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Improvement of Photoluminescent and Photovoltaic Properties of Poly(thienylene vinylene) by Carboxylate Substitution

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Conjugated polymers have been a popular research field in the past three decades since the discovery of conducting polymers in 1977,[1] owing to their novel properties and promising applications in optoelectronic devices such as polymer light-emitting diodes,[2] polymer solar cells (PSCs),[3−5] chemical sensors,[6] and nonlinear optical devices.[7] Recently, conjugated polymers with low bandgaps have drawn much attention due to their potential to be intrinsic conductive polymers and red-emitting luminescent polymers as well as for their better spectral matching with the solar spectrum for the application in PSCs.[3b,4c,8]

Poly(thienylene vinylene) (PTV) derivatives are well-known low-bandgap polymers.[9] PTVs have already proven to be interesting polymers with high conductivity upon doping.[10] In addition, PTVs have high hole mobility (ca. 0.22 $cm^2 V^{-1} s^{-1}$)[11] and low bandgap (1.5−1.8 eV), which makes them attractive candidates for photovoltaic applications.[12] However, PTVs are inherently nonluminescent,[13,14] and thus far the photovoltaic efficiencies of the devices based on PTVs as donor materials are rather low.[15,16] The lifetime of the singlet excited-state of PTVs is extremely short due to the fast thermal decay,[17] and their photoexcitation decay primarily occurs via intrachain relaxation rather than photoinduced electron transfer from the PTVs to the acceptor.[14] Consequently, research on PTV in PSCs is rather limited compared with its parent polymer, polythiophene (PT).[3a,5]

Here, we synthesized a new poly(thienylene vinylene) derivative, poly(3-carboxylated thienylenevinylene), P3CTV (see Scheme 1), containing a carboxylate substituted group in the 3-position of thiophene by Stille coupling reaction (M_w = 16.5K; polydispersity = 2.8). P3CTV is readily soluble in common organic solvents such as chlorobenzene, dichlorobenzene, and chloroform and possesses excellent film-forming ability. To study the effect of the carboxylate substituent on the optoelectronic properties of PTVs, poly(3-hexyl thienylenevinylene) (P3HTV) was also synthesized with the method reported previously.[12b] TGA plots of the two polymers, as shown in Figure 1, display that the onset points of the weight loss of P3CTV and P3HTV are both close to ca. 300 °C.

Figure 2 shows the absorption spectra of the polymers in a dilute chloroform solution and in solid film. The absorption peak of P3CTV solution appears at ca. 553 nm, almost the same position as that for P3HTV. For the polymer films, the absorption bands were broadened than their solutions, which should result from the interchain interactions in the polymer films. The absorption peak of P3CTV film is at 556 nm, 5 nm bathochromic shifted as compared with that (ca. 551 nm) of P3HTV. This result indicates that the carboxylate group in the side chain did not produce much steric hindrance. The absoprtion band-edge of P3CTV film is located at 736 nm, red-shifted by 21 nm than that of P3HTV. The optical band gap (E_g^{opt}) of the P3HTV and P3CTV films calculated from the absorption band edges are 1.73 and 1.68 eV, respectively.

It is well-known that PTVs are nonluminescent materials;[13−15] our photoluminescence (PL) spectrum of P3HTV solution (also shown in Figure 2) confirms its nonluminescent property. Surprisingly, the P3CTV solution shows a PL peak at ca. 724 nm (see Figure 2). Probably, the observation of increased photoluminescence of P3CTV in solution is mainly related to the reduction of nonradiative relaxation pathways after the introduction of carboxylate group. The appearance of PL of P3CTV could indicate a longer lifetime of the excited state and more possibility for the photoinduced charge transfer from P3CTV to PCBM before the photoexcitations decay via intrachain relaxation.[14] On the other hand, the electron-withdrawing effect of the carboxylate group may create an internal charge transfer that could favor the charge separation.

