

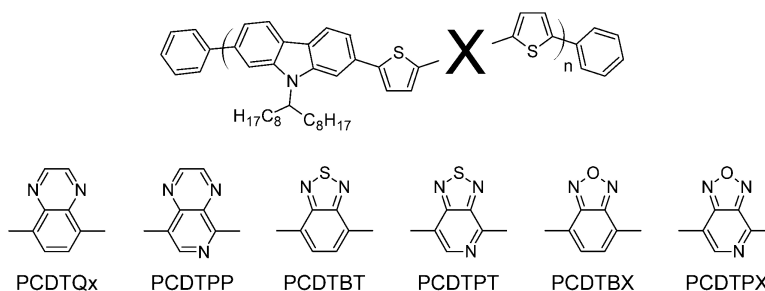
Article

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## Toward a Rational Design of Poly(2,7-Carbazole) Derivatives for Solar Cells

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**Abstract:** On the basis of theoretical models and calculations, several alternating polymeric structures have been investigated to develop optimized poly(2,7-carbazole) derivatives for solar cell applications. Selected low band gap alternating copolymers have been obtained via a Suzuki coupling reaction. A good correlation between DFT theoretical calculations performed on model compounds and the experimental HOMO, LUMO, and band gap energies of the corresponding polymers has been obtained. This study reveals that the alternating copolymer HOMO energy level is mainly fixed by the carbazole moiety, whereas the LUMO energy level is mainly related to the nature of the electron-withdrawing comonomer. However, solar cell performances are not solely driven by the energy levels of the materials. Clearly, the molecular weight and the overall organization of the polymers are other important key parameters to consider when developing new polymers for solar cells. Preliminary measurements have revealed hole mobilities of about  $1 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$  and a power conversion efficiency (PCE) up to 3.6%. Further improvements are anticipated through a rational design of new symmetric low band gap poly(2,7-carbazole) derivatives.

### 1. Introduction

Solar cells are one key technology for solving world energy needs. The development of new materials such as the semiconducting conjugated polymers as active components in bulk heterojunction<sup>1–4</sup> (BHJ) photovoltaic devices could help to significantly reduce the fabrication cost of such devices. For these purposes, two polymeric materials have been extensively studied in the past decade: poly[2-methoxy-5-(3',7'-dimethyl-octyloxy)-*p*-phenylenevinylene] (MDMO-PPV)<sup>5,6</sup> and regio-regular poly(3-hexylthiophene) (P3HT).<sup>7–9</sup> The utilization of these polymeric materials has led to power conversion efficiencies between 3.0 and 5.0% when mixed with [6,6]-Phenyl C61

butyric acid methyl ester (PCBM), as the electron acceptor. To further improve the device performances, one can develop new device architectures,<sup>10,11</sup> synthesize new polymers<sup>12,13</sup> and new electron acceptors,<sup>5,14–16</sup> or work on both ends.

In the past few years, several groups of chemists proposed new polymer structures as alternatives to P3HT and MDMO-PPV since the performances of these two polymers are somehow limited by their relatively large band gap.<sup>17,18</sup> For many years, internal charge transfer (ICT) from an electron-rich unit to an electron deficient moiety has been extensively used to obtain low band gap conjugated polymers.<sup>19–23</sup> Using an ICT strategy,

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new polymers have been developed to better harvest the solar spectrum, especially in the 1.4–1.9 eV region. Several low band gap polythiophene derivatives have been reported by Krebs<sup>24–26</sup> and Reynolds,<sup>27,28</sup> but until now, relatively low performances in solar cells have been obtained. Polyfluorene derivatives<sup>29–32</sup> show promising features with power conversion efficiencies (PCE) between 2.0 and 4.2%. However, these polymers show relatively low carrier mobility, limiting the device performances. Recently, benzothiadiazole and cyclopentadithiophene copolymers showed very interesting PCE values (3.2–5.5%)<sup>33,34</sup> and high carrier mobility ( $10^{-2}$ – $10^{-1}$  cm<sup>2</sup>·V<sup>-1</sup>·s<sup>-1</sup>)<sup>33,35</sup> demonstrating that one can synthesize ICT polymers having low band gap and high carrier mobility.

Poly(2,7-carbazole) derivatives are other excellent potential candidates for BHJ solar cells. Indeed, as observed with poly(2,7-fluorene)s,<sup>36,37</sup> the physical properties of poly(2,7-carbazole)s<sup>38</sup> can be easily modulated. As an electron-rich molecule,<sup>38–40</sup> the carbazole unit is perfect for the development of ICT polymers. Moreover, poly(*N*-vinylcarbazole) (PVK) is among the best photoconductive polymeric materials.<sup>39</sup> Initial studies by K. Müllen<sup>41</sup> and our group<sup>42</sup> have produced polycarbazole materials that exhibit relatively low efficiency in solar cells (0.6–0.8%). In general, those polymers were poorly soluble and showed a lack of organization. However, we recently reported a new polycarbazole derivative (PCDTBT)<sup>43</sup> bearing a secondary alkyl side chain on the nitrogen atom of the carbazole unit that shows high solubility and some organization, resulting in a very good PCE (3.6%). It was concluded that, by improving the electronic properties of the polymeric materials, much higher efficiencies could be reached.

Recently, several models have been proposed to estimate the polymer performance in BHJ solar cells.<sup>12,27,44</sup> First, the polymer must be air-stable; therefore, the HOMO energy level needs to

be below the air oxidation threshold (ca. –5.27 eV or 0.57 V vs SCE).<sup>45</sup> Furthermore, this relatively low value assures a relatively high open circuit potential ( $V_{OC}$ ) in the final device. Second, the LUMO energy level of the polymer must be positioned above the LUMO energy level of the acceptor (i.e., [6,6]-Phenyl C61 butyric acid methyl ester (PCBM)) by at least 0.2–0.3 eV to ensure efficient electron transfer from the polymer to the acceptor.<sup>46,47</sup> Therefore, the ideal donor LUMO energy level should be between –3.7 and –4.0 eV. Finally, the optimal band gap, considering the solar emission spectrum and the open circuit potential of the resulting solar cell, should range between 1.2 and 1.9 eV. Therefore, the ideal polymer HOMO energy level should range between –5.2 and –5.8 eV. Taking into account the LUMO energy level of PCDTBT (–3.60 eV), one needs to reduce this parameter to further increase the performance of a polymeric cell while keeping the HOMO energy level within the same energy value (i.e., –5.45 eV).

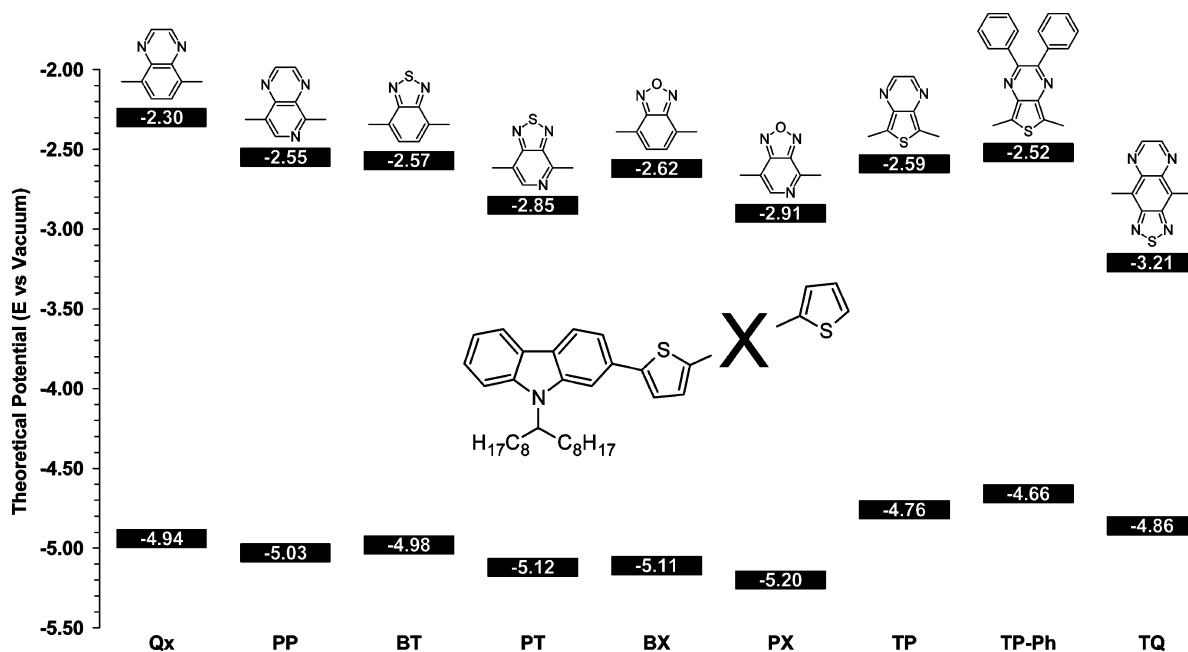
On the basis of these initial data and theoretical models, we investigated several alternating polymeric structures to develop the most suitable poly(2,7-carbazole) derivatives for BHJ solar cell devices.<sup>12,27,44</sup> To estimate the polycarbazole performances using those models, we performed quantum calculations on the repeat unit of the planned polymers to determine both the HOMO and LUMO energy levels. These values were then compared to the experimental values of the polymers. These new polymers were tested in solar cell devices, and their performances were analyzed in terms of polymer organization, molecular weight, charge carrier mobility, and LUMO energy level.

