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A diketopyrrolopyrrole molecule end-capped with furan-2-carboxylate moiety: planarity of molecular geometry and photovoltaic property

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We designed and synthesized a diketopyrrolopyrrole (DPP) molecule with fully-planar molecular geometry, 3,6-bis{5-[(ethylfuran-2-carboxylate)-2-yl]thiophene-2-yl}-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (**DPP(CF)**₂), for solution-processable organic solar cells (OSCs). It is theoretically

¹⁰ calculated that the dihedral angels between the two furan-2-carboxylate end-groups and DPP core are both only 0.56°. Due to this negligible steric distortion, the molecular conformation of **DPP(CF)**₂ can be considered fully coplanar, leading to a higher crystallinity for **DPP(CF)**₂ film. As a result, the hole mobility of **DPP(CF)**₂ is one order of magnitude higher than that of the DPP derivative with thiophene-2carboxylate as the end-group (**DPP(CT)**₂). And **DPP(CF)**₂ exhibits both a low optical band gap (*Eg*) of

¹⁵ 1.60eV and a low-lying highest occupied molecular orbital (HOMO) energy level of -5.33 eV, implying that **DPP(CF)**₂ is a promising electron donor for OSCs. OSCs with **DPP(CF)**₂ or **DPP(CT)**₂ as the electron donor and [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₁BM) as the electron acceptor were fabricated. It is found that the **DPP(CF)**₂-based devices exhibit much better photovoltaic performance than the **DPP(CT)**₂-based devices, with the highest power conversion efficiency of 5.37% and a short-²⁰ circuit current density of 11.4mA cm⁻². This phenomenon can be ascribed to the superior charge-

transporting ability of **DPP(CF)**₂ caused by its fully-planar molecular geometry.

Introduction

Organic solar cells (OSCs) have attracted tremendous scientific and industrial interests in recent years due to their promising advantages, such as low-cost, simple manufacturing process, flexibility, and light weight¹⁻⁵. Bulk heterojunction (BHJ) structure which involves a

²⁵ blend of organic electron donor (conjugated polymers or small molecules) and electron acceptor ([6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) or other fullerene derivatives) has emerged as a robust way to fabricate high-performance OSCs. In the last decade, the PCE of OSCs has rapidly improved⁶⁻¹⁴, which can be mainly attributed to the development of many high performance polymer donors with near ideal optical and electron properties. Meanwhile, OSCs with small molecules as electron donors also received increasing attention for the advantages of easy synthesis and purification, well-defined structures, absence of end group contaminants, high charge

³⁰ carrier mobility, and better batch-to-batch reproducibility^{5,15,16}. Through persistent investigations by scientists, power conversion efficiency (PCE) of over 8% has been achieved for small molecule organic solar cells (SMOSCs)¹⁷⁻¹⁹. For instance, Chen and co-workers achieved a PCE of 8.12% by developing a series of novel small molecule donors, with a benzodithiophene core, a terthiophene spacer, and a rhodamine end-group²⁰. Very recently, Bazan *et al.* reported an OSC based on the small molecule donor of p-DTS(FBTTh₂)₂²¹⁻²³ and found that barium cathode layer can significantly enhance the fill factor (*FF*) of the device *via* increasing the charge collection at the ³⁵ cathode. Ultimately the PCE is improved to 9.02% and is the record value for SMOSCs.

Nowadays, several strategies to design organic donors for high-performance OSCs have been established: (1) to form a conjugated donor-acceptor (D-A) molecular backbone to achieve broad and strong light absorptions in the visible and near-infrared regions, (2) to incorporate planar molecular structures which are closely packed for crystallization to enhance the charge carrier mobility and yield large short-circuit current (J_{SC}), and (3) to realize a low-lying the highest occupied molecular orbital (HOMO) energy level to ensure high 40 open-circuit voltage (V_{OC}) and a suitable the lowest unoccupied molecular orbital (LUMO) energy level to provide enough energy offset

for efficient exciton dissociation²⁴.

