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# A Low-Bandgap Poly(2,7-Carbazole) Derivative for Use in High-Performance Solar Cells\*\*

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Harvesting energy directly from sunlight using photovoltaic cells (PCs) is a very important way to address growing global energy needs with a renewable resource while minimizing detrimental effects on the environment. For this purpose, the development of polymeric solar cells has received a great deal of attention from both academic and industrial laboratories.<sup>[1–3]</sup> Indeed, the utilization of semiconducting conjugated polymers as active components in bulk heterojunction photovoltaic devices offers significant potential advantages over existing inorganic materials in terms of ease of processing, formation of large surface areas, and costs. For example, poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylenevinylene] (MDMO-PPV),<sup>[4]</sup> regioregular poly(3-hexylthiophene) (P3HT),<sup>[5,6]</sup> and other polythiophene derivatives<sup>[7]</sup> have been extensively studied over the last decade, resulting in PCs with a power conversion efficiency between 3.0 and 5.0 %. However, the performances of these polymers are somehow restricted by their relatively large bandgap and the limited possibilities to modulate their physical properties by synthetic methods. New low-bandgap polymers have been developed over the years to better harvest the solar spectrum, especially in the 1.4–1.9 eV region. Promising copolymers based on fluorene units have been proposed by Andersson/Inganäs<sup>[8,9]</sup> and Cao,<sup>[10]</sup> with power conversion efficiencies between 2.0 and 2.8 %. Interestingly, the physical properties of polyfluorene derivatives can be easily modulated through the design of various alternating copolymers.<sup>[11]</sup> However, relatively low hole mobilities were reported for low-bandgap polyfluorene derivatives. Therefore, besides those recent advances, there is still a need for new polymeric materials to go beyond the 5 % efficiency of actual materials.<sup>[3,12,13]</sup>

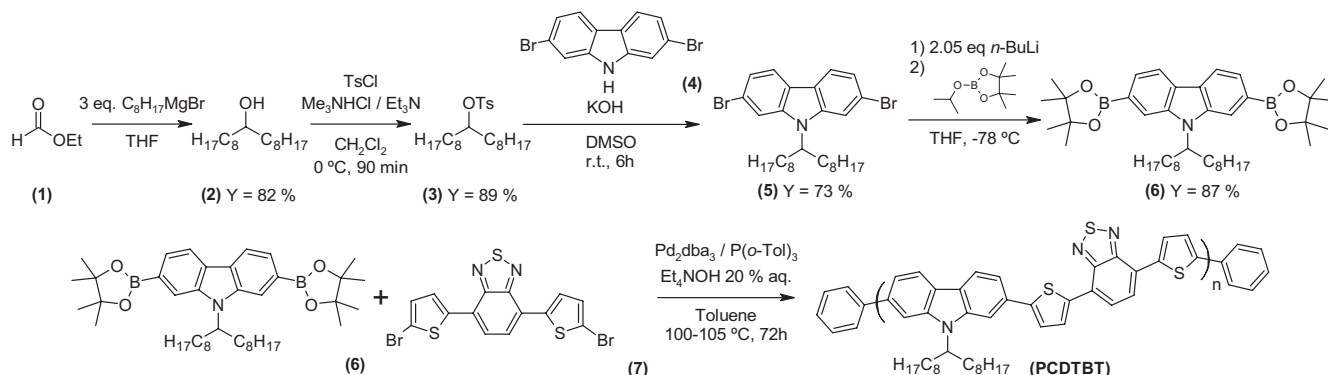
Along these lines, poly(*N*-vinylcarbazole) (PVK) is well known as an excellent photoconductor.<sup>[14,15]</sup> Furthermore, studies have demonstrated that PVK photoconduction increases when doped with sensitizers like 2,4,7-trinitrofluorenone (TNF) or C<sub>60</sub>.<sup>[15,16]</sup> In parallel, oligo- and poly(2,7-carba-

