

Supporting Information

Tunable Control of the Performance of Aqueous-based Electrochemical Devices by Post-polymerization Functionalization

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1. Materials and measurements

Materials: Solvents used in our work are all spectroscopic grade, purchased from Sigma Aldrich, and used as received. 4,7-dibromo-5-fluoro-2,1,3-benzothiadiazole was purchased from Nanjing Zhiyan Technology Co., Ltd. The monomers were purified by column chromatography using silica gel (General-Regent, 300-400 mesh) and the copolymers were purified by Soxhlet extraction. $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$ were conducted in chloroform-d (CDCl_3) or 1, 1, 2, 2-tetrachloroethane-d₂ (TCE-D₂) with a 400 HMZ or 500 HMZ Bruker Avance III spectrometer.

Molecular weight: The number-average molecular weights (M_n) and dispersity were determined using a PL-GPC 220 in DMF at 45 °C using a calibration curve with standard linear polyethylene glycol as a reference.

UV–Vis–NIR absorption spectroscopy: Spectra was measured using an Agilent Technologies (Cary 5000/6000i) Cary Win UV-Vis-NIR spectrophotometer. Solution spectra was recorded in a quartz cuvette with a 1cm path length at a concentration of 1.0×10^{-5} M (chloroform). Thin films were prepared by spin-coating 6 mg mL^{-1} solution (chloroform) on ITO-coated glass substrates.

Cyclic voltammetry (CV): The CV measurements were performed using a standard commercial electrochemical analyzer (Shanghai Chenhua Instrument co. LTD., CHI760E) with a three-electrode single-compartment cell equipped with an Ag/AgCl reference electrode and a Pt wire counter electrode. The copolymers were drop casted on a glassy carbon, which were utilized as working electrode. For the measurement in organic electrolyte, it was carried out in anhydrous acetonitrile (HPLC grade) under nitrogen and degassed. 0.1 M tetrabutylammonium hexafluorophosphate ($\text{n-Bu}_4\text{NPF}_6$) was used as the supporting electrolyte and the ferrocene/ferrocenium couple (Fc/Fc^+) was applied as an external standard. For the measurement in aqueous electrolyte, it was conducted in 0.1 M NaCl solution.

Gravimetric capacitance was obtained from CV measurement in 0.1 M aqueous NaCl solution. 30 μL of a solution (6 mg mL^{-1} , chloroform) of copolymers was drop casted on ITO coated glass substrates with the same area (2.85 cm^2). The gravimetric capacitance was calculated for copolymers from CV recorded at 50 mV s^{-1} by integrating the current from -0.3 V to 0.7 V and normalizing for copolymer mass.

Galvanostatic charge–discharge (GCD) measurement was carried out using a commercial electrochemical analyzer (Shanghai Chenhua Instrument co. LTD., CHI760E) with a three-

electrode set-up. Ag/AgCl was used as the reference electrode and a Pt wire was used as the counter electrode. 30 μL of copolymer solution (6 mg mL^{-1} , chloroform) was drop casted on ITO coated glass substrates with same area (2.85 cm^2), which was applied as a working electrode. Chronopotentiometry model was applied to perform the measurement between -0.3 V and 0.7 V.

Spectroelectrochemistry: The measurements were performed by fitting the CV setup inside a quartz cuvette in the UV-vis-NIR absorption spectrophotometer. The polymers were spin-casted onto the substrates from solutions in chloroform with a concentration of 6 mg mL^{-1} . Potentials were applied for 30 s prior to recording the UV-vis-NIR absorption spectrum at each voltage to ensure stabilization of the optical trace. Potential step of 0.1 V was then used to evaluate the electrochromic behavior of the polymers. All spectroelectrochemical measurements were conducted using a 0.1 M NaCl solution as the supporting electrolyte.

Grazing-incidence wide-angle X-ray scattering (GIWAXS): Samples for X-ray scattering were prepared by spin-coating 6 mg mL^{-1} solution (chloroform) on Si substrates. An incidence angle of 0.18° and photon energy of 8 keV were used to record the scattering patterns.

OECTs Device Fabrication: Electrode contacts were prepared by subsequently evaporating titanium (as an adhesion layer) and gold on glass using a custom-made mask. The channel was $L = 10 \mu\text{m}$ and width $W = 100 \mu\text{m}$. Solutions of the copolymers (6 mg mL^{-1}) in chloroform were spin-coated (500 rpm/5 s + 1000 rpm/30 s) on the electrodes. Film thicknesses were measured with a Tencor-P15 stylus profilometer. A solution of 0.1 M NaCl in water was used as the electrolyte and a silver pellet as the gate. Device characterization was performed in air at room temperature using a Keithley 4200A-SCS parameter analyzer. OECTs were gated with aqueous 0.1 M NaCl using an Ag/AgCl pellet as the gate electrode. Electrical characterization (output, transfer, and pulsed stability) of the OECTs were carried out using NI source-measure units controlled by custom LabView code. Data analysis was performed using OriginPro 2021, and transconductance lines were smoothed by adjacent averaging to attenuate instrument and environmental noise. μC^* was calculated from the slope of the transfer curves, which is the gate transconductance ($g_m = \partial I_d / \partial V_g$), using the relation $g_m = Wd/L \times \mu C^* \times (V_{th} - V_G)$.

Electrochemical impedance spectroscopy (EIS): EIS was performed with a three-electrode set-up same as CV measurement. EIS measurements were conducted in 0.1 m NaCl at a DC offset potential and a sinusoidal AC amplitude of 10 mV, spanning a frequency range from 10 kHz to 0.1 Hz. The $R_s (R_p // C)$ fits were generated using EC-Lab software V10.44. The

capacitance was calculated the film capacitances according to the equation below^[S1]:

$$C = \frac{1}{2\pi f \times |Img(Z)|}$$

where C is the capacitance, f is the frequency, and $|Img(Z)|$ is the magnitude of the imaginary part of the impedance. The capacitance values were normalized by film volume to determine the volumetric capacitance (C^*).

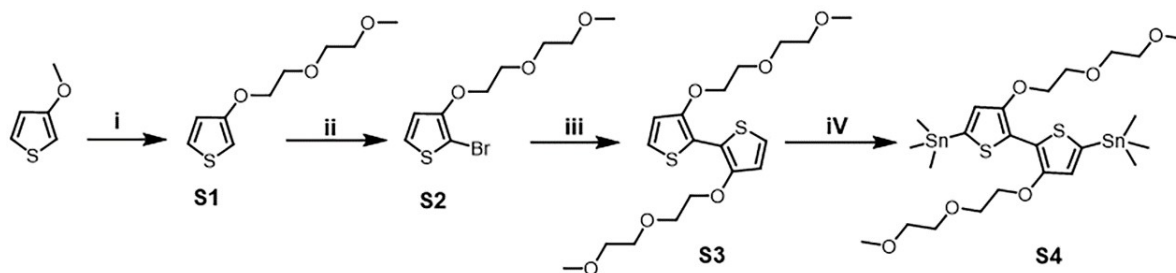
EQCM-D measurement: EQCM-D was carried out using a Q-sense analyzer (QE401, Biolin Scientific). Passive swelling measurements were performed as follows. First, the QCM-D response of bare Au sensors was recorded in air, followed by injection of a 0.1 M NaCl solution into the chamber. The measurements were then stopped when f and D were stable, the sensors were removed, and the polymer layers were spin-casted on the same sensors from polymer solutions in chloroform (6 mg/ml). The absolute f value for each polymer-coated sensor was obtained in both air and 0.1 M NaCl after the system was in equilibrium. EQCM-D was performed using an SP-300 (BioLogic Science Instruments) as the voltage source. The three-electrode setup was composed of Ag/AgCl (reference electrode), Pt (counter electrode), and an Au/polymer EQCM-D sensor (working electrode). A +0.7 V bias for 60 s was applied to the working electrode for the measurement of active swelling. Three cycles of cyclic voltammetry from 0 V to 0.7 V were performed for calculate the ions and water uptake.

Using the QSoft software function “stitch data” provided the difference between the f and D signals before and after the sensor was coated with a polymer film in both dry state and with electrolyte. This difference was used to calculate the film areal mass in dry and swollen states, using the Sauerbrey equation ^[S2]:

$$\frac{\Delta m}{A} = -\Delta f_n \frac{\rho_q V_q}{2f_0^2 n} \approx \frac{-\Delta f_n}{n} 17.9 \text{ ng/cm}^2$$

Where Δf_n represents the frequency shift of the n th overtone, A is the sensor active area, ρ_q is the density of quartz, V_q is the shear wave velocity in quartz, f_0 is the fundamental frequency and n is the overtone number.

2. Synthesis of Monomers and Copolymers



Scheme S1. Monomers synthesis

Reaction conditions: (i) toluene, *p*-TsOH, 110 °C; (ii) *n*-bromosuccinimide, anhydrous DCM, 0 °C, 2h; (iii) Ni(COD)₂, COD, BPy, THF; (iv) *n*-BuLi, Me₃SnCl, THF, -78 °C. **S1-S4** were synthesized according to the literature. [S3-S5]

Monomer S1

3-methoxythiophene (20.0 g, 175.2 mmol), 2-(2-methoxyethoxy)ethanol (31.6 g, 263.0 mmol) and *p*-toluenesulfonic acid monohydrate (3.0 g, 17.4 mmol) were dissolved in 200 mL toluene and the resulting mixture was heated at 110 °C for 5 h under nitrogen. After cooling the reaction to room temperature, the solution was diluted with dichloromethane (DCM) and washed with water and brine, before drying the combined organic phases over anhydrous MgSO₄. Excess solvent was removed under reduced pressure. The crude product was purified by silica flash column chromatography to give the target product, which is stored protected from light at -10 °C. (14.2 g, 40 % yield). ¹H NMR (400 MHz, chloroform-*d*, 300 K), δ (ppm): 7.18 (t, *J* = 3.92 Hz, 1H), 6.80 (d, *J* = 4.84 Hz, 1H), 6.28 (d, *J* = 3.12 Hz, 1H), 4.14 (t, *J* = 4.76 Hz, 2H), 3.86 (t, *J* = 4.92 Hz, 2H), 3.72 (t, *J* = 4.52 Hz, 2H), 3.59 (t, *J* = 4.88 Hz, 2H), 3.41 (s, 3H).

