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n-Type Core Effect on Perylene Diimide Based Acceptors for Panchromatic Fullerene-Free Organic Solar Cells

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Abstract

Perylene diimide (PDI) based high bandgap acceptors, DTBTP, DTF2BTP, and DTF2TZP, are synthesized for use in fullerene-free organic solar cells. The two PDI rings are conneced to the end of the n-type core, forming a PDI-n-type core-PDI structure. Several n-type core materials, 4,7-dithieno-2,1,3-benzothiadiazole (DTBT), 5,6-difluoro-4,7-dithieno-2,1,3-benzothiadiazole (DTF2BT), and 4,6-difluoro-2H-benzo[d][1,2,3]triazole (DTF2TZ), are incorporated in the PDI acceptors and the n-type core effect on photovoltaic properties is studies. The introduction of alkyl side chains onto the core structure weakened the intermolecular interaction, whereas fluorination of the core structure improved the backbone planarity and intermolecular ordering. DTF2BTP having a planar core structure without bulky alkyl chains yielded the best power conversion efficiency, 4.41%, when mixed with PTB7-Th donor. The n-type core structure was beneficial in terms of increasing the electron accepting properties and the absorption in the high bandgap region of non-fullerene acceptors.

Keywords: Non-fullerene acceptor; Fullerene-free organic solar cells; n-Type core effect; Perylene diimide; Panchromatic absorption

1. Introduction

Remarkable progress has been achieved in the development of bulk-heterojunction (BHJ) organic solar cells (OSCs) in both academia and industry in efforts to exploit their potential for portable and flexible photoelectric devices.[1-4] The active layer composed of electron donors and acceptors plays a key role in light harvesting, exciton separation, and charge transport in the devices.[5-7] Thus, extensive studies have been performed to develop new active materials to improve the absorption properties, intermolecular ordering, nanomorphology, etc.[8-10] During the past two decades, fullerene acceptor-based BHJ OSCs have been leading the efficiency table with power conversion efficiencies (PCEs) of over 10 %[11-14], owing to the excellent charge transporting properties of fullerene acceptors in the blended system.[15] However, fullerene derivatives have limited absorption at the long wavelength and it is difficult to prevent phase separation behaviour in blend films during the thermal treatment. Thus, the development of novel alternative organic acceptors is important for further improvement of the PCE value and the long-term stability, and vigorous efforts have been dedicated toward developing non-fullerene acceptors.[16-22]

Due to the strong light harvesting property of non-fullerene acceptors, the formation of complimentary absorption between a donor polymer and a non-fullerene acceptor is important in the active layer.[23-30] There are two ways to realize panchromatic light absorption in the active layer: blending a high bandgap donor and a low bandgap acceptor, and mixing a low bandgap donor and a high bandgap acceptor. In the former case, the combination of high bandgap donor polymers and malononitrile-terminated low bandgap acceptors has yielded the highest PCE, exceeding 13%.[16, 31-33] In the latter case, the combination of low bandgap donor polymers

and diimide-terminated high bandgap acceptors provides PCEs over 7%.[34-37] Thus, it is necessary to explore and understand the high bandgap non-fullerene acceptors.

In this study, we explored perylene diimide (PDI) terminated high bandgap acceptors having a PDI-n-type core-PDI structure. PDI is a well-known diimide-functionalized material showing strong electron withdrawing characteristics and high electron mobility.[34] As the core structure, p-type conjugated materials such as thiophene, fluorene, and benzodithiophene derivatives are commonly used to control the three dimensional molecular structure of the electron acceptor,[38-43] but the incorporation of n-type moieties in the core structure can enhance the electron withdrawing properties and finely tune the energy levels. Thus, herein we introduce n-type core moieties in the PDI-core-PDI structure.

To date, n-type core materials have rarely been introduced to the PDI-core-PDI structure, likely due to the difficulty in synthesizing stannylated or borylated n-type materials to make carbon-carbon (C-C) coupling with a halogenated PDI moiety. Thus, Welch et al. reported direct heteroarylation to make C-C bonding between diketopyrrolopyrrole (or isoindigo) and a monobrominated PDI unit.[44]

However, to explore a more general way to achieve C-C coupling in a PDI-n-type core-PDI structure, we synthesized stannylated n-type core materials based on 4,7-dithieno-2,1,3-benzothiadiazole (DTBT), 5,6-difluoro-4,7-dithieno-2,1,3-benzothiadiazole (DTF2BT), and 4,6-difluoro-2H-benzo[d][1,2,3]triazole (DTF2TZ), and then successfully synthesized novel electron acceptors, DTBTP, DTF2BTP, and DTF2TZP, via a Stille coupling reaction with a monobrominated PDI unit. The introduction of n-type core units intensifed the n-type properties of the PDI-core-PDI acceptor and showed complementary absorption with that of the PTB7-Th donor.

