

Supporting Information

Design, Synthesis and Characterization of Fused Bithiazole- and Dithiophene-Based Low Bandgap Thienylenevinylene Copolymers

Dhananjaya Patra,^{‡1} Marc Comí,^{‡1} Xianhe Zhang,² Gururaj P. Kini,³ Malsha Udayakantha,⁴ Alex Kalin,⁴ Sarbajit Banerjee,⁴ Lei Fang,⁴ Xugang Guo² and Mohammed Al-Hashimi^{1*}

¹ Department of Chemistry, Texas A&M University at Qatar, Education City, Doha, P.O. Box 23874, Qatar.

² Department of Materials Science and Engineering, Southern University of Science and Technology (SUSTech), No. 1088, Xueyuan Road, Shenzhen, Guangdong 518055, China

³ Nano and Information Materials (NIMs) Laboratory, Department of Chemical Engineering, Konkuk University, 120, Neungdong-ro, Gwangjin-gu, Seoul 05029, Korea.

⁴ Department of Chemistry, Texas A&M University, College Station, TX 77843-3012, United States

Table of contents:

- Materials and Methods
- Experimental Procedures
- NMR Characterization
- Polymer Thermal Properties
- Fluorescence
- AFM
- Computational Calculations
- OTFT Analysis

Materials and Methods

All commercially available solvents, reagents, and chemicals were used as received without further purification unless otherwise stated. Anhydrous solvent tetrahydrofuran (THF) was distilled from sodium under argon. Sodium sulfide hydrate, sodium, dibutyltin dichloride, selenium powder, tetrakis(triphenylphosphine)palladium (0), tetrabutylammonium fluoride solution 1.0 M in THF and N-bromosuccinimide were purchased from Sigma Aldrich. Unless otherwise stated, all operations and reactions were carried out under argon using standard Schlenk line techniques. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-400 (400 MHz), using the residual solvent resonance of CDCl_3 or TMS as an internal reference and are given in ppm. Number-average (M_n) and weight average (M_w) were determined by Agilent Technologies 1200 series GPC running in chlorobenzene at 80 °C, using two PL mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards. UV-vis spectra were recorded on a UV- 1601 Shimadzu Uv-vis spectrometer. Flash chromatography (FC) was performed on silica gel (Merck Kieselgel 60 F254 230-400 mesh) unless otherwise indicated. Thin Layer Chromatography (TLC) was performed on Merck aluminium-backed plates pre-coated with silica (0.2 mm, 60 F254). Microwave experiments were performed in a Biotage initiator V 2.3. Differential scanning calorimetry (DSC) analysis were recorded on Mettler in nitrogen at 10 °C min^{-1} of heating rate from 30 °C to 350 °C in two cycles heating-cooling, and thermogravimetric analysis (TGA) curves were collected on Mettler in nitrogen at 10 °C min^{-1} of heating rate from 30 °C to 600 °C. Cyclic voltammetry (CV) measurements of polymers films were performed under argon atmosphere using a CHI760E Voltammetry analyzer with 0.1 M tetra-n-butylammonium hexafluorophosphate in acetonitrile as the supporting electrolyte. A platinum disk working electrode, a platinum wire counter electrode, and a silver wire reference electrode were employed, and the ferrocene/ferrocenium (Fc/Fc^+) was used as the internal reference for all measurements. The scanning rate was 100 mV/s. Polymer films were drop-casted from chloroform solutions on a Pt working electrode (2 mm in diameter).

