Electronic Supplementary Information

High Performance, Low-Voltage Organic Field-Effect Transistors Using Thieno[3,2-*b*]thiophene and Benzothiadiazole Co-Polymers

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1. Materials

All reagents were purchased from Aldrich, Merck and Acros Organics and used without further purification. All solvents used in the syntheses were of technical grade and freshly distilled prior to use. The solvents used in spectroscopic measurements were of spectroscopic grade. Synthesized compounds were purified by column chromatography using a Merck Silica Gel (0.015–0.040 mesh) as the adsorbent (stationary phase) packed into a glass column. Commercial TLC (Merck TLC Silica Gel 60 F254) was used for the determination of the extent of reaction as well as to find out the eluent (mobile phase) for the column chromatography.

2. Methods

2.1. Chemical structure confirmation:

^{1}H NMR and ^{13}C NMR spectra of polymers were measured in deuterated chloroform with a Varian 500 and 125 MHz spectrometer, respectively using trimethylsilane, TMS as an internal standard. Proton and carbon chemical shifts were reported in parts per million (ppm).

2.2. Photophysical properties

UV measurements were recorded on HITACHI U-0080D. Fluorescence spectra were measured on HITACHI F-4500 Fluorescence Spectrophotometer.

2.3. Thermal properties

Thermalgravimetric analysis (TGA) as performed on PerkinElmer Diamond TA/TGA with a heating rate of 10 °C min $^{-1}$ under a nitrogen flow.

2.4. Electrochemical measurements

Cyclic voltammetry was performed using a CH-Instruments Model 400A electrochemical analyzer. Electrodes were used Pt wire as a working and counter, and an Ag reference electrode. The supporting electrolyte was 0.1 M Bu_4NPF_6 in ACN in all the measurements (**Fig. S1**).

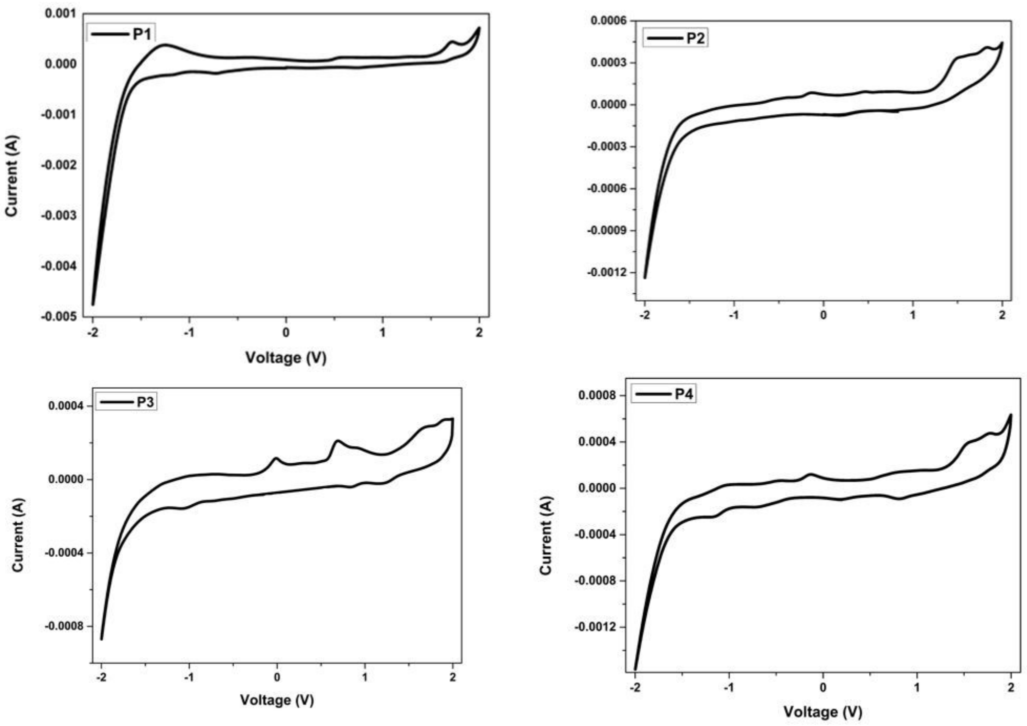
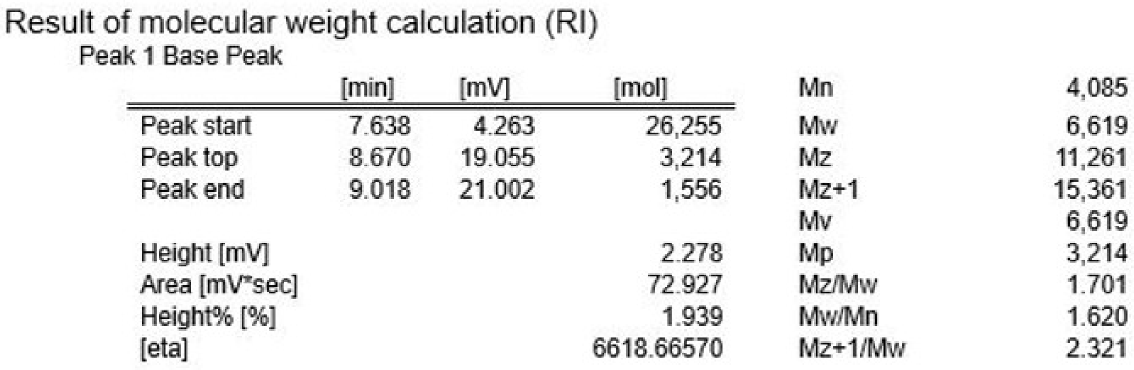


