Solution-Processable Platinum-Acetylide-based Small Molecular Bulk Heterojunction Solar Cells

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Two new solution-processable A’−D−≡Pt(PEt3)2−≡-D′-structured molecules, namely, CNPT and DRPT, were synthesized and characterized for photovoltaic applications. Their optoelectronic properties were investigated by UV-vis absorption and cyclic voltammograms. Grazing-incidence wide-angle X-ray scattering and resonant soft X-ray scattering studies revealed that the DIO additive could enhance the crystallization of CNPT and reduce the size of phase separation of CNPT:PC71BM blends, while the addition of DIO showed little influence on the crystallization and morphology of the DRPT:PC71BM blends. Processing with the DIO additive, CNPT:PC71BM based solar cells showed a best power conversion efficiency of 1.4%, with a Jsc of 4.14 mA·cm−2, a Voc of 0.75 V, and a fill factor of 45.4%.

Keywords platinum, acetylide, optoelectronic property, morphology, organic solar cells

Introduction

Bulk heterojunction (BHJ) organic solar cells (OSCs) have drawn great attention as a promising technology for renewable energy in recent years due to their advantage of solution processability, low cost, light weight, and flexibility.[1,2] Recently, there has been significant interest in platinum(II)-containing polyynes and their oligomers as donor materials in BHJOSCs.[4,5] When Pt atom is conjugated with an alkyne unit, the d orbitals (dxy and dxz) of Pt overlap with the π orbitals (π* and πxy) of the C≡C unit, which facilitates π-electron delocalization.[6] Insertion of [-≡Pt(L2)≡-] units, where L is the ligands, into a conjugated backbone has been demonstrated to enhance the formation of the triplet excitons, which is reported to increase the exciton diffusion length and decrease geminate recombination, thereby probably increasing the efficiency of charge generation.[7] For this reason, efforts have been paid to explore the potential of using triplet states of polyacetylenes for photovoltaic applications. Wong and coworkers reported a successful strategy to create narrow band gap organometallic polymers by incorporating platinum-acetylide into donor-acceptor (D-A) structure. And a series of platinum-acetylide based oligomers and polymers have been explored, which absorb photons through out the visible region and achieve a power conversion efficiency (PCE) of ca. 4%. [8] Fréchet et al. reported solution-processable crystalline platinum-acetylide oligomers with broad band absorption with PCEs up to 3%.[9]

Solution-processed small-molecule BHJs OSCs are drawing more and more attention recently due to their good device performance and intrinsic advantages such as well-defined structures, easy synthesis and purification, and little batch to batch variations.[10] And impressive PCE up to 10% has been obtained, which is comparable to their polymer counter parts.[11-13] In our recent work, we reported an A’−D−A−D−A’-type small molecule CNDPP with a PCE value of ca. 5%, where 3,3’-dioctyl-2,2’:5’,2”-terthiophene acts as donor, and diketopyrrolopyrrole (DPP) and octylecycanoacetate units are central and terminal acceptors, respectively.[14] We adjusted the BHJ morphology by the solution additive (1,8-diiodooctane, DIO). The role of the additive in CNDPP:PC71BM system is similar to, but not identical to, its role in polymer-based BHJ blends. On the basis of the success of CNDPP, we exchange the DPP center with a platinum-acetylide to build a new class of A’−D−≡Pt(PEt3)2−≡-D′-structured molecules CNPT and DRPT. The oligomers have been designed to (1) investigate the influence of platinum-acetylide central unit on the optoelectronic properties; (2) build multichromophoric systems to extend the absorption into the long wavelength range; (3) prevent strong aggregation using

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tetrahedral trialkylphosphine ligands on the platinum center, thus providing good solution process ability; (4) change the terminal acceptor group with 3-ethylrhodamine to induce different photon physical, morphological and device properties. The optoelectronic properties of both oligomers have been studied by UV-vis absorption spectroscopy and cyclic voltammetry. The crystalline properties and BHJ morphology have been analyzed by Grazing-incidence wide-angle X-ray scattering and resonant soft X-ray scattering. Solution processable small-molecule BHJ solar cells with moderate performances were demonstrated.