Since firstly reported by Nguyen and co-workers²⁵⁻²⁸, diketopyrrolopyrrole (DPP) unit, with two fused electron-deficient lactams, has been widely used to design D-A polymers and small molecules for applications in the optoelectronic field. The thienyl groups chemically decorated at 3,6-positions of the lactam improve intramolecular π -electron delocalization and π - π intermolecular interaction, leading to

⁴⁵ intense absorptions in the visible region²⁹. In the last few years, significant progress has been made for the application of DPP-containing materials in semiconductors. Liu's group³⁰ reported two donor-acceptor (D–A) copolymer based on diketopyrrolopyrole and (*E*)-2-(2-(thiophen-2-yl)vinyl) thiophene (TVT) units for solution-processed field-effect transistors (FETs), with a highest hole mobility of 8.2 cm² V⁻¹ s⁻¹. A linear solution-processable small molecule based on 5-alkylthiophene-2-yl-substituted benzodithiophene and DPP was reported by two different groups, and the resulting OSCs show PCEs of 5.79%³¹ and 5.29%³², respectively. Recently, our group designed

⁵⁰ a DPP molecule end-capped with two thiophene-2-carboxylate moieties (**DPP(CT)**₂), which owns appropriate energy levels (both narrow band gap and low-lying HOMO) as the donor in SMOSCs. The **DPP(CT)**₂-based OSCs gave a PCE of 4.02%³³. We found that the relatively low hole mobility of **DPP(CT)**₂ is one of main reasons for the moderate device performance. Nguyen and co-workers

presented that changing heteroatom substitutions in the aromatic end-groups may significantly affect their thermal properties, solubility, crystallinity, film morphology, charge carrier mobility, and solar cell performance³⁴. Therefore, to obtain high performance SMOSCs, in this work, while remaining the ester functionalization to tune its solubility and energy level, we replace thiophene-2-carboxylate with furan-2-carboxylate unit to design a new DPP derivative, 3,6-bis {5-[(ethyl furan-2-carboxylate)-2-yl]thiophene-2-yl}-2,5-bis(2s ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (**DPP(CF)**₂). It is expected that **DPP(CF)**₂ would exhibit better planarity of the molecular structure than **DPP(CT)**₂ because the oxygen atom in furan ring is smaller than the sulfur atom in thiophene ring. We demonstrate that this improved molecular structure decreases the steric hinderance³⁵ and results in stronger π - π stacking, and the electronegative oxygen atom stabilizes the HOMO energy level³⁶. As a result, improved photovoltaic performance can be expected. Herein, molecular geometries, crystallinities, charge-transporting abilities, and photovoltaic properties of **DPP(CF)**₂ and **DPP(CT)**₂ are investigated and ¹⁰ compared, in order to verify the feasibility of the above molecular design strategy.

Scheme 1

Results and discussion

Synthesis and Thermal Property

DPP(CF)₂ was synthesized *via* traditional Pd(0)-catalyzed Stille coupling reaction between ethyl 5-bromo-furan-2-carboxylate and the ¹⁵ stannyl derivative of DPP, as shown in Scheme 1. The obtained **DPP(CF)**₂, as well as **DPP(CT)**₂, was soluble in either chloroform (more than 20 mg/ml), chlorobenzene, or dichlorobenzene, due to the alkyl chain in the end heteroatom substitutions. Thermal properties of **DPP(CF)**₂ were investigated by thermogravimetric analysis (TGA) (Fig. 1a) and differential scanning calorimetry (DSC) (Fig. 1b). The DSC heating trace for **DPP(CF)**₂ shows a melting peak at 198 °C, suggesting that this molecule is crystalline. During the cooling process, a broad exothermic peak with a shoulder is observed from 75 to 130 °C, due to its quite slow crystallization process. From TGA curves, ²⁰ it is found thatthe decomposition temperature (*T*_d) with 5% weight loss of **DPP(CF)**₂ is 398 °C (39 °C higher than that of **DPP(CT)**₂), indicating a better thermal stability. This thermal stability is good enough for the application in optoelectronic devices^{37, 38}.

Optical Property

Optical measurements provide essential information on the electronic properties and the ongoing electron-transfer process within materials³⁹. UV-Vis absorption spectra of **DPP(CF)**₂ and **DPP(CT)**₂ in dilute chloroform (CF) solutions and corresponding thin films are ²⁵ compared in Fig. 2. Two molecules display similar characteristic absorption peaks due to the similar molecular structures ^{40, 41}. However, the absorption of **DPP(CF)**₂ red-shifts by ~ 12 nm than that of **DPP(CT)**₂ when they exist as monomeric dyes in solutions, implying stronger conjugation effect between furan rings and DPP core in **DPP(CF)**₂. The red-shift of the absorption becomes more obvious in their solid films. Compared to the solutions, both films exhibit an additional absorption peak located at longer wavelength region, which originates from strong intermolecular π - π overlapping in the condensed state³⁶. Because of the improved molecular arrangement caused ³⁰ by better intramolecular conjugation and more planar molecular geometry, the absorption peak (representing π - π stacking) of **DPP(CF)**₂ film is more red-shifted and intense. As a result, the band-edge (λ_{onset}) of **DPP(CF)**₂ film extends to 773 nm, whereas that of **DPP(CT)**₂

is 752 nm The optical band gaps (E_g^{opt}) are calculated as 1.60 eV and 1.65 eV for **DPP(CF)**₂ and **DPP(CT)**₂, respectively.

