### Platinum(II)–Bis(aryleneethynylene) Complexes for Solution-Processible Molecular Bulk Heterojunction Solar Cells

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Abstract: Four new solution-processible small-molecular platinum(II)-bis(aryleneethynylene) complexes consisting of benzothiadiazole as the electron acceptor and triphenylamine and/ or thiophene as the electron donor were conveniently synthesized and characterized by physicochemical and computational methods, and utilized as the electron-donor materials in the fabrication of solution-processed bulk heterojunction (BHJ) solar cells. The effect of different electron-donor groups in these small molecules on the optoelectronic and photovoltaic properties was also examined. The optical and time-dependent density functional theory studies showed that the incorporation of stronger electron-donor groups significantly enhanced the solarabsorption abilities of the complexes. These molecular complexes can serve as good electron donors for fabricating BHJ devices by blending them with the [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>70</sub>BM) as the electron accept-

**Keywords:** organic photovoltaics • organic solar cells • platinum • solution processing • synthetic methods • voltammetry or. The best power conversion efficiency of 2.37% was achieved with the open-circuit voltage of 0.83 V, short-circuit current density of 7.10 mA cm<sup>-2</sup> and fill factor of 0.40 under illumination of an AM 1.5 solar-cell simulator. The spin-coated thin films showed pchannel field-effect charge transport with hole mobilities of up to  $2.4 \times$  $10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  for these molecules. The present work illuminates the potential of well-defined organometallic complexes in developing light-harvesting small molecules for efficient power generation in organic photovoltaics implementation.

#### Introduction

Since the first organic photovoltaics (OPVs) by Tang in 1986,<sup>[1]</sup> considerable effort has been devoted to develop photovoltaic device technology, photovoltaic materials, and device architectures to improve the device performance. Bulk heterojunction (BHJ) solar cells comprising a donor–acceptor (D–A) system of electron donating conjugated polymers and electron-withdrawing fullerene derivatives

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- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201102598.

have led to improvements in the power conversion efficiencies (PCEs).<sup>[2]</sup> To date, many fullerene derivatives have been investigated, such as the most commonly used [6,6]phenyl- $C_{61}$ -butyric acid methyl ester (PCBM)<sup>[3]</sup> and the  $C_{70}$ analogue of PCBM, [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>70</sub>BM).<sup>[4]</sup> Moreover, the use of numerous  $\pi$ -conjugated polymers as donor materials, including organic polymers based on phthalocyanines,<sup>[5]</sup> thiophene<sup>[2c,6]</sup> and/or arylacetylenes,<sup>[7]</sup> and metal-containing derivatives such as platinum(II)-polyynes<sup>[8,9]</sup> allows the fabrication of efficient devices. At present, PCE values in excess of 7-8% have been demonstrated based on the polymer-based BHJ solar cell under simulated AM1.5 solar illumination.<sup>[10]</sup> In the case of device fabrication, the primary thin-film preparation methods typically include high-vacuum vapor deposition of thermally stable molecules and the solution processing of soluble organic materials. Solution processing is more cost efficient than vacuum vapor deposition and can also improve the material utilization efficiency, simplify the manufacturing process and reduce the size/cost of the manufacturing apparatus. Although the polymers used in the BHJ solar cells have shown great promise in the improvement of the absorption and film processing abilities, the molecular weight and purification of these polymers are still the most pressing problems to be addressed and can severely influence the reproducibility of the device performance. In particular, the Hagihara-type condensation polymerization usually gives polymers of large molecular weight distribution with polydispersity of >2 and undefined end groups.<sup>[11]</sup> The amorphous nature of these polymers has also generally rendered them with lower charge carrier mobilities.<sup>[9h,12]</sup> Recently, solution-processed small-molecule bulk heterojunction (SMBHJ)<sup>[13]</sup> solar cells have attracted considerable attention because the small molecules and oligomers employed in the devices are easier to synthesize and purify and possess well-defined structures, in contrast to polymeric systems that intrinsically display large structural variations in the molecular weight, polydispersity, and regioregularity. In this new research frontier, PCE values have evolved from <1% to a recent value of about 5%.<sup>[13c]</sup> Li et al. recently reported a star-shaped molecule for SMBHJ with a high PCE of 4.3%,<sup>[14]</sup> whereas an even higher PCE of 5.08% was obtained by Chen and co-workers.<sup>[15]</sup> An impressive PCE of 5.2% has recently been achieved for small-molecule devices using a three-layered p-i-n structure based on solution-processed fabrication.<sup>[16]</sup> Therefore, the judicious design and synthesis of new molecular donor materials to improve the energy conversion efficiency of these devices is still a great challenge. However, to our knowledge, related work using organometallic molecular compounds is very scarce in the literature.

Recently, we and others have demonstrated a number of highly efficient BHJ solar cells based on platinum-containing polyynes.<sup>[9]</sup> Although the charge transport in platinum(II)-acetylides has been demonstrated,<sup>[17]</sup> solutionprocessible organometallic polymer semiconductors possessing donor-acceptor (D-A) architecture and platinum center in the backbone were recently shown to exhibit broad absorption bands due to the intramolecular charge transfer (ICT) between the donor and acceptor units and small bandgaps (even down to near-infrared) suitable for photovoltaic devices.<sup>[9]</sup> The complexation of an electron-rich platinum(II) ion into the conjugated chain was reported to enhance the intrachain charge transport of  $\pi$ -conjugated polymers.<sup>[9]</sup> When the metal is conjugated with an alkyne unit, the d orbitals  $(d_{xy} \text{ and } d_{xz})$  of the Pt atom overlap with the  $\pi$ orbitals ( $\pi_v^*$  and  $\pi_z^*$ ) of the C=C unit, thereby facilitating  $\pi$ -electron delocalization and enhanced solubility in organic solvents (due to the presence of bulky PBu<sub>3</sub> ligands that prevent strong aggregation). However, these polymers often suffer from inconvenient synthesis procedures and purification. Our ultimate goal here is to develop an alternative for these Pt-acetylide polymers simply by using aryleneethynylene ligands to form soluble and tractable symmetric platinum(II)-bis(aryleneethynylene) small molecules. The benzothiadiazole units were introduced as the electron-accepting group to tailor the energy levels of the frontier molecular orbitals for the complexes. Our strategy was to molecularly design and utilize different electron-donating groups based on triphenylamine and/or thiophene moieties to modify the ICT strength of the D-A component. Here, we report the synthesis and characterization of a series of platinum(II)-bis(aryleneethynylene) complexes for SMBHJ solar cells. The synthetic processes are convenient and provide very good yields. All of the products are very easy to