Electrochemical cyclic voltammetry has been widely employed to investigate the redox behavior and to estimate the HOMO and LUMO energy levels of conjugated polymers from their onset oxidation and onset reduction potentials.[18] Figure 3a shows the cyclic voltammograms of P3CTV and P3HTV. The onset oxidation potential (E_{ox}) is 0.34 V vs Ag/Ag^+ for P3HTV and 0.55 V for P3CTV, and the onset reduction potential (E_{red}) is −1.36 V for P3HTV and −1.15 V for P3CTV. Obviously, the introduction of carboxylate group shifts both the oxidation and reduction potentials positively by ca. 0.21 V. From the E_{ox} and E_{red} values of the polymers, the HOMO and LUMO energy levels were calculated according to the following equations:[19] $E_{LUMO} = -e(E_{red} + 4.71)$ (eV) and $E_{HOMO} = -e(E_{ox} + 4.71)$ (eV), where the units of E_{ox} and E_{red} are in V vs Ag/Ag^+. The E_{LUMO} and the E_{HOMO} values of the polymers are shown in Figure 3b. The E_{LUMO} and the E_{HOMO} of P3HTV are located at −3.35 and −5.05 eV, respectively, while those of P3CTV are decreased to −3.56 and −5.26 eV, respectively. The results indicate that the introduction of the electron-deficient carboxylate group in the side chains can lower both E_{LUMO} and E_{HOMO} values of PTVs. The lower HOMO energy level of P3CTV could be beneficial to a higher open-circuit voltage of the PSCs with the polymer as donor.

Charge carrier mobility is another important parameter for conjugated polymers. The hole mobility of P3CTV was measured by the space-charge-limited current (SCLC) method[12b] with a device structure of ITO/PEDOT:PSS/polymers/Au. The hole mobility obtained for the P3CTV film is ca. 3.1×10^{-3} $cm^2 V^{-1} s^{-1}$, which is similar to that of P3HTV of 1.6×10^{-3} $cm^2 V^{-1} s^{-1}$ under the same experimental conditions.

The above experimental results, including the stronger photoluminescent emission, lower HOMO energy levels, and higher (about 2 times) hole mobility of P3CTV as compared with P3HTV, indicate that P3CTV could show improved photovoltaic properties. Therefore, photovoltaic performance of P3CTV was

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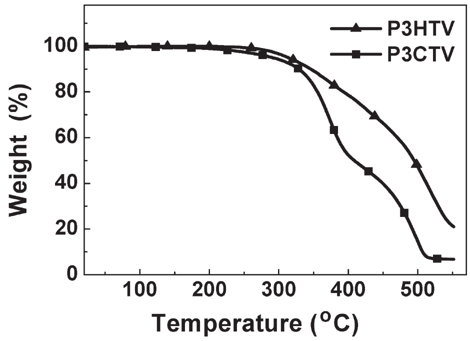


Figure 1. TGA plots of the polymers with a heating rate of 10 °C/min in an atmosphere of N_2.

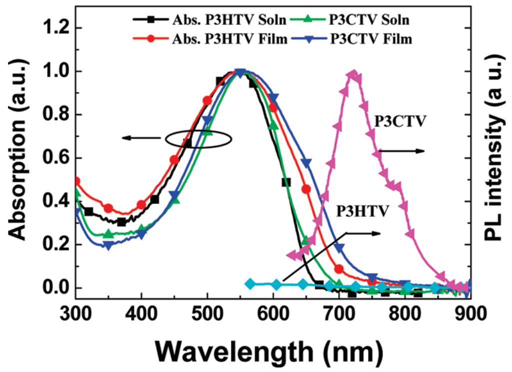
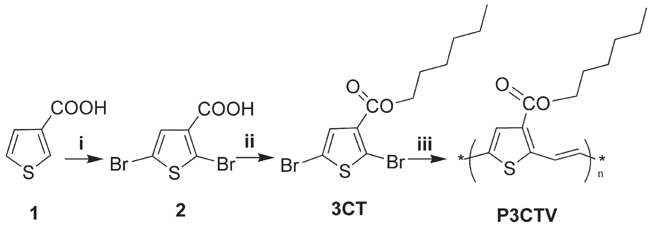


Figure 2. Normalized UV−vis absorption spectra of P3HTV and P3CTV solutions and films and PL spectra of P3HTV and P3CTV solutions in dilute $CHCl_3$.

