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Influence of *N*-Substituents on Photovoltaic Properties of Singly Bay-Linked Dimeric Perylene Diimides

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Abstract: The influence of N-substituents on the photovoltaic properties of singly bay-linked perylene diimides (diPDIs) was systematically investigated to understand the aromatic-aliphatic balance, which is beneficial for achieving high device performance in organic photovoltaic (OPV) systems. The synthesis of various N-substituted diPDIs was successfully achieved using a newly developed one-step procedure, resulting in sufficiently high yields. Detailed investigations of seven variants of diPDIs demonstrated that the primary alkyl substituents, particularly the 2-ethylhexyl group, induce the self-organized growth of thin films with high crystallinity. This is beneficial for enhancing the device performance of bulk heterojunction (BHJ) systems. The results presented herein reveal the important roles of alkyl side chains as hydrophobic solubilizing auxiliaries or primary determinants in the control of the active layer nanomorphology. This offers a valuable guideline that is essential for developing high-performance organic semiconductor materials for future practical applications.

Introduction

Organic photovoltaics (OPVs) that are based on a combination of polymeric donors and small molecular nonfullerene acceptors (NFAs) have attracted considerable attention.^[1] This is because of the significant advances made in current state-of-the-art systems in the improvement of photovoltaic performance with a

power conversion efficiency (PCE) close to 18%^[2], while retaining many practical advantages, such as flexibility, light weight, low production costs of solution-processed bulk films, and low waste disposal costs for hazardous element-free materials.^[3] The compatibility of the donor-acceptor pair is considered a principle determinant governing the surface morphology and photovoltaic properties of the bulk heterojunction (BHJ) layers.^[4] According to the proposed strategy for the rational design of efficient organic semiconductive materials, the presence of aliphatic auxiliaries at the outer edges of the π -extended aromatic structures stabilizes the face-on oriented π - π stacking of the aromatic units through a layer-by-layer self-organization into lamellar architectures.^[5] The so-called "zipper effect" caused by van der Waals interactions among the alkyl side chains improves the crystallinity of the composite materials to adapt the microcrystalline film morphologies of the BHJ blends.^[6] This develops the intermolecular charge transport properties, which eventually improve the photovoltaic device performances.^[7] Therefore, it is assumed that the enhancement in the OPV efficiency can be ensured by a proper alkyl substituent placed on the π -conjugated backbones of the donor and acceptor materials.^[8]

For the molecular design of NFAs, regarding highly efficient OPVs, perylene diimide (PDI) has been considered as one of the most promising functional components with attractive n-type semiconductive properties.^[9] However, a well-known drawback in PDIs is the tendency to excessively aggregate. This is associated

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with an inherent poor solubility because of their high backbone planarity, rendering them unsuitable for device fabrication with solution processing.^[10] Many efforts to develop PDI systems with enhanced solubility have demonstrated the potential of a singly baylinked dimeric PDI (diPDI) system, in which two PDI units are connected through single bonding at the bay positions to adopt twisted conformations.^[11] Considering that the diPDI system has been shown to serve as a superior NFA material, compared to the mononuclear PDI,^[12] extensive studies have been conducted to investigate the potential of diPDIs for photovoltaic applications,[13-^{16]} including the investigation of optimal donor materials, device structures, and additives for device fabrication.^[17,18] Additionally, previous studies have elucidated the mechanisms of the photoelectric conversion processes and discovered their unique optical and electronic properties.^[19-23] In this context, the diPDI systems can be regarded as an ideal platform to investigate the influence of the alkyl side chains on the photovoltaic properties because of their greater structural tunability and material reliability, although the diPDIs have recently lost their superiority by comparison with the state-of-the-art NFAs.^[2] Despite the increasing interest in diPDI systems, attempts to undertake further derivatization have been hampered by the unavailability of general synthetic strategies to overcome insolubility encountered using relevant synthetic precursors. Thus, conventional diPDI systems have been designed by introducing branched long alkyl chains (the so-called swallow tails), at the imide positions to impart sufficient solubility.^[24] However, this molecular design degrades the film crystallinity, which is detrimental to the OPV performance^[25] and emphasizes the need for a general synthetic approach with a high tolerance for the imide functionality in diPDI systems.

Consequently, we developed a new synthetic strategy that enables the preparation of diverse *N*-substituted diPDIs for exploratory studies focusing on photovoltaic applications. Herein, we describe our efforts to adapt the conventional synthetic method (Path A in Scheme 1) for initial investigations and to explore an alternative synthetic pathway (Path B) for a wide range of diPDI products. Herein, we report the practical synthesis of diPDIs and their applications in OPVs, highlighting the significant impact of structural differences in the *N*-substituents on the morphological and photovoltaic properties of the BHJ active layers.

Results and Discussion

We synthesized a diPDI, 1, using a variety of substitution patterns for comparison purposes. Conventionally, a diverse library of diPDIs had been prepared via an Ullmann-type reductive homocoupling of bay-monobrominated PDIs with nanosized copper powder.^[12] Regarding this, our recently reported approaches that ensure the ready availability of various N-substituted PDI monobromides from commercially available 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) enabled the preparation of the reaction precursors with 6-undecyl (2a) and 2-ethylhexyl (2b) moieties (Path A in Scheme 1).^[26] The initial attempt to access the diPDI systems by subjecting 2a and 2b to a previously used procedure^[12] for the reductive homocoupling led to different reaction outcomes, whose production yields were greatly affected by the solubility of the PDI substrates. The swallow-tail PDI, 2a, containing solubilizing moieties, provided a moderate yield of 1a, while 2b did not react under similar conditions (entries 1 and 2 in Table 1). However, **2b** reacted in the presence of catalytic tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄),^[27] with a high efficiency and 21% yield. Although partial success was achieved in the synthesis of **1a** and **1b**, the aforementioned approach had critical limitations in terms of functional group tolerance for the structural variations of the substituents at the imide positions.



Scheme 1. Synthetic routes to variously N-substituted diPDIs.

Table 1.	Synthesis	of diPDIs	1 from	2 ^[a] (or 3 ^[b]
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E	ntry	1	Substrate	R	<i>T</i> [°C]	<i>t</i> [h]	Yield
	1 ^[a]	1a	2a	6-undecyl	100	5.5	39%
2	2 ^[a]	1b	2b	2-ethylhexyl	150	6	0% ^[c]
3	3 ^[b]	1b	2b	2-ethylhexyl	150	12	21%
	4	1b	3	2-ethylhexyl	150	6	56%
0	5	1c	3	phenyl	150	8	45%
	6	1d	3	benzyl	150	6	32%
	7	1e	3	cyclohexyl	150	8	54%
	8	1f	3	cyclohexylmethyl	150	2	67%

[a] The reaction was carried out in the absence of Pd(PPh₃)₄. [b] The reaction was carried out in the presence of Pd(PPh₃)₄. [c] The starting material was recovered intact with no noticeable degradation.

