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Low band gap conjugated small molecules containing benzobisthiadiazole and thienothiadiazole central units: synthesis and application for bulk heterojunction solar cells

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Two novel conjugated low band gap small molecules (SMs), **M1** and **M2**, containing benzobisthiadiazole and thienothiadiazole central units, respectively, were synthesized. Both SMs carried terminal cyanovinylene 4-nitrophenyl at both sides which were connected to the central unit with a thiophene ring. The long-wavelength absorption band was located at 591–643 nm and the optical band gap was 1.62–1.63 eV, which is lower than that of P3HT. These two SMs were investigated as electron donor materials along with PCBM or **F** as electron acceptors for fabrication of bulk heterojunction (BHJ) organic photovoltaic devices. **F** is a modified PCBM which has been previously synthesized and used as an electron acceptor for poly(3-hexylthiophene) (P3HT). The power conversion efficiency (PCE) for **M1**:PCBM, **M1**:**F**, **M2**:PCBM and **M2**:**F** was 1.05%, 2.02%, 1.23% and 2.72%, respectively. The higher PCE for the devices with **M2** as the electron donor has been related to the improved hole mobility for **M2**. However, the improved PCE for the devices with **F** as the electron acceptor has been attributed to the more intense absorption of **F** in the visible region than that of PCBM and also to the higher open circuit voltage resulting from the higher LUMO level of **F**. We have also fabricated devices with **M2**:**F** cast film from mixed solvents. The PCE for the BHJ devices with the as cast and thermally annealed **M2**:**F** (mixed solvents) is 3.34% and 3.65%, respectively.

Introduction

Organic solar cells using conjugated molecular materials have become increasingly feasible through the development of bulk heterojunction (BHJ) structures based on intimate blends of polymeric donors and soluble fullerene acceptors,¹⁻⁴ where efficient exciton separation is enabled by a large-area donor– acceptor interface.^{5,6} The attractive features of this type of solar cells include the ease of solution-processing, low costs, light weight, and the potential application in flexible large-area devices.⁷⁻⁹ So far, such devices based on polymer/fullerene blends have achieved high power conversion efficiencies (PCEs) of more than 6%.¹⁰⁻¹⁴ Recently, Liang *et al.* have reported PCE about 7.4% for the BHJ photovoltaic (PV) device based on the blend film of PTB7 with PC71BM. 15

In recent years, BHJ solar cells utilizing solution-processable small molecules as the active layer have been also actively studied.^{16–26} Although the PCEs are still behind those of polymer-based devices, solution-processable small molecule-based solar cells have the advantage that, for example, they are intrinsically monodisperse, have well-tunable physicochemical properties, provide important reproducibility in device fabrication, and typically show higher charge carrier mobilities.²⁷ At the same time, devices of this class can improve the efficiency of the process and greatly reduce fabrication costs, compared with the vacuum-deposited small molecule-based devices. Up to now, the best results of organic PV cells made by solution-processable small molecule heterostructures were reported by Nguyen^{24–26} and coworkers. According to these results, the PCEs have been improved to 2.3%, 3.0% and 4.4% very recently.

The benzo[1,2-c;4,5-c']bis[1,2,5]thiadiazole (BBT) unit (structure **A**, Scheme 1) is a strong electron accepting unit that has been used to make low band gap donor–acceptor materials. This has potential applications in light-emitting devices (LED), ambipolar organic field-effect transistors (OFETs), and solar cells. As a sign of the effectiveness of BBT in promoting low band gaps, even the small oligomers of **B** and **C** (Scheme 1) are reported to possess band gaps of only 1.5 eV.²⁸⁻³⁰ Oligomer **C** has been used as

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Scheme 1 Chemical structures of BBT (A) and some low band gap 4,8disubstituted BBT derivatives (B and C). Chemical structure of 4,6-di-(2-thieny)thieno[3,4-*c*][1,2,5]thiadiazole (D).

emissive material in an LED displaying efficient emission in the near-infrared region (NIR).²⁸ Polymeric films obtained by electropolymerization of **B** and **C** display band gaps of about 0.5 eV.^{29,30} The small band gaps observed in these materials can be attributed to the high electron affinity and large quinoid contribution of the BBT unit.²⁸⁻³⁰ A literature survey revealed that structure **B** has been introduced in the design of low band gap copolymers,³¹⁻³⁴ which however have not been used for solar cells. Moreover, a one-pot synthesis of the dibromo derivative of **A** has been recently reported.³⁵

On the other hand, 4,6-di(2-thienyl)thieno[3,4-c][1,2,5]thiadiazole (structure **D**, Scheme 1) is a highly planar terthiophene derivative first prepared by Tanaka and Yamashita.³⁶ Its central thienothiadiazole (TTD) moiety has an electron-acceptor nature; its longest wavelength UV-vis absorption maximum lies at 620 nm. It is, therefore, interesting as a dopant for BHJ PV cells in blends with polythiophenes, but even more as a building block for the syntheses of low band-gap thiophene-based oligomers and donor–acceptor copolymers absorbing light in a great part of the solar spectrum. Certain low band gap copolymers containing the structure **D** have been synthesized, but not used for solar cells.^{37–39}

Recently, a series of low band gap small molecules (SMs) containing cyanovinylene 4-nitrophenyl segments have been synthesized and used as donors with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as acceptor for BHJ solar cells.⁴⁰⁻⁴⁴ Moreover, we have very recently synthesized a modified PCBM derivative **F** (Scheme 2) which contains cyanovinylene 4-nitrophenyl segments.⁴⁵ In particular, PCBM has been hydrolyzed to carboxylic acid and then it was converted to the corresponding carbonyl chloride. The latter was condensed with 4-nitro-4'-hydroxy- α -cyanostilbene to afford **F**. It was more soluble than PCBM in common organic solvents due to the increase of the organic moiety. Both solutions and thin films of **F** showed stronger absorption than PCBM in the range of 250–900 nm. BHJ solar cells based on P3HT as electron donor with **F** as electron acceptor displayed a PCE of 4.23%, while the device

F

Scheme 2 Chemical structure of F.