## 2. Results and Discussion

**2.1. Theoretical Calculations.** Predicting the behavior of both the HOMO and LUMO energy levels for new polymers is crucial to make a rational design of optimized BHJ solar cells. Recently, semiempirical calculations (MNDO) have been successfully applied on several similar low band gap fluorene derivatives.<sup>48</sup> In the present work, we have estimated the HOMO and LUMO energy levels of the repetitive units of the corresponding alternating copolymers by using the density functional theory (DFT) as approximated by the B3LYP functional and employing the 6-31G\* basis set. The computational methodology is described in the Supporting Information. DFT/B3LYP/6-31G\* has been found to be an accurate formalism for calculating the structural and optical properties of many molecular systems.<sup>49–55</sup>

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**Figure 1.** Theoretical energy levels for some carbazole derivatives. Insert: repeating unit of the correlated alternating copolymer.

As shown in Figure 1, we first investigated several potential polycarbazole analogues to the low band gap polyfluorenes reported by Andersson/Inganäs.<sup>30,56–58</sup> The TQ comonomer should lead to a relatively low band gap polymer, but as found with polyfluorene derivatives,<sup>57,58</sup> the resulting polycarbazole should have a too low LUMO energy level, assuming that PCBM is used as an electron acceptor. Other candidates (TP and TP-Ph) raise also some concerns. For these two copolymers, the calculations revealed an important increase of the HOMO energy value without any major decrease of the LUMO energy value compared to the other candidates. This phenomenon could result in lower  $V_{oc}$  and, more importantly, to air-unstable polymers. In contrast, pyridine-based candidates (PP, PT, and PX) revealed an interesting trend; the pyridine moiety decreases both the HOMO and LUMO energy levels. The resulting polymers should therefore exhibit higher open circuit potentials while being air-stable. Replacing the sulfur atom (BT, PT) by an oxygen atom (BX, PX) has a similar effect. Based on these calculations, it was decided to synthesize the BX, PP, PT, PX copolymers. For comparison purposes, we also synthesized the Qx polycarbazole derivative and the previously reported BT derivative.

**2.2. Synthesis. 2.2.1. Monomer Synthesis.** The synthetic route to the chosen five new comonomers is depicted in Scheme 1. First, this synthetic strategy required an electron-deficient dibromoheteroarene as the elementary block, as already proposed by Yamashita and co-workers for similar compounds.<sup>59</sup> Starting from the 2,3-diaminopyridine (**1**), compound **2** was obtained from bromine in hydrobromic acid according to the work of Lee and Yamamoto.<sup>60</sup> An alternative purification process was used to eliminate any remaining mineral residues.

Without this additional purification, the ring closing reaction leading to compounds **3** and **4** is significantly affected. Compound **3** was prepared from a double imide formation using aqueous glyoxal in butanol. The conversion of compound **2** to compound **4** was only possible with thionyl chloride (75 equiv), following a strategy similar to that reported by Thomas and Sliwa.<sup>61</sup> Surprisingly, the bromine atom at the 4-position is converted into a chlorine atom, as demonstrated from both mass spectra and monocystal X-ray analyses (Figure 1S). Reaction concentration, addition of base (pyridine or triethylamine), or substitution of thionyl chloride for thionylaniline or thionyl bromide did not improve the reaction yield and generally resulted in undesired products. The only viable way found to obtain the 4,7-dibromo-2,1,3-benzoxadiazole (**6**) was from melted 2,1,3-benzoxadiazole (**5**) mixed with iron as catalyst and bromine. The product was subsequently treated with a  $K_2CO_3$  saturated aqueous solution according to already reported procedures.<sup>62,63</sup> Under milder conditions, nearly pure starting compound is recovered. To ensure that the bromine atoms insert at the 4,7-positions, monocystals were grown from ethanol and subsequently analyzed by X-ray diffraction. Figure 2S (Supporting Information) confirms the structure of the desired compound, demonstrating a perfect selectivity for the 4,7-positions.

From these electron-deficient dibromoheteroarene building blocks, the comonomers **12** to **15** were synthesized. Starting from the dibromoheteroarene compounds **3**, **4**, **6**, or **7**<sup>64</sup> and 2-tributylstannylthiophene, a Stille coupling reaction<sup>65</sup> in dimethylformamide (DMF) afforded precursors **8** to **11**. These precursors were treated with *n*-bromosuccinimide (NBS) in 1,2-dichlorobenzene (ODCB) at 55 °C, according to a methodology previously reported for 4,7-di(2'-bromothien-5'-yl)-2,1,3-ben-

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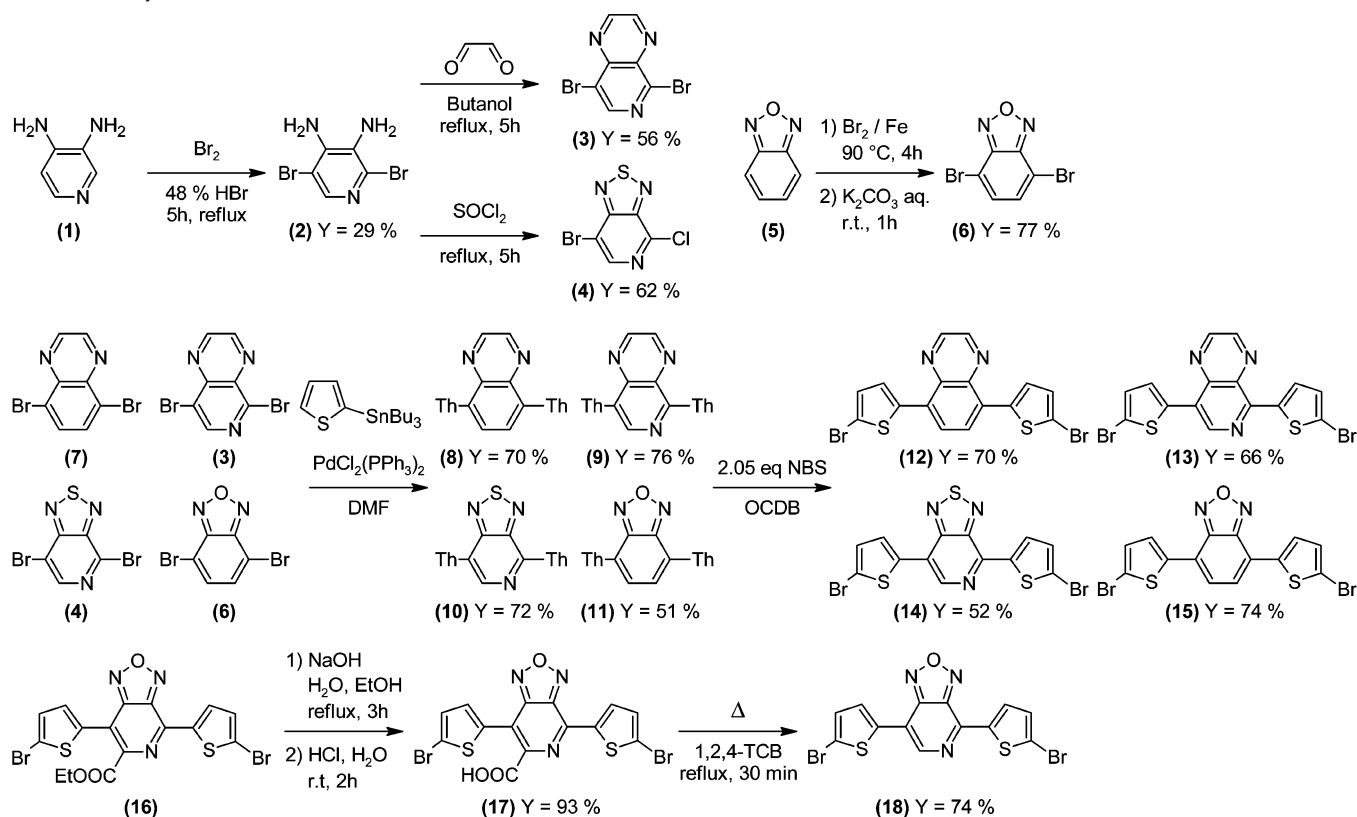
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Scheme 1. Synthesis of the Comonomers