In particular, we modified the molecular structure of the core materials by incorporating a fluorine moiety and an alkyl side group to investigate the structural effect on the photovoltaic performance, and found that the intermolecular ordering, electron mobility, and current density of the PDI-n-type core-PDI acceptors were highly affected by the molecular structure of the core moieties.

Fullerene-free OSCs were fabricated using the synthesized high bandgap acceptors with a low bandgap donor polymer (PTB7-Th)[45], and the DTF2BTP acceptor having a planar core backbone without alkyl side chains provided the best PCE of 4.41% among the three synthesized acceptors.

2. Materials and methods

2.1. Synthesis

Synthesis of 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c] [1,2,5] thiadiazole (4). A solution of compound 1 (0.77 g, 2.56 mmol) in anhydrous THF (40 mL) was added dropwise at -78 °C to 2.0 M lithium diisopropylamine (LDA, 3.20 mL, 6.4 mmol). After stirring for 1 h at -78 °C, trimethyltin chloride (7.69 mL, 7.68 mmol, 1 M in hexanes) was added dropwise to the reaction mixture. Subsequently, the reaction flask was warmed to room temperature and stirred overnight. The reaction mixture was quenched with distilled water and extracted with diethyl ether. The organic layer was washed twice with brine and dried over MgSO₄. After drying the extracts, the obtained residue was purified by recrystallization from ethanol to yield red crystals. Yield: 75% (1.2 g). ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.18 (d, J = 3.3 Hz, 2H), 7.87 (s, 2H), 7.30 (d, J = 3.6 Hz, 2H), 0.43 (s, 18H).

Synthesis of 5,6-difluoro-4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (5). Compound 5 was synthesized by the same synthetic route, as described above for 4. The desired product was obtained as a yellow solid (0.7 g, 82%). ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.43 (d, J = 3.0 Hz, 2H), 7.35 (d, J = 3.3 Hz, 2H), 0.44 (s, 18H).

General Stille coupling reaction

In degassed toluene (10 ml), dibrominated conjugated core material (compound 4, 5 or 6) and 1bromo-N,N'-bis(2-ethylhexyl)-3,4,9,10-perylene tetracarboxylic diimide and palladium catalyst, Pd(PPh₃)₄ (20 mg, 0.017 mmol), were dissolved. After refluxing the reaction mixture at 110 \Box for 48 hours, it was cooled to room temperature and poured into distilled water. The organic layer was extracted with methylene dichloride and dried over magnesium sulfate. After removing the solvent under reduced pressure, the crude solid was purified by column chromatography on silica gel with dichloromethane. The resulting product was recrystallized twice using chloroform and acetone to give a pure product.

DTBTP: Compound 4 (0.15 g, 0.24 mmol) and 1-bromo-N,N'-bis(2-ethylhexyl)-3,4,9,10perylene tetracarboxylic diimide (0.50 g, 0.54 mmol) were used and then yielded DTBTP of 0.36 g (76%) . ¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.59 (d, J = 7.6 Hz, 2H), 8.53 (d, J = 9.2 Hz, 4H), 8.44 (m, 4H), 8.37 (d, J = 8.0 Hz, 2H), 8.22 (d, J = 8.0 Hz, 2H), 8.11 (d, J = 3.6 Hz, 2H), 7.75 (s, 2H), 7.31 (s, 2H), 4.02 (d, J = 6.4 Hz, 4H), 3.93 (d, J = 5.2 Hz, 4H), 1.92 (br, 4H), 1.23 (m, 96H), 0.82 (t, 24H). MALDI-TOF-MS: *m*/*z* Calcd. for C₁₂₆H₁₅₂N₆O₈S₃: 1996.07 [M+Na]⁺; found 1996.297 [M+Na]⁺.

DTF2BTP: Compound 5 (0.16 g, 0.24 mmol) and 1-bromo-N,N'-bis(2-ethylhexyl)-3,4,9,10perylene tetracarboxylic diimide (0.51 g, 0.56 mmol) were used and then yielded DTF2BTP of 0.34 g (70%). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.60 (m, 6H), 8.50 (br, 4H), 8.40 (d, J = 4.0 Hz, 2H), 8.28 (d, J = 8.0 Hz, 2H), 8.20 (d, J = 8.0 Hz, 2H), 7.39 (s, 2H), 4.01 (br, 8H), 1.93 (br, 4H), 1.22 (m, 96H), 0.82 (t, 24H). MALDI-TOF-MS: *m*/*z* Calcd. for C₁₂₆H₁₅₀F₂N₆O₈S₃: 2032.05 [M+Na]⁺; found 2032.278 [M+Na]⁺.

