Regioisomerically Pure 1,7-Dicyanoperylene Diimide Dimer for Charge Extraction from Donors with High Electron Affinities

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ABSTRACT: Perylene diimide (PDI) has attracted widespread interest as an inexpensive electron acceptor for photovoltaic applications; however, overcrystallization in the bulk heterojunction typically leads to low device performance. Recent work has addressed this issue by forming bay-linked PDI dimers and oligomers, where the steric bulk of adjacent PDI units forces the molecule to adopt a nonplanar structure. This disrupts the molecular packing and limits domain sizes in the bulk heterojunction. Unfortunately, the introduction of electron-donating/-withdrawing groups in the bay region is also the best way to fine-tune the frontier molecular orbitals (FMOs) of PDI, which is highly desirable from a device optimization standpoint. This competition for the bay region has made it difficult for PDI to keep pace with other non-fullerene acceptors. Here, we report the synthesis of regioisomerically pure 1,7-dicyanoperylene diimide and its dimerization through an imide linkage. We show that this is an effective strategy to tune the energies of the FMOs while simultaneously suppressing overcrystallization in the bulk heterojunction. The resulting acceptor has a low LUMO energy of −4.2 eV and is capable of accepting photogenerated electrons from donor polymers with high electron affinities, even when conventional acceptors such as PDI, PC71BM, and ITIC cannot.

INTRODUCTION

The field of organic photovoltaics (OPVs) has long-promised to produce colorful, flexible, solar cells with unique form factors and low embodied energies; however, it is only recently that the power conversion efficiencies (PCEs) of OPVs have started to become competitive with other technologies. Fine-tuning of both chemical structure and device architecture has led to single-junction devices with PCEs of over 15%3,4 and tandem cells with PCEs as high as 17.3%.5 This progress shows that OPVs are able to exceed the performance limits6 previously thought to restrict their utility. Modern OPVs typically use a bulk heterojunction architecture, which is a partially phase-separated blend of an electron donor and acceptor. These two materials need to be carefully matched in terms of their optoelectronic and physicochemical properties. The energies of the frontier molecular orbitals (FMOs) must be offset enough to facilitate exciton splitting and charge transfer but without an excess of driving force that would lower the operating voltage of the cell. Overcrystallization is also a key challenge; if the two materials lack sufficient miscibility, they will separate into large, phase-separated domains within the bulk heterojunction. This leads to extensive geminate recombination and a loss of PCE.8

Among NFAs, perylene imides (PDIs, Figure 1) have attracted a great deal of interest for their low LUMO, high photoinduced electron transfer, and their ability to fine-tune the energy levels of the FMOs of the bulk heterojunction. However, overcrystallization is a key challenge for these materials; if the two materials do not mix well, they will separate into large, phase-separated domains within the bulk heterojunction. This leads to extensive geminate recombination and a loss of PCE.8 Among NFAs, perylene imides (PDIs, Figure 1) have attracted a great deal of interest for their low LUMO, high photoinduced electron transfer, and their ability to fine-tune the energy levels of the FMOs of the bulk heterojunction. However, overcrystallization is a key challenge for these materials; if the two materials do not mix well, they will separate into large, phase-separated domains within the bulk heterojunction. This leads to extensive geminate recombination and a loss of PCE.8

Figure 1. Structure of perylene diimide; the bay region includes the 1, 6, 7, and 12 positions.
extinction coefficients, and low cost.\textsuperscript{14,16,17} The key challenge with PDI is preventing overcrystallization.\textsuperscript{18} Careful optimization of the alkyl chains at the imide position can be moderately effective at disrupting $\pi$-stacking,\textsuperscript{8,19−22} but dimerization or oligomerization has proven to be the most effective in OPVs. Early examples of dimers made use of imide linkages, which led to efficiencies of up to 3.2%.\textsuperscript{18,23} Exploiting the bay region to link two PDI units together pushed efficiencies to 4.0%.\textsuperscript{24} Further modifications to the alkyl chain length, selenium annulation, and donor pairing led to efficiencies of 8.4%.\textsuperscript{25} Similar strategies have joined PDIs together by either ring fusion\textsuperscript{26,27} or the use of spacers,\textsuperscript{26−29} and $N$-annulation has also proven effective at improving miscibility with donors.\textsuperscript{30,31} The introduction of steric bulk in the bay region of PDI has now led to PCEs of up to 10.6%.\textsuperscript{29}