**Experimental**

All chemicals and reagents were used as received from commercial sources without purification. trans-[PtCl₂(PEt₃)₂] was purchased from J&K Scientific Ltd. Anhydrous tetrahydrofuran was distilled from sodium/benzophenoneketyl prior to use. 5-Bromo-3,3''-dioctyl-2,2':5',2''-terthiophene was synthesized according to the literature.[15]

¹H, ¹³C, and ³¹P nuclear magnetic resonance (NMR) spectra were collected on a Varian Mercury Plus 500 spectrometer with tetramethylsilane as the internal standard. Matrix-assisted laser desorption/ionization (MALDI) experiments were carried out using a Shima-dzu AXIMA-CFR plus time-of-flight mass spectrometer (Kratos Analytical, Manchester, UK.). Elemental microanalyses were carried out on a Vario EL III CHNOS Elementar analyzer. FT-IR spectra were recorded on a JASCO FT/IR-470 plus Fourier transform infrared spectrometer and measured as KBr pellets. UV-vis spectra were recorded on a Shimadzu 3150 PC spectrophotometer. Cyclic voltammetry (CV) was performed at a scanning rate of 50 mV•s⁻¹ on an AUTOLAB. PGSTAT30 potentiostat/galvanostat system (Ecochemie, Netherlands), which was equipped with a three-electrode cell. The sample was cast onto a glass carbon disk as a working electrode and Pt wire was used as the counter electrode. An Ag/Ag⁺ was used as a reference electrode. Tetrabutylammoniumhexafluorophosphate (n-Bu₄NPF₆, 0.1 mol•L⁻¹) was used as a supporting electrolyte. Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed on Beamline 7.3.3 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. An X-ray beam impinged onto the sample at a grazing angle above the critical angle of the sample film (α = 0.16) but below the critical angle of the silicon substrate (α = 0.24). The wavelength of X-rays used was 1.240 Å, and the scattered intensity was detected by using PILATUS 1M detector. RSoXS was performed at ALSbeamline 11.0.1.2, Lawrence Berkeley National Lab. Thin films were flowed and transferred onto Si₃N₄ substrate and experiments were done in transition mode.

**Scheme 1** Synthetic routes of target compounds CNPT and DRPT
The indium tin oxide (ITO)-coated glass substrates (20 ± 5 ohms/sq) were bought from Thin Film Devices Inc., and were cleaned through ultrasonic treatment in detergent, DI water, acetone, and isopropyl alcohol and then dried in an oven overnight. PEDOT:PSS (Baytron P VP A1 4083 (ca. 35 nm) was spin-coated on the ultraviolet ozone-treated ITO substrates. After annealing at 150 °C for 3 min in air, the substrates were transferred to the glove box. Oligomer/PC 71BM chloroform solution (20 mg/mL) with or without DIO additive were spin-coated on top of the PEDOT:PSS layer at 1500 r/min. The thickness of film was ca. 80–100 nm (KLA-TENCOR Alpha-Step IQ Surface Profiler). Finally, 10 nm of Ca and then 100-nm-thick Al cathode was deposited (area 5.65 mm²) on the active layer under high vacuum (2 × 10⁻⁵ Pa) using a thermal evaporator. All current-voltage (J-V) characteristics of the devices were measured under simulated AM1.5G irradiation (100 mW·cm⁻²) using a Xe lamp-based Newport 91160-300-W solar simulator. A Xe lamp equipped with an AM1.5G filter was used as the white light source. The light intensity was adjusted with an NREL-calibrated Si solar cell with a KG-5 filter.

