



HAL
open science

Hydrogen-bonded oligothiophene rosettes with a benzodithiophene terminal unit: self-assembly and application to bulk heterojunction solar cells

Hayato Ouchi, Xu Lin, Takahiro Kizaki, Deepak D. Prabhu, Fabien Silly, Takashi Kajitani, Takanori Fukushima, Ken-Ichi Nakayama, Shiki Yagai

► To cite this version:

Hayato Ouchi, Xu Lin, Takahiro Kizaki, Deepak D. Prabhu, Fabien Silly, et al.. Hydrogen-bonded oligothiophene rosettes with a benzodithiophene terminal unit: self-assembly and application to bulk heterojunction solar cells. *Chemical Communications*, 2016, 52, pp.7874. 10.1039/C6CC03430F . cea-01485666

HAL Id: cea-01485666

<https://cea.hal.science/cea-01485666>

Submitted on 9 Mar 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.


 Cite this: *Chem. Commun.*, 2016, 52, 7874

 Received 24th April 2016,
 Accepted 21st May 2016

DOI: 10.1039/c6cc03430f

www.rsc.org/chemcomm

Hydrogen-bonded oligothiophene rosettes with a benzodithiophene terminal unit: self-assembly and application to bulk heterojunction solar cells†

 Hayato Ouchi,^a Xu Lin,^{*a} Takahiro Kizaki,^b Deepak D. Prabhu,^a Fabien Silly,^c Takashi Kajitani,^{de} Takanori Fukushima,^d Ken-ichi Nakayama^{bf} and Shiki Yagai^{*af}

Benzodithiophene-functionalized oligothiophene with barbituric acid hydrogen-bonding unit self-assembles into nanoscopic structures via the formation of rosettes. The nanostructures show a power conversion efficiency of 3% upon mixing with PC₆₁BM in bulk-heterojunction solar cells without thermal annealing.

Bulk heterojunction (BHJ) small molecular organic photovoltaic (OPV) devices, despite their inferior performance compared to the polymer or inorganic hybrid counterparts, still attract much attention owing to their outstanding cost-effectiveness and large-area applicability through solution processing in addition to diversity in available organic semiconductors.^{1,2} For BHJ-OPV devices, control over the self-assembly of semiconducting materials through solvent processing is of primary importance in view of creating ideal p–n heterojunction nanostructures.³ Thus, enormous supramolecular insight into how molecular aggregation can be controlled in solution as well as in the bulk state, provided by a myriad of research examples, must contribute largely to this advanced research field.⁴ However, multiple hydrogen-bonding interactions, a typical supramolecular tool to control molecular assembly, have been rarely applied for organic photovoltaic materials, due to the requirements of installing solubilizing yet non-conducting long alkyl chains into molecular scaffolds.⁵

As a promising supramolecular design for hydrogen-bonding semiconductors applicable to the organic photovoltaic application, we have recently developed barbituric acid-functionalized oligothiophenes, wherein solubilizing short alkyl chains are grafted onto the π -conjugated backbone.⁶ For example, compound **1** is organized into semiconducting nanorods through the formation of hexameric hydrogen-bonded aggregates (rosettes) *via* solution processing (Fig. 1). This self-assembly pathway occurred in the presence of PC₆₁BM ([6,6]-phenyl-C₆₁-butyric acid methyl ester), and the resulting p–n blend film showed a power conversion efficiency (PCE) of 2.1% in the BHJ-OPV device under optimized conditions. To further improve the functionality of this supramolecular design, herein we have devised a strategy to end-functionalization of **1** with the semiconducting backbone (Fig. 1).

An alkoxy substituted benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) unit is a promising electron donating building block for organic photovoltaics due to its excellent charge carrier transporting properties arising from a large and planar π -conjugated structure.⁷ We expect that a low charge carrier mobility ($\sim 10^{-7}$ cm² V⁻¹ s⁻¹, *vide infra*) of our parent compound **1** can be improved by its end-functionalization with the BDT unit. We thus synthesized **1-BDT** according to Scheme S1 (ESI†). In the previous study, we confirmed the formation of a hexameric rosette for **1** by means of scanning tunneling microscopy (STM) at the liquid–solid interface. To understand the impact of the BDT unit on this self-assembling motif, we performed the STM analysis of **1-BDT**.

