Synthesis and Photovoltaic Characteristics of Novel Copolymers Containing Poly(phenylenevinylene) and Triphenylamine Moieties Connected at 1,7 Bay Positions of Perylene Bisimide

Yang Liu,[†,‡] Chunhe Yang,[†] Yongjun Li,[†,‡] Yuliang Li,*[,†] Shu Wang,[†] Junpeng Zhuang,[†] Huibiao Liu,[†] Ning Wang,[†,‡] Xiaorong He,[†,‡] Yongfang Li,[†] and Daoben Zhu*[,†]

CAS Key Laboratory of Organic Solids, Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P.R. China, and Graduate School of Chinese Academy of Sciences

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ABSTRACT: Two novel copolymers containing PPV and triphenylamine moieties connected at 1,7 bay positions of perylene bisimide were successfully synthesized by means of the Wittig reaction. Both of them were characterized by FT-IR, ^{1}H NMR, UV−vis, and FL spectra as well as GPC, TGA, and DSC measurements. The introduction of PPV and TPA moieties into the bay positions of perylene bisimide enhanced the solubility of polymers and quenched the fluorescence of perylene bisimide obviously. The photovoltaic devices ITO/PEDOT:PSS/copolymers/Ca/Al were fabricated, and their $I-V$ characteristics indicated that the copolymerization in PERY−PPV and PERY−PPV−TPA improved the device performance for some extent.

Introduction

In recent years, conjugated polymers and organic materials have attracted much attention for their applications in light-emitting diodes (LEDs) and plastic solar cells.[1−3] Poly(phenylenevinylene) (PPV) and its derivatives are one of the most promising classes of conjugated polymers for LEDs due to their high luminescence and easy modification of the chemical structure.[4−8] Triphenylamine (TPA) and its derivatives, with excellent solubility, good stability, and high PL efficiency, have been extensively used as hole-transporting species in photoelectronic devices.[9] Perylene bisimides represent a class of organic semiconductors with a variety of different structures,[10−13] with possible applications such as optical switching,[14] photovoltaic devices,[15] and dye lasers.[16] They have excellent chemical, thermal, and photochemical stability. Perylene bisimides are potential candidates as electron-accepting materials in organic photovoltaic solar cells.[17] Both PPV and perylene bisimide chromophores have been applied in bulk-heterojunction-like solar cell configurations as donor and as acceptor materials, respectively.[18,19] Recently, Janssen's group reported a new class of donor−acceptor polymers consisting of alternating oligo(*p*-phenylenevinylene) (OPV) and perylene bisimide connected via saturated spacers.[20] However, little attention was paid to the synthesis of copolymers containing PPV and TPA moieties covalently introduced into bay positions of perylene bisimide.[13] In this paper, we present the synthesis and characterization of two copolymers containing perylene bisimide and PPV and TPA moieties. The PPV and TPA groups were connected through ether linkages at 1,7 bay positions of perylene bisimide, and the photovoltaic characteristics of two copolymers were measured. In our case, introducing moieties with different properties into the bay positions of perylene bisimide led to polymers with good solubility compared with that of perylene bisimide, which may be a useful strategy for the synthesis of other functional polymers. These polymer donor−acceptor molecular systems have shown that the charge transfer from the excited state occurs. These data imply fabricating improved polymer photovoltaic cells with higher efficiency. We hope that these new designed donor−acceptor copolymers could be of importance for future studies on polymer materials applied in the field of photoelectric devices.

Experimental Section

Materials. Most of chemical reagents were purchased from Acros or Aldrich Corp. and were utilized as received unless indicated otherwise. *N,N′*-Dioctyl-1,7-dibromoperylene-3,4,9,-10-tetracarboxylic acid bisimide **(1)**, 1,4-bis(triphenylphosphonionmethyl)-2,5-bis(octyloxy)benzene dibromide (**3**), and triphenylamine diandehyde (**4**) were prepared according to literature procedures.[21−23] All solvents were purified using standard procedures.