Monomer S2

A solution of **S1** (4.0 g, 19.8 mmol) in dry DCM (100 mL) was cooled to 0 °C. *N*-bromosuccinimide (3.5 g, 19.8 mmol) was added in small portions over 30 minutes. After the addition, the reaction was stirred at 0 °C for 2 h. The reaction was then warmed to room temperature and was quenched by 100 mL water. The reaction was extracted three times with DCM (50 mL), the combined solvent was washed with brine (200 mL), dried over MgSO₄, filtered, concentrated in vacuo to give an oil. The oil was purified by silica flash column chromatography to give the target product (5.1 g, 92 % yield), which is stored protected from

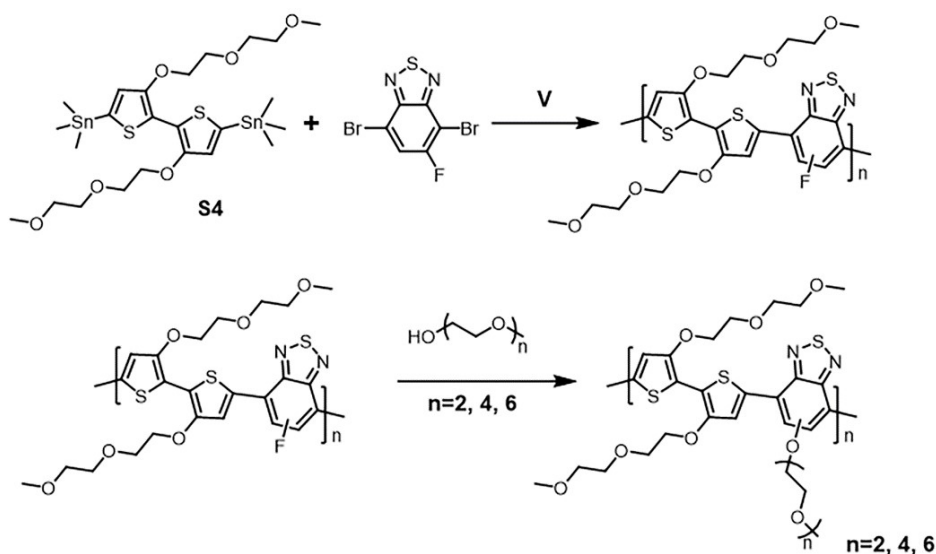
light at -10 °C. ¹H NMR (400 MHz, chloroform-d, 300 K), δ (ppm): 7.18 (d, J = 5.92 Hz, 1H), 6.78 (d, J = 6.00 Hz, 1H), 4.22 (t, J = 4.88 Hz, 2H), 3.84 (t, J = 4.84 Hz, 2H), 3.74 (t, J = 4.24 Hz, 2H), 3.58 (t, J = 4.88 Hz, 2H), 3.41 (s, 3H).

Monomer S3

S2 (2.0 g, 7.1 mmol), 1,5-cyclooctadiene (0.8 g, 7.1 mmol) and 2,2'-bipyridine (1.7 g, 10.7 mmol) were dissolved in anhydrous THF (100 mL). Bis(1,5-cyclooctadiene) nickel (0) (2.9 g, 10.7 mmol) was added in one portion to the reaction mixture, leading to the formation of a purple solution. The resulting solution was heated at 60 °C overnight. After cooling to room temperature, the reaction mixture was filtered, and the excess solvent was removed under reduced pressure. The crude product was purified by silica flash column chromatography to give the pure product as a solid (0.8 g, 55 % yield), which is stored protected from light at -10 °C. ¹H NMR (400 MHz, chloroform-d, 300 K), δ (ppm): 7.10 (d, J = 6.00 Hz, 2H), 6.87 (d, J = 5.60 Hz, 2H), 4.28 (t, J = 4.88 Hz, 4H), 3.92 (t, J = 5.32 Hz, 4H), 3.77-3.75 (m, 4H), 3.60-3.57 (m, 4H), 3.41 (s, 6H).

Monomer S4

S3 (0.8 g, 2.0 mmol) was dissolved in 30 mL anhydrous THF and the solution was cooled down to -78 °C. Then, a 1.6 M solution of n-butyllithium in hexane (5.0 mL, 8.0 mmol) was added dropwise. After stirring the solution for 1 h at -78 °C, trimethyltin chloride (8.4 mL, 1 M in hexane, 8.4 mmol) was added in one portion. After that, the solution was allowed to warm to room temperature and stirred overnight. The mixture was diluted with DCM and washed with water before drying the combined organic phases over MgSO₄. Excess solvent was removed under reduced pressure to afford a solid. The solid was recrystallized from isopropanol to give the product, which is stored protected from light at -10 °C. (1.1 g, 73 % yield). ¹H NMR (400 MHz, chloroform-d, 300 K), δ (ppm): 6.92 (s, 2H), 4.30 (t, J = 4.96 Hz, 4H), 3.94 (t, J = 5.28 Hz, 4H), 3.80-3.77 (m, 4H), 3.60-3.58 (m, 4H), 3.41 (s, 6H), 0.38 (s, 18H).



Scheme S2. Copolymers synthesis by post-polymerization modification^[S6]

g2T2-BTf

S4 (240.22 mg, 0.33 mmol), 4,7-dibromo-5-fluoro-2,1,3-benzothiadiazole (102.92 mg, 0.33 mmol), Pd₂(dba)₃ (6.04 mg, 6.6 × 10⁻³ mmol) and P(o-tol)₃ (12.05 mg, 0.04 mmol) were added to a microwave vial. The tube was sealed and flushed with nitrogen, and then degassed toluene (3 mL) was added. The mixture was degassed under nitrogen for 30 mins. The vial was stirred at 110 °C for 24 h. After cooling to room temperature, the solution was precipitated into methanol, and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus with methanol, acetone, hexane, and chloroform. The chloroform solution was concentrated and precipitated into methanol again. The precipitate was filtered and dried under vacuum to afford **g2T2-BTf** (142.73 mg, 78 %). ¹H NMR (500 MHz, 1, 1, 2, 2-tetrachloroethane-d₂, 373K), δ (ppm) : 7.72-7.56 (m, 2H), 7.27-7.15 (m, 1H), 4.06-3.94 (m, 4H), 3.62-3.48 (m, 4H), 3.43-3.27 (m, 4H), 3.21-3.07 (m, 4H), 2.95-2.88 (s, 6H). ¹⁹F NMR (400 MHz, chloroform-d, 300 K), δ (ppm): -103.1.

General procedure for the post-polymerization modification^[S6]: A mixture of **g2T2-BTf** (50 mg, 0.09 mmol) and NaOH (80 mg, 2.0 mmol) was added to a high pressure microwave vial. The vial was sealed with a septum and degassed with nitrogen before anhydrous chlorobenzene and DMF (3:1, v:v, 4 ml in total) and the desired alcohol (0.2 mmol) was added. The solution was heated at 120 °C for 48 h. During this time, the reaction was monitored by ¹⁹F NMR spectroscopy. After reaction, the solution was cooled down, diluted with DCM (20 mL) and washed with water to remove residual DMF and NaOH.

The solvent was then removed under reduced pressure. To remove the excess alcohol, the residue was repeatedly washed in refluxing acetone, resulting in a solid.

g2T2-gBT2: ^1H NMR (500 MHz, 1, 1, 2, 2-tetrachloroethane- d_2 , 373K), δ (ppm) : 8.08-7.94 (broad, 1H), 7.67-7.53 (broad, 1H), 7.47-7.30 (broad, 1H), 4.17-3.95 (m, 4H), 3.72-2.98 (m, 20H), 2.98-2.78 (broad, 9H). ^{19}F NMR (400 MHz, chloroform- d , 300 K), no signal.

g2T2-gBT4: ^1H NMR (500 MHz, 1, 1, 2, 2-tetrachloroethane- d_2 , 373K), δ (ppm) : 8.08-7.94 (broad, 1H), 7.68-7.53 (broad, 1H), 7.45-7.27 (broad, 1H), 4.15-3.99 (m, 4H), 3.68-3.46 (m, 6H), 3.41-2.91 (m, 22H), 2.93-2.85 (broad, 6H), 2.85-2.79 (s, 3H). ^{19}F NMR (400 MHz, chloroform- d , 300 K), no signal.

g2T2-gBT6: ^1H NMR (500 MHz, 1, 1, 2, 2-tetrachloroethane- d_2 , 373K), δ (ppm) : 8.13-7.94 (broad, 1H), 7.69-7.50 (broad, 1H), 7.47-7.30 (broad, 1H), 4.13-3.99 (m, 4H), 3.70-3.53 (m, 6H), 3.41-3.00 (m, 30H), 2.91-2.87 (broad, 6H), 2.87-2.82 (s, 3H). ^{19}F NMR (400 MHz, chloroform- d , 300 K), no signal.