DTF2TZP: Compound 6 (0.20 g, 0.20 mmol) and 1-bromo-N,N'-bis(2-ethylhexyl)-3,4,9,10perylene tetracarboxylic diimide (0.48 g, 0.52 mmol) were used and then yielded DTF2TZP of 0.29 g (62%). ¹H NMR (CDCl₃, 400 MHz, ppm): δ 8.62 (br, 6H), 8.53 (br, 4H), 8.38 (m, 4H), 8.26 (br, 2H), 7.34 (s, 2H), 4.74 (br, 2H), 4.04 (br, 8H), 2.32 (m, 1H), 1,93 (br, 4H), 1.23-1.06 (m, 136H), 0.85 (t, 30H). MALDI-TOF-MS: *m/z* Calcd. for C₁₅₀H₁₉₉F₂N₇O₈S₂: 2353.39 [M+Na]⁺; found 2353.073 [M+Na]⁺.

2.2. Two-dimensional grazing-incidence X-ray diffraction (2D-GIXD)

2D-GIXD measurements were performed under vacuum at the 9A beamline at Pohang Light Source, Korea. The samples were prepared on ZnO-modified Si substrates under the same conditions as those used for the fabrication of solar cell devices. The wavelength of the X-ray was 0.11997 nm and the incidence angle (i.e., the angle between the critical angle of the sample and that of Si) was 0.12°. The 2D-GIXRD patterns were recorded using a 2D-CCD detector (MX225-HS, Rayonix L.L.C., USA), and the X-ray irradiation time was 10 s. The 2D-GIXRD images from the films were analyzed based on the relationship between the scattering vector (q) and the d spacing ($q = 2\pi/d$).

2.3. Device fabrication

Fullerene-free OSCs were prepared on a commercial indium tin oxide (ITO)-coated glass substrate with a structure of ITO/ZnO/ PTB7-Th:acceptor (DTBTP, DTF2BTP, and DTF2TZP) /MoO₃/Ag. Prior to use, the patterned ITO covered glass substrates were cleaned with deionized water, acetone, and isopropyl alcohol via ultrasonication for 20 minutes, followed by treatment with UV-ozone for 20 minutes. A ZnO precursor was prepared by dissolving zinc acetate (Aldrich, 99.9%, 1 g) and ethanolamine (Aldrich, 99.5%, 0.28 g) in 2-methoxyethanol (Aldrich, 99.8%, 10 mL) under stirring for 12 hours in air. The ZnO precursor solution was spin-coated (2800 rpm, 40 s) onto the cleaned ITO-glass and dried at 200 °C for 10 minutes in the ambient environment. The thickness of the ZnO layer was around 25~30 nm. Blends of PTB7-Th (concentration, 8 mg/mL): acceptor (DTBTP, DTF2BTP, and DTF2TZP) with a 1:1.5 weight ratio were dissolved in chlorobenzene (CB) with 1.5 vol% 1-chloronathphalene (CN). The blending solution was subsequently spin-coated at 2000 rpm for 60 seconds (thickness, 50~60 nm,) onto the ZnO layer covered on the ITO. The resulting films were dried for 3 h under N₂ in a glove box. The devices were completed by the deposition of a 7 nm film of MoO₃ and a 100 nm Ag layer. These layers were thermally evaporated at a pressure of 1×10^{-6} Torr. There were four devices per substrate, with an active area of 0.09 cm^2 per each device. The electron-only devices were constructed as ITO/ZnO/PTB7-Th:acceptor (DTBTP, DTF2BTP and DTF2TZP) /LiF (0.8 nm)/Al (100 nm). The fabrication process was identical to that of OSC fabrication except for the electrodes.

2.4. Device Analysis

Device characterization was carried out under light illumination at AM 1.5G using a solar simulator (Yamashita Denso) at 100 mW/cm², adjusted with a standard PV reference (2×2 cm²),

and a mono-crystalline silicon solar cell (calibrated at NREL, Colorado, USA). The current– voltage (J–V) characteristics were measured with a Keithley 2635B source-measure unit. The external quantum efficiency (EQE) was detected under monochromatic illumination (McScience, K3100 spectrometer equipped with 400 W Xenon lamp) and the calibration of the incident light was performed with a monocrystalline silicon diode. The electron mobility of active layers was measured by the steady-state space-charge-limited current (SCLC) method in dark condition. From plots of $J^{1/2}$ vs. V, the mobility was determined by the Mott-Gurney law in the steady-state space-charge-limited current (SCLC) trap free regime.