***N,N′*-Dioctyl-1,7-bis(4-formalphenoxy)perylene-3,4,9,-10-tetracarboxylic Acid Bisimide (PERY) (2).** A mixture of *p*-hydroxybenzaldehyde (97.6 mg, 0.8 mmol), K_2CO_3 (442 mg, 3.2 mmol), and 18-crown-6 (1.69 g, 6.4 mmol) was stirred under nitrogen in toluene (50 mL) at room temperature. Then *N,N′*-dioctyl-1,7-dibromoperylene-3,4,9,10-tetracarboxylic acid bisimide **(1)** (154 mg, 0.2 mmol) was added. The reaction mixture was refluxed with stirring for 5 h. After cooling to room temperature, the reaction mixture was filtered and filtrate was collected. The crude product was obtained by drying solvent and purified by column chromatography on silica with CH_2Cl_2 to give **2** (98.3 mg, 58%): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 10.00 (s, 2H), 9.44 (d, 2H, J = 9.5 Hz), 8.64 (d, 2H, J = 9.5 Hz), 8.36 (s, 2H), 7.96 (d, 4H, J = 9.5 Hz), 7.24 (d, 4H, J = 9.5 Hz), 4.15 (t, 4H, J = 7.7 Hz), 1.71 (m, 4H), 1.40−1.26 (m, 20H), 0.86 (m, 6H). UV/vis ($CHCl_3$) λ_{max}: 526, 492, 392 nm. Fluorescence ($CHCl_3$) λ_{max}: 562 nm. FT-IR (KBr), ν [cm^{-1}]: 2733, 1700, 1659, 853. MS (MALDI−TOF): 854.9 (M^-). Elemental analysis calcd (%) for $C_{54}H_{50}N_2O_8$ (854.4): C, 75.86; H, 5.89; N, 3.28. Found: C, 75.61; H, 6.02; N, 3.36.

Synthesis of Copolymer PERY−PPV (5). To a solution of 17.1 mg (0.02 mmol) of compound **2** and 20.8 mg (0.02 mmol)

† Chinese Academy of Sciences.
‡ Graduate School of Chinese Academy of Science.
* Corresponding author. E-mail: ylli@iccas.ac.cn.

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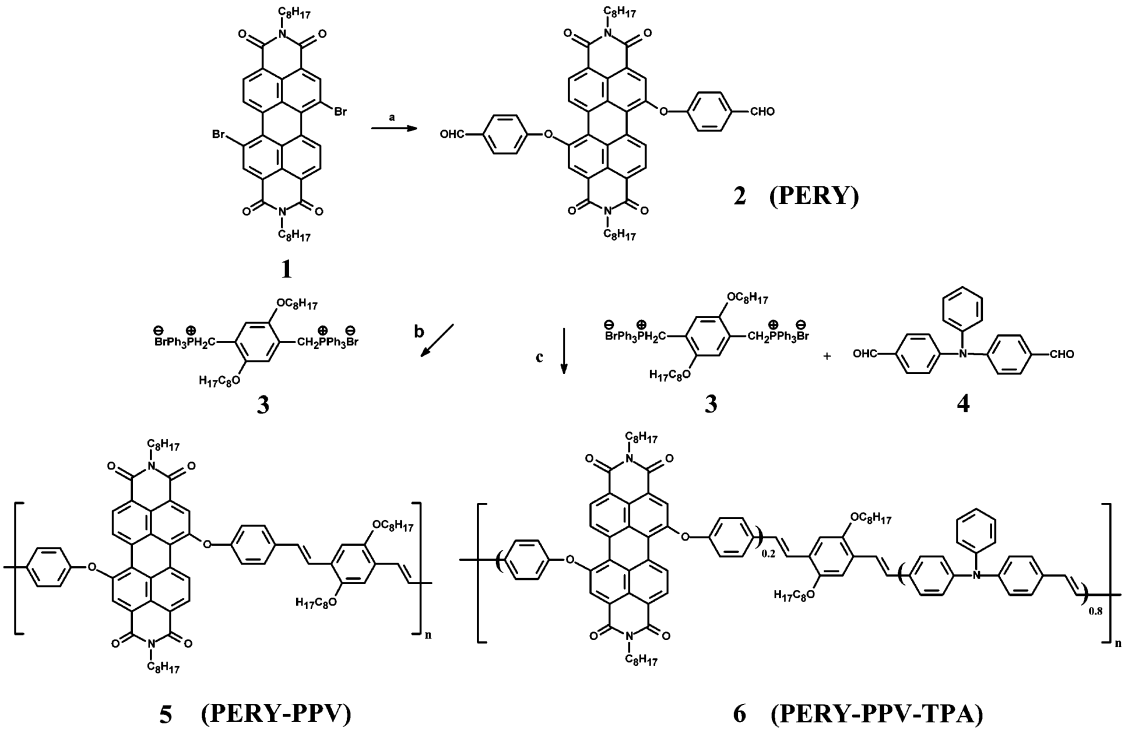
Scheme 1. Synthesis of Monomer and Copolymers[a]



