

# Twisting Charge Transfer Complex Crystals for Organic Optoelectronics

Joel Grayson, Pallavi Sundaram, Stephanie Lee

Keywords: organic optoelectronics, organic solar cell, twisted crystal, charge transfer complex, cocrystallization

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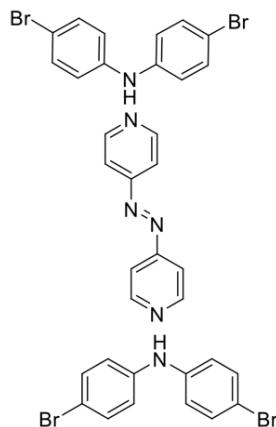
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## Abstract

It is important to study and advance the understanding of organic optoelectronics because organic devices (organic photovoltaic cells [OSCs], organic photodetectors, organic thin film transistors, etc.) are more flexible, lightweight, and cheaper to process than their inorganic counterparts.<sup>1</sup> Charge transfer complexes (CTCs) are a promising material for optoelectronic devices because of their chemical properties. Making crystal fibers twist is helpful because it exposes different orientations of the substance for investigation, increases conductivity between the

active and transport layers, and twisted crystals have been shown to perform better in devices than straight crystals.<sup>2</sup> Herein, the CTC formed by bis(4-bromophenyl)amine and 4,4'-azopyridine, abbreviated as BrDPA-AzoBipy (see **Figure 1**), is twisted and examined. The optimal cooling temperature, cooling pressure, additive, and additive weight ratio for twisting were found by varying these values while making BrDPA-AzoBipy thin films. Films made with the optimal conditions were analyzed with UV-visible absorbance spectroscopy, microspectroscopy, and scanning electron microscopy (SEM).

BrDPA-AzoBipy was synthesized at the National Autonomous University of Mexico as part of a study of new CTCs. It consists of a trans azobipyrindine core, the donor, with two bis(4-bromophenyl)amines, the acceptors. It was made by mixing bis(4-bromophenyl)amine with azobipyrindine in a 2:1 stoichiometric ratio in the solvent dichloromethane. Given its broad absorbance spectrum, it is a candidate compound for OSCs' active layer and photodetectors.



**Figure 1.** BrDPA-AzoBipy

# Introduction

As the third generation of solar cells, organic solar cells (OSCs) could become a cheaper electricity source than silicon cells in the future. For applications, until production costs go down, OSCs' light weight makes the space industry a potential early customer since rockets often use solar panels but want to be as light as possible.<sup>1</sup> They can be placed in windows, absorbing infrared light but being transparent to visible light.<sup>3</sup> Their flexibility allows for usage in wearable electronics.<sup>4</sup> Also, unlike second-generation and other third-generation solar cells, OSCs are not made of toxic materials, such as arsenic in gallium arsenide, cadmium in cadmium telluride, and lead in perovskites, or rare or expensive chemicals, such as tellurium in copper tellurides and indium in copper indium gallium selenide.<sup>5</sup> Finally, it is possible for organic materials to be used with other materials in tandem cells to reach even higher efficiencies.<sup>6</sup>

OSCs have advanced to 11% efficiency in the last few decades thanks in part to investigations into new absorber materials.<sup>7, 8</sup> Improving power conversion efficiency (PCE) and device lifespan are necessary to advance the technology. PCE can be improved by finding materials that absorb a wide spectrum, reducing thermalization and recombination losses, and creating new device architectures. Device lifespan can be increased by preventing photochemical degradation and better encapsulating the device from water and oxygen ingress.<sup>7-9</sup> Historically, absorbers have been fullerenes, such as C<sub>60</sub>. Today, many non-fullerene charge transfer complexes in the form acceptor-donor-acceptor are being investigated, an early example being TCNQ.<sup>10</sup> BrDPA-AzoBipy is one of these non-fullerene charge transfer complex absorbers.