zole) derivatives have been successfully used in polymer light-emitting diodes (PLEDs)<sup>[17]</sup> and organic field-effect transistors (OFETs),<sup>[17,18]</sup> demonstrating good *p*-type transport properties. Recently, Müllen and co-workers<sup>[19]</sup> have reported solar cells with an efficiency of 0.6 % with poly(*N*-alkyl-2,7-carbazole), whereas Leclerc and co-workers<sup>[20]</sup> have shown an efficiency of 0.8 % with poly(2,7-carbazolenevinylene) derivatives. Moreover, in contrast with the fluorene unit the carbazole moiety is fully aromatic, providing a better chemical and environmental stability. Taking all of these results into account, the development of new low-bandgap copolymers based on carbazoles should therefore lead to interesting features for photovoltaic applications. However, poly(*N*-alkyl-2,7-carbazole)s generally exhibit poor solubilities and low molecular weights.<sup>[21]</sup> To solve these problems, bulky side chains are usually attached onto the conjugated backbone.<sup>[19,22]</sup> Therefore, in this Communication we report the development of a new processable, high-molecular-weight, highly conjugated poly(*N*-alkyl-2,7-carbazole) derivative, namely poly[*N*-9'-heptadecan-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]. The combination of a low bandgap with good mechanical and transport properties has led to a power conversion efficiency of 3.6 % in bulk heterojunction solar cells.

Different linear and branched alkyl and aryl substituents were tested to get processable and high-molecular-weight poly(2,7-carbazole) derivatives, and the best results were obtained with a secondary alkyl side chain on the nitrogen atom of the carbazole unit (a structure that looks like that of 9,9-dialkylfluorene<sup>[23]</sup>). We first attempted to obtain the *N*-9'-heptadecan-2,7-dibromocarbazole (**5**) using 9-bromoheptadecane,<sup>[24]</sup> but low conversion yields were obtained (10–15 %) despite the utilization of various synthetic pathways.<sup>[25,26]</sup> These results are similar to the ones observed on indole derivatives by Marzoni and Garbrecht.<sup>[26]</sup> For this reason, and as shown in Scheme 1, 9-heptadecane *p*-toluenesulfonate (**3**) was prepared. The reaction between ethyl formate (**1**) and octylmagnesium bromide led to heptadecan-9-ol (**2**)<sup>[27]</sup> with a good yield and high purity after distillation under reduced pressure. The tosylate derivative (**3**) was obtained from compound **2** and *p*-toluenesulfonyl chloride through a high-performance reaction by Yoshida et al.<sup>[28]</sup> with an excellent yield (89 %). Finally, the alkylation reaction of 2,7-dibromo-9-*H*-carbazole<sup>[29]</sup> with compound **3** was carried out following a procedure described by Marzoni and Garbrecht.<sup>[26]</sup> Compound **6** was synthesized through a double lithiation of compound **5** with *n*-butyllithium and subsequent quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, as re-

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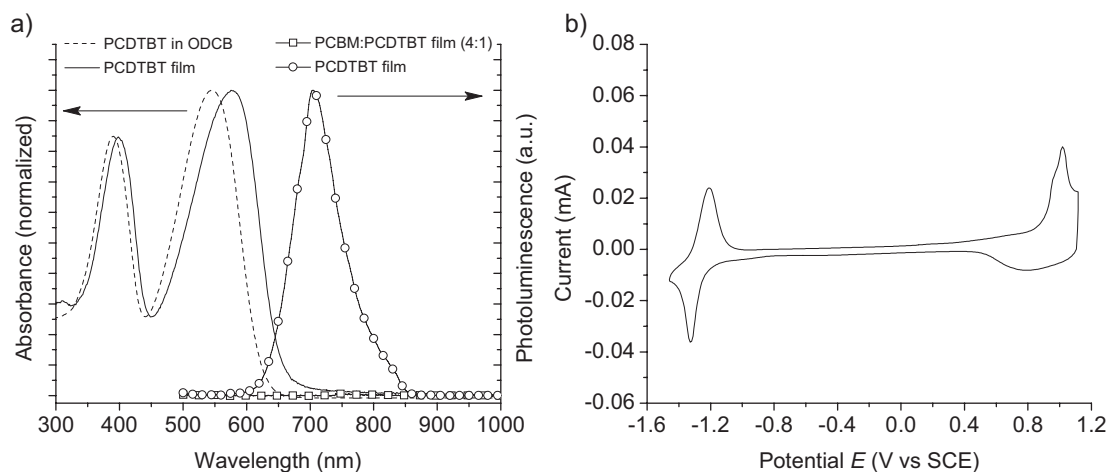