[a] Reaction conditions: (a) *p*-hydroxybenzaldehyde, K_2CO_3, 18-crown-6, toluene, nitrogen, reflux, 5 h, 58%; (b) compound **3**, $CHCl_3$, EtOH, EtONa/EtOH, at room temperature, 48 h, 45%; (c) compounds **3** and **4**, $CHCl_3$, EtOH, EtONa/EtOH, at room temperature, 24 h, 12%.

of compound **3** in 40 mL of dry $CHCl_3$ and 10 mL of anhydrous EtOH, 10 mL of fresh EtONa/EtOH (10 mL of EtOH + 115 mg of Na) was added. The reaction mixture was stirred at room temperature for 48 h. Then the resulting solution was poured into 50 mL of 2 N hydrochloric acid. The organic phase was collected and washed with ethanol/water (3/1) to remove the byproducts triphenylphosphine oxide and NaBr. The product was extracted by dichloromethane and dried by anhydrous sodium sulfate. The solvent was removed, and the residue was redissolved in CH_2Cl_2 and precipitated in methanol and dried in a vacuum to give 17.2 mg of dark solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ: 9.44 (br, 2H), 8.63 (br, 2H), 8.39 (s, 2H), 7.95 (d, 4H), 7.65−7.46 (br, 2H), 7.23−7.17 (br, 4H), 7.05−6.72 (br, 4H), 4.14 (br, 4H), 4.04−3.85 (br, 4H), 1.71 (m, 8H), 1.55−1.24 (m, 40H), 0.86 (m, 12H). UV/vis ($CHCl_3$) λ_{max}: 536, 502, 394 nm. Fluorescence ($CHCl_3$) λ_{max}: 565 nm. FT-IR (KBr), ν [cm^{-1}]: 1700, 1659, 984. GPC (THF, g/mol): M_n, 6801; M_w, 15 419; M_z = 35 380; PDI: 2.27.

Synthesis of Copolymer PERY−PPV−TPA (6). A mixture of compound **2** (17.2 mg, 0.02 mmol), compound **3** (104.2 mg, 0.1 mmol), and compound **4** (24 mg, 0.08 mmol) was dissolved in 50 mL of dry chloroform and 10 mL of anhydrous EtOH. Then 10 mL of fresh EtONa/EtOH (10 mL of EtOH + 115 mg of Na) was added. The reaction mixture was stirred at room temperature for 24 h. Then the resulting solution was poured into 50 mL of 2 N hydrochloric acid. The organic phase was collected and washed with water. The product was extracted by chloroform and dried by anhydrous sodium sulfate. The solvent was removed by reduced pressure. The residue was redissolved in $CHCl_3$ and precipitated in methanol to purification. The product was dried in a vacuum to give 17.3 mg of dark solid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ: 9.60 (br, 2H), 8.66 (br, 2H), 8.39 (s, 2H), 7.98 (d, 4H), 7.68−7.42 (br, 2H), 7.23−7.17 (br, 12H), 7.05−6.72 (br, 6H), 4.15 (br, 4H), 4.01−3.75 (br, 4H), 1.72 (m, 8H), 1.43−1.20 (m, 40H), 0.86 (m, 12H). UV/vis ($CHCl_3$) λ_{max}: 539, 518, 509, 389 nm. Fluorescence ($CHCl_3$) λ_{max}: 568, 530 nm. FT-IR (KBr), ν [cm^{-1}]: 1700, 1659, 968. GPC (THF, g/mol): M_n, 6849; M_w, 16 769; M_z = 35 203; PDI: 2.45.