2.5. General Characterizations

¹H NMR spectra were recorded on a Bruker AscendTM-400 spectrometer, with tetramethylsilane as an internal reference. The UV-vis (SHIMADZU UV-2550) of each compound was measured in chlorobenzene (CB) solution and the corresponding film state. Cyclic voltammetry (CV) measurements were performed with WonATech BAS 100B under N₂ at a scan rate of 50 mVs⁻¹ at room temperature, wherein a Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively, in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu₄NPF₆) as an electrolyte. The reference electrode was calibrated with Fc/Fc⁺ as an external standard. The samples were prepared onto a Pt wire electrode by drop casting from a 20 mg/mL CB solution.

- 3. Results and Discussion
- 3.1. Synthesis and Characterizations

The synthetic procedure of the synthesized acceptors, DTBTP, DTF2BTP, and DTF2TZP, is described in **Scheme 1**. Compounds 1, 2, and 3 [46-49] were lithiated using lithium diisopropylamide (LDA), followed by distannylation using trimethyltin-chloride to obtain compounds 4, 5, and 6, respectively. The pure di-stannylated compounds 4 and 5 were obtained from the recrystallization, but compound 6 contains a small amount of mono-stannylated by-product, which was eliminated at the next step. The final products DTBTP, DTF2BTP, and DTF2TZP were successfully synthesized by Stille coupling reaction of 1-bromo-N,N'-bis(2-ethylhexyl)-3,4,9,10-perylene tetracarboxylic diimide with compounds 4, 5, and 6, respectively. All the acceptors showed excellent solubility in common organic solvents, such as dichloromethane, chloroform, and chlorobenzene. In addition, all the synthesized acceptors had extremely high thermal stability, which was evaluated by a thermal gravimetric analysis (TGA) under a N₂ atmosphere. The temperature for 5% weight loss of DTBTP, DTF2BTP, and DTF2TZP reached 442, 435, and 433 °C, respectively. ¹H NMR, matrix-assisted laser desorption ionization-time of flight mass (MALDI-TOF MS) and TGA thermograms of the synthesized acceptors are shown in Supporting Information (**Figures S1 – S9**).

3.2. Optical and Electrochemical Properties

The ultraviolet-visible (UV-vis) absorption spectra of the synthesized acceptors in solution and film are shown in **Figures 1a** and **b**, respectively. All the acceptors showed strong absorption in the range of 450 – 650 nm. The double-hump absorption characteristic of DTF2TZP is attributed to the absorption of the DTF2TZ backbone at 400 nm[50], whereas the single-hump absorption of DTBTP (or DTF2BTP) acceptor is due to the similar absorption range of PDI and DTBT (or DTF2BT) monomers. As a result, the combination of PDI and the n-type core minimized their

intramolecular charge transfer interaction (ICT) interaction, leading to strong large bandgap absorption in the range of 400 - 650 nm.

The absorption of the films was red-shifted and broadened compared to that of the solutions, indicating enhanced intermolecular interaction in the film. The red-shifts of the absorption maximum of DTBTP, DTF2BTP, and DTF2TZP from solution to film were 4 nm, 8 nm, and 6 nm, respectively. In particular, the shoulder absorption of DTF2BTP in the film was the most developed and increased. Thus, the fluorinated and non-alkylated DTF2BT core structure induced the strongest intermolecular stacking of DTF2BTP in the film.

The fluorinated DTF2BTP acceptor showed a blue-shifted absorption maximum compared to that of non-fluorinated DTBTP because the electron-withdrawing fluorine atom has a stronger influence on the HOMO level than on the LUMO level.[51-53] The LUMO level of the acceptors was determined by cyclic voltammetry (CV), as shown in **Figure 1c**. The reduction onset potentials of DTBTP, DTF2BTP, and DTF2TZP were quite similar at -0.88, -0.88, and -0.89 V, respectively, and the corresponding LUMO levels were -3.82, -3.82, and -3.81 eV, respectively. However, the oxidation potentials of the acceptors were not obtained from CV due to the strong n-type characteristics of the synthesized acceptors. This strong electron accepting property was realized by a combination of the electron withdrawing PDI and the n-type core.