purify by flash column chromatography on silica gel using the appropriate eluent. The photophysical, time-dependent density functional theory (TD-DFT) and cyclic voltammetry (CV) studies of these platinum(II) complexes were conducted, and the photovoltaic properties of these small molecules were investigated by fabricating solution-processed BHJ devices based on the active blends consisting of these complexes as donors and  $PC_{70}BM$  as the acceptor.

#### **Results and Discussion**

Syntheses and chemical characterization: The general synthetic routes for the preparation of the new platinum(II)bis(aryleneethynylene) compounds are illustrated in Scheme 1. The palladium-catalyzed Suzuki<sup>[18]</sup> and Stille<sup>[19]</sup> coupling reactions of 4-bromo-7-(4-hexyl-2-thienyl)-2,1,3benzothiadiazole with N,N-di-p-tolyl-4-aminophenylboronic acid and N,N-di-p-tolyl-4-(5-(tributylstannyl)thiophen-2-yl)benzenamine yielded compounds 1a and 1b, respectively. Bromination of compounds 1a and 1b with N-bromosuccinimide (NBS) gave compounds 2a and 2b, respectively. Compound 2c was obtained from the reaction of 4,7-dibromo-2,1,3-benzothiadiazole with 0.9 equivalents of N,N-di-p-tolyl-4-(5-(tributylstannyl)thiophen-2-yl)benzenamine using the Stille coupling. The trimethylsilyl protected compounds 3a-3d were conveniently synthesized in good yields using the Sonogashira coupling of 2a-2d with trimethylsilylacetylene, respectively.<sup>[20]</sup> After desilylation with K<sub>2</sub>CO<sub>3</sub> in a mixture of MeOH/CH2Cl2, compounds L1-L4 were obtained and then reacted with trans-[PtCl<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub>] in a CH<sub>2</sub>Cl<sub>2</sub>/NEt<sub>3</sub> mixture and in the presence of a catalytic amount of CuI at room temperature to afford the platinum(II)-bis(aryleneethynylene) compounds PT1-PT4 in good synthetic yields (Scheme 1).

These platinum(II) compounds were purified by chromatography on silica gel, and fully characterized by UV/Vis, FTIR, and <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy. The resonance peaks observed at 3.46–3.51 ppm for the platinum(II) complexes in the <sup>31</sup>P {<sup>1</sup>H} NMR spectra indicate a *trans* geometry of the square-planar Pt(PBu<sub>3</sub>)<sub>2</sub>(C=C-)<sub>2</sub> component. The <sup>1</sup>J<sub>P.Pt</sub> values of 2321–2341 Hz for the PBu<sub>3</sub> moieties are typical of those for related *trans*-PtP<sub>2</sub> systems. The FTIR spectra of the ethynyl ligands and platinum(II) complexes show  $v_{(C=C)}$  absorption bands at 2078–2153 cm<sup>-1</sup>, and the terminal acetylenic C=C-H stretching vibrations occur at 3276– 3292 cm<sup>-1</sup> for L1–L4.

The solid-state structure of **PT4** was also determined by single-crystal X-ray diffraction analysis. Selected bond lengths and angles are summarized in Table S1 in the Supporting Information. The ORTEP drawing of **PT4** is depicted in Figure 1, and two halves of the molecule are related by a center of symmetry at the central metal atom. The coordination geometry of the Pt center is square planar with two PBu<sub>3</sub> groups and two ethynyl ligands in a *trans* arrangement. The tricyclic push–pull di(thienyl)benzothiadiazole unit is almost coplanar with dihedral angles of 8.9 and 17.8°





Scheme 1. Synthetic routes to the platinum(II)-bis(aryleneethynylene) compounds.



Figure 1. ORTEP drawing of **PT4** with the atom-labeling scheme, showing 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

between the thiophene rings and benzothiadiazole unit, and 12.7° between the two thiophene rings, hence leading to improved absorption. Although the steric requirements of the PBu<sub>3</sub> groups on the Pt atom prevent close packing of the individual molecules in the unit cell, there exists an intermo-

lecular  $\pi$ -stacking interaction between the edge thiophene rings and the thiadiazole rings with the centroid-centroid distance of 3.543 Å (Figure S1, Supporting Information). These structural features of **PT4** should be beneficial for enhancing the absorption and charge transport of the material.

**Optical properties**: The photophysical properties of the new ethynyl ligands and their corresponding platinum(II) complexes were investigated by UV/Vis and photoluminescence (PL) spectroscopy in dichloromethane at 293 K. The photophysical data are collected in Table 1. Figure 2 shows the UV/Vis spectra and normalized PL spectra of **PT1–PT4** in dichloromethane at 293 K. Compounds **L1–L4** and **PT1–PT4** showed two or three broad and structureless absorption bands in the range of 300–700 nm. The absorption bands at short wavelengths centered at 307–382 nm are ascribed to the  $\pi \rightarrow \pi^*$  transitions of the aryleneethynylene segment.

Table 1. Photophysical data for compounds L1-L4 and PT1-PT4 in dichloromethane at 293 K.