based on P3HT:PCBM displayed a PCE of 2.93% under the same conditions. 45

Herein, we describe the synthesis of two novel symmetrical conjugated low band gap SMs, M1 and M2, containing BBT and TTD central units, respectively. These SMs have certain common structural characteristics. In particular, they carry terminal cyanovinylene 4-nitrophenyl segments at both sides, which were connected to the central unit with a thiophene ring. Both central unit and terminal segments are strong electron acceptors. M1 and M2 were successfully synthesized by eight- and seven-step reaction respectively. The last step of their synthesis included the condensation of a key dialdehyde with 4-nitrobenzylcyanide. These SMs were used as candidates (electron donors) along with PCBM or modified PCBM i.e. F (electron acceptors) for BHJ organic solar cells. To the best of our knowledge, other materials based on **B** and **D** (Scheme 1) have not been previously utilized for PV applications. The PCE for the devices with M1:PCBM, M1:F, M2:PCBM and M2:F blends is 1.05%, 2.02%, 1.23% and 2.72%, respectively. The PCE for the devices based on the as cast and thermally annealed M2:F blend cast from mixed solvents (chlorobenzene/THF) has been further improved to 3.34% and 3.65%, respectively. We show here that, unlike the conjugated polymer based blended films, the absorption and crystallinity as well as the solar cell device characteristics of both as cast and thermally blended films based on SM donors and PCBM acceptor are significantly affected.

Experimental

Reagents and solvents

Nitrobenzylcyanide was synthesized from the nitration of benzyl cyanide with concentrated nitric and sulfuric acid.⁴⁶ It was recrystallized from ethanol. *N*,*N*-Dimethylformamide (DMF) and tetrahydrofuran (THF) were dried by distillation over CaH₂. All other reagents and solvents were commercially purchased and were used as supplied.

Preparation of compounds

Compound 7. A flask was charged with a solution of **6** (0.3662 g, 1.02 mmol) in DMF (1.19 g, 16.32 mmol). POCl₃ (1.72 g, 11.22 mmol) was added dropwise to the solution at 0 °C. The mixture was subsequently refluxed for 20 h. After cooling to room temperature, a saturated aqueous solution of CH₃COONa (10 mL) was added and the mixture was stirred for 2 h at room temperature. Then, it was concentrated under reduced pressure and water was added to the concentrate. The precipitate was filtered and washed with water. The crude product was recrystallized from DMF/water (0.24 g, 56%).

FT-IR (KBr, cm⁻¹): 1704 (formyl); 2926, 1614, 1504, 1454 (aromatic); 852 (N=S).

¹H NMR (DMSO-d₆) ppm: 10.18 (s, 2H, formyl); 7.20–7.12 (m, 4H, thiophene).

Anal. Calcd for $C_{16}H_6N_4O_2S_4$: C, 46.36; H, 1.46; N, 13.52. Found: C, 45.86; H, 1.37; N, 13.68%.

Compound M1. A flask was charged with a solution of 7 (0.2285 g, 0.551 mmol) and 4-nitrobenzylcyanide (0.1787 g, 1.102 mmol) in DMF (15 mL). Sodium hydroxide (0.20 g. 5.00 mmol)

dissolved in ethanol (5 mL) was added to this solution. The reaction mixture was stirred for 1 h at room temperature under N_2 and then was concentrated under reduced pressure. Water was added to the concentrate and **M1** precipitated as a dark green solid. It was recrystallized from DMF/water (0.2685 g, 69%).

FT-IR (KBr, cm⁻¹): 2158 (cyano); 1520, 1346 (nitro); 2924, 1600, 1500, 1438 (aromatic); 852 (N=S).

¹H NMR (DMSO-d₆) ppm: 8.19 (m, 4H, phenylene *ortho* to nitro); 7.83 (s, 2H, cyanovinylene); 7.52 (m, 4H, phenylene *meta* to nitro); 7.04–6.97 (m, 4H, thiophene).

Anal. Calcd for C₃₂H₁₄N₈O₄S₄: C, 54.69; H, 2.01; N, 15.94. Found: C, 53.97; H, 1.96; N, 15.73%.

Compound 13. This compound was prepared in 49% yield (0.40 g) from the reaction of **12** (0.6280 g, 2.25 mmol) with DMF (2.63 g, 18.70 mmol) and POCl₃ (3.79 g, 24.75 mmol) according to the procedure described for compound **7**.

FT-IR (KBr, cm⁻¹): 1702 (formyl); 2922, 1592, 1508, 1458 (aromatic); 850 (N=S).

¹H NMR (DMSO-d₆) ppm: 10.02 (s, 2H, formyl); 7.21–7.11 (m, 4H, thiophene).

Anal. Calcd for $C_{14}H_6N_2O_2S_4$: C, 46.39; H, 1.67; N, 7.73. Found: C, 45.93; H, 1.75; N, 7.64%.

Compound M2. This compound was prepared in 75% yield (0.54 g) from the reaction of **13** (0.4004 g, 1.10 mmol) with 4nitrobenzylcyanide (0.3582 g, 2.20 mmol) in DMF (15 mL) in the presence of NaOH (0.20 g, 5.00 mmol) dissolved in ethanol (5 mL) according to the procedure described for compound **M1**.

FT-IR (KBr, cm⁻¹): 2158 (cyano); 1518, 1344 (nitro); 2926, 1600, 1500, 1436 (aromatic); 848 (N=S).

¹H NMR (DMSO-d₆) ppm: 8.14 (m, 4H, phenylene *ortho* to nitro); 7.83 (s, 2H, cyanovinylene); 7.53 (m, 4H, phenylene *meta* to nitro); 7.05–6.95 (m, 4H, thiophene).

Anal. Calcd for $C_{30}H_{14}N_6O_4S_4$: C, 55.37; H, 2.17; N, 12.91. Found: C, 54.82; H, 2.03; N, 12.86%.

Characterization methods

IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer with KBr pellets. ¹H NMR (400 MHz) spectra were obtained using a Bruker spectrometer. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. UV-vis spectra were recorded on a Beckman DU-640 spectrometer with spectrograde THF. Elemental analyses were carried out with a Carlo Erba model EA1108 analyzer.

The electrochemical properties (*i.e.* onset oxidation and reduction potentials) of SMs were studied by cyclic voltammetry (CV) (CH Instruments). We used an electrochemical cell with three electrodes in tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) in anhydrous acetonitrile solution at a scan rate of 100 mV s⁻¹ at room temperature. SM was deposited on a Pt disk, which was used as working electrode, while a Pt wire and an Ag/Ag⁺ were used as counter electrode and reference electrode, respectively.