Figure S1. Cyclic voltammograms of polymers **P1**, **P2**, **P3** and **P4**

2.5. Determination of the molecular weights

Mass spectra (HRMS) of the monomers were recorded on Thermo LCQ-Deca ion trap mass instruments. The molecular weights of newly synthesized co-polymers were determined using a TOSOH EcoGPC system equipped with an auto sampler unit, a column oven, a temperature-controlled pump, a purge and degasser unit, and a TSK gel superhZ2000 column with 4.6 mm ID × 15 cm × 2 cm dimensions. THF was used as the eluent at the flow rate of 10 Ml min^{-1} at 40 °C. A refractive index (RI) detector calibrated with polystyrene standard was used for the measurements. GPC data were analyzed using Eco-GPC Analysis software (**Fig. S2-S5**).



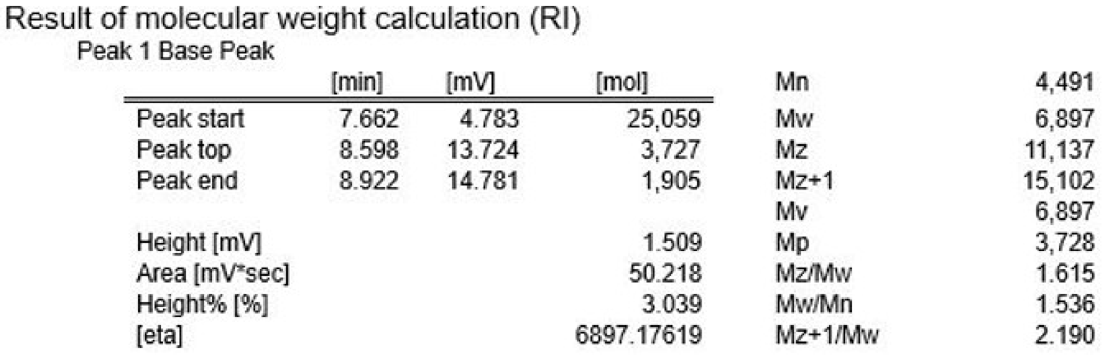
Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]
Peak start	7.638	4.263	26,255
Peak top	8.670	19.055	3,214
Peak end	9.018	21.002	1,556
Height [mV]			2.278
Area [mV*sec]			72.927
Height% [%]			1.939
[eta]			6618.66570

Mn	4,085
Mw	6,619
Mz	11,261
Mz+1	15,361
Mv	6,619
Mp	3,214
Mz/Mw	1.701
Mw/Mn	1.620
Mz+1/Mw	2.321

Figure S2: GPC result of **P1**



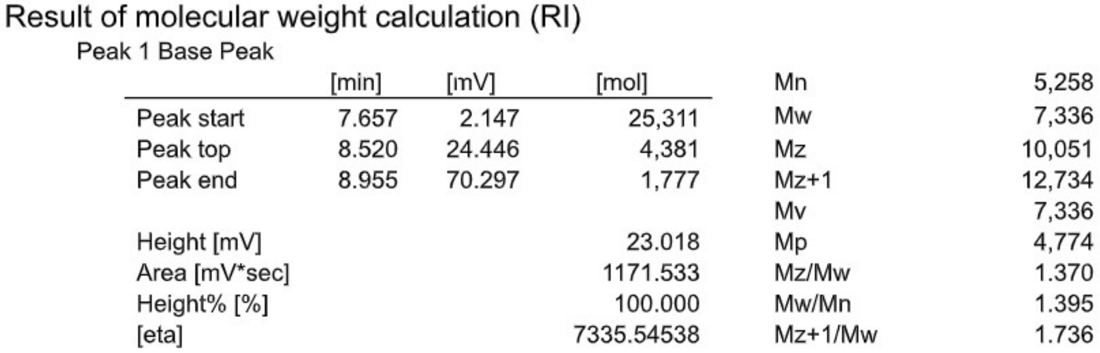
Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]
Peak start	7.662	4.783	25,059
Peak top	8.598	13.724	3,727
Peak end	8.922	14.781	1,905
Height [mV]			1.509
Area [mV*sec]			50.218
Height% [%]			3.039
[eta]			6897.17619

