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High Open-Circuit Voltage Solar Cells Based on New Thieno[3,4-*c*]pyrrole-4,6-dione and 2,7-Carbazole Copolymers

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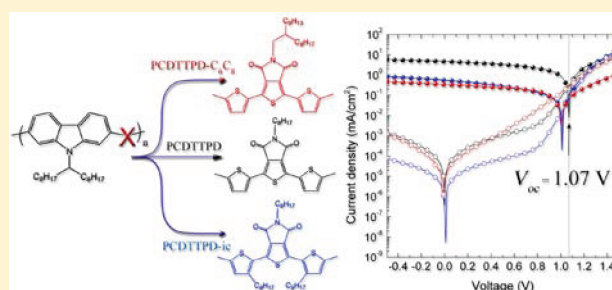
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S Supporting Information

ABSTRACT: New alternating copolymers derived from thieno[3,4-*c*]pyrrole-4,6-dione (TPD) and 2,7-carbazole moieties have been synthesized by Suzuki cross-coupling reaction and characterized. These polymers combine interesting properties such as good solubility and excellent thermal and air stability. The present studies indicate that the combination of TPD and 2,7-carbazole building blocks can be a very effective way to lower the HOMO energy level and ultimately to enhance the V_{oc} of polymer solar cells. The V_{oc} reported here (up to 1.07 V) is one of the highest observed for polymer:[60]PCBM bulk heterojunction devices, and preliminary results on the photovoltaic devices (power conversion efficiencies up to 1.8%) indicate that performance could probably be improved by increasing the molecular weights and by fine-tuning the electronic properties and the morphology.



INTRODUCTION

Polymer bulk heterojunction (BHJ) solar cells offer a compelling option for tomorrow's photovoltaics due to many interesting features such as low cost, light weight, and flexibility.^{1–3} BHJ solar cells based on the blends of regioregular poly(3-hexylthiophene)s (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester ([60]PCBM) have been investigated extensively in the past decade, and power conversion efficiencies (PCE)s as high as 4–5% have been reported.^{4–6} However, the PCE is critically limited by the relatively low open-circuit voltage ($V_{oc} \approx 0.5–0.6$ V). Usually, the V_{oc} originates from the energy difference between the highest occupied molecular orbital (HOMO) of the polymer and the lowest unoccupied molecular orbital (LUMO) of the fullerene derivative.⁷ Therefore, polymers with a deep HOMO level will potentially lead to an enhanced V_{oc} and a possibly higher PCE when blended with PCBM. Along these lines, some push–pull copolymers based on 2,7-carbazole derivatives have demonstrated promising potential as photovoltaic materials.^{8–11} Among them, poly(*N*-9'-heptadecan-2,7-carbazole-*alt*-5,5-(4',7'-dithienyl-2',1',3'-benzothiadiazole) (PCDTBT) has a low-lying HOMO energy level of -5.5 eV, showing a V_{oc} of 0.9 V when mixed with [70]PCBM. Tao et al. have achieved a PCE of 7.1% using PCDTBT:[70]PCBM on an area of 1.0 cm².¹² Also, Heeger et al. reported a PCE of 7.2% based on

PCDTBT and using [70]PCBM as electron acceptor, TiO_x as an optical spacer, and a structured antireflection coating.¹³

Because the HOMO level of alternating push–pull copolymers is mainly determined by the donor moiety, the relatively low-lying HOMO energy level of PCDTBT seems to be related to the presence of the weak electron-donating carbazole unit. Indeed, when this moiety is copolymerized with different electron-withdrawing units as benzothiadiazole BT,^{8,9,12,13} 1,4-diketopyrrolopyrrole (DPP),^{10,14} or pyridine derivatives,⁹ the HOMO energy levels of the resulting copolymers remain most of the time between -5.3 and -5.5 eV. For all these reasons, the 2,7-carbazole unit can be an excellent candidate to generate a high V_{oc} in bulk heterojunction polymer solar cells.

