Support Information

Pyridinium-pended Conjugated Polyelectrolyte for Efficient Photocatalytic Hydrogen Evolution and Organic Solar Cells

Muhammad Rafiq, Jianhua Jing, Yuanying Liang, Zhicheng Hu, Xi Zhang, Haoran Tang, Li Tian, Yingwei Li*, Fei Huang*

Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, State Key Laboratory of Pulp and Paper Engineering, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640, P. R. China

* Y. Li, liyw@scut.edu.cn; F. Huang, msfhuang@scut.edu.cn.

Experimental Section:

Materials and Methods: Monomers M1¹ and M2² were synthesised according to reported procedure. The neutral polymer, DPTF was synthesised by Suzuki polymerization method. The conjugated polymers with quaternary ammonium and N-oxide salts (DPTFBr and DPTFNO) were synthesised from their neutral precursor (DPTF) with quaternarization reaction³.



Scheme S1: Synthetic routes of monomers M1.

Photo-induced doping tests of Polymers

Typically, 3 mg of DPTFBr polymer was dissolved in 1mL of methanol. Triethanolamine (10wt% or 25 wt% of DPTFBr) was added. The solution sample was degassed for 10 minutes. Afterwards, the sample was irradiated under Xe light source (>300 nm) for 30 minutes. It can be observed that the color of sample was gradually changed from yellow to red brown. The obtained sample was then submitted for characterizations, including UV-vis, CV, ESR and ¹H-NMR *etc*.

Characterizations

The ¹H NMR spectra of these conjugated polymers and monomers were recorded in a Bruker-600 spectrometer that working at 600-MHz in CDCl₃ or MeOD solution. Tetramethylsilane was used as internal standard and the chemical shifts were measured as δ values (ppm). The weight average molecular weights (*Mw*) and number average (*Mn*) of conjugated polymers were determined in a Waters GPC-2410.

The UV-visible absorption spectra of these conjugated polymers (DPTF, DPTBr and DPTFNO) both in film state and solution state were measured from HP-8453 spectrophotometer. Cyclic voltammetry tests were recorded on an electrochemical workstation CHI-660E, equipped with electrode coated by glassy carbon. A sheet of Pt was applied as the counter electrode, and a saturated calomel electrode was used as a reference electrode. The measurements were recorded in the presence of supporting electrolyte (Bu₄NPF₆, 0.1M in CH₃CN) under nitrogen environment. Ferrocene/ferrocenium (Fc/Fc⁺) was used as internal standard. The Electron spin resonance spectroscopic characterization of these conjugated polymers in solid state and solution state were studied under dark condition. Samples with equal amount were prepared for characterization.

Photocatalytic measurements: For the photocatalytic hydrogen evolution, triethanol amine (TEOA) was used as the sacrificial donor. Polymer (2.5 mg) were firstly dissolved in 200 μ L of methanol and then dispersed into a mixture of 10 mL of triethanolamine and 40 mL of water. Pt co-catalysts (3 wt% of polymers) were made by dissolving H₂PtCl₄ aqueous solution into the polymer reaction and irradiated for 0.5 h to enable the formation of Pt nanoparticles before testing. The reaction was held in a vacuum for 30 min before testing to remove the dissolved oxygen and methanol. The photocatalytic reactions were illuminated with a solar simulator (300-W Xe light source, $\lambda > 300$ nm). The luminous power reaching the surface of the reaction solution was calibrated to be 150 mWcm⁻² by a power meter. The produced gas was analyzed by a GC7900 gas chromatograph. Hydrogen were detected with a thermal conductivity detector, referencing against standard gas with a known concentration of hydrogen.

Device Measurement.

The photovoltaic devices were fabricated with the structure of ITO/PEDOT:PSS/PBDB-T-2F:BTPTT-4F/CPE/Ag. The effective area of device is 0.04 cm². The ITO-coated glass substrates was firstly cleaned by sequentially sonicating in a detergent bath with surfactant scrub, deionized water and isopropanol for 30mins and dried at 60 °C oven over night. PEDOT:PSS(4083) was spin-coated on the top of UVO-treated ITO substrate at 3500 rpm for 30 s and annealed at 150 °C for 15 mins on a hot plate. Then, those substrates were transferred into N₂ protected glove box. The active layer solutions (D:A=1:1.2, wt:wt) with the donor concentration of about 6mg/mL in chloroform and 0.5% 1-chloronaphthalene as solvent additive were spin-coated onto the PEDOT:PSS layer at ~2000 rpm to obtain ~100 nm active layers. After that, the active layers were thermally annealed at 110 °C for 10 mins. For different interlayers, PFN-Br, DPTFBr and DPTFNO were separately dissolved in methanol at a concentration of 0.5 mg mL⁻¹. All of these interlayers were spin-coated at 2000rpm for 30s on the top of active layer. Finally, 100nm Ag was thermally evaporated as the top electrode through a shadow mask under ~10⁻⁷ mbar. The average device parameters were calculated from 16 dependent photovoltaic devices.



Fig. S1 GPC result of DPTF



Fig. S2 ¹HNMR analysis of DPTFBr: (a) pristine DPTFBr in CD₃OD; (b) pristine DPTFBr with TEOA in CD₃OD (c) DPTFBr in CD₃OD with 25 wt% TEOA and illuminated for 30 min; (d) TEOA and illumination-treated DPTFBr stored for 20 days.



Fig. S3 Unnormalized UV-vis absorption spectra of DPTFBr in solution in response with 25%TEOA and illumination.



Fig. S4 CV curve of TEOA



Fig. S5 Photocatalytic hydrogen evolution of DPTF, DPTFBr, and DPTFNO by using Ascorbic Acid as a sacrificial donor.



Fig. S6 TEM image of DPTF, DPTFNO and DPTFBr.



Fig. S7 TEM image of DTPFBr with/without TEOA (It can be observed that DPTFBr with TEOA samples showed smaller but irregular aggregates in aqueous solution, indicating slightly better dispersity of DPTFBr + TEOA sample than that without TEOA. This phenomenon might be explained that TEOA could act as a second solvent to assist the dissolution of DPTFBr.)



Fig. S8 Photocurrent response of the conjugated polymers at applied voltage of -0.2V (with 0.1 M Na₂SO₄ as the electrolyte).



Fig. S9 Absorption spectra of polymers before and after photocatalytic experiment.

References

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