Electronic Supplementary Information

for

Tuning of HOMO Energy Levels and Open Circuit Voltages in Solar Cells Based on Statistical Copolymers Prepared by ADMET Polymerization

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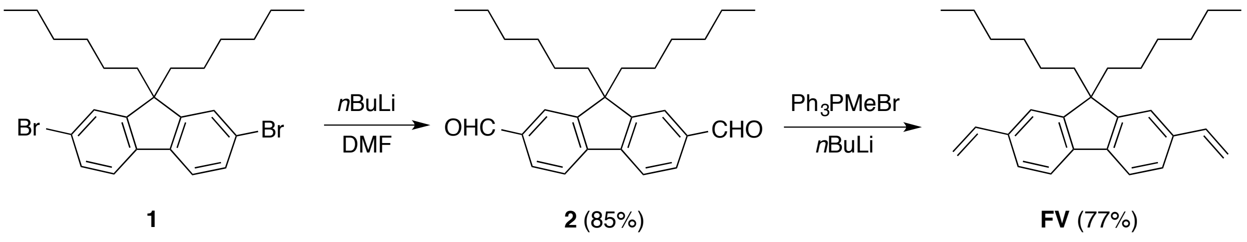
Monomer synthesis

The 2,7-divinyl-9,9'-di-n-hexylfluorene (**FV**) monomer was prepared by treating commercially available 2,7-dibromo-9,9'-dihexylfluorene (**1**) with n-butyllithium at -78 °C to form the dilithiated species (Scheme S1). This species was reacted with N,N-dimethylformamide to yield the dialdehyde (**2**) which was isolated after acidic workup. Standard Wittig chemistry saw the conversion of the dialdehyde intermediate to **FV**, a low melting white solid, with 65% overall yield. Note: The synthesis of the dipropenyl electron acceptor (4,7-bis(4-hexadecyl-5-propenyl-2-thienyl)-2,1,3-benzothiadiazole (TBTV)) and the resulting homopolymer (PTBTV), is thoroughly documented in a previous report.[1]

Scheme S1 Synthesis of FV.



2,7-Diformyl-9,9'-di-*n*-hexylfluorene (2). A 250 mL reaction flask was equipped with a magnetic stirring bar and flame dried. Commercially available 2,7-dibromo-9,9'-dihexylfluorene (5.00 g, 10.2 mmol) was added, and the flask was evacuated and refilled with argon. Anhydrous THF (70 mL) was cannulated into the flask, and the solution was cooled to -78 °C. Using a syringe, *n*-butyllithium (2.5 M hexanes, 8.60 mL, 21.4 mmol) was slowly added. The reaction became cloudy and was stirred at -78 °C for 1 h. Anhydrous DMF (2.40 mL, 31.6 mmol) in a solution of anhydrous THF (20 mL) was added via syringe. The reaction was allowed to warm to room temperature and stirred for 20 h. The reaction was quenched with 50 mL 1 M HCl and extracted with diethyl ether (2 × 100 mL). The combined organics were washed with 100 mL water and dried over Na_2SO_4. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography with 8:1 hexanes/ethyl acetate to afford a light yellow solid (3.4 g, 85%). ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): δ_H = 10.11 (s, 2H), 7.96-7.90 (m, 6H), 2.10-2.04 (m, 4H), 1.12-0.95 (m, 12H), 0.74 (t, J = 6.9 Hz, 6H), 0.57-0.52 (m, 4H).

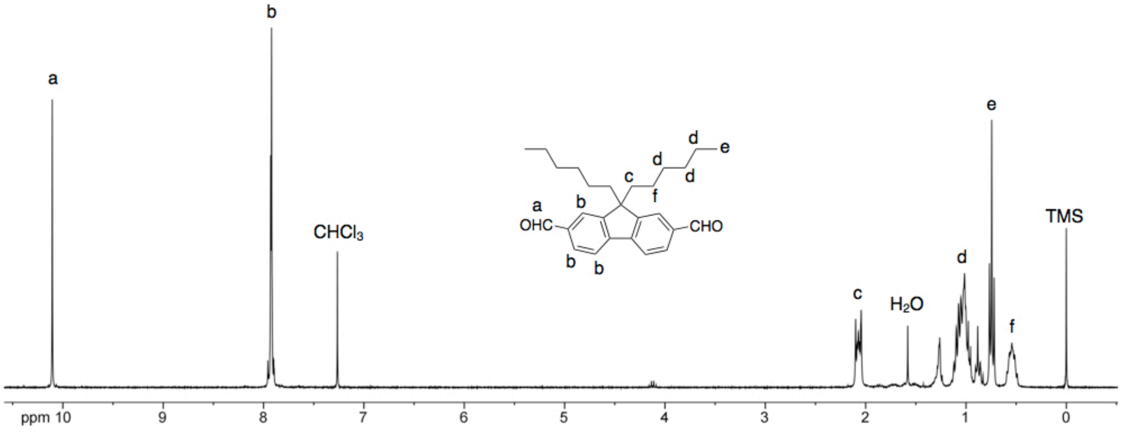


Figure S1 ^{1}H NMR of **2**.