	Absorption	Emission			
	$\lambda_{\rm abs}  [{\rm nm}]  (\epsilon  [10^4 {\rm M}^{-1} {\rm cm}^{-1}])$	$\lambda_{em} [nm]$	$arPsi_{ m F}[\%]^{[a]}$	$\tau_{\rm F}  [{\rm ns}]$	
PT1	315 (5.78), 366 (6.14), 526 (5.52)	665	2.79	4.40	
PT2	307 (4.85), 382 (8.77), 561 (7.51)	697	1.47	1.23	
PT3	310 (5.13), 367 (6.47), 524 (6.97)	656	0.76	4.07	
PT4	318 (3.53), 364 (5.13), 518 (4.88)	649	1.09	0.91	

[a] Quantum yields were measured with an excitation wavelength of 488 nm using Rhodamine 6G in ethanol as the reference ( $\Phi_{\rm F}$ =0.95).



Figure 2. a) UV/Vis absorption spectra and b) normalized photoluminescence spectra of **PT1-PT4** in dichloromethane at 293 K.

The low-energy broad absorption bands centered at 483– 561 nm can be assigned to the ICT transition from the triphenylamine and/or thiophene donating groups to the benzothiadiazole withdrawing unit. Compared to the free ethynyl ligands, there is a slight redshift (ca. 31–63 nm) in the long-wavelength absorption peak for their corresponding platinum(II) compounds.

Commonly, a stronger electron-donating strength can result in a higher degree of electronic delocalization and hence a stronger ICT in the molecular donor materials. Compared to **PT4**, each of the compounds **PT1–PT3** showed a significant redshift and enhancement of the absorption intensities for the ICT transition, which is due to the stronger electron-donating ability of triphenylamine unit in these small molecules. In the cases of **PT1** and **PT3**, which have almost the same  $\pi$ -conjugated length of the molecular structure, compound **PT3** showed a significantly higher molar absorption coefficient (69700  $M^{-1}$  cm<sup>-1</sup> at 524 nm) than **PT1** (55200  $M^{-1}$  cm<sup>-1</sup> at 526 nm). It may be -FULL PAPER

caused by the addition of a long alkyl chain on the thiophene ring, which would result in a less coplanar configuration for the aromatic rings, making it less conjugated in **PT1** than **PT3**.<sup>[21]</sup> Among these platinum(II) compounds, **PT2** exhibits the strongest and broadest ICT transition. The highest molar absorption coefficient  $(75100 \,\mathrm{m^{-1}\,cm^{-1}}$  at 561 nm) was obtained for compound **PT2**, which could be explained by the stronger electron-donating ability of the D groups and longer  $\pi$ -conjugation length of **PT2**. The optical band gaps  $(E_{g,opt})$  of **PT1–PT4** are in the range of 1.93–2.11 eV (Table 2). As expected, **PT2**, with the strongest ICT interaction, has the lowest  $E_{g,opt}$  (1.93 eV), which is lower than that of **PT1** (2.06 eV), **PT3** (2.09 eV), and **PT4** (2.11 eV).

Table 2. Electrochemical data and hole-carrier mobilities of PT1-PT4.

	$E_{\text{Ox}}^{\text{onset}}$ [V]	HOMO [eV] <sup>[a]</sup>	$E_{ m Red}^{ m onset}$ [V]	LUMO [eV] <sup>[b]</sup>	$E_{\rm g,ec}$ $[\rm eV]^{[c]}$	$E_{\rm g,opt}$ [eV] <sup>[d]</sup>	$\mu \ [cm^2V^{-1}s^{-1}]$
PT1	0.42	-5.10	-1.68	-3.00	2.10	2.06	$0.7 \times 10^{-4}$
PT2	0.35	-5.03	-1.55	-3.13	1.90	1.93	$2.4 \times 10^{-4}$
РТ3	0.39	-5.07	-1.72	-2.96	2.11	2.09	$1.2 \times 10^{-5}$
PT4	0.53	-5.21	-1.60	-3.08	2.13	2.11	[e]

[a] Calculated from  $E_{\rm HOMO} = -(E_{\rm Ox}^{\rm onset} + 4.68)$  eV. [b] Calculated from  $E_{\rm LUMO} = -(E_{\rm Red}^{\rm onset} + 4.68)$  eV. [c] Electrochemical band gap was obtained from -(HOMO-LUMO). [d] Optical band gap was determined from onset of absorption in dichloromethane. [e] Field effects were not observed.

All of the platinum(II) bis(aryleneethynylene) compounds are photoluminescent in dichloromethane at 293 K (Table 1 and Figure 2b). Compounds **PT1–PT4** display red emission peaks with maxima at 665, 697, 656, and 649 nm, respectively, and their respective emission lifetimes are 4.4, 1.23, 4.07 and 0.91 ns, indicative of their fluorescent origin. Triplet emissions were not observed, which is in accordance with the energy gap law for low bandgap Pt-containing ethynylenic conjugated polymers and monomers.<sup>[22]</sup>

Electrochemical properties: To calculate the oxidation and reduction potentials and evaluate the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of these complexes, cyclic voltammetry (CV) was performed in the THF containing  $[Bu_4N]PF_6$  (0.1 M) with a platinum working electrode, Pt wire counter electrode, and a Ag/AgCl reference electrode under N<sub>2</sub> atmosphere. The potential measured was referenced to the half-wave potential of the ferrocenium/ferrocene couple  $(E_{1/2}=0.12 \text{ V in } [Bu_4N]PF_6 (0.1 \text{ M})$  in THF), which has an absolute energy level of -4.8 eV relative to the vacuum level for calibration.<sup>[23]</sup> So, the onset oxidation  $(E_{\text{Ox}}^{\text{onset}})$  and reduction  $(E_{\text{Red}}^{\text{onset}})$  potentials were used to determine the HOMO and LUMO energy levels using the equa- $E_{\rm HOMO} = -(E_{\rm Ox}^{\rm onset} + 4.68) \, {\rm eV}$ tions and  $E_{\rm LUMO} =$  $-(E_{Red}^{onset}+4.68)$  eV, in which the unit of potential is V versus Ag/AgCl. The difference between the oxidation and reduction potentials gives access to the so-called electrochemical band gap  $(E_{g,ec})$ . The results of the electrochemical measurements and calculated energy levels of PT1-PT4 are listed in Table 2 and the CV curves are shown in Figure 3. Com-