Device Fabrication

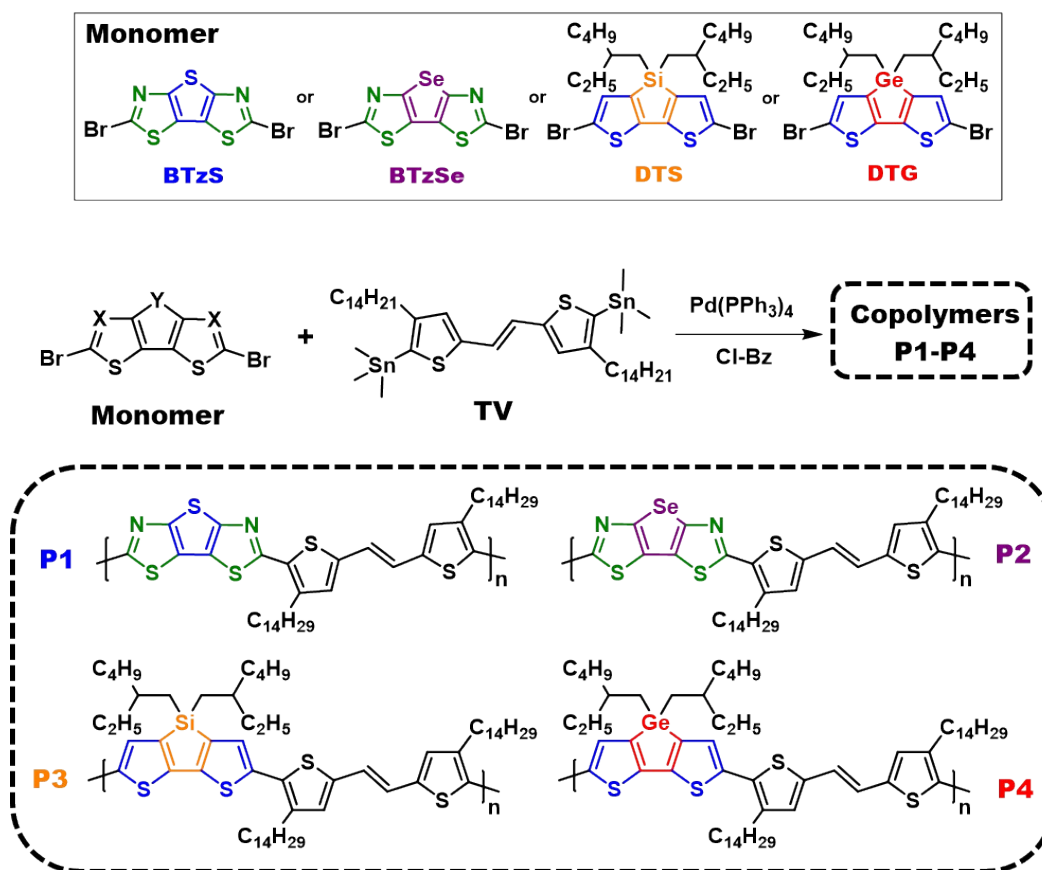
Borosilicate glass was used as substrate on which source and drain electrodes (3 nm Cr and 30 nm Au) were patterned by standard photolithography process. The glass with pattern were cleaned by sonicated in acetone and isopropanol for 10 min. Then substrates were transferred into glove box filled with N₂ after UV-ozone (30 min) and plasma (15 min) treatment. All the semiconductors were solved in dichlorobenzene/chlorobenzene/chloroform with concentration of 5 mg/ml. The solution was spin-coated on the substrate with speed of 3000 rpm for 1 min followed by annealing at different temperature for 10 min then cooled to room temperature.

Then diluted CYTOP solution (CTL-809M: CT-SOLV180 = 2:1 volume ratio, Asahi Glass Co., Ltd.) was spin-coated with speed 1500 rpm for 1 min as dielectric layer followed by annealing at 100 °C for 20 min. Eventually, 50 nm Al was evaporated on the top of substrate as gate electrodes.

The maximum values were extracted from saturated region at optimal annealing temperature based on the equation: $I_{SD} = \mu_{sat} C_i (W/2L) (V_G - V_T)^2$, where W is the width of channel, L is the length of channel. I_{DS} is the source–drain saturation current after gate leakage current correction, C_i is the capacitance per unit area of CYTOP dielectric layer (4.4 nF cm⁻²), μ_{sat} is the mobility, V_G is the gate voltage, and V_T is the threshold voltage. μ_{sat} is extracted using $\mu_{sat} = 2L(\partial |I_{SD}|^{1/2} / \partial V_G) / (C_i W)$, where $\Delta = \partial |I_{SD}|^{1/2} / \partial V_G$ is the slope of the square root plot of I_{SD} versus V_G .

Experimental Procedures

General Procedure for the Synthesis of TV-Copolymers P1-P4.