The bay positions also serve as a way of tuning the FMO energies, thus allowing the energy offsets with donor materials to be optimized. The addition of nitrile groups to the bay region has long been known to lower $E_{\text{LUMO}}$,\textsuperscript{32−36} while pyrrolidine groups have been used to produce a higher-lying LUMO.\textsuperscript{32} Fortunately, overcrystallization remains an issue with these materials. As a result, the highest-performing PDI NFAs rarely employ this strategy, and nearly, all PDI acceptors have an $E_{\text{LUMO}}$ of 3.8 ± 0.3 eV.\textsuperscript{35} To continue improving the performance of PDI NFAs, it is necessary to expand upon these strategies to prevent overcrystallization, while also leaving the bay region open for tuning the FMO energies.

Here, we show that 1,7-dicyanoperylene diimide can be linked through the imide position to form a dimer; the dimerization prevents overcrystallization, while the nitrile-substitution substantially lowers the $E_{\text{LUMO}}$. We first report a method of preparing regioisomerically pure 1,7-dicyanoperylene-3,4,9,10-tetracarboxy tetrabutylester. This allowed us to isolate regioisomerically pure 1,7-PDI(CN)$_2$ and 1,7-diPDI(CN)$_2$, which were compared to PDI and diPDI (Chart 1). Our results show that the nitrile-substitution results in a pronounced drop in $E_{\text{LUMO}}$, while the dimerization results in smaller domain sizes in bulk heterojunction blends. As a result, 1,7-diPDI(CN)$_2$ is able to accept electrons from high electron affinity donors in situations where neither PDI, PC$_{71}$BM, nor ITIC had a low-enough LUMO to drive charge separation.

**RESULTS AND DISCUSSION**

**Synthesis.** The synthetic scheme for 1,7-diPDI(CN)$_2$ is shown in Scheme 1. Beginning with Sengupta et al.’s methodology,\textsuperscript{34} we first prepared the regioisomerically pure 1,7-dicyanoperylene-3,4,9,10-tetracarboxy tetrabutylester. Previous reports of cyanation via standard metal-catalyzed cross-
coupling procedures yielded mixtures of the 1,6 and 1,7-dicyanoperylene regioisomers, even when starting from the regioisomerically pure 1,7-dibromoperylene.\(^5\)\(^,\)\(^7\) Once formed, these two regioisomers co-cryocrystallize and cannot be separated by column chromatography, making it impossible to separate and isolate the desired 1,7-dicyano regioisomer. To address this issue, we developed a synthesis involving milder reaction conditions and the use of Pd(PPh\(_3\))\(_4\) as the catalyst, which yields good yields of the desired 1,7-dicyano regioisomer. To address this issue, we developed a synthesis involving milder reaction conditions and the use of Pd(PPh\(_3\))\(_4\) as the catalyst, which yields good yields of the desired 1,7-dicyano regioisomer. To address this issue, we developed a synthesis involving milder reaction conditions and the use of Pd(PPh\(_3\))\(_4\) as the catalyst, which yields good yields of the desired 1,7-dicyano regioisomer. To address this issue, we developed a synthesis involving milder reaction conditions and the use of Pd(PPh\(_3\))\(_4\) as the catalyst, which yields good yields of the desired 1,7-dicyano regioisomer. To address this issue, we developed a synthesis involving milder reaction conditions and the use of Pd(PPh\(_3\))\(_4\) as the catalyst, which yields good yields of the desired 1,7-dicyano regioisomer.

