Supporting Information

Molecular Design of Semiconducting Polymers for High-Performance Organic Electrochemical Transistors

Christian B. Nielsen,*,†,⊥ Alexander Giovannitti,† Dan-Tiberiu Sbircea,† Enrico Bandiello,& Muhammad R. Niazi,# David A. Hanifi,$ Michele Sessolo,& Aram Amassian,# George G. Malliaras,‡ Jonathan Rivnay,‡§ Iain McCulloch†,#

† Department of Chemistry and Centre for Plastic Electronics, Imperial College London, London SW7 2AZ, United Kingdom.

⊥ Materials Research Institute and School of Biological and Chemical Sciences, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom.

‡ Department of Bioelectronics, École Nationale Supérieure des Mines, CMP-EMSE, MOC Gardanne, 13541, France.

King Abdullah University of Science and Technology (KAUST), PSE, Thuwal, 23955-6900, Saudi Arabia.

$ Department of Chemistry, Stanford University, Stanford, CA 94305, USA.

& Instituto de Ciencia Molecular, Universidad de Valencia, 46980 Paterna, Spain.

§ Palo Alto Research Center, Palo Alto, CA 94304, USA.

Table of Contents

1. Methods

Column chromatography was carried out with silica gel for flash chromatography from VWR Scientific. Microwave experiments were performed in a Biotage Initiator V 2.3. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AV-400 spectrometer at 298 K. UV-Vis absorption spectra were recorded on a UV-1601 Shimadzu UV-Vis spectrometer. Number-average (M_n) and weight-average (M_w) molecular weights were determined with an Agilent Technologies 1200 series GPC in either N,N-dimethylformamide at 40 °C or in 1,2,4-trichlorobenzene at 130 °C, using two PL mixed B columns in series, and calibrated against narrow weight-average dispersity ($Dw < 1.10$) polystyrene standards. Film thicknesses were measured with a Dektak profilometer.

X-ray diffraction (XRD) measurements were carried out with a Panalytical Model X'Pert PRO MRD diffractometer equipped with a nickel-filtered Cu $K\alpha_1$ beam and a X'Celerator detector, using a current of $I = 40$ mA and an accelerating voltage of $U = 40$ kV.

Cyclic voltammograms were obtained using an Autolab PGSTAT101 potentiostat with a standard three-electrode setup with an ITO coated glass slide as the working electrode, a platinum mesh counter electrode and a Ag/Ag^+ reference electrode calibrated against Fc/Fc^+. The measurements were carried out with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte at a scan rate of 100 mV/s. Ionization potentials were obtained using the equation: $IP = (E_{ox} – E_{Fc} + 4.8V)$.

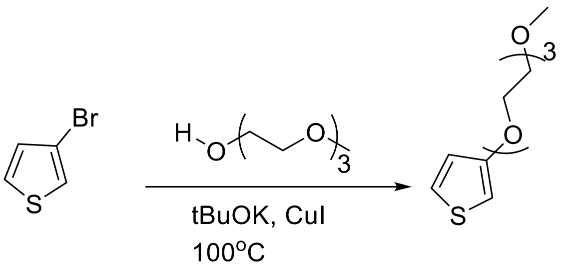
Spectroelectrochemistry was carried out using an Ocean Optics Spectrometer and an Autolab potentiostat with a standard three-electrode setup with a platinum wire working electrode and a Ag/Ag^+ reference electrode in 0.1 M NaCl in deionized water. Thin films were prepared by spin coating on ITO coated glass substrates.

The OECT fabrication process, similar to that reported previously,[1] included the deposition and patterning of metal, parylene, and the conducting polymers. We used photolithography to define the channels of the transistors with Au source and drain electrodes and interconnects on glass substrates. These interconnects were insulated from the aqueous electrolyte by a vapour-polymerized parylene-C layer. The active channel and the insulating parylene layer were simultaneously patterned by using a second sacrificial parylene layer. After the polymer film was spin cast, the device was baked at 110 °C for 60 min with subsequent rinsing in DI water. The thickness of the films at each channel was measured using a Dektak profilometer.

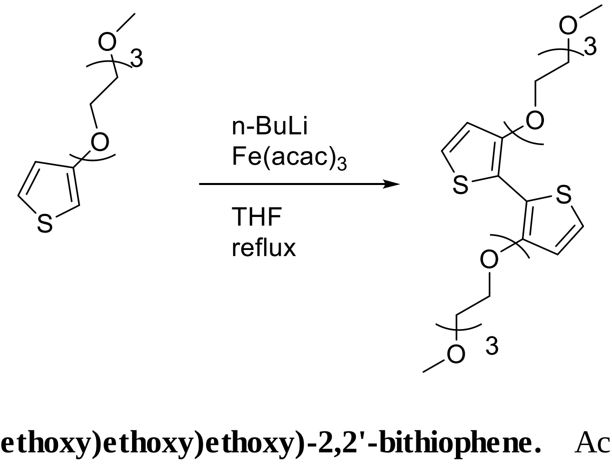
Device Characterization: Devices were operated in the common source configuration. The electrolyte was a 0.1 M NaCl water solution dropped on top of the transistors. The gate electrode was a Ag/AgCl pellet which was immersed in the electrolyte. The IV-characteristics of the OECTs were measured using a National Instruments PXIe-1062Q system. An NI-PXI-4071 digital multimeter was used to measure drain current, and a NI-PXI 6289 measured drain and gate voltage. All the measurements were triggered through the built-in PXI architecture. The recorded signals were saved and analyzed using customized LabVIEW software.

Field-effect transistor devices: substrates were sonicated in Acetone, IPA, and ethanol for 15 minutes. UV ozone cleaning 15 minutes before OTS treatment. After PFBT treatment baked at 150 °C. Polymers were deposited by spin coating at 2500 rpm. Thermal annealing for 30 min at 100 °C in air. Various device architectures were tested: BCBG (short channels), BCBG (long channels), TCBG and TCTG (CYTOP dielectric); best results reported herein were achieved with BCBG and short channels. Output curves could not be obtained for **gBDT-T** due to device instabilities.

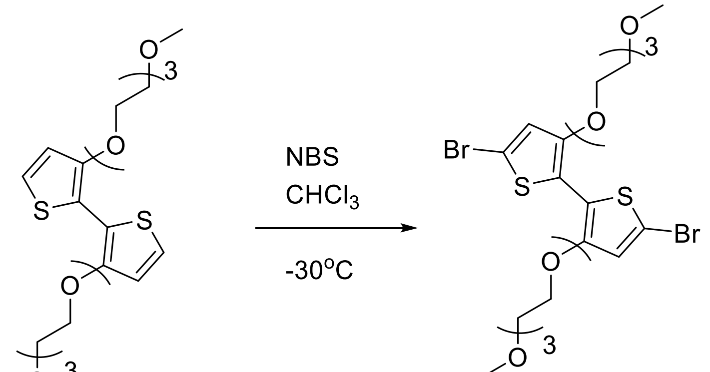
2. Experimental Details



3-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)thiophene. According to a modified procedure by Marks,[2] a dry 250 mL round bottom flask was charged with copper iodide (2.80 g, 14.70 mmol, 0.20 equiv), potassium tert-butoxide (12.40 g, 110.71 mmol, 1.5 equiv). The flask was purged with Argon after which triethylene glycol monomethyl ether (16.10 mL, 147.20 mmol, 2.00 equiv) was added and left to stir for 1 h at room temperature. 3-Bromothiophene (6.90 mL, 73.60 mmol, 1.00 equiv) was added and the reaction was heated to 100°C for 24h. After cooling to room temperature, the mixture was put through a short silica plug eluting with DCM:MeOH 95:5 to remove inorganics. The crude material was concentrated *in vacuo* and purified *via* column chromatography, eluting with 3:2 hexanes:ethyl acetate (v/v). The desired product was isolated as a pale yellow oil (11.41 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (dd, J = 5.4, 3.1 Hz, 1H), 6.77 (dd, J = 5.1, 1.7 Hz, 1H), 6.25 (dd, J = 3.1, 1.6 Hz, 1H), 4.11 (t, J = 4.8 Hz, 2H), 3.84 (t, J = 4.7 Hz, 2H), 3.72 (dd, J = 6.3, 3.5 Hz, 2H), 3.70 – 3.62 (m, 4H), 3.55 (dd, J = 5.6, 3.6 Hz, 2H), 3.38 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.8, 124.9, 119.8, 97.7, 72.2, 70.9, 70.8, 70.7, 69.8, 69.7, 59.2.

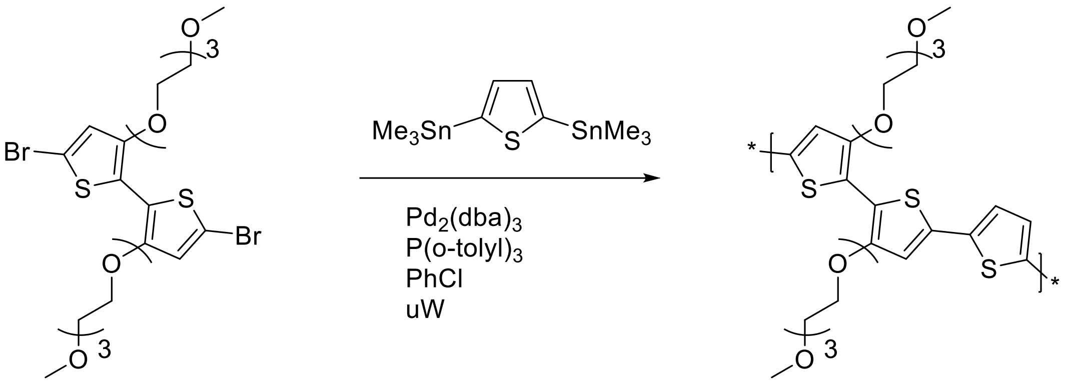


3,3'-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2'-bithiophene. According to a modified procedure by Marks,[2] a dry 100 mL round bottom flask with magnetic stir bar was charged with 2.40 g 3-(2-(2-(2-methoxyethoxy)ethoxy)-ethoxy)thiophene (9.76 mmol) and 20 mL of dry THF. The reaction mixture was cooled to 0°C in an ice bath over 15 min. 3.90 mL of 2.5 M n-butyllithium in hexanes (9.75 mmol) was then added dropwise over 10 min, and the reaction was stirred for two h at 0 °C. This solution was then added to a dry 250 mL two-neck round bottom flask with condenser and magnetic stir bar that had been charged with 3.46 g iron(iii) acetylacetonate (9.80 mmol) and 70 mL of dry THF. The reaction mixture was then heated to reflux and stirred for two h. After cooling to room temperature, the mixture was put through a short silica plug eluting with DCM:MeOH 95:5 to remove inorganics. The crude material was concentrated *in vacuo* and purified *via* column chromatography, eluting with 97:3 dichloromethane:methanol (v/v) giving of a yellow tinted oil that solidified at reduced temperature. The material was recrystallized from diethyl to afford white crystals (1.25 g, 52%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.09 (d, J = 5.6 Hz, 2H), 6.87 (d, J = 5.5 Hz, 2H), 4.26 (t, J = 4.9 Hz, 4H), 3.92 (dd, J = 5.5, 4.6 Hz, 4H), 3.81 – 3.76 (m, 4H), 3.72 – 3.65 (m, 8H), 3.59 – 3.54 (m, 4H), 3.39 (s, 6H). ^{13}C-NMR (100 MHz, CDCl$_3$): δ 151.8, 122.0, 116.7, 114.9, 72.1, 71.5, 71.0, 70.8, 70.7, 70.1, 59.1.