Characterization. UV/vis spectra were taken on a Hitachi U-3010 spectrometer, and fluorescence spectra were measured on a Hitachi F-4500 spectrofluorometer. ^{1}H NMR spectra were obtained on a Bruker Avance DPS-400(400 MHz) spectrometer. FT-IR spectra were measured on a Bruker EQUINOX55 spectrometer. MALDI−TOF mass spectrometric measurements were performed on Bruker Biflex MALDI−TOF. Elemental analyses were carried out on the Carlo-Erba 1160 elemental analyzer. Gel permeation chromatography (GPC) analysis was performed on a Waters 2410 GPC instrument, using THF as eluant and polystyrene standards for calibration. Thermal gravimetric analysis (TGA) was carried out using Perkin-Elmer 7 series thermal analysis system. Differential scanning calorimetry (DSC) was run on a DSC822e at a heating rate of 10 °C/min in nitrogen. The current−voltage (I−V) measurements of photovoltaic devices were conducted on a computer-controlled Keithley 236 source measure unit. A xenon lamp simulated a white-light source; the optical power at the sample was 75 mW/cm^2.

Results and Discussion

Scheme 1 outlines the synthetic routes of monomer **2** and two copolymers **5** and **6**. The monomer **2** was prepared by the nucleophilic substitution of the two bromine atoms of compound **1** using *p*-hydroxybenzaldehyde. Two copolymers **5** and **6** can be obtained by Wittig polycondensation reaction.[24]

Figure 1 showed the FT-IR spectra of the dialdehyde monomer PERY and the two copolymers PERY−PPV and PERY−PPV−TPA. In Figure 1a, the dialdehyde monomer PERY showed the characteristic absorption peak of aldehyde group at 2733 cm^{-1}. But in Figure 1b, the absorption peak at 2733 cm^{-1} disappeared after polymerization. At the same time, a weak absorption peak at 984 cm^{-1} corresponding to the out-of-plane bending mode of the trans-vinylene groups appeared, suggesting that the generated double bonds are mainly

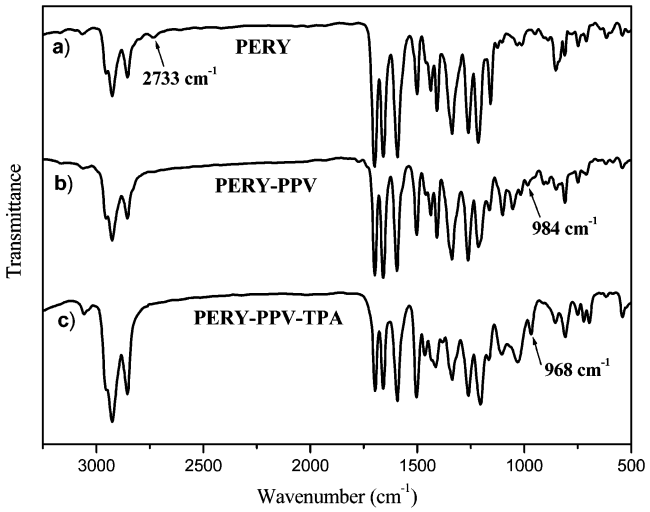


Figure 1. FT-IR spectra of PERY (a), PERY−PPV (b), and PERY−PPV−TPA (c).

