





Fig. 2 Normalized UV-vis absorption spectra of thin films of bay-linked PBIs (diPBIs, 1–3) on quartz.

previously synthesized by some of us from isomeric dibromoPBI gave a promising PCE of 4.03%,<sup>13</sup> and here we explore further structurally defined PBI dimers. Our synthetic route to bay-linked dimers is particularly based on monobrominated PBI, which render more precise control of molecular conformation and fine tuning of energy levels. Moreover, branched alkyl chains were introduced to balance the molecular aggregation as a result of strong  $\pi$ - $\pi$  interactions.

As expected, the flexibly twisted s-diPBIs (1) showed much broadened absorption bands in the range of 400 to 600 nm, while d-diPBI (2) showed a narrowed spectrum similar to that of the parent PBI. In contrast, new and pronounced red-shifted absorption peaks throughout from 300 to 800 nm in t-diPBI (3) were observed (Fig. 2). The donor polymer absorbed in the wavelength range from 500 to 750 nm, which well matched with these diPBIs that will enhance light harvesting in the range of the solar spectrum. The optical energy gaps were determined from the absorption onsets in film with 2.03–2.08 eV for s-diPBIs, and 2.22 eV for d-diPBI, and 1.69 eV for t-diPBI, respectively (Table S2, ESI<sup>†</sup>). Calculated by their onset of reduction potentials in film, the LUMO levels were –3.91, –3.87, –3.82, –3.79 and –4.09 eV for s-diPBI to t-diPBI, which are slightly upward shifted of about 0.2–0.5 eV to that of PCBM (Fig. S4, ESI<sup>†</sup>). The differences can be ascribed to the different degrees of twisting and flexibility by bay-linkages that results in different conjugation over the whole  $\pi$ -system.<sup>11</sup>

Electron transporting properties of five diPBIs were also measured by field-effect transistors (FETs) in air at room temperature and listed in Table S3 (ESI<sup>†</sup>). It is observed that the doubly- and triply-linked diPBIs with the same alkyl substituents (8-pentadecyl) showed higher mobilities by two orders of magnitude than that of the singly-linked one. However, the electron transporting properties can be largely enhanced by reducing the branched alkyl chain length to achieve a moderate mobility of  $\sim 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for 6-undecyl substituted s-diPBI (1b), suggesting that structural modification by appropriate substituents indeed exert influences on crystallinity and self-assembly morphology of s-diPBI in the solid state. These electron mobilities without intense optimization, comparable to that of PCBM usually measured in nitrogen, are necessary for functioning as electron acceptors in OSCs.<sup>14</sup>

The photovoltaic properties of the PBDTTT-C-T/diPBI blends have been assessed in typical solar cell devices with the structure of ITO|PEDOT:PSS ( $\sim 35 \text{ nm}$ )|PBDTTT-C-T:diPBI|Ca ( $\sim 20 \text{ nm}$ )|Al



Fig. 3 (a) Comparison of photovoltaic performances based on PBDTTT-C-T-diPBI systems, processed without and with the use of 3% DIO processing. (b) EQE curves of the OSCs with the optimized PBDTTT-C-T-diPBI combinations.

( $\sim 80 \text{ nm}$ ). The ratio of donor to acceptor (D:A) was initially optimized by using dichlorobenzene (DCB) as the processing solvent. The best D:A ratio is 1:1 for all the studied diPBIs with the exception of t-diPBI (3). Then, we carefully examined their performances as electron acceptors by gradually adding 1,8-diiodooctane (DIO) additive (1, 3 or 5 vol%). The detailed photovoltaic parameters of the OSC devices with different D:A ratios and additive amounts are listed in Tables S4–S8 (ESI<sup>†</sup>). As presented in Fig. 3a, distinct photovoltaic characteristics were observed from the different bay-linked diPBIs with or without DIO processing. The promoted PCEs can be obtained accompanied with increased  $J_{\text{sc}}$ <sup>15</sup> when using 3% DIO processing with the exception of t-diPBI (3). Comparing the three diPBIs with same alkyl substituents, s-diPBI showed better PCEs than those of other two analogues. As summarized in Table 1,