An alternative method of synthesizing **1** is the late-stage installation of the imide substituents onto the perylene core (Path B in Scheme 1). Considering that this method requires the use of an anhydride derivative of the bay-linked dimeric perylene tetracarboxylic acid **3**, an efficient pathway was provided for this molecular precursor. We envisaged that this type of compound could be provided by the acidic removal of ester groups from a dimeric derivative of perylene tetraesters (PTEs), which may be represented by the relevant benzyl ester, **4**, because of its synthetic accessibility ^[28] and ease of processing for scalable solution-based reactions.^{[29],[30]} The preparation was conducted according to our reported synthetic method in which PTCDA was efficiently converted on a multigram scale to tetrabenzyl 1-bromoperylene tetra-

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carboxylate 5 in two steps.^[31] The application of the aforementioned preparation method to this substrate led to a successful reaction. It afforded the corresponding dimeric product, 4, with an isolated yield of 44%. The treatment of this compound with p-toluenesulfonic acid (PTSA) in refluxing toluene resulted in the complete conversion of all benzyl ester groups to the cyclic anhydride functionalities to provide a practically quantitative formation of 3, which was precipitated out of the reaction mixture.^[32] With the key intermediate, a series of condensation experiments were performed with amines to explore the synthesis of diPDIs that could not be accessed with the initial preparative route. Table 1 includes the scope of the methodology for the construction of diPDIs 1b-f via the multiple imidation of small aliphatic and aromatic amines with 3. All products were characterized by proton nuclear magnetic resonance (¹H NMR) spectroscopy and high-resolution mass spectrometry (HRMS). The main skeleton of the diPDI structure was elucidated by preliminary results of the X-ray crystallographic analysis of **1e**, while the structure could not be fully refined, owing to the presence of highly disordered solvent molecules (Figure S1 in Supporting Information).^[33] The high thermal stabilities of these compounds were confirmed by differential scanning calorimetry (DSC) measurements on 1a and 1b and thermogravimetric analysis (TGA) on 1b, showing superimposable DSC traces at a temperature range of 60-200 °C and a weight loss of less than 2% when heated to 350 °C under an argon atmosphere (Figures S2a-c in Supporting Information). These results illustrate the remarkable generality of this one-step procedure and the potential of this synthetic approach toward diPDI derivatives with desired imide functionalities.



Figure 1. (a) Absorption and (b) fluorescence spectra of 1a-f (coloured solid lines) and 6 (black dashed line) in CHCl₃ for all samples. Excitation wavelengths at 453 nm for all cases. The fluorescence spectra are normalized to the emission maxima.

Figure 1a shows the absorption spectra of **1a**–**f** in CHCl₃ solutions, superimposed with that of a comparative monomeric PDI, *N*,*N'*-di(6-undecyl)-3,4,9,10-perylenetetracarboxylic diimide **6**.^[34] In comparison with PDI **6**, the series of diPDIs exhibited broad and red-shifted absorption, probably because of 1) a narrow highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap associated with extensive conjugation over the entire π system and 2) the excitonic interaction between the bay-linked PDI moieties. This is consistent with the prior report

by Schwartz and coworkers,^[23] who offered the mechanistic rationale for the spectral broadness relying on the conformational variability and strong π -stacking interactions of the diPDI systems. As shown in Figure 1, the diPDIs **1a**-f displayed inherently weaker molar absorptivity than that of the monomeric PDI **6**,^[30] which is in good agreement with other published works.^{[21],[22]} The fluorescence spectra of **1a**-f show broad and red-shifted profiles (Figure 1b). The observed absorption and emission spectra were essentially unaffected by the substituents on the imide nitrogen atoms.

Cyclic voltammetry (CV) measurements were conducted on **1a**, **1b**, and **6** to analyze the electrochemical properties of the diPDI systems. Based on previous studies,^{[21],[22]} **1a** exhibited a reduction peak at -1.07 V, significantly higher than that of **6** ($E_{red} =$ -1.17 V), while **1b** showed an unclear reduction wave around -1.01 V, probably due to the high aggregation tendency of this compound (Figure 2). Based on the aforementioned observation, the energy levels of the LUMO of **1a** and **1b** (E_{LUMO}) were calculated to be -3.73 and -3.79 eV, respectively, which correlate with that of a previous study (-3.76 eV).^[22] Furthermore, the energy levels of the HOMO for **1a** and **1b** (E_{HOMO}) were determined to be -5.81 and -5.86 eV, respectively, by subtracting the optical energy gaps ($E_g = -2.08$ and -2.07 eV, respectively) from E_{LUMO} .



Figure 2. Cyclic voltammograms of **1a** (blue solid, enlarged by 30 times), **1b** (red solid, enlarged by 3 times), and **6** (black dashed) in THF containing (*n*-Bu₄N)PF₆ at *c* 0.1 mol/L. Scan rate: 50 mV/s. The inset zooms into the range from -1.4 to -0.8 V. Platinum wire as the working and counter electrodes. Ag/AgCl (Ag/Ag⁺) as a reference electrode. The potentials were externally calibrated against the ferrocene/ferrocenium couple and calculated from the inflection points of the curves.

Density functional theory (DFT) calculations were conducted to understand the electronic structures of diPDI (Figure S3, Supporting Information). All calculations employed the Gaussian 16 program at the B3LYP theory level with a basis set of 6-31G. To simplify the calculations, the imide substituents were replaced with methyl groups. In comparison with the monomeric PDI with an E_{LUMO} and E_{HOMO} at -3.46 and -6.00 eV, respectively, it was revealed that the diPDI system possessed a significantly stabilized E_{LUMO} of -3.66 eV and a comparable E_{HOMO} of -6.01 eV. Thus, the diPDI was shown to have a smaller E_g (2.35 eV) than that of the monomeric PDI (2.54 eV). This corresponds with the bathochromic spectral shifts and low reduction potentials observed for **1b**. According to the optimized structure of the diPDI, two PDI rings are forced to twist at an average dihedral angle of 67° (61°

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for the dihedral angle of the single bond that connects the junctional bay carbon atoms), owing to the steric interference of the rigid π -systems, which is comparable to the preliminary X-ray results (Figure S1 in Supporting Information). This suggests that nonnegligible electronic couplings exist between the two PDI systems, which would influence the E_{LUMO} and E_{HOMO} ; antibonding and bonding interactions were confirmed in the HOMO and LUMO, respectively, between the junctional bay carbon atoms.

Next, the absorptive behavior of diPDIs in the thin-film state was investigated. Figure 3a shows the thin-film absorption spectra of **1a–f** spin-coated on quartz substrates from CHCl₃ with and without 3% 1,8-diiodooctane (DIO).^[35] For compounds **1a** and **1e** possessing secondary alkyl groups, the spectra were virtually similar to the solution spectra, exhibiting a comparable full width at half maximum (FWHM) of ca. 5000 cm⁻¹, regardless of the addition of DIO. The *N*-arylated diPDI, **1c**, showed a similar spectrum to that in solution, when fabricated without DIO. The DIO-affected film of **1c** showed an ill-defined spectral profile, probably due to its low solubility, which hampered a suitable film formation.