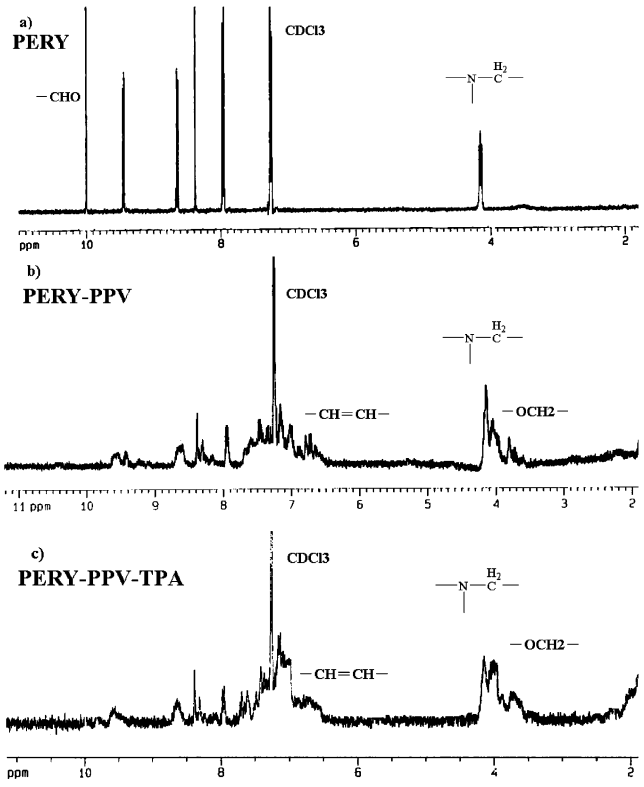


Figure 2. Partial ^{1}H NMR spectra of PERY, PERY−PPV, and PERY−PPV−TPA in $CDCl_3$ at room temperature.

the trans configuration. Figure 1c also showed a weak absorption peak at 968 cm^{-1}, corresponding to the out-of-plane bending mode of the trans-vinylene groups.

Figure 2 shows the partial ^{1}H NMR spectra of PERY, PERY−PPV, and PERY−PPV−TPA. Figure 2a represents the spectrum of monomer PERY. The characteristic peaks at δ 10.00, 9.44−8.36, and 7.96−7.17 ppm are due to the resonance of protons on formyl group, perylene ring, and aromatic rings, respectively. And the triplets of $-CH_2-$ linked to the imide group are at 4.15 ppm. In Figure 2b,c, we can see that the peaks of copolymers are broader than those of monomer. It can be found that the characteristic peak for the formyl proton of monomer PERY disappeared completely, while a new peak at about 6.8 ppm appeared, which is the

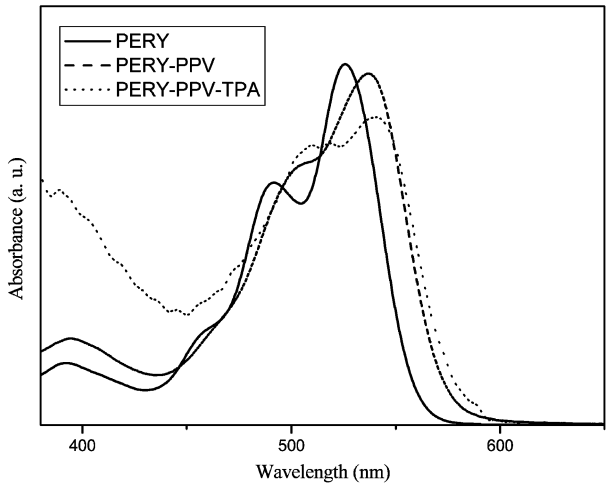


Figure 3. UV−vis absorbance spectra of PERY, PERY−PPV, and PERY−PPV−TPA in $CHCl_3$.

resonance of protons on the newly formed vinylene group, and broad peaks at about 4.04−3.75 ppm appeared due to the resonance of protons on $-OCH_2-$ linked to aromatic ring. These results indicate that the Wittig reaction is successful and complete.

The UV−vis absorption spectra of monomer PERY and two copolymers in $CHCl_3$ are shown in Figure 3. The main absorption band of pure PERY showed a peak at 526 nm. The absorption maximum of PERY−PPV and PERY−PPV−TPA were red-shifted by 10 and 13 nm compared with that of pure PERY, respectively. This is similar to the phenomenon that perylene bisimides exhibit a red shift upon aggregation.[25] It was found that UV−vis spectra of both copolymers were broader at around 400 nm due to the $\pi-\pi^*$ transition of the PPV conjugated backbone.[26]

Figure 4 showed the fluorescence spectra of pure PERY and two copolymers in chloroform at excitation wavelength 402 nm. Pure monomer PERY showed intense fluorescence, and the fluorescence of PERY−PPV and PERY−PPV−TPA showed significant quenching compared with that of pure PERY (Figure 4a). This is due to electron transfer from the PPV moiety to the perylene unit leading to strong fluorescent quenching.[20] As shown in Figure 4b, PERY−PPV−TPA also showed obvious quenching compared with that of PERY−PPV. Significant quenching of the emission in the triad of copolymer indicates interaction and electron transfer from the PPV and TPA moieties to the perylene unit. In $CHCl_3$ solution, PERY−PPV and PERY−PPV−TPA displayed poor fluorescence with maximum at 565 and 568 nm, which were slightly but distinctly red-shifted by 3 and 6 nm compared to that of pure PERY, respectively. As can be seen in Figure 4a, the shoulder peak of the fluorescence spectrum of pure PERY was at 598 nm, which almost disappeared in the fluorescence spectra of PERY−PPV and PERY−PPV−TPA. And a new shoulder peak of the fluorescence spectrum of PERY−PPV−TPA at 530 nm was observed (Figure 4b), which may be caused by the conjugated structure of PPV backbone and TPA moiety.[27]