Electrochemical Property

The electrochemical properties of **DPP(CT)**₂ and **DPP(CF)**₂ were investigated by cyclic voltammetry (CV). Fig. 3 shows the cyclic ³⁵ voltammograms of the two molecules in dichloromethane solutions. The CV curve was recorded versus the potential of standard calomel electrode (SCE), which was calibrated by the ferrocene-ferroceium (Fc/Fc⁺) redox couple (4.8 eV below the vacuum level). In the positive potential region, the $E_{1/2}$ values for the first oxidation/reduction waves are calculated as the oxidation potential. From the empirical formula E_{HOMO} = -(E_{ox} +4.4) eV, the HOMO energy level of **DPP(CF)**₂ can be calculated as -5.33 eV. Compared to **DPP(CT)**₂, **DPP(CF)**₂ also presents slightly lower LUMO energy level of -3.58 eV, due to the increased electron affinity of the furan ring. The ⁴⁰ increased electron affinity of the furan ring can reduce both the HOMO and LUMO levels of **DPP(CF)**₂ (induction effect). Moreover, the furan ring possesses conjugation effect with DPP core, leading to the increasing of HOMO level and the decreasing of LUMO level of **DPP(CF)**₂ (conjugation effect). Therefore, the combination of the above two effects gives the identical HOMO level and the lower LUMO level of **DPP(CF)**₂.

	Fig. 1
45	Fig. 2
	Fig. 3

Geometry and Front Orbitals Simulated by Theoretical Calculations

To demonstrate the improved π -conjugation and molecular planarity of **DPP(CF)**₂ ensured by the end-groups of furan-2-ylcarboxylate, the molecular conformation and front orbitals of **DPP(CF)**₂, in the free states, were simulated by theoretical calculations^{35, 40}.

⁵⁰ The simulated front orbitals, energy levels, and dihedral angels between the end-groups and DPP core are presented in Fig. 4 and Table 1. It is found that the dihedral angle between DPP core and end-group is merely 0.56° for **DPP(CF)**₂, which is much smaller than that of **DPP(CT)**₂ (5.27°)³³. Due to this negligible steric distortion, the two furan moieties at end-groups can be considered to show complete

Fig. 4

Table 1

Charge-Transporting Property

Organic field-effect transistors (OFETs) were fabricated to reveal the enhanced charge-transporting property of **DPP(CF)**₂ due to molecular planarity. For an average of 15 devices, the transfer curves of the corresponding devices are shown in Fig. 5. The as-cast films show an average hole mobility of $1.1\pm0.4\times10^{-4}$ cm² V⁻¹ s⁻¹ for **DPP(CT)**₂ and $2.0\pm0.3\times10^{-6}$ cm² V⁻¹ s⁻¹ for **DPP(CF)**₂, respectively. ¹⁰ Through thermal annealing for 10 min at 100 °C, the hole mobility of **DPP(CF)**₂ increases significantly by three orders of magnitude to $5.1\pm2.3\times10^{-3}$ cm² V⁻¹ s⁻¹. However, the hole mobility of **DPP(CT)**₂ increases moderately to $3.1\pm1.1\times10^{-4}$ cm² V⁻¹ s⁻¹ after thermal annealing. The highest mobilities of the annealed **DPP(CF)**₂ and **DPP(CT)**₂ films are 1.3×10^{-2} and 6.3×10^{-4} cm² V⁻¹ s⁻¹, respectively.