The LUMO energy levels of the fullerenes such as [6,6]-Phenyl C₇₁ butyric acid methyl ester (PC₇₁BM) are known to be around -4.0 ~ 4.2 eV.[54] The high-lying LUMO energy levels of the synthesized non-fullerene acceptors increase the potential energy between HOMO energy level of the donor and the LUMO energy level of the acceptor, improving the open circuit voltage (V_{oc}) in the photovoltaic devices.

Thus, the HOMO levels of the acceptors were calculated from the LUMO levels and the optical bandgap. The optical bandgap of DTBTP, DTF2BTP, and DTF2TZP was determined by the absorption onset wavelength in the film, and the corresponding bandgaps were 1.66, 1.69, and 1.73 eV, respectively. Even though they showed major absorption in the high bandgap area of 450 - 550 nm, their optical onset bandgap was quite narrow due to the strong intermolecular stacking behaviour of the synthesized acceptors; the absorption maximum peak of DTBTP,

DTF2BTP, and DTF2TZP in the film was 498, 494, and 504 nm, respectively, but the onset absorption wavelength appeared at 745, 733, and 717 nm, respectively. In the case of DTF2TZP, it showed the largest bandgap (1.73 eV) in spite of having the most red-shifted absorption maximum wavelength (504 nm), which is ascribed to the weakened intermolecular stacking of DTF2TZP due to the bulky alkyl side group on the core unit.

The calculated HOMO levels of DTBTP, DTF2BTP, and DTF2TZP were -5.48, -5.51, and -5.54 eV, respectively. The fluorinated DTF2BTP showed a similar LUMO level with DTBTP, but a deeper HOMO level than that of DTBTP. This is in a good agreement with a typical fluorination effect.[51-53] The results of the optical and electrochemical properties are summarized in **Table 1**.

3.3. Theoretical Calculations

The geometric structures of the acceptors in the ground state (S_o) were calculated by density functional theory (DFT) using the B3LYP functional and 6-31G(d, p) basis set (**Figure 2**) and the dihedral angles of the bonding in the acceptors are summarized in **Table 2**. All the acceptors showed a typical 3D molecular structure where PDI is linked to the core backbone in a 48° twisted manner. The difference was found in the core structure. The dihedral angle of DTF2BTP

at the A2 and A3 positions was close to zero, which indicates strong intramolecular interaction between thiophene and fluorine atoms,[55, 56] whereas that of DTBTP was approximately 10°, implying somewhat free rotation. Thus, the fluorination in the core structure improved the backbone planarity, implying better intermolecular ordering in the film state. In the case of DTF2TZP, the isobutyl side group on the core unit slightly increased the dihedral angle at the A2 and A3 positions, indicating a geometric influence of the bulky side group on the DT2TZP structure.

3.4. Photovoltaic Properties

Bulk heterojunction OPV devices were fabricated using configurations of indium tin oxide (ITO)/ZnO/active layer/MoO₃/Ag. The active layer was composed of a donor polymer, PTB7-Th, and the newly synthesized acceptors, DTBTP, DTF2BTP, and DTF2TZP. The current density-voltage (*J-V*) characteristics of the devices were optimized by controlling the thickness of the active layer, the weight ratio between the donor and acceptor, and the amount and variety of solvent additives. When the active layers were formed at a 1.0:1.5 weight ratio of PTB7-Th:acceptor in chlorobenzene (CB) with 1.5 vol% 1-chloronathphalene (CN), all the devices showed optimum power conversion efficiencies. PTB7-Th:DTF2BTP devices showed a best power conversion efficiency of 4.41% with a V_{oc} of 0.80 V, a J_{sc} of 9.79 mAcm⁻¹, and a FF of 0.56, while the PTB7-Th:DTBTP and PTB7-Th:DTF2TZP devices exhibited PCEs of 3.81% (V_{oc} of 0.82 V, a J_{sc} of 8.38 mA cm⁻¹ and FF of 0.56) and 2.23% (V_{oc} of 0.81 V, a J_{sc} of 6.39 mAcm⁻¹ and FF of 0.43), respectively. The *J-V* characteristics of the photovoltaic devices are shown in **Figure 3a** and the photovoltaic parameters are summarized in **Table 3**.