**Synthesis of compound 2**

Phosphoryl chloride (0.16 mL, 1.7 mmol) was added dropwise into DMF (2 mL) at 0 °C and stirred for 30 min. Solution of 1 (551.7 mg, 1 mmol) in 1,2-dichloroethane (15 mL) was added into the prepared Vilsmeier reagent. After being stirred at 70 °C for 12 h, the mixture was poured into ice water (100 mL), neutralized with Na₂CO₃, and then extracted with dichloromethane. The combined organic layer was washed with water and brine, dried over Na₂SO₄, and then extracted with dichloromethane. The combined organic layer was washed with water and brine, dried over Na₂SO₄. After removal of solvent it was purified by column chromatography on silica gel using petroleum ether as eluant to afford compound 3 as orange solid in 92% yield. ¹H NMR (500 MHz, CDCl₃) δ: 9.80 (s, 1H), 7.55 (s, 1H), 7.19 (d, J = 3.81 Hz, 1H), 7.10–7.06 (m, 2H), 2.78 (t, J = 7.75 Hz, 2H), 2.70 (t, J = 7.75 Hz, 2H), 1.67–1.60 (m, 4H), 1.32–1.28 (m, 20H), 0.91–0.87 (m, 6H), 0.27 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ: 182.24, 140.61, 140.61, 139.00, 138.93, 137.36, 135.67, 134.93, 131.62, 127.68, 126.45, 121.50, 100.23, 97.40, 31.91, 30.39, 30.31, 29.57, 29.53, 29.46, 29.45, 29.38, 29.31, 29.29, 22.72, 14.16, –0.12.

**Synthesis of compound 4**

To a stirred solution of 3 (850 mg, 1.42 mmol) in the mixture of THF (100 mL) and methanol (25 mL) was added tetrabutylammonium fluoride (896 mg, 2.84 mmol). The mixture was stirred for 2 h at room temperature and concentrated. The residue was diluted with diethyl ether, washed with brine, and dried over Na₂SO₄. After removal of solvent, the resulting organic compound was purified by column chromatography on silica gel using petroleum ether as eluant to afford compound 4 as dark solid in 95% yield. ¹H NMR (500 MHz, CDCl₃) δ: 9.83 (s, 1H), 7.60 (s, 1H), 7.24 (d, J = 3.77 Hz, 1H), 7.13 (s, 1H), 7.12 (d, J = 3.87 Hz, 1H), 3.41 (s, 1H), 2.84 (t, J = 7.64 Hz, 2H), 2.75 (t, J = 7.83 Hz, 2H), 1.71–1.63 (m, 4H), 1.42–1.28 (m, 20H), 0.91–0.88 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ: 182.46, 140.67, 140.51, 140.41, 139.90, 139.00, 137.18, 136.09, 135.12, 131.86, 127.77, 126.75, 120.36, 82.43, 31.89, 30.46, 30.33, 29.53, 29.52, 29.50, 29.43, 29.33, 29.28, 22.70, 14.14.

**Synthesis of compound 5**

Compound 4 (110.2 mg, 0.21 mmol) and trans-[PtCl₂(PEt₃)₂] (50.2 mg, 0.1 mmol) were added to a mixture of THF and Et₃N (V : V = 1 : 1) in the presence of a catalytic amount of Cul (10 mol%) under nitrogen. The reaction mixture was stirred at room temperature overnight. The solvent was then removed under reduced pressure to obtain the crude product, which was then purified by column chromatography on silica gel using ethyl acetate/petroleum ether (V : V = 5 : 95) as eluant to afford compound 5 as red solid in 87% yield. ¹H NMR (500 MHz, CDCl₃) δ: 9.84 (s, 2H), 7.61 (s, 2H), 7.23 (d, J = 3.92 Hz, 2H), 7.07 (d, J = 3.90 Hz, 2H), 6.72 (s, 2H), 2.84 (t, J = 7.78 Hz, 4H), 2.73 (t, J = 7.78 Hz, 4H), 2.20–2.15 (m, 12H), 1.74–1.62 (m, 8H), 1.40–1.20 (m, 58H), 0.92–0.88 (m, 12H); ¹³C NMR (125 MHz, CDCl₃) δ: 182.42, 141.34, 140.05, 140.00, 139.12, 138.86, 133.67, 130.75, 128.27, 127.75, 126.95, 125.49, 116.39, 116.28, 116.16, 101.76, 31.92, 31.88, 30.55, 30.32, 29.65, 29.55, 29.53, 29.50, 29.48, 29.43, 29.32, 29.28, 22.70, 16.70, 16.56, 16.42, 14.14; ³¹P NMR (202 MHz, CDCl₃) δ: 11.52 (J₉,₀₂ = 2340 Hz).

