Cruciform Oligo(phenylenevinylene) with a Bipyridine Bridge: Synthesis, its Rhenium (I) Complex and Photovoltaic Properties

Feng He, Yinghua Zhou, Shuijun Liu, Leilei Tian, Hai Xu, Houyu Zhang, Bin Yang, Qingfang Dong, Wenjing Tian, Yuguang Ma* and Jiacong Shen

State Key Laboratory for Supramolecular Structure and Materials, Jilin University, Changchun 130012, P. R. China. Fax: +86-431-85168480;

E-mail: ygma@jlu.edu.cn;

1. General experiment.

Nuclear magnetic resonance spectra were recorded on AVANCZ 500 spectrometers at 298K by utilizing deuterated chloroform or Dimethyl Sulphoxide (DMSO) as solvents and tetramethylsilane (TMS) as standard. The compounds were characterized by Flash EA 1112, CHNS-O elemental analysis instrument. The MALDI-TOF mass spectra were recorded using a KRATOS instrument. The TGA analysis was determined using a PE instrument at 10 °C min^{-1} under nitrogen flushing. For the device fabrication, ITO-coated glass substrates were spin-coated with PEDOT and annealed in a vacuum at 100 °C for 15 min. And then complex were spin-coated onto the PEDOT coated ITO glass. At last LiF and an aluminum electrode were thermally evaporated under a vacuum of 5×10^{-4} Pa. The electrode was deposited through a mask resulting in multiple devices, each with an area of 2.5 mm^2. The

illumination source is a Xe lamp FL-1039 passed through a mono-chromator TRIAX320. The devices were tested under 410 nm light (4.2 mW/cm^2) and white light illumination (100 mW/cm^2) through the ITO electrode. The current density-voltage (*I-V*) curve was measured using a Keithley 2400 source generator by varying the voltage from -1.0 to 1.5 V in 0.05 V by steps across the ITO and Al electrodes. All the compounds studied were stable under the experimental conditions described here, and no bleaching of the solutions was observed at the end of the set of measurements.

2. Characterization data of the materials.

Compound **2**: ^{1}H NMR (500Hz, $CDCl_3$,) δ [ppm] 8.717 (d, 2H, ArH), 8.317 (d, 2H, ArH) , 7.962 (dd, 2H, ArH). Elemental analysis: calculated: $C_{10}H_6N_2Br_2$: C, 38.25; H, 1.93; N, 8.92; found: C, 38.35; H, 2.00; N, 8.76.

Compound **3**: ^{1}H NMR (500 MHz, DMSO-d_6): δ [ppm] δ8.696 (s, 2H, ArH), 8.503-8.487 (d, 2H, ArH), 7.975-7.959 (d, 2H, ArH), 7.261-7.245 (d, 2H, ArH), 7.173-7.158 (d, 2H, ArH), 7.158 (s, 2H, ArH), 2.339 (s, 6H, CH_3), 2.262 (s, 6H, CH_3); Elemental analysis: calculated: $C_{26}H_{24}N_2$: C, 85.68; H, 6.64; N, 7.69; found: C, 85.48; H, 6.72; N, 7.50.

Compound **4**: ^{1}H NMR (500 MHz, $CDCl_3$): δ [ppm] 8.81 (s, 2H, ArH), 8.61-8.58 (d, 2H, ArH), 8.09-8.07 (d, 2H, ArH), 7.67-7.65 (d, 2H, ArH), 7.61-7.60 (d, 2H, ArH), 7.54 (s, 2H, ArH), 4.79 (s, 4H, CH_2Br), 4.68 (s, 4H, CH_2Br); Elemental analysis: calculated: $C_{26}H_{20}N_2Br_4$: C, 45.92; H, 2.96; N, 4.12; found: C, 45.82; H, 2.90; N, 4.01.

Compound **5**: ^{1}H NMR (500 MHz, DMSO-d_6): δ [ppm] 8.716 (s, 2H, ArH), 8.526-8.510 (d, 2H, ArH), 8.026-8.010 (d, 2H, ArH), 7.445-7.428 (d, 2H, ArH),

7.336-7.320 (d, 2H, ArH), 7.260 (s, 2H, ArH), 3.998-3.853 (m, 16H, OCH_2), 3.306-3.159 (m, 8H, $ArCH_2O$), 1.236-1.099 (m, 24H, CH_3).

