Comparison of the Optical and Electrochemical Properties of Bi(perylene diimide)s Linked through Ortho and Bay Positions

Yeli Fan,‡,‡ Kostiantyn Ziatrev,‡,§ Siyuan Zhang,‡∥ Baoping Lin, ‡ Stephen Barlow,‡ and Seth R. Marder,‡,*

‡School of Chemistry and Chemical Engineering, Southeast University, Nanjing, Jiangsu 211189, P. R. China
‡Center for Organic Photonics and Electronics and School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, United States

ABSTRACT: The Ullmann homocoupling of 2-bromo-perylene diimides (PDIs) gave [2,2′-biperylene]-3,4:9,10,3′,4′:9′,10′-tetrakis(dicarboximide), 2,2′-bi(PDI)s, and the Suzuki coupling of a PDI-2-boronic ester and a 1-bromo-PDI gave a [1,2′-biperylene]-3,4:9,10,3′,4′:9′,10′-tetrakis(dicarboximide), 1,2′-bi(PDI). These were compared with [1,1′-biperylene]-3,4:9,10,3′,4′:9′,10′-tetrakis(dicarboximide), 1,1′-bi(PDI)s. Solution absorption spectra suggest that the PDIs in 2,2′-bi(PDI)s are more planar and less strongly coupled than those in 1,1′-bi(PDI)s, which is consistent with density functional theory calculations. 2,2′-Bi(PDI)s are less easily reduced than 1,1′- and 1,2′-bi(PDI)s by ca. 70–90 mV. Bulk heterojunction organic solar cells incorporating a 2,2′-bi(PDI) acceptor behaved similarly to those employing its 1,1′-bi(PDI) analogue.

INTRODUCTION

Perylene-3,4:9,10-bis(dicarboximide) (perylene diimides, PDIs) have attracted interest as dyes and pigments, electron-transporting semiconductors in organic field-effect transistors, two-photon-absorbing chromophores, fluorophores, and acceptors in photoinduced electron-transfer reactions for both fundamental studies and optical limiting. They have also been extensively used as light-harvesting electron-transporting materials in organic solar cells; indeed, the first donor–acceptor organic solar cell used a PDI-like acceptor in a bilayer heterojunction with copper phthalocyanine. A wide range of PDI architectures have been used in bulk-heterojunction (BHJ) organic photovoltaics (OPV), including simple small molecules, molecules with bulky substituents to hinder aggregation, molecules that form columnar discotic liquid–crystal phases, and conjugated side-chain polymers. Nonfullerene acceptors for solar cells are still an active subject of research, and PDIs remain one of the major classes under investigation. Many of the most efficient examples have three-dimensional (3D) architectures, whereby two or more PDIs are forced out of plane with one another and/or a bridging group. One simple approach to such 3D structures is to directly link two PDIs through their “bay” (1,1′) positions (see Figure S1 for the numbering scheme for PDIs), with the PDI units being sterically precluded from achieving coplanarity. A variety of 1,1′-bi(PDI)s, 1a–j, have been reported (Figure 1). Delocalization in 1a was investigated, and excitonic coupling and electron/energy transfer were studied in 1b.

RESULTS AND DISCUSSION

Scheme 1 shows the synthesis of 1, 2, and 3. Previously reported 1b (1c) was made in a similar way to other 1,1′-Bi(PDI)s that is, by the Ullmann homocoupling of S25,26 in dimethyl sulfoxide (DMSO) (but with added toluene to improve solubility). Boronic esters (S3) were synthesized using the previously described conditions and, without purification or characterization, they were treated with CuBr2 to yield 2-Br-PDIs (S4), which were converted to 2,2′-PDIs (3) using Ullmann conditions similar to those used for the formation of 1a–j.

Received: December 21, 2016
Accepted: January 23, 2017
Published: February 3, 2017

DOI: 10.1021/acsomega.6b00537
ACS Omega 2017, 2, 377–385

Supporting Information

© 2017 American Chemical Society

http://pubs.acs.org/journal/acsodf

377

ACS Omega

February 3, 2017

Published: December 21, 2016

377

ACS Omega

February 3, 2017

Published: December 21, 2016

377

ACS Omega

February 3, 2017

Published: December 21, 2016

377

ACS Omega

February 3, 2017

Published: December 21, 2016

377

ACS Omega

February 3, 2017

Published: December 21, 2016

377

ACS Omega

February 3, 2017

Published: December 21, 2016

377

ACS Omega

February 3, 2017

Published: December 21, 2016

377

ACS Omega

February 3, 2017

Published: December 21, 2016

377
for 1,1‘-PDIs. Boronic ester S3a was also subjected to Suzuki coupling conditions with S2a to obtain 1,2‘-bi(PDI) (2a). The new dimers were all characterized by 1H and 13C NMR spectroscopy, mass spectrometry, and combustion analysis. Although several of the derivatives show broadened 1H and/or 13C spectra, likely as a result of restricted rotation around the PDI–PDI bond, especially in the case of 2,2‘-isomers, and about the N-alkyl bonds of the derivatives with CH(C5H11)2, the isomers can be readily distinguished by NMR (see Experimental Section and spectra in the Supporting Information).

Differential scanning calorimetry (DSC) (10 °C min⁻¹, Figure S2) gave melting points of 167, 188, and 275 °C for 1a, 2a, and 3a, respectively, all considerably higher than that of monomeric S1a (108 °C) under the same conditions. In contrast, the bi(PDI)s with secondary alkyl substituents, 1b and 3b, showed no evidence of crystallinity, consistent with GIWAXS measurements on 1b, 30 but exhibited glass transitions at 132 and 85 °C, respectively (Figure S3). The decomposition temperatures (5 wt % loss, thermogravimetric analysis, 10 °C min⁻¹), which vary slightly with linkage motif, are similar to those of monomeric PDIs and are slightly lower for compounds with secondary alkyl amide substituents than for those with branched primary substituents (432, 432, 440, 420, 383, and 381 °C for 1a, 2a, 3a, S1a, 1b, and 3b, respectively).