GPC analysis was performed on a Waters 2410 GPC instrument, using THF as eluant and polystyrene standards for calibration. Table 1 displayed polymerization results and molecular weights of PERY−PPV and PERY−PPV−TPA. The number-average and weight-average molecular weights for PERY−PPV were 6801

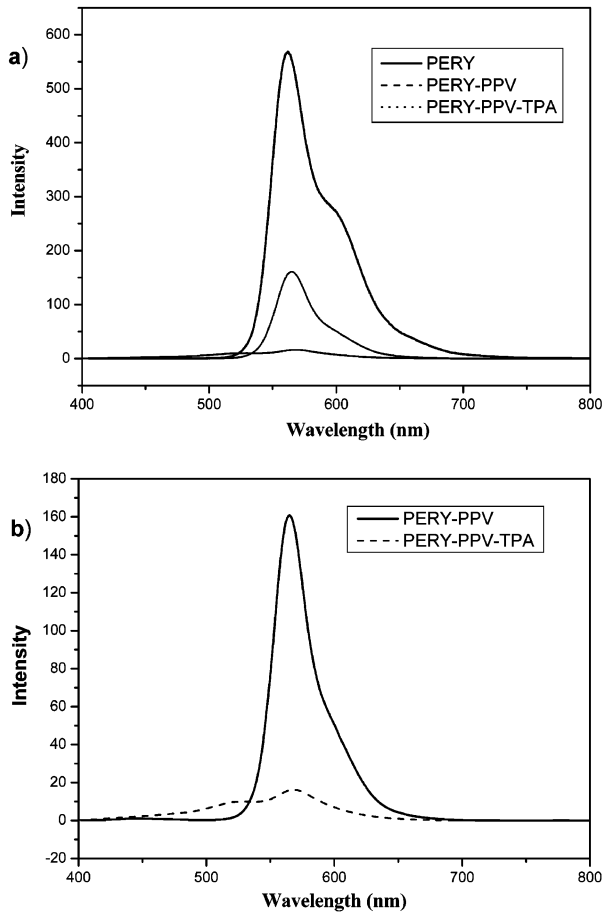


Figure 4. Fluorescence spectra of PERY, PERY−PPV, and PERY−PPV−TPA in $CHCl_3$ (λ_{ex} = 402 nm).

Table 1. Polymerization Results and Molecular Weights of Copolymers PERY−PPV and PERY−PPV−TPA[a]

copolymers	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI	yield (%)
PERY−PPV	6801	15 419	35 380	2.27	45
PERY−PPV−TPA	6849	16 769	35 203	2.45	12

[a] GPC in THF using polystyrene standards.

and 15 419, respectively, whereas those for PERY−PPV−TPA were 6849 and 16 769, respectively. In fact, two copolymers were partially soluble in THF; their actual molecular weights should be higher than the measured values because the insoluble parts possessed higher molecular weights. The thermal property of PERY−PPV was measured by TGA measurement (Figure 5), which showed thermal stability up to 370 °C. Figure 6 showed the DSC curves of two copolymers at a heating rate of 10 °C/min under flowing nitrogen. PERY−PPV−TPA showed a higher glass transition temperature (T_g) of 146 °C than PERY−PPV (103 °C), owing to the attachment of the triphenylamine unit that can efficiently enhance the T_g of the polymers.[9c] These values of T_g were comparable with those of PPV derivatives with bulky pendants (140 °C,[27] 106 and 122 °C[28]) but lower than those of PPV derivatives with cyanophenyl pendant (180 and 192 °C).[29] The T_g values of the present copolymers were around 40−80 °C higher than that of MEH−PPV (∼65 °C)[30] but lower than those of some main chain copolyimides containing perylene units (170−210,[31a] 340−360,[31b] and 374 °C[31c]).

