor as well.

Although $E_{cb}$ can be shifted following adsorption of sensitizers on TiO$_2$ surface$^{112}$, different types of sensitizers can shift $E_{cb}$ to a different extent. In addition, different lifetimes change electron densities on the TiO$_2$ surface. Taking the effects of lifetimes on $V_{oc}$ into account, lifetimes turned out to have a strong relationship with observed voltage parameters. For example, the lifetimes of Series 1 based devices extracted from EIS showed an increase order as in the following sensitizers with: N-methyl pyrrole (40 ms) > benzene (16 ms) > thiophene (8 ms) > furan (3 ms) > thiazole (1 ms). This order was consistent with $V_{oc}$, where $V_{oc}$ values recorded were 0.664 V, 0.627 V, 0.618 V, 0.609 V, and 0.555 V, respectively. On the other hand, Series 2 also exhibited the same order for lifetime values as in Series1, except that the D7 (furan based) device gave the lowest lifetime (vide section 3.4.2), still giving same orders of $V_{oc}$ as Series 1 based DSSCs. This finding implies that there is an additional factor affecting $V_{oc}$ which would account for $E_{cb}$ movement. It is known that the dipole moment and surface concentration of dyes would affect change in $E_{cb}$$^{112}$. Even if both normal dipole moment and dye loads are taken into consideration, there is not a strong relationship between dipole moment (or dye loads) and recorded voltages. Therefore, a significant $V_{oc}$ dependence on lifetimes was strongly evident from these results. However, judging from the results of Series 2, the effect of electron lifetimes on $V_{oc}$ is somewhat lower due to the low and similar dye loads among devices sensitized with different types of
sensitizers. Instead, $E_{cb}$ movement may become determinant of $V_{oc}$ variations in the range of ~ 20 mV (e.g. D7 versus D8). Even though $E_{cb}$ influence on $V_{oc}$ was small compared to the effects of electron lifetimes, it is expected that the 3D modeling or capacitance calculations would be a further step to broaden our understanding of the effects of sensitizers on $E_{cb}$ movement.

In order to get insight into the effects of additives on photovoltaic parameters, DSSCs were fabricated with the addition of DCA or TBP and the resultant photovoltaic parameters were compared to DSSCs constructed in the absence of those additives. Fig. 3.20 and Fig. 3.22 show change in current-potential characteristics in the presence of additives. Regarding the effects of DCA, an increase in current was observed in the range of 0.3 – 35 % depending on the choice of sensitizer in Series 1, while Series 2 dyes gave current densities at higher levels (33 – 58 %) compared with Series 1 dyes. That is, the dependence on increased current in the presence of DCA become larger when dye aggregates or/and non-efficient packing of dyes on TiO$_2$ surface was present to a high extent. Moreover, reductions in charge recombination led to increases in voltage, especially in the case of Series 2 dyes. On the other hand, DCA gave no (or very little) contribution to voltage increases for Series 1. Nonetheless, the D3 based device recorded a slight increase (3 %) in voltage which might arise from surface blocking by DCA. The surface blocking effect is supported by the 2 fold lifetime increase obtained from impedance measurements.

Concerning the contribution of TBP on photovoltaic performance, increased voltage was evident for both series of dyes. However, current decreases accompanied by the addition of TBP counteracted increase in voltage, resulting in reduced efficiencies. The decrease in current density by the addition of TBP was significant, especially in cases of having small driving force for electron injection from sensitizers in DSSCs. For example, D3 or D1 based devices gave considerable decreases (26 - 28 %) in current and devices based on D2 and D5 exhibited relatively slight decreases in current instead. Furthermore, DSSCs based on D8, which has the thiazole based sensitizer, gave the lowest short circuit current (2.34 mA·cm$^{-2}$) which is a reflection of a 39 % decrease in current compared to devices assembled in the absence of TBP. Therefore, as reported by other research$^{26-c, 28-c}$ which showed that TBP can
shift $E_{cb}$ negatively by $\sim 0.3$ V, it is suggested that TBP could be used under large driving force of sensitizers for the injection process of electrons generated by photo-excitation in DSSCs. However, differences in driving force for electron injection are not enough to fully explain reduced currents caused by the addition of TBP. Examples include the unexpected large decreases in currents for D7 and D8 based device, despite even largely secured driving forces of Series 2 dyes with respect to Series 1. Here, the assumption is that the $E_{cb}$ of TiO$_2$ is -0.5 V (vs NHE) regardless of the sensitizers adsorbed in DSSCs. As a result, there might be other factors to weigh in explaining the decrease in current caused by the addition of TBP. One possible explanation is that TBP could change the packing of dyes on the TiO$_2$ surface in DSSCs. (e.g. change the alignment of sensitizers on the TiO$_2$ surface).