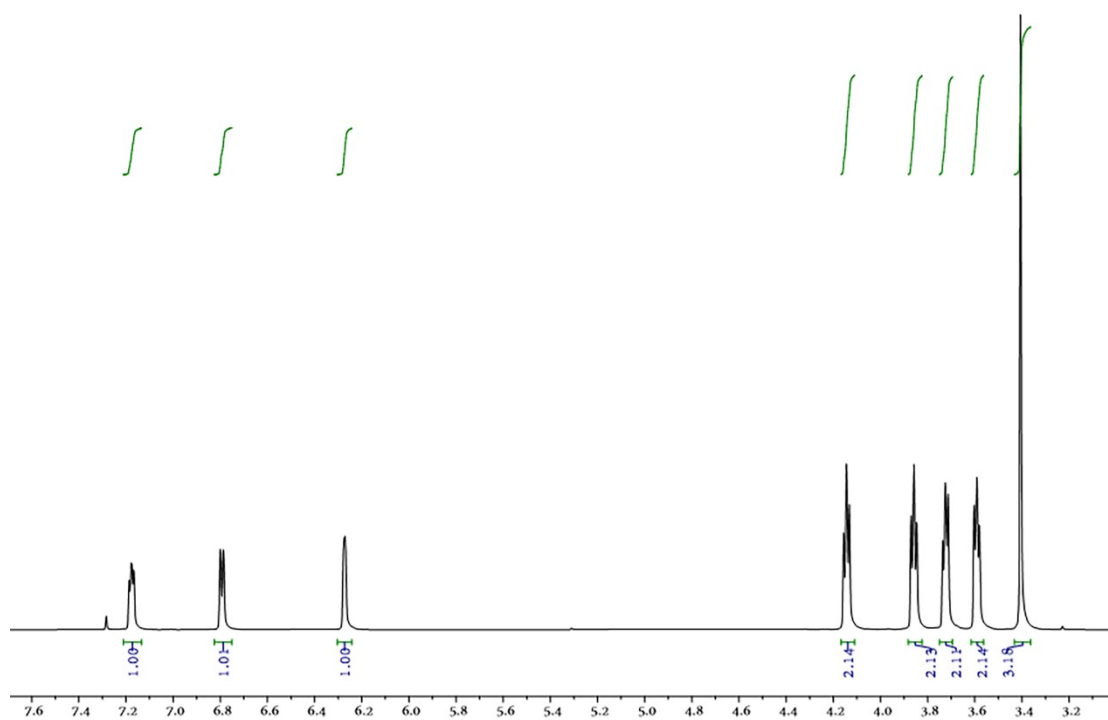


Figure S1. ^1H NMR of monomer S1

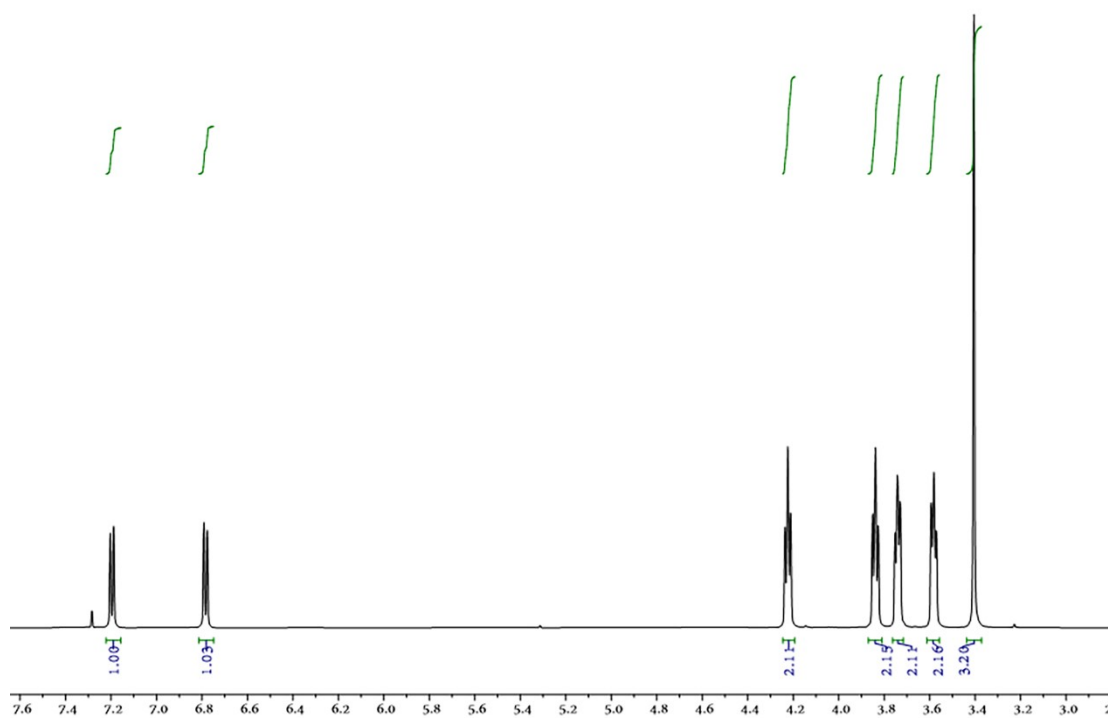


Figure S2. ^1H NMR of monomer S2

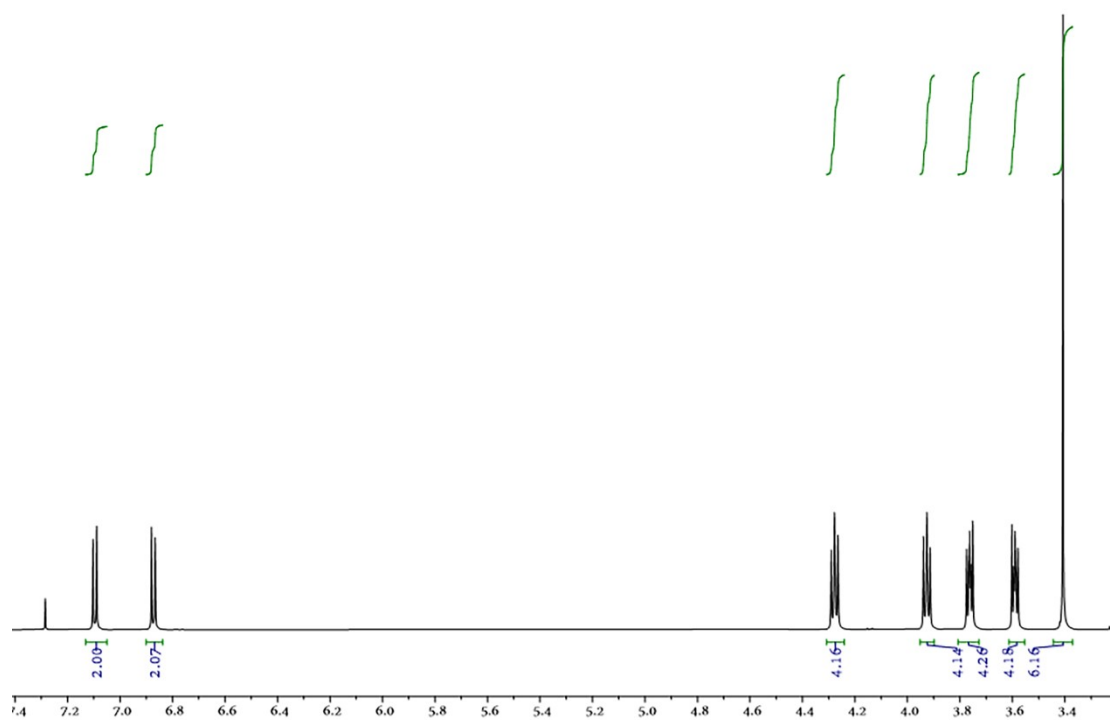


Figure S3. ^1H NMR of monomer S3

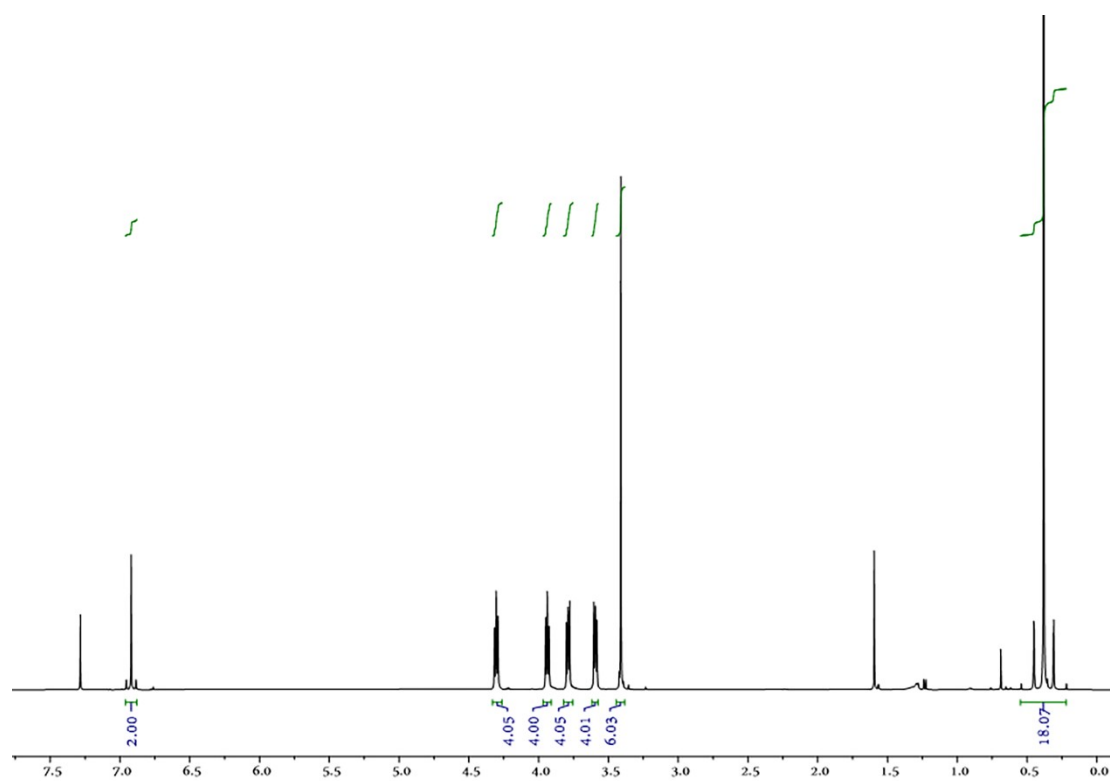


Figure S4. ^1H NMR of monomer S4

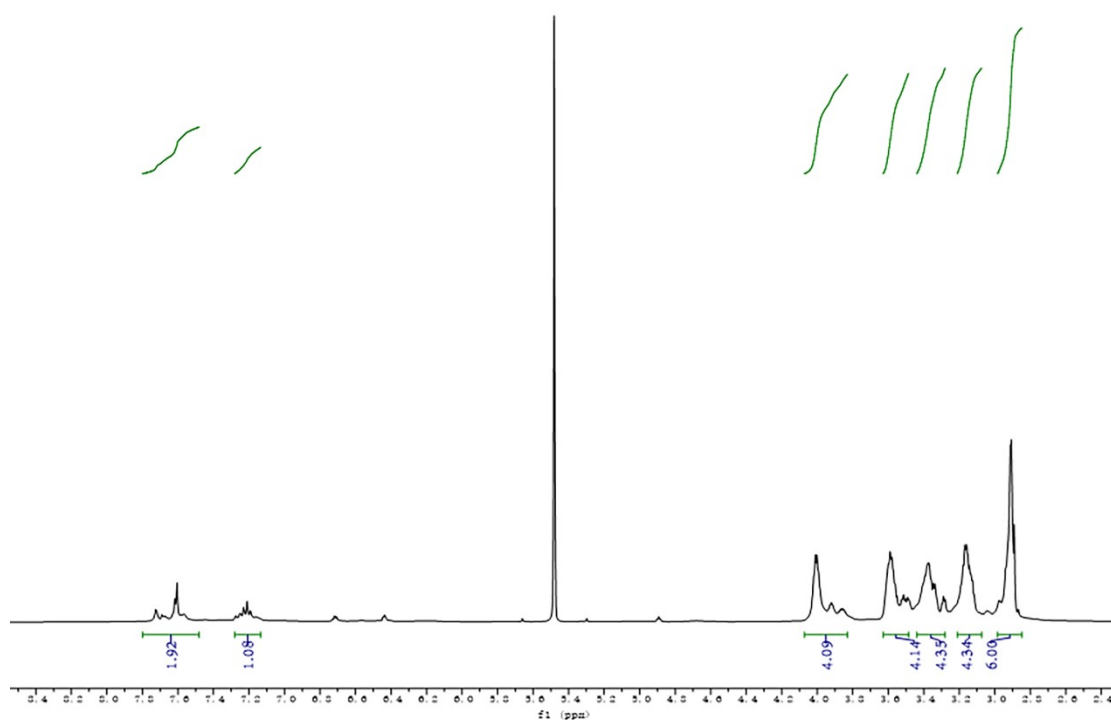


Figure S5. ^1H NMR of polymer **g2T2-BTf** (1, 1, 2, 2-tetrachloroethane- d_2 , 500 MHz, 373 K)

