# ChemComm



**View Article Online** 

# **FEATURE ARTICLE**



Cite this: Chem. Commun., 2015, 51, 4936

Received 6th December 2014, Accepted 23rd January 2015

DOI: 10.1039/c4cc09758k

www.rsc.org/chemcomm

# A–D–A small molecules for solution-processed organic photovoltaic cells

Wang Ni, Xiangjian Wan, Miaomiao Li, Yunchuang Wang and Yongsheng Chen\*

A–D–A small molecules have drawn more and more attention in solution-processed organic solar cells due to the advantages of a diversity of structures, easy control of energy levels, *etc.* Recently, a power conversion efficiency of nearly 10% has been achieved through careful material design and device optimization. This feature article reviews recent representative progress in the design and application of A–D–A small molecules in organic photovoltaic cells.

## Introduction

The conversion of solar energy to electricity in an efficient and environmentally friendly way would be an important solution to man's energy needs. Inorganic silicon-based solar cells have shown a high power conversion efficiency (PCE) of over 20%.<sup>1</sup> However, due to the disadvantages of inorganic solar cells such as their high cost, environmental issues and limited flexibility, great effort has been made to search for new types of photovoltaic technologies. Among those novel types of solar cells, the organic photovoltaic cell (OPV) has been considered one of the most promising photovoltaic technologies due to its low cost, solution-processing, light weight, flexibility, *etc.*<sup>2–6</sup>

The typical photoactive layer of an organic solar cell is composed of low band gap polymers/small molecule electron

Key Laboratory of Functional Polymer Materials, Center for Nanoscale Science and Technology, Institute of Polymer Chemistry, College of Chemistry, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China. E-mail: yschen99@nankai.edu.cn

donor materials and substituted fullerenes as electron acceptor materials. The most widely used fullerene derivatives are [6,6]phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) and [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM). Among numerous electron donor materials, conjugated polymer electron donor materials are, to date, the most studied materials for OPV devices.<sup>7-9</sup> A series of carefully designed polymers with an electron push and pull structure (also called donor-acceptor (D-A)) have been developed to finely tune the energy level, solubility, planarity, etc.<sup>9-14</sup> In the last few years, D-A structure polymer based organic solar cells with PCEs of over 9% for a single junction<sup>15-18</sup> and over 11% for a tandem junction organic solar cell have been achieved.19,20 Meanwhile, conjugated small molecules have drawn more and more attention because of their well defined structures and thus less batch-tobatch variation, versatile chemical structures, and thus easier energy level control, etc.<sup>21-24</sup> Inspired by the successful development of D-A narrow band-gap conjugated polymers, small molecules with different types of electron push-pull structure have been developed.<sup>25-30</sup> A class of D-A structure molecules,



Wang Ni

Wang Ni is a graduate student pursuing a PhD under the supervision of Prof. Yongsheng Chen at Nankai University. He received his BA in Chemical Engineering and Technology from Tianjin University in 2011. His PhD research focus is on the design and synthesis of small molecules for organic solar cells.



Xiangjian Wan received his PhD degree in 2006 at Nankai University. He joined Prof. Yonsheng Chen's group at Nankai University in 2006. His current research interests include the syntheses of novel small molecule donor materials and device optimization.

Xiangjian Wan



A–D–A small molecules, has attracted more and more attention in the last two years due to their outstanding photovoltaic performance.<sup>31–33</sup> As indicated in Fig. 1, A–D–A small molecules generally consist of an electron-donating segment (D) as the central building block and two electron-accepting segments (A) as terminal groups. In the backbone of these A–D–A molecules, oligothiophene or other electron donor units are chosen as bridges to link the central donor unit and the terminal acceptor unit. The commonly used central electron donor segments include thiophene, benzodithiophene (BDT), dithienosilole (DTS), dithienocyclopenta (DTC), indacenodithiophene (IDT),



Miaomiao Li is a graduate student pursuing a PhD under the supervision of Prof. Yongsheng Chen at Nankai University. She received her BA in Chemistry from Lanzhou University in 2011. Her PhD research focus is on the fabrication and optimization of small-moleculebased organic solar cells.

Miaomiao Li



Yunchuang Wang



Yongsheng Chen

Prof. Yongsheng Chen graduated from the University of Victoria with a PhD degree in chemistry in 1997 and then joined the University of Kentucky and the UCLA for his postdoc studies from 1997 to 1999. Since 2003 he has held a Chair Professor at Nankai University. His main research interests focus on carbon-based nanomaterials and organic functional materials for green energy applications.

silafluorene (SFL), fluorene (FL), carbazole (CZ), thiophene, etc.11 Widely used electron withdrawing units for the terminal acceptor segment usually involve dyes and pigments such as dicyanovinyl, alkyl cyanoacetate, rhodanine, and 1,3-indanedione.<sup>34-36</sup> Clearly, donor and acceptor units as well as oligothiophene  $\pi$ -conjugation bridges all have a great impact on the overall optical, electrochemical and charge transport properties of the resulting small molecules.<sup>25,32</sup> Meanwhile, the position and length of alkyl side chains on these units also play a crucial role in improving the solubility and could finely tune the  $\pi$ -stacking, energy level and charge transport properties of these small molecules.<sup>33</sup> In this article, we summarize the recent representative progress in the design and synthesis of these A-D-A small molecules for solution-processed OPV devices and discuss the relationship between their molecular structures and their OPV performance.37

The most important parameter for an organic solar cell is its PCE which is given by the following equation: PCE =  $V_{oc} \times J_{sc} \times$  FF/ $P_{in}$ , where  $V_{oc}$  is the open circuit voltage,  $J_{sc}$  is the short circuit current density, FF is the fill factor and  $P_{in}$  is the given incident light power density (Fig. 2). It is most widely accepted that  $V_{oc}$  mainly depends on the energy level difference between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor.<sup>9,11,25</sup>  $J_{sc}$  is much more complicated and is determined



**Fig. 2** Typical J-V curve of an OPV device indicating the meaning of  $J_{sc}$ .  $V_{oc}$  and FF. The current density and voltage at the maximum power point are denoted as  $J_m$  and  $V_m$ , respectively.

by the efficiencies of light absorption, exciton generation, diffusion and separation, *etc.* The FF represents the quality of OPV devices and there are several factors that can significantly influence it, such as series resistance, shunt resistance and competition between charge carrier recombination and transport processes.<sup>38</sup>

Ideal photoactive materials are one of the most fundamental and important issues for high performance OPV devices. Since substituted fullerenes are very effective electron acceptor materials, much more attention has been devoted to the design and synthesis of donor materials which need to match substituted fullerenes in terms of energy levels, mobility, etc. Reducing the HOMO energy level of donor materials is an efficient way to obtain a high  $V_{oc}$ . On the other hand, the absorption coverage of donor materials, which is a key factor that determines  $J_{sc}$ , depends on the difference between the HOMO and LUMO energy level of the donor materials. Thus, ideally, a donor material with a low band gap (good absorption) but a low HOMO level (high  $V_{oc}$ ) is needed. With fullerene derivatives as the electron acceptor, the LUMO energy level of the donor material cannot be too low in order to guarantee efficient exciton splitting and charge dissociation between the donor and acceptor materials at the interface. Although PCE is determined by the three factors, these factors are not independent of each other and in most cases depend on each other, particularly  $J_{sc}$  and FF. For this reason, the design of donor materials for a high performance OPV device needs a careful balance of many factors including HOMO/LUMO energy levels, band gap, mobility and so on. Besides, solubility, planarity and stability also need to be considered in the materials design.

#### Oligothiophene based small molecules

Thiophene is an efficient conjugated unit that has been widely used in organic functional materials.<sup>22,23</sup> Oligothiophenes are

among the best-studied semiconducting materials due to their good transport properties and easy tunable optical and electrochemical properties.<sup>39,40</sup> However, the OPV performance of general thiophene materials including polymers and small molecules is restricted by their limited absorption in the visible and near infrared regions. Introducing electron withdrawing units thus forming an intramolecular D–A structure is one of the efficient ways to broaden the molecular absorption region. In 2006, Bäuerle *et al.* reported an oligothiophene derivative DCV5T produced by introducing a strong electron withdrawing unit end group dicyanovinyl (DCV) to the molecule and the OPV devices fabricated using vacuum processing indeed gave a higher performance.<sup>41</sup> The introduction of electron acceptor end-capping groups leads to a large red shift of the absorption edge and thus a high photovoltaic performance.

Based on these previous studies on oligothiophene derivatives and with the goal of solution-processing, we have designed and synthesized a series of oligothiophene derivatives terminated by various electron withdrawing acceptor units. Molecules 1-3 ending with DCV and with different conjugated lengths were reported by our group in 2009 (Fig. 3).42 We found that molecule 3 showed the best device performance among the three owing to its long conjugated backbone. A PCE of 2.45% was obtained for 3:PC<sub>61</sub>BM based devices (Table 1).<sup>43</sup> Further device optimization of the 3:PC<sub>61</sub>BM blend film exhibited a PCE of 3.7% with a  $V_{\rm oc}$  of 0.88 V, a  $J_{\rm sc}$  of 12.4 mA cm<sup>-2</sup>, but a low FF of 0.34.<sup>44</sup> Roncali *et al.* developed two septithiophene derivatives (molecules 4 and 5) by replacing DCV with thiobarbituric acid (TB).45 The unsymmetrical A-D-A small molecule 4 which was synthesized by replacing only one DCV group with TB led to a lower oxidation potential in solution but to the reverse effect in the solid state. Replacing both DCV end groups with TB led to a much lower LUMO energy level (-3.42 and -4.00 eV for molecules 3 and 5,respectively) and thus a reduced band gap. Parallel heterojuction solar cells based on molecules 4 and 5 with PC61BM as the acceptor layer showed PCEs of 1.21% and 0.36%, respectively.



Fig. 3 Molecular structures of A-D-A small molecules 1-13.