Fig.5

15 Photovoltaic Property

Photovoltaic properties of **DPP(CT)**₂ and **DPP(CF)**₂ were investigated by fabricating OSCs with a conventional structure of ITO/PEDOT:PSS/DPP molecule:PC₇₁BM/LiF/Al. *J-V* characteristics of the devices under one sun (simulated AM 1.5G irradiation at 100 mW cm⁻²) are shown in Fig. 6a, with the performance parameters summarized in Table 2. It is found that **DPP(CF)**₂:PC₇₁BM blends with weight ratios of either 2:1, 1:1, or 1:1.5 induce very poor device performances (PCE<0.5%). The composition ratio of 1.5:1 results a ²⁰ relatively better PCE of 0.52% with a short-circuit current density (J_{SC}) of 1.47 mA cm⁻², fill factor (*FF*) of 0.37 and a high open-circuit voltage (V_{OC}) of 0.96 V. This composition ratio is fixed for further device optimization by thermal annealing and incorporating additive. Thermal annealing leads to a decrease in V_{OC} by 0.07-0.10 V. However, an increase in *FF* by 0.05-0.15 and a remarkable improvement in J_{SC} by several times are obtained. The devices exhibit the best PCE of 2.86% with a J_{SC} of 6.23 mA cm⁻², V_{OC} of 0.89 V, and a *FF* of 0.52 after annealing at 100 °C for 10 min. Incorporating 0.2% v/v additive of 1,8-diiodooctane (DIO)²³ can only slightly increase the J_{SC} and 25 *FF*, leading to a PCE of 0.86%. Nevertheless, after combined with annealing at 100 °C for 10 min, the PCE of 8.80 mA cm⁻², V_{OC} of 0.89 V, and a *FF* of 0.56. To further improve the photovoltaic performance of the **DPP(CF)**₂-based OSCs, a Ca layer is used to replace LiF layer, so that the cathode can collect electrons more efficiently³⁷. Thus, the PCE is elevated to 5.37%, with a much larger J_{SC} of 11.40 mA cm⁻², V_{OC} of 0.89 V, and a *FF* of 0.53. This efficiency of 5.37% achieved by **DPP(CF)**₂ is higher than those from most reported DPP-based small molecule donors (4.0-4.8%)⁴⁴⁻⁴⁶, and even higher than 30 that from the polymer alternating DPP and furan rings (5.0%)³⁶. Under the same device conditions, the PCE of the **DPP(CT)**₂-base

is 3.89% due to a smaller J_{SC} of 8.89 mA cm⁻².

Table 2

Fig. 6

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The external quantum efficiency (EQE) curves of the **DPP(CF)**₂-based OSCs are shown in Fig. 6b. All of the devices show broad photovoltaic response ranging from 300 to 770 nm. The highest EQE value of the devices without any active layer treatment is only \sim 10%. Thermal annealing improves EQE in the whole spectrum, and the maximum value reaches 35% at 680 nm. Incorporating additives slightly improves EQEs all over the response range, especially in the absorption range of **DPP(CF)**₂ (500-700 nm). After combining a these two treatments, remarkable increase of EQE values covering the whole absorption range is observed, with the maximum EQE value of the spectrum.

⁴⁰ these two treatments, remarkable increase of EQE values covering the whole absorption range is observed, with the maximum EQE value of 58.9% at 629nm.

To understand the underlying mechanism for the above improvements of the device performances, the effects of thermal annealing and additive on the morphology of the active layer were investigated. Fig. 7 shows the height and the corresponding phase images obtained by atomic force microscopy (AFM) for **DPP(CF)**₂:PC₇₁BM blended films with different treatment. It is found that the film without

⁴⁵ treatment shows large domains in a scale of ~ 100 nm and thermal annealing cannot alter the phase separation degree of the blended films. After 0.2% ν/ν DIO is added, the film becomes smoother and large domains disappeared. Further annealing at 100 °C for 10 min, phase separation with very clear boundaries is observed with the domain size of about 40 nm, and domains are much more interconnected. These interpenetrating networks of donors and acceptors not only provide interfaces for exciton dissociations but also percolate pathways for charge carrier transport to corresponding electrodes, responsible for the enhancement of the device performance.

Fig. 7

Fig. 8

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Fig. 8 presents X-ray diffraction (XRD) patterns of the active layers spin-coated on ITO substrates. As shown in Fig. 8a, the as-cast

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DPP(CF)₂:PC₇₁BM film exhibits a broad and weak peak at 2θ = 5.45°, indicating a low degree of crystallinity. This peak becomes much stronger by incorporating 0.2% *v/v* additive, indicating that DIO can promote the crystallization of **DPP(CF)**₂. The annealed **DPP(CF)**₂:PC₇₁BM film shows a shifted sharp peak at 2θ = 7.25°, indicating higher crystallinity with different molecular arrangement than that in the as-cast film⁴¹. While the blended film is treated by thermal annealing together with DIO, this sharp peak gets more ⁵ pronounced, giving the highest crystallinity and ordered molecular packing. In Fig. 8b, it is shown that, under the conditions for best device performances, the obtained **DPP(CT)**₂:PC₇₁BM film exhibits a much weaker peak at 2θ = 6.45°, due to lower cystallinity induced by less molecular coplanarity of **DPP(CT)**₂.