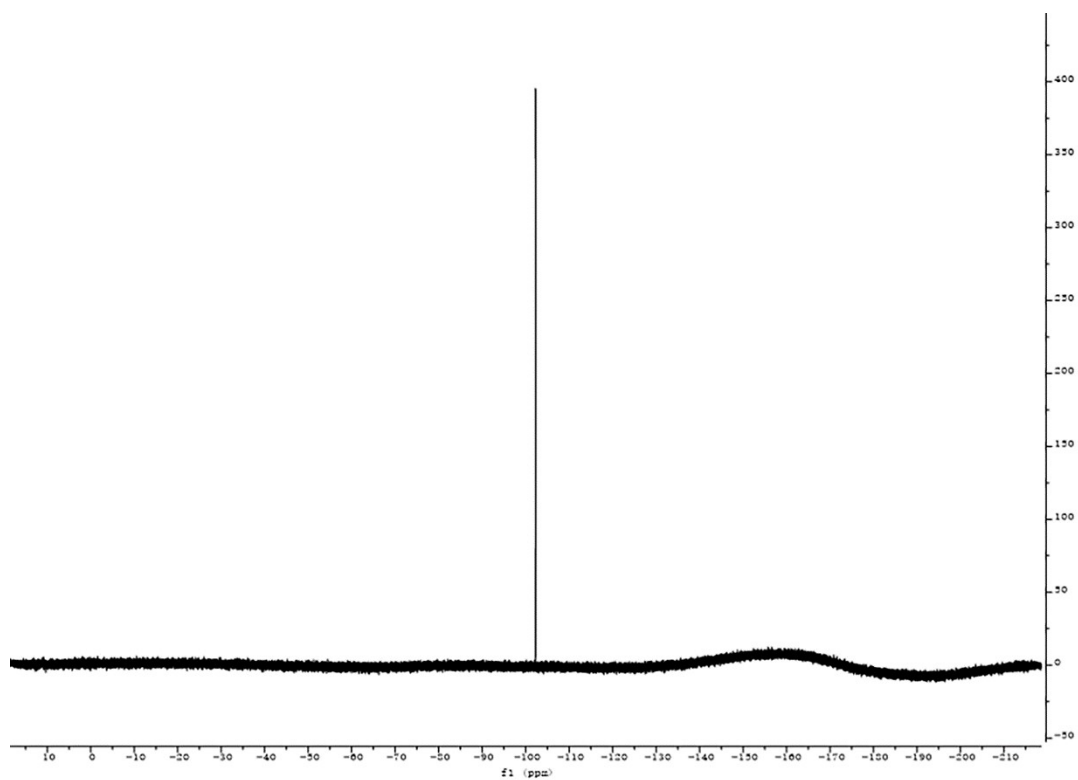


Figure S6. ^{19}F NMR of polymer **g2T2-BTf** (chloroform- d , 400 MHz, 300 K)

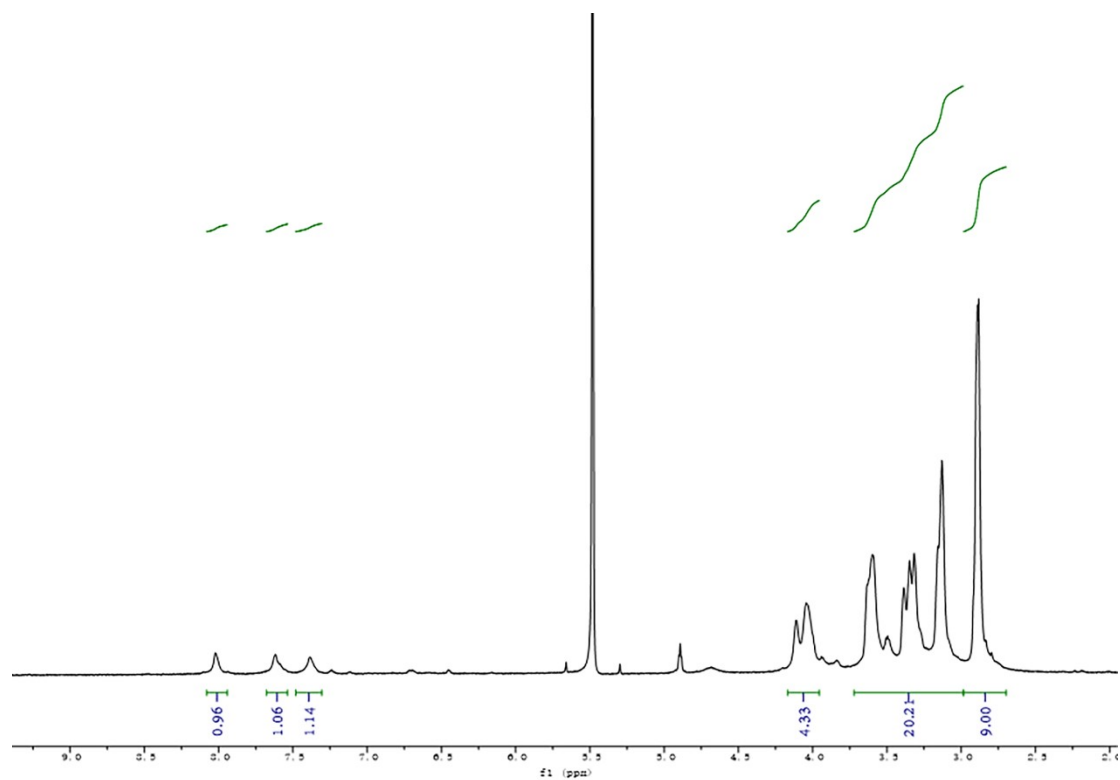


Figure S7. ^1H NMR of polymer **g2T2-gBT2** (1, 1, 2, 2-tetrachloroethane- d_2 , 500 MHz, 373 K)

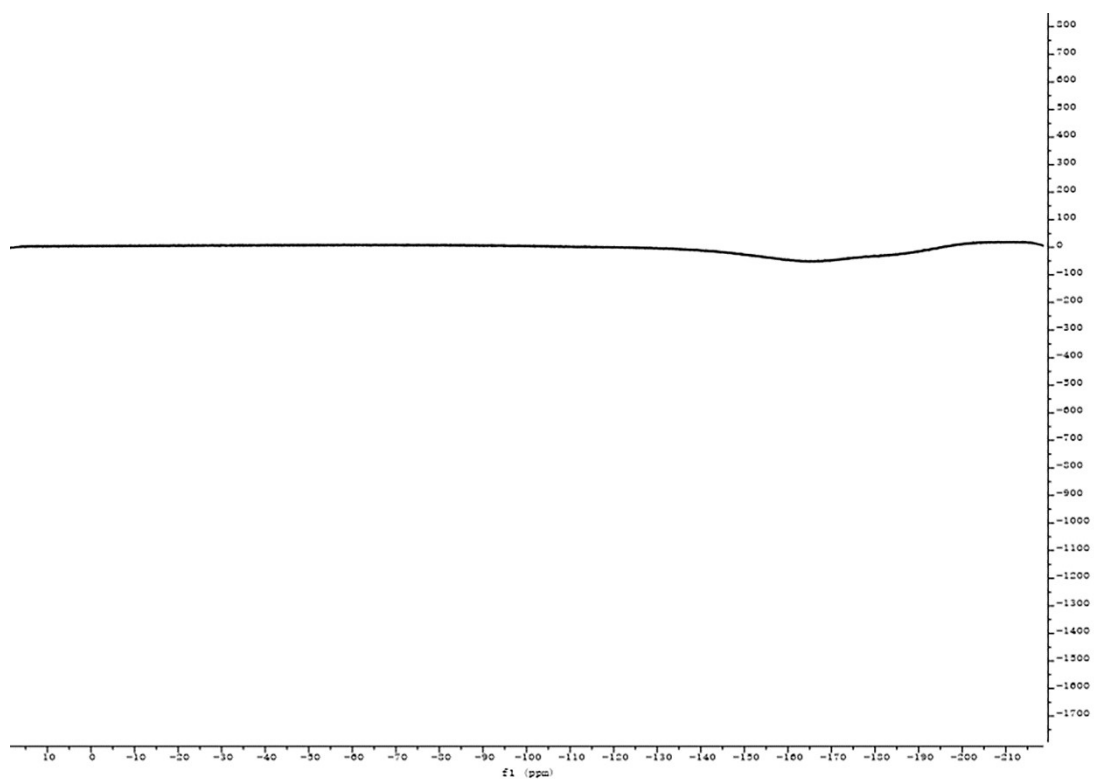


Figure S8. ^{19}F NMR of polymer **g2T2-BT2** (chloroform- d , 400 MHz, 300 K)

