DESIGN OF MULTILAYER OPTICAL MEDIA:
ORGANIC PHOTOVOLTAICS
AND OPTICAL DATA STORAGE

by

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*We also certify that written approval has been obtained for any proprietary material contained therein.
Dedication

To my wife, Jen.
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List of Abbreviations

2PA Two Photon Absorption
BHJ Bulk Hetero-Junction
BR Blu-ray
DSC Differential Scanning Calorimetry
DVD Digital Video Disc
EQE External Quantum Efficiency
FWHM Full-Width at Half-Maximum
HDD Hard Drive Disk
HOMO Highest Occupied Molecular Orbital
IAD Ion-Assisted Deposition
ICT Intramolecular Charge Transfer
IPCE Internal Power Conversion Efficiency
ITO Indium Tin Oxide
LUMO Lowest Unoccupied Molecular Orbital
ML Multi-layer
MPP Maximum Power Point
MT Magnetic Tape
NA Numerical Aperture
NLO Nonlinear Optical
NMR Nuclear Magnetic Resonance
ODS Optical Data Storage
<table>
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<th>Abbreviation</th>
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<tr>
<td>OLED</td>
<td>Organic Light Emitting Diode</td>
</tr>
<tr>
<td>OPV</td>
<td>Organic Photovoltaic</td>
</tr>
<tr>
<td>PB</td>
<td>Petabyte ($10^{15}$ bytes)</td>
</tr>
<tr>
<td>PCE</td>
<td>Power Conversion Efficiency</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
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<tr>
<td>POM</td>
<td>Polarized Optical Microscopy</td>
</tr>
<tr>
<td>SVEA</td>
<td>Slowly Varying Envelope Approximation</td>
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<tr>
<td>TB</td>
<td>Terabyte ($10^{12}$ bytes)</td>
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<tr>
<td>VASE</td>
<td>Variable Angle Spectroscopic Ellipsometry</td>
</tr>
<tr>
<td>WAXS</td>
<td>Wide Angle X-ray Scattering</td>
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Design of Multilayer Optical Media: 
Organic Photovoltaics and Optical Data Storage

Abstract

by

BRENT VALLE

The optical properties of one-dimensional layered materials provides a wealth of interesting phenomena. Fine control of the optical properties of the constituent materials and the thicknesses of each layer allows for sophisticated design of useful optical devices. Optical devices based on one-dimensional layered structures may have significant contributions in solving some of society’s greatest problems in the coming century.

The first of these challenges is to transition from fossil fuel energy generation to low-carbon, renewable energy replacements. Among the many proposed solutions is solar photovoltaic energy capture. In solar photovoltaics, light is converted to electric current by generating charge carriers in semiconductors. These charge carriers are then moved to opposing electrodes generating an electric current. These components: semiconductor, electrodes, and a supporting substrate form a layered optical system that can be studied.

The interaction between absorbing material and the weak optical cavity formed by
these electrodes causes enhanced absorption. By carefully designing the layer thicknesses, the absorption in the semiconductor layer can be tuned. In addition, the total absorbed solar photons vary as functions of the layer thicknesses requiring optimization by calculation and experiment.

The second challenge is to store digital data for several decades at low-cost and with minimal use of power-consuming magnetic hard drive disks. Using scalable polymer processing techniques, it is possible to fabricate a multilayer optical data storage medium that satisfies the need for low-cost, scalable storage capacity. With a large number of physical layers, only small changes are needed to optical read/write hardware avoiding the pitfalls encountered with holographic and other exotic optical data storage technologies.

The design and optimization of solar photovoltaic and optical data storage devices is considered. In addition, characterization of the optical, thermal, and electronic properties of these devices and their constituent materials is presented.
Chapter 1

Introduction

1.1 Overview and Impact

Some of nature’s most fascinating optical phenomena are produced by layered materials. The brilliant iridescence of bubbles, oil-slicks and butterfly wings\[1\] are produced by interference of layered interfaces. Deriving inspiration from nature, these structures have been mimicked\[2\] and refined\[3\] to produce sophisticated mirrors, filters and anti-reflective coatings. One-dimensional stratified optical media are easily fabricated and have a wide range of customizable optical behavior, and therefore enjoy widespread use. Despite their seeming simplicity of both form and fabrication, one might wonder how these layered materials can be used to address some of humanity’s greatest problems in the coming century? In particular:

1. How will our civilization generate sufficient energy while lowering fossil fuel use and carbon emissions?
2. How will our society store the vast quantities of data generated by our information revolution?

Solar photovoltaic energy generation is a renewable means of extracting a small portion of the immense amount of energy incident on the Earth’s surface. This method uses the photo-electric effect to convert solar photons to electric charge-carriers in semiconductors. These charge-carriers are then driven to electrodes generating a photocurrent. A layered optical structure is formed by the sandwiching of the absorbing semiconductors by an optically transparent front electrode and highly reflective back electrode. Understanding how this optical structure affects the absorption spectrum of the semiconductor layers is important to increase efficiency and optimize device design.

Today, digital information is primarily stored using magnetic media: Hard Drive Disks (HDDs) and magnetic tape (MT). For applications where read/write speed is the primary consideration, flash media is also increasingly used. Increases in storage densities of magnetic media has resulted in single MT and HDD capacities of a few terabytes. However, magnetic storage media has limited lifetime, relatively large costs, and in the case of HDDs, longterm power consumption to keep platters spinning. An alternative storage technology is Optical Data Storage (ODS). Storage capacity in ODS has remained much less than a terabyte due to saturation of areal storage density. ODS technology leaders have not developed an inexpensive and scalable way to increase capacity by adding many layers. For this reason, ODS research have focused their efforts on holographic and other novel storage mechanisms requiring expensive media and read/write hardware. However, by instead developing a low-cost, scalable way to
fabricate layered media, these hurdles can be avoided.

1.2 Organic Photovoltaics

1.2.1 Photovoltaics and Organic Photovoltaics

The origin of nearly all energy on Earth (geothermal, nuclear, and tidal energy being the exceptions) is the sun. The sun drives weather patterns that contribute to wind and hydroelectric. Plants, which store energy in chemical bonds, are used in biomass energy schemes and fossil hydrocarbons. Since the discovery of the photoelectric effect, the means of directly and efficiently harvesting light from the sun has been the crown-jewel of carbon-neutral energy generation. Considering the energy generating capacity of competing technologies, it is easy to see why this is the case.

In recent years, as the cost of producing silicon photovoltaic cells has decreased, solar energy generation has made gains into penetrating the energy generation market. Solar energy has also benefited from favorable government economic policies\[4\] and competition between national governments seeking manufacturing dominance of this new energy technology\[5\]. For this reason, the efficiency of amorphous silicon photovoltaics is approaching the Shockley–Queisser limit\[6, 7\], and manufacturing techniques are unlikely to produce drastic reductions in cell prices. For this reason, researchers are exploring several alternative photovoltaic technologies. For example, thin-film semiconductors utilizing CdTe\[8, 9\] or CIGS may have a future for moderately efficient photovoltaics with considerably lower materials costs\[10\].
Indeed a number of relatively new technologies have made significant gains in efficiency. The National Renewable Energy Lab’s National Center for Photovoltaics maintains a fascinating plot (shown in Fig. 1.1) of record-breaking research cell efficiencies for various technologies over the past four decades. Progress in increased efficiency of record-breaking cells for various emerging photovoltaic technologies appears to be proceeding at the fastest pace in history. These emerging photovoltaic technologies are being researched and their efficiencies optimized by a large number of workers around the world, both in commercial enterprises and by government funded research.

![Best Research-Cell Efficiencies](http://www.nrel.gov/ncpv/images/efficiency_chart.jpg)

**Figure 1.1:** Certified efficiency of lab solar cells during the last few decades. For the most up-to-date version see [http://www.nrel.gov/ncpv/images/efficiency_chart.jpg](http://www.nrel.gov/ncpv/images/efficiency_chart.jpg)

The technology considered in this thesis, organic photovoltaics (OPVs), is one of the youngest. Success using organics as the semiconducting materials in a solar cell was first reported by Tang in 1986[11]. There are a number of reasons to employ organic
semiconductors as the active materials in photovoltaics. The wide range of material properties that can be tuned by chemical synthesis presents both a challenge and opportunity. The potential for low-cost, low-temperature manufacturing techniques stands in contrast to the costly, high-temperature processing of inorganic photovoltaics[12]. Finally, the mechanical properties of organics could drastically change the economics of photovoltaic transportation and installation costs. If the best hopes of those working on organic photovoltaics are realized, we may all enjoy the benefits of solar cells, produced using inexpensive roll-to-roll[13] or inkjet printed processes[14–16], installed by simply unrolling a photovoltaic film on roofs or in solar power plants.

![Figure 1.2: Fabricated organic solar cells.](image)

Despite such an optimistic outlook, organic photovoltaics have significant challenges that have yet to be fully solved. Significant gains in both efficiency and lifetime are needed to produce a more competitive module cost[17]. The organic semiconductors used are generally susceptible to degradation by oxygen and atmospheric moisture[18, 19]. In addition, organic semiconductors suffer from reduced conductivity and higher
concentration of charge traps[20] as well as higher recombination rates[21, 22] than
in inorganics. All of these challenges present research topics for materials scientists,
and are the subject of considerable effort worldwide. Indeed, significant progress has
been made in recent years in each of these areas, and new laboratory records for power
conversion efficiency are reported nearly every few months.

Physics of Photovoltaics

There are many similarities between inorganic and organic photovoltaics, and also
considerable differences in the physics of their operation. The device physics of inorganic
photovoltaics results from the behavior of a $p-n$ junction. In this device, an interface
between $p$-doped and a $n$-doped semiconductor materials are formed. Diffusion of
electrons and holes into the $p$ and $n$-type materials respectively creates a charged region
left behind by the diffused charges. This charged depletion region produces an electric
field that opposes charge diffusion and in steady state prevents further recombination.
The built-in electric field is the driver for the physics of the $p-n$ junction. As photons
are absorbed within this depletion region producing charge carriers, this built-in electric
field is responsible for sweeping charge carriers to their respective electrodes.

The solar cell can be modeled as a current source that depends on incident light
intensity, $I_L$, in parallel with a diode and shunt resistance, $R_{SH}$, in series with a parasitic
resistance, $R_S$, resulting mainly from the resistance of the front and back electrodes. The
photocurrent is solved numerically as a function of bias voltage by finding the zeros of

$$0 = I - I_L + I_0 \left\{ \exp \left[ \frac{q}{nk_B T} (V + IR_S) \right] - 1 \right\} + \frac{V + IR_S}{R_{SH}} \tag{1.1}$$
<table>
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<th>Parameter</th>
<th>Description</th>
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<tr>
<td>$I_0$</td>
<td>Dark Saturation Current</td>
<td>$1\times 10^{-7}$</td>
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<tr>
<td>$I_L$</td>
<td>Photocurrent</td>
<td>15</td>
<td>mA</td>
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</table>

Table 1.1: Description and example values for the solar cell equivalent circuit parameters.

Several important values can be obtained from a solar cell $J - V$ curve. The first two are the open circuit voltage, $V_{OC}$, and short circuit current $J_{SC}$. As they are named these are the values of the voltage across the device when operated with no load, and the current produced while shorted, respectively. For the largest power conversion efficiency (PCE), these two values should be maximized. Instead of the short and open condition, a solar cell under operation will be under some load so as to operate as close to the maximum power point (MPP) as possible. At this point, the power, $V_{MPP} \times I_{MPP}$, is maximized. This power will always be smaller than $V_{OC} \times I_{SC}$. The ratio between these two is the fill factor:

$$FF = \frac{V_{MPP}I_{MPP}}{V_{OC}I_{SC}}$$

(1.2)

The fill factor is largely determined by the series and shunt resistances, and incorporates many possible flaws in material and fabrication quality. Finally, the power conversion efficiency of solar photovoltaics is easily determined given the area, $A$, of the cell being
Figure 1.3: $J - V$ curve of a solar cell under illumination using the parameters in Table 1.1. The important features: open circuit voltage ($V_{OC}$), short circuit current density ($J_{SC}$), maximum power point voltage ($V_{MPP}$), and maximum power point current density ($J_{MPP}$). Finally, the fill factor ($FF$) is the ratio of area of the rectangle with corners at the origin and the maximum power point (light green) to the area of the rectangle with corners at the origin and the point $V_{OC}$, $J_{SC}$ (light red). (inset) Equivalent circuit of a solar cell.
tested and the irradiance of solar simulated light, $E_s$.

$$\eta = FF \frac{V_{oc} J_{sc}}{E_s}$$  \hspace{1cm} (1.3)

**Physics of Organic Photovoltaics**

Significant differences occur in organic materials. The main difference is due to their lower dielectric constant causing exciton binding energies to be appreciably larger than room temperature energies. For this reason, a means of dissociating the exciton before recombination is needed. By placing another material with slightly lower Lowest Unoccupied Molecular Orbital (LUMO) nearby, the electron can be donated to the new material, breaking up the exciton. This charge-transfer process\cite{23–26} is quite efficient given a large-enough LUMO-LUMO energy difference and provided proximity between charge transfer species. However, the open-circuit voltage, a crucial factor in the power conversion efficiency of the photovoltaic, is given by the energy difference between the LUMO of the acceptor and Highest Occupied Molecular Orbital (HOMO) of the donor\cite{26}. This need for charge transfer, driven by the LUMO-HOMO energy difference reduces the open-circuit voltage, and thus the overall efficiency of organic solar cells.

After exciton dissociation, charges must move to their respective electrodes. In organic photovoltaics, this process is governed by both drift and diffusion\cite{27, 28}. Whereas charges are driven in opposite directions by the built-in electric field, resulting in rectification behavior, organics are rectified using charge-selective layers at the electrodes: hole-transport layer at the anode, and electron transport layer at the cathode.

Because of the short-lived lifetimes of these excitons, the mean exciton diffusion
Figure 1.4: Steps to collecting photo-generated charge in a BHJ depicted as a cartoon (left) and as an energy diagram (right). (a) A bound electron-hole pair (exciton) is created when a photon is absorbed. This typically occurs in the electron donor material. (b) The exciton diffuses with a mean diffusion length of about 10 nm before recombination. (c) If the exciton encounters an acceptor/donor interface before recombination, charge transfer dissociates the exciton. (d) Charge carriers drift/diffuse to their respective electrodes. Charge selective layers prevent recombination at the incorrect electrode.

length is about 10-20 nm[29]. If the exciton is not dissociated within that distance, recombination occurs resulting in no photocurrent. Bilayer heterojunctions with donor and acceptor thicknesses of about one exciton diffusion length are indeed the first examples of organic photovoltaics in the literature[11]. However, the low efficiency in these devices obviously results from the low fraction of solar light absorbed in such thin films of these organic photovoltaic materials. Absorption lengths for even the strongest absorbing organics are on the order of a few hundred nm. The two extremes then are a bilayer heterojunction thick enough to capture a large fraction of the solar irradiance, but too thick to dissociate the charges, or a heterojunction thin enough to efficiently dissociate charges, but too thin to absorb much light.

The incompatibility between exciton diffusion length and absorption length in OPV active layers provides the primary motivation for the
absorption enhancement approach used in this thesis.

An intriguing work-around to this incompatible length scale problem is the use of a bulk-heterojunction (BHJ)\(^{30, 31}\), an interpenetrating network of acceptor and donor material phase separated so that junctions between the two materials occur within about 10 nm throughout the 100 nm active layer. A BHJ film is usually formed by mixing acceptor and donor molecules or polymers in solution and spin-casting or inkjet printing. After drying, the film can be further processed by vapor\(^{32, 33}\) or thermal annealing\(^{34–36}\) to influence the nanoscale morphology or the distribution of donor and acceptor densities throughout the film\(^{37–39}\). Alternatively, addition of selectively soluble additives are used to influence morphology\(^{40}\). Even with the BHJ solution, large recombination rates and poor conductivity of organic donor and acceptor materials\(^{41, 42}\) favor using the thinnest possible active layer that can absorb a significant fraction of the solar irradiance. For this reason, we will next explore means used to increase absorption of light in thin active layer organic photovoltaics in the following section.

![Figure 1.5: A bulk-heterojunction solar cell is depicted with the donor and acceptor materials in blue and red. The bi-continuous mixture of materials allows charges to flow to their respective electrodes. The small distance to a junction throughout the film ensures efficient exciton dissociation.](image-url)
1.2.2 An overview of techniques for improving absorption in OPVs

Chemical synthesis

There are several approaches to modifying absorption in OPV devices. The first is to use chemical synthesis to change the absorption strength and spectra of the materials themselves. Increasing the oscillator strength of the constituent materials is one of the most straightforward ways to increase absorption of solar energy. Another chemical synthetic approach is to adjust the HOMO and LUMO levels of the donor material to shift the "bandgap" capturing a larger portion of the solar irradiance.

![Spectral Irradiance](image.png)

Figure 1.6: NREL standard solar irradiance spectra depicting the solar spectrum before passing through the Earth's atmosphere (extraterrestrial), after traversing 1.5 standard air-mass (direct+circumsolar), and incident upon surface tilted at 37° towards the equator (global tilt).

Much of the solar spectrum lies at energies lower than about one electron-volt, a region of the spectrum largely untapped by organic photovoltaics. The theoretical efficiency limit and optimal bandgap for a single-junction solar cell was derived by
Shockley and Queisser[7] by accounting for thermalization of above-band photons, lack of absorption of below-band photons, thermal radiation and charge recombination. One problem with lowering the HOMO-LUMO energy difference in the donor material is the constraints of the energy levels of the BHJ system. The electron donor must have a low-lying Highest Occupied Molecular Orbital (HOMO) energy level to provide a large open circuit voltage. It must also have a LUMO energy level with enough energy difference between itself and the LUMO of the acceptor species to drive the exciton dissociation charge-transfer. Although work on new acceptor species continues, fullerene-based acceptors (PC$_{60}$BM, PC$_{71}$BM, and C$_{60}$) produce the highest efficiency devices; so we can consider the LUMO of the acceptor as essentially fixed for the time being. Therefore, if we lower the LUMO of the donor to decrease the bandgap, we will not have enough energy offset to drive the exciton dissociation; if we raise the HOMO of the donor to decrease the bandgap, we will lower the open circuit voltage[43]. This effectively places a limit on the long-wavelength absorption of organic photovoltaics.

**Photonic crystals**

Photonic crystals are periodic arrangements of dielectric materials characterized by a photonic bandgap, a set of frequencies for which light cannot propagate through the material. The unique dispersion of photonic crystals has a strong effect on the velocity of light within the crystal and also serves to suppress any radiative relaxations[44]. Several different types of photonic crystal have been applied to the goal of influencing absorption in photovoltaics. A narrow spectral enhancement of absorption can be seen in absorbing media embossed with a periodic structure. Ko and coworkers reported a
three-fold enhancement in absorption over a narrow band at energies slightly lower than the low-energy edge of TDPTD using an enhancement produced by a columnar periodic crystal embossed into the TDPTD:PCBM bulk-heterojunction\cite{45}. Zeng, et. al. improved the long-wavelength absorption of Si solar cells by implementing a photonic crystal-textured back reflector etched on top of an efficient Distributed Bragg Reflector. This combination of diffractive elements provided nearly an order of magnitude External Quantum Efficiency enhancement between 1000 and 1200 nm\cite{46}. Inverse opals of TiO$_2$ infiltrated with an organic dye may be a promising future application for photonic crystal solar cell enhancement, but processing and morphological control must be demonstrated\cite{47}.

**Optical scattering effects and plasmonics**

Optical scattering effects can be used in photovoltaics to effectively increase the optical path within the absorbing medium\cite{48–53} by causing light to take a less direct path before the possibility of escaping via the transparent front face. Excitation of plasmonic modes by patterning electrodes results in local field enhancements and increased scattering that can improve absorption\cite{49, 54, 55}.

**Optical interference effects**

These approaches include optical multilayer designs to take advantage of interference effects\cite{27, 56–59} that optimize the distribution of optical fields and effective absorption length within thin-film photovoltaics. Typically these techniques find an active layer thickness that maximizes solar cell photocurrent. Alternatively, transparent layers such
as an optical spacer[58] are added to influence optical field distributions within the solar cells.

Inherited OLED design

Analogous work in the field of organic light-emitting diodes (OLEDs) demonstrates that luminescence intensity and spectra versus emission angle can be finely tuned through cavity design[60]. Novel cavity designs including optical spacer layers[61], Bragg reflectors[62, 63], and tandem designs[64] occur first in the OLED literature and are then "re-discovered" in the organic photovoltaic field.

1.2.3 Cavity enhanced absorption for organic photovoltaics

The approach presented in this thesis is to use the weak cavity formed by the highly reflective metal back electrode and semi-reflective transparent conducting oxide front electrode. This approach is similar to the optical interference approach in the previous section. However, this previous work has ignored the spectral component of this type of absorption enhancement, instead integrating over the solar spectral irradiance to approximate total photocurrent. It is true that the end goal is to maximize the total photocurrent, a more full understanding of how these weak cavities shape the absorption spectra, can guide design of new materials and architectures. In this thesis, I will explore how these interference effects and especially their interaction with the optical absorption of the photovoltaic materials can be used to understand and improve device performance by spectral modification. Control of absorption spectra of the active layer is achieved simply by controlling thicknesses of the layers within the device; a much easier method.
than synthesizing new semiconductors. In addition, because the HOMO and LUMO levels of the donor and acceptor materials remain unchanged, no change in open-circuit voltage is needed.

This spectral sculpting will be explored in two ways. First, optical transfer matrix calculations will be used to demonstrate the controllability of absorption spectra via tuning device layers. These calculations show how device absorption in very thin layers (∼70 nm) can be similar to that seen in much thicker layers (300+ nm). They also show the degree to which the absorption can be extended to longer wavelengths. Second, OPV devices will be fabricated for various active layer thicknesses. Using External Quantum Efficiency (EQE), specular reflectance, and current density-voltage (J – V) measurements, the results of the transfer matrix modeling will be confirmed establishing the sound approach of the spectral sculpting approach presented in this thesis.

1.3 A Brief Introduction to Transfer Matrix Theory

1.3.1 Motivation

Solving problems in electrodynamics is usually accomplished by solving Maxwell’s equations. Computational solutions to Maxwell’s equations come in many forms[65–68], and both commercial¹, open-source², and home-made solutions abound. One particularly interesting approach for one-dimensional, multilayer dielectric structures is to use optical transfer matrix theory[69, 70]. In this approach, the continuity relations

¹COMSOL Multiphysics, CrystalWave
²MIT Electromagnetic Equation Propagation (MEEP)
of Maxwell’s equations across dielectric boundaries is used to cast the problem in terms of a simple matrix algebra. In the 1-D isotropic case of discussed here, two modes (s and p-polarized waves) are uncoupled and can be treated independently as 2x2 matrices. For birefringent media, these two modes are coupled and therefore the matrix representation is 4x4\textsuperscript{[71]}. The solutions rendered by this matrix algebra are exact, however it is important to note the following assumptions constrain their applicability and may require additional or alternative treatment.

- Steady state. The transfer matrix method is not appropriate for dynamic solutions.
- Perfectly coherent. The formalism described here does not account for scattering, coherence length of light\textsuperscript{3}, re-emission, saturable absorption or any other change in optical constants.

The inputs to the optical transfer matrix calculation are the complex refractive index and thickness of each layer, the refractive index of the incident and substrate materials, and the wavelength of incident light. Each interface and layer within a dielectric stack is represented by a 2x2 matrix. By multiplying these matrices, the optical properties of the stack can be obtained. There are several quantities that can be derived from this input via the TM calculations. The most straightforward are the complex transmittance and reflectance of the dielectric stack. To derive other interesting quantities, the transfer matrix calculations can be extended to determine optical intensity within the dielectric stack and from that optical absorption of individual layers. In the next section, a basic outline of the transfer matrix calculation is given. Next, is a

\textsuperscript{3}For much thicker layers such as the glass substrate, phase information can be discarded to model incoherent layers.
brief description of spectroscopic ellipsometry, a technique used to measure the optical constants of materials. Finally, we outline how the transfer matrix method can be extended to calculate optical intensity and absorption within individual layers and provide interesting insights into the interaction between absorbing layers and their surrounding environment.

1.3.2 Transfer Matrix Derivations

Derivation of the Transfer Matrix

In a scattering matrix method the first goal is to calculate the reflected and transmitted flux (be it electrons, photons, or some other quantity) in terms of the incident flux. In order to calculate the matrix that relates these quantities we need some building blocks first.