We further investigated the effect of thermal annealing and additive on charge-transporting properties of the active layers by using the space-charge-limited current (SCLC) method. As shown in Fig. 9 and Table 3, films without annealing exhibit very low hole mobilities ¹⁰ and relatively high electron mobilities, no matter they are incorporated additive or not. The low hole mobilities and the unbalanced electron/hole transport are the main reasons for the poor performance of these two types of devices prepared without annealing. Thermal annealing can significantly enhance the hole mobilities in both types of devices. In addition, the electron mobilities are also improved slightly, and the more balanced electron/hole transport is obtained. Under the same conditions, both hole and electron mobilities of **DPP(CF)**₂:PC₇₁BM film are much higher than those of **DPP(CT)**₂:PC₇₁BM. Therefore, based on the above analysis, we conclude: (1) the excellent photovoltaic property of **DPP(CF)**₂ is mainly ascribed to its superior charge-transporting ability. This is because the fully-planar molecular geometry of **DPP(CF)**₂ is in favor of ordered molecular packing in the condensed state, especially after the treatment of thermal annealing; (2)additive improves photovoltaic performance basically through the reduction of domain size in the active layer.

Table 3 Fig. 9

Conclusions

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In summary, a DPP molecule end-capped with two furan-2-carboxylate moieties, **DPP(CF)**₂ is successfully synthesized and demonstrated as a promising donor for solution-processable OSCs. The end-groups of furan-2-carboxylate endow **DPP(CF)**₂ with a ²⁵ narrow E_g of 1.60 eV, a low-lying HOMO energy level of -5.33 eV, and typically complete planar molecular geometry, which is in favor of ordered molecular packing in the condensed state. Incorporating furan-2-carboxylate can efficiently improve the molecular planarity and crystallinity, resulting in higher charge-transporting property and photovoltaic performance. As a result, **DPP(CF)**₂ exhibits excellent charge-transporting property with the highest FET hole mobility of 0.013 cm² V⁻¹ s⁻¹, and a high PCE of 5.37% after the optimizations of thermal annealing and additive.

30 Experimental Section

Materials and Instrument

All reagents and solvents were purchased from Aldrich and used without further purification. **DPP(CT)**₂was synthesized according to our previous published precedures³⁰. ¹H-NMR and ¹³C-NMR spectra were measured on a Bruker Advance DMX300 (300 MHz) and 600 (600 MHz) nuclear magnetic resonance spectroscope. UV-visible absorption spectra were taken on a Shimadzu UV-2450 ³⁵ spectrophotometer. Elemental analyses were conducted on a Flash EA 1112 elemental analyzer. Thermogravimetric analysis (TGA) was carried out on a WCT-2 thermal balance under protection of nitrogen at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) was recorded on a Perkin-Elmer Pyris 1 differential scanning calorimeterunder protection of nitrogen at a heating rate of 5°C/min. Cyclic voltammetry (CV) was done on a CHI 660C electrochemical workstation with Pt disk, Pt plate, and standard calomel electrode (SCE) as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L ⁴⁰ tetrabutylammoniumhexafluorophosphate (Bu₄NPF₆) CH₂Cl₂ solution. Topographic images of the films were obtained on a Veeco Multi Mode atomic force microscopy (AFM) in the tapping mode using an etched silicon cantilever at a nominal load of ~2 nN and the

Mode atomic force microscopy (AFM) in the tapping mode using an etched silicon cantilever at a nominal load of ~ 2 nN, and the scanning rate for a 5 μ m × 5 μ m image size was 1.0 Hz. X-ray diffraction (XRD) patterns were recorded on a Bede D1 system high-solution X-ray diffractometer.

Theoretical Calculations

⁴⁵ Geometry optimizations were carried out by the density functional theory (DFT) method at the B3LYP/6-31G(d) level. Energies of front orbitals (HOMOs and LUMOs) were evaluated with the basis set of 6-311+G(d,p). All the calculations were performed using the Gaussian 03 program. Model compounds of the two DPP derivatives were simplified by replacing pendant alkyl side chains with methyl groups to save computational time due to the fact that the geometries and energies negligibly depended on the pendant alkyl groups^{33, 48}.