Mn	4,491
Mw	6,897
Mz	11,137
Mz+1	15,102
Mv	6,897
Mp	3,728
Mz/Mw	1.615
Mw/Mn	1.536
Mz+1/Mw	2.190

Figure S3: GPC result of **P2**



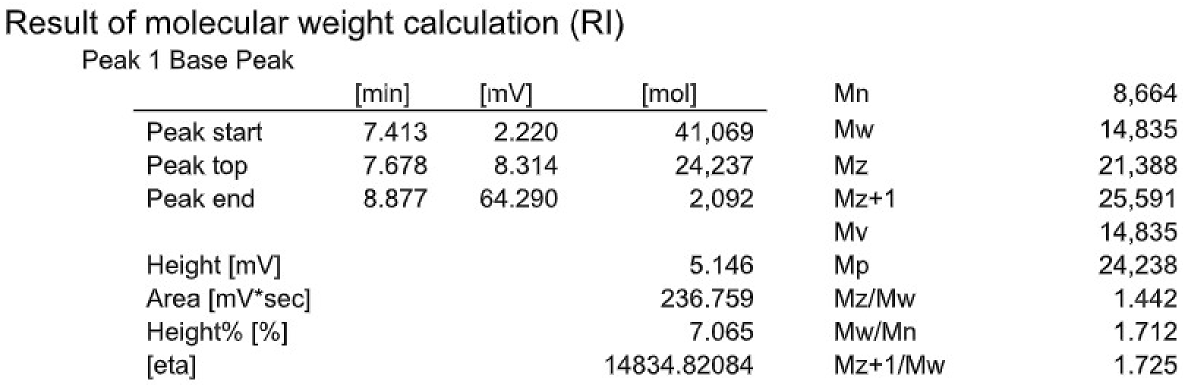
Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]
Peak start	7.657	2.147	25,311
Peak top	8.520	24.446	4,381
Peak end	8.955	70.297	1,777
Height [mV]			23.018
Area [mV*sec]			1171.533
Height% [%]			100.000
[eta]			7335.54538

Mn	5,258
Mw	7,336
Mz	10,051
Mz+1	12,734
Mv	7,336
Mp	4,774
Mz/Mw	1.370
Mw/Mn	1.395
Mz+1/Mw	1.736

Figure S4: GPC result of **P3**



Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	7.413	2.220	41,069	Mn	8,664
Peak top	7.678	8.314	24,237	Mw	14,835
Peak end	8.877	64.290	2,092	Mz	21,388
				Mz+1	25,591
				Mv	14,835
Height [mV]			5.146	Mp	24,238
Area [mV*sec]			236.759	Mz/Mw	1.442
Height% [%]			7.065	Mw/Mn	1.712
[eta]			14834.82084	Mz+1/Mw	1.725