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Figure 3. Cyclic voltammograms of **PT1–PT4** in THF containing  $[Bu_4N]PF_6 (0.1 \text{ M})$  at a scan rate of 100 mVs<sup>-1</sup>.

pounds **PT1–PT4** have their LUMO level at around -3.00 eV which is higher than the PC<sub>70</sub>BM level (-4.3 eV),<sup>[24]</sup> making the photoinduced ICT and charge separation possible at the interface between the donor and acceptor (vide infra). Compared with **PT4** ( $E_{\text{HOMO}} = -5.21 \text{ eV}$ ), the HOMO energy levels of **PT1** (-5.10 eV), **PT2** (-5.03 eV) and **PT3** (-5.07 eV) are significantly increased, due to the enhancement of the electron donating abilities of these compounds with the stronger donating triphenylamine group in the structure. The  $E_{\text{g.ec}}$  order of **PT4** (2.13 eV) > **PT3** (2.11 eV) > **PT1** (2.10 eV) > **PT2** (1.90 eV) is consistent with the increase in the  $\pi$ -conjugated strength of **PT1–PT4**. The  $E_{\text{g.ec}}$  values are in good agreement with the optical band gaps ( $E_{\text{g.opt}}$ ) for these four platinum(II)-based small molecules.

**Theoretical studies:** Density functional theory (DFT) calculations were carried out for **PT1–PT4** to gain better insight into the electronic and spectroscopic properties as well as the nature of absorption bands for these platinum(II) complexes. On the basis of the ground-state optimized geometry,

50 singlet excited states for PT3 and PT4, and 60 singlet excited states for PT1 and PT2 were calculated at the PBE1PBE/ LANL2DZ (Pt), 6-31G(d, p) (all other atoms) level with the TD-DFT approach. The relative compositions of the different energy levels in terms of the composing fragments and the absorption transition characters are summarized in Tables S2-S5 (Supporting Information). The energy and electron density diagrams of important frontier molecular orbitals for PT1-PT4 are depicted in Figure 4.

Complexes **PT1–PT4** display similar frontier orbital features.

The HOMOs of these four complexes are mainly delocalized over the organic aryleneethynylene ligands, with minor contribution from the d orbitals of Pt (8, 8, 10 and 12% for **PT1–PT4**, respectively), whereas the HOMO–1 orbitals are primarily contributed from the electron-donating triphenylamine (61, 44 and 69% for **PT1–PT3**, respectively) and/or thiophene (16, 33, 18 and 51% for **PT1–PT4**, respectively) groups. Their LUMOs and LUMO+1 orbitals have amplitudes mostly on the electron-accepting benzothiadiazole unit, in which the benzothiadiazole character accounts for about 76–84% of the contribution.

As indicated in Tables S2-S5, the calculated lowest energy absorption (from the HOMO→LUMO (72-87%) and HOMO-1 $\rightarrow$ LUMO+1 (8-27%) transitions) can be primarily assigned as the ICT transitions from the electrondonating thiophene and/or triphenylamine group to the electron-accepting benzothiadiazole unit. The contribution of the electron-donating groups to the HOMOs displays the order of PT2 (65%)>PT1 (63%)>PT3 (59%)>PT4 (46%), which indicates that introduction of the strong triphenylamine donor and/or enhancement of the  $\pi$ -conjugation strength leads to an increase in the absorbance for the ICT transition. The calculated absorption peaks at 371 nm for PT1, 399 nm for PT2, 390 nm for PT3 and 365 nm for **PT4** from the HOMO $\rightarrow$ LUMO+2 and HOMO-1 $\rightarrow$ LUMO+3 transitions result from the  $\pi \rightarrow \pi^*$  transitions of the aryleneethynylene ligands, which are in reasonable agreement with the experimentally measured absorption data (366 nm for PT1, 382 nm for PT2, 367 nm for PT3 and 364 nm for PT4). The absorption peak at the shorter wavelength at 312 nm, 307 nm and 306 nm for PT1-PT3, respectively, corresponds to the  $\pi \rightarrow \pi^*$  transition of the aryleneethynylene ligands, although the transitions from the aryleneethynylene ligands to the Pt(PBu<sub>3</sub>)<sub>2</sub> unit (45%) were observed in PT4 at 322 nm. The main absorption energies for each complex from the TD-DFT calculations agree well with the experimental values. The TD-DFT calculations suggest that addition of the triphenylamine and/or thiophene



es. Figure 4. Selected frontier molecular orbitals of PT1-PT4.

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groups can increase the HOMO and HOMO-1 energy levels [HOMO: **PT2** (-4.699 eV>**PT3** (-4.730 eV)>**PT1** (-4.753 eV)>**PT4** (-4.933 eV); HOMO-1: **PT2** (-4.799 eV)>**PT1** (-4.858 eV)>**PT3** (-4.886 eV)>**PT4** (-5.104 eV)], resulting in the enhancement of the absorption ability of the corresponding compound by reducing the energy gap for the HOMO/HOMO-1 $\rightarrow$ LUMO+*n* transitions.

Performance of BHJ solar cells: To demonstrate the potential of these platinum(II)-bis(aryleneethynylene) molecular species as electron-donor materials in photovoltaic applications, BHJ devices were fabricated using PC70BM as the acceptor in a structure of ITO/PEDOT:PSS/active layer/LiF/ (PEDOT:PSS = poly(3,4-ethylene-dioxythiophene):po-Al ly(styrene sulfonate)). The active layers were prepared by spin-coating compounds PT1-PT4 and PC70BM in chlorobenzene with a weight ratio of 1:4. The surface of the active area was 0.12 cm<sup>2</sup>. The devices were characterized in the dark and under white-light illumination (solar simulator AM 1.5, 100 mW cm<sup>-2</sup>). Since the active-layer thickness had an influence on the performance of the photovoltaic devices, the optimized active layer thickness was 80 nm for PT1 and PT2, 45 nm for PT3, and 60 nm for PT4. It was shown that both thinner and thicker active layers resulted in lower PCEs, due to the fact that a very thin active layer reduces the absorption of the irradiated light, and, on the other hand, a very thick active layer slows down the charge transport in the active layer of the solar cells.

