# Polymer Chemistry

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### **Graphic Abstract**

Diindenocarbazole-based large landgap copolymers for high-performance organic solar cells with large open-circuit voltages

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# **ARTICLE TYPE**

## Diindenocarbazole-based large bandgap copolymers for highperformance organic solar cells with large open circuit voltages

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Three donor-acceptor alternating copolymers abbreviated as PC1, PC2, and PC3, respectively, have been designed and synthesized by using diindenocarbazole (DIC) and dithienylbenzothiadiazole (DTBT) units. Through backbone manipulation, copolymers with large bandgaps (~2.0 eV) and deep-lying HOMO energy levels (below -5.41 eV) are obtained. The side chains have also been investigated to tune the

<sup>10</sup> intermolecular interactions and morphology of the copolymers blended with  $PC_{71}BM$ . Polymer solar cells (PSCs) based on PC2:PC<sub>71</sub>BM exhibit an outstanding power conversion efficiency (PCE) of 7.26%, which represents one of the highest PCEs ever reported for PSCs while combining an open-circuit voltage ( $V_{oc}$ ) of 0.93 V and a large optical bandgap of 2.01 eV. Under the similar device fabrication conditions, regular PSCs based on PC1 and PC3 achieve PCEs of 2.45% and 6.68%, respectively. Moreover, inverted

<sup>15</sup> PSCs derived from PC2 also exhibit an attractive PCE of 6.17% with a high  $V_{oc}$  of 0.92 V. In view of its similar optical profiles to P3HT, but a deeper-lying HOMO energy level, PC2 should be a promising candidate as a short wavelength absorbing material for tandem solar cells.

#### Introduction

- <sup>20</sup> Solution-processed bulk-heterojunction (BHJ) polymer solar cells (PSCs) have been under extensive investigation in the past decade<sup>1</sup>. So far, PSCs with power conversion efficiencies (PCEs) well over 9% for single-junction devices<sup>2</sup> and as high as 10.6% for tandem modules<sup>3</sup> have been achieved. To explore novel *p*-
- <sup>25</sup> type conjugated polymer materials to further improve the PCE, the donor-acceptor (D-A) approach is one of the most successful and universal strategies, because it enables tunable absorption spectra and tailored frontier molecular orbital energy levels of the resulting polymers. To efficiently capture photons from the solar
- <sup>30</sup> irradiation to maximize the short-circuit current density  $(J_{sc})$ , many studies have been focused on the development of lowbandgap (LBG) conjugated copolymers. However, there is usually a trade-off between the  $J_{sc}$  and the open-circuit voltage  $(V_{ac})$  of a photovoltaic device<sup>4</sup>. Another effective way to increase
- the total absorption of solar light is to adopt a tandem device architecture which stacks two or more subcells with complementary absorption spectra, i.e., active layer materials with different bandgaps. In this regard, it is desirable to develop new high-performance large bandgap copolymers with a high  $V_{oc}$
- <sup>40</sup> to serve as potential candidates for the efficient tandem PSC application<sup>5</sup>.

Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) is an excellent example of poly(N-alkyl-2,7-carbazole) derivatives<sup>6</sup>, which 45 possesses a deep-lying HOMO level to guarantee an attainable high  $V_{oc}$ , high hole mobility for a large  $J_{sc}$ , and remarkable thermal stability. Since its inception in 2007, the PCE has progressed from 3.6% to 7.9% for classical PCDTBT-based BHJ PSCs<sup>7</sup>. Although there is no doubt that carbazole-based 50 derivatives are deserved to be explored, the number of highperformance carbazole-based polymer donors for PSCs is still limited<sup>8</sup>. Previously, we reported a carbazole-based ladder-type heteroheptacene (HHA)<sup>9</sup>, where the central carbazole core is connected with two outer thienyl rings through two embedded 55 cyclopentadienyl rings (in Scheme 1). Subsequently, Cheng et al. explored the photovoltaic characteristics when its analogue was copolymerized with various electron-deficient units, and a moderate PCE of 4.6% was demonstrated<sup>10</sup>. Back to our original intention to design the carbazole-based heteroheptacene as a 60 donor unit, considering its extended and rigid planarization that is favorable for intermolecular  $\pi$ - $\pi$  stacking, we expect that based on some carbazole derived multi-fused polycyclic aromatic system, a comparable photovoltaic performance relative to the best results of PCDTBT would be achieved through stepwise 65 molecular engineering.

Herein, we adopt two benzene fragments to replace the outer thiophenes in our previously reported carbazole-cored heteroheptacene to form another ladder-type heptacyclic arene, namely, diindenocarbazole (Scheme 1). As for the acceptor unit, 70 2,1,3-benzothiadiazole (BT) is chosen. At the same time, two thiophenes are used to connect the donor and the acceptor similar

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Scheme 1 Molecular design strategy for high-performance diindenocarbazole-based copolymers.

- <sup>5</sup> to PCDTBT. In addition, different aliphatic side chains are introduced to the donor/acceptor segments to tune the polymer's intrinsic solubility and miscibility with fullerene derivatives. As such, three carbazole-based copolymers, i.e., PC1, PC2, and PC3, are synthesized and tested for PSCs. These three copolymers
- <sup>10</sup> possess larger bandgaps than P3HT, but show a significantly improved  $V_{oc}$  of up to 0.99 V (0.60 V for P3HT:PC<sub>71</sub>BM) for the PSCs based on them. An optimal PCE of 7.26% with a  $V_{oc}$  of 0.93 V, a  $J_{sc}$  of 14.22 mA cm<sup>-2</sup>, and an *FF* of 54.7% has been demonstrated in conventional single-junction devices based on
- <sup>15</sup> PC2:PC<sub>71</sub>BM. To the best of our knowledge, this  $V_{oc}$  value is the highest ever reported for carbazole-based single-junction PSCs while maintaining a PCE over 7%, promising its good potential as a large bandgap material for the tandem PSC application.