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The formation of the second anhydride was then followed by condensation with m-xylene diamine to prepare 1,7-diPDI(CN)\(_2\), as shown in Scheme 1. 1,7-PDI(CN)\(_2\) was prepared using similar methods in two steps, starting from the same 1,7-dicyanoperylene-3,4,9,10-tetracarboxy tetrabutylester (Scheme S2). It should be noted that the nitrile-substituted derivatives required longer reaction times than the non-substituted analogues to form either the anhydride or the imide. The preparation of PDI and diPDI was carried out using previously established procedures\(^31\)\(^,\)\(^38\) and the synthetic scheme for diPDI is shown in Scheme S3.

**Computational.** Having successfully synthesized each of the four acceptors, we investigated the effects of dimerization and nitrile substitution computationally. We optimized molecular geometries and calculated the electronic structure using density functional theory with B3LYP functional and a 6-31G(d) basis set. The alkyl chain length was truncated to reduce convergence time. We were primarily interested in how dimerization and nitrile substitution would impact the LUMO of these electron acceptors; the LUMO isosurfaces are shown in Figure 2, and a summary of the HOMO and LUMO eigenvalues is shown in Table S1. The results suggest that the dimers should have the same LUMO energies as the monomers, with PDI and diPDI having a predicted \(E_{\text{LUMO}}\) of \(-3.5\) eV, while 1,7-PDI(CN)\(_2\) and 1,7-diPDI(CN)\(_2\) have a predicted \(E_{\text{LUMO}}\) of \(-4.1\) eV. The two halves of the PDI dimers are effectively electronically isolated, and only the cyano substitution has an effect on the \(E_{\text{LUMO}}\). This can also be seen from the LUMO isosurfaces shown in Figure 2, where the two PDI \(\pi\)-systems in diPDI and 1,7-diPDI(CN)\(_2\) are spatially separated and oriented orthogonally to one another. From Figure 2, it can also be seen that nitrile substitution leads to a slight twist about the aromatic core in 1,7-PDI(CN)\(_2\) and 1,7-diPDI(CN)\(_2\). Both this twist and the conformational flexibility of the \(\pi\)-methylene linkage in the dimers are expected to disrupt the \(\pi\)-stacking of PDI, leading to improved solubility and reduced domain size within bulk heterojunction active layers.

**Optical Properties.** In order to determine the effect of substitution and dimerization on the optical properties of the PDI acceptors, we measured their UV/vis and photoluminescence (PL) spectra in chloroform solution (Figure 3). The absorption spectra of all four materials consist of three vibronic peaks at 527, 490, and 459 nm, which arise from the lowest energy \(\pi \rightarrow \pi^*\) transition.\(^39\) The relative intensities of these peaks are similar for both the monomers and the dimers, again suggesting that each PDI chromophore is electronically isolated. This is in contrast to PDI dimers linked through the bay region, where the intensity ratio of the 0–0 and 0–1 vibronic bands at 527 and 490 nm, respectively, is often lower in solution.\(^31\) Compared to the monomers, the dimers display a very slight decrease in the energy of the 0–0 transition (\(E_{00}\)), as shown in Table S2. The emission profiles of both the monomers and dimers are near-mirror images of the UV/vis spectra. The nitrile-substituted PDI derivatives have a slightly larger Stokes shift (\(\approx400\) cm\(^{-1}\)) as compared to the unsubstituted acceptors (200 cm\(^{-1}\)), consistent with the small increase in conformational flexibility (Table S2). The nitrile substitution does not greatly affect the molar extinction coefficients (Table S2).