Judging from the performance of DSSCs based on molecular structures (D-\pi-A framework) employed in this study, it appears that better DSSC performance was achieved by DCA-induced increase in current, with a slight gain in voltage. The use of both DCA and TBP gave the best performance, when increase in voltage was large enough to counteract a decrease in current, resulting in the best overall performance (e.g. D5, D6, D9, and D10). Therefore, further optimization of photovoltaic parameters by the addition of additives will lead to best performance of DSSCs for a given sensitizer.

The best D1 based DSSCs only reached 50% of the efficiency of N719, which emphasizes the importance of high photon collection by DSSC sensitizers. On the other hand, best voltage was achieved by N-methyl pyrrole based sensitizers and this value obtained was the same as that from the N719 based device. From this finding, molecular modification of N-methyl pyrrole based sensitizer opens the possibility of achieving high performance DSSCs.
Table 3-11. Photovoltaic performances of DSSCs based on Series 1 dyes.ª)

<table>
<thead>
<tr>
<th>Series 1</th>
<th>J_sc (mA·cm⁻²)</th>
<th>V_oc (V)</th>
<th>ff</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No add.</td>
<td>8.19</td>
<td>0.618</td>
<td>0.697</td>
<td>3.53</td>
</tr>
<tr>
<td>w/ DCA</td>
<td>8.21</td>
<td>0.618</td>
<td>0.696</td>
<td>3.53</td>
</tr>
<tr>
<td>w/ TBP</td>
<td>6.09</td>
<td>0.700</td>
<td>0.668</td>
<td>2.85</td>
</tr>
<tr>
<td>w/ D &amp; T</td>
<td>6.77</td>
<td>0.691</td>
<td>0.749</td>
<td>3.50</td>
</tr>
<tr>
<td>D2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No add.</td>
<td>6.40</td>
<td>0.609</td>
<td>0.717</td>
<td>2.80</td>
</tr>
<tr>
<td>w/ DCA</td>
<td>6.90</td>
<td>0.600</td>
<td>0.729</td>
<td>3.01</td>
</tr>
<tr>
<td>w/ TBP</td>
<td>6.11</td>
<td>0.691</td>
<td>0.749</td>
<td>3.16</td>
</tr>
<tr>
<td>w/ D &amp; T</td>
<td>5.96</td>
<td>0.691</td>
<td>0.749</td>
<td>3.08</td>
</tr>
<tr>
<td>D3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No add.</td>
<td>5.06</td>
<td>0.555</td>
<td>0.709</td>
<td>1.99</td>
</tr>
<tr>
<td>w/ DCA</td>
<td>6.81</td>
<td>0.573</td>
<td>0.646</td>
<td>2.52</td>
</tr>
<tr>
<td>w/ TBP</td>
<td>3.64</td>
<td>0.645</td>
<td>0.703</td>
<td>1.65</td>
</tr>
<tr>
<td>w/ D &amp; T</td>
<td>4.01</td>
<td>0.645</td>
<td>0.699</td>
<td>1.81</td>
</tr>
<tr>
<td>D4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No add.</td>
<td>5.85</td>
<td>0.664</td>
<td>0.738</td>
<td>2.86</td>
</tr>
<tr>
<td>w/ DCA</td>
<td>6.08</td>
<td>0.655</td>
<td>0.761</td>
<td>3.03</td>
</tr>
<tr>
<td>w/ TBP</td>
<td>4.55</td>
<td>0.718</td>
<td>0.724</td>
<td>2.37</td>
</tr>
<tr>
<td>w/ D &amp; T</td>
<td>4.53</td>
<td>0.736</td>
<td>0.776</td>
<td>2.59</td>
</tr>
<tr>
<td>D5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No add.</td>
<td>6.89</td>
<td>0.627</td>
<td>0.715</td>
<td>3.09</td>
</tr>
<tr>
<td>w/ DCA</td>
<td>7.38</td>
<td>0.627</td>
<td>0.749</td>
<td>3.47</td>
</tr>
<tr>
<td>w/ TBP</td>
<td>6.18</td>
<td>0.727</td>
<td>0.756</td>
<td>3.40</td>
</tr>
<tr>
<td>w/ D &amp; T</td>
<td>6.50</td>
<td>0.718</td>
<td>0.750</td>
<td>3.50</td>
</tr>
</tbody>
</table>

ª) No add. indicates DSSCs fabricated with no additives. w/DCA, w/TBP, w/ D & T indicates devices produced with DCA, TBP, and both DCA and TBP, respectively.