Device fabrication and characterization

BHJ organic PV devices were fabricated through the solution processing technique. The patterned indium tin oxide (ITO)

glasses were subsequently cleaned with detergent, deionized (DI) water, acetone and isopropanol and then dried at room temperature for 30 min in ambient conditions. A thin layer of (3,4-ethylene di-oxythiophene):poly(styrenesulfonate) poly (PEDOT:PSS) with a thickness of 60 nm was formed on the ITO substrate by spin coating a PEDOT:PSS aqueous solution (Baytron) and baked at 80 °C for 30 min. The photoactive layers containing SMs (M1 or M2) and PCBM or F in a weight ratio of 1:1 were spin cast from THF solution or from chlorobenzene/ THF mixed solvents. The concentration of M1 or M2 and PCBM or F was kept 10 mg mL⁻¹ to make the blend. The thickness of the active layer was in the range of 80-85 nm. The organic films were dried in vacuum at room temperature. An aluminium (Al) cathode (80 nm) was then thermally evaporated under high vacuum ($\sim 10^{-5}$ Torr) through a shadow mask defining an active area of 0.05 cm².

The mixed solvents blend of **M2:F** was developed as follows. The blend solution of **M2:F** (1 : 1, w/w) was first prepared using THF at a concentration of 10 mg mL⁻¹ and stirred for 4 h. A 0.5 mL of chlorobenzene was added to 1 mL **M2:F** solution prepared in THF solvent, then stirred for another 2 h. The prethermal annealing of the active layer was carried out at 120 °C for 2 min on a hot plate before the deposition of the Al electrode.

The crystallinity of the films was studied using the X-ray diffraction (XRD) technique (panalytical make USA) having CuK α , as radiation source of wavelength $\lambda = 1.5405$ Å with the films coated on the quartz substrates.

Current–voltage (J-V) characteristics of the devices were measured using a computer controlled Keithley 238 source meter in the dark and under an illumination intensity of 100 mW cm⁻² under ambient conditions. A xenon light source (100 W) was used to give a simulated irradiance of 100 mW cm⁻² (equivalent to AM 1.5 irradiation) at the surface of the device. The J-Vcharacteristics of the devices having structure of ITO/ PEDOT:PSS/M1 or M2/Au were recorded and fitted with the space charge limited current model to find the hole mobilities. The hole and electron devices having structures ITO/ PEDOT:PSS/M2:F/Au and Al/M2:F/Al were fabricated, respectively to measure the hole and electron mobilities in the BHJ active layer.

The incident photon to current efficiency (IPCE) of the devices was measured by illuminating the device with a xenon lamp using a monochromator and measuring the resulting photocurrent with a Keithley electrometer under short circuit conditions. The IPCE was determined from the following expression:

IPCE (%) =
$$1240J_{sc}/\lambda P_{in}$$

where J_{sc} is the short circuit photocurrent and λ and P_{in} are the wavelength and illumination intensity of the incident light, respectively.

Results and discussion

Synthesis and characterization

Schemes 3 and 4 outline the synthetic route to M1 and M2 respectively. Compounds $1,^{47} 2,^{47} 3,^{48} 4,^{48} 5,^{48} 6,^{33} 8,^{49} 9,^{50} 10,^{51} 11^{48}$ and 12^{52} were synthesized according to the reported methods. Compounds 6 and 12 were formylated by reacting with





Scheme 4 Synthesis of M2.

DMF and POCl₃ to afford dialdehydes 7 and 13 respectively. The latter were condensed with 4-nitrobenzylcyanide in the presence of NaOH to give the target SMs M1 and M2 respectively. Even though these SMs lacked solubilising aliphatic chains and contained a rigid and compact central unit, they dissolved in common organic solvents. Specifically, they dissolved in THF, acetonitrile, dioxane as well as in polar aprotic solvents such as DMF, N,N-dimethylacetamide and N-methylpyrolidone. M1 showed lower solubility than M2, because BBT is more rigid than TTD.

The structural characterization of SMs was accomplished by FT-IR and ¹H NMR spectroscopy. They displayed common absorption bands approximately at 2158 (cyano); 1520, 1346 (nitro); 2930, 1600, 1500, 1436 (aromatic) and 850 cm⁻¹ (N=S inphase and out-of-phase stretching). On the other hand, the ¹H NMR spectra were very similar, since the proton-containing moieties were identical in both SMs. They showed upfield signals around 8.19 (aromatic *ortho* to nitro), 7.83 (cyanovinylene) and 7.52 ppm (aromatic *meta* to nitro). Finally, thiophene resonated approximately at 7.0 ppm.

Photophysical properties

Fig. 1 presents the UV-vis absorption spectra of SMs in both dilute (10^{-5} M) THF solution and thin film. These spectra were normalized by their long-wavelength absorption peak. Table 1 summarizes all photophysical and electrochemical properties of SMs. The absorption spectra covered the whole visible spectral region and extended from 300 nm up to approximately 760 nm, which is desirable for PV applications. The long-wavelength absorption maximum ($\lambda_{a,max}$) was at 591–643 nm. The $\lambda_{a,max}$ of **M1** was red shifted by 13–45 nm as compared to **M2** in both solution and thin film. This indicates that the absorption of structure **B** is bathochromically shifted relative to that of **D** (Scheme 1), because these SMs are differentiated only by their



Fig. 1 UV-vis absorption spectra of SMs in THF solution (top) and thin film (bottom).

central unit. In addition, the $\lambda_{a,max}$ of both SMs was red shifted by 7–39 nm upon going from solution to thin film due to intermolecular interactions in the solid state. **M1** and **M2** displayed Table 1 Optical and electrochemical properties of SMs

M1	M2
636	591 $(650)^d$
643	630
768	763
1.62	1.63
0.55	0.46
-1.20	-1.29
-5.25	-5.15
-3.50	-3.40
1.75	1.75
	M1 636 643 768 1.62 0.55 -1.20 -5.25 -3.50 1.75

^{*a*} $\lambda_{a,max}$: the absorption maxima from the UV-vis spectra in THF solution or thin film. ^{*b*} E_g^{opt} : optical band gap determined from the absorption onset in thin film. ^{*c*} E_g^{el} : electrochemical band gap determined from cyclic voltammetry. ^{*d*} Shoulder in the absorption spectrum.

similar thin film absorption onset at 768 and 763 nm, corresponding to an optical band gap (E_g^{opt}) of 1.62 and 1.63 eV respectively. These E_g^{opt} values are slightly lower than those (~1.67 eV) of other related SMs containing terminal cyanovinylene 4-nitrophenyl.⁴⁰⁻⁴⁴ This feature was attributed to the contribution of the central unit.