**Electrochemical Properties.** Using cyclic (Figure S1) and differential pulse voltammetry (DPV, Figure 4), we measured the oxidation and reduction potentials of the four acceptors. As a benchmark, we first consider PDI, which possesses cathodic peaks at \(-1.06\) and \(-1.25\) V (vs Fe/C) corresponding to the first and second reduction events. The same two distinct reduction events are seen for 1,7-PDI(CN)\(_2\), except that the potentials have shifted to \(-0.67\) and \(-0.98\) V. The pronounced shift to more positive potentials is consistent with the electron-withdrawing nature of the nitrile groups and is consistent with previous reports of the reduction of 1,7-PDI(CN)\(_2\).\(^40\) From cyclic voltammetry (Figure S1), we see that both reduction events are quasi-reversible for both PDI and 1,7-PDI(CN)\(_2\).

We then consider the effect of dimerization on the electrochemical behavior. For an electronically isolated PDI dimer, we would expect to see reduction occurring at the same potentials as for the monomer, only with increased current.

![Figure 2](https://example.com/figure2.png)  
*Figure 2. LUMO isosurfaces calculated at the B3LYP/6-31G(d) level of theory for: (a) PDI, (b) 1,7-PDI(CN)\(_2\), (c) diPDI, and (d) 1,7-diPDI(CN)\(_2\).*

![Figure 3](https://example.com/figure3.png)  
*Figure 3. UV/vis and PL spectra of PDI-based acceptors in chloroform solutions.*
flow because of the greater number of electrons being transferred. As can be seen in Figure 4, this is not the case for either diPDI or 1,7-diPDI(CN)2; both acceptors show two smaller reduction peaks (likely one-electron reductions), followed by a third, larger peak (likely a two-electron reduction). This is most easily seen for 1,7-diPDI(CN)2, which has three distinct peaks at −0.58, −0.74, and −1.03 V. Previous work has shown that this phenomenon is due to conformational flexibility of the m-xylylene linkage.41 Similar to what has been shown previously,41 we hypothesize that PDI dimers start in an unfolded conformation (similar to Figure 2c,d); after the first reduction event, rotation about the m-xylylene linkage puts the two PDI units in close proximity. This reorientation means that the two PDI units are no longer electronically isolated, shifting the subsequent reduction event to −0.74 V in 1,7-diPDI(CN)2. The same electrochemical behavior is seen for diPDI, except that the conformationally induced shifts are less clearly resolved. Although the results suggest that dramatic conformational changes can occur upon reduction in solution, these are unlikely to occur in thin films, making them less relevant to OPV device performance.

We next used the reduction potentials to estimate ΔE_LUMO; this was combined with measurements of ΔE_HOMO (Table S2) to yield estimates of ΔE_HOMO as summarized in Figure 5. These data can then be used to predict whether electron transfer from the donor to acceptor is energetically favorable. We considered two different donors: PTB7-th, a well-established donor polymer for OPV applications, and bis-il-3T, a low-band gap donor polymer with a particularly high electron affinity (Chart 2).42,43 We would expect all four acceptors to readily accept an electron from PTB7-th (ΔE_LUMO ≥ 0.1 eV), which is supported by PL quenching experiments (Figure S3). However, the LUMO of bis-il-3T is isoenergetic with that of PDI, and we would expect bis-il-3T to only pair well with the nitrile-substituted acceptors. Similar PL quenching experiments were not possible for bis-il-3T because the polymer is nonemissive.