In a microwave vial equimolar amounts of ((E)-1,2-bis(4-tetradecyl-5-(trimethylstannyl)thiophen-2-yl)ethene (TV) (0.20 mmol) and 2,6-dibromothieno[2,3-d:5,4-d']bis(thiazole) or 2,6-dibromoselenopheno[2,3-d:5,4-d']bis(thiazole) or 2,6-dibromo-4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene or 2,6-dibromo-4,4-bis(2-ethylhexyl)-4H-germolo[3,2-b:4,5-b']dithiophene were dissolved in anhydrous chlorobenzene (0.5 mL) followed by addition of tetrakis(triphenylphosphine)palladium(0) (2 mol%, 5.02 mg), the resultant mixture was degassed for 30 min with argon and securely sealed. The glass vial was placed into a microwave reactor and heated at 140 °C for 2 min, 160 °C for 2 min, and followed by 180 °C for 30 min. After being cooled to room temperature, the reaction mixture was precipitated into a mixture of methanol (200 mL) and concentrated HCl (2 mL) and stirred for 1 h at RT. The precipitate was filtered and extracted (Soxhlet) with methanol, acetone, n-hexane, chloroform. The remaining polymer was

dissolved in chlorobenzene and precipitated into methanol, filtered and dried under vacuum to achieve the desired polymers as a dark purple solid. The ^1H NMR spectrum for all polymers exhibited considerable broadening of the aromatic and alkenyl hydrogen peaks and only alkyl sidechain protons were observable. We attribute this to the aggregation effects.

P1: Yield 101 mg, ^1H NMR (400 MHz, CDCl_3) δ 7.12 (2H), 6.92 (2H), 1.53 (4H), 1.10-1.50 (48H), 0.87 (6H); GPC: $M_n = 24,200$ g/mol, $\mathcal{D} = 2.0$; UV-Vis: $\lambda_{max} = 546$ nm (dilute chlorobenzene solution).

P2: Yield 100 mg, ^1H NMR (400 MHz, CDCl_3) δ 7.13 (2H), 6.92 (2H), 1.54 (4H), 1.10-1.50 (48H), 0.86 (6H); GPC: $M_n = 21,100$ g/mol, $\mathcal{D} = 1.9$; UV-Vis: $\lambda_{max} = 557$ nm (dilute chlorobenzene solution).

P3: Yield 123 mg, ^1H NMR (400 MHz, CDCl_3) δ 7.15 (4H), 6.95 (2H), 2.67 (4H), 1.66 (4H), 1.10-1.60 (72H), 0.90 (12H); GPC: $M_n = 36,400$ g/mol, $\mathcal{D} = 2.1$; UV-Vis: $\lambda_{max} = 560$ nm (dilute chlorobenzene solution).

P4: Yield 119 mg, ^1H NMR (400 MHz, CDCl_3) δ 7.13 (4H), 6.93 (2H), 2.65 (4H), 1.64 (4H), 1.10-1.60 (72H), 0.86 (12H); GPC: $M_n = 37,600$ g/mol, $\mathcal{D} = 2.1$; UV-Vis: $\lambda_{max} = 566$ nm (dilute chlorobenzene solution).

NMR characterization

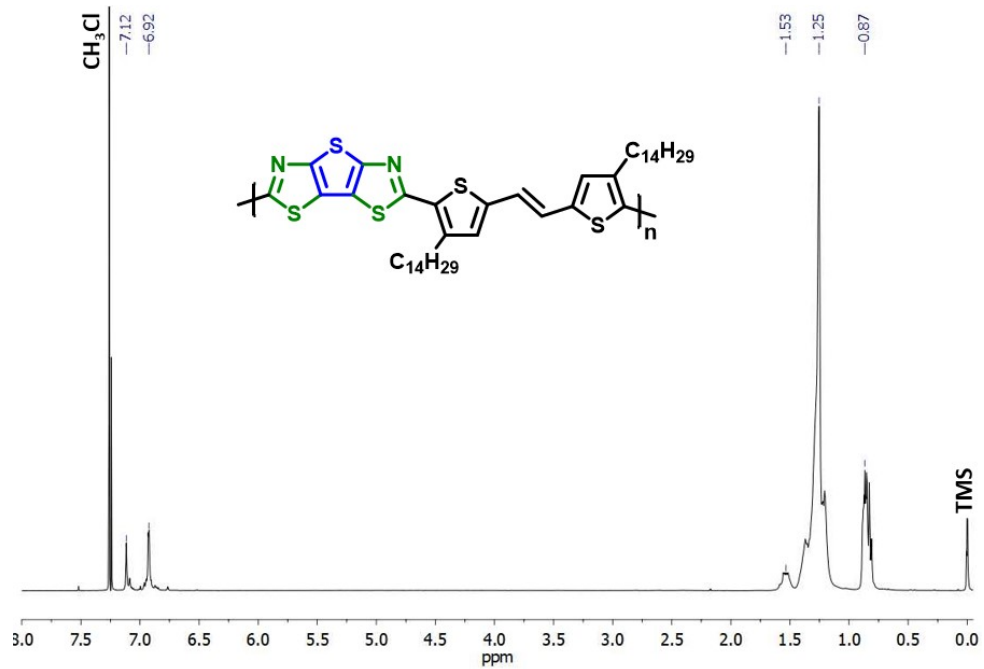


Figure S1. ^1H NMR spectrum of P1.