Table 1 Photophysical properties and device performance of molecules 1–23

|                 | HOMO/LUMO (eV)          | $\varepsilon^a/M^{-1} \mathrm{~cm}^{-1}$ | $E_{\mathrm{g}}^{\mathrm{opt}}\left(\mathrm{eV}\right)$ | ${\mu_{\rm h}}^b/{\rm cm}^2~{\rm V}^{-1}~{\rm S}^{-1}$   | Active layer           | $V_{\rm oc}/{\rm V}$ | $J_{\rm sc}/{ m mA~cm^{-2}}$ | FF    | PCE (%) | Ref. |  |  |  |  |  |
|-----------------|-------------------------|--|---|--|------------------------|----------------------|------------------------------|-------|---------|------|--|--|--|--|--|
| 1               | -5.73/-3.59             | $6.70	imes10^4$                          | 2.16  | _  |                        | _                    |                              | _     | _       | 42   |  |  |  |  |  |
| 2               | -5.32/-3.44             | $7.63	imes10^4$                          | 2.02  | —  | —                      | _                    | —                            | _     | _       | 42   |  |  |  |  |  |
| 3               | -5.31/-3.42             | $1.10 \times 10^5$                       | 1.96  | $1.5 	imes 10^{-4}$ (S, N)   | 3:PC61BM               | 0.82                 | 10.23                        | 0.292 | 2.45    | 43   |  |  |  |  |  |
| 3               |                         |  |   |  | 33:PC61BM              | 0.88                 | 12.4                         | 0.34  | 3.7     | 44   |  |  |  |  |  |
| 4               | -5.66/-3.97             | $7.41	imes10^4$                          | 1.53  | $3.28 	imes 10^{-5}$ (S, N)  | $4/PC_{61}BM$          | 0.81                 | 3.70                         | 0.36  | 1.21    | 45   |  |  |  |  |  |
| 5               | -5.67/-4.00             | $7.24 \times 10^4$                       | 1.55  | $6.9 \times 10^{-5} (S, N)$  | 5/PC <sub>61</sub> BM  | 0.51                 | 2.16                         | 0.28  | 0.36    | 45   |  |  |  |  |  |
| 6               | -5.09/-3.33             | $7.6 \times 10^4$                        | 1.73  | $4.51 \times 10^{-4}$ (S, N)   | 6:PC <sub>61</sub> BM  | 0.88                 | 9.94                         | 0.51  | 4.46    | 34   |  |  |  |  |  |
| 7               | -5.13/-3.29             | $6.0	imes10^4$                           | 1.75  | $1.94 \times 10^{-4}$ (S, N)   | 7:PC61BM               | 0.93                 | 9.91                         | 0.491 | 4.52    | 34   |  |  |  |  |  |
| 8               | -5.10/-3.26             | $6.3	imes10^4$                           | 1.74  | $3.26 \times 10^{-4}$ (S, N)   | 8:PC <sub>61</sub> BM  | 0.86                 | 10.74                        | 0.55  | 5.08    | 34   |  |  |  |  |  |
| 9               | -5.11/-3.44             | $7.85	imes10^4$                          | 1.63  | $7.7 	imes 10^{-5}$ (S, N)   | 9:PC <sub>61</sub> BM  | 0.83                 | 5.50                         | 0.50  | 2.26    | 46   |  |  |  |  |  |
| 10              | -5.11/-3.44             | $7.70	imes10^4$                          | 1.66  | _  | —                      |                      | —                            |       |         | 46   |  |  |  |  |  |
| 11              | -5.19/-3.58             | —  | 1.78  | $1.1	imes10^{-4}~(\mathrm{S,N})$   | 11:PC <sub>61</sub> BM | 0.78                 | 6.34                         | 0.643 | 3.18    | 47   |  |  |  |  |  |
| 12              | -5.25/-3.56             | —  | 1.77  | $1.2	imes10^{-4}~(\mathrm{S,N})$   | 12:PC <sub>61</sub> BM | 0.85                 | 7.43                         | 0.716 | 4.52    | 47   |  |  |  |  |  |
| 13              | -5.26/-3.58             | —  | 1.72  | $1.6 	imes 10^{-4}$ (S, N)   | 13:PC <sub>61</sub> BM | 0.85                 | 10.79                        | 0.671 | 6.15    | 47   |  |  |  |  |  |
| 14              | -5.00/-3.28             | $9	imes 10^4$                            | 1.69  | $1.5	imes10^{-4}~(\mathrm{S,N})$   | 14:PC <sub>61</sub> BM | 0.92                 | 13.98                        | 0.474 | 6.10    | 35   |  |  |  |  |  |
| 15              | -5.09/-3.39             | $8.86 \times 10^4$                       | 1.70  | $2.4 	imes 10^{-5} \ ( m{S, N})$   | 15:PC <sub>61</sub> BM | 0.92                 | 6.77                         | 0.39  | 2.46    | 36   |  |  |  |  |  |
| 16              | -5.12/-3.50             | $5.53	imes10^4$                          | 1.67  | $4.7 	imes 10^{-5}$ (S, N)   | 16:PC <sub>61</sub> BM | 0.90                 | 7.54                         | 0.60  | 4.05    | 36   |  |  |  |  |  |
| 17              | -4.97/-3.44             | $7.80 \times 10^4$                       | 1.49  | $1.73 \times 10^{-4}$ (S, N)   | 17:PC61BM              | 0.80                 | 8.56                         | 0.72  | 4.93    | 48   |  |  |  |  |  |
| 18              | -5.02/-3.72             | $8.45 \times 10^4$                       | 1.33  | _  | —                      |                      | —                            |       |         | 48   |  |  |  |  |  |
| 19              | -4.90/-3.86             | $6.99\times 10^4$                        | 1.20  | $3.0	imes 10^{-4}~({ m S,~N})$   | 19:PC <sub>61</sub> BM | 0.76                 | 3.14                         | 0.28  | 0.66    | 48   |  |  |  |  |  |
| 20              | -4.95/-3.36             | $7.77	imes10^4$                          | 1.62  | $5.91 	imes 10^{-4} ( m S, B)$   | 20:PC71BM              | 0.91                 | 14.87                        | 0.687 | 9.30    | 49   |  |  |  |  |  |
| 21              | -5.25/-3.23             | $4.34	imes10^4$                          | 1.80  | $3.94	imes 10^{-4}~({ m S,~B})$  | 21:PC <sub>61</sub> BM | 0.88                 | 7.02                         | 0.53  | 3.2     | 50   |  |  |  |  |  |
| 22              | -5.09/-3.20             | $5.54	imes10^4$                          | 1.65  | $3.86 	imes 10^{-4} \ ( m S, B)$   | 22:PC <sub>61</sub> BM | 1.02                 | 9.26                         | 0.49  | 4.6     | 50   |  |  |  |  |  |
| 23              | -5.11/-3.36             | $6.94	imes10^4$                          | 1.56  | $5 	imes 10^{-4}$ (S, B)   | 23:PC61BM              | 0.78                 | 8.13                         | 0.63  | 4.0     | 50   |  |  |  |  |  |
| <sup>a</sup> Ab | sorption coefficient in | solution. $b$ O an                       | d S: measur   | $^{a}$ Absorption coefficient in solution $^{b}$ O and S measured by OEET or SCLC method N and B in next or blend film |                        |                      |                              |       |         |      |  |  |  |  |  |

In order to improve the solubility and film quality of oligothiophene derivatives, we have developed three small molecules (molecules 6-8) by introducing an electron-withdrawing alkyl cyanoacetate group to replace DCV as the terminal unit in the septithiophene backbone.34 These small molecules all exhibited relatively good film quality and high PCEs (PCEs over 4%) for solution-processed small molecule-based OPV, and among these three molecules, the highest PCE of 5.08% was achieved based on the blended film of molecule 8 and PC61BM without any post treatment. Later, we synthesized small molecules 9 and 10 based on our previous molecules 6 and 8 by introducing fluorinated alkyl chains into the terminal unit.46 The introduction of a fluorinated substituted alkyl group in the terminal unit led to decreased LUMO energy levels (-3.44 eV for molecules 9 and 10)compared to molecules 6 and 8 (-3.33 eV for molecule 6 and-3.26 eV for molecule 8). The fluoro-substituted alkyl chains also had a great influence on the film forming properties. As the fluorinated alkyl group length increased, the surface energy decreased and the lipophobicity increased. Molecule 8 was not able to produce a uniform film by spin coating due to its high lipophobicity and the problem of wettability. Molecule 9 based organic solar cells showed a PCE of 2.26% with a  $V_{\rm oc}$  of 0.83 V, a  $J_{\rm sc}$ of 5.55 mA cm<sup>-2</sup> and a FF of 0.50.

Yang *et al.* also designed and synthesized a series of solution processable small molecules (**11–13**) using furan, thiophene and selenophene as electron linkers respectively, for bulk hetero-junction organic solar cells.<sup>47</sup> Using these different electron linkers could tune the HOMO and LUMO energy levels. Molecule **11** showed a lower band gap than molecules **12** and **13**, due to the decreased electronegativity of the heteroatoms in the linkers. Among these three molecules, the highest PCE achieved was 6.15% using a **13**:PC<sub>71</sub>BM blend



Fig. 4 Molecular structures of A-D-A small molecules 14-20.

film with a high  $V_{oc}$  of 0.85 V, a  $J_{sc}$  of 10.79 mA cm<sup>-2</sup> and a notable FF of 67.1%.

Looking for better solar absorption, we designed and synthesized molecule **14** by introducing a stronger electron withdrawing unit, 3-ethylrhodanine, as the terminal acceptor unit on the oligothiophene backbone (Fig. 4).<sup>35</sup> As expected, the absorption band of molecule **14** showed a red-shift of about 100 nm compared to that of molecule **8**, which improved the value of  $J_{sc}$ . The device based on a **14**:PC<sub>61</sub>BM blend film showed a high PCE of 6.10% with a high  $V_{oc}$  of 0.92 V and a  $J_{sc}$  of 13.98 mA cm<sup>-2</sup> but a relatively low FF of 0.474. To investigate the effect of dye

end groups on their optical and electrochemical properties and OPV performance, we synthesized a series of molecules (molecules 15-19) with different dye end groups.<sup>36,48</sup> The band gaps of these molecules in a wide range from 1.70 to 1.20 eV demonstrated that the band gaps and energy levels of these A-D-A small molecules could be fine tuned by changing the terminal group. Meanwhile, the terminal acceptor groups of these A-D-A molecules also had a great influence on molecular packing in the solid state, thus affected the and thus affected the morphologies of the active layers and device performance. Molecules 15, 16 and 19, showed poor packing in the solid state and lower hole mobilities, resulting in relatively low PCEs of 4.05%, 2.46% and 0.66%, respectively. Molecule 17 exhibited good packing in the solid state, and a PCE of 4.93% with a high FF of 0.72 was obtained for the device based on  $17:PC_{61}BM$ . Recently, we designed a new molecule 20 using 2-(1,1-dicyanomethylene)rhodanine as the terminal unit, this new molecule showed a high PCE of 9.30% with  $V_{\rm oc}$  of 0.91 V,  $J_{\rm sc}$  of 14.87 mA cm<sup>-2</sup> and FF of 0.687.49 The high performance was due to its optimized morphology with an interpenetrating network consisting of  $\sim$ 10 nm-diameter highly crystalline fibrils in the donor and acceptor blend film.

In order to obtain a higher  $V_{oc}$ , we synthesized three quinquethiophene derivatives with different end groups (molecules **21**, **22** and **23**) (Fig. 5).<sup>50</sup> Compared to their septithiophene analogs (molecule **8**, **14** and **17**), the quinquethiophene derivatives showed lower HOMO energy levels and thus increased  $V_{oc}$ , but an overall lower OPV performance was observed for these molecules mainly due to the poor FF.

The above results demonstrate that the physical and chemical properties of these A–D–A oligothiophene derivatives, such as absorption, energy levels and mobilities, *etc.* could be finely turned through careful molecule design. To date, among these A–D–A oligothiophene derivatives, molecule **20** based on septithiophene with end caps of 2-(1,1-dicyanomethylene)-rhodanine exhibits the highest PCE of 9.30%. The terminal acceptors play an important role in the absorption and packing properties of A–D–A oligothiophene derivatives. The device performance could be further improved by designing small molecules with new terminal acceptors that have a strong electron withdrawing ability, good solubility and



Fig. 5 Molecular structures of A-D-A small molecules 21-23.

good intermolecular  $\pi$ - $\pi$  packing for A-D-A molecules with oligothiophene backbones.