The photovoltaic characteristics of the various devices are summarized in Table 3. The current density versus voltage (J-V) curves of the BHJ devices based on **PT1– PT4**:PC<sub>70</sub>BM (1:4, w/w) blends with different active layer thicknesses are plotted in Figure 5 and Figures S4–S6 (Supporting Information). The devices based on **PT4**, which exhibited the shortest  $\pi$ -conjugated system, showed a minimum PCE of 0.54%, an open-circuit photovoltage ( $V_{oc}$ ) of 0.86 V, a short-circuit photocurrent density ( $J_{sc}$ ) of 2.44 mA cm<sup>-2</sup>, and a fill factor (FF) of 0.26 with the active layer thickness of 60 nm. The photovoltaic performance can

Table 3. Device performance of the BHJ devices based on **PT1–PT4**:PC<sub>70</sub>BM=1:4 (w/w). The data represent an average from 12 to 16 devices.

Donor	Film thick- ness [nm]	$V_{\rm oc}$ [V]	$J_{\rm sc}$ [mA cm <sup>-2</sup> ]	FF	PCE [%]
PT1	100	0.83	6.34	0.40	2.08
	80	0.83	7.10	0.40	2.37
	45	0.80	4.40	0.43	1.52
PT2	100	0.80	5.87	0.38	1.77
	80	0.80	7.15	0.41	2.34
	50	0.73	4.76	0.41	1.42
PT3	90	0.82	3.64	0.36	1.08
	75	0.82	4.29	0.38	1.32
	45	0.81	4.99	0.36	1.45
PT4	80	0.85	2.30	0.22	0.42
	60	0.86	2.44	0.26	0.54
	40	0.64	2.59	0.27	0.45



Figure 5. Current-density-voltage (J-V) curves of the photovoltaic devices based on **PT1** with different active layer thicknesses under AM 1.5 simulated solar illumination at 100 mW cm<sup>-2</sup>.

be significantly improved by introducing a strong donor group in the molecules. The devices based on PT3, which has a strong triphenylamine donor group, showed a better performance with comparable  $V_{\rm oc}$  of 0.81 V, higher  $J_{\rm sc}$  of 4.99 mA cm<sup>-2</sup>, higher FF of 0.36 and higher PCE of 1.45 % with an active layer thickness of 45 nm. The higher  $J_{sc}$  of the device based on PT3 may plausibly be caused by the stronger ICT interaction between the electron-donating triphenylamine unit and the electron-accepting benzothiadiazole unit in PT3, which leads to more efficient absorption of the solar spectrum. PT1- and PT2-based devices showed the best overall performances, in which high  $J_{sc}$  values of  $7.10 \text{ mA cm}^{-2}$  and  $7.15 \text{ mA cm}^{-2}$ , respectively, were obtained. Combined with the  $V_{\rm oc} = 0.83$  V and FF = 0.40 for **PT1**, and  $V_{\rm oc} = 0.80$  V and FF = 0.41 for **PT2**, the PCE up to 2.37 % and 2.34% were secured in the photovoltaic devices based on PT1 and PT2, respectively, even without the post thermal annealing step.

The charge-carrier mobility is an essential property for efficient photovoltaic devices, which is one of the important factors that affect the  $J_{sc}$  of the devices.<sup>[25]</sup> In order to ensure effective charge carrier transport to the electrodes and reduce the photocurrent loss in solar cells by recombination, a high hole mobility is required for the electron donor. The hole mobilities of these platinum(II) compounds were studied using organic field-effect transistors (OFETs). The mobilities calculated at  $V_{\rm DS} = -100 \,\text{V}$  of **PT1-PT4** are given in Table 2. Although field-effect mobility was not detected for PT4 due to its low charge carrier mobility, typical p-type characteristics were observed for PT1-PT3 (Figure S8). The field-effect hole mobilities of  $0.7 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ,  $2.4 \times$  $10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  and  $1.2 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  were observed in OFETs based on PT1-PT3, respectively, which are consistent with the notion that charge mobility is dependent on the molecular packing and film morphology. The hole mobility of PT3 is significantly lower than that of PT1 and PT2, which is consistent with the relatively low  $J_{sc}$  of the photovoltaic device based on PT3. In addition, the mobility of the active material was also shown to exert a great influence on the FF of the photovoltaic device.<sup>[6c]</sup> The FF of the photovoltaic devices based on **PT1–PT4** were not very impressive, partly due to the low hole mobilities of **PT1–PT4** and their poor charge mobility balance.

Because the photoconversion efficiencies are also greatly influenced by the active layer thin film morphologies, we investigated the morphology of the **PT1–PT4**/PC<sub>70</sub>BM blend films by atomic force microscopy (AFM) techniques (see Figure S3, Supporting Information). The surfaces of these four blend films are quite smooth, with very similar rootmean-square (rms) values of 0.289, 0.305, 0.314 and 0.244 nm for **PT1**/PC<sub>70</sub>BM, **PT2**/PC<sub>70</sub>BM, **PT3**/PC<sub>70</sub>BM, and **PT4**/PC<sub>70</sub>BM, respectively. The morphological similarity between the AFM images of **PT1–PT4** and PC<sub>70</sub>BM blend films implies that the observed PCE difference in the photovoltaic devices based on **PT1–PT4** may be ascribed to variations on the electronic structure, HOMO–LUMO energies and, most importantly, the absorption properties of **PT1– PT4**.

