Electronic Supplementary Information

Porphyrin-Containing D-π-A Conjugated Polymer with Absorption over the Entire Spectrum of Visible Light and its Applications in Solar Cells

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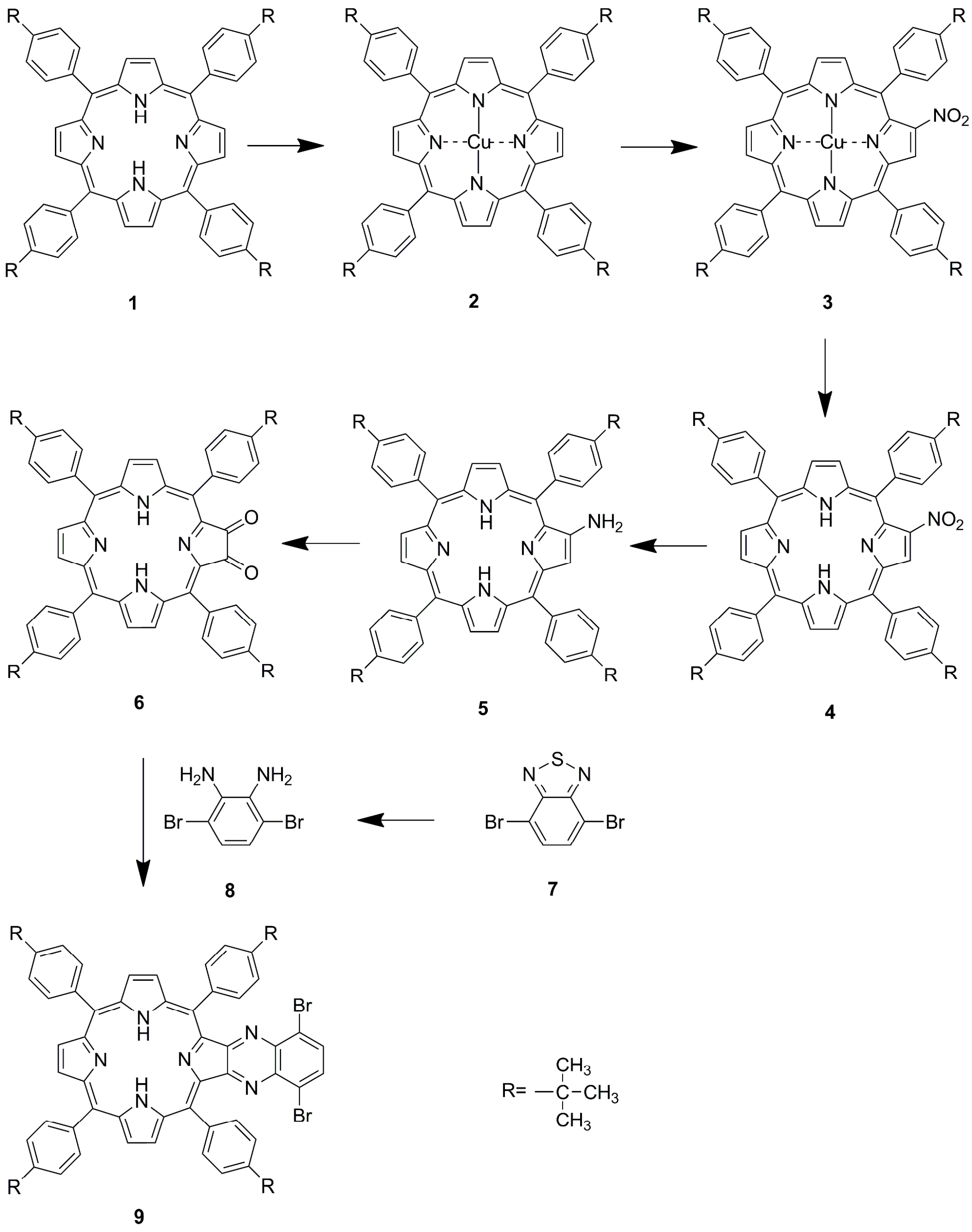
Experimental Section

Materials. Tetrahydrofuran (THF) was dried over Na/benzophenone ketyl and freshly distilled before use. 2,7-Dibromo-9-dodecyl-9H-carbazole (**CZ**), 2,2':5',2'' - Terthiophene-5,5''-bis(trimethylstannane) (**TT**) and 5,10,15,20-Tetra(4-*tert*-butylphenyl)porphyrin **1** were synthesized as reported in the literature.[1-3] Other reagents and solvents were commercial grade and used as received without further purification.