zothiadiazole.<sup>66</sup> The resulting comonomers **12** to **15** are then easily recovered. In contrast, when treated under more classical conditions (i.e., chloroform/acetic acid, 1:1), the resulting products are not suitable for polymerization reactions. The last comonomer (**18**) is prepared from an alternative synthetic pathway originally proposed by Gorohmaru et al.<sup>67</sup> The ethyl 4,7-bis(5-bromothiophen-2-yl)[1,2,5]oxadiazolo[3,4-c]pyridine-6-carboxylate<sup>67</sup> (**16**) is hydrolyzed with aqueous NaOH and neutralized with aqueous hydrochloride to obtain the carboxylic acid **17**. This compound was decarboxylated at high temperature in 1,2,4-trichlorobenzene to afford comonomer **18**.

**2.2.2. Polymer Synthesis.** The five new polymers were synthesized according to Scheme 2. The same polymerization

reaction as that already reported for PCDTBT<sup>43</sup> was chosen to obtain these new copolymers. Indeed, 2,7-bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-N-9''-heptadecanilcarbazole<sup>43</sup> (**20**) and the desired comonomers were copolymerized through a Suzuki coupling reaction<sup>68</sup> and produced three symmetric copolymers (PCDTQx, PCDTBT, and PCDTBX) and three asymmetric copolymers (PCDTPP, PCDTPT, and PCDTPX). PCDTBT and PCDTBX have higher molecular weights than the other polymers even if each monomer showed similar purities and was polymerized using the same conditions (Table 1). Other Suzuki coupling polymerization conditions were tried, especially for PCDTPT and PCDTPX, to improve the molecular weight but, up to now, without any success. We attribute these results to the possible complexation<sup>69–71</sup> of the palladium catalyst by monomers **14** and **18** or the resulting polymers, slowing down or stopping the polymerization reaction.

The parent symmetric PCDTQx and asymmetric PCDTTPP show similar number-average molecular weights (9.0 kDa and 11 kDa, respectively). Therefore, comparisons of the polymer properties and device performances are possible without taking into account the influence of the molecular weight, as generally observed for P3HT.<sup>72,73</sup> In general, the asymmetric polymers are more soluble in common solvents (i.e., chloroform and

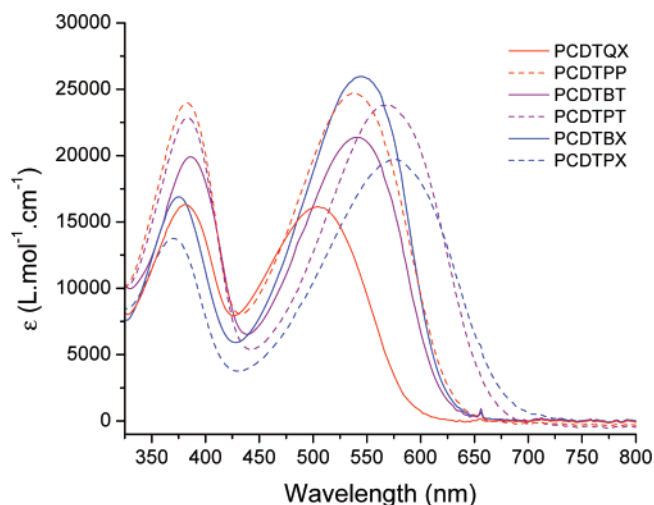


Figure 2. UV-vis spectra at 135 °C in 1,2,4-trichlorobenzene for the six polycarbazoles derivatives.

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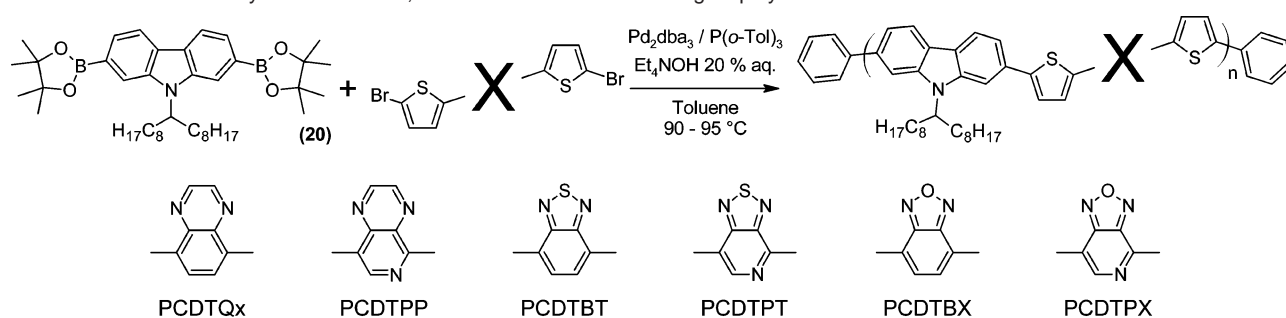
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**Scheme 2.** Structure and Synthesis of the 2,7-Carbazole-Based Alternating Copolymers**Table 1.** Number-Average Molecular Weight ( $M_n$ ), Polydispersity Index (PDI), Glass Transition Temperature ( $T_g$ ), Degradation Temperature ( $T_d$ ), and Optical and Electrochemical Properties of Polycarbazole Derivatives

polymer	$M_n$ kDa	PDI	$T_g$ , °C	$T_d$ , °C	$E_{\text{HOMO}}^a$ , eV	$E_{\text{LUMO}}^b$ , eV	$E_g^{\text{elec}}$ , eV	$E_g^{\text{opt thin}}$ , eV
PCDTQx	9.0	1.53	116	440	-5.46	-3.42	2.04	2.02
PCDTPP	11	1.70	133	420	-5.52	-3.67	1.85	1.89
PCDTBT	36	1.54	130	470	-5.45	-3.60	1.85	1.88
PCDTPT	4.0	1.50	111	410	-5.53	-3.80	1.73	1.75
PCDTBX	26	1.97	145	380	-5.47	-3.65	1.82	1.87
PCDTPX	4.5	1.33	-	340	-5.55	-3.93	1.62	1.67

<sup>a</sup> Ionization potential ( $E_{\text{HOMO}}$ ; HOMO: highest occupied molecular orbital) measured from the cathodic onset. The SCE level used for the HOMO calculation was -4.7 eV.<sup>27</sup> <sup>b</sup> Electron affinity ( $E_{\text{LUMO}}$ ; LUMO: lowest unoccupied molecular orbital) measured from the anodic onset. The SCE level used for the LUMO calculation was -4.7 eV.<sup>27</sup> <sup>c</sup> Measurements performed on spin-coated films from the onset of the absorption band.

tetrahydrofuran) than their symmetric counterparts. Surprisingly, PCDTBT is soluble in chloroform, chlorobenzene (CB), or orthodichlorobenzene (OBCB), whereas PCDTBX is far less soluble in these solvents. This explains the lower soluble content recovered after Soxhlet extractions. It was also noticed that 16 h of polymerization for the PCDTBT were more efficient than the 72 h previously reported,<sup>43</sup> leading to an improved polymerization yield (soluble fraction in chloroform) and a less polydisperse polymer. Similar attempts to improve PCDTBX and PCDTQx polymerization reactions did not result in the same improvements.