Device Performance: PTB7-th. Based on our electrochemical data, we selected PTB7-th as the electron donor for initial device optimization studies (Table S3); the ΔE_LUMO offset was expected to allow efficient electron transfer from PTB7-th to each of the four acceptors (Figure 5). The J−V curves of the best devices are shown in Figure 6a, and average data are reported in Table 1. We first consider the effect of nitrile substitution and dimerization on V_oc. The V_oc is directly related to the E_LUMO(acceptor) − E_HOMO(donor) energy difference;44 however, all of the V_oc’s here are significantly lower than this gap, indicating high levels of recombination in the cells. Cells made using PDI and 1,7-PDI(CN)2 had an average V_oc of 0.8 and 0.30 V, while diPDI and 1,7-diPDI(CN)2 had an average V_oc of 0.63 and 0.36 V, respectively. In both cases, there is a significant drop in V_oc upon nitrile substitution (0.5 and 0.27 V); although recombination losses may be present to a greater or lesser degree in each system, the main driver of this trend is most likely the decrease in E_LUMO (0.2 eV for PDI and 1,7-PDI(CN)2 and 0.3 for diPDI and 1,7-diPDI(CN)2). In terms of photocurrent generation, we observed a considerable increase in J_sc for diPDI (J_sc = 2.07 mA/cm²) compared to PDI (J_sc = 1.76 to 1.42 mA/cm² for 1,7-PDI(CN)2 and 1,7-diPDI(CN)2, respectively. Although many factors can contribute to these differences in J_sc, the PTB7-th excited state is efficiently quenched by each of the PDI-based acceptors (Figure S3). This suggests that the lower photocurrents of the nitrile-substituted acceptors are not due to poor exciton separation but are more likely due to either recombination through a nonradiative charge transfer state or inefficient carrier extraction and bimolecular recombination. The lower photocurrent of 1,7-diPDI(CN)2 (as opposed to 1,7-PDI(CN)2) is also consistent with an observed increase in series resistance (Table 1). Although this is not necessarily the only contributor to the lower J_sc, it does lead to substantially lower fill factors for 1,7-diPDI(CN)2. The incident photon-to-current efficiency (IPCE) spectra for the PTB7-th devices (Figure 6b) are consistent with the observed changes in J_sc.

The different film morphologies, which were evaluated using atomic force microscopy (AFM), can help explain the observed trends in J_sc, FF, and series/shunt resistance. The phase images (Figure 7) and topography images (Figure S6) show that the PDI-based films have feature sizes (corresponding to either donor-rich or acceptor-rich domains) on the order of 300 nm. Although AFM cannot quantitate the phase purity of these domains, the large spatial extent of phase separation suggests that the acceptor has overcrystallized. For 1,7-PDI(CN)2, these features are much smaller, roughly 100 nm in size. The
Figure 6. (a) J–V curves and (b) IPCE spectra of the highest-performing ITO/ZnO/PTB7-th:acceptor/MoO3-x/Ag devices prepared using the PDI acceptors.

Table 1. Average Device Parameters for Optimized ITO/ZnO/PTB7-th:acceptor/MoO3-x/Ag Devicesa

| acceptor          | N  | Voc (V) | Jsc (mA/cm²) | FF (%) | PCE (%) | Rs (Ω cm²) | Rsh (Ω cm²) |
|-------------------|----|---------|--------------|--------|---------|------------|-------------|
| PDIb              | 14 | 0.8 ± 0.1 (0.9) | 2.07 ± 0.07 (2.20) | 42 ± 2 (43) | 0.7 ± 0.1 (0.8) | 60 ± 20 | 890 ± 80 |
| 1,7-PDI(CN)2c     | 15 | 0.30 ± 0.07 (0.32) | 1.8 ± 0.2 (2.0) | 47 ± 3 (50) | 0.26 ± 0.04 (0.31) | 40 ± 10 | 700 ± 200 |
| diPDIb            | 16 | 0.63 ± 0.03 (0.67) | 3.7 ± 0.3 (4.1) | 39 ± 4 (47) | 0.9 ± 0.1 (1.2) | 50 ± 11 | 370 ± 70 |
| 1,7-diPDI(CN)2e   | 16 | 0.355 ± 0.005 (0.365) | 1.42 ± 0.05 (1.48) | 37.9 ± 0.4 (38.5) | 0.191 ± 0.009 (0.205) | 85 ± 7 | 510 ± 20 |

aThe uncertainties are plus-or-minus one standard deviation. The values for champion cells are given in parentheses. bD/A = 0.3. cD/A = 0.1, 0.5% DIO. dD/A = 0.3. eD/A = 0.3.