#### DTS based small molecules

The DTS unit is a well known unit for developing efficient organic solar cell due to its highly planar structure and good electron-donating ability.51-54 Bazan and co-workers have designed and synthesized a series of D1-A-D2-A-D1 structure small molecules with DTS as the core unit (D2).<sup>26,55,56</sup> Among these D1-A-D2-A-D1 small molecules, p-DTS(FBDTTh<sub>2</sub>)<sub>2</sub> (Fig. 6) showed the highest performance with a PCE of 9.02% reported by Heeger et al.57 In this part, we will focus on DTS based molecules with the A-D-A structure for solution processed OPV devices. Our group reported an A-D-A molecule 24 with a DTS unit as the central building block, terthiophene as the  $\pi$ -bridge and octyl cyanoacetate as the end acceptor group (Fig. 7).<sup>58</sup> It exhibited a well organized assembly in a thin film and a device based on molecule 24 gave a PCE of 5.84% (Table 2). Wang and co-workers synthesized three molecules (25-27) comprised of DTS as the central block unit, different alkyl side chains substituted bithiophene as  $\pi$ -bridges, and octyl cyanoacetate or dicyano as end groups.<sup>59</sup> The absorption, energy levels and solubilities of these molecules were finely tuned by using different alkyl chains-substituted on the bithiophene  $\pi$ -bridge unit. Compared to octyl cyanoacetate end-capped molecules (25 and 26), molecule 27 with dicyano end groups showed a relatively lower band gap. The devices based on these molecules exhibited PCEs of 3.27% for molecule 25, 2.88% for molecule 26 and 3.81% for molecule 27. Recently, Kim et al. reported a series of small molecules (28-33) with DTS as the central donor unit, two different terminal groups of octyl-2-cyanoacetate and 2-cyano-N-octylacetamide and different alkyl chains-substituted terthiophene as the conjugated  $\pi$ -bridge to investigate the influence of the intermolecular interactions of small molecules on molecular packing and photovoltaic properties.<sup>60</sup> Compared to the molecules based on octyl-2-cyanoacetate terminal group, molecules with 2-cyano-N-octylacetamide terminal groups showed strong intermolecular interactions due to the hydrogen bonds. Moreover, changing the length of the alkyl side chains is an efficient way to control the distance between adjacent molecules during assembly and thus to finely tune the interaction between the small molecules in the film. Controlling the intermolecular interactions in small molecules could result in different interfacial interactions with PC61BM, thus significantly changing their active layer morphology and photovoltaic performance in OPV devices. Among devices based on these



Fig. 6 Structure of typical D1-A-D2-A-D1 molecule p-DTS(FBDTTh<sub>2</sub>)<sub>2</sub>.



Fig. 7

| Table 2 | Photophysical | properties and | device | performance | of molecules | 24-35 |
|---------|---------------|----------------|--------|-------------|--------------|-------|
|---------|---------------|----------------|--------|-------------|--------------|-------|

|                 | HOMO/LUMO (eV)   | $\varepsilon^a/M^{-1} \mathrm{~cm}^{-1}$ | $E_{\mathrm{g}}^{\mathrm{opt}}\left(\mathrm{eV}\right)$ | $\mu_{\rm h}{}^{b}\!/{\rm cm}^2~{\rm V}^{-1}~{\rm S}^{-1}$ | Active layer           | $V_{\rm oc}/{ m V}$ | $J_{\rm sc}/{ m mA~cm^{-2}}$ | FF     | PCE (%) | Ref. |  |
|-----------------|--|--|---|--|------------------------|---------------------|------------------------------|--------|---------|------|--|
| 24              | -4.95/-3.26  |  | 1.73  | $1.8 \times 10^{-4}$ (S, N)                                | 24:PC <sub>61</sub> BM | 0.80                | 11.51                        | 0.64   | 5.84    | 58   |  |
| 25              | -5.17/-3.37  | _  | 1.84  | _  | 25:PC <sub>61</sub> BM | 0.92                | 6.37                         | 0.56   | 3.27    | 59   |  |
| 26              | -5.08/-3.31  | _  | 1.75  | _  | 26:PC <sub>61</sub> BM | 0.89                | 6.61                         | 0.49   | 2.88    | 59   |  |
| 27              | -5.12/-3.45  | _  | 1.72  | _  | 27:PC <sub>61</sub> BM | 0.92                | 8.73                         | 0.48   | 3.81    | 59   |  |
| 28              | -5.28/-3.52  | _  | 1.76  | $1.37 	imes 10^{-2}$ (O, N)                                | 28:PC <sub>61</sub> BM | 0.82                | 9.79                         | 0.54   | 4.35    | 60   |  |
| 29              | -5.27/-3.52  | _  | 1.75  | $2.82 \times 10^{-2}$ (O, N)                               | 29:PC <sub>61</sub> BM | 0.82                | 9.30                         | 0.57   | 4.34    | 60   |  |
| 30              | -5.47/-3.65  | _  | 1.82  | $2.70 \times 10^{-4}$ (O, N)                               | 30:PC <sub>61</sub> BM | 0.94                | 7.75                         | 0.41   | 3.00    | 60   |  |
| 31              | -5.35/-3.50  | _  | 1.85  | $2.18 \times 10^{-3}$ (O, N)                               | 31:PC <sub>61</sub> BM | 0.87                | 7.94                         | 0.47   | 3.22    | 60   |  |
| 32              | -5.34/-3.53  | _  | 1.81  | $2.99 \times 10^{-3}$ (O, N)                               | 32:PC <sub>61</sub> BM | 0.86                | 8.38                         | 0.52   | 3.75    | 60   |  |
| 33              | -5.02/-3.10  | _  | 1.92  | $6.54 \times 10^{-2}$ (O, N)                               | 33:PC61BM              | 0.64                | 1.25                         | 0.26   | 0.21    | 60   |  |
| 34              | -5.55/-3.44  | _  | 1.92  | _  | 34:PC <sub>61</sub> BM | 0.97                | 2.60                         | 0.4758 | 1.20    | 61   |  |
| 35              | -5.52/-3.57  | —  | 1.87  | _  | 35:PC61BM              | 0.88                | 2.59                         | 0.3290 | 0.75    | 61   |  |
| <sup>a</sup> Ab | Absorption coefficient in solution. <sup>b</sup> O and S: measured by OFET or SCLC method. N and B: in neat or blend film. |  |   |  |                        |                     |                              |        |         |      |  |

molecules, molecules 28 and 29 afforded relatively high PCEs of 4.35% and 4.34%, respectively.

Chen et al. designed and synthesized two molecules (34 and 35) with thiophene or bithiophene as the  $\pi$ -conjugated bridge and thieno[2,3-*c*]pyrrole-4,6-dione as the terminal groups.<sup>61</sup> Due to the slightly increased delocalization of the  $\pi$ -bridge bithiophene compared to that of thiophene, molecule 35 showed a narrower optical band gap than molecule 34. The devices fabricated with PC61BM provided PCEs of 1.20% for molecule 34 and 0.75% for molecule 35 and molecule 34 with a shorter  $\pi$ -bridge exhibited a higher  $V_{\rm oc}$  (Table 2).

These studies indicate that different methods such as changing the length of alkyl side chain and the number of oligothiophene  $\pi$ -conjugation bridges, and choosing different terminal acceptor unit could be used to finely tune the optical properties, energy levels, solubility and intermolecular interactions of DTS corebased A-D-A small molecules. For DTS core-based small molecules, molecule 24 with octyl chains-substituted terthiophene as the  $\pi$ -conjugated bridge and octyl-2-cyanoacetate as the terminal acceptor units exhibits the highest device performance. The octyl-substituted thiophene has been demonstrated to be a good fundamental unit to provide not only good solubility but also good intermolecular  $\pi$ - $\pi$  packing. However, the  $I_{sc}$  and FF of DTS-based A-D-A small molecules are relatively low. Design and synthesis of new small molecules with more efficient terminal acceptor units and optimization of the photovoltaic device could be useful ways to improve the device performance.

#### BDT based small molecules

Benzo[1,2-b:4,5-b']dithiophene (BDT), as an electron-donating unit, has been widely used in polymer-based OPVs.62-68 The symmetric and plain conjugated structure of the BDT unit could facilitate the formation of  $\pi$ - $\pi$  stacking. Recently, devices based on BDT-based polymer with high PCEs over 9% have been reported by several research groups.<sup>15-18</sup>

In 2011, we synthesized molecule 36 with the unsubstituted BDT as the central building block, trioctylterthiophene as the  $\pi$ -conjugation bridge and octyl cyanoacetate groups as the terminal acceptor units (Fig. 8).<sup>69</sup> This small molecule showed a PCE of 5.44% with a  $V_{\rm oc}$  of 0.93 V, a  $J_{\rm sc}$  of 11.86 mA cm<sup>-2</sup> and a FF of 0.599 for solution-processed organic solar cells (Table 3). For molecule 36, the  $\pi$ -conjugation bridge unit of trioctylterthiophene was used to ensure its solubility and film quality when using a solution process to produce organic solar cells. Therefore, the synthesis of this molecule is not efficient, and the route is long. Later, we designed and synthesized two molecules (37 and 38), with 2-ethylhexoxy-substituted BDT block as the central building block, octyl cyanoacetate and 3-ethylrhodanine as the terminal group and bioctylterthiophene as the  $\pi$ -conjugated bridge.<sup>31</sup> Molecule 37 exhibited an absorption band from 350 nm to 670 nm. The introduction of the 3-ethylrhodanine terminal group to the A-D-A molecule improved the solar light absorption significantly with a broader absorption from 350 nm to 750 nm and solar cell devices based on molecule 38 have a much higher

 $J_{\rm sc}$  (11.8 mA cm<sup>-2</sup>) compared to the device based molecule 37  $(8 \text{ mA cm}^{-2})$  with the octyl cyanoacetate terminal. The devices based on molecules 37 and 38 showed PCEs of 4.56% and 6.92%, respectively. With polydimethylsiloxane (PDMS) as a processing additive, the device exhibited a higher PCE of 7.38%.<sup>31</sup> Following this work, new efficient transport layers were also used in optimizing device performance. After replacing the highly acidic and hygroscopic poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) by more stable graphene quantum dots (GQDs) as the hole transport layer of the OPV device, its performance showed a comparable value of 6.82%.<sup>70</sup> Using ZnO nanoparticles or poly [(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) as electron transport layer, the devices based on molecule 38 showed PCEs of 7.30% and 8.32%, respectively.<sup>71</sup> To achieve a lower HOMO energy level and thus a higher  $V_{\rm oc}$ , we synthesized molecule **39** by replacing the bulky branched 2-ethylhexyloxy side chain on the BDT unit with a less electron-donating octyl side chain.<sup>72</sup> and this molecule exhibited a lower HOMO energy level (-5.08 eV), thus a higher  $V_{\text{oc}}$  of



Fig. 8 Molecular structures of A-D-A small molecules 36-54

Table 3 Photophysical properties and device performance of molecules 36-44

|    | HOMO/LUMO (eV) | $\epsilon^{a}/M^{-1}cm^{-1}$ | $E_{\mathrm{g}}^{\mathrm{opt}}\left(\mathrm{eV}\right)$ | $\mu_{\rm h}{}^{b}/{\rm cm}^2~{\rm V}^{-1}~{\rm S}^{-1}$ | Active layer                          | $V_{\rm oc}/{\rm V}$ | $J_{\rm sc}/{ m mA~cm^{-2}}$ | FF    | PCE (%) | Ref. |
|----|----------------|------------------------------|---|--|---------------------------------------|----------------------|------------------------------|-------|---------|------|
| 36 | -5.11/-3.54    | $3.1	imes10^4$               | 1.74  | $4.50 \times 10^{-4}$ (S, N)                             | 36:PC <sub>61</sub> BM                | 0.93                 | 9.77                         | 0.599 | 5.44    | 69   |
| 37 | -5.04/-3.24    | $7.2	imes10^4$               | 1.84  | $1.38 \times 10^{-4}$ (S, B)                             | 37:PC <sub>61</sub> BM                | 0.95                 | 8.00                         | 0.600 | 4.56    | 31   |
| 38 | -5.02/-3.27    | $8.1 \times 10^4$            | 1.74  | $1.76 \times 10^{-4}$ (S, B)                             | 38:PC71BM                             | 0.93                 | 11.40                        | 0.653 | 6.92    | 31   |
| 38 |                |                              |   |  | $38:PC_{71}BM^c$                      | 0.93                 | 12.21                        | 0.651 | 7.38    | 31   |
| 38 |                |                              |   |  | $38:PC_{71}BM^d$                      | 0.92                 | 11.36                        | 0.652 | 6.86    | 70   |
| 38 |                |                              |   |  | 38:PC <sub>71</sub> BM <sup>c,e</sup> | 0.94                 | 11.77                        | 0.66  | 7.30    | 71   |
| 38 |                |                              |   |  | 38:PC <sub>71</sub> BM <sup>c,f</sup> | 0.92                 | 12.92                        | 0.70  | 8.32    | 71   |
| 39 | -5.08/-3.27    | $8.4 \times 10^4$            | 1.79  | $4.08 	imes 10^{-4}$ (S, B)                              | 39:PC71BM                             | 0.98                 | 8.52                         | 0.52  | 4.34    | 72   |
| 39 |                |                              |   |  | 39:PC <sub>71</sub> BM <sup>g</sup>   | 0.94                 | 12.56                        | 0.70  | 8.26    | 72   |
| 40 | -5.07/-3.30    | $1.01	imes10^5$              | 1.74  | $6.13 	imes 10^{-4}  ( m S,  B)$                         | 40:PC <sub>71</sub> BM <sup>g</sup>   | 0.92                 | 14.61                        | 0.74  | 9.95    | 73   |
| 41 | -5.02/-3.27    | —                            | 1.72  | $2.88 \times 10^{-4}$ (S, B)                             | 41:PC <sub>71</sub> BM                | 0.93                 | 13.17                        | 0.663 | 8.12    | 76   |
| 42 | -5.06/-3.29    | —                            | 1.76  | $1.52 \times 10^{-4}$ (S, B)                             | 42:PC71BM                             | 0.96                 | 11.92                        | 0.594 | 6.79    | 76   |
| 43 | -5.07/-3.29    | _                            | 1.76  | $3.29 \times 10^{-4}$ (S, B)                             | 43:PC <sub>71</sub> BM                | 0.92                 | 12.09                        | 0.721 | 8.02    | 76   |
| 44 | -5.50/-3.60    | _                            | 1.77  | $3.3 \times 10^{-4}$ (S, B)                              | 44:PC <sub>71</sub> BM                | 0.94                 | 12.50                        | 0.69  | 8.10    | 77   |
|    |                |                              |   |  | $44:PC_{71}BM^h$                      | 1.82                 | 7.7                          | 0.72  | 10.1    | 77   |