Scheme 1. Synthetic Route of P3CTV[a]



[a] Conditions: (i) Br_2, acetic acid, 60 °C, reflux, 15 h; (ii) $SOCl_2$, reflux, 6 h, then *n*-$C_6H_{13}OH$, pyridine, 60 °C, 10 h; (iii) (*E*)-1,2-bis(tributylstannyl)ethane, $Pd(PPh_3)_4$, toluene, reflux, 5 h.

investigated in comparison with that of P3HTV. Polymer solar cells (PSCs) were fabricated with a structure of ITO/PEDOT:PSS/polymers:PCBM (1:2 w/w) /Ca/Al. Figure 4 shows the *I*−*V* curves of the devices.[20] The PSC based on P3HTV shows open-circuit voltage (V_{oc}) of 0.54 V, short-circuit current (J_{sc}) of 1.14 mA/cm^2, fill factor (FF) of 32.0%, and a power convency efficiency (PCE) of only 0.20% under the illumination of AM 1.5G, 100 mW/cm^2. The PCE (0.20%) of the device based on P3HTV is close to the results for the PTVs reported by Smith et al. with a value of 0.24%[15] and by Hou et al. with a value of 0.26%.[16] Under the same experimental conditions, the photovoltaic performance of the PSC based on P3CTV improves significantly; the corresponding V_{oc} increases to 0.82 V from 0.54 V, J_{sc} increases from 1.14 to 4.78 mA/cm^2, and a PCE of 1.59% was obtained. After annealing the P3CTV-based PSC device at 110 °C for 5 min, the V_{oc} further increased to 0.86 V, J_{sc} to 5.47 mA, and FF also increased slightly to 42.8%, resulting in a higher PCE of 2.01%. The PCE of 2.01% is significant improvement for the PSCs based on the PTVs reported so far.

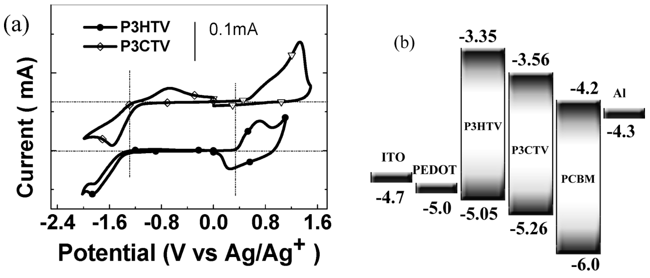


Figure 3. (a) Cyclic voltammograms of P3HTV and P3CTV films on platinum electrode in acetonitrile solution containing 0.1 mol/L Bu_4NPF_6 at a scan rate of 20 mV/s. (b) Energy level diagrams for P3HTV, P3CTV, and PCBM.

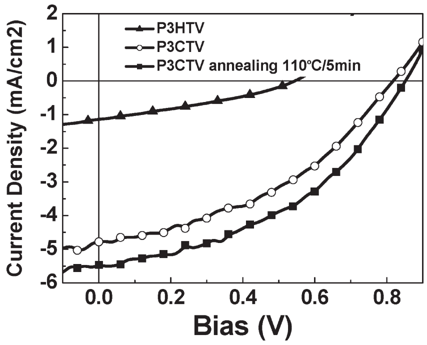


Figure 4. *I*−*V* curves of the PSCs based on P3HTV and P3CTV under illumination of AM1.5G, 100 mW/cm^2.

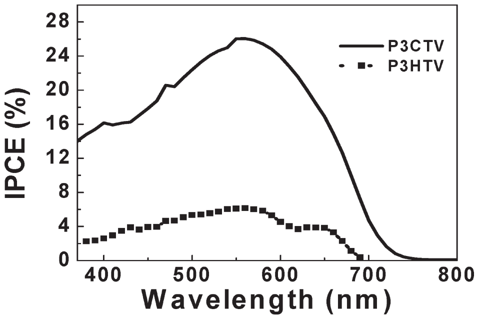


Figure 5. IPCE curves of the PSCs based P3CTV and P3HTV.