Table 1 Photovoltaic parameters of the OSCs based on PBDTTT-C-T/diPBI systems, processed without and with the use of 3% DIO

Acceptor	D:A ratio	Additives	$V_{\text{oc}}/\text{V}$	$J_{\text{sc}}/\text{mA cm}^{-2}$	FF (%)	PCE <sup>a</sup> (%)
1a	1:1	N	0.62	6.09	35.39	1.34
		3% DIO	0.67	6.68	42.94	1.92
1b	1:1	N	0.68	8.47	40.80	2.35
		3% DIO	0.72	10.36	42.08	3.11
1c	1:1	N	0.69	7.51	33.87	1.77
		3% DIO	0.72	8.86	39.75	2.54
2	1:1	N	0.66	4.76	37.43	1.18
		3% DIO	0.74	5.76	36.41	1.54
3	1:3	N	0.46	5.77	50.58	1.36
		3% DIO	0.50	0.50	23.45	0.06

<sup>a</sup> Tested under illumination of AM 1.5G 100 mW  $\text{cm}^{-2}$ .

**Table 2** Photovoltaic performances of C5,5-s-diPBI (**1b**) as electron acceptors by different solvent processing

Acceptor	Additives	$V_{OC}/V$	$J_{SC}/\text{mA cm}^{-2}$	FF (%)	PCE <sup>a</sup> (%)
<b>1b</b>	N	0.68	8.47	40.80	2.35
	3% DIO	0.72	10.36	42.08	3.11
	3% CN	0.75	10.01	45.25	3.39
	1.5% DIO/1.5% CN	0.73	10.58	46.80	3.63

<sup>a</sup> Tested under illumination of AM 1.5G 100 mW cm<sup>-2</sup>.

the open circuit voltage ( $V_{OC}$ ) values of devices based on s-diPBI (**1c**) are similar to that of d-diPBI (**2**) and much higher than that of t-diPBI (**3**), which is mainly ascribed to their different arrangement of LUMO energy levels, while the obtained  $J_{SC}$  values of s-diPBI are significantly increased in comparison with those of d-diPBI and t-diPBI. The primary reason is traceable to the flexibility and twisting of the singly-linked derivatives with disrupting the crystallinity and appropriate charge-transporting properties.<sup>16</sup> In contrast, the device based on t-diPBI (**3**) exhibited a PCE of 1.36% at the ratio of 1:3 when pure DCB was used, but almost vanished when using 3% DIO as the additive, resulting from the sharply decreased  $J_{SC}$  and the reduced FF by a half due to  $\pi$ -stacked aggregation that is induced by its almost-planar structure.

We speculated that further alkyl modification might play an important role on crystallinity and interpenetrating nanostructure formed by the two components, which also influence corresponding  $J_{SC}$  and FF, and thus PCE. As a result, much better performance of 3.11% for C5,5-s-diPBI (**1b**) by binary co-solvent (DCB/3% DIO) processing was obtained when shortened 6-undecyl was adopted. Further optimization by selecting another binary solvent mixture of DCB/3% CN (1-chloronaphthalene), and a ternary solvent mixture of DCB/1.5% DIO/1.5% CN, we found that a PCE of 3.63% with a  $V_{OC}$  of 0.73 V, a  $J_{SC}$  of 10.58 mA cm<sup>-2</sup> and a FF of 46.80% was recorded by the use of the ternary solvent with finely tuning the morphology of the composites (Table 2).<sup>17</sup> It can be seen that the EQE curves of all these devices cover the wavelength range from 300 to 800 nm (Fig. 3b). Their quantum yields become much higher when a 3% DIO additive was added, with the exception of a sharp decrease for t-diPBI. It is also noteworthy that the maximum EQE peak approaches 48.62% at 530 nm for devices utilizing **1b** as electron acceptor.