### 2.3. Polymer Characterization. 2.3.1. UV-vis Absorption.

The characterization of the UV-visible absorption features of our polymers is essential for photovoltaic applications and has been performed both in solution (in 1,2,4-trichlorobenzene (TCB) at 135 °C, see Figure 2) and in the solid state. For solution measurements, such a high temperature was required since a significant bathochromic shift (ca. 15–25 nm) is observed at 25 °C (Figures 3S to 8S, Supporting Information), suggesting, in agreement with SEC data, the presence of aggregation.

The solid-state UV-vis spectra of the polymers show a bathochromic shift (ca. 30–40 nm) compared to the solution spectra obtained in TCB at 135 °C (Figures 3S to 8S, Supporting Information). The red shift observed from solution to the solid state suggests a higher structural organization in the solid state. As expected, the optical band gap (Table 1) varies as a function of the electron-withdrawing properties of the comonomers. Therefore, the optical band gap (Table 1) ranges from 2.02 eV (614 nm) for PCDTQx to 1.67 eV (743 nm) for PCDTPX.

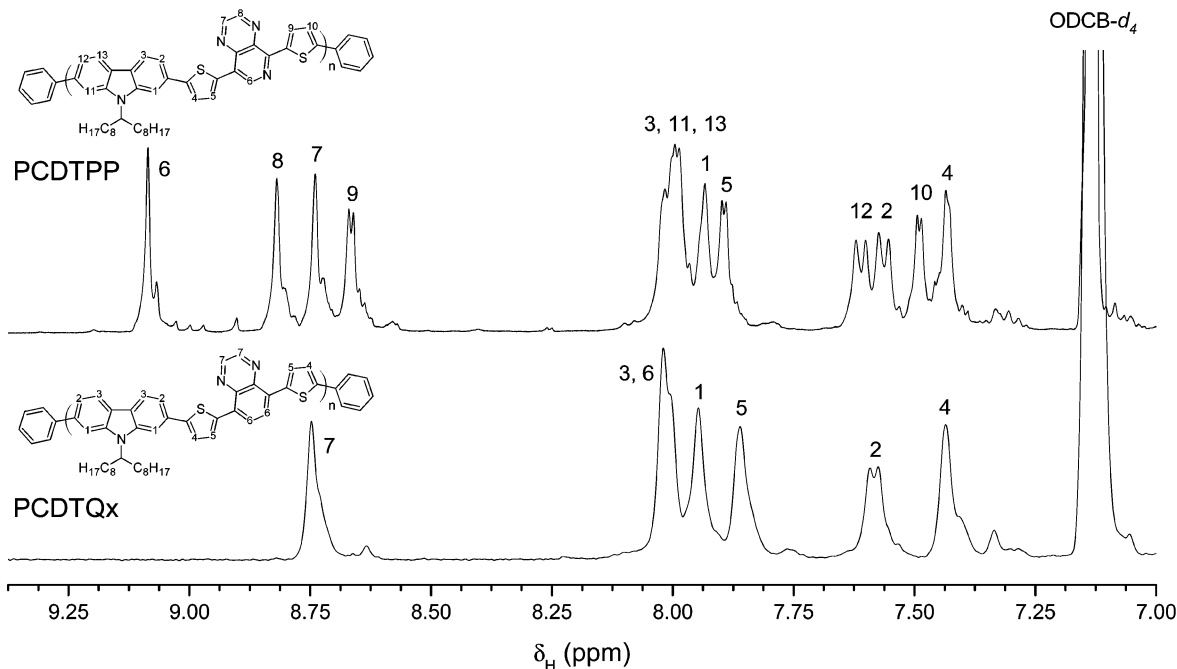
**2.3.2. <sup>1</sup>H NMR Analyses of the Polymers.** The symmetric (PCDTQx, PCDTBT, PCDTBX) and asymmetric (PCDTPP, PCDTPT, PCDTPX) natures of the copolymers were clearly revealed by <sup>1</sup>H NMR analyses. For such measurements, a high temperature (in ODCB at 130 °C) was necessary to suppress both the polymer aggregation and alkyl side chain atropisomerism configuration observed at room temperature.<sup>43</sup> Differences between the two structures are particularly evident in the aromatic region (see Figure 3). For instance, the signal of proton-2 on the PCDTQx is split into two proton signals (2, 12) for PCDTPP. Moreover, the two other proton signals (1 and 3) for PCDTQx result in four different signals (1, 3, 11, and 13) for PCDTPP although the splitting is less evident. Overall, there are three proton signals associated with the carbazole for the PCDTQx, whereas there are six peaks for the PCDTPP. The asymmetry in the polymer backbone is therefore attributable to the additional nitrogen atom present on the pyridine core and its relative position to both sides of the carbazole unit. Similar but less evident observations have been made for the other copolymers.

**2.3.3. Thermal Properties.** The thermal stability of these polymers is also a very important parameter for the performance of the BHJ devices. All present copolymers are thermally stable up to 340 °C and show a glass transition temperature ( $T_g$ ) over 100 °C (Table 1), except for PCDTPX whose  $T_g$  was not detected by DSC. Clearly, the oxygen-containing polymers (PCDTBX and PCDTPX) show lower thermal stability than the sulfur-containing polymers (PCDTBT and PCDTPT). Interestingly, PCDTBT melts into a liquid crystalline state around 268 °C and recrystallizes around 259 °C (Figure 4). Similar transitions have been reported for poly(fluorene-*alt*-dithienylbenzothiadiazole)s (175–180 °C).<sup>74</sup> The low supercooling and the very low energy involved (between 0.34 and 0.39 J/g in both heating and cooling) support a mesophase nature. This assumption is also supported by observations made with polarized optical microscopy (POM) since the melting of PCDTBT and PCDTQx leads to birefringent liquids. The third symmetric polymer, PCDTBX, shows some birefringence but degrades before melting. No birefringence was noticed for the asymmetric polymers, and this fact confirms a higher ordering capability for the symmetric structures. The same alkyl side chain has a similar impact over the polymer solubility and organization of other *N*-substituted heterocycles,<sup>75</sup> demonstrating the importance to better understand the role also played by the alkyl side chain.

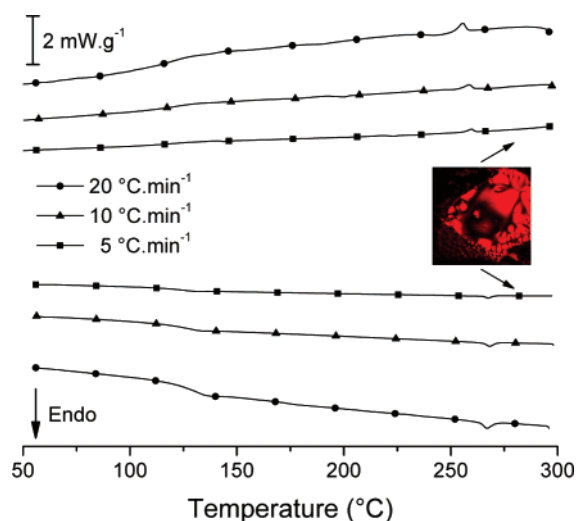
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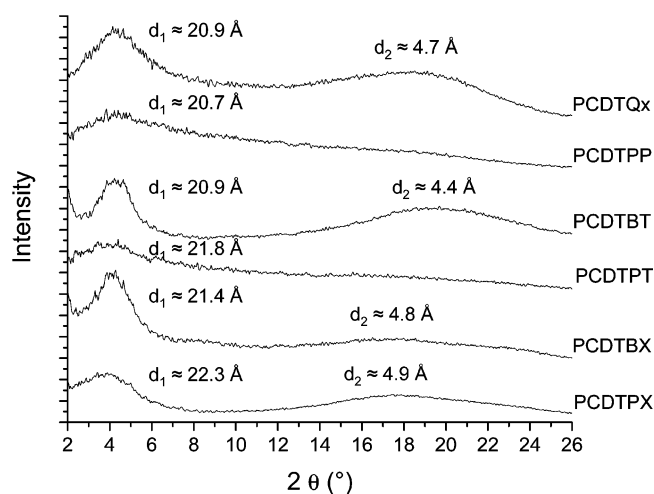


**Figure 3.** Aromatic region of the  $^1\text{H}$  NMR spectra of PCDTQx and PCDTTP in 1,2-dichlorobenzene- $d_4$  at 130  $^\circ\text{C}$ .