**Scheme 1.** Synthesis of the co-monomers and PCDTBT. THF: tetrahydrofuran; Et: ethyl; Bu: butyl; TsCl: *p*-toluenesulfonyl chloride; DMSO: dimethyl sulfoxide; Pd<sub>2</sub>dba<sub>3</sub>: tris(dibenzylideneacetone)dipalladium(0).

ported for 2,7-bromo-9,9-dialkylfluorene.<sup>[30]</sup> Interestingly, the resulting aromatic structure should present a better stability compared to the fluorene moiety, which is known to degrade partially into fluorenone subunits.<sup>[31]</sup> NMR experiments have revealed that compounds **5** and **6** present atropisomeric configurations at room temperature,<sup>[32]</sup> clearly illustrating the side-chain-limited rotation around the carbazole backbone. As a co-monomer, we utilized the well-documented 4,7-dithien-2-yl-2,1,3-benzothiadiazole unit.<sup>[8,33]</sup> The co-monomer (**7**) was prepared according to a highly efficient procedure reported in the literature.<sup>[34]</sup>

As also shown in Scheme 1, both co-monomers were copolymerized through Suzuki coupling<sup>[35]</sup> to yield poly[*N*-9'-heptadecanyl-2,7-carbazole-*alt*-5,5'-(4',7'-di-2-thienyl-2',1'-benzothiadiazole)] (PCDTBT). To increase the stability of the polymer, an end-capping reaction was performed using bromobenzene and phenyl boronic acid. After purification and according to size-exclusion chromatography (SEC) experiments based on monodisperse polystyrene standards, the chloroform-soluble fraction seems to have a relatively high

molecular weight (number- ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights 37 and 73 kDa, respectively (1 Da =  $1.661 \times 10^{-27}$  kg)). Indeed, free-standing films can be easily obtained from solutions of this polymer. Moreover, the resulting aromatic polymer shows a high glass transition temperature ( $T_g$ ; ca. 130 °C), excellent thermal stability (5% degradation at 430 °C), and is soluble in tetrahydrofuran (THF), chloroform, chlorobenzene (CB), orthodichlorobenzene (ODCB), and 1,2,4-trichlorobenzene (TCB). The combination of such good physical properties has never been reported for other poly(2,7-carbazole) derivatives, and is highly suitable for photovoltaic applications. Although PCDTBT gives colored but clear solutions in tetrahydrofuran and chloroform, SEC data suggest some aggregation in those two solvents. However, no aggregation was observed at 135 °C in TCB. In a good solvent (ODCB at 90 °C), the PCDTBT presents two absorption bands at 390 and 545 nm (see Fig. 1A). A pure PCDTBT thin film shows two broad absorption bands with peaks at 398 and 576 nm and an absorption onset at 660 nm (1.88 eV). The solid-state photoluminescence of the polymer



**Figure 1.** a) UV-vis spectrum in ODCB at 90 °C (dashed line) and in the solid state (solid line), photoluminescence in the solid state (○) and photoluminescence quenching for PCBM:PCDTBT (4:1) (□). b) Cyclic voltammogram (second scan) of PCDTBT films cast on platinum wire in Bu<sub>4</sub>NBF<sub>4</sub>/acetonitrile at 50 mV s<sup>-1</sup>. SCE: standard calomel electrode.

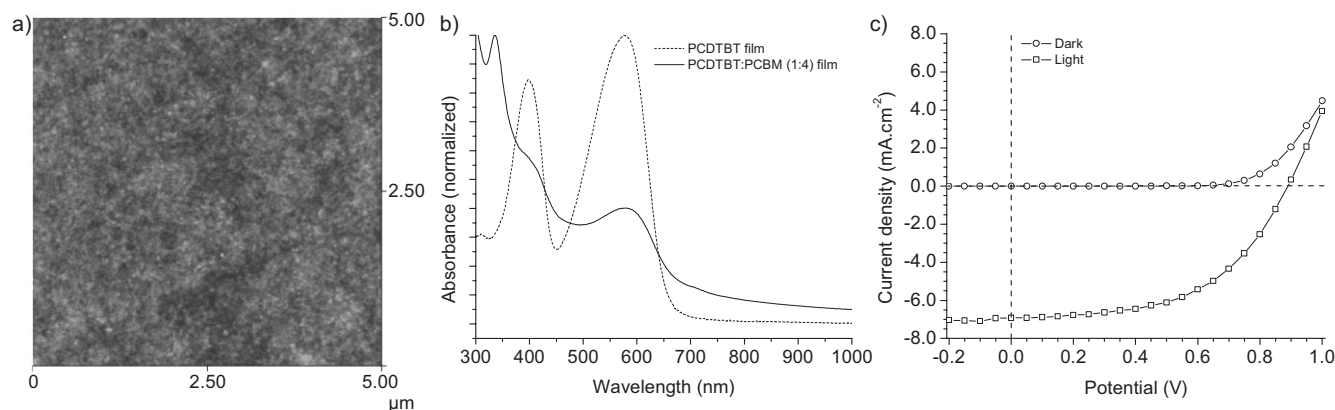
lies near the red region with a maximum of emission at 705 nm and is almost completely quenched by the addition of [6,6]-phenyl- $C_{61}$  butyric acid methyl ester (PCBM) (Fig. 1A). This highly efficient photoluminescence quenching is the consequence of ultrafast photoinduced charge transfer from the polymer to PCBM. On the basis of all these optical measurements, one can assume that PCDTBT is a viable candidate for applications in PCs.