M1

5,5′-Dibromo-3,3′-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2′-bithiophene (M1). Following a modified procedure by Facchetti,[3] a solution of 3,3'-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2'-bithiophene (0.80 g, 1.63 mmol, 1.00 equiv) in dry degassed chloroform (30 mL) was cooled to -30 °C. N-bromosuccinimide (0.58 g, 3.27 mmol, 2.0 equiv) was added in small portions over 10 minutes at -30°C. After the addition, the reaction was stirred at -30 °C for 2 h. The reaction was then warmed to room temperature and was quenched by the addition of 30 mL saturated aqueous sodium sulphite. The reaction was extracted three times with dichloromethane (30 mL), the combined organic were washed with brine (50 mL), dried over magnesium sulphate, filtered, concentrated *in vacuo* to give a green oil. The oil was put through a short silica plug eluting with 95:5 dichloromethane:methanol (v/v), concentrated *in vacuo* to give a pale yellow oil which solidified upon cooling. The residue was recrystallized two times from diethyl ether, to give yellow microcrystals (0.81 g, 77%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.87 (s, 2H), 4.27 – 4.18 (m, 4H), 3.94 – 3.85 (m, 4H), 3.80 – 3.74 (m, 4H), 3.74 – 3.66 (m, 8H), 3.61 – 3.55 (m, 4H), 3.40 (s, 6H); ^{13}C-NMR (100 MHz, CDCl$_3$): δ 150.2, 119.7, 115.9, 110.1, 72.0, 71.7, 70.9, 70.7, 70.6, 69.9, 59.0. MS (TOF-LD^{+}) m/z: [M]$^{+}$ Calcd for $C_{22}H_{32}Br_2O_8S_2$ 648.0; Found 648.2



g2T-T: A dry, argon purged 20 mL microwave vial was charged with **M1** (50.00 mg, 0.0774 mmol), 2,5-bis(trimethylstannyl)thiophene (31.89 mg, 0.0774 mmol), tris-(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (1.42 mg, 0.0015 mmol) and tris(o-tolyl)-phosphine ($P(o\text{-}tolyl)_3$) (1.88 mg, 0.0062 mmol). The flask and its contents were next subjected to three pump/purge cycles with argon, followed by addition of anhydrous chlorobenzene (1 mL) via syringe. The vial was sealed and further purged with argon for 20 min. The flask was subjected to microwave heating: 5 min 100 °C, 5 min 140 °C, 5 min 160 °C, 5 min 180 °C, 25 min 200 °C. The vial was cooled, 20 µL of 2-(tributylstannyl)-thiophene was added and the contents were subjected to microwave heating: 2 min 100 °C, 2 min 140 °C, 2 min 160 °C, 2 min 180 °C, 5 min 200 °C. Finally, 50 µL 2-bromothiophene was added and the reaction was subjected to microwave heating: 2 min 100 °C, 2 min 140 °C, 2 min 160 °C, 2 min 180 °C, 5 min 200 °C. After cooling to room temperature, the deep-coloured reaction mixture was slowly dripped into 100 mL of methanol with stirring. After stirring for 30 min, the solid precipitate was transferred to a Soxhlet thimble. The crude product was subjected to subsequent Soxhlet extractions with n-hexane (16 h), diethyl ether (16 h), acetone (16 h), methanol (16 h) and chloroform (6 h). After final extraction with chloroform, the polymer solution was concentrated *in vacuo* to approximately 5 mL, and then dripped into 100 mL of methanol with stirring. The polymer was collected by filtration and dried under reduced pressure to afford the product as a blue solid (28 mg, 64%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.10 (br s, 2H), 6.99 (br s, 2H), 4.37 (br s, 4H), 4.00 (br s, 4H), 3.85 (br m, 4H), 3.75 (br m, 4H), 3.69 (br m, 4H), 3.56 (br m, 4H), 3.38 (br s, 6H).

gBDT-g2T: A dry, argon purged 20 mL microwave vial was charged with **M1** (40.00 mg, 0.049 mmol), (4,8-bis(TEG)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (32.95 mg, 0.049 mmol), tris-(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (0.90 mg, 0.0009 mmol) and tris(o-tolyl)-phosphine ($P(o\text{-}tolyl)_3$) (1.20 mg, 0.0040 mmol). The flask and its contents were next subjected to three pump/purge cycles with argon, followed by addition of anhydrous chlorobenzene

(1 mL) via syringe. The vial was sealed and further purged with argon for 20 min. The flask was subjected to microwave heating: 5 min 100 °C, 5 min 140 °C, 5 min 160 °C, 5 min 180 °C, 25 min 200 °C. The vial was cooled, 20 µL of 2-(tributylstannyl)-thiophene was added and the contents were subjected to microwave heating: 2 min 100 °C, 2 min 140 °C, 2 min 160 °C, 2 min 180 °C, 5 min 200 °C. Finally, 50 µL 2-bromothiophene was added and the reaction was subjected to microwave heating: 2 min 100 °C, 2 min 140 °C, 2 min 160 °C, 2 min 180 °C, 5 min 200 °C. After cooling to room temperature, the deep-coloured reaction mixture was slowly dripped into 100 mL of methanol with stirring. After stirring for 30 min, the solid precipitate was transferred to a Soxhlet thimble. The crude product was subjected to subsequent Soxhlet extractions with n-hexane (16 h), diethyl ether (16 h), acetone (16 h), methanol (16 h) and chloroform (6 h). After final extraction with chloroform, the polymer solution was concentrated *in vacuo* to approximately 5 mL, and then dripped into 100 mL of methanol with stirring. The polymer was collected by filtration and dried under reduced pressure to afford the product as a dark blue solid (24 mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (s, 2H), 7.19 (s, 2H), 4.60-4.48 (br, 8H), 4.47-3.38 (br, 8H) , 4.09-3.99 (br, 8H), 3.80-3.73 (m, 8H), 3.72-3.63 (m, 8H), 3.62- 3.47 (m, 8H), 3.38 (br s, 6H), 3.35 (br s, 6H).

Microwave Heating Program 1: 100 °C for 5 min, 120 °C for 5 min, 140 °C for 5 min, 160 °C for 5 min, 180 °C for 5 min, 200 °C for 25 min. **Microwave Heating Program 2:** 100 °C for 1 min, 120 °C for 1 min, 140 °C for 1 min, 160 °C for 1 min, 180 °C for 5 min. **Polymer end-capping procedure:** End-capping: 0.1 mL of 0.6 M 2-(tributylstannyl)thiophene (or (tributylstannyl)benzene) dissolved in chlorobenzene was added and heating program 2 was carried out. Finally, 0.1 mL of 1.2 M 2-bromothiophene (or bromobenzene) solution in chlorobenzene was added and heating program 2 was applied.

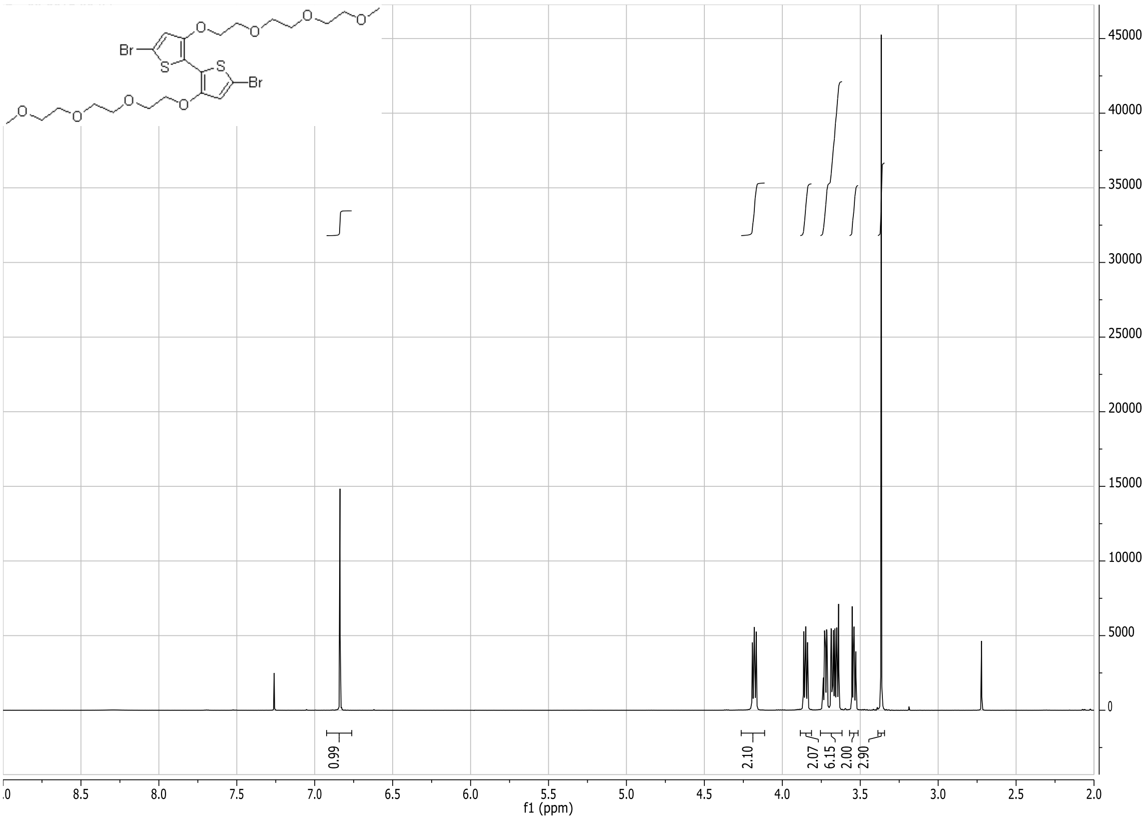
gBDT: In a 2.00 mL microwave vial 65.46 mg of 2,6-dibromo-4,8-bis(2-TEG)benzo[1,2-b:4,5-b']dithiophene[4] (0.10 mmol, 1.00 eq.) and 81.80 mg of (4,8-bis(TEG)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane)[4] (0.10 mmol, 1.00 eq.) were dissolved in 1.00 mL of degassed anhydrous chlorobenzene. 1.80 g tris(dibenzylideneacetone)-dipalladium(0) $Pd_2(dba)_3$ (2.00 mol%) and 2.44 mg tri(*o*-tolyl)phosphine $P(o\text{-tol})_3$ (8.00 mol%) were added and the reaction mixture was purged with argon for 10 min. The microwave heating programme 1 was carried out. After the reaction was cooled down the end capping procedure was carried out. The red coloured reaction mixture was precipitated in cold methanol and filtered into a Soxhlet thimble. Extraction with methanol, hexane, acetone, THF and chloroform was carried out and the product was dissolved in hot chloroform and precipitated in methanol. 42.6 mg (0.041 mmol) of an orange/red polymer was obtained with a yield of 41 %. GPC results: Mn = 4.2 kg/mol, Mw = 6.5 kg/mol. ^{1}H NMR (400 MHz,

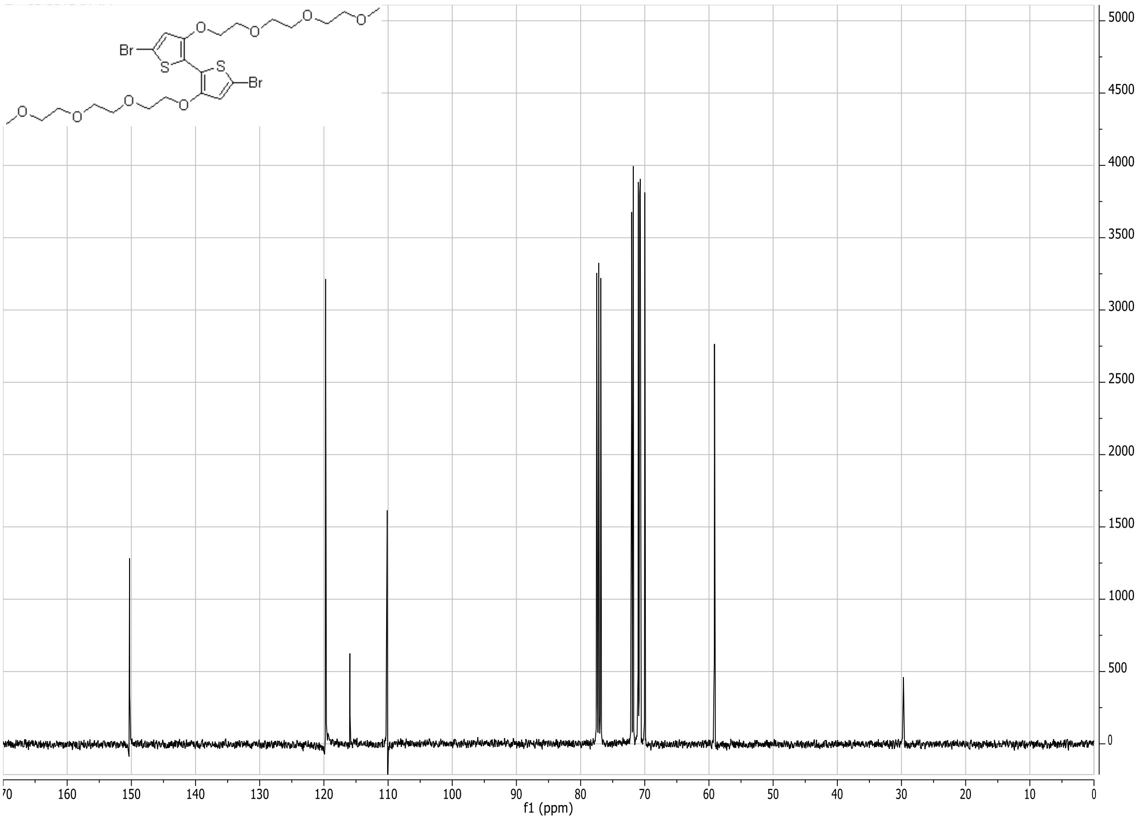
$CDCl_3$): δ 7.77 (m, 2H), 4.61 – 4.47 (m, 4H), 4.04 – 3.95 (m, 4H), 3.89 – 3.77 (m, 8H), 3.77 – 3.63 (m, 4H), 3.64 – 3.53 (m, 4H), 3.44 – 3.32(m, 6H).