Figure S5: GPC result of **P4**

3. NMR Spectra

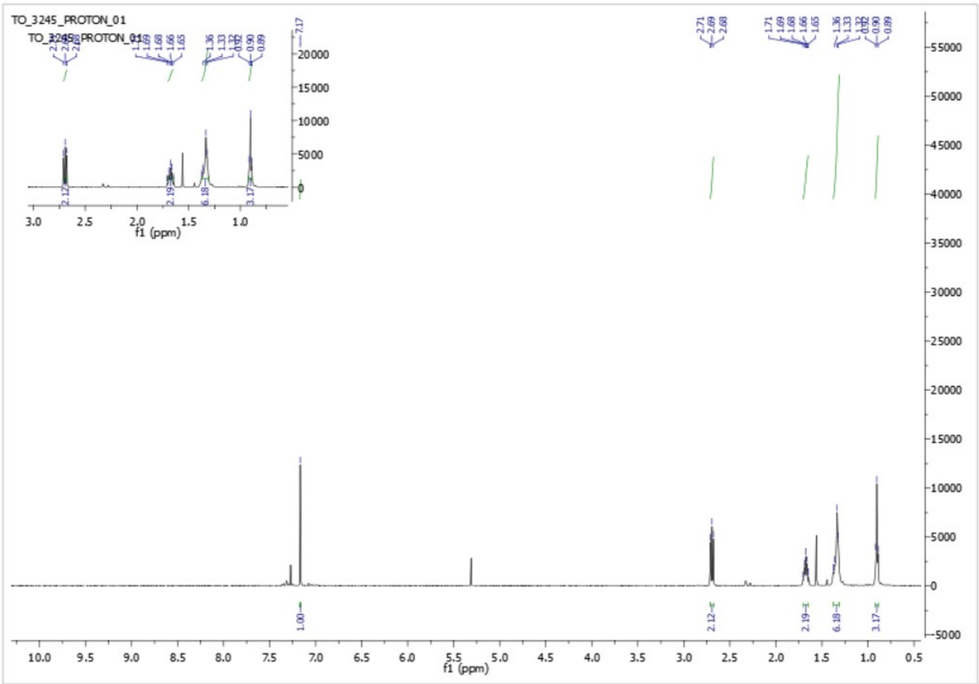


Figure S6. ^{1}H NMR of **M3**

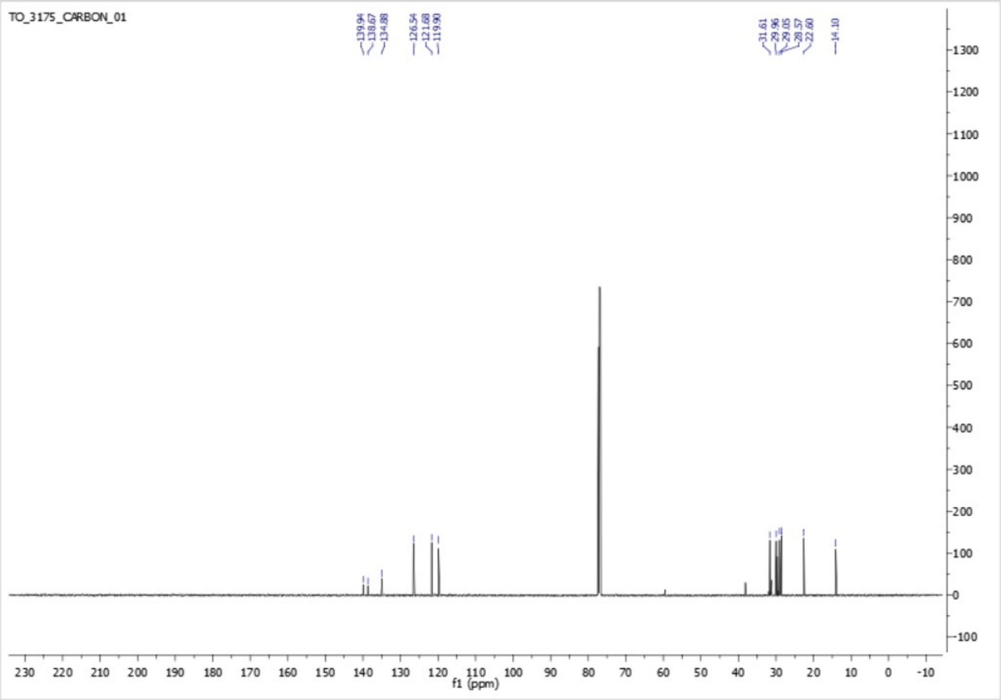