The ITO/PEDOT:PSS (50 nm)/copolymers/Ca (5 nm)/Al (88 nm) devices were fabricated by sequential spin-coating of the polymer layer onto an ITO-coated glass substrate. Each of the copolymers was sandwiched between PEDOT:PSS-covered indium tin oxide (ITO) and calcium and aluminum electrodes. The organic active layers were prepared by spin-coating from toluene solutions. In Figure 6 the current−voltage ($I-V$) characteristics of the photovoltaic devices were plotted in a logarithmic and linear scale. Figure 7A showed that the characteristic data of the ITO/PEDOT:PSS/PERY−PPV/Ca/Al device were a short-circuit current (I_{SC}) of 0.45 mA/cm^2, an open-circuit voltage (V_{OC}) of 0.3 V, the fill factor (FF, defined as $(IV)_{max}/(I_{SC}V_{OC})$ where $(IV)_{max}$ is the maximum power rectangle[32]) of 36%, and the power conversion efficiency (η_e) of 0.07% under illumination at an intensity of 75 mW/cm^2. However, reported polymers[20] introducing OPV moieties into the imide of perylene bisimides had I_{SC} of 0.008−0.012 mA/cm^2, V_{OC} of 0.97−1.20 V, and the fill factors of 25−26%. Figure 7B displayed that the characteristic data of the ITO/PEDOT:PSS/PERY−PPV−TPA/Ca/Al device were a short-circuit current (I_{SC}) of 0.0167 mA/cm^2, an open-circuit voltage (V_{OC}) of 0.42 V, and a fill factor of 28%. The relevant data of the $I-V$ characteristics of photovoltaic devices are shown in Table 2. The I_{SC} of the PERY−PPV photocell was almost 30 times higher than that of the PERY−PPV−TPA photocell, probably because of the much higher content of perylene in PERY−PPV than that in PERY−PPV−TPA. The absorber in

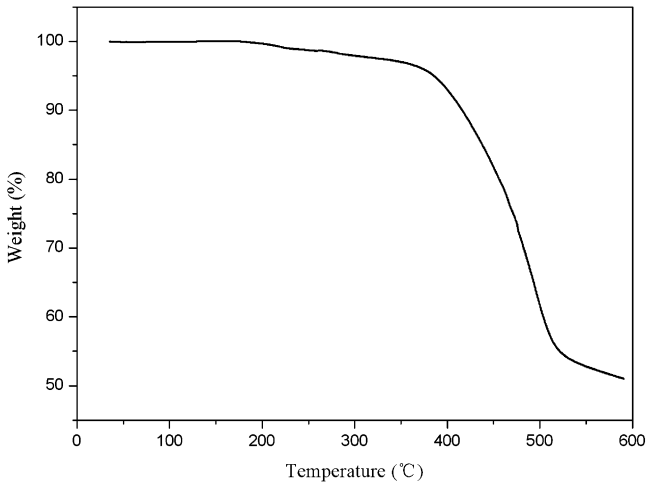


Figure 5. TGA spectrum of copolymer PERY−PPV.

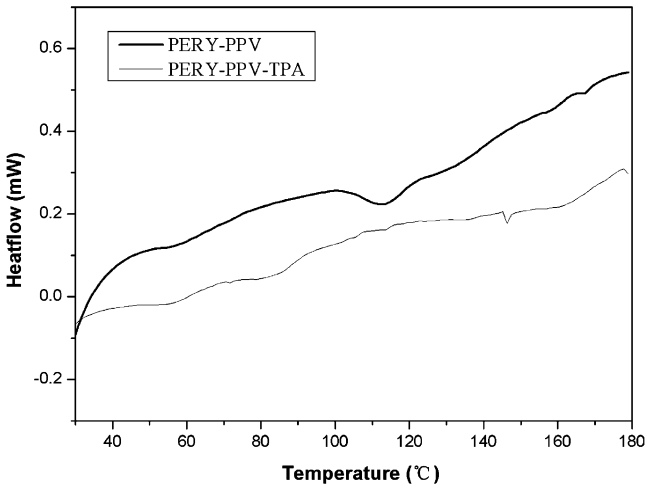


Figure 6. DSC scan for copolymers PERY−PPV and PERY−PPV−TPA in flowing nitrogen at a heating rate of 10 °C/min.