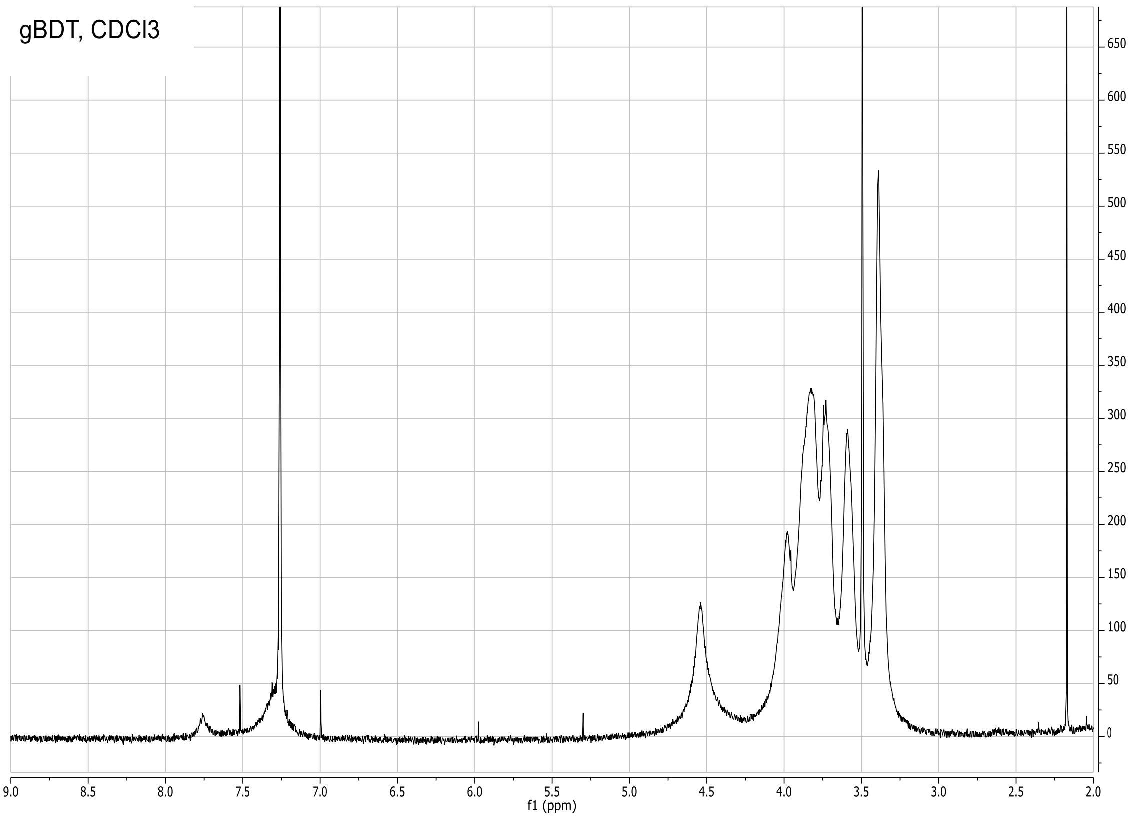
gBDT-T: In a 2.00 mL microwave vial 93.89 mg of 2,6-dibromo-4,8-bis(2-TEG)benzo[1,2-b:4,5-b']dithiophene[4] (0.14 mmol, 1.00 eq.) and 57.21 mg 2,5-bis(trimethylstannyl)thiophene (0.14 mmol, 1.00 eq.) were dissolved in 1.00 mL of degassed anhydrous chlorobenzene. 2.56 g $Pd_2(dba)_3$ (2.00 mol%) and 3.40 mg $P(o\text{-}tol)_3$ (8.00 mol%) were added and the reaction mixture was purged with argon for 10 min. The microwave heating programme 1 was carried out. After the reaction was cooled down the end capping procedure was carried out. The red reaction solution was precipitated in cold methanol, filtered in a Soxhlet thimble and subjected to Soxhlet extractions with methanol, hexane, acetone, THF and chloroform. The product was dissolved in hot chloroform and precipitated in methanol. 59.51 mg (0.10 mmol) of a red polymer was obtained with a yield of 72 %. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.25 (m, 2H), 4.59 – 4.27 (m, 4H), 4.06 – 3.91 (m, 4H), 3.90 – 3.78 (m, 8H), 3.77 – 3.66 (m, 4H), 3.66 – 3.49 (m, 4H), 3.44 – 3.30(m, 6H).

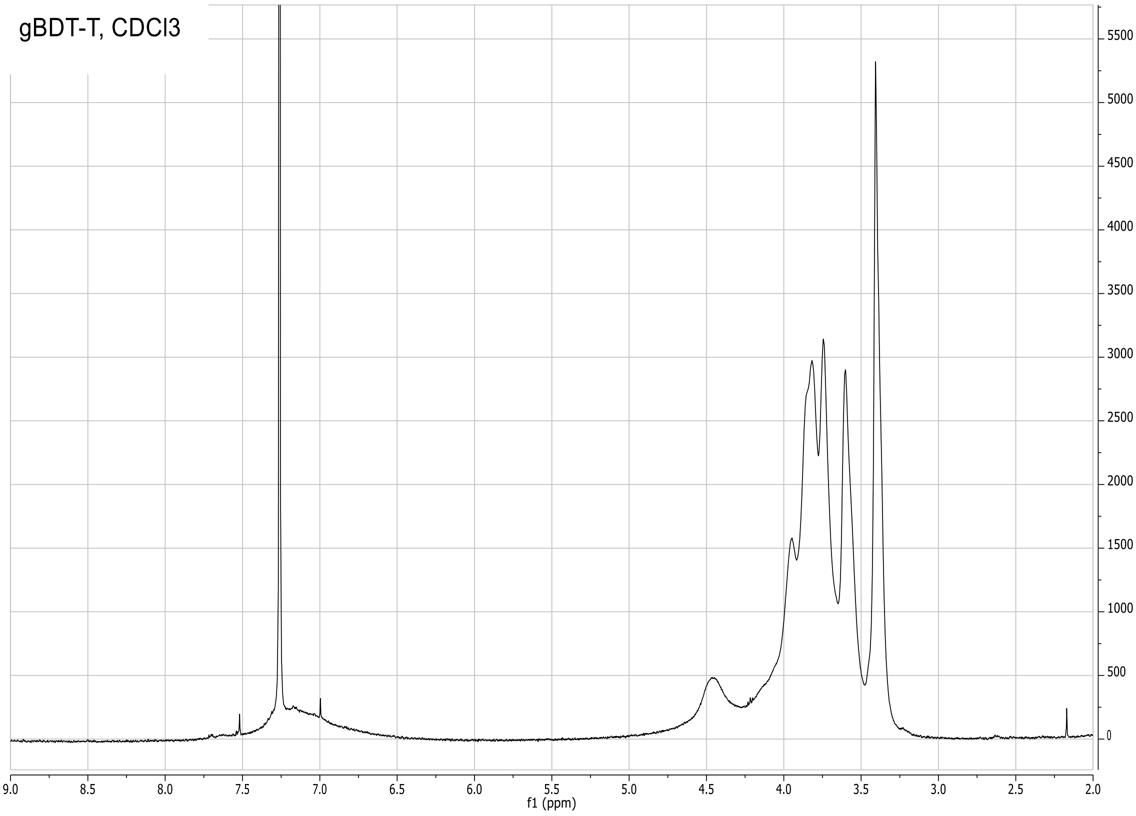
gBDT-2T: In a 2.00 mL microwave vial 102.4 mg 2,6-dibromo-4,8-bis(2-TEG)benzo[1,2-b:4,5-b']dithiophene[4] (0.15 mmol, 1.00 eq.) and 74.91 mg 5,5′-bis(trimethylstannyl)-2,2′-bithiophene (0.15 mmol, 1.00 eq.) were dissolved in anhydrous 1.00 mL chlorobenzene. 2.77 mg $Pd_2(dba)_3$ (2.00 mol%) and 3.75 mg $P(o\text{-}tol)_3$ (8.00 mol%) were added and the reaction mixture was purged with argon for 5 min. The vial was transferred to a microwave and the heating programme 1 was applied. A red solid was obtained and the solid was washed with methanol and filtered into a Soxhlet thimble. Extractions with methanol, hexane, acetone, tetrahydrofuran, chloroform was carried out and the main polymer product was isolated and is soluble in 1,1,2,2-tetrachloroethane. 68.1 mg (0.10 mmol) of a red polymer was obtained with a yield of 66 %. ^1H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2): 7.40 – 7.2 (m, 2H), 4.56 – 4.30 (m, 4H), 4.01 – 3.92 (m, 4H), 3.97 – 3.88 (m, 8H), 3.87 – 3.66 (m, 4H), 3.66 – 3.47 (m, 4H), 3.45 – 3.25 (m, 6H).