Figure S7. ^{13}C NMR of **M3**

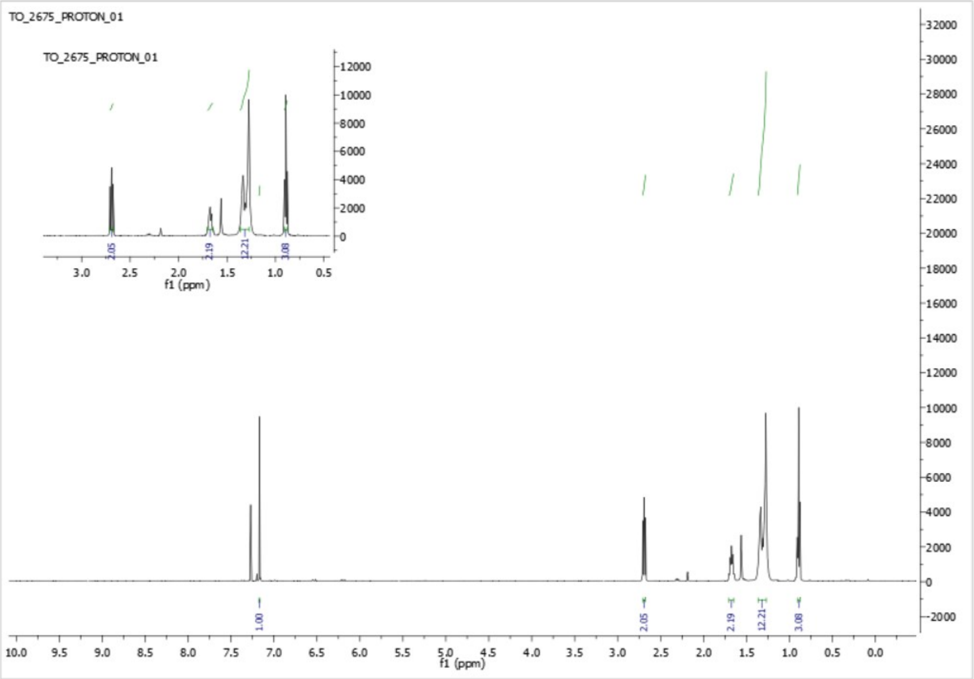


Figure S8. ^{1}H NMR **M4**

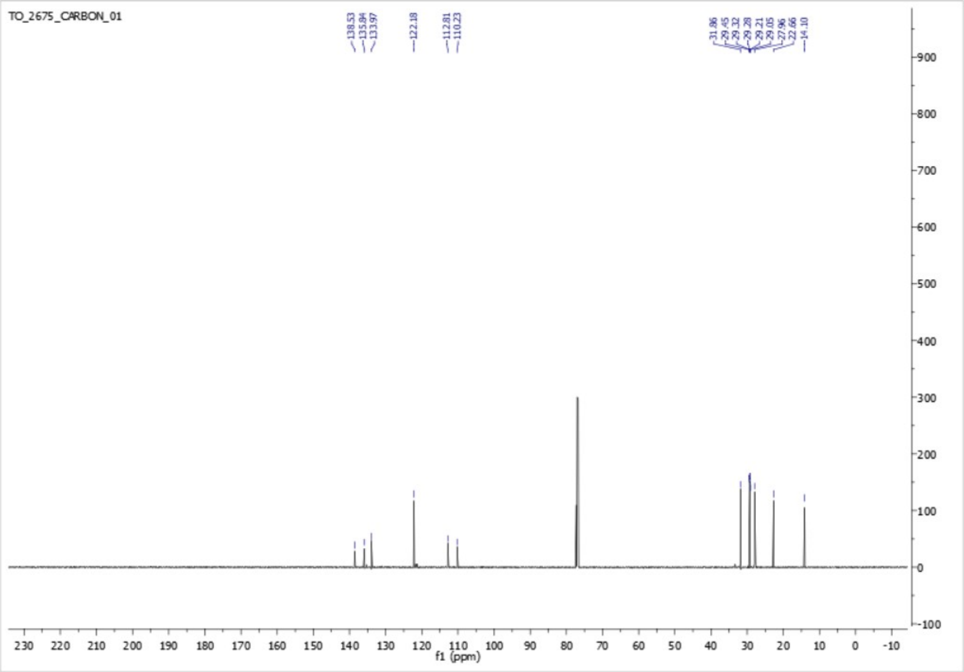
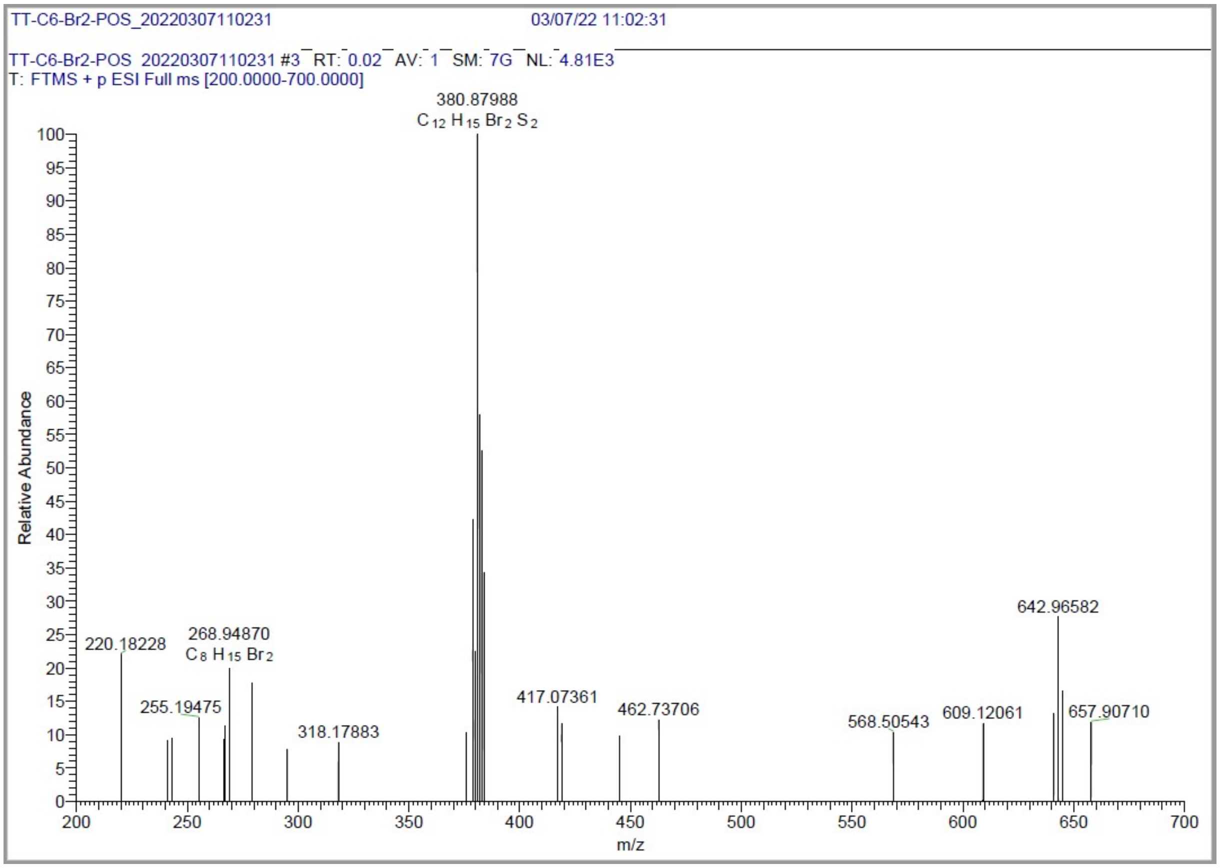