Density functional theory (DFT) (B3LYP/6-31G**) calculations for 1c, 2c, and 3c (in which the N,N’-dialkyl groups are simplified to CH₃ Scheme 1) provide insight into their conformations and energetics. The two PDI units are severely twisted relative to one another, which is consistent with the previous calculations for 1,1‘-bi(PDIs); 20,25,28 ψ, the CH–C–C–CH torsion angle across the PDI–PDI bond, increases from 1,1‘- to 1,2‘- and 2,2‘-linkages (Figure 2, Table 1). On the other hand, the two naphthalene subunits of the bay-substituted PDIs of 1c and 2c are somewhat twisted from coplanarity (as quantified by ɸ), whereas the ortho-functionalized PDIs of 2c and 3c are virtually planar. Twisted cores are often found for bay-substituted PDIs, even with medium-sized substituents, and they help relieve steric interactions between the 1-substituent and the hydrogen or other substituent in the 12-position. 38–40 However, steric interaction between 2-substituents and the 3-oxo-group cannot be relieved by an intra-PDI twist, ɸ, and hence results in a larger inter-PDI twist, ψ. Similar differences in bridge/PDI twists and intra-PDI distortion were seen between bay- and ortho-linked species. 38,39

Frontier molecular orbitals for 1c–3c were also calculated (DFT, B3LYP/6-31G**); the wavefunctions and energies for 1c are similar to those previously reported for 1a. 20 The LUMO and LUMO + 1 of the symmetric bi(PDI)s (1c and 3c) are bonding and antibonding combinations, respectively, of two PDI LUMOs (see Table S2). The LUMO/LUMO + 1 energetic separation (Table 1) is much smaller for 3c than that for 1c; this can be attributed to the larger ψ in 3c, which reduces the inter-PDI π-overlap, and to the ortho positions of PDIs having smaller LUMO coefficients than the bay positions. Similarly, HOMO and HOMO – 1 resemble, respectively, antibonding and bonding combinations of two PDI HOMOs; again, a larger separation is seen for 1c. The large LUMO/LUMO + 1 and HOMO/HOMO – 1 separations seen for 2c are partly due to its inherent asymmetry; the LUMO and HOMO – 1 are localized on the ortho-substituted PDI, whereas the LUMO + 1 and HOMO are localized on the bay-substituted PDI.

Figure 3 compares solution absorption spectra of 1a–3a and S1a (Figure S4 shows spectra of 1b and 3b, which are very similar to those of their analogues). Spectra for 1a,b are consistent with previous reports on 1,1‘-bi(PDIs); 20–22 and are considerably broader and more complex than those of monomeric PDIs, such as S1a, with lower peak absorptivities (εmax). The broadening and consequent lowering of εmax are partially attributed to the nonplanarity of the PDI units; 44,45 however, inter-PDI electronic coupling helps to determine the vibrational structure. 21 Spectra of 3a,b more closely resemble those of monomeric PDIs, suggesting the PDI units of 2,2‘-bi(PDIs) are more planar and less strongly coupled than those of 1,1‘-bi(PDIs), consistent with DFT results (see above). The differences in the linewidth and absorptivity seen here between 1,1‘- and 2,2‘-PDIs are reminiscent of those previously seen for the PDI-based transitions of II and V, although the additional complexity attributable to PDI–PDI coupling for 1a,b is not seen for II. 46c Finally, the spectrum of 2a is quite similar to that.
of 3a, but with a lower $\epsilon_{\text{max}}$ and broadened vibronic sub-bands, consistent with the superposition of the spectra of a planar (ortho-substituted) and less planar (bay-substituted) PDI and with small coupling. Despite a large variation in $\epsilon_{\text{max}}$, the oscillator strengths of the main PDI-like bands are similar for all three linkages and only a little less than twice those of S1a (Table 2).

PDI–PDI $\pi$–$\pi$ interactions typically result in a retained vibronic structure but a decreased ratio of the absorbances of 0.0 to 0.1 sub-bands. Thus, spectra of bi(PDI) thin films (Figure 3) can be understood as resulting from the effects of the planarity and through-bond electronic coupling responsible for the solution spectra and these intermolecular interactions. The variation in $\pi$–$\pi$ interactions between bi(PDI)s with different connectivities cannot be easily gauged because of the variation of the solution spectra. However, these effects are more pronounced for the branched primary alkyl derivatives, 1a and 3a, than for their secondary alkyl analogues, 1b and 3b.

Figure 2. Molecular conformations of isolated molecules of, from left to right, 1,1′-, 1,2′-, and 2,2′-Bi(PDI)s (1c–3c) according to DFT calculations (B3LYP/6-31G**).
consistent with the trends for monomeric PDIs and indicating a more disrupted π-stacking when the alkyl branching is immediately adjacent to the nitrogen atoms. The effects of π–π interactions appear to be less severe for the bi(PDI)s than for monomeric PDIs (see Figure S4 and spectra of secondary alkyl PDIs in ref 7).

Monomeric PDIs show two successive reversible one-electron reductions. The bi(PDI)s show four solution reductions (Table 2, Figures 3 and S5), consistent with other 1,1'-bi(PDI)s.20-22,26,28,32 Splittings between redox potentials in compounds with linked equivalent redox centers result from an interplay of effects, including electronic contributions in the mixed-valence species, solvent-mediated Coulombic effects, and through-bond inductive effects.48 Here, electronic coupling is likely weak: the absorption spectrum of 1a causes the excess electron to be localized on one PDI unit and the coupling is small, and the DFT LUMO + 1 splittings (Table 1) suggest an even weaker coupling in 2,2'-bi(PDI)s. For 1,2'-bi(PDI) (2a), the inequivalence of the two PDIs may also contribute to the electrochemical splitting.

