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Synthesis and characterization of push-pull organic semiconductors with various acceptors for solution-processed small molecule organic solar cells

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ABSTRACT

New efficient push–pull organic semiconductors comprising of the bis(9,9-dimethyl-9*H*-fluoren-2-yl) aniline (bisDMFA) donor and the various acceptors such as NO₂, DCBP, and TCF, which were linked with bithiophene or vinyl bithiophene π -conjugation bridges, were synthesized, and their photovoltaic characteristics were investigated in solution-processed small molecule organic solar cells (SMOSCs). The intramolecular charge transfers of these materials were effectively appeared in between bisDMFA donor and acceptors, depending on the electron-withdrawing strength of acceptors. The organic semiconductors having NO₂ and DCBP acceptors exhibited the most efficient photovoltaic performance, showing power conversion efficiency (PCE) of 1.98% (±0.17) and 2.01% (±0.21), respectively. When the TiO_x thin layer was treated on photoactive layer, the organic semiconductor having NO₂ showed the best PCE of 2.70% with short circuit current of 8.19 mA/cm², fill factor of 0.40, and open circuit voltage of 0.83 V in SMOSC devices.

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1. Introduction

Solution-processed organic solar cells (OSCs) fabricated by means of versatile printing techniques such as doctor blade, inkjet, and rollto-roll can provide the most attractive advantages of device such as low cost, light weight, solution processability. Over the last few years, enormous efforts have intensively focused on improving the device performances toward power conversion efficiency (PCE) of 10% though developments of photoactive materials such as π -conjugated (semiconducting) polymer and fullerene derivatives, or functional layers such as buffering, charge transporting, and optical spacing.¹ And recently great achievement of promising PCEs of above 8% in OSC has offered special attention as a strong candidate on next generation solar cell with threatening inorganic thin film solar cell as well as dye-sensitized solar cells (DSSCs).² Most of high efficiencies have been reported in OSC fabricated with bulk-heterojunction (BHJ) materials comprising of low-bandgap semiconducting polymers and [6,6]-phenyl-C_{61(or 71)}-butyric acid methyl ester (C_{61(or 71)}-PCBM).³ Nevertheless, small molecule organic semiconductor seems to fascinate more than these polymers from the viewpoint of mass production for commercial application due to their low reproducibility for characteristics such as average molecular weight (M_w) and polydispersity index (PDI) as well as difficulty in purification. Motivated by this, considerable research effort has been focused on developing efficient small molecule materials for improved device performance, with the near-term goal being a power conversion efficiency (PCE) comparable to polymer-based solar cells (PSCs).⁴ Indeed, recent breakthroughs in realizing PCEs of above 6% have placed solution-processed small molecule organic solar cells (SMOSCs) in competition with PSCs.⁵

The efficient organic semiconductors reported in SMOSC often have the structural symmetric motifs containing the electronwithdrawing cores such as benzothiadiazole,⁶ squaraine,⁷ or diketopyrrolopyrrole,^{4c} which were motivated by low-bandgap semiconducting polymers or push–pull molecular structures in nonlinear optics (NLO) and DSSC due to their superior optoelectronic properties. Recently, we have also reported various symmetric push–pull organic semiconductors comprising triphenylamine (TPA) donor and squaraine (or diketopyrrolopyrrole) acceptor for solution-processed SMOSC.⁸ These push–pull structures in SMOSC enable an efficient intramolecular charge transfer (ICT) to give the better molar absorptivity. And an TPA electron-donating unit can play an important role of stabilizing the separated hole from exciton and improving the transporting property of hole carrier.⁹

On the other hand, we have interestingly found that the unsymmetric push—pull organic semiconductor having the different end groups of TPA donor and squaraine acceptor presented the



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better PCE than the symmetric structures of these donor and acceptor,¹⁰ and that the new organic semiconductor, bisDM-FA-diTh-MMN comprising bis(9,9-dimethyl-9H-fluoren-2-yl) aniline (bisDMFA) donor, methylene-malononitrile (MMN) acceptor, and bithiophene bridge exhibited the superior photovoltaic performance in solution-processed BHI SMOSC even its small molecular size, which should be a obstacle for forming the selfnetwork domains in BHI composite with PCBM, showing the PCE of 3.6%.¹¹ In this study, we also tried to develop new semiconducting push-pull type organic small molecules having various acceptor motifs, especially 4-dicyanomethylene-6-tert-butyl-4H-(DCBP). 2-dicyanomethylene-3-cyano-5-dimethyl-2,5pyran dihydrofuran (TCF), and nitrogen dioxide (NO₂). To the best our knowledge, the electron accepting features can significantly affect the energy bandgap and molar absorptivity as well as the ICT strength of push-pull organic materials. Beside, the structural variation of acceptor motifs often afford its unique features that when integrated into bulk heterojunction composite with PCBM can critically affect the performance characteristics of BHJ OSC.

