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## A new class of three-dimensional, p-type, spirobifluorene-modified perylene diimide derivatives for small molecular-based bulk heterojunction organic photovoltaic devices

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A new class of non-planar and three-dimensional spirobifluorene-modified perylene diimide compounds has been successfully designed and synthesized. The functionalization of the perylene diimide core with different spirobifluorene moieties can alter the molecular geometry as well as extend the spectral coverage into the red region. In addition, these compounds can be utilized as donor materials in combination with fullerene to form bulk heterojunctions, and particularly efficient organic photovoltaic (OPV) devices demonstrating high open-circuit voltages of 0.97 V and a power conversion efficiencies of up to 4% have been prepared. These values are the highest among the cells utilizing p-type perylene diimide as photoactive material in OPV devices. This work opens up a new avenue for the design and synthesis of a new class of p-type perylene diimide compounds that are promising candidates as donor materials in the fabrication of OPV devices.

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### Introduction

Organic photovoltaic (OPV) devices are considered as a promising renewable energy source due to their distinct properties, including light weight, flexibility, and low manufacturing cost, over their inorganic counterparts. Significant advances in the developments of smart materials and innovative device architectures have boosted the power conversion efficiencies (PCEs) of up to 9.2% for a single cell and 10.6% for a tandem device.<sup>1,2a</sup> Heliatek recently reported a world-record OPV device with a PCE of 12% based on oligomers with a tandem architecture.<sup>1b</sup> While most of the record-high OPV devices are based on employing newly synthesized polymers or oligomers as donor materials in combination with fullerene acceptors,<sup>2b-e</sup> the difficulty to produce high quality thin films and to obtain a high batch-to-batch reproducibility poses a major challenge for achieving efficient polymeric OPV devices. In addition, it is quite difficult to control the morphology and phase separation of active layer blends, which play a vital role in governing the device performance. On the other hand, small molecules are monodisperse in nature with well-defined chemical structures and can be synthesized with high purity and reproducibility. More importantly, it is much easier to produce high quality and uniform

thin films based on small molecules *via* a vacuum deposition technique.

While small molecules can in principle give rise to OPV devices of better performance, the development of small molecular-based OPV devices is lagging much behind those of the polymer counterparts.<sup>3a-d,f-h</sup> A major challenge lies in the much smaller carrier mobility in small molecules than those of the polymers that leads to a low fill factor (FF), and hence a relatively low PCE of the OPV devices. This is especially the case for the devices with bulk heterojunctions, in which the carrier mobility in the blended layer is two or three orders of magnitude lower than that in the homogeneous layer.<sup>4</sup> In addition, the planar geometry of small molecular-based donor materials would favor a mutually parallel orientation or polaron-pair recombination with fullerene acceptors, which would inevitably induce significant charge recombination to lower the device performance.<sup>5,6</sup> As recently reported by Adachi and coworkers, the planar structure of donor materials, such as pentacene and copper phthalocyanine, would disrupt the molecular stacking of the fullerenes, resulting in a low PCE of the OPV devices.<sup>6</sup>

Apart from the metal phthalocyanine or aromatic compounds,<sup>7</sup> perylene diimide (PDI) is another class of small molecules that has aroused much interest in organic field-effect transistors (OFETs) and more recently in OPV.<sup>8-10</sup> PDI is a traditional dye with large molar extinction coefficients, high photo-stability and good chemical robustness. Owing to the  $\pi$ - $\pi$  stacking in the conducting direction, it has an excellent electron-accepting property with a high electron mobility.

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Particularly, PDI and its derivatives have been widely studied for their self-assembly behavior and have been extensively used as semiconducting materials in the fabrication of organic field-effect transistors.<sup>8</sup> Taking the advantages of the high electron mobility, PDI compounds are prototypes of n-type acceptors in OPV devices.<sup>9</sup> However, the performance based on PDI is rather poor, in which the strong  $\pi$ - $\pi$  stacking of the PDI molecules may be the major reason for the occurrence of severe exciton quenching and results in a considerably low PCE of such devices.<sup>10</sup> It was only until very recently that Zhao and coworkers demonstrated a series of PDI dimers connected with different spirobifluorene linkers that served as an acceptor in a PDI dimer:poly(3-hexylthiophene-2,5-diyl)-based device to give a satisfactory PCE of up to 2.3%.<sup>9e</sup> The introduction of spirobifluorene linkers has been suggested to effectively suppress the self-aggregation and crystallization of the PDI units and enhance the exciton dissociation at the organic heterojunction. Narayan and coworkers also reported another twisted PDI compound as an acceptor.<sup>9a</sup> A high PCE of 2.8% has been achieved when this compound was blended into a polymer donor. These results demonstrate that non-planar PDI molecules can disrupt the crystallinity and enhance the short-circuit current density ( $J_{SC}$ ) and PCE of OPV devices.

As the planarity of the PDI molecules has proven to have an impact on the photovoltaic responses, this would provide new insights and open up new opportunities for the design and synthesis of efficient PDI molecules as donors or acceptors for the fabrication of OPV devices. Indeed, there are very limited reports on the synthesis of the p-type PDI counterparts.<sup>11</sup> Herein, we report the synthesis, electrochemical and photovoltaic properties of a novel class of p-type, non-planar and three-dimensional spirobifluorene-modified PDI derivatives. By functionalizing the PDI core with various spirobifluorene groups, both the optical and electronic properties of the PDI derivatives can be significantly manipulated. In particular, the electronic absorption spectral properties of such PDI compounds can cover the entire visible region with a low optical bandgap. In addition, this class of compounds has been explored as donor materials in the fabrication of efficient bulk heterojunction OPV devices.

## Experimental section

### Materials

All chemicals used for synthesis were of analytical grade and were purchased and used as received from Sigma-Aldrich Chemical Co. and Strem Chemicals Inc.

### Synthesis

**TPA-SPIRO-Br.** 4-(Diphenylamino)phenylboronic acid (289 mg, 1 mmol) and 2,7-dibromo-9,9'-spirobifluorene (1.89 g, 4 mmol) were added into a mixture of tetrahydrofuran and aqueous  $K_2CO_3$  (2 M). The reaction mixture was degassed for at least 15 minutes. Then,  $[Pd(PPh_3)_4]$  (58 mg, 0.05 mmol) was added and the reaction mixture was heated at reflux overnight. After that, the reaction was cooled down and extracted three

times with dichloromethane. The combined organic layer was washed with deionized water several times. The organic layer was dried over anhydrous  $MgSO_4$ , and the solvent was evaporated to dryness under vacuum. The crude product was purified by column chromatography using dichloromethane-hexane as eluent. Further purification was achieved by recrystallization of the product with dichloromethane-methanol. Yield: 414 mg (65%).  $^1H$  NMR (400 MHz, acetone- $d_6$ , 298 K, relative to  $Me_4Si$ ):  $\delta$  6.77 (t, 3H, 8.0 Hz, spiro- $H_{1'}$ ,  $H_{8'}$  and  $H_1$ ), 6.92 (s, 1H, spiro- $H_8$ ), 6.96–7.04 (m, 8H, TPA), 7.19 (t, 2H, 8.0 Hz, spiro- $H_{2'}$  and  $H_{7'}$ ), 7.27 (t, 4H, 8.0 Hz, TPA), 7.37 (d, 2H, 8.0 Hz, TPA), 7.44 (t, 2H, 8.0 Hz, spiro- $H_4$  and  $H_5$ ), 7.59 (d, 1H, 8.0 Hz, spiro- $H_6$ ), 7.73 (d, 1H, 8.0 Hz, spiro- $H_3$ ), 7.96–8.02 (m, 3H, spiro- $H_{4'}$ ,  $H_{5'}$  and  $H_{6'}$ ), 8.08 (d, 1H, 8.0 Hz, spiro- $H_{3'}$ ). HRMS (positive-EI) calcd for  $C_{43}H_{28}BrN$ :  $m/z = 637.1400$ ; found: 637.1415  $[M]^+$ .