The first reduction potentials of the bi(PDI)s are similar to one another and to that of 1a; however, both the 1,1'- and 1,2'-bi(PDI)s (1a,b and 2a, respectively) are somewhat more readily reduced than the 2,2' dimers (3a,b), consistent with the DFT LUMO energies (Table 1), or than 1a. The differences between 1a,b and 3a,b may be due to the effects of not only planarity but also differences in the inductive and electronic coupling effects of the linkage motifs. The potential of 2a is close to that of 1a, which might suggest its bay-linked PDI that is reduced first; however, DFT indicates that the LUMO of 2a is localized on the ortho-linked PDI (Table S2), perhaps suggesting that PDI is a more effective inductively electron-withdrawing group through its bay position.

The feasibility of using 2,2'-bi(PDI)s as nonfullerene acceptors in BHJ OPVs was investigated using “inverted” devices with the structure of indium tin oxide (ITO)/ZnO/PTB7-Th:bi(PDI)/MoO3/Ag. We compared 1b and 3b because (a) 1b (1c) has been used as a nonfullerene acceptor in previous studies22-24,26,27,30 and (b) monomeric PDIs with secondary alkyl substituents often give more favorable morphologies and better performance than those with linear or branched primary alkyl groups.7 The device structure and the donor polymer, PTB7-Th (also known as PCE10 and PBDTT-F-TT),49 were selected on the basis of their previous use with 1b (1c), which gave an optimized power conversion efficiency (PCE) of 5.3% (even higher with a surface modifier applied to ZnO);24 the same PTB7-Th:1b ratio and additives afforded very similar device parameters in our experiment (Table 3, Figure 4). With 3b as acceptor, the same ratios, additives, and processing gave PCE = 4.8%. However, varying the donor/acceptor ratios and additives led to PCE values close to those for PTB7-Th:1b devices (Table 3; see Supporting Information for additional characterization of blends and devices). The similarity in the behavior of the optimized blends is consistent with similar EQE spectra (Figure 4), where, at least for the additive-containing films, the acceptor and donor contributions increase and decrease, respectively, for 3b versus 1b films, consistent with a higher acceptor content of the films. The similarity in behavior is also consistent with a fairly small difference in the electron mobility of the blend films (5.0 × 10−5 and 2.2 × 10−5 cm2 V−1 s−1, respectively, for the 1b and 3b optimized blends; see Figure S8). AFM also suggests similar surface morphologies, although phase images indicate somewhat larger feature sizes for optimized 3b blends (Figure S7). Overall, at least with PTB7-Th, the 2,2'-bi(PDI) offers no clear advantage over its 1,1' analogue. However, different optimum donor/acceptor/additive compositions found for the two bi(PDI) substituents indicates they are not interchangeable and suggests that which performs best may vary from system to system.

Table 1. Geometric and Energetic Characteristics of 1,1'-, 1,2'-, and 2,2'-Bi(PDI)s (Isolated Molecules) from DFT Calculations (B3LYP/6-31G**)

| torsion angles (deg) | ψ° | ϕ° | orbital energies (eV) |
|----------------------|----|----|-----------------------|
|                      | LUMO + 1 | LUMO | HOMO | HOMO − 1 |
| 1c 70 13             | −3.492 | −3.659 | −6.005 | −6.225 |
| 2c 70 15,0°          | −3.426 | −3.662 | −5.927 | −6.204 |
| 3c 80 0             | −3.458 | −3.500 | −6.025 | −6.032 |

“Inter-PDI CH–C–C–CH angle, C2–C1–C1′–C2′, C2–C1–C2′–C1′, and C1–C2–C2′–C1′ for 1c, 2c, and 3c, respectively (see Figure S1 for numbering scheme). Intr-PDI angles C1–C12b–C12a–C6b (Figure S1) quantifying twisting of each PDI core. For 1- and 2-substituted PDIs, respectively.

Figure 3. Left: Absorption spectra of bi(PDI)s with different linkages and the corresponding monomeric PDI in CHCl3. Center: Absorption spectra of films of bi(PDI)s with different linkages and alkyl substituents. Right: Reductive differential pulse voltammograms of bi(PDI)s in THF/0.1 Bu4NPF6.
Table 2. Electrochemical and Solution Optical Properties of a PDI and 1,1′-, 1,2′-, and 2,2′-Bi(PDI)s

| acceptor | D/A wt ratio | additives | V_{OC} (V) | J_{SC} (mA cm⁻²) | FF (%) | PCE (%) |
|----------|--------------|-----------|------------|------------------|--------|---------|
| 1a       | 1:1          |           | 0.74 ± 0.01| 12.63 ± 0.35     | 40.78 ± 1.03 | 3.81 ± 0.19 | 3.99 |
| 1b       | 1:1          | 1 wt % DIO + 2 wt % CN | 0.76 ± 0.00 | 12.57 ± 0.29 | 55.02 ± 0.75 | 5.24 ± 0.14 | 5.44 |
| 3b       | 1:1.5        |           | 0.74 ± 0.01| 11.38 ± 0.30     | 39.85 ± 0.56 | 3.34 ± 0.15 | 3.49 |
| 3b       | 1:1.5        | 2 wt % DIO | 0.78 ± 0.01| 12.57 ± 0.17     | 52.36 ± 1.07 | 5.16 ± 0.19 | 5.43 |

“The values are averages from over eight devices; the error bars are standard deviations, and the value of PCE in parentheses is the highest value obtained. "DIO = 1,8-diiodooctane; CN = 1-chloronaphthalene.