As shown in Figure 1B, the cyclic voltammogram of PCDTBT presents one oxidation process ( $E_{\text{ox}}^{1/2} = 0.91$  V vs. the standard calomel electrode (SCE)) and one reduction process ( $E_{\text{red}}^{1/2} = -1.26$  V versus SCE). Based on the recorded oxidation potential, the neutral PCDTBT should show a good air stability.<sup>[36]</sup> Furthermore, the highest occupied molecular orbital (HOMO, ca. 5.5 eV;  $E_{\text{onset}}^{\text{ox}} = 0.78$  V vs. SCE) and lowest unoccupied molecular orbital (LUMO, ca. 3.6 eV;  $E_{\text{onset}}^{\text{red}} = -1.09$  V vs. SCE) energy levels calculated from these electrochemical measurements fit reasonably well with the required electronic levels<sup>[12,13,37]</sup> ( $E_{\text{HOMO}}$  level between 5.2–5.8 eV;  $E_{\text{LUMO}}$  level between 3.7–4.0 eV) for polymeric bulk heterojunction solar cells utilizing PCBM as the acceptor. On the basis of these electrochemical data, and taking into account a LUMO level for PCBM at -4.3 eV using semi-empirical estimation equation,<sup>[12]</sup> the calculated open circuit potential ( $V_{\text{OC}}$ ) is ca. 0.9 V. Interestingly, the optical bandgap (1.88 eV) and electrochemical bandgap (1.87 eV) are similar within the experimental error.

Following all these physical characterizations, photovoltaic solar cells were fabricated by spin-coating a chloroform solution made from a mixture of PCBM and PCDTBT (4:1). Films obtained using this method were uniformly deposited onto an indium tin oxide (ITO)/glass substrate coated with poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS). Atomic force microscopy (AFM) studies showed that the films had an average thickness of 70 nm and a root mean square (RMS) roughness lower than 0.8 nm (Fig. 2A). The absorption spectra of the blend (4:1, PCBM:PCDTBT) and the pure polymer are reported in Figure 2B. Photovoltaic

cells, when tested under an AM1.5G solar illumination at  $90 \text{ mW cm}^{-2}$  source intensity, demonstrated power conversion efficiencies up to 3.6 % on a regular basis. A typical  $I$ - $V$  curve demonstrating the behavior of the device is presented in Figure 2C. A good current density ( $J_{\text{SC}}$ ) was obtained ( $6.92 \text{ mA cm}^{-2}$ ) along with a relatively high fill factor (FF; 0.63) and open-circuit potential ( $V_{\text{OC}} = 0.89$  V). The latter value agrees quite well with the calculated  $V_{\text{OC}}$  (0.9 V) determined from electrochemical data. Interestingly, a similar polymer obtained via a Stille coupling reaction presented similar photovoltaic performances. The high FF shows that the charge flow is well-balanced and that no significant recombination loss occurs within the active material at this thickness.<sup>[5,38]</sup> Furthermore, the high FF and  $J_{\text{sc}}$  indicate that there are low serial resistances from the materials in this configuration.<sup>[2]</sup> All samples were fabricated and characterized in air, without protecting environment, and demonstrated the high stability of PCDTBT.