<sup>&</sup>lt;sup>*a*</sup> Absorption coefficient in solution. <sup>*b*</sup> O and S: measured by OFET or SCLC method, N and B: in neat or blend film. <sup>*c*</sup> Blend film with PDMS as additive. <sup>*d*</sup> Device with GQD as electron transport layer. <sup>*e*</sup> Device with ZnO as electron transport layer. <sup>*f*</sup> Device with PFN as electron transport layer. <sup>*g*</sup> Blend film with TSA treatment. <sup>*h*</sup> Homo-tandem solar cells.

0.98 V. Using a simple two-step annealing approach, the device based on a **39**:PC<sub>71</sub>BM blend film gave a high PCE of 8.26%, with significantly improved  $J_{\rm sc}$  and FF. Based on these previous studies, we designed and synthesized molecule **40** with alkylthio-substituted BDT as the central building block.<sup>73</sup> The device based on molecule **40** blended with PC<sub>71</sub>BM showed a high PCE of 9.95% with a  $V_{\rm oc}$  of 0.92 V, a  $J_{\rm sc}$  of 14.61 mA cm<sup>-2</sup> and a FF of 0.74.

In 2010, Yang *et al.* reported a series of polymers that used 2-alkylthienyl groups to replace the commonly used alkoxyl groups at the 4- and 8-positions of the BDT units.<sup>74</sup> The two dimensional conjugated BDT has been demonstrated to be an efficient block unit in high performance polymer-based photovoltaic devices.<sup>75</sup> Recently, we designed and synthesized three small molecules (**41–43**) by introducing thiophene or bithiophene units at the 4- and 8-positions of the BDT unit, and investigated their optical, electrochemical and photovoltaic properties.<sup>76</sup> The optical properties and energy levels could be finely tuned by changing the substitution on the BDT unit. Devices based on these molecules all showed high PCEs over 6%. In particular, the devices based on molecule **41** showed high PCE of 8.12% with a  $V_{oc}$  of 0.93 V, a  $J_{sc}$  of 13.17 mA cm<sup>-2</sup> and a FF of 0.663.

Later, Yang *et al.* reported a BDT based A–D–A molecule (44) with thiophene-substituted BDT as the core unit and 3-octyl-rodanine as the electron with-drawing end group for use in small molecule-based OPV.<sup>77</sup> The introduction of 3-octylrodanine end-capped units with long linear alkyl chains as the electron-withdrawing acceptor units improved solubility and film quality. The single junction device and homo-tandem solar cells based on 44:PC<sub>71</sub>BM exhibited high PCE of 8.02% and 10.1%, respectively.

Li *et al.* reported a series of small molecules (**45–48**) with alkoxy or thiophene substituted BDT as the central building block, thiophene or bithiophene as the  $\pi$ -conjugated bridges and indenedione as the end groups. Generally, molecules with bithiophene  $\pi$ -conjugated bridges demonstrate stronger absorbance and higher hole mobilities ( $\sim 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> S<sup>-1</sup> for **47** and **48**) than those with thiophene  $\pi$ -conjugated bridges ( $\sim 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> S<sup>-1</sup> for **45** and **46**).<sup>32</sup> The two molecules with thiophene-substituted BDT showed higher mobilities than molecules with alkoxy-substituted BDT. Devices based on these molecules gave PCEs of 4.15% for **45**, 5.67% for **46**, 5.11% for **47** and 6.75% for **48**, respectively (Table 4).

Recently, Chu and co-workers reported two A-D-A molecules (49 and 50) with thiophene-substituted BDT as the central block unit, cyanoacetate or dicyanovinyl units as the terminal acceptor unit and terthiophene as the  $\pi$ -conjugated bridges.<sup>78</sup> Molecule 50 showed better packing and charge transport properties than molecule 49, thus led to higher photovoltaic performance. The device based on a 50:PC<sub>61</sub>BM blend film provided a PCE of 5.42%, with a  $V_{\rm oc}$  of 0.90 V, a  $J_{\rm sc}$  of 9.08 mA cm<sup>-2</sup> and a FF of 66%, while the device based on molecule 49 showed a much lower PCE of 2.13%. Yang et al. reported molecule 51 which showed a high PCE of 7.93% with a  $V_{\rm oc}$  of 0.95 V, a  $J_{\rm sc}$  of 11.86 mA cm<sup>-2</sup> and a FF of 70%.<sup>79</sup> Zhan *et al.* reported a linear A-D-A molecule (52) with thiophene-substituted BDT as the core and terthiophene end-caps with n-octyl cyanoacetate as the arms.<sup>80</sup> The solution-processed layer-by-layer organic solar cell based on 52/PC<sub>61</sub>BM showed a PCE of 4.16% with a high FF of 0.75. Molecules 50, 51 and 52, with the same conjugated backbone but different alkyl groups substituents show different optical properties, energy levels and photovoltaic performance, which demonstrates that the position and length of the substituted alkyl chains played an important role in device performance. Recently, Wei and co-workers reported two molecules (53 and 54) based on a conjugated backbone with thiophene-substituted BDT as the central block, octyl and hexyl chains substituted terthiophene as the  $\pi$ -conjugated bridge and octyl/pentyl chains substituted oxo-alkylated nitrile as the terminal unit to investigate the effect of shortened alkyl chains on the packing properties and device performance.<sup>81</sup> The results demonstrated that molecule 54 substituted by shorter chains showed tighter molecular stacking and higher crystallinity in the mixture with PC71BM and

Table 4 Photophysical properties and device performance of molecules 44-60

|    | HOMO/LUMO (eV) | $\varepsilon^a/M^{-1} \mathrm{~cm}^{-1}$ | $E_{\mathrm{g}}^{\mathrm{opt}}\left(\mathrm{eV}\right)$ | $\mu_{\rm h}{}^{b}/{\rm cm}^2~{\rm V}^{-1}~{\rm S}^{-1}$ | Active layer           | $V_{\rm oc}/{\rm V}$ | $J_{\rm sc}/{ m mA~cm^{-2}}$ | FF    | PCE (%) | Ref |
|----|----------------|--|---|--|------------------------|----------------------|------------------------------|-------|---------|-----|
| 45 | -5.18/-3.56    | $7.76	imes10^4$                          | 1.59  | $1.71 \times 10^{-4}$ (S, N)                             | 45:PC71BM              | 0.91                 | 9.47                         | 0.482 | 4.15    | 32  |
| 46 | -5.19/-3.56    | $7.37	imes10^4$                          | 1.61  | $2.04 \times 10^{-4}$ (S, N)                             | 46:PC <sub>71</sub> BM | 1.03                 | 10.07                        | 0.547 | 5.67    | 32  |
| 47 | -5.16/-3.52    | $9.45	imes10^4$                          | 1.60  | $2.63 \times 10^{-2}$ (S, N)                             | 47:PC <sub>71</sub> BM | 0.92                 | 8.58                         | 0.648 | 5.11    | 32  |
| 48 | -5.16/-3.54    | $1.00	imes10^5$                          | 1.60  | $2.82 \times 10^{-2}$ (S, N)                             | 48:PC71BM              | 0.92                 | 11.05                        | 0.664 | 6.75    | 32  |
| 49 | -5.45/-3.61    | _  | 1.72  | $1.21 \times 10^{-4}$ (S, B)                             | 49:PC <sub>61</sub> BM | 0.91                 | 5.17                         | 0.46  | 2.13    | 78  |
| 50 | -5.40/-3.63    | _  | 1.75  | $1.72 \times 10^{-4}$ (S, B)                             | 50:PC <sub>61</sub> BM | 0.90                 | 8.60                         | 0.66  | 5.42    | 78  |
| 51 | -5.37/-3.42    | _  | 1.80  | $3 \times 10^{-2}$ (O, N)                                | 51:PC <sub>61</sub> BM | 0.95                 | 11.86                        | 0.70  | 7.93    | 79  |
| 52 | -5.20/-2.90    | $1.15 \times 10^5$                       | 1.87  | $2.5 \times 10^{-3}$ (S, N)                              | $52/PC_{61}BM$         | 0.88                 | 6.30                         | 0.75  | 4.16    | 80  |
| 53 | -5.19/-3.46    | $9.52	imes10^4$                          | 1.76  | $1.4 \times 10^{-4}$ (S, B)                              | 53:PC71BM              | 0.94                 | 5.26                         | 0.70  | 5.26    | 81  |
| 54 | -5.11/-3.37    | $8.03 \times 10^4$                       | 1.77  | $1.1 \times 10^{-4}$ (S, B)                              | 54:PC71BM              | 0.87                 | 9.94                         | 0.65  | 5.64    | 81  |
| 55 | -5.48/-3.61    | —  | 1.75  | _ ``   | 55:PC71BM              | 0.88                 | 6.32                         | 0.536 | 2.98    | 82  |
| 56 | -5.41/-3.57    | —  | 1.72  | $6.61 	imes 10^{-4} \ (	ext{S}, 	ext{B})$                | 56:PC71BM              | 0.86                 | 9.94                         | 0.591 | 5.05    | 82  |
| 57 | -5.15/-3.00    | $1.12 	imes 10^5$                        | 2.14  | $7.62 \times 10^{-6}$ (S, B)                             | 57:PC <sub>61</sub> BM | 0.96                 | 10.32                        | 0.59  | 5.84    | 83  |
| 58 | -5.15/-3.06    | $1.34	imes10^5$                          | 2.09  | $2.99 \times 10^{-6}$ (S, B)                             | 58:PC <sub>61</sub> BM | 0.97                 | 8.67                         | 0.60  | 5.03    | 83  |
| 59 | -5.12/-2.91    | $1.38\times 10^5$                        | 2.21  | $4.82 \times 10^{-6}$ (S, B)                             | 59:PC <sub>61</sub> BM | 0.97                 | 8.91                         | 0.62  | 5.31    | 83  |
| 60 | -5.33/-3.44    | $5.33	imes10^4$                          | 1.83  | $6.09 \times 10^{-4}$ (S, B)                             | 60:PC <sub>71</sub> BM | 0.92                 | 6.89                         | 0.63  | 4.0     | 84  |
|    |                | ,  |   |  |                        |                      |                              |       |         |     |

<sup>a</sup> Absorption coefficient in solution. <sup>b</sup> O and S: measured by OFET or SCLC method, N and B: in neat or blend film.

thus a higher PCE (5.26% for molecule 53 and 5.64\% for molecule 54) in optimized devices.