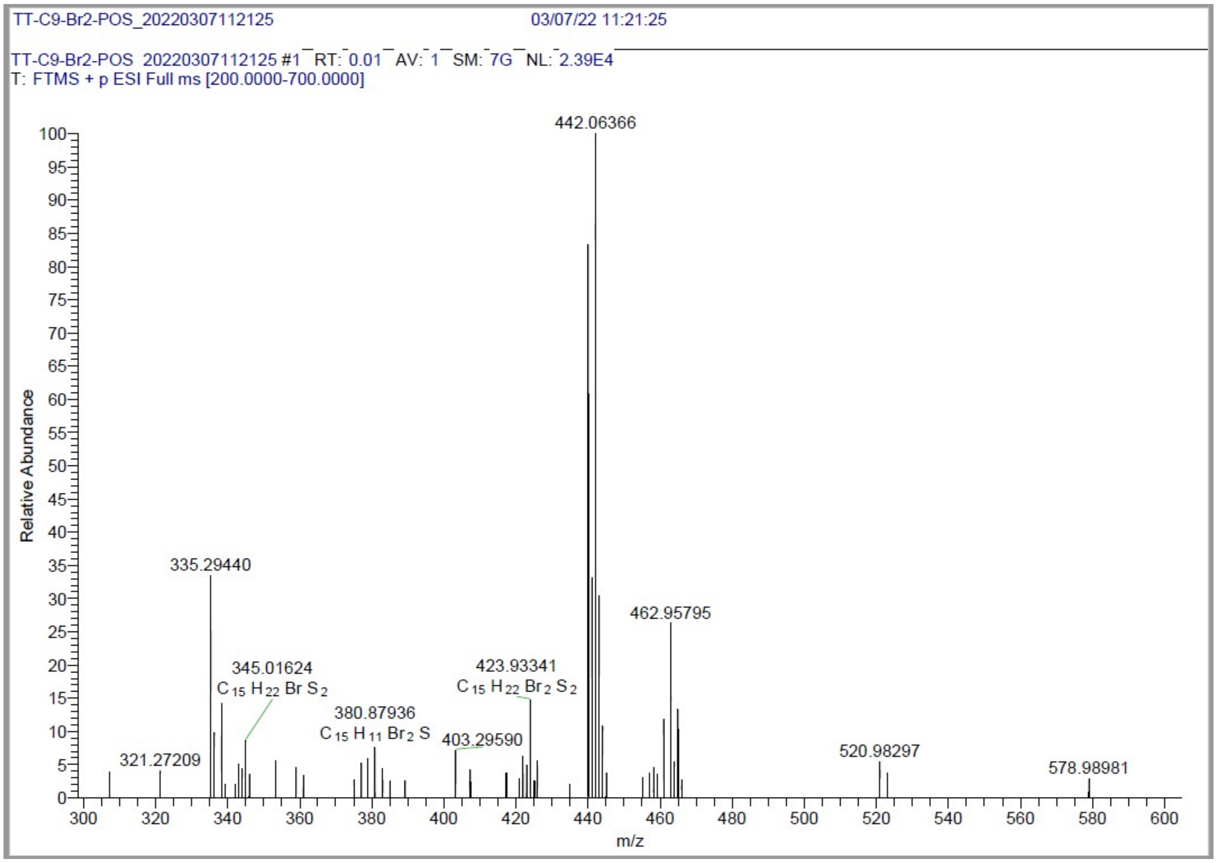
Figure S9. ^{13}C NMR of **M4.**

4. Mass Spectra



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
380.87946	380.89764	-47.74	4.5	$C_{12}H_{15}Br_2S_2$