**TPA-tert-SPIRO-Br.** The procedure was similar to that for **TPA-SPIRO-Br**, except 2,7-dibromo-2',7'-di-tert-butyl-9,9'-spirobifluorene (2.34 g, 4 mmol) was used in place of 2,7-dibromo-9,9'-spirobifluorene. Yield: 562 mg (75%).  $^1H$  NMR (400 MHz,  $CDCl_3$ , 298 K, relative to  $Me_4Si$ ):  $\delta$  1.16 (s, 18H,  $^tBu$ ), 6.67 (s, 2H, spiro- $H_{1'}$  and  $H_{8'}$ ), 6.84 (s, 1H, spiro- $H_1$ ), 6.89 (s, 1H, spiro- $H_8$ ), 6.96–7.06 (m, 8H, TPA), 7.21 (t, 4H, 8.0 Hz, TPA), 7.29 (d, 2H, 8.0 Hz, TPA), 7.39 (t, 2H, 8.0 Hz, spiro- $H_4$  and  $H_5$ ), 7.48 (d, 1H, 8.0 Hz, spiro- $H_6$ ), 7.59 (d, 1H, 8.0 Hz, spiro- $H_3$ ), 7.71 (m, 3H, spiro- $H_{4'}$ ,  $H_{5'}$  and  $H_{6'}$ ), 7.85 (d, 1H, 8.0 Hz, spiro- $H_{3'}$ ). HRMS (positive-EI) calcd for  $C_{51}H_{44}BrN$ :  $m/z = 749.2652$ ; found: 749.2652  $[M]^+$ .

**TPA-SPIRO-Bpin.** 4-(2-Bromo-9,9'-spirobifluorene-7-yl)-*N,N*-diphenylaniline (637 mg, 1 mmol), potassium acetate (294 mg, 3 mmol) and bis(pinacolato)diboron (381 mg, 1.5 mmol) were dissolved in dry toluene. Then,  $[Pd(dppf)Cl_2] \cdot CH_2Cl_2$  (43 mg, 0.05 mmol) was added. The reaction mixture was heated at 90 °C overnight. After that, the reaction was quenched with deionized water and extracted three times with dichloromethane. The combined organic layer was washed with deionized water several times. The organic layer was dried over anhydrous  $MgSO_4$ , and the solvent was evaporated to dryness under vacuum. The crude product was purified by column chromatography using dichloromethane-hexane as eluent. Further purification was achieved by recrystallization of the product with dichloromethane-methanol. Yield: 417 mg (61%).  $^1H$  NMR (400 MHz, acetone- $d_6$ , 298 K, relative to  $Me_4Si$ ):  $\delta$  1.22 (s, 12H,  $CH_3$ ), 6.71 (d, 2H, 8.0 Hz, spiro- $H_{1'}$  and  $H_{8'}$ ), 6.94–7.09 (m, 10H, TPA, spiro- $H_1$  and  $H_8$ ), 7.17 (t, 2H, 8.0 Hz, spiro- $H_{2'}$  and  $H_{7'}$ ), 7.27 (t, 4H, 8.0 Hz, TPA), 7.37–7.45 (m, 4H, TPA and spiro- $H_4$  and  $H_5$ ), 7.74 (d, 1H, 8.0 Hz, spiro- $H_6$ ), 7.81 (d, 1H, 8.0 Hz, spiro- $H_3$ ), 8.01–8.04 (m, 3H, spiro- $H_{4'}$ ,  $H_{5'}$  and  $H_{6'}$ ), 8.11 (d, 1H, 8.0 Hz, spiro- $H_{3'}$ ). HRMS (positive-EI) calcd for  $C_{49}H_{39}O_2NB$ :  $m/z = 684.3068$ ; found: 684.3158  $[M]^+$ .

**TPA-tert-SPIRO-Bpin.** The procedure was similar to that for **TPA-SPIRO-Bpin**, except 4-(2-bromo-2',7'-di-tert-butyl-9,9'-spirobifluorene-7-yl)-*N,N*-diphenylaniline (749 mg, 1 mmol) was used in place of 4-(2-bromo-9,9'-spirobifluorene-7-yl)-*N,N*-diphenylaniline. Yield: 493 mg (62%).  $^1H$  NMR (400 MHz, Acetone- $d_6$ , 298 K, relative to  $Me_4Si$ ):  $\delta$  1.12 (s, 18H,  $^tBu$ ), 1.20 (s, 12H,  $CH_3$ ), 6.74 (d, 2H, 8.0 Hz, spiro- $H_{1'}$  and  $H_{8'}$ ), 6.93–7.08 (m, 10H, TPA, spiro- $H_1$  and  $H_8$ ), 7.24–7.29 (m, 4H, TPA), 7.38 (d, 2H, 8.0 Hz, TPA), 7.48 (d, 2H, 8.0 Hz, spiro- $H_4$  and  $H_5$ ), 7.76 (d, 1H,

8.0 Hz, spiro-H<sub>6</sub>), 7.82 (d, 1H, 8.0 Hz, spiro-H<sub>3</sub>), 7.89 (d, 2H, 8.0 Hz, spiro-H<sub>4</sub> and H<sub>5</sub>), 8.02 (d, 1H, 8.0 Hz, spiro-H<sub>6</sub>), 8.09 (d, 1H, 8.0 Hz, spiro-H<sub>3</sub>). HRMS (positive-EI) calcd for C<sub>57</sub>H<sub>55</sub>O<sub>2</sub>NB:  $m/z = 796.4320$ ; found: 796.4425 [M]<sup>+</sup>.

**PDI(OPh)<sub>4</sub>.** Precursor **PDI(OPh)<sub>4</sub>** was synthesized according to the modified literature procedure.<sup>12d,ef</sup> Tetrachloro-PDI precursor (694 mg, 1 mmol) and 4-iodophenol (8 mmol) were dissolved in dry 1-methyl-2-pyrrolidinone. K<sub>2</sub>CO<sub>3</sub> (12 mmol) was added to the reaction mixture, followed by heating at 90 °C overnight. After that, the reaction was quenched with water and extracted with dichloromethane for three times. The combined organic layer was washed with deionized water several times. The organic layer was dried over anhydrous MgSO<sub>4</sub>, and the solvent was evaporated to dryness under vacuum. The crude product was purified by column chromatography using dichloromethane–hexane as eluent. Further purification was achieved by recrystallization of the product with dichloromethane–ethanol. Yield: 1.07 g (75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si): δ 0.86 (t, 6H, 8.0 Hz, –NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.25–1.43 (m, 12H, –NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>–), 1.54–1.68 (m, 4H, –NCH<sub>2</sub>CH<sub>2</sub>–), 4.09 (t, 4H, 8.0 Hz, –NCH<sub>2</sub>–), 6.67 (d, 8H, 8.0 Hz, Ph), 7.58 (d, 8H, 8.0 Hz, Ph), 8.16 (s, 4H, PDI). MS (positive-FAB):  $m/z = 1430.6$  [M]<sup>+</sup>.