#### **Experimental section**

#### 20 Materials

All commercially available chemicals were used as received unless otherwise specified. THF was distilled over sodium/

- benzophenone, and other dry solvents were dried over molecular sieves. DTBT (5a)<sup>11</sup> and 5,6-bis(butoxy)-4,7-di(thiophen-2-<sup>25</sup> yl)benzo-[c][1,2,5]-thiadiazole (5b)<sup>12</sup> were prepared according to
- the literature procedures.  $PC_{71}BM$  (99%) was purchased from American Dye Source Inc., and MoO<sub>3</sub> (99.9%) was purchased from Alfa Aesar. The synthesis of PIFB has been described by us previously<sup>13</sup>.

#### 30 Synthesis

**Compound 2a.** To a precooled suspension (*ca.* 5 °C) of 2,7dibromo-N-(ethyl)carbazole (4.85 g, 13.74 mmol) and AlCl<sub>3</sub> (7.33 g, 4.0 equiv.) in dry CH<sub>2</sub>Cl<sub>2</sub> (80 ml) was added dropwise heptanoyl chloride (6.10 g, 3.0 equiv.) over 25 min. After the addition was available the stirring mixture was warmed to

<sup>35</sup> addition was completed, the stirring mixture was warmed to reflux for 8 h. When cooling to room temperature, the reaction was quenched upon slowly pouring the mixture into some crashed ice. The inorganic precipitate was dissolved with 2 M HCl, and the aqueous phase was extracted with dichloromethane 40 (3 × 50 ml). The combined organic fractions were washed with water, saturated aq. NaHCO<sub>3</sub> and brine, dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. The obtained residue was purified by silica gel chromatography using 5% ethyl acetate in petroleum ether as the eluent to afford the title
45 compound as a pale yellow solid (4.3 g, 54%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.17 (s, 2H), 7.65 (s, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 3.04 (t, *J* = 7.6 Hz, 4H), 1.76 (quintet, *J* = 7.6 Hz, 4H), 1.46-1.33 (m, 15H), 0.89 (m, 6H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, δ): 203.60, 141.90, 133.18, 121.48, 121.29, 117.45, 114.30, 42.68, 50 38.24, 31.64, 28.95, 24.64, 22.51, 14.12, 13.79. HRMS (MALDITOF) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>28</sub>H<sub>36</sub>Br<sub>2</sub>NO<sub>2</sub> 576.1113; found 576.1107. Elemental analysis (%), calcd. for C<sub>28</sub>H<sub>35</sub>Br<sub>2</sub>NO<sub>2</sub>: C, 58.24; H, 6.11; N, 2.43; found: C, 58.13; H, 6.04; N, 2.39.

- 55 Compound 3a. In a 250 ml round-bottom flask, equipped with a stirrer and a condenser with a nitrogen inlet needle, compound 2a (4.3 g, 7.45 mmol), phenylboronic acid (2.8 g, 3 equiv.), and aq.  $Na_2CO_3$  (6.3 g, 8.0 eq., 30 ml  $H_2O$ ) were dissolved in THF (65 ml). The solution was purged with nitrogen for 30 min, and then 60 Pd(PPh<sub>3</sub>)<sub>4</sub> was added. After being flushed with nitrogen for another 20 min, the reaction was carried out at reflux under N<sub>2</sub> until completion (ca. 24 h) as indicated by TLC. The cooled mixture was diluted with water, and the aqueous layer was extracted with ethyl acetate for three times. The combined 65 organic layer was dried with MgSO<sub>4</sub>, filtered, and concentrated via a rotary evaporator. The crude product was purified by column chromatography on silica gel, eluting with EtOAc/petroleum ether (1/20) to get the title compound as a colorless oil (3.7 g, 87%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.36 (s, <sup>70</sup> 2H), 7.45-7.42 (m, 10H), 7.37 (s, 2H), 4.41 (q, J = 7.2 Hz, 2H), 2.38 (t, J = 7.6 Hz, 4H), 1.48 (m, 8H), 1.10 (m, 8H), 0.83 (m, 9H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, δ): 207.02, 141.99, 141.83, 139.72, 133.49, 129.15, 128.58, 127.64, 121.76, 121.46, 110.36, 42.92, 38.06, 31.45, 28.76, 25.03, 22.42, 14.00, 13.91. HRMS (MALDI-75 TOF) m/z:  $[M+H]^+$  calcd for C<sub>40</sub>H<sub>46</sub>NO<sub>2</sub> 572.3529; found
- 572.3523. Elemental analysis (%), calcd. for  $C_{40}H_{45}NO_2$ : C, 84.02; H, 7.93; N, 2.45; found: C, 84.10; H, 7.89; N, 2.29.

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**Compound 4a.** To a dry THF solution (30 ml) in a 100 ml Schlenk flask at -78 °C and under nitrogen protection was added slowly 24.5 ml of n-hexyllithium (1.6 M in n-hexane, 6.0 equiv.).

- <sup>5</sup> After being kept at the same temperature for several minutes, a solution of compound 3a (3.7 g, 6.47 mmol) in THF (20 ml) was dropped into the mixture over 40 min under -60 °C. When the addition was completed and another 10 min continued, the resulting mixture was slowly warmed to room temperature and
- <sup>10</sup> stirred overnight, followed by quenching with a saturated NH<sub>4</sub>Cl solution (15 ml). The organic layer was separated, and the aqueous phase was extracted with EtOAc for three times. The combined organic layer was washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated via rotary evaporator to obtain <sup>15</sup> the product of a crude diol as a viscous oil which could be used
- directly for next step without chromatography purification.

To a solution of the crude diol obtained above in dichloromethane (80 ml) under nitrogen atmosphere was added a  $BF_3$ /etherate solution (5 ml) at ambient temperature. A color

- <sup>20</sup> change was observed somewhat upon the addition. After being stirred for 45 min, 100 ml of dry MeOH was added into the mixture to quench the reaction. The mixture was further stirred overnight, and concentrated to give a viscous oil which was loaded onto a silica gel column and eluted with n-hexane to yield
- <sup>25</sup> compound 4a as a white solid (1.52 g, 33 % for two steps). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.03 (s, 2H), 7.84 (d, J = 7.2 Hz, 2H), 7.69 (s, 2H), 7.40-7.31 (m, 6H), 4.52 (q, J = 7.2 Hz, 2H), 2.10 (m, 8H), 1.60 (t, J = 7.2 Hz, 3H), 1.16-1.03 (m, 24H), 0.78-0.66 (m, 20H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, δ): 151.59, 142.05, 30 141.77, 140.57, 139.42, 126.78, 126.67, 122.98, 119.38, 114.00,
- 99.15, 54.40, 41.34, 37.81, 31.59, 29.89, 23.87, 22.66, 14.06, 14.01. HRMS (MALDI-TOF) m/z: [M]<sup>+</sup> calcd for C<sub>52</sub>H<sub>69</sub>N 707.5430; found 707.5425. Elemental analysis (%), calcd. for C<sub>52</sub>H<sub>69</sub>N: C, 88.20; H, 9.82; N, 1.98; found: C, 88.47; H, 9.74; N, <sup>35</sup> 1.85.