Electrochemical properties

The HOMO and LUMO levels of donor materials strongly affect the open circuit voltage (V_{oc}) and the charge separation efficiency of the OPVs. The HOMO and LUMO levels of **M1** and **M2** were studied by CV as shown in Fig. 2. The oxidation (E_{onset}^{ox}) and reduction (E_{onset}^{red}) potentials vs. Ag/Ag⁺ summarized in Table 1 were used for the calculation of the HOMO and LUMO according to the following equations:⁵³

$$E_{\rm HOMO} = -q \ (E_{\rm onset}^{\rm ox} + 4.70) \ eV$$

$$E_{\text{LUMO}} = -q \left(E_{\text{onset}}^{\text{red}} + 4.70 \right) \text{eV}$$

The HOMO and LUMO levels are -5.25 eV and -3.50 eV for M1, and -5.15 eV and -3.40 eV for M2, respectively. The electrochemical band gap (E_g^{el}) , calculated from CV, is slightly higher than the optical band gap (E_g^{opt}) , estimated from the onset absorption edge in films, which is a common phenomenon for organic semiconducting materials reported in the literature.⁵⁴ Compared with the P3HT, the HOMO and LUMO of both M1 and M2 shift to lower energy values, indicating higher stability against oxidation which is an advantage for solar cell applications.55 It has been already reported that the LUMO level of the acceptor should be at least 0.3 eV lower than that of the donor to drive charge separation after exciton generation. These deep lying HOMO levels and sufficient LUMO offsets allow these new SMs to act as electron donors, when they are coupled with an electron acceptor i.e. PCBM or F. In addition, the deeper HOMO level of M1 and M2 is beneficial for higher $V_{\rm oc}$ of organic solar cells as donor materials. The energy levels of M1 and M2 (donor) together with those of PCBM and F (acceptor) are schematically shown in Fig. 3. The LUMO levels of M1 and M2



Fig. 2 Cyclic voltammetry curves for M1 and M2 film on Pt electrode in acetonitrile solution of 0.1 mol L^{-1} Bu₄NPF₆ electrolyte with a scan rate of 100 mV s⁻¹.



Fig. 3 Energy level diagram of M1, M2, PCBM and F.

are higher than the LUMO level of PCBM or F. An effective charge separation is expected between M1 or M2 and PCBM or F.

The hole mobilities of an organic semiconductor film can be estimated from the J-V characteristics in the dark using space charge limited current (SCLC).⁵⁶

$$J_{\rm SCLC} = (9/8) \varepsilon_{\rm o} \varepsilon_{\rm r} \mu_{\rm h} V^2 / L^3$$

where J_{SCLC} is the current density in SCLC region, ε_0 is the permittivity of free space, ε_r is the dielectric constant of the material, μ_h is the hole mobility, V is the applied voltage corrected for the built in voltage (V_{bi}) arising from the difference between the work function of the contacts, and L is the thickness of the organic film. The hole mobilities of **M1** and **M2** films were studied by measuring the J-V characteristics of the hole only devices having structure of ITO/PEDOT/PSS/**M1** or **M2**/Au. The variation of current density with the voltage *i.e.* $V_{\text{appl}} - V_{\text{bi}}$ value for **M1** and **M2** organic films is shown in Fig. 4. The hole mobilities estimated from these curves with SCLC model were 3.2×10^{-5} cm² V⁻¹ s⁻¹ for **M1** and **M2** respectively. The hole mobility of **M2** is higher than that of **M1** due to the presence of the thienothiadiazole central unit in the former.

Photovoltaic properties of the BHJ devices

Fig. 5 shows the thin film absorption spectra of M2:PCBM (1 : 1) and M2:F (1 : 1 w/w) blends. Similar absorption spectra were

Fig. 4 Variation of current density with the $(V_{appl} - V_{bi})$ for ITO/ PEDOT:PSS/M1 or M2/Au devices in the dark at room temperature.

Fig. 5 Absorption spectra of blend film spin cast from THF solution of **M2**:PCBM and **M2**:F.

observed for M1:PCBM and M1:F blends. The film absorption of the blends shows two bands *i.e.* one in shorter wavelength region corresponding to the PCBM or F and another in longer wavelength region corresponding to M2. The blended film gives a very good solar coverage. A broader absorption through the whole solar spectrum is observed for the M2:F blend as compared to M2:PCBM and this has been attributed to the absorption of F.⁴⁵ The broader absorption spectrum of M2:F indicates higher light harvesting efficiency and exciton generation for the device.

We have carefully examined the PV performance of the devices with different blend ratios and found that the best performance was obtained for the devices with a 1 : 1 weight ratio of **M1** or **M2**:PCBM or **F**. Fig. 6 shows the J-V characteristics of the devices with **M1**:PCBM or **F** and **M2**:PCBM or **F** (1 : 1), under an illumination intensity of 100 mW cm⁻². Table 2 summaries the

Fig. 6 Current–voltage (J-V) characteristics of the devices based on the blend (a) **M1**:PCBM or **F** and (b) **M2**:PCBM or **F**, under an illumination intensity of 100 mW cm⁻².

various device characteristics, *i.e.*, short circuit current (J_{sc}) , open circuit voltage (V_{oc}) , fill factor (FF) and power conversion efficiency (PCE). Short circuit current densities of 3.5 mA cm⁻² and 5.0 mA cm⁻² have been achieved for M1:PCBM and M1:F, respectively. Combined the values of J_{sc} with FF (0.42 and 0.46 for M1 and M1:F respectively), the devices based on M1 and M1:F show PCEs of 1.05% and 2.02%, respectively. PCE values of 1.23% and 2.72% have been achieved for the devices based on M2:PCBM and M2:F respectively. Fig. 7 shows the incident photon to current efficiency (IPCE) for the devices based on M2 as electron donor and PCBM or F as electron acceptor. The shape of the IPCE curves of the devices is similar to the corresponding absorption spectra of the blend active layers employed in the devices. The IPCE value of the devices based on PCBM as electron acceptor is lower than that based on F. Since the absorption of PCBM is very low in the range of 400-500 nm, it