3. ^{1}H NMR spectra.

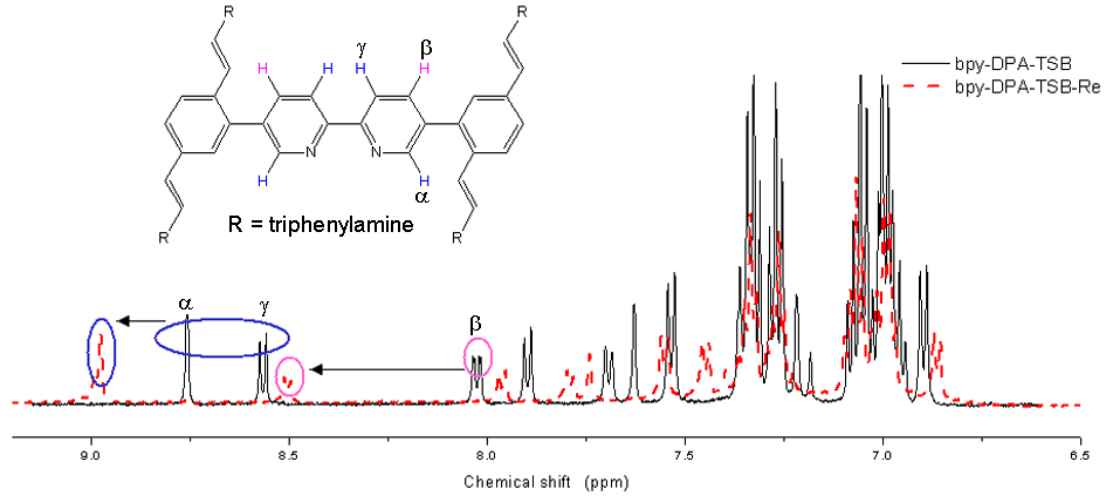

Fig. S1. ^{1}H NMR spectra of two oligomers.

4. MALDI-TOF mass spectrum.

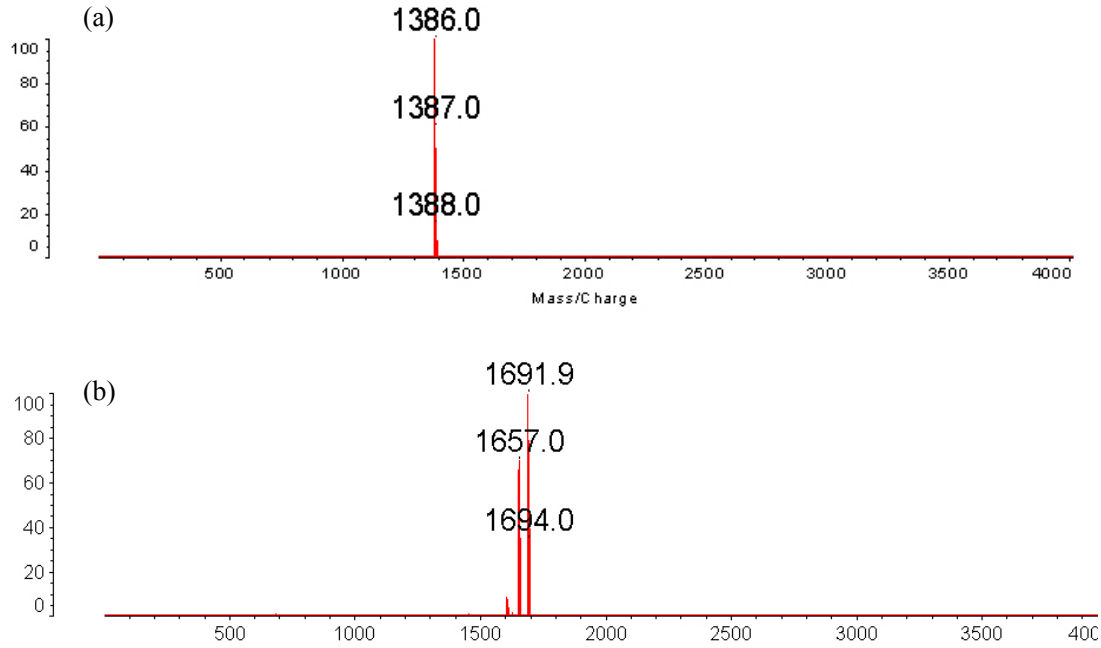

Fig. S2. MALDI-TOF mass spectra: a) bpy-DPA-TSB (**6**); b) bpy-DPA-TSB-Re (**7**).