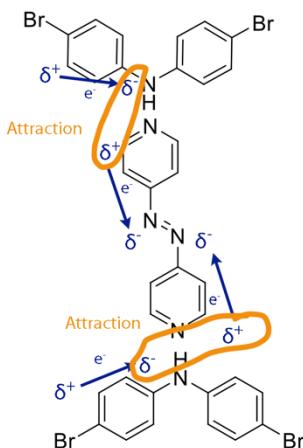
Charge transfer complexes (CTCs) are a group of molecules that exchange electrons. The molecule(s) that gives away its electrons is called the donor and the molecule(s) receiving those electrons is called the acceptor. Since this exchange makes the acceptor relatively more negative and the donor relatively more positive, there is electrostatic attraction from van der Waals and dipole–dipole forces, holding the complex together. As a supramolecular entity, a CTC has its own electron bands.<sup>11</sup>

CTCs offer great conductivity because electrons can pass through the CTCs' overlapping pi bonds. CTCs form reversible reactions ( $D+A \rightleftharpoons DA$ ) in which the change of energy when the complex is formed is the sum of the electrostatic attraction between the donor and acceptor and the difference between the acceptor's electron affinity and the donor's ionization potential.<sup>11</sup> Temperature, concentration, and solvent also affect whether or not the CTCs form.<sup>11</sup> In BrDPA-AzoBipy, there is hydrogen bonding between BrDPA's hydrogen and AzoBipy's nitrogen and dipole–dipole forces (shown in **Figure 2**). CTCs in which the acceptor's lowest unoccupied molecular orbital (LUMO) is a lower energy state than the donor's highest occupied molecular orbital (HOMO) are ground-state complexes, and those in which the acceptor's LUMO is the higher energy state are excited complexes. Excited complexes require light to excite an electron to the acceptor's LUMO.

In an organic solar cell whose active layer is made from an excited complex, the donor absorbs incident light, exciting an electron in the HOMO to the donor's LUMO. The electron in the LUMO and the absence of an electron in the HOMO are collectively called an exciton. The electron then moves from the donor's LUMO to the acceptor's LUMO. Then, if the electron can break out of its electrostatic attraction to its hole (exciton dissociation), it becomes a free electron and moves from acceptor to acceptor of neighboring CTCs in the direction of the electron transport layer (ETL), which it is electrostatically attracted to. The hole left behind hops from CTC to CTC towards the hole transport layer (HTL). This movement of the electrons and holes to their transport layers is exciton diffusion. If there is more energy in the absorbed photon than the band gap, the excess energy is converted into heat, a process called thermalization. To find the optimal band gap size, it is important to balance not making the gap too small, which increases heat loss from thermalization, and not making it too large so that less light is absorbed. Another area of loss is the premature recombination of excitons. Even after excitons have dissociated, if the free electron encounters a hole while moving around, recombination can occur with a different hole. By making thin films, the distance to the ETL and HTL is small, reducing the probability of recombination.

Crystal engineering is necessary to find the crystallization conditions creating optimal crystal morphologies and behavior for device functionality.<sup>12</sup> As crystal fibers grow outwards, they can twist from face-on to edge-on orientations. This behavior was observed in BrDPA-AzoBipy under SEM. Additives affect crystal growth by favoring certain polymorphs.<sup>12</sup> Additives can help understand mechanisms of crystallization, find locations of dislocations, and induce twisting.<sup>12</sup> Herein, additives are used to make BrDPA-AzoBipy twist.

BrDPA and AzoBipy cocrystallized together after having been dissolved in a solution. A cocrystal is a multi-component crystal resulting from multiple solids combining in a stoichiometric ratio to form a crystalline material. BrDPA-AzoBipy is a cocrystal. Intermolecular forces holding together the cocrystal include hydrogen bonding, van der Waals forces, π-π interactions, and halogen bonding among others.<sup>13</sup>



**Figure 2.** BrDPA-AzoBipy's dipole–dipole attractions.

## Experimental Methods

Crystal thin films were prepared by melting powder between two glass slides on a Kofler hot bench (Wagner & Munz). The films were then analyzed under a polarized light microscope (Olympus BX53 using LambdaFire). The presence or absence of banded spherulites determined if the film twisted. Melting temperatures, cooling temperatures, cooling pressure, and additives and their weight ratios were varied to find optimal conditions for crystal twisting. Pressure was varied by placing small cylindrical calibration blocks with flat bottoms onto the sample as it cooled. The photos of the crystal were only taken in areas where the block was placed. The pressure was calculated by dividing the weight of the block by the area it covered on the film.