Layer and Interface Matrices An electromagnetic wave traveling in the ±z direction is given by

\[ E^\pm(z) = E_0 e^{i(\omega t \mp kz)} \]  

(1.4)

where

\[ k = \frac{\omega}{c} = \frac{2\pi}{\lambda} \]  

(1.5)
We would like to determine the scattering matrix that can be used to determine the field and has propagated a distance $L$ in the positive or negative $z$ direction.

\[
\begin{bmatrix}
E^+(z + L) \\
E^-(z + L)
\end{bmatrix} =
\begin{bmatrix}
L_{11} & L_{12} \\
L_{21} & L_{22}
\end{bmatrix}
\begin{bmatrix}
E^+(z) \\
E^-(z)
\end{bmatrix}
\]

(1.6)

\[
E_0 e^{i(\omega t - k(z + L))} = L_{11}E_0 e^{i(\omega t - k z)} + L_{12}E_0 e^{i(\omega t + k z)} \tag{1.7a}
\]

\[
E_0 e^{i(\omega t + k(z + L))} = L_{11}E_0 e^{i(\omega t - k z)} + L_{12}E_0 e^{i(\omega t + k z)} \tag{1.7b}
\]

By inspection we determine that the appropriate layer matrix is

\[
L = \begin{bmatrix}
 e^{-ikL} & 0 \\
0 & e^{ikL}
\end{bmatrix}
\]

(1.8)

This makes sense; a wave propagating in some medium simply acquires phase and is attenuated. For a wave propagating a distance $L$ through the medium, but at an angle $\theta$ we can replace $k$ by $\xi$ where

\[
\xi = \frac{2\pi}{\lambda} \tilde{n} \cos \theta \tag{1.9}
\]

It is important to note here, that $\tilde{n}$ is the complex index of refraction ($\tilde{n} = n + i\kappa$).

The other crucial scattering matrix we need is the one that describes the phase and
intensity change of reflected and transmitted waves across a dielectric interface. Here we can use the well-known Fresnel reflection and transmission coefficients, seen in undergraduate Electrodynamics textbooks[72], so that we have

\[
\begin{bmatrix}
E_1^+ \\
r_{12}E_1^++t_{21}E_2^-
\end{bmatrix} = \begin{bmatrix}
I_{11} & I_{12} \\
I_{21} & I_{22}
\end{bmatrix} \begin{bmatrix}
t_{12}E_1^+ + r_{21}E_2^- \\
E_2^-
\end{bmatrix}
\] (1.10)

This gives the following two equations that can be solved to obtain the matrix elements of \( I \).

\[
E_1^+ = I_{11}t_{12}E_1^+ + I_{11}r_{21}E_2^- + I_{12}E_2^- \quad (1.11a)
\]

\[
r_{12}E_1^++t_{21}E_2^- = I_{21}t_{12}E_1^+ + I_{21}r_{21}E_2^- + I_{22}E_2^- \quad (1.11b)
\]

\( I_{11} \) and \( I_{21} \) can be solved by inspection. To find the other matrix elements we use two relations.

1. The reflection coefficient from layer 1 to layer 2 is equal and opposite \((r_{21} = -r_{12})\).
2. Energy is conserved \((t_{12}t_{21} - r_{12}r_{21} = 1)\).

Finally, we obtain the interface matrix in terms of the Fresnel coefficients:

\[
I = \frac{1}{t_{12}} \begin{bmatrix}
1 & r_{12} \\
r_{12} & 1
\end{bmatrix}
\]  

(1.12)

**Derivation of Reflection and Transmission Coefficients**

Given the transfer matrix of some optical system, which is calculated by matrix multiplication of all the \(I\) and \(L\) matrices of the dielectric stack, we would like to determine the complex reflection and transmission coefficients of the entire structure[73]. The situation is depicted in Figure 1.8. An incident wave \(E_0\) is propagating rightward and is incident on the left side of the dielectric stack represented by the total transfer matrix \(M\). The reflected wave is propagating leftward on the left side of the stack. The complex coefficient \(r\) describes the amplitude and phase change of the reflected wave with respect to the incident beam. Similarly, a transmitted wave is propagating rightward on the right side and is characterized by a complex coefficient \(t\). Our goal is to determine \(t\) and \(r\) in terms of the matrix elements of \(M\).

![Figure 1.8: Diagram of the electric fields used to calculate the \(t\) and \(r\) coefficients in terms of the matrix elements of a scattering matrix.](image)

21
The situation depicted in Figure 1.8 is described in the transfer matrix formalism in eq. 1.13.

\[
\begin{bmatrix}
E_0 \\
rE_0
\end{bmatrix}
= 
\begin{bmatrix}
M_{11} & M_{12} \\
M_{21} & M_{22}
\end{bmatrix}
\begin{bmatrix}
tE_0 \\
0
\end{bmatrix}
\]  
(1.13)

Solving for \( t \) and subsequently for \( r \) yields

\[
t = \frac{1}{M_{11}} \tag{1.14a}
\]

\[
r = \frac{M_{21}}{M_{11}} \tag{1.14b}
\]

This usage of the transfer matrix formalism, to calculate reflection and transmission, has been used for decades to develop anti-reflection coatings and dielectric mirrors. The success of this method and the ability to finely control film thicknesses allows for very precise optical design of coatings. The transfer matrix method has been employed in a wide variety of applications including in ellipsometric analysis of nanometer-scale films, harmonic generation and wave-mixing in multilayer structures\[74\], spectroscopy of single quantum dots\[75\], and to analyze birefringent elements used for polarimetry measurements of the Cosmic Microwave Background\[76\]. Here it will be shown how the simple 2x2 isotropic calculation can be extended\[27, 59\] to calculate optical intensities and absorption within dielectric stacks that is important especially in opto-electronic devices.
1.3.3 Using transfer matrices to calculate optical field distributions and absorption

As we have just seen, using matrices to describe propagating electromagnetic waves can be used to calculate reflection and transmission of a complicated one-dimensional dielectric system. This was accomplished by multiplying $I$ and $L$ matrices to obtain a total transfer matrix $M$. In order to calculate optical electric fields within a layer $j$ of the dielectric stack, the calculation of $M$ will be broken into three components. The transfer matrix to the left of layer $j$ will be $S^L_j$, and to the right of layer $j$ will be $S^R_j$. So the total transfer matrix is the product $M = S^L_j L_j S^R_j$.

Figure 1.9: This figure illustrates how the multilayer optical transfer matrix calculation can be split up to calculate the fields entering and leaving a single layer.

$$S^L_j = \begin{bmatrix} S^L_{j11} & S^L_{j12} \\ S^L_{j21} & S^L_{j22} \end{bmatrix} = \left( \prod_{i=1}^{j-1} I_{i(i-1)} L_i \right) I_{(j-1)(j)} \quad (1.15)$$
The electric field within layer $j$ is the sum of a rightward and leftward traveling wave within the layer and can be calculated from these two $S_j$ matrices in terms of the incident field.

\[
E_j(x) = t_j^+[e^{i\xi_jx} + r_j^Re^{i\xi_j(2d_j-x)}]E_0 \tag{1.17}
\]

\[
t_j^+ = [S_j^{L11} + S_j^{L12}r_j^Re^{2i\xi_jd_j}]^{-1}; r_j^R = S_j^{R21}/S_j^{R11} \tag{1.18}
\]

Once the light intensity $I(x,\lambda)$ has been obtained from the square modulus of the electric field, we can determine the optical energy dissipated within the structure using

\[
Q(x,\lambda) = \alpha(x,\lambda)I(x,\lambda) \tag{1.19}
\]

where $\alpha(x,\lambda)$ is the absorption coefficient.

Layers much thicker than the coherence length of incident light must be handled as a special case. Assuming perfect coherence between interfaces in these thick layers will produce unrealistic, narrow oscillations in the modeling of reflection, transmission
and absorption. The solution is to treat these thick layers as completely incoherent. To do this, the absolute squares of Fresnel coefficients are used, thus throwing away their phase information[77, 78]. This is how thick (1 mm) glass substrates can be modeled for organic photovoltaics.

An example of the optical field distribution within an organic photovoltaic is shown in Figure 1.10. The layers of the photovoltaic are the following: Indium Tin Oxide (ITO) serves as a transparent anode. The polymer mixture poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) is a hole-transport layer. The organic semiconducting layer is a mixture of the donor, poly(3-hexylthiophene) (P3HT), and acceptor, [6,6]-phenyl C61-butyric acid methylester (PCBM). The reflective cathode is a vapor-deposited Al layer.
1.3.4 Spectroscopic Ellipsometry

Several inputs are needed to ensure a meaningful optical transfer matrix method calculation. Estimates or measurements of the thickness of each layer within the stack of materials is one input. The other primary input is refractive index and extinction coefficient spectra for each material used. This data must be accurate and reliable over the calculation's spectral range. Because the photovoltaic materials absorption is the focus of the calculation, the dispersion of the refraction and extinction is critically important. In order to obtain reliable data for these spectra we use spectroscopic ellipsometry.

Ellipsometry is a non-destructive, optical measurement[79–81]. Light of a known polarization state illuminates a thin film sample. The polarization of light, which has now changed in amplitude and relative phase by being reflected from or transmitted through the sample, is analyzed. In spectroscopic ellipsometry, this process is carried out across the desired spectrum.

The ellipsometry technique can be used to acquire the full Mueller matrix of a given sample by measuring the output polarization for several different configurations of the
input polarizations. Typically for isotropic materials, however, a material’s refractive index and extinction coefficient can be obtained using an linearly polarized light at 45°. The difference in phase, \( \Delta \), and the ratio of electric field amplitudes, \( \tan \Psi \) of \( p \) to \( s \)-polarized light is measured. The reflection coefficients are then related as follows:

\[
\frac{r_p}{r_s} = \tan \Psi e^{i\Delta}.
\] (1.20)

Using optical transfer matrix methods \( \Psi \) and \( \Delta \) can be calculated given the thickness and optical constants of the materials within the sample. Typically one of layers contains a material under investigation. The task then becomes developing a dispersion model for the optical constants of the material that gives the experimentally measured \( \Psi \) and \( \Delta \). Starting with simple dispersion models, such as a series of Lorentz oscillators, a dispersion can usually be developed that starts by fitting a small spectral window at low energies, and is gradually extended to fit the entire measured spectrum by adding new terms. When the fit is sufficient, the refractive index and extinction coefficient can be exported for use in optical transfer matrix modeling or other purposes.

### 1.3.5 Applications of Transfer Matrix Theory in this Thesis

As a reminder: in this thesis, optical transfer matrix calculations will be used to investigate the spectral shaping of an absorbing layer by modification of a surrounding cavity. Surprisingly the absorption spectrum of a medium can be modified very strongly even in very weak cavities. This effect will be exploited in organic photovoltaic devices where absorption shape and its relation to the solar spectral irradiance are of extreme
importance. It will be shown that rather than modifying absorption spectra via chemical
synthesis of organic semiconductors (which also alters the open-circuit voltage of pho-
tovoltaic devices), absorption spectra can be shaped by adjusting the layer thicknesses
within the solar cell.

Because adjusting the thicknesses of device layers is much easier than synthesizing
novel organic optoelectronic materials, it is expected that a more full understanding
of the tunability of absorption will enable higher efficiency, more customizable devices.
Additionally the relaxed optical constraints on novel materials can enable the focus
of chemical synthesis to remain focused on higher mobility, improved environmental
stability, fewer electronic traps, and better film morphologies that will in-turn improve
organic photovoltaic device performance.

1.4 A Brief Introduction to Nonlinear Optics

In the second section of this thesis, nonlinear absorbing organic chromophores and
their inclusion in thermally processable polymers are explored. The nonlinear optical
properties of some novel chromophores, designed for thermal processability and polymer
solubility will be reported. In addition applications of these chromophores to optical
data storage applications will be demonstrated in the final section.

1.4.1 Overview of Nonlinear Optics

Nonlinear optics is the study of optical effects that occur with incident intensities many
orders of magnitude larger than is experienced in everyday life. On a bright sunny day,
with the sun directly overhead, the incident intensity is about 1 kW/m². This is the intensity of our normal experience. In this intensity regime, absorption, reflection, and refraction are constant over short time scales. However, at very large intensities, this is no longer the case. These intensity-dependent effects are known as nonlinear optics. The origin of this nonlinear response arises from the nonlinear polarization induced by large optical fields.

Dipoles are induced within a dielectric material with the application of electric fields. On average, these dipoles yield a bulk response resulting in an electric polarization of the material. In linear optics the polarization response is linearly proportional to the applied field.

\[
<\vec{\mu}> = \vec{P} = \varepsilon_0 \chi^{(1)} \vec{E}
\]  

(1.21)

The response function relating the polarization to the electric field is called the dielectric response tensor and it is common to consider its frequency domain analogue the susceptibility tensor. In the linear optical regime these tensors contain nine elements, however for isotropic materials, the susceptibility is commonly treated as a scalar. The familiar index of refraction and extinction coefficient are related to the susceptibility.

\[
\sqrt{\frac{\varepsilon(\omega)}{\varepsilon_0}} = \sqrt{1 + \chi^{(1)}(\omega)} = n(\omega) + i \frac{\alpha(\omega)}{4\pi}
\]

(1.22)

In nonlinear optics we will no longer limit ourselves to the case that the polarization response is linearly proportional to the electric field. Instead we expand the susceptibility
in a power series expansion.

\[ P_i = \chi^{(1)}_{ij}E_j + \chi^{(2)}_{ijk}E_jE_k + \chi^{(3)}_{ijkl}E_jE_kE_l \]  

(1.23)

For the first nonlinear term, the polarization in the \( i \)th direction at frequency \( \omega_3 \) induced by two electric fields (one in the \( j \)th direction at frequency \( \omega_1 \), and the other in the \( k \)th direction at frequency \( \omega_2 \)) can be written as

\[
\vec{P}_i^{(2)}(\omega_3) = \chi^{(2)}_{ijk}(\omega_3; \omega_1, \omega_2)E_j(\omega_1)E_k(\omega_2)
\]  

(1.24)

This is the second-order susceptibility and is responsible for the nonlinear optical effects of second harmonic generation and the electro-optic effect. By symmetry we can see that if the material has an inversion center, then \( \chi^{(2)} \) must be identically 0 (\( \vec{P} \rightarrow -\vec{P} \) and \( \vec{E} \rightarrow -\vec{E} \)). Therefore with centro-symmetric materials, it is necessary to consider the next term in the series.

Analogously, this next term is written as

\[
\vec{P}_i^{(3)}(\omega_4) = \chi^{(3)}_{ijkl}(\omega_4; \omega_1, \omega_2, \omega_3)E_j(\omega_1)E_k(\omega_2)E_l(\omega_3)
\]  

(1.25)

An interesting case occurs for the degenerate second order nonlinear optics case.

\[
\vec{P}_x^{(3)}(\omega) = \chi^{(3)}_{xxxx}(-\omega; \omega, \omega, -\omega)E_x(\omega)E_x(\omega)E_x(\omega) = \chi^{(3)}_{xxxx} |E_x(\omega)|^2 E_x(\omega)
\]  

(1.26)

Now we have something that looks very much like the linear case (i.e. \( \vec{P} \propto \vec{E} \)), but
now the proportionality between polarizability and electric field is intensity dependent. Remember that the susceptibility defines the material’s refractive index and extinction coefficient. So in this degenerate second-order nonlinear optics, the result of a $\chi^{(3)}$ nonlinear optical response is an intensity dependent refractive index and extinction coefficient. For simplicity, we will assume an isotropic system. The nonlinear refractive index and absorption are

$$n_2 = \frac{1}{\epsilon_0 c n_0^2} \Re \left( \chi^{(3)} \right)$$  \hspace{1cm} (1.27)$$

$$\alpha^{(2)} = \frac{3\omega}{2\epsilon_0 c^2 n_0^2} \Im \left( \chi^{(3)} \right)$$  \hspace{1cm} (1.28)$$

in SI units ($m^2 W^{-1}$ and $mW^{-1}$ for $n_2$ and $\alpha^{(2)}$ respectively so that multiplication by irradiance ($W m^{-2}$) gives a unit-less refractive index and per-unit-length absorption).

Next we will explore a simple experiment to measure these intensity dependent absorption and refractive indices.

Z-Scan Experiment

Nonlinear refraction and absorption can be measured simultaneously using an experimental technique called Z-scan[82–84]. In the Z-scan experiment, the sample under investigation is translated through the focus of an extremely intense laser. Near the focus, the nonlinear refraction and absorption changes the intensity and divergence of
Figure 1.12: Experimental schematic for the simultaneous open and closed aperture Z-scan measurement. The signal from three photodiodes (R = Reference, O = Open Aperture, C = Closed Aperture) is collected by a boxcar integrator and recorded by computer. A computer controlled translation stage is used to move the sample through the focus.

Figure 1.13: Example closed aperture (red) measurement (circles) and theory fit (solid line) using Eq. 1.33 and open aperture (black) measurement (squares) and theory fit (solid line) using Eq. 1.36.
the laser beam in the far field. The experimental setup is shown in Figure 1.12. The signal from the three photodiodes is measured while the sample is moved through the focus by a computer controlled translation stage. The shot-to-shot laser noise is reduced by dividing the closed and open aperture signals by a reference signal (R in Figure 1.12). After the sample, a beamsplitter is used to split the light transmitted through the sample into two signal arms. In the closed aperture arm an aperture is placed in the beam to measure changes in divergence resulting from nonlinear refractive index changes. In the open aperture arm, reductions in the transmitted light due to nonlinear absorption is monitored. The data, measured as open and aperture signals versus z-position, is normalized to the transmittance and then these two curves are fit to obtain the sample's nonlinear optical properties.

**Closed Aperture Z-scan**

Under the Slowly Varying Envelope Approximation (SVEA) and the thin sample approximation \( L \ll n_0 z_0 \) the change in phase and amplitude of the incident beam as it propagates a depth \( z' \) into the sample are\[83\]

\[
\frac{d\Delta \phi}{dz'} = \frac{2\pi}{\lambda} \Delta n(I) \approx \frac{2\pi}{\lambda} (n_2 I + \ldots)
\]

(1.29)

\[
\frac{dI}{dz'} = -\alpha(I)I
\]

(1.30)
Here $\alpha$ includes both linear and nonlinear absorption, but the following analysis will assume no nonlinear absorption. The measurement of nonlinear refraction in the presence of nonlinear absorption is discussed below. Solving these equations simultaneously, the irradiance and phase shift at the exit surface ($z' = L$) follow the intensity distribution of the Gaussian input beam[84].

$$\Delta \varphi(z, r, t) = \frac{\Delta \Phi_0(t)}{1 + (z/z_0)^2} \exp \left( -\frac{2r^2}{w^2(z)} \right)$$

(1.31)

with the on-axis focal intensity

$$\Delta \Phi_0(t) = k\Delta n_0(t)L_{eff}$$

(1.32)

Using the Gaussian decomposition method to determine the electric field to the aperture in the far field. Assuming the aperture is placed far from the focus ($d \gg z_0$), the transmittance function can be calculated as a function of the sample position, $z$, and on-axis focal intensity, $\Delta \Phi_0$.

$$T(z, \Delta \Phi_0) \approx 1 - \frac{4\Delta \Phi_0(z/z_0)}{((z/z_0)^2 + 9)((z/z_0)^2 + 1)}$$

(1.33)

Several convenient features of the transmittance function provide for ease of data analysis. The peak and valley locations are found[82] by finding the solutions to the derivative of Eq. 1.33 with respect to $z$. These occur at $z = \pm 0.858z_0$ which gives an easy sanity check on the measurement via independent measurement of the Rayleigh length ($\Delta z_{p-v} \approx 1.7z_0$). Plugging these positions back into Eq. 1.33, it is found that the
Figure 1.14: Transmittance of the closed aperture Z-scan for phase shifts of $\Delta \Phi_0 = (0.05, 0.10, 0.20)$.

The difference between peak valley height is linearly proportional to the nonlinear phase shift\cite{82}.

$$\Delta T_{p-v} \approx 0.406 \Delta \Phi_0$$

(1.34)

Due to the noise associated with the measurement it is preferable to determine $\Delta \Phi_0$ as a fit parameter to $T(z)$. From this value, it is straightforward to determine $n_2$.

$$\Delta \Phi_0 = \frac{2\pi}{\lambda} n_2 I_0 L_{eff}$$

(1.35)

From Eq. 1.35, it is clear that $n_2$ can best be determined from a linear fit of $\Delta \Phi_0$ versus the incident beam intensity.
Open Aperture Z-scan

The open aperture Z-scan analysis and experiment are more straight-forward. The nonlinear absorption will follow the Lorentzian irradiance distribution of the pump beam[82, 84].

\[
T(z) \approx -\frac{q_0}{2\sqrt{2}} \frac{1}{1 + (z/z_0)^2}
\]  

(1.36)

with the single fit parameter \( q_0 = \beta I_0 L_{\text{eff}} \). As above an accurate determination of \( \beta \) can be obtained with a linear fit to \( q_0 \) versus incident beam intensity. This two photon absorption coefficient \( \beta \) is then used to determine the molecularly intrinsic two photon absorption cross-section, \( \sigma \) as follows:

\[
\sigma = \frac{\beta \hbar \omega}{N}
\]  

(1.37)

or to fit the two photon absorption coefficient versus concentration (\( \beta = \sigma / (\hbar \omega N) \)). The units for \( \sigma \) are

In the presence of nonlinear absorption, the closed aperture Z-scan signal will be modified. By simply dividing the closed aperture transmittance by the open aperture transmittance[84], the result is approximately the closed aperture Z-scan transmittance that would be measured without any nonlinear absorption\(^4 \) (\( \Delta \alpha = 0 \)).

\(^4\)Note that this simple division of curves is only possible for the lowest-order Gaussian mode. For the higher-order Gaussian modes, the open and closed aperture scans are not coupled so simply. For that reason, it is important that the Z-scan beam be spatially filtered and beam quality verified to ensure that this procedure can be used.
Figure 1.15: Transmittance of the open aperture Z-scan for nonlinear absorption coefficients of $q_0 = (0.05, 0.10, 0.20)$.

1.5 Summary

This thesis can be roughly broken into three sections. In the first section (Chapters 2 and 3), I will describe how weak optical cavity effects formed from the stratified architecture in organic photovoltaics can be designed to change the absorption of the active materials. In the next section (Chapters 4 and 5), I will describe the optical and nonlinear optical properties of novel organic chromophores possessing high-temperature stability as potential additives for use in melt-processed fabrication of layered polymer optical films. Finally, in the third section (Chapters 6 and 7), a demonstration of how these layered polymer films can be used for optical data storage is presented.

- Ch. 2 Spectral Sculpting by Cavity Enhanced Absorption
- Ch. 3 Device Optimization of Inverted PTB7:PC$_{71}$BM OPVs
- Ch. 4 An Indole-Squaraine Nonlinear Optical Glass
References


Chapter 2

Spectral Sculpting by Cavity Enhanced Absorption

This chapter is adapted from:

B. Valle, S. Loser, J. W. Hennek, V. DeGeorge, C. Klosterman, J. H. Andrews, K. D. Singer, T. J. Marks,

2.1 Introduction

As interest in renewable energy has surged, research in organic photovoltaics (OPVs) has rapidly expanded because of their potential as an inexpensive, lightweight, flexible, and easy-to-install alternative to inorganic semiconductors. OPV device performance can be significantly enhanced through facile customization of the constituent materials’ electronic properties and phase behavior via rational chemical synthesis. This effort has focused, for example, on providing lower band gaps[1–6], larger open-circuit
voltages[7–11], and improved environmental stability[12–17]. Note, however, that
device design also provides other opportunities for performance optimization. Although
typical OPV polymers have relatively large optical oscillator strengths, device thicknesses
in the hundreds of nanometer range are still necessary for complete light absorption.
However, the large exciton binding energies and limited exciton lifetimes require that a
donor-acceptor interface be accessible within the exciton diffusion length of the material,
typically in the low 10s of nm. A common solution to bridge the gap between these
length scales is to create co-continuous networks of donor and acceptor materials, the
bulk-heterojunction (BHJ)[18, 19], filling the film with donor-acceptor junctions so
that any point within the film has access to donor/acceptor interfaces within about one
exciton diffusion length, while allowing thicker films for complete optical absorption.
These structures provide an array of charge generation pathways. The energy level
diagram demonstrating charge extraction is depicted in Fig. 2.1.

$$\begin{array}{c}
3.5 \text{ eV} \\
5.0 \text{ eV} \\
5.2 \text{ eV} \\
6.1 \text{ eV}
\end{array}$$

\begin{array}{c}
\text{ITO} \\
PEDOT:PSS \\
P3HT \\
PCBM \\
Al
\end{array}

Figure 2.1: Energy diagram of the P3HT:PCBM photovoltaic. The BHJ is
formed by the blending of P3HT:PCBM domains. Holes are
extracted to the ITO electrode from P3HT and electrons are
extracted by PCBM to the Al electrode.