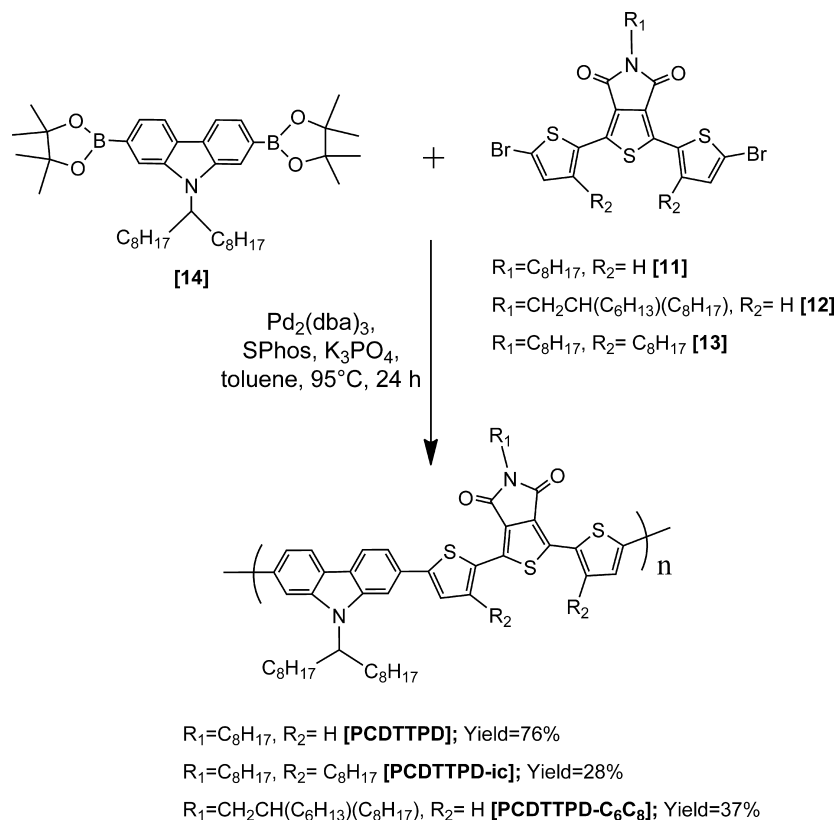
In parallel, thieno[3,4-*c*]pyrrole-4,6-dione (TPD)-based polymers were first introduced by Tour and Zhang,¹⁵ and recently, Leclerc et al. have reported for the first time the use of these copolymers in solar cells.¹⁶ For instance, the electron-withdrawing TPD moiety copolymerized with an electron-donating benzo[1,2-*b*:3,4-*b'*]dithiophene (BDT) unit presented a HOMO energy level (-5.56 eV) which led to a V_{oc} of 0.85 V

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Scheme 1. Synthesis of Polymers



in the resulting photovoltaic devices.¹⁷ By using the same polymer, Fréchet et al.¹⁸ reported a power conversion efficiency up to 6.8% with the addition of 1,8-diiodooctane (DIO) during the processing of the film. Tao et al.¹⁹ achieved a PCE of 7.3% (V_{oc} of 0.88 V) with a new copolymer made of dithienosilole and TPD units (PDTSTPD). By using a dithienogermole comonomer (DTG-TPD), Reynolds et al.²⁰ reported a comparable performance (PCE of 7.3% with a V_{oc} of 0.85 V). Finally, Wei et al.²¹ have fabricated a BHJ solar cell device incorporating a bithiophene comonomer (PBTTPD) which also exhibited a PCE of 7.3% (V_{oc} of 0.92 V). In short, most bulk heterojunction solar cells based on thieno[3,4-*c*]pyrrole-4,6-dione derivatives exhibit also relatively high open-circuit voltage.²² In other words, the electron-withdrawing TPD unit contributes to slightly decrease the HOMO energy level of the resulting push–pull copolymers while keeping the LUMO energy levels around -3.8 eV.