Table 3. Performance of ITO/ZnO/PTB7-Th:biBPI/MoO3/Ag Solar Cells

| acceptor | V° (V) | J° (A cm⁻²) | \(\lambda_{max} (\text{nm})\) | \(\varepsilon_{max} (10^3 \text{ M}^{-1} \text{ cm}^{-1})\) | \(f^{\ell}\) |
|----------|--------|-------------|-----------------------------|---------------------------------|---------|
| S1a      |        |             |                             |                                 |         |
| 1a       |        |             |                             |                                 |         |
| 2a       |        |             |                             |                                 |         |
| 3a       |        |             |                             |                                 |         |

“Peak reduction potentials from differential pulse voltammetry in tetrahydrofuran (THF)/0.1 M Bu4NPF6. In chloroform. Estimated solid-state electron affinity obtained from \(EA = e^\frac{E°}{2} + 4.8 \text{ eV}\). Oscillator strength obtained as \(f = 4.32 \times 10^{-3} \int \varepsilon d\lambda / \varepsilon \) (and \(\varepsilon\) are in M⁻¹ cm⁻¹ and cm⁻¹, respectively) over the PDI-like absorption band (\(\varepsilon > 25 \text{ 000 cm}^{-1}\)).

Figure 4. J−V curves (left) and EQE (right) spectra for ITO/ZnO/PTB7-Th:biBPI/MoO3/Ag solar cells (1:1 and 1:1.5 wt ratios for 1b and 3b, respectively) with and without additives (1 wt % DIO + 2 wt % CN for 1b; 2 wt % DIO for 3b). See Figure S6 for the absorption spectra of blend films.

1,1′-, 1,2′-, and 2,2′-bi(PDI)s differ subtly in their solution absorption spectra and electrochemistry; these changes are consistent with DFT geometries and frontier orbital energies. However, solid-state spectra are more strongly dependent on the nature of the N,N'-substituents. A 2,2′-bi(PDI) has been shown to act as a nonfullerene acceptor in BHJ solar cells, and it exhibits a similar performance to its 1,1′- analogue, albeit with a different optimum active-layer composition, indicating the 2,2′-bi(PDI) moiety is also a viable building block for nonfullerene acceptors.

**CONCLUSIONS**

**EXPERIMENTAL SECTION**

General Synthesis and Characterization. Chromatographic separations were performed with standard flash column chromatography methods using silica gel purchased from Sorbent Technologies (60 Å, 40–63 μm). Electrochemical measurements were carried out under nitrogen in dry deoxygenated 0.1 M tetra-n-butylammonium hexafluorophosphate in THF using a conventional three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and a Ag wire coated with AgCl as the pseudoreference electrode. Potentials were referenced by using ferrocenium/ferrocene as an internal reference. Cyclic voltammograms were recorded at a scan rate of 50 mV s⁻¹.

1-Bromo-N,N'-di(2-decyltetradecyl)perylene-3,4:9,10-bis(dicarboximide), S2a. This compound was previously reported in ref 50 but its synthesis and characterization were not. An alternative preparation involving imidization of a mixture of brominated perylene dianhydrides was reported in ref 51; the characterizing data in ref 51 are consistent with those reported below. N,N'-Di(2-decyltetradecyl)perylene-3,4:9,10-bis(dicarboximide), S1a. This compound was previously reported in ref 50 but its synthesis and characterization were not.
temperature and poured into a saturated Na₂S₂O₅ solution (500 mL). The mixture was extracted with CHCl₃ (2 × 200 mL) and dried over Na₂SO₄. After the solvent was removed, the residue was purified by column chromatography on silica gel, with CHCl₃/hexane (1:1) as the eluent. After the solvent was removed under reduced pressure, S2a was obtained as a red solid (2.7 g, 42%). ¹H NMR (500 MHz, CDCl₃): δ 9.62 (d, J = 8.0 Hz, 1H), 8.72 (s, 1H), 8.51 (m, 3H), 8.36 (m, 2H), 4.09 (d, J = 7.0 Hz, 2H), 4.06 (d, J = 7.0 Hz, 2H), 1.95 (m, 2H), 1.5−1.1 (m, 80H), 0.82 (m, 12H). ¹³C(¹H) NMR (125 MHz, CDCl₃): δ 163.5, 163.2, 163.1, 162.3, 138.9, 133.5, 133.1, 133.0, 130.8, 130.3, 128.3, 127.9, 127.6, 126.6, 123.5, 123.4, 123.3, 122.92, 122.7, 122.5, 120.9, 44.79, 44.72, 36.63, 36.58, 31.9, 31.7, 30.1, 30.0, 29.7, 29.6 (2 close peaks), 29.6, 29.4, 26.5 (2 close peaks), 22.7, 14.1 (2 aromatic carbon peaks and 31 alkyl carbon peaks were not observed, presumably due to overlap).

HRMS (MALDI-TOF): calcd for C₇₂H₁₀₅BrN₂O₄ (M⁺) 1140.728; found, 1140.734. Anal. Calcd for C₇₂H₁₀₅BrN₂O₄: C, 75.69; H, 9.26; N, 2.45. Found: C, 75.77; H, 9.26; N, 2.50.