Herein, we report the synthesis and photovoltaic characteristics of new efficient push-pull organic semiconductors comprising of on the bisDMFA donor and the various 4-(bis((9,9-dimethyl-9H-fluoren-2-yl)amino)pheacceptors, nyl)-2-(5'-nitrothiophen-2'-yl)thiophen (bisDMFA-diTh-NO₂, **1**), (*E*)-2-(2-(2-(5'-(4-(bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino) phenyl)-2,2'-bithiophen-5-yl)vinyl)-6-*tert*-butyl-4H-pyran-4-ylidene) malononitrile (bisDMFA-diTh-DCBP, 2), and (E)-2-(4-(2-(5'-(4-(bis(9.9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-2.2'-bithiophen-5-vl)vinvl)-3-cvano-5.5-dimethvlfuran-2(5H)-vlidene)malononitrile (bisDMFA-diTh-TCF, 3), which were linked with bithiophene or vinyl bithiophene π -conjugation bridges, in solution-processed SMOSC. Scheme 1 shows the structures of the synthesized organic semiconductors and device architecture of solution-processed SMOSC.

malononitrile (iv), and 2-(3-cyano-4,5,5-trimethylfuran-2(5H)vlidene)malononitrile (\mathbf{v}) could be effectively synthesized through modifying the procedures reported previously.¹² BisDM-FA-diTh-DCBP ($\mathbf{2}$) (and bisDMFA-diTh-TCF ($\mathbf{3}$)) were readily prepared through Knoevenagel condensation reaction with **i** and iii (and iv). And the borate compound of ii, which was produced from reaction of **ii** and pinacol borate using the *n*-BuLi, successfully performed the palladium-catalyzed Suzuki coupling reaction with 2-bromo-5-nitrothiophene using phase-transfer catalyst, Aliquat 336 mixture in biphase solution of anhydrous toluene and deionized water, producing the bisDMFA-diTh- $NO_2(1)$ with good yield above 85%. The chemical structure of the synthesized products, bisDMFA-diTh-acceptor series, (1, 2, and 3) were verified with ¹H NMR, ¹³C NMR, ATR-FTIR, and MALDI-TOF mass analysis. And the corresponding further characteristic data of these materials were summarized in Fig. S1 and Table S1 (see Supplementary data). These materials have good solubility in common organic solvents, such as methylene chloride, chloroform, chlorobenzene, and toluene

Fig. 1 shows the UV–vis absorption spectra of the bisDM-FA–diTh–acceptor series, (**1**, **2**, and **3**) in chlorobenzene solution and thin films, and the corresponding optical properties are summarized in Table 1. As shown in Fig. 1, the absorption spectra of **1** (black) and **2** (red) in chlorobenzene (solid line) showed typical two transition bands with the moderate molar absorptivities in wavelength region of 300–700 nm¹³: (**1**) 38,000 M⁻¹ cm⁻¹ at 367 nm, 22,000 M⁻¹ cm⁻¹ at 493 nm and (**2**) 66,500 M⁻¹ cm⁻¹ at 356 nm, 34,000 M⁻¹ cm⁻¹ at 510 nm. The first peak at shorter wavelength could be assigned to the π – π * transition and the second peak at longer wavelength should result from an ICT between TPA donor and 2,2′-bithiophene (BT) acceptor. These π – π * and ICT transitions originate in the highest occupied molecular orbital (HOMO)–1 → lowest unoccupied molecular orbital (LUMO) and the HOMO→LUMO monoexcitations, respectively. The ICT band between bisDMFA donor and DCBP acceptor



Scheme 1. Molecular structures of the bisDMFA-diTh-acceptors and device architecture of solution-processed small molecule organic solar cell.