In contrast to the above picture, bimolecular recombination [20–22] of dissociated
excitons as the charges drift to their respective electrodes limits power conversion efficiency (PCE) in thicker BHJ films. The limited mobility of polymer semiconductors then suggests that a thinner film should be preferable due to the higher electric field obtained and shorter mean path to the electrodes, both of which should suppress recombination. Because of these trade-offs, significant effort has been aimed at decreasing the physical active layer thickness while enhancing light absorption. These approaches include optical multilayer designs to take advantage of interference effects \([23–27]\) that optimize the distribution of optical fields and effective absorption length within thin-film photovoltaics, the use of photonic crystals\([28–31]\) that guide and slow light, and the use of optical scattering\([32–37]\) that also increases the effective absorption length. Indeed, analogous work in the field of organic light-emitting diodes (OLEDs) demonstrates that luminescence intensity and spectra versus emission angle can be finely tuned through cavity design\([38]\). Novel cavity designs including optical spacer layers\([39]\), Bragg reflectors\([40, 41]\), and tandem designs\([42]\) occur first in the OLED literature.

While reducing the thickness of an absorbing medium generally reduces its optical absorbance, the presence of the indium tin oxide (ITO) and Al electrodes in OPVs creates an optical cavity that enhances absorption for standing waves of the optical fields. Thus, Pettersson et al. used optical modeling to calculate, and demonstrated experimentally, that an oscillatory dependence of the short circuit current density \((J_{SC})\) in BHJ OPVs arises from optical interference effects\([26]\). In addition, consideration of interference effects has motivated the design of novel thin-film photovoltaic architectures \([23–25]\). While the oscillations in the short circuit current have been correctly
attributed to interference effects, the detailed mechanism is far from obvious given
the broadband spectrum involved and the strong dispersion of the complex refractive
index near resonance. Other researchers have modeled absorption spectra in OPVs as a
function of BHJ thickness and optimized cavity effects for device performance[43, 44].
In the present contribution, we aim to elucidate the detailed mechanism of the inter-
action of the optical cavity defined by the electrodes in an OPV device with the highly
dispersive spectrum of the complex refractive index in the absorptive spectral region
of the photovoltaic polymers. We also provide a simple model to predict conditions
for cavity enhanced absorption and use reflection spectroscopy measurements to verify
modeling results.

To perform this analysis, we employ transfer matrix theory with complex index
of refraction dispersion data as measured by spectroscopic ellipsometry, to simulate
reflection, transmission, absorption, and electric field distributions in the device for
various wavelengths, while varying the thickness of both the ITO anode and the ab-
sorbing medium. We focus on two different absorbing layers. The first is a BHJ active
layer formed from a blend of the donor polymer poly-3-hexylthiophene (P3HT) and
the fullerene derivative phenyl-C_{60}-butyric acid methyl ester (PCBM). The second is a
neat absorbing film of thieno[3,4-b]thiophene-alt-benzodithiophene copolymer (PTB7).
We calculate the absorption within the active layer of the device as a function of its
thickness and wavelength. We then compare our transfer matrix modeling results to
experimental measurements of the optical absorption spectra derived from reflectance
measurements in “half-cavity” films as semiconductors deposited between the ITO and
reflecting aluminum. In determining how the spectral aspects of cavity-enhanced absorp-
tion effects result from the interaction of the cavity modes with the highly dispersive material, we find that:

• strong thickness-dependent spectral tuning reveals features consistent with the concept of frequency-pulling\cite{45},

• these features include significant spectral broadening to both longer and shorter wavelengths,

• these significant spectral changes, including the spectral broadening to longer wavelengths, result in a larger low-energy response to the solar spectrum that is independent of the BHJ HOMO and LUMO energies and thus do not affect the open circuit voltage ($V_{OC}$), but can significantly increase the PCE, and

• the observed oscillations in the PV response directly emerge from these spectral changes.

In addition, we find that varying the thickness of the ITO can affect these pronounced spectral changes, and thus, additional optical layers may be unnecessary. Measurements of optical characteristics in films of varying layer thicknesses are consistent with the modeling results.
2.2 Experimental

2.2.1 Device fabrication:

Devices were fabricated with varying P3HT/PCBM and ITO layer thicknesses to evaluate optical and electrical behavior. Glass substrates (1 mm) were cleaned by successive 15 min. sonications at 50 °C in a weak detergent water solution, DI water, isopropanol, methanol, and acetone. Indium tin oxide was deposited on glass substrates by ion-assisted deposition (IAD), which is known to produce dense, highly conductive films[46]. The sheet resistance of these films was 50 Ω/□. The ITO coated substrates were patterned with electrical tape and etched in boiling HCl acid. The residual acid was then neutralized in aqueous NaHCO₃ solution, and residual tape removed by sonication in hexanes. Patterned ITO substrates were then recleaned using the same procedure as above. Next, PEDOT:PSS (Clevios P VP AI 4083) was spin-cast at 5.0 kRPM for 30 s, after passing through a 0.45 µm PVDF filter, and then annealed for 15 min. at 150 °C.

The BHJ active layer was prepared by dissolving poly-3-hexylthiophene (P3HT), purchased from Rieke Metals, and [6,6]-phenyl-C₆₀-butyric acid methyl ester (PCBM), purchased from American Dye Source, in distilled o-dichlorobenzene under an N₂ purge. The active layer solution was then spin-cast in an N₂ filled glove box at various speeds to control the BHJ layer thickness. The resulting films were allowed to slow-dry in a petri dish for 20 min. Next, a 1.0 nm LiF layer followed by a 120 nm Al cathode were deposited by thermal evaporation at 1x10⁻⁶ Torr. The thickness of the two cathode materials was monitored during deposition using a quartz crystal monitor. For additional fabrication information see appendix A.
Devices with the PTB7 neat films were deposited on patterned 150 nm thick ITO coated glass substrates (XinYan) that were cleaned as above. PTB7 films were spin-cast from o-dichlorobenzene at various speeds to control the film thickness. Resulting films were slowly dried before coating with 100 nm Al cathode as above.

2.2.2 Specular reflectance:

Normal incidence specular reflectance measurements were obtained using a UV-VIS-NIR spectrophotometer (Varian Cary 500). Devices were masked using a 1.0 mm diameter round pinhole. A highly reflective standard was used to calibrate the reflectance. Angular-dependent reflectance measurements were obtained from an fiber optic spectrometer with variable incidence angle attachment (Ocean Optics).

2.2.3 Spectroscopic Ellipsometry

Variable Angle Spectroscopic Ellipsometry (VASE) was used to obtain the optical constants of each material in the organic photovoltaic device. In this measurement, light with equal intensities of \( p \) and \( s \) polarization is incident on the measured material at some incidence angle between 55 and 80°. The specular reflection is collected and the ratio of intensity and phase difference of \( s \) to \( p \) polarizations is collected. This data is then fit using a user-defined model composed of the thickness and dispersion of the material and substrate being measured. The complex optical dispersion of the material under investigation can then be used as fitting parameters and optimized to produce the best fit. Care must be taken to minimize the number of parameters and their range.
to ensure a physically sensible model. Fig. 2.2 shows an example of experimental data and fit functions for PC$_{60}$BM. The dispersion function used to fit the PC$_{60}$BM data is a sum of oscillators with a cut-off frequency:

$$n(\omega) = n_{\infty} + \sum_j \frac{B(\omega - \omega_j) + C}{(\omega - \omega_j)^2 + \Gamma_j^2}$$

(2.1)

where

$$B = \frac{f_j}{\Gamma_j} \left( \Gamma_j^2 - (\omega_j - \omega_g)^2 \right)$$

(2.2a)

$$C = 2f_j\Gamma_j(\omega_j - \omega_g)$$

(2.2b)

and

$$\kappa(\omega) = \begin{cases} 
\frac{f_j(\omega - \omega_j)^2}{(\omega - \omega_j)^2 + \Gamma_j^2}, & \omega > \omega_g \\
0, & \omega \leq \omega_g 
\end{cases}$$
The best fit is produced from a sum of five oscillators with oscillator strength, $f_j$, frequency, $\omega_j$, and width, $\Gamma_j$. The ellipsometry software uses these fit parameters, the known dispersion of the substrate, and the thickness of the PCBM layer to simulate $r_p$ and $r_s$ to match the experimental data. The optimum dispersion fit parameters used to produce Fig. 2.2 are shown in Table 2.1 below. The dispersion equation and the fit parameters are then used to calculate the complex index of refraction of material under investigation (PCBM in this example). The resulting dispersion function is shown in Fig. 2.3.

<table>
<thead>
<tr>
<th>$j$</th>
<th>$f_j$ [eV]</th>
<th>$\omega_j$ [eV]</th>
<th>$\Gamma_j$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.060</td>
<td>2.286</td>
<td>0.509</td>
</tr>
<tr>
<td>2</td>
<td>0.002</td>
<td>3.247</td>
<td>0.246</td>
</tr>
<tr>
<td>3</td>
<td>0.003</td>
<td>4.155</td>
<td>0.516</td>
</tr>
<tr>
<td>4</td>
<td>0.015</td>
<td>4.420</td>
<td>0.558</td>
</tr>
<tr>
<td>5</td>
<td>0.005</td>
<td>5.099</td>
<td>0.369</td>
</tr>
</tbody>
</table>

Table 2.1: Summary of oscillators contributing to PCBM dispersion.

Figure 2.3: PCBM dispersion function obtained by ellipsometry.
2.3 Results

2.3.1 Transfer Matrix Results and ITO Thickness Dependence

Using the optical transfer matrix calculations and spectroscopic ellipsometric measurements of optical constants for ITO, PEDOT:PSS, PTB7 and P3HT:PCBM, we model the absorption in our PV devices at normal incidence. For each film structure, the absorbance of the active layer was calculated as a function of the active layer thickness and wavelength. Additionally, the absorbance was multiplied by the AM1.5G solar spectrum to obtain the spectral dependence of absorbed light as a function of active layer thickness. Finally, the solar absorbance spectra are integrated to obtain the total absorbed photons as a function of active layer thickness.

In Fig. 2.4a we plot the calculated absorbance spectra of a free-standing P3HT/PCBM blend film surrounded by air as a contour of the film thickness and wavelength. As would be expected, the absorption spectra remain relatively unchanged and the absorbance increases nearly monotonically as the thickness is increased. However, even in the case of a free-standing film, small interference effects are observed due to reflection at the interfaces. Near 600 nm, for example, the absorbance decreases as the BHJ thickness is increased from 155 nm to 200 nm. As can be seen in Fig. 2.4b, by surrounding the absorbing medium with more reflective materials, these interference effects are enhanced. Figure 2.4c depicts the same spectrum multiplied by the AM1.5 solar spectrum, thus depicting the spectrum of absorbed sunlight, showing long wavelength absorption enhancement near 200 and 350 nm thickness. A typical OPV device architecture consists of a thick glass substrate that can be treated incoherently[47, 48] with subsequent
layers of 150 nm ITO, 40 nm PEDOT:PSS, P3HT:PCBM of varying thickness, and 200 nm Al. The absorbance calculation for this device is shown in Fig. 2.4b as a contour plot. The darkened contours indicate wavelength/thickness regions where the absorption is much greater than observed in the bare P3HT/PCBM film. These regions coincide with resonance conditions for the coupled material-cavity system. The appearance of a remarkable series of diagonal contour structures indicates significant interaction between the first several cavity modes and the absorbing semiconducting materials. This interaction can be described by frequency pulling, similar to that described in lasers, and discussed further below. Interestingly, the absorption edges at both high and low energy are broadened.

We next performed additional calculations for various ITO thicknesses between 50 and 200 nm. We find, generally, that the first cavity resonance (BHJ thickness below 100 nm) is strongest for ITO thicknesses of less than 140 nm. By plotting the total absorbed photons versus P3HT/PCBM thickness for a series of ITO thicknesses, we find that the cavity enhancement at the first interference peak can be significantly increased (Fig. 2.4d). In fact, the peak absorption for a P3HT/PCBM thickness of about 80 nm is very sensitive to the thickness of the ITO layer, and significant spectral changes can be effected merely by adjusting the ITO thickness from 150 nm to 110 nm with no other optical layers required. This result confirms that the thickness and optical constants of the transparent anode should be optimized during device design to control absorption in the BHJ layer. We find a particularly interesting design, its absorption contour depicted in Fig. 2.5, where the absorption is concentrated across most of the visible spectrum for a BHJ layer thicknesses around 80 nm. Based on our transfer matrix
Figure 2.4: (a) Absorptance of a free-standing P3HT:PCBM film in air calculated by optical transfer matrix theory for thicknesses ranging from 0 to 400 nm. (b) Absorptance of the P3HT:PCBM layer calculated by optical transfer matrix theory for a photovoltaic structure consisting of ITO (150 nm) / PEDOT:PSS (40 nm) / P3HT:PCBM (0-400 nm) / Al (120 nm). (c) Total absorbed photons in the P3HT:PCBM layer calculated by transfer matrix theory for a photovoltaic structure consisting of ITO (150 nm) / PEDOT:PSS (40 nm) / P3HT:PCBM (0-400 nm) / Al (120 nm). (d) Total absorbed photons in the P3HT:PCBM layer calculated by transfer matrix theory for a photovoltaic structure consisting of various thicknesses of ITO / PEDOT:PSS (40 nm) / P3HT:PCBM (0-400 nm) / Al (20 nm).
calculations, we expect that these 80 nm active layers would capture only slightly less optical energy than a 230 nm active layer thickness device. However, due to the arguments above, we would expect PCEs in these devices to be comparable or larger, due to reduced bimolecular recombination\[20–22\]. As OPV devices of various thicknesses are fabricated, the morphology must be optimized in each case in order to realize the expected increase in power conversion efficiency.

![Figure 2.5: Total absorbed photons in the P3HT:PCBM layer calculated by transfer matrix theory for a photovoltaic structure consisting of various thicknesses of ITO / PEDOT:PSS (40 nm) / P3HT:PCBM (0-400 nm) / Al (20 nm).](image)

### 2.3.2 Weak Cavity Model

To understand the origin of the distinctive diagonal spectral features in Fig. 2.4b, we calculate the resonant frequency of the multilayer cavity, \( \nu \), using a simple frequency pulling model, that depends on the bare cavity frequency, \( \nu_m \), and the cavity bandwidth,
\( \delta \nu_c \), as well as the absorber's transition frequency, \( \nu_{21} \), and bandwidth, \( \delta \nu_{21} \).

\[
\nu = \frac{\nu_{21} \delta \nu_c + \nu_m \delta \nu_{21}}{\delta \nu_c + \delta \nu_{21}}
\]  

(2.3)

This model describes the frequency dependence of the observed coupled modes arising from dispersion of the material's refractive index interacting with the cavity. Using this model, we calculate the first several resonant modes of the cavity for various device thicknesses and plot them overlaid on the transfer matrix contours described above (see Fig. 2.6). We find excellent agreement between the areas of cavity-enhanced absorbance and the calculated cavity resonances. The non-trivial modal structure is due in large part to the strong wavelength dependence of the material dispersion near resonance. To compare with experiment, we use specular reflectance spectroscopy. The peaks and troughs correspond to strong and weak absorption, respectively, for structures with varying active layer thickness. The transmittance for these structures is negligible due to the high reflectance of the aluminum cathode, so the absorbance is plotted as \( A = (1 - R) \). Figure 2.8(a) clearly shows features of the reflectance spectra shifting to longer wavelengths as the P3HT/PCBM thickness is increased. Additionally, for structures with P3HT/PCBM thickness between 200 and 250 nm, the absorption near the 600 nm edge is extended and enhanced, which is important for capturing the peak solar irradiance near 600 nm, hence increasing PCE. By plotting the points where these absorbance peaks or troughs occur on top of the calculated absorbance for devices with identical architecture (see Fig. 2.8(b)), we find significant correlation in that areas of predicted absorption enhancement coincide with peaks in the absorption spectra and,
conversely, areas predicted to have low absorbance coincide with absorption dips. As the P3HT/PCBM thickness is varied, no changes to the materials’ HOMO and LUMO energies is made, and yet the cavity interference effects can shift absorption features by 50 or 100 nm (up to 400 meV). This optical method of extending the absorption spectrum of OPV active layers is an approach with no trade-off to other device parameters contributing to the PCE.

![Figure 2.6: Absorptance contour calculated by the transfer matrix method with the first four cavity modes plotted as black dots on top for a typical photovoltaic architecture: ITO (150 nm) / PEDOT:PSS (40 nm) / P3HT:PCBM (0-400 nm) / Al (120 nm).](image)

The cavity quality factor $Q$ for these devices is very small. This explains why the cavity enhancement is spectrally broad. However, it is then surprising to see such strong spectral shaping. The cavity quality factor for these modes depends on the cavity length $L$ and the reflectivity of the electrodes. Due to the dispersion of the materials, $Q$ is also a function of incident wavelength.
Figure 2.7: Quality factor versus incident wavelength of P3HT:PCBM photovoltaics for several different active layer thicknesses, $L$.

\[ Q(L, \lambda) = \frac{\omega}{2\delta\nu_c} \]  \hspace{1cm} (2.4)

where the cavity bandwidth, $\delta\nu_c$ is given by

\[ \delta\nu_c = \left| \frac{1}{4\pi} \frac{c}{2L} \ln \left( \frac{1}{|r_1r_2|} \right) \right| \]  \hspace{1cm} (2.5)

These cavity $Q$s are plotted in the visible spectrum in Fig. 2.7 for several different thicknesses.
Figure 2.8: (a) Normal incidence absorbance spectra of a series of structures with varying active layer thickness consisting of ITO (150 nm) / PEDOT:PSS (40 nm) / P3HT:PCBM (80 - 250 nm) / Al (100 nm). Notable peaks and troughs are observed to shift with active layer thickness and distinct features are highlighted by symbols. For comparison, the material extinction spectrum is also shown as a dashed curve. (b) A zoomed-in view of the simulation results of Fig. 2.4b with peaks (green circles, black squares) and troughs (blue triangles) from normal incidence absorbance measurements (Fig. 2.8(a)) plotted on top showing agreement between calculations and experiment.
2.3.3 Specular Reflectance

In addition to normal incidence modeling and experiments, transfer matrix calculations and specular reflectance measurements were performed on a 100 nm P3HT:PCBM active layer and 150 nm ITO thickness sample\[49\] (see Figure 2.9). As the angle of incidence is tuned, the most noticeable effect observed in the transfer matrix calculations is a reflectance dip that shifts to shorter and shorter wavelengths. Additionally, the absorption edge at 630 nm is seen to move to longer wavelengths. In specular reflectance measurements, these features are plotted versus incidence angle overlaid onto the transfer matrix calculations. The shifting of these features with incidence angle is confirmed by the specular reflectance measurements. Surprisingly, these shifts are fairly inconsequential to the overall device absorbance. Unlike high-Q cavities, these weaker cavities have much less sensitive angular dependence.

2.3.4 PTB7

In the next series of experiments, we fabricated a series of samples with PTB7 as the absorbing medium to determine the applicability of spectral design shaping of the active layer by thickness control for next generation alternating co-polymers. PTB7 is known to have a large extinction coefficient and an absorption edge extending further into the red\[50, 51\]. As a result of careful chemical design and device optimization, very large power conversion efficiencies have been reported using this material\[52, 53\]. Using a neat film rather than a mixture of two materials allows the most straightforward conclusions regarding any spectral shifts. As with the P3HT/PCBM samples, thickness
Figure 2.9: Transfer matrix simulation of reflectance of a 150 nm ITO, 100 nm P3HT:PCBM device. The inset shows the specular reflectance at a 40.5°. Features observed in the reflectance are overlaid onto a contour plot of reflectance versus angle and wavelength.

dependent absorption features demonstrate a large degree of spectral control especially in tuning the low energy absorption edge. It can be seen in Fig. 2.8(b) that long wavelength absorption enhancements occur periodically as a function of thickness. Careful engineering of the active layer thickness and ITO thickness can be used to extend absorption, and importantly this enhancement occurs even in materials that have been carefully designed to capture low energy photons. In addition, oscillations in the absorption spectrum especially at shorter wavelengths appear as peaks and dips whose location depends strongly on thickness (see Fig. 2.10(a)). Comparing these measured absorption peaks and dips with simulations, we find that there is a strong match with corresponding absorption characteristics observed in the active layer with the transfer matrix formulation calculations. In particular, the strong agreement between
measurement and calculation of the location of absorption resonant enhancement or suppression as well as their shift as a function of active layer thickness is seen in Fig. 2.10(b).

![Figure 2.10](image)

Figure 2.10: (a) Normal incidence absorbance spectra of a series of PTB7 films of various thickness consisting of ITO (150 nm) / PTB7/ Al (100 nm). The material extinction spectrum is also shown. (b) A contour plot simulated by optical transfer matrix calculations overlaid by data with blue corresponding to peaks in Fig. 2.10(a), and black corresponding to valleys.

We note that in comparing the extinction coefficients in Figs. 2.8(a) and 2.10(a) with their corresponding cavity absorption, that the cavity effects are considerably larger in the PTB7 samples than in the P3HT/PCBM samples. This observation is consistent with the values of the extinction coefficients and oscillator strengths indicating that the cavity tuned absorption is stronger for larger oscillator strengths due to stronger coupling between the cavity modes and the material.

In order to provide the maximum range of efficiency control by spectral shaping using this method, it is highly desirable to use active layers that are less subject to decreases in charge collection efficiency as the active layer thickness is modified. This could be
achieved by developing new materials or by optimizing processing conditions during the BHJ deposition and annealing\cite{54}. One thickness dependent morphology study that optimized processing\cite{55} suggests that 100 nm P3HT/PCBM thickness produces a higher degree of P3HT crystallinity and nanowire formation that should lead to higher photocurrent collection. We believe that further optimization of nanoscale morphology for various active layer thickness BHJ films could yield large photocurrents in especially thin, spectrally optimized devices. Additionally, consideration of optical interference effects may serve to guide work on novel materials designed to interact favorably with the cavity to influence absorption spectra and efficiency in devices.

### 2.4 Conclusions

Transfer matrix theory has been utilized to model the absorption of organic photovoltaic devices as a function of active layer thickness and incident wavelength, with results consistent with experiment. In particular, we have examined the optical enhancements that arise from the design of the ITO and Al electrodes, and identified a high efficiency cavity structure not requiring additional optical spacer layers due to the high sensitivity of the design to the thickness of the ITO layer, within the thickness range of high-performance ITO. Significant spectral effects are observed, including frequency pulling that tunes the optical absorption and extends the absorption spectrum to longer wavelengths, decoupled from the open circuit voltage, hence also the HOMO/LUMO energetics. The absorption features can be shifted by as much as 0.4 eV, without the deleterious change in open-circuit voltages that accompany other approaches. This
independence of the shift from the open-circuit voltage suggests the ability to adjust
the absorption spectrum of photovoltaic devices independently of the material, which
could have major implications as the extended spectrum leads to increased PCE. Note
that these cavity pulling effects are highly dependent on the details of the absorption
spectrum, such as oscillator strength, and refractive index dispersion for particular ma-
terials, so that such studies for other materials should be routinely carried out and used
to select the optimum coupled material/device-design combination. Regardless, this
modeling provides additional degrees of freedom in optimizing organic photovoltaics.
Future work is aimed in this direction, taking into account that optimized processing is
also a critical consideration.