**Figure 4.** Differential scanning calorimetry of PCDTBT at 5, 10, and 20  $^\circ\text{C}/\text{min}$ . Insert: micrograph under polarized light.

**2.3.4. X-ray Analyses.** To confirm the structural order observed by POM and DSC measurements, X-ray diffraction analyses on powdery polymers were performed (Figure 5). All six polymers show a peak at  $d_1 \approx 21\text{--}22$  Å, but only a very weak diffraction is observed for PCDTTP and PCDTPT. Contrastingly, the three symmetric polymers show  $d_2 \approx 4.4\text{--}4.9$  Å, whereas only PCDTPX shows a peak at the same distance spacing. These  $d$  values ( $d_1$  and  $d_2$ ) are similar to those reported for poly(9,9-dioctylfluorene) in a nematic form.<sup>76–78</sup> It is reasonable to assume that  $d_1$  values correspond to the distance between  $\pi$ -conjugated main chains separated by the long alkyl side chain, whereas  $d_2$  values correspond to the distance between the coplanar  $\pi$ -conjugated main chains. Logically, the comono-



**Figure 5.** X-ray diffraction patterns of powdery polycarbazole derivatives.

mers have no effect on the  $d_1$  distance. In contrast, the nature of the comonomers has an important effect on the  $d_2$  distance. For instance, PCDTBT exhibits the shortest  $\pi$  stacking distance ( $d_2 \approx 4.4$  Å). Such a phenomenon could be related to the highly favorable dipole–dipole and  $\pi$ – $\pi$  interactions between benzothiadiazole units and conjugated polymer chains.<sup>79–81</sup> These results suggest a higher structural organization in the solid state for the symmetric polymers (PCDTQx, PCDTBT, and PCDTBX) compared to the asymmetric polymers (PCDTTP and PCDTPT) with an exception for the PCDTPX.

**2.3.5. HOMO–LUMO Energy Levels.** Copolymer energy levels depend on several factors and have been characterized from electrochemical analyses. The anodic peak potential ( $E_{pa}$ ) for the three symmetric polymers (PCDTQx, PCDTBT, PCDTBX) is, within the experimental error, the same (ca. 1.01 V), as

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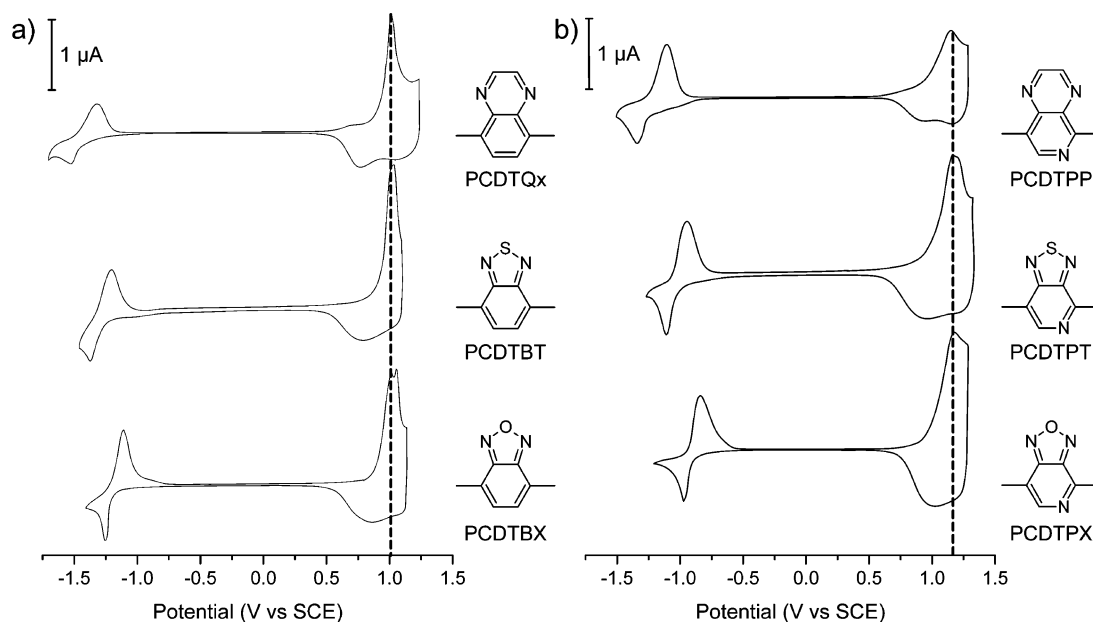
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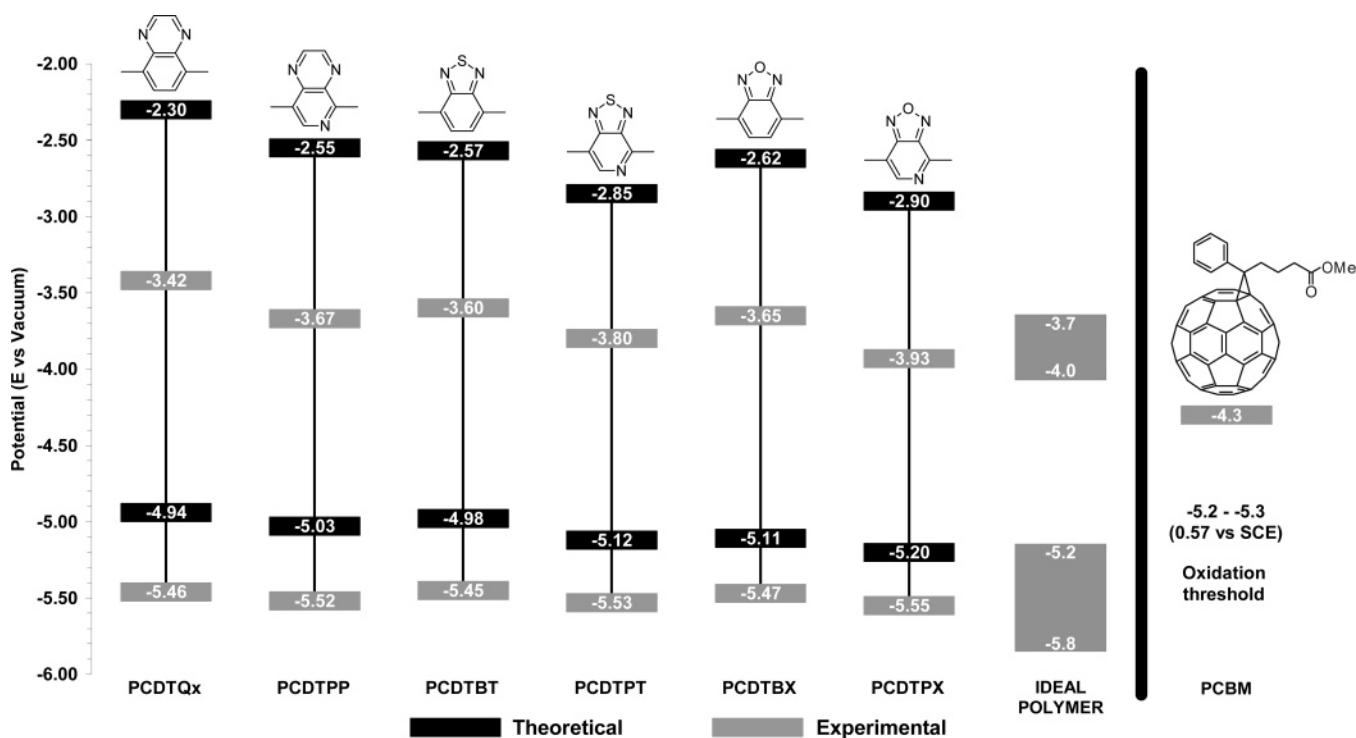
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**Figure 6.** Cyclic voltammogram (second scan) of (a) symmetric and (b) asymmetric polymer films cast on a platinum wire in  $\text{Bu}_4\text{NBF}_4/\text{acetonitrile}$  at 50 mV/s.