The identical LUMO energy levels of the three acceptors resulted in quite similar V_{oc} values in the devices because the energy gap between the HOMO level of the donor polymer and the LUMO level of the acceptor is closely related to the V_{oc} .[57] Incident photon to current efficiency (IPCE) was measured to verify the J_{sc} values of PTB7-Th:acceptor (DTBTP, DTF2BTP and DTF2TZP) based devices (**Figure 3b**). A significantly enhanced external quantum efficiency (EQE) was obtained for the PTB7-Th:DTF2BTP based device in nearly the entire visible range from 400nm to 750nm. In contrast, the EQE of the PTB7-Th:DTF2TZP device is noticeably small. The higher photon-to-current response in the entire spectrum suggests that both the PTB7-Th donor and the DTF2BTP acceptor have an efficient photon conversion process, implying balanced charge transport by an improved active layer morphology such as molecular ordering and phase separation. Thus, the huge difference in FF and J_{sc} was attributed to the morphological differences of the three acceptors.

Morphological properties are investigated by two-dimensional grazing-incidence X-ray diffraction (2D-GIXD) (**Figure 4**) and transmission electron microscopy (TEM) (**Figure 5**). The molecular ordering of the pristine acceptor films and blend films (donor:acceptor) is evaluated from 2D-GIXD. As shown in **Figures 4a**, **b**, and **g**, the DTBTP and DTF2BTP identically showed a clear layered ordering, as indicated by the (100, 200, 300) peaks with a repeat interval of 0.24 Å⁻¹ in out-of-plane (Qz), corresponding to a d-spacing of 26.2 Å. However, DTF2TZP only showed a (100) peak at 0.20 Å⁻¹ in Qz, corresponding to d-spacing of 31.4 Å, without any reflection peak (**Figure 4c**). This clearly indicates that alkylation of the core unit increases the distance of intermolecular ordering and suppresses efficient molecular ordering, whereas the rigid core unit enhanced the long-distance ordering of the acceptor.

In the blend film, the fluorination effect was clearly observed. The layered structure of DTBTP almost disappeared in the PTB7-Th:DTBTP film, and only the (010) peak at 1.31 Å⁻¹ (π - π stacking distance, 4.8 Å) from the donor polymer was observed in the Qz direction (**Figure 4d**). However, PTB7-Th:DTF2BTP blend films clearly showed layered ordering of the DTF2BTP acceptor with (h00) reflections as well as the (010) π - π stacking peak of PTB7-Th (**Figure 4e**). This means that fluorination in the core unit improves the intermolecular ordering of the acceptors, and thus in the presence of the donor polymer, acceptors can form long-distance ordering, which is favourable for electron transport.

These ordering behaviours directly affected the electron transport properties of the devices. The electron mobility (μ_e) of the blend films was determined from the space-charge-limited current (SCLC) trap free regime using electron-only devices with configurations of ITO/ZnO/active layer/LiF/Al. The resulting *J*-*V* characteristics are shown in **Figure S11** and the mobilities are listed in **Table 3**. PTB7-Th:DTF2BTP blend films showed the highest electron mobility, 2.2 × 10^{-4} cm²V⁻¹s⁻¹, PTB7-Th:DTF2TZP films the lowest value, 0.4×10^{-4} cm²V⁻¹s⁻¹, and PTB7-Th:DTF2TZP films the lowest value, 0.4×10^{-4} cm²V⁻¹s⁻¹, and PTB7-Th:DTF2TZP films the lowest value, 0.4×10^{-4} cm²V⁻¹s⁻¹, and PTB7-Th:DTF2TZP films the lowest value, 0.4×10^{-4} cm²V⁻¹s⁻¹, and PTB7-Th:DTF2TZP films the lowest value, 0.4×10^{-4} cm²V⁻¹s⁻¹, and PTB7-Th:DTF2TZP films the lowest value, 0.4×10^{-4} cm²V⁻¹s⁻¹, and PTB7-Th:DTF2TZP films the lowest value, 0.4×10^{-4} cm²V⁻¹s⁻¹, and PTB7-Th:DTBTP films showed a median value of 1.8×10^{-4} cm²V⁻¹s⁻¹. The better intermolecular ordering in blend films, as shown in the 2D-GIXD results, yielded better electron transport properties in the devices. The electron mobility and photovoltaic performance was thereby improved in the following order: alkylated core structure < non-fluorinated core structure < fluorinated planar core structure.

The interfacial morphology of the blend films was investigated from TEM images (**Figure 5**). As shown in TEM, the PTB7-Th:DTBTP and PTB7-Th:DTF2TZP films showed a sizable phase separation in the blend films. It is expected that the alkylated core structure of DTBT and the non-fluorinated core structure of DTF2TZ diminish the intermolecular interaction in blend states,

leading to phase separation. However, PTB7-Th:DTF2BTP films showed the most uniform bicontinuous network in all the blend films, forming the best charge transport pathway. Thus, the fluorinated and planar core structure of DTF2BT effectively increases the intermolecular and interfacial interaction in blend films, leading to a uniformly mixed nano-morphology and the best photovoltaic performance.