2. Results and discussion

The synthetic methods are outlined in Scheme 2. All reactions were carried out under a nitrogen atmosphere. 5'-(4-(Bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)phenyl)-2,2'-bithiophene-5-car-baldehyde (**i**), *N*-(4-bromophenyl)-*N*-(9,9-dimethyl-9*H*-fluoren-2-yl)-9,9-dimethyl-9*H*-fluoren-2-amine (**ii**), 5-iodo-5'-nitro-2,2'-bithiophene (**iii**), 2-(2-*tert*-butyl-6-methyl-4*H*-pyran-4-ylidene)

of **2** showed ~ 17 nm red-shift and ~ 1.6 times higher intensity than that of **1** due to the more elongated π -conjugation length and the higher electron-withdrawing strengths of DCBP acceptor compared to that of NO₂ acceptor. Meanwhile, **3** (blue) exhibited three transition bands, showing the absorption in whole visible region. The three peaks at 365 nm, 489 nm, and 630 nm could be also assigned to the transition conducted by the HOMO–2→LUMO (365 nm), HOMO– $-1 \rightarrow$ LUMO, (489 nm) and the HOMO→LUMO (630 nm)



Scheme 2. Schematic diagram for the synthesis of the bisDMFA-diTh-acceptors (NO₂ (1), DCBP (2), TCF (3)).



Fig. 1. UV–vis absorption spectra of the bisDMFA–diTh–acceptors [**1** (black), **2** (red), and **3** (blue)] in chlorobenzene solution (solid line) and thin films (dashed line).

monoexcitations, respectively.¹⁴ Also, the ICT transition observed as third peak of **3** was more intensive than the other π – π * transitions, which provide the ICT transition state between TPA donor and TCF acceptor as dominant excitation, even though the ICT bands of **1** and **2** showed the less intensive than their π – π * transition bands. Moreover, the ICT band of **3** exhibited the ~2 times and ~1.4 times more

intensive and significantly \sim 137 nm and \sim 120 nm red-shifted absorption compared to those of **1** and **2**, respectively, because of the better electron-withdrawing characteristics by three CN groups of TCF acceptor.

In solid-state thin film, the π -conjugated organic materials often show the red-shifted absorption bands and broaden spectra by the intermolecular π – π packing interaction than those in solution.¹⁵ But, **1** in solid-state exhibited a little bit red-shifted absorption spectrum and **2** and **3** in solid-state exhibited only broaden spectra without significant band-shifts to longer wavelength region. On the basis of these observations, it seems that the intermolecular packing interactions in solid-state film could be interrupted by the amorphous non-planar bisDMFA and affected by the spatial size of acceptors.

Fig. 2 shows the optimized structure of bisDMFA—diTh—acceptor series, (**1**, **2**, and **3**), which were calculated by the time dependentdensity functional theory (TD-DFT) using the B3LYP functional/6-31G* basis set. The orbital density of highest occupied molecular orbital (HOMO) of **1**, **2**, and **3** were evenly distributed on bisDM-FA—bithophene—acceptor, but the orbital density of lowest unoccupied molecular orbital (LUMO) of these materials was predominantly located on the electron accepting core and thiophene bridge, showing a general orbital distribution like push—pull organic semiconductors. These calculations reveal that the ICT from bisDMFA to acceptor core can effectively occur in **1**, **2**, and **3**, absorbed the photon energy, and the bisDMFA can especially play a role for stabilizing of hole separated from exciton and improve the transport property of hole carrier.

Table 1

Optical, redox parameters of the bisDMFA-diTh-acceptors [1, 2, and 3]

Compounds	$\lambda_{abs}^{a}/nm (\epsilon/M^{-1} cm^{-1})$	$E_{\text{onset,ox}}$ (V)/HOMO (eV) ^b	$E_{\text{onset,red}}$ (V)/LUMO (eV)	E_{onset}^{c} (eV)	E_{0-0}^{d} (eV)
1	367 (38,000), 493 (22,000)	0.308/-5.108	-1.202/-3.51	2.08	1.97
2	356 (66,500), 510 (34,000)	0.197/-4.997	-1.287/-3.513	2.05	1.99
3	365 (40,500), 489 (25,000), 630 (46,000)	0.221/-5.021	-1.000/-3.800	1.69	1.58

^a Absorption spectra were measured in chlorobenzene solution.

^b Redox potential of the compounds were measured in CH₂Cl₂ with 0.1 M (*n*-C₄H₉)₄NPF₆ with a scan rate of 100 mVs⁻¹.

^c *E*_{onset} was calculated from the onset from absorption spectra in chlorobenzene solution.

^d E_{0-0} was calculated from the absorption thresholds from absorption spectra in chlorobenzene solution.