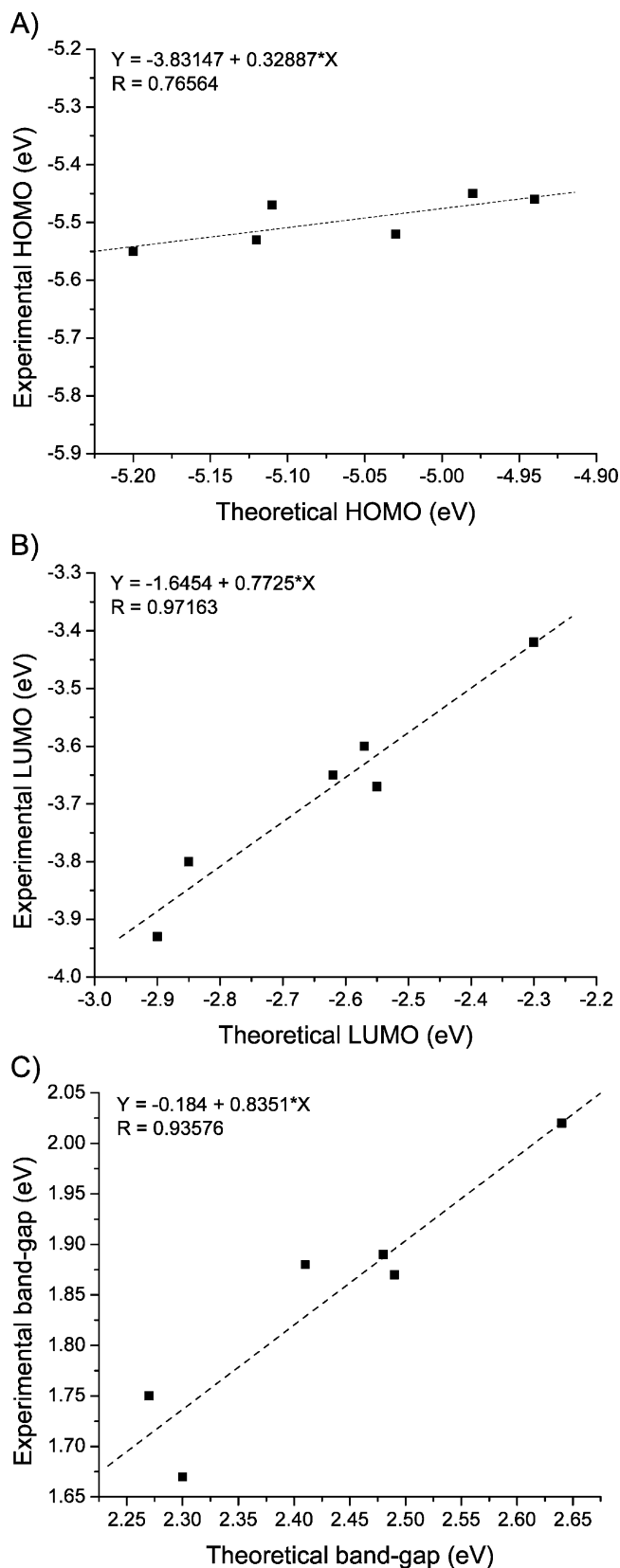


**Figure 7.** Experimental and theoretical energy levels for the six polycarbazole derivatives.

shown in Figure 6a. The same observation is also true for the three asymmetric polymers (PCDTPP, PCDTPT, PCDTPX) with an  $E_{\text{pa}}$  value of ca. 1.12 V (Figure 6b). Therefore, the substitution of the electron-deficient center unit has almost no effect on the polymer oxidation potential. However, replacing the benzene core on the electron-deficient center unit by a pyridine core induces an increase of the  $E_{\text{pa}}$  by ca. 0.10 V. From these CV curves, it was calculated that the three symmetric polymers (PCDTQx, PCDTBT, PCDTBX) show HOMO energy levels at ca.  $-5.46$  eV and the three asymmetric polymers (PCDTPP, PCDTPT, PCDTPX) at ca.  $-5.53$  eV (Table 1 and Figure 7). More importantly, based on the oxidation potential data, the

neutral polymers should show good air stability, the HOMO energy level being largely below the air oxidation threshold (ca.  $-5.27$  eV or 0.57 V vs SCE).<sup>45</sup> On the other hand, the polymer LUMO energy level behaves quite differently. The LUMO energy level is clearly affected by the electron-deficient center on the bithiophene comonomer, a stronger electron-deficient unit resulting in a lower LUMO energy level. The pyridine core also affects the LUMO energy level, lowering the LUMO energy level by ca. 0.25 eV when compared to the benzene core polymers. It is worth also noting that the electrochemical and optical band gap values are relatively in good agreement (Table 1).





**Figure 8.** Theoretical and experimental HOMO (A), LUMO (B), and band gap (C).

**2.3.6. Validation of the Theoretical Calculations.** An excellent correlation can be established between the theoretical LUMO energy levels of the repetitive units and the experimental LUMO energy levels of the polymers (Figure 8b). On the other

hand, the correlation for the small energy variations of the HOMO energy levels is not as good, resulting in a lower correlation factor (Figure 8a). Nevertheless, DFT calculations on model compounds provide a good estimation of the HOMO energies considering the small energy difference between the lowest and highest values. As expected, theoretical energy band gaps of the repeating units of the polymers are overestimated compared to the experimental values of the polymers (see Figure 7), but a useful correlation can be found between the theoretical and experimental band gaps as shown in Figure 8c. From these data, one can conclude that DFT calculations performed on the repetitive units can indeed provide good estimations of the HOMO, LUMO, and band gap energy trends, thus allowing a rapid screening of the most promising polymeric structures.

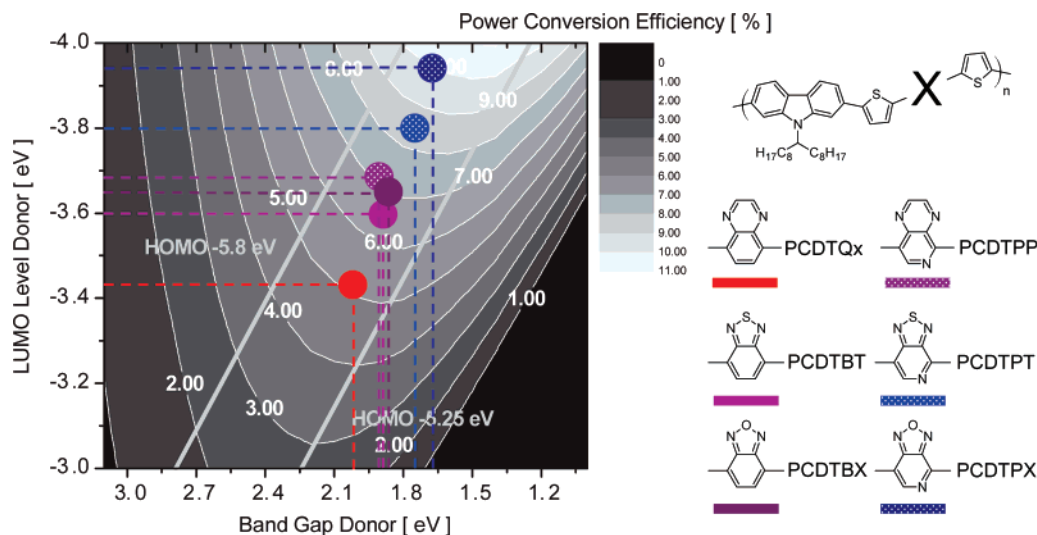
**2.3.7. Performance Predictions.** All six copolymers have a HOMO energy level within the desired range (−5.2 to −5.8 eV), assuring both an air-stable photovoltaic device and a relatively high  $V_{OC}$ . One can also expect similar  $V_{OC}$  values from all devices made with these polymers since they have very similar HOMO energy level values. In contrast, only two polymers (PCDTPT and PCDTPX) have an ideal LUMO energy level (−3.7 to −4.0 eV). The four other polymers have higher LUMO energy levels and, consequently, should present lower efficiencies. Using the design rules proposed by Scharber et al.<sup>12</sup> which assume a charge carrier mobility of  $10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ , a fill factor of 0.65, and an optimal morphology, one can estimate the overall power conversion efficiency from the optical band gap and the LUMO values of the copolymers (Figure 9). This model predicts that the asymmetric polymers (PCDTPP, PCDTPT, and PCDTPX) should be more efficient than the symmetric polymers (PCDTQx, PCDTBT, PCDTBX). Furthermore, based on this model, predicted device performances made from PCDTPP, PCDTBT, and PCDTBX should be similar. Finally, one can expect a power conversion efficiency near 10% for PCDTPX (Figure 9).