In this work, we therefore present new alternating copolymers based on thieno[3,4-*c*]pyrrole-4,6-dione (TPD) and 2,7-carbazole moieties, namely PCDTTPD, PCDTTPD-ic, and PCDTTPD-C₆C₈ (see Scheme 1). It is believed that by combining both comonomers promising conjugated copolymers for photovoltaic applications could emerge.

RESULTS AND DISCUSSION

First, a TPD unit (monomer 6, see Supporting Information) was directly copolymerized with a 2,7-carbazole unit (monomer 14, see Scheme 1) without any spacer (PCTPD, see Supporting Information), but a low number-average molecular weight, \bar{M}_n , of 3 kg/mol (polymerization degree (PD) ~ 5) was obtained with a polydispersity index (PDI) of 1.5. As previously observed, Suzuki coupling does not seem to be a useful tool

with TPD units.²³ However, TPD units are highly suitable moieties for direct arylation reactions,^{24,25} and the same polymer was then prepared by direct arylation polycondensation reaction (see Supporting Information). This reaction gave a PCTPD with a \bar{M}_n of 34 kg/mol and PDI of 1.3. The resulting copolymer has electrochemical (E_g^{el}) and optical (E_g^{opt}) bandgaps of 2.36 eV. The HOMO and LUMO energy levels are localized at -5.88 and -3.52 eV, respectively. However, this large band gap copolymer is clearly not promising for photovoltaic applications, and it was not further investigated in this study. In fact, the optimal band gap, considering the solar emission spectrum, should range between 1.3 and 1.9 eV.¹⁷

To decrease the band gap, unsubstituted and substituted thiophene spacers were added. As shown in Scheme 1, different comonomers were polymerized through Suzuki cross-coupling polymerization to afford PCDTTPD, PCDTTPD-ic, and PCDTTPD-C₆C₈. Further details about the synthesis of monomers ([1] to [13]) and related polymers are described in the Supporting Information. An end-capping reaction was performed by using bromobenzene and phenylboronic acid to increase the stability of the polymer.²⁶ PCDTTPD, PCDTTPD-ic, and PCDTTPD-C₆C₈ have a \bar{M}_n of 13, 18, and 6 kg/mol, respectively (see Table 1). Thermogravimetric

Table 1. Polymerization and Thermal Data of Polymers

polymers	\bar{M}_n (kg/mol)	\bar{M}_w (kg/mol)	PDI	T_g (°C)	T_d (°C)
PCDTTPD	13	24	1.8		450
PCDTTPD-ic	18	24	1.3	80	425
PCDTTPD-C ₆ C ₈	6	10	1.7		390