Instruments and measurements. The molecular weight of the polymer was measured using gel permeation chromatography (GPC). The GPC measurements were performed on Waters 515-2410 with polystyrenes as reference standard and THF as an eluent. All new compounds were characterized by nuclear magnetic resonance (NMR) spectra. The NMRs were recorded on a Bruker AV 600 spectrometer in $CDCl_3$ at room temperature. Chemical shifts of ^1H NMR were reported in ppm. Splitting patterns were designated as s (singlet), t (triplet), d (doublet), m (multiplet), and br (broaden). Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were made on a Shimadzu KOMPACT MALDI II using CHCA as a matrix. Elemental analyses were performed on a Flash EA 1112 analyzer or Elementar vario EL III. Thermal gravimetric analysis (TGA, NetzschTG209C) was performed under a nitrogen atmosphere at a heating rate of 10°C /min. UV–Vis absorption spectra were recorded on a Shimadzu spectrometer model UV-3150. Absorption spectra measurements of the polymer solutions were performed in chloroform (analytical reagent) at 25°C. Absorption spectra measurements of the polymer films were performed on the quartz plates with the polymer films spin-coated from the polymer solutions in chlorobenzene (analytical reagent) at 25°C. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with Pt disk coated with the polymer film, Pt plate, and Ag/Ag+ electrode as working electrode, counter electrode and reference electrode respectively in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution.

Device Fabrication and Characterization of PSCs. PSCs were fabricated with ITO glass as a positive electrode, Ca/Al as a negative electrode and the blend film of the polymer/$PC_{71}BM$ between them as a photosensitive layer. The ITO glass was pre-cleaned and modified by a thin layer of PEDOT:PSS which was spin-cast from a PEDOT:PSS aqueous solution (Clevious P VP AI 4083 H. C. Stark, Germany) on the ITO substrate, and the thickness of the PEDOT:PSS layer is about 30 nm. The photosensitive layer was prepared by spin-coating a blend solution of polymers and $PC_{71}BM$ in o-dichlorobenzene on the ITO/PEDOT:PSS electrode. Then the Ca/Al cathode was deposited on the active layer by vacuum evaporation under $3x10^{-4}$ Pa. The effective area of one cell is 4 mm^2 and the thickness of the photosensitive layer is ca. 80 nm. The current-voltage (*J*-*V*) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit in drybox under inert atmosphere. A xenon lamp with AM 1.5 filter was used as the white light source, and the optical power at the sample was 100 mW/cm^2. The external quantum efficiency (EQE) was measured using a Stanford Research Systems model SR830 DSP lock-in amplifier coupled with a WDG3 monochromator and 500W xenon lamp. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. All the measurements were performed under ambient atmosphere at room temperature.

Synthesis of Monomers. The synthetic route of the monomers is shown in Scheme S1. And the detailed synthesis processes were described in the following.



Scheme S1. Synthetic route of the monomers

5,10,15,20-Tetrakis(4-*tert*-butylphenyl)porphyrinatocopper(II) (2)

A mixture of 1 (3.00 g, 3.57 mmol), copper (II) acetate monohydrate (1.50 g, 7.5 mmol), chloroform (300 ml), and methanol (90 ml) was heated at reflux for 2 h. The reaction mixture was allowed to cool and the solvent removed. The residue was passed through a plug of silica using chloroform as eluent. The main fraction was collected and the solvent completely removed to give a purple solid of **2** (3.12 g, 97%) and the product was used without further purification.