**DICBr-Et**. A suspension of compound 4a (1.0 g, 1.41 mmol), copper (II) bromide on aluminum oxide (4.8 g, 5 equiv., CuBr<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 1:2 w%) in CCl<sub>4</sub> (50 ml) was refluxed for about 5 <sup>40</sup> h. The cooled mixture was filtered, and concentrated *via* a rotary evaporator to get a solid residue, which was purified by column chromatography on silica gel using petroleum ether as the eluent to yield the monomer as a light yellow solid (0.23 g, 19%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.98 (s, 2H), 7.67 (d, *J* = 8.8 Hz,

- <sup>45</sup> 2H), 7.62 (s, 2H), 7.49-7.47 (m, 4H), 4.47 (q, J = 7.2 Hz, 2H), 2.12-1.98 (m, 8H), 1.15-0.98 (m, 27H), 0.76-0.64 (m, 20H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>, δ): 153.79, 141.69, 140.71, 140.62, 138.42, 129.85, 126.20, 123.18, 120.75, 114.09, 99.29, 54.76, 41.19, 37.80, 31.54, 29.78, 23.81, 22.63, 14.02, 13.99. HRMS

**DICBr-EH**.<sup>14</sup> The same procedures as described above for <sup>55</sup> monomer DICBr-Et synthesis were employed for DICBr-EH starting from 2,7-dibromo-N-(2-ethylhexyl)carbazole (28% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 7.98 (s, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.59 (s, 2H), 7.49-7.46 (m, 4H), 4.26-4.22 (m, 2H), 2.172.13 (m, 1H), 2.11-1.96 (m, 8H), 1.52-1.37 (m, 6H), 1.32-1.26 (m, 60 2H), 1.11-0.99 (m, 27H), 0.88 (t, J = 7.2 Hz, 3H), 0.77-0.63 (m, 20H). Elemental analysis (%), calcd. for C<sub>58</sub>H<sub>79</sub>NBr<sub>2</sub>: C, 73.32; H, 8.38; N, 1.47; found: C, 73.82; H, 8.40; N, 1.32.

#### RODTBT-Sn. Compound 5b (0.43 g, 0.97 mmol) was dissolved

<sup>65</sup> in dry THF (15 ml) in a 50 ml flame-dried flask, and the solution was cooled to -78 °C under a nitrogen atmosphere. Lithium diisopropylamide (1.95 ml, 4.0 equiv. 2.0 M in heptanes) was added dropwise into the solution, upon which a purple color would develop. The resulting mixture was stirred at -78 °C for an

<sup>70</sup> hour, followed by the addition of trimethyltin chloride (0.70 g, dissolved in 3 ml of THF, 3.5 equiv.) at -78 °C. After the addition is completed, the liquid N<sub>2</sub>/acetone bath was removed and the reactant was recovered to room temperature with stirring overnight. When the reaction was quenched by slowly adding of <sup>75</sup> water, the mixture was poured into plenty of water, and the aqueous layer was extracted with EtOAc. After evaporation of the solvent, the residue was recrystallized from methanol to afford the monomer as an orange crystal (0.55 g, 74%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, δ): 8.52 (d, *J* = 3.6 Hz, 2H), 7.34 (d, *J* = 3.6 Hz, 2H), 4.14 (t, *J* = 7.2 Hz, 4H), 1.92 (m, 4H), 1.52 (m, 4H), 0.99 (t, *J* = 7.2 Hz, 6H), 0.45 (s, 18H). MS (MALDI-TOF) *m/z*: [M]<sup>+</sup> calcd for C<sub>28</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub>Sn<sub>2</sub> 772.03; found 772.05. Elemental analysis (%), calcd. for C<sub>28</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>S<sub>3</sub>Sn<sub>2</sub>: C, 43.66; H, 5.23; N,

3.64; found: C, 43.43; H, 5.26; N, 3.58.

85 Polymer PC2. Into a 50 ml round-bottom flask were charged monomer DICBr-Et (0.22 g. 0.25 mmol), monomer RODTBT-Sn (0.21 g, 0.27 mmol), and dry toluene (15 ml). The solution was flushed with N<sub>2</sub> for 30 min, then Pd<sub>2</sub>(dba)<sub>3</sub> (10 mg) and P(o-tol)<sub>3</sub> 90 (25 mg) were added quickly. After bubbling the mixture with N<sub>2</sub> for another 30 min, it was heated to 100 °C for 2 days. After cooling to room temperature, the mixture was precipitated into methanol and filtered. The crude polymer was dissolved in chloroform, filtered through a short florisil column, concentrated 95 and precipitated again. The recovered polymer was purified by Soxhlet extraction sequentially with methanol, acetone, hexane and chloroform. The chloroform extract was concentrated and precipitated in methanol. The polymer was collected by filtration and dried under vacuum to yield a red solid (100 mg, 35%). <sup>1</sup>H <sup>100</sup> NMR (400MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.62 (d, J = 3.6 Hz, 2H), 8.09 (s, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.82-7.78 (m, 4H), 7.72 (s, 2H), 7.59 (d, J = 3.6 Hz, 2H), 4.53 (br, 2H), 4.30 (br, 4H), 2.20 (s, 8H), 2.10-2.07 (m, 4H), 1.69-1.62 (m, 7H), 1.17-1.08 (m, 32H), 0.81-0.77 (m, 18H). GPC (THF):  $M_n = 23.3 \text{ kDa}$ ,  $M_w = 44.8 \text{ kDa}$ , PDI = 1.9.