Fig. 3-19. IPCE spectra of DSSCs sensitized by Series 1 dyes.
Fig. 3-20. Current-voltage curves of DSSCs based on **Series 1** dyes as a function of additives used.

(w/d, w/t, w/d_t indicates devices produced with DCA, TBP, and both DCA and TBP, respectively.)
Table 3-12. Photovoltaic performances of DSSCs based on Series 2 dyes. a)

<table>
<thead>
<tr>
<th></th>
<th>J_{sc} (mA cm^{-2})</th>
<th>V_{oc} (V)</th>
<th>ff</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D6</td>
<td>No add.</td>
<td>5.35</td>
<td>0.564</td>
<td>0.681</td>
</tr>
<tr>
<td></td>
<td>w/ DCA</td>
<td>7.11</td>
<td>0.582</td>
<td>0.677</td>
</tr>
<tr>
<td></td>
<td>w/ TBP</td>
<td>4.95</td>
<td>0.655</td>
<td>0.698</td>
</tr>
<tr>
<td></td>
<td>w/ D &amp; T</td>
<td>6.29</td>
<td>0.673</td>
<td>0.720</td>
</tr>
<tr>
<td>D7</td>
<td>No add.</td>
<td>3.38</td>
<td>0.555</td>
<td>0.698</td>
</tr>
<tr>
<td></td>
<td>w/ DCA</td>
<td>5.45</td>
<td>0.582</td>
<td>0.715</td>
</tr>
<tr>
<td></td>
<td>w/ TBP</td>
<td>2.43</td>
<td>0.627</td>
<td>0.739</td>
</tr>
<tr>
<td></td>
<td>w/ D &amp; T</td>
<td>4.20</td>
<td>0.673</td>
<td>0.758</td>
</tr>
<tr>
<td>D8</td>
<td>No add.</td>
<td>3.82</td>
<td>0.536</td>
<td>0.686</td>
</tr>
<tr>
<td></td>
<td>w/ DCA</td>
<td>6.02</td>
<td>0.555</td>
<td>0.653</td>
</tr>
<tr>
<td></td>
<td>w/ TBP</td>
<td>2.34</td>
<td>0.618</td>
<td>0.700</td>
</tr>
<tr>
<td></td>
<td>w/ D &amp; T</td>
<td>2.65</td>
<td>0.650</td>
<td>0.760</td>
</tr>
<tr>
<td>D9</td>
<td>No add.</td>
<td>3.86</td>
<td>0.582</td>
<td>0.689</td>
</tr>
<tr>
<td></td>
<td>w/ DCA</td>
<td>5.76</td>
<td>0.627</td>
<td>0.725</td>
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<tr>
<td></td>
<td>w/ TBP</td>
<td>3.67</td>
<td>0.691</td>
<td>0.726</td>
</tr>
<tr>
<td></td>
<td>w/ D &amp; T</td>
<td>4.97</td>
<td>0.736</td>
<td>0.763</td>
</tr>
<tr>
<td>D10</td>
<td>No add.</td>
<td>3.88</td>
<td>0.564</td>
<td>0.682</td>
</tr>
<tr>
<td></td>
<td>w/ DCA</td>
<td>5.70</td>
<td>0.609</td>
<td>0.645</td>
</tr>
<tr>
<td></td>
<td>w/ TBP</td>
<td>3.69</td>
<td>0.664</td>
<td>0.695</td>
</tr>
<tr>
<td></td>
<td>w/ D &amp; T</td>
<td>5.52</td>
<td>0.682</td>
<td>0.701</td>
</tr>
</tbody>
</table>

No add. indicates DSSCS fabricated with no additives. w/DCA, w/TBP, w/ D & T indicates devices produced with DCA, TBP, and both DCA and TBP, respectively.

Fig. 3-21. IPCE spectra of DSSCs sensitized by Series 2 dyes.
Fig. 3-22. Current-voltage curves of DSSCs based on **Series 2** dyes as a function of additives used.