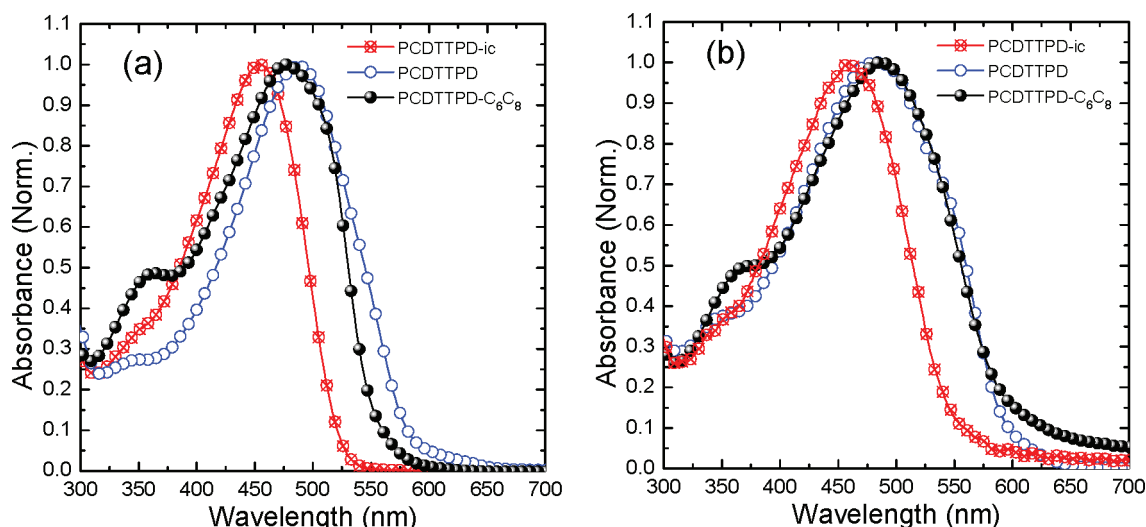


Figure 1. UV-vis absorption spectra of PCDTTPD, PCDTTPD-ic, and PCDTTPD-C₆C₈ in CHCl₃ solution (a) and in the solid state (b).

Table 2. Optical and Electrochemical Properties of the Polymers

polymers	UV-vis absorption spectra				cyclic voltammetry (vs Ag/Ag ⁺)				
	solution		film		p-doping ^a		n-doping ^a		E_g^{el} (eV)
	λ_{max} (nm)	λ_{onset} (nm)	λ_{max} (nm)	λ_{onset} (nm)	$E_{\text{on}}^{\text{ox}}$ (V)	HOMO ^b (eV)	$E_{\text{on}}^{\text{red}}$ (V)	LUMO ^b (eV)	
PCDTTPD	487	484	604	2.05	1.01	-5.71	-0.96	-3.74	1.97
PCDTTPD-ic	454	458	560	2.21	0.77	-5.47	-1.31	-3.39	2.02
PCDTTPD-C ₆ C ₈	480	487	602	2.06	0.80	-5.50	-1.20	-3.50	1.93

^ap-doping and n-doping represent the electrochemical oxidation and reduction, respectively. The term electrochemical p-doping and n-doping is generally understood as a process that involves both oxidation and reduction of the conducting polymer backbone and the concomitant changes in the electronic structure. ^bHOMO = $-e(E_{\text{on}}^{\text{ox}} + 4.7)$ (eV) and LUMO = $-e(E_{\text{on}}^{\text{red}} + 4.7)$ (eV).

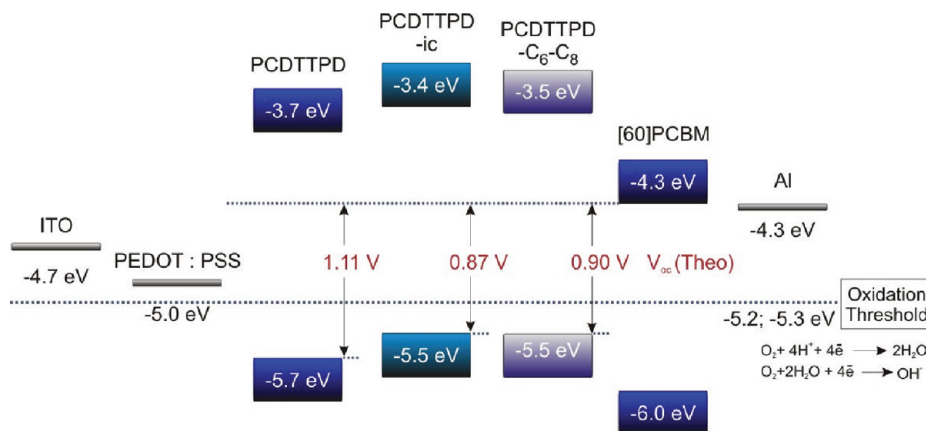


Figure 2. Energy levels diagram of the polymers and [60]PCBM.

analyses (TGA) (Figure 1S) show that these polymers possess a good stability up to 450 °C under nitrogen. DSC measurements did not indicate any glass transition temperature (T_g) for PCDTTPD and PCDTTPD-C₆C₈ but revealed a T_g around 80 °C for PCDTTPD-ic. All polymers are soluble in common solvents such as chloroform, THF, chlorobenzene (CB), 1,2-dichlorobenzene (ODCB), and 1,2,4-trichlorobenzene (TCB).