Figure 3. (a) Absorption spectra of non-DIO-processed (blue solid line) and DIO-processed (3% (v/v), red dashed line) films for 1a–f. (b) Comparison of absorption spectra of non-DIO-processed films fabricated without (blue solid) and with thermal annealing at 100 (green dotted), 150 (green dashed), and 200 (green solid) °C for 1a and 1b.

These results show no significant enhancement in the intermolecular electronic coupling during the film formation process in **1a**, **1c**, and **1e**. In contrast, compounds **1b**, **1d**, and **1f**, which possess primary alkyl groups, showed remarkable spectral changes driven by the film formation process. When fabricated without DIO, the spectra of 1b, 1d, and 1f were broadened and red-shifted, indicating an enhancement in the intermolecular electronic coupling. The observed N-substituent dependence can be ascribed to the steric nature of the PDI core. The small steric hindrance of the primary alkyl groups may allow the diPDI molecules to closely contact each other. Thus, diPDIs possessing primary alkyl groups are assumed to form enhanced $\pi-\pi$ intermolecular interactions. Furthermore, the use of a DIO additive can significantly change the spectral features of 1b, 1d, and 1f. Among these compounds, 1f demonstrated a narrow spectral width when DIO was used, similar to those for the solution sample. Meanwhile, the DIObased films of 1b displayed split absorption bands covering a broad range of wavelengths. This suggests that the J-aggregation induced by face-to-face molecular stacking slipped through the long axis of the PDI chromophores.[36] The prominent sensitivity observed for these three compounds toward the additive may be explained in terms of the accessibility of DIO molecules to the less congested PDI planes with primary alkyl groups. The observed additive effect suggests high controllability in the film formation process of the sterically less-hindered materials. Therefore, we considered if a similar effect could be obtained by applying the thermal annealing treatment. Contrarily, no morphological transition occurred for 1a and 1b upon thermal annealing up to 200 °C (Figure 3b).



Figure 4. Current density-voltage (*J-V*) characteristics of OPV devices fabricated with **1a** (blue) and **1b** (red) in the absence (dashed) and presence (solid) of 3% (v/v) DIO under 1000 W/cm² AM 1.5G illumination. The bold dashed line represents *J*–*V* curve of thermally annealed device fabricated from **1a**.

Next, using a variety of prepared diPDIs, a systematic study was conducted to understand the photovoltaic behavior of these materials when combined with a representative low band-gap polypoly([2,6'-4,8-di(5-ethylhexylthienyl)benzo[1,2meric donor. b;3,3-b]dithiophene]{3-fluoro-2[(2-ethylhexyl)carbonyl]thieno[3,4b]thiophenediyl}) (PTB7-Th), to fabricate active layer blends.[37] Consequently, we fabricated and characterized a device with an inverted structure, indium tin oxide (ITO)/polyethylenimine ethoxylated (PEIE)/active layer (1:2 (w/w) donor:acceptor ratios)/MoO₃/Ag. The active layers were spin-coated from CHCl₃ solutions of PTB7-Th and 1. Concurrently, comparative fabrication experiments were conducted using a 3% (v/v) DIO additive. Experiments were conducted by replacing PEIE with ZnO as an alternative electron transport material to eliminate detrimental defects for J-V measurements. Among the diPDIs examined here, 1c and 1d were observed to be unsuitable for solution processing

because of their extremely low solubility. Instead, the others provided sufficient solubility to form high-quality homogeneous films. Figures 4 and S4 (Supporting Information) show the photocurrent density–voltage curves of the OPV devices under air mass (AM) 1.5 simulated sunlight at a light intensity of 100 mW/cm². The detailed photovoltaic parameters including short-circuit current (J_{SC}), open-circuit voltage (OCV) (V_{OC}), fill factor (FF), and photon conversion efficiency (PCE), are summarized in Table 2.

Table 2. The photovoltaic parameters of PTB7-Th:1-based inverted OPV devices processed with and without ${\rm DIO}^{\rm [a]}$

Entry	1	DIO ^[b] [v/v]	J _{SC} [mA/cm ²]	V _{oc} [V]	FF [%]	PCE [%]
1	1a	0%	7.15	0.742	44.3	2.35
2 ^[c]	1a	0%	7.15	0.710	44.7	2.27
3	1a	3%	6.02	0.746	36.0	1.62
4	1b	0%	11.82	0.719	51.7	4.40
5 ^[d]	1b	0%	9.01	0.537	31.4	2.95
6	1b	3%	10.95	0.789	51.8	4.48
7	1c	0%	1.53	0.537	31.4	0.258
8	1c	3%	1.27	0.524	28.9	0.192
9	1d	0%	0.898	0.542	25.9	0.126
10	1d	3%	0.195	0.394	18.6	0.0143
11	1e	0%	7.78	0.782	42.9	2.61
12	1e	3%	7.99	0.786	45.5	2.85
13 ^[d]	1f	0%	9.63	0.691	54.3	3.61
14 ^[d]	1f	3%	7.58	0.723	58.3	3.19
15	1g	0%	8.77	0.76	47.2	3.13
16	1g	3%	7.90	0.78	53.7	3.29

[a] All the photovoltaic devices were made with PTB7-Th and 1 at a ratio of 1:2 (w/w). [b] The amount of DIO used for solution processing. [c] The spin-cast film was thermally annealed at 100 °C for 5 min. [d] ZnO was used as an electron transport material instead of PEIE.

In the first instance, the OPV system based on compound 1a, which had been investigated in a previous study,[38] exhibited a modest photovoltaic performance with a PCE estimate of 2.35% (entry 1 in Table 2 and Figure 4). After the thermal annealing (100 °C for 5 min) and addition of 3% DIO, no positive effect was observed on the performance with virtually comparable or low photovoltaic parameters of J_{SC}, V_{OC}, and FF (entries 2 and 3 in Table 2).^[39] Oppositely, 1b delivered a significantly superior performance of 4.40% with the highest J_{SC} of 11.82 mA/cm², V_{OC} of 0.719 V, and FF of 51.7% (entry 4 in Table 2), illustrating a meaningful candidate for efficient photovoltaic applications. For further improvement, the PEIE was substituted with ZnO. This was unsuccessful, resulting in a deterioration of the charge transport in the BHJ system, as shown in the low estimates of the parameters (entry 5 in Table 2). Consequently, it was observed that the DIO treatment with PEIE optimized the morphology of the active layer

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to achieve the best performance of 4.48% with a slightly enhanced V_{oc} of 0.789 V and a comparably high FF of 51.8% (entry 6 in Table 2 and Figure 4). Figure S5 (Supporting Information) shows the light intensity (I) dependences of J_{SC} values for the devices. As illustrated by the linear relationship in the J_{SC} -I plots, which follows the power law behavior $(J_{SC} \sim I^{\alpha})$, the scale exponents (α) were calculated to be 0.84 and 0.80 for the **1a** films with and without DIO, respectively, and 0.90 for both 1b films. These results suggest that the degree of bimolecular decay on charge recombination loss is more suppressed in the BHJ systems of 1b, compared with that of 1a.[40] Furthermore, space charge limited current (SCLC) measurements demonstrated that the active layer with **1b** exhibited higher electron mobility (μ_e) of 1.16 × 10⁻⁵ cm²/Vs than that with **1a** ($\mu_e = 3.87 \times 10^{-6}$ cm²/Vs), although the DIO processing led to a lower μ_e estimate for **1b** (1.66 × 10⁻⁶ cm²/Vs). This was presumably due to the change in molecular orientation, which was unsuitable for electron transport in the vertical direction (Figure S6, Supporting Information), These results show that the improvement of the carrier transport in the BHJ films of 1b will undoubtedly enhance the FF and PCE, relative to those of 1a. Further investigation with different donor candidates such as PBDB-T and PBDB-T-2F (PM6) was undertaken to discover compatible alternatives. However, all attempts to obtain a better photovoltaic performance failed (Figure S7 and Table S1, Supporting Information).