(w/d, w/t, w/d_t indicates devices produced with DCA, TBP, and both DCA and TBP, respectively.)
3.5.2. Dark current-voltage characteristics

Results of dark current measurements are depicted in Fig. 3.23 and Fig. 3.24. For all cases, onset voltages at 1 mAcm$^{-2}$ followed changes in lifetimes obtained from EIS measurements. This was consistent with the differences in recombination of generated electrons with oxidizing species in electrolyte in DSSCs as a function of sensitizer and co-adsorbed additives.

**Fig. 3-23.** Dark current-voltage characteristic of device based on **Series 1** dyes as a function of additives used.
**Fig. 3-24.** Dark current-voltage curves of DSSCs sensitized with Series 2 dyes as a function of additives used.
Chapter 4. Conclusion

In an effort to investigate dye structure-performance relationship in DSSCs, methodological changes in spacer and donor groups in a D-π-A system were designed. The final candidates consisted of 2 series of structures. **Series 1** contains a diphenylamine donor with different spacer units while **Series 2** employs a carbazole based donor in the D-π-A system. All 10 novel dyes were synthesized and used in DSSCs. Photovoltaic performances based on the new sensitizers were measured under AM 1.5G irradiation. The resultant photovoltaic parameters were analyzed using spectroscopic and electrochemical techniques. Changes in photovoltaic parameters by the addition of DCA and TBP were also determined.

1. **Molecular modeling studies**
   - Examination of the frontier orbitals calculated for the target dyes showed that homolumo excitation moved electron density from the donor moiety to the anchoring group.
   - All 10 dyes can participate in a thermodynamically favorable electron injection process. (Homo and lumo were located at energy levels corresponding to the order of N-methyl pyrrole > furan > thiophene > thiazole based dyes)
   - Calculated polarizabilities were increased by introducing the more bulky strong carbazole based amine unit. Polarizabilities among the different dyes followed the order of **D3 > D1 > D5 > D4 > D2** for **Series 1** and **D3 > D1 > D5 > D2 > D4** in the case of **Series 2**.
   - Normal dipole moments did not give a consistent pattern between **Series 1** and **Series 2**. **(D2 > D1 > D3 > D5 > D4 for Series 1 and D5 > D3 > D1 > D4 > D2 for Series 2)**
   - TDDFT calculations based on B3LYP correlation functional predicted relative orders of the bathochromic shifts obtained from UV-Vis spectroscopy, at the expense of overestimation while the BHandH method having increased HF led to the values closer to experimental absorption maxima (average deviation of ~ 30 nm).
However, both B3LYP and BHandH did not predict the oscillator strength at each given transition.

2. Spectroscopic studies

- Absorption maxima of all dyes in solution were in the range of 390 – 530 nm, with molar extinction coefficient of \( \sim 17,000 – 27,000 \text{ M}^{-1}\text{cm}^{-1} \). Introduction of a carbazole based donor unit induced both batho- and hypochromic shifts by average of 41 nm and \( \sim 2,000 \text{ M}^{-1}\text{cm}^{-1} \), respectively. Changes in absorption maxima arising from different heterocyclic spacers followed the order of N-methyl pyrrole < benzene < furan < thiophene < thiazole.

- Absorption behavior of dyes in the film state varied with types of sensitizers absorbed on TiO\(_2\) surface. Typically, broaden and red shifted spectra were found for both Series compared to those of solution state. Also, shifts in absorption maxima on TiO\(_2\) film were somewhat higher in Series 1 (vs Series 2), except for furan based sensitizers with D2, D7 giving 21 and 20 nm bathochromic shifts. The differences in absorption maxima were significantly reduced by co-adsorption of DCA.

- The absorbed amount of Series 1 dyes on TiO\(_2\) was \( \sim 1.3 \) times higher compared to Series 2 dyes. In general, D1 and D6 having a thiophene spacer showed the highest dye loads, while D4 and D9 having an N-methyl pyrrole spacer gave the lowest dye loads from each series. Addition of DCA resulted in reduced dye loads by competition for TiO\(_2\) sites with dyes. Adsorbed dye losses on the TiO\(_2\) surface were 5 - 20 % and 11 - 20 % for Series 1 and Series 2, respectively.

- Emission maxima reflected absorption maxima

- In fluorescence emission lifetime, both series had slower relaxation times of excited electrons at more than \( 10^2 \) orders under assumption of electron injection time of at least picosecond scale.
3. Electrochemical studies

- Reduction potentials obtained from linear sweep voltammetry gave the values less than -0.5 V for both series, providing the driving force required for injection of generated electrons into a TiO\textsubscript{2} semiconductor. The reduction potential increased in the order of N-methyl pyrrole > furan > thiophene > thiazole based dyes. **Series 2** having a carbazole based donor unit conferred a more negative shifted reduction potential with respect to **Series 1**.