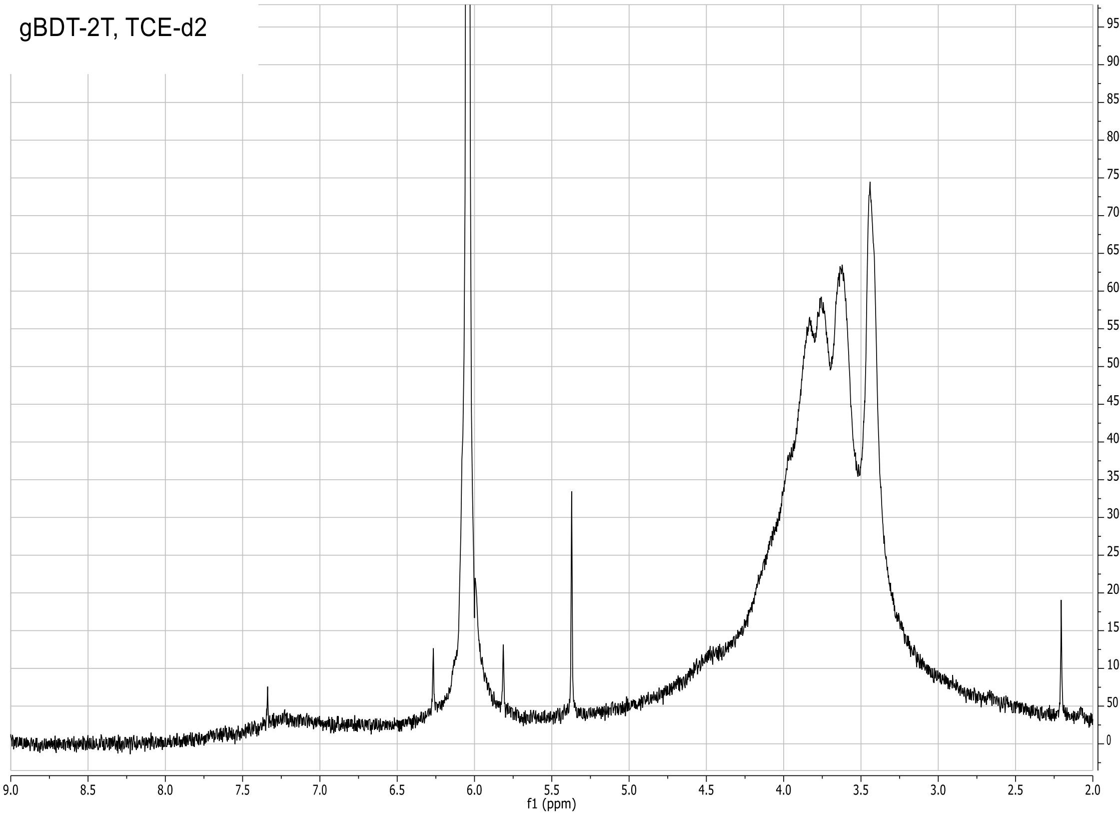
3. NMR Spectra

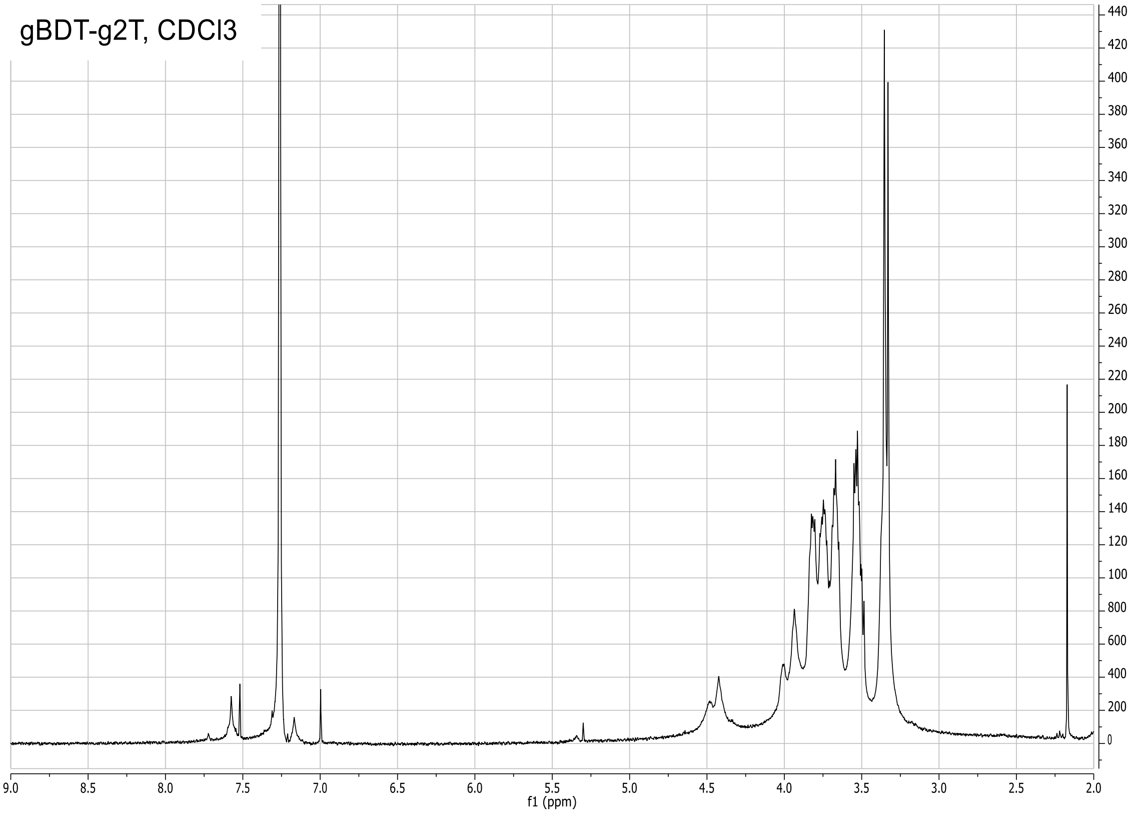





gBDT, CDCl3
650
600
550
500
450
400
350
300
250
200
150
100
50
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


gBDT-T, CDCl3
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


gBDT-2T, TCE-d2
950
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


gBDT-g2T, CDCl3
4400
4200
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

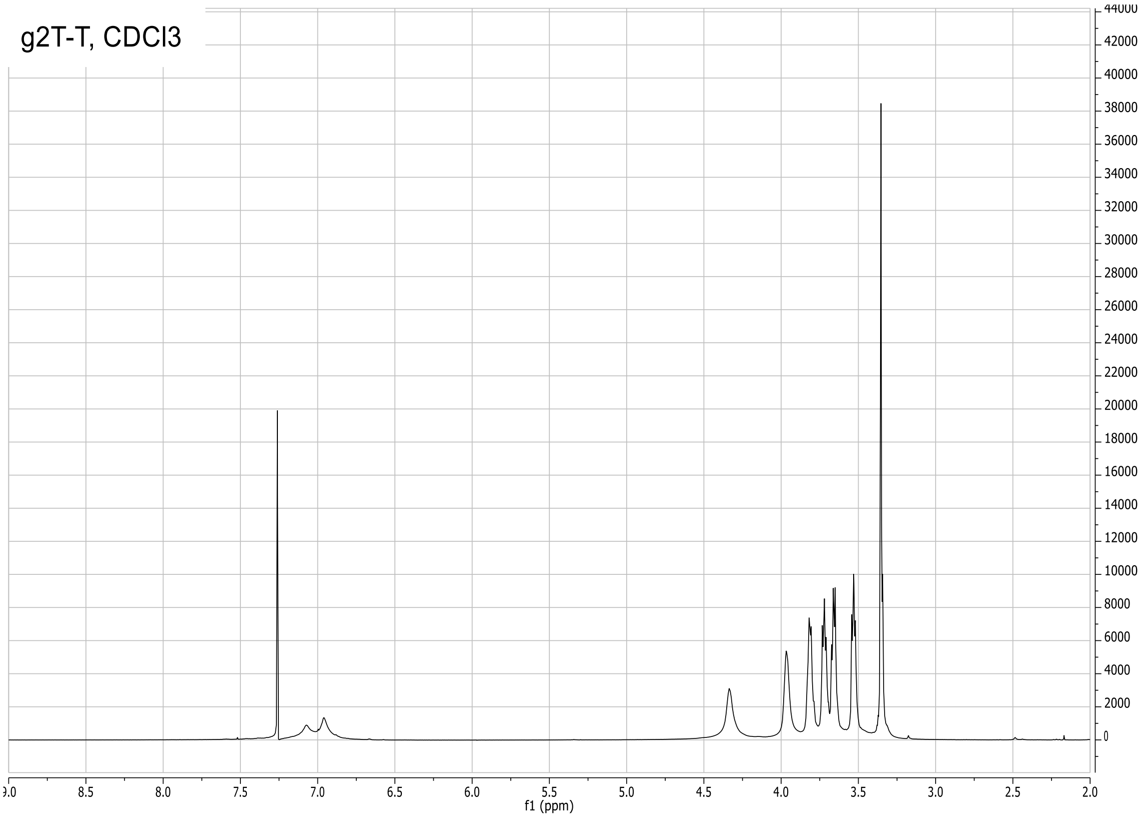


Figure S1 ^{1}H-NMR and ^{13}C-NMR spectra of 5,5′-dibromo-3,3′-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2′-bithiophene and ^{1}H-NMR spectra of all the polymers.

4. Molecular Weight Data and Optical Properties

Polymer	M_n (kDa)	Đ	λ_{max} (nm)	E_g (eV)
gBDT	4.2[a]	1.54[a]	495, 533	2.18
gBDT-T	-	-	510, 549	2.12
gBDT-2T	-	-	525, 562	2.07
gBDT-g2T	22.1[b]	1.89[b]	585	1.88
g2T-T	62.5[b]	1.59[b]	613, 650	1.73

Table S1 Molecular weight data measured as polystyrene-equivalent molecular weights by size exclusion chromatography in a) chlorobenzene at 80°C and b) N,N-dimethylformamide at 40°C.

5. DFT Data

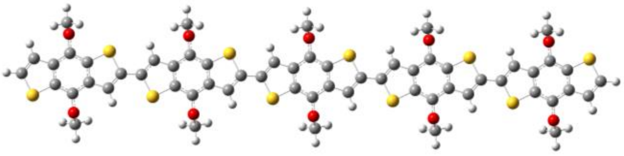
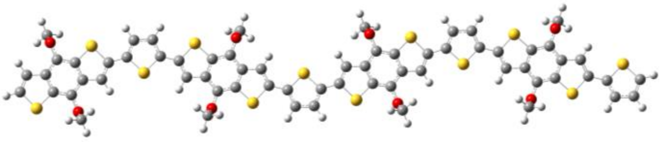
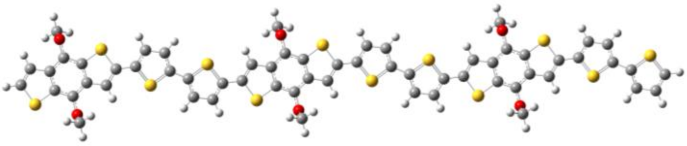
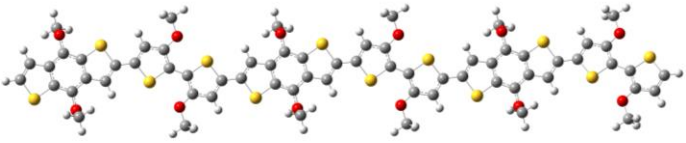
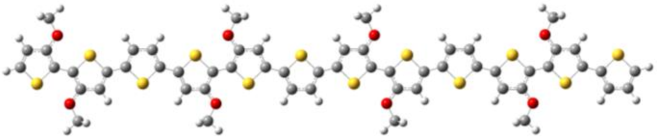
Polymer	Oligomer Conformation	HOMO (eV)	ΔE (eV)
gBDT		-4.98	2.68
gBDT-T		-4.88	2.50
gBDT-2T		-4.83	2.44
gBDT-g2T		-4.33	2.19
g2T-T		-4.04	1.95

Table S2 Energy-minimized molecular conformations of the polymers approximated using similar length oligomers with methoxy groups instead of PEG chains for reduced computational time (Gaussian B3LYP/6-31G*; gas phase).

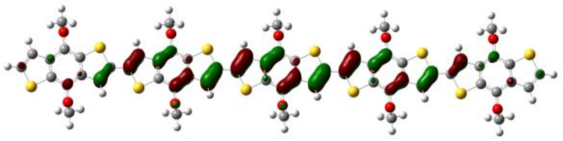
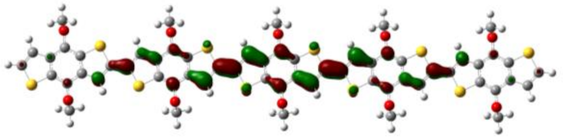
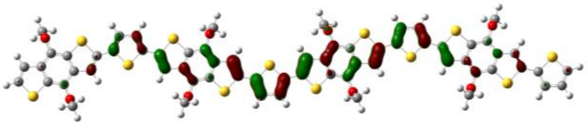
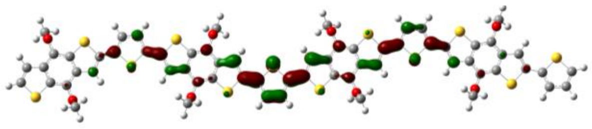
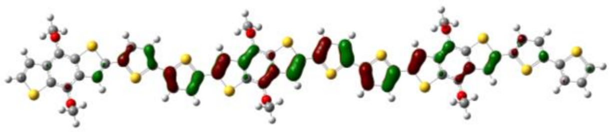
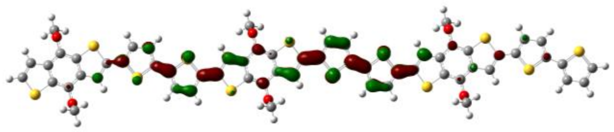
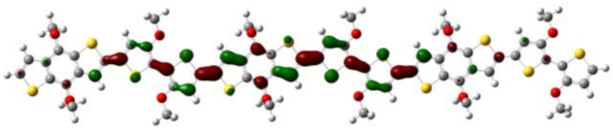
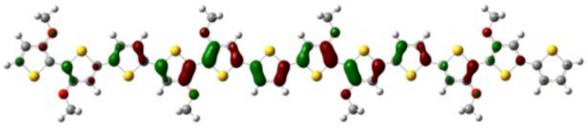
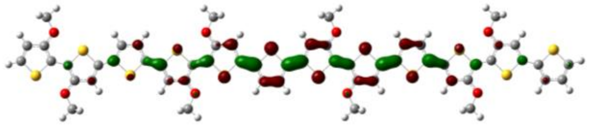
gBDT 	**gBDT** 
gBDT-T 	**gBDT-T** 
gBDT-2T 	**gBDT-2T** 
gBDT-g2T 	**gBDT-g2T** 
g2T-T 	**g2T-T** 

Table S3 Spatial distributions of the HOMO (left) and LUMO (right) of the polymers approximated using similar length oligomers with methoxy groups instead of PEG chains for reduced computational time (Gaussian B3LYP/6-31G*; gas phase).