In conclusion, we reported a new fully aromatic poly(2,7-carbazole) derivative (i.e., poly[*N*-9'-heptadecan-yl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]) that combines a high glass transition temperature, good solubility, relatively high molecular weight, and air-stability. Photovoltaic cells based on this polymer blended with PCBM have revealed a power conversion efficiency of 3.6 % which makes this class of materials among the best conjugated polymers reported up to now. It is firmly believed that further improvements from device fabrication (e.g., film thickness, annealing, solvent) should lead to even better performances. Moreover, the utilization of this innovative 2,7-carbazole building block and a more powerful electron-accepting unit (e.g., thieno[3,4-*b*]pyrazine, pyrazino[2,3-*g*]quinoxaline)<sup>[39]</sup> should lead to polymers with lower bandgaps (in the range of 1.4–1.8 eV). Those new low-bandgap polycarbazole derivatives should also exhibit fine-tuned HOMO (5.2–5.8 eV) and LUMO (3.7–4.0 eV) energy levels,<sup>[12,13,37]</sup> increasing the total number of collected photons and the open circuit potential.



**Figure 2.** a) Height image (scale 15 nm, size  $5 \mu\text{m} \times 5 \mu\text{m}$ ) obtained by tapping-mode AFM on the surface for PCBM:PCDTBT (4:1) spin-coated thin film. b) Optical spectra of a PCDTBT film (dashed line) and a PCBM:PCDTBT (4:1) blend film on glass. c) Current density-potential characteristic of a diode made of PCDTBT:PCDTBT (4:1) under illumination with AM1.5G solar simulated light ( $\square$ ) and in the dark ( $\circ$ ).

## Experimental

**Characterization:**  $^1\text{H}$  and  $^{13}\text{C}$ NMR spectra were recorded on a Varian AS400 apparatus in appropriated deuterated solvent solution at 298 K, unless specified otherwise. Chemical shifts were reported as  $\delta$  values (ppm) relative to an internal tetramethylsilane (TMS) standard. Number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights were determined by SEC with a Viscotek High Temperature GPC System (Model 350 HTGPC) and two Viscotek H-MBHMW-3078 columns using a refraction index (RI) detector at 135 °C in 1,2,4-trichlorobenzene (HPLC grade, Mallinckrodt). The calibration curve was made with a series of monodispersed polystyrene standards (Shodex). Differential scanning calorimetry (DSC) analyses were performed on a Perkin–Elmer DSC-7 instrument, calibrated with ultrapure indium. Glass transition temperatures ( $T_g$ ) were measured at a scanning rate of 20 °C min $^{-1}$ , under a nitrogen flow. Thermogravimetric analysis (TGA) measurements were carried out with a Mettler Toledo TGA SDTA 851e apparatus at a heating rate of 20 °C min $^{-1}$  under a nitrogen atmosphere. The temperature of degradation ( $T_d$ ) corresponds to a 5 % weight loss. UV-visible absorption spectra were taken using a Varian Cary 500 UV-vis-NIR spectrophotometer whereas fluorescence spectra were recorded on a Varian Eclipse spectrofluorometer. Cyclic voltammograms (CVs) were recorded on a Solartron 1287 potentiostat using platinum electrodes at a scan rate of 50 mV s $^{-1}$  and a Ag/Ag $^+$  (0.10 M of AgNO $_3$  in acetonitrile) reference electrode in an anhydrous and argon-saturated solution of 0.1 M of tetrabutylammonium tetrafluoroborate (Bu $_4$ NBF $_4$ ) in acetonitrile. In these conditions, the oxidation potential ( $E_{\text{ox}}^{1/2}$ ) of ferrocene was 0.11 V versus Ag/Ag $^+$ , whereas the  $E_{\text{ox}}^{1/2}$  of ferrocene was 0.42 V versus SCE. The HOMO and LUMO energy levels were determined from the oxidation and reduction onset of the second scan from CV data taking into account the SCE level at –4.7 eV [37,40]. Electrochemical onsets were determined at the position where the current starts to differ from the baseline. A Nanoscope III, Dimension 3100, atomic force microscope (Digital Instrument) was used to examine the surface topology of thin PCDTBT films and to determine their thickness. A 90  $\mu\text{m}$  scanner was operated in tapping mode with an etched silicon tip. To determine their thickness, each film was indented with a razor blade and topographic images were recorded by AFM; the thickness of the film was taken as the difference between the height of the film surface (an average made on both sides of the indentation) relative to the surface of the substrate (at the bottom of the indentation).