In summary, a series of bay-linked (singly, doubly and triply) perylene bisimides featuring branched alkyl chains as non-fullerene acceptors have been designed and demonstrated their electron accepting properties in solution-processed BHJ OSC devices by utilizing PBDTTT-C-T as the polymer donor. By screening the bay-linkage and further alkyl modification, the singly-linked diPBIs have proved their superior performances up to 3.63% owing to their better matching energy levels resulting from the flexibility and twisted structure. In addition, the triply-linked analogue also revealed its promising nature owing to broad absorptions and preferable charge transporting. Further improvements in non-fullerene solar cells could be achieved by molecular design of bay-linkage and alkyl

modification in PBIs towards suitable energy levels as well as enhanced mobility.

For financial support of this research, we thank 973 Program (Grant 2014CB643500 and 2012CB932903), the National Natural Science Foundation of China (21225209, 91027043, 21190032, and 51203164), NSFC-DFG Joint Project TRR61, and the Chinese Academy of Sciences.

## Notes and references

- G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, **270**, 1789.
- (a) J. You, L. Dou, K. Yoshimura, T. Kato, K. Ohya, T. Moriarty, K. Emery, C.-C. Chen, J. Gao and Y. Yang, *Nat. Commun.*, 2013, **4**, 1446; (b) Z. He, C. Zhong, S. Su, M. Xu, H. Wu and Y. Cao, *Nat. Photonics*, 2012, **6**, 591.
- (a) Y. Sun, G. C. Welch, W. L. Leong, C. J. Takacs, G. C. Bazan and A. J. Heeger, *Nat. Mater.*, 2011, **11**, 44; (b) Y.-X. Xu, C.-C. Chueh, H.-L. Yip, F.-Z. Ding, Y.-X. Li, C.-Z. Li, X. Li, W.-C. Chen and A. K.-Y. Jen, *Adv. Mater.*, 2012, **24**, 6356; (c) J. Zhou, Y. Zuo, X. Wan, G. Long, Q. Zhang, W. Ni, Y. Liu, Z. Li, G. He, C. Li, B. Kan, M. Li and Y. Chen, *J. Am. Chem. Soc.*, 2013, **135**, 8484; (d) U. Mayerhöffer, K. Deing, K. Gruf, H. Braunschweig, K. Meerholz and F. Würthner, *Angew. Chem., Int. Ed.*, 2009, **48**, 8776.
- For examples: (a) Y. Lin, Y. Li and X. Zhan, *Adv. Energy Mater.*, 2013, **3**, 724; (b) Y. Zhou, L. Ding, K. Shi, Y.-Z. Dai, N. Ai, J. Wang and J. Pei, *Adv. Mater.*, 2012, **24**, 957; (c) G. Ren, E. Ahmed and S. A. Jenekhe, *Adv. Energy Mater.*, 2011, **1**, 946; (d) Y. Zhou, Y.-Z. Dai, Y.-Q. Zheng, X.-Y. Wang, J.-Y. Wang and J. Pei, *Chem. Commun.*, 2013, **49**, 5802; (e) Y. Zhou, Q. Yan, Y.-Q. Zheng, J.-Y. Wang, D. Zhao and J. Pei, *J. Mater. Chem. A*, 2013, **1**, 6609.