Figure 7. AFM phase images of the optimized PTB7-th:acceptor bulk heterojunctions: (a) PDI, (b) 1,7-PDI(CN)2, (c) diPDI, and (d) 1,7-diPDI(CN)2.
smaller domain sizes are consistent with the predicted torsion of the PDI unit in 1,7-PDI(CN)2 (Figure 2). The imide-linked diPDI leads to greater film heterogeneity, likely owing to its low solubility. The film is noticeably rougher (R$_{\text{rms}}$ = 15 nm, as opposed to 3.1 and 1.9 nm for PDI and 1,7-PDI(CN)$_2$, respectively), which likely contributes to the lower shunt resistances observed for these devices (Table 1). In the case of 1,7-diPDI(CN)$_2$, the AFM image shows little evidence of phase separation, and the film is quite smooth and homogeneous (R$_{\text{rms}}$ = 0.7 nm). Clearly, dimerization prevents overcrystallization of the nitrile-substituted PDI; unfortunately, overly small domain sizes may contribute to the observed increase in series resistance (Table 1).

Device Performance: Bis-il-3T. Figure 5 shows that finding an acceptor to pair with PTB7-th is a relatively easy task; however, the high electron affinity of Bis-il-3T makes finding a compatible acceptor much more difficult. In order to provide sufficient driving force for exciton separation, acceptors with electron affinities >4.0 eV (such as 1,7-PDI(CN)$_2$ and 1,7-diPDI(CN)$_2$) would likely be required. It is in these situations—when paired with a high electron affinity donor—that the nitrile-substituted acceptors are most advantageous.

To test this point, we prepared a number of OPV devices using Bis-il-3T as the donor (Table S5); the polymer was paired with each of the four PDI-based acceptors, as well as two commonly used acceptors, PC$_7$BM and ITIC. The data show that the monomeric PDI acceptors (PDI and 1,7-PDI(CN)$_2$) performed poorly (PCE <0.02%), based on their propensity for overcrystallization (Figure 7). diPDI and ITIC (both of which have an electron affinity of 3.9 eV) performed better (PCE ~0.05%), but the best results (PCE ~0.2%) were achieved with the strongest acceptors, PC$_7$BM and 1,7-diPDI(CN)$_2$ (which have electron affinities of 4.0 and 4.2 eV, respectively).

The IPCE spectra of the devices (Figure 8a) and the solid-state UV/vis spectra of the active layer components (Figure 8b) provide important insight into the photophysical processes occurring in the cells. It can be seen from Figure 8a that neither the PDI nor the diPDI devices produce photocurrent at wavelengths >600 nm, despite the fact that Bis-il-3T absorbs strongly out to ~950 nm (Figure 8b). This indicates that excitons generated on Bis-il-3T are not able to dissociate and form charge carriers, a result of the low $\Delta E_{\text{LUMO}}$ ($\leq$0.2 eV). The photocurrent in these devices arises entirely from photon absorption by the acceptor because there is more than sufficient driving force provided by the $\Delta E_{\text{HOMO}}$ offsets ($\geq$0.8 eV). The situation is similar when PC$_7$BM is used as the acceptor; the IPCE spectrum of the Bis-il-3T/PC$_7$BM devices closely matches the absorption spectrum of PC$_7$BM, with no contribution from Bis-il-3T (Figure 8c). The results clearly show that even a relatively high electron affinity of 4.0 eV (PC$_7$BM) provides insufficient driving force to dissociate a Bis-il-3T exciton. In contrast, the IPCE spectra of the nitrile-substituted acceptors, both 1,7-PDI(CN)$_2$ and 1,7-diPDI(CN)$_2$, show photocurrent being generated in the range of 600–950 nm. This is a clear signature of charge transfer from the donor to acceptor (Figure 8d). The difference in performance of the 1,7-diPDI(CN)$_2$- and 1,7-PDI(CN)$_2$-based devices is therefore most likely due to differences in morphology, rather than any electronic effect. Ultimately, these data highlight the importance of tuning the FMOs of the acceptor to match those of the donor, while simultaneously controlling active layer morphology. We have clearly shown that 1,7-PDI(CN)$_2$ can act as an electron acceptor in situations where both state-of-the-art fullerene (PC$_7$BM) and non-fullerene (ITIC) acceptors fail.
CONCLUSIONS