As shown above, the extended  $\pi$ -conjugation of two dimensional conjugated BDT with introducing thiophene or bithiophene units at the 4- and 8-positions of the BDT has been demonstrated to be an efficient central block unit in an A–D–A small molecule based-OPV. Besides, more effort has been made to synthesize extended  $\pi$ -conjugation of BDT-based A–D–A small molecules. Recently, Chu and co-workers synthesized two molecules **55** and **56** using an electron-rich benzotrithiophene unit as the core (Fig. 9).<sup>82</sup> Compared with BDT, the more planar and more sulfur-rich benzotrithiophene improved intermolecular  $\pi$ - $\pi$  stacking, charge transport, and mobility. The devices based on blends of **56**:PC<sub>71</sub>BM and **55**:PC<sub>71</sub>BM gave PCEs of 5.05% and 2.98%, respectively.

Recently, Ko and co-workers reported a series of molecules 57–59 with an alkylsilylethynyl-substituted BDT unit as the central block unit.<sup>83</sup> The rigid and extended  $\pi$ -conjugation of the alkylsilylethynyl-substituted BDT unit facilitated intramolecular charge transfer and intermolecular  $\pi$ - $\pi$  packing interactions of these molecules in the active blend films. The molecules showed low HOMO levels and high  $V_{\rm oc}$  values of ~1.0 V. Among these molecules, molecule 57 showed the highest PCE of 5.84%. Recently, Wong and co-workers reported a new two-dimensional small molecule **60** with oligothiophene-carrying 2-(2-ethylhexyl)-thiophene conjugated side chains as the arm.<sup>84</sup> It showed good packing and a relatively high hole mobility of 6.09 × 10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. The device based on molecule **60** exhibited a PCE of 4.0% with a  $V_{\rm oc}$  of 0.92 V, a  $J_{\rm sc}$  of 6.89 mA cm<sup>-2</sup> and a FF of 0.63.

Diketopyrrolopyrrole (DPP), an efficient electron acceptor unit, has also been widely used in organic semi-conductor materials.<sup>85–88</sup> Recently, Yao *et al.* and Zhan *et al.* independently and almost simultaneously reported a small molecule (**61**) based on thiophene-substituted BDT as the core and DPP as the arms (Fig. 10).<sup>89,90</sup> The device based on molecule **61** showed a PCE of 5.79%. Replacing the central thiophene-substituted BDT with alkoxy-substituted BDT, Nguyen *et al.* and Marks *et al.* 



Fig. 9 Molecular structures of A-D-A small molecules 55-60.

independently reported molecule **62**.<sup>91,92</sup> The device based on molecule **62** showed a PCE of 3.8%. Tu *et al.* designed and synthesized molecule **63** with longer alkoxy side chains on the central BDT unit and the device based on molecule **63** gave a PCE of 2.19% with a  $V_{\rm oc}$  of 0.76, a  $J_{\rm sc}$  of 5.22 mA cm<sup>-2</sup> and a FF of 0.55 (Table 5).<sup>93</sup>

Recently, Aso *et al.* reported two A–D–A molecules (**64** and **65**) based on isoindigo and thienoisoindigo acceptor units.<sup>94</sup> By replacing one of the benzopyrrolidone parts of isoindigo with a



Fig. 10 Molecular structures of A-D-A small molecules 61-65.

more planar and thus more effective conjugated thienopyrrolidone unit, molecule **65** showed much broader absorption (from 300 nm to 850 nm) than molecule **64** (from 300 nm to 740 nm). The device based on molecule **65** showed a PCE of 1.51% while the device based on molecule **64** did not show a photocurrent response.

These studies indicate that BDT based A–D–A molecules generally had a good absorption spectrum and suitable energy levels and most of the devices based on these molecules exhibited PCEs over 5% with a high  $V_{oc}$ . Molecules **38–44** based on BDT with different substituted groups as the central building block, bioctylterthiophene as the  $\pi$ -conjugated bridge and 3-alkyl-rhodanine as the terminal acceptor units exhibited high PCEs over 6% and among them, the device based on molecule



Fig. 11 Molecular structures of A-D-A small molecules 66-77.

**40** shows a high PCE of 9.95%, which is the highest value in small molecule-based OPVs. Compared with high performance polymer-based OPVs, molecule **40** showed a higher  $V_{oc}$ , a similar FF but a lower  $J_{sc}$ . The design and synthesis of BDT

| Table           | able 5 Photophysical properties and device performance of molecules 61–65 |  |  |  |                        |                     |                              |       |         |      |  |
|-----------------|---|--|--|--|------------------------|---------------------|------------------------------|-------|---------|------|--|
|                 | HOMO/LUMO (eV)  | $\varepsilon^a/M^{-1} \mathrm{~cm}^{-1}$ | $E_{g}^{\mathrm{opt}}\left(\mathrm{eV}\right)$ | $\mu_{\rm h}{}^{b}\!/{\rm cm}^2~{\rm V}^{-1}~{\rm S}^{-1}$ | Active layer           | $V_{\rm oc}/{ m V}$ | $J_{\rm sc}/{ m mA~cm^{-2}}$ | FF    | PCE (%) | Ref. |  |
| 61 <sup>c</sup> | -5.15/-3.44   | $1.25	imes10^5$                          | 1.64   | $1.6 \times 10^{-3}$ (O, N)                                | 61:PC <sub>61</sub> BM | 0.72                | 11.86                        | 0.62  | 5.29    | 89   |  |
| 61 <sup>d</sup> | -5.23/-3.46   | —  | 1.65   | $4.0 \times 10^{-2}$ (O, N)                                | 61:PC <sub>61</sub> BM | 0.84                | 11.97                        | 0.576 | 5.79    | 90   |  |
| 62 <sup>e</sup> | -5.39/-3.57   | —  | 1.72   | _  | 62:PC71BM              | 0.78                | 8.27                         | 0.444 | 2.85    | 91   |  |
| 62 <sup>f</sup> | -5.50/-3.70   | —  | 1.75   | —  | 62:PC <sub>61</sub> BM | 0.85                | 8.7                          | 0.55  | 3.8     | 92   |  |
| 63              | -5.30/-3.44   | $9.89\times10^4$                         | 1.71   | $5.9 	imes 10^{-6}$ (S, B)                                 | 63:PC71BM              | 0.76                | 5.22                         | 0.55  | 2.19    | 93   |  |
| 64              | -5.25/-3.52   | $4.8\times10^4$                          | 1.71   | $3.8 \times 10^{-5}$ (S, B)                                | _                      | _                   | _                            | _     | _       | 94   |  |
| 65              | -5.18/-3.45   | $4.0	imes10^4$                           | 1.49   | $3.8 \times 10^{-5}$ (S, B)                                | 65:PC71BM              | 0.72                | 4.89                         | 0.43  | 1.51    | 94   |  |

<sup>*a*</sup> Absorption coefficient in solution. <sup>*b*</sup> O and S: measured by OFET or SCLC method; N and B: in neat or blend film. <sup>*c*</sup> Data from Zhan's results. <sup>*d*</sup> Data from Yao's results. <sup>*e*</sup> Data from Nguyen's results. <sup>*f*</sup> Data from Marks's results.

Table 6 Photophysical properties and device performance of molecules 66-77

|                 | HOMO/LUMO (eV)          | $\varepsilon^a/M^{-1} \mathrm{~cm}^{-1}$ | $E_{\mathrm{g}}^{\mathrm{opt}}\left(\mathrm{eV}\right)$ | $\mu_{\rm h}{}^{b}/{\rm cm}^2~{\rm V}^{-1}~{\rm S}^{-1}$ | Active layer           | $V_{\rm oc}/{\rm V}$ | $J_{ m sc}/ m mA~cm^{-2}$ | FF    | PCE (%) | Ref.   |
|-----------------|-------------------------|--|---|--|------------------------|----------------------|---------------------------|-------|---------|--------|
| 66              | -5.28/-3.68             | $7.01 	imes 10^4$                        | 1.61  | $9 \times 10^{-5}$ (S, N)                                | 66:PC <sub>61</sub> BM | 0.829                | 8.8                       | 0.63  | 4.8     | 33, 95 |
| 67              | -5.28/-3.64             | $7.69	imes10^4$                          | 1.61  | $6 \times 10^{-5}$ (S, N)                                | 67:PC <sub>61</sub> BM | 0.810                | 10.5                      | 0.66  | 5.6     | 33, 95 |
| 68              | -5.27/-3.67             | $7.96 \times 10^4$                       | 1.60  | $1.1 \times 10^{-4}$ (S, N)                              | 68:PC <sub>61</sub> BM | 0.840                | 8.4                       | 0.66  | 4.6     | 33     |
| 69              | -5.30/-3.75             | $5.87	imes10^4$                          | 1.58  | $1.2 \times 10^{-4}$ (S, N)                              | 69:PC <sub>61</sub> BM | 0.829                | 8.2                       | 0.65  | 4.4     | 33     |
| 70              | -5.31/-3.75             | $5.55	imes10^4$                          | 1.59  | $1.1 \times 10^{-4}$ (S, N)                              | 70:PC <sub>61</sub> BM | 0.841                | 11.4                      | 0.63  | 6.1     | 33     |
| 71              | -5.30/-3.73             | $5.84	imes10^4$                          | 1.58  | $1.6 \times 10^{-4}$ (S, N)                              | 71:PC <sub>61</sub> BM | 0.843                | 10.1                      | 0.72  | 6.1     | 33     |
| 72              | -5.23/-3.23             | $9.42	imes10^4$                          | 2.0   | $5.19 \times 10^{-5}$ (S, B)                             | 72:PC <sub>61</sub> BM | 1.07                 | 4.54                      | 0.49  | 2.38    | 96     |
| 73              | -5.14/-3.21             | $8.32 \times 10^4$                       | 1.94  | $6.47 \times 10^{-5}$ (S, B)                             | 73:PC <sub>61</sub> BM | 0.97                 | 6.15                      | 0.61  | 3.63    | 96     |
| 74              | -5.22/-3.28             | $1.1	imes 10^5$                          | 1.92  | $7.5 \times 10^{-5}$ (S, B)                              | 74:PC <sub>71</sub> BM | 0.88                 | 7.98                      | 0.331 | 2.53    | 97     |
| 75              | -5.21/-3.27             | $1.1	imes 10^5$                          | 1.86  | $5.0 \times 10^{-5}$ (S, B)                              | 75:PC <sub>71</sub> BM | 0.93                 | 10.11                     | 0.445 | 4.38    | 97     |
| 76              | -5.18/-3.29             | $1.6	imes10^5$                           | 1.90  | $1.7 \times 10^{-4}$ (S, B)                              | 76:PC <sub>71</sub> BM | 0.91                 | 10.52                     | 0.496 | 5.00    | 97     |
| 77              | -5.19/-3.27             | $1.3 	imes 10^5$                         | 1.88  | $3.0 \times 10^{-4}$ (S, B)                              | 77:PC <sub>71</sub> BM | 0.90                 | 11.55                     | 0.49  | 5.32    | 97     |
| <sup>a</sup> Ab | sorption coefficient in | solution. $^{b}$ O at                    | nd S: measu   | red by OFET or SCLC                                      | method N and           | l B∙ in ne           | eat or blend film         |       |         |        |

units substituted with new groups and having better absorption could be a promising way to further improve the OPV performance.

#### Other A–D–A molecules

Because of the large number of possible donor and acceptor units, many A–D–A molecules with different central block units and terminal units have been designed and synthesized.