**Polymer PC1**. Using a procedure similar to that described above for PC2, monomer DICBr-EH (0.7 g, 0.73 mmol) and monomer DTBT-Sn (0.49 g, 1.05 equiv.) were copolymerized in dry toluene (15 ml) for 3 days to yield PC1 as a purple black solid <sup>110</sup> (0.45 g, 57%). <sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>, *δ*): 8.19-8.09 (m, 4H), 7.78 (br, 4H), 7.57-7.35 (m, 6H), 7.30-7.22 (m, 2H), 2.18 (br, 8H), 1.56 (br, 8H), 1.19 (br, 32H), 0.93-0.81 (m, 21H). GPC (THF): M<sub>n</sub> = 13.8 kDa, M<sub>w</sub> = 16.8 kDa, PDI = 1.2.

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Scheme 2 Synthesis of the monomers and copolymers. Conditions: a) heptanoyl chloride, AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, reflux; b) phenylboronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, aq. Na2CO3 THF, N2, reflux; c) n-hexyllithium, THF, -78 °C, then r.t., N2; d) boron trifluoride/etherate, CH2Cl2, r.t., then MeOH; e) CuBr2/alumina, CCl4, 75 5 °C; f) LDA, THF, -78 °C, N2, then Me3SnCl, r.t.; g) Pd2(dba)3, P(0-tol)3, toluene, 110 °C, N2.

Polymer PC3. Following the same procedure as that used for the synthesis of PC2, PC3 was obtained as a deep red solid (0.18 g, 69%) through copolymerization between monomer DICBr-EH (0.20 g, 0.21 mmol) and monomer RODTBT-Sn (171 mg, 1.06

- 10 equiv.) in dry toluene (12 ml) for 60 h. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ,  $\delta$ ): 8.62 (d, J = 3.2 Hz, 2H), 8.08 (s, 2H), 7.88 (d, J = 8.0Hz, 2H), 7.82-7.77 (m, 4H), 7.69 (s, 2H), 7.60 (d, J = 3.6 Hz, 2H), 4.30 (br, 6H), 2.20 (s, 8H), 2.12-2.05 (m, 5H), 1.71-1.62 (m, 5H), 1.56-1.49 (m, 4H), 1.39 (m, 2H), 1.17-1.06 (m, 32H), 0.97 (m, 15 4H), 0.85-0.77 (m, 21H). GPC (THF):  $M_n = 14.7 \text{ kDa}$ ,  $M_w = 23.1$
- kDa, PDI = 1.6.

#### Instruments and measurements

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were acquired from a Bruker AVANCE-400 spectrometer with tetramethylsilane (TMS) as the

- 20 internal reference, and the peaks are given in ppm relative to TMS. Molecular weights of the polymers were measured using the GPC method with polystyrene standards. UV-vis absorption spectra were recorded on a Perkin-Elmer Lamada 35 UV-vis spectrophotometer. For the measurements of thin films, polymers
- 25 were spin-coated onto precleaned glass slides from 5 mg/ml polymer solutions in chlorobenzene. AFM images were collected by a Veeco Multimode NS3A-02 Nanoscope III microscope. Blend films for AFM measurements were prepared on PEDOT: PSS-coated ITO substrates following the same procedure
- 30 as described for the device fabrication.

#### Electrochemistry

Cyclic voltammetry (CV) measurements were conducted in a solution of 0.1M tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in acetonitrile at a scan rate of 100 mV/s, using Pt

 $_{35}$  disk coated with the polymer film, Pt wire, and Ag/Ag<sup>+</sup> (0.01 M AgNO<sub>3</sub> in anhydrous acetonitrile) as working electrode, counter electrode, and reference electrode, respectively. The polymers

were deposited onto the working electrode from a 2 mg/ml chloroform solution and dried under ambient circumstance prior 40 to the measurements. The onset oxidation potential  $(E_{1/2} \text{ ox})$  of the ferrocene was -0.02 V vs  $Ag/Ag^+$  electrode under the same conditions. With an assumption that the redox potential of Fe/Fe<sup>+</sup> has an absolute energy level of -4.80 eV relative to vaccum, the HOMO and LUMO energy levels were calculated consulting the 45 following equations, where  $E_{ox}$  and  $E_{red}$  are the onset oxidation and onset reduction potentials vs Ag/Ag<sup>+</sup>, respectively.

$$E_{\text{HOMO}} = -(E_{\text{ox}} + 4.82) \text{ (eV)}$$
 (1)  
 $E_{\text{LUMO}} = -(E_{\text{red}} + 4.82) \text{ (eV)}$  (2)

#### Hole mobility measurement

<sup>70</sup> and turned out to be 90.5  $\Omega$ .

50 Hole-only devices with a configuration of ITO/PEDOT:PSS/ polymer:PC71BM/Au were fabricated to evaluate the hole mobilities of the resulting polymers using the space charge limited current (SCLC) model. Unipolar devices were prepared by following the same procedure as described for PSC fabrication 55 except that the PIFB/A1 cathode was replaced by the gold electrode. The dark current was measured by an Agilent 4155C source measurement kit, and the  $J^{0.5}$ -V curves were fitted according to the following equation: J =

$$(9/8)\varepsilon_{\rm r}\varepsilon_0 (V^2/L^3)$$
 (3)

<sup>60</sup> where  $\varepsilon_0$  is the permittivity of free space (8.85 × 10<sup>-12</sup> F/m),  $\varepsilon_r$  is the dielectric constant of the polymer (assumed to be 3),  $\mu$  is the hole mobility, V is the voltage drop across the device, and L is the average active layer thickness (92 nm for PC1, 106 nm for PC2, and 73 nm for PC3).  $V = V_{appl} - V_s - V_{bi}$ , where  $V_{appl}$  is the applied <sup>65</sup> voltage to the device,  $V_s$  is the voltage drop due to contact resistance and series resistance across the electrodes, and  $V_{\rm bi}$  is the built-in voltage due to the difference in work function of the two electrodes (0.3 V). The resistance of the device was measured using a blank configuration of ITO/PEDOT:PSS/Au

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Table 1 Molecular weights, UV-vis data, electrochemical energy levels and hole mobilities of the copolymers

