Topological Considerations for the Design of Molecular Donors with Multiple Absorbing Units

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Supporting Information

ABSTRACT: The molecule AT1, with two weakly conjugated chromophores, was designed, synthesized, and examined within the context of its film forming tendencies. While the addition of the second chromophore to the central core enables broadening of the absorption spectrum, this change is mostly apparent in films that are grown slowly. Grazing incidence X-ray scattering (GI-XWSX) analysis indicates that these spectral characteristics correspond to an increase in solid state ordering. This information, in combination with differential scanning calorimetry, suggests that the overall molecular shape provides a kinetic barrier to crystallization. As a result, one finds the absence of molecular order when AT1 is combined with PC71BM in solution-cast blends. These findings highlight the importance of molecular topology when designing molecular components for solar cell devices.

Improvements in materials design, processing techniques, and device architectures have led to improvements in the power conversion efficiencies (PCE) of organic photovoltaic (OPV) devices. Significant effort on blends comprised of narrow band gap polymer donors with fullerene acceptors in a bulk heterojunction (BHJ) architecture has led to PCE values on the order of 10%. However, recent successes with molecular donors have led to renewed efforts to understand and optimize this class of materials because of their monodisperse nature and ease of purification relative to their polymeric counterparts.

A molecular design that has garnered significant attention and led to high PCEs couples electron-rich donor (D) units and electron-deficient acceptor (A) units. An example of this class of molecules is p-DTS(FBTTh2)2 shown in Figure 1, which has achieved a PCE of 9%. As the internal quantum efficiency of molecular devices approaches unity, further advancements in molecular OPVs will likely require new strategies in molecular design. Such novel chemical architectural features must either tune frontier energy levels to increase open circuit voltages (VOC) or increase the number of absorbed photons and thereby the short-circuit current density (JSC).

Broad absorption may be achieved by coordinating different chromophores within a single molecule. This strategy has been successfully applied to oligothiophenes, with dye units as end caps. In these examples, the dye units extend the conjugation length, and therefore adjust the electronic structure of the entire molecule. In this contribution we examine a different design strategy, which is based on integrating independent absorbing units at two ends of a symmetric core. Figure 1 shows the specific molecule AT1. The central chromophore C1 (red) is linked on both sides with chromophore C2 (blue). Although C1 and the two C2 units appear on paper to be conjugated, it was anticipated that they would absorb nearly independently as a result of the molecular topology, namely the twist in the conjugated backbone from steric interference between the hexyl side chains on the internal thiophene units. It also seemed reasonable that the internal

Figure 1. Compounds p-DTS(FBTTh2)2 and AT1.
core of AT1 would have the lowest energy transition and would determine the highest occupied molecular orbital (HOMO) energy level, due to the extended conjugation length and the presence of the electron-rich dithieno(3,2-b:2',3'-d)silole (DTS) unit.

The synthesis of AT1 is shown in Scheme S1, and the full synthetic and characterization details are provided in the Supporting Information (SI). Thin film cyclic voltammetry (CV) measurements show oxidation and reduction waves from which we estimate that the HOMO and lowest unoccupied molecular orbital (LUMO) energies are −5.29 and −3.14 eV, respectively, corresponding to a band gap of 2.1 eV (Figure S6). These data indicate that the frontier molecular orbitals of AT1 are very similar to those of p-DTS(FBTTh2)2, suggesting that the levels are primarily determined by the C1 core.

Figure 2a shows that the absorption spectrum of AT1 in chlorobenzene (CB) exhibits an onset of absorption (λonset) at 664 nm, corresponding to an optical band gap of 1.9 eV, and a broad absorption maximum (λmax) at ∼757 nm. These features are similar to those of p-DTS(FBTTh2)2; however, in AT1 a second absorption band is discernible as a shoulder at ∼475 nm. This second band is reasonably attributed to absorption of the C2 chromophores, effectively broadening the range of absorption, compared with C1 alone.