We estimated the maximum PCEs of the PTB7-Th:DTF2BTP devices according to the literature reported by Brabec et al.[54] The maximum PCE was calculated by a function of the bandgap of donor and the difference between LUMO energy levels of donor and acceptor. The LUMO energy levels measured from CV was approximately -3.2 eV for PTB7-Th[6] and -3.8 eV for DTF2BTP, respectively, and the bandgap of PTB7-Th was approximately 1.6 eV.[6] Thus, the maximum possible PCE of PTB7-Th:DTF2BTP devices is calculated to be around 7%. We believe that further understanding and optimization of nanomorphology between donor and non-fullerene acceptor can reach this theoretical value.

4. Conclusions

Non-fullerene acceptors incorporating an n-type core were synthesized and their photovoltaic properties were investigated. The combination of electron withdrawing PDIs and n-type core moieties enhanced electron accepting properties and absorption in high bandgap area, thereby providing a good candidate for high bandgap n-type acceptors suitable for panchromatic absorption with a well-known low bandgap electron donor (PTB7-Th).

2D-GIXD revealed that the core structure is highly important for intermolecular ordering in pristine and blend films. The fluorination effect was clear. The non-fluorinated acceptor (DTBTP) showed sizable ordering in pristine films, but not in blend films. However, the

fluorinated acceptor (DTF2BTP) showed sizable ordering in both pristine and blend films, resulting in the highest electron mobility. In addition, alkylation of the core structure diminished intermolecular interaction in both pristine and blend films, and resulted in poor electron transport properties. Thus, the DTF2BTP acceptor incorporating a fluorinated and planar core showed the best PCE, 4.41%, among the synthesized acceptors. We suggest that planarity and bulkiness of the core structure are important for designing the PDI-core-PDI acceptor.

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Appendix A. Supporting Information

Supplementary data associated with this article can be found in the online version at...

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Scheme 1. i) LDA, trimethyltin chloride, THF, -78 [], ii) 1-bromo-N,N'-bis(2-hexyldecyl)-

3,4,9,10-perylene tetracarboxylic diimide, $Pd(PPh_3)_4$, Toluene, 110 \Box



Figure 1. UV-vis absorption spectra (a) in solution and (b) in film, and (c) cyclic

voltammograms of DTBTP, DTF2BTP, and DTF2TZP



Figure 2. The geometric structures of DTBTP, DTF2BTP, and DTF2TZP, calculated by the DFT method using B3LYP/6-31G(d, p).



Figure 3. (a) Current density-voltage (J-V) characteristics of PTB7-Th:acceptor (DTBTP, DTF2BTP, and DTF2TZP) devices under AM 1.5G, 100 mWcm⁻² illumination and (b) the corresponding EQE spectra.



Figure 4. 2D-GIXD images of pristine and blend films: (a) DTBTP, (b) DTF2BTP, (c) DTF2TZP , and (d) PTB7-Th:DTBTP, (e) PTB7-Th:DTF2BTP, and (f) PTB7-Th:DTF2TZP (1.0:1.5 w/w). Line-cut data along the q_z axis (g) pristine films and (h) blend films



Figure 5. TEM images of (a) PTB7-Th:DTBTP, (b) PTB7-Th:DTF2BTP, and (c) PTB7-

Th:DTF2TZP (1.0:1.5 w/w) blend film.

				λ_{max} (n	n)	$E_{ m g}$	opt		Em	мо Ено	MO
DTF27	ſZP	•									
Table	1.	Summary	of	optical	and	electrochemical	properties	of	DTBTP,	DTF2BTP,	and

		λ_{\max} (nm)		$E_{ m g}^{ m opt}$	$\mathbf{F}_{\mathbf{r}}$, (\mathbf{V})	ELUMO	E _{HOMO}	
	solution ^[a]	film ^[b]	onset	$(eV)^{[c]}$	L _{Red} (V)	(eV) ^[d]	(eV) ^[e]	
DTBTP	494	498	745	1.66	-0.88	-3.82	-5.48	
DTF2BTP	486	494	733	1.69	-0.88	-3.82	-5.51	
DTF2TZP	498	418, 504	717	1.73	-0.89	-3.81	-5.54	

^[a] In dilute chloroform; ^[b] formed by spin-coating on a quartz plate; ^[c] bandgap calculated from absorption onset wavelength in film; ^[d] LUMO levels were determined from the reduction onset potential (E_{Red}); ^[e] HOMO levels were estimated from E_g^{opt} and E_{LUMO} .