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Chapter 3

Device Optimization of Inverted

PTB7:PC\textsubscript{71}BM OPVs

3.1 Introduction

Polymer photovoltaics represent one of several technologies to fill the need for renewable energy sources for the replacement of current carbon-based energy production. Desirable mechanical properties, low-cost manufacturing, and straightforward customization through chemical synthesis have spurred rapid innovation and efficiency increases. Further improvement in efficiency and stability are needed for commercial viability and widespread market adoption. Two of the main challenges being addressed to raise power conversion efficiency are to redden the absorption spectra without lowering open circuit voltage, and to absorb as much light as possible despite an excitation diffusion length much shorter than the extinction length of light. The first challenge has been addressed largely by synthesizing molecule and polymer donors with smaller bandgaps\cite{1–5}. This
strategy has resulted in donors that achieve state-of-the-art efficiencies with absorption extended through most of the visible spectrum. To the second challenge: there are many means by which light absorption can be increased despite a short diffusion length. One of the most successful has been the use of bulk heterojunction architectures that provide charge separating interfaces throughout the bulk of a thick absorbing layer. However, even using BHJs, very thick layers become disadvantageous due to poor charge carrier mobility\[6\], charge recombination, and high densities of trap states\[7\] that has fueled interest in other means of absorption enhancement. Among these are the use of textures\[8, 9\], photonic crystals and diffractive elements, and optical interference effects.

Here we focus on BHJ active layers using the donor Poly\[4,8-bis(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl] [3-fluoro-2-[(2-ethylhexyl)carbonyl] thieno[3,4-b]thiophenediyl] (PTB7) and acceptor [6,6]-phenyl C_{71} butyric acid methyl-ester (PC_{71}BM), shown in Fig 3.1(a), which have previously been shown to yield large internal quantum efficiencies and exhibit absorption across much of the visible spectrum[10–12]. In addition, the donor's large oscillator strength enhances the customizability of absorption spectra achievable by cavity tuning.

In inverted OPVs, increasing the work function of the metal anode prevents reaction with atmosphere. In addition, omission of the corrosive[13], hygroscopic[14], and thermally unstable[15] poly(3,4-ethylenedioxylenethiophene):poly(styrenesulphonic acid) (PEDOT:PSS) hole transport layer extends device lifetime. Instead of the PEDOT:PSS hole-transport layer, an electron transport layer is used on the ITO cathode. Solution deposited ZnO is well-suited for an electron transport layer in inverted organic solar
cells with a large bandgap[16], high electron mobility[17], solar transparency[18], and well-positioned HOMO energy level for use with PC$_71$BM acceptor.

In this work we aim to use optical transfer matrix theory[19, 20] to guide design of inverted organic photovoltaic devices via optimization of the thickness of BHJ and charge selective layers. Using a spectral sculpting enhancement of absorption using cavity effects[21], we demonstrate a large range of absorption spectra achievable by simple tuning of device layer thicknesses. Finally, we compare external quantum efficiency measurements to transfer matrix simulations to demonstrate the agreement between simulations and fabricated devices.

3.2 Experimental

3.2.1 Materials and Sample Fabrication

The inverted device structure of cells fabricated for this study is shown in Fig. 3.1(b) and consists of the following: glass/ITO/ZnO/PTB7:PC$_71$BM/MoO$_3$/Ag. Transfer matrix calculations guided design of the range of thicknesses used and will be described below. Patterned ITO-coated glass substrates were obtained from Thin Film Devices, Inc. ITO thickness was measured using a stylus profilometer to be 270 nm and the sheet resistance was 10 $\Omega/\square$. Substrates were cleaned by subsequent sonications in detergent water, DI water, methanol, isopropanol, and acetone followed by a 20 min. UV-ozone treatment at 150 °C. Various thicknesses of ZnO layers were deposited on the clean substrates by spin-coating from several solutions with a range of molar concentrations.
A stock 0.5 M Zn-precursor was prepared by adding 329.4 mg Zn(CH$_3$COO)$_2$·2H$_2$O (99.9% Sigma-Aldrich) in 3 mL 2-methoxyethanol (anhydrous, Sigma-Aldrich) in 90 µL ethanolamine (distilled, Sigma-Aldrich). This solution was aged 24 hrs. to ensure complete dissolution. Then, a 0.25 M, 0.1 M, and 0.05 M solution were prepared by diluting the 0.5 M stock solution appropriately with 2-methoxyethanol. The 0.5 M ZnO layer was spun-cast at both 2000 RPM and 4000 RPM for 40 seconds to afford a 40 and 30 nm film respectively. The 0.25 M, 0.1 M and 0.05 M solutions were all spun at 4000 RPM for 40 s to afford a 20, 10, and 6 nm film, respectively. All films were then baked at 170°C for 10 min. and then transferred to a N$_2$-filled glovebox. Solutions of PTB7:PC$_{71}$BM (1:1.5 wt.) at a concentration of 10 mg/mL were prepared in chlorobenzene with the additive 1,8-diiodoctane (DIO) (97:3 % vol.). The thickness of the deposited active layer was controlled by varying the speed and acceleration of the spin-coating process. Finally,
the MoO$_3$ (10 nm) and Ag (100 nm) anode were deposited by thermal evaporation through a shadow mask to give a defined active area of 0.07 cm$^2$. The active layer solution preparation and all subsequent fabrication was performed under dry nitrogen atmosphere.

### 3.2.2 Device Characterization

The $J - V$ curves of all devices were measured using a Keithley 2400 source meter and an Oriel Sol2A solar simulator (AM1.5G, 100 mW/cm$^2$) integrated into a N$_2$-filled glovebox. Spectrally resolved External Quantum Efficiency (EQE) was measured using a benchtop QEX10 measurement system provided by PV Measurements Inc.. Each device was briefly exposed to room atmosphere during the 5 min. EQE measurement.

Absorption calculations within each layer of the device between wavelengths of 350 and 900 nm were performed using optical transfer matrix theory. Complex refractive index spectra for the materials used were determined using variable angle spectroscopic ellipsometry (Uvisel DUV-NIR, Horiba).

### 3.3 Results

#### 3.3.1 Transfer Matrix Calculations

Led by optical transfer matrix calculations, we sought to explore changes in device performance as the thickness of both the active and ZnO layers are varied. Transfer matrix calculations predict a range of active layer thicknesses near 100 nm for which
the number of solar photons absorbed reaches a local maximum. As the thickness of this layer is increased, the solar absorption decreases slightly before continuing to increase. However, inefficient charge collection due to recombination in these thickest active layer devices is expected to decrease power conversion efficiency. In addition, the thin active layers will produce a larger internal electric field that will result in more efficient charge-collection. It was also found that in order to increase solar absorption within the active layer, the thickness of the ZnO layer should be kept to a minimum. Of course the ZnO thickness must be thick enough to serve as an effective hole-blocking layer. In addition, we calculate the spectrum of light absorbed by the active layer and its strong dependence on thickness due to optical interference effects. This cavity enhanced absorption that has been reported previously using non-inverted architectures[21] is used here to optimize device design and shape absorption within the PTB7:PC$_{71}$BM layer.

Using optical transfer matrix theory the total number of absorbed solar photons within the active layer was obtained by multiplying active layer absorption by the AM1.5G spectrum. This simulation was performed as functions of the thickness of active and ZnO layers and is presented as a contour in Fig 3.2a. For all active layer thicknesses studied, more solar photons are absorbed within the active layer as the thickness of the ZnO layer is decreased. Near 100 nm active layer thickness, more photons are absorbed than in slightly thicker (125 nm) layers. The reason for this can be illustrated more clearly by examining the absorption spectra within the active layer as a function of active layer thickness which is shown in Fig 3.2b. For active layer thicknesses of approximately 100 nm, a region of enhanced absorption is predicted.
between wavelengths of 550 and 700 nm. A similar absorption enhancement occurs near 250 nm active layer thickness. Diagonal features of the absorption enhancement of the contour in Fig 3.2b are described by a frequency-pulling model described previously[21]. These calculated diagonal features will appear as absorption peaks that shift wavelengths as the active layer thickness is increased and can be compared later with External Quantum Efficiency (EQE) measurements.

![Figure 3.2: (a) Absorption contour calculated by optical transfer matrix theory as functions of ZnO and active layer thicknesses. Total absorbed photons increases as ZnO thickness is decreased. In general, thicker active layer thicknesses result in more absorption except in the region near 100 nm and 250 nm active layer thicknesses resulting from cavity effects. (b) Active layer absorption spectral contour calculated by optical transfer matrix theory as a function of active layer thickness. Control of absorption spectra is exercised via careful control of active layer thickness.](image)

Transfer matrix calculations were also used to determine optical field distribution within the device (see Figure 3.4). At 100 nm PTB7:PC_{71}BM layer thickness, optical fields for each wavelength have one peak in the active layer and for all but 400 nm, have no minimum. This optical field distribution demonstrates concentration of light
within the active layer and results in a large simulated photocurrent. For the 150 nm PTB7:PC$_7$1BM layer thickness, optical fields have a maximum in the active region, but most also have a minimum. This minimum lowers the overall average optical energy density within the active region and results in lower performance. With increased thickness, more maxima and minima are brought into the active region that produces an oscillating average optical energy density within the active region as a function of PTB7:PC$_7$1BM layer thickness. This also qualitatively explains why the amplitude of these oscillations diminishes with increased active layer thickness as the average optical energy density is less and less affected by the addition of a new minimum or maximum for very thick devices.
Figure 3.4: (a) Normalized optical field distribution within a device with ITO (270 nm)/ZnO (5 nm)/PTB7:PCBM (100 nm)/MoO$_3$ (5 nm)/Ag(200 nm) for incident wavelengths of 400, 500, 600, 700, and 800 nm. (b) Normalized optical field distribution within a device with ITO (270 nm)/ZnO (5 nm)/PTB7:PCBM (150 nm)/MoO$_3$ (5 nm)/Ag(200 nm) for incident wavelengths of 400, 500, 600, 700, and 800 nm.

3.3.2 Electrical Characterization

Measuring $J$-$V$ performance of the fabricated cells, we find relatively good agreement with calculations. Short circuit current increased as the active layer thickness increased as expected. The shape of the thickness dependent short circuit current is well-matched with transfer matrix simulations (see Fig. 3.5c). Scatter within our experimental data do not allow us to resolve the slight peak in $J_{SC}$ near 100 nm as is predicted in the transfer matrix calculations. Additionally, short circuit current for the thinnest devices outperforms transfer matrix calculations. This underestimation of absorption could be due to scattering within the device or changes in optical properties for the thinner films that is not accounted for in these simulations. Thickness dependent morphology within the BHJ layer may substantially change the optical constants of this layer.
Fill factor decreased for the thickest active layers as is expected\[22, 23\]. The decrease in fill factor is the chief contribution to decreasing PCE for the thickest devices, and the resulting curve of PCE vs active layer thickness produces a peak near 100 nm. Variation of the open-circuit voltage is small and does not depend strongly on active layer thickness, despite the shifts in absorption spectra.

In addition to the 5 nm ZnO thickness samples discussed above, samples with a range of ZnO layer thicknesses were also prepared. In these samples, a small decrease in short circuit current is observed for thicker ZnO layer thickness (see Fig. 3.6b. This is consistent with the optical transfer matrix results shown in Fig. 3.2a. This decreased photocurrent for thick ZnO layers in inverted structures stands in contrast to the so-called "optical spacer" effect\[24\]. The result of an optical spacer adjacent to the highly-reflective cathode in a standard architecture OPV cell is to maintain large optical field density in the BHJ region by using a spacer where the optical field has nearly completely decayed near the cathode. In inverted architectures, the ZnO layer is next to the ITO electrode. Here the transparent "optical spacer" is not filling the region of decayed field; instead it is taking up valuable space in the weak optical cavity formed by the electrodes. Therefore, the thickness of this layer should be minimized so that a larger fraction of the optical cavity is filled by the active layer.

External quantum efficiency measurements allow us to examine the spectrum of light that is absorbed within the active layer and then subsequently measured as an external device current. Comparing absorbance within the active layer predicted by optical transfer matrix theory and measured EQE, we see very good agreement. This comparison is equivalent to assuming an internal quantum efficiency of unity. The wavelengths that
Figure 3.5: (a) Open circuit voltage, (b) fill factor, (c) short circuit current, and (d) power conversion efficiency measurements versus active layer thickness for samples with ZnO thickness of 5 nm are depicted as points connected by lines to guide the eye. The theoretical short circuit current (c) is plotted as a solid black line. Open circuit voltage remains relatively constant with active layer thickness. Fill factor decreases versus active layer thickness due to recombination and trapping in thick BHJ films. The trend of short circuit current versus active layer thickness compares favorably with theory. Power conversion efficiency peaks near 100 nm due to a balance of falling fill factor for the thickest devices (b) and the increasing short circuit current (c).
Figure 3.6: (a) Example illuminated $J - V$ curves for active layer thicknesses of 40, 65, 100, 195, and 250 nm. (b) Short-circuit current values versus ZnO thickness for active layer thicknesses of 100, 90, 85, 65, and 55 nm.

Optical peaks occur are predicted to shift as the active layer thickness is increased are seen to coincide with the EQE spectra. This agreement between simulated absorption within the active layer and measured EQE spectra indicate the sound approach of using optical transfer matrix theory to optimize and shape absorption spectra in polymer photovoltaics.

## 3.4 Conclusions

Optical Transfer Matrix modeling was used to investigate and optimize absorption within the active layer of inverted PTB7:PC$_{71}$BM solar cells. Using ZnO and active layer thicknesses as design parameters, total absorbed solar photons were maximized for optimal device performance. Two design guidelines were developed by transfer matrix modeling and then realized in physical devices: 1) The ZnO layer thickness should be
Figure 3.7: External quantum efficiency (black dots) and absorption calculated by optical transfer matrix theory (blue solid lines) for PTB7:PCBM thicknesses of (from top to bottom) 250, 195, 100, 90, 85, 65, 55, and 40 nm.
minimized so that a maximal fraction of the weak optical cavity formed by reflective and transparent electrodes be composed of PTB7:PC$_{71}$BM. This result stands in contrast to the concept of an "optical spacer" advanced by others[24]. 2) A local maximum in total absorbed photons occurs for active layer thickness near 100 nm, and this local maximum should be preferred to avoid recombination losses in much thicker devices. Strong spectral agreement between External Quantum Efficiency Measurements and Transfer Matrix calculations demonstrate the degree of spectral design that can be accomplished by optical modeling. These design guidelines and optimization by optical modeling resulted in inverted PTB7:PC$_{71}$BM devices with large short-circuit currents, fill factors, and ultimately power conversion efficiencies validating this approach.

References


Chapter 4

An Indole-Squaraine Nonlinear Optical Glass

This chapter is adapted from:


4.1 Introduction

The synthesis and properties of a new indole-based squaraine dye functionalized with ethylhexyl substituents are reported. The chromophore displays a large two-photon absorption cross-section of 1490 GM at a resonance wavelength of 1160 nm. The crystalline material exhibits a melting temperature of 222°C, which is sufficiently low to allow for melt-processing without significant thermal decomposition. Crystallization of the dye from the melt is exceedingly slow, so that amorphous glasses with a glass
transition temperature of 60°C can easily be produced, even without particularly rapid cooling. This allows the fabrication of thin films and more complex shapes, which offer a maximum of dye content, yet lack the scattering effects associated with organic crystalline materials.

Nonlinear optical (NLO) materials that possess large two-photon absorption (2PA) cross-sections (σ) are useful in a plethora of applications such as optical switching[1] and limiting[2], two-photon photoluminescence (PL) microscopy[3], photo-dynamic therapy[4], and 3D optical data storage[5]. For many devices, such as optical switches or multiplexers based on macroporous silicon that is locally infiltrated with a NLO dye[6] or polymer-based adaptive dielectric mirrors[7], it would be desirable or even required that the NLO material could be melt-processed and quenched into an amorphous glass. This would allow the fabrication of thin films and more complex shapes, which offer a maximum of dye content, yet lack the scattering effects associated with organic crystalline materials. However, low-molecular weight nonlinear optical compounds that can be melt-processed into amorphous glasses are rare. We here report a new indole-based squaraine dye that exhibits these properties and also a large σ.

Squaraines have been long known to possess unusually large third-order intensity dependent refractive indices[8–10]. Renewed interest in squaraines has focused on 2PA[11]. The unusually large nonlinear optical response in both the real and imaginary response functions derives from efficient symmetric intramolecular charge transfer (ICT) in dominant low-lying excited states. The ICT results from efficient electron distribution between the electron-rich indole functionalities and the highly electron-deficient squarylium core. The high polarizability of squaraines has also led to their
exploitation in applications that do not exploit their optical nonlinearity[12], including ion sensors[13], light-emitting field-effect transistors[14], and dye-sensitized solar cells[15]. Unfortunately, the high rigidity, polarity, and polarizability render squaraines rather intractable; their solubility is usually low, and few examples are known that can be melted without decomposition[8–16]. The introduction of bulky aliphatic substituents has, however, afforded highly soluble squaraine derivatives, which can be solution-processed into crystalline or amorphous films[17]. However, squaraine derivatives, which can be melt-processed and quenched into an amorphous glass, are to the best of our knowledge unknown. As a high-number-density solid is formed, the bulk response would be highly enhanced over amorphous polymeric materials. We here report the synthesis and properties of a new indole-based squaraine dye functionalized with ethylhexyl substituents (Fig. 4.1, 3). This structural modification was based on our experience that ethylhexyl groups are very effective in lowering thermal transition temperatures and hindering the formation of ordered structures[18–20].

4.2 Experimental

Methods and General Remarks. 2,3,3-Trimethylindolenine (98%), 2-ethylhexyliodide, anhydrous acetonitrile, and 3,4-dihydroxy-3-cyclobutene-1,2-dione (99%) were obtained from Sigma Aldrich and used as received. All other solvents were of highest commercial quality and obtained from Fisher Scientific. Linear absorption, two-photon absorption, and photoluminescence measurements were carried out in anhydrous toluene, which was purchased from Burdick & Jackson. Reagent grade chloroform (Sigma Aldrich)
was used for the concentration-dependent PL measurements. 1H NMR spectroscopic data were measured in CDCl$_3$, and chemical shifts are expressed in ppm relative to the CDCl$_3$ peak at 7.26 ppm. The 1HNMR spectrum of 2 was obtained on a Varian 300 MHz NMR spectrometer and the spectrum of 3 was obtained on a Bruker 360 MHz NMR spectrometer. Elemental analysis was provided by the School of Engineering at the University of Fribourg, Switzerland.

**Synthesis of 1-(2-ethylhexyl)-2,3,3-trimethyl-3H-indol-1-ium iodide (2).**

2-Ethylhexyl iodide (14.15 g, 62.5 mmol) was combined with 2,3,3-trimethylindolenine (1) (3.99 g, 25 mmol) and anhydrous acetonitrile (38 mL) and the reaction mixture was heated under reflux for 8 days. The reaction mixture was cooled to room temperature and reduced in vacuo. A solution of concentrated hydrochloric acid (4 mL) in methanol (60 mL) was added to the residue and the mixture was stirred for 105 min. The volatiles were evaporated in vacuo, the organic residue was dissolved in CHCl$_3$, and the organic phase was washed with distilled water (3 x 100 mL). The organic layer was separated off, and the solvent was evaporated. Drying in vacuo overnight yielded 2 as a viscous dark red oil (6.2 g, 62 %). 1H NMR (300 MHz, CDCl$_3$): δ 7.61 (m, 4H), 4.59 (d, 2H), 3.05 (s, 3H), 2.11-2.00 (m, 1H), 1.69 (s, 3H), 1.57-1.25 (m, 8H), 1.01 (t, 3H), 0.91 (t, 3H).

**Synthesis of 2,4-Bis[(1-(2-ethylhexyl)-3,3-dimethyl-2,3-dihydroindol-2-ylidene)methyl]cyclobutene-diylium-1,3-diolate (3).**

Compound 2 (3.06 g, 7.6 mmol) and squaric acid (0.416 g, 3.7 mmol) were dissolved in a mixture of toluene (39 mL) and 1-butanol (39 mL) and the reaction mixture was heated under reflux for 42 h in a 250 mL round bottom flask using a Dean Stark trap for
the azeotropic removal of water. The reaction mixture was cooled to room temperature and reduced in vacuo at 75°C. The remaining residue was dissolved in a minimal amount of dichloromethane and purified by column chromatography (silica gel, eluent 6:4 ethyl acetate:hexanes). The resulting product was dried at 40°C in vacuo to yield 3 in the form of green crystals with a metallic luster (0.91 g, 40%). 1H NMR (360 MHz, CDCl₃): δ 7.37-7.26 (m, 4H), 7.16 (m, 2H), 6.99 (d, 2H), 5.99 (s, 2H), 3.89 (d, 4H), 2.20-2.01 (m, 2H), 1.80 (s, 12H), 1.50-1.21 (m, 16H), 0.97 (t, 6H), 0.88 (t, 6H). Anal. Calcd. for C₄₂H₅₆N₂O₂: C, 81.24; H, 9.09; N, 4.51. Found: C, 81.11; H, 9.34; N, 4.36.

**UV-VIS Spectroscopy.**

Absorbance spectra were recorded on a Perkin Elmer Instruments Lambda 800 UV-VIS spectrophotometer. Solution experiments were carried out in toluene at a concentration of 1.6x10⁻⁶ M against toluene as a reference. A spin-cast sample was also measured. In this case, 3 was dissolved at a concentration of 1.3x10⁻³ M in toluene and spin-cast at 500 RPM onto a glass substrate. The melt-processed film was prepared by melting the dye at 235°C on a Gel Instrumente AG hotstage with a TC2 temperature controller, placing a coverslip on top, turning off the hot stage and letting cool to room temperature under ambient conditions. A glass microslide was used as a reference for the spin and melt-casted films.

**Steady-State Photoluminescence Spectroscopy.**

Photoluminescence (PL) measurements on dye-solutions in toluene, spin-cast and melt-processed films, prepared as described above, were acquired using a Photon Technology International C720 spectrophotometer with excitation at 615 nm. All spectra were corrected for the spectral dispersion of the Xe lamp, the instrument throughput, and the
detector response. A reference detector accounted for fluctuation in lamp intensity. A series of 3 solutions in chloroform with concentrations between $8.3 \times 10^{-6}$ and $1.3 \times 10^{-4}$ M was also measured under the same conditions.

**Thermal Characterization.**

The differential scanning calorimetry (DSC) traces were recorded using a Mettler-Toledo DSC-1 equipped with a Huber TC-100 cooling regulation system. All traces were recorded in a nitrogen atmosphere and were recorded with the heating and cooling rates indicated. The polarized optical microscopy images were taken on an Olympus BX51 Polarized Optical Microscope equipped with an Instec STC200 temperature controller and an Instec HCS402 hot stage. Here, the heating rate was 10K/min and cooling was done by allowing the sample reach room temperature after switching off the hot stage, leading to an average cooling rate of 10-15K/min. The nucleation experiments (both the mechanical scratching with the spatula and the nucleation via addition of crystals) were performed on a Gel Instrumente AG hotstage with a TC2 temperature controller.

**Wide-Angle X-Ray Scattering.**

The 1D wide angle X-ray scattering (WAXS) experiments of 3 were carried out at ambient temperature in the reflection mode in a Rigaku diffractometer with a sealed-tube source of CuKα radiation ($\lambda = 0.154$ nm) operated at 40 kV and 40 mA at ambient temperature. The scanning was performed at 0.3 °/min rate.

**Two-Photon Absorption Measurements.**

Two photon absorption spectra were measured using the open-aperture Z-scan technique. A Ti:Sapphire regenerative amplifier (CPA-2010, from Clark-MXR) with 200 fs pulse duration and 1 mJ pulse energy pumped a traveling-wave optical parametric amplifier
of superfluorescence (TOPAS, Light Conversion Ltd.). The second harmonic of the signal was passed through a spatial filter to isolate the lowest-order transverse mode of the beam. The beam was then split into a signal and reference arm that was used to divide by shot-to-shot noise. The beam waist and confocal parameter were determined through measurements of the beam size using a rotating slit beam profiler (BP104-VIS, Thorlabs Inc.) at several z-positions and then fitting these points to the well-known gaussian beam propagation equation.

Data was acquired from photodiodes in combination with a gated boxcar integrator (SR200 series, Stanford Research Systems) while the sample was translated through the focus by a computer-controlled translation stage. The accuracy of the Z-scan measurement was probed by measuring as standards the 2PA cross-section of Rhodamine 6G (standard dye for visible region) and Styryl-9m (purchased from Exciton, standard dye for infrared region). The 2PA cross-section was measured in spectroscopic grade toluene in a 1 mm path-length fused quartz cuvette.