**Synthesis of CNPT**

Bis-aldehyde derivative 5 (147.9 mg, 0.1 mmol) was dissolved in CHCl₃ (10 mL), several drops of triethylamine ether as eluant to afford compound 3 as orange solid in 92% yield. ¹H NMR (500 MHz, CDCl₃) δ: 9.80 (s, 1H), 7.55 (s, 1H), 7.19 (d, J = 3.81 Hz, 1H), 7.10–7.06 (m, 2H), 2.78 (t, J = 7.75 Hz, 2H), 2.70 (t, J = 7.75 Hz, 2H), 1.67–1.60 (m, 4H), 1.32–1.28 (m, 20H), 0.91–0.87 (m, 6H), 0.27 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ: 182.24, 140.61, 140.35, 139.79, 138.93, 137.36, 135.67, 134.93, 131.62, 127.68, 126.45, 121.50, 100.23, 97.40, 31.91, 30.39, 30.31, 29.57, 29.53, 29.46, 29.45, 29.38, 29.31, 29.29, 22.72, 14.16, –0.12.
amine and octyleynoacetate (394.5 mg, 2 mmol) were added, and the resulting solution was stirred for 2 d under nitrogen at room temperature. The reaction mixture was then extracted with CH₂Cl₂, washed with water, and dried over Na₂SO₄. After removal of solvent, it was purified by column chromatography on silica gel using a mixture of dichloromethane/petroleum ether (V : V = 6 : 4) as eluent to afford CNPT as deep red solid in 74% yield. ¹H NMR (500 MHz, CDCl₃) δ: 8.21 (s, 2H), 7.60 (s, 2H), 7.29 (d, J = 3.95 Hz, 2H), 7.08 (d, J = 3.95 Hz, 2H), 6.72 (s, 2H), 4.30 (t, J = 6.80 Hz, 4H), 2.84 (t, J = 7.74 Hz, 4H), 2.73 (t, J = 7.74 Hz, 4H), 2.22—2.15 (m, 12H), 1.80—1.61 (m, 16H), 1.40—1.22 (m, 74H), 0.93—0.88 (m, 18H); ¹³C NMR (125 MHz, CDCl₃) δ: 163.17, 145.91, 142.12, 140.88, 140.23, 140.13, 139.40, 133.25, 132.69, 130.78, 128.38, 128.18, 126.97, 125.52, 116.51, 116.06, 101.80, 97.40, 66.49, 31.91, 31.86, 31.78, 30.48, 30.22, 29.74, 29.54, 29.48, 29.40, 29.38, 29.31, 29.27, 29.20, 29.17, 28.5, 25.82, 22.70, 22.68, 22.66, 16.69, 16.55, 16.41, 14.41, 18.31. ³¹P NMR (202 MHz, CDCl₃) δ: 11.52 (Jₚ₋ₚ = 2340 Hz); FT-IR (KBr) ν = 2088 cm⁻¹. MS (MALDI-TOF) celled for C₉₆H₁₄₂N₂O₄P₂S₆Pt [M⁺]: 1837.58, found 1836.90. Anal. calcd for C 84H118N2-O4P2S6Pt: C 77.19, H 6.82, N 1.59, S 18.16; found C 75.19, H 6.82, N 1.67, S 18.11.