Since the V_{oc} of PSCs is proportional to the difference between the LUMO level of the electron acceptor and the HOMO level of the electron donor,[21] the higher V_{oc} of 0.82 V for the PSC based on P3CTV should result from its lower HOMO energy level of P3CTV. On the other hand, the higher J_{sc} of the device based on P3CTV could be benefited from the appearance of PL which makes the more effective photoinduced charge separation and the higher hole mobility which favors a higher charge transporting efficiency.

The incident photon to current conversion efficiency (IPCE) plots of the PSCs based on the P3HTV and P3CTV polymers were measured and are shown in Figure 5. It can be seen that the photoresponse curve of the PSC based on P3CTV covers a wide wavelength range from 380 nm up to 740 nm, which coincides with the absorption spectrum of the photoactive film. The maximum IPCE value of the device based on P3CTV reached 26% at 560 nm, which is around 5 times higher than that of the device based on P3HTV. The higher IPCE value of P3CTV-based device justifies the higher J_{sc} value of the device.

In conclusion, we synthesized a PTV derivative with carboxylate substituent, P3CTV, by the Stille coupling reaction. P3CTV shows unexpected PL emission, narrower E_g of 1.68 eV, lower

HOMO energy level at −5.26 eV, and higher hole mobility of 3.1×10^{-3} cm^2 V^{-1} s^{-1} in comparison with those of P3HTV. The PCE of the PSC based on P3CTV as donor and PCBM as acceptor with a weight ratio of 1:2 reached 2.01% under the illumination of AM1.5G, 100 mW/cm^2, which is about 10 times increased than that of the device based on P3HTV. The PCE of 2.01% is the highest efficiency for the PSCs based on the PTVs reported so for. The significant improvement of the photovoltaic properties of PTVs by the carboxylate substitution indicates that PTVs could be also promising photovoltaic materials after suitable structural modification.

Experimental Section. *Materials.* (*E*)-1,2-Bis(tributylstannyl)ethane was prepared according to the adapted literature method,[16] and thiophene-3-carboxylic acid was prepared according to the literature.[22] Pd(PPh$_3$)$_4$ was obtained from Aldrich Chemical Co., and 3-thenaldehyde was purchased from Acros Chemical Co. and used as received. Hexane was dried over Na/benzophenone ketyl and freshly distilled prior to use. The other materials are common commercial level and used as received.

Measurements. ^{1}H NMR spectra were measured on a Bruker DMX-300 spectrometer. Absorption spectra were taken on a Hitachi U-3010 UV−vis spectrophotometer. Photoluminescence spectra were measured using a Hitachi F-4500 spectrophotometer. The molecular weight of polymers was measured by the GPC method, and polystyrene was used as a standard. TGA measurement was performed on a Perkin-Elmer TGA-7 at a heating rate of 10 °C/min in an atmosphere of N$_2$ at a flow rate of 60 cm^3/min, and the weight of the samples was about 5 mg. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e electrochemical workstation with Pt disk, Pt plate, and Ag/Ag$^+$ electrode as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$)−acetonitrile solution.

Synthesis. The synthetic route of P3CTV is shown in Scheme 1. The detailed synthetic processes are as follows:

*2,5-Dibromothiophene-3-carboxylic Acid (**2**)*[23]. Thiophene-3-carboxylic acid (**1**) (1.28 g, 0.01 mol) was added to glacial acetic acid (25 mL). Then Br$_2$ (2.56 mL, 0.05 mol) was added to the flask dropwise at room temperature. The mixture was warmed and stirred at 60 °C for 15 h. After the reaction was completed, the mixture was poured into 200 mL of deionized water, and some Na$_2$SO$_3$ was added to decolorize. After dehydration and evaporation of the solvent, the crude product was purified by recrystallization from EtOH−H$_2$O to give product **7** as white needles (2.49 g, yield 87%); mp 178 °C. ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm): 13.31 (s, 1H), 7.40 (s, 1H). ^{13}C NMR: 164.8, 131.6, 130.5, 120.9, 110.9.

