

Electronic Supporting Information

Molecular modulation of fluorene-dibenzothiophene-*S,S*-dioxide based conjugated polymers for enhanced photoelectrochemical water oxidation under visible light

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ESI 1. Materials and Measurements

All solvents and reagents were commercially available and analytical-reagent-grade. 9,9-dihexyl-2,7-di(1,3,2-dioxaborolan-2-yl)fluorene and 9,9-didodecylfluorene-2,7-diboronic acid were purchased from sigma-aldrich and used without further purification. NMR spectra of the polymers were acquired from a Bruker DRX-400 spectrometer. C, H, and S of elemental analyses were performed on an Elementar vario MICRO cube. Molecular weights of the polymers were determined by GPC with Waters-244 HPLC pump and THF was used as solvent and relative to polystyrene standards. UV-vis spectra were measured with a Shimadzu 3600 UV-vis-NIR spectrophotometer (reflectance spectra of polymer powder was obtained using an integrating sphere attachment with the BaSO₄ reference). The XRD patterns of film samples were collected on a Bruker D8 Advance X-ray powder diffractometer (Cu K α X-ray source) operating at a voltage of 40 kV and a current of 30 mA. Fluorescence spectra of the polymers were recorded on a FS5 Spectrofluorometer (Edinburgh Instruments). The morphology of polymer film was characterized by field emission scanning electron microscope (FESEM, JEOL, JSM-7610F) at an accelerating voltage of 5.0 kV. Thermogravimetric analyses (TGA) of the polymers were performed on Shimadzu DTG-60AH thermal analyzer with a heating rate of 15 °C/min under N₂ atmosphere. Fourier Transform Infrared spectra (FTIR) were recorded by using a Bio-Rad FTS-3500 ARX FTIR spectrometer in the range 4000-400 cm⁻¹. The slice was made with powder constituted of KBr and sample by a tablet machine.

Electrochemical measurements: The cyclic voltammograms of as-prepared conjugated polymers were conducted in a deoxygenated anhydrous acetonitrile solution of tetrabutylammonium hexafluorophosphate (TBAPF₆, 0.1 M). A platinum electrode was used as the counter electrode, glassy carbon electrodes (GCE) was used as working electrode, and

Ag/Ag⁺ electrode (0.01 M AgNO₃ and TBAPF₆ in acetonitrile) was used as reference electrodes calibrated with ferrocene/ferrocenium couple (Fc/Fc⁺). HOMO and LUMO (eV) were calculated using the equation: $-4.8 + E_{1/2, \text{Fc, Fc}^+}$ oxidation or reduction onset.

Photoelectrode preparation: The photoelectrode was prepared by spin coating (rpm: 2000) THF solution of the polymer on a fluorine-doped tin oxide (FTO) conductive glass, which was cleaned in turn with acetone, ethanol, and DI water under continuous sonication, and then allowed to dry at room temperature. The composite film was prepared by spin coating the THF solution (10 mg/mL) of C12 onto the TiO₂ nanorods grown onto the FTO glass.

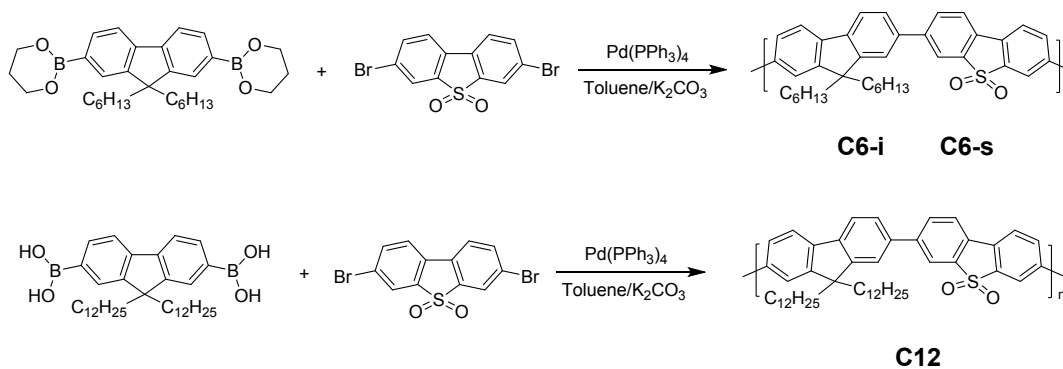
Photoelectrochemical activity measurement: PEC measurements were performed using a conventional three-electrode cell system and an electrochemical workstation (CHI 852C, chenhua, China). The prepared electrode was employed as the working electrode. Meanwhile, a saturated Ag/AgCl electrode and a platinum electrode served as the reference and counterelectrode, respectively. All the potentials were referred to the saturated Ag/AgCl unless otherwise stated. MAX-302 xenon lamp (Asahi Spectra) equipped with an ultraviolet cut-filter ($\lambda > 420$ nm) was used as light source to provide a visible light. Linear sweep voltammetry (LSV) curves were measured at a scanning rate of 10 mV s⁻¹, ranging from -1.0 V to 1.0 V vs Ag/AgCl. Electrochemical impedance spectroscopy (EIS) was carried out with a frequency range from 100 mHz to 100 kHz at a bias of +0.6 V (vs Ag/AgCl) in 0.5 M Na₂SO₄ solution.