Recently, Bäuerle et al. designed and synthesized a series of molecules (66-71) with dithienopyrrole (DTP) as the central donor unit, alkyl bithiophene as the  $\pi$ -conjugation bridge and dicyanovinyl groups as terminal acceptor units (Fig. 11).<sup>33,95</sup> The type and length of the alkyl chains on the DTP and the position of the hexyl side chains on the thiophene units had a great influence on the solubility of these molecules. With the hexyl group at the outer positions, molecules 66-68 showed solubilities of 10 mg  $mL^{-1},\,66$  mg  $mL^{-1}$  and 77 mg  $mL^{-1}$  in chloroform solution, respectively. With the hexyl chains at the inner positions, molecules 69-71 had increased solubilities of 19 mg  $mL^{-1},~\geq 120~mL^{-1}$  and  $\geq 120~mg~mL^{-1}$  relative to molecules 66-68, respectively. Molecules 69-71 also exhibited lower HOMO and LUMO energy levels than molecules 66-68. The much lower LUMO energy level of molecules 69-71  $(\sim -3.75 \text{ eV})$  compared to molecules 66-68  $(\sim -3.68 \text{ eV})$  lead to narrower band gaps. The devices based on these molecules exhibited PCEs of 4-6%, and molecules 70 and 71 showed relatively high PCEs of 6.1% (Table 6).

Recently, we synthesized two molecules (72 and 73), using two weak electron-donating units, fluorene and carbazole as the central building blocks and octyl cyanoacetate as the terminal units.<sup>96</sup> With weak electron-donating units as the cores, molecules 72 and 73 showed high  $V_{oc}$  of 1.07 and 0.97 V, respectively. Zhan and co-workers reported four molecules (74–77) with 4,4,9,9-tetrakis(4-hexylphenyl)-indaceno[1,2-*b*:5,6-*b'*]dithiophene (IDT) as the central building block, bithiophene or terthiophene as the  $\pi$ -conjugated bridges, and alkyl cyanoacetate or rhodanine as the end acceptor groups.<sup>97</sup> The absorptions and energy levels of the molecules were slightly affected by the  $\pi$ -bridge length. Extending the  $\pi$ -bridges from bithiophene to terthiophene led to higher hole mobilities (7.5 × 10<sup>-5</sup> cm<sup>2</sup> V<sup>-1</sup> S<sup>-1</sup> for molecule 74,  $5.0 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$  for molecule 75,  $1.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$  for molecule 76,  $3.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$  for molecule 77) thus giving better device performance. The devices based on these molecules showed PCEs of 2.53% for 74, 4.38% for 75, 5.00% for 76 and 5.32% for 77.

Jo and co-workers reported two A–D–A molecules (**78** and **79**) based on thiophene and phenylene as the central units and DPP as the terminal groups (Fig. 12).<sup>98</sup> Since the electrondonating ability of phenylene between DPP units is weaker than that of thiophene, molecule **79** exhibited a lower HOMO energy level (-5.17 eV for **78** and -5.31 eV for **79**), thus a higher  $V_{\rm oc}$  in OPV devices. The device based on molecule **79** showed a PCE of 4.01% with  $V_{\rm oc}$  of 0.93 V while molecule **78** gave a PCE of 1.49% with a lower  $V_{\rm oc}$  of 0.80 V (Table 7). To further investigate the relationship between structure and properties, they designed and synthesized four molecules (**80–83**) with bithiophene, thienothiophene, biphenylene, and naphthalene as the



Fig. 12 Molecular structures of A–D–A small molecules 78–87.

Table 7 Photophysical properties and device performance of molecules 78–92

|                        | HOMO/LUMO (eV) | $\varepsilon^a/M^{-1} \mathrm{cm}^{-1}$ | $E_{\mathrm{g}}^{\mathrm{opt}}\left(\mathrm{eV}\right)$ | $\mu_{\rm h}{}^{b}/{\rm cm}^2~{\rm V}^{-1}~{\rm S}^{-1}$ | Active layer           | $V_{\rm oc}/{ m V}$ | $J_{\rm sc}/{ m mA~cm^{-2}}$ | FF    | PCE (%) | Ref. |
|------------------------|----------------|---|---|--|------------------------|---------------------|------------------------------|-------|---------|------|
| <b>78</b> <sup>c</sup> | -5.17/-3.68    | _                                       | 1.51  | $2.5 	imes 10^{-5}$ (S, B)                               | 78:PC <sub>71</sub> BM | 0.80                | 4.30                         | 0.43  | 1.49    | 98   |
| <b>78</b> <sup>d</sup> | -5.29/-3.43    | $8.68\times10^4$                        | 1.62  | $2.4 \times 10^{-5}$ (S, B)                              | 79:PC <sub>71</sub> BM | 0.82                | 7.48                         | 0.54  | 3.30    | 93   |
| 79                     | -5.31/-3.65    | _                                       | 1.66  | $8.8 \times 10^{-5}$ (S, B)                              | 79:PC <sub>71</sub> BM | 0.93                | 9.09                         | 0.47  | 4.01    | 98   |
| 80 <sup>c</sup>        | -5.14/-3.55    | —                                       | 1.65  | $5.1 \times 10^{-4}$ (S, B)                              | 80:PC71BM              | 0.78                | 6.8                          | 0.57  | 3.0     | 99   |
| $80^d$                 | -5.20/-3.30    | $8.60\times10^4$                        | 1.60  | $7.4 \times 10^{-5}$ (S, B)                              | 81:PC71BM              | 0.79                | 6.57                         | 0.50  | 2.58    | 93   |
| 81                     | -5.11/-3.56    | —                                       | 1.60  | $7.7 \times 10^{-4}$ (S, B)                              | 81:PC71BM              | 0.81                | 9.3                          | 0.53  | 4.0     | 99   |
| 82                     | -5.21/-3.57    | —                                       | 1.80  | $6.1 	imes 10^{-4} (S, B)$                               | 82:PC71BM              | 0.86                | 8.3                          | 0.53  | 3.8     | 99   |
| 83                     | -5.18/-3.58    | —                                       | 1.75  | $1.1 	imes 10^{-3}$ (S, B)                               | 83:PC71BM              | 0.87                | 9.5                          | 0.53  | 4.4     | 99   |
| 84                     | -5.03/-3.32    | _                                       | 1.78  | _ ```  | 84:PC71BM              | 0.66                | 4.12                         | 0.44  | 1.50    | 100  |
| 85                     | -5.01/-3.33    | —                                       | 1.80  | —  | 85:PC71BM              | 0.64                | 1.95                         | 0.34  | 0.53    | 100  |
| 86                     | -5.04/-3.34    | —                                       | 1.69  | —  | 86:PC71BM              | 0.65                | 2.63                         | 0.35  | 0.75    | 100  |
| 87                     | -5.16/-3.36    | —                                       | 1.85  | —  | 87:PC71BM              | 0.66                | 3.17                         | 0.30  | 0.78    | 100  |
| 88                     | -5.21/-3.60    | $1.1	imes 10^5$                         | 1.70  | $5.7	imes 10^{-2}~({ m O,~N})$                           | 88:PC <sub>61</sub> BM | 0.844               | 11.2                         | 0.427 | 4.0     | 101  |
| 89                     | -5.11/-3.39    | —                                       | 1.70  | $4.6 \times 10^{-2}$ (O, N)                              | 89:PC <sub>61</sub> BM | 0.755               | 11.7                         | 0.501 | 4.4     | 102  |
| 90                     | -5.20/-3.42    | —                                       | 1.78  | $1.2 	imes 10^{-2}$ (O, N)                               | 90:PC61BM              | 0.77                | 5.91                         | 0.40  | 1.80    | 103  |
| 91                     | -5.28/-3.50    | —                                       | 1.78  | $1.9 \times 10^{-2}$ (O, N)                              | 91:PC <sub>61</sub> BM | 0.72                | 3.92                         | 0.508 | 1.40    | 103  |
| 92                     | -5.11/-3.32    | $1.3\times10^{5}$                       | 1.74  | $1.27 \times 10^{-3}$ (S, B)                             | 92:PC71BM              | 0.88                | 8.53                         | 0.376 | 2.82    | 104  |

<sup>*a*</sup> Absorption coefficient in solution. <sup>*b*</sup> O and S: measured by OFET or SCLC method, N and B: in neat or blend film. <sup>*c*</sup> Data from Jo's results. <sup>*d*</sup> Data from Tu's results.

central block units and DPP as the terminal acceptor.99 The HOMO energy levels of these molecules could be tuned by changing the central units and the LUMO energy levels were similar due to the same terminal group. Photovoltaic devices based on 82 and 83 exhibited higher  $V_{\rm oc}$  than the devices using molecules 80 and 81 as donor materials. The introduction of a planar fused aromatic ring (thienothiophene and naphthalene) in the small molecules benefited molecular crystallinity, lowered the band gap and enhanced the hole mobility, thus gave a higher J<sub>sc</sub> and improved photovoltaic performance. Among these molecules, molecule 83 showed the highest PCE of 4.4% with a  $V_{\rm oc}$  of 0.87 V, a  $J_{\rm sc}$  of 9.5 mA cm<sup>-2</sup>, and a FF of 0.53. Tu et al. reported two molecules (78 and 80) with thiophene and bithiophene as the central units and DPP as the end groups.<sup>93</sup> Molecule 78 showed a lower HOMO energy level (-5.29 eV) than that of molecule 80 (-5.20 eV). The devices based on molecules 78 and 80 exhibited PCEs of 3.30% and 2.58%, respectively.

Wang and co-workers reported a series of molecules **84–87** based on alkylated carbazole, diphenylamine, phenothiazine and fluorene as the central donor units and DPP as the terminal acceptors.<sup>100</sup> The HOMO energy levels varied from -5.01 to -5.16 eV and the LUMO energy levels were around -3.35 eV. The results demonstrated that the HOMO energy levels could be fine-tuned by choosing a central block unit with different electron donor ability. Among these molecules, molecule **84** exhibited the highest PCE of 1.50% with a  $V_{\rm oc}$  of 0.66 V, a  $J_{\rm sc}$  of 4.12 mA cm<sup>-2</sup> and a FF of 0.44.

Marks *et al.* reported a small molecule **88** based on linear naphtho[2,3-*b*:6,7-*b'*]dithiophene (NDT) as the core and DPP as the terminal units (Fig. 13).<sup>101</sup> The device based on this molecule showed a PCE of 4.1%. They then synthesized molecule **89** with a novel 4,9-bis(2-ethylhexyloxy)naphtho[1,2-*b*:5,6-*b'*]-dithiophene (zNDT) "zig-zag" core.<sup>92,102</sup> Compared with linear NDT, the angular geometry of zNDT altered the electronic structure to appreciably raise the HOMO and LUMO energy levels (-5.21 and -3.60 eV for molecule 88 based on linear



Fig. 13 Molecular structures of A-D-A small molecules 88-92.

NDT, -5.11 and -3.39 eV for molecule 89 based on zBDT). The hole mobility of molecule **89** (1 × 10<sup>-4</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) is higher than that of molecule **88** (7 × 10<sup>-5</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>). The device based on molecule **89** exhibited higher PCE (4.4%) than molecule **88** (4.0%). Yagai *et al.* reported two molecules (**90** and **91**) with regioisomeric indolo[3,2-*b*]carbazoles as cores and DPP as the end groups.<sup>103</sup> Molecule **90** with the more linear molecular geometry showed higher crystallinity and a stronger intermolecular interaction than did molecule **91**. Photovoltaic devices showed PCEs of 1.80% for molecule **90** and 1.40% for molecule **91**.

Zhan *et al.* synthesised a small molecule (92) with IDT as the core and DPP as the terminal acceptor units.<sup>104</sup> The device

based on molecule **92** blended with  $PC_{71}BM$  exhibited PCE of 2.82% with a  $V_{oc}$  of 0.88, a  $J_{sc}$  of 8.53 mA cm<sup>-2</sup> and a FF of 0.376.