Figure S10. HRMS Spectra of **M3**



m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
423.95242	423.93341	-44.84	4.0	$C_{15}H_{21}Br_2S_2$

Figure S11. HRMS Spectra of **M4**

5. Organic Field-Effect Transistors

The structure of the fabricated bottom-gate, top-contact (BGTC) OFET and the chemical structure of CEC are depicted in **Fig. 5**. OFETs were fabricated by firstly a 100 nm thick aluminum layer was thermally evaporated to serve as the bottom gate electrode (Fig. S12a) onto a pre-washed corning glass substrate. To enable low-voltage operation of OFETs, cyanoethyl cellulose (CEC) with a high dielectric constant ($k \sim 14$) and low values of dielectric loss compared to other common organic insulating polymers[1,2] is used as the dielectric thin film. When compared with poly(vinylidene fluoride) and its copolymers, CEC has good heat and acid stability, low moisture uptake and is mechanically robust. Most recently, Faraji *et al.* reported low-voltage operating

OFETs using solution-deposited, high-*k* gate dielectric layers based on nanocomposites of cyanoethylated cellulose (CEC) and barium strontium titanate (BST).[3] CEC shavings purchased from Sigma Aldrich was dissolved in *N,N*-dimethylformamide (DMF) at 5 wt% and stirred for 3 h at room temperature until a homogenous solution was obtained. The solution was then filtered through 0.45mm PTFE membrane and spin-coated at 3000 rpm onto the gate electrode. The dielectric layer was then annealed at 90 °C for 90 min to form a solid, robust thin film. The thickness (*d*) of the CEC thin film measured using a DEKTAK 3ST profilometer was 280 ± 1 nm.

The dielectric properties of the CEC layer were determined by the fabrication of parallel-plate capacitors. The capacitance per unit area (C_i) was measured 40 ± 2 Nf/cm^2 using an Agilent E4980A Precision LCR Meter in frequency range of 100 Hz–1 MHz. The dielectric constant (k) was calculated based on $Ci = \varepsilon_0 k/d$ *as 13 ± 1.* Subsequently, to complete the OFET design, a prepared solution of each thienothiophene-based (TT) OSC in chloroform was spin-coated at 2000 rpm for 2 min on top the gate dielectric layer and annealed at 90 °C for 60 min. Finally, gold source and drain electrodes (~50 nm) were deposited through a shadow mask (Fig. S12b) by thermal evaporation. A typical substrate, consisting of 20 identical BGTC OFETs, fabricated in this work is illustrated in (Fig. S12c). The transistor characterisation was performed in ambient conditions (air with 40%-50% relative humidity) using an Agilent E5270B measurement mainframe with Karl Suss PH100 micromanipulator probes.

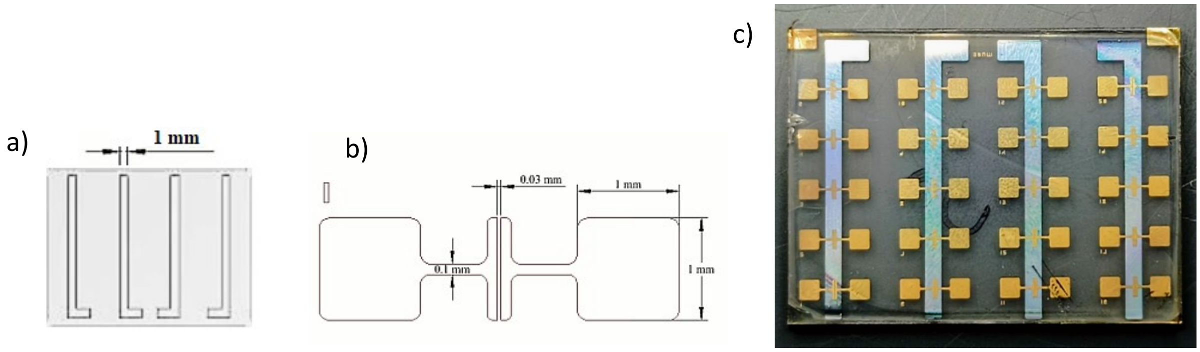


Fig. S12. (a) Gate and (b) source/drain electrodes shadow mask designs and dimensions and (c) a typical substrate consisting of 20 identical BGTC OFETs fabricated in this work

