Cruciform oligo(phenylenevinylene) with a bipyridine bridge: synthesis, its rhenium(I) complex and photovoltaic properties†

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A cruciform-shaped oligo(phenylenevinylene) (OPV) with a phosphorescent rhenium(I) chromophore incorporated at the centre and grafted triphenylamines around the periphery was designed as a new organic photovoltaic material, in which the chelation of rhenium(I) to the cruciform successfully constructs a three-dimensional intramolecular charge transfer system and extends the exciton lifetime; as a result, the rhenium-OPV complex shows a power conversion efficiency almost two times that of the metal ion-free parent compound.

Organic solar cells have been under intensive investigation because of their cost effectiveness and potential as flexible and lightweight solar cells.[1] The power conversion efficiency of organic photovoltaic devices is dependent on three key processes: light absorption, exciton dissociation and charge collection.[2] Donor–acceptor-type interfaces and bulk heterojunctions have been demonstrated to be effective for exciton dissociation.[3] However, in most cases, the photo generated excitons could not fully reach the junction due to poor exciton mobility,[4] which limits the power conversion efficiency up to the theoretical prefigure. It is considered that establishing donor–acceptor junctions at the molecular level can make the excitons have a natural tendency towards charge separation in the whole system,[5] which is an efficient synthetic strategy for photovoltaic materials design.

Recently, the cruciform π-conjugated compounds (Chart 1) have been paid much attention for their excellent opto-electronic properties.[6] Such a cruciform shape disrupts the crystallization tendency of the material as well as enhances the likelihood of glass formation and the solubility in common organic solvents. Biphenyl is a special kind of building block for cruciform π-conjugated oligomers, which can provides a large degree of crossing for linear conjugated segments.[6a,7] At the same time, the relatively free rotation of biphenyl results in the conformational multiformity and mild molecular flexibility in these cruciform systems, which determines their excellent film forming abilities.[6c,d] High performance OLEDs[6b] based on biphenyl-linked olig(phenylenevinylene)s and OFETs[6d] based on biphenyl-linked oligo(thiophene)s have been achieved. When electron donating groups are attached to the periphery of the cruciform oligomer, named 2,5,2′,5′-tetra(4′-*N*,*N*-diphenylaminostyryl)biphenyl (DPA-TSB, Chart 1), a three-dimensional donor–π–donor meshwork has been achieved in this oligomer, which exhibits strong intramolecular charge transfer and enhanced two-photo excited fluorescence properties.[6c] Reports herein are based on an advancement in molecular structure design. The strategy is inserting a metal ion ligand 2,2′-bipyridine (bpy) into the central biphenyl of DPA-TSB. On the one hand, being similar with a dendrimer, this new cruciform system (named bpy-DPA-TSB) has an electronic withdrawing core (2,2′-bipyridine) and electronic donating branches (diphenylamine substituted styrene), in which the charge separation ability will be improved compared with its analog DPA-TSB. On the other hand, the chelating function of the 2,2′-bipyridine core provides an easy way to further tune the electronic structure of the molecule. The phosphorescent rhenium(I) chromophore, chelated bpy-DPA-TSB (bpy-DPA-TSB-Re), was synthesized, in which the electronic withdrawing core was further strengthened. And more importantly, due to the nature of the triplet state phosphorescent chromophore, rhenium(I) incorporation endows bpy-DPA-TSB-Re with a long exciton lifetime, which is helpful for the enhancement of exciton dissociation efficiency.[8,9] Herein, we report the synthesis of such a phosphorescent rhenium(I) chelated cruciform oligomer as well as its application in organic photovoltaic devices.

As shown in the Scheme 1, the synthesis of the starting material **1** was performed by bubbling hydrogen bromide gas in the anhydrous methanol solution of bipyridine, and then the collected precipitates were dried and reacted with bromine at 180 °C in a sealed tube to give the bromination product **2**. In a typical Suzuki coupling experiment, compound **2** and 2,5-dimethylphenylboronic acid were heated to 80 °C for two days to give the compound **3**. The tetrakis-bromomethyl product **4** was then obtained by NBS bromization of **3** as a white powder. The compound **4** was further converted into the