These photovoltaic devices showed similar  $V_{\rm oc}$  values of around 0.80 V, except that the  $V_{\rm oc}$  became slightly lower in the case of PT2 and PT4 based devices when a thinner active layer was employed. This is probably because the  $V_{
m oc}$ value mostly depends on the HOMO energy level of the complexes, and it can also be modified by other parameters such as processing conditions, resistance related to the thickness of the active layer, the degree of phase separation between components in the blend, and so forth. As shown in Table 3, the  $J_{sc}$  values for these devices range from 2.30 to 7.15 mA cm<sup>-2</sup>, as a result of the differences in the spectral overlap between the absorption of the active material and the solar spectrum, the absorption strength, and the charge transport properties of the active layer. The influence of the absorption properties of the active layer was confirmed by comparing the incident photon-to-current conversion efficiency (IPCE) spectrum of the photovoltaic devices based on PT1-PT4 (Figure 6). High IPCE values of 49.3% and 45.1% at 474 nm were achieved for PT1- and PT2-based devices, respectively, but the PT2-based device exhibited a slightly broader curve than the PT1-based device. So, the device based on **PT2** showed a slightly higher  $J_{sc}$  value than



Figure 6. IPCE spectra of the photovoltaic devices based on **PT1–PT4**:PC<sub>70</sub>BM=1:4 (w/w) under monochromatic AM1.5 solar illumination.

the device based on **PT1**. The IPCE values of 33.3% at 463 nm and 17.8% at 477 nm were obtained for **PT3** and **PT4** based devices, respectively, which resulted in the lower  $J_{sc}$  values of the devices based on **PT3** and **PT4** than the devices fabricated from **PT1** and **PT2**.

#### Conclusion

A new series of multichromophoric small molecular systems of platinum(II)-bis(aryleneethynylene) compounds containing triphenylamine and/or thiophene as the donor and benzothiadiazole as the acceptor were designed and obtained by straightforward synthesis and purification procedures with reasonably good yields. These metal complexes were fully characterized by spectroscopic and TD-DFT techniques. As demonstrated by the absorption spectral studies, the increase in the electron-donating strength in such a push-pull conjugated system resulted in the broadening and the enhancement of the ICT transition. Using the platinum groups as exciton confinement centers, we can easily extend the absorption into the long-wavelength range beyond 600 nm by introducing ICT chromophores. In addition, the TD-DFT calculations indicated that the LUMOs are highly localized on the benzothiadiazole units and the HOMOs are mainly delocalized over the aryleneethynylene moieties, and these further confirm that the absorption ability can be reasonably enhanced by reducing the energy gap for the HOMO→LUMO transition using a stronger electron donor. Although high PCE values of 2.37 and 2.34% and IPCE values of 49.3 and 45.1% at 474 nm were achieved for PT1and PT2-based solar cells, respectively, under illumination of an AM 1.5 solar-cell simulator in a 1:4 (PT1/ PT2:PC<sub>70</sub>BM) blend ratio with the active layer thickness of 80 nm, these results correlate well with the absorption intensity of the ICT band. Hence, this innovative class of solution processible platinum(II)-bis(aryleneethynylene) based small molecules and other related compounds have great potential to excel in realizing highly efficient BHJ devices without the molecular weight problem common for the corresponding polymers, and further improvement in the device efficiency could be achieved by tuning the ICT absorption and energy levels of this type of material as well as the oligomeric chain length and thin film morphology.

#### **Experimental Section**

**Materials and reagents**: All of the manipulations were performed under a dry nitrogen atmosphere by using Schlenk techniques. Solvents were dried by standard methods and distilled prior to use except for those of spectroscopic grade for the spectroscopic measurements. *Trans*-[PtCl<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub>] was synthesized by a literature method.<sup>[26]</sup> The syntheses of all of the organic precursors are given in the Supporting Information. **Physical measurements**: Fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT SSQ710 system. NMR spectra were measured in CDCl<sub>3</sub> or [D<sub>6</sub>]DMSO on a Bruker AM400 MHz FT-NMR spectrometer, and the chemical shifts are quoted relative to tetramethyl-

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silane for <sup>1</sup>H and <sup>13</sup>C and an 85% H<sub>3</sub>PO<sub>4</sub> external reference for <sup>31</sup>P. UV/ Vis spectra were obtained on an HP-8453 diode array spectrophotometer. Cyclic voltammograms were measured on a CHI model 600D electrochemistry station in THF containing 0.1 M [Bu<sub>4</sub>N]PF<sub>6</sub> as the supporting electrolyte. A conventional three-electrode configuration consisting of a platinum working electrode, a Pt-wire counter electrode and a Ag/AgCl reference electrode was used. All of the potentials reported are quoted with reference to the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) couple at a scan rate of 100 mV s<sup>-1</sup>.

X-ray crystallography: X-ray diffraction data were collected at 293 K using graphite monochromated  $Mo_{K\alpha}$  radiation ( $\lambda\!=\!0.71073\; \text{\AA})$  on a Bruker Axs SMART 1000 CCD diffractometer. The collected frames were processed with the software SAINT+[27] and an absorption correction (SADABS)<sup>[28]</sup> was applied to the collected reflections. The structure was solved by direct methods (SHELXTL)<sup>[29]</sup> in conjunction with standard difference Fourier techniques and subsequently refined by fullmatrix least-squares analyses on  $F^2$ . Hydrogen atoms were generated in their idealized positions and all of the non-hydrogen atoms were refined anisotropically. CCDC-833362 (PT4) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Crystal data for **PT4**:  $C_{56}H_{68}N_4P_2S_6Pt M_w = 1246.58$ , triclinic, space group  $P\bar{1}$ , a=10.2319(3), b=10.5176(3), c=13.7347(4) Å,  $\alpha = 92.897(2), \beta = 98.372(2), \gamma = 96.858(2)^{\circ}, V = 1448.37(7) \text{ Å}^3, Z = 1,$  $\rho_{\text{calcd}} = 1.429 \text{ mg m}^{-3}, \ \mu(\text{Mo}_{\text{K}\alpha}) = 2.733 \text{ mm}^{-1}, \ F(000) = 636. \ 25502 \text{ reflec-}$ tions measured, of which 5101 were unique ( $R_{int} = 0.0400$ ). Final  $R_1 =$ 0.0367 and  $wR_2 = 0.0948$  for 4816 observed reflections with  $I > 2\sigma(I)$ .