Synthesis

50 5-bromofuran-2-carboxylic acid (1)

Furan-2-carboxylic acid (2.50 g, 22.3 mmol) and 50 mL of glacial acetic acid were poured into a 100 mL three-necked flask. Then, 1.32 mL (22.0 mmol) of bromine was added dropwise to the flask at room temperature. The mixture was warmed and stirred at 60 °C for 1 h. The mixture was poured into 50 mL of cold water and sodium sulfite was added to remove excess bromine. After that, the mixture was

filtered, and a white solid was obtained. The crude product was recrystallized from 30 mL of ethanol/water (1:2) to give 3.14 g (yield 78%) of product **1** as white needles. ¹H NMR (600 MHz, DMSO) δ 13.31 (s, 1H), 7.22 (d, *J* = 3.6 Hz, 1H), 6.77 (d, *J* = 3.6 Hz, 1H). ¹³C NMR (600 MHz, DMSO) δ 167.35, 145.19, 138.93, 127.33, 119.83.

Ethyl 5-bromo-furan-2-carboxylate (2)

s 1.2 g (6.51 mmol) compound 1 was soluble in 30 ml ethanol, and 1.24 ml trimethylchlorosilane was added into the solution under nitrogen. After being stirred at the ambient temperature for 1 h, the mixture was heated at 65 °C for 24 h. After cooling to room temperature, the solvent was removed by reduced pressure distillation. The crude product was purified by column chromatography (silica gel) with dichloromethane and petroleum mixture (1:1, v/v) to yield a light yellow liquid 2(1.48 g, yield 86%).¹H NMR (300 MHz, CDCl₃) δ 7.08 (d, *J* = 3.5 Hz, 1H), 6.42 (d, *J* = 3.5 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).¹³C NMR (300 MHz, CDCl₃) δ 157.80, 146.70, 127.46, 120.04, 114.05, 61.39, 14.47.

3,6-Bis[5-(trimethylstannyl)thiophene-2-yl]-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (3)

10 ml dry tetrahydrofuran (THF) was cooled to -10 °C under argon followed by addition of 3.19 ml *n*-butyllithium (1.6 M in hexane). Then a solution of 0.72 ml diisopropylamine was added slowly and the reaction mixture was stirred for 30 min. Then, the freshly prepared solution of lithium diisopropylamine (LDA) in THF was added slowly to a cooled solution (-78 °C) of 3,6-bis(5-thiophene-2-15 yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (1.07 g, 2.04mmol) in dry THF (20 ml). The reaction mixture was stirred for 1 h at -78 °C under argon followed by addition of trimethyltin chloride (7.64 ml, 1M in hexane). The reaction mixture was allowed to warm

to room temperature and stirred for 2 h. Water was added to the reaction mixture followed by extraction with ether. The combined organic phase was washed with water, dried over magnesium sulfate, filtered and concentrated in vacuum. Compound 3 was obtained as sticky dark purple oil (1.68 g) with a yield of 97.5% and used without any further purification.

20 3,6-Bis{5-[(ethylfuran-2-carboxylate)-2-yl]thiophene-2-yl}-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4-dione (DPP(CF)₂)

1.42 g (1.32 mmol) compound **3** and compound **2** (1.15 g, 3.31 mmol) were put into a two-neck 100mL round flask and were purged three times with successive vacuum and nitrogen fill cycles. Then 30 mL of dry degassed toluene was added under the protection of nitrogen and the solution was flushed with nitrogen before the addition of 70 mg of tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄). The reaction mixture was further degassed and subsequently sealed before being heated to 110 °C for 48h. Removal of the solvent on a

²⁵ rotary evaporator afforded the crude product, which was purified using column chromatography (silica gel)with dichloromethane and petroleum mixture (5:1, v/v) to give a dark blue powder(0.48g, yield 54%).¹H NMR (600 MHz, CDCl₃) & 8.93 (d, *J* = 4.2 Hz, 2H), 7.54 (d, *J* = 4.2 Hz, 2H), 7.24 (d, *J* = 3.6 Hz, 2H), 6.75 (d, *J* = 3.6 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 4H), 4.12 – 3.97 (m, 4H), 1.88-1.97 (m, 2H), 1.40 (t, *J* = 7.1 Hz, 6H), 1.40 – 1.27 (m, 16H), 0.90(t, *J* = 7.1 Hz, 6H), 0.86 (t, *J* = 7.1 Hz, 6H).¹³C NMR (600 MHz, CDCl₃) & 161.41, 158.37, 151.45, 144.47, 139.56, 136.62, 136.28, 129.91, 124.59, 119.89, 117.42, 109.00, 61.19, 46.04, 39.23, 30.28, 28.44, 23.66, 23.05, 30 14.35, 14.03, 10.54.Anal.Calcd for C₄₄H₅₂N₂O₈S₂: C, 65.97; H, 6.54; N, 3.50. Found: C, 65.94; H, 6.56; N, 3.51.