# Conclusion and outlook

Many excellent small molecules have been designed and synthesized for use in solution-processed organic solar cells in the past few years, and a maximum PCE of nearly 10% has been achieved. The D–A structure has been confirmed to be an efficient strategy to achieve good light absorption not only for polymers but also for small molecules. In addition the absorption, energy levels, mobility, solid packing mode and solubility, *etc.* could also be controlled quite well through careful molecule design, especially for small molecules with A–D–A structures. Various central electron donor cores, terminal units, as well as bridges with different conjugation lengths have been used in the molecule design.

For the outlook, the following issues need to be addressed:

(1) Improving  $J_{\rm sc}$  without sacrificing high  $V_{\rm oc}$  and FF. In general, small molecule-based OPV devices have a relatively higher  $V_{\rm oc}$  compared to that of polymer-based devices. This is one of the advantages of small molecule devices though the reason is not clear. In addition, a high FF now is not out-of-reach for small molecule devices. In fact, FF values over 0.70 have been reported in many small molecule based organic solar cells. It seems that the relatively low  $J_{\rm sc}$  is the limiting factor in further improving the performance of small molecule-based devices. Note that design and synthesis of small molecules with a strong and wide absorption band is only the first and relatively easily realized step. High mobility, matched energy levels with acceptors, and morphology control in the device optimization are all big issues as well.

(2) Small molecule structure-physical property correlations. A systematic investigation of the correlation between small molecule structures and their properties such as absorption, energy levels and mobilities and OPV device performance is greatly needed to understand the intrinsic potential of small molecules and to optimize their efficiency. As shown in this article, molecules 20 and 40, are outstanding for A-D-A based OPV devices. Both exhibited suitable HOMO/LUMO energy levels ( $\sim 5.0$  eV for HOMO and  $\sim 3.3$  for LUMO) which could provide both a high V<sub>oc</sub> and broad absorption (from 350 nm to 750 nm) and therefore a relatively high  $J_{sc}$ . For BDT-based A-D-A small molecules, the symmetric and plain conjugated structure of the BDT central building block facilitates the formation of  $\pi$ - $\pi$  stacking thus giving high hole mobilities  $(>10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1})$  and leading to relatively high FF  $(\geq 65\%)$ . However, due to the fact that the data in the tables are cited from many research groups, tested by different methods (e.g. mobility data were investigated by SCLC or FET methods), comparison and analysis of the structurephysical property relationships of these reported molecules is not rigorous. More comprehensive studies of molecule structures-physical property relations should be done. In fact, the advantage of small molecules in having a definite

chemical structure presents the possibility and opportunity for conducting this study.

(3) Fully understand the morphology of the active layer and controlling/predicting the morphology. Since molecular level properties such as absorption and HOMO/LUMO levels are relatively well understood, it seems to be even more urgent to carry out a full study of the morphology which is only partially understood. This is because an ideal morphology with proper phase separation and domain size is one of the most determining factors for achieving high device performance. The control of phase separation of donor-acceptor blend film is one of the most important issues for optimization of OPV devices. The phase separation could be determined by the chemical properties of the small molecule donor materials such as the intrinsic packing modes and miscibility with acceptors. Besides, the phase separation could be further tuned by the device optimization process. It has been demonstrated that a little change in the chemical structure can give a big difference in the active layer morphology and thus final device performance, such as for molecule 14 relative to molecule 20. To investigate the intrinsic determining factors that lead to different packing modes and phase separation behaviour in the active layer with only a small change in the molecule structure could provide important hints for the design of new molecules to realize better phase separation. On the other hand, different approaches such as thermal annealing, solvent vapor annealing and processing with additives have been used in the optimization of morphology. The phase separation of active layer could be tuned by these methods. However, developing systematic process methods to finely control the phase separation of different donor-acceptor systems and thus to realize ideal morphology is still a big challenge for device fabrication.

(4) Stability issue. Only few reports mentioned the stability issue for small molecule based devices. Device structures, interface layer stability, active layer morphology and its intrinsic chemical stability, all have great impact on the final device stability. Generally, lots of small molecule based devices exhibited good thermal stability, which is one of promising factors for high stability devices. More study are needed to conduct the stability issue. Currently, the lifetime of devices is still a challenge for organic solar cells including polymer and small molecule based devices.

Besides, almost all high performance small molecule organic solar cells are fabricated with fullerene derivatives as acceptors. Although with well known excellent properties, fullerene derivatives have some disadvantages such as limited absorption in the visible region and high cost for preparation and purification. Therefore, non fullerene acceptors have drawn more and more attentions. Developing small molecules based devices with non fullerene acceptors would be a promising alternative way for even low cost and high performance organic solar cells.

Nowadays, devices based on A–D–A small molecule donor materials have provided PCEs over 9%, with the highest PCE of nearly 10%. Through further careful efforts in the design and synthesis of new A–D–A small molecules, together with morphology control and device optimization, it is believed that a PCE of up to 12% for a single junction small molecule-based OPV can be achieved in the near future.

## Acknowledgements

The authors gratefully acknowledge financial support from MoST (2014CB643502), NSFC (51373078, 51422304), PCSIRT (IRT1257) and Tianjin city (13RCGFGX01121).

#### Notes and references

- 1 J. Zhao, A. Wang, M. A. Green and F. Ferrazza, *Appl. Phys. Lett.*, 1998, **73**, 1991–1993.
- 2 L.-M. Chen, Z. Hong, G. Li and Y. Yang, Adv. Mater., 2009, 21, 1434–1449.
- 3 A. C. Arias, J. D. MacKenzie, I. McCulloch, J. Rivnay and A. Salleo, *Chem. Rev.*, 2010, **110**, 3–24.
- 4 A. J. Heeger, Chem. Soc. Rev., 2010, 39, 2354-2371.
- 5 D. J. Lipomi and Z. Bao, Energy Environ. Sci., 2011, 4, 3314-3328.
- 6 F. C. Krebs, Sol. Energy Mater. Sol. Cells, 2009, 93, 394-412.
- 7 H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu and G. Li, *Nat. Photonics*, 2009, **3**, 649–653.
- 8 G. W. P. Van Pruissen, F. Gholamrezaie, M. M. Wienk and R. A. J. Janssen, *J. Mater. Chem.*, 2012, **22**, 20387–20393.
- 9 F. He and L. Yu, J. Phys. Chem. Lett., 2011, 2, 3102-3113.
- 10 Y. Liang and L. Yu, Acc. Chem. Res., 2010, 43, 1227-1236.
- 11 H. Zhou, L. Yang and W. You, *Macromolecules*, 2012, 45, 607–632.
- 12 L. Dou, J. You, Z. Hong, Z. Xu, G. Li, R. A. Street and Y. Yang, Adv. Mater., 2013, 25, 6642–6671.
- 13 C. Duan, F. Huang and Y. Cao, J. Mater. Chem., 2012, 22, 10416–10434.
- 14 A. C. Stuart, J. R. Tumbleston, H. Zhou, W. Li, S. Liu, H. Ade and W. You, J. Am. Chem. Soc., 2013, 135, 1806–1815.
- 15 Z. He, C. Zhong, S. Su, M. Xu, H. Wu and Y. Cao, *Nat. Photonics*, 2012, 6, 591–595.
- 16 S.-H. Liao, H.-J. Jhuo, Y.-S. Cheng and S.-A. Chen, Adv. Mater., 2013, 25, 4766–4771.
- 17 X. Guo, M. Zhang, W. Ma, L. Ye, S. Zhang, S. Liu, H. Ade, F. Huang and J. Hou, *Adv. Mater.*, 2014, **26**, 4043–4049.
- 18 W. Zhang, Y. Wu, Q. Bao, F. Gao and J. Fang, *Adv. Energy Mater.*, 2014, 4, 1400359.
- 19 C.-C. Chen, W.-H. Chang, K. Yoshimura, K. Ohya, J. You, J. Gao, Z. Hong and Y. Yang, *Adv. Mater.*, 2014, 26, 5670–5677.
- 20 A. R. B. Mohd Yusoff, D. Kim, H. P. Kim, F. K. Shneider, W. J. da Silva and J. Jang, *Energy Environ. Sci.*, 2015, **8**, 303–316.
- 21 Y. Lin, Y. Li and X. Zhan, Chem. Soc. Rev., 2012, 41, 4245-4272.
- 22 A. Mishra and P. Bäuerle, Angew. Chem., Int. Ed., 2012, 51, 2020–2067.
- 23 J. Roncali, Acc. Chem. Res., 2009, 42, 1719-1730.
- 24 B. Walker, C. Kim and T.-Q. Nguyen, Chem. Mater., 2010, 23, 470-482.
- 25 Y. Chen, X. Wan and G. Long, Acc. Chem. Res., 2013, 46, 2645-2655.
- 26 J. E. Coughlin, Z. B. Henson, G. C. Welch and G. C. Bazan, Acc. Chem. Res., 2013, 47, 257–270.
   27 H. V. Lin, W. G. H. Scholl, C. L. Scholl, C. Sc
- 27 H.-Y. Lin, W.-C. Huang, Y.-C. Chen, H.-H. Chou, C.-Y. Hsu, J. T. Lin and H.-W. Lin, *Chem. Commun.*, 2012, **48**, 8913–8915.
- 28 A. B. Tamayo, X.-D. Dang, B. Walker, J. Seo, T. Kent and T.-Q. Nguyen, *Appl. Phys. Lett.*, 2009, **94**, 103301.
- 29 X. Liu, Y. Sun, L. A. Perez, W. Wen, M. F. Toney, A. J. Heeger and G. C. Bazan, *J. Am. Chem. Soc.*, 2012, **134**, 20609–20612.
- 30 Y. Wu and W. Zhu, Chem. Soc. Rev., 2013, 42, 2039-2058.
- 31 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.
- 32 S. Shen, P. Jiang, C. He, J. Zhang, P. Shen, Y. Zhang, Y. Yi, Z. Zhang, Z. Li and Y. Li, *Chem. Mater.*, 2013, 25, 2274–2281.
- 33 C. D. Wessendorf, G. L. Schulz, A. Mishra, P. Kar, I. Ata, M. Weidelener, M. Urdanpilleta, J. Hanisch, E. Mena-Osteritz, M. Lindén, E. Ahlswede and P. Bäuerle, *Adv. Energy Mater.*, 2014, 4, 1400266.