5. UV absorption and photoluminescence spectra.

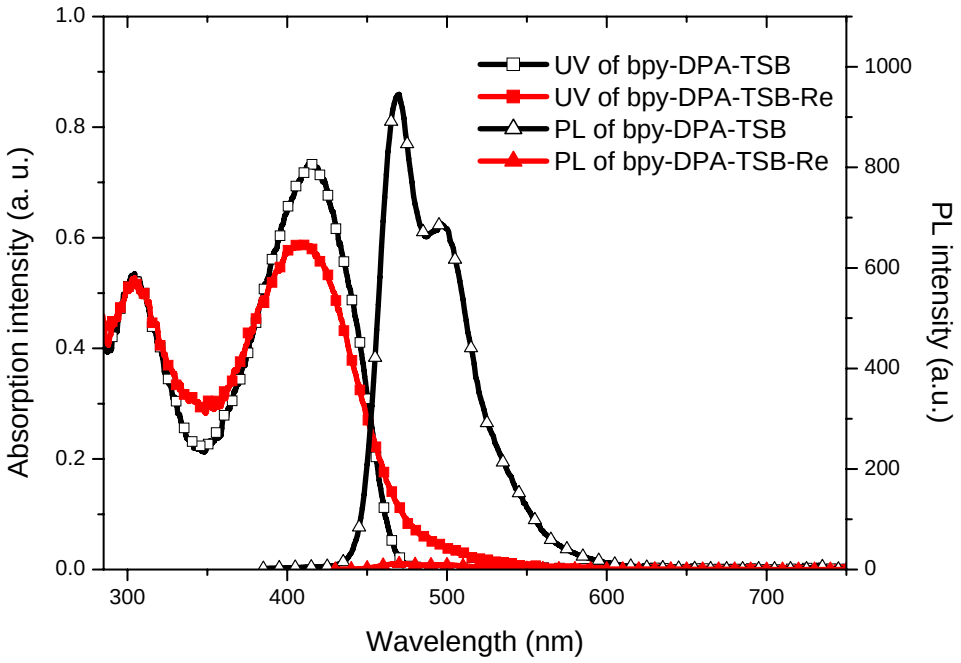

Fig. *S3.* Absorption and photoluminescence spectra in toluene solution for bpy-DPA-TSB (**6**) and bpy-DPA-TSB-Re (**7**) at 298 K.

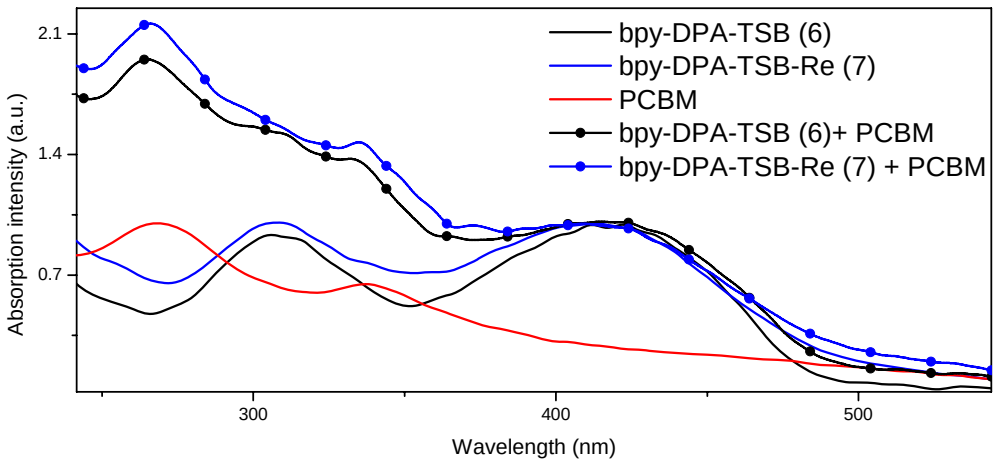

Fig. *S4.* The thin film absorption spectra of bpy-DPA-TSB (**6**), bpy-DPA-TSB-Re (**7**), PCBM and their blends with PCBM (1:1, w/w), all films were prepared by spin-coating using 5 mg mL^{-1} solution.