6. UV-Vis Spectra

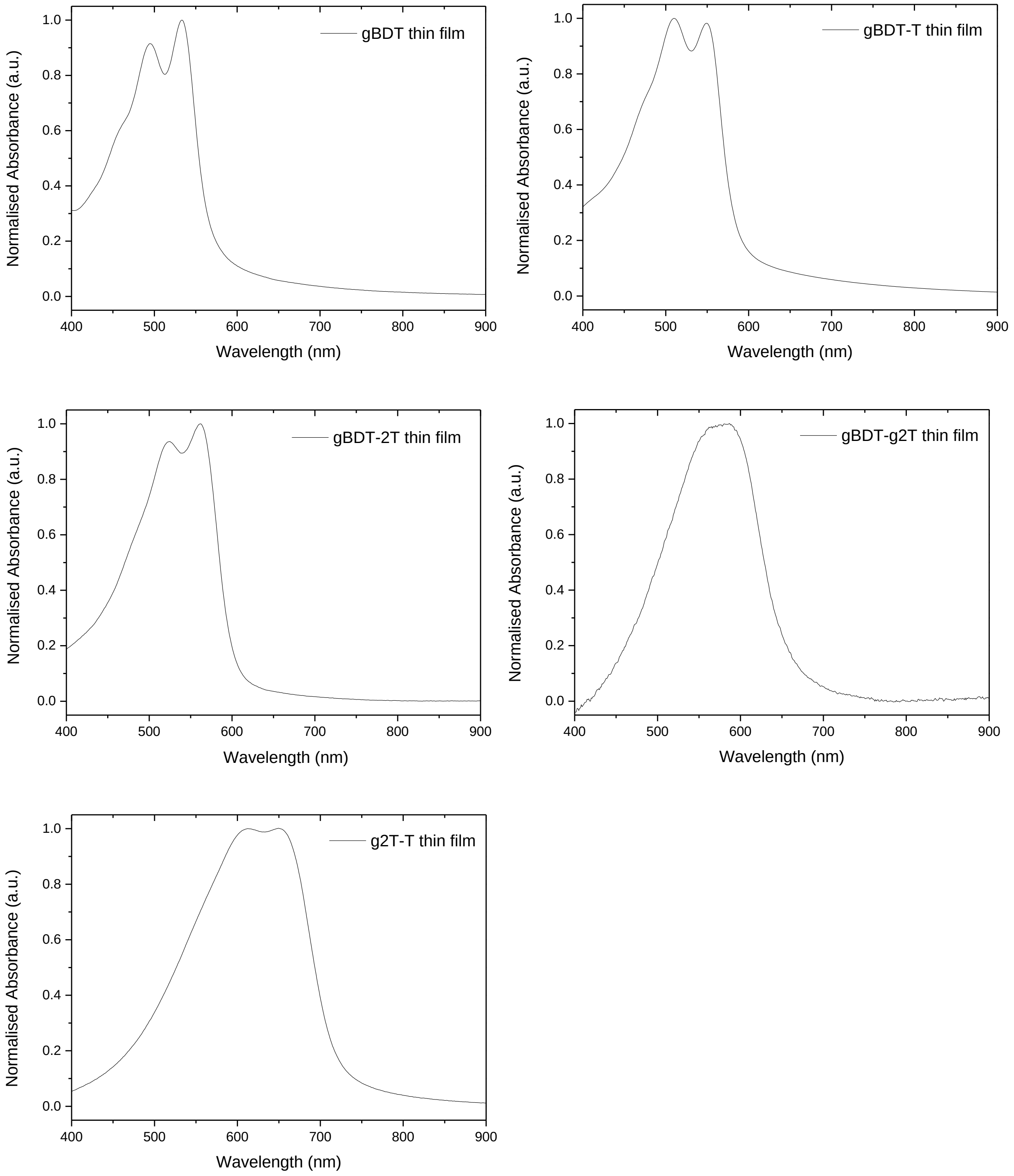


Figure S2 UV-Vis spectra of all polymers as thin spin-cast films.

7. Cyclic Voltammograms (Acetonitrile)

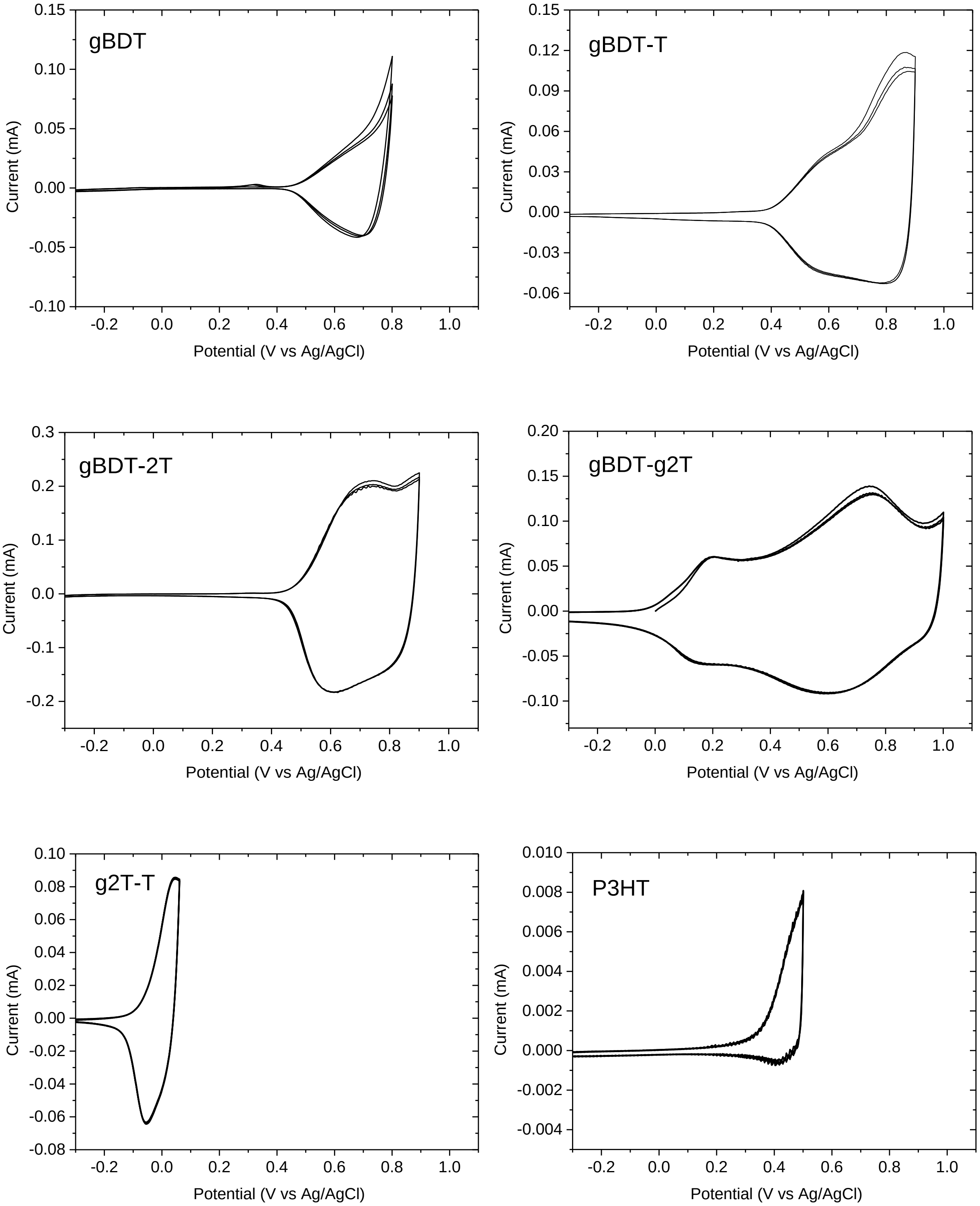


Figure S3 Cyclic voltammograms of all polymers; polymer thin films on ITO coated glass substrates in a) acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte.

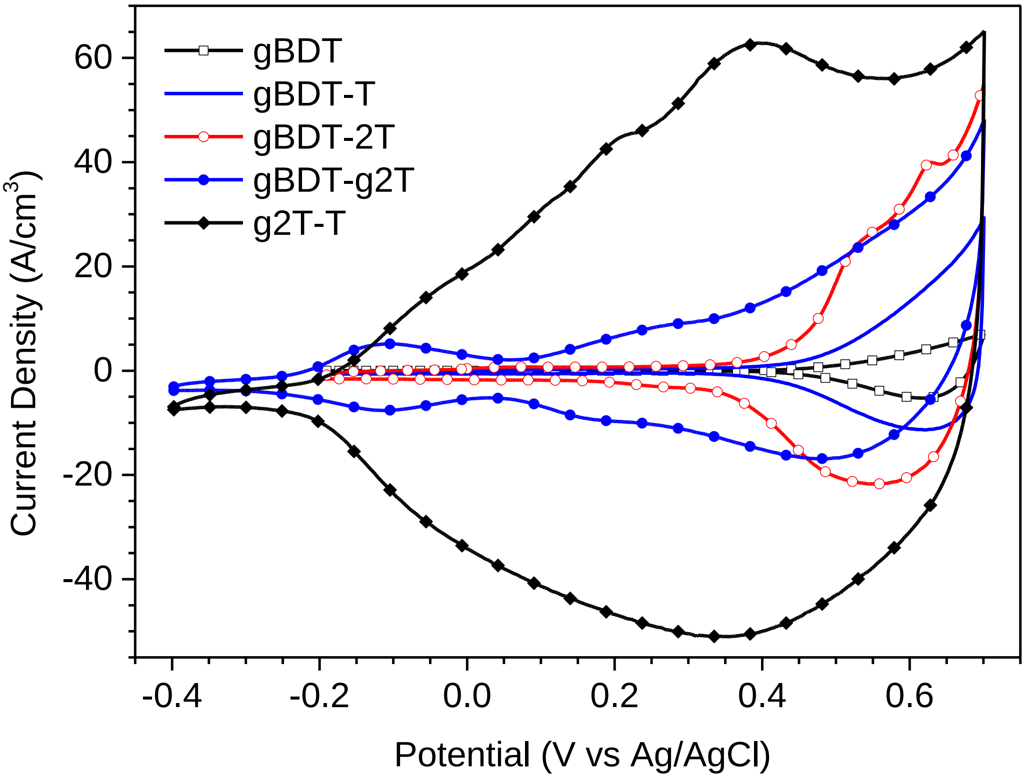


Figure S4 Cyclic voltammograms showing current density for all polymers; polymer thin films on ITO coated glass substrates in a) acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte.