2-Nitro-5,10,15,20-tetrakis(4-*tert*-butylphenyl)porphyrinatocopper(II) (3)

To a solution of **2** (1.00 g, 1.11 mmol) in chloroform (800 ml), a solution of copper nitrate trihydrate (0.80 g, 3.33 mmol) in a mixed solution of acetic anhydride (100 mL) and acetic acid (50 mL) was added. The reaction mixture was stirred at room temperature for 10-15 min until the reactant was not detected by silica TLC (Thin-Layer Chromatography) (hexane/CH_2Cl_2 = 2:1). Then the reaction mixture was poured into water and the organic layers were washed with water, saturated $NaHCO_3$ solution, and water, dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The residue was recrystallised from a chloroform–methanol mixture to give **3** as a violet solid (0.85 g, 81%) and was used directly for the next step. FT-IR (KBr) v_{max} 1526, 1341(NO_2).

2-Nitro-5,10,15,20-tetrakis(4-*tert*-butylphenyl)porphyrin (4)

To a vigorously stirred solution of **3** (1.00 g, 1.06 mmol) in trifluoroacetic acid (90 mL) was added a concentrated sulfuric acid (98%, 20 mL). The reaction mixture was stirred at room temperature for 2.5h and then it was poured into ice water and neutralized with saturated aqueous $NaHCO_3$ and extracted with chloroform. The extract was washed with water, dried over anhydrous $MgSO_4$, and concentrated in vacuo. Purification by silica column chromatography (hexane/CH_2Cl_2 = 3:1-2:1) to give a **4** as a purple solid (0.75 g, 80%). FT-IR (KBr) v_{max} 1525, 1350 (NO2), 3325（NH）; ^{1}H NMR ($CDCl_3$, 600 MHz) δ(ppm): δ 2.54 (s, 2H), 1.56–1.62 (m, 36H), 7.73–7.80 (m, 8H), 8.13–8.22 (m, 8H), 8.75 (s, 2H), 8.90–9.00 (m, 3H), 9.04–9.08 (m, 2H).

2-Amino-5,10,15,20-tetrakis(4-*tert*-butylphenyl)porphyrin (5)

Palladium (10% on carbon, 2.00 g) were added to a mixed solution of compound **4** (2.00 g, 2.26 mmol) in dichloromethane (480 ml) and dry methanol (120mL). The solution was purged with nitrogen and stirred at room temperature for 1 h, and placed into the ice-bath. Sodium borohydride (2.14g, 56.60mmol) was added to the solution in small portions over a 30 min period. The reaction was stirred overnight under N_2 in the dark. The mixture was then filtered and the solution was evaporated to dryness and the solid residue extracted with dry CH_2Cl_2.

The solvent was then evaporated, and the air-sensitive product was carried on to the next reaction without further purification.

2,3-Dioxo-5,10,15,20-tetrakis(4-*tert*-butylphenyl)chlorine (6)

This procedure was based upon the literature protocol for similar compound.[4-5] To a solution of **5** (0.47 g, 0.55 mmol) in a dichloromethane (150 mL) was added Dess-Martin periodinane (0.25 g, 0.59 mmol). The reaction mixture was stirred at room temperature in the dark for 30h .Then Hydrochloric acid (1 M, 90 ml) was added and the reaction mixture was stirred for a further 1h to hydrolyze undesirable imine products. The reaction mixture was treated with saturated aqueous $NaHCO_3$ and washed with water. Organic layer was collected, dried over anhydrous $MgSO_4$, and then remove the solvent in vacuo. Column chromatography on silica gel (hexane/CH_2Cl_2 = 1:1) afforded **6** as a greenish brown solid with a distinctive smell (182mg , 38%). ^1H NMR ($CDCl_3$, 600 MHz) δ(ppm): δ -1.95 (s, 2H), 1.57–1.60 (m, 36H), 7.71 (d, 4H), 7.73 (d, 4H), 7.85 (d, 4H), 8.08 (d, 4H), 8.58–8.63 (m, 4H), 8.74–8.80 (m, 2H); MS (MALDI-TOF) m/z 865.5 ($M+H^+$).

3,6-Dibromobenzene-1,2-diamine (8)

To a suspension of 4,7-dibromo-2,1,3-benzothiadiazole (7.00 g, 23.8 mmol) in ethanol (200 ml). $NaBH_4$ (18.00 g, 476.3 mmol) was added into the solution slowly and at 0°C under nitrogen, and the mixture was stirred at room temperature overnight. After evaporation of the solvent, water (250ml) was added, and the mixture was extracted with ether, washed with brine, dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure to obtain pale-yellow solid (4.10g，65%). ^1H NMR ($CDCl_3$, 600 MHz) δ(ppm): δ 5.00 (s, 4H), 6.63 (s, 2H).