**PDI(OPh)<sub>2</sub>.** The precursor **PDI(OPh)<sub>2</sub>** was synthesized according to a procedure similar to that of precursor **PDI(OPh)<sub>4</sub>**, except that the dichloro-PDI precursor (628 mg, 1 mmol) was used in place of the tetrachloro-PDI precursor. Yield: 795 mg (80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si): δ 0.82 (t, 6H, 8.0 Hz, –NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.25–1.43 (m, 12H, –NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>–), 1.69–1.74 (m, 4H, –NCH<sub>2</sub>CH<sub>2</sub>–), 4.15 (t, 4H, 8.0 Hz, –NCH<sub>2</sub>–), 6.65 (d, 4H, 8.0 Hz, Ph), 7.58 (d, 4H, 8.0 Hz, Ph), 8.19 (s, 2H, PDI-H<sub>2</sub> and H<sub>5</sub>), 8.57 (d, 2H, 8.0 Hz, PDI-H<sub>9</sub> and H<sub>10</sub>), 8.65 (d, 2H, 8.0 Hz, PDI-H<sub>8</sub> and H<sub>11</sub>). HRMS (positive-EI) calcd for C<sub>48</sub>H<sub>40</sub>O<sub>6</sub>N<sub>2</sub>I<sub>2</sub>:  $m/z = 994.0970$ ; found: 994.0960 [M]<sup>+</sup>.

**Compound 1 [(TPA-PhO)<sub>4</sub>-PDI].** The product was synthesized according to the standard Suzuki coupling reaction conditions. The precursor **PDI(OPh)<sub>4</sub>** (1.43 g, 1 mmol) was dissolved in a mixture of aqueous K<sub>2</sub>CO<sub>3</sub> (2 M) solution (8 ml) and THF (80 ml). After that, 4-(diphenylamino)phenylboronic acid (1.73 g, 6 mmol) was added to the reaction mixture. The solvent was degassed for 15 minutes and [Pd(PPh<sub>3</sub>)<sub>4</sub>] (0.2 mmol) was added. The reaction mixture was heated at reflux overnight. The crude reaction mixture was extracted with dichloromethane at least three times. Then, the organic layer was washed with deionized water several times. The organic layer was dried over anhydrous MgSO<sub>4</sub>, and the solvent was evaporated to dryness under vacuum. The crude product was purified by column chromatography using dichloromethane–methanol. Yield: 1.57 g (83%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K, relative to Me<sub>4</sub>Si): δ 0.81–0.85 (m, 6H, –NCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.21–1.40 (m, 12H, –NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>–), 1.53–1.65 (m, 4H, –NCH<sub>2</sub>CH<sub>2</sub>–), 4.04 (t, 4H, 8.0 Hz, –NCH<sub>2</sub>–), 6.98–7.09 (m, 40H, TPA), 7.22–7.26 (m, 16H, TPA), 7.38 (d, 4H, 8.0 Hz, Ph), 7.44 (d, 8H, 8.0 Hz, Ph), 8.21 (s, 4H, PDI). HRMS (MALDI-TOF)

calcd for C<sub>132</sub>H<sub>102</sub>O<sub>8</sub>N<sub>6</sub>:  $m/z = 1900.2577$ ; found: 1901.6255 [M + 1]<sup>+</sup>.

**Compound 2 [(TPA-SPIRO-PhO)<sub>4</sub>-PDI].** The product was synthesized according to a procedure similar to that of compound 1, except that precursor **TPA-SPIRO-Bpin** (4.1 g, 6 mmol) was used in place of 4-(diphenylamino)phenylboronic acid. Yield: 2.27 g (72%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K, relative to Me<sub>4</sub>Si): δ 0.81–0.87 (m, 6H, –NCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.19–1.41 (m, 16H, –NCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>–), 3.94 (t, 4H, 8.0 Hz, –NCH<sub>2</sub>–), 6.77 (d, 8H, 7.6 Hz, Ph), 6.82 (d, 8H, 8.3 Hz, spiro), 6.87 (d, 8H, 3.8 Hz, spiro), 6.96–7.02 (m, 32H, TPA and spiro), 7.11 (t, 8H, 7.6 Hz, spiro), 7.20 (t, 16H, 8.0 Hz, TPA), 7.29 (t, 16H, 8.4 Hz, TPA), 7.37 (t, 8H, 7.6 Hz, spiro), 7.53 (d, 4H, 8.0 Hz, spiro), 7.63 (d, 4H, 7.6 Hz, spiro), 7.86 (d, 8H, 7.6 Hz, Ph), 7.91 (d, 4H, 7.7 Hz, spiro), 7.94 (d, 4H, 8.0 Hz, spiro), 8.00 (s, 4H, PDI). HRMS (MALDI-TOF) calcd for C<sub>232</sub>H<sub>158</sub>O<sub>8</sub>N<sub>6</sub>:  $m/z = 3157.7723$ ; found: 3157.8599 [M]<sup>+</sup>.

**Compound 3 [(TPA-tert-SPIRO-PhO)<sub>4</sub>-PDI].** The product was synthesized according to a procedure similar to that of compound 1, except that precursor **TPA-tert-SPIRO-Bpin** (4.77 g, 6 mmol) was used in place of 4-(diphenylamino)phenylboronic acid. Yield: 2.45 g (68%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si): δ 0.83–0.85 (m, 6H, –NCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.16 (s, 72H, <sup>t</sup>Bu), 1.24–1.36 (m, 16H, –NCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>–), 4.00 (t, 4H, 8.0 Hz, –NCH<sub>2</sub>–), 6.74 (d, 8H, 7.6 Hz, Ph), 6.85 (d, 8H, 8.7 Hz, spiro), 6.91 (d, 8H, 5.1 Hz, spiro), 6.97–7.08 (m, 32H, TPA and spiro), 7.22 (t, 16H, 8.0 Hz, TPA), 7.34 (t, 16H, 8.4 Hz, TPA), 7.40 (d, 8H, 8.0 Hz, spiro), 7.50 (d, 4H, 7.9 Hz, spiro), 7.62 (d, 4H, 8.0 Hz, spiro), 7.73 (d, 8H, 7.9 Hz, Ph), 7.88 (d, 4H, 8.1 Hz, spiro), 7.92 (d, 4H, 8.2 Hz, spiro), 8.06 (s, 4H, PDI). HRMS (MALDI-TOF) calcd for C<sub>264</sub>H<sub>222</sub>O<sub>8</sub>N<sub>6</sub>:  $m/z = 3606.6229$ ; found: 3606.0172 [M]<sup>+</sup>.