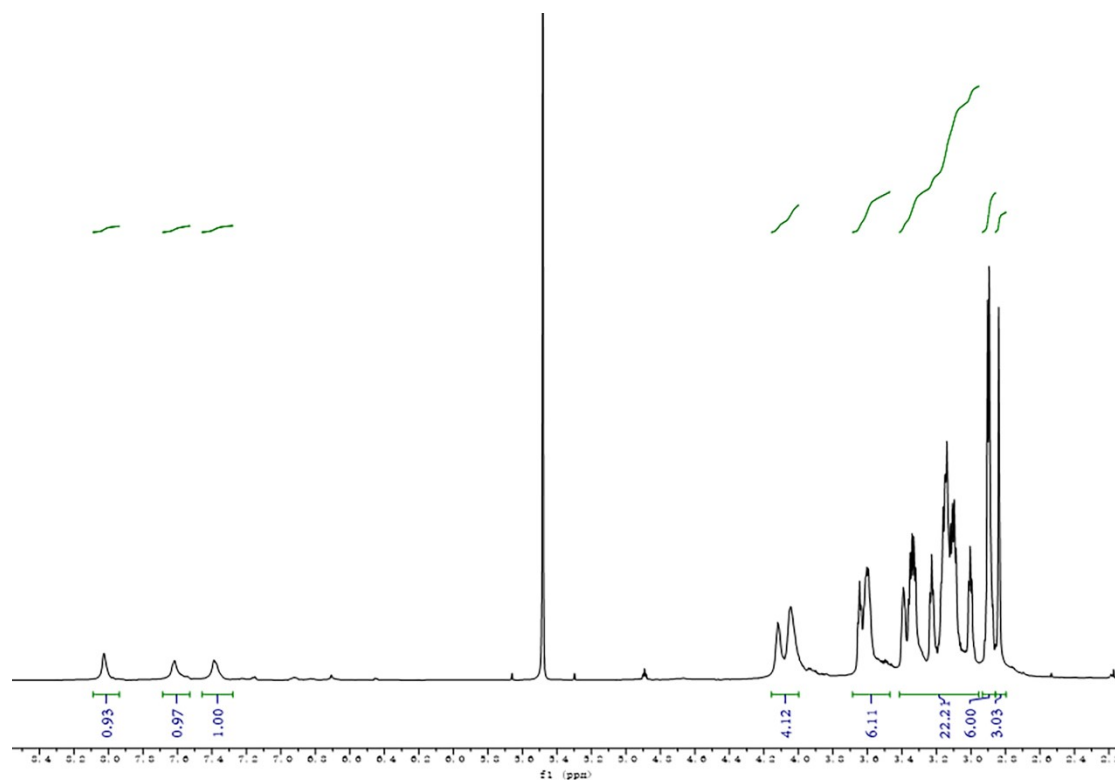


Figure S9. ^1H NMR of polymer **g2T2-gBT4** (1, 1, 2, 2-tetrachloroethane- d_2 , 500 MHz, 373 K)

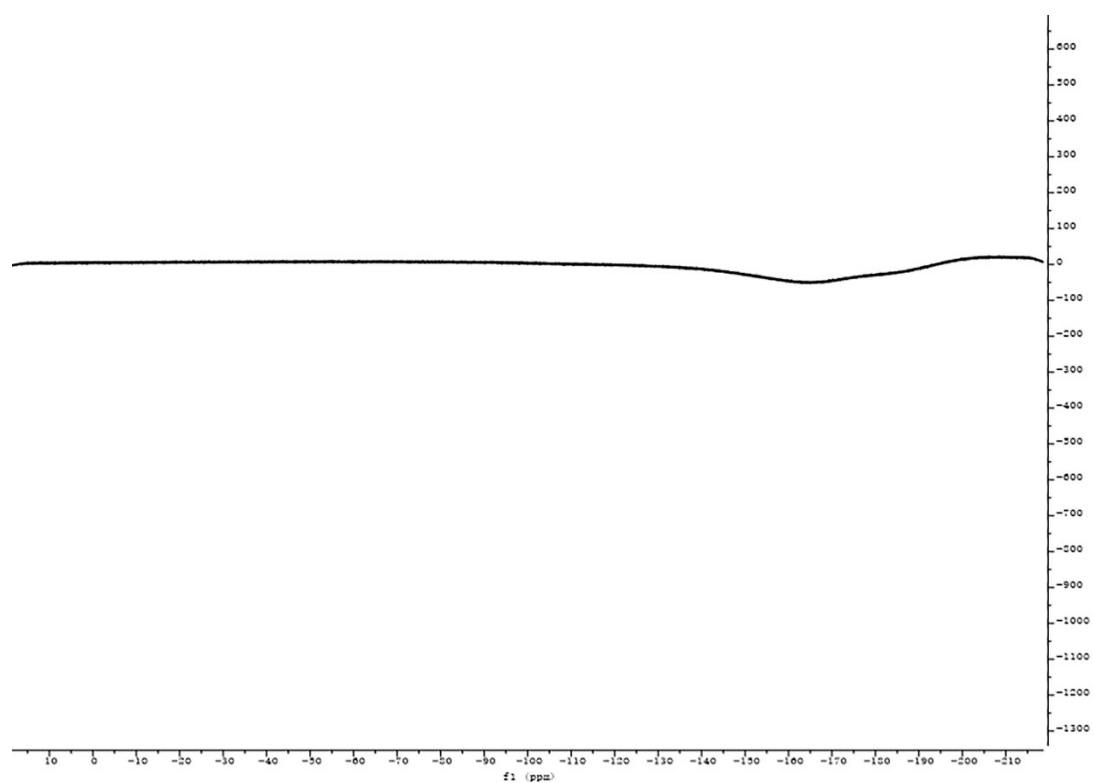


Figure S10. ^{19}F NMR of polymer **g2T2-BT4** (chloroform- d , 400 MHz, 300 K)

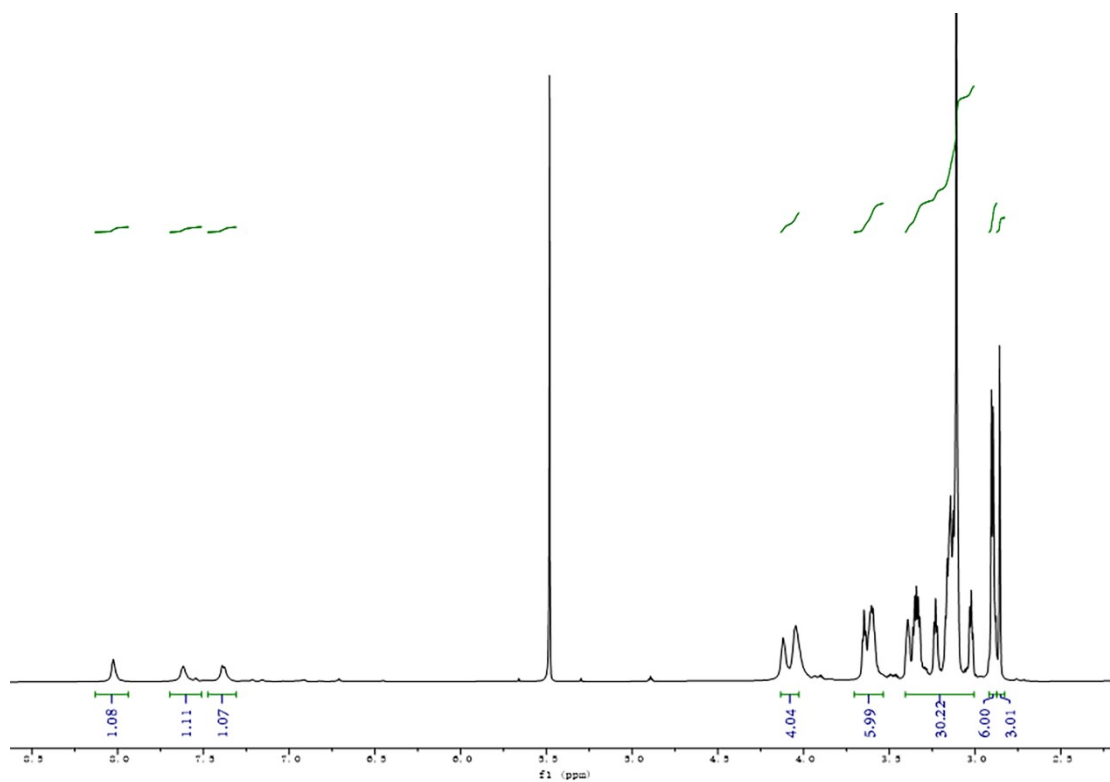


Figure S11. ^1H NMR of polymer **g2T2-gBT6** (1, 1, 2, 2-tetrachloroethane- d_2 , 500 MHz, 373 K)