Density functional theory (DFT) calculations were employed using CAM-B3LYP/6-31G(d,p). The minimum energy structure of AT1 was calculated to have a dihedral twist angle of 57° between the two internal thiophenes; see Figure 3. Time-dependent DFT studies were completed using a dielectric model to determine excitation energies, and the calculated spectrum matches well with the experimentally determined spectrum (Figure S7). Natural transition orbitals show that the transition around 480 nm is mainly from C2 groups and the transition at 590 nm arises from C1 almost exclusively (Table S3); see dashed lines in Figure 2a. Therefore, the twist angle of 57° effectively breaks electronic communication between C1 and C2. The dependence of the absorption spectrum as a function of twist angle is provided in the SI.

Figure 2a also shows that the absorption of AT1 films exhibits a large red shift compared to solution. The features are dependent on the evaporation rate of the CB. When spin-cast for 60 s and allowed to dry under nitrogen, λonset = 620 nm. A broad, ill-defined shoulder peak appears at low energies that shifts λonset to 775 nm. A significantly different absorption is observed if the film is allowed to dry slowly in a closed Petri dish containing CB vapor. These conditions lead to shifts of λonset to 760 nm and of λmax to 825 nm (band gap = ∼1.5 eV). The sharpness of these features suggests increased molecular order relative to the as-cast samples and highlights the influence of processing history.

Differential scanning calorimetry (DSC) measurements of AT1 were performed at different heating rates (Figure 2b and Figures S9–S10). At a rate of 5 °C/min, a cold crystallization is observed at 67 °C during the heating cycle, followed by a melting transition at 87 °C. No recrystallization peak is observed upon cooling. At the slower rate of 1 °C/min, a distinct melting temperature of 85 °C is observed with no indication of cold crystallization. However, upon cooling at the slower rate, the emergence of an exothermic peak at 56 °C was observed, identified as crystallization from the melt. Both the UV–visible absorption and DSC data therefore indicate that AT1 has a substantial resistance to crystallization.

Figure 3. Top-down and side-on view of the lowest energy conformation of AT1.

Figure 4. GIWAXS profiles of as-cast films of AT1 spin coated from CB solution for 10 s: (a) slow drying; (b) fast drying.

GIWAXS pattern of the fast-dried film exhibits two isotropic peaks at approximately q = 0.37 and 1.77 Å−1, corresponding to d-spacings of 17.0 and 3.5 Å, respectively. We assign the higher q reflection as the π−π stacking peak and the lower q reflection as an “alkyl chain stacking peak”, or arising from π-stacked units separated by alkyl side chains. These spacings are consistent with structurally similar molecules and common conjugated polymers. The slow-dried film exhibits the same reflections, as well as additional reflections at q = 0.74, 1.09, and 1.46 Å−1. These additional reflections are attributed to higher order alkyl chain stacking peaks. The π−π stacking peak in the slow-dried film is highly anisotropic, appearing primarily in the in-plane direction. This suggests AT1 preferentially π-stacks in the plane of the substrate, though a more specific understanding of molecular orientation is not possible at this stage, as attempts to grow a suitable single crystal were unsuccessful. The presence of higher order
reflections and a preferred orientation of crystallites indicate that AT1 films are able to achieve a greater degree of order when evolved more slowly.

Atomic force microscopy reveals that slow versus fast drying leads to considerably different surface topographic features; see Figure S13. Specifically, coarser and blockier features are observed for the slow dried film, compared to a fiber-like morphology when the film dries more quickly.