**Compound 4 [(TPA-tert-SPIRO-PhO)<sub>2</sub>-PDI].** The product was synthesized according to a procedure similar to that of compound 3, except that precursor **PDI(OPh)<sub>2</sub>** (994 mg, 1 mmol) was used in place of precursor **PDI(OPh)<sub>4</sub>**. Yield: 1.58 g (76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si): δ 0.82 (t, 6H, 8.0 Hz, –NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.16 (s, 36H, <sup>t</sup>Bu), 1.28–1.43 (m, 12H, –NCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>–), 1.60–1.69 (m, 4H, –NCH<sub>2</sub>CH–), 4.11 (t, 4H, 8.0 Hz, –NCH<sub>2</sub>–), 6.74 (d, 4H, 7.6 Hz, Ph), 6.84 (d, 4H, 8.7 Hz, spiro), 6.90 (d, 4H, 5.1 Hz, spiro), 7.00–7.08 (m, 16H, TPA and spiro), 7.22 (t, 8H, 8.0 Hz, TPA), 7.33 (t, 8H, 8.4 Hz, TPA), 7.40 (d, 4H, 8.0 Hz, spiro), 7.50 (d, 2H, 7.9 Hz, spiro), 7.62 (d, 2H, 8.0 Hz, spiro), 7.75 (d, 4H, 8.0 Hz, Ph), 7.88 (d, 2H, 8.0 Hz, spiro), 7.92 (d, 2H, 8.1 Hz, spiro), 8.19 (s, 2H, PDI-H<sub>2</sub> and H<sub>5</sub>), 8.56 (d, 2H, 8.0 Hz, PDI-H<sub>9</sub> and H<sub>10</sub>), 8.63 (d, 2H, 8.0 Hz, PDI-H<sub>8</sub> and H<sub>11</sub>). HRMS (MALDI-TOF) calcd for C<sub>150</sub>H<sub>128</sub>O<sub>6</sub>N<sub>4</sub>:  $m/z = 2082.6445$ ; found: 2082.6904 [M]<sup>+</sup>.

### Physical measurements and instrumentation

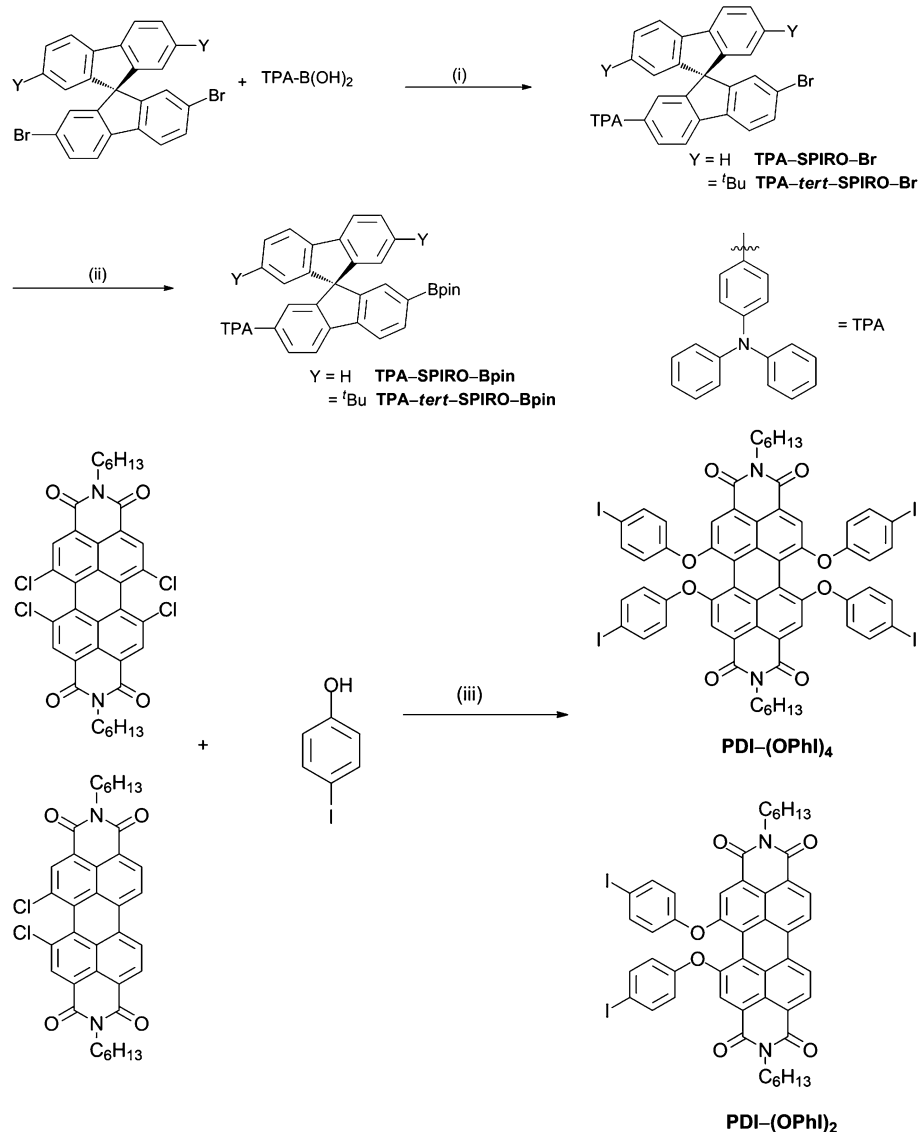
<sup>1</sup>H NMR spectra were recorded using a Bruker Avance 400 (400 MHz) Fourier-transform NMR spectrometer with chemical shifts reported relative to tetramethylsilane ((CH<sub>3</sub>)<sub>4</sub>Si). Positive-ion EI and FAB mass spectra were recorded using a Thermo Scientific DFS high-resolution magnetic sector mass spectrometer. The electronic absorption spectra were obtained using a Hewlett-Packard 8452A diode array spectrophotometer. Cyclic voltammetric measurements were performed with a CH

Instruments, Inc. model CHI 620A electrochemical analyzer. Electrochemical measurements were performed in dichloromethane solutions with  $0.1 \text{ mol dm}^{-3} \text{ } ^n\text{Bu}_4\text{NPF}_6$  as supporting electrolyte at room temperature. The reference electrode was a  $\text{Ag}/\text{AgNO}_3$  ( $0.1 \text{ mol dm}^{-3}$  in acetonitrile) electrode, and the working electrode was a glassy carbon electrode (CH Instruments, Inc.) with a platinum wire as the counter electrode. The working electrode surface was first polished with  $1 \mu\text{m}$  alumina slurry (Linde) on a microcloth (Buehler Co.), and then with a  $0.3 \mu\text{m}$  alumina slurry. It was then rinsed with ultrapure deionized water and ultrasonically mixed in a beaker that contained ultrapure water for five minutes. The polishing and ultrasonic mixing steps were repeated twice, and then the working electrode was finally rinsed under a stream of ultrapure deionized water. The ferrocenium/ferrocene couple ( $\text{Fc}^+/\text{Fc}$ ) was used as the internal reference. All solutions for electrochemical studies were deaerated with prepurified argon gas prior to the

measurements. Current–voltage characteristics of the solar cells were measured using a programmable Keithley model 2400 power source. The photocurrent was measured under illumination from an Oriel 300 W solar simulator equipped with AM 1.5G (AM: air mass; G: global) filter, and the light intensity was measured using an Oriel silicon reference cell. For the external quantum efficiency measurements, devices were irradiated with monochromatic light of variable wavelength by using an Oriel Cornerstone 260 1/4 m monochromator with a 300 W xenon arc lamp (Oriel Model no. 74125). Thermogravimetric analysis was performed with a thermal gravimetric analyzer (Perkin-Elmer TGA 7) with a heating rate of  $10 \text{ } ^\circ\text{C min}^{-1}$  under a nitrogen atmosphere.