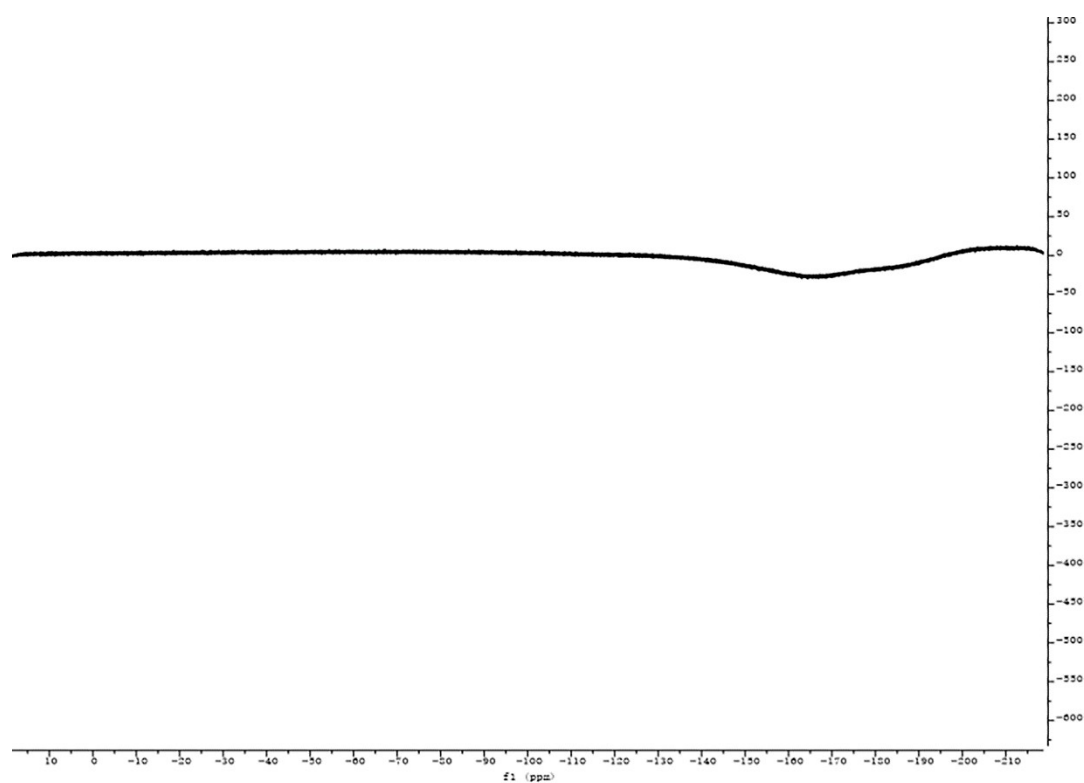


Figure S12. ^{19}F NMR of polymer **g2T2-BT6** (chloroform- d , 400 MHz, 300 K)

3. Molecular Weight

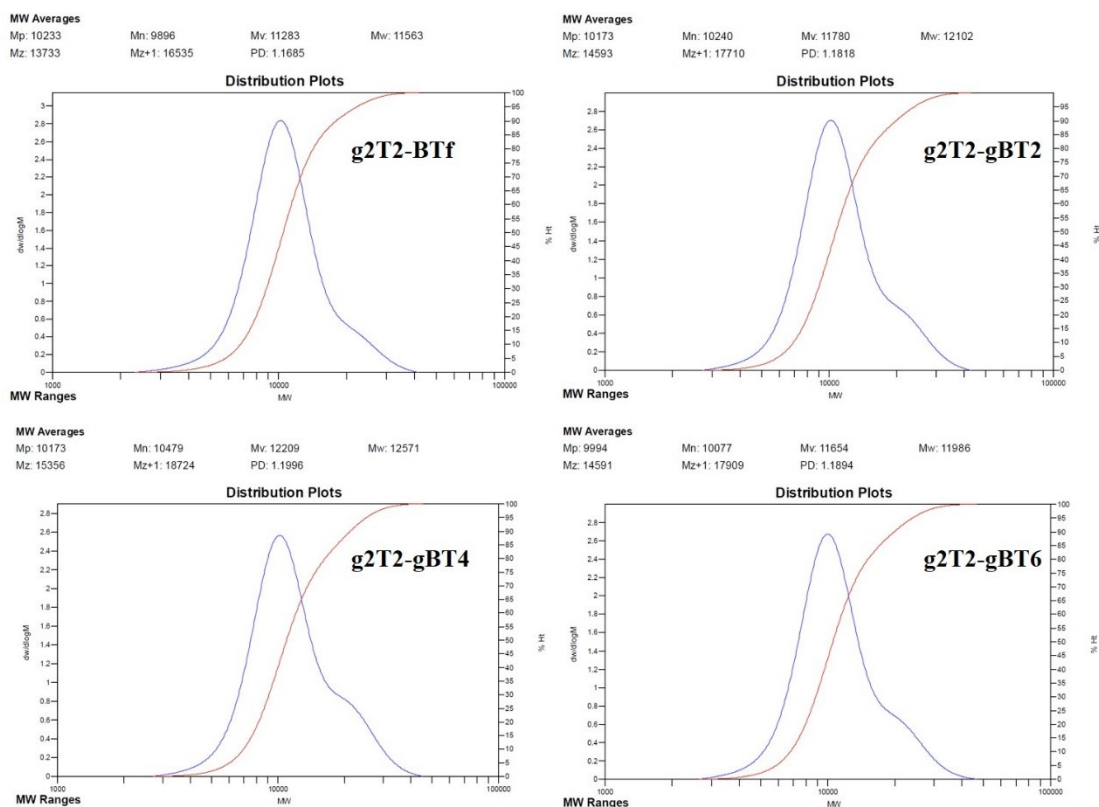


Figure S13. GPC data of the polymers synthesized

Table S1. The molecular weights of polymers synthesized

Polymers	M_n (kg mol ⁻¹)	Dispersity
g2T2-BTf	9.9	1.17
g2T2-gBT2	10.2	1.18
g2T2-gBT4	10.5	1.20
g2T2-gBT6	10.1	1.19

4. UV-vis-NIR Absorption

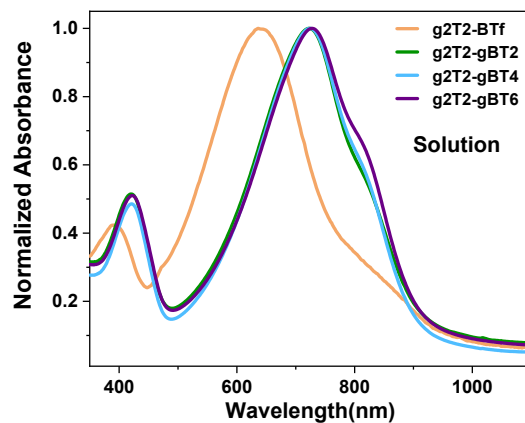


Figure S14 Normalized UV-vis-NIR absorption spectra in solution (chloroform)

5. Spectroelectrochemistry

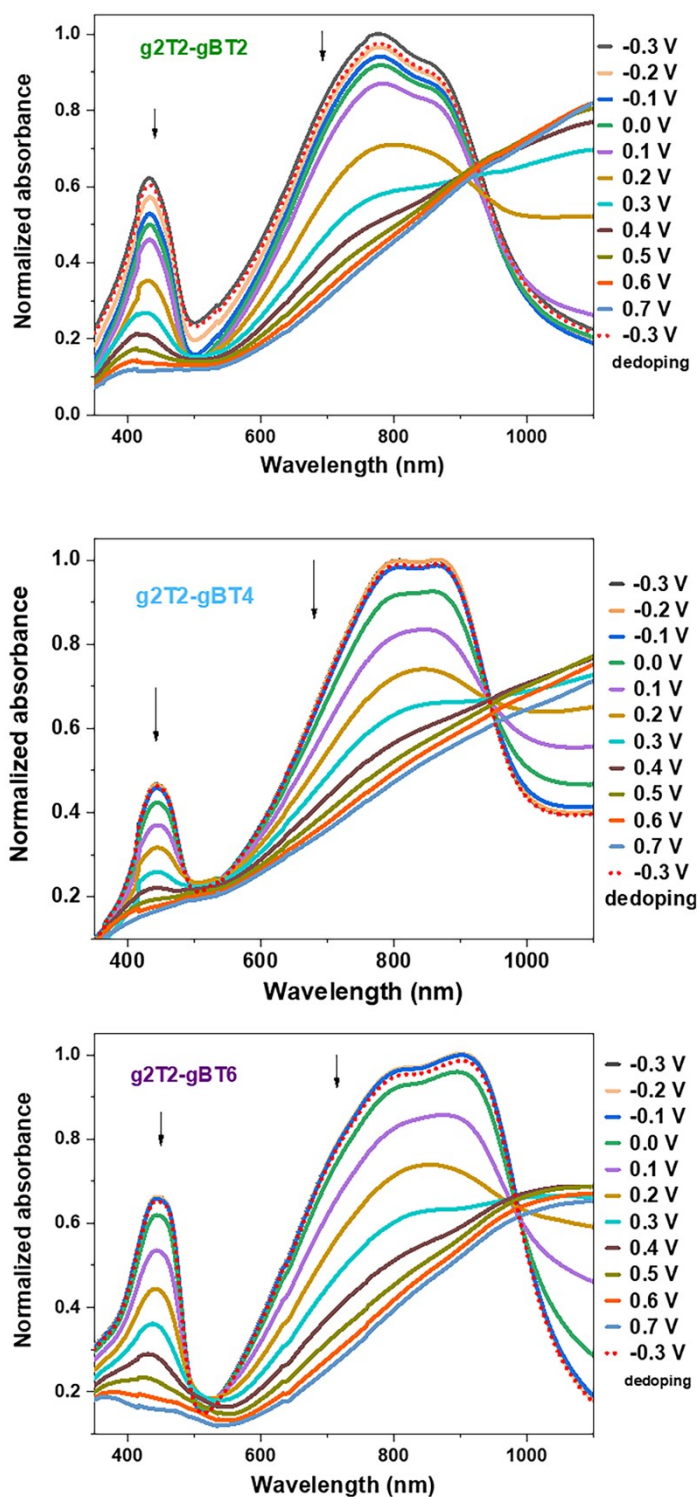


Figure S15. Spectroelectrochemical measurements of copolymers, monitoring the evolution of the absorption spectrum during the charging cycle of polymer thin films on ITO substrates between -0.3 V and 0.7 V vs Ag/AgCl at a scan rate of 50 mV/s.

6. OECTs Measurements

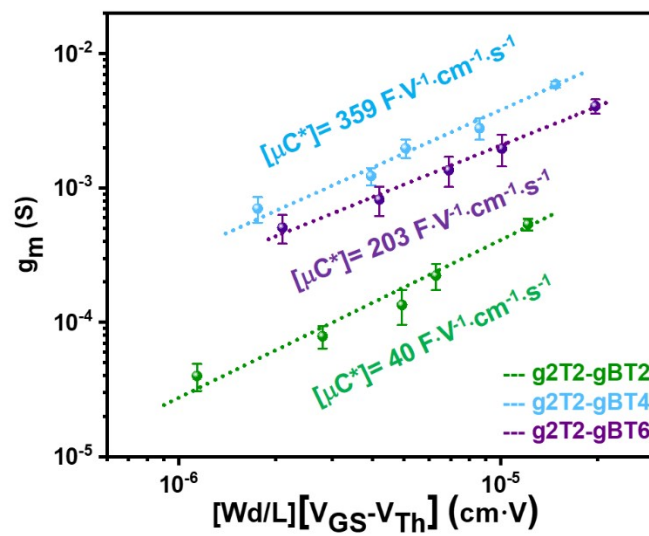


Figure S16. The value μC^* was determined by a series of transistor measurements with different channel dimension.