ESI 2. Synthesis of the monomers and polymers

Synthesis of C6-s and C6-i: A mixture of 3,7-dibromodibenzothiophene-*S,S*-dioxide (0.25 mmol, 93.5 mg), 9,9-dihexyl-2,7-di(1,3,2-dioxaborolan-2-yl)fluorene (0.25 mmol, 125.6 mg), and Pd(PPh₃)₄ (2% mmol, 2.9 mg) was added in a 25 mL flask. 2 mL of dioxane, 6 mL of

toluene, and 3 mL of K_2CO_3 aqueous solution (2 M) added by syringe after the tube was evacuated and refilled with Ar three times. The reaction mixture was stirred at 85 °C for 5 hours under argon, and then cooled down to room temperature. The mixture was poured into methanol and collected by filtration. The solids were washed with CH_3OH , H_2O and acetone and then purified using a Soxhlet apparatus with THF. The soluble polymer C6-s was obtained concentration of THF solution as a yellow powder (35 mg, yield: 22%) and the insoluble polymer C6-i was obtained as a green powder (80 mg, yield: 51%). **C6-s**: 1H NMR (400 MHz, $CDCl_3$): δ 8.19-8.13 (m, 1H), 7.99-7.86 (m, 3H), 7.76-7.57 (m, 2H), 2.14 (d, 3H), 1.26 (m, 7H), 0.89-0.71 (m, 6H). GPC results: $M_n = 4810$; $M_w = 7310$; PDI = 1.52. Anal. Calcd for **C6-s** ($C_{43}H_{52}O_2S$)_n: C, 81.60; H, 8.28; S, 5.07. Found: C, 78.11; H, 7.67; S, 4.18. Anal. Calcd for **C6-i** ($C_{43}H_{52}O_2S$)_n: C, 81.60; H, 8.28; S, 5.07. Found: C, 79.54; H, 7.85; S, 4.29.

Synthesis of C12: **C12** was synthesized from 9,9-didodecylfluorene-2,7-diboronic acid in 83% yield by the same procedure as the preparation of C6-s with the reaction time of 24 h: yellow solid. 1H NMR (400 MHz, $CDCl_3$): δ 8.20-8.13 (m, 1H), 8.01-7.85 (m, 3H), 7.73-7.62 (m, 2H), 2.12 (s, 2H), 1.19-1.11 (d, 19H), 0.86-0.71 (m, 5H). GPC results: $M_n = 12040$; $M_w = 15290$; PDI = 1.27. Anal. Calcd for ($C_{49}H_{64}O_2S$)_n: C, 82.07; H, 9.00; S, 4.47. Found: C, 78.94; H, 7.17; S, 3.69.