### Fabrication of OPV devices

OPV devices were fabricated on patterned ITO-coated glass substrates with a sheet resistance of  $30 \Omega \text{ sq.}^{-1}$ . The substrates



**Scheme 1** Synthetic schemes for the precursors. (i) THF–aq. 2 M  $\text{K}_2\text{CO}_3$ ,  $[\text{Pd}(\text{PPh}_3)_4]$ , reflux; (ii)  $\text{B}_2\text{pin}_2$ , KOAc, Toluene,  $[\text{Pd}(\text{dppf})\text{Cl}_2]$ ,  $90 \text{ } ^\circ\text{C}$ ; (iii)  $\text{K}_2\text{CO}_3$ , NMP,  $90 \text{ } ^\circ\text{C}$ .

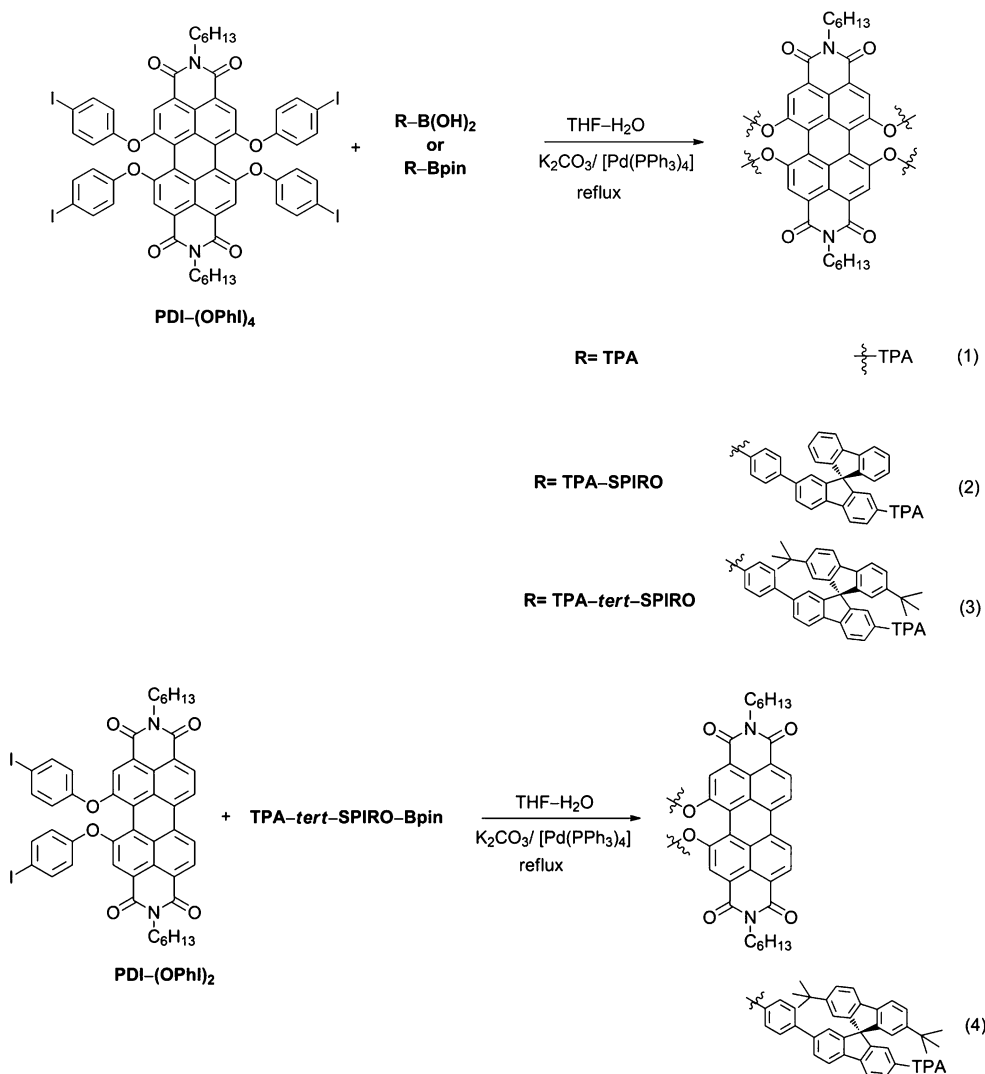
were cleaned with Decon 90, rinsed with de-ionized water, dried in an oven, and then treated in an ultraviolet ozone chamber. After that, the substrates were transferred into a vacuum deposition chamber for thermal evaporation of organic materials and metal, and all the films were sequentially deposited at a rate of 0.1–0.2 nm s<sup>-1</sup> without a vacuum break. A shadow mask was used to define the cathode and to make four 0.1 cm<sup>2</sup> devices on each substrate. All devices were measured under ambient conditions without encapsulation.

## Results and discussion

### Synthesis and characterization

4-(Diphenylamino)phenylboronic acid,<sup>12a</sup> 2,7-dibromo-9,9'-spirobifluorene<sup>12b</sup> and 2,7-dibromo-2',7'-di-*tert*-butyl-9,9'-spirobifluorene<sup>12c</sup> were synthesized according to the reported literature procedures. Precursors **TPA-SPIRO-Br** and **TPA-*tert*-SPIRO-Br** were synthesized by a controlled mono-Suzuki coupling reaction of the corresponding 2,7-dibromo-9,9'-spirobifluorene or