- 34 Y. Liu, X. Wan, F. Wang, J. Zhou, G. Long, J. Tian, J. You, Y. Yang and Y. Chen, *Adv. Energy Mater.*, 2011, 1, 771–775.
- 35 Z. Li, G. He, X. Wan, Y. Liu, J. Zhou, G. Long, Y. Zuo, M. Zhang and Y. Chen, *Adv. Energy Mater.*, 2012, 2, 74–77.
- 36 G. He, Z. Li, X. Wan, Y. Liu, J. Zhou, G. Long, M. Zhang and Y. Chen, J. Mater. Chem., 2012, 22, 9173–9180.
- 37 W. Li, W. S. C. Roelofs, M. Turbiez, M. M. Wienk and R. A. J. Janssen, *Adv. Mater.*, 2014, 26, 3304–3309.
- 38 B. Qi and J. Wang, *Phys. Chem. Chem. Phys.*, 2013, 15, 8972–8982.
  39 L. Zhang, N. S. Colella, B. P. Cherniawski, S. C. B. Mannsfeld and
- A. L. Briseno, ACS Appl. Mater. Interfaces, 2014, 6, 5327–5343.
  40 S. Chen, Y. Liu, W. Qiu, X. Sun, Y. Ma and D. Zhu, Chem. Mater.,
- 2005, 17, 2208–2215.
  41 K. Schulze, C. Uhrich, R. Schüppel, K. Leo, M. Pfeiffer, E. Brier, E. Reinold and P. Bäuerle, *Adv. Mater.*, 2006, 18, 2872–2875.
- 42 Y. Liu, J. Zhou, X. Wan and Y. Chen, *Tetrahedron*, 2009, **65**, 5209–5215.
- 43 Y. Liu, X. Wan, B. Yin, J. Zhou, G. Long, S. Yin and Y. Chen, J. Mater. Chem., 2010, 20, 2464–2468.
- 44 B. Yin, L. Yang, Y. Liu, Y. Chen, Q. Qi, F. Zhang and S. Yin, Appl. Phys. Lett., 2010, 97, 023303.
- 45 D. Demeter, T. Rousseau, P. Leriche, T. Cauchy, R. Po and J. Roncali, Adv. Funct. Mater., 2011, 21, 4379–4387.
- 46 G. He, X. Wan, Z. Li, Q. Zhang, G. Long, Y. Liu, Y. Hou, M. Zhang and Y. Chen, J. Mater. Chem. C, 2014, 2, 1337–1345.
- 47 Y. Liu, Y. Yang, C.-C. Chen, Q. Chen, L. Dou, Z. Hong and G. Li, *Adv. Mater.*, 2013, **25**, 4657–4662.
- 48 G. He, Z. Li, X. Wan, J. Zhou, G. Long, S. Zhang, M. Zhang and Y. Chen, J. Mater. Chem. A, 2013, 1, 1801–1809.
- 49 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.
- 50 G. Long, X. Wan, B. Kan, Y. Liu, G. He, Z. Li, Y. Zhang, Y. Zhang, Q. Zhang, M. Zhang and Y. Chen, *Adv. Energy Mater.*, 2013, 3, 639–646.
- 51 C. Cui, X. Fan, M. Zhang, J. Zhang, J. Min and Y. Li, *Chem. Commun.*, 2011, **47**, 11345–11347.
- 52 T.-Y. Chu, J. Lu, S. Beaupré, Y. Zhang, J.-R. Pouliot, J. Zhou, A. Najari, M. Leclerc and Y. Tao, *Adv. Funct. Mater.*, 2012, 22, 2345–2351.
- 53 L. Liao, L. Dai, A. Smith, M. Durstock, J. Lu, J. Ding and Y. Tao, *Macromolecules*, 2007, **40**, 9406–9412.
- 54 P. M. Beaujuge, W. Pisula, H. N. Tsao, S. Ellinger, K. Müllen and J. R. Reynolds, J. Am. Chem. Soc., 2009, 131, 7514–7515.
- 55 Y. Sun, G. C. Welch, W. L. Leong, C. J. Takacs, G. C. Bazan and A. J. Heeger, *Nat. Mater.*, 2012, **11**, 44–48.
- 56 N. D. Eisenmenger, G. M. Su, G. C. Welch, C. J. Takacs, G. C. Bazan, E. J. Kramer and M. L. Chabinyc, *Chem. Mater.*, 2013, 25, 1688–1698.
- 57 V. Gupta, A. K. K. Kyaw, D. H. Wang, S. Chand, G. C. Bazan and A. J. Heeger, *Sci. Rep.*, 2013, **3**, 1965.
- 58 J. Zhou, X. Wan, Y. Liu, G. Long, F. Wang, Z. Li, Y. Zuo, C. Li and Y. Chen, *Chem. Mater.*, 2011, 23, 4666–4668.
- 59 D. Ye, X. Li, L. Yan, W. Zhang, Z. Hu, Y. Liang, J. Fang, W.-Y. Wong and X. Wang, *J. Mater. Chem. A*, 2013, 1, 7622–7629.
- 60 K.-H. Kim, H. Yu, H. Kang, D. J. Kang, C.-H. Cho, H.-H. Cho, J. H. Oh and B. J. Kim, *J. Mater. Chem. A*, 2013, 1, 14538–14547.
- 61 L. Fu, H. Pan, T. T. Larsen-Olsen, T. R. Andersen, E. Bundgaard, F. C. Krebs and H.-Z. Chen, *Dyes Pigm.*, 2013, 97, 141–147.
- 62 Y. Liang, D. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray and L. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 7792–7799.
- 63 Y. Liang, Y. Wu, D. Feng, S.-T. Tsai, H.-J. Son, G. Li and L. Yu, *J. Am. Chem. Soc.*, 2008, **131**, 56–57.
- 64 L. Huo and J. Hou, Polym. Chem., 2011, 2, 2453-2461.
- 65 C. Cabanetos, A. El Labban, J. A. Bartelt, J. D. Douglas, W. R. Mateker, J. M. J. Fréchet, M. D. McGehee and P. M. Beaujuge, *J. Am. Chem. Soc.*, 2013, 135, 4656–4659.
- 66 J. Min, Z.-G. Zhang, S. Zhang and Y. Li, *Chem. Mater.*, 2012, 24, 3247-3254.
- 67 J. Hou, M.-H. Park, S. Zhang, Y. Yao, L.-M. Chen, J.-H. Li and Y. Yang, *Macromolecules*, 2008, **41**, 6012–6018.
- 68 S. C. Price, A. C. Stuart, L. Yang, H. Zhou and W. You, *J. Am. Chem. Soc.*, 2011, **133**, 4625–4631.
- 69 Y. Liu, X. Wan, F. Wang, J. Zhou, G. Long, J. Tian and Y. Chen, Adv. Mater., 2011, 23, 5387–5391.

- 70 M. Li, W. Ni, B. Kan, X. Wan, L. Zhang, Q. Zhang, G. Long, Y. Zuo and Y. Chen, *Phys. Chem. Chem. Phys.*, 2013, 15, 18973–18978.
- 71 G. Long, X. Wan, B. Kan, Z. Hu, X. Yang, Y. Zhang, M. Zhang, H. Wu, F. Huang, S. Su, Y. Cao and Y. Chen, *ChemSusChem*, 2014, 7, 2358–2364.
- 72 W. Ni, M. Li, X. Wan, H. Feng, B. Kan, Y. Zuo and Y. Chen, *RSC Adv.*, 2014, 4, 31977–31980.
- 73 B. Kan, Q. Zhang, M. Li, X. Wan, W. Ni, G. Long, Y. Wang, X. Yang,
   H. Feng and Y. Chen, J. Am. Chem. Soc., 2014, 136, 15529–15532.
- 74 L. Huo, J. Hou, S. Zhang, H.-Y. Chen and Y. Yang, Angew. Chem., Int. Ed., 2010, 49, 1500–1503.
- 75 L. Ye, S. Zhang, L. Huo, M. Zhang and J. Hou, Acc. Chem. Res., 2014, 47, 1595–1603.
- 76 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, 8484–8487.
- 77 Y. Liu, C.-C. Chen, Z. Hong, J. Gao, Y. Yang, H. Zhou, L. Dou and G. Li, *Sci. Rep.*, 2013, 3, 3356.
- 78 D. Patra, T.-Y. Huang, C.-C. Chiang, R. O. V. Maturana, C.-W. Pao, K.-C. Ho, K.-H. Wei and C.-W. Chu, ACS Appl. Mater. Interfaces, 2013, 5, 9494–9500.
- 79 Z. Du, W. Chen, Y. Chen, S. Qiao, X. Bao, S. Wen, M. Sun, L. Han and R. Yang, *J. Mater. Chem. A*, 2014, **2**, 15904–15911.
- 80 Y. Lin, L. Ma, Y. Li, Y. Liu, D. Zhu and X. Zhan, *Adv. Energy Mater.*, 2014, 4, 1300626.
- 81 D. Deng, Y. Zhang, L. Yuan, C. He, K. Lu and Z. Wei, Adv. Energy Mater., 2014, 1400538.
- 82 D. Patra, C.-C. Chiang, W.-A. Chen, K.-H. Wei, M.-C. Wu and C.-W. Chu, *J. Mater. Chem. A*, 2013, **1**, 7767–7774.
- 83 N. Lim, N. Cho, S. Paek, C. Kim, J. K. Lee and J. Ko, *Chem. Mater.*, 2014, **26**, 2283–2288.
- 84 C. Cui, J. Min, C.-L. Ho, T. Ameri, P. Yang, J. Zhao, C. J. Brabec and W.-Y. Wong, *Chem. Commun.*, 2013, **49**, 4409–4411.
- 85 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.
- 86 Y. Han, L. Chen and Y. Chen, J. Polym. Sci., Part A: Polym. Chem., 2013, 51, 258–266.

- 87 J. Yuan, X. Huang, F. Zhang, J. Lu, Z. Zhai, C. Di, Z. Jiang and W. Ma, J. Mater. Chem., 2012, 22, 22734–22742.
- 88 S. Qu and H. Tian, Chem. Commun., 2012, 48, 3039-3051.
- 89 Y. Lin, L. Ma, Y. Li, Y. Liu, D. Zhu and X. Zhan, *Adv. Energy Mater.*, 2013, 3, 1166–1170.
- 90 J. Huang, C. Zhan, X. Zhang, Y. Zhao, Z. Lu, H. Jia, B. Jiang, J. Ye, S. Zhang, A. Tang, Y. Liu, Q. Pei and J. Yao, ACS Appl. Mater. Interfaces, 2013, 5, 2033–2039.
- 91 B. Walker, J. Liu, C. Kim, G. C. Welch, J. K. Park, J. Lin, P. Zalar, C. M. Proctor, J. H. Seo, G. C. Bazan and T.-Q. Nguyen, *Energy Environ. Sci.*, 2013, 6, 952–962.
- 92 A. Guerrero, S. Loser, G. Garcia-Belmonte, C. J. Bruns, J. Smith, H. Miyauchi, S. I. Stupp, J. Bisquert and T. J. Marks, *Phys. Chem. Chem. Phys.*, 2013, 15, 16456–16462.
- 93 C. Li, Y. Chen, Y. Zhao, H. Wang, W. Zhang, Y. Li, X. Yang, C. Ma, L. Chen, X. Zhu and Y. Tu, *Nanoscale*, 2013, 5, 9536–9540.
- 94 M. Karakawa and Y. Aso, RSC Adv., 2013, 3, 16259-16263.
- 95 M. Weidelener, C. D. Wessendorf, J. Hanisch, E. Ahlswede, G. Gotz, M. Linden, G. Schulz, E. Mena-Osteritz, A. Mishra and P. Bauerle, *Chem. Commun.*, 2013, **49**, 10865–10867.
- 96 W. Ni, M. Li, B. Kan, Y. Zuo, Q. Zhang, G. Long, H. Feng, X. Wan and Y. Chen, Org. Electron., 2014, 15, 2285–2294.
- 97 H. Bai, Y. Wang, P. Cheng, Y. Li, D. Zhu and X. Zhan, ACS Appl. Mater. Interfaces, 2014, 6, 8426–8433.
- 98 J. W. Lee, Y. S. Choi and W. H. Jo, Org. Electron., 2012, 13, 3060–3066.
- 99 Y. S. Choi and W. H. Jo, Org. Electron., 2013, 14, 1621-1628.
- 100 L. Zhang, S. Zeng, L. Yin, C. Ji, K. Li, Y. Li and Y. Wang, New J. Chem., 2013, 37, 632–639.
- 101 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.
- 102 S. Loser, H. Miyauchi, J. W. Hennek, J. Smith, C. Huang, A. Facchetti and T. J. Marks, *Chem. Commun.*, 2012, 48, 8511–8513.
- 103 X. Lin, Y. Tani, R. Kanda, K.-I. Nakayama and S. Yagai, J. Mater. Chem. A, 2013, 1, 14686–14691.
- 104 H. Bai, P. Cheng, Y. Wang, L. Ma, Y. Li, D. Zhu and X. Zhan, *J. Mater. Chem. A*, 2014, **2**, 778–784.