Scheme S1 Synthetic procedures for the polymers

ESI 3. NMR spectra of the polymers

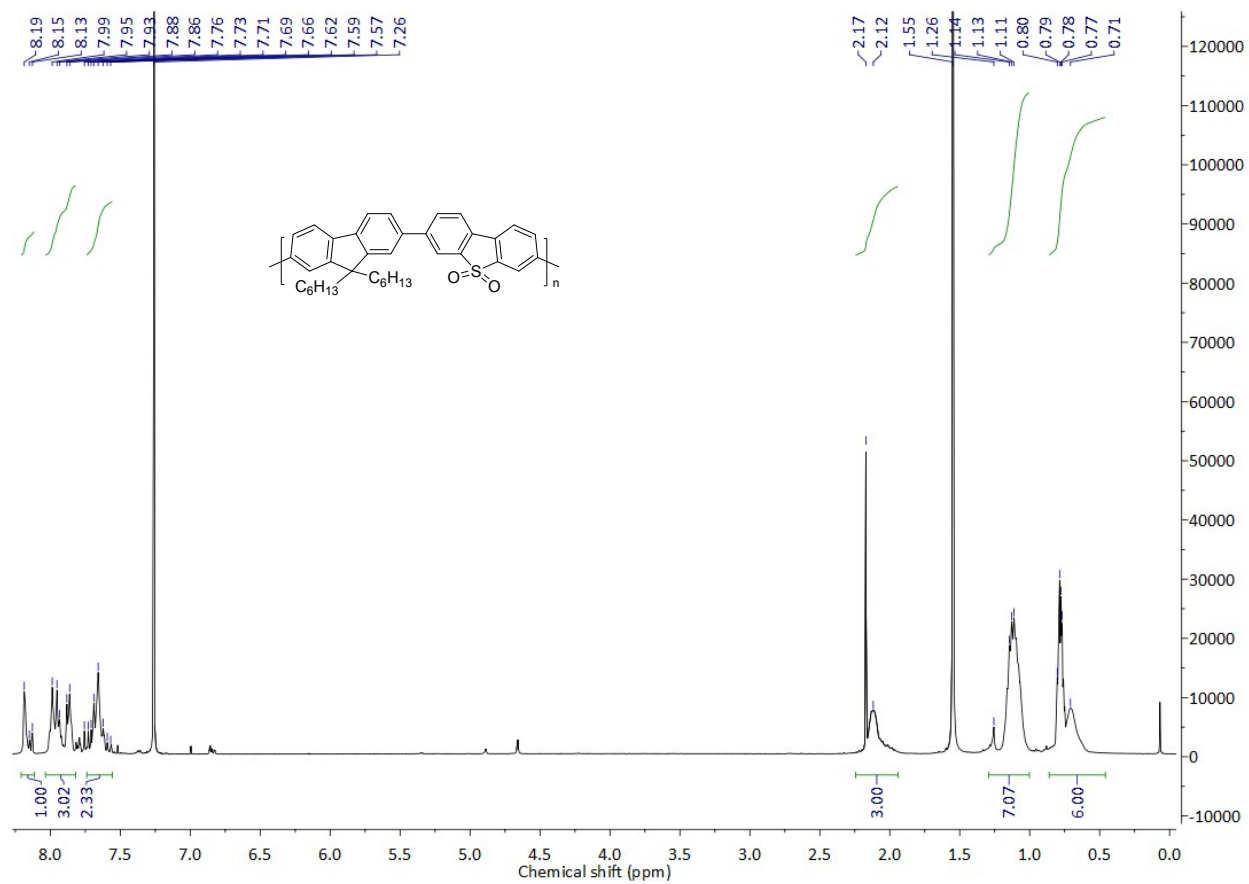


Fig. S1 ^1H NMR spectra of C6-s

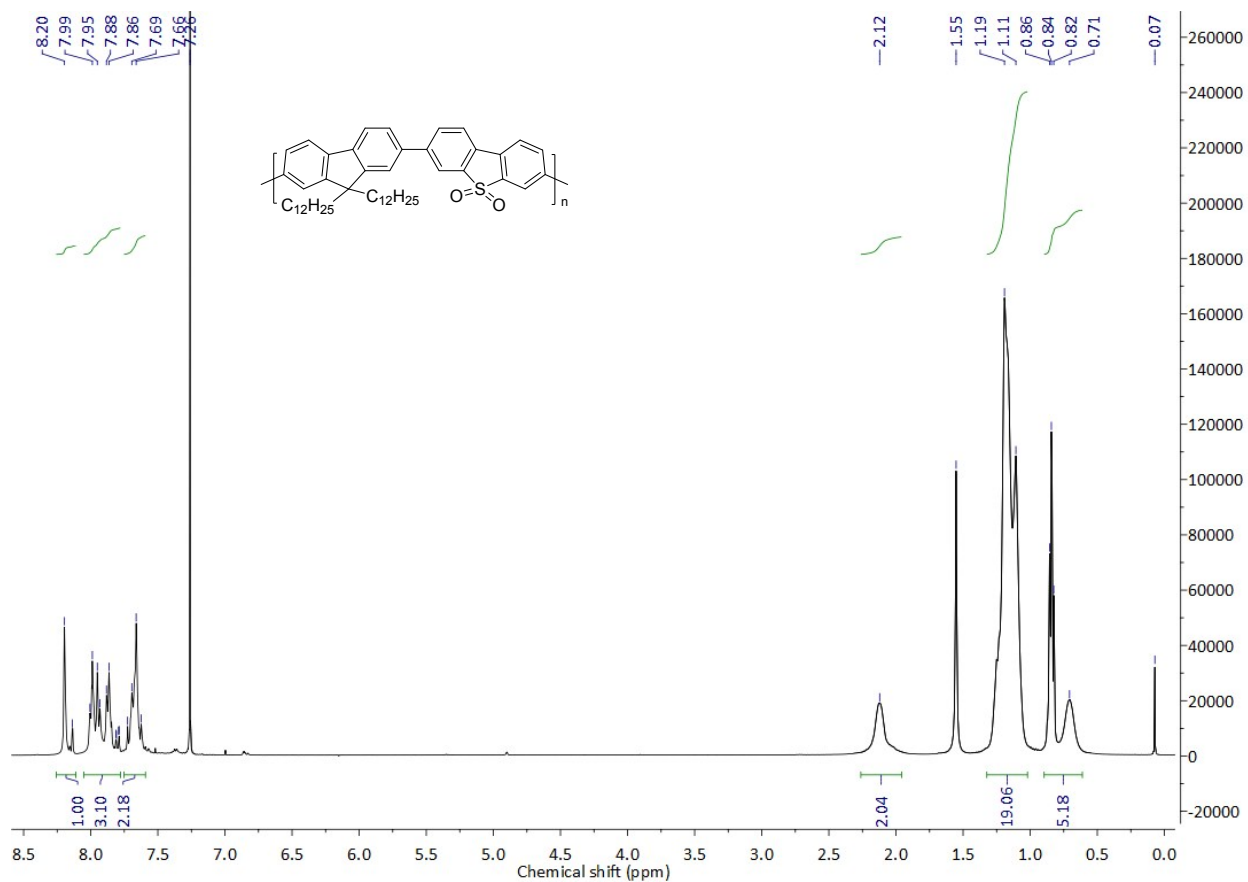


Fig. S2 ¹H NMR spectra of C12