The powder was made by grinding up BrDPA-AzoBipy chunks and mixing it at different weight ratios with additives. The additives damar gum, polyethylene, and Canada balsam were tested because they have a lower melting point than BrDPA-AzoBipy. BrDPA-AzoBipy melts at 127°, damar gum at 110°, polyethylene at 105°, and Canada balsam at circa 120°. Additive ratios were calculated using the weights from a Mettler Toledo XS104 balance. BrDPA-AzoBipy showed little sign of degradation after being remelted and recrystallized eight times. Therefore, to conserve the small amount of BrDPA-AzoBipy available, the films were melted multiple times to test different conditions within the same experiment.

Once finding optimal twisting conditions, the film was characterized. Absorbance and photoluminescence data were measured with a Craic Axioskop 40. Absorbance data was collected on the micro and macro levels using unpolarized light, light polarized at 0° by placing the polarizer in, and light polarized at 90° by placing both the polarizer and analyzer in perpendicular to each other. For micro absorbance data (**Figure 9**), the individual light and dark bands were analyzed by zooming with a 40x objective and placing a small aperture within a spherulite band. The data was smoothed to reduce noisiness caused by measuring small amounts of light. The macro absorbance data (see **Figure 10**) was collected across multiple bands zooming with a 10x and using a larger aperture (aperture 5), averaging out the absorbance of the

different bands. Photoluminescence data (see **Figure 11**) was collected by shining light on the sample and seeing what light it fluoresces. The detector measured for 365, 436, and 546 nm emission. The peak for 436 nm emission around 436 nanometers was caused by a device leakage, not the sample. Scanning electron microscopy (SEM) was collected on two optimal samples, one sputter coated with gold and the other with iridium.

## **Results and Discussion**

### **Optimal Twisting Conditions**

The optimal crystallization conditions were found to be mixing BrDPA-AzoBipy with 12 wt% damar gum, melting the film at 140°, and cooling at 70°. At best, a film slightly larger than a square centimeter in size was able to cool entirely as one twisted spherulite (see **Figure 7**). BrDPA-AzoBipy is anisotropic and its fibers twist in parallel at optimal conditions, meaning banded spherulites are visible under cross-polarized light. Twisting was determined by looking at the crystal under a microscope for banded spherulites. SEM of the crystal at optimal conditions confirmed the twisting by showing the individual fibers twisting from face-on to edge-on orientations (see **Figure 8**). Even in twisted films processed from the melt, BrDPA-AzoBipy remained in the complexed crystalline state.

BrDPA-AzoBipy occasionally twists on its own, but with additives (see **Figure 3**), it can be made to twist consistently. With polyethylene, it did not form banded spherulites at 50°, 70°, or 90°. With damar gum, it twisted consistently. It twisted with Canada balsam, but not as well as with damar gum, and the spherulites had huge nuclei of a non-twisting polymorph.

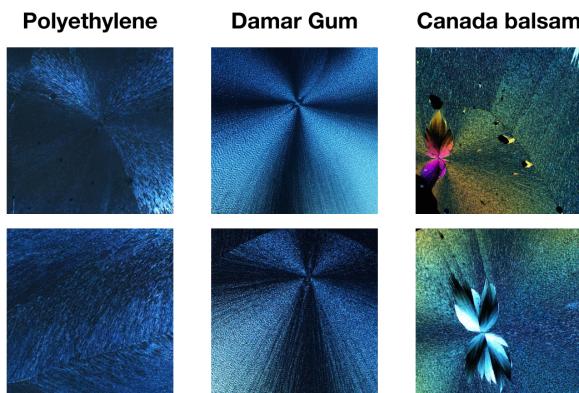
The optimal damar gum weight ratio was 12 wt%. In **Figure 4**, different weight ratios are compared. It was observed that the higher the wt%, the more numerous the nucleation sites, the smaller the spherulites, and the more twisted the spherulites. It is

advantageous to have the entire film be one spherulite because boundaries between spherulites can act as charge traps. 15 wt% was too high a ratio because it was too dense with spherulites, and 4.7 wt% was too low a ratio because much of the film was not twisting or even part of a spherulite. 8.9 wt%, 12 wt%, and 13.6 wt% all had good twisting results. 12 wt% was a good balance between not having too many tiny spherulites and not having enough twisting. Damar gum does not crystallize as seen at 100 wt% damar gum, but rather helps BrDPA-AzoBipy crystallize.