The optical properties were investigated by UV-vis-NIR absorption spectroscopy (see Figure 1 and Table 2). The UV-vis-NIR absorption spectra show broad absorption bands in solution and in the solid state around 480–487 nm for PCDTTPD and PCDTTPD-C₆C₈, while those of PCDTTPD-

ic are observed around 458 nm. These results seem to indicate that the substituted thiophene spacers seem to affect the optical properties of those copolymers. Indeed, this blue shift could be explained by a slightly twisted conformation due to the presence of alkyl chains.²⁷ The optical bandgap determined from the polymers film absorption onset are around 2.0 eV for the polymers having unsubstituted thiophene spacers and 2.2 eV for PCDTTPD-ic.

The HOMO and LUMO energy levels of polymers were determined by cyclic voltammetry (CV). These data are summarized in Figure 2 and Table 2. Based on the recorded oxidation potentials for PCDTTPD, PCDTTPD-ic, and PCDTTPD-C₆C₈ (HOMO energy levels at -5.71, -5.47,

Table 3. Photovoltaic Data for ITO/PEDOT:PSS/Polymer:[60]PCBM/Al Devices

polymers	thickness (nm)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	PCE (%)	J_0 (A/m ²)
PCDTTPD	53	-4.72	1.07	0.36	1.82	3.5×10^{-17}
PCDTTPD-ic	82	-0.56	1.01	0.25	0.14	4.8×10^{-17}
PCDTTPD-C ₆ C ₈	91	-0.35	1.00	0.39	0.13	4.4×10^{-17}

and -5.50 eV, respectively), the polymers should be stable in ambient air conditions.²⁸ The HOMO and LUMO energy levels of the polymers were estimated from the onset oxidation and reduction potentials, assuming a SCE level to be at -4.7 eV below the vacuum level.²⁹ It should be noted that the structural difference between the PCDTTPD and PCDTTPD-C₆C₈ is almost negligible, but a HOMO energy level difference of 0.2 eV is observed between both polymers. This observation could be explained by the presence of the chain in the TPD unit. Indeed, compared to a linear chain, a branched side chain increases the electron density in the polymer, so in this case the oxidation may be easier. However, it is important also to mention that the electrochemistry is a dynamic method and different parameters need to be taking into account as the thickness of the film, the porosity of the polymer, etc.

On the basis of these electrochemical data and taking into account a LUMO energy level at -4.3 eV for [60]PCBM and using the semiempirical estimation of the eq 1,⁷ the theoretical open-circuit voltages (V_{oc}) calculated for PCDTTPD, PCDTTPD-ic, and PCDTTPD-C₆C₈ should be around 1.10, 0.87, and 0.90 V, respectively (Figure 2)

$$V_{oc} = \frac{1}{e} [|E_{HOMO}^{donor}| - |E_{LUMO}^{PCBM}|] - 0.3 \quad (1)$$

where e is the elementary charge and the value of 0.3 V is an empirical factor.³⁰ Indeed, Vanderwal et al. have observed that there is a correlation between the V_{oc} and the energetic difference between the HOMO of the donor (polymer) and the LUMO of the acceptor (PCBM).³¹ As the authors highlighted, an increase of the LUMO level of the fullerene or the utilization of donor polymers with optimized energetic levels represent the most efficient pathways for increasing the V_{oc} of a polymer-PCBM solar cells. Also, the reduction of nonradiative pathways and the increase of the carrier lifetime should result to a decrease of the dark saturation current (J_0) and, therefore, to an increase of the V_{oc} value. By using the eq 2,³¹ J_0 was estimated around to $(3.0\text{--}4.0) \times 10^{-17}$ A/m² for all polymers (see Table 3)

$$V_{oc} = \frac{k_B T}{e} \ln \left(\frac{J_{sc}}{J_0} + 1 \right) \quad (2)$$

where k_B is the Boltzmann constant and T is the temperature.