Fig. 2a shows that **1-BDT** forms a sophisticated self-assembled structure at the interface between 1-phenyloctane and highly oriented pyrolytic graphite (HOPG). The molecules preferentially

^a Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan. E-mail: yagai@faculty.chiba-u.jp; Fax: +81-(0)43-290-3039; Tel: +81-(0)43-290-3368

^b Department of Organic Device Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

^c TITANS, SPEC, CEA, CNRS, Université Paris-Saclay, CEA Saclay, F-91191 Gif sur Yvette, France

^d Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

^e RIKEN SPring-8 Center, 1-1-1 Kouto, Sayo, Hyogo 679-5148, Japan

^f CREST-JST, Chiyoda-ku, Tokyo 102-0075, Japan

† Electronic supplementary information (ESI) available: Detailed synthesis and characterization of **1-BDT**; the absorption spectra and transfer OFET characteristics of **1** and **1-BDT**. See DOI: 10.1039/c6cc03430f

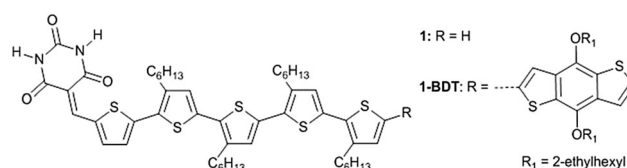


Fig. 1 Molecular structures of **1** and **1-BDT**.

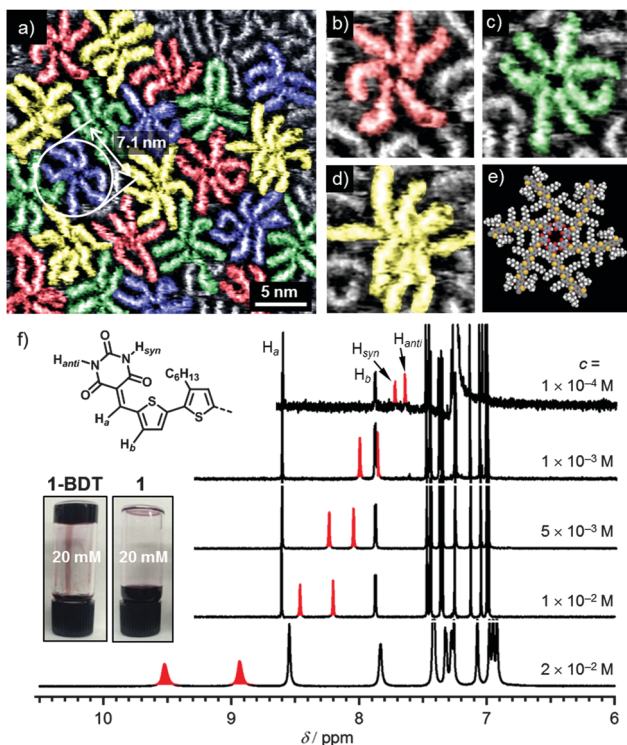


Fig. 2 (a) STM image of **1-BDT** at the 1-phenyloctane–HOPG interface. ($I_t = 9$ pA, $V_s = -0.55$ V. Concentration of solution is 5.0×10^{-6} M. (b)–(d) Rosettes composed of (b) 6, (c) 7, and (d) 8 molecules, respectively. Image size: 9×9 nm². (e) Molecular modelled 6-membered rosette of **1-BDT**. (f) Concentration-dependent ¹H NMR spectra of **1-BDT** ($c = 1 \times 10^{-4}$ – 2×10^{-2} M) in CDCl₃. Inset: CHCl₃ gel of **1-BDT** and CHCl₃ solution of **1**, obtained after 0.5 h upon cooling homogeneous hot solutions ($c = 2 \times 10^{-2}$ M) to room temperature.

form closely packed rosette structures on the surface. The different rosettes have been colored in green, red, blue and yellow as a guide to the eye. Isolated molecules are shown in grey. The majority of rosettes are composed of 6 molecules (Fig. 2b), but rosettes composed of 7 and 8 molecules were also observed (Fig. 2c and d). The arms of the rosette can adopt different conformations on the surface, due to the flexibility of the oligothiophene backbone.⁸ Despite the variation in conformation and the number of molecules, the average diameter of rosettes is uniform and is ~ 7 nm, similar to the diameter of the molecular modelled rosette structure composed of 6 molecules (7.1 nm, Fig. 2e).