7. V_{th}

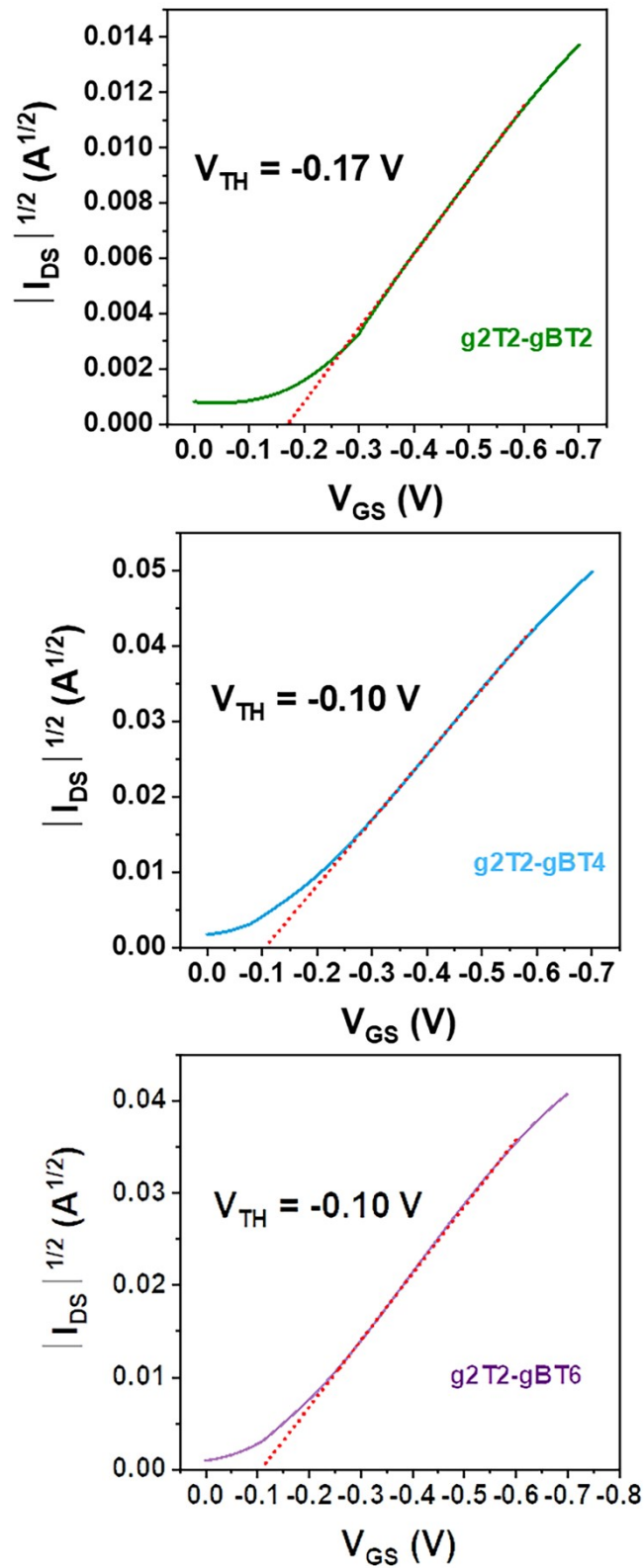


Figure S17. V_{th} of g2T2-gBT2, g2T2-gBT4 and g2T2-gBT6.

8. Electrochemical Impedance Spectroscopy

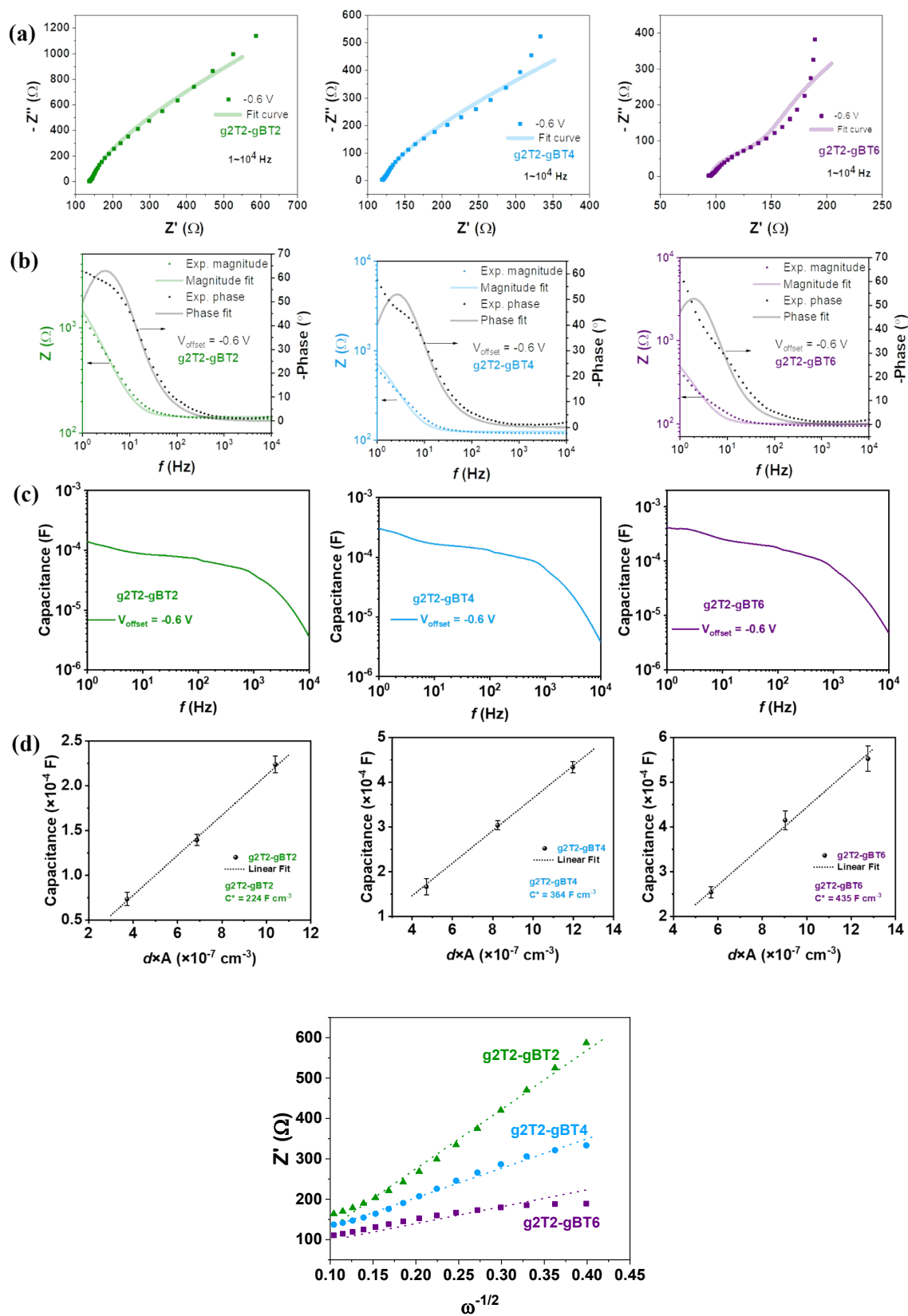


Figure S18. (a) The Nyquist plots and (b) Bode plots acquired employing the bias voltage -0.6 V vs Ag/AgCl. (c) The capacitance dependence frequency was characterized under the

bias voltage of -0.6 V vs Ag/AgCl , and capacitance was calculated according to the equation $C=1/(2\pi f \times |Z_{\text{img}}|)$. (d) The volumetric capacitance (C^*) was obtained from the slope of the capacitance values extracted at 1 Hz versus the film volume plot. (e) The relationships between Z' (Ω) and $\omega^{-1/2}$ in the low-frequency region for **g2T2-gBT2**, **g2T2-gBT4** and **g2T2-gBT6**.