![Figure 4.1: Synthesis of squaraine 3.](image)
4.3 Results and Discussion

4.3.1 Synthesis and Optical Characterization

The preparation of 3 involved the alkylation of 2,3,3-trimethylindolenine (1) with 2-ethylhexyliodide and two equivalents of the resulting N-(2-ethylhexyl)indolinium (2) were subsequently reacted with squaric acid to produce 3 in appreciable yield. The dye displays high (>10\(^{-3}\) M) solubility in solvents such as chloroform, methanol, toluene, and DMF. The dye’s linear absorption and PL spectra in dilute toluene solution and the absorption spectra of a spin-cast thin film and a melt-processed thin film are shown in Fig. 4.2(a). The narrow solution spectra with absorption and PL maxima at 646 and 658 nm are characteristic of molecular solutions of indole-based squaraines\[16\]. The PL spectra are broadened and red-shifted if the concentration is increased from 8.3 x 10\(^{-6}\) to 1.3 x 10\(^{-4}\) M and the PL intensity is severely reduced (Fig. 4.3). This is consistent with self-quenching, a well-known effect for squaraines\[13\]. In both spin-cast and melt-processed films of 3, the PL is completely quenched. The films display absorption spectra that are broadened and somewhat red-shifted (maximum around 676 nm) compared to those of the solution. The optical properties of the spin-cast and melt-processed film are consistent with observations by Wang et al\[21\], who reported broad, red-shifted absorption spectra in a solid thin film of a highly soluble squaraine derivative and attributed these to the strong excitonic interaction between neighboring molecules. The same derivative was reported by Wei et al\[22\], to exhibit similar optical properties and X-ray diffraction confirmed that spin-cast films are indeed amorphous.
Figure 4.2: (a) Optical absorption and PL spectra of 3 in toluene ($1.6 \times 10^{-6}$ M) and absorption spectra of a spin-cast film processed from toluene and a melt-processed film. The PL spectrum was recorded under excitation at 615 nm. (b) Linear absorption spectrum of 3 in toluene ($1.6 \times 10^{-6}$ M) and $\sigma$ of 3 in toluene ($0.01$ M) as a function of wavelength.

Figure 4.3: Photoluminescence spectra of 3 in chloroform as a function of dye concentration (excitation 615 nm).
4.3.2 Z-Scan

Open-aperture Z-scan measurements of toluene solutions were used to establish the $\sigma$ of 3 as a function of wavelength (Fig. 4.2b). The dispersion curve (Fig. 4.2) mirrors that of similar dyes[11] and shows maxima of 1600 and 1490 GM at 720 and 1160 nm, respectively, the former ascribed to resonant enhancement of the adjacent one-photon absorption peak. The latter is the 2PA resonance and is positioned exquisitely for applications in telecommunications where the transparency of optical fibers is high in the near infrared. In order to compare the merit of 3 as a 2PA chromophore with similar molecules, we normalized $\sigma$ to the number of $\pi$-electrons effectively involved in the conjugation[23] ($N_e = 17$); this resulted in a value of $94GM/N_e$, which compares favorably to that of other squaraine chromophores[24].

4.3.3 Thermal and Morphological Characterization

The thermal properties of 3 were studied as a function of thermal history by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The first DSC heating scan (Fig. 4.4(a)) shows a dominant, sharp, endothermic transition, which by way of POM (Fig. 4.4(b) and (c)) and changes of visual appearance (Fig. 4.5(a) and (b)) is ascribed to the formation of an isotropic melt. A closer inspection of the first heating scan reveals a weak endothermic transition at 60°C that is followed by a broad, weak exothermic transition with maximum at 109°C. Taking also into consideration the experiments discussed below, these transitions are assigned as glass transition and crystallization of residual amorphous domains in the as-prepared material. The first
DSC cooling scan (Fig. 4.2(a)) is void of any crystallization peak, even at a cooling rate of 1°C min\(^{-1}\). POM images of samples that were melted and cooled (Fig. 4.2(c)) display no birefringence and wide-angle X-ray diffraction data provide further evidence for the amorphous nature of melted and cooled samples (Fig. 4.6). Thus, these experiments show that, even if cooled at an exceedingly slow rate, 3 solidifies as an amorphous glass. The second DSC heating scan of a melted and slowly cooled sample (Fig. 4.2(a)) shows a well-defined exothermic transition with a considerable enthalpy around 158°C, which corresponds to the crystallization of the sample, as confirmed by POM (Fig. 4.2(d)). Upon further heating, the DSC trace shows a melting transition at 222°C (Fig. 4.2(a)), which is slightly broader than that of the as-prepared material and is of slightly lower enthalpy. Given that the sample has been crystallized under dynamic heating, this is not very surprising. The fact that the crystallization peak is seen at a considerably higher temperature than in the as-produced material (109 vs. 158°C) suggests that the crystallization of 3 upon heating a quenched sample is limited by nucleation. To further probe this aspect, we attempted to promote nucleation by external influences. Fig. 4.5 shows images of samples of 3 that were cooled from the melt and in one case (Fig. 4.5(e)) scratched with a spatula during cooling. The side-by-side comparison shows clearly that the latter perturbation indeed triggers crystallization. The same effect was observed when 3 was quenched into a glass, heated to 80°C and the supercooled melt was similarly treated (Fig. 4.5(f) and (g)). Crystallization could also be induced by adding a few crystals of 3 as seeds into a supercooled melt (Fig. 4.5(c) and (d)). Compound 3 was also cooled at different rates ranging from 1 to 500°C min\(^{-1}\) and the effect on the crystallization during the second heating was studied. The extent of crystallization
decreased as the first cooling rate was increased (Fig. 4.7) and the maximum of the crystallization peak shifted to higher temperatures. Gratifyingly, at a cooling rate of 500°C min⁻¹ no crystallization could be observed upon second heating, suggesting that rapid cooling suppresses the formation of nuclei. When a rapidly quenched sample was stored for 8 days before being heated to 235°C at 10°C min⁻¹, it was found to crystallize with a maximum peak temperature of ca. 135°C (Fig. 4.8), suggesting the formation of some nuclei upon ageing. However, the significant enthalpy of this transition indicates that the stability of the amorphous state under ambient conditions is high. This was further confirmed by POM images of an amorphous sample that was aged for 20 days (Fig. 4.9). Sample decomposition is not an issue as confirmed by NMR experiments (Fig. 4.10).

Figure 4.4: (a) DSC traces for the 1st heating, 1st cooling, and 2nd heating of 3, conducted at the rates indicated. The inset is a magnification (y-axis multiplied by 30) of the 1st heating scan. (b-d) Polarized optical microscopy images (picture widths are 300 μm) of 3: (b) as-synthesized; (c) after heating the sample to 230°C at a rate of 10°C min⁻¹ and cooling to 25°C at a rate of 10 to 15°C min⁻¹ and (d) after re-heating the sample shown in (c) to 180°C at a rate of 10°C min⁻¹.
4.4 Conclusions

In conclusion, we have shown that the functionalization of an indole-based squaraine dye with ethylhexyl groups lowers the melting temperature to below the decomposition temperature, so that melt-processing is possible. The structure also frustrates nucleation, so that the new dye can be cooled to form an amorphous glass, even without particularly rapid cooling. This allows the fabrication of thin films and more complex shapes, which offer a maximum of chromophore number density with potentially high concomitant bulk response (measurements in progress), yet lack the scattering effects associated with organic crystalline materials. These features and its appreciable $\sigma$ of 1490 GM at a resonance wavelength of 1160 nm, suitable for operation at telecommunication wavelengths, suggest that 3 could be an attractive candidate for devices that require
Figure 4.6: Wide-angle X-ray scattering data of 3 as a function of thermal history (as described in the figure).

Figure 4.7: DSC traces of 3. Left: First heating scans. The samples were subsequently cooled at the cooling rates indicated in the figure. Right: Subsequent second heating scans, conducted with a heating rate of 10K/min; the rate of the preceding cooling scan is indicated and the samples correspond to those shown on the left. To enable a comparison of the data in the right, the heat flow of the two graphs was normalized on the basis of equal melting enthalpies in the first heating scan.
Figure 4.8: DSC traces of 3 as a function of thermal history. Shown are the 1st heating trace of an as-prepared sample (1st heating), and the heating trace of that same sample immediately after quenching it with a cooling rate of 500 K/min (2nd heating). The heating trace of the same sample was observed after storing under ambient conditions for 8 days (3rd heating) and immediately after quenching it with a cooling rate of 500 °K/min (4th heating).

Figure 4.9: Optical microscopy images of an amorphous film of 3 that was cooled from the melt under ambient conditions and stored at room temperature for 20 days. The same section (750 x 750 µm) was imaged without polarizer (left) and between crossed-polarizers (right).
Figure 4.10: NMR spectra of 3 as-produced (top) and after melting and冷却回室温（bottom）
integration of a (non-fluorescent) nonlinear optical solid in complex shapes, such as Si-organic-hybrid waveguides[6].

References


Chapter 5

Two-Photon Absorbing

Melt-Processable Cyano-OPVs

This chapter is adapted from:


5.1 Introduction

Two-photon absorption (2PA) is a nonlinear optical (NLO) process that involves the simultaneous absorption of two photons of identical or different frequencies, leading to the excitation of a molecule from the ground state to a higher energy electronic state[1]. Nonlinear transmission and intensity-dependent refraction or other 2PA-related processes can be exploited in a plethora of optoelectronic devices such as waveguides[2], optical switches[3], lasers[4], optical limiters[5], and 3-dimensional
Fluorescence or chemical reactions can also be triggered by 2PA, which enable applications such as biological imaging, photodynamic therapy, and 3-dimensional lithography. Significant efforts have been directed towards the development of organic 2PA chromophores that possess large 2PA cross-sections, which permit one to exploit NLO processes with lower-energy light sources. Strategies to maximize a chromophore’s cross-section include extending the conjugation length and dimensionality, as well as the introduction of electron donating/accepting (D/A) groups to create “push-pull” systems. An effective design involves symmetrically substituted D–π–D chromophores in which two donors are conjugated by a bridge so that excitation leads to large changes of the quadrupole moment. The integration of additional electron-accepting groups in the conjugated system, so that D–π–A–π–D structures are created, further increases the cross-section.

Maximization of the cross-section, however, often comes at the expense of processability, since extended π-systems usually exhibit high melting and dissolution enthalpies and low melting and dissolution entropies, leading to limited solubility and high melting temperatures. Nevertheless, for many devices, such as optical switches, multiplexers based on macroporous silicon structures that are locally infiltrated with a neat NLO dye, or multilayered adaptive dielectric mirrors, it would be desirable if the NLO material could be melt-processed at low temperatures and/or processed from high-concentration solutions. We here report the investigation of several cyano-substituted oligo(phenylenevinylene)s (cyano-OPVs, Fig. 5.1), which can offer rather large two-photon absorption cross-sections and are readily melt-processed at temperatures as low as 100°C. These properties, together with their propensity to form excimers, render them...
attractive for use in polymer-based optical storage systems that operate on the basis of 2PA-induced switching of the aggregation state and fluorescence\cite{6}.

![Chemical structures of the nonlinear optical dyes investigated in this study.](image)

#### Table 5.1: Chemical structures of the nonlinear optical dyes investigated in this study.

<table>
<thead>
<tr>
<th>Dye</th>
<th>R1</th>
<th>R2</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>OMe</td>
<td>OMe</td>
</tr>
<tr>
<td>A2</td>
<td>OC_{18}H_{37}</td>
<td>OMe</td>
</tr>
<tr>
<td>A3</td>
<td>H</td>
<td>OMe</td>
</tr>
<tr>
<td>A4</td>
<td>H</td>
<td>OMe</td>
</tr>
<tr>
<td>B1</td>
<td>OMe</td>
<td>H</td>
</tr>
<tr>
<td>B2</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>C1</td>
<td>NO_{2}</td>
<td>H</td>
</tr>
<tr>
<td>C2</td>
<td>NO_{2}</td>
<td>H</td>
</tr>
</tbody>
</table>

Many low-molecular weight oligo(phenylene vinylene) dyes (OPVs) have already been reported to display appreciable 2PA cross-sections of between 400 and 2000 GM, depending upon the detailed chemical structure and also the solvent\cite{16}. The largest nonlinearities are seen in OPVs in which donor and acceptor groups are connected to create D-\(\pi\)-A-\(\pi\)-D structures, with the objective to maximize the extent of intramolecular charge transfer (ICT). For example, Pond et al. showed that the attachment of cyano groups to the central benzene ring in OPVs with peripheral donor groups increases \(\sigma\) by as much as 900 GM\cite{17}. Interestingly, the 2PA response of OPVs featuring cyano groups attached to the vinylene bridge, and which may be viewed as compact D-\(\pi\)-A-\(\pi\)-D-\(\pi\)-A-\(\pi\)-D systems, has been little explored. The compounds found in the literature all carry the cyano groups in the vinylene positions close to the central benzene ring (CN'-OPVs)\cite{18}.
With respect to maximizing $\sigma$, this configuration is not ideal, since cyano groups in this position are known to twist the molecule out of plane\cite{18}, thereby limiting conjugation and ICT\cite{19}. By contrast, the placement of cyano groups on the vinylene position away from the central ring (CN’’-OPVs) results in planar molecules\cite{18}. Such CN’’-OPVs have attracted our attention as fluorescent “chameleon dyes” due to their propensity to form highly fluorescent excimer complexes and the ability to change their emission color upon (dis)assembly\cite{20–22}. In this context, the high stability of these molecules has been exploited to melt-process them either in their neat form or as blends with a range of different polymers\cite{23–30}. Nonetheless, the 2PA of such CN’’-OPVs has received little attention, perhaps on account of the comparably low 2PA properties of CN’-OPVs. Departing from one CN’’-OPV derivative whose 2PA cross-section was recently reported (Fig. 5.1, A2), we here explore systematic structural variations with the objective to maximize $\sigma$ and minimize the melting temperature ($T_m$) for optimum processability. All of the new dyes form highly fluorescent excimer complexes and display significant emission color changes upon transition from solution to the solid state, which makes them also interesting for sensor applications\cite{23–30} and optical data storage schemes\cite{31}.

### 5.2 Experimental

All commercial reagents were used as received unless otherwise stated in the text. 4-(2-Ethylhexyloxy)phenylacetonitrile\cite{26}, and molecules A1\cite{32}, A2\cite{33}, A3\cite{20}, and B1\cite{32} were prepared as previously described. 1H NMR spectra were recorded
on Varian 300 MHz and 600 MHz NMR spectrometers. Chemical shifts were expressed in ppm relative to the internal chloroform peak at 7.26 ppm. Elemental analyses were conducted by Galbraith Laboratories, Inc.

**Synthesis of (2Z,2'Z)-3,3'-(2,5-bis(octyloxy)-1,4-phenylene)bis(2-(4-((2-ethylhexyl)oxy)phenyl)acrylonitrile) (A4)**

4-(2-Ethylhexyloxy)phenylacetonitrile (156 mg, 0.64 mmol), 2,5-bis(octyloxy)terephthaldehyde (112 mg, 0.29 mmol), THF (4 mL) and t-buOH (11 mL) were combined and heated to 50°C while stirred. t-buOK (0.058 mL of a 1 M solution in THF) and Bu4NOH (0.58 mL of a 1 M solution in methanol) were added quickly and the mixture turned green. The reaction mixture was stirred for another 15 min, cooled to room temperature, and poured into acidified methanol (30 mL containing 1 drop of concentrated acetic acid). The precipitate was filtered off, excessively washed with methanol, and dried in vacuo at 50°C to yield A4 in the form of an orange powder (151 mg, 60%). 1H NMR (CDCl$_3$): $\delta = 7.90$ (s, 2H), 7.85 (s, 2H), 7.62 (d, 4H), 6.97 (d, 4H), 4.14 (t, 4H), 3.93 (d, 4H), 1.86 (m, 4H), 1.80 (m, 2H), 1.57-1.20 (m, 36H), 0.99 (3t, 18H). Calcd: C, 79.57; H, 9.54; N, 3.31. Found: C, 79.39; H, 9.35; N, 3.43%.

**Synthesis of (2Z,2'Z)-3,3'-(1,4-phenylene)bis(2-(4-((2-ethylhexyl)oxy)phenyl)acrylonitrile) (B2)**

4-(2-Ethylhexyloxy)phenylacetonitrile (340 mg, 1.4 mmol), terephthaldehyde (91 mg, 0.68 mmol), THF (5.7 mL) and t-buOH (17 mL) were combined and heated to 50°C while stirred. t-buOK (0.136 mL of a 1 M solution in THF) and Bu4NOH (1.35 mL of a 1 M solution in methanol) were added quickly and a yellow precipitate formed. The reaction mixture was stirred for another 15 min, cooled to room temperature, and
poured into acidified methanol (34 mL containing 1 drop of concentrated acetic acid). The precipitate was filtered off, excessively washed with methanol, and dried in vacuo at 50° to yield B2 in the form of a red powder (240 mg, 60%). 1H NMR (CDCl3): δ = 7.95 (s, 4H), 7.63 (d, 4H), 7.43 (s, 2H), 6.98 (d, 4H), 3.91 (d, 4H), 1.76 (m, 4H), 1.55-1.30 (m, 16H), 0.88 (2t, 12H). Calcd: C, 81.59; H, 8.22; N, 4.76. Found: C, 81.49; H, 7.85; N, 4.86%.

Synthesis of (2Z,2′Z)-3,3’-(1,4-phenylene)bis(2-(4-nitrophenyl)acrylonitrile) (C1)

Terephthaldehyde (0.529 g, 4.0 mmol) and 4-nitrophenylacetonitrile (1.376 g, 8.5 mmol) were combined in a 250 mL 3-neck round-bottom flask. Methanol (100 mL) was added and the mixture was stirred at 50° until the reactants had dissolved. Piperidine (0.86 mL) was quickly added via a syringe. The color of the reaction mixture instantly turned purple and a yellow precipitate formed after 2 min. The reaction mixture was stirred for another 30 min at 50°, cooled to room temperature, and poured into acidified methanol (380 mL containing 8 drops of concentrated acetic acid). The precipitate was filtered off and dried in vacuo at 50° overnight. Recrystallization from DMF yielded C1 in the form of an orange powder (1.18 g, 71%). Calcd: C, 68.24; H, 3.34; N, 13.26. Found: C, 67.57; H, 3.35; N, 13.30%.

Synthesis of (2Z,2′Z)-3,3’-(2,5-bis((3,7-dimethyloctyl)oxy)-1,4-phenylene)bis(2-(4-nitrophenyl)acrylonitrile) (C2)

2,5-Bis(3,7-dimethyloctyloxy)terephthaldehyde (0.200 g, 0.45 mmol) and 4-nitrophenyl acetonitrile (0.1597 g, 0.99 mmol) were combined in a 25 mL 3-neck round-bottom flask. THF (2.6 mL) and t-buOH (7.8 mL) were added and the mixture was stirred at
60° until the reactants had dissolved. Piperidine (0.11 mL) was quickly added via a syringe. The color of the reaction mixture instantly turned orange. The reaction mixture was stirred for another 60 min at 60° and subsequently cooled to room temperature. The solvents were removed using a rotary evaporator. The remaining solid was dissolved in CHCl₃, the solution was filtered through a plug of silica gel, and the solvent was removed using a rotary evaporator. The crude orange product was recrystallized from 2-propanol to yield C₂ in the form of a deep red powder (0.200 g, 60%). 1H NMR (CDCl₃): δ = 8.34 (d, 4H), 8.19 (s, 2H), 7.95 (s, 2H), 7.86 (s, 4H), 4.21 (t, 4H), 1.93 (m, 2H), 1.69-1.12 (m, 14H), 0.98 (d, 6H), 0.84 (d, 12H). Calcd: C, 71.91; H, 7.41; N, 7.62. Found: C, 71.49; H, 7.07; N, 7.58%.

**Synthesis of (2Z,2′Z)-3,3′-(2,5-bis(octyloxy)-1,4-phenylene) bis(2-(pyridin-4-yl)acrylonitrile) (D₁)**

2,5-Bis(3,7-dimethyloctyloxy)-terephthaldehyde (0.150 g, 0.33 mmol) and 4-pyridine acetonitrile hydrochloride (0.115 g, 0.74 mmol) were combined in a 25 mL 3-neck round-bottom flask. THF (2.0 mL) and t-buOH (5.9 mL) were added and the mixture was heated to 60°, while stirring. H₂O (1.0 mL) was added and the mixture was stirred until the reactants had dissolved. Piperidine (0.07 mL) was quickly added via a syringe and the reaction color instantly turned yellow. The reaction mixture was stirred for another 90 min at 60°, cooled to room temperature, and poured into acidified methanol (50 mL containing 1 drop of concentrated acetic acid). The precipitate was filtered off and dried in vacuo at 50° overnight. Recrystallization from boiling methanol to which a few drops of H₂O had been added yielded D₁ in the form of an orange powder (0.978 g, 45%). 1H NMR (CDCl₃): δ = 8.73 (d, 4H), 8.25 (s, 2H), 7.95 (s, 2H), 7.58 (d, 4H),
Synthesis of (2Z,2′Z)-3,3’-(2,5-bis(octyloxy)-1,4-phenylene)

bis(2-(pyridin-2-yl)acrylonitrile) (D2)

2,5-Bis(3,7-dimethyloctyloxy)-terephthaldehyde (0.150 g, 0.33 mmol) and 2-pyridine acetonitrile (0.087 g, 0.88 mmol) were combined in a 25 mL 3-neck round-bottom flask. THF (2.0 mL) and t-buOH (5.9 mL) were added and the mixture was stirred at 55° until the reactants had dissolved. A solution of Bu4NOH (3 drops of a 1.0 M solution in methanol) in THF (5.0 mL) was added drop-wise to the reaction mixture over the course of 10 min. The reaction mixture was stirred for another 60 min at 55°, cooled to room temperature, and poured into acidified methanol (50 mL containing 1 drop of concentrated acetic acid). The precipitate was filtered off and dried in vacuo at 50° overnight. Recrystallization from boiling methanol to which a few drops of H2O had been added yielded D2 in the form of an orange powder (0.117 g, 54%). 1H NMR (CDCl3): δ = 8.87 (s, 2H), 8.67 (d, 2H), 7.96 (s, 2H), 7.74 (m, 4H), 7.30 (m, 2H), 4.20 (t, 4H), 1.92 (m, 2H), 1.76-1.11 (m, 18H), 0.97 (d, 6H), 0.84 (d, 12H). Calcd: C, 77.98; H, 8.41; N, 8.66. Found: C, 77.27; H, 8.16; N, 8.67%.

Differential scanning calorimetry

The differential scanning calorimetry (DSC) traces were recorded using a Mettler-Toledo DSC-1 equipped with a Huber TC-100 cooling regulation system. All traces were recorded in a nitrogen atmosphere with heating and cooling rates of 10 K min⁻¹, except for dye A3, which was recorded at a rate of 5 K min⁻¹.

UV-Vis spectroscopy
UV-Vis absorbance spectra were recorded in chloroform (>99.8% containing 0.75% ethanol as stabilizer) on a Perkin Elmer Instruments Lambda 800 UV-VIS spectrophotometer. For quantum yield measurements, absorbances were measured on a CARY 500 UV-VIS-NIR spectrophotometer.

**Steady-state photoluminescence spectroscopy**

All photoluminescence (PL) measurements were acquired using a Photon Technology International QuantaMaster 40 spectrophotometer under excitation at the wavelength of maximum absorption; the spectra were corrected for instrument throughput and detector response. Quantum yields in degassed toluene ($n = 1.497$) were determined according to the general protocol given in ref. [34] using Rhodamine 6G in EtOH ($n = 1.361$) as reference. Experiments were conducted with samples that had an absorbance of 0.05-0.1 in a 1 cm cuvette on a Horiba Fluorolog 3 with Xenon arc lamp source. Rhodamine has a known fluorescence quantum yield of 0.95[35]. To obtain the quantum yield of the measured chromophores the following equation is used:

$$Q_{dye} = Q_{R6G} \frac{A_{R6G}(530nm)}{A_{Dye}(\lambda_{ex})} \frac{n_{EtOH}^2}{n_{toluene}^2} \frac{F_{Dye}(\lambda_{ex})}{F_{R6G}(530nm)}$$

(5.1)

Where $A$ is the absorbance of the dye in solution at wavelength $\lambda_{ex}$, $n$ is the index of refraction of the solvent used, and $F$ is the integrated fluorescence at the excitation wavelength $\lambda_{Ex}$.

**Determination of solubility in chloroform**

The solubility was determined by weighing a known amount of the respective dye and adding chloroform in small increments while periodically sonicating the solution until
the dye appeared to be visually dissolved. Since these dyes tend to form excimers and therefore should emit light at longer wavelengths when not fully dissolved, the solutions were also observed under 365 nm UV-light.