The formation of hydrogen-bonded rosettes using **1-BDT** was supported by the ¹H NMR study in CDCl₃. Fig. 2f shows the concentration-dependent ¹H NMR spectra of **1-BDT**. At 1×10^{-4} M, sharp signals of NH protons of the barbituric acid moiety (H_{syn} and H_{anti}) appeared at 7.73 and 7.65 ppm, respectively.⁶ Upon increasing the concentration, the NH signals showed gradual downfield shifts, indicating hydrogen bonding. The difference in the chemical shift value between the two proton signals increased from $\Delta\delta = 0.13$ ppm at $c = 1 \times 10^{-4}$ M to $\Delta\delta = 0.58$ ppm at $c = 2 \times 10^{-2}$ M, which indicates that these protons experience distinct deshielding effects from the neighboring molecules. The finding may indicate the formation

of a screw-shaped hydrogen-bonded rosette motif, as shown in Fig. 2b. The signals of the olefinic proton (H_a) and the thiophene proton (H_b) did not show such a large change upon increasing the concentration to 1×10^{-2} M. These spectral changes are similar to those of the previously reported molecule **1**, and suggest that **1-BDT** forms well-defined hydrogen bonded oligomers, rather than polymeric assemblies arising from a competing tape-like hydrogen-bonding motif in CDCl₃. Interestingly, the solution at $c = 2 \times 10^{-2}$ M turned into a gel upon standing for 30 min at room temperature (inset in Fig. 2f). The gelation in CDCl₃ was not observed for **1**, suggesting that the BDT units decrease the solubility appreciably.

Since the formation of gel in CDCl₃ implies that **1-BDT** organizes into higher-order nanoscopic aggregates through the formation of rosettes, the chloroform gel ($c = 2 \times 10^{-2}$ M) was studied by atomic force microscopy (AFM) upon spin-coating onto the HOPG substrate. However, only granular objects with 50 nm in size were visualized (Fig. S5, ESI[†]). In order to observe individual columnar aggregates formed by stacked rosettes, a dilute solution of **1-BDT** (1×10^{-4} M) in toluene, which is less polar than CHCl₃, was drop-cast onto the HOPG substrate and the solvent was allowed to evaporate slowly under ambient conditions to grow the columnar aggregates.⁶ The AFM images of the substrate displayed islands composed of densely aligned short nanorods with lengths of 20–80 nm (Fig. 3a). The cross-sectional analysis of the aligned nanorods showed that the average top-to-top distance between neighbouring rods was 5.3 nm whereas their average height was 4.0 nm. The discrepancy between these dimensions may indicate a tilted stacking of rosettes to form a column with an ellipsoidal cross-section.

The UV-vis absorption spectrum of a dilute CHCl₃ solution ($c = 1 \times 10^{-5}$ M) of **1-BDT** showed two absorption bands similarly to **1** (Fig. S6, ESI[†]). However, the absorption intensity of the lower wavelength band is much higher for **1-BDT**. The increased absorption intensity in the lower wavelength region is ascribable to the contribution of BDT units.^{7c} Interestingly, the spectrum of the thin film prepared by spin-coating a chloroform solution exhibited a strong bathochromic and hypochromic shift for the transition of the BDT unit, suggesting strong aggregation of this unit in the solid state. The absorption band of the oligothiophene scaffold is broadened due to π – π

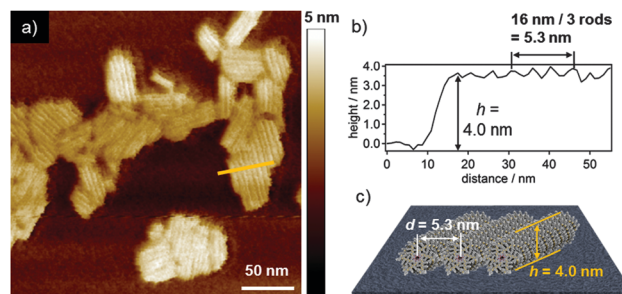


Fig. 3 (a) AFM image of thin film prepared by drop-casting toluene solution ($c = 1 \times 10^{-4}$ M) of **1-BDT** onto HOPG. (b) Cross-sectional analysis along the yellow line in (a). (c) Schematic representations of aligned nanorods of **1-BDT** on the substrate.