Figure 5. (a) Thin film absorption spectra for OPV devices fabricated with **1b** in the absence (blue solid line) and presence of 1% (v/v) (red dashed line) and 2% (v/v) DIO (red solid line), (b) IPCE spectra for OPV devices fabricated with **1b** in the absence (blue circles) and presence of 2% (v/v) DIO (red circles), (c) Gaussian curve-fittings (dashed lines) to highly sensitive EQE and electroluminescence (EL) profiles for the OPV devices processed with 2% (v/v) DIO (EQE: red circles, EL: red line) and without DIO (EQE: blue circles, EL: blue line), respectively.

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Interestingly, the contrasting behaviors regarding the DIO effect on the photovoltaic properties shown between 1a and 1b correlate with the sensitivity differences for the absorption changes in thin films. Therefore, it was considered that the DIO effect on the fine-tuning of BHJ morphology followed the trend shown in the absorption experiments with thin films. To verify this hypothesis, additional detailed studies were conducted focusing on the active layer of the device with 1b because of the prominent DIO effect observed in the film properties. The initial step in this approach entailed a comparison of the thin-film absorption spectra of the BHJ layers fabricated with and without DIO. Figure 5a shows the spectral changes associated with the use of 1% and 2% (v/v) DIO. The characteristic sharp peaks centered at 598 nm, which are attributed to J-aggregation, were well reproduced by the influence of DIO, concomitant with a further improvement in the photovoltaic performance (Table S2, Supporting Information). The incident photon-to-current efficiency (IPCE) spectra of the devices are shown in Figure 5b. In comparison, the DIO-processed devices display external quantum efficiency (EQE) maxima covering a bathochromic region of visible light (400-800 nm) more efficiently than those made without DIO, demonstrating that DIO processing is significantly beneficial to the photovoltaic properties and performance.

Furthermore, the OCV loss (V_{loss}) in each device was analyzed based on Marcus theory, to discuss the difference in the photovoltaic behaviors of the BHJ systems. With the optical band gap (E_0^{opt}) of 1.57 eV determined from the absorption edge of PTB7-Th, the degrees of V_{loss} for the nonDIO- and DIO-processed films were quantified using the equation, $V_{\text{loss}} = E_{g^{\text{opt}}}/q - V_{\text{OC}}$, where q is the optical band gap of the elementary charge; they were determined to be 0.88 and 0.81 V, respectively. The Vloss comprises three constituent elements: charge separation (V_{CS}), radiative recombination (V_r), and nonradiative recombination (V_{nr}); the relationship is expressed by $V_{loss} = V_{CS} + V_r + V_{nr}$. It has been recognized that the V_{CS} is closely related to the LUMO-LUMO offset between the donor and acceptor. By employing the charge transfer (CT) state energy (E_{CT}) of the device, V_{CS} can be expressed by the equation, $V_{CS} = (E_g^{opt} - E_{CT})/q$. Gaussian curve-fitting of the spectral edges of the BHJ films observed in highly sensitive IPCE spectra allowed for the determination of E_{CT} (1.28 and 1.44 eV) for the nonDIO- and DIO-processed films, respectively (Figure 5c). Notably, the E_{CT} for the DIO-processed film was abnormally higher than that for the nonDIO-processed film, despite the bathochromically shifted absorption character of the former film. According to the aforementioned equation, the V_{CS} for the DIO-processed film ($V_{CS} = 0.13$) was significantly lower than that for the nonDIO-processed film ($V_{CS} = 0.29$). This result can be attributed to the destabilization of the CT state in the DIO-processed film. As shown in Figure 5c, V_r and V_{nr} were quantified by the Gaussian curve-fitting of the CT state absorption.^[41] $V_{\rm f}$ is the inevitable voltage loss in all types of photovoltaic (PV) devices, which proved to be virtually comparable to each other ($V_r = 0.23$), irrespective of the film processing. In general, the V_{nr} is larger for OPVs, compared to their inorganic counterparts, which is the primary cause of minute PCE estimates for OPVs. The Vnr values are estimated to be 0.36 and 0.45 for the nonDIO- and DIO-processed films, respectively. Thus, the DIO processing produced a substantial increase in the $V_{\rm OC}$ with a minimal $V_{\rm loss}$ as a result of the low $V_{\rm CS}$ estimate.

To gain a better insight into the aggregation behavior in the bulk state, the thin-film morphology of 1b was probed by two-dimensional grazing incidence X-ray diffraction (2D GIXD). For the pristine nonDIO-processed film, the position of the reflection produced a d spacing value, which represents the monolayer thickness, equal to 20.3 Å (0.31 Å⁻¹), as shown in Figure 6a. In contrast, the DIO-processed film showed high-order diffraction peaks at 15.6 Å (0.40 Å⁻¹) in an out-of-plane (OOP) direction and 7.43 Å (0.85 Å⁻¹) in an in-plane (IP) direction (Figure 6b). These results corresponded with those observed in our previous study on N,N'di(n-hexyl)PDI with the OOP and IP directions at 18.5 and 8.4 Å, respectively.^[7] Therefore, it was concluded that the DIO-processed films exhibit high crystallinity with a preference for edgeon orientation, where the growth of supramolecular columns is aligned perpendicular to the PDI cores with narrowed interplanar spacing in the longitudinal direction.



Figure 6. Two-dimensional grazing incidence X-ray diffraction (2D-GIXD) profiles for pristine films of 1b fabricated in the (a) absence and (b) presence of 3% (v/v) DIO.

The morphological features of the blend films based on **1a** and **1b** were further investigated using atomic force microscopy (AFM). As shown in Figure S8 (Supporting Information), the BHJ systems of **1b** preferentially produced highly aligned crystalline grains, while only ill-defined and amorphous aggregates were observed for those of **1a**. These observations support the theory that **1b** effectively leads to more highly crystalline active layers with PTB7-Th than **1a**.