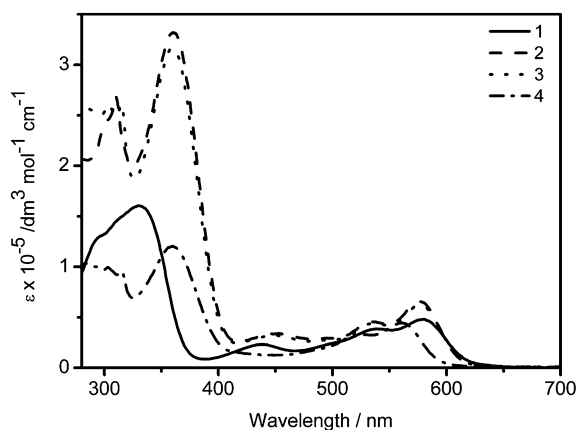
2,7-dibromo-2',7'-di-*tert*-butyl-9,9'-spirobifluorene with 4-(diphenylamino)phenyl-boronic acid in a mixture of tetrahydrofuran and aqueous K<sub>2</sub>CO<sub>3</sub> (2 M) in the presence of [Pd(PPh<sub>3</sub>)<sub>4</sub>] catalyst. Precursors **TPA-SPIRO-Br** and **TPA-*tert*-SPIRO-Br** were obtained in moderate yields, and they were then converted to their corresponding boronic ester precursors **TPA-SPIRO-Bpin** and **TPA-*tert*-SPIRO-Bpin** by palladium-catalyzed borylation with KOAc and B<sub>2</sub>pin<sub>2</sub> in toluene. Precursors **PDI-(OPh)<sub>4</sub>** and **PDI-(OPh)<sub>2</sub>** were synthesized according to modification of a procedure reported in the literature.<sup>12d–f</sup> A mixture containing 4-iodophenol and tetrachloro/dichloro-PDI (8 : 1) were heated at 90 °C in dry 1-methyl-2-pyrrolidinone (NMP) overnight in the presence of excess K<sub>2</sub>CO<sub>3</sub>. Finally, compounds **1–4** were synthesized by the Suzuki coupling reaction of precursors **PDI-(OPh)<sub>4</sub>** and **PDI-(OPh)<sub>2</sub>** with an excess amount of the respective boronic acid/ester. Compounds **1–4** were characterized by <sup>1</sup>H NMR spectroscopy and HR-EI or HR-MALDI-TOF mass spectrometry. The synthetic schemes of precursors and compounds **1–4** are shown in Schemes 1 and 2.



Scheme 2 Synthetic scheme for compounds **1–4**.

Table 1 Electronic absorption data of compounds 1–4 recorded in dichloromethane at 298 K

Compound	Medium	Absorption
		$\lambda_{\max}$ (nm) ( $\epsilon_{\max}$ (dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup> ))
1	CH <sub>2</sub> Cl <sub>2</sub>	330 (159 260), 436 (22 770), 537 (38 100), 580 (47 530)
2	CH <sub>2</sub> Cl <sub>2</sub>	310 (265 800), 360 (331 260), 450 (33 980), 533 (45 790), 576 (64 630)
3	CH <sub>2</sub> Cl <sub>2</sub>	314 (260 910), 359(317 330), 449 (32 050), 533 (43 930), 577 (61 720)
4	CH <sub>2</sub> Cl <sub>2</sub>	314 (90 910), 359(119 890), 520 (32 790), 560 (43 850)

Fig. 1 Electronic absorption spectra of compounds 1–4 in CH<sub>2</sub>Cl<sub>2</sub> at 298 K.

### Electronic absorption properties

The electronic absorption spectra of spirobifluorene-modified perylene diimide derivatives 1–4 were recorded in dichloromethane at 298 K. In general, the electronic absorption spectra of all the compounds show broad absorption bands ranging from 300 to 650 nm with extinction coefficients on the order of  $10^5$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>. The characteristic vibronic absorption bands of PDI located at around 400–600 nm with extinction coefficients of  $4 \times 10^4$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> correspond to the  $\pi$ - $\pi^*$  transition of the PDI core. The electronic absorption band at 400–500 nm is assigned to the  $S_0 \rightarrow S_2$  electronic transition

caused by the dipole moment perpendicular to the long perylene axis, while the absorption band at 500–600 nm is assigned to the  $S_0 \rightarrow S_1$  electronic transition caused by the dipole moment parallel to the long perylene axis. These assignments are based on the grounds of previous spectroscopic work on PDI compounds.<sup>13</sup> The higher-energy absorption bands located at approximately 280–400 nm with extinction coefficients of  $3 \times 10^5$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> correspond to the mixing of  $\pi$ - $\pi^*$  transitions of the pendant triphenylamine and spirobifluorene linker. The  $\pi$ - $\pi^*$  transition of the PDI core is found to be slightly blue-shifted in 4 as a result of the less electron-donating substituents on the PDI core. In addition, the extinction coefficients of the absorption bands of the pendant triphenylamine and spirobifluorene linker, *i.e.* the  $\pi$ - $\pi^*$  transition bands located at approximately 280–400 nm, are found to be correlated to the number of pendant groups attached to the PDI core. It is worth noting that no intramolecular charge transfer band can be found, indicating that there is no significant ground-state electronic interaction between PDI and the pendant triphenylamine-spirobifluorene groups, as expected for the twisted structural configuration of these compounds. The photo-physical data of compounds 1–4 are summarized in Table 1, and the UV-vis spectra are shown in Fig. 1.

### Electrochemical properties

The electrochemical behaviors of compounds 1–4 were studied by cyclic voltammetry. The cyclic voltammograms were recorded in dichloromethane in the presence of 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub>. In general, all the spirobifluorene-modified PDI compounds

Table 2 Electrochemical properties of 1–4

Compound	Oxidation $E_{1/2}$ (V) <sup>a,b</sup> vs. SCE	Reduction $E_{1/2}$ (V) <sup>a,b</sup> vs. SCE	HOMO <sup>c</sup> (eV)	LUMO <sup>d</sup> (eV)	HOMO–LUMO gap (eV)
1	+0.92	−0.67	−5.26	−3.67	1.59
	+1.42	−0.81			
2	+0.91	−0.72	−5.25	−3.62	1.63
	+1.45	−0.85			
3	+0.81	−0.80	−5.15	−3.54	1.61
	+1.33	−0.95			
4	+0.90	−0.66	−5.24	−3.68	1.56
	+1.40	−0.81			

<sup>a</sup> 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte at room temperature; scan rate 100 mV s<sup>-1</sup>. <sup>b</sup>  $E_{1/2} = (E_{pa} + E_{pc})/2$ ;  $E_{pa}$  and  $E_{pc}$  are peak anodic and peak cathodic potentials, respectively. <sup>c</sup>  $E_{HOMO} = -(E_{ox} + 4.34)$  eV. <sup>d</sup>  $E_{LUMO} = -(E_{red} + 4.34)$  eV.

showed two quasi-reversible oxidation couples at around +0.8 to +1.5 V *versus* standard calomel electrode (SCE). The first oxidation couple is assigned to the oxidation of the triphenylamine moiety, whereas the second oxidation couple is assigned to the oxidation of the spirobifluorene linker. With the introduction of the more electron-rich *tert*-butyl groups on the spirobifluorene linker, *i.e.*, compound 3, the potentials for the oxidation were found to be less positive relative to that of compound 2. Two quasi-reversible reduction couples ranging from -0.6 to -1.0 V that arise from the PDI-centered reduction are observed. With the attachment of less electron-donating groups to the PDI core, the reduction peak potentials became less negative, whereas the potentials for the oxidation peaks remained almost unchanged. For example, with compounds 1 and 2, the introduction of spirobifluorene linker between the triphenylamine and PDI core would increase the distance between the two chromophores and simultaneously reduce the efficiency of the intramolecular electron transfer, and thus increase the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy gap. There is also an increased possibility of  $\pi$ - $\pi$  stacking between the PDI molecules for compound 4, which in turn results in a narrowing of the energy bandgap. Table 2 summarizes the electrochemical data for compounds 1–4, and their cyclic voltammograms are given in Fig. 2.