**Two-photon absorption measurements**

Two photon absorption spectra were measured at wavelengths between 625 and 725 nm using the open-aperture Z-scan technique.[36] A Ti:Sapphire regenerative amplifier (CPA-2010, from Clark-MXR) with 200 fs pulse duration and 1 mJ pulse energy pumped a traveling-wave optical parametric amplifier of superfluorescence (TOPAS, Light Conversion Ltd.). The second harmonic of the signal was passed through a spatial filter to isolate the lowest-order transverse mode of the beam. The beam was then split into a signal and reference arm which was used to divide by shot-to-shot noise. The beam waist and confocal parameter were determined through measurements of the beam size using a rotating slit beam profiler (BP104-VIS, Thorlabs Inc.) at several Z-positions and then fitting these points to the well-known Gaussian beam propagation equation[37].

Data were acquired from photodiodes in combination with a gated boxcar integrator (SR200 series, Stanford Research Systems) while the sample was translated through the focus by a computer-controlled translation stage. The accuracy of the Z-scan measurement was probed by measuring the 2PA cross-section of Rhodamine 6G (2.13 x 10⁻³ M in methanol) at a wavelength of 685 nm and the measured value (76.9 GM [1 GM ≡ 1

<table>
<thead>
<tr>
<th>Dye</th>
<th>Solvent</th>
<th>n&lt;sub&gt;Solvent&lt;/sub&gt;</th>
<th>λ&lt;sub&gt;Ex&lt;/sub&gt; /nm</th>
<th>A(λ&lt;sub&gt;Ex&lt;/sub&gt;) / cm⁻¹</th>
<th>F(λ&lt;sub&gt;Ex&lt;/sub&gt;) / counts</th>
</tr>
</thead>
<tbody>
<tr>
<td>R6G</td>
<td>EtOH</td>
<td>1.361</td>
<td>530</td>
<td>0.0185</td>
<td>2.248 x 10⁸</td>
</tr>
<tr>
<td>A4</td>
<td>toluene</td>
<td>1.497</td>
<td>440</td>
<td>0.0486</td>
<td>3.522 x 10⁸</td>
</tr>
<tr>
<td>B2</td>
<td>toluene</td>
<td>1.497</td>
<td>400</td>
<td>0.0975</td>
<td>7.092 x 10⁸</td>
</tr>
</tbody>
</table>

Table 5.1: Optical properties used to calculate quantum yield of A4 and B2.
$x 10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$) is consistent with values in the literature (55 to 97 GM\cite{38}). The 2PA cross-section of each dye was measured in spectroscopic grade toluene in a 1 mm path-length fused quartz cuvette.

![Nonlinear absorption versus irradiance data obtained during the Z-scan calibration using Rhodamine-6G at a wavelength of 685 nm.](image)

Figure 5.2: Nonlinear absorption versus irradiance data obtained during the Z-scan calibration using Rhodamine-6G at a wavelength of 685 nm.

### 5.3 Results and discussion

In connection with the development of 3-dimensional optical data storage materials, we recently reported the 2PA cross-section of chromophore A2\cite{31}, a 1,4-bis-(α-cyano-4-(2-alkyloxystyryl))-2,5-dialkoxybenzene derivatized with methoxy and octadecyloxy groups in the central and peripheral positions, respectively (Fig. 5.1)\cite{31, 33}. The nonlinear optical characteristics of this dye were explored, because its structure offers several features typically associated with a large $\sigma$, including extended conjugation\cite{39}, a large extent of symmetric charge transfer upon excitation\cite{13}, and donor/acceptor
functionalization[11]. The 2PA cross-section of A2, determined using the open-aperture Z-scan method as a function of wavelength in the range of 625 to 725 nm, where the linear absorption is negligible, was found to reach a maximum of 650 GM at 675 nm[31].

Using this data point, the $T_m$ ($154^\circ$), the solubility (1 x 10$^{-3}$ M), the UV-Vis absorption maximum ($\lambda_{abs} = 371$ nm), and the PL emission maximum ($\lambda_{em} = 507$ nm) in CHCl$_3$ solution as starting points (Table 5.2), we explored systematic structural variations with the objective to create an OPV with maximum $\sigma$ and solubility and minimal $T_m$. Compounds A1[32], A3[20], and A4 with identical electronic structure, but different peripheral substituents, were synthesized via the Knoevenagel reaction of (4-alkyloxyphenyl)acetonitriles, which are readily accessible through alkylation of the parent (4-hydroxyphenyl)acetonitriles[20, 32, 33], with 2,5-dimethoxyterephthalaldehyde (A1, A3) or 2,5-dioctyloxyterephthalaldehyde (A4). As expected, the UV-Vis absorption and PL emission spectra of these chromophores in CHCl$_3$S solution (Table 5.2, Fig. 5.3 and ref. [20, 32, 33]) are essentially identical and match that of A2 (Fig. 5.7). Fig. 5.5, which shows $\sigma$ of selected dyes as a function of wavelength measured by an open-aperture Z-scan measurement, reveals that the 2PA cross-sections of the series A1-A4 are comparable, with a maximum of between 630 and 858 GM at 675 nm (i.e., within the commonly accepted error of ±15%)[40, 41]. We note that in these symmetric dyes, 2PA will probe two-photon allowed $A_g$ symmetry states rather than the one-photon allowed $B_u$ states. Indeed, Z-scan measurements conducted at pump energies near half the one photon absorption maxima yielded negligible 2PA signal.

The common dispersion among these various chromophores is interesting and worthy
<table>
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<tr>
<th>Dye</th>
<th>( \lambda_{\text{max}}^{\text{Abs}} ) (nm) in CHCl(_3)</th>
<th>( \lambda_{\text{max}}^{\text{PL}} ) (nm) in CHCl(_3)</th>
<th>( \lambda_{\text{max}}^{\text{PL}} ) (nm) in solid</th>
<th>( T_m(\degree) ) in CHCl(_3)</th>
<th>Solubility(M) in CHCl(_3)</th>
<th>( \sigma ) (GM)(^{†})</th>
<th>( \sigma/N_{\text{eff}} )</th>
</tr>
</thead>
<tbody>
<tr>
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<td>365, 436</td>
<td>513, 536</td>
<td>644</td>
<td>248</td>
<td>2x10(^{-2})</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>A2</td>
<td>371, 437</td>
<td>507, 538</td>
<td>644</td>
<td>154</td>
<td>1x10(^{-3})</td>
<td>666</td>
<td>26</td>
</tr>
<tr>
<td>A3</td>
<td>371, 440</td>
<td>508, 541</td>
<td>619</td>
<td>141</td>
<td>1x10(^{-1})</td>
<td>858</td>
<td>33</td>
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<td>A4</td>
<td>371, 434</td>
<td>511, 544</td>
<td>594</td>
<td>84</td>
<td>2x10(^{-1})</td>
<td>632</td>
<td>24</td>
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<tr>
<td>B1</td>
<td>389</td>
<td>461, 486</td>
<td>550</td>
<td>279</td>
<td>9x10(^{-3})</td>
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<tr>
<td>B2</td>
<td>397</td>
<td>464, 487</td>
<td>552</td>
<td>157</td>
<td>5x10(^{-2})</td>
<td>378</td>
<td>15</td>
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<tr>
<td>C1</td>
<td>374</td>
<td>no PL</td>
<td>543</td>
<td>325</td>
<td>«4x10(^{-4})</td>
<td>—</td>
<td>—</td>
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<td>360, 458</td>
<td>553</td>
<td>618</td>
<td>191</td>
<td>8x10(^{-3})</td>
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<td>28</td>
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<td>531</td>
<td>584</td>
<td>113</td>
<td>5x10(^{-3})</td>
<td>413</td>
<td>16</td>
</tr>
</tbody>
</table>

Table 5.2: Optical properties and isotropic melting temperatures of the dyes investigated in this study.

\( a \) Absorbance, emission, and thermal data for dyes A1\([32]\), A2\([33]\), A3\([20]\), and B1\([32]\) were reproduced from earlier publications.

\( b \) The isotropic melting temperature is listed here. Dyes A2 and B1 exhibit solid to liquid crystalline transitions below this temperature\([32, 33]\).

\( c \) C1 was not dissolved at this concentration.

\( d \) The 2PA resonance for all dyes was between 650 and 700 nm. In the case of A1, B1, and C1 the solubility in toluene was too low for an accurate determination of \( \sigma \).

\( e \) All molecules studied have an \( N_{\text{eff}} \) value (number of \( \pi \)-electrons effectively involved in conjugation )\([42]\) of 26.

Figure 5.3: UV-Vis absorbance and fluorescence spectra (excitation at 365 nm) of a CHCl\(_3\) solution and solid powder of a) C1 and b) D2.
of quantum chemical studies. The processability of these dyes, however, was found to vary considerably (Table 5.2). The $T_m$ of A1, carrying four methoxy groups, is almost 250°. Substitution of the two peripheral methoxy against octadecyloxy groups (A2) led to a reduction of $T_m$ by almost 100°, but proved to decrease the solubility in CHCl₃. The introduction of two peripheral ethylhexyloxy groups (A3) caused a similar reduction of $T_m$, but increased the solubility by an order of magnitude in comparison to A1. A4, featuring the sterically hindered ethylhexyloxy groups in the peripheral position and two octadecyloxy groups on the central benzene ring, displayed by far the best processability, with a melting temperature of 84°, i.e., 55-70° lower than that of A3 and A2, and a higher solubility than A3. This behavior is consistent with the large melting and dissolution entropies imparted by both substituent types, in particular the sterically demanding ethylhexyloxy groups[34, 43, 44]. Fig. 5.6 shows this by comparing differential scanning calorimetry (DSC) traces of the first heating of A1, A3, and A4 (note that the small endothermic transition observed for A3 at 137° is not seen in the second heating trace and appears to be related to polymorphs; also note that dye A2 exhibits a solid to liquid crystalline transition below $T_m$)[33].

Chromophores B1 and B2 are simple structural variations of the A-series and simply lack the two methoxy groups attached to the central benzene ring. Consistent with the lower degree of substitution, the solubility of these dyes is somewhat lower than that of the corresponding A1 and A3 and the melting temperatures are somewhat higher. The absorption and emission spectra of the B-dyes are blue-shifted and $\sigma$ is considerably reduced (Table 5.2 and Fig. 5.7). These changes are consistent with a reduction of symmetric charge transfer brought about by the omission of the two donor groups.
Figure 5.4: 2PA fit coefficient, $q_0$, versus irradiance at $\lambda = 750\, nm$. Concentration of the dyes in toluene solution is shown in the table inset. Solid curves are fits to the measured data. These fits are linear except for the three curves marked with arrows that were also fit with a quadratic term. Only the linear portion of the fit was used in calculating the 2PA coefficient.

Figure 5.5: 2PA cross-section of OPV dyes investigated in this study as a function of wavelength measured by open-aperture Z-scan measurements ($1\, GM = 10^{-50} \, cm^4s^{-1} photon^{-1}$) in toluene.
In order to increase the extent of symmetric charge transfer, and therewith $\sigma$, C1 and C2, carrying electron-withdrawing nitro groups in the peripheral positions, were investigated. Not surprisingly, C1, bare of any substituent on the central ring, showed the highest $T_m$ and lowest solubility of all compounds investigated here, preventing any characterization in solution. The introduction of 3,7-dimethyloctyloxy groups (C2) had the expected effect on the processability, dropping $T_m$ to below 200° and increasing the solubility by almost two orders of magnitude. The absorption spectrum shows a slight red-shift compared to the B-series on account of the strongly electron withdrawing nitro substituents. However, unlike dye B1, the fluorescence of C1 was completely quenched, likely because the nitro groups stabilize the excited state via inductive effects[45]. The fluorescence intensity of C2 is much higher than that of C1, presumably on account of an increased ICT, resulting in a smaller HOMO/LUMO gap. The $\sigma$ of C2 is among
Figure 5.7: (a) UV-Vis absorbance and (b) fluorescence spectra (excitation at 365 nm) of solutions of dyes A4, B2, C2, and D1 in chloroform (ca. 2.5 x 10^{-5} M).
the highest measured here. Interestingly, however, it does not surpass the values of
the A-series that possesses weaker electron accepting functional groups (cyano), likely
because it lacks the same compact $D - \pi - A - \pi - D - \pi - A - \pi - D$ motif.

In the case of $D_1$ and $D_2$, the peripheral 4-alkyloxyphenyl moieties were substituted
with slightly less electron-rich 4-pyridinyl ($D_1$) and 2-pyridinyl ($D_2$) groups. By and
large, the optical properties of these molecules are comparable to those of the A-series,
although the 2PA cross-section is somewhat lower (359 GM for $D_1$ and 413 GM for $D_2$).
The melting points of the dyes are at the low end of the spectrum ($149^\circ$ for $D_1$ and $113^\circ$
for $D_2$), and their solubility is high. This is clearly the result of the 3,7-dimethyloctyloxy
groups that induce large melting and dissolution entropies. The difference in melting
points reflects the lower symmetry of $D_2$ in comparison to $D_1$.

Several CN′′-OPVs, including $A_1$ and $A_2$, have previously been shown to form ex-
cimers upon aggregation so that solutions and solid materials display rather different
fluorescence spectra. This “chameleon behavior” is the result of intramolecular interac-
tions and in the case of static (as opposed to dynamic) complexes strongly depends on
the molecular packing[24]. The previously reported dyes of the A-series (A1-A3) display green emission in CHCl₃ solution, with \( \lambda_{em} = 507-511 \text{ nm} \) (Table 5.2). Their solid-state emission is orange-red, with identical \( \lambda_{em} = 644 \text{ nm} \) for A1[32] and A2[33]. The solid-state emission of A3[20] is blue-shifted by 25 nm compared to A1 and A2, presumably due to a less compact crystal structure by the bulky ethylhexylgroups. In fact, the crystal structure for A1 shows a strong twisting of the molecular backbone, a likely effect of accommodating the strong intermolecular charge transfer interactions[24]. The twisting is much less pronounced in A3; its crystal structure reveals a rather planar molecule, suggesting that the bulky substituents reduce the intermolecular charge transfer due to less effective orbital overlap between adjacent molecules (Fig. 5.9).

![Figure 5.9: Crystal structure for (a) A1 and (b) A3.](image)

The absorption and fluorescence spectra of the new dyes A4, B2, C2, and D1, both in chloroform and solid state, are shown in Fig. 5.10, together with pictures of the
corresponding samples. The quantum yield of \textbf{A4} and \textbf{B2}, which serve as prototype for the respective series, was for both dyes determined to be 0.47 in toluene solution. As can be seen, the emission spectra of solution and solid state (also evident from the digital images shown in Fig. 5.10) of all dyes display pronounced differences, and in particular \textbf{A4} and \textbf{B2} show featureless broadened solid-state spectra that are indicative of excimer formation\cite{32}. Aggregation experiments in mixed solvent systems (MeOH/CHCl\textsubscript{3} for \textbf{B2}, C\textsubscript{2} and THF/H\textsubscript{2}O for \textbf{A3}) have not revealed any changes in the absorption spectra that are indicative of ground-state interactions. This observation is in line with the previous findings for \textbf{A} and \textbf{B} series dyes, with the exception of \textbf{A2}, which displays considerable charge-transfer interactions in the solid state\cite{33}.

\textbf{A4} continues the trend set by \textbf{A3} vis a vis \textbf{A1} and \textbf{A2} in that functionalization with bulky substituents (i.e. the combination of octyloxy groups attached to the aromatic core and 2-ethylhexyloxy groups in the peripheral positions) blue-shifts the solid state spectra by another 25 nm in comparison to \textbf{A3}. The emission characteristics of \textbf{B2} are identical to those of \textbf{B1}. In view of the hypsochromic shift observed between \textbf{A3} and \textbf{A1} (\textit{vide supra}) and the fact that dyes of the \textbf{B}-series with long linear peripheral alkyl oxy groups (dodecyloxy and octadecyloxy) show blue monomer emission\cite{24}, this finding is quite intriguing, as a low-melting, yellow-blue color-changing excimer-forming cyano-OPV has so far not been available. As was shown previously, the formation of ground-state excimers in cyano-OPVs is usually the result of crystal structures, in which adjacent molecules are shifted with respect to one another so that the electron-poor cyano-group overlaps with the electron-donating central ring of its neighbor\cite{24}. In the case of \textbf{B}-series derivatives with long linear peripheral alkyl oxy groups, interactions between
Figure 5.10: Fluorescence spectra (excitation at the wavelength of absorbance maximum) and digital images (under excitation at 365 nm) of (a) A4, (b) B2, (c) C2, and (d) D1 in chloroform and as a solid powder.
the latter prevail over $\pi-\pi$ interactions, imparting crystal structures that do not lend themselves to excimer emission[24]. In this context, the 2-ethylhexyloxy tails appear to be ideal, as they impart the new B2 with low melting temperature and high solubility without providing strong interactions that have a governing influence on the dye’s solid state structure.

C2 displays a deep red solid-state emission (Table 5.2 and Fig. 5.10c) centered around 618 nm, which is shifted by 65 nm compared to the emission maximum in solution. The contrast between solution and solid state for C2 is smaller than that of any dye in the A or B-series that is perhaps a result of the bulky 3,7-dimethyloctyloxy groups, which prevent compact crystal packing, much in the same way as was suggested for the A and B-series based upon the trend of higher energy emission for increasing bulkiness seen for those dyes.

Molecules D1 and D2 are almost identical in structure and their spectra are indeed very similar. The D series also has bulky 3,7-dimethyloctyloxy groups much like the C-series that can frustrate excimer formation. Furthermore, the weakly electron donating nitrogen accounts for much less ICT as the nitro substituents in the C-series or the alkyloxy substituents in the A or B-series, so it is not surprising that the D-series exhibits the smallest contrast between emission of solution and solid state (49 and 53 nm for D1 and D2, respectively). Indeed the digital images in Fig. 5.10 show the least impressive contrast between emission of solution and solid state.

The excimer-forming propensity of the new chromophores is useful for the design of stimuli-responsive, color-changing fluorescent polymers that are produced by incorporating small amounts of excimer-forming dyes into a host polymer of interest[23–30].
The general approach relies on the stimulus-driven self-assembly (e.g. upon exposure to heat, chemicals) or dissociation (e.g. upon mechanical deformation, exposure to light) of nanoscale aggregates of these dyes in a host polymer that results in a pronounced change in the fluorescence color. Some representatives of the A and B series have already proven to be very useful in this context. They have been shown to be stable under melt-processing conditions at temperatures of over 250° in a variety of host polymers, which bodes well for the exploitation of the new dyes in such a context.

5.4 Conclusions

In conclusion, we have measured large 2PA cross-sections in the range of 400-850 GM for several CN′′-OPVs, a class of molecules whose optical nonlinearities have previously little been studied. The functionalization with bulky alkyloxy substituents has afforded derivatives that display a melting point as low as 84° and a solubility in chloroform as high as 2 x 10⁻¹ M while exhibiting a σ of 630 GM. These CN′′-OPVs have the propensity to form excimers and exhibit a wide array of absorption/emission colors that are dependent on the functionalization of the OPV motif with electron accepting and donation groups.

The combination of significant optical nonlinearity, low melt-processing temperature, high thermal stability, and the propensity for excimer-formation makes the new CN′′-OPVs interesting candidates for a range of applications, in particular optical data storage systems that function on the basis of 2PA-induced switching of the aggregation state and fluorescence color[31]. The availability of such dyes that cover a range of emission
colors makes the design of complex systems with a multitude of switching states for each voxel possible.

References


Chapter 6

Optical Data Storage by Aggregate Switching of Excimer-Forming Dyes Using Two-Photon Absorption

This chapter is adapted from:

J. Lott, C. Ryan, B. Valle, J. R. Johnson, D. A. Schiraldi, J. Shan, K. D. Singer, and C. Weder,

6.1 Introduction

Current optical data storage (ODS) technologies use one-photon-absorption processes to write data by locally changing the optical properties of the medium[1, 2]. Since the lateral dimensions of spots that can be written are near the diffraction limit, signifi-
cant capacity increases require new approaches such as storage in three dimensions. DVDs, which comprise up to four individually addressable storage layers, exemplify the potential of this concept, but the complexity of producing and using multilayer systems increases with the number of layers. In bulk materials, changes can be confined in the third dimension via nonlinear optical processes, such as two-photon absorption (2PA)[3–6]. We have developed a novel ODS system that relies on the optically-induced switching of the aggregation state and fluorescence of a 2PA dye in a polymer matrix. Well-defined, $3 \times 3 \times 6$ $\mu$m-large voxels were written with single focused laser pulses and read by confocal laser scanning microscopy. Such ODS systems are easily produced and promise a storage capacity of up to several TB on a DVD-size disk, which is $100\times$ higher than that of current commercial ODS technologies[6, 7].

The optical changes considered for rewritable and write-once read-many three-dimensional (3D) ODS storage media based on 2PA include reversible and irreversible photochemical reactions such as photoisomerizations[8–10], photo-induced dimerizations[11, 12], photo-decompositions[13, 14], and photo-polymerizations[15–17]. Fluorescent photochromic systems have attracted particular interest, because the exploitable photophysical processes are fast, efficient, and reversible[18–20]. However, it has been challenging to create fluorescent photochromic materials, which combine high stability, high fluorescence quantum yield, and large 2PA cross-section. We here demonstrate a novel approach to 3D ODS materials, which relies on the switching of the aggregation state of an excimer-forming fluorescent dye with an appreciable 2PA cross-section in an inert host polymer.
6.2 Experimental

6.2.1 Materials

The chromophore 1,4-bis(α-cyano-4-octadecyloxystyryl)-2,5-dimethoxybenzene (C18-RG) was synthesized as previously described[21]. Poly(ethylene terephthalate glycol) (PETG) Eastar 6763 and spectroscopic grade toluene were obtained from Eastman Chemical Company and Burdick & Jackson and were used as received.

6.2.2 Sample Preparation

A blend of C18-RG and PETG (nominal dye content 2% w/w) was prepared using a Haake Rheocord 9000 batch mixer at 230 °C for 5 min. This blend was compression-molded between Kapton sheets into thin films of a thickness of 150 µm in a Carver melt press at 230 °C and 4 tons for 3 min. Aluminum spacers were used to control the film thickness. Upon removal from the press the films were quenched by immediate immersion into ice water. Some of the films thus produced were annealed for 2 days at 90 °C under an N₂ (g) atmosphere.

6.2.3 UV–vis Spectroscopy

UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 800 spectrophotometer and used to determine the actual dye concentration in the blend (1.1% w/w) based on the film thickness and the extinction coefficient of C18-RG (31250 L·mol⁻¹·cm⁻¹).
6.2.4 Photoluminescence Spectroscopy

Photoluminescence (PL) spectra were recorded using a Photon Technology International QuantaMaster 40 spectrophotometer under excitation at 423.5 nm; the spectra were corrected for the instrument throughput and the detector response.

6.2.5 Z-Scan Measurements

The TPA cross-section of C18-RG was measured at various wavelengths using the open-aperture Z-scan technique\cite{22,23}. A Ti:Sapphire regenerative amplifier (CPA-2010, from Clark-MXR) with 200 fs pulse duration and 1 mJ pulse energy was used to pump a traveling-wave optical parametric amplifier of superfluorescence (TOPAS, Light Conversion Ltd.). The output from the TOPAS was passed through a spatial filter to isolate the lowest-order transverse mode of the beam. The Z-scan setup included a reference channel to minimize shot-to-shot noise and to ignore pulses deviating more than two standard deviations from the mean. Beam waists were measured using a rotating slit beam profiler (BP104-VIS, Thorlabs Inc.). Data was acquired from the photodiodes in combination with a gated boxcar integrator (SR200 series, Stanford Research Systems) while the sample was translated through the focus of a 20 cm focal length lens by a computer-controlled translation stage. The accuracy of the Z-scan measurement was probed by measuring the TPA cross-section of Rhodamine 6G (2.13 x 10^{-3} M in methanol) at a wavelength of 685 nm and the measured value (76.9 GM) is consistent with values in the literature (55–97 GM)\cite{24}. The TPA cross-section of C18-RG was subsequently measured in a fused quartz cuvette (1 mm path-length) at
wavelengths between 625 and 725 nm.