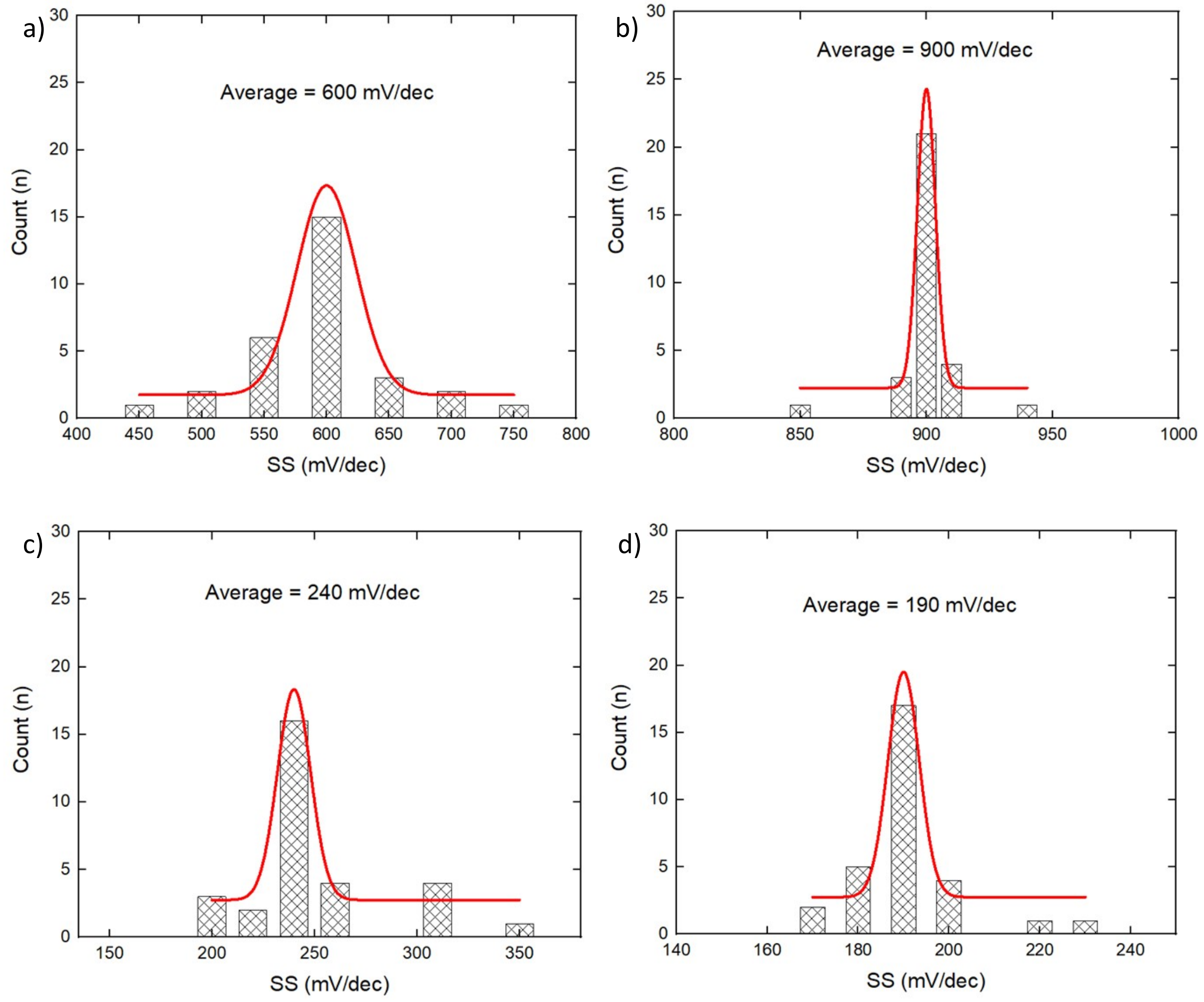


Fig. S13a-d. P1-P4 OFETs' subthreshold swing statistics obtained from at least 30 devices.

References

1. K. W. Saunders, N. M. Bikales, Cyanoethylated cellulose solutions, *US Patent*, 1963, 3097956 A
2. M.L. Hassan, Dielectric properties of cyanoethylated bagasse composites, *Polym.-Plast. Technol. Eng.* 2002, **41**, 589-600.
3. S. Faraji, E. Danesh, D.J. Tate, M.L. Turner, L.A. Majewski, Cyanoethyl cellulose-based nanocomposite dielectric for low-voltage, solution-processed organic field-effect transistors (OFETs), *J. Phys. D: Appl. Phys*. 2016**, 49,** 185102.