Table 1 Optical and electronic properties of **1**-BDT and **1**

Compounds	$\lambda_{\text{max}}^{\text{solution}}$ (nm)	$\lambda_{\text{max}}^{\text{film}}$ (nm)	E_g^{film} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
1 -BDT	418, 550	555	1.80	-5.00	-3.20
1	388, 552	334, 418, 542	1.84	-5.06	-3.22

stacking aggregation. The optical bandgap of **1**-BDT in the film state, estimated from the absorption onset ($\lambda_{\text{onset}} = 688$ nm), is $E_g = 1.80$ eV. The HOMO energy level of **1**-BDT was evaluated using photoelectron yield spectroscopy under atmospheric pressure and was found to be -5.00 eV, which is almost identical to that of **1** (-5.06 eV). The value of the LUMO energy level, thus estimated by subtracting the value of the HOMO energy level from the optical band gap, is -3.20 eV, which is also comparable to that of **1** (Table 1). These results indicate that the introduction of the BDT unit has a minimal impact on the electronic structure of the π -conjugated system.

BHJ solar cells were fabricated using **1**-BDT as a donor material and PC₆₁BM as an acceptor material. The active layer composed of **1**-BDT and PC₆₁BM (denoted as **1**-BDT:PC₆₁BM) was prepared by spin-coating a chloroform solution of 1:1 (w:w) blends of the donor and acceptor materials onto the ITO/PEDOT:PSS substrates under a N₂ atmosphere followed by vapour depositing Ca/Al as an anode.⁹ In our previous studies,⁶ we reported BHJ solar cells of **1**:PC₆₁BM, whose active layers were prepared by using a solvent mixture of chloroform and toluene (1:1 v/v). For these devices, we observed the highest PCE of 2.1% after thermal annealing. However, the addition of toluene, even in 10% to chloroform, as a co-solvent for the preparation of

1-BDT:PC₆₁BM seriously decreased the solubility of **1**-BDT. In the present study, we thus fabricated solar cells of **1**:PC₆₁BM under the same condition as **1**-BDT:PC₆₁BM in order to focus on the introduction of the BDT unit.

In Fig. 4a and Table 2, the device properties of solar cells using as-cast and thermally annealed films of **1**-BDT:PC₆₁BM and **1**:PC₆₁BM are compared. The as-cast device of **1**-BDT:PC₆₁BM showed significant improvements in J_{sc} and FF compared to that of **1**:PC₆₁BM, leading to a PCE of 2.98%, far greater than that of **1**:PC₆₁BM (0.76%). The improved J_{sc} is rationalized by a higher charge carrier mobility of **1**-BDT (1.2×10^{-5} cm² V⁻¹ s⁻¹) than that of **1** ($\sim 10^{-7}$ cm² V⁻¹ s⁻¹), as estimated by the top-contact bottom-gate configuration organic field effect transistor (OFET) fabricated using solution-processed thin films (Fig. S7, ESI†). The external quantum efficiency (EQE) spectrum of the **1**-BDT:PC₆₁BM device exhibited a panchromatic spectral response over the entire excitation spectral range, indicating the contribution of both **1**-BDT and PC₆₁BM on the photocurrent generation. The maximum EQE value of 42% was observed at 420 nm and 580 nm, which corresponds to the absorption maxima of the BDT unit and the oligothiophene backbone, respectively (Fig. 4b and Fig. S8, ESI†). The increased EQE response in the shorter wavelength region reflects the positive influence of the BDT unit both on light harvesting and on the charge carrier mobility. Unlike **1**:PC₆₁BM, the device performance was reduced upon annealing the film of **1**-BDT:PC₆₁BM.¹⁰

The surface morphology of **1**-BDT:PC₆₁BM was studied by AFM (Fig. S9, ESI†). Although no well-defined nanostructure was imaged for the as-cast film, the thermally annealed films exhibited rod-like nanostructures. The rod-like morphology became well-defined with the increasing annealing temperature. The similar effect of thermal annealing on the nanostructure change was observed for **1**:PC₆₁BM, wherein the growth of nanorods improved the solar cell performance. The reason why the solar cell performance of **1**-BDT:PC₆₁BM was decreased by thermal annealing albeit the growth of rod-like nanostructures is unclear at the present, presumably a phase-separated structure optimum for this semiconducting material was already achieved through solution processing.¹¹