Fig. 2. Isodensity surface plots of bisDMFA-diTh-acceptors [1, 2, and 3], calculated by the time dependent-density functional theory (TD-DFT) using the B3LYP functional/6-31G* basis set.

Fig. 3 shows the cyclic voltammograms of the bisDM-FA-diTh-acceptor series, (**1**, **2**, and **3**) in methylene chloride solution. And the corresponding electrochemical properties are also



Fig. 3. Electrochemical characterization of the bisDMFA-diTh-acceptors [1 (black), 2 (red), and 3 (blue)] in dichloromethane/TBAHFP (0.1 M), scan speed 100 mV/s, potentials.

summarized in Table 1. The energy levels of HOMO and LUMO of these materials were determined from these cyclic voltammetry (CV) spectra. A platinum rod electrode, a platinum wire, and an Ag/ AgNO₃ (0.10 M) electrode were used as the working electrode, as the counter electrode, and as the reference electrode, respectively. The analysis were performed in an electrolyte consisting of a solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in methylene chloride at room temperature under nitrogen with a scan rate of 100 mV/s and ferrocenium/ferrocene redox couple was used as an external reference. The HOMO and LUMO levels can be deduced from the oxidation and reduction onsets with the assumption that the energy level of ferrocene (Fc) is 4.8 eV below vacuum level. The CV of these materials in solid-state thin film could not be measured due to the stripping of film on electrode. Therefore, we determined the optical bandgap from calculation of the absorption thresholds from absorption spectra of bisDM-FA-diTh-acceptor series in chlorobenzene. The HOMO levels of 1, 2, and 3 determined in solution by CV are calculated as 5.108 eV, 4.997 eV, and 5.021 eV, respectively. From these results, we can roughly guess that the Voc of devices fabricated using these materials/PCBM BHJ active layers may be in 0.7–0.9 eV, respectively.¹⁶

The photophysical characteristics of bisDMFA-diTh-acceptor series, (1, 2, and 3) were investigated through the application of

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photovoltaic device fabricated with these materials/ $C_{61(or 71)}$ -PCBM BHJ films. In the course of studying the characteristics of over 200 solar cells, the most efficient photovoltaic cells fabricated using of [bisDMFA–diTh–acceptor/ C_{71} -PCBM were optimized at ratio of 1:3 (**1** and **3**) or 1:2 (**2**) approximately. These BHJ films were cast on top of PEDOT:PSS (Heraeus, AI 4083) layer. The optimum thicknesses of these materials, **1**, **2**, and **3** based BHJ films obtained under these conditions were approximately 90 nm, 95 nm, and 80 nm, respectively. Fig. 4a shows the UV–vis absorption spectra of the bisDMFA–diTh–acceptor [**1** (black), **2** (red), and **3** (blue)]/ C_{71} -PCBM (1:3) films. As shown in Fig. 4a, the absorption bands of these materials in BHJ composites with C_{71} -PCBM were red-shifted ~10 nm and broaden to the longer wavelength compared to that of its pristine films shown in Fig. 1.

To investigate the space-charge effects, we extracted the hole mobilities of these organic semiconductors from the space-charge limitation of current (SCLC) J-V characteristics obtained in the dark for hole-only devices. We measured the average of hole mobility for 20 cells at three times per one cell in order to compensate for causable error. Fig. 4b shows the dark-current characteristics of hole-only ITO/PEDOT:PSS/bisDMFA-diTh-acceptor:C₇₁-PCBM/Au devices as a function of the bias corrected by the built-in voltage determined from the difference in work function between Au and the HOMO level of these materials. The Ohm's law can be observed at low voltages as an effect of thermal free carriers. For the presence of carrier traps in the active layer, there is a trap-filled-limit (TFL) region between the ohmic and the trap-free SCLC regions. The SCLC behavior in the trap-free region can be characterized using the Mott–Gurney square law (Eq. 1).¹⁷



Fig. 4. (a) UV–vis absorption spectra and (b) space-charge limitation of current J-V characteristics of the bisDMFA–diTh–acceptors/C₇₁-PCBM [**1** (black), **2** (red), and **3** (blue)] BHJ films, which hole-only devices (ITO/PEDOT:PSS/Donor:C₇₁-PCBM/Au).