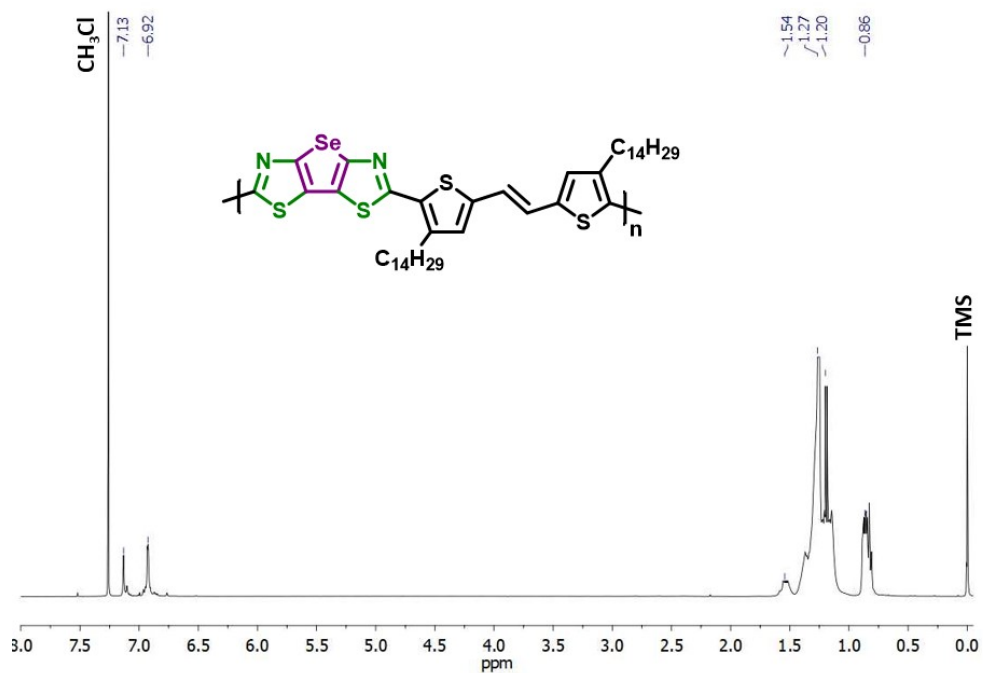


Figure S2. ^1H NMR spectrum of P2.