Table 2Photovoltaic parameters of the devices based on M1:PCBM,M1:F, M2:PCBM and M2:F blends

Blend	$J_{\rm sc}/{\rm mA~cm^{-2}}$	$V_{\rm oc}/{ m V}$	FF	PCE (%)
M1:PCBM	3.50	0.72	0.42	1.05
M1:F	5.00	0.88	0.46	2.02
M2:PCBM	3.94	0.68	0.46	1.23
M2:F	6.75	0.84	0.48	2.72

Fig. 7 Incident photon to current conversion efficiency (IPCE) spectra of the **M2**:PCBM or **F** photovoltaic devices.

does not contribute to the light absorption in this region. The IPCE spectra also are correlated very well with the absorption spectra of M1 or M2 film in the respective devices. Compared to the PCBM based device, the improved PCE for the device based on **F** is due to the large increment of both J_{sc} and V_{oc} . The increase in J_{sc} could be attributed to the more intense absorption of F in the visible region than that of PCBM as evident from the IPCE spectra.⁵⁷ It can be seen that the $V_{\rm oc}$ is increased from 0.72 V for the M1:PCBM and 0.68 V for the M2:PCBM based device to 0.88 V for M1:F and 0.84 V for M2:F based device, respectively. Obviously, the $V_{\rm oc}$ increment of the PV device based on F is benefited from the higher LUMO energy level of F as compared to that of PCBM, because it is well known that the V_{oc} of the organic BHJ solar cells is proportional to the difference between the HOMO of the donor (M1 or M2) and the LUMO of the acceptor.58 The higher value of PCE for the devices based on M2 as donor material is also attributed to the higher value of hole mobility for M2 as compared to M1, which improves the charge collection efficiency. The HOMO level of M2 is almost the same with that of PEDOT:PSS, indicating that holes can be more easily transported from M2 to PEDOT:PSS than from M1 to PEDOT:PSS.

Since the **M2:** F blend gives higher PCE than other blends, we have investigated the effect of mixed solvents and subsequent thermal annealing only for this blend. A mixed solvents approach has been shown to be effective in several other polymer solar cells including P3HT,⁵⁹ as well as several other low band gap conjugated polymers.⁶⁰ This approach has also been

Fig. 8 Current–voltage (J-V) characteristics of the devices based on the M2:F blend cast from mixed solvents (chlorobenzene/THF) and subsequently thermally annealed.

successfully applied to other SM:fullerene derivatives, BHJ devices⁶¹ and planar heterojunction solar cells.⁶² The J-V characteristics of the device based on mixed solvents (chlorobenzene/THF) under illumination are shown in Fig. 8 and the PV data are summarized in Table 3. The J_{sc} and FF of the PV device prepared from mixed solvents increased up to 7.5 mA cm⁻² and 0.53, respectively, resulting in overall PCE of 3.34%. The PCE has also been further increased up to 3.65% when the blend cast from mixed solvents is thermally annealed. The increase in the PCE has been attributed to the improved J_{sc} and FF. The raise in the J_{sc} has been attributed to the increase in crystallinity of the blend cast from mixed solvents, and more balanced charge transport in the device as it is discussed below.

The UV-visible spectra of the M2:F blend cast from mixed solvents were used to monitor the degree of M2:F self-organization. As shown in Fig. 5, the blend prepared from THF contained an absorption band with absorption peak centered at 630 nm corresponding to M2. The absorption spectrum of M2:F blend cast from mixed solvents is shown in Fig. 9. Upon addition of chlorobenzene to the blend solution, the absorption peak, corresponding to M2, shifts towards the longer wavelength region and also the intensity of the absorption band increases. The absorption spectra of the thin film cast from mixed solvents also clearly show a vibronic shoulder around 730 nm. The high degree of M2 crystallinity was indicated by a red shift in the absorption band, a clear vibronic shoulder appeared at long

 Table 3
 Photovoltaic parameters of the devices based on the as cast and thermally annealed M2:F blend cast from mixed solvents (chlorobenzene/THF)

Blend	$J_{\rm sc}/{ m mA~cm^{-2}}$	$V_{\rm oc}/{ m V}$	FF	PCE (%)
M2:F (as cast) M2:F (thermally annealed)	7.50 8.30	0.84 0.80	0.53 0.56	3.34 3.65

Fig. 9 Absorption spectra of the as cast and thermally annealed thin films using mixed solvents.

wavelengths due to the enhanced interchain π - π * stacking, and an increased absorption intensity as has been observed in conjugated polymers.⁶³ The blend cast from mixed solvents showed higher crystallinity than the film cast from THF solvent. Fig. 9 clearly shows that the crystallinity of the blend film was further enhanced by thermal annealing. The additional application of thermal annealing associated with the mixed solvents cast film allowed the film to crystallize more extensively, as indicated by the increased absorption intensity and prominent vibronic features. The improved crystallinity of **M2**, facilitated through self-organized chain stacking, can enhance not only the hole transport but also the light harvesting capabilities, improving the cell photocurrent.

The crystallinity of M2:F blend films was also evaluated by X-ray diffraction (XRD) measurements on the spin coated blend films. Fig. 10 and 11 show the XRD patterns of blend films cast from THF solvent, cast from mixed solvents (chlorobenzene/THF) and thermally annealed films cast from mixed solvents, respectively. The XRD band with a peak at $2\theta = 6.4^{\circ}$ was observed on the M2 film, corresponding to an interplanar distance of 13.8 Å. Annealing leads to higher peak intensity, indicating higher degree of crystallinity. When M2 was blended

Fig. 10 Diffraction patterns for (a) the as cast and (b) thermally annealed pure M2 films.

Fig. 11 Diffraction patterns of (a) the as cast film from THF solvent, (b) the as cast film from mixed solvents (chlorobenzene/THF) and (c) thermally annealed film cast from mixed solvents.

with **F**, this diffraction peak becomes weak, suggesting an effective mixing of **F** with **M2**, which interferes with the molecular packing of **M2**. When the blend is cast from mixed solvents, the diffraction peak corresponding to $2\theta = 6.4^{\circ}$ reappears. This indicates that the film cast from the THF solvent was not sufficiently crystallized. However, when the same blend was cast from mixed solvents, the diffraction intensity peak is higher than that for the film cast from the THF solvent, which is attributed to the increased crystalline nature of the blend. The intensity of this diffraction peak has been further increased when the blend film cast from mixed solvents is thermally annealed at 120 °C for 2 min. This also indicates that the thermal annealing further increases the film crystallinity. These changes in film crystallinity after thermal annealing agree with what has been observed in the absorption data.