In addition to the surface morphology, the packing structure of the **1**-BDT:PC₆₁BM film was investigated by powder X-ray diffraction (PXRD) in addition to that of **1**-BDT in the neat film. A thin film of **1**-BDT, prepared by the evaporation of CHCl₃ solution ($c = 3.8 \times 10^{-3}$ M, 5 mg mL⁻¹), displayed two broad

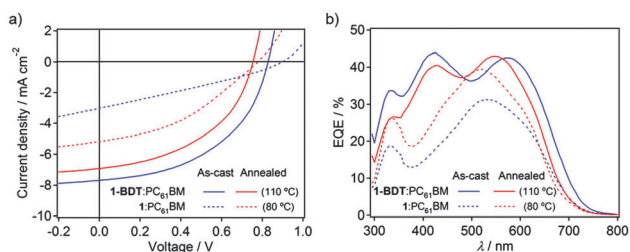


Fig. 4 (a) Current–voltage (J – V) characteristics of BHJ solar cells using 1:1 (w:w) blend films of **1**-BDT and PC₆₁BM (solid lines) and **1** and PC₆₁BM (dotted lines) before (blue) and after annealing (red). (b) EQE spectra of the devices of **1**-BDT:PC₆₁BM (solid lines) and **1**:PC₆₁BM (dotted lines) before (blue) and after annealing (red). Film thickness: 100–120 nm.

Table 2 Photovoltaic properties of the BHJ solar cells based on **1**-BDT and **1** as the donor and PC₆₁BM as the acceptor under the illumination of AM 1.5G, 100 mW cm⁻²

BHJ films	Annealing temp. (°C)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
1 -BDT:PC ₆₁ BM	as-cast	0.83 ± 0.01	7.74 ± 0.06	46.6 ± 1.4	2.98 ± 0.08
	50	0.79 ± 0.05	7.02 ± 0.23	47.7 ± 0.9	2.63 ± 0.08
	80	0.73 ± 0.05	6.76 ± 0.28	48.7 ± 1.0	2.38 ± 0.06
	110	0.69 ± 0.01	6.98 ± 0.07	51.2 ± 0.8	2.47 ± 0.05
1 :PC ₆₁ BM	as-cast	0.88 ± 0.03	2.97 ± 0.06	28.9 ± 0.6	0.76 ± 0.04
	50	0.80 ± 0.09	2.53 ± 0.04	28.4 ± 1.1	0.58 ± 0.09
	80	0.77 ± 0.01	5.18 ± 0.00	37.8 ± 0.6	1.51 ± 0.04
	110	0.74 ± 0.03	2.67 ± 0.04	35.6 ± 0.3	0.70 ± 0.02

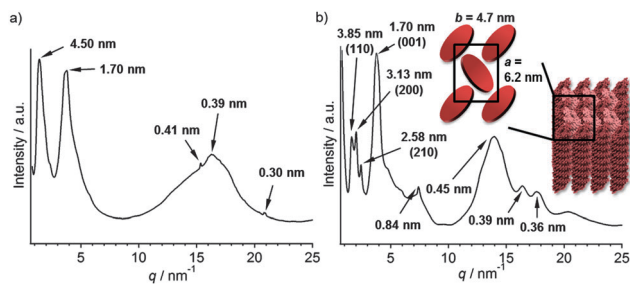


Fig. 5 PXRD patterns of bulk samples of (a) **1-BDT** and (b) **1-BDT**:PC₆₁BM at 25 °C in a glass capillary (diameter: 1.0 mm). Values in parentheses denote Miller indices.