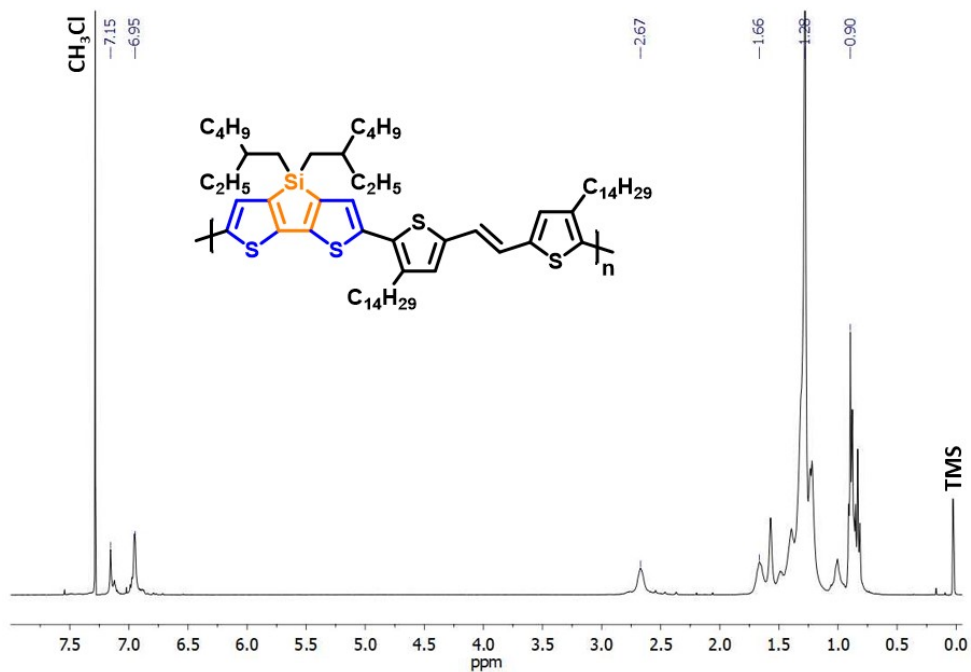


Figure S3. ^1H NMR spectrum of P3.

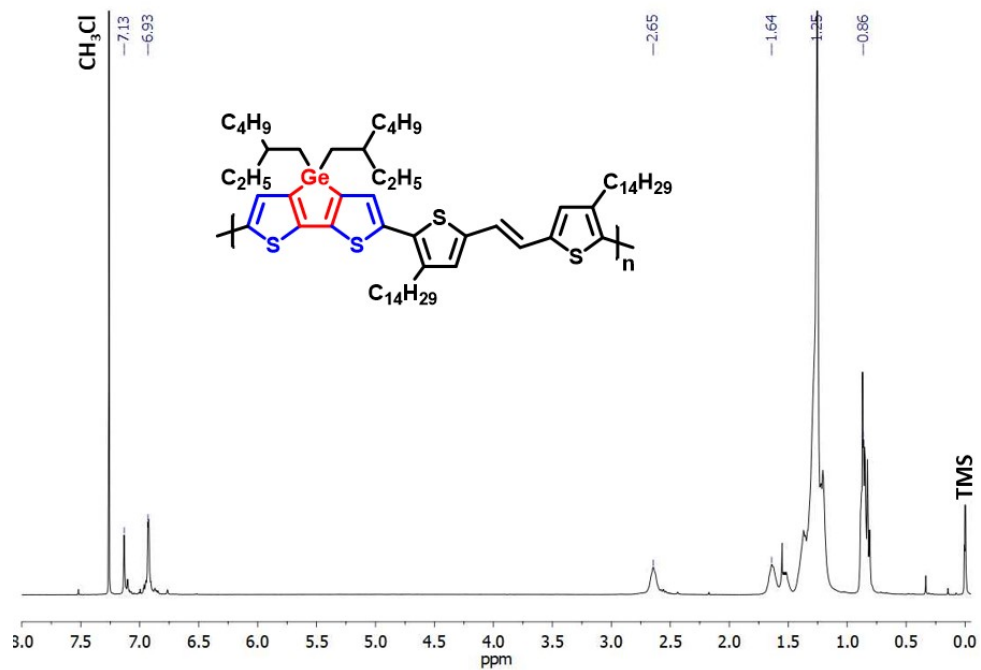


Figure S4. ^1H NMR spectrum of **P4**.