The DIO effect on the photovoltaic characteristics of the BHJ systems was again investigated for all other entries to understand the morphological transformations in detail and to guide the design of more effective systems for potential applications. As shown in the results obtained with 1c-f, no significant difference was observed in the photovoltaic outcomes, regardless of DIO processing in the BHJ blends (Figure S4, Supporting Information). Notably, 1c and 1d displayed only negligible PCEs of less than 1% with extremely low photovoltaic parameters (entries 7-10, Table 2). These inefficiencies can be explained in terms of excessively strong aggregation due to the inherently poor solubility of these compounds to form phase-segregated domains, which are unfavorable for charge separation. The high solubility of 1e and 1f in CHCl₃ allowed for easy fabrication of high-quality films to achieve high efficiencies in the photovoltaic systems. In the 1e experiment, modestly attenuated but relatively high photovoltaic performances with PCEs of 2.61 and 2.85% were obtained for the nonDIO- and DIO-processed devices, respectively, when compared with the others (entries 11 and 12, Table 2). The significantly higher efficiency obtained for 1e, relative to that of 1a, can be explained based on the enhanced crystallinity of the active

layer, which is mostly attributed to the restricted conformational flexibility of the cyclohexyl substituents. Nevertheless, the device efficiency of **1e** remained below 3%, which is low compared to that of **1b**. This may be ascribed to the difference in molecular close contacts and interlayer π – π stacking distances, as probably reflected by the difference in the steric encumbrance around the PDI core. Therefore, it can be assumed that the sterically less hindered substituents including the methylene chain adjacent to the nitrogen atom of the PDI system would enhance film properties and device performance, as shown by the positive DIO effect for the single-layer films of **1b**, **1d**, and **1f**. This assumption was further supported by the enhanced photovoltaic efficiencies of the devices made with **1f**, exhibiting PCEs beyond 3% with a remarkably high FF as high as 58.3%, using ZnO as an electron transporting layer (entries 13 and 14, Table 2).

Finally, to clarify the influence of structural differences in the imide substituents on the photovoltaic properties, we performed an additional control experiment with an asymmetric diPDI, **1g**, which possesses 2-ethylhexyl and cyclohexyl moieties in the different PDI units. This synthesis was achieved by cross-coupling **2b** and a bay-borylated PDI, **7e**, as shown in Scheme 2. The conversion of **2e** into **7e** was accomplished with bis(pinacolato)diboron (B₂pin₂) in the presence of dipotassium hydrogen phosphate (K₂HPO₄) and the catalytic [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (Pd(dppf)Cl₂) under heating in *o*-xylene to obtain **7e** in 42% yield.^[42] This reaction was successful under conventional conditions and afforded **1g** with a yield of 19%.^[43]



Scheme 2. Synthetic sequence to asymmetric diPDI 1g.

Similar to the structurally related compounds 1b and 1e, 1g showed high chemical stability (Figure S2d, Supporting Information) and excellent solubility in CHCl₃ (~ 10 mg/mL), enabling easy processing to obtain stable spectroscopic and photovoltaic results. Figure S9 (Supporting Information) shows the optical absorption and emission properties of 1g, which provide spectral shapes essentially homogeneous to those of 1b and 1e in virtually the same wavelength regions. This molecular system was studied to determine which character of the two different substituents is dominant in the nature of thin films. The absorption spectra for the pristine films of 1g prepared with and without DIO are shown in Figure S9c (Supporting Information). This molecular system displays a significantly enhanced DIO sensitivity, which induces a prominent bathochromic shift in the absorption band, closely resembling that observed for 1b. The thermal annealing up to 200 °C was observed to have no positive effect on the thin-film morphologies (Figure S9d, Supporting Information). Expectedly, the devices based on 1g further improved in photovoltaic performance from 3.13 to 3.29% after the treatment with DIO (Figure S10, Supporting Information), which is not up to that of 1b but is superior to that of 1e (entries 15 and 16, Table 2). The light intensity dependences of J_{SC} for these two additional devices were studied to understand the charge transport properties of the devices based on 1g. Following the aforementioned analytical method, linear relationships were obtained in the J_{SC} -I plot with α values of 0.93 and 0.92 for the nonDIO- and DIO-processed films, respectively, comparably high to those for 1b (Figure S11, Supporting Information). These results suggest that the bimolecular recombination loss is likely to be more suppressed, as observed for the devices based on 1b. Based on these features, it was observed that the sterically less demanding 2-ethylhexyl group, not the cyclohexyl moiety, dominantly contributes to the morphological and photovoltaic properties of the BHJ layers. Inversely, the blend film morphology can be controlled by a judicious choice of alkyl chains present in the imide positions. This shows that primary solubilizing substituents with minimum molecular volumes favorably enhance the bulk crystallinity and overall device performance of BHJ films. According to the previous literatures, many examples of the swallow-tail diPDIs have boosted PCEs exceeding 5%.^{[13],[14],[20],[38],[44]-[46]} one of which has reached up to 6.51%.^[16] In this respect, it is believed that the effective utilization of the primary alkyl derivatives will provide significant improvements in the performances through further optimization of the device fabrication conditions.

Conclusion

In this study, we developed a new strategy for the efficient synthesis of diPDIs with desired functional groups. Systematic investigations with seven variants of diPDIs demonstrated that steric factors of the N-substituents largely influence the morphological and photovoltaic properties of either the pristine or BHJ films. Therefore, it was concluded that the primary alkyl substituents, particularly the 2-ethylhexyl group, induce the self-organized growth of thin films with high crystallinity, which enhances the device performance of the diPDI systems, as mentioned in a related study.^[47] The functional superiority of the primary alkyl substituents over the sterically more demanding secondary alkyl substituents was further substantiated by their prominent sensitivity toward the DIO additive, which significantly changed the film-forming properties. Finally, we highlighted the important roles of alkyl side chains as either hydrophobic solubilizing auxiliaries or primary determinants in the control of the active layer nanomorphology, offering a valuable guideline that is essential for developing high-performance organic semiconductive materials for future practical applications. Given that several efforts with multiply PDIloaded materials composed of more than three PDI units have achieved great successes in obtaining better photovoltaic performances than those with diPDIs, [45], [48]-[50] the oligomeric PDIs designed by following the lessons learned in this work hold great promise for advancing the PDI-based NFAs with superior performances,^[9] which are currently under investigation in our laboratory.

Experimental Section

UV-vis and fluorescence spectra were recorded on a JASCO V-630 spectrophotometer and a JASCO FP-6200 spectrofluorometer, respectively. The ¹H and ¹³C NMR spectra operating at the frequencies of 300 and 75