8. Spectroelectrochemistry Data (Water)

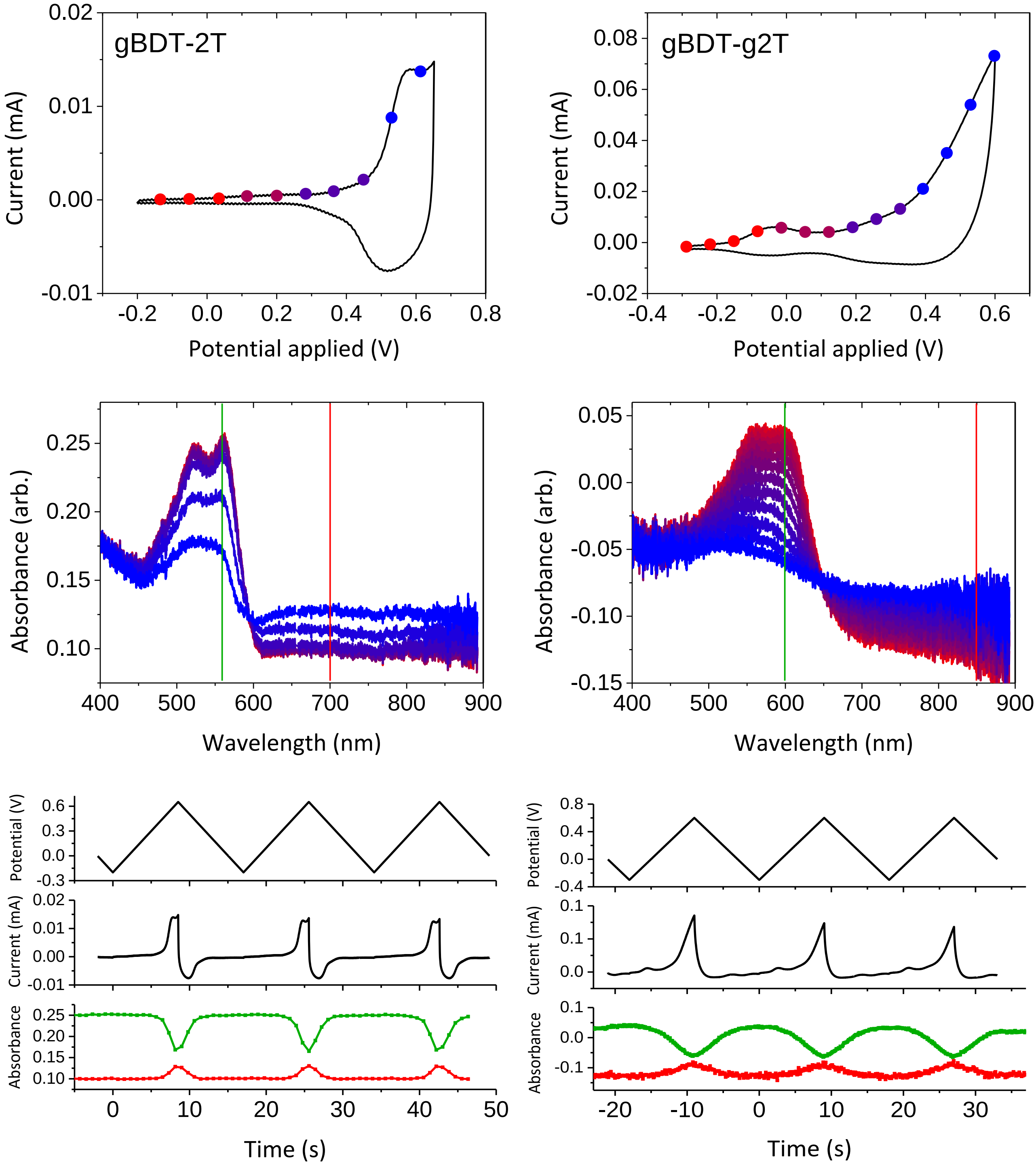
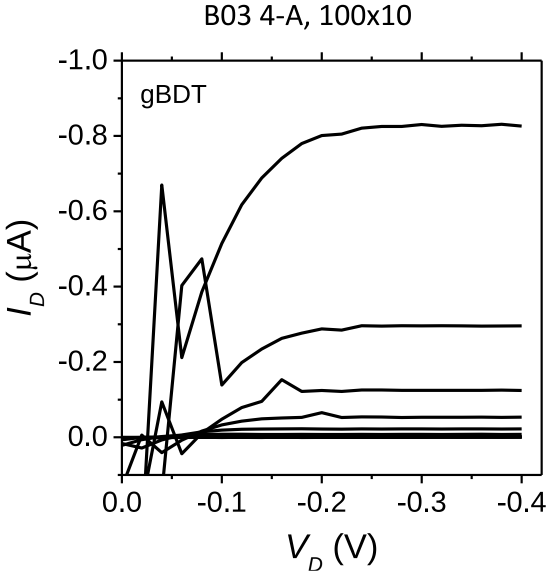


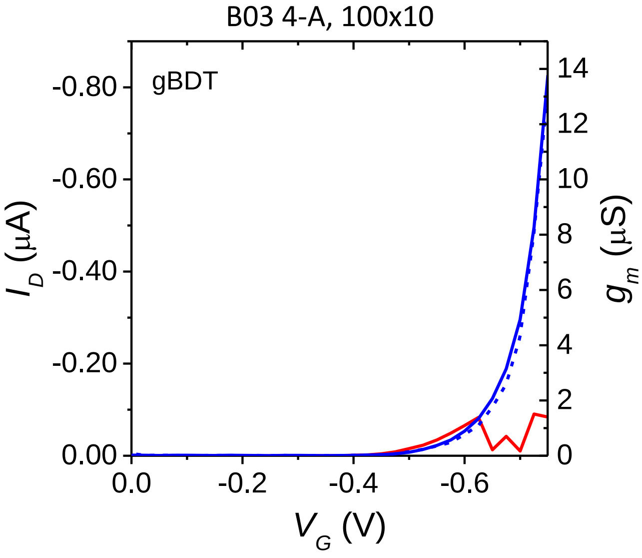
Figure S5 Cyclic voltammograms (top pane; polymer thin films on ITO coated glass substrates in water with 0.1 M sodium chloride as the supporting electrolyte) and corresponding UV-Vis absorption spectra (middle pane) with color coding indicating the applied potential during recording of the UV-Vis spectrum. Bottom pane shows the switching behaviors with the two wavelengths used for monitoring the optical switching indicated in the corresponding UV-Vis spectra by the green and red lines.

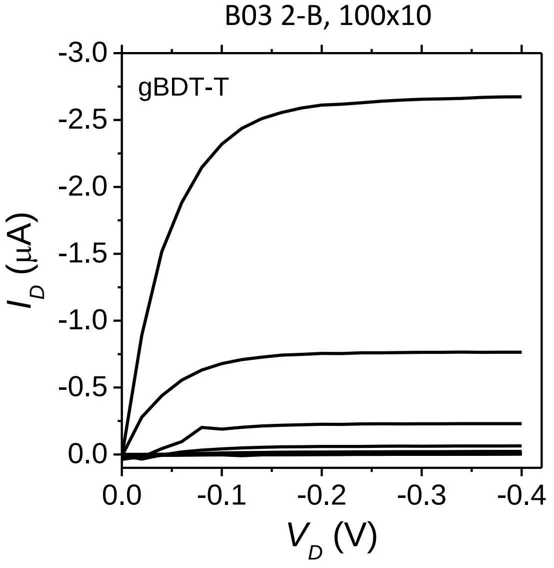
9. OECT Device Data

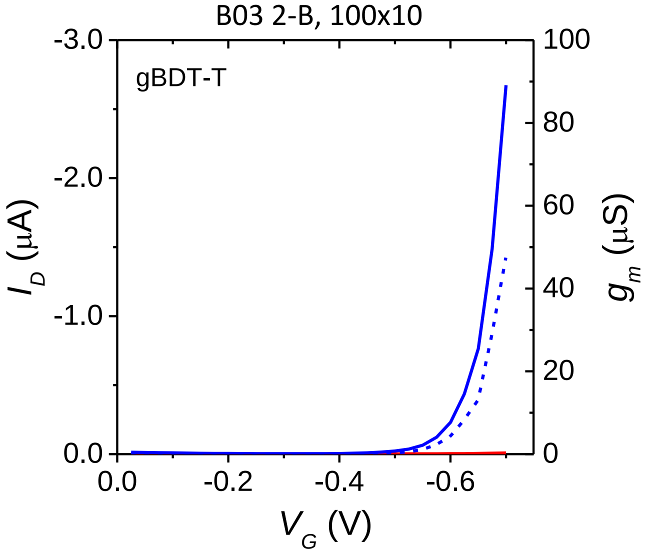
Polymer	Batch	Dimensions	Peak current (A)	Peak g_m (S)	$I_{ON/OFF}$	V_{th} (V)
gBDT	B03-3A	100x10	-1.58E-08	1.74E-07	$2.78\cdot10^{1}$	-0.65
	(drop-cast)	50x50	-7.23E-09	6.83E-08	$2.28\cdot10^{1}$	-0.64
	(112-236 nm)	10x10	-1.76E-08	2.06E-07	$4.19\cdot10^{1}$	-0.65
	B03-4A	100x10	-8.26E-07	1.32E-05	$7.80\cdot10^{2}$	-0.66
	(drop-cast)	50x50	-2.03E-07	3.24E-06	$1.32\cdot10^{2}$	-0.66
	(2.22-2.35 um)	10x10	-9.97E-09	1.43E-07	$1.96\cdot10^{1}$	-0.50
	B03-9A	100x10	-2.91E-08	1.21E-07	$2.70\cdot10^{1}$	-0.65
	(spin-cast)	50x50	---	---	---	---
	(80-90 nm)	10x10	---	---	---	---
gBDT-T	B03-1A	100x10	-1.80E-07	3.42E-06	$2.25\cdot10^{2}$	-0.51
	(drop-cast)	50x50	-3.64E-08	5.99E-07	$6.86\cdot10^{1}$	-0.50
	(215-248 nm)	10x10	-1.08E-07	2.11E-06	$1.29\cdot10^{2}$	-0.51
	B03-2A	100x10	-2.67E-06	4.75E-05	$8.51\cdot10^{2}$	-0.62
	(drop-cast)	50x50	---	---	---	---
	(2.3-3.0 um)	10x10	-1.21E-07	2.53E-06	$1.22\cdot10^{2}$	-0.64
	B03-5A	100x10	-3.32E-08	5.45E-07	$1.88\cdot10^{1}$	-0.68
	(spin-cast)	50x50	---	---	---	---
	(80-84 nm)	10x10	-3.39E-08	6.21E-07	$6.78\cdot10^{1}$	-0.62
gBDT-2T	B01-3	100x10	-3.40E-06	5.98E-05	$4.06\cdot10^{3}$	-0.58
	(spin-cast)	50x50	-2.65E-07	5.47E-06	$3.01\cdot10^{2}$	-0.58
	(100-120 nm)	10x10	-4.77E-07	1.00E-05	$9.67\cdot10^{2}$	-0.53
	B06-5	100x10	---	---	---	---
	(drop-cast)	50x50	---	---	---	---
	thin	10x10	-6.55E-05	0.000878	$2.88\cdot10^{5}$	-0.61
	B07-4	100x10	-7.16E-05	0.00099	$2.70\cdot10^{5}$	-0.62
	(drop-cast)	50x50	-5.29E-06	7.41E-05	$3.38\cdot10^{4}$	-0.62
	thick	10x10	-9.76E-06	0.000186	$6.40\cdot10^{4}$	-0.58
gBDT-g2T	B06-8	100x10	-0.00015	0.00084	$3.48\cdot10^{4}$	-0.51
	(drop-cast)	50x50	-7.92E-06	8.07E-05	$3.52\cdot10^{3}$	-0.49
	(400 nm)	10x10	-1.71E-05	0.000176	$9.62\cdot10^{3}$	-0.49
	B06-7	100x10	-4.92E-05	0.000469	$9.84\cdot10^{3}$	-0.49
	(spin-cast)	50x50	-5.35E-06	5.38E-05	$1.80\cdot10^{3}$	-0.49
	(110 nm)	10x10	-6.50E-06	6.67E-05	$2.86\cdot10^{3}$	-0.49
g2T-T	B04-5	100x10	-0.00326	0.007886	$1.73\cdot10^{5}$	-0.36
	(spin-cast)	50x50	-0.00054	0.001395	$4.13\cdot10^{4}$	-0.39
	(103 nm)	10x10	-0.0004	0.002513	$6.91\cdot10^{4}$	-0.33
	B04-7	100x10	-0.007	0.023378	$6.64\cdot10^{4}$	-0.10
	(drop-cast)	50x50	-0.0047	0.01202	$6.56\cdot10^{4}$	-0.18
	(2.89 um)	10x10	-0.00601	0.017829	$1.24\cdot10^{5}$	-0.16
	B04-8	100x10	-0.00656	0.015196	$4.12\cdot10^{5}$	-0.25
	(drop-cast)	50x50	-0.00109	0.002634	$3.61\cdot10^{4}$	-0.34
	(111 nm)	10x10	-0.00316	0.007127	$5.14\cdot10^{5}$	-0.28
	B05-9	100x10	-0.00766	0.021148	$2.55\cdot10^{5}$	-0.18
	(drop-cast)	50x50	-0.00367	0.008723	$1.45\cdot10^{5}$	-0.28
	(162 nm)	10x10	-0.00494	0.011659	$4.34\cdot10^{5}$	-0.24
	B05-10	100x10	-0.00921	0.029864	$2.89\cdot10^{5}$	-0.17
	(drop-cast)	50x50	-0.0035	0.008112	$2.08\cdot10^{4}$	-0.23
	(335 nm)	10x10	-0.0061	0.014498	$5.09\cdot10^{5}$	-0.24

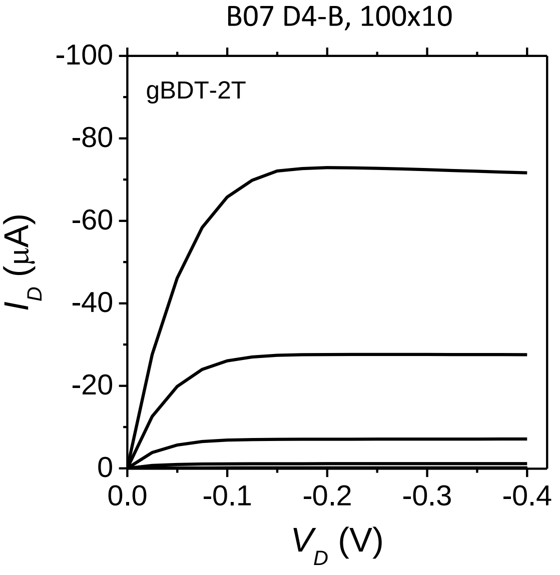
Table S4 Summary of OECT figures of merit for representative devices of all polymers encompassing both thin and thick devices obtained by both spin- and drop-casting.