The morphology of the PV active layer used in the device is very important for the performance of the OSCs and in some cases the performance of the device strongly depends on the morphological features.⁶⁴ To investigate in more detail the reason for higher PCE for **M2:F** (as cast from chlorobenzene/THF and subsequently thermally annealed) as compared to the **M2:F** cast from THF, we have recorded atomic force microscopy (AFM) images (Fig. 12). The surface root mean square (rms) roughness of the **M2:F** cast from THF and chlorobenzene/THF solvents is 1.8 nm and 2.7 nm, respectively and further increases up to 3.2 nm, when the blend cast from chlorobenzene/THF solvents is thermally annealed. These results indicate that there is a significant change, which increases the charge carrier mobility leading to an improvement in the overall PCE.

The space charge limited current (SCLC) method was employed to estimate the hole and electron mobilities of the devices prepared from the as cast and thermally annealed films (**M2**:**F** blend) cast from mixed solvents.^{56,65} The hole and electron mobilities of the blend films cast from mixed solvents and subjected to thermal annealing are estimated and the results are compared with the mobilities of the devices fabricated from THF solvent. Highly ordered π - π * conjugation, as has been described above, is known to improve the enhancement of the charge carrier mobility in the blend films.⁶⁶ To obtain efficient charge transport of carriers in the device, it is necessary to enhance the hole and electron mobilities to achieve a balanced mobility ratio. SCLC *J*-*V* characteristics were obtained in the dark from the

Fig. 12 AFM images of M2:F blends cast under different conditions (image size 3 μ m \times μ m).

hole only devices (ITO/PEDOT:PSS/M2:F/Au) and the electron only devices (Al/M2:F/Al) as a function of the applied bias, which was corrected for built in potential *i.e.* $V = V_{appl} - V_{bi}$. The hole and electron mobilities were estimated by the dark J-Vcharacteristics and fitting the data in SCLC region as described earlier. The hole mobility for the film cast from mixed solvents has been increased to $4.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, more than two orders of magnitude higher than the mobility of $1.8 \times 10^{-6} \text{ cm}^2$ $V^{-1} s^{-1}$ in the film cast from THF solvent. The electron mobility was also enhanced by a factor of twenty for the blend cast from mixed solvents. Therefore, the addition of chlorobenzene (mixed solvents) and thermal annealing increase both hole and electron mobilities. The ratio between the electron and hole mobilities approached unity, resulting in highly balanced charge transport as compared to the device based on the THF solvent. The hole mobility in the device fabricated from THF solvent was insufficient to ensure efficient charge transport as well as the hole and electron mobilities were less balanced than those measured for the thin films cast from mixed solvents with thermal annealing. The increase in the hole mobility for the film cast from mixed solvents may be due to the increased crystallinity of the blend, which is further enhanced by thermal annealing of the blend as has been evidenced by the absorption spectrum and XRD patterns of the films.

Conclusions

Two conjugated SMs M1 and M2 were synthesized. They showed long-wavelength absorption maximum at 591-643 nm and an optical band gap of 1.62-1.63 eV. The HOMO and LUMO levels of M1 and M2 were estimated from cyclic voltammetry data and it is found that the electrochemical band gap is slightly higher than the optical band gap. The hole mobility of pure M1 and M2 has been estimated from the J-V characteristics fitting in SCLC region. The BHJ PV devices based on M1 or M2 as donor and PCBM or F as acceptor were fabricated. It is found that the device based on M2 as donor (1.23% and 2.72% for PCBM and F as acceptor, respectively) shows improved PCE as compared to the device based on M1 (1.05% and 2.02% for PCBM and F as acceptor, respectively). This has been attributed to the higher hole mobility of M2 and better matching of the HOMO levels of M2 and PEDOT:PSS, leading to better charge transport and collection respectively. It has been found that the BHJ device with F as electron acceptor is higher than that with PCBM which may be attributed to the better absorption

capability of **F** in visible region, resulting in high J_{sc} and improved V_{oc} due the higher LUMO level of **F** as compared to PCBM.

We have also investigated the BHJ devices based on the as cast and thermally annealed **M2:F** blend cast from mixed solvents. The crystallization of the **M2:F** blend was significantly enhanced by spin casting from mixed solvents as has been evidenced by the absorption spectrum and XRD patterns of the films. The improved crystallinity with the as cast and thermally annealed blend cast from mixed solvents yields PCE of 3.34% and 3.65%, respectively. This improved PCE of the BHJ PV devices based on the as cast and thermally annealed **M2:F** blend cast from mixed solvents, has been attributed to the improved charge transport in the devices.

References

- 1 A. Dhanabalan, J. K. J. van Duren, P. A. van Hal, J. L. J. van Dongen and R. A. J. Janssen, *Adv. Funct. Mater.*, 2001, 11, 255–262.
- P. Peumans, S. Uchida and S. R. Forrest, *Nature*, 2003, **425**, 158–162.
 P. Schilinsky, U. Asawapirom, U. Scherf, M. Biele and C. J. Brabec, *Chem. Mater.*, 2005, **17**, 2175–2180.
- 4 M. M. Wienk, J. M. Kroon, W. J. H. Verhees, J. Knol, J. C. Hummelen, P. A. van Hal and R. A. J. Janssen, *Angew. Chem.*, *Int. Ed.*, 2003, 42, 3371–3375.
- 5 N. S. Sariciftci, L. Smilowitz, A. J. Heeger and F. Wudl, Science, 1992, 258, 1474–1476.
- 6 J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti and A. B. Holmes, *Nature*, 1995, **376**, 498–500.
- 7 G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, **270**, 1789–1791.
- 8 J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T. Q. Nguyen, M. Dante and A. J. Heeger, *Science*, 2007, **317**, 222–225.
- 9 (a) F. C. Krebs, M. Jorgensen, K. Norrman, O. Hagemann, J. Alstrup, T. D. Nielsen, J. Fyenbo, K. Larsen and J. Kristensen, *Sol. Energy Mater. Sol. Cells*, 2009, **93**, 422–441; (b) F. C. Krebs, T. D. Nielsen, J. Fyenbo, M. Wadstrom and M. S. Pedersen, *Energy Environ. Sci.*, 2010, **3**, 512–525; (c) F. C. Krebs, J. Fyenbo and M. Jorgensen, *J. Mater. Chem.*, 2010, **20**, 8994–9001.
- 10 H. Y. Chen, J. H. Hou, S. Q. Zhang, Y. Y. Liang, G. W. Yang, Y. Yang, L. P. Yu, Y. Wu and G. Li, *Nat. Photonics*, 2009, 3, 649–653.
- 11 S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee and A. J. Heeger, *Nat. Photonics*, 2009, **3**, 297–303.
- 12 Y. Y. Liang, D. Q. Feng, Y. Wu, S. T. Tsai, G. Li, C. Ray and L. P. Yu, J. Am. Chem. Soc., 2009, 131, 7792–7799.
- 13 J. H. Hou, H. Y. Chen, S. Q. Zhang, R. I. Chen, Y. Yang, Y. Wu and G. Li, J. Am. Chem. Soc., 2009, 131, 15586–15587.
- 14 G. J. Zhao, Y. J. He and Y. F. Li, Adv. Mater., 2010, 22, 4355-4358.
- 15 Y. Liang, Z. Xu, J. Xia, S. T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, *Adv. Mater.*, 2010, **22**, E135–E138.
- 16 O. Hagemann, M. Jorgensen and F. C. Krebs, J. Org. Chem., 2006, 71, 5546–5559.