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MHz, respectively, were recorded on a JEOL JNM-AL300 spectrometer in CDCl₃. Chemical shifts are reported in parts per million (ppm) relative to CDCl₃ (77.16 ppm for ¹³C NMR) or tetramethylsilane (0.00 ppm for ¹H NMR), and the coupling constants are reported in hertz (Hz). High resolution matrix assisted laser desorption ionization mass spectra (HR-MALDI-MS) were measured on a Shimadzu AXIMA Resonance mass spectrometer using α-cyano-4-hydroxycinnamic acid (α-CHCA) matrix as a cationization agent. High resolution electrospray ionization (ESI) mass spectra were measured on a Waters Xevo Q-TOF UPLC-MS system. Redox potentials were measured by cyclic voltammetry on a Hokuto Denko potentiostat/galvanostat HAB-151 A. The thermal characterisation was carried out using a Shimadzu differential scanning calorimeter DSC-60 Plus, and TGA thermogram for **1b** was recorded with a Shimadzu DTG-60A. The samples were heated at a heating rate of 10 °C/min for all the measurements. The measurement for X-ray crystallographic analysis was made on a Bruker Smart APexII CCD area detector with monochromated Mo-Ka radiation (λ 0.71073 Å). The structure was solved by direct methods with SHELXL-97 and refined with SHELXL-2014/7. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Deposition Number <url href="https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/chem.202102318"> 2083264 (for 1e)</url> contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre Karlsruhe Fachinformationszentrum and <url href=" http://www.ccdc.cam.ac.uk/structures ">Access Structures service</url>. Nanosized Cu powder was purchased from io-li-tec nanomaterials. Unless otherwise noted, all solvents and reagents were of reagent grade quality from Wako Pure Chemicals and Tokyo Chemical Industry (TCI) used without further purification. The requisite synthetic intermediates 2a and 2b were prepared by our previously reported procedures.^[26] The reference PDI 6 was synthesized by following the literature procedure.^[34] The OPV devices were fabricated on indium tin oxide (ITO)-coated glass substrates (ITO thickness: 150 nm; sheet resistance: 10.3 Ωs/q; Techno Print). The ITO substrates were cleaned by UV-O3 treatment for 20 min. PEIE 80% ethoxylated solution (Aldrich) was diluted by 2-methoxyethanol (Wako), and the solution was spin-coated on the ITO substrates at a spinning rate of 5,000 rpm for 50 s, dried at 100°C for 10 min. CHCl₃ solutions containing 3.33 g/L of donor polymer (PTB7-Th, PBDB-T, or PBDB-T-2F (PM6)) (Aldrich), and 6.66 g/L of 1 were spin-coated onto the ITO/PEIE substrates at a spinning rate of 2,500 rpm for 30 s in a glove box (UNICO). The MoO₃ hole-transporting layer (10 nm, 0.01 nm/s) and Al electrodes (100 nm, 0.03 nm/s) were deposited by thermal evaporation under high vacuum (~10⁻⁵ Pa) in a vacuum evaporation system (VTS-350M, ULVAC) housed in the glove box. The devices were characterized in a vacuum container for optical measurements (Epitech) without exposure to air. The J-V characteristics of the devices were measured under simulated solar illumination (AM 1.5 G, 100 mW/cm²) from a solar simulator based on a 300 W Xe lamp (HAL-320, Asahi Spectra) using a source meter (R6243, Advantest). The light intensity was calibrated with a standard silicon solar cell (CS-20, Asahi Spectra). The active area of the devices was defined using a 0.04 cm² photomask. The highly sensitive EQE of the devices was measured on a Hypermonolight SM 250F system with NF LI5640 lock in amplifier (Bunkoh Keiki). EL was measured on a spectrofluorometer equipped with an InGaAs detector (NanoLog, Horiba) with a constant DC voltage applied to the devices by a DC power supply (2400, Keithley). Two dimensional grazing incidence wide angle X-ray scattering patterns were measured at an incident angle of 0.12° by using the synchrotron radiation at beam line BL19B2 of Spring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI). Atomic force microscope (AFM) images were measured on a SPI3800 (SII).

Synthesis of 1a (Path A in Scheme 1, entry 1 in Table 1): To a mixture of 2a (50 mg, 0.072 mmol) and copper powder (46.8 mg, 0.74 mmol), was added anhydrous dimethyl sulfoxide (DMSO, 6.4 mL) under an argon atmosphere. The resulting mixture was heated under stirring at 100 °C for 5.5 hours, and then cooled to ambient temperature. To this reaction mixture, was added water until precipitates appeared, which were collected by filtration through a pad of Celite. The residue removed carefully from the

Celite pad was dissolved in dichloromethane (DCM), and the resulting solution was filtered to remove insoluble materials. The solution was transferred to a separatory funnel, and then washed once with water. The solution was dried over anhydrous Na₂SO₄, filtered, and then concentrated in vacuum to obtain a solid crude residue. This material was purified by silica gel chromatography with CHCl₃/ethyl acetate (AcOEt, 100/1 (v/v)) as an eluent. Further purification was performed by gel permeation chromatography using an eluent of toluene/CHCl₃ (2/1 (v/v)). The purified material was dissolved in CHCl₃, and then reprecipitated by adding MeOH to obtain **1a** (19.5 mg, 0.014 mmol, 39%) as a reddish brown solid. ¹H NMR spectrum was in accordance with the literature data.^[12]

Synthesis of 1b (Path A in Scheme 1, entry 3 in Table 1): To a mixture of **2b** (215 mg, 0.311 mmol), copper powder (213 mg, 3.35 mmol), and Pd(PPh₃)₄ (50 mg, 0.0433 mmol), was added anhydrous DMSO (2.9 mL) under a nitrogen atmosphere. The resulting mixture was heated under stirring at 150 °C for 12 hours, and then cooled to ambient temperature. To this reaction mixture, was added water until precipitates appeared, which were collected by filtration. The residue was dissolved in CHCl₃, and the resulting solution was filtered to remove insoluble materials. The solution was concentrated in vacuum to obtain a solid crude residue. This material was purified by silica gel chromatography with CHCl₃/AcOEt (100/1~80/1 (v/v)) as an eluent. Further purification was performed by gel permeation chromatography using an eluent of toluene/CHCl₃ (2/1 (v/v)). The purified material was dissolved in CHCl₃, and then reprecipitated by adding MeOH to obtain **1b** (40.5 mg, 0.033 mmol, 21%) as a reddish brown solid.

Compound data of 1b: ¹H NMR (300 MHz, CDCl₃) δ 8.83–8.70 (m, 8H, Ar*H*), 8.46 (d, *J* = 7.9 Hz, 2H, Ar*H*), 8.20 (s, 2H, Ar*H*), 8.12 (d, *J* = 8.1 Hz, 2H, Ar*H*), 4.04 (brs, 8H, C*H*₂), 1.88 (brs, 4H, C*H*), 1.32–1.26 (m, 32H, Ar*H*), 0.914–0.792 (m, 24H, C*H*₃); ¹³C NMR (75 MHz, CDCl₃) δ 163.6, 163.3, 163.1, 142.0, 135.1, 134.7, 134.17, 134.13, 133.1, 131.7, 130.7, 130.6, 129.3, 128.9, 128.8, 127.8, 127.4, 124.4, 124.1, 123.6, 123.5, 123.4, 123.2, 44.6, 44.5, 44.3, 38.0, 30.8, 28.8, 28.6, 24.23, 24.15, 24.1, 24.0, 23.1, 14.23, 14.15, 10.7, 10.5; HR-MALDI-MS: *m/z* = 1227.6192 [M+H]⁺, calc. for C₈₀H₈₃N₄O₈: 1227.6211.