We have shown that the dimerization of PDI through the imide region can be an effective way of preventing overcrystallization, while leaving the bay region available for further functionalization. Using this strategy, we were able to shift the frontier molecular orbital energies of PDI dimers by regioselective nitrile substitution at the 1,7 positions. We demonstrated that the resulting acceptor (1,7-diPDI(CN)$_2$) can produce working OPV devices in situations where other acceptors (including unsubstituted PDI, PC$_2$BM, and ITIC) lack sufficient driving force for exciton separation. This development is expected to be particularly important for low band gap donor materials, which often have relatively low LUMO energies and high electron affinities.

METHODS

Characterization. NMR spectra were obtained using a Bruker Avance 500 MHz spectrometer. Mass spectra were acquired on a JEOL AccuToF 4G GGc mass spectrometer with an Etten field desorption ionization source. UV/vis spectra were measured in chloroform solutions using either a Cary 50 or 600i UV/vis spectrophotometer. AFM measurements were performed using a PicoSPM microscope operating in the tapping mode. Cyclic and differential pulse voltammetry was carried out in 0.05 mol L$^{-1}$ tetrabutylammonium hexafluorophosphate dissolved in either dry, degassed dichloromethane as the working OPV devices in situations where other acceptors (including unsubstituted PDI, PC$_2$BM, and ITIC) lack sufficient driving force for exciton separation. This development is expected to be particularly important for low band gap donor materials, which often have relatively low LUMO energies and high electron affinities.

OPV Fabrication and Testing. ITO-coated glass substrates ($R_s = 20 \Omega/$sq, Xin Yan Technology Ltd.) were cleaned by sequential sonication in Extraxn 300 detergent (2% v/v in Millipore H$_2$O), Millipore H$_2$O, acetone, and isopropanol for 20 min each, blown dry with filtered nitrogen (0.45 $\mu$m PTFE syringe filter), and UV/ozone-cleaned for 15 min. A ZnO sol–gel precursor solution was prepared by dissolving ZnOAc-2H$_2$O (0.108 g) and ethanolamine (30 $\mu$L) in 2-methoxyethanol (1.0 mL) and stirred vigorously overnight. The ZnO precursor solution was spin-cast onto the cleaned ITO/glass substrates and annealed at 180 °C for 15 min; the substrates were placed into a nitrogen-filled glovebox while still hot. Bis-IL-3T/acceptor active layer solutions were prepared by dissolving in chlorobenzene to a total solid concentration of 20 mg mL$^{-1}$ (18 mg/mL for PBT7-th) by heating to 60 °C. The active layer was spin-coated at 2500 rpm. After the active layer was deposited, MoO$_3$-x (5 nm, 0.1 Å s$^{-1}$) and Ag (70 nm, 0.1–0.3 Å s$^{-1}$) were thermally evaporated at a base pressure of 1 × 10$^{-6}$ mbar. Current–voltage measurements were performed inside a nitrogen-filled glovebox using a Keithley 2400 source-measure unit. The cells were illuminated using a 450 W Class AAA solar simulator equipped with an AM1.5G filter (Sol3A, Oriel instruments) at a calibrated intensity of 100 mW cm$^{-2}$, as determined using a standard silicon reference cell (91150V, Oriel Instruments). The cell area was defined to be 0.0708 cm$^2$ by a nonreflective anodized aluminum mask. IPCE measurements were performed in air on the best-performing devices using a QE-PV-Si system (Oriel Instruments) consisting of a 300 W Xe arc lamp, monochromator, chopper, lock-in amplifier, and certified silicon reference cell, operating at a 30 Hz beam-chopping frequency.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01217.

Computational details, cyclic voltammograms, optical data, OPV performance, AFM images, synthetic procedures, and NMR spectra (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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