- 17 L. Schmidt-Mende, A. Fechtenkotter, K. Mullen, E. Moons, R. H. Friend and J. D. MacKenzie, *Science*, 2001, 293, 1119–1122.
- 18 S. Roquet, A. Cravino, P. Leriche, O. Aleveque, P. Frere and J. Roncali, J. Am. Chem. Soc., 2006, 128, 3459–3466.
- 19 F. Silvestri, M. D. Irwin, L. Beverina, A. Facchetti, G. A. Pagani and T. J. Marks, J. Am. Chem. Soc., 2008, 130, 17640–17641.
- 20 C. Q. Ma, M. Fonrodona, M. C. Schikora, M. M. Wienk, R. A. J. Janssen and P. Bauerle, *Adv. Funct. Mater.*, 2008, 18, 3323–3331.
- 21 M. T. Lloyd, A. C. Mayer, S. Subramanian, D. A. Mourey, D. J. Herman, A. V. Bapat, J. E. Anthony and G. G. Malliaras, J. Am. Chem. Soc., 2007, 129, 9144–9149.
- 22 C. H. Huang, N. D. McClenaghan, A. Kuhn, J. W. Hofstraat and D. M. Bassani, Org. Lett., 2005, 7, 3409–3412.
- 23 A. B. Tamayo, X. D. Dang, B. Walker, J. Seo, T. Kent and T. Q. Nguyen, *Appl. Phys. Lett.*, 2009, 94, 103301.
- 24 A. B. Tamayo, B. Walker and T. Q. Nguyen, J. Phys. Chem. C, 2008, 112, 11545–11551.
- 25 B. Walker, A. B. Tamayo, X. D. Dang, P. Zalar, J. H. Seo, A. Garcia, M. Tantiwiwat and T. Q. Nguyen, *Adv. Funct. Mater.*, 2009, **19**, 3063– 3069.
- 26 (a) J. Zhang, D. Deng, C. He, Y.-J. He, M.-J. Zhang, Z.-G. Zhang, Z.-J. Zhang and Y. Li, *Chem. Mater.*, 2010, **23**, 817–822; (b) J. Zhang, Y. Yang, C. He, Y. He, G. Zhao and Y. Li, *Macromolecules*, 2009, **42**, 7619–7622; (c) C. He, Q. He, Y. Yi, G. Wu, F. Bai, Z. Shuai and Y. Li, *J. Mater. Chem.*, 2008, **18**, 4085–4090.
- 27 I. N. Hulea, S. Fratini, H. Xie, C. L. Mulder, N. N. Iossad, G. Rastelli, S. Ciuchi and A. F. Morpurgo, *Nat. Mater.*, 2006, 5, 982–986.
- 28 Y. Yang, R. T. Farley, T. T. Steckler, S. H. Eom, J. R. Reynolds, K. S. Schanze and J. Xue, J. Appl. Phys., 2009, 106, 044509.
- 29 T. T. Steckler, K. A. Abboud, M. Craps, A. G. Rinzler and J. R. Reynolds, *Chem. Commun.*, 2007, 4904–4906.
- 30 M. Karikomi, C. Kitamura, S. Tanaka and Y. Yamashita, J. Am. Chem. Soc., 1995, 117, 6791-6792.
- 31 T. Kono, D. Kumaki, J.-I. Nishida, S. Tokito and Y. Yamashita, *Chem. Commun.*, 2010, 46, 3265–3267.
- E. Bundgaard and F. C. Krebs, *Macromolecules*, 2006, **39**, 2823–2831.
 C. Kitamura, S. Tanaka and Y. Yamashita, *Chem. Mater.*, 1996, **8**,
- 570–578.
 34 M. Karikomi, C. Kitamura, S. Tanaka and Y. Yamashita, J. Am. Chem. Soc., 1995, 117, 6791–6792.
- 35 T. L. Tam, H. Li, F. Wei, K. J. Tan, C. Kloc, Y. M. Lam, S. G. Mhaisalkar and A. C. Grimsdale, *Org. Lett.*, 2010, **12**, 3340– 3343.
- 36 S. Tanaka and Y. Yamashita, Synth. Met., 1995, 69, 599-600.
- 37 I. Kminek, V. Cimrova, D. Vyprachticky and P. Pavlackova, *Macromol. Symp.*, 2008, 268, 100–104.
- 38 I. Kminek, D. Vyprachticky, J. Kriz, J. Dybal and V. Cimrova, J. Polym. Sci., Part A: Polym. Chem., 2010, 48, 2743–2756.
- 39 S. Tanaka and Y. Yamashita, Synth. Met., 1993, 55, 1251-1254.
- 40 J. A. Mikroyannidis, S. S. Sharma, Y. K. Vijay and G. D. Sharma, ACS Appl. Mater. Interfaces, 2010, 2, 270–278.
- 41 J. A. Mikroyannidis, M. M. Stylianakis, P. Balraju, P. Suresh and G. D. Sharma, ACS Appl. Mater. Interfaces, 2009, 1, 1711–1718.
- 42 J. A. Mikroyannidis, M. M. Stylianakis, P. Suresh, P. Balraju and G. D. Sharma, Org. Electron., 2009, 10, 1320–1333.
- 43 J. A. Mikroyannidis, A. N. A. KabanakisKumar, S. S. Sharma, Y. K. Vijay and G. D. Sharma, *Langmuir*, 2010, 26, 12909–12916.
- 44 J. A. Mikroyannidis, P. Suresh and G. D. Sharma, Org. Electron., 2010, 11, 311–321.
- 45 J. A. Mikroyannidis, A. N. Kabanakis, S. S. Sharma, Y. K. Vijay and G. D. Sharma, *Adv. Funct. Mater.*, 2010, DOI: 10.1002/ adfm.201001807.