N,N′,N″,N‴-Tetra(2-decyldodecyl)-[1,1′-biphenylene]-3,4,9,10,3′,4′-9′,10′-tetrakis(dicarboximide), 1a. A mixture of S2a (0.25 g, 0.22 mmol), dry toluene (8 mL), and dry DMSO (23 mL) was loaded into a pressure vessel and deoxygenated with a flow of nitrogen; copper powder (40−60 nm particle size, 0.14 g, 2.2 mmol) was then added, and the reaction vessel was sealed and heated to 100 °C for 5 h. The reaction mixture was cooled to room temperature and diluted with dichloromethane (50 mL); after deoxygenation by bubbling with argon for 30 min, the resulting residue was purified by column chromatography on silica gel, with CHCl₃/hexane (1:1) as the eluent. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography (silica gel; 3:2 dichloromethane/hexane), followed by size-exclusion chromatography (SX-1 BioRad; THF) to afford a red solid (0.146 g, 63%). Mp (DSC): 167 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.84−8.79 (m, 8H), 8.47 (d, J = 8.0 Hz, 2H), 8.24 (s, 2H), 8.16 (d, J = 8.0 Hz, 2H), 4.08−3.99 (m, 8H), 1.93−1.91 (m, 4H), 1.34−1.17 (m, 16H), 0.87−0.81 (m, 24H). ¹³C(¹H) NMR (125 MHz, CDCl₃): δ 163.85, 163.72, 163.45, 163.36, 142.01, 135.05, 134.49, 134.33, 133.27, 131.92, 131.88, 130.97, 129.53, 129.05, 128.91, 127.81, 127.67, 124.47, 124.28, 123.82, 123.70, 123.65, 123.52, 44.96, 44.84, 36.81, 36.81, 32.13, 32.09, 31.89, 31.82, 31.80, 31.77, 30.26, 30.22, 30.21, 30.18, 29.90, 29.87, 29.86, 29.84, 29.82, 29.58, 29.56, 29.53, 26.64, 26.46, 22.89, 22.86, 14.32 (1 aromatic carbon peak and 22 alkyl carbon peaks were not observed, presumably due to overlap). HRMS (MALDI-TOF): calcd for C₁₄₄H₂₁₅BrN₂O₄ (MH⁺) 2124.6227; found, 2124.6271. Anal. Calcd for C₁₄₄H₂₁₅BrN₂O₄: C, 75.80; H, 9.29; N, 2.52.

N,N′,N″,N‴-Tetra(2-decyldodecyl)-[1,2′-biphenylene]-3,4,9,10,3′,4′-9′,10′-tetrakis(dicarboximide), 2a. A solution of K₂CO₃ (0.087 g, 0.63 mmol) in water (6 mL) was added to a solution of S3a (0.32 g, 0.27 mmol) and S2a (0.24 g, 0.21 mmol) in a mixture of toluene (60 mL) and EtOH (0.8 mL); after deoxygenation by bubbling with argon for 30 min, Pd(PPh₃)₄ (0.026 g, 0.022 mmol) was added, and the resulting mixture was heated to 80 °C under argon overnight. After the conversion of the starting material (according to TLC) was complete, the product was extracted with dichloromethane. The organic phase was washed with water, dried over MgSO₄, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; 3:2 dichloromethane/hexane, followed by size-exclusion chromatography (SX-1 BioRad; THF) to give 2a as a red solid (0.13 g, 29%). Mp (DSC): 188 °C. ¹H NMR (500 MHz, CDCl₃, 325 K): δ 8.76 (d, J = 8.0, 1H), 8.71−8.52 (m, 7H), 8.46 (d, J = 7.0, 1H), 8.41 (s, 1H), 8.37 (d, J = 7.0, 1H), 8.30−8.20 (m, 1H), 8.02 (d, J = 8.5, 1H), 7.83 (d, J = 8.5, 1H), 4.14 (d, J = 6.5, 2H), 3.96 (d, J = 6.5, 2H), 3.91−3.60 (m, 4H), 2.03−1.78 (m, 4H), 1.41−1.01 (m, 160H), 0.87−0.78 (m, 24H). ¹³C NMR (125 MHz, CDCl₃): δ 163.79, 163.73, 163.56, 163.40, 163.29, 148.82, 141.25, 135.84, 134.84, 134.66, 134.64, 134.09, 133.39, 131.39, 131.47, 131.09, 130.99, 130.80, 129.43, 129.32, 128.99, 128.27, 128.77, 128.17, 126.24, 125.97, 124.26, 123.96, 123.58, 123.27, 122.90, 121.12, 120.07, 45.08, 44.83, 44.72, 37.01, 36.77, 36.65, 36.43, 32.13, 32.11, 32.10, 31.95, 31.70, 31.61, 30.31, 30.27, 30.22, 30.19, 29.90, 29.86, 29.81, 29.75, 29.67, 29.51, 26.76, 26.73, 26.68, 25.68, 25.60, 26.41, 26.34, 22.88, 14.31, 14.30, 14.25 (6 sp² and 61 alkyl resonances were not observed, presumably due to overlap). HRMS (MALDI-TOF): calcd for C₁₄₄H₂₁₅BrN₂O₄ (MH⁺), 2124.6227; found,
2H), 1.41 3,4:9,10;3

Am x t u r e o f 3,4:9,10-bis(dicarboximide), S4b.

N

S3b, and 2-Bromo-

dioxane (200 mL), and aqueous CuBr2 (2.70 g, 12.1 mmol) fi

24 h. The solvent was removed under reduced pressure after

residue was puriﬁed Si cell. The solar-cell performance was

determined using an Air Mass 1.5 G solar simulator with an

light source, the intensity of which was calibrated

Solar-Cell Fabrication and Testing. ITO-coated glass

substrates were ultrasonically cleaned in detergent (sodium
dodecyl sulfate), deionized water, acetone, and isopropanol in

successive steps. The substrates were treated with UV−ozone

for 10 min before use. A thin layer of sol−gel ZnO (ca. 10 nm)

was spin-coated onto precleaned ITO-coated glass substrates at

4000 rpm and then annealed at 150 °C for 10 min in air. The

ZnO precursor solution was prepared by dissolving Zn(OAc)2·

2H2O and ethanolamine in 2-methoxethanol and then stirred

overnight. A 24 mg/mL total concentration solution of PTB7-

Th and the relevant bi[PD1] in chlorobenzene with different

mass ratios and additive concentrations was spin-coated on ZnO

layer in a nitrogen-filled glovebox. At the ﬁnal stage, the

substrates were transferred to high vacuum, and MoOx (10 nm)
topped with silver (100 nm) was thermally evaporated onto the

active layer. The active area deﬁned by shadow masks was 0.1

cm2. The current density−voltage characteristics of the

photovoltaic devices were measured in the glovebox using a

Keithley 2400 source meter. A xenon arc lamp (300 W) was

used as the light source, the intensity of which was calibrated

using a KG5−scaled Si cell. The solar-cell performance was

measured using an Air Mass 1.5 G solar simulator with an

irradiation intensity of 100 mW/cm2. The thickness of ﬁlms

was measured by a KLA-Tencor P-15 profiler.