**2.4. Device Performances and Characterization. 2.4.1. Field-Effect Transistors.** As indicated above, transport properties are important parameters for efficient photovoltaic devices. The electron transport properties of pure PCBM have been already reported in details and are known to be sufficient for high photovoltaic performances ( $\sim 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ ).<sup>46,47</sup> In order to avoid important photocurrent loss by recombination, a hole mobility of  $\geq 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$  is required for the donor conjugated polymer.<sup>12</sup>

The hole mobilities of our pure copolymers or in blends with PCBM were studied using organic field-effect transistors (OFETs) as the testing vehicle. Top contact OFETs of these poly(2,7-carbazole) derivatives were fabricated on OTS-treated  $\text{SiO}_2/\text{Si}$  substrates as described in the Supporting Information. All these poly(2,7-carbazole) derivatives were found to exhibit typical *p*-type organic semiconductors characteristics. The hole mobilities calculated in the saturation regime<sup>82</sup> at  $V_{DS} = -100 \text{ V}$ , the on/off current ratios, and the threshold potentials of these polymers are summarized in Table 2.

Pure polymers spin-coated on OTS-treated substrates and heated at 50 °C for 10 min show hole mobilities between  $2 \times 10^{-5}$  and  $1 \times 10^{-3} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ . PCDTBT exhibits the highest

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**Figure 9.** Estimated power conversion efficiency for the six polycarbazole derivatives. (Adapted with permission from Wiley-VCH from the work of Scharber and collaborators.<sup>12</sup>)

**Table 2.** Open Circuit Potential ( $V_{oc}$ ), Short Circuit Current ( $I_{sc}$ ), Fill Factor (FF), Power Conversion Efficiency ( $\eta_e$ ), Hole Carrier Mobility ( $\mu$ ), On/Off Current Ratios ( $I_{on}/I_{off}$ ), and Threshold Voltage ( $V_T$ ) for Polycarbazole Derivatives

polymer	PCBM/polymer (4:1)			Pristine <sup>a</sup>				PCBM/polymer (4:1) <sup>a</sup>		
	$V_{oc}$ , V	$I_{sc}$ , mA·cm <sup>-2</sup>	FF	$\eta_e$ , %	$\mu$ , cm <sup>2</sup> ·V <sup>-1</sup> ·s <sup>-1</sup>	$I_{on}/I_{off}$	$V_T$ , (V)	$\mu$ , cm <sup>2</sup> ·V <sup>-1</sup> ·s <sup>-1</sup>	$I_{on}/I_{off}$	$V_T$ , (V)
PCDTQx	0.95	-3.0	0.56	1.8	$3 \times 10^{-4}$	$1 \times 10^4$	-21	$7 \times 10^{-6}$	30	-29
PCDTPP	0.90	-2.6	0.44	1.1	$2 \times 10^{-5}$	$1 \times 10^2$	-40	no FE <sup>b</sup>	-	-
PCDTBT	0.86	-6.8	0.56	3.6	$1 \times 10^{-3}$	$3 \times 10^4$	-16	$4 \times 10^{-4}$	$2 \times 10^2$	-1
PCDTPT	0.71	-2.9	0.32	0.7	$4 \times 10^{-5}$	$1 \times 10^2$	-48	$6 \times 10^{-5}$	$2 \times 10^2$	-32
PCDTBX	0.96	-3.7	0.60	2.4	$1 \times 10^{-4}$	$5 \times 10^3$	-21	c	c	c
PCDTPX	0.85	-1.4	0.60	0.8	$5 \times 10^{-4}$	$1 \times 10^3$	-46	$3 \times 10^{-4}$	$4 \times 10^2$	-9

<sup>a</sup> Polymers and polymer/PCBM blends were deposited from a chloroform solution on OTS-treated SiO<sub>2</sub>/Si substrates and heated at 55 °C before Au contact deposition. <sup>b</sup> No field effect (FE). <sup>c</sup> No thin films were obtained on OTS-treated SiO<sub>2</sub>/Si substrates.

hole mobility and on/off current ratio. As one can see in Table 2, the hole mobilities and on/off current ratios of symmetric polymers are higher (by more than 1 order of magnitude) than those of their asymmetric counterparts, except for PCDTBX and PCDTPX which exhibit similar performances. This difference between the symmetric and asymmetric polymers could be attributed to different solid-state packings and/or molecular weights. The structural organization present in both PCDTBX and PCDTPX, as observed in the X-ray diffraction pattern (Figure 5), may explain the similar mobilities observed for both polymers. Comparing PCDTQx and PCDTPP, which have similar molecular weights, one can suggest that the higher mobility of PCDTQx is due to its symmetric structure which could induce some structural ordering in the thin film, as revealed by polarized optical microscopy and X-ray measurements. First attempts for OFET optimization by film annealing at 150 °C for 20 min demonstrated interesting enhancement (about 3 times) in performances for PCDTPP and PCDTBT. For example, in the case of PCDTBT, a hole mobility and an on/off current ratio up to  $3 \times 10^{-3}$  cm<sup>2</sup>·V<sup>-1</sup>·s<sup>-1</sup> and  $1 \times 10^5$  were obtained, respectively (Figure 10).

All these polymers, except PCDTPP, when blended with PCBM in a 1:4 stoichiometry show hole mobility values between  $5 \times 10^{-6}$  and  $4 \times 10^{-4}$  cm<sup>2</sup>·V<sup>-1</sup>·s<sup>-1</sup> in OFETs (Table 2). The PCDTBT/PCBM blend exhibits the highest hole mobility. The higher structural organization present in PCDTBT, as observed in DSC, POM, and X-ray analyses, is consequent with such results. Despite the high ratio of PCBM in the blends

which should introduce more defects and consequently should reduce the hole mobility, we note that the hole mobilities of these polymers in the blends are very close to those obtained with the pure polymers, except for PCDTQx and PCDTPP. In fact, different research groups have found from studies on OFETs and diodes that the blends of different polymers give higher hole mobility values with increasing fractions of PCBM.<sup>83–86</sup>

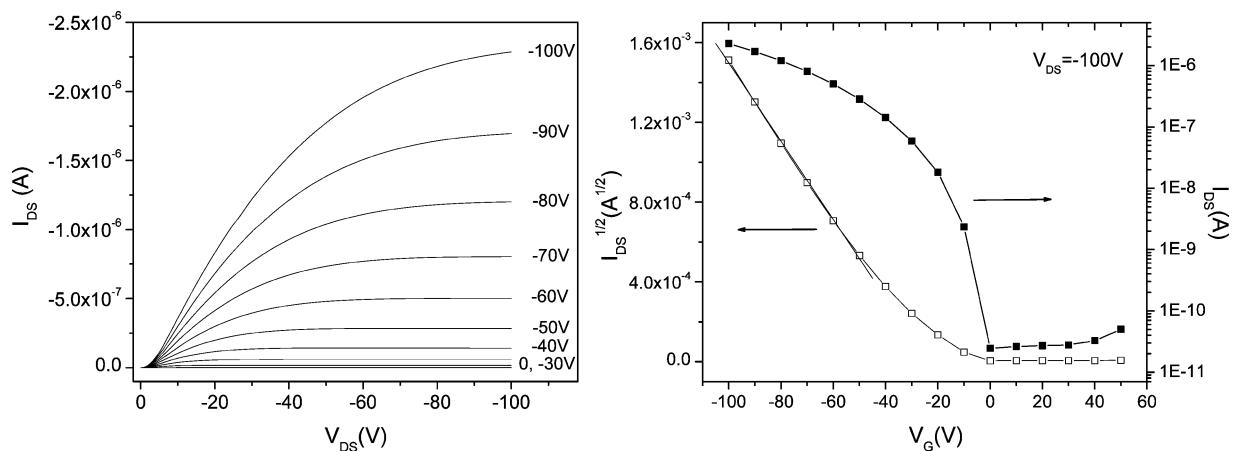
**2.4.2. Photovoltaic Solar Cells.** Devices using each of the polymers were then made according to procedures described in the Supporting Information. AFM images (see Supporting Information, Figure 9S) reveal no important variation in the morphology of PCBM/polymer (4:1) thin films. However, larger structures are observed for the PCBM/PCDTBX and PCBM/PCDTPP blends. We attribute those structures to polymer aggregates present in chloroform solution. Indeed, these two polymers have a lower solubility in chloroform compared to the other polymers. Photovoltaic results are summarized in Table 2 and Figure 11. At first glance, and contrary to what was proposed from the theoretical calculations, the most efficient polymers are those with a symmetric structure. One can conclude that the structural organization observed for the