6. Theoretical simulation.

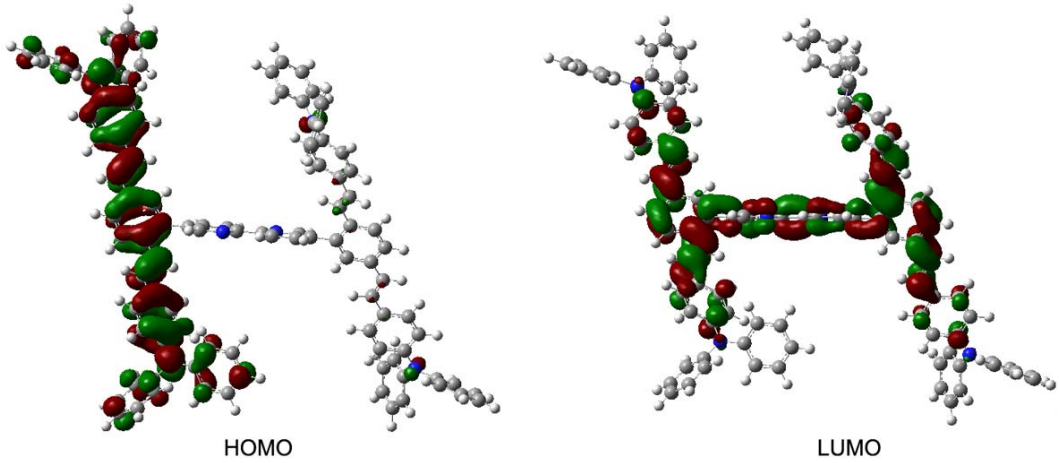

Fig. *S5*. Frontier molecular orbitals of bpy-DPA-TSB (**6**).

7. TGA of two oligomers.

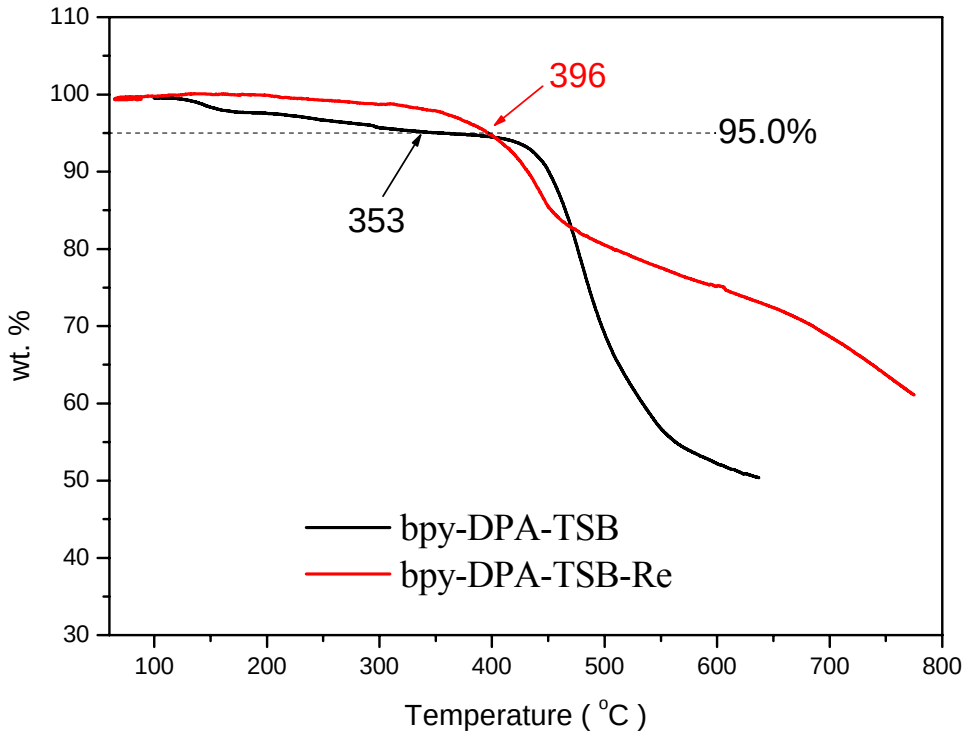

Fig. *S6*. TGA of of bpy-DPA-TSB (**6**) and bpy-DPA-TSB-Re (**7**).