DFT Calculations. DFT calculations were carried out using

the B3LYP functional, which combines Becke’s three-

parameter hybrid-exchange functional with the Lee−Yang−

Parr correlation functional, and the 6-31G** basis set as

implemented within the Spartan14 package. Frequency

calculations on the optimized geometries indicated no imaginary

frequencies.
PDI atom numbering and definitions of torsion angles; DSC data; additional electrochemical and optical data; additional data characterizing OPV devices and blends; NMR spectra for the bi(PDI)s and new intermediates; additional data and plots from DFT calculations; and Cartesian coordinates for minimized structures (PDF)

Author Information
Corresponding Author
*E-mail: seth.marder@chemistry.gatech.edu.

Present Addresses
§Department of Radiation, Optical Radiation Laboratory, Washington University in St. Louis, School of Medicine, 4515 McKinley Avenue, St. Louis, Missouri 63101, United States (K.Z.).

Notes
The authors declare no competing financial interest.

Acknowledgments
This work was supported by the Department of the Navy, Office of Naval Research Award No. N00014-14-1-0580 (CAOP MURI). Y.F. thanks the State-Sponsored Scholarship for Graduate Students from China Scholarship Council. The authors thank Yuting Gao for help with some of the synthetic work and Timothy Parker for help with the DFT calculations.

Additional Notes
“In addition to the compounds shown in Figure 1, halosubstituted derivatives have been reported as precursors to I$_{3}^\text{−}$ but have not been studied extensively spectroscopically and electrochemically or in devices.28,32

Comparisons between the spectra of III, IV and VI, VII are complicated by the effects of aggregation, even in a dilute solution.39

Electronic coupling (V) in a localized mixed-valence monoanion is given by

\[ 2V = E_{\text{LUMO}+1} - E_{\text{LUMO}} \]

where the orbital energies refer to the corresponding neutral species, assuming (i) Koopmans’ theorem and (ii) that the neutral geometry is a good approximation to that of the monoanion at the symmetric transition state, which connects the two unsymmetrical minima.

Expected J$_{SC}$ values obtained from convolution of the four EQE spectra shown in Figure 4 with the AM1.5 spectrum are 12.4, 13.1, 11.4, and 12.4 mA cm$^{-2}$, roughly consistent with the values obtained by J–V measurements (note that the values given in Table 3 are averages over eight devices).

References
(1) Würtzner, F. Perylene Bisimide Dyes as Versatile Building Blocks for Functional Supramolecular Architectures. Chem. Commun. 2004, 1564–1579.

(2) Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Waselewski, M. R.; Marder, S. R. Rylene and Related Diimides for Organic Electronics. Adv. Mater. 2011, 23, 268–284.

(3) Huang, C.; Barlow, S.; Marder, S. R. Perylene-3,4,9,10-Tetracarboxylic Acid Diimides: Synthesis, Physical Properties, and Use in Organic Electronics. J. Org. Chem. 2011, 76, 2386–2407.

(4) Liu, Z.; Zhang, G.; Cai, Z.; Chen, X.; Luo, H.; Li, Y.; Wang, J.; Zhang, D. New Organic Semiconductors with Imide/Amide-Containing Molecular Systems. Adv. Mater. 2014, 26, 6965–6977.

(5) Fernández-Lázaro, F.; Zink-Lorre, N.; Sastre-Santos, Á. Perylenediimides as Non-Fullerene Acceptors in Bulk-Heterojunction Solar Cells (BHJSCs). J. Mater. Chem. A 2016, 4, 9336–9346.

(6) Tang, C. W. Two-Layer Organic Photovoltaic Cell. Appl. Phys. Lett. 1986, 48, 183–185.

(7) Sun, J.-P.; Hendsbee, A. D.; Dobson, A. J.; Welch, G. C.; Hill, I. G. Perylene Diimide Based All Small-Molecule Organic Solar Cells: Impact of Branched-Alkyl Side Chains on Solubility, Photophysics, Self-Assembly, and Photovoltaic Parameters. Org. Electron. 2010, 35, 151–157.

(8) Sharma, G. D.; Balajee, P.; Mikroyannidis, J. A.; Stylianakis, M. M. Bulk Heterojunction Organic Photovoltaic Devices Based on Low Band Gap Small Molecule BTD-TNP and Perylene–Anthracene Diimide. Sol. Energy Mater. Sol. Cells 2009, 93, 2025–2028.

(9) Schmidt-Mende, L.; Fechtenkötter, A.; Mullen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. Self-Organized Discotic Liquid Crystals for High-Efficiency Organic Photovoltaics. Science 2001, 293, 1119–1122.

(10) Zhan, X.; Tan, Z.; Domercq, B.; An, Z.; Zhang, X.; Barlow, S.; Li, Y.; Zhu, D.; Kippelen, B.; Marder, S. R. A High-Mobility Electron-Transport Polymer with Broad Absorption and Its Use in Field-Effect Transistors and All-Polymer Solar Cells. J. Am. Chem. Soc. 2007, 129, 7246–7247.

(11) Zhang, Q.; Cirpan, A.; Russell, T. P.; Emrick, T. Donor–Acceptor Poly(Thiophene-Block-Perylene Diimide) Copolymers: Synthesis and Solar Cell Fabrication. Macromolecules 2009, 42, 1079–1082.

(12) Lin, Y.; Zhan, X. Non-Fullerene Acceptors for Organic Photovoltaics: An Emerging Horizon. Mater. Horiz. 2014, 1, 470–488.

(13) Eftaiha, F. E.; Sun, J.-P.; Hill, I. G.; Welch, G. C. Recent Advances in Non-Fullerene, Small Molecular Acceptors for Solution Processed Bulk Heterojunction Solar Cells. J. Mater. Chem. A 2014, 2, 1201–1213.