Cooling temperatures were tested for BrDPA-AzoBipy with different weight percentages of damar gum. 8.9 wt% was the most comprehensive cooling temperature test (see **Figure 5**). In the temperature range 25–105°, lower cooling temperatures had lower pitch sizes. The same needle-like polymorph was formed at high temperatures as at 1887 Pa.

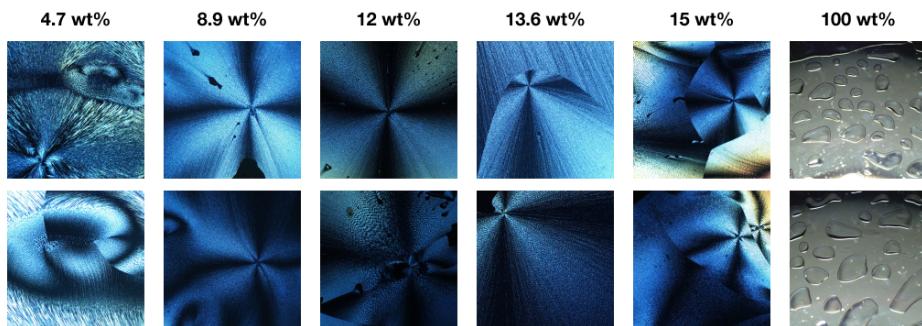
Pressure (see **Figure 6**) did not help. With pressure, samples became more inconsistent. The same sample had spherulite with greatly varying pitch sizes and non-spherulite areas. Since consistency is important in device-making, pressure is disadvantageous.

### Additive Comparison



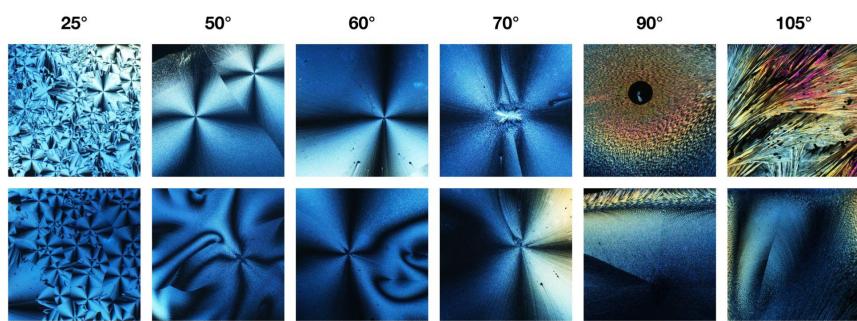
**Figure 3.** Comparing the crystallization of BrDPA-AzoBipy with different additives.

### Damar Gum Ratio Comparison



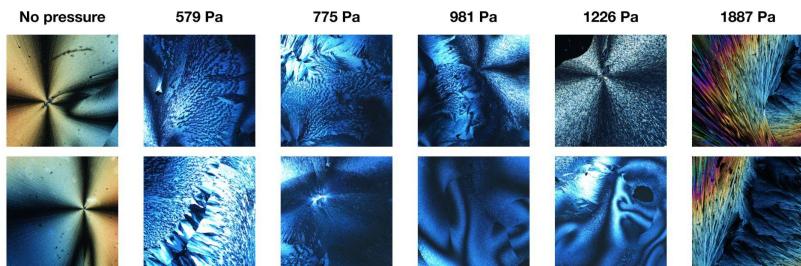
**Figure 4.** Comparing the crystallization of BrDPA-AzoBipy with different weight ratios of damar gum.