Synthesis of 4: To a mixture of **5** (300 mg, 0.346 mmol), copper powder (220 mg, 3.46 mmol), and Pd(PPh₃)₄ (59.9 mg, 0.0519 mmol) was added anhydrous DMSO (3.5 mL) under a nitrogen atmosphere. The resulting mixture was heated under stirring at 150 °C for 3 hours, cooled to ambient temperature, and then quenched by water (10 mL) to afford precipitates. The precipitates were then collected by filtration through a pad of Celite. The residue was washed successively with water and MeOH. After removal of the filtrate, the residue collected on the Celite pad was dissolved by washing with CHCl₃. The resulting solution was dried over anhydrous Na₂SO₄, filtered, and then concentrated in vacuum to give a dark brown oily crude residue. This material was purified by silica gel chromatography (toluene /AcOEt = 50/1, 25/1, and 15/1 (v/v)). Further purification was performed by gel permeation chromatography using an eluent of toluene to give **4** (111 mg, 0.0758 mmol, 44%) as a dark violet solid.

Compound data of 4: ¹H NMR (300 MHz, CDCl₃) δ 8.41 (d, J = 8.0 Hz, 2H, Ar*H*), 8.38 (d, J = 8.0 Hz, 2H, Ar*H*), 8.23 (d, J = 8.1 Hz, 2H, Ar*H*), 8.17 (d, J = 8.1 Hz, 4H, Ar*H*), 7.62 (d, J = 8.0 Hz, 4H, Ar*H*), 7.44–7.28 (m, 30H, Ar*H*), 7.25–7.14 (m, 10H, Ar*H*), 5.29–5.04 (m, 16H, C*H*₂); ¹³C NMR (75 MHz, CDCl₃) δ 168.2, 168.2, 167.8, 167.5, 140.3, 135.7, 135.6, 135.5, 135.2, 134.0, 133.5, 133.3, 132.6, 131.6, 131.2, 131.0, 130.8, 130.4, 130.3, 130.0, 129.0, 128.7, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 126.5, 122.7, 122.0, 67.4, 67.2; HR-MALDI-MS: m/z = 1597.4535 [M+Na]⁺, calc. for C₁₀₄H₇₀NaO₁₆: 1597.4562.

Synthesis of 3: To a mixture of 4 (316 mg, 0.201 mmol) and PTSA monohydrate (123 mg, 0.647 mmol), was added toluene (2.2 mL) under ambient atmosphere. The resulting mixture was heated under stirring at 95 °C for 7 hours, and then cooled to ambient temperature to afford precipitates. The precipitates were then collected by filtration, washed successively with MeOH (20 mL) and CHCl₃ (20 mL) to obtain **3** (156 mg, 0.199 mmol, 99%)

as a reddish solid. Unfortunately, all our attempts to obtain ¹³C NMR spectrum failed due to high insolubility of the material. Alternatively, this compound was characterized by combustion ¹H NMR and HRMS spectral analyses of its sodium salt prepared prior to measurement.

Compound data of 3: ¹H NMR (300 MHz, sodium salt, D₂O with 0.3 M NaOH) δ 8.48–8.44 (m, 4H, Ar*H*), 8.12 (d, J = 7.9 Hz, 2H, Ar*H*), 7.89 (d, J = 7.2 Hz, 2H, Ar*H*), 7.86 (d, J = 7.2 Hz, 2H, Ar*H*), 7.44 (s, 2H, Ar*H*), 7.27 (d, J = 7.9 Hz, 2H, Ar*H*), T.86 (d, J = 7.2 Hz, 2H, Ar*H*), 7.44 (s, 2H, Ar*H*), 7.27 (d, J = 7.9 Hz, 2H, Ar*H*). HR-ESI-MS: m/z = 823.0468 [M+Na+H₂O]⁺, calc. for C₄₈H₁₆NaO₁₃: 823.0489.

General synthetic procedure for 1b-f via imidation of 3 (Path B in Scheme 1, entry 4 in Table 1): The synthesis by imidization was performed according to a general procedure exemplified by the synthesis of 1b as follows. To a mixture of 3 (50.0 mg, 0.0639 mmol), 2-ethylhexylamine (0.20 mL, 1.2 mmol), and propionic acid (26 µL, 0.35 mmol) was added N-methyl pyrrolidone (NMP, 1.0 mL) under ambient atmosphere. The resulting mixture was heated under stirring at 150 °C for 6 hours, cooled to ambient temperature, and then quenched by 3% HCl_{aq} (10 mL). The mixture was extracted by CHCl₃ (20 mL), washed successively with water (20 mL) and saturated brine (30 mL), dried over anhydrous sodium sulfate, filtered, and then concentrated under vacuum to give a dark brown crude residue. The residue was purified by silica gel column chromatography (toluene/AcOEt = 25/1 (v/v) to toluene/MeOH = 10/1), gel permeation chromatography (toluene/CHCl₃ =2/1). The sample was further purified by reprecipitation from CHCl₃/MeOH to obtain 1b (43.8 mg, 0.0360 mmol, 56%) as a reddish brown solid. Analytical data were in accordance with those described above.

Compound data of 1c: ¹H NMR (300 MHz, CDCl₃) δ 8.89–8.83 (m, 8H, Ar*H*), 8.54 (d, *J* = 8.1 Hz, 2H, Ar*H*), 8.33 (s, 2H, Ar*H*), 8.30 (d, *J* = 7.9 Hz, 2H, Ar*H*), 7.57–7.49 (m, 12H, Ar*H*), 7.34–7.32 (m, 8H, Ar*H*); HR-MALDI-MS: *m*/*z* = 1083.2459 [M+H]⁺, calc. for C₇₂H₃₅N₄O₈: 1083.2455. Unfortunately, the distinguishable resonance signals could not be observed by ¹³C NMR measurement due to high insolubility of the material.

Compound data of 1d: ¹H NMR (300 MHz, CDCl₃) δ 8.84–8.73 (m, 8H, Ar*H*), 8.37 (d, *J* = 8.2 Hz, 2H, Ar*H*), 8.23 (s, 2H, Ar*H*), 8.14 (d, *J* = 7.9 Hz, 2H, Ar*H*), 7.48–7.45 (m, 8H, Ar*H*), 7.30–7.21 (m, 12H, Ar*H*), 5.30 (s, 8H, C*H*₂); ¹³C NMR (75 MHz, CDCl₃) δ 163.4, 163.3, 163.0, 162.9, 141.8, 136.9, 136.8, 135.1, 134.5, 134.3, 133.3, 132.0, 131.9, 131.1, 129.4, 129.2, 128.9, 128.6, 127.8, 127.7, 124.4, 123.70, 123.67, 123.63, 123.54, 123.4, 44.0, 43.8; HR-MALDI-MS: *m*/*z* = 1161.2875 [M+Na]⁺, calc. for C₇₆H₄₂N₄NaO₈: 1161.2900.