6.2.6 3D Data Storage

Patterns were written by translating the C18-RG/PETG blend films through a focused writing beam. A Nd:YAG laser (Surelite II-10, Continuum) was used to pump an optical parametric oscillator (Surelite OPO, Continuum) to produce light pulses of wavelength of 675 nm, pulse duration of 10 ns, and pulse energy of 3 mJ. These pulses were then attenuated, and focused onto the sample films by an oil-immersed objective lens with a numerical aperture of 0.85. Films were placed on a computer controlled 3-axis translation stage. Data was written into the film by single laser pulses as the film was translated. This was achieved through simultaneous computer control of the Q-switch of the Nd:YAG pump laser and the position of the film. The pulse energy was varied between 1 and 1000 nJ by inserting neutral density filters into the beam path. Energy measurements were made at the sample position with a calibrated silicon diode to determine the amount of energy delivered to the sample.

6.2.7 Data Read-Out

The written data was read with a Fluoview 1000 confocal scanning microscope operated in fluorescence detection mode using an excitation wavelength of 400 nm. For the results reported here an objective (100×, 1.0 NA) was used to provide a spatial resolution of 250 nm. The fluorescence from the sample was passed through a set of dichroic mirrors and band pass filters and fluorescence in the range of 500–525 nm and in the range of
650–800 nm was detected by two photomultiplier tubes.

### 6.3 Results

We have previously reported a range of materials, which change their fluorescence and/or absorption properties upon exposure to heat\[^{[21, 25, 26]}\], chemicals\[^{[27]}\], or mechanical forces\[^{[28–30]}\], on account of reversible or irreversible stimulus-induced changes of the aggregation state of the dye molecules. We surmised that such changes could be induced in small volumes by 2PA-induced local heating and therefore explored a melt-processed blend of poly(ethylene terephthalate glycol) (PETG) and 1.1% w/w of 1,4-bis(α-cyano-4-octadecyloxystyryl)-2,5-dimethoxybenzene\[^{[21, 26]}\] (C18-RG, Fig. 6.1a) as 2PA-addressable ODS medium. C18-RG was selected on account of its significant changes in absorption and emission spectra upon aggregation/dissociation, its high thermal and photochemical stability, and, as demonstrated here, its appreciable 2PA cross-section. PETG was chosen as the matrix due to its glassy nature and transparency in the relevant optical window. Its glass transition temperature \(T_g\) of 78 °C, which defines the write/erase temperature \(\text{(vide infra)}\) is sufficiently above ambient temperature and provides excellent stability of the storage medium as discussed below. The solubility phase diagram and aggregation kinetics of C18-RG/PETG blends and similar materials have been previously investigated\[^{[21, 26]}\] (Fig. 6.1b). Figures 6.1b and 6.2 illustrate the aggregation state and fluorescence properties of the 1.1% w/w C18-RG/PETG blend as a function of thermal history. The corresponding normalized absorption and fluorescence spectra are shown in Figure 6.3. The temperature at which 1.1% w/w of C18-RG is
thermodynamically soluble in PETG is 130 °C (Figure 6.1b); note that the dissolution temperature varies with the dye content. Thermodynamically unstable, but kinetically trapped molecular mixtures of the dye and the polymer can be produced by quenching a thermodynamically miscible, melted mixture of the two components (230°C for a blend comprising 1.1% w/w dye) to below $T_g$. In this state, the blend film appears yellow (peak wavelength of the absorption spectrum $\lambda = 447$ nm, Figure 6.3a) and displays the green fluorescence (peak wavelength of the fluorescence spectrum $\lambda = 508$ nm, Figure 6.2(a), 3b) that is characteristic of a molecularly mixed blend. Subjecting the quenched blend to temperatures above $T_g$ but below the dissolution temperature leads to stable and pronounced changes in absorption (orange appearance, $\lambda = 387$ nm, Figure 6.3a) and fluorescence (orange, $\lambda = 542$ nm), due to aggregation of the dye molecules. These changes are retained if the blend is cooled back to ambient temperature (Figures 6.2(b), 6.3b). The original state can be restored by subsequently heating the phase-separated blend to above the dissolution temperature (all erase experiments reported here were carried out at 160°C) (Figures 6.1b, 6.2(c), 6.3). Thus, the blend employed here can be used as an optically readable storage medium, in which local exposure to well-defined temperatures allows one to write and erase information in two dimensions. In principle, two different modes of operation are possible. Data can be written into a quenched blend (in which the dye molecules are dissolved) by heating to a temperature above $T_g$ but below the dissolution temperature, and erased through heating above the dissolution temperature. Alternatively, data is written into a phase-separated material by heating above the dissolution temperature and erased by annealing above $T_g$. The cycles illustrated in Figures 6.2 and 6.3 show that either starting point is a viable option.
and that, in principle, many write/read/erase cycles are possible.

The choice to utilize C18-RG for the present optical data storage systems was based on the expectation that this dye, like other cyano-substituted oligo(phenylene vinylene)s\cite{31–33} possesses an appreciable 2PA cross-section, so that the above-described write/erase schemes could be achieved by 2PA-induced local heating. The 2PA cross-section of C18-RG was measured using the open-aperture Z-scan method\cite{22, 23} Figure 6.4 shows the 2PA cross-section of C18-RG as a function of wavelength in the range of 625 to 725 nm, where the linear absorption is negligible (Figure 6.3a). The 2PA cross-section of the dye varies between 0 and 650 GM with a maximum at 675 nm. The non-linear absorption is thus significant and comparable to that of similar molecules reported in the literature\cite{31–33}.

For 2PA-based writing experiments, 1.1% w/w C18-RG/PETG blend films of a thickness of 150 µm were annealed at 90°C for 2 days to ensure complete aggregation of the chromophores. Data writing was accomplished by using a Nd:YAG laser in combination with an optical parametric oscillator (OPO), which produced light pulses with a center wavelength of 675 nm, duration of 10 ns, and maximum output energy of 3 mJ. The pulse-to-pulse energy stability was 20%. These pulses were attenuated and focused onto the storage medium through an oil-immersed objective lens with a numerical aperture of 0.85. The resulting Gaussian beam was measured to have a waist of 3 µm and Rayleigh range of 10 µm. Each data spot was written by exposing the samples to a single laser pulse. The samples were positioned in 3D by a computer-controlled 3-axis translation stage. In initial experiments, the average pulse energy was systematically varied. For each trial, a set of spots was written while the average pulse
Figure 6.1: (a) Chemical structure of C18-RG, the dye employed in this study. (b) Plot of the (inverse) dissolution temperature of C18-RG/PETG blends as function of dye content. The vertical lines represent the glass transition temperature (red, 78°C) below which the dye is ‘immobilized’, and the temperature of 160°C, where blends of all compositions form molecularly mixed melts. Arrows represent the thermal pathways involved in quenching, annealing, and melting. The cartoons depict the dye aggregation state in each temperature regime.
Figure 6.2: Photographs of a 1.1% w/w C18-RG/PETG blend film demonstrating thermally introduced aggregation (write, 125°C) and dispersion (erase, 160°C) of the dye. (a) After compression-molding at 230°C and quenching by immersion in ice water. (b) After heating a portion of the sample (orange rectangle) through contact with a rectangular copper block (9.0 × 3.0 mm, 125°C, 2.5 min) and subsequent quenching. (c) After heating a portion of the sample with the same copper block (turned by 90°, 160°C, 30 s) and subsequent quenching. (d,e) After heating portions of the sample (new orange squares) with a quadratic copper block (3.0 × 3.0 mm, 125 °C, 2.5 min) and subsequent quenching. All scale bars represent 3 mm.

Figure 6.3: Normalized optical absorption (a) and fluorescence (b) spectra of the sample shown in Figure 6.2. a) The absorption spectra show the appearance of a band around 387 nm upon annealing an originally quenched sample at 125°C, due to aggregation of the dye. The band disappears if the sample is heated to 160°C and re-quenched, due to dissolution of the dye. (b) Similarly, an emission band around 542 nm appears and disappears under these conditions.
energy was held constant. At pulse energies above 100 nJ permanent localized damage was observed, while pulse energies below 25 nJ brought about no visible optical changes. The energy range of 50–65 nJ was found to afford the desired changes. An average pulse energy of 55 nJ was used for the data writing experiments presented below.

Confocal laser scanning microscopy was used to characterize the voxels written into the C18-RG/PETG blend films. A continuous-wave laser operating at a wavelength of 400 nm was used to excite the samples and the fluorescence was recorded in two channels corresponding to the integrated intensity in the spectral ranges of 500–525 nm and 650–800 nm, respectively. These spectral windows were chosen to monitor the aggregated and dispersed state of the chromophores. Confocal microscopy images of a representative sample show eight written data spots at ~10 µm below the surface of the film in Figures 6.5 and 6.6. The variations in these data spots were caused by the pulse-
to-pulse energy variation of the output of the OPO. Figure 6.5a shows the intensity image of the sample in a plane parallel to the film surface (XY plane) for fluorescence in the spectral range of 650–800 nm. Orange excimer emission of aggregated dye molecules is observed across the entire sample, except for the written spots, which appear as darker areas, indicative of dispersion of the dye aggregates due to the 2PA-induced local heating. The result is further confirmed by the corresponding fluorescence intensity image recorded for the spectral range of 500–525 nm (Figure 6.5(b)). The image shows a complementary behavior; the written spots appear bright, reflecting an increase of the green emission in these areas. No appreciable photo-induced degradation of the films upon writing was observed. The ratio of the emission intensities in the above short and long wavelength windows has been shown to represent a good measure of the aggregation state\[21, 26\]. Thus, it was used to generate a composite image (Figure 6.5(c), which indeed shows a significantly improved contrast. The image contrast can be further enhanced by applying a low pass intensity filter (Figure 6.5(d)), which eliminated the effect of the dye aggregates from the image. Further processing involving converting the signal to binary format by applying a threshold value could in principle further enhance the contrast. As is evident from Figure 6.5, the spot sizes written with the setup employed here have a diameter of 3 \( \mu \text{m} \) in the XY plane. Figure 6.6 shows the emission intensity profile of the top four spots shown in Figure 6.5c as recorded in the ZX plane. The dimensions of the data spots in the ZX direction (6 \( \mu \text{m} \)) are a bit larger than those in the XY-plane (3 \( \mu \text{m} \)), which are mostly limited by the dimensions of the beam focus. The current results reveal clearly that the 2PA-based writing process allows one to write voxels that are microscopically localized in all 3Ds. Because the
writing process requires a threshold temperature, it should be possible to achieve a
data spot substantially smaller than the writing beam size. Below the polymer’s $T_g$, the
translational mobility of the dye molecules is negligible\cite{21, 26} and the morphology
of the dye/host systems should be stable for years. Erasing data is possible by heating
above $T_g$ and re-aggregate the chromophores\cite{21}, as has been illustrated in Figure 6.2,
either by direct exposure to heat or 2PA-induced heating.

![Diagram](image)

Figure 6.5: Confocal scanning fluorescence microscopy images of a
photo-patterned 1.1% w/w C18-RG/PETG blend film acquired in the plane of the film (XY plane). (a) Raw image recorded by the channel monitoring fluorescence in the range of 650–800 nm. (b) Raw image recorded by the channel monitoring fluorescence in the range of 500–525 nm. (c) Composite image corresponding to the ratio of the intensities of the two channels. (d) As in (c) but after applying low pass filtering.
6.4 Conclusions

In summary, we have demonstrated a new ODS system that relies on the optically-initiated, thermally induced switching of the aggregation state of an excimer-forming, fluorescent 2PA dye in a polymer matrix. Such blends can be easily, inexpensively and rapidly fabricated in large quantities using simple melt-processing techniques. Well-defined voxels with dimensions of \( \sim 3 \times 3 \times 6 \, \mu m \) have been written through the exposure of the blend to single laser pulses. The voxel size is comparable to the focal point volume of the writing laser, suggesting that thermal transport does not place a lower limit to the voxel size, at least not at the length scales used here. A diffraction limited laser beam can be achieved by optimizing the optical setup. In that case the volume for efficient 2PA is limited to a space slightly smaller than 0.4 \( \mu m \) in each dimension given the wavelength and numerical aperture used. Such a scheme can be used to potentially write several terabytes of binary data in a disk of size of common CDs and DVDs.
References


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Chapter 7

A Scalable, Low-Cost Optical Data Storage Medium Fabricated by Multilayer Coextrusion

This chapter is adapted from:


7.1 Introduction

Optical data storage (ODS) has led to transformative advances in information storage and distribution technology. Conventional two-dimensional ODS media have allowed storage capacities necessary for high-definition video. The capacity is limited, however, by the size of the disk and the number of layers that can be addressed using highly
scattering phase-change materials employed in these media[1]. Here we report on a co-extrusion process for fabricating roll-to-roll multilayer (ML) films for high-density ODS. This process can easily produce a continuous, complete storage medium hundreds of meters in length and meters in width, ready for fabrication into the standard 120 mm diameter disk or a variety of other potential formats, with total writable areas sufficient for terabyte (TB) to petabyte (PB)-scale capacity. The co-extrusion process is also low-cost and far simpler than current manufacturing approaches, such as spin-coating[2, 3] and lamination[4–6]. We demonstrate data storage in 23 layers of a 78 µm thick ML film using a continuous-wave Blu-Ray (BR) laser by fluorescence (FL) quenching of an organic dye. The areal density is found to be similar to that of commercial disks, and the small layer spacing allowed by a FL-based scheme leads to a bit density of $1.2 \times 10^{12}$ cm$^{-3}$. Given the mechanism and high axial density, the cross-talk during writing is also examined. The approach is generic so that materials already developed for high-density ODS can be exploited for innovations including “cloud”-scale data storage.

Commercial ODS disks are made by first injection molding of the thick, plastic substrate. The reflective and active layers are added by a combination of sputtering and spin-coating[1]. For simple read/write systems based on a bit-wise one-photon write scheme, a multilayer architecture would require a multiplicity of steps with the current manufacturing processes. Several organic dye/polymer schemes suitable for three-dimensional (3D) ODS have been developed[2, 7–11], and have afforded storage media with TB-level capacity[12], but the fabrication methods are intricate, not easily scalable and require the development of expensive hardware systems. The simple co-extrusion process reported here is a new approach, where many layers can be extruded
at once as a single roll-to-roll film, a mode of manufacturing that has attracted attention from a number of different photonics fields, such as organic photovoltaics\cite{13} and flexible displays\cite{14}, as it allows for large area devices at low cost. The simplicity of this process, along with its high degree of scalability both in area and number of layers, is utilized here to produce long and continuous ML ODS films for a novel storage medium whose low-cost and compatibility with many organic polymers suggests suitability for economically viable products.

![Figure 7.1: Diagram of the co-extrusion process illustrating the polymer flow for the first two multipliers. The ratio of PETG to PVDF is preserved during each multiplication step, but the number of layers are doubled.]

As an illustrative model, we employ highly transparent ML polymer films with a FL organic molecule in the active layers. The FL mechanism is used because, for the large number of layers produced and recorded here, coherent cross-talk during reading would be significant with reflective schemes. The co-extrusion technique\cite{15, 16} used to manufacture these films is illustrated in Figure 7.2(a). It has already been successfully applied to the fabrication of photonic crystals\cite{17}, lasers\cite{18}, and gradient refractive index lenses\cite{19}. In this process, two thermoplastic polymers (A and B) are heated to form a melt with matching viscosities, and then coextruded into a bilayer.
feedblock. The AB bilayer is sent through a series of multiplication dies, which cut, spread, and stack the melt, doubling the number of layers each time. Films with over four thousand layers and layer thickness as low as 10 nm have been produced using this technique[20]. The laboratory process employed in the present study allows fabricating films up to 36 cm in width and 200 µm in thickness at a speed of approximately 200 m hr⁻¹, which can be scaled up in commercial applications. The use of removable multipliers makes the number of layers highly scalable, in the range of a few hundreds to thousands. The production process has broader applicability than to just the particular dye/polymer material reported here, and can be used to realize more sophisticated device architectures, such as multiple functional dopants or distinct layers, or even metal reflective layers[21] that are needed for phase change materials.

Figure 7.2: (a) Schematic of the co-extruder used to manufacture the films, and (b) the resulting roll of films. The neat polymer and polymer/dye blend are loaded into the extruders, melted, and pumped through the two-layer feedblock, and then into a series of layer multiplication dies, each of which doubles the number of entering layers. A final extruder adds surface layers for mechanical stability. The film in (b) is 6 cm wide and on the order of 100 m long.
7.2 Experimental

7.2.1 Materials

The chromophore C18-RG was synthesized as previously described\cite{22}. PETG Eastar 6763 was obtained from Eastman Chemical Company and used as received. A blend of C18-RG and PETG (nominal dye content 2 wt.%) was prepared using a Haake Rheocord 9000 batch mixer at 230°C for 5 minutes.

7.2.2 Co-extrusion

The PETG/dye blend and PVDF were loaded into separate hoppers and heated to 230°C where the polymers have matching viscosities. The bilayer extruded after these hoppers was sent sequentially through 5 dies. Each die cut perpendicular to the bilayers, spread, and stacked the film to multiply the number of layers by 2\cite{16}. The final film produced consisted of 64 layers with an overall thickness of approximately 200 µm.

7.2.3 Absorption and Fluorescence

The absorption spectrum was measured using a Cary 500 spectrophotometer on the entire 200 µm thick, ML film with 64 active layers. The FL was measured using an Olympus FV1000 confocal microscope fiber-coupled to an Acton 2300i spectrometer and a Princeton PIXIS 100BR CCD. A square region was first read using the same parameters as for reading the images (\textit{vide infra}) except the scan rate was 6 µm ms$^{-1}$ to reduce the signal-to-noise ratio. Then, the square region was bleached using a 405 nm wavelength
CW laser under the same conditions as described below for writing. The FL spectra before and after bleaching were collected using the same laser under similar conditions for reading described below.

7.2.4 Writing and Reading

The data were written with the Olympus FV1000 confocal microscope. A 405 nm, 25 mW Olympus FV5-LD405 laser was coupled to the microscope using a single mode fiber focused into the film through an Olympus M Plan Apochromatic, 100x, 1.4 NA oil-immersed objective. Patterns were recorded using the confocal microscope by scanning the laser beam along a customized path at a rate of 75 nm ms$^{-1}$. The incident power was about 150 $\mu$W and the intensity was varied from 1.0 mW $\mu$m$^{-2}$ (topmost) to 1.5 mW $\mu$m$^{-2}$ (lowest layer). The reading was performed in the same setup, except at a faster rate and much reduced power (0.01 mW $\mu$m$^{-2}$ at 5 $\mu$m ms$^{-1}$) to avoid destructive read-out. An intensity on the order of 0.1 mW $\mu$m$^{-2}$ or greater is required to obtain measurable quenching with sub-ms exposures.

7.3 Results

7.3.1 Materials and Data Storage Medium

We fabricated a storage medium consisting of 23 data storage layers interleaved between inactive buffer layers, which serve to confine the bits within discrete regions. A photograph of approximately 100 m sample of the film produced in this study is
shown in Figure 7.2(b), which possesses a writable area a factor of 1000 more than conventional 120 mm disks. Data storage layer A is composed of a transparent host polymer, poly(ethylene terephthalate glycol) (PETG) that is doped with 2.0 wt.% of the fluorescent chromophore 1,4-bis(α-cyano-4-octadecyloxystyryl)-2,5-dimethoxybenzene (C18-RG, Figure 7.3(a)[23]. Buffer layer B consisted of poly(vinylidene fluoride) (PVDF), is optically inactive and refractive index-matched to layer A. This material is also particularly effective in limiting diffusion of the dye during processing[24]. The average thicknesses of layers A and B are 0.3 and 3.1 µm, respectively.

![Chemical structure of C18-RG](image)

Figure 7.3: (a) Chemical structure of the dye (C18-RG). (b) Absorption (black) of the entire 200 µm thick ML film, containing 64 active layers, and the FL spectra of a single layer before (grey) and after (dashed) writing indicating a typical level of FL reduction induced by writing.

C18-RG is a cyano-substituted oligo(p-phenylene vinylene) dye exhibiting both
excimer and monomer states, which we have previously used for ODS by two-photon absorption\[23\]. If molecularly dispersed in PETG, the monomer exhibits absorption and FL peaks at 450 and 510 nm, respectively. The excimer exhibits absorption and FL peaks at 370 and 540 nm, respectively. The absorbance and FL spectra are shown in Figure 7.3(c), along with the FL spectra after photobleaching by 20\%, approximately the same level used during data writing as we discuss below. Note that the quenching is fairly uniform in the region of the peaks, indicating negligible shift in the relative concentration of monomers and excimers. In this work, molecularly dispersed dye in PETG was used for data storage by bleaching the green FL using single photon absorption.

### 7.3.2 Writing and Reading of Data

The data writing was performed in a scanning confocal microscope using a 405 nm CW laser beam focused onto a chosen layer, making the process compatible with compact BR sources. The FL changes caused by writing were observed to be permanent and stable over the time period of more than 2 years, while the samples were kept under ambient temperature and lighting conditions. Figure 7.4(a) depicts FL images written into the storage layers. The written regions correspond to areas of reduced FL intensity (black). Here writing was done layer-by-layer from the lowest to the topmost storage layer. The same confocal microscope and laser source subsequently collected 3D FL images of the sample at a reduced intensity and increased scan rate. See the Supplementary Information for a movie of a continuous downward scan of all layers after writing. For
Figure 7.4: (a) Patterned images stored in the 23 layer film (false color). Top left is the topmost layer and bottom right is the lowest layer, with subsequent layers going from left to right. (b) Cross-section of two layers after writing complementary images. The top cross-section is along the blue line, and the bottom along the red line. Images are normalized to the background. Each image is 22 $\mu$m square, containing 512 pixels.

Figure 7.4(b) illustrates a cross-section of two adjacent layers after writing simple geometric images. Even though the images are complementary, the data in each layer is distinct and sufficiently confined to the layer of interest. From the images shown in Figures 7.4(a) and 7.4(b), it is evident that data can readily be recorded and retrieved from each of the individual storage layers. Figure 7.4(a) also shows that the quality of the retrieved images decreases for the deeper layers due to aberrations and the limited working distance of the objective used in this study. This can be improved with a longer...
objective[14] or the dynamic lenses employed in commercial systems. However, it is readily possible to retrieve information from 23 layers, which is the largest number of recorded layers that has been reported, to our knowledge, in a heterogeneous ML ODS medium.

7.3.3 Spot Shape and Aberration

Another concern with a multilayer system such as this, is the role of beam aberration in either the writing or excitation beam. In order to investigate the role of aberration, simulations of the diffracted beam were performed[25]. The main aberration concern is spherical aberration, especially as spherical aberration may cause spots to deviate from the diffraction limited spot size in the axial direction. Two simulations were performed. In the first, the writing beam is focused 50 $\mu$m deep into a slab of material with index of refraction of 1.55. It is assumed that index matching fluid of 1.5 is used between the objective and the medium. This produces some spherical aberration in the focused beam and shifts the focal point towards the objective. In the next simulation, the beam is focused into a similar slab, but with alternating layers of 5 $\mu$m thickness with index of refraction 1.5 and 1.6. The beam spot size and focal positions can be compared in Figure 7.5. It is observed that the axial beam size for the two situations is the same. The beam focal position is shifted slightly in the layered case due to the focus being in the high-index material at this focal depth.

Plotting electric field amplitude as a function of axial and radial distance from the focal point in the layered sample described above is used to illustrate the deviation from
the Gaussian beam caused by a layered sample. Oscillations in both the radial and axial directions are seen for the light polarized in the same direction as the incoming light (see Fig. 7.6a). In addition a much smaller portion of laser beam energy is polarized in the axial direction and is seen to surround the focal spot at a radius of about 100 nm (see Fig. 7.6b).

### 7.3.4 Spot Size and Cross-Talk

The axial spacing of state-of-the-art, two to four layer BR disks is greater than 10 \( \mu m \) in order to limit the coherent cross-talk that occurs due to multiple reflections of the reading beam at the reflective layer and spacer layer interfaces[26]. The FL detection scheme employed here greatly reduces the multiple reflections as well as emitting at a non-degenerate wavelength, allowing much smaller spacing to be used. Thus, the spacing of our layers (3 \( \mu m \)) is one of the smallest explored.3 The areal density of ODS,
on the other hand, is constrained by the beam waist at the diffraction limit. To examine the data bit dimension of our ML films, single lines were written into a monolithic film of the active layer under the same writing conditions as used above. The resulting profile is shown in Figure 7.7. A fit yields a full-width-half-maximum (FWHM) of 380 nm, which is approximately the minimum bit spacing achievable in the current system, and is consistent with the diffraction-limited beam size. Given the close layer spacing and BR laser diffraction limited writing, the bit density achievable here is estimated to be $1.2 \times 10^{12}$ cm$^{-3}$. Optical aberrations limit the thickness of BR disks to less than 140 µm.[27] Thus, in a commercial disk format, our co-extruded medium is sufficient for TB storage within the BR system specifications.