Because of the interesting electronic and optical of the copolymers (preferred energy levels and proper absorption spectra), BHJ solar cells were fabricated with a configuration of glass/ITO/PEDOT:PSS/polymer:[60]PCBM/Al. After spin-coating a layer of 50 nm of poly(3,4-ethylene dioxothiophene):poly(styrenesulfonate) (PEDOT:PSS) onto a precleaned indium-tin oxide (ITO)-coated glass substrate, polymer/[60]PCBM blends (1:1 (PCDTTPD) or 1:2 (PCDTTPD-ic and PCDTTPD-C₆C₈), w/w) solution in ODCB were deposited by spin-coating and dried under vacuum at room temperature for 15 h. The devices were completed by evaporating Al metal as the electrode. The solar cells active area is 25 mm². The detailed conditions of the device fabrication

and characterization are fully described in the Supporting Information. The photovoltaic performance presented in Figure 3 was realized under AM 1.5G illumination of 100 mW cm⁻².

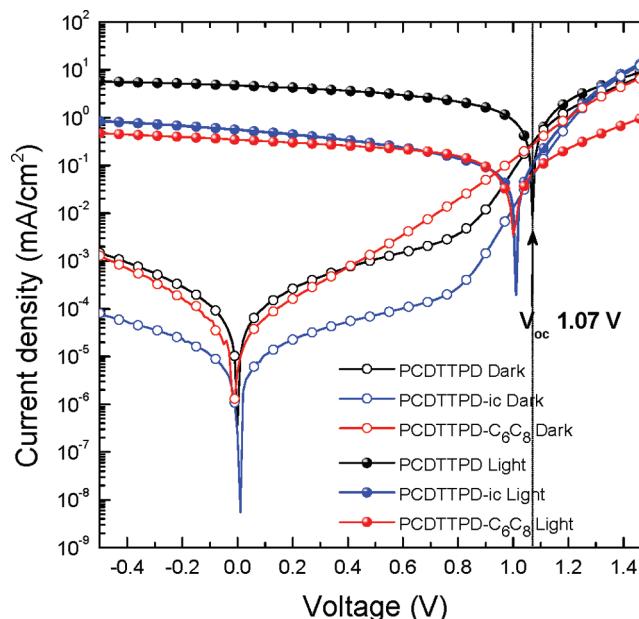


Figure 3. J - V curves of the polymer solar cells based on PCDTTPD in the dark and under the illumination of AM 1.5 G, 100 mW cm⁻².

The polymer PCDTTPD was able to reach a current density of 4.72 mA cm⁻², a moderate fill factor of 0.36, and a very high open-circuit voltage (V_{oc}) of 1.07 V. It is worth noting that this open-circuit voltage agrees with its anticipated value. As a result, a power conversion efficiency (PCE) of 1.82% has been achieved in these first measurements. In the case of PCDTTPD-ic and PCDTTPD-C₆C₈, very low PCEs were achieved. However, for fair comparisons, it could be important to vary the device configurations (such as annealing, solvents, additives, electrodes, acceptors, etc.) for each polymer. Such optimizations should be carried out in the near future.

Photovoltaic properties such as PCE, open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and the dark saturation current (J_0) are listed in Table 3. These performances can be partially explained by the morphology observed using atomic force microscopy (AFM) (see Figure 4). In fact, AFM images of PCDTTPD:[60]PCBM show some percolation pathways compared to those obtained with PCDTTPD-ic:[60]PCBM and PCDTTPD-C₆C₈:[60]PCBM blends, where the presence of holes (more or less wide and deep, see Figure 3S) into the bulk heterojunction could easily disturb or limit the transport of the charges to the electrodes. The presence of different chains on the polymers probably implies a steric hindrance in solid state in the case of PCDTTPD-ic and PCDTTPD-C₆C₈ which involve a change of the conformation and the morphology. In this regard, the