ESI 4. FTIR spectra of polymers

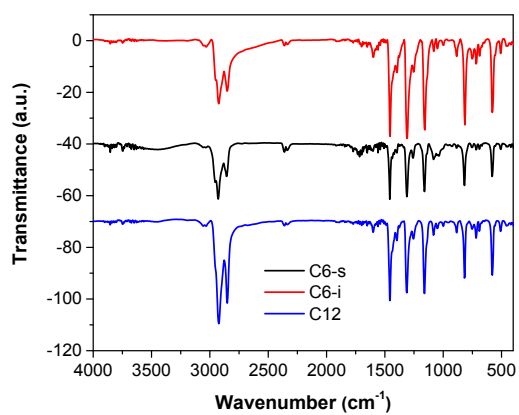


Fig. S3 FTIR spectra of polymers

ESI 5. Thermogravimetric analysis of polymers

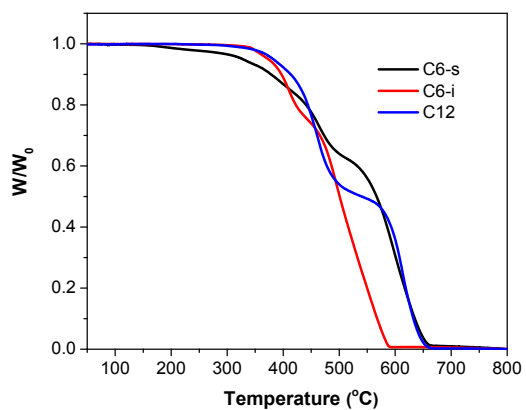
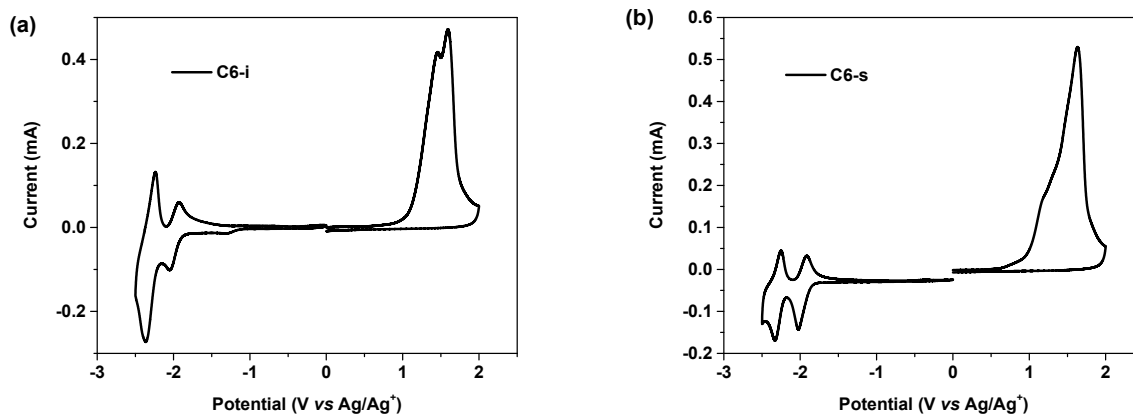