Synthesis of DRPT

Bis-aldehyde derivative 5 (221.8 mg, 0.15 mmol) was dissolved in CHCl₃ (10 mL), several drops of triethylamine and 3-ethylrhodanine (483.7 mg, 3 mmol) were added, and the resulting solution was stirred for 2 d under nitrogen at room temperature. The reaction mixture was then extracted with CH₂Cl₂, washed with water, and dried over Na₂SO₄. After removal of solvent, it was purified using silica gel column chromatography, and the final products were fully characterized by ¹H NMR, ¹³C NMR, ³¹P NMR, FT-IR and MALDI-TOF mass analysis. The NMR spectra and MALDI-TOF mass spectra of both compounds were shown in the supporting information (Figures S1—S8). After post-functionalized by octylcyanacetate and 3-ethylrhodanone in chloroform and triethylamine gave the target platinum(II) compounds CNPT and DRPT, respectively.

Both CNPT and DRPT were purified using silica gel column chromatography, and the final products were fully characterized by ¹H NMR, ¹³C NMR, ³¹P NMR, FT-IR and MALDI-TOF mass analysis. The NMR spectra and MALDI-TOF mass spectra of both compounds were shown in the supporting information (Figures S1—S8). After post-functionalized by octylcyanacetate and 3-ethylrhodanone, the characteristic signal of aromatic aldehyde protons at δ 9.84 disappeared in the ¹H NMR spectra of compound 5, and new signals of olefinic protons of CNPT and DRPT at around δ 8.20 and 7.80 were observed, respectively. The ³¹P NMR spectra of compounds 5, CNPT and DRPT all showed a single signal at δ 11.52, which confirmed the highly symmetrical structure of these oligomers. The observed Jₚ₋ₚ values of 2340 Hz for these platinum(II) compounds are typical of those for related trans-Pt-P-P complexes. The FT-IR spectra of the platinum(II) complexes exhibited a single sharp characteristic ν(C≡C) absorption band at 2085—2088 cm⁻¹. Both oligomers reported here showed only a single peak corresponding to the molecular weights of 1836.90 for CNPT, and 1764.20 for DRPT, respectively. The perfect agreement between the calculated and experimentally determined m/z ratios confirms the monodispersity of the oligomers.

Optical properties

The UV-vis absorption spectra of the oligomers in diluted dichloromethane solution and thin films are shown in Figure 1. The corresponding optoelectronic data are summarized in Table 1. In general, both oligomers feature two primary absorption bands, one appearing in the blue-violet absorbing region and the other at lower energy with a maximum absorption at 498 nm for CNPT and 508 nm for DRPT, respectively. The former band at the low wavelength region can be assigned to π-π* transition of the conjugated backbone, while the lowest energy band is due to intramolecular charge transfer (ICT) between the conjugated backbone

Results and Discussion

Synthesis and characterization

The synthetic route to the target platinum(II) oligomers was shown in Scheme 1. The key platinum(II)-bis(arylennethylenylene) unit 5 was started with tertithiophene, which was brominated with NBS in CHCl₃/AcOH at 0 °C to afford the corresponding bromomertithiophene (I) in 67% yield. Vilsmeier-Haack formulation of bromomertithiophene (I) afforded aldehyde intermediate 2. The trimethylsilyl protected compound 3 was conveniently synthesized in good yields using the Sonogashira coupling of 2 with trimethylsilylacetylene. After desilylation with tetrabutylammonium fluoride in a mixture of THF/MeOH, compound 4 was obtained and then reacted with trans-[PtCl₂(PÉt₃)₂] in a THF/NEt₃ mixture and in the presence of a catalytic amount of Cu at room temperature to afford the core platinum(II)-bis(arylennethylenylene) unit 5. Finally, Knoevenagel condensation of dialdehyde precursors 5 with octyleynoacetate and 3-ethylrhodanone in chloroform and triethylamine gave the target platinum(II) compounds CNPT and DRPT, respectively.