$$J = (9/8)\varepsilon \cdot \mu \left(V^2 / L^3 \right) \tag{1}$$

where ε is the static dielectric constant of the medium and μ is carrier mobility. The hole mobilities of bisDMFA-diTh-acceptor series, [1 (black), 2 (red), and 3 (blue)] evaluated using the above Mott–Gurney Law $(\varepsilon = 3\varepsilon_0)$, were $4.03 \times 10^{-5} \text{ cm}^2/\text{V s}$ $2.00 \times 10^{-5} \text{ cm}^2/\text{V} \text{ s}$, and $1.28 \times 10^{-5} \text{ cm}^2/\text{V} \text{ s}$, respectively. Compound **1** exhibited about 2 times and 3.1 times higher hole mobility than those of **2** and **3**, respectively. It was interestingly found that these hole mobilities were contrary to the electron-withdrawing strength of acceptors. The hole mobilities of p-type organic semiconductors observed in these BHI films might be closely related to the charge stability separated from excition as well as the intermolecular packing interaction, leading to the increase of transporting property of hole carrier. The bisDFMA donor can stabilize the separated hole from exciton. Therefore, we note that the bulk substituents such as *tert*-butyl group of DCBP acceptor or dimethyl group of TCF acceptor might spatially interrupt the intermolecular packing interaction in BHJ system with PCBM. These BHJ films of C₇₁-PCBM and **2** (or **3**) containing the bulk DCBP (or TCF) also exhibited the rougher surface morphology than that of 1, showing higher root mean square (rms) values, which were investigated with atomic force microscopy (AFM) analysis (see Fig. S3 of Supplementary data).

Fig. 5 shows the current (J)–voltage (V) curves under AM 1.5 conditions (100 mW/cm²) and incident-photon-to-current efficiency (IPCE) spectra of bisDMFA–diTh–acceptors [**1** (black), **2** (red), and **3** (blue)]/C₇₁-PCBM BHJ solar cells fabricated under



Fig. 5. (a) Current (*J*)–voltage (*V*) curves under AM 1.5 conditions (100 mW/cm²) and (b) IPCE spectra of the bisDMFA–diTh–acceptors/C₇₁-PCBM [**1** (black), **2** (red), and **3** (blue)] BHJ solar cells fabricated under optimized processing condition with (solid line)/without (dashed line) insertion of TiO_x layer.

optimized processing condition. The corresponding values are summarized in Table 2. The IPCE spectra of these devices as shown in Fig. 5b exhibit well-matched curves with their optical absorptions, resulting in the close correlation with their photocurrents in J-V curves.

Table 2

Photovoltaic performances of the devices fabricated with the bisDM-FA-diTh-acceptors $[1, 2, and 3]/C_{71}$ -PCBM BHJ films^a

Organic semiconductor	Functional layer	$J_{\rm sc}$ (mA cm ⁻²)	$V_{\rm oc}\left({\sf V}\right)$	FF (%)	η (%)
1	None	7.40 ± 0.1	$\textbf{0.77} \pm \textbf{0.1}$	35 ± 2.0	1.98 ± 0.25
1	TiO _x	8.19 ± 0.3	$\textbf{0.83} \pm \textbf{0.1}$	40 ± 2.2	$\textbf{2.70} \pm \textbf{0.3}$
2 ^b	None	6.80 ± 0.13	0.85 ± 0.08	35 ± 1.8	2.01 ± 0.21
3 ^b	None	$\textbf{6.26} \pm \textbf{0.2}$	0.80 ± 0.09	33 ± 1.7	1.68 ± 0.18

^a The photovoltaic characteristics are performed under simulated 100 mW/cm² AM 1.5G illumination. The light intensity using calibrated standard silicon solar cells with a proactive window made from KG5 filter glass traced to the National Renewable Energy Laboratory (NREL). The masked active area of device is 4 mm².

 $^{\rm b}$ The devices fabricated with this BHJ films were optimized after post-annealing at 100 $^\circ \rm C$ for 10 min.