**Synthetic Procedures:** All starting organic compounds were purchased from Aldrich, Alfa Aesar, or TCI America and used without further purification. Tetrabutylammonium tetrafluoroborate (98 %, Aldrich) was recrystallized three times in a 50:50 mixture of methanol/water and dried at 100 °C under reduced pressure, as reported in the literature [41]. All reactions were carried out under argon at 1 atmosphere unless mentioned otherwise. Some reaction solvents were distilled before use (THF from sodium/benzophenone, acetonitrile and dichloromethane from CaH $_2$ ). Column chromatography was carried out on silica gel (size 40–63  $\mu\text{m}$ , pore size 60 Å, Silicycle). The 2,7-dibromo-9-*H*-carbazole [29] (**4**), 4,7-di(2'-bromothien-5'-yl)-2,1,3-benzothiadiazole [34] (**7**) have been already reported in the literature. All other compounds have been synthesized following procedures described below.

**Heptadecan-9-ol (**2**)** [24,27]: In a three neck flame-dried 1 L round-bottom flask, ethyl formate (7.408 g, 100.0 mmol, 8.04 mL) was dissolved in 167 mL of THF and cooled to –78 °C. Octylmagnesium bromide (300.0 mmol, 300 mL of a 1 M solution in THF) was then added dropwise and the reaction mixture was allowed to stir overnight at room temperature. The reaction was quenched by the addition of methanol (MeOH) and then saturated aqueous NH $_4$ Cl. This mixture was transferred to a separatory funnel, extracted with ether (750 mL), and then washed once with a saturated aqueous NaCl solution (750 mL). The ether fraction was dried over MgSO $_4$ . The crude product was distilled under reduced pressure (b.p. 130 °C at 0.45 mmHg) to obtain 21.07 g of pure product as a white solid (yield: 82 %). m.p.

28–31 °C.  $^1\text{H}$  NMR (400 MHz, CDCl $_3$ , ppm):  $\delta$  3.58 (m, 1H); 1.42 (m, 8H); 1.27 (m, 21H); 0.87 (t,  $J$  = 7.1 Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz, CDCl $_3$ , ppm):  $\delta$  72.16; 37.63; 32.04; 29.87; 29.75; 29.44; 25.81; 22.82; 14.25. HRMS: Calculated for C $_{17}$ H $_{34}$  ( $M$ –H $_2$ O): 238.2660, Found: 238.2665  $\pm$  0.0007; Calculated for C $_{17}$ H $_{35}$ O ( $M$ –H): 255.2688, Found: 255.2694  $\pm$  0.0008.

**9-Heptadecane *p*-Toluenesulfonate (**3**):** *p*-Toluenesulfonyl chloride (11.13 g, 48.49 mmol) in CH $_2$ Cl $_2$  (39 mL) was added to a stirred solution of heptadecan-9-ol (**2**) (10.00 g, 38.99 mmol), Et $_3$ N (13.55 mL, 97.25 mmol) and Me $_3$ N·HCl (3.718 g, 38.99 mmol) in CH $_2$ Cl $_2$  (39 mL) in a 250 mL flask at 0–5 °C. The mixture was stirred for 90 min, water was added, and the mixture was extracted three times with CH $_2$ Cl $_2$ . The organic phase was washed with water and brine, dried (Na $_2$ SO $_4$ ), and concentrated under reduced pressure. The crude product was purified by silica-gel column chromatography (90 % hexanes/10 % ethyl acetate as eluent) to give 14.25 g of colorless oil, which crystallized overtime as the title product (yield: 89 %). m.p. 31–32 °C.  $^1\text{H}$  NMR (400 MHz, CDCl $_3$ , ppm):  $\delta$  7.79 (d,  $J$  = 8.2 Hz, 2H); 7.32 (d,  $J$  = 8.1 Hz, 2H); 4.53 (qt,  $J$  = 5.9 Hz, 1H); 2.44 (s, 3H); 1.55 (m, 4H); 1.22 (m, 24H); 0.88 (t,  $J$  = 7.1 Hz, 6H).  $^{13}\text{C}$  NMR (100 MHz, CDCl $_3$ , ppm):  $\delta$  144.40; 134.92; 129.75; 127.86; 84.81; 34.25; 31.98; 29.50; 29.43; 29.30; 24.82; 22.79; 21.74; 14.25. HRMS: Calculated for C $_{24}$ H $_{46}$ NO $_3$ S ( $M$  + NH $_4$  $^+$ ): 428.3198, Found: 428.3205  $\pm$  0.0012.