	М		2 (1	nm)	F opt	номо	LUMO	F elec	
Polymer	IVI n	PDI <sup>a</sup>	$\lambda_{\rm max}$ (IIIII)		Lg	nowio	LUMO	$L_{g}$	$\mu_{\text{hole}}$
	(kDa) <sup>a</sup>		solution	film	(eV) <sup>b</sup>	$(eV)^{c}$	$(eV)^{c}$	(eV)	$[\mathrm{cm}^2 \mathrm{V}^2 \mathrm{s}^2]^{\mathrm{d}}$
PC1	13.8	1.2	539	549	1.90	-5.41	-3.67	1.74	$(6.7 \pm 0.3) \times 10^{-6}$
PC2	23.3	1.9	515	520	2.01	-5.43	-3.56	1.87	$(5.4 \pm 0.6) \times 10^{-5}$
PC3	14.7	1.6	517	537	1.97	-5.44	-3.65	1.79	$(4.3 \pm 0.2) \times 10^{-5}$

<sup>a</sup> The number-average molecular weight and polydispersity index measured by GPC. <sup>b</sup> The optical bandgap estimated from the onset of the film absorption spectrum. <sup>c</sup> Determined by onset of the CV curve from thin film. <sup>d</sup> Calculated by the SCLC model, the data have been averaged over 8 devices.

#### PSCs fabrication and characterization

- s Devices with the structure of ITO/PEDOT:PSS/polymer: PC<sub>71</sub>BM/PIFB/Al were fabricated as follows: Indium-tin oxide (ITO) coated glass substrates (15  $\Omega$ /sq) were ultrasonically cleaned with detergent, deionated water, acetone and isopropanol for 30 min each, then dried overnight in an oven, subsequently
- <sup>10</sup> subjected to UV-O<sub>3</sub> treatment for 15 min prior to use. Poly(3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron PVPAI-4083) was filtered through a 0.45 $\mu$ m filter before being deposited onto ITO at 3000 rpm for 30s. The film-loaded substrate was baked at 140 °C for 10 min in air and then
- <sup>15</sup> transferred to a glove box to spin-cast the active layer. A solution containing a mixture of polymer/PC<sub>71</sub>BM at different weight ratios (20 mg/ml) in a mixed *o*-DCB:CB (1:4, v/v) solvent was stirred overnight at 50 °C and filtered through a 0.45 µm filter before being spin-cast onto the PEDOT:PSS layer at 800-1200
- <sup>20</sup> rpm for 60s. In the case of with additive, different volume fractions of DIO was added into the mixed solvent. Before the aluminum deposition, a conjugated polyelectrolyte PIFB was introduced as an interlayer to facilitate efficient electron injection. The PIFB layer was spin-coated at 1500 rpm for 30 s from a
- $_{25}$  methanol solution (0.3 mg/mL, containing 30 eq. of acetic acid). Finally, a layer of aluminum cathode was thermally deposited through a shadow mask under a high vacuum about  $1 \times 10^{-6}$  Torr. For the inverted devices, the ZnO precursor solution (0.23 M in 2-methoxyethanol) was spin-coated onto the ITO substrate, which
- <sup>30</sup> was pre-treated by UV-ozone for 15 min. The resulting film was then annealed<sup>15</sup>. The fabrication of the active layer followed the same fashion described as above for the classical structure. Eventually, an anode interfacial layer of MoO<sub>3</sub> (8 nm) and the Ag electrode (100 nm) were thermally deposited. Each sample
- <sup>35</sup> consists of eight independent devices with an active area of 6 mm<sup>2</sup>. Device characterization was performed under AM 1.5 G irradiation (100 mW cm<sup>-2</sup>) on an Oriel sol3A simulator (Newport) with a NREL-certified silicon reference cell. The current density–voltage curves were tested by a Keithley 2440 source <sup>40</sup> measurement unit. EQE spectra were measured on a Newport
- <sup>40</sup> measurement unit. EQE spectra were measured on a Newpor EQE measuring system.

#### **Results and discussion**

#### Synthesis of monomers and polymers

The synthetic routes toward the monomers and polymers are 45 depicted in Scheme 2. Starting from 2,7-dibromo-9-alkyl-9Hcarbazole (1), the 3,6-diketo-2,7-dibromo-9-alkyl-9H-carbazole (2) was prepared via Friedel-Crafts acylation with heptanoyl chloride. Compound 2 was coupled with phenylboronic acid by the Suzuki reaction to afford the intermediate 3 in 80% yield. 50 Subsequently, a nucleophilic attack reaction at the keto site of compound 3 by n-hexyllithium produced a crude diol, which underwent cyclization with boron trifluoride/etherate to give the key heptacyclic arene (4) in 33% overall yield. Finally, selective bromination at the linear end positions by copper (II) bromide on 55 an alumina matrix in carbon tetrachloride accomplished the monomer (DICBr-alkyl) synthesis. In parallel, lithiation of DTBT or its dibutoxy-substituted derivative (5) at low temperature followed by quenching with trimethyltin chloride afforded the corresponding stannylated DTBT or its derivative. Three 60 copolymers were prepared by the Stille coupling polycondensation between brominated carbazole-based heptacene (DICBr-Et and DICBr-EH) and corresponding stannylated DTBT or its derivative, using toluene as solvent and Pd<sub>2</sub>(dba)<sub>3</sub>/P(o-tol)<sub>3</sub> as the catalytic system. Two thiophenes were flanked on both 65 sides of the BT unit to isolate the donors and acceptors for reducing if any the steric hindrance, which is beneficial to improve the planarity and  $\pi$ - $\pi$  stacking of the polymer chains. All polymers were purified by Soxhlet extraction with methanol, acetone, and hexane to remove oligomers and residual catalyst. 70 Polymers PC2 and PC3 exhibit excellent solubility in common solvents such as chloroform, chlorobenzene, and 0dichlorobenzene. Polymer PC1 has relatively poor but sufficient solubility in these solvents at the ambient temperature. As determined by gel permeation chromatography (GPC), using 75 monodispersed polystyrene as standard and THF as eluent, the number-average molecular weights  $(M_n)$  and polydispersity indices (PDIs) of PC1, PC2, and PC3 are 13.8 kDa (PDI = 1.2), 23.3 kDa (PDI = 1.9), and 14.7 kDa (PDI = 1.6), respectively (Table 1). The comparatively low molecular weight observed for 80 PC1 can be attributed the fact that there are no alkyl chains on the

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BT unit. And large molecular weight portions of PC1 are not collected because they are barely soluble in chloroform. Therefore, PC1 has a low  $M_n$  of 13.8 K and a narrow PDI of 1.2. Thermo gravimetric analysis (TGA) under nitrogen suggests all  $_5$  polymers are favorably stable with the 5% weight-loss

temperature ( $T_d$ ) values of 420, 340 and 338 °C for PC1, PC2 and PC3, respectively (Fig. S1†).