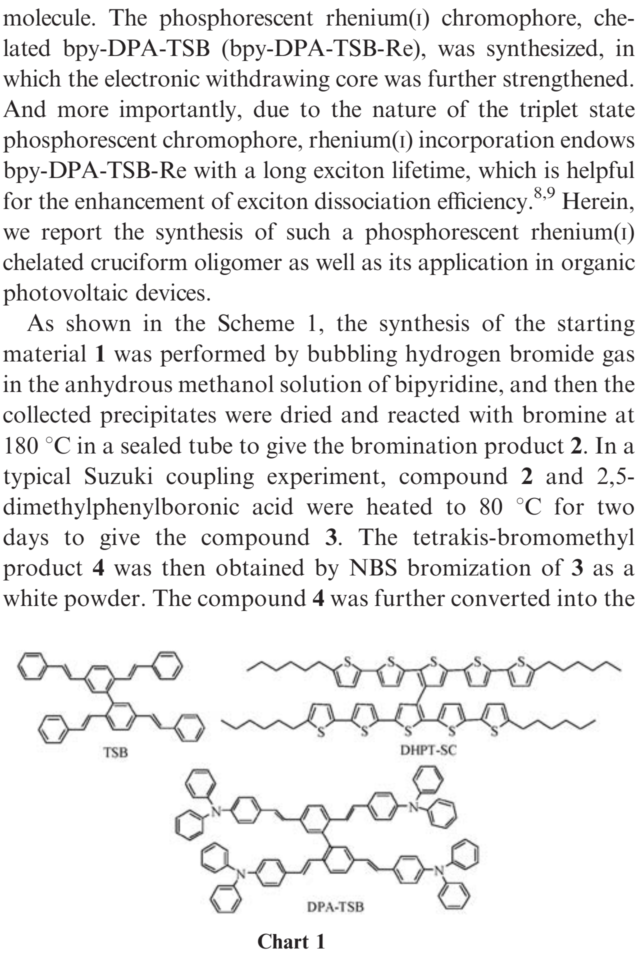

Chart 1

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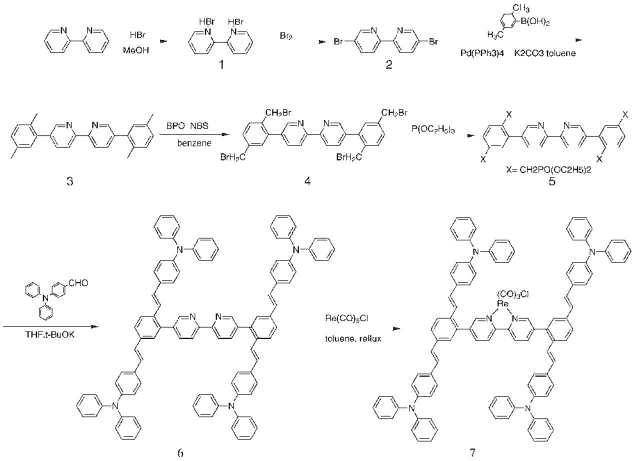
† Electronic supplementary information (ESI) available: Characterization of compounds, absorption and photoluminescence spectra and photovoltaic properties data. See DOI: 10.1039/b804995e



Scheme 1 Synthesis of the cruciform oligo(phenylenevinylene)s with a bipyridine bridge (bpy-DPA-TSB (**6**) and bpy-DPA-TSB-Re (**7**)).

tetra(phosphonate) **5** in hot triethyl phosphite. The reaction of monomer **5** with 4-(diphenylamino)benzaldehyde under Wittig–Honer conditions in the presence of excess *t*-BuOK in degassed THF at room temperature gave the oligomer **6** (bpy-DPA-TSB). The resulting oligomer was precipitated out from methanol twice and then purified by column chromatography to give bright yellow solid (yield 80%). The complex **7** (bpy-DPA-TSB-Re) was prepared in refluxing toluene solution containing pentacarbonylrhenium chloride and excess diimine ligand **6** and was obtained as crystalline solids with a deep-red color in nearly 100% yield. Although these two oligomers have relatively larger molecular weights without alkyl chain substituents, they both show good solubility in common organic solvents due to their swivel-cruciform structure, which allows for wet processing of materials by spin-coating or inkjet printing. ^{1}H NMR spectroscopy was used to examine the electron structure of cruciform oligomers before and after metal ion chelation (Fig. S1†). The protons of the two oligomers are both located in the aromatic region and in good agreement with their structures. After Re ion chelation, the protons at the central bipyridine shift downfield (0.2–0.5 ppm) comparing with that of bpy-DPA-TSB, which indicates that the electron withdrawing ability in the bpy-DPA-TSB-Re complex is dramatically enhanced by the Re ion chelation.‡