9. ON/OFF-time Constant

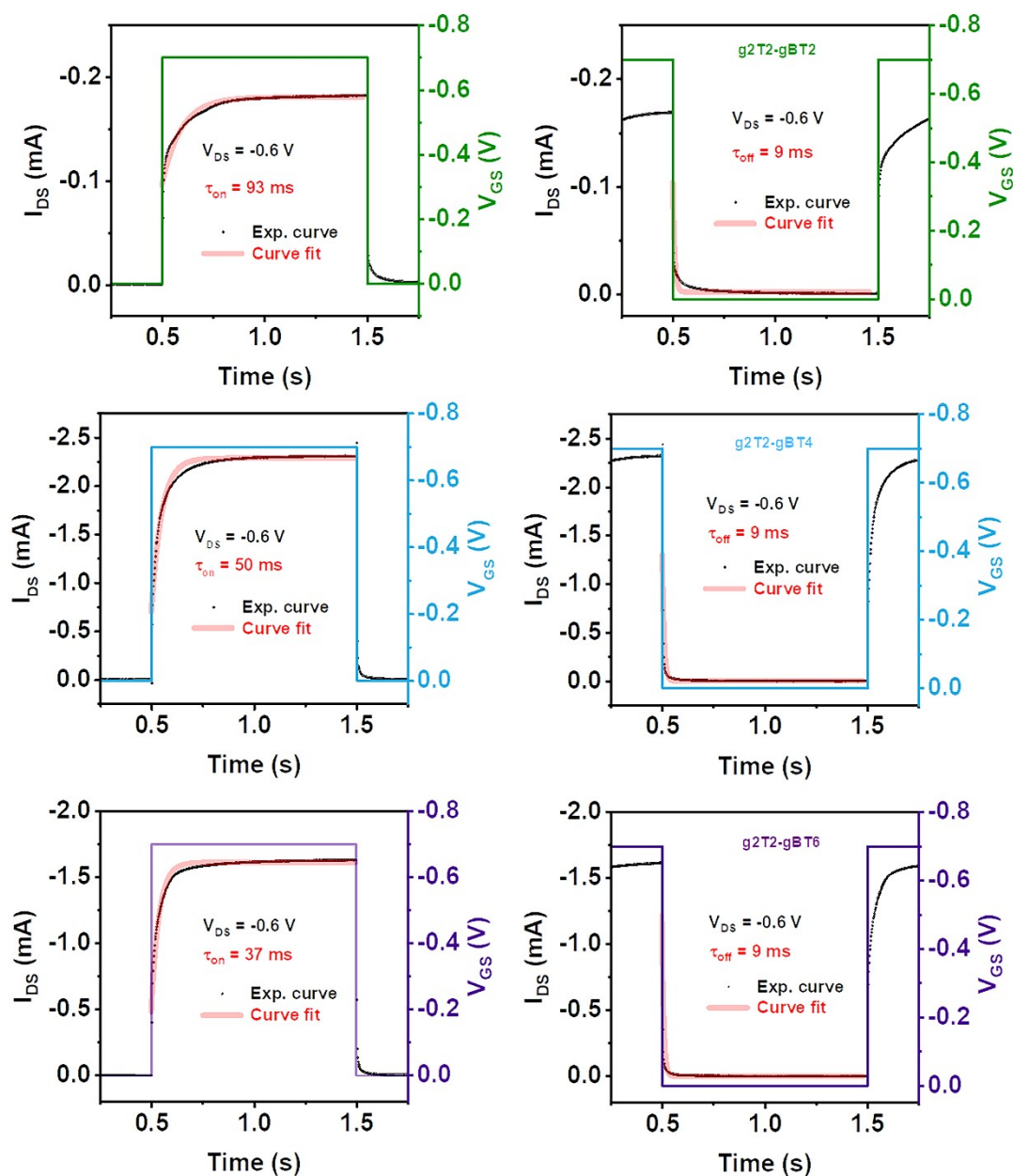


Figure S19. ON/OFF-time constant of three copolymers as active materials in OECT devices.

10. OECTs Device Stability

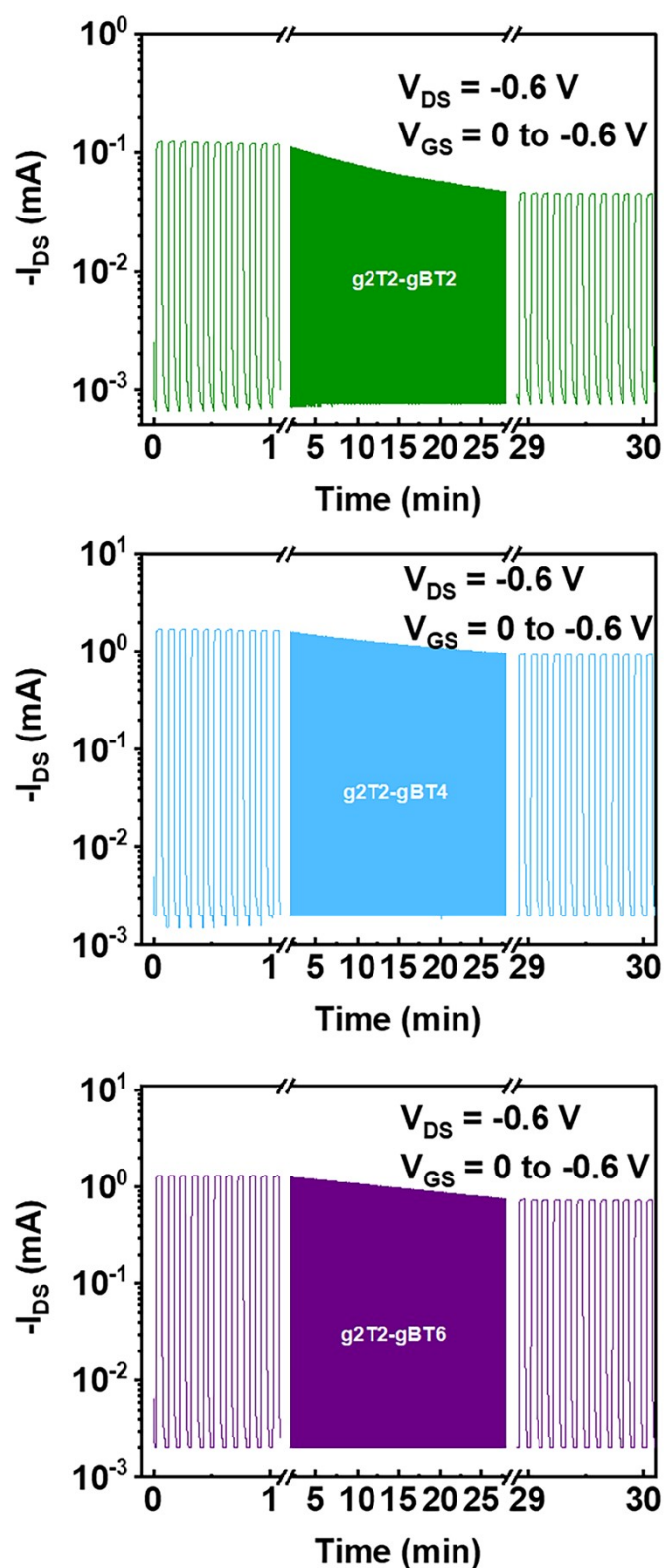


Figure S20. Operation stability of g2T2-gBT2, g2T2-gBT4 and g2T2-gBT6-based OECTs under sequential square wave gate voltage for 30 mins.

Table S2. Oxidized state of molecular packing parameters for the copolymers

Polymers	Lamellar stacking		π -stacking		Dominant texture
	$q(\text{\AA}^{-1})$	$d(\text{\AA})$	$q(\text{\AA}^{-1})$	$d(\text{\AA})$	
g2T2-gBT2 in-plane	0.391	16.06	1.631	3.85	edge-on
g2T2-gBT2 out-of-plane	0.392	16.02	1.641	3.82	
g2T2-gBT4 in-plane	0.316	19.87	1.648	3.81	edge-on
g2T2-gBT4 out-of-plane	0.316	19.87	1.661	3.78	
g2T2-gBT6 in-plane	0.292	21.51	1.620	3.88	edge-on
g2T2-gBT6 out-of-plane	0.289	21.73	1.632	3.85	

(010) peaks were fit with the summation of pseudo-Voigt distributions.

11. Atomic Force Microscopy

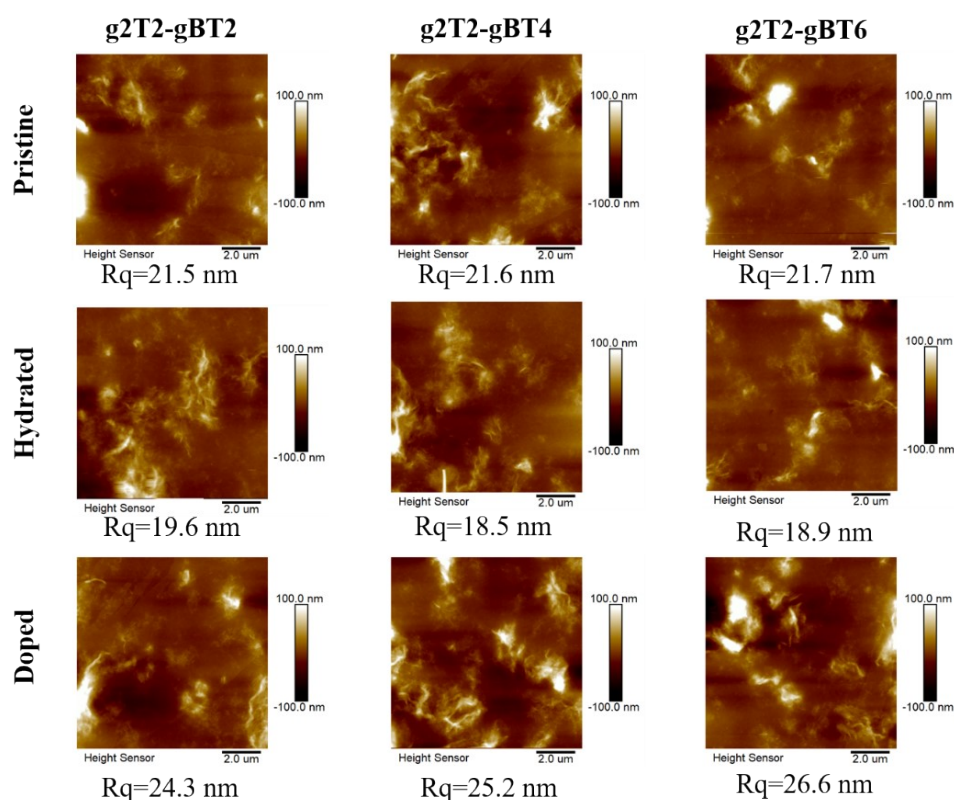


Figure S21. Atomic force microscopy (AFM) height images of **g2T2-gBT2**, **g2T2-gBT4** and **g2T2-gBT6**, along with the Rq denotes root mean square (RMS) values in dry (as-cast), electrolyte swollen and after being subject to five oxidized CV cycles.

12. EQCM-D measurement

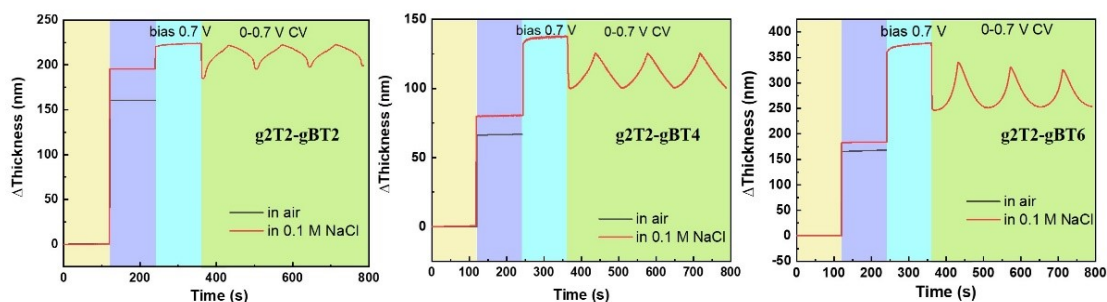


Figure S22. EQCM-D traces recorded for three EG functionalized polymers.

13. References

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