diffraction peaks in the lower angle region, corresponding to $d = 4.5$ nm and 1.7 nm (Fig. 5a). The d -value of 4.5 nm is close to the width of the rosette column (5.3 nm) observed by AFM, and the d -value of 1.7 nm can be attributed to the periodic length along the stacking direction of rosettes. The absence of other diffractions in the small angle region suggests that the **1-BDT** rosette is organized in a columnar architecture without 2D ordering. In contrast, the thin film of **1-BDT**:PC₆₁BM showed explicit diffraction peaks with d -spacings which can be assigned to the diffractions from the (110), (200), (210), and (001) planes of a rectangular 2D lattice (space group: $P2_1/a$, lattice parameters: $a = 6.2$ nm, $b = 4.7$ nm) in the ab plane, which is complemented by the formation of one-dimensional columns along the c axis, formed by the stacking of rosettes with a periodic length of 1.7 nm (Fig. 5b).¹² These results show that **1-BDT** can organize into a one-dimensional columnar architecture *via* the formation of rosettes in the presence of PC₆₁BM.¹³

In summary, we have shown that the functionalization of the rosette-forming hydrogen-bonding oligothiophene with semi-conducting π -units does not affect the formation of rosettes followed by the hierarchical organization into columnar structures. Further modification and functionalization of our supramolecular material design may provide unprecedented low-molecular-weight materials exhibiting outstanding optoelectronic properties as well as processability in addition to the unique self-organization motif.

The PXRD and STM studies of this work were supported by a Grant-in-Aid for Scientific Research on Innovative Areas “ π -System Figuration: Control of Electron and Structural Dynamism for Innovative Functions” from the Ministry of Education, Culture, Sports, Science and Technology, Japan. Synchrotron XRD experiments were carried out at the BL45XU beamline of SPring-8, with the approval of the RIKEN SPring-8 Center (Proposal No. 20140056 and 20150068).

Notes and references

- (a) S. Loser, C. J. Bruns, H. Miyauchi, R. P. Ortiz, A. Facchetti, S. I. Stupp and T. J. Marks, *J. Am. Chem. Soc.*, 2011, **133**, 8142–8145; (b) H. Shang, H. Fan, Y. Liu, W. Hu, Y. Li and X. Zhan, *Adv. Mater.*, 2011, **23**, 1554–1557; (c) Y. Sun, G. C. Welch, W. L. Leong,