### Thermal properties

The thermal properties of compounds 1–4 were studied by thermogravimetric analysis (TGA). All of the compounds exhibit no apparent glass transitions. In addition, all the compounds show high decomposition temperatures  $>400$  °C

(defined as the temperature at which the material showed a 5% weight loss under a nitrogen atmosphere), indicating that this class of compounds are thermally stable. Fig. 3 shows the TGA curves of compounds 1–4, and the thermal decomposition temperature of the compounds are tabulated in Table 3.

### Photovoltaic properties

To study the applicability of compounds 1–4 as donor materials for the fabrication of OPV devices, bulk heterojunction devices with the configuration of indium tin oxide (ITO)/molybdenum oxide ( $\text{MoO}_3$ ) (2 nm)/*x*% 1–4:  $\text{C}_{70}$  (60 nm)/bathophenanthroline (BPhen) (8 nm)/aluminum (Al) (100 nm) were prepared, where *x* has been varied from 3% to 9%. ITO,  $\text{MoO}_3$ ,  $\text{C}_{70}$ , BPhen and Al were used as the anode, anodic buffer layer, acceptor, exciton blocking layer and cathode, respectively. A control device without the donor (*i.e.*  $\text{C}_{70}$ -only) was also prepared for comparison. Under light illumination of 1 sun, the  $\text{C}_{70}$ -only device shows a poor photovoltaic response with a  $J_{\text{SC}}$  of 1.27  $\text{mA cm}^{-2}$ , an  $V_{\text{OC}}$  of 0.98 V and a FF of 0.37, corresponding to a low PCE of 0.46%, consistent with other studies.<sup>14</sup> On the other hand, the doping of PDI compounds as donor into  $\text{C}_{70}$  to form bulk heterojunctions had significantly improved the photovoltaic responses. For instance, the  $J_{\text{SC}}$  sharply increases from 1.27  $\text{mA cm}^{-2}$  for the  $\text{C}_{70}$ -only device to 9.74  $\text{mA cm}^{-2}$  for the device doped with 7% compound 3. Together with the high  $V_{\text{OC}}$  of 0.94 V, this corresponds to the best device with a PCE of 3.94%. Similar performance has been obtained when the  $\text{C}_{70}$  is doped with other PDI compounds. Table 4 summarizes the key parameters of devices without and with PDI as donor materials. It should be mentioned that the doping of the PDI compounds

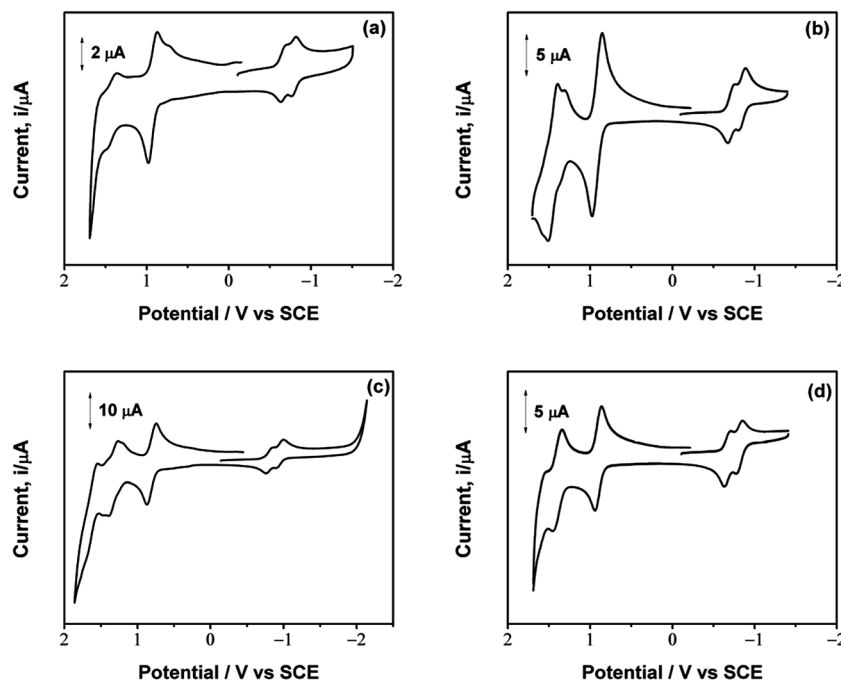


Fig. 2 Cyclic voltammograms of (a) 1, (b) 2, (c) 3, and (d) 4 in dichloromethane ( $0.1 \text{ M } ^t\text{Bu}_4\text{PF}_6$ ). Scan rate:  $100 \text{ mV s}^{-1}$ .

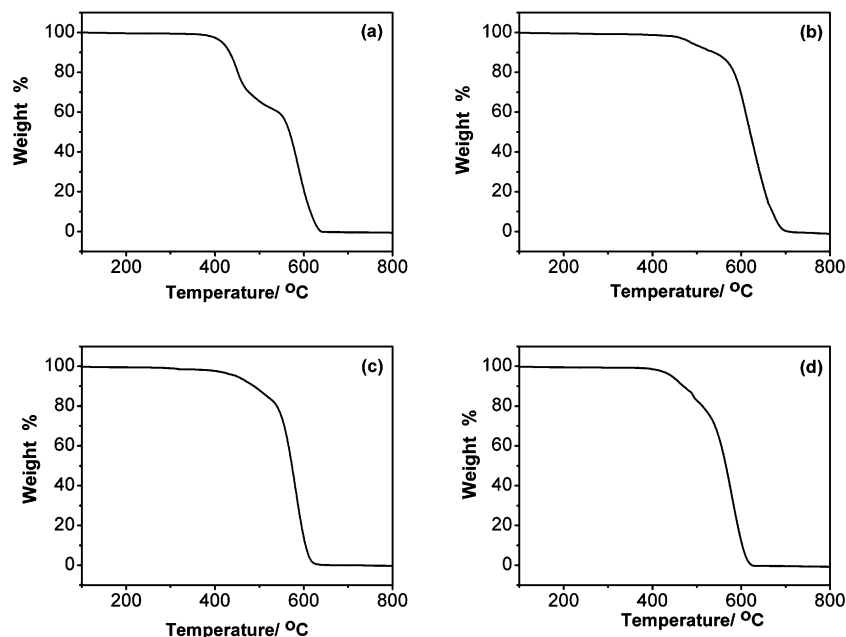


Fig. 3 TGA thermograms of (a) 1, (b) 2, (c) 3, and (d) 4. Heating rate:  $10\text{ }^{\circ}\text{C min}^{-1}$  under a nitrogen atmosphere.

Table 3 Thermal properties for compounds 1–4

Compounds	$T_{\text{decomp}}^a$ ( $^{\circ}\text{C}$ )
1	417
2	486
3	449
4	444

<sup>a</sup> Determined by thermogravimetric analysis. Heating rate:  $10\text{ }^{\circ}\text{C min}^{-1}$  under a nitrogen atmosphere.  $T_{\text{decomp}}$  was determined at 5% weight loss.