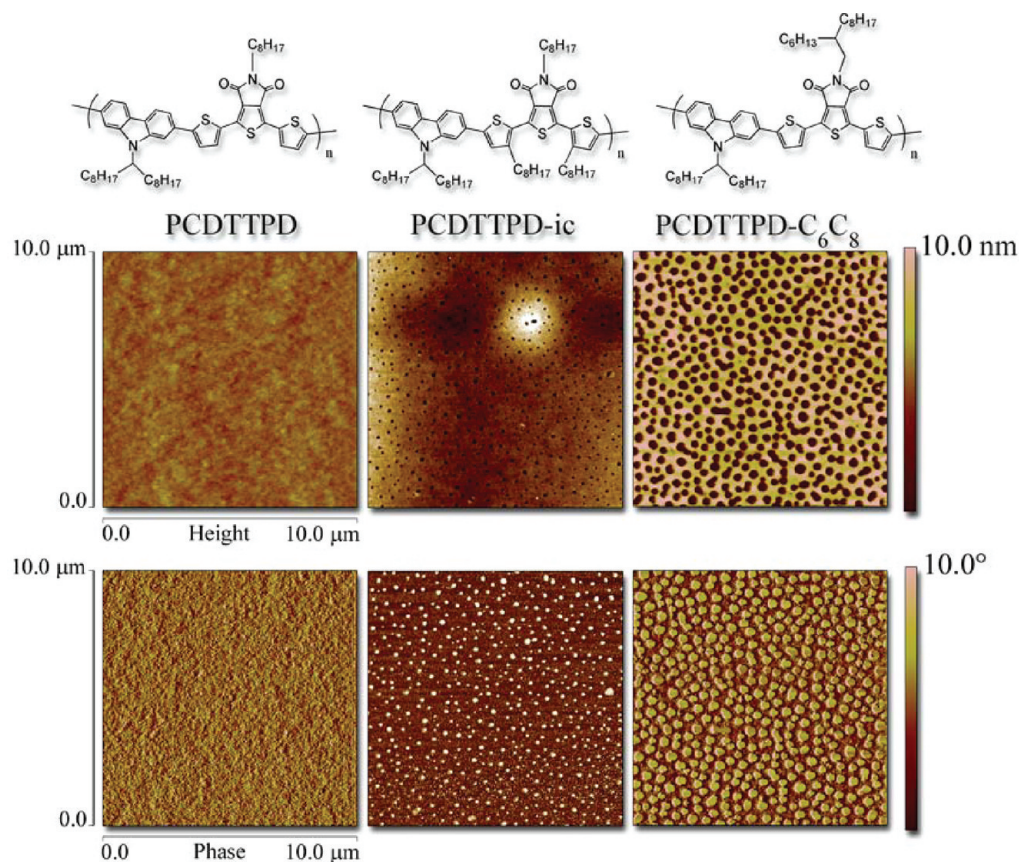


Figure 4. AFM images acquired by tapping mode (height and phase images are shown for polymers/[60]PCBM blends).

interaction with [60]PCBM is completely different for these polymers compared to PCDTTPD.

CONCLUSION

New poly(2,7-carbazole-*alt*-TPD) derivatives (PCDTTPD, PCDTTPD-ic, and PCDTTPD-C₆C₈) were designed and synthesized. These polymers combine interesting properties such as good solubility and excellent thermal and air stability. Preliminary results with photovoltaic devices based on PCDTTPD:[60]PCBM show a power conversion efficiency close to 2.0% with a high V_{oc} of 1.07 V. The present studies indicate that the combination of TPD and 2,7-carbazole building blocks can be a very effective way to lower the HOMO energy level and ultimately to enhance the V_{oc} of polymer solar cells. The V_{oc} reported here is one of the highest observed for a polymer:[60]PCBM bulk heterojunction devices.^{32–36} We also firmly believe that by optimizing nanoscale morphology of these PCDTTPD-based devices through different polymer/[60 or 70]PCBM ratios, processing additives, or annealing, higher PCE values should be obtained. Higher molecular weights through direct arylation polycondensation reactions could also be an asset.

ASSOCIATED CONTENT

Supporting Information

Experimental details, synthesis of the monomers and polymers, instrumentation, fabrication details, and characterization procedures of the organic photovoltaic devices. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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