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and the end acceptor units. Commonly, a stronger electron-donating and electron-accepting strength can result in a higher degree of electronic delocalization and hence a stronger ICT in the molecular donor materials. By changing the end acceptor from octylcyananoacetate to 3-ethylrhodanine, a slightly red-shift of the ICT absorption band is observed, which is due to the stronger electron-accepting ability of 3-ethylrhodanine unit.\[16\] The absorption coefficients of CNPT and DRPT are $6.13 \times 10^4 \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 498 nm and $3.76 \times 10^4 \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 508 nm, respectively. Compared to the platinum-free A-D-A analogue DCAO7T and DERHD7T reported by Chen and co-workers,\[16\] the molar absorption coefficients of the complexes decrease slightly, which may be due to the weak absorption of Pt(II) complexes of this kind in the visible light. The absorption spectra of these oligomers in thin films show an obvious broadening and red-shift compared to the solution spectra of these oligomers in thin films.

The absorption maxima for CNPT and DRPT were found to be 579 and 629 nm with shoulders at 380 and 409 nm, respectively, which may be due to the intermolecular aggregation in the solid states. The optical band gaps of CNPT and DRPT are estimated from the onset of the film absorption spectra to be 1.62 eV for CNPT, and 1.58 eV for DRPT, respectively.

Electrochemical properties

In addition to the absorption properties, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the donor material are key parameters that influence the overall performance of a photovoltaic device by affecting the efficiency of charge separation and the maximum attainable open-circuit voltage ($V_{oc}$). We carried out cyclic voltammetry to investigate the redox properties of the oligomers. And according to de Leeuw et al.,\[17\] the HOMO and LUMO energy levels are approximately equal to the onset oxidation potential and reduction potentials (vs. Ag/Ag⁺) plus 4.83 eV, respectively. Cyclic voltammograms of both compounds show one irreversible oxidation and reduction waves (Figure 2). The anodic scan shows that the onsets of oxidation for CNPT and DRPT occur at 0.57 and 0.31 V, respectively, which correspond to HOMO levels of −5.4 and −5.14 eV.

When scanning cathodically, the onset potentials of reduction for CNPT and DRPT are −1.29 and −1.33 eV, respectively, corresponding to LUMO levels of −3.54 and −3.5 eV. The electrochemical band gaps estimated from redox properties are 1.86 and 1.64 eV for CNPT and DRPT, respectively, which are in consistent with the optical band gaps.

**Table 1** UV-vis absorption and cyclic voltammetric data of oligomers

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>$\lambda_{max}$ (sol)/nm</th>
<th>$\lambda_{max}$ (film)/nm</th>
<th>$\epsilon_{max}$ (L·mol⁻¹·cm⁻¹)</th>
<th>$E_{g,opt}$ /eV</th>
<th>$E_{onset}$ /V</th>
<th>$E_{red}\text{/onset}$ /V</th>
<th>HOMO /eV</th>
<th>LUMO /eV</th>
<th>$E_{F}^{\text{w,eff}}$ /eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNPT</td>
<td>498</td>
<td>579</td>
<td>61376</td>
<td>1.62</td>
<td>0.57</td>
<td>−1.29</td>
<td>−5.4</td>
<td>−3.54</td>
<td>1.86</td>
</tr>
<tr>
<td>DRPT</td>
<td>508</td>
<td>630</td>
<td>37665</td>
<td>1.58</td>
<td>0.31</td>
<td>−1.33</td>
<td>−5.14</td>
<td>−3.5</td>
<td>1.64</td>
</tr>
</tbody>
</table>

*Extinction coefficient at $\lambda_{max}$ in solution. \(b\) Estimated from the absorption edge in thin films. Optical band gap = $1240/\epsilon_{onset}$ (eV).