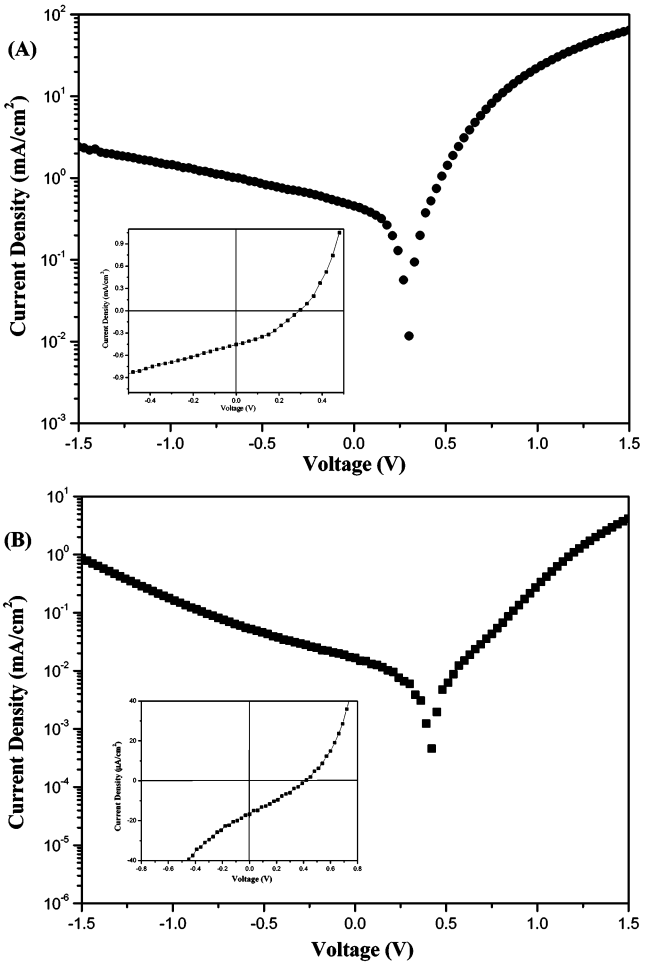


Figure 7. $I-V$ characteristics under illumination at an intensity of 75 mW/cm^2 for (A) an ITO/PEDOT:PSS/PERY−PPV/Ca/Al device and (B) an ITO/PEDOT:PSS/PERY−PPV−TPA/Ca/Al device in a logarithmic scale. The insets are linear plots of the same $I-V$ data.

Table 2. Performance of ITO/PEDOT:PSS/Copolymers/Ca/Al Devices

copolymers	I_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)
PERY−PPV	0.45	0.3	36
PERY−PPV−TPA	0.0167	0.42	28

these two coplymers should be mainly perylene unit, since the stilbene or triphenylamine was almost transparent in the visible region. Therefore, the content of perylene units in the copolymers played an important role for the performance of the photocells. To investigate the copolymerization effect on the photovoltaic performance, the photovoltaic cell with the blend of PERY and TPA (weight ratio of 1:1) as the active layer was also fabricated and characterized. The I_{SC} and V_{OC} of the photovoltaic cell were 0.013 mA/cm^2 and 0.12 V, respectively. The performance of the device based on the blend of PERY and TPA was poorer than that of the device based on PERY−PPV−TPA, indicating that the copolymerization in PERY−PPV and PERY−PPV−TPA improved the device performance for some extent.

Conclusions

Two novel copolymers PERY−PPV and PERY−PPV−TPA were successfully synthesized by means of the Wittig reaction. Both of them were characterized by FT-IR, ^{1}H NMR, UV−vis, and FL spectra as well as GPC, TGA, and DSC measurements. The introduction of PPV and TPA moieties into the bay positions of perylene bisimide enhanced the solubility of polymers and quenched the fluorescence of perylene bisimide obviously. The photovoltaic devices, ITO/PEDOT:PSS/copolymers/Ca/Al, were fabricated, and their $I-V$ characteristics indicated that the copolymerization in PERY−PPV and PERY−PPV−TPA improved the device performance for some extent.

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