Fig. S4 Thermogravimetric analysis (TGA) curves for three polymers, recorded under a nitrogen atmosphere with a heating rate of 15 $^{\circ}\text{C}/\text{min}$

ESI 6. Cyclic voltammograms curves of Fc/Fc^+



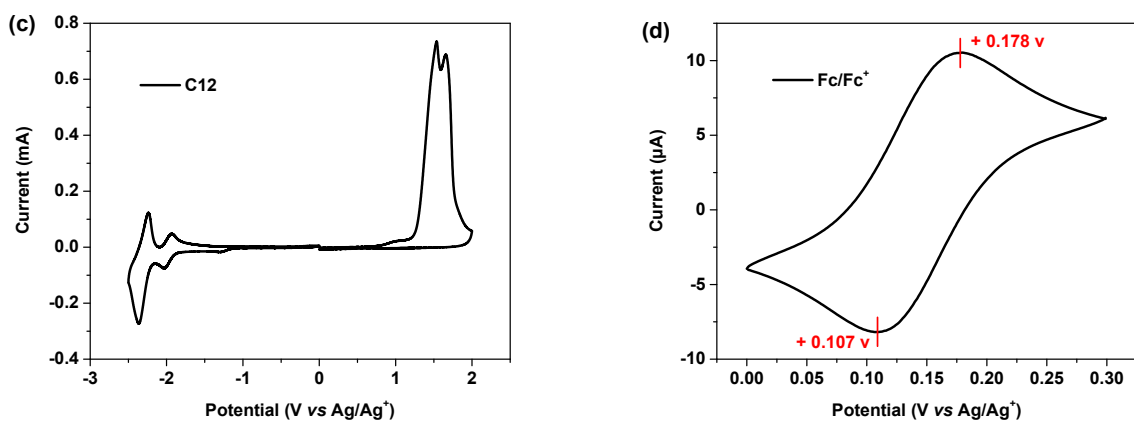


Fig. S5 (a) Cyclic voltammograms curves of Fc/Fc⁺ in anhydrous CH₃CN solution of TBAPF₆ (0.1 M). The half-wave potential of the Fc/Fc⁺ redox couple ($E_{1/2, \text{Fc,Fc}^+}$) was found to be 0.145 V $\{E_{1/2, \text{Fc,Fc}^+} = (E_{\text{ap}} + E_{\text{cp}})/2 = (0.178+0.107)/2 = 0.145 \text{ V}\}$ versus the Ag/Ag⁺ reference electrode.

ESI 7. XRD pattern of C6-i

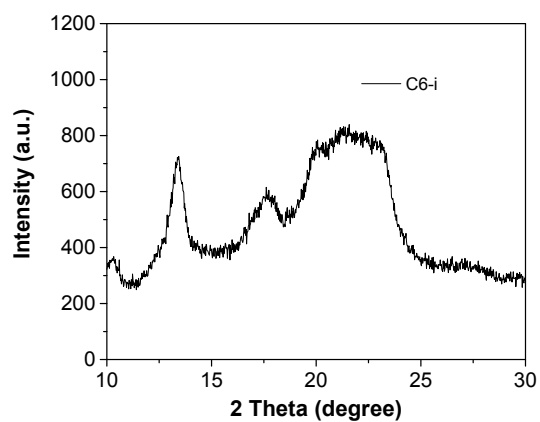


Figure S6. The XRD pattern of C6-i on FTO substrate.