5,10,15,20-Tetrakis(4-*tert*-butylphenyl) -5',8'-dibromo-quinoxalino[2,3-b']porphyrin (9)

Compound **6** (0.50 g, 0.575 mmol)and compound **8** (0.15 g, 0.575 mmol) were dissolved in 200ml CH_2Cl_2 and 5ml acetic acid was added. The reaction was stirred at room temperature for 24h. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, hexane/CH_2Cl_2 = 1:1) to give a red purple solid (0.55 g, 87%). ^1H NMR ($CDCl_3$, 600 MHz) δ(ppm): δ -2.52 (s, 2H), 1.60-1.65 (m, 36H), 7.78 (d, 4H), 7.84 (d, 4H), 7.93 (s, 2H), 8.16 (m, 8H), 8.75–8.83 (m, 6H); MS (MALDI-TOF) m/z 1101.2 ($M+H^+$).

Synthesis of the Polymer. PCTTQP: To a 25 mL two-necked flask were added monomer **CZ** (49.30 mg, 0.10mmol), **9** (109.90 mg 0.10 mmol), **TT** (114.8 mg, 0.2 mmol), and chlorobenzene (6mL). The mixture was purged with nitrogen for 15 min and then $Pd_2(dba)_3$ (10.00 mg, 0.01 mmol) and P(*o*-tol)$_3$ (25.00 mg, 0.08mmol) were added. After being purged for 15 min, the reaction mixture was heated at 140°C for 72 h. After cooled to room temperature, the reaction mixture was added dropwise to 200 ml methanol and then collected by filtration and washed with methanol. Then the solid was subjected to Soxhlet extraction with methanol, hexane and chloroform. Subsequently, the fraction that was extracted by chloroform was evaporated under reduced pressure, then precipitated in methanol, filtered and finally dried under vacuum to obtain a black solid (98.1mg, yield 55.6%, Mn =61.1 kDa, Mw= 130.3 kDa, PDI = 2.13. ^{1}H NMR (CDCl3, 600 MHz) δ(ppm): δ -2.34–-2.24（br, NH）,0.85–2.53(br, alkyl-H), 7.40–8.45(br, Ar-H), 8.65–9.31(br, pyrrolic-H) Elemental analysis: Calculated for $C_{114}H_{107}N_7S_6$, C, 77.46; H, 6.10; N, 5.55 S, 10.88; found: C, 76.25; H, 6.06; N, 5.04 S, 12.67.

Thermal Analysis

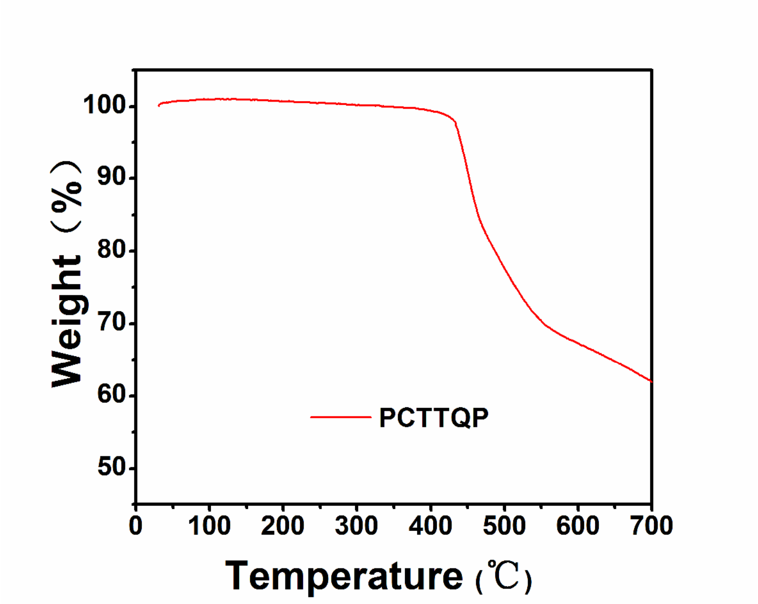


Figure S1. Thermal Analysis: TGA scan curve

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