- Kinetic properties regarding electron recombination were achieved using impedance measurement. Devices based on **Series 1** dyes more efficiently suppressed recombination of generated electrons and oxidizing species in electrolyte. Notably, DSSCs assembled with sensitizers based on N-methyl pyrrole or benzene dyes conferred relatively longer electron lifetimes while DSSCs containing sensitizers based on furan or thiazole showed inferior kinetic constants for electron recombination. Co-adsorption of DCA gave no (or little) increase in electron lifetimes. However, TBP gave a significant increase in lifetimes compared to DSSCs in the absence of additives.

4. Photovoltaic measurements of DSSCs

- IPCE spectra reflected absorption spectra of dye-loaded films but maximum quantum efficiencies did not match the absorption spectra of dyes in solution. Maximum quantum efficiencies (max. Q.E.) was achieved with devices containing D\textsubscript{5} and D\textsubscript{9}. On the other hand, DSSCs sensitized with the thiazole based spacer gave the lowest maximum quantum efficiency. By the addition of DCA, max. Q.E. was increased while TBP resulted in reduced max. Q.E. The greatest reduction in max. Q.E was resulted in combination with device D\textsubscript{3}.

- From the current-potential curves, current densities obtained were consistent with IPCE trends. The highest short circuit current was found for the device containing D\textsubscript{1} (8.19 mA·cm\textsuperscript{-2}) and device D\textsubscript{6} (5.35 mA·cm\textsuperscript{-2}) for each Series. On the other hand, the
lowest current densities were produced by devices sensitized by dyes having a thiazole spacer.

- Open circuit voltage parameters gave a strong correlation with electron recombination lifetime. Enhancement in voltage, in general, was obtained in the order of devices based on N-methyl pyrrole > benzene > thiophene > furan > thiazole incorporated sensitizers. DSSCs constructed with furan based sensitizers gave somewhat lower voltage (e.g. 0.609 V for D2, 0.555 for D7) Increased lifetime by the addition of TBP contributed to an increase in $V_{oc}$.

- Best photovoltaic performance was attained with the device derived from D1 ($\eta = 3.5 \%$, $J_{sc} = 8.19 \text{ mA}\cdot\text{cm}^{-2}$, $V_{oc} = 0.618 \text{ V}$, $ff = 0.697$). On the other hand, the lowest performance was noted for devices based on dyes having a thiazole unit as a spacer, due to both inferior current densities and voltage parameters.

- According to the efficiencies of DSSCs obtained by construction of cells with (or without) additives, DCA added devices resulted in better performance, when compensating for possible voltage loss in conjunction with a large increase in current densities.

From these results, the dependence of DSSC efficiency on molecular structures (especially, the effects of heterocyclic spacers) was unveiled to some extent. Even small changes in molecular structures had significant effects on optical and electrochemical properties, and kinetics in DSSCs, all of which contribute to DSSC efficiencies.

Results from spectroscopic analysis indicate that the broad absorption properties in the solar spectrum will be crucial to high levels of solar capture. However, this should be complemented by ease of dye adsorption on TiO$_2$ surfaces in DSSCs (e.g. efficient packing and prevention of disordered dye aggregation on the TiO$_2$ surface). Importance of efficient surface packing of dyes on TiO$_2$ was evident from the study on kinetics in DSSCs. Based on the extracted electron lifetime constants from EIS studies, there might be generic issues that are related to the suppression of charge recombination arising from different heterocyclic spacer based sensitizers. Even though a relationship between electron lifetimes and the
different types of spacers was found, dependence of lifetime on the types of heterocyclic units became less significant in the case of Series 2, where relatively low dye-loads were found compared to Series 1. Therefore, further studies on aggregation phenomena of dyes on TiO₂ would be a key next step towards enhancing current understanding of DSSC efficiency and consequently, the development of high performance DSSCs.

Based on the results of this study, sensitizers with N-methyl pyrrole or benzene as a spacer in D-π-A systems are suggested for further structural modification, to develop more efficient sensitizers. This structural modification should be aimed at bathochromic shift in the absorption spectra, with aggregation control as well. Studies pertaining to modeling molecular dynamics of dyes on TiO₂ should be included.
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