### Cooling Temperature Comparison

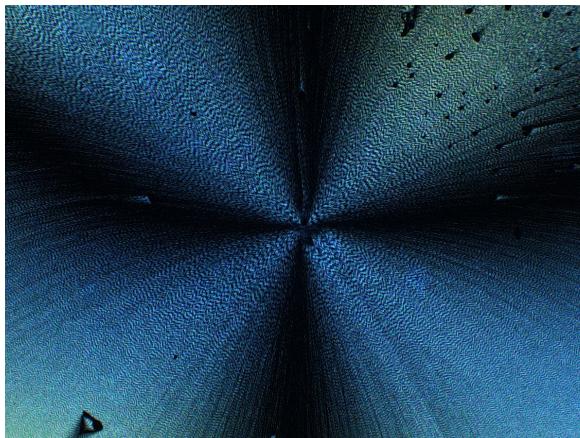


**Figure 5.** Comparing cooling temperatures on a BrDPA-AzoBipy 8.9 wt% damar gum sample.

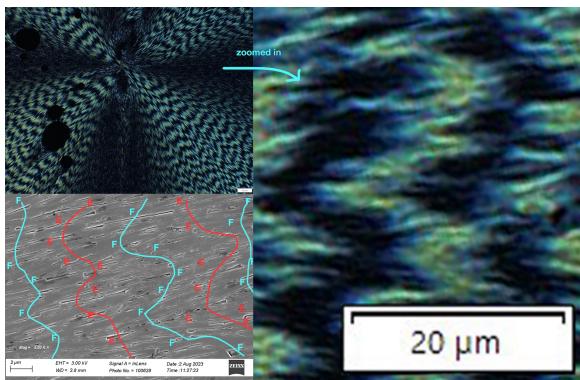
### Cooling Pressure Comparison



**Figure 6.** Comparing the crystallization of BrDPA-AzoBipy with 8.5 wt% damar gum cooled under different pressures.



**Figure 7.** Twisted crystal at optimal conditions.

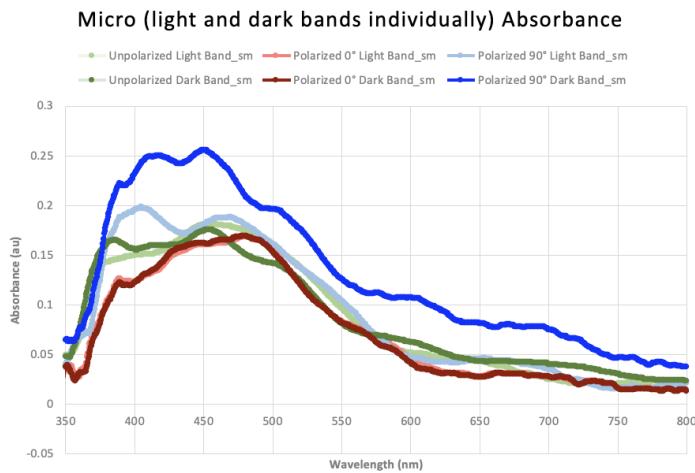


**Figure 8.** SEM shows the twisting fibers: the top left image is the sample for reference under a microscope, the right image is the same image but zoomed in to match the same size as the bottom left image, and the bottom left image is an SEM photo of the sample coated in gold with the inferred annotations “E” for edge-on and “F” for face-on regions.