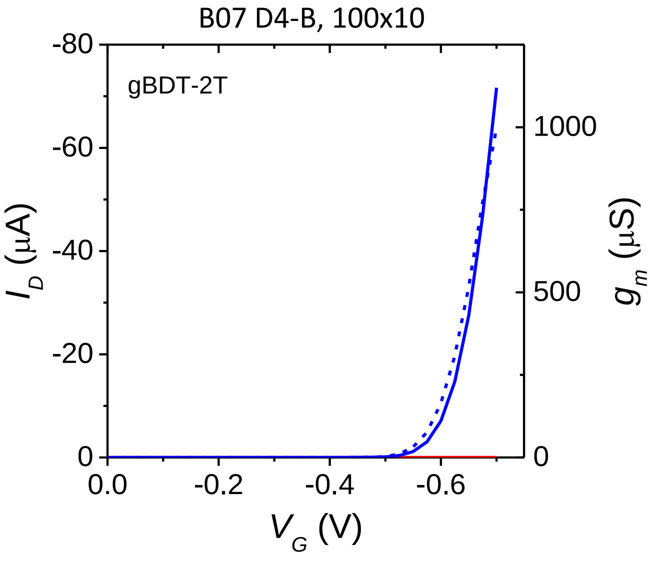

B03 4-A, 100x10
gBDT
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
0.0
-0.1
-0.2
-0.3
-0.4
I_D (µA)
V_D (V)


B03 4-A, 100x10
gBDT
-0.80
-0.60
-0.40
-0.20
0.00
0.0
-0.2
-0.4
-0.6
14
12
10
8
6
4
2
0
I_D (µA)
g_m (µS)
V_G (V)


B03 2-B, 100x10
gBDT-T
-3.0
-2.5
-2.0
-1.5
-1.0
-0.5
0.0
0.0
-0.1
-0.2
-0.3
-0.4
I_D (µA)
V_D (V)


B03 2-B, 100x10
gBDT-T
-3.0
-2.0
-1.0
0.0
0.0
-0.2
-0.4
-0.6
100
80
60
40
20
0
I_D (µA)
g_m (µS)
V_G (V)


B07 D4-B, 100x10
gBDT-2T
-100
-80
-60
-40
-20
0
0.0
-0.1
-0.2
-0.3
-0.4
I_D (µA)
V_D (V)


B07 D4-B, 100x10
gBDT-2T
-80
-60
-40
-20
0
0.0
-0.2
-0.4
-0.6
1000
500
0
I_D (µA)
g_m (µS)
V_G (V)

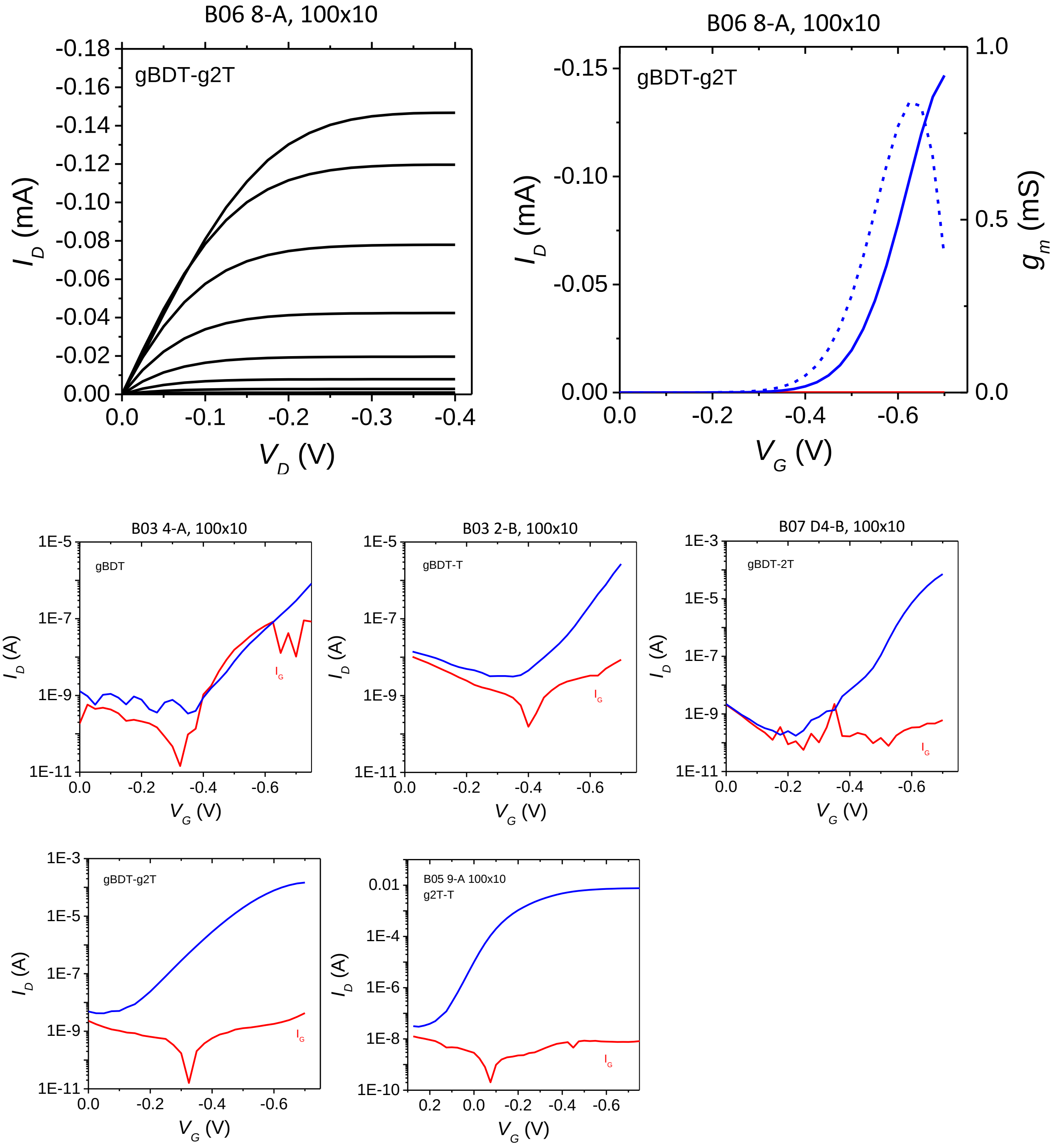


Figure S6 Output characteristics (left) and transfer characteristics and related transconductances (right) for OECT devices measured in 0.1 M NaCl aqueous solution. Bottom graphs show drain and gate currents plotted on a log scale for all five polymers. All transfer characteristics are recorded at a drain voltage of -0.4 V.

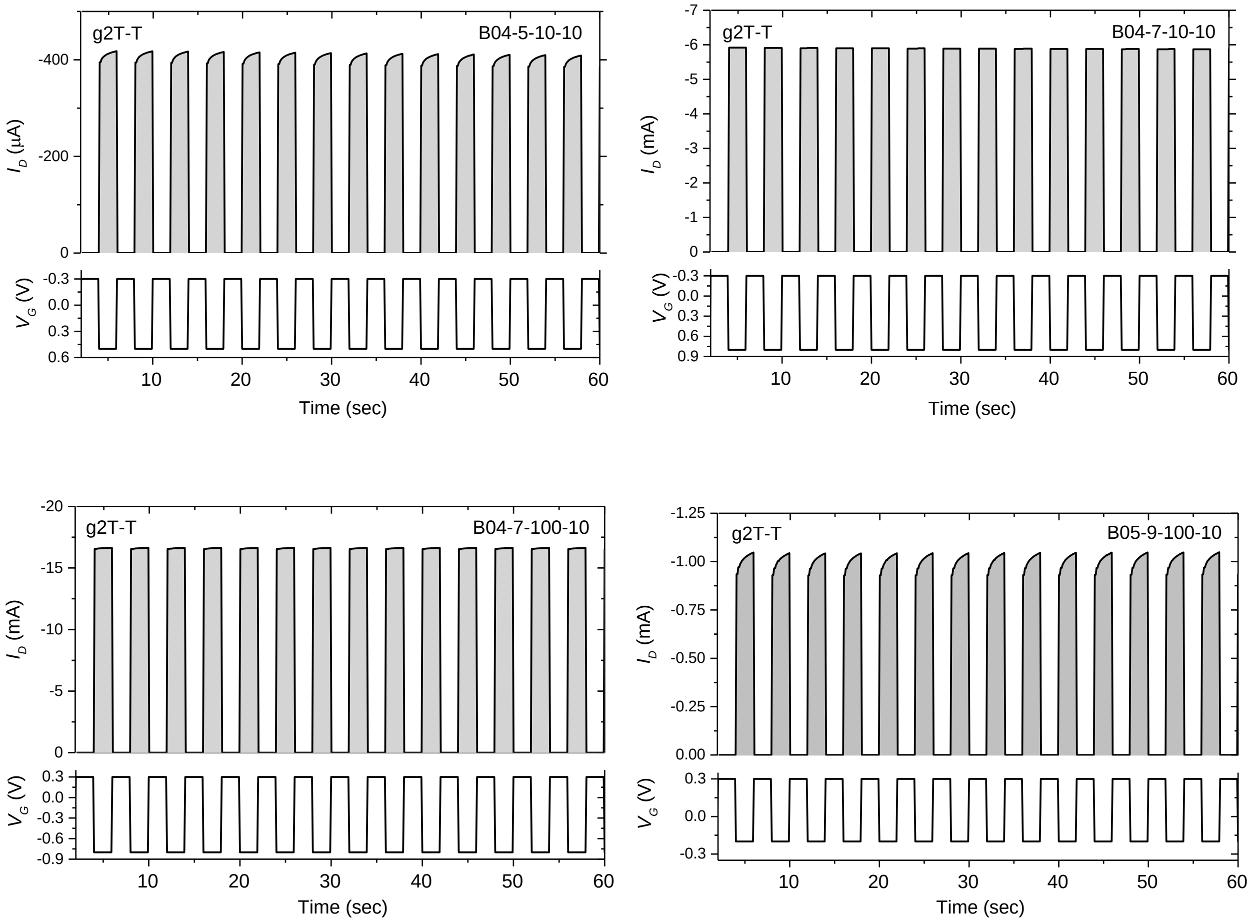


Figure S7 Switching characteristics of **g2T-T** based OECT devices; for device thicknesses see table S3.