- C. J. Takacs, G. C. Bazan and A. J. Heeger, *Nat. Mater.*, 2012, **11**, 44–48; (d) T. Bura, N. Leclerc, S. Fall, P. L ev eque, T. Heiser, P. Retailleau, S. Rihn, A. Mirloup and R. Ziessel, *J. Am. Chem. Soc.*, 2012, **134**, 17404–17407; (e) K. Sun, Z. Xiao, S. Lu, W. Zajaczkowski, W. Pisula, E. Hanssen, J. M. White, R. M. Williamson, J. Subbiah, J. Ouyang, A. B. Holmes, W. W. H. Wong and D. J. Jones, *Nat. Commun.*, 2015, **6**, 6013–6021.
- (a) H. Yamada, T. Okujima and N. Ono, *Chem. Commun.*, 2008, 2957–2974; (b) Y.-J. Cheng, S.-H. Yang and C.-S. Hsu, *Chem. Rev.*, 2009, **109**, 5868–5923; (c) A. W. Hains, Z. Liang, M. A. Woodhouse and B. A. Gregg, *Chem. Rev.*, 2010, **110**, 6689–6735; (d) J. L. Delgado, P. A. Bouit, S. Filippone, M. A. Herranz and N. Martin, *Chem. Commun.*, 2010, **46**, 4853–4865; (e) A. Mishra and P. B auerle, *Angew. Chem., Int. Ed.*, 2012, **51**, 2020–2067; (f) A. J. Heeger, *Adv. Mater.*, 2014, **26**, 10–27.
- (a) H. Hoppe and N. S. Sariciftci, *J. Mater. Chem.*, 2006, **16**, 45–61; (b) F. W urthner and K. Meerholz, *Chem. – Eur. J.*, 2010, **16**, 9366–9373; (c) B. Walker, C. Kim and T.-Q. Nguyen, *Chem. Mater.*, 2011, **23**, 470–482; (d) P. M. Beaujuge and J. M. J. Fr chet, *J. Am. Chem. Soc.*, 2011, **133**, 20009–20029; (e) M. T. Dang, L. Hirsch, G. Wantz and J. D. Wuest, *Chem. Rev.*, 2013, **113**, 3734–3765; (f) Y. Huang, E. J. Kramer, A. J. Heeger and G. C. Bazan, *Chem. Rev.*, 2014, **114**, 7006–7043.
- (a) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491–1546; (b) A. C. Grimsdale and K. M ullen, *Angew. Chem., Int. Ed.*, 2005, **44**, 5592–5629; (c) S. S. Babu, V. K. Praveen and A. Ajayaghosh, *Chem. Rev.*, 2014, **114**, 1973–2129.
- (a) A. El-ghayoury, A. P. H. J. Schenning, P. A. van Hal, J. K. J. van Duren, R. A. J. Janssen and E. W. Meijer, *Angew. Chem., Int. Ed.*, 2001, **40**, 3660–3663; (b) A. Wicklein, S. Ghosh, M. Sommer, F. W urthner and M. Thelakkat, *ACS Nano*, 2009, **3**, 1107–1114; (c) R. B. K. Siram, K. Tandy, M. Horecha, P. Formanek, M. Stamm, S. Gevorgyan, F. C. Krebs, A. Kiriy, P. Meredith, P. L. Burn, E. B. Namdas and S. Patil, *J. Phys. Chem. C*, 2011, **115**, 14369–14376.
- S. Yagai, M. Suzuki, X. Lin, M. Gushiken, T. Noguchi, T. Karatsu, A. Kitamura, A. Saeki, S. Seki, Y. Kikkawa, Y. Tani and K. Nakayama, *Chem. – Eur. J.*, 2014, **20**, 16128–16137.
- (a) Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray and L. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 7792–7799; (b) Y. Zou, A. Najari, P. Berrouard, S. Beaupr e, B. R. Aich, Y. Tao and M. Leclerc, *J. Am. Chem. Soc.*, 2010, **132**, 5330–5331; (c) J. Zhou, X. Wan, Y. Liu, Y. Zuo, Z. Li, G. He, G. Long, W. Ni, C. Li, X. Su and Y. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 16345–16351; (d) Q. Zhang, B. Kan, F. Liu, G. Long, X. Wan, X. Chen, Y. Zuo, W. Ni, H. Zhang, M. Li, Z. Hu, F. Huang, Y. Cao, Z. Liang, M. Zhang, T. P. Russell and Y. Chen, *Nat. Photonics*, 2015, **9**, 35–41.
- Y. Kervella, E. Shilova, S. Latil, B. Joussetme and F. Silly, *Langmuir*, 2015, **31**, 13420–13425.
- After careful screening of various parameters for device fabrication, we have chosen chloroform as a processing solvent, 1 : 1 (w : w) for the optimum D/A blend ratio and 100–120 nm for thicknesses of the active layer, which can be prepared with a total concentration of 10 mg mL^{−1} of the organic materials.
- We also fabricated solar cells of **1-BDT** and PC₇₁BM. However, the devices showed lower performance than those using PC₆₁BM. The highest PCE of the **1-BDT**:PC₇₁BM device is = 2.77%. This might be due to the fact that both **1-BDT** and PC₇₁BM are highly aggregative, which induces a significant phase separation.
- (a) A. Saeki, S. Yoshikawa, M. Tsuji, Y. Koizumi, M. Ide, C. Vijayakumar and S. Seki, *J. Am. Chem. Soc.*, 2012, **134**, 19035–19042; (b) T. Ghosh, A. Gopal, A. Saeki, S. Seki and V. C. Nair, *Phys. Chem. Chem. Phys.*, 2015, **17**, 10630–10639.
- (a) S. Yagai, Y. Goto, T. Karatsu, A. Kitamura and Y. Kikkawa, *Chem. – Eur. J.*, 2011, **17**, 13657–13660; (b) S. Yagai, Y. Goto, X. Lin, T. Karatsu, A. Kitamura, D. Kuzuhara, H. Yamada, Y. Kikkawa, A. Saeki and S. Seki, *Angew. Chem., Int. Ed.*, 2012, **51**, 6643–6647.
- (a) R. Pacios, D. D. C. Bradley, J. Nelson and C. J. Brabec, *Synth. Met.*, 2003, **137**, 1469–1470; (b) C. Melzer, E. J. Koop, V. D. Mihailetschi and P. W. M. Blom, *Adv. Funct. Mater.*, 2004, **14**, 865–870.