A significant factor that determines the minimum bit spacing in both the axial and lateral dimension is cross-talk, especially for these films with a large number of
layers that are closely spaced. One attractive feature of ML films in the context of 3D storage is the confinement of the bits in the axial direction, which reduces cross-talk between neighboring bits and layers during writing and reading. To directly measure the writing cross-talk, an array of bits was written into 10 successive layers and the contrast modulation in the middle (“probe”) layer was read as information was written in the others. Similar writing conditions as described above were employed. The laser was modulated with a square wave generator to produce on-off bit pairs separated by 1.0 \( \mu \text{m} \) in both lateral directions, and the total area written (40 \( \times \) 40 \( \mu \text{m} \)) was larger than the beam diameter in any given layer, so as not to underestimate the total cross-talk between any two layers. This also leads to results that are not dependent on which of the 10 layers is chosen as the probe. A subsection of the FL pattern and modulation after select writing steps is shown in Figures 7.8(a) and (b). The main effect of cross-talk appears to be an overall reduction in the average FL level.
Figure 7.8: (a) FL images of a series bits in layer 1 after recording layer 1 itself (top), layers 1-5 (middle), and layers 1-10 (bottom). Images have the same brightness and contrast settings. Scale bar is 1 µm. The curves in (b) show the modulation signal of the images in (a). (c) The experimentally measured CBR of layer 1 versus the number of layers of recorded, along with results of simulation assuming a photobleaching process which is linear in optical fluence.
The ratio of signal modulation to the background FL depletion (carrier-to-background ratio, or CBR) is used to quantify the cross-talk. The CBR after writing each of the 10 layers (starting with the probe layer) is plotted in Figure 7.8(c) (triangles). The value decreases from 2 to 0.15 with increasing number of layers, and is in good agreement with numerical simulations. While this is not insignificant, this CBR is more than sufficient to resolve individual bit information, as shown in Figure 7.4. Note that the total background depletion is accumulated over many small exposures, and due to the high numerical aperture of the writing objective and the inert buffer layers, the fluence in the layer adjacent to one that is being written, is reduced by more than a factor of 10. Thus, exposure while writing the bit of interest is still the dominant contribution compared to any other single exposure.

Improved contrast and longer reading lifetime would be enabled by new one-photon write schemes that are nonlinear in fluence or intensity, which is the subject of our ongoing research. This will be studied in conjunction with the development of an optical and electronic system suitable for a complete device, allowing optimization of features such as speed and vertical drift of layers over long distances. This will be important since the long, flexible film suggests new formats are possible allowing much larger volumes to be written and stored compactly, leading to PB capacity.

### 7.4 Conclusions

In conclusion, we have demonstrated fabrication and use of a novel 3D optical storage medium. Co-extrusion can create a complete medium scalable both in size and number
of layers for low-cost using well established thermoplastic polymers. We have written in films containing 23 active layers with independent images, the largest number of layers of any stratified storage medium, at the diffraction limit of BR lasers. Work is currently ongoing to incorporate other promising materials into the co-extrusion process, such as plasmonic nanostructures[2, 28] and organic photopolymers[29]. Since the medium and process is compatible with either write-once-read-many or rewritable schemes, many other materials and applications are possible.

References


Chapter 8

Future Work

8.1 Organic Photovoltaics

8.1.1 Cavity Polaritons

Future work should focus on connecting this cavity enhanced absorption in weak cavities with the cavity polariton\cite{1, 2} formalism. The physics describing the interaction between cavity and material resonances has a rich history. In 1946 Purcell showed that spontaneous emission of a two-level system could be enhanced by placing the system in a cavity tuned to the transition frequency\cite{3}. The interaction between cavity and material resonances have two distinct regimes: weak and strong coupling. In the weak-coupling regime, the cavity perturbs the absorption spectra and decay rate of the absorbing medium. In the strong-coupling regime, the excitations of the system oscillate between excitons and cavity modes. The strength of the coupling is determined by the oscillator strength of the material, the reflectivity of the cavity, and the mismatch.
between the cavity and material bandwidths\cite{1}. Until recently exciton polaritons have been observed mainly in inorganic semiconductor quantum wells using Bragg reflectors as cavity mirrors\cite{4, 5}. Polaritons in organics have also been observed using similar highly reflective cavities\cite{6, 7}. Because the interaction strength requires matching cavity and material bandwidths, we would expect to see the strong coupling regime in widely absorbing materials like polymer photovoltaics in cavities with large bandwidths and correspondingly weakly reflecting mirrors.

The weak cavity, broad oscillator regime is one that is largely unexplored and that has obvious applications to organic photovoltaics as described in this work. This research can take several areas. In addition to the transfer matrix theory described here, the cavity polariton theory can be applied for a simple oscillator-cavity model. Experiments should focus on:

- Varying absorber oscillator strength. This will adjust the coupling between cavity and absorber, and can easily be accomplished by diluting chromophores with a polymer host.

- Varying cavity $Q$. The coupling between cavity and absorber is decreased as the cavity and absorber bandwidths are mismatched. Adjusting cavity $Q$ should be an efficient way to vary this without changing chromophores.

- Time dependence. The Rabi oscillations present in the strong-coupling regime should be easily detectable in the time domain as well. These could be time-dependent absorbance or fluorescence measurements.

In addition to the new weak cavity polariton regime described here, what may be
more interesting and novel is the application to nonlinear optics. In nonlinear optical switching, an important figure of merit[8] for a material’s switching efficiency is the ratio of nonlinear refractive index $n_2$ to two photon absorption cross-section $\sigma$. This ratio is fixed for a given material and is governed by a Kramers-Kronig relation. However, the absorption can be strongly influenced by cavity effects, allowing for customization of this ratio. Developing the theoretical tools and experiments to explore this problem should be a high-priority for continued research in this area.

### 8.1.2 Extending Transfer Matrix Simulations

Within this work optical transfer matrix theory was used to simulate absorption within organic photovoltaic devices. A reasonable estimate of the generated photocurrent can be made by assuming some constant Internal Power Conversion Efficiency (IPCE) over the absorption range of the active material. A slightly better approximation would use experimentally measured IPCE spectra. Device architecture was then optimized to maximize solar absorption. However, absorption is only this first step in generating photocurrent within organic solar cells. By simulating the drift/diffusion of dissociated excitons using optical transfer matrix simulated absorption, these calculations could be extended to fully simulate photocurrent.

The combination of two effects indicate that these simulations could prove insightful. First, it is known that organic photovoltaics have vertical concentration gradients of the donor/acceptor materials throughout the active layer. These regions with large donor/acceptor concentration especially near the electrodes plays a crucial role in
the charge-extraction phase of photocurrent generation. Second, due to the cavity effects described in this work, we know that the location of absorption is not uniform throughout the active layer. To summarize: in a full simulation

- the transfer matrix modeling will account for material concentration gradients
- the transfer matrix modeling yields the exciton generation rate throughout the active layer, and
- the drift diffusion of these generated excitons is then solved for the photocurrent taking into account electron and hole mobility in the donor and acceptor material distributed throughout the active layer.

8.1.3 Modified Transparent Electrodes for Cavity Enhanced Absorption

In Chapter 2, it was shown that the thickness dependence of the transparent conducting oxide layer could be used as a design parameter that would optimize absorption within the active layer. An interesting design architecture was found that provided an absorption enhancement across much of the visible spectrum using a much thinner ITO layer (∼50 nm). However, the surface resistivity of an ITO film this thin would result in very low fill factor for solar cells. The goal is to use a modified transparent electrode that posses a very low surface resistivity, but with controllable optical properties. Some progress has been made in electrodes formed by sandwiching a very thin metal layer with ITO[9–11]. By controlling the thickness of the metal and ITO layers, surface resistivity and
optical properties can be modified. Research should focus first on exploring the range of layer thickness that yield acceptable surface resistivity and optical measurements that characterize these electrodes. Then transfer matrix simulations can be used to find optimal electrode designs that maximize absorption. Numerous permutations of transparent conducting oxide and metal materials should allow for a wide range of optical and electronic properties.

8.2 Optical Data Storage

8.2.1 Understanding of Bleaching Phenomena

In 3-dimensional data storage, non-destructive reading and low inter-layer cross-talk require a writing response that is very strong for large optical intensities present during writing and small or nonexistent response during reading or in adjacent data layers. If the written contrast exhibits a nonlinear or threshold relationship to writing intensity, one might infer a lack of interlayer cross-talk during writing and durable contrast in reading, leading to large or unlimited number of read cycles. In a nonlinear or threshold writing process, the much higher intensities at the focus during writing produces a strong response (in this case bleaching) of the material. At low intensities (in adjacent layers during writing, or during reading) little or no writing response ensures that data can be written and read without unintended changes in the material. A nonlinear or threshold writing process also ensures longevity of the data storage medium by ensuring little to no data loss from ambient light exposure. This problem has already been solved in
multilayer holographic media on which threshold response linear writing schemes were used to create refractive holographic gratings\cite{12, 13}. The materials development effort for the medium presented in Chapter 7 is aimed at developing responsive materials for optical data storage, particularly ones possessing quenchable fluorescence with a nonlinear or threshold response.

Bleaching in this medium may have several different mechanisms that have yet to be fully understood. Photo-chemical and photo-thermal processes are currently being modeled to explain the behavior. The photochemical model is based on the published values and estimates for energy levels and transition rates of the molecule, and describes the population of the bleached state under a given exposure intensity and time. The nonlinear photochemical effects sought for this application are likely to be due to excited state absorption transitions that can be difficult to measure and are not generally reported. The thermal model describes the temperature rise induced by a laser beam and is based on a numerical solution to the heat diffusion equation inside an absorbing polymer film\cite{14}. Thermal bleaching mechanisms could be due to dye decomposition, thermally activated chemical reactions, or temperature-dependent bleaching or transition rates.

In order to understand the bleaching mechanisms at work in this medium as well as those that would be desirable in an ideal optical data storage system work should focus on both modeling and experiment. Experiments to measure transition and bleaching rates should be conducted using transient absorption techniques. It may be possible to measure temperature-dependent bleaching or transition rates by placing the sample on a temperature-controlled stage. In addition, measurements of bleaching rates under
nitrogen atmosphere could indicate photochemical a bleaching mechanism.

### 8.2.2 Medium Lifetime Measurements

One of the key features of optical data storage is its relatively long data lifetime and high integrity compared with magnetic media such as hard disk drives or magnetic tape. This added life has fostered trust in optical data storage formats in such a strong fashion, that brand new optical drive technologies are generally compatible with media nearly three-decades, and two-technology generations old. Optical discs that can withstand several decades or even up to 100 years of ambient exposure have previously been reported and are highly desirable to significantly reduce the total cost of ownership for data that must be archived long-term.

The longevity and integrity of data in a multilayer optical data storage medium depends upon several different types of data loss. The most likely source of data loss expected in the optical data storage medium presented in Chapter 7 is bleaching of the active medium in ambient light, and environmental conditions. Due to the short-wavelength of light and high intensity of the light used to write data within the medium, it is expected that ambient exposure of discs formed from this medium will result in very slow bleaching of the active materials. Samples of the coextruded roll that have been kept under fluorescent lights in ambient conditions demonstrate very slow bleaching and give some indication that ambient bleaching is a small contributor to data loss. Samples in which data was written were exposed to fluorescent room lighting for 11 months. The contrast degraded at most 10% in that time period. This preliminary result
is quite promising as no efforts were made to reduce degradation, and the materials optimization process has not even started. Discs stored under fluorescent lights could be expected to last several decades. It is also noteworthy that the shape of the data spots did not change within measurement uncertainty during the 11 month period. This suggests an absence of dye diffusion, and that the degradation process is likely photochemical.

Many highly photostable dyes are known suggesting development efforts will identify an appropriate dye. Indeed several classes of organic dyes are used in CDs, DVDs, and BRs including phthalocyanines or other cyanines, azo-dyes and azo-metal complexes, and quinones. With usable lifetimes of many decades, these and similar stable dyes are suitable candidates to be used in multilayer ODS. Combined with preliminary data showing slow photobleaching under fluorescent lighting, prospects for multi-decade lifetimes in multilayer ODS media are quite favorable.

In order to further evaluate bleaching in ambient conditions, accelerated photo-stability studies should be pursued using a multi-sun solar simulator to measure photobleaching of the active materials in both written and unwritten media. The solar spectrum includes a large variety of wavelengths not present in fluorescent lighting and includes wavelengths in the ultraviolet that are the same as those used to write and read data. Exposure to this spectrum should give a much more useful estimate of data loss due to light exposure. Temperature and light-intensity dependence studies and accelerated lifetime modeling will allow estimation of the contribution of each of these two factors. These accelerated aging tests and models will give an estimate of the usable lifetime of the data storage media, a crucial metric for adoption of our
media and/or appropriate environmental conditions for the use thereof. Although some current holographic developments use light-tight cartridges, we expect that these will not be needed keeping cost and complexity to a minimum.

From the relative bleaching observed in multiple intensity exposures, the usable lifetime of the data storage film will be extrapolated if stored in sunlight spectrum conditions. Bleaching rates and the shape of data written as a function of temperature will also be measured. The range of temperatures to be tested should be from room temperature to at least above 100 °C. PETG has a glass transition temperature of 88 °C, and above this temperature more diffusion of the dye may be expected. Demonstrating both the photostability and lack of dye diffusion is a key milestone for establishing the longevity of this ODS medium. If the dye becomes mobile above PETG’s glass transition temperature, this establishes important environmental constraints for the medium and may prompt reconsideration of the active layer host polymer material. Methods to stabilize against diffusion include the use of bulky side-groups on the dye or synthesis as a side-chain dye copolymer.

8.3 Other Topics

During my research, there were several times where interesting discoveries were made, but with no time or ability to pursue further, they were set aside.
Figure 8.1: (a) A film of P3HT is submerged in water and manipulated by tweezers. (b) 1/30 of a second before the film snaps to the surface. The film is starting to flatten. (c) The moment the film has snapped to the surface and flattened. (d) The film quickly moves from the tweezers, which disturb the water tension. This repulsion makes the films difficult to manipulate after they have snapped to the surface.
8.3.1 Floated P3HT Films

Films of P3HT and films of the bulk-heterojunction P3HT:PCBM were spun coat on top of a water soluble polymer layer (PEDOT:PSS or PVA) and then placed in water to obtain free-standing films. The hope was to place the free-standing films on top of a spun-coat PCBM film and then use thermal processing to control the polymer distribution throughout a bulk-heterojunction. This ability to control the polymer distribution especially at the interface could reduce recombination and improve efficiency. Interestingly, it was found that these P3HT-containing films had interesting behavior when floated to the water-air interface. When brought to the interface, the film would orient so that the side of the film spun on top of the water-soluble polymer would remain in the water. As the film came very near to the water-air interface it would "snap" onto the water's surface. The film that was pliable and ribbon-like when submerged became rigid, very flat, and much more brittle. It seems that this process that produces very flat, uniform films could be a very interesting thin film fabrication technique. In order to investigate further, other amphiphilic polymers should be investigated to see how widely this process could be used. Interfaces other than water-air can be used to influence the strength of this effect. Film morphology can be varied by mixing other polymers, by thermal processing, or by spin coating on top of self-assembled monolayers with various functional groups. Measurements of the mechanical properties that were observed only qualitatively should be pursued. Does the film really become more brittle on the water's surface? What morphological changes does the film undergo when it snaps to the surface?
8.3.2 Color Change in Scratched DCDHF Films

Dicyanomethylenedihydrofuran (DCDHF) chromophores are known for large extinction coefficients and are commonly used in biological applications as single-molecule fluorescent markers. We were investigating several of these molecules to see if neat films made of a molecule with extremely large oscillator strength could be made. During this investigation, it was found that one of these molecules (TH-DCDHF-6V\cite{15, 16}) changed color when scratched. This behavior is relatively rare and would have excellent applications as a sensor. After scratching, the color change reverses over the course of several hours. It appears that the molecule remains unchanged, as the scratched area absorbance returns to its initial value after a long period of time. X-ray crystallography of the film in each state should be performed to investigate the possibility of crystallization that is being disturbed mechanically during scratching. Although mechanochromic effects are known\cite{17, 18}, they have not yet been reported in DCDHF chromophores.

![Figure 8.2](image)

Figure 8.2: (a) Spun-coat film of TH-DCDHF. (b) TH-DCDHF film just after scratching with a razor blade. (c) TH-DCDHF film after two drops of chloroform were deposited.
Figure 8.3: (a) Absorbance spectra of a TH-DCDHF film after scratching as the blue color disappears. (b) Absorbance spectra in (a) versus time for wavelengths of 473 nm (blue) and 650 nm (red).

8.3.3 Nonlinear Optical Measurements of Squaraine Glass

Measurement of bulk response in the squaraine material in Chapter 4 provides a challenge to sample fabrication. To date, measurements in dense optical glass samples of 3 have suffered from material wedge, and inappropriate thickness. Fabrication of an optical quality, flat film of appropriate thickness has been difficult. In addition, if the nonlinear optical dispersion of the glass is desired, then samples of various thickness but the same optical quality will be required so that the nonlinear optical response at each wavelength is similar. Sample fabrication requires heating above the melting temperature and then rapid quenching. To obtain the appropriate thickness, 3 was placed between glass slides (with or without spacers), melted, and then a large weight was placed on top to thin and spread the sample. Quenching was achieved by passing liquid nitrogen through a copper block. Nonlinear optical measurements of this material are still of great interest, but until problems of sample fabrication are solved, this
Figure 8.4: Digital photos of glass sample 3 illustrating the optical flaws experienced during sample fabrication under backlit (top) and direct (bottom) illumination. Wedge is seen under backlit illumination as the sample thickness decreases from bottom right to top left. Crystalline or aggregates of 3 are seen in the lower right portion in the direct illuminated image. Non-uniformity seen usually as bubbles or holes are also visible in this sample.
measurement cannot be performed.

References


Appendix A

Organic Solar Cell Fabrication

Here is a detailed procedure for fabricating high efficiency P3HT:PCBM solar cells.

A.1 Materials

- P3HT - Purchased from Rieke metals. 4002-E is their highly regioregular (91-94%), electronic grade P3HT. As an alternative, Rieke offers 4002-EE which has undergone additional purification. Do not substitute regiorandom or non-electronic grade.

- PCBM - Purchased from SES Research. 99.5% PC$_{60}$BM is what was used for the P3HT work in chapter 2. PC$_{70}$BM is also available from this company.

- o-dichlorobenzene - Purchased from Sigma-Aldrich. 99% anhydrous was only opened inside the nitrogen glovebox.

- PEDOT:PSS - Purchased from Clevios. Product identifier: P VP AI 4083. Kept
A.2 Substrate Preparation

Patterned ITO-coated glass substrates are from Xin Yan Technology Ltd. I ordered coatings two coatings of different thickness (XY15S and XY20S) which were 15 and 20 $\Omega/\square$. respectively. The pattern is L-shaped and obtained from Tobin Marks’ group at Northwestern. The design allows for very simple measurement of cells using the setup in the MORE center. The only downside to this pattern is the decreased performance of cells along the busbar to the finite ITO conductivity. This could be improved by depositing a thin metal strip along the top ITO edge, but this would require a new shadow mask.

The substrates were cleaned by 20 min sonications in:

1. detergent water (1% Liquinox in DI water) w/heat

2. DI water w/heat

3. DI water w/heat (It is important to do this twice)

4. Acetone

5. Methanol

6. 2-propanol

Substrates were removed from the isopropanol with CLEAN tweezers and blown dry with nitrogen air gun. The air gun was used to blow the isopropanol to the corner of the
substrate with no ITO. Any impurities left in the isopropanol will end up in that corner which should not affect any devices. Just before fabrication (Preferably within hours of fabrication), the substrates were further cleaned by UV-Ozone cleaner for 20 min @ 150 °C. This seems to be sufficient cleaning, but oxygen plasma cleaning would be faster if available.

A.3 Layer Deposition

A.3.1 PEDOT:PSS

PEDOT:PSS (Clevios 4083) in aqueous solution was spin-cast at 4000 RPM for 60 s, and then annealed for 10 min at 120°C. The PEDOT:PSS was cleaned from the left busbar using a DI-water dampened cotton swab. Any PEDOT:PSS on the glass-side of the substrate should also be removed by cotton swab. As a hint: the best way to tell if the PEDOT:PSS has been sufficiently removed is to watch the drying of the DI water. Any PEDOT:PSS left on the substrate will dry last because of its hygroscopic nature. When clean, the DI water should dry quickly and VERY uniformly.

A.3.2 P3HT:PCBM solution

All the following materials are stored in oxygen and moisture free atmosphere. The P3HT and PCBM can be removed from the glovebox to be weighed. This will be much easier because the glovebox gloves are very electrostatic. The optimum ratio of P3HT to PCBM is approximately (1:0.8 wt.), but this is very dependent on processing conditions.
Figure A.1: Steps during solar cell fabrication. (a) Patterned ITO substrate. (b) PEDOT:PSS after spin coating on substrate and then cleaning of excess PEDOT:PSS off of ITO strip for anode connection. (c) P3HT:PCBM deposited after PEDOT:PSS which has also been cleaned from anode strip. (d) Patterned cathodes deposited by vacuum deposition process. The overlap of ITO pattern and metalized cathode pattern form each solar cell. Electrical connections are made via the anode strip and each cathode finger leading to a cell.
Each worker should probably vary this ratio slightly given his/her fabrication method for optimum results. The vial of weighed P3HT:PCBM is then transferred back into the glovebox to be dissolved. Anhydrous o-dichlorobenzene is used. The concentration to achieve appropriate film thicknesses is about 50 - 70 mg/mL. The solution was then heated to 50 °C until fully dissolved (in about an hour the solution will appear fully dissolved, but 24 - 48 hours at 50 °C using a magnetic stirbar is best). The solution is then filtered using 0.45 μm PTFE filter (use the smallest filter possible to avoid wasting solution) into another sample vial or directly onto substrates during spin-coating.

The P3HT:PCBM solution was spin-cast onto the PEDOT:PSS coated substrates at 1000 - 1500 RPM for 40 - 60 s. Optimize spin coating speeds and times for your desired thickness. Immediately after spin-coating, the samples were covered by a a glass petri dish and allowed to slow dry for 30 min or until the color changed to a dark purple. This vapor-annealing step is crucial for forming efficient BHJ morphologies in P3HT:PCBM.

A.3.3 Annealing and cleaning

Samples were then annealed for 5 min at 140 °C. The time and temperature can be varied slightly. A noticeable change in the color of the BHJ layer is visible in less than 30 s of annealing.

A.4 Cathode Deposition

1 nm LiF was thermally evaporated onto the masked substrate with a deposition rate of 0.1 Å/s. LiF is a difficult material to deposit. Thermal evaporation in a boat with a
small hole will help control the deposition rate. I have always had to manually control this deposition. In order to start depositing, the current will have to slowly be ramped. Eventually the deposition rate will spike to several Å/s, at which point the current can be returned to the normal deposition current (about 19% on the Angstrom deposition system). It will take a few minutes until the deposition rate stabilizes before the shutter should be opened for deposition.

100 nm Al was thermally evaporated next at an initial rate of 0.5 Å/s and after a few nanometers ramped up to 3 Å/s. Aluminum is fairly easy to deposit by thermal evaporation.
Appendix B

Material Dispersions Used for Transfer Matrix Calculations

Figure B.1: Dispersion of ITO used in the P3HT experiments of Ch. 2.
Figure B.2: Dispersion of PEDOT:PSS used in the P3HT experiments of Ch. 2.

Figure B.3: Dispersion of P3HT:PCBM used in the P3HT experiments of Ch. 2.
Figure B.4: Dispersion of LiF used in the P3HT experiments of Ch. 2.

Figure B.5: Dispersion of Al used in the P3HT experiments of Ch. 2.
Figure B.6: Dispersion of ITO used in the PTB7 experiments of Ch. 3.

Figure B.7: Dispersion of ZnO used in the PTB7 experiments of Ch. 3.
Figure B.8: Dispersion of PTB7:PC$_{71}$BM used in the PTB7 experiments of Ch. 3.

Figure B.9: Dispersion of Ag used in the PTB7 experiments of Ch. 3.


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