Photovoltaic properties

OSC devices based on these two small molecules were fabricated and tested with a configuration of indium tin oxide (ITO)/PEDOT:PSS/oligomer: PC71BM/Ca/Al. Figure 3 shows the $J$-$V$ curves of OSC devices based on oligomer:PC71BM (w : w = 1 : 1) under illumination of AM 1.5G, 100 mW·cm⁻². And the corresponding open-circuit voltage ($V_{oc}$), short-circuit current ($J_{sc}$), fill factor (FF) and PCEs of the devices are summarized in Table 2. For CNPT, when chloroform
(CF) was used as the solvent, a PCE of 0.9% was obtained, with a $J_{sc}$ of 3.11 mA cm$^{-2}$, a $V_{oc}$ of 0.78 V, and an FF of 36.7%. In order to optimize the morphology of the blend films and thus to enhance photovoltaic performance, 1,8-diiodooctane (DIO) was added into CF during the film casting process. By the use of 0.3 vol% DIO as an solvent additive, $J_{sc}$ and FF of the devices increased to 4.14 mA cm$^{-2}$ and 45.4%, respectively, while $V_{oc}$ reduced slightly. The combined effect led to the optimal PCE of 1.4%. DRPT showed an inferior device performance compared to CNPT. A low PCE of 0.47% was recorded in chloroform processed BHJ devices under the same device configuration. The major reason came from the reduced $J_{sc}$ and FF. Adding DIO additive (0.3 vol%) led to decrease of $V_{oc}$ and FF, which further reduced the device performance.

**Figure 3** Current density-voltage characteristics of the OSC devices based on the blend of CNPT or DRPT:PC$_{71}$BM under the illumination of AM. 1.5G, 100 mW cm$^{-2}$.

**Table 2** The photovoltaic performances of the OSC devices based on oligomers:PC$_{71}$BM blends

<table>
<thead>
<tr>
<th>Oligomer:PC$_{71}$BM</th>
<th>$V_{oc}$/V</th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
<th>FF/%</th>
<th>PCE/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNPT (CF)</td>
<td>0.78</td>
<td>3.11</td>
<td>36.7</td>
<td>0.90</td>
</tr>
<tr>
<td>CNPT (CF+DIO)</td>
<td>0.75</td>
<td>4.14</td>
<td>45.4</td>
<td>1.40</td>
</tr>
<tr>
<td>DRPT (CF)</td>
<td>0.84</td>
<td>2.01</td>
<td>27.6</td>
<td>0.47</td>
</tr>
<tr>
<td>DRPT (CF+DIO)</td>
<td>0.67</td>
<td>2.01</td>
<td>25.5</td>
<td>0.34</td>
</tr>
</tbody>
</table>