**DFT and TD-DFT computational methods**: All of the calculations were performed using the Gaussian 03 program package.<sup>[30]</sup> The DFT method at the gradient-corrected correlation functional level PBE1PBE<sup>[31]</sup> was used to optimize the ground-state geometries of **PT1-PT4**. The PBE1PBE functional gave the best results in the simulations of the UV/ Vis properties by comparison of different functionals (B3LYP, BHandH-LYP and MPWB1K). On the basis of the ground-state optimized geometries, 50 singlet excited states for **PT3** and **PT4**, and 60 singlet excited states for **PT1** and **PT2** were calculated to determine the vertical excitation energies using the TD-DFT method at the PBE1PBE level. The LAN2DZ effective core potential basis set was applied for Pt atoms and 6-31G(d, p) for other atoms.

Fabrication and characterization of bulk heterojunction solar cells: The device structure was ITO/PEDOT:PSS/active layer/LiF/Al, in which the active layer is a blend film of the platinum(II)-bis(aryleneethynylene) small molecule as the electron donor and PC70BM as the electron acceptor in a weight ratio of 1:4 (w/w). Indium tin oxide (ITO) glass substrates (10  $\Omega$  per square) were cleaned by sonication in toluene, acetone, ethanol, and deionized water, dried in an oven, and then cleaned with UV ozone for 300 s. PEDOT:PSS (Baytron P AI 4083) was spin-coated onto the pre-cleaned ITO substrate to form a 40 nm-thick layer, followed by drying at 120°C for 30 min in air. Then, the substrates were transferred to a glove box filled with nitrogen. The prepared solution containing a mixture of PT1-PT4:PC70BM (1:4, by weight ratio) in chlorobenzene was spin-coated on top of the PEDOT:PSS layer. Finally, the samples were transferred into an evaporator where 1 nm of LiF and 80 nm of Al were thermally deposited under vacuum at 10<sup>-6</sup> Torr. The effective area was 0.12 cm<sup>2</sup>. The devices were encapsulated in the glove box and measured in air.

Current-voltage characteristics were measured using a computer controlled Keithley 236 source meter. The photocurrent was measured under AM 1.5G illumination at 100 mW cm<sup>-2</sup> from a solar simulator (Oriel, 91160 A-1000). The EQE was measured at a chopping frequency of 275 Hz with a lock-in amplifier (Stanford, SR830) during illumination with the monochromatic light from a xenon lamp. The AFM measurements were performed on a SPA300HV instrument with an SPI3800 controller (Seiko Instruments). The images were taken with the tapping mode.

**Fabrication and characterization of organic field-effect transistors** (**OFETs**): Silicon wafers (n-type) with a thermal oxide layer (500 nm) were used as the substrates. The 5 nm chromium (as an adhesion layer) and 40 nm gold films were evaporated on the surface of  $SiO_2$  through a shadow mask as source and drain electrodes. The channel width (W) and length (L) were 2.0 mm and 0.1 mm, respectively. Organic semiconductors were dissolved in toluene with a concentration of 10 mgmL<sup>-1</sup>. The solutions were stirred for 12 h at 60 °C and then spin-coated onto the substrates, followed by thermal annealing (60 °C) process in a glovebox filled with high purity N<sub>2</sub>.

The OFETs were characterized in the glovebox with a semiconductor parameter analyzer (Agilent 4156C). For transfer characteristics  $(I_D \approx V_G)$ , the channel current  $(I_D)$  between the source and drain was measured as a function of gate voltage  $(V_G)$  under a constant drain voltage. For output characteristics  $(I_D \approx V_{DS})$ , the channel current  $(I_D)$  was measured as a function of drain voltage  $(V_{DS})$  under a constant gate voltage  $(V_G)$  and different  $V_G$  values resulted in different curves for  $I_D$  versus  $V_{DS}$ . The field effect mobility of each transistor was calculated in the saturation regime  $(V_{DS} = -100 \text{ V})$  by plotting the square root of channel current  $(I_D)$  versus the gate voltage  $(V_G)$  and fitting the curve by Equation(1), in which  $C_i$  is the capacitance of the gate oxide with a unit area.

$$\mu = \frac{2L}{WC_i} \left(\frac{\mathrm{d}\sqrt{I_D}}{\mathrm{d}V_G}\right)^2 \tag{1}$$

General procedure for the synthesis of platinum(II) complexes: Under a N<sub>2</sub> atmosphere, each of the appropriate ethynyl ligands (L1–L4) and *trans*-[PtCl<sub>2</sub>(PBu<sub>3</sub>)<sub>2</sub>] (0.49 equiv) were added to a mixture of Et<sub>3</sub>N and CH<sub>2</sub>Cl<sub>2</sub> (1:1, v/v) in the presence of a catalytic amount of CuI (10 mol%). The reaction mixture was stirred at room temperature overnight. The solvent was then removed under reduced pressure to obtain the crude product. The mixture was purified by chromatography over a silica column using the appropriate eluent to produce a pure sample of **PT1–PT4** in high yields (84–88%) after evaporation of the solvent and drying in vacuo.

**Compound PT1:** Yield: 87%; dark red solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =7.94 (s, 2H, Ar), 7.84–7.81 (m, 4H, Ar), 7.09–7.07 (m, 2H, Ar), 7.63–7.61 (m, 2H, Ar), 7.15–7.12 (m, 4H, Ar), 7.09–7.06 (m, 16H, Ar), 2.76–2.72 (m, 4H, alkyl), 2.32 (s, 12H, Me), 2.20–2.16 (m, 12H, alkyl), 1.73–1.69 (m, 4H, alkyl), 1.64–1.60 (m, 12H, alkyl), 1.57–1.49 (m, 12H, alkyl), 1.42–1.34 (m, 12H, alkyl), 0.99–0.95 (m, 18H, alkyl), 0.92–0.88 ppm (m, 6H, alkyl); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =154.09, 152.91, 148.27, 145.00, 143.41, 134.42, 132.99, 131.35, 130.00, 129.67, 128.86, 127.24, 126.02, 125.12, 124.81, 123.32, 121.76, 119.82 (Ar), 101.38, 77.28 (C=C), 32.01, 30.66, 29.96, 29.51, 26.48, 24.43, 23.80, 22.81, 20.92, 14.24, 14.03 ppm (alkyl); <sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>):  $\delta$ =3.50 ppm (J<sub>P-P1</sub> = 2341 Hz); IR (KBr):  $\tilde{\nu}$ =2080 cm<sup>-1</sup> (w, v(C=C)); FAB-MS: *m*/z: 1793.1 [*M*]<sup>+</sup>; elemental analysis calcd (%) for C<sub>100</sub>H<sub>122</sub>N<sub>6</sub>P<sub>2</sub>PtS<sub>4</sub>: C 66.97, H 6.86, N 4.69; found: C 67.10, H 6.64, N 4.78.