- (a) R. B. Ross, C. M. Cardona, D. M. Guldi, S. G. Sankaranarayanan, M. O. Reese, N. Kopidakis, J. Peet, B. Walker, G. C. Bazan, E. V. Keuren, B. C. Holloway and M. Greer, *Nat. Mater.*, 2009, **8**, 208; (b) Y. He, H.-Y. Chen, J. Hou and Y. Li, *J. Am. Chem. Soc.*, 2010, **132**, 1377.
- (a) C. Li and H. Wonneberger, *Adv. Mater.*, 2012, **24**, 613; (b) B. Liu, W. Zhu, W. Wu, K. Mu Ri and H. Tian, *J. Photochem. Photobiol., A*, 2008, **194**, 268.
- (a) B. A. Jones, M. J. Ahrens, M. H. Yoon, A. Facchetti, T. J. Marks and M. R. Wasielewski, *Angew. Chem., Int. Ed.*, 2004, **43**, 6363; (b) M. Gsänger, J. H. Oh, M. Könemann, H. W. Höffken, A.-M. Krause, Z. Bao and F. Würthner, *Angew. Chem., Int. Ed.*, 2010, **49**, 740.
- For recent examples: (a) E. Zhou, J. Cong, Q. Wei, K. Tajima, C. Yang and K. Hashimoto, *Angew. Chem., Int. Ed.*, 2011, **50**, 2799; (b) A. Sharenko, C. M. Proctor, T. S. van der Poll, Z. B. Henson, T.-Q. Nguyen and G. C. Bazan, *Adv. Mater.*, 2013, **25**, 4403; (c) Q. Yan, Y. Zhou, Y.-Q. Zheng, J. Pei and D. Zhao, *Chem. Sci.*, 2013, **4**, 4389.
- (a) J. J. Dittmer, E. A. Marseglia and R. H. Friend, *Adv. Mater.*, 2000, **12**, 1270; (b) T. W. Holcombe, J. E. Norton, J. Rivnay, C. H. Woo, L. Goris, C. Piliago, G. Griffini, A. Sellinger, J.-L. Brédas, A. Salleo and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2011, **133**, 12106.
- (a) H. Qian, Z. Wang, W. Yue and D. Zhu, *J. Am. Chem. Soc.*, 2007, **129**, 10664; (b) H. Qian, F. Negri, C. Wang and Z. Wang, *J. Am. Chem. Soc.*, 2008, **130**, 17970; (c) Y. Zhen, W. Yue, Y. Li, W. Jiang, S. Di Motta, E. Di Donato, F. Negri, S. Ye and Z. Wang, *Chem. Commun.*, 2010, **46**, 6078; (d) J. Zhang, L. Tan, W. Hu and Z. Wang, *J. Mater. Chem. C*, 2013, **1**, 3200.
- W. Jiang, C. Xiao, L. Hao, Z. Wang, H. Ceymann, C. Lambert, S. Di Motta and F. Negri, *Chem.-Eur. J.*, 2012, **18**, 6764.
- L. Huo, S. Zhang, X. Guo, F. Xu, Y. Li and J. Hou, *Angew. Chem., Int. Ed.*, 2011, **50**, 9697.
- X. Zhang, Z. Lu, L. Ye, C. Zhan, J. Hou, S. Zhang, B. Jiang, Y. Zhao, J. Huang, S. Zhang, Y. Liu, Q. Shi, Y. Liu and J. Yao, *Adv. Mater.*, 2013, **25**, 5791.
- C.-Z. Li, C.-C. Chueh, H.-L. Yip, J. Zou, W.-C. Chen and A. K.-Y. Jen, *J. Mater. Chem.*, 2012, **22**, 14976.
- J. K. Lee, W. L. Ma, C. J. Brabec, J. Yuen, J. S. Moon, J. Y. Kim, K. Lee, G. C. Bazan and A. J. Heeger, *J. Am. Chem. Soc.*, 2008, **130**, 3619.
- S. Rajaram, R. Shivanna, S. K. Kandappa and K. S. Narayan, *J. Phys. Chem. Lett.*, 2012, **3**, 2405.
- L. Ye, S. Zhang, W. Ma, B. Fan, X. Guo, Y. Huang, H. Ade and J. Hou, *Adv. Mater.*, 2012, **24**, 6335.