***N*-9'-Heptadecanyl-2,7-dibromocarbazole (**5**):** A flame-dried three neck flask fitted with an addition funnel and a magnetic stirring bar was charged with 6.500 g (20.00 mmol) of 2,7-dibromo-9-*H*-carbazole (**4**), dimethyl sulfoxide (48 mL), and 5.611 g (100.0 mmol) of freshly powdered potassium hydroxide. When the carbazole was completely dissolved, a solution of 12.32 g (30.00 mmol) of **3** in DMSO (32 mL) was added dropwise through the addition funnel over 1.5–2 h at room temperature. After 6 h, the reaction was poured into 300 mL of distilled water, and the aqueous layer was extracted three times with hexanes (350 mL). The combined organic fractions were dried over magnesium sulfate and the solvent was removed under reduced pressure. The crude product was dissolved in dichloromethane, preadsorbed on silica gel, and purified by column chromatography (silica gel, hexanes as eluent) resulting in a white solid. (8.203 g, yield: 73 %) m.p. 59–61 °C.  $^1\text{H}$  NMR (400 MHz, CDCl $_3$ , ppm):  $\delta$  7.90 (br, 2H); 7.70 (br, 1H); 7.54 (br, 1H); 7.33 (br, 2H) 4.42 (br, 1H); 2.19 (br, 2H); 1.90 (br, 2H); 1.14 (br, 22H); 0.97 (br, 2H); 0.83 (t,  $J$  = 6.3 Hz, 6H) (Multiple and broad peaks are due to the phenomenon of atropisomerism [32]).  $^{13}\text{C}$  NMR (100 MHz, CDCl $_3$ , ppm):  $\delta$  143.03; 139.56; 122.44; 121.61; 121.36; 120.97; 119.90; 119.31; 114.66; 112.29; 57.09; 33.61; 31.87; 29.42; 29.40; 29.26; 26.86; 22.74; 14.21 (Multiple carbon peaks are due to the phenomenon of atropisomerism [32]). HRMS: Calculated for C $_{29}$ H $_{41}$ Br $_2$ N: 561.1606, Found: 561.1611  $\pm$  0.0017.

**2,7-Bis(4',4'',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-*N*-9'-heptadecanycarbazole (**6**):** To a solution of compound **5** (6.000 g, 10.65 mmol) in THF (107 mL) in a flame-dried 250 mL flask at –78 °C was added dropwise 8.73 mL (21.83 mmol) of *n*-butyllithium (2.5 M in hexane). The mixture was stirred at –78 °C for 1 h and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.78 mL, 4.359 g, 23.43 mmol) was added rapidly to the solution. After one additional hour at –78 °C, the resulting mixture was warmed to room temperature and stirred overnight. The mixture was poured into water, extracted with diethyl ether four times and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by recrystallisation in methanol/acetone (ca. 10:1) to obtain the title product as a white crystal (6.081 g, Yield: 87 %). m.p. 128–130 °C.  $^1\text{H}$  NMR (400 MHz, C $_6$ D $_6$ , ppm):  $\delta$  8.61 (br, 1H); 8.41 (br, 1H); 8.19 (d,  $J$  = 7.8 Hz, 1H); 8.14 (t,  $J$  = 8.1 Hz, 2H); 8.09 (d,  $J$  = 7.7 Hz, 1H); 4.50 (m, 1H); 2.33 (m, 2H); 1.61 (m, 2H); 1.22 (br, 4H); 1.19 (br, 12H); 1.17 (br, 12H); 1.03 (br, 20H); 0.87 (t,  $J$  = 7.1 Hz, 6H) (Multiple and broad protons are due to a phenomenon of atropisomerism [32]).  $^{13}\text{C}$  NMR (100 MHz, C $_6$ D $_6$ , ppm):  $\delta$  142.81; 139.42; 127.59; 126.94; 125.77; 125.57; 125.44; 121.06; 120.67; 118.66; 116.26; 116.22; 83.81; 83.79; 56.82; 34.20; 32.18; 29.78; 29.62; 29.60; 27.10; 25.09; 23.03; 14.39 (Multiple carbon peaks are due to a phenomenon of atropisomerism [32]). HRMS: Calculated for C $_{41}$ H $_{65}$ B $_2$ NO $_4$ : 657.5099, Found: 657.5105  $\pm$  0.0020.

*Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5'-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT)*: In a 50-mL flame dried flask, 723.3 mg (1.100 mmol) of compound **6**, 504.0 mg (1.100 mmol) of 4,7-di(2'-bromothien-5'-yl)-2,1,3-benzothiadiazole (**7**), 5.0 mg (0.0055 mmol) of tris(dibenzylideneacetone)dipalladium(0) and 6.7 mg (0.022 mmol) of tri(*o*-tolyl)phosphine were dissolved in 11.0 mL of degassed toluene and 3.7 mL of degassed 20 % aqueous tetraethylammonium hydroxide. The reaction mixture was vigorously stirred at 90–95 °C. After a few hours, the mixture became very viscous and 5.0 mL of toluene was added. After 72 h, bromobenzene (12 µL, 0.110 mmol) was added to the reaction then one hour later, phenylboronic acid (13.4 mg, 0.110 mmol) was added and the reaction refluxed overnight to complete the end-capping reaction. The polymer was purified by precipitation in methanol/water (10:1), filtered through 0.45 µm nylon filter and washed on Soxhlet apparatus with acetone, hexanes, toluene, dichloromethane and chloroform. The chloroform fraction (550–600 mL) was reduced to 40–50 mL under reduced pressure, precipitated in methanol/water (10:1, 500 mL), filtered through 0.45 µm nylon filter and finally air dried overnight. (178.1 mg, Yield: 23 %). <sup>1</sup>H NMR (400 MHz, ODCB-*d*<sub>4</sub>, 130 °C, ppm): δ 8.11 (d, *J* = 3.5 Hz, 2H); 8.02 (d, *J* = 8.1 Hz, 2H); 7.94 (br, 2H); 7.74 (br, 2H); 7.56 (d, *J* = 7.8 Hz, 2H); 7.45 (d, *J* = 3.6 Hz, 2H); 4.73 (br, 1H); 2.42 (br, 2H); 2.05 (m, 2H); 1.23 (br, 8H); 1.22 (br, 16H); 0.70 (t, *J* = 6.8 Hz, 6H).

*Photovoltaic Cells Fabrication and Testing*: The organic photovoltaic cells, with the sandwiched structure of glass/ITO/PEDOT:PSS/PCDTBT-PCBM(1:4)/Aluminum, were prepared on commercial ITO-coated glass substrate (25 × 25 mm<sup>2</sup>) with a sheet resistance of ca. 10 Ω/square (Präzisions Glas & Optic GmbH, Germany). Each substrate was patterned using photolithography techniques to produce a segment with an active area of 90 mm<sup>2</sup>. Prior to use, the substrates were cleaned with detergent and deionized water. Then, they were ultrasonicated in deionized water and in isopropanol. ITO substrates were spin-coated (2000 rpm, 60 s) with a thin film (50 nm) of PEDOT: PSS, Baytron P, H. C. Starck and dried at 120 °C for 10 min. A blend of [6,6]-phenyl-C<sub>61</sub> butyric acid methyl ester (PCBM) (Nano-C, USA) and PCDTBT (4:1, 4.0 mg mL<sup>-1</sup> of PCDTBT in CHCl<sub>3</sub>) was solubilized overnight in chloroform, filtered through a 0.45 µm poly(tetrafluoroethylene) (PTFE) filter, spin-coated at 2000 rpm for 60 s. The resulting films were dried at 50 °C for 10 minutes and then under vacuum at room temperature for 12 h. The devices were completed by deposition of a 70 nm Al layer. This layer was thermally evaporated at a pressure of 1 × 10<sup>-6</sup> Torr at room temperature. Note that LiF was not used between the active layer and the Al electrode. Current versus potential curves (*I*-*V* characteristics) were measured with a Keithley 2400 Digital SourceMeter under a collimated beam. Illumination of the cells was done through the ITO side using light from 150 W Oriel Instruments Solar Simulator and xenon lamp with AM1.5G filter (No. 81094) to provide an intensity of 90 mW cm<sup>-2</sup>. All fabrications and characterizations were performed in an ambient environment without a protective atmosphere.

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