**Compound PT2:** Yield: 85 %; purple solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =8.08–8.07 (m, 2H, Ar), 7.94 (s, 2H, Ar), 7.81–7.79 (m, 2H, Ar), 7.73–7.71 (m, 2H, Ar), 7.53–7.51 (m, 4H, Ar), 7.29–7.28 (m, 2H, Ar), 7.10–7.02 (m, 20H, Ar), 2.76–2.72 (m, 4H, alkyl), 2.32 (s, 12H, Me), 2.20–2.17 (m, 12H, alkyl), 1.73–1.69 (m, 4H, alkyl), 1.67–1.59 (m, 12H, alkyl), 1.54–1.49 (m, 12 H, alkyl), 1.42–1.35 (m, 12 H, alkyl), 0.99–0.95 (m, 18 H, alkyl), 0.92–0.89 ppm (m, 6H, alkyl); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ = 152.68, 147.93, 145.32, 144.95, 143.53, 137.86, 134.34, 132.93, 129.99, 129.05, 128.35, 127.21, 126.78, 126.47, 126.00, 125.33, 124.88, 124.54, 122.96, 122.28 (Ar), 101.49, 100.00 (C=C), 32.01, 30.65, 29.95, 29.51, 26.47, 24.43, 23.80, 22.81, 20.91, 14.23, 14.03 ppm (alkyl); <sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>):  $\delta$ =3.51 ppm ( $J_{P-Pt}$ =2335 Hz); IR (KBr):  $\bar{\nu}$ = 2078 cm<sup>-1</sup> (w, v(C=C)); FAB-MS: *m*/z: 1956.7 [*M*]\*; elemental analysis calcd (%) for C<sub>108</sub>H<sub>126</sub>N<sub>6</sub>P<sub>2</sub>PtS<sub>6</sub>: C 66.26, H 6.49, N 4.29; found: C 66.37, H 6.65, N 4.34.

**Compound PT3**: Yield: 84%; dark red solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =8.07-8.05 (m, 2H, Ar), 7.74-7.72 (m, 2H, Ar), 7.52-7.50 (m, 4H, Ar), 7.48-7.46 (m, 2H, Ar), 7.29-7.27 (m, 2H, Ar), 7.09-7.06 (m, 8H, Ar), 7.04-7.01 (m, 12H, Ar), 2.36-2.33 (m, 12H, Bu), 2.32 (s, 12H, Me), 1.69-1.66 (m, 12H, Bu), 1.49-1.44 (m, 12H, Bu), 0.93-0.87 ppm (m, 18H, Bu); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =156.81, 152.22, 147.85, 144.99, 144.82, 138.34, 132.89, 130.14, 130.00, 127.93, 127.37, 126.44,

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125.56, 124.87, 124.05, 122.96, 122.36, 120.89 (Ar), 106.83, 77.30 (C=C), 26.50, 24.46, 23.81, 20.92, 13.97 ppm (alkyl); <sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>):  $\delta = 3.46$  ppm ( $J_{P-Pt} = 2322$  Hz); IR (KBr):  $\tilde{v} = 2078$  cm<sup>-1</sup> (w, v(C= C)); FAB-MS: m/z: 1624.7 [M]<sup>+</sup>; elemental analysis calcd (%) for C88H98N6P2PtS4: C 65.04, H 6.08, N 5.17; found: C 65.18, H 6.13, N 5.32. Compound PT4: Yield: 88%; dark red solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.09-8.07$  (m, 2H, Ar), 8.00–7.99 (m, 2H, Ar), 7.81–7.19 (m, 2H, Ar), 7.73-7.71 (m, 2H, Ar), 7.43-7.42 (m, 2H, Ar), 7.20-7.18 (m, 2H, Ar), 6.95-6.94 (m, 2H, Ar), 2.20-2.14 (m, 12H, Bu), 1.66-1.62 (m, 12H, Bu), 1.55-1.50 (m, 12H, Bu), 1.01-0.97 ppm (m, 18H, Bu); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 152.69$ , 152.57, 139.61, 135.94, 131.48, 128.61, 128.00, 127.89, 127.17, 126.52, 126.22, 125.97, 125.04, 124.68 (Ar), 118.02, 102.12 (C=C), 26.46, 24.50, 24.09, 13.98 ppm (alkyl); <sup>31</sup>P NMR (161.9 MHz, CDCl<sub>3</sub>):  $\delta = 3.46$  ppm ( $J_{P-Pt} = 2321$  Hz); IR (KBr):  $\tilde{v} =$ 2085 cm<sup>-1</sup> (w,  $v(C \equiv C)$ ); FAB-MS: m/z: 1246.8 [M]<sup>+</sup>; elemental analysis calcd (%) for C56H68N4P2PtS6: C 53.96, H 5.50, N 4.49; found: C 54.12, H 5.39. N 4.42.

#### Acknowledgements

This work was supported by the University Grants Committee Areas of Excellence Scheme (AoE/P-03/08), the Faculty Research Grant from Hong Kong Baptist University (FRG2/09–10/091), the General Research Fund (HKBU202410) from the Hong Kong Research Grants Council and Open Research Fund of State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. We also thank the State Administration of Foreign Experts Affairs International Partnership Program for Creative Research Teams, Chinese Academy of Sciences. The authors would like to thank Dr. Shu-Ping Huang for the TD-DFT calculations and Vincent Ho-Yuen Ng for the cyclic voltammetry measurements.

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> Received: August 21, 2011 Published online: December 23, 2011