2,7-Divinyl-9,9'-di-*n*-hexylfluorene (FV). A 250 mL reaction flask was equipped with a magnetic stirring bar and flame dried. Methyltriphenylphosphonium bromide (8.25 g, 23.1 mmol) was added, and the flask was placed under vacuum for 30 min. Anhydrous THF (100 mL) was cannulated into the flask, and the suspension was cooled to 0 °C. Using a syringe, *n*-butyllithium (2.5 M hexanes, 9.40 mL, 23.5 mmol) was slowly added. The reaction was stirred for 30 min at 0 °C to form the Wittig reagent. **2** (3.0 g, 7.7 mmol) was added in a solution of anhydrous THF (25 mL) via cannula. The reaction was allowed to warm to room temperature and stirred for 4 h. The solvent was removed by rotary evaporation. The brown residue was dissolved in MeOH (30 mL) and extracted with hexanes (3 × 100 mL). The hexanes were removed by rotary evaporation, and the resultant residue was purified by column chromatography with hexanes to afford product as a low melting white solid (2.3 g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ_H = 7.62 (d, *J* = 7.8 Hz, 2H), 7.39 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.35 (s, 2H), 6.80 (dd, *J* = 17.6, 10.9 Hz, 2H), 5.80 (dd, *J* = 17.6, 0.8 Hz, 2H), 5.26 (dd, *J* = 10.9, 0.7 Hz, 2H), 1.98-1.93 (m, 4H), 1.14-1.00 (m, 12H), 0.75 (t, *J* = 6.9 Hz, 6H), 0.67-0.57 (m, 4H).

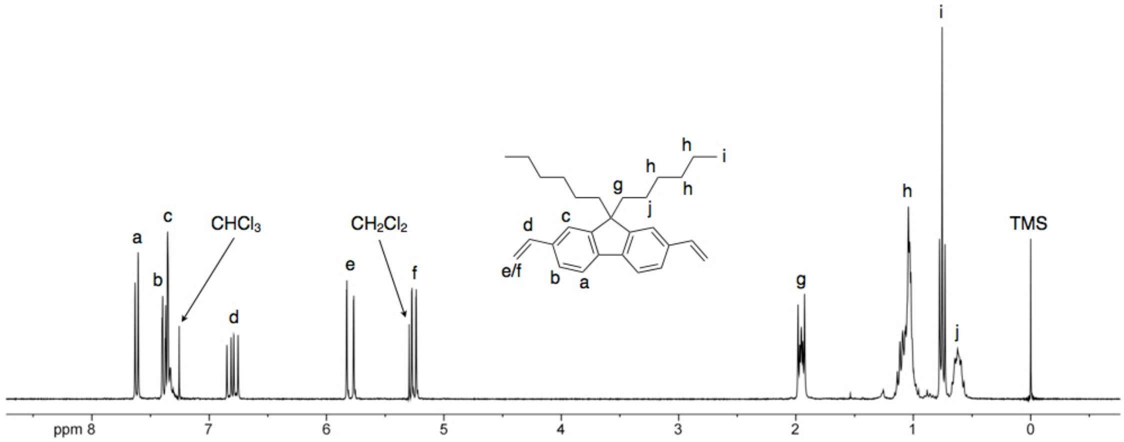


Figure S2 ^{1}H NMR of **FV**.