Charge transport was examined by using a hole-only diode structure in which a film of AT1 was sandwiched between an ITO/poly(3,4-ethylendioxythiophene)poly(styrene sulfonate) (PEDOT:PSS) bottom electrode and an evaporated Au top contact. Devices containing slow dried films were all electrically shorted, presumably because of the inhomogeneous surface features. Diodes fabricated with the quickly dried films were fit with the space charge limited current model described by the Mott–Gurney law (SI) to give a hole mobility of \( \mu_h = 2.5 \times 10^{-4} \text{ cm}^2/(\text{Vs}) \), comparable with other BHJ donor materials.\textsuperscript{25,26}

Using solution casting conditions which have been successful for structurally similar molecules\textsuperscript{8,27} (35 mg/mL chlorobenzene, 50:50 AT1:PC\textsubscript{71}BM), the initial examination of solar cells utilized the device architecture of glass/ITO(\~150 nm)/PEDOT:PSS(\~35 nm)/BHJ(\~80 nm)/Al(\~100 nm). Blends were cast from pure solvent, as well as with small amounts of the solvent additive diiodooctane (DIO); see Figure S11. As cast from CB, AT1:PC\textsubscript{71}BM solar cells show negligible performance (PCE = 0.3\%, \( \text{V}_\text{OC} = 0.59 \text{ V}, \text{J}_{\text{SC}} = 1.78 \text{ mA/cm}^2 \), \( \text{FF} = 26\% \)). Addition of 0.4\% DIO by volume to the casting solution enhances the PCE to 1.3\% (\( \text{V}_\text{OC} = 0.75 \text{ V}, \text{J}_{\text{SC}} = 6.39 \text{ mA/cm}^2 \), \( \text{FF} = 27\% \)). This increase in \( \text{V}_\text{OC} \) begins to approach what would be expected empirically based on the energy levels of AT1.\textsuperscript{5}

Crystallization of the donor within the BHJ blend has proven paramount to providing effective molecular OPVs.\textsuperscript{21,27,28} We therefore examined the order within any AT1 phase in the BHJ blend films first by examining the absorption profiles of AT1:PC\textsubscript{71}BM films obtained from a number of conditions (Figure S11). Despite different solvent, additive, and thermal annealing conditions, the absorption of the blends exhibit no evidence of the vibronic structure related to AT1 crystallization; see the green trace in Figure 2a for a representative example. GIWAXS spectra for blend films with and without DIO, provided in Figure S12, appear almost identical. Although there is some scattering in the region where one would expect alkyl chain stacking reflections from AT1, there are no clear features. There is also no apparent indication of any \( \pi-\pi \) stacking peak. It is evident that the incorporation of PC\textsubscript{71}BM prevents AT1 from overcoming the kinetic barrier to crystallization resulting in a very poorly organized BHJ blend. Additionally, blends of AT1 with two other common acceptor molecules, a perylenediimide and vinazene derivative, showed no evidence of vibronic structure in the absorption traces either (Figure S14) indicating that difficulties in crystallization are specific to the structure of the donor material.

In conclusion, AT1 is a single molecule with nearly independent chromophores. The key structural feature is the breakup of delocalization between the C1 and C2 absorbing units via the nonplanar relationship between the two internal thiophene heterocycles. While this feature achieves the desirable objective within the context of the molecule’s electronic structure, as inferred from absorption characteristics and DFT analysis, it provides AT1 with an overall nonplanar topology; see Figure 3. This “awkward” structure is reminiscent of spiro-type and tetrahedral multichromophore systems that are resistant to crystallization and often provide amorphous thin films.\textsuperscript{29,30} A combination of GIWAXS and absorption spectroscopy shows that it is possible to find growth conditions through slow solvent evaporation that yield ordered films of pure AT1. However, the introduction of PC\textsubscript{71}BM exacerbates the kinetic barriers for AT1 crystallization from solution. This absence of crystallization likely impedes achieving the BHJ morphology necessary for achieving high PCE. Looking forward, the work highlights the need for developing new processing strategies that allow different film growth profiles of BHJ blends and for design strategies that allow incorporation of multiple absorbing units within a planar molecular topology.

**ASSOCIATED CONTENT**

Supporting Information

Full experimental information, solar cell fabrication, thin film characterization, and full computational report are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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