Table 4 Key photovoltaic responses for devices with PDI as donor materials

Compound		$J_{\text{SC}}$ ( $\text{mA cm}^{-2}$ )	$V_{\text{OC}}$ (V)	FF	PCE (%)
$\text{C}_{70}$ -only	0%	1.27	0.98	0.37	0.46
1	3%	8.83	0.76	0.48	3.22
	5%	9.06	0.79	0.46	3.29
	7%	9.04	0.79	0.44	3.14
	9%	9.20	0.80	0.44	3.24
2	3%	8.69	0.97	0.33	2.78
	5%	10.26	0.97	0.37	3.68
	7%	10.15	0.96	0.38	3.70
	9%	10.23	0.95	0.37	3.60
3	3%	8.27	0.89	0.39	2.87
	5%	9.37	0.93	0.41	3.57
	7%	9.74	0.94	0.43	3.94
	9%	9.87	0.94	0.41	3.80
4	3%	3.36	0.67	0.38	0.86
	5%	6.43	0.87	0.38	2.13
	7%	5.78	0.80	0.33	1.53
	9%	5.23	0.80	0.24	1.00

as donors can broaden the spectral coverage and increase the incident photon-to-current efficiency (IPCE) of the OPV devices. Fig. 4 shows the IPCE spectra of devices doped with 7% PDI compound as the donor. Without the donor material, the maximum IPCE of the control device (*i.e.* the  $\text{C}_{70}$ -only device) is only 24.6% at 385 nm. The employment of the PDI compounds as donor significantly increased the IPCE of up to 62.9%, 73.0%, 70.6%, and 54.4% for devices doped with 1, 2, 3, and 4 respectively. In addition, the plateau sensitivity of the doped devices can fully cover the visible spectrum between 380 and 700 nm, which corresponds well to the superposition of the spectral absorption of  $\text{C}_{70}$  and the PDI compounds. The IPCE of devices doped with 1, 2, 3, and 4 has been shown to be dramatically increased to 63.2%, 75.6%, 67.5%, and 58.6% at 500 nm, respectively, approaching an order of magnitude higher than that of the  $\text{C}_{70}$ -only device (7.8%). Note that the  $J_{\text{SC}}$  obtained by integrating the product of the IPCE data and the AM 1.5G solar spectrum perfectly matches the observed  $J_{\text{SC}}$  in the  $J$ - $V$  curves (*i.e.* within 5% error). For instance, from the integration of the IPCE spectrum with an AM 1.5G solar spectrum, the  $J_{\text{SC}}$  calculated for devices doped with 7% of compound 3 is  $9.65\text{ mA cm}^{-2}$ , in excellent agreement with that observed from the  $J$ - $V$  characteristic ( $9.74\text{ mA cm}^{-2}$ ). The inset in Fig. 4 shows the product of the IPCE data and the AM 1.5G solar spectrum for devices doped with 3.

The increase in  $J_{\text{SC}}$  and IPCE are found to be dependent on the planarity of the PDI molecules. The tetra-substituted PDI (*i.e.* compound 1) has a non-planar and three-dimensional structure, in which the 7%-doped device gives a moderate PCE of 3.14% with a  $J_{\text{SC}}$  of  $9.04\text{ mA cm}^{-2}$ . Introduction of a spirobifluorene linker between the triphenylamine and PDI core to prepare compounds 2 and 3 would increase the three-dimensional molecular size. Such larger molecular sizes of 2 and 3 can



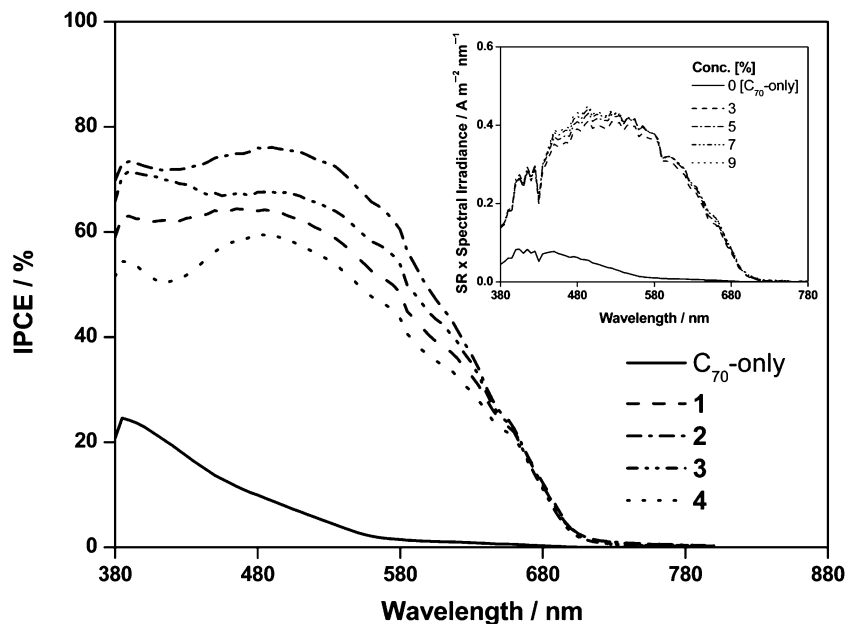


Fig. 4 IPCE spectra of devices based on different PDI compounds as donor materials. Inset: The product of the IPCE data and the AM 1.5G solar spectrum for devices doped with compound 3.

minimize the exciton quenching resulting from the mutual parallel orientation between the donor and acceptor,<sup>5,9a,e</sup> and thus enhance the possibility for charge dissociation. This, in turn, results in an increased  $J_{SC}$  of up to 10.15 and 9.74  $\text{mA cm}^{-2}$ , respectively, for devices doped with 2 and 3. In sharp contrast, reducing the number of substitutions on the PDI core (*i.e.* compound 4) would not alter the planarity of the rigid PDI molecule, in which rapid charge recombination would occur that would quench the photogenerated excitons and results in a lower  $J_{SC}$  of 5.78  $\text{mA cm}^{-2}$  and a PCE of 1.53%. Nevertheless, the present findings demonstrate an effective approach for synthesizing a new class of p-type PDI compounds that are suitable candidates to serve as the donor materials in the fabrication of efficient OPV devices. Particularly, to the best of our knowledge, the PCE of 3.94% is one of the highest ever reported for a cell utilizing a p-type PDI moiety.

## Conclusion

A new class of p-type, spirobifluorene-modified PDI derivatives has been synthesized and characterized. The functionalization of the perylene diimide core with different spirobifluorene moieties has been shown to effectively alter the molecular geometry, as well as extend the spectral coverage into the red region of up to 700 nm, with high molar extinction coefficients of up to  $3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ . More importantly, these modified-PDI compounds are promising donor materials for the fabrication of OPV devices. Bulk heterojunction devices based upon a fullerene acceptor demonstrated a high  $J_{SC}$  of up to 10.26  $\text{mA cm}^{-2}$  and high  $V_{OC}$  of up to 0.97 V. In addition, a high PCE of up to 3.94% has been achieved. This is one of the highest ever reported for a cell utilizing p-type PDI moiety.

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