As shown in Fig. 5 and Table 2, the devices conventionally fabricated with 1/C71-PCBM, 2/C71-PCBM, and 3/C71-PCBM exhibited a PCE of 1.98% (± 0.17) with short circuit current (I_{sc})= 7.40 mA/cm², fill factor (FF)=0.35, and open circuit voltage (V_{oc})= 0.77 V, a PCE of 2.01% (\pm 0.21) with I_{sc} =6.80 mA/cm², FF=0.35, and $V_{0c}=0.84$ V, and a PCE of 1.68% (±0.23) with $I_{sc}=6.26$ mA/ cm^2 , FF=0.33, and V_{oc} =0.80 V, respectively. Although **3** showed the absorption band covering the whole visible region, the solution-processed SMOSCs fabricated with 3/C71-PCBM exhibited the less J_{sc} value than those of $1/C_{71}$ -PCBM or $2/C_{71}$ -PCBM BHJ film. This might be mainly originated from the low IPCE value in longer wavelength region, indicating the facile recombination of separated charges from the excitons conducted by monoexcitation in ICT transition band especially. These results were consistent with their hole mobilities obtained by SCLC J-V characteristics shown in Fig. 4b. For these results, in order to increase the efficiency of the device with especially 1 due to its highest photocurrent, we used the TiO_x thin layer that can play the effective roles of optical spacer and buffer layer through the insertion between $1/C_{71}$ -PCBM BHJ layer and Al electrode.¹⁸ The best PCE of 2.70% (\pm 0.25) in devices fabricated using $1/C_{71}$ -PCBM film with TiO_x layer was observed with J_{sc} =8.19 mA/cm², FF=0.40, and $V_{\rm oc}$ =0.83 V, which showed the further improvements of all photovoltaic parameters, resulting in \sim 36% higher efficiency than that without TiO_x layer.

In conclusion, we have demonstrated the synthesis and photovoltaic characteristics of new efficient push-pull organic semiconductors comprising of on the bis(9,9-dimethyl-9H-fluoren-2-yl) aniline (bisDMFA) donor and the various acceptors, bisDM-FA-diTh-NO₂ (1), bisDMFA-diTh-DCBP (2), and bisDMFA-diTh-TCF (3), which were linked with bithiophene or vinyl bithiophene π conjugation bridges, in solution-processed SMOSC. These materials showed the strong intramolecular charge transfer between bisDMFA donor and acceptors (NO₂, DCBP, or TCF). Especially, the ICT band of **3** was significantly red-shifted above 120 nm compared to those of **1** and **2** because of the better electron-withdrawing characteristics by three CN groups of TCF acceptor. We also found that the bulk substituents such as tert-butyl group of DCPB acceptor or dimethyl group of TCF acceptor might spatially interrupt the intermolecular packing interaction in BHJ system with PCBM. The best performances were observed in the devices fabricated with $1/C_{71}$ -PCBM BHJ material that could be significantly improved by means of insertion of TiO_x thin layer between photoactive layer and Al electrode. These results obtained from the facile structural modifications using various accepting units of organic semiconductor shown in this study can give an important guide for developing new materials in solution-processed small molecule BHJ solar cell.

3. Experimental section

3.1. General methods

Solvents were distilled from appropriate reagents. All reagents were purchased from Sigma-Aldrich, TCI, and Alfa Aesar. All reactions were carried out under a nitrogen atmosphere. And [6,6]phenyl-C71-butyric acid methyl ester (C71-PCBM) was obtained from Nano-C. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury 300 spectrometer. Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard unless otherwise indicated, and coupling constants in hertz. Elemental analyses were performed with a Carlo Elba Instruments CHNS-O EA 1108 analyzer. Mass spectra were recorded on a JEOL JMS-SX102A instrument. UV-vis data were measured with a Perkin-Elmer Lambda 2S UV-visible spectrometer. Optimized structures calculated by TD-DFT using the B3LYP functional and the 6-31G* basis set. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies were determined using minimized singlet geometries to approximate the ground state. Cyclic voltammetry was carried out with a BAS 100B (Bioanalytical System, Inc.). A threeelectrode system was used and consisted of non-aqueous reference electrode (0.1 M Ag/Ag⁺ acetonitrile solution; MF-2062, Bioanalytical System, Inc.), platinum working electrode (MF-2013, Bioanalytical System, Inc.), and a platinum wire (diam. 1.0 mm, 99.9% trace metals basis, Sigma-Aldrich) as counter electrode. Redox potentials of materials were measured in CH₂Cl₂ with 0.1 M $(n-C_4H_9)_4N-PF_6$ with a scan rate between 100 mVs⁻¹ (vs Fc/Fc⁺). Atomic force microscope (AFM) measurements were performed with a Digital Instruments NanoScope IV in the tapping mode. All FTIR measurements were performed using a Nicolet 6700 FT-IR (Thermo Scientific) spectrometer operating in the 4000–400 cm⁻¹ wavenumber range (mid-infrared). Melting point was measured by Melting Point B-540 (BÜCHI).