Fabrication and Characterization of Organic Field-effect Transistors (OFETs)

A heavily doped silicon wafer was used as the gate electrode and substrate, with a 300 nm thermal oxidation SiO₂ layer as gate insulator covered with divinyltetramethyldisiloxanebis(benzocyclobute) (BCB). The **DPP(CF)**₂or **DPP(CT)**₂film was casted from chloroform (CF) solution and annealed for 10 min at 100°C.Organic field-effect transistors (OFETs) were constructed in a bottom-gated ³⁵ configuration by depositing top-contact source and drain electrodes (70 nm Au), with channel length of 50 µm and width of 1 mm. Transfer characteristics of the devices were measured in air using a Agilent 4155C semiconductor parameter analyzer. The measured capacitance of the BCB-covered SiO₂/Si substrates was 10 nF/cm², and this value was used for mobility calculation.

Fabrication and Characterization of Organic Solar Cells (OSCs)

Organic solar cells (OSCs) were fabricated on glass substrates commercially pre-coated with a layer of indium tin oxide (ITO). Prior to 40 fabrication, the substrates were cleaned using detergent, deionized water, acetone, isopropanol consecutively for every 15 min, and then treated in an ultraviolet ozone generator for 15 min before being spin-coated with a layer of 35 nm poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). After baking the PEDOT: PSS in air at 140 °C for 15 min, the substrates were transferred to a glovebox. The BHJ layer was spin-cast at 2500 rpm from a solution of **DPP(CF)**₂(or **DPP(CT)**₂) and PC₇₁BM in chloroform with or without 0.2% (ν/ν) 1,8-diiodooctane (DIO) at a total solids concentration of 16 mg/mL. The thickness of the active

⁴⁵ layers is 90-100 nm, which was calibrated by an Ambios XP-2 profilometer. Then the samples were loaded into a vacuum deposition chamber (background pressure $\approx 5 \times 10^{-4}$ Pa) to deposit 0.6 nm thick LiF(or 20nm thick calcium) and 100 nm thick aluminum cathode with a shadow mask (device active area of 9 mm²).

Current density-voltage (J-V) curve was measured with Keithley 2400 measurement source units at room temperature in air. The photocurrent was measured under a calibrated solar simulator (Abet 300 W) at 100 mW cm⁻², and the light intensity was calibrated with a ⁵⁰ standard silicon photovoltaic reference cell. External quantum efficiency (EQE) spectrum was measured with Stanford lock-in amplifier

8300 unit. The hole mobility of the blends was measured using the space-charge-limited current (SCLC) method. Hole-only devices were

fabricated in a structure of Al(120 nm)/DPP(CF)₂(or DPP(CT)₂):PC₇₁BM/Al(100 nm). The device characteristics were extracted by ⁵⁵ modeling the dark current under forward bias using the SCLC expression described by the Mott-Gurney law:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3}$$

Here, $\varepsilon_r \approx 3$ is the average dielectric constant of the blended film, ε_0 is the permittivity of the free space, μ is the carrier mobility, $L \approx 70$ nm is the thickness of the film, and V is the applied voltage.

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Notes and references

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Table 1 Energy levels and dihedral angels of the two DPP derivatives obtained by CV experiment and theoretical simulations.

Molecule	E _{HOMO} ^{CV} (eV)	E _{LUMO} CV (eV)	E_g^{opt} (eV)	E _{HOMO} DFT (eV)	E _{LUMO} DFT (eV)	E_g^{DFT} (eV)	Dihedral angels between the two end-groups and DPP core (°)
DPP(CT) ₂	-5.33	-3.55	1.60 ^a	-5.35	-3.24	2.11	5.27; 5.27 ^b
DPP(CF) ₂	-5.33	-3.58	1.65ª	-5.33	-3.28	2.05	0.56; 0.56

^a $E_g^{opt} = 1240/\lambda_{onset}$ ^b Ref 33.

Active layer	Solvent	Cathode	Thermal annealing	V _{OC} (V)	J_{SC} (mA cm ⁻²)	FF	PCE (%)
DPP(CF) ₂ :PC ₇₁ BM	CF	LiF/Al	w/o	0.96	1.47	0.37	0.52
DPP(CF) ₂ :PC ₇₁ BM	CF	LiF/Al	90°C 10 min	0.89	4.18	0.42	1.56
DPP(CF)2:PC71BM	CF	LiF/Al	100°C 10 min	0.89	6.23	0.52	2.86
DPP(CF)2:PC71BM	CF	LiF/Al	110°C 10 min	0.86	6.00	0.51	2.64
DPP(CF)2:PC71BM	CF/DIO (0.2% v/v)	LiF/Al	w/o	0.95	2.24	0.40	0.86
DPP(CF)2:PC71BM	CF/DIO (0.2% v/v)	LiF/Al	100 °C 10 min	0.89	8.80	0.56	4.35
DPP(CF)2:PC71BM	CF/DIO (0.2% v/v)	Ca/Al	100 °C 10 min	0.89	11.4	0.53	5.37
DPP(CT) ₂ :PC ₇₁ BM	CF/DIO (0.2% v/v)	Ca/Al	100 °C 10 min	0.94	8.89	0.46	3.89