Polymer Thermal Properties

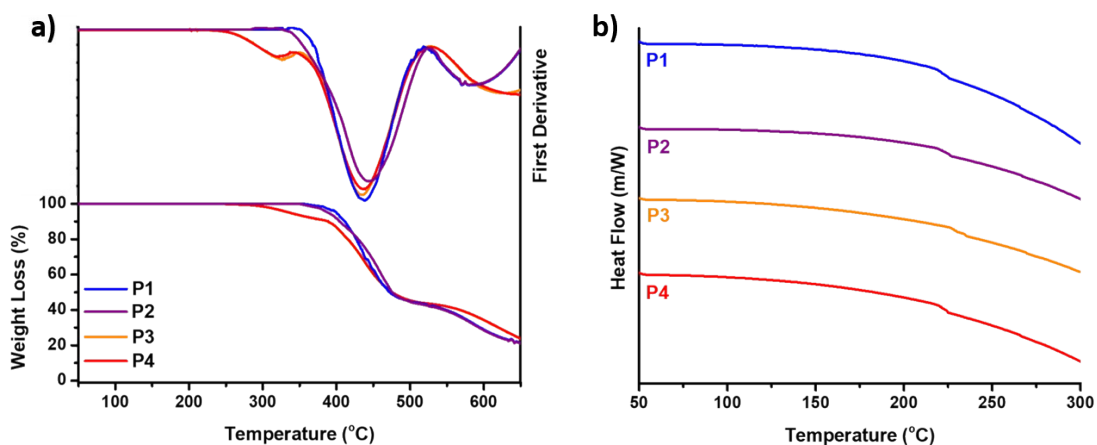


Figure S5. (a) TGA thermograms of copolymers **P1-4** under nitrogen flow at $10\text{ }^\circ\text{C min}^{-1}$ of heating rate from $30\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$. (b) DSC thermograms of second heating scan for copolymers **P1-4**, $30\text{ }^\circ\text{C}$ to $350\text{ }^\circ\text{C}$, in heating-cooling-heating scans with a ramp rate of $10\text{ }^\circ\text{C min}^{-1}$ under N_2 as the purge gas.

Fluorescence

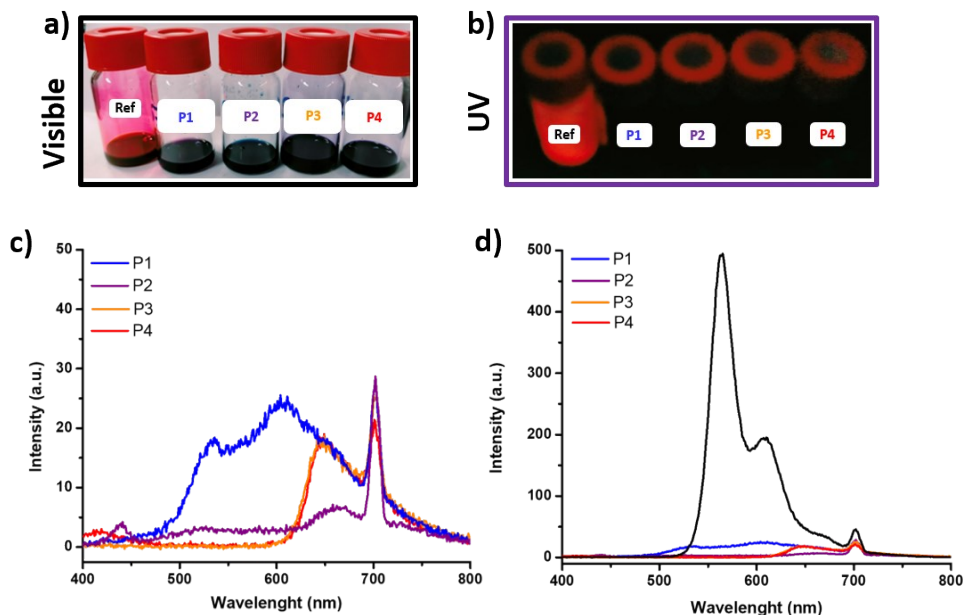


Figure S6. Photograph of **P1-P4** and fluorescence **reference** in solution under a) visible and b) UV light. Emission spectra of c) copolymers **P1-P4** in solution and d) comparison of intensity between fluorescence **reference** and copolymers **P1-P4** in solution upon excitation at 350 nm .