8. Photovoltaic properties.

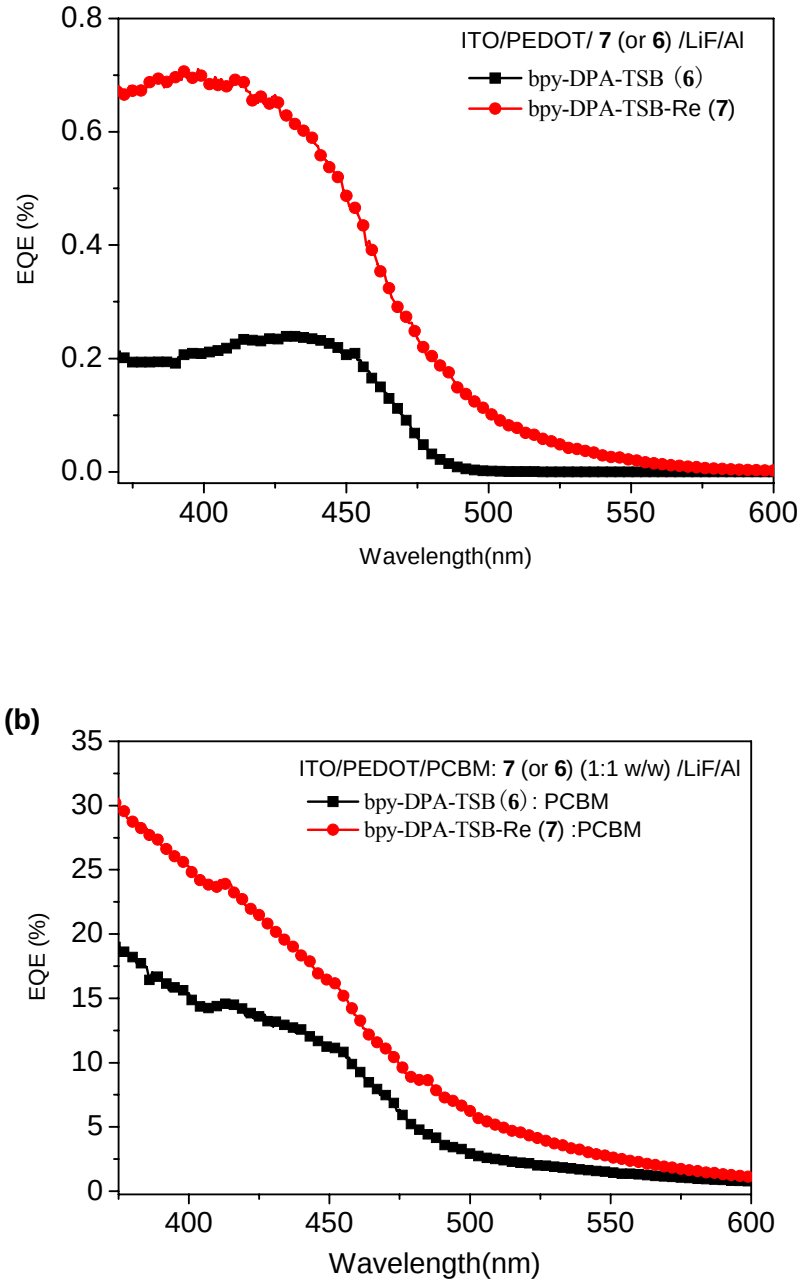

Fig. *S7*. a) Comparison of the external quantum efficiency (EQE) spectra of photovoltaic devices based on bpy-DPA-TSB (**6**) and bpy-DPA-TSB-Re (**7**); b) Comparison of the EQE spectra of photovoltaic devices based on bpy-DPA-TSB (**6**) : PCBM (1:1, w/w) and bpy-DPA-TSB-Re (**7**) : PCBM (1:1, w/w).