#### **Optical and electrochemical properties**



<sup>10</sup> Fig. 1 Normalized UV-vis absorption spectra of the copolymers (a) in dilute chlorobenzene solution  $(1 \times 10^{-5} \text{ M})$  and (b) as pristine films.

The UV-vis absorption spectra of the three copolymers in chlorobenzene (CB) solution and in thin film are shown in Fig. 1, and the relevant data are collected in Table 1. Both in solution <sup>15</sup> and in solid state, two main absorption bands are observed which is typical for D-A copolymers. The lower energy absorbance comes from the intramolecular charge transfer (ICT) between the donor and acceptor units, while the shorter wavelength band is

- attributed to  $\pi$ - $\pi^*$  transition of the heteroheptacene. Originating <sup>20</sup> from the same donor skeleton of the carbazole-based heptacyclic arenes, all copolymers possess nearly identical spectroscopic profiles in the shorter wavelength regions. As for the longer wavelength bands, polymers PC2 and PC3 exhibit blue-shifted absorption maxima compared to PC1, which can be attributed to
- <sup>25</sup> the weakened electron-withdrawing ability of the BT moiety induced by the introduction of two alkoxy groups. In solution, absorption peaks in long wavelength regions are located at 539 nm, 515 nm, and 517 nm for PC1, PC2, and PC3, respectively, which correspondingly red-shift to 549 nm, 520 nm, and 537 nm
- <sup>30</sup> for the spectra in thin film. These bathochromic shifts in going from the solution to the solid state suggest a stronger interchain  $\pi$ - $\pi$  stacking and a higher degree of ordered arrangement in thin film. It is worth noting that only a minimal red-shift occurs for the absorption maximum of PC2 in going from solution to thin <sup>35</sup> film. It may be attributed to the fact that the polymer chains

aggregate somewhat in solution for PC2 because the bulky alkyl substituents are only present on one side of the backbone, imposing less barrier to the chains interacting compared to PC3 with bulkier chains on both sides<sup>16</sup>. To verify this speculation, the 40 same solution was heated to 80 °C, as shown in Fig. S2(ESI<sup>+</sup>), a blue-shift of 12 nm appears for the absorption maximum as compared to that measured at 20 °C, indicating partial disaggregation of the polymer chains at higher temperature. All three polymers exhibit strong absorption ability in the wavelength 45 range from 375 nm to 600 nm, for example, with a maximum extinction coefficient of  $6.2 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup> for PC2 and  $7.2 \times 10^4$ M<sup>-1</sup> cm<sup>-1</sup> for PC3 at 418 nm in solution, which is benefical to harvest more sunlight and thus may lead to enhanced  $J_{sc}$  in PSCs. In comparison with its thiophene-substituted backbone analogue, <sup>50</sup> i.e., PCDCTDTBT-C8<sup>10</sup>, PC1 exhibits noticeable blue-shifts of the absorption maxima (low energy absorption band) with 50 nm for thin film and 46 nm for solution, which is due to the weaker electron donating ability of the benzene unit compared to the thiophene ring, resulting in decreased electron delocalization ss along the PC1 backbone. The optical bandgaps  $(E_g^{opt})$  deduced from onsets of the film spectra were determined to be 1.90 eV for PC1, 2.01 eV for PC2, and 1.97 eV for PC3, respectively. With similar or larger optical bandgaps relative to P3HT ( $E_g^{opt} = 1.90$ eV)17 which is the state-of-the-art large bandgap (short-60 wavelength absorbing) polymer for tandem PSCs, these polymers can be promising candidates as the front cell ingredient for multijunction devices with high efficiencies and large open circuit voltages.



65 Fig. 2 Cyclic voltammograms of the polymer thin films on Pt electrode, performed in 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> acetonitrile solution at 100 mV min<sup>-1</sup>.

Cyclic voltammetry (CV) was employed to investigate the electrochemical behaviors of these copolymers in thin film. The cyclic voltammograms are shown in Fig. 2, and the relevent 70 results are summarized in Table 1. On the basis of onset oxidation potentials in the CV curves, the estimated HOMO levels are -5.41 eV, -5.43 eV, and -5.44 eV for PC1, PC2, and PC3, respectively. These HOMO levels are similar to those of the 2,7-carbazole-based analogues and are significantly deeper-lying than those of 75 their thiophene-substituted backbone counterpart, which is helpful for achieving a high  $V_{oc}$  in PSCs. As expected, through donor structural modification, i.e., changing the more electron-donating thiophene moieties as shown in PHHA-BT into benzenes, lower-lying HOMO levels are acquired. It is common 80 that the HOMO levels of D-A copolymers are mainly governed

<sup>6 |</sup> Journal Name, [year], [vol], 00-00

by the electron donors<sup>18</sup>, and therefore similarly located HOMO energies are found in view of their same donor skeleton. Meanwhile, it is found that side chains can exert an influence on HOMO energy levels through the effect on molecular s conformation/molecular interactions, i.e., more twisted polymer backbones have been shown to achieve lower-lying HOMO

- levels<sup>19</sup>, so it is reasonable for a slightly descending HOMO levels from PC1 to PC3, accompanied by the strengthened backbone torsion with more or bulkier side chains attached. On <sup>10</sup> the other hand, deduced from the onset reduction potentials of the
- film CV curves, the LUMO levels were calculated to be -3.67 eV, -3.56 eV, and -3.65 eV for PC1, PC2, and PC3, respectively. These LUMO values are located within a suitable range and are sufficiently higher (>0.3 eV) than the LUMO level of [6,6]-
- <sup>15</sup> phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM, *ca.* -4.3 eV)<sup>20</sup> to overcome exciton binding energy and thus guarantee efficient exciton splitting and electron transfer.