AFM

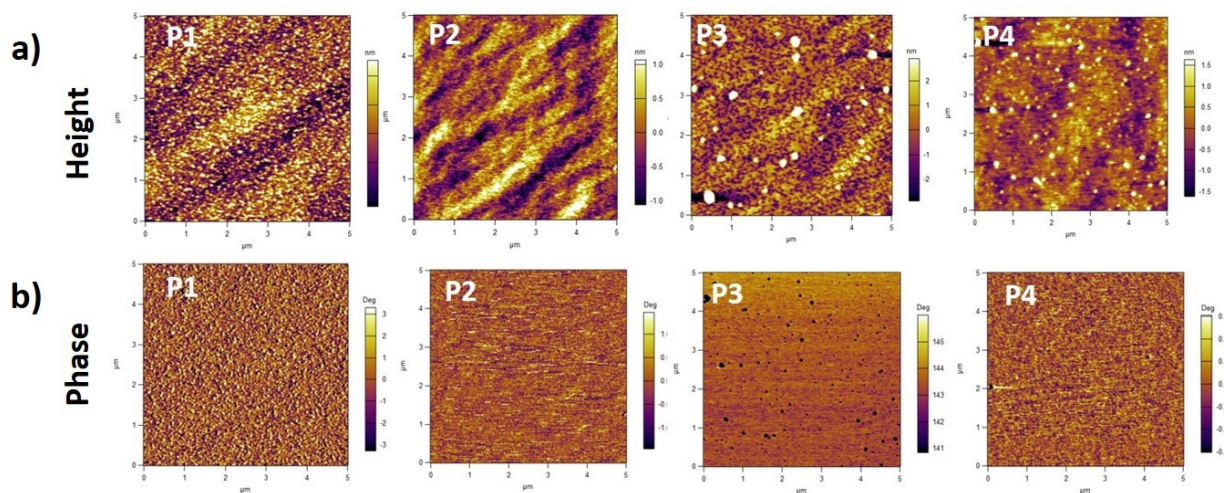


Figure S7. Tapping-mode AFM (a) height image and (b) phase image of as-cast films of copolymers **P1-4** and root-mean-square (RMS) roughness values **P1** = 1.16, **P2** = 0.53, **P3** = 0.80 and **P4** = 0.46 nm.

Computational Calculations

Polymer	θ_1 (°)	θ_2 (°)	θ_3 (°)	HOMO (eV)	LUMO (eV)
P1	0.01	0.01	0.02	-4.90	-2.67
P2	0.02	0.01	0.01	-4.88	-2.65
P3	3.97	5.69	5.4	-4.92	-4.02
P4	3.37	5.44	5.22	-4.90	-4.03

Table S1. Torsion angle and HOMO/LUMO energy level

of model dimers for **P1- P4** calculated by DFT.

OTFT Analysis

Table S2. Electrical parameters of field-effect transistors devices based on TV copolymers **P1-P4** fabricated with different chlorinated solvent.

Materials	Solvent	Annealing Temperature (°C)	μ_{Lin} (cm ² /Vs)		μ_{Sat} (cm ² /Vs)		V_{th} (V)	I_{On}/I_{off}
			Max	Avg	Max	Avg	Avg	
P1	CF	160	0.0028	0.0017	0.0036	0.0021	25	10 ³
	CB		0.0095	0.0069	0.013	0.0073	30	10 ³
	DCB		0.033	0.031	0.055	0.038	43	10⁶
P2	CF	160	<10 ⁻⁴		<10 ⁻³			
	CB		<10 ⁻⁴		<10 ⁻³			
	DCB		0.0026	0.0021	0.0029	0.0028	61	10⁶
P3	CF	160	0.079	0.053	0.29	0.11	26	10 ⁴
	CB		0.055	0.030	0.070	0.048	41	10 ⁴
	DCB		0.096	0.075	0.36	0.17	27	10⁶
P4	CF	160	0.134	0.052	0.35	0.14	23	10⁴
	CB		0.077	0.048	0.17	0.081	20	10 ⁴
	DCB		0.11	0.089	0.34	0.15	28	10⁶

Table S3. Electrical parameters of field-effect transistors devices based on TV copolymers **P1-P4** at

Materials	Annealing Temperature (°C)	μ_{Lin} (cm ² /Vs)		μ_{Sat} (cm ² /Vs)		V_{th} (V)	I_{On}/I_{off}
		Max	Avg	Max	Avg	Avg	
P1	Cast	0.034	0.029	0.041	0.035	46	10 ⁶
	130	0.043	0.033	0.047	0.043	45	10 ⁶
	160	0.033	0.031	0.055	0.038	43	10 ⁶
	190	0.039	0.033	0.055	0.044	41	10 ⁷
	220	0.060	0.049	0.086	0.069	43	10⁶
P2	Cast	0.00092	0.00071	0.0015	0.0014	62	10 ⁵
	160	0.0026	0.0021	0.0029	0.0028	61	10 ⁶
	190	0.0022	0.0011	0.0033	0.0029	60	10⁶
P3	Cast	0.036	0.032	0.073	0.042	30	10 ⁶
	130	0.047	0.041	0.096	0.062	30	10 ⁷
	160	0.096	0.075	0.36	0.17	27	10⁶
	190	0.077	0.068	0.30	0.14	32	10 ⁷
	220	0.025	0.021	0.047	0.034	28	10 ⁶
P4	Cast	0.038	0.025	0.037	0.028	30	10 ⁶
	130	0.038	0.032	0.088	0.049	32	10 ⁴
	160	0.11	0.089	0.34	0.15	28	10⁶
	190	0.57	0.049	0.16	0.090	29	10 ⁵
	220	0.039	0.031	0.12	0.06	28	10 ⁴

different annealing temperatures.