Poly(9,9-di-*n*-hexylfluorene-2,7-vinylene) (PFV). An apparatus like that shown previously[2] was assembled and flame dried under vacuum. A 50 mL Schlenk tube was charged with **FV** (200 mg, 0.52 mmol) in a solution of anhydrous TCB (4 mL). The solution was heated to 80 °C and dynamic vacuum was applied for 30 min to remove oxygen. The flask was placed under an argon atmosphere and G2 (14 mg, 0.016 mmol) was added as a solution in TCB (0.25 mL). Dynamic vacuum was reapplied. After 15 h the reaction was quenched by the addition of ethyl vinyl ether (3 drops). The polymer was precipitated in MeOH (150 mL, 0 °C) and filtered through a Soxhlet thimble. The polymer was purified by Soxhlet extraction with methanol (ca. 100 mL) and chloroform (ca. 100 mL). The chloroform fraction was concentrated to ca. 10 mL under reduced pressure and precipitated in MeOH (100 mL, 0 °C). The polymer was filtered and dried under vacuum to obtain the target material as a bright yellow solid (149 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$, Me_4Si): δ_H = 7.70-7.28 (m, 8H), 2.06-1.99 (m, 4H), 1.14-1.05 (m, 12H), 0.79-0.75 (m, 6H), 0.67 (s, 4H), vinyl end groups: 6.82 (dd, J = 17.5, 10.9 Hz), 5.82 (d, J = 17.6 Hz), 5.27 (d, J = 10.9 Hz).

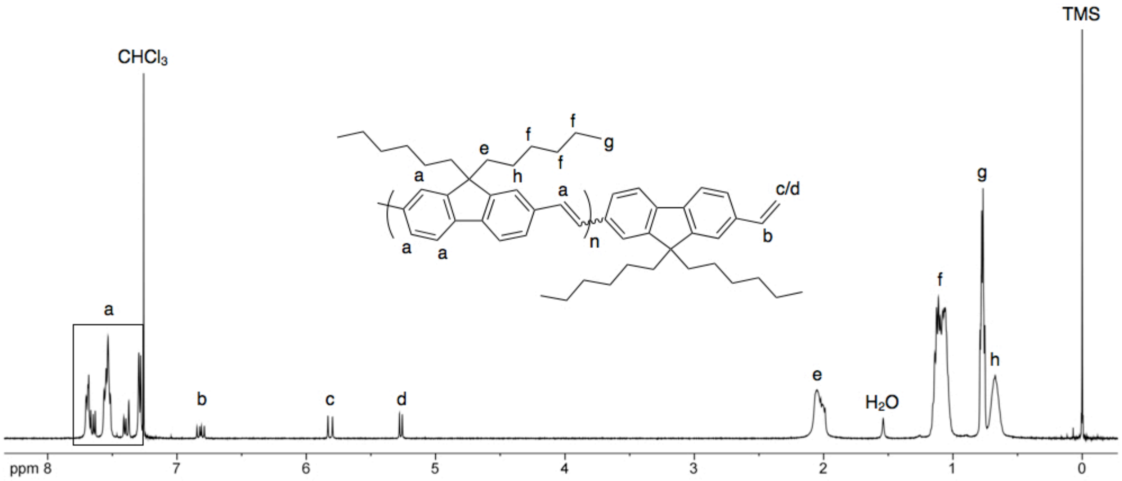


Figure S3 ^{1}H NMR of **PFV**.

General Copolymerization Procedure. The Schlenk tube was charged with monomers in a solution of anhydrous TCB (ca. 0.15 M). The solution was heated to 80 °C and dynamic vacuum was applied for 30 min. to remove oxygen. The flask was placed under an argon atmosphere and G2 (1 mol%) was added as a solution in TCB (0.5 mL). Dynamic vacuum was reapplied and the polymerization was run for 15–48 h. The reaction was quenched by the addition of ethyl vinyl ether (3 drops), and the polymer was precipitated into a 20-fold excess of a non-solvent (methanol or acetone) held at 0 °C. The precipitate was filtered through a Soxhlet thimble and purified by Soxhlet extraction with non-solvent (ca. 100 mL). The polymer was extracted into chloroform (ca. 100 mL) and concentrated under reduced pressure before precipitating into the same non-solvent (0 °C). The polymer was collected via filtration and dried under vacuum to obtain the target material. Copolymer composition was determined by ^{1}H NMR analysis.