#### Photovoltaic performance and film morphology

Photovoltaic properties of the copolymers were investigated in <sup>20</sup> conventional single-junction PSCs with a configuration of ITO/PEDOT:PSS/polymer:PC<sub>71</sub>BM/PIFB/AI. All the active layers were spin-coated from a mixed solvent of *ortho*dichlorobenzene:chlorobenzene (*o*-DCB:CB=1:4, v/v) with or without processing additives. The current density-voltage (*J-V*) <sup>25</sup> curves of the optimized PSCs measured under the AM 1.5G 100 mW cm<sup>-2</sup> illumination are plotted in Fig. 3a, and the

- mW cm<sup>-2</sup> illumination are plotted in Fig. 3a, and the corresponding device parameters are summarized in Table 2. Parameters including the blend ratio and the additive amount were screened toward device optimization (Table 3). Through
- <sup>30</sup> systematic optimization, PSCs based on PC2:PC<sub>71</sub>BM (1:4, w/w) using 0.5% (v/v) 1,8-diiodooctane (DIO) as the additive exhibit the best performance with a high  $V_{oc}$  of 0.93 V, a  $J_{sc}$  of 14.22 mA cm<sup>-2</sup>, an *FF* of 54.7%, and an intriguing PCE of 7.26%. From Table 3, one may find that the devices with the 1:3 blend ratio
- <sup>35</sup> also exibit a high averged PCE of 6.95 %. However, the devices with 1:3 blend ratio have a slightly larger averaged  $J_{sc}$  value with a decreased FF. It can be explained when one considers the relatively better light-harvesting ability and lower carrier mobility of PC2 in comparison with those of PC<sub>71</sub>BM. To the best of our
- <sup>40</sup> knowledge, this  $V_{oc}$  is a record high value ever reported for carbazole-based single-junction PSCs with a PCE over 7%, and this PCE value is also among the highest of ladder-type or large bandgap donor materials for PSCs. In comparison with its thiophene-substituted backbone counterpart ( $V_{oc} = 0.74$  V)<sup>10</sup> or
- <sup>45</sup> PCDTBT (maximum  $V_{oc} = 0.92 \text{ V})^6$ , PC2 based devices exhibit a higher  $V_{oc}$  benefiting from its deep-lying HOMO level. It is worth noting that a high  $V_{oc}$  of 0.99 V (PCE = 6.02%) was obtained when no additive of DIO was applied (Table 3). Compared to the devices fabricated without DIO, the reduction of  $V_{oc}$  in DIO
- <sup>50</sup> processed devices may come from the lowering of the charge transfer states upon using the additive<sup>21</sup>. It is well recognized that the molecular weight of a polymer has a large impact on the BHJ solar cell performance<sup>22</sup>. Therefore, we also prepared a batch of PC2 with relatively low molecular weight ( $M_n = 17.0$  kDa, PDI =
- ss 2.0), and the corresponding devices exhibit an optimal PCE of 6.54% with  $V_{oc} = 0.95$  V,  $J_{sc} = 12.04$  mA cm<sup>-2</sup>, and FF = 57.2% (Fig. S3, ESI†). While these results demonstrate the importance of molecular weight consideration, they also suggest the

possibility that even better performance based on PC2 could be o obtained by a systematic optimization on the molecular weight. When the best device based on PC3:PC<sub>71</sub>BM was prepared under the same conditions, it also exhibits an impressive PCE of 6.68% with  $V_{oc} = 0.93$  V,  $J_{sc} = 11.45$  mA cm<sup>-2</sup>, and FF = 62.7%. Whereas, the best cell based on PC1 only has a low PCE of

<sup>65</sup> 2.45% with  $V_{oc} = 0.88$  V,  $J_{sc} = 6.25$  mA cm<sup>-2</sup>, and FF = 44.7%, using 0.5% (v/v) DIO as an additive. The inferior maximum performance of PC1 and PC3 as compared to that of PC2 may be ascribed to the their lower hole mobilities (see Table 1) and the unfavorable morphology induced by their lower molecular

70 weights (vide infra). As expected, all devices based on these three polymers exhitit high  $V_{oc}$  values which is in accordance with their low-lying HOMO levels. Nevertheless, PC1 based devices afford the smallest  $J_{sc}$  and consequently the lowest PCE, which may be ascribed to its decreased solubility that would result in decreased 75 miscibility upon blending with PC71BM, and accordingly deteriorated film quality which in turn unfavorablely contributing to exciton dissociation and charge transport. External quantum efficiencies (EQE) of the devices prepared with DIO were measured and the EQE spectra are shown in Fig. S4a (ESI<sup>†</sup>). All 80 devices show a broad photon response range from 300 to 700 nm, which is consistent with the absorption spectra of the blend films (Fig. S5, ESI<sup>†</sup>). Obviously, the EQE values of PC2 based device are higher than those of PC1 or PC3 across the whole photon response range, and high values above 80% in the wavelength 85 region from 360 to 570 nm have been demonstrated, which agrees with the higher  $J_{sc}$  observed for the PC2 based device. Besides, the  $J_{sc}$  values calculated by integrating the EQE curves with the AM 1.5G spectrum agree with those obtained from the J-V measurements.



**Fig. 3** *J-V* characteristics of the optimized PSCs based on polymer: PC<sub>71</sub>BM and fabricated (a) in conventional architecture and (b) with inverted geometry, under AM 1.5G illumination, 100 mW/cm<sup>2</sup>.