Compounds **6** and **7** both exhibited the maximal absorption peaks at 415 nm, corresponding to the π–π^* transition of the backbone. However, complex **7** showed clear additional absorption tails at long wavelengths (450–550 nm), corresponding to its ^{1}MLCT transition (Fig. S3†). Although compound **6** displayed very strong sky-blue emission in solution (fluorescence quantum yield: 0.8), the Re ion chelated complex **7** showed almost no emission in solution (fluorescence quantum yield: 0.01). This strongly fluorescent quenching in complex **7** could be attributed to the classic charge-transfer (CT) excited-state characteristic.[10] Based on the results of theoretical simulation (density functional theory, B3LYP/6-31G),[11] the charge separation structure for complex **7** had been further revealed. The simulated electronic structure of complex **7** is given in Fig. 1: the highest occupied molecular orbital (HOMO) is completely localized on the diphenylamine substituted π-conjugated units while the lowest unoccupied molecular orbital (LUMO) is mainly localized on the central Re-chelated bipyridine part. As a comparison, much more HOMO and LUMO orbital overlap was observed in compound **6**, its LUMO is almost extended across the whole molecular fragment (Fig. S5†). Such results indicate that the excited electron in the LUMO has a tendency to localize on the Re chelated bipyridine centre after the Re ions chelated in complex **7**, which will greatly enhance the exciton dissociation and decrease their recombination with charged species in peripheral conjugated sites. Such natural properties of charge carrier separation in Re incorporating sites meet the requirement of photovoltaic cell applications.

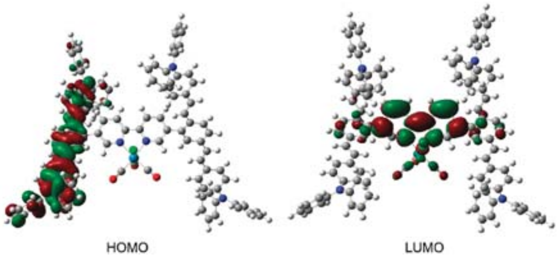


Fig. 1 Frontier molecular orbital of bpy-DPA-TSB-Re (**7**).

Because the film-forming ability and morphological stability of the organic materials strongly influence the performance of organic optoelectronic device, the spin-coated films of complex **7** were investigated by atomic force microscopy (AFM). The thin film was prepared on a indium-tin-oxide (ITO) substrate by spin-coating and then annealed at 90 °C for 2 h under a nitrogen atmosphere. The annealed film showed a height variation in the range of less than ±3 nm (Fig. 2), which changes little comparing to the original spin-coated film. It suggests that the thin film of complex **7** is suitable for practice applications as film devices with good film-forming ability and morphological stability under Joule heat during the device operation. Meanwhile, complex **7** exhibited a high onset degradation temperature above 396 °C (5% weight loss) measured by thermogravimetric analysis (Fig. S6†), which was about 40 °C higher than its parent compound **6**, suggesting that the thermostabilization has been enhanced after metal ion chelation.

The single-layer organic photovoltaic devices ITO/PEDOT/**7** (or **6**)/LiF/Al using **6** or **7** as the active layer were fabricated. Under white light illumination at 100 mW cm^{-2}, the photovoltaic cells showed marked photocurrents (Fig. 3). The complex **7** based device shows a typical photovoltaic response: the short circuit current (I_{sc}) was 0.082 mA cm^{-2}, the open-circuit voltage (V_{oc}) was 0.72 V and the fill factor (FF) was 0.21

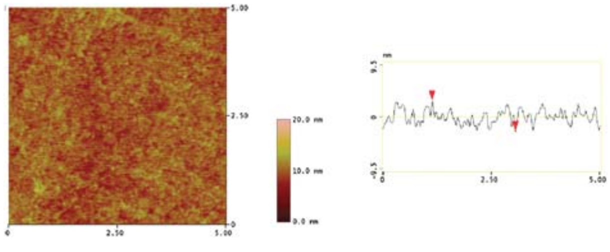


Fig. 2 AFM image (5 × 5 μm) of bpy-DPA-TSB-Re (**7**) after annealing at 90 °C for 2 h under a nitrogen atmosphere.

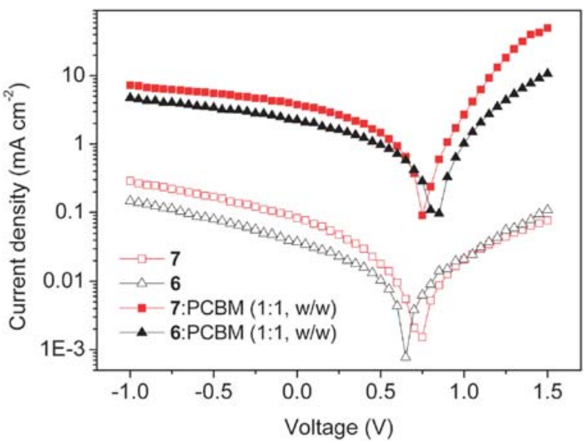


Fig. 3 Current–voltage characteristics of devices under white light illumination (100 mA cm^{-2}).