Table 2. Dihedral angles of the acceptors shown in Figure 2.

	Dihedral angle						
	A1 (°)	A2 (°)	A3 (°)	A4 (°)			
DTBTP	48.2	9.9	9.8	48.2			
DTF2BTP	48.2	0.5	0.5	48.2			
DTF2TZP	49.5	1.9	2.3	47.7			

Table 3. Summary of photovoltaic properties.

PTB7-Th: acceptors	SCLC mobility ($cm^2 V^{-1} s^{-1}$)	$V_{OC}\left(\mathbf{V}\right)$	J_{SC} (mA cm ⁻²)	Fill factor	PCE (%) ^[a]
DTBTP	1.8×10^{-4}	0.82 ± 0.00	8.38 ± 0.14	0.555 ± 0.41	3.81 ± 0.05
DTF2BTP	2.2×10^{-4}	0.80 ± 0.00	9.79 ± 0.13	0.562 ± 0.35	4.41 ± 0.03
DTF2TZP	$0.4 imes 10^{-4}$	0.81 ± 0.00	6.39 ± 0.09	0.425 ± 0.39	2.23 ± 0.02

^[a] The average values were obtained from 16 devices.

Supporting Information

n-Type Core Effect on Perylene Diimide Based Acceptors for Panchromatic Fullerene-Free Organic Solar Cells

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Figure S1. ¹H NMR spectrum of 4,7-bis(5-(trimethylstannyl)thiophen-2-

yl)benzo[c][1,2,5]thiadiazole (compound 4)



Figure S2. ¹H NMR spectrum of 5,6-difluoro-4,7-bis(5-(trimethylstannyl)thiophen-2-

yl)benzo[c][1,2,5]thiadiazole (compound 5)



Figure S3. ¹H NMR spectrum of 5,5'-(benzo[c][1,2,5]thiadiazole-4,7-diylbis(thiophene-5,2-diyl))bis(2,9-bis(2-hexyldecyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone) (DTBTP)



Figure S4. ¹H NMR spectrum of 5,5'-((5,6-difluorobenzo[c][1,2,5]thiadiazole-4,7diyl)bis(thiophene-5,2-diyl))bis(2,9-bis(2-hexyldecyl)anthra[2,1,9-def:6,5,10d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone) (DTF2BTP)



Figure S5. ¹H spectrum of 5,5'-((2-(2-decyltetradecyl)-5,6-difluoro-2H-benzo[d][1,2,3]triazole-4,7-diyl)bis(thiophene-5,2-diyl))bis(2,9-bis(2-hexyldecyl)anthra[2,1,9-def:6,5,10d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone) (DTF2TZP)







Figure S7. MALDI-TOF-MS of DTF2BTP



Figure S8. MALDI-TOF-MS of DTF2TZP



Figure S9. TGA thermogram of the synthesized acceptors



Figure S10. Calculated HOMO and LUMO of the acceptors using DFT method with B3LYP/6-

31G(d, p)



Figure S11. The structures of electron-only devices were ITO/ZnO/PTB7-Th:acceptor/LiF/Al. The mobility of the blend films was determined by Mott-Gurney law in the SCLC trap free regime, by using the slope of $J^{1/2}$ vs V.



Figure S12. *J-V* characteristics of PTB7-Th:DTF2BTP devices under AM 1.5G illumination at different amount of 1-chloronaphthalene (CN) in chlorobenzene (CB).

Donor:Acceptor	additive	J_{sc} (mA cm ⁻²)	$V_{oc}\left(\mathrm{V} ight)$	FF (%)	PCE (%)
	W/O	8.24	0.81	42.59	2.85
	0.75 Vol% of CN	8.67	0.80	50.71	3.53
PTB7-Th: DTF2BTP	1.00 Vol% of CN	9.87	0.80	52.93	4.17
	1.50 Vol% of CN	9.99	0.80	55.73	4.47
	2.00 Vol% of CN	9.28	0.81	54.00	4.04

Table S1. Summary of photovoltaic properties in Figure S12.

 Highlights

- We synthesized novel n-type core incorporated perylene diimide (PDI) acceptors
- Panchromatic absorption was achieved via high bandgap PDI acceptors and a low bandgap

donor, PTB7-Th.

- The n-type core effect of non-fullerene acceptors was systemically analyzed by morphological studies.
- The fluorinated planar core structure provided the best PCE of 4.41%.