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Table 2 Photovoltaic results of the optimized classical PSCs, under the AM 1.5G, 100 mW/cm<sup>2</sup> condition

Polymer	D:A <sup>a</sup>	$V_{\rm oc}$ [V]	$J_{sc} [\mathrm{mA \ cm}^{-2}]$	FF [%]	PCE <sup>c</sup> [%]	-	
PC1	1:4 <sup>b</sup>	$0.88\pm0.02$	$5.77\pm0.48$	$44.1 \pm 0.6$	2.30 ± 0.22 (2.45)		
PC2	1:4 <sup>b</sup>	$0.94\pm0.01$	$12.84 \pm 1.38$	$58.7\pm3.9$	$7.10 \pm 0.16$ (7.26)		
PC3	1:4 <sup>b</sup>	$0.93 \pm 0.01$	$11.18 \pm 0.49$	$63.3 \pm 2.6$	$6.60 \pm 0.10$ (6.68)		
<sup>a</sup> Blend ratio of polymer: PC <sub>71</sub> BM. <sup>b</sup> A mixed solvent of <i>o</i> -DCB:CB (1:4, v/v) is used, 0.5% (v/v) DIO as an additive. <sup>c</sup> The data have been averaged over 8							

Table 3 Photovoltaic properties of the regular PSCs based on PC2:PC71BM with different D/A ratios and volume fractions of DIO<sup>a</sup>

Blend ratio <sup>b</sup>	DIO (v/v) [%]	$V_{\rm oc}$ [V]	$J_{sc}$ [mA cm <sup>-2</sup> ]	FF [%]	$PCE^{c}$ [%]		
1:4	w/o	$0.98 \pm 0.01$	$10.86 \pm 0.35$	53.9±1.0	5.75 ± 0.27 (6.02)		
1:4	1.0	$0.95\pm0.01$	$11.21\pm0.42$	$57.1 \pm 1.5$	$6.07 \pm 0.21$ (6.21)		
1:3	0.5	$0.95\pm0.01$	$13.40 \pm 0.98$	$54.7 \pm 2.5$	$6.95 \pm 0.29$ (7.24)		
<sup>a</sup> A mixed solvent of o-DCB:CB (1:4, $v/v$ ) is used. <sup>b</sup> Blend ratio of polymer: PC <sub>71</sub> BM. <sup>c</sup> The data have been averaged over 8 devices of different batches.							
The performance of the best device is given in parentheses.							



**Fig. 4** Tapping-mode AFM height (top), phase (middle), and 3D images of the blend films: (a) PC1:PC<sub>71</sub>BM with 0.5% (v/v) DIO, (b) PC2:PC<sub>71</sub>BM with 0.5% DIO, (c) PC3:PC<sub>71</sub>BM with 0.5% DIO, (d) PC2:PC<sub>71</sub>BM without DIO. The scan size is 0.5  $\mu$ m × 0.5  $\mu$ m. All samples were prepared following the same procedure as the fabrication of the optimized PSCs.

<sup>10</sup> We also investigated the photovoltaic properties of these three copolymers with an inverted device structure of ITO/ZnO/polymer:PC<sub>71</sub>BM/MoO<sub>3</sub>/Ag. The *J-V* characteristics of the optimized inverted PSCs are depicted in Fig. 3b, and the corresponding performance data are listed in Table S1. The best <sup>15</sup> performance was obtained based on PC2 with a PCE of 6.17% and a  $V_{oc}$  of 0.92V. The integrated  $J_{sc}$  values from the EQE curves (Fig. S4b, ESI<sup>†</sup>) are consistent with respective values from the *J*-*V* measurements (within 3% error).

To disclose the relationship between optimized performance <sup>20</sup> and microstructures, the surface morphology of the polymer:PC<sub>71</sub>BM blends were screened by tapping mode atomic force microscopy (AFM). As can be seen in Fig. 4a, due to the poor solubility of PC1 and the resulting bad miscibility with  $PC_{71}BM$ , the PC1:PC<sub>71</sub>BM film features discrete dark and bright regions with a root mean square (RMS) roughness value of 2.78

- 5 nm, which also corresponds to the inferior phase separation as indicated by the clear and large scale fibrils in the phase image (also see Fig. S6, ESI<sup>†</sup>). Under such condition, photo-induced excitons can not realize effective dissociation, and interfacial defects between the active layer and the buffer layer modified
- <sup>10</sup> electrode may induce more traps. Therefore, the PC1 based device exhibits the smallest  $J_{sc}$ , *FF* and thus the lowest PCE among all the three polymers. In contrast, the PC2:PC<sub>71</sub>BM blend film with 0.5% DIO exhibits well-defined nanoscale phase separation with an RMS of 0.64 nm (Fig. 4b), indicating good
- <sup>15</sup> demixing of the polymer and PC<sub>71</sub>BM. However, in the case of PC2:PC<sub>71</sub>BM processed without DIO, rather smooth (RMS = 0.23 nm) and uniform film with obscure domains (shown in Fig. 4d) accounts for the corresponding decreased  $J_{sc}$  compared with that of the film with DIO. As for the PC3:PC<sub>71</sub>BM blend film
- <sup>20</sup> (Fig. 4c), the relatively rough surface (RMS = 1.13 nm) and large scale phase separation with randomly distributed polymer or PC<sub>71</sub>BM aggregates may be correlated to its suboptimal  $J_{sc}$  and PCE compared to PC2.

#### Conclusions

- <sup>25</sup> We have developed three D-A copolymers using DTBT derivatives as acceptor units and new carbazole-based heteroheptacenes, i.e., diindenocarbazoles, as donor units. Through polymer backbone manipulation and side chain tuning, eventually, a champion device based on PC2:PC<sub>71</sub>BM (1:4, w/w)
- <sup>30</sup> with 0.5 vol% DIO exhibited an impressive PCE of 7.26% with a high  $V_{oc}$  of 0.93 V. To the best of our knowledge, this represents the highest PCE ever reported for carbazole-based single-junction PSCs while maintaining a  $V_{oc}$  of up to 0.93 V. In addition, inverted PSCs also showed a PCE of 6.17% with a large  $V_{oc}$  of
- <sup>35</sup> 0.92 V. In view of the better light harvesting ability in the short wavelength region with a deep-lying HOMO energy level, PC2 should be a promising candidate for the use as a short wavelength absorbing material in tandem solar cells.

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  - $\dagger$  Electronic Supplementary Information (ESI) available: Experimental details including figures showing the absorption spectra of PC2 at different temperatures, the absorption spectra of blend films, the *J-V*
- 55 characteristics for PSCs based on PC2 (low molecular weight), EQE

spectra of the devices and other relevant data. See DOI: 10.1039/b000000x/

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