(Table 1). These values corresponded to a power conversion efficiency (η_e) of 0.012%, which was a satisfied result for single layer organic photovoltaic device compared with previous reports.[12] On the other hand, the device based on compound **6** was also been inspected. The I_{sc}, V_{oc} and FF were 0.038 mA cm^{-2}, 0.65 V and 0.24, respectively. The value of η_e is 0.006%, which was only half of that obtained from **7** based devices. Obviously, both the I_{sc} and V_{oc} of the devices were highly influenced by the Re ion chelation. These two factors, especially I_{sc} increased significantly for the device based on complex **7**. In addition, the external quantum efficiency value of the **7** based device is also nearly two times higher than that of the **6** based device (Fig. S7‡). These improvements after Re ion chelation can be attributed to enhanced exiton dissociation ability in complex **7** compared with compound **6**. Meanwhile, since the donor and acceptor components are covalently linked in complex **7**, the problem of phase separation in some heterojunction devices could be avoided.[13] In a further experiment, the organic bulk heterojunction photovoltaic cells were fabricated by using PCBM as the acceptor for a more efficient charge collection with a device structure ITO/PEDOT/PCBM: **7** (or **6**) (1 : 1 w/w)/LiF/Al. The power conversion efficiency of the **7**/PCBM based device is 0.8%, which is about 1.6 times of that in the compound **6** based device (0.5%).

In conclusion, we report here the synthesis, characterization and photovoltaic properties of the photoactive molecular material bpy-DPA-TSB-Re bearing efficient charge separation, good film-forming ability and morphological stability. The power conversion efficiency under white light illumination was found to be moderated about 0.012% for bpy-DPA-TSB-Re based device and showed twice larger efficiency comparing with that of bpy-DPA-TSB (0.006%), which is an encouraging result for possible application of such molecular donor–acceptor ensembles for photovoltaic devices. Further investigation will be necessary to optimize the devices structure and fully clarify the photophysical features.

Table 1 Photovoltaic data for the materials studied under white light illumination (100 mW cm^{-2})

Materials	I_{sc}/mA cm^{-2}	V_{oc}/V	FF	η_e (%)
7	0.082	0.72	0.21	0.012
6	0.038	0.65	0.24	0.006
7 : PCBM(1 : 1, w/w)	3.8	0.75	0.28	0.8
6 : PCBM(1 : 1, w/w)	2.3	0.85	0.26	0.5

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Notes and references

‡ Selected data of the compounds. **6**: ^{1}H NMR (500 MHz, DMSO-D$_6$): δ [ppm] 8.760 (s, 2H, ArH), 8.575–8.558 (d, 2H, ArH), 8.037–8.016 (d, 2H, ArH), 7.906–7.890 (d, 2H, ArH), 7.702–7.685 (d, 2H, ArH), 7.630 (d, 2H, ArH), 7.544–7.527 (d, 2H, ArH), 7.362–7.184 (m, 26H), 7.090–6.945 (m, 30H), 6.907–6.890 (d, 4H, ArH); Elemental analysis: calculated: $C_{102}H_{76}N_6$: C, 88.41; H, 5.53; N, 6.06; found: C, 88.43; H, 5.91; N, 5.33; MALDI-TOF MS: m/z = 1386.0 ([M + H]$^+$), calcd.: 1384.6.

7: ^{1}H NMR (500 MHz, DMSO-D$_6$): δ [ppm] 8.991–8.976 (d, 2H, ArH), 8.976 (s, 2H, ArH), 8.512–8.495 (d, 2H, ArH), 7.969–7.953 (d, 2H, ArH), 7.798–7.783 (d, 2H, ArH), 7.741 (s, 2H, ArH), 7.560–7.544 (d, 2H, ArH), 7.456–7.440 (d, 2H, ArH), 7.398–7.227 (m, 22H), 7.097–6.969 (m, 30H), 6.871–6.855 (d, 4H, ArH); Elemental analysis: calculated: $C_{105}H_{76}Cl\ N_6O_3Re$: C, 74.56; H, 4.53; N, 4.97; found: C, 73.76; H, 4.71; N, 4.11; MALDI-TOF MS: m/z = 1691.9 ([M + H]$^+$), calcd.: 1690.5.

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