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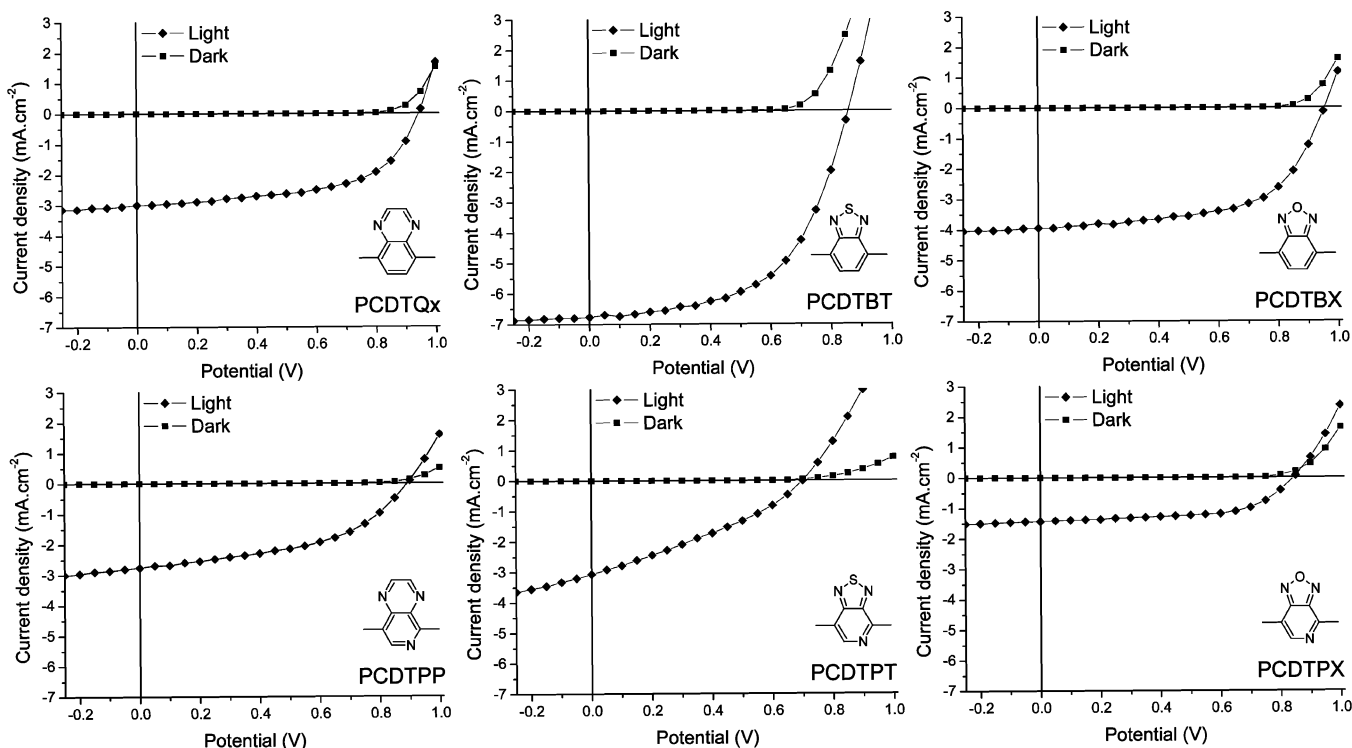
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**Figure 10.** Output at different gate voltages ( $V_G$ ) and transfer characteristics in the saturation regime at constant source–drain voltage ( $V_{DS} = -100$  V) for OFETs using spin-coated PCDTBT on OTS-treated  $\text{SiO}_2/\text{Si}$  substrates.



**Figure 11.** Current density–potential characteristics of a diode made of PCBM/Polymer (4:1) under illumination with AM1.5G solar simulated light (◆) and in the dark (■).

symmetric polymers has also a major impact on the device performances. Comparisons between PCDTTPP and PCDTQx, which have similar molecular weights, clearly illustrate this behavior. In BHJ solar cells, their PCE is respectively of 1.1% and 1.8%. These results are also in good agreement with the OFET measurements. The hole mobility in pure PCDTQx is about 1 order of magnitude higher than that obtained with PCDTTPP. Therefore, this higher hole mobility in PCDTQx, presumably related to a better organization, could explain the higher value of the short-circuit current ( $I_{sc}$ ) with PCDTQx, despite the lower band gap for PCDTTPP which is supposed to increase its  $I_{sc}$ .

According to the predicted performances, one can expect relatively high PCEs for PCDTPT and PCDTPX. In contrast, these polymers showed very low PCEs (under 1%). These results can be explained by different factors. First, the low molecular

weight polymers (ca. 4–5 KDa) generally exhibit low mobilities,<sup>72,73</sup> resulting in low  $I_{sc}$ . However, in the case of PCDTPX, the low  $I_{sc}$  could not be explained solely by a low mobility of the material as the hole mobility of PCDTPX (pure and in the blend with PCBM) is about  $4 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ . The cause for the low efficiencies for PCDTPX is poorly understood at this time, but it is likely to be related to geminate charge recombination at the interface due to stable charge-transfer states, which limits the photocurrent.<sup>87</sup> Moreover, low molecular weight also has an impact on the film mechanical properties, the interface resistance, and the nanoscale morphology, resulting in a low open-circuit potential ( $V_{oc}$ ) and a low fill factor (FF).

PCDTBT gave the best results with a PCE of 3.6%. We note here that this high efficiency is obtained due to the excellent  $I_{sc}$

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and FF values both attributed to the good hole mobility (see Table 2) resulting from the higher structural organization present in PCDTBT, as previously noted. However, one cannot exclude the possibility of better contact electrode interfaces, better charge transfers at the blend interface, or specific interactions induced by the benzothiadiazole unit, since other benzothiadiazole-based copolymers<sup>32–34,88–90</sup> also demonstrated high PCE values.

### 3. Conclusions

We have demonstrated a versatile synthetic strategy to obtain various low band gap polycarbazole derivatives via a Suzuki coupling reaction. DFT theoretical calculations performed on the repeat unit of the polymers provided good estimations of the trends to be observed for the HOMO, LUMO, and band gap energies of the corresponding polymers. Overall, the HOMO energy level seems to be fixed by the carbazole moiety, whereas the LUMO energy level seems to be directly related to the nature of the electron-withdrawing unit. From these data, one can expect to easily fine-tune the LUMO energy level for optimal solar cell performances while synthesizing air-stable polymers since the HOMO is more or less constant. The polymer organization is also influenced by the polymer backbone (benzene or pyridine core). As revealed by DSC, polarized optical microscopy, and X-ray diffraction measurements, the symmetric polymers show better structural organization than

the asymmetric polymers (except for PCDTPX). For all these reasons, the polymer backbone (pyridine or benzene core) has an important impact on the polymer hole mobility and power conversion efficiency.

Taking all these data into account, one can conclude that, up to now, PCDTBT has the best potential for photovoltaic devices. It is anticipated that this value could be improved through modifications in the device fabrication (film thickness, annealing, solvent, etc.). Optimization of the PCDTBX and PCDTPX polymerization reactions should also provide better materials with higher solubility and higher molecular weight and, hopefully, better performances in BHJ solar cell devices. Finally, symmetric and lower band gap polycarbazole derivatives with a LUMO energy level value similar to that of PCDTPX will certainly be good candidates for BHJ solar cells.

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**Supporting Information Available:** Details of syntheses, characterization, computation method, device fabrication and testing (pdf), and X-ray crystallographic information files of compounds **4** and **6** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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