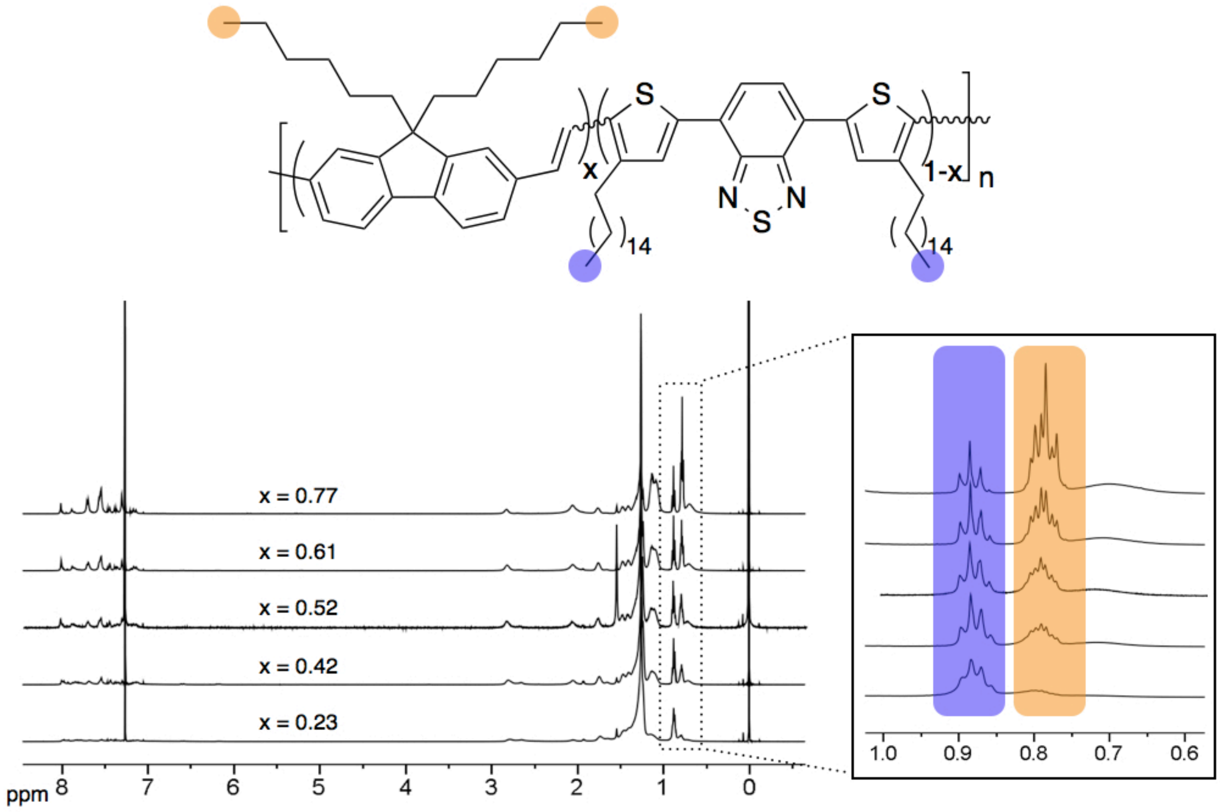


Figure S4 ^{1}H NMR spectra of PFV-TBTV series. Colored circles correspond to resonances used to quantify copolymer composition.

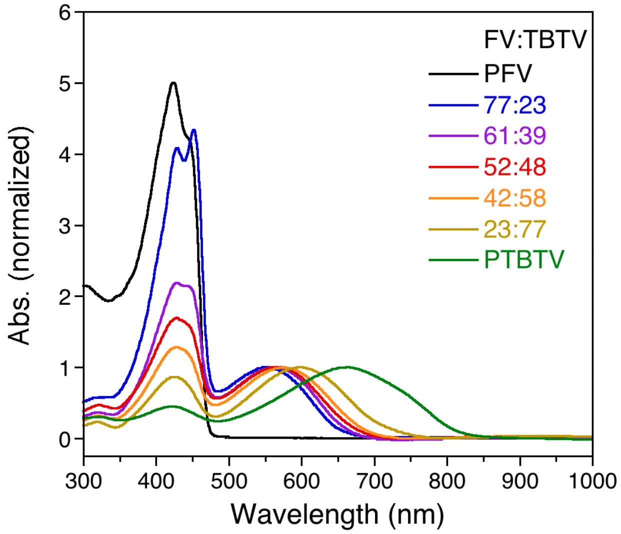


Figure S5 UV–vis solution spectra of the PFV-TBTV copolymer series and corresponding homopolymers. All spectra except PFV normalized to the second (TBTV) absorption peak.