Table 2 Device parameters of OSCs with or without additive DIO and with or without thermal annealing. The blend weight ratio of donor: acceptor is 1.5:1.

Table 3 Summary of hole and electron mobilities of DPP(CF)2:PC71BM and DPP(CT)2:PC71BM films prepared by different procedures.

Active layer	Solvent	Thermal annealing	$\substack{ (\times 10^{-5} \\ cm^2 V^{-1} \ s^{-1}) }^{\mu_h}$	$\substack{ (\times 10^{-4} \\ cm^2 V^{-1} s^{-1}) }^{\mu_e}$	μ_e/μ_h
DPP(CF) ₂ :PC ₇₁ BM	CF	w/o	0.80±0.06	3.02±1.06	38
DPP(CF) ₂ :PC ₇₁ BM	CF	100°C 10 min	4.11±0.27	4.93±0.55	12
DPP(CF) ₂ :PC ₇₁ BM	CF/DIO (0.2% v/v)	w/o	1.12±0.19	4.10±0.58	37
DPP(CF) ₂ :PC ₇₁ BM	CF/DIO (0.2% v/v)	100 °C 10 min	4.65±0.87	8.08±1.73	17
DPP(CT) ₂ :PC ₇₁ BM	CF/DIO (0.2% v/v)	100 °C 10 min	0.97±0.15	0.43±0.12	4.4

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(i) Br₂, acetic acid, reflux 24 h; (ii) ClSi(CH₃)₃/C₂H₅OH, 60 °C for 12 h; (iii) LDA/ClSn(CH₃)₃, THF -78 °C; (iv) Pd(PPh₃)₄, toluene, reflux 24 h.

Scheme 1Synthesis route of DPP(CF)2

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Fig. 1(a) TGA traces of DPP(CF)₂ and DPP(CT)₂. The heating rate is 20 °C/min. (b) DSC curve of DPP(CF)₂ at the heating rate of 5 °C/min.

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 $V_{G}(V)$

Fig.5 Transfer characteristics of the OFETs based on (a) DPP(CF)2 and (b) DPP(CT)2 with the highest mobilities

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Fig. 6 Current density-voltage (*J-V*) characteristics (a) and external quantum efficiency (EQE) curves (b) of OSCs with DPP(CF)₂:PC₇₁BM (1.5:1, by wt.) blend as the active layer with or without additive and with or without thermal annealing.



Fig. 7 AFM height images (a, b, c, d) and phase images (e, f, g, h) of DPP(CF)₂:PC₇₁BM blended films obtained by different procedures.

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Fig. 8 XRD patterns of (a) DPP(CF)₂:PC₇₁BM blended films obtained by different procedures and (b) DPP molecule:PC₇₁BM blended films prepared under the optimized conditions (thermal annealing at 100 °C for 10 min and 0.2 % v/v DIO).





Fig. 9 $J^{0.5}$ -V curves of (a) hole-only devices (ITO/PEDOT:PSS/DPP(CF)₂:PC₇₁BM/MoO₃/Al) and (b) electron-only devices (Al/DPP(CF)₂:PC₇₁BM/Al). The symbols represent experimental data and the solid lines are fitted according to the Mott-Gurney Law.

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Table of Content

A diketopyrrolopyrrole molecule end-capped with furan-2-carboxylate moiety: planarity of molecular geometry and photovoltaic property

⁵ Lei Fu,^{*a*} Weifei Fu,^{*a*} Pei Cheng,^{*b*} Zhixin Xie,^{*a*} Congcheng Fan,^{*a*} Minmin Shi,*^{*a*} Jun Ling,^{*a*} Jianhui Hou,^{*b*} Xiao-wei Zhan^{*c*} and Hongzheng Chen*^{*a*}

DPP(CF)₂ exhibits fully-planar molecular geometry, which comes with excellent hole mobility of 0.013 cm² V⁻¹ s⁻¹ and a high power conversion efficiency of 5.37%.