**Grazing-incidence wide-angle X-ray scattering**

Grazing incidence wide-angle X-ray scattering (GIWAXS) experiments were carried out to investigate the structure order of pure and BHJ thin films based on CNPT and DRPT molecules. The 2D diffraction profiles were shown in Figure 4. Thin films were prepared on a silicon/PEDOT:PSS substrate by spin-coating process, which was exactly the same with device fabrication. In pristine films, CNPT showed semicrystalline properties, and preferentially adopted edge-on orientation with respect to the substrate, indicated from the strong (100) and (010) reflections in the out-of-plane and in-plane directions. The azimuthal angle spreading of (100) peak was quite broad, which indicated the orientation effect was weak. In DRPT pristine thin film, no obvious scatterings were observed in GIWAXS, indicating that as spun film took an amorphous morphology. Thermal annealing under 100 °C for 5 min was used to induce structure order of CNPT and DRPT. After thermal treatment, both CNPT and DRPT showed enhanced crystallinity, showing strong diffraction spots in the 2-D detector. In CNPT, the azimuthal angle of (100) peak strongly reduced and centered in the out-of-plane direction, and thus the edge-on orientation strongly improved. DRPT showed a large array of scattering spots, which were hard to interpretate. In CNPT blends, a broad diffraction halo ring existed at ca. 1.35 Å$^{-1}$ was seen in all cases, which was attributed to scattering from PC$_{71}$BM. Comparing with the pristine films, the crystallization and orientation of both oligomers were not significantly influenced in the presence of PC$_{71}$BM. Using additive, GIWAXS similar to that of annealed CNPT thin film was observed, indicating additive processing could induce structure order of CNPT molecules in blends. The well-structured crystalline solids of CNPT would enhance mobilities and thus enhance the solar
cell performance. DRPT blends showed the PC$_{71}$BM diffraction ring at ca. 1.35 Å$^{-1}$, and no obvious crystallization information could be observed from the molecule. Adding DIO additive into blends did not change the feature of this film. The low crystallinity in this case could be the major reason for its low device performances, showing low $J_{sc}$, FF and PCE.

**Resonant soft X-ray scattering (RSoXS)**

Resonant soft X-ray scattering was carried out to investigate the global phase separation of BHJ blends by taking advantage of the high contrast between conjugated material and fullerenes as well as large sized photons.$^{[19]}$ In RSoXS experiment, the beam energy was tuned to 284.2 eV, which is at the carbon K-edge to enhance the contrast of the PCBM and oligomers. The scattering experiments were carried out in transmission mode. BHJ thin films that used in device fabrication were transferred onto Si$_3$N$_4$ window and mounted onto high vacuum scattering chamber. Typically a few seconds of exposure was used to record signals. Figure 5 showed the RSoXS profiles of oligomer:PC$_{71}$BM blend films. In CNPT:PC$_{71}$BM blends, the film processed without the additive showed a scattering peak located at ca. 0.00087 Å$^{-1}$, corresponding to a 722 nm center-to-center spacing. This size scale of phase separation could be even larger since the peak was not fully developed within the probing length scale of the experiment. After adding DIO, the scattering peak shifted to the high $q$ value at ca. 0.0027 Å$^{-1}$, corresponding to a 230 nm center-to-center spacing. This result indicated that the addition of DIO leads to a reduction in the size of phase separation in CNPT:PC$_{71}$BM blends, together with the increased crystallization of CNPT discussed above, the two factors determined that CNPT:PC$_{71}$BM blends have improved $J_{sc}$ and FF after processed with the additive. In DRPT:PC$_{71}$BM blends, identical RSoXS profiles were observed for both as cast and additive processed thin films. The quick decay of the profile that showed no feature of scattering peak or hump indicated either a homogeneous mixture or super large phase separation far beyond the RSoXS probing ability in these films. This morphology feature plus the observation of weak crystallinity in BHJ blends, cause more exciton recombination, and thus limits the $J_{sc}$ and FF of the devices.

**Conclusions**

In conclusion, we have designed and synthesized two new platinum-acetylide-based small molecules CNPT and DRPT for solution-processable BHJ photovoltaic application. CNPT and DRPT exhibit the maximum absorptions at 579 and 629 nm in the thin film, respectively. And the HOMO and LUMO levels are $-5.4$ and $-3.54$ eV for CNPT, $-5.14$ and $-3.5$ eV for DRPT, respectively. For CNPT:PC$_{71}$BM devices, processing with 0.3 vol% DIO as a solvent additive, $J_{sc}$ and FF of the devices increased obviously while $V_{oc}$ reduced slightly, as a result, the optimal PCE of 1.4% was obtained. This may be due to the increase of crystallization of CNPT and reduction in the size of phase separation of CNPT:PC$_{71}$BM blends. However, DIO additive showed little influence on the crystallization and morphology of the DRPT:PC$_{71}$BM blends.

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**References**


(Zhao, C.)