(14) Nielsen, C. B.; Hollliday, S.; Chen, H.-Y.; Cryer, S. J.; McCulloch, I. Non-Fullerene Electron Acceptors for Use in Organic Solar Cells. Acc. Chem. Res. 2015, 48, 2803–2812.

(15) Sauvé, G.; Fernando, R. Beyond Fullerenes: Designing Alternative Molecular Electron Acceptors for Solution-Processable Bulk Heterojunction Organic Photovoltaics. J. Phys. Chem. Lett. 2015, 6, 3770–3780.

(16) Zhan, C.; Zhang, X.; Yao, J. New Advances in Non-Fullerene Accepter Based Organic Solar Cells. RSC Adv. 2015, 5, 93002–93026.

(17) Zhan, C.; Yao. More Than Conformational “Twisting” or “Coplanarity”: Molecular Strategies for Designing High-Efficiency Nonfullerene Organic Solar Cells. Chem. Mater. 2016, 28, 1948–1964.

(18) Lin, Y.; Zhan, X. Oligomer Molecules for Efficient Organic Photovoltaics. Acc. Chem. Res. 2016, 49, 175–183.

(19) Lin, Y.; Wang, Y.; Wang, J.; Hou, J.; Li, Y.; Zhu, D.; Zhan, X. A Star-Shaped Perylene Diimide Electron Acceptor for High-Performance Organic Solar Cells. Adv. Mater. 2014, 26, 5137–5142.

(20) Jiang, W.; Xiao, C.; Hao, L.; Wang, Z.; Ceymann, H.; Lambert, C.; Di Motta, S.; Negrì, F. Localization/Delocalization of Charges in Bay-Linked Perylene Bisimides. Chem. Eur. J. 2012, 18, 6764–6775.

(21) Horinouchi, H.; Sakai, H.; Araki, Y.; Sakanoue, T.; Takenobu, T.; Wada, T.; Tkachenko, N. V.; Hasobe, T. Controllable Electronic Structures and Photoinduced Processes of Bay-Linked Perylenediimides.
Activation and Use in the Synthesis of Bis(Perylene Diimide)-Donor Org. Lett.
Tetraborylation of Perylene Bisimides. Org. Lett.
to the Imide Groups.

J. M.; Dicke, J. W.; Marks, T. J.; Wasielewski, M. R. Photophysics and Marder, S. R. 2-Bromo Perylene Diimide: Synthesis Using C

ACS Omega 2015, 3, 13000−13010.

Ye, L.; Sun, K.; Jiang, W.; Zhang, S.; Zhao, W.; Yao, H.; Wang, Z.; Hou. J. Enhanced Efficiency in Fulleren-Free Polymer Solar Cell by Incorporating Fine-Designed Donor and Acceptor Materials. ACS Appl. Mater. Interfaces 2015, 7, 9274−9280.

Wu, C.-H.; Chueh, C.-C.; Yi, Y.-Y; Zhong, H.-L.; Gao, G.-P.; Wang, Z.-H.; Pozzo, L. D.; Wen, T.-C.; Jen, A. K.-Y. Influence of Molecular Geometry of Perylene Diimide Dimers and Polymers on Bulk Heterojunction Morphology toward High-Performance Non-fullerene Polymer Solar Cells. Adv. Funct. Mater. 2015, 25, 5326−5332.

Sun, D.; Meng, D.; Cai, Y.; Fan, B.; Li, Y.; Jiang, W.; Huo, L.; Sun, Y.; Wang, Z. Non-Fullerene-Acceptor-Based Bulk-Heterojunction Organic Solar Cells with Efficiency over 7%. J. Am. Chem. Soc. 2015, 137, 11156−11162.

Zhao, J.; Li, Y.; Lin, H.; Liu, Y.; Jiang, K.; Mu, C.; Ma, T.; Lai, J. Y. L.; Hu, H.; Yu, D.; Yan, H. High-Efficiency Non-Fullerene Organic Solar Cells Enabled by a Difluorobenzothiadiazole-Based Donor Polymer Composed with a Properly Matched Small Molecule Acceptor. Energy Environ. Sci. 2015, 8, 520−525.

Feng, G.; Xu, Y.; Zhang, J.; Wang, Z.; Zhou, Y.; Li, Y.; Wei, Z.; Li, C.; Li, W. Small-Molecule Organic Solar Cells Based on an Electron Donor Incorporating Binary Electron Deficient Units. J. Mater. Chem. A 2016, 4, 6056−6063.

Meng, D.; Sun, D.; Zhong, C.; Liu, T.; Fan, B.; Huo, L.; Li, Y.; Jiang, W.; Choi, H.; Kim, T.; Kim, J. Y.; Sun, Y.; Wang, Z.; Heeger, A. J. High-Performance Solution-Processed Non-Fullerene Organic Solar Cells Based on Selenophene-Containing Perylene Bismide Acceptor. J. Am. Chem. Soc. 2016, 138, 375−380.

Yu, Y.; Yang, F.; Ji, Y.; Wu, Y.; Zhang, A.; Li, C.; Li, W. A Perylene Bismide Derivative with a LUMO Level of −4.56 eV for Non-Fullerene Solar Cells. J. Mater. Chem. C 2016, 4, 4134−4137.

Nakazono, S.; Easwaranmoorthi, S.; Kim, D.; Shinokubo, H.; Osaka, A. Synthesis of Arylated Perylene Bismides through C−H Bond Cleavage under Ruthenium Catalysis. Org. Lett. 2009, 11, 5429−5432.

Bullock, J. E.; Vagnini, M. T.; Ramanan, C.; Co, D. T.; Wilson, T. M.; Dicke, J. W.; Marks, T. J.; Wasielewski, M. R. Photophysics and Redox Properties of Rylen Imide and Diimide Dyes Alkylated Ortho to the Imide Groups. J. Phys. Chem. B 2010, 114, 1794−1802.