3.2. Fabrication of solar cell devices

The BHJ films were prepared under optimized conditions according to the following procedure reported previously:¹⁹ the indium tin oxide (ITO)-coated glass substrate was first cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried overnight in an oven. PEDOT:PSS (Heraeus, Clevios P VP.AI 4083) in aqueous solution was spin-cast to form a film with thickness of approximately 35 nm. The substrate was dried for 10 min at 140 °C in air, then transferred into a glove box to spin-cast the photoactive layer. The optimized bisDM-FA-diTh-acceptor series:C₇₁-PCBM BHJ materials were blended with 1:2 or 1:3 weight ratio in chlorobenzene at a concentration of 30 mg/mL. These solutions were then spin-cast on top of the PEDOT layer. The substrate was dried for 10 min at 80 °C in air. Then, the device was pumped down to lower than 10^{-7} Torr and a ~ 100 nm thick Al electrode was deposited on top.

3.3. Characterization of solar cell devices

Solar cells efficiencies were characterized under simulated 100 mW/cm² AM 1.5G irradiation from a Xe arc lamp with an AM 1.5 global filter. The light intensity was adjusted with a Si solar cell that was double-checked with an NREL-calibrated Si solar cell (PV Measurement Inc.). The applied potential and measured cell current were measured using a Keithley model 2400 digital

source meter. The current—voltage characteristics of the cell under these conditions were determined by biasing the cell externally and measuring the generated photocurrent. This process was fully automated using Wavemetrics software. The IPCE spectra for the cells were measured on an IPCE measuring system (PV measurements).

3.4. Synthesis of 4-(bis((9,9-dimethyl-9H-fluoren-2-yl)amino) phenyl)-2-(5'-nitrothiophen-2'-yl)thiophen (bisDMFA-diTh-NO₂, 1)

Under nitrogen atmosphere and at -10 °C, n-BuLi (0.68 ml, 1.6 M in hexane, 1.09 mmol) was added drop-wise to a dry THF solution containing N-(4-bromophenyl)-N-(9,9-dimethyl-9H-fluoren-2-yl)-9,9-dimethyl-9H-fluoren-2-amine (i, 0.5 g, 0.89 mmol). After 30 min stirring at -10 °C, 0.3 ml (1.47 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added slowly to the reaction solution at -10 °C. The temperature of the solution was warmed to room temperature and the reaction mixture was stirred for 1 h. Then, guench the reaction with deionized water. The solution was extracted with dichloromethane, dried with MgSO₄, and then a solvent was evaporated with a rotary evaporator. A light yellow solid (silica gel TLC plate, ethyl acetate/hexane=1:10, R_{f} =0.2) was obtained. Without further purification, this compound (0.2 g, 0.33 mmol) was mixed with 5-iodo-5'-nitro-2,2'-bithiophene (E, 0.1 g, 0.296 mmol), Pd(PPh₃)₄ (0.02 g, 0.017 mmol), K₂CO₃ (0.18 g, 1.3 mmol), a drop of Aliguat 336, and degassed water (2 M) in dry toluene (25 ml), then refluxed under nitrogen atmosphere for overnight. After cooling to room temperature, the solution was extracted with dichloromethane, dried with MgSO₄, and subjected to column chromatography (silica gel, dichloromethane/ hexane=1:4, R_f=0.1). A purple solid was obtained. Yield: 85% (0.17 g). Mp: 136–138 °C. Mass: m/z 668.50 [M⁺]. IR: 1322 cm⁻¹, 1446 cm⁻¹ (NO₂). ¹H NMR (300 MHz, CDCl₃): δ 7.86 (d, 1H, J=4.5 Hz), 7.68 (d, 2H, J=6.9 Hz), 7.64 (d, 2H, J=7.8 Hz), 7.51 (d, 2H, J=8.4 Hz), 7.41 (d, 2H, J=7.8 Hz), 7.35-7.18 (m, 10H), 7.15 (dd, 2H, J=7.8, 1.8 Hz), 7.08 (d, 1H J=4.2 Hz), 1.43 (s, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 155.31, 153.63, 148.55, 147.41, 146.79, 145.65, 138.89, 134.93, 132.93, 130.01, 129.58, 127.87, 127.16, 126.81, 123.74, 123.38, 123.27, 122.64, 121.94, 120.83, 119.64, 119.24, 47.06, 27.24. Anal. Calcd for C44H34N2O2S2: C, 76.94; H, 4.99. Found: C, 76.77; H, 4.90.