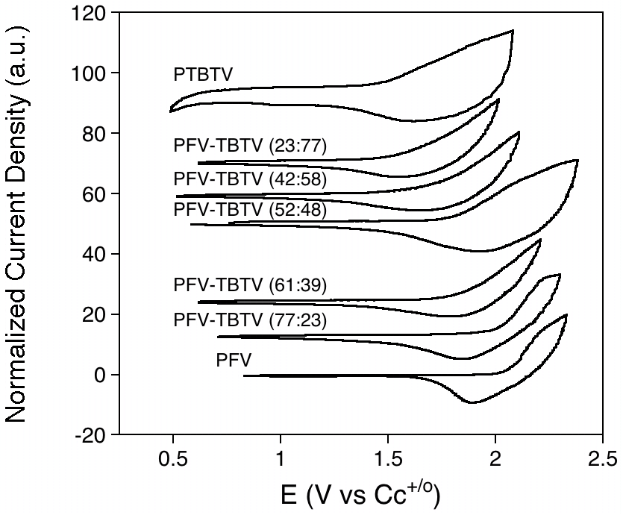


Figure S6 Cyclic voltammograms of the PFV-TBTV series and corresponding homopolymer thin films collected in [P14][TFSA] ionic liquid electrolyte at 50 mV sec^{-1}.

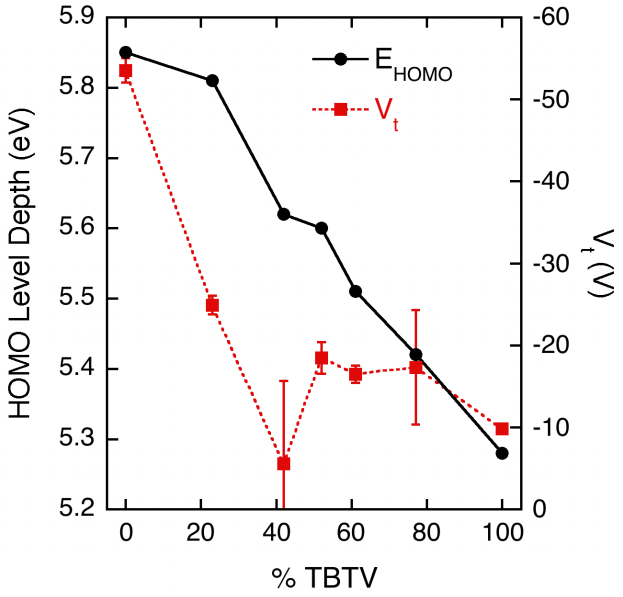


Figure S7 HOMO energy level (E_{HOMO}) and transistor threshold voltage (V_t) of the PFV-TBTV series and corresponding homopolymers.

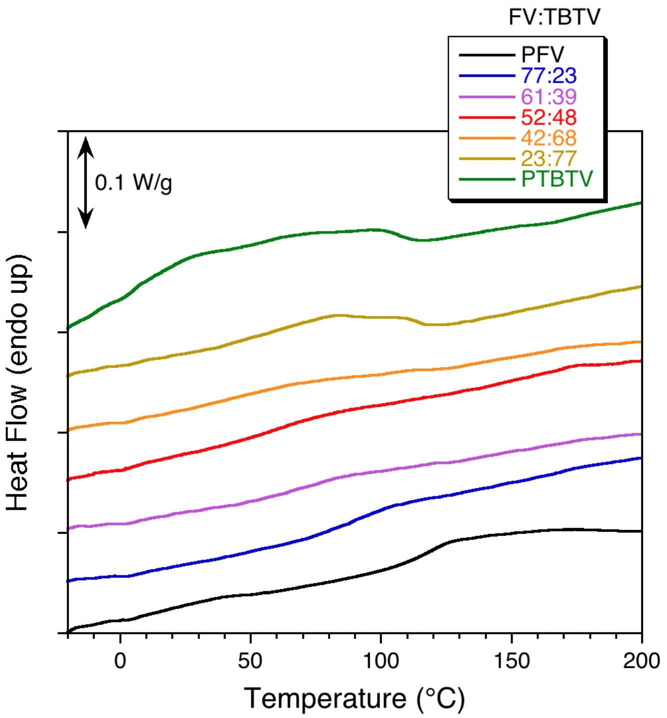


Figure S8 DSC thermograms (2nd heat) of homopolymers and copolymers. DSC was acquired following a heat-cool-heat protocol in the range of -30 to 230 °C at 10 °C min^{-1}.

[1] J. C. Speros, B. D. Paulsen, B. S. Slowinski, C. D. Frisbie and M. A. Hillmyer, *ACS Macro Lett.*, 2012, **1**, 986–990.

[2] J. C. Speros, B. D. Paulsen, S. P. White, Y. Wu, E. A. Jackson, B. S. Slowinski, C. D. Frisbie and M. A. Hillmyer, *Macromolecules*, 2012, **45**, 2190–2199.