Compound data of 1e: ¹H NMR (300 MHz, CDCl₃) δ 8.78 (m, 8H, Ar*H*), 8.40 (d, *J* = 8.2 Hz, 2H, Ar*H*), 8.18 (s, 2H, Ar*H*), 8.15 (d, *J* = 8.2 Hz, 2H, Ar*H*), 5.02–4.94 (brs, 4H, C*H*), 2.56–2.43 (brs, 8H, C*H*₂), 1.86 (brs, 10H, C*H*₂), 1.70 (brs, 10H, C*H*₂), 1.45–1.26 (m, 12H, C*H*₂); ¹³C NMR (75 MHz, CDCl₃) δ 163.9, 163.74, 163.66 163.3, 141.9, 134.8, 134.3, 134.1, 133.1, 131.67, 131.60, 131.5, 130.91, 130.87, 129.4, 128.9, 128.8, 127.7, 127.5, 124.9, 124.18, 124.11, 123.9, 123.5, 54.3, 54.2, 29.2, 26.6, 25.5; HR-MALDI-MS: *m*/z = 1129.4129 [M+Na]⁺, calc. for C₇₂H₅₈N₄NaO₈: 1129.4152.

Compound data of 1f: ¹H NMR (300 MHz, CDCl₃) δ 8.82–8.70 (m, 8H, Ar*H*), 8.45 (d, *J* = 8.2 Hz, 2H, Ar*H*), 8.19 (s, 2H, Ar*H*), 8.13 (d, *J* = 8.1 Hz, 2H, Ar*H*), 4.06–3.92 (brs, 8H, C*H*₂), 1.84 (brs, 4H, C*H*), 1.69–1.61 (m, 16H, C*H*₂), 1.25–1.07 (m, 24H, C*H*₂); ¹³C NMR (75 MHz, CDCl₃) δ 163.62, 163.57, 163.22, 163.18, 141.9, 135.3, 135.0, 134.8, 134.23, 134.16, 133.0, 131.8, 130.7, 129.3, 128.85, 128.78, 127.7, 127.4, 124.4, 124.1, 123.6, 123.5, 123.45, 123.42, 46.6, 46.3, 36.8, 31.0, 26.4, 25.9; HR-MALDI-MS: *m*/z = 1163.4983 [M+H]⁺, calc. for C₇₆H₆₇N₄O₈: 1163.4959.

Synthesis of 7e: To a mixture containing **2e** (115 mg, 0.182 mmol), B_2pin_2 (158 mg, 0.622 mmol), K_2HPO_4 (181 mg, 1.04 mmol), and Pd(dppf)Cl₂ (17.0 mg, 0.0208 mmol) was added *o*-xylene (2.0 mL) under a nitrogen atmosphere. The resulting mixture was heated under stirring at 140 °C for 9 hours, cooled to ambient temperature, quenched by addition of water,

extracted by CHCl₃, washed with water, and then concentrated in vacuum. The residue was purified by silica gel column chromatography (toluene /AcOH = 50/1, 25/1, and 10/1 (v/v)) to obtain **7e** (52 mg, 0.0764 mmol, 42%) as a reddish violet solid.

Compound data of 7e: ¹H NMR (300 MHz, CDCl₃) δ 8.75 (s, 1H, Ar*H*), 8.64 (d, *J* = 8.1 Hz, 2H, Ar*H*), 8.59–8.52 (m, 3H, Ar*H*), 8.27 (d, *J* = 7.9 Hz, 1H, Ar*H*), 5.05 (brs, 2H, C*H*), 2.64–2.55 (m, 4H, C*H*₂), 1.96–1.91 (m, 4H, C*H*₂), 1.82–1.78 (m, 6H, C*H*₂), 1.48 (s, 12H, C*H*₃), 1.56–1.26 (m, 6H, C*H*₂); HR-ESI-MS: *m*/*z* = 681.3135 [M+H]⁺, calc. for C₄₂H₄₂BN₂O₆: 681.3136. Unfortunately, the distinguishable resonance signals could not be observed by ¹³C NMR measurement due to the insolubility of the material.

Synthesis of 1g: To a mixture containing 7e (33.0 mg, 0.0485 mmol) and 2b (33.3 mg, 0.0481 mmol), and aqueous solution of Na₂CO₃ (3.0 M, 0.48 mL, 1.44 mmol), was added a 2:1 (v/v) mixture of toluene and EtOH (0.96 mL) under an argon atmosphere. The temperature of the mixture was elevated to 80 °C, and Pd(PPh₃)₄ (8.32 mg, 0.0072 mmol) was then added to this mixture. The resulting mixture was kept under reflux for 4 hours, cooled to ambient temperature, quenched by addition of saturated NH₄Cl_{ad} (10 mL), filtered through a pad of Celite. The residue collected on the Celite pad was washed twice with DCM (20 mL). The resulting solution was transferred to a separatory funnel and washed successively with water (20 mL) and saturated brine (30 mL). The solution was dried over anhydrous Na₂SO₄, filtered, and then concentrated in vacuum to obtain a solid crude residue. This material was purified by silica gel chromatography with CHCl₃/AcOEt (100/1, 50/1, and 25/1 (v/v)) as an eluent. Further purification was performed by gel permeation chromatography using an eluent of toluene/CHCl₃ (2/1). The purified material was dissolved in CHCl₃, and then reprecipitated by adding MeOH to obtain 1g (11.0 mg, 0.00943 mmol, 19%) as a dark violet solid.

Compound data of 1g: ¹H NMR (300 MHz, CDCl₃) δ 8.83–8.76 (m, 8H, Ar*H*), 8.44 (d, *J* = 8.4 Hz 2H, Ar*H*), 8.23 (s, 1H, Ar*H*), 8.19 (s, 1H, Ar*H*) 8.15 (d, *J* = 8.4 Hz, 2H, Ar*H*), 4.98–4.92 (m, 2H, C*H*), 4.11–4.03 (m, 4H, C*H*₂), 2.52–2.48 (m, 4H, C*H*₂), 1.87 (brs, 6H, C*H* (2H) and C*H*₂ (4H)), 1.70 (brs, 4H, C*H*₂), 1.48–1.25 (m, 24H, C*H*₂), 0.91–0.83 (m, 12H, C*H*₃); ¹³C NMR (75 MHz, CDCl₃) δ 163.8, 163.7, 163.54, 163.47, 163.32, 163.27, 142.0, 141.8, 135.03, 134.93, 134.8, 134.4, 134.3, 134.2, 134.0, 133.2, 133.1, 131.8, 131.78, 131.69, 131.58, 131.0, 130.9, 129.4, 129.3, 129.0, 128.84, 128.78, 127.5, 124.9, 124.30, 124.25, 124.12, 123.86, 123.66, 123.56, 123.52, 123.46, 123.38, 54.3, 54.2, 44.5, 44.4, 44.3, 38.0, 30.8, 29.1, 28.8, 26.6, 25.5, 24.2, 24.15, 24.12, 24.03, 23.2, 23.1, 14.21, 14.18, 10.8, 10.75, 10.70, 10.5; HR-MALDI-MS: *m*/*z* = 1189.5067 [M+H]⁺, calc. for C₇₆H₇₀N₄NaO₈: 1189.5091.

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By developing a general synthetic strategy, we synthesized a new series of bay-linked dimeric perylene diimides (diPDIs), some of which possess primary *N*-alkyl substituents or unsymmetric *N*-substitution pattern. The systematic investigation on their photovoltaic properties revealed that the primary alkyl substituents are advantageous for enhancing the device performance in terms of crystallinity improvement and film-forming controllability.