- 46 (a) G. R. Robertson, Org. Synth., 1941, Coll. Vol. I, 396; (b)
 G. R. Robertson, Org. Synth., 1922, Coll. Vol. II, 57.
- 47 F. S. Mancilha, B. A. Da Silveira Neto, A. S. Lopes, P. F. Moreira, Jr, F. H. Quina, R. S. Goncalves and J. Dupont, *Eur. J. Org. Chem.*, 2006, 4924–4933.
- 48 E. Perzon, X. Wang, S. Admassie, O. Inganas and M. R. Andersson, *Polymer*, 2006, **47**, 4261–4268.
- 49 X. Liu, X. Zhou, X. Shu and J. Zhu, *Macromolecules*, 2009, 42, 7634– 7637.
- 50 D. Kenning, K. A. Mitchell, T. R. Calhoun, M. R. Funfar, D. J. Sattler and S. C. Rasmussen, *J. Org. Chem.*, 2002, **67**, 9073– 9076.
- 51 A. P. Zoombelt, M. Fonrodona, M. G. R. Turbiez, M. M. Wienk and R. A. J. Janssen, J. Mater. Chem., 2009, 19, 5336–5342.
- 52 M. C. Ruiz Delgado, V. Hernandez, J. T. Lopez Navarrete, S. Tanaka and Y. Yamashita, *J. Phys. Chem. B*, 2004, **108**, 2516–2526.
- 53 (a) Y. Li, Y. Cao, J. Gao, D. Wang, G. Yu and A. J. Heeger, *Synth. Met.*, 1999, **99**, 243–248; (b) Q. J. Sun, H. Q. Wang, C. H. Yang and Y. F. Li, *J. Mater. Chem.*, 2003, **11**, 800–806.
- 54 (a) T. Johansson, W. Mammo, M. Svensson, M. R. Anderson and O. Inganas, *J. Mater. Chem.*, 2003, **13**, 1316–1323; (b) W. C. Chen, C. I. Liu, C. T. Yen, F. C. Tsai, C. J. Tonzola, N. Olson and S. A. Jeneke, *Macromolecules*, 2004, **37**, 5959–5964.
- 55 J. H. Hou, Z. A. Tan, Y. Yan, Y. J. He, C. H. Yang and Y. P. Li, J. Am. Chem. Soc., 2006, **128**, 4911–4916.
- 56 A. M. Goodman and A. Rose, J. Appl. Phys., 1971, 42, 2823-2830.
- 57 (a) M. M. Wienk, J. M. Kroon, W. J. M. Verhees, J. Knol, J. C. Hummelen, P. A. van Hal and R. A. J. Janssen, *Angew. Chem., Int. Ed.*, 2003, **42**, 3371–3375; (b) A. P. Zoombelt, M. Fonrodona, M. G. R. Turbiez, M. M. Wienk and R. A. J. Janssen, *J. Mater. Chem.*, 2009, **19**, 5336–5342.
- 58 (a) C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez and J. C. Hummelen, Adv. Funct. Mater., 2001, 11, 374–380; (b) M. C. Scharber, D. Muhlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. J. Brabec, Adv. Mater., 2006, 18, 789–794.
- 59 Y. Yao, J. H. Hou, Z. Hu, G. Li and Y. Yang, Adv. Funct. Mater., 2008, 18, 1783–1789.
- 60 J. Peet, Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger and G. C. Bazan, *Nat. Mater.*, 2007, 6, 497–500.
- 61 (a) A. Tamayo, T. Kent, M. Tantitiwat, M. A. Dante, J. Rogers and T. Q. Nguyen, *Energy Environ. Sci.*, 2009, 2, 1180–1186; (b) H. Fan, H. Shang, Y. Li and X. Zhan, *Appl. Phys. Lett.*, 2010, 97, 133302; (c) B. Walker, C. Kim and T. Q. Nguyen, *Chem. Mater.*, 2010, 23, 470–482.
- 62 (a) J. Sakai, T. Taima, T. Yamanari and K. Saito, *Sol. Energy Mater. Sol. Cells*, 2009, **93**, 1149–1153; (b) H. X. Wei, J. Li, Z. Q. Xu, Y. Cai, J. X. Tang and Y. Q. Li, *Appl. Phys. Lett.*, 2010, **97**, 083302.
- 63 (a) Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulia, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C. S. Ha and M. Ree, *Nat. Mater.*, 2006, **5**, 197–203; (b) L. Li, G. Lu and X. Yang, J. Mater. Chem., 2008, **18**, 1984–1990; (c) Y. D. Park, H. S. Lee, Y. J. Choi, D. Kwak, J. H. Cho, S. Lee and K. Cho, Adv. Funct. Mater., 2009, **19**, 1200–1206.
- 64 R. Qin, W. Li, C. Li, C. Du, C. Veit, H.-F. Schleiermacher, M. Andersson, Z. Bo, Z. Liu, O. Inganas, U. Wuerfel and F. Zhang, J. Am. Chem. Soc., 2009, 131, 14612–14613.
- 65 L. J. A. Koster, E. C. P. Smits, V. D. Mihailetchi and P. W. M. Blom, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, 72, 085205.
- 66 (a) J. H. Park, J. S. Kim, J. H. Lee, W. H. Lee and K. Cho, J. Phys. Chem. C, 2009, **113**, 17579–17584; (b) X. Yang, J. Loos, S. C. Veenstra, W. J. H. Verhees, M. M. Wienk, J. M. Kroon, M. A. J. Michels and R. A. J. Janssen, Nano Lett., 2005, **5**, 579– 583.