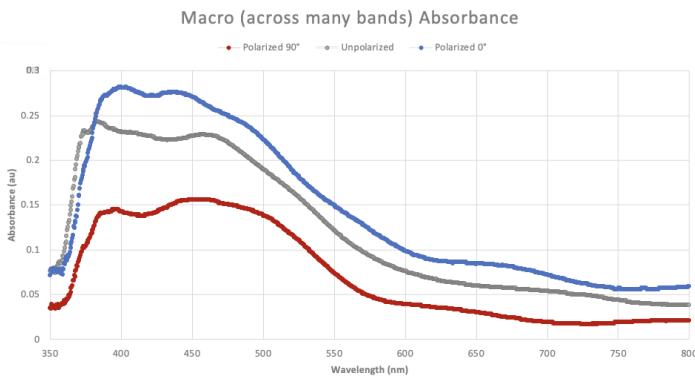
## Characterization

Once optimal twisting conditions were found, films were made at these conditions to be optically characterized. The sample was found to absorb light from a wide spectrum (see **Figure 9** and **Figure 10**), close to 300 nm in range. Being a CTC instead of a regular donor-acceptor combination helped it reach this broad range. The broad absorbance spectrum indicates its potential usage in light-to-electricity devices, such as organic solar cells and photodetectors. Without reaching as high an external quantum efficiency as other materials, it can still achieve high PCE by absorbing a large range of wavelengths. The photoluminescence data (**Figure 11**) shows that it

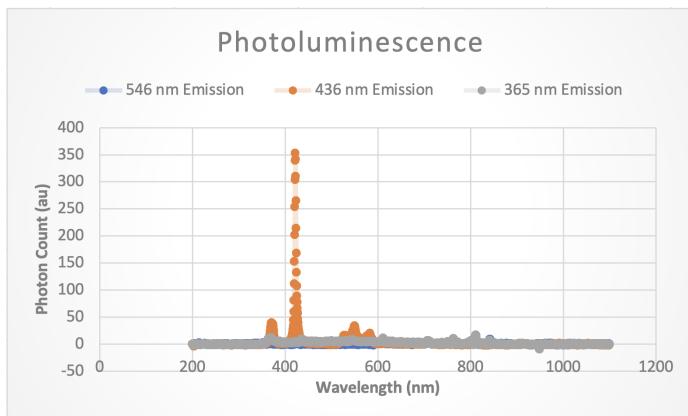
does not fluoresce and, hence, should not be used in electricity-to-light devices, such as OLEDs.



**Figure 9.** Absorbance data for the individual bands (smoothed).



**Figure 10.** Absorbance data across multiple bands.



**Figure 11.** Photoluminescence data.

# Conclusion

BrDPA-AzoBipy has promising absorbance properties deserving further study. Its broad absorbance spectrum compared to other compounds indicates it could be a good material for OSCs and photodetectors. Now that the optimal crystallization conditions for twisting have been found, a next step is creating devices using BrDPA-AzoBipy to compare to other materials. All data is available [here](#) to help future researchers.

# Terms

**Absorption efficiency** - the ratio of excitons' energy to the incident photons' energy.

**Active layer** - the part of the OSC that absorbs light to excite electrons. This paper explores a potential material (BrDPA-AzoBipy) for the active layer. Also known as the absorber layer.

**Anisotropic** - emitting light differently in different directions. This means it looks different from different angles.

**Band gap** - the difference in energy between the LUMO and HOMO of an entity.

**Carrier mobility** - how fast a charge carrier (electron or hole) can move in a material when under a voltage gap.

**Electron affinity** - energy released when it gains an electron.

**Ionization potential** - energy required to remove an electron.

**External quantum efficiency (EQE)** - the ratio of electricity produced to the amount of absorbed photon energy. This metric is useful when benchmarking the material in an OSC's active layer.

**Mesoscale** - between 10 nm and 10 microns (between the macroscale and microscale).

**Power conversion efficiency (PCE)** - the ratio of power outputted by an OSC to the energy of the incoming light.

**Recombination** - the merging of the electron and hole of an exciton. A related term, decay, means the relaxation of an electron to its lower energy state.

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## Author Information

**Joel Grayson** — *Department of Chemistry and Molecular Design Institute, New York University, New York, New York 10003, United States; [orcid.org/0009-0006-9340-9455](https://orcid.org/0009-0006-9340-9455); Email: [joelbaograyson@gmail.com](mailto:joelbaograyson@gmail.com)*

**Pallavi Sundaram** — Department of Chemistry and Molecular Design Institute, New York University, New York, New York 10003, United States; Email: pallavisundaram01@gmail.com

**Stephanie S. Lee** — Department of Chemistry and Molecular Design Institute, New York University, New York, New York 10003, United States; [orcid.org/0000-0003-0964-6353](https://orcid.org/0000-0003-0964-6353); Email: stephlee@nyu.edu

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