3.5. Synthesis of (*E*)-2-(2-(2-(5'-(4-(bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)phenyl)-2,2'-bithiophen-5-yl)vinyl)-6*tert*-butyl-4*H*-pyran-4-ylidene)malononitrile (bisDMFA-diTh-DCBP, 2)

2-(2-tert-Butyl-6-methyl-4H-pyran-4-ylidene)malononitrile (iii, 39 mg, 0.18 mmol) and piperidine (3-5 drops) were added to a solution of 5'-(4-(bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-2,2'-bithiophene-5-carbaldehyde (ii, 80 mg, 0.12 mmol) in CHCl₃/CH₃CN (1:1, 10 ml:10 ml) at room temperature. The reaction mixture was heated under reflux for 24 h. Concentration and purification of the residue by flash column chromatography (hexane/ ethyl acetate=5:1, R_f =0.3) gave the product (dark red solid, 69 mg, 70%). Mp: 185–188 °C. Mass: *m*/*z* 865.21[M⁺]. IR: 2210 cm⁻¹ (CN). ¹H NMR (300 MHz, DMSO-*d*₆): δ 7.79–7.71 (m, 5H), 7.65–7.62 (m, 2H), 7.54-7.40 (m, 6H), 7.34-7.28 (m, 6H), 7.12-7.05 (m, 5H), 6.97 (s, 1H), 6.44 (s, 1H), 1.38 (s, 9H), 1.36 (s, 12H). ¹³C NMR (75 MHz, DMSO-d₆): δ 185.1, 172.3, 166.3, 159.0, 156.0, 154.7, 153.0, 146.1, 138.5, 137.9, 133.9, 132.5, 129.8, 128.5, 126.7, 126.4, 126.1, 124.6, 123.2, 123.0, 122.8, 122.6, 122.2, 120.7, 119.2, 118.4, 117.3, 117.1, 106.3, 50.5, 46.1, 29.0, 27.2, 26.4. Anal. Calcd for C₅₈H₄₇N₃OS₂: C, 80.43; H, 5.47. Found: C, 80.20; H, 5.42.

3.6. Synthesis of (*E*)-2-(4-(2-(5'-(4-(bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)phenyl)-2,2'-bithiophen-5-yl)vinyl)-3-cyano-5,5-dimethylfuran-2(5*H*)-ylidene)malononitrile (bisDMFA-diTh-TCF, 3)

2-(3-Cvano-4.5.5-trimethylfuran-2(5H)-vlidene)malononitrile (iv. 35.9 mg, 0.18 mmol) and piperidine (3–5 drops) were added to a solution of 5'-(4-(bis(9.9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-2,2'-bithiophene-5-carbaldehyde (ii, 80 mg, 0.12 mmol) in CHCl₃/CH₃CN (1:1, 10 ml:10 ml) at room temperature. The reaction mixture was heated under reflux for 24 h. Concentration and purification of the residue by flash column chromatography (hexane/ ethyl acetate=2:1, R_f =0.2) gave the product (dark blue solid, 68 mg, 69%). Mp: 317–319 °C. Mass: *m*/*z* 850.18 [M⁺]. IR: 2225 cm⁻¹ (CN). ¹H NMR (300 MHz, DMSO- d_6): δ 8.14 (d, 1H J=15.9 Hz), 7.83–7.75 (m, 6H), 7.68-7.51 (m, 7H), 7.31-7.27 (m, 6H), 7.12-7.06 (m, 3H), 6.76 (d, 1H, J=15.9 Hz), 1.79 (s, 6H), 1.38 (s, 12H). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 176.3, 174.1, 154.7, 153.0, 147.5, 146.0, 145.1, 144.1, 139.4, 138.2, 137.9, 137.2, 134.1, 133.3, 127.8, 126.7, 126.4, 126.3, 125.5, 124.0, 123.2, 122.4, 122.2, 120.7, 119.2, 118.5, 112.7, 112.3, 111.5, 110.5, 98.3, 55.7, 46.1, 26.4, 25.1, 18.1. Anal. Calcd for C₅₆H₄₂N₄OS₂: C, 79.03; H, 4.97. Found: C, 78.85; H, 4.88.

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Supplementary data

Supplementary data related to this article can be found in the online version, at doi:10.1016/j.tet.2012.03.061.

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