Teraoka, T.; Hiroto, S.; Shinokubo, H. Iridium-Catalyzed Direct Tetraarylation of Perylene Bismides. Org. Lett. 2011, 13, 2532−2535.

Battaglini, G.; Li, C.; Enkelmann, V.; Müllen, K. 2,5,8,11-Tetrabronic Ester Perylenediamides: A Next Generation Building Block for Dye-Stuff Synthesis. Org. Lett. 2011, 13, 3012−3015.

Battaglini, G.; Zhao, Y.; Li, C.; Müllen, K. Efficient Tuning of Lumo Levels of 2,5,8,11-Substituted Perylenediamides Via Copper Catalyzed Reactions. Org. Lett. 2011, 13, 3399−3401.

Zhao, J.; Singh, S.; Hwang, D. K.; Barlow, S.; Kippelen, B.; Marder, S. R. 2-Bromo Perylene Diimide: Synthesis Using C−H Activation and Use in the Synthetic of Bis(Perylene Diimide)-Donor Electron-Transport Materials. J. Mater. Chem. C 2013, 1, 5093−5100.

Zhao, D.; Wu, Q.; Cai, Z.; Zheng, T.; Chen, W.; Lu, J.; Yu, L. Electron Acceptors Based on A-Substituted Perylene Diimide (PDI) for Organic Solar Cells. Chem. Mater. 2016, 28, 1139−1146.

Schmidt, C. D.; Lang, N.; Jux, N.; Hirsch, A. A Facile Route to Water-Soluble Coronenes and Benzo[ghi]Perylenes. Chem. Eur. J. 2011, 17, 5289−5299.

To, S.; Hiroto, S.; Shinokubo, H. Synthesis of Pyrindine-Fused Perylene Imides with an Amidine Motie for Hydrogen Bonding. Org. Lett. 2013, 15, 3110−3113.

Wescott, L. D.; Mattern, D. L. Donor-acceptor Molecules Incorporating a Nonadecyl-Swallowed Perylenediimide Acceptor. J. Org. Chem. 2003, 68, 10058−10066.

Huang, C.; Potsavage, W. J.; Tiwari, S. P.; Sutcu, S.; Barlow, S.; Kippelen, B.; Marder, S. R. Polynorbornenes with Pendant Perylene Dimides for Organic Electronic Applications. Polym. Chem. 2012, 3, 2996−3006.

Wüthrich, F.; Stepanenko, V.; Chen, Z.; Saha-Müller, C. R.; Kocher, N.; Stalke, D. Preparation and Characterization of RegioisomERICALLY Pure 1,7-Disubstituted Perylene Bismide Dyes. J. Org. Chem. 2004, 69, 7933−7939.

Chao, C.-C.; Leung, M.-K.; Su, Y. O.; Chiu, K.-Y.; Lin, T.-H.; Shieh, S.-J.; Lin, S.-C. Photophysical and Electrochemical Properties of 1,7-DIaryl-Substituted Perylene Dimides. J. Org. Chem. 2005, 70, 4323−4331.

Schmidt, R.; Oh, J. H.; Sun, Y.-S.; Deppisch, M.; Krause, A.-M.; Radacki, K.; Braunschweig, H.; Köinemann, M.; Erk, P.; Bao, Z.; Wüthrich, F. High-Performance Air-Stable n-Channel Organic Thin Film Transistors Based on Halogenated Perylene Bismide Semiconductors. J. Am. Chem. Soc. 2009, 131, 6215−6228.

Li, A. D. Q.; Wang, W.; Wang, L.-Q. Folding versus Self-Assembling. Chem. Eur. J. 2009, 3, 4594−4601.

Winter, R. F. Half-Wave Potential Splittings ΔE1/2 as a Measure of Electronic Coupling in Mixed-Valent Systems: Triumphs and Defeats. Organometallics 2014, 33, 4517−4536.

Liao, S.-H.; Jhoo, H.-J.; Cheng, Y.-S.; Chen, S.-A. Fulleren Derivative-Doped Zinc Oxide Nanoi Lm as the Cathode of Inverted Polymer Solar Cells with Low-Bandgap Polymer (PTB7-Th) for High Performance. Adv. Mater. 2013, 25, 4766−4771.

Shoae, S.; Clarke, T. M.; Huang, C.; Barlow, S.; Marder, S. R.; Heeney, M.; McCulloch, I.; Durrant, J. R. Acceptor Energy Level Control of Charge Photogeneration in Organic Donor/Acceptor Blends. J. Am. Chem. Soc. 2010, 132, 12919−12926.

Zhan, X.; Zhang, J.; Tang, S.; Lin, Y.; Zhao, M.; Yang, J.; Zhang, H.-L.; Peng, Q.; Yu, G.; Li, Z. Pyrene Fused Perylene Dimides: Synthesis, Characterization and Applications in Organic Field-Effect Transistors and Optical Limiting with High Performance. Chem. Commun. 2015, 51, 7156−7159.

Odom, S. A.; Kelley, R. F.; Ohira, S.; Ensley, T. R.; Huang, C.; Paddula, L. A.; Webster, S.; Coropceanu, V.; Barlow, S.; Hagan, D. J.; Van Stryland, E. W.; Bréda, J. L.; Anderson, H. L.; Wasielewski, M. R.; Marder, S. R. Photophysical Properties of an Alkyne-Bridged Bis(Zinc Porphyrin)-Perylene Bis(dicarboximide) Derivative. J. Phys. Chem. A 2009, 113, 10826−10832.

Demmig, S.; Langhals, H. Leichtlösliche, Lichtechte Perylen-Fluoreszenzfarbstoffe. Chem. Ber. 1988, 121, 225−230.

Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. J. Phys. Chem. 1994, 98, 11623−11627.

Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. Phys. Rev. A 1988, 38, 3098−3100.

Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. Phys. Rev. B 1988, 37, 785−789.

Spartan'14: Wavefunction Inc.: Irvine, CA.