Hexyl 2,5-Dibromothiophene-3-carboxylat (3CT). A mixture of 2,5-dibromo-3-thiophenecarboxylic acid (1.15 g, 0.004 mol) and SOCl$_2$ (10 mL) was refluxed for 6 h, and the excess SOCl$_2$ was removed under vacuum. To the residue, n-C$_6$H$_{13}$OH (10 mL) and dry pyridine (2 mL) were added to the flask dropwise through an addition funnel. The mixture was stirred for 10 h at 60 °C and was cooled to room temperature, poured into a mixture of ice and chlorohydric acid (20 mL, 1 M), and stirred. The solution was washed with ether for three times, and the combined organic layer was washed with saturated NaHCO$_3$ and dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified by distillation in vacuum to get a pale yellow liquid (1.18 g, yield 80%). GC-MS: m/z = 370. ^{1}H NMR (300 MHz, CDCl$_3$, δ/ppm): 7.34 (s, 1H), 4.27 (t, 2H), 1.75 (p, 2 H), 1.46−1.32 (m, 6H), 0.90 (t, 3H). ^{13}C NMR: 160.7, 131.9, 131.5, 118.4, 110.8, 65.3, 30.8, 28.0, 25.2, 22.5, 13.9.

P3CTV. The polymer was prepared by a typical Stille coupling reaction of 2,5-dibromo-3-ester substituted-thiophene monomer 3CT with (*E*)-1,2-bis(tributylstannyl) ethane. 1.0 mmol of the monomer was put into a three-neck flask. Then 15 mL of degassed toluene and 1.0 mmol of (*E*)-1,2-bis(tributylstannyl)ethane were added under the protection of argon. The solution was flushed with argon for 10 min, and then 50 mg of Pd(PPh$_3$)$_4$ was added. After another flushing with argon for 20 min, the reactant was heated to reflux for 5 h. Then the reactant was cooled to room temperature; the polymer was precipitated by adding 50 mL of methanol and filtered through a Soxhlet thimble and was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The polymer was recovered as solid from the chloroform fraction by rotary evaporation. The solid was dried under vacuum for 1 day to obtain a deep purple-red solid; yield 26.5%. ^{1}H NMR (300 MHz, CDCl$_3$, δ/ppm): 8.25−7.08 (m, Ar−H and vinyl protons 3H), 4.27 (br, 2H), 1.88 (br, 2H), 1.50−1.37 (m, 6H), 0.91 (br, 3H). Anal. Calcd for C$_{13}$H$_{16}$O$_2$S: C 66.07, H 6.82. Found: C 65.81, H 6.36. M_w = 16.5K; polydispersity = 2.8.

Hole Mobility Measurement and Fabrication of Polymer Solar Cells. We used a device structure of ITO/PEDOT:PSS/polymer/Au for the hole mobility measurement, based on the space-charge-limited current (SCLC) model.[12b] The thickness of the P3HTV and P3CTV films was 96 and 107 nm, respectively. Hole mobility was calculated according to the equation $\ln(JL^3/V^2) \cong 0.89(1/E_0)^{0.5}(V/L)^{0.5} + \ln(9\varepsilon\varepsilon_0\mu_0/8)$, where μ_0 is the zero-field mobility, E_0 is the characteristic field, J is the current density, ε is the dielectric constant of the polymer, ε_0 is the permittivity of the vacuum, L is the thickness of the polymer layer, $V = V_{\mathrm{appl}} - V_{\mathrm{bi}}$, V_{appl} is the applied potential, and V_{bi} is the built-in potential (in this device structure, $V_{\mathrm{bi}} = 0.2$ V).

Polymer solar cell devices with the structure of ITO/PEDOT−PSS/polymers:PCBM (1:2, w/w)/Ca/Al were fabricated under conditions as follows: After spin-coating a 30 nm layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) onto a precleaned indium−tin oxide (ITO)-coated glass substrates, the polymer/PCBM blend solution was spin-coated. The typical concentration of the blend solution used in this study for spin-coating the active layer was 10 mg/mL, and dichlorobenezene was used as the solvent. The thickness of the active layer was ~80 nm. The fabrication of the devices was completed by evaporating Ca/Al metal electrodes with an area of 12.5 mm^2 as defined by masks.

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