10. FET Device Data

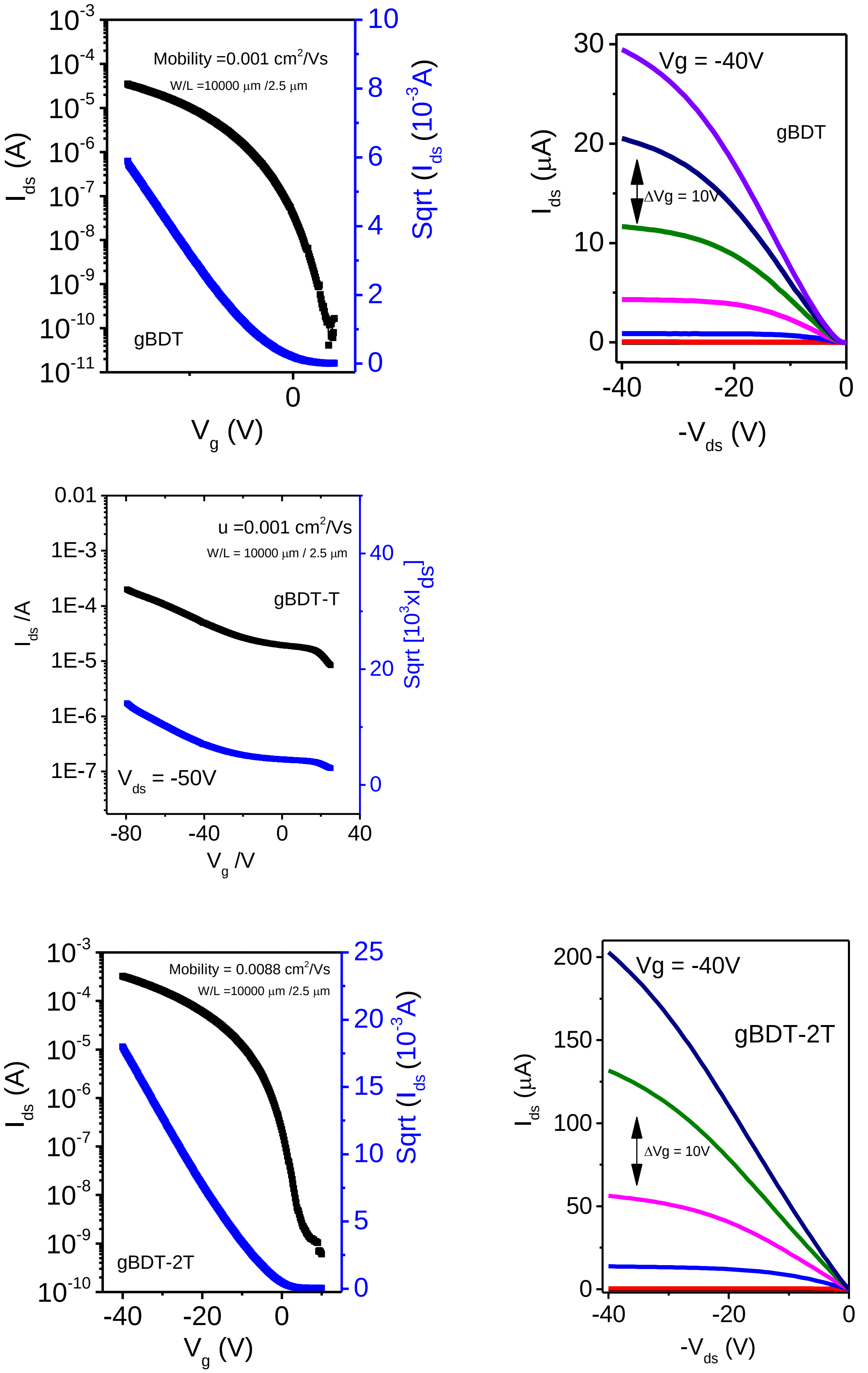


Figure S8 Transfer (left) and output (right) curves for OFET devices.

11. XRD and GIWAXS Data

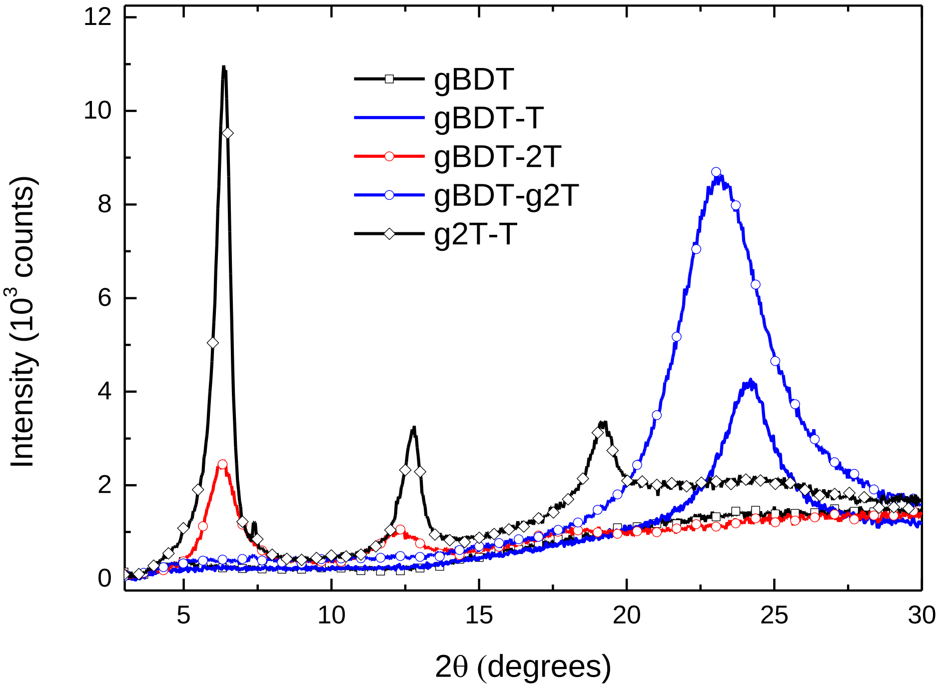
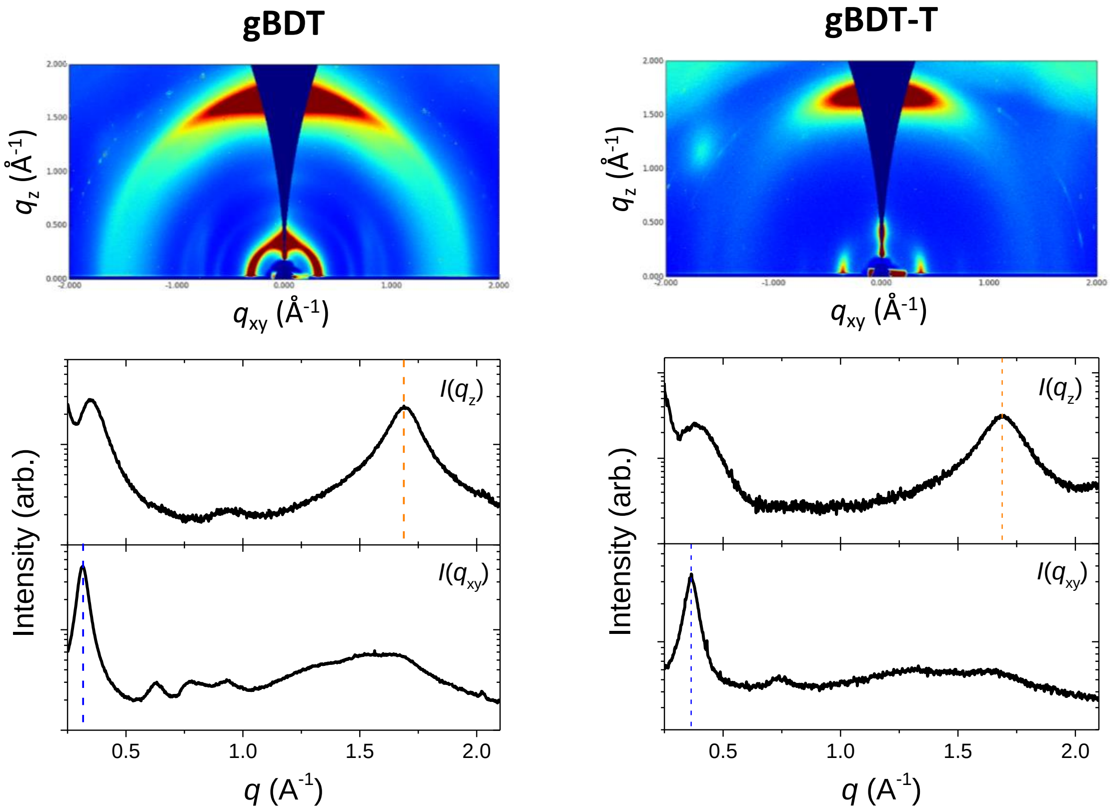


Figure S9 Specular X-Ray diffractograms for drop-cast films of all polymers.



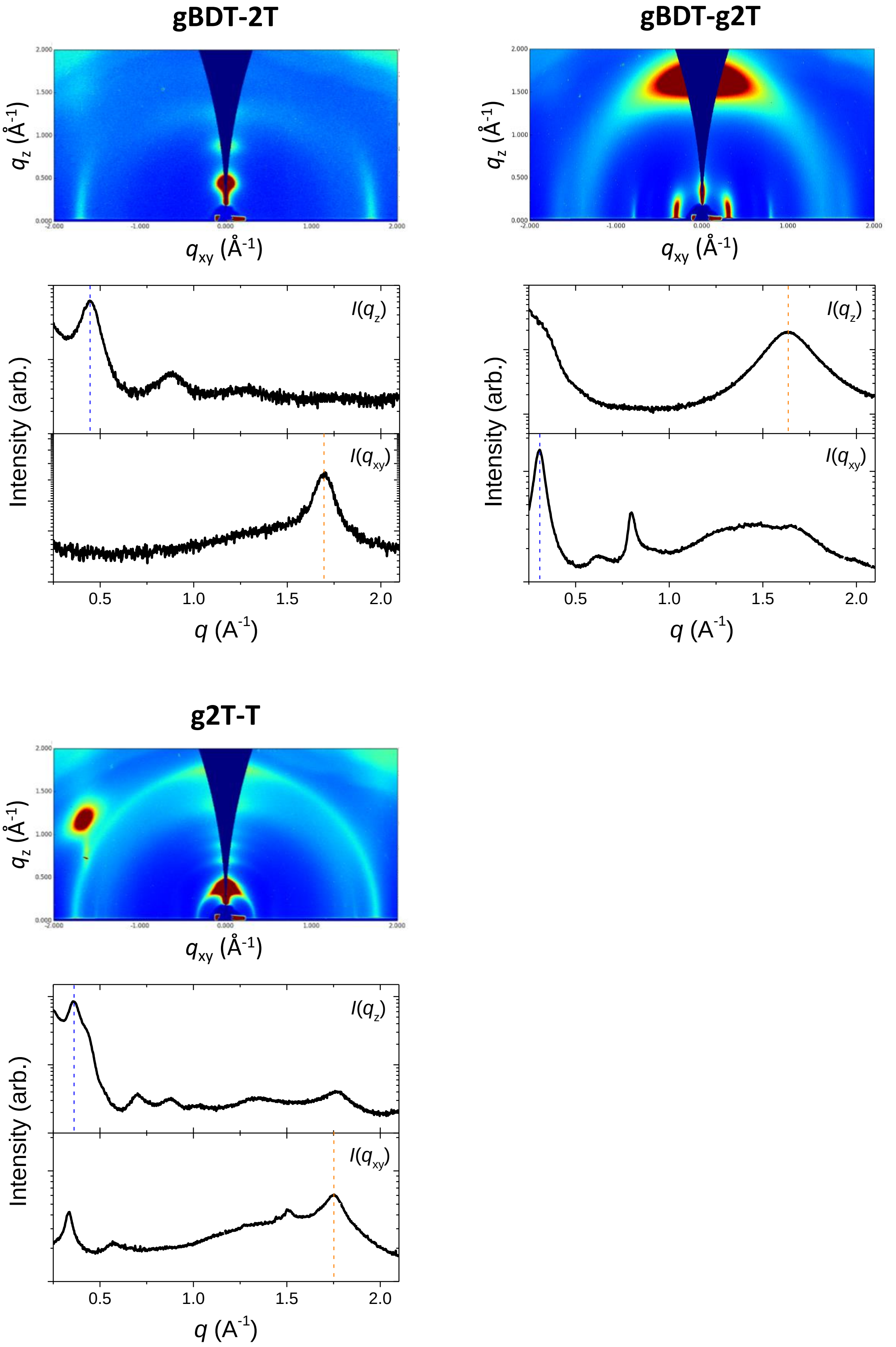


Figure S10 GIWAXS plots for spin-cast films of all polymers.

12. References

(1) Rivnay, J.; Leleux, P.; Sessolo, M.; Khodagholy, D.; Hervé, T.; Fiocchi, M.; Malliaras, G. G. *Adv. Mater.* **2013**, *25*, 7010-7014.

(2) Song, C. K.; Eckstein, B. J.; Tam, T. L. D.; Trahey, L.; Marks, T. J. *ACS Appl. Mater. Interfaces* **2014**, *6*, 19347-19354.

(3) Guo, X.; Quinn, J.; Chen, Z.; Usta, H.; Zheng, Y.; Xia, Y.; Hennek, J. W.; Ortiz, R. P.; Marks, T. J.; Facchetti, A. *J. Am. Chem. Soc.* **2013**, *135*, 1986-1996.

(4) Giovannitti, A.; Nielsen, C. B.; Rivnay, J.; Kirkus, M.; Harkin, D. J.; White, A. J. P.; Sirringhaus, H.; Malliaras, G. G.; McCulloch, I. *Adv. Funct. Mater.* **2016**, *26*, 514-523.