Supporting Information

Modular Synthesis and Dielectric Properties of Fluorinated Poly(arylene ether-1,3,4-oxadiazole)s

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Materials

2,5-Bis(pentafluorophenyl)-1,3,4-oxadiazole (**FPOx**) was synthesized according to the literature procedure in reference 14. All other chemicals and solvents were commercially available from Aldrich and used as received unless otherwise noted.

General procedure for synthesis of monomer 1a-1h

The synthesis of monomers **1a-1h** was conducted in a similar approach, and a typical procedure for monomer **1c** was described as follows. In a 250 ml four-neck round bottom flask equipped with a mechanical stirrer, a condenser and a thermometer, 12.2 g (0.1 mol) of 2-ethylphenol was dissolved in 100 ml of 1,2-dichloroethane in the ice-water bath. Subsequently, 40.0 g (0.3 mol) of anhydrous aluminum chloride (anh. $AlCl_3$) and 14.8 g (0.1 mol) of phthalic anhydride were added to the solution slowly in several portions. The resulting mixture was stirred intensively at room temperature for 2 h and 45 ˚C for another 2 h followed by being poured into hydrochloric acid (37.5 wt %, 50 ml) containing crushed ice. The coarse cream mixture was separated by steam distillation. After filtrated and dried, the coarse compound γ-ketone acid and about 100 ml 1-buntanol was added into a 250 ml three-necked round bottom flask equipped with a mechanical stirred and a condenser. Then excessive hydrazine

monohydrate (30 ml, 85 wt %) was carefully dropped into the mixture when the solution was heated to reflux. The reaction was accomplished within 3 h and the white power product was obtained by filtration. The product was then purified by recrystallization in DMAc for at least two times followed by dried under vacuum at 80 ˚C for 24 h prior to polymerization.

4-(4'-hydroxyphenyl) (2*H*)phthalazin-1-one (1a)

White solid, yield based on two steps: 72%, mp: 309-310˚C. ^{1}H NMR (400 MHz, DMSO-d_6/TMS int, ppm) δ: 6.95(m, 2H, 2'-H), 7.42(m, 2H, 3'-H), 7.75(d, 1H, 5-H), 7.89(m, 2H, 6,7-H), 8.34(m, 1H, 8-H), 9.83(s, 1H, O*H*), 12.76(s.1H, N-*H*), Elemental Analysis (%) Found (Calcd.): C: 70.37(70.58), H: 4.17(4.23), N: 11.63(11.76)

4-(3'-methyl-4'-hydroxyphenyl) (2*H*)phthalazin-1-one (1b)

White solid, yield based on two steps: 80 %, mp: 297-298˚C. ^{1}H NMR (400 MHz, DMSO-d6/TMS int, ppm) δ: 2.21 (s, 3H, 30-CH3), 6.93 (d, 1H,50-H), 7.22 (d, 1H, 60-H), 7.29 (s, 1H, 20-H), 7.75(m, 1H, 5-H), 7.88 (m, 2H, 6-,7-H), 8.32 (m, 1H, 8-H), 9.69 (s, 1H, O-*H*), 12.72 (s, 1H, N-*H*), Elemental Analysis (%) Found (Calcd.): C: 71.18(71.42), H: 4.67(4.79), N: 11.03(11.10)

4-(3'-ethyl-4'-hydroxyphenyl) (2*H*)phthalazin-1-one (1c)

White solid, yield based on two steps: 71 %, mp: 246-247 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6/TMS int, ppm) δ: 1.99 (t, 3H, 2'-CH_3), 3.32(q, 2H, 2'-CH_2), 6.73 (d, 1H, 2'-H), 6.77 (s, 1H, 5'-H), 7.10 (d, 1H, 6'-H), 7.27 (m, 1H, 5-H), 7.83 (m, 2H, 6-,7-H), 8.31(m, 1H, 8-H), 9.62 (s, 1H, O-*H*), 12.72 (s, 1H, N-*H*), Elemental Analysis (%) Found (Calcd.): C: 71.31(72.17), H: 5.08(5.30), N: 10.06(10.52)

4-(3'-isopropyl-4'-hydroxyphenyl) (2*H*)phthalazin-1-one (2d)

White solid, yield based on two steps: 82 %, mp: 281-282 ˚C. ^{1}H NMR (400 MHz, DMSO-d_6/TMS int, ppm) δ: 1.21 (d, 6H, -CH_3), 3.35(h, 1H, -C*H*(CH_3)), 6.93 (d, 1H, 5'-H), 7.21 (s, 1H, 6'-H), 7.30 (d, 1H, 2'-H), 7.73 (m, 1H, 5-H), 7.86 (m, 2H, 6-,7-H), 8.31(m, 1H, 8-H), 9.72 (s, 1H, O-*H*), 12.74 (s, 1H, N-*H*), Elemental Analysis (%) Found (Calcd.): C: 71.80(72.84), H: 5.33(5.75), N:8.71(9.99)

4-(3'-phenyl-4'-hydroxyphenyl) (2*H*)phthalazin-1-one (1e)

White solid, yield based on two steps: 85%, mp: 300-301˚C. ^{1}H NMR (400 MHz, DMSO-d_6/TMS int, ppm) δ: 7.11(d, 1H, Ar-H), 7.22-7.54(m, 6H, Ar-H), 7.62(d, 1H, Ar-H), 7.79-7.97(m. 3H, 5, 6, 7-H), 8.38(dd, 1H, 8-H), 8.82(s, 1H, O-*H*), 10.00(s, 1H, N-*H*), Elemental Analysis (%) Found (Calcd.): C: 75.37(76.42), H: 4.27(4.49), N: 7.97 (8.91)

4-(3'-5'-dimethyl-4'-hydroxyphenyl) (2*H*)phthalazin-1-one (1f)

White solid, yield based on two steps: 85%, mp: 280-281˚C. ^{1}H NMR (400 MHz, DMSO-d6/TMS int, ppm) δ: 2.25 (s, 6H, 3'-,5'-CH3), 7.14 (s, 2H, 2'-,6'-H), 7.76 (m, 1H, 5-H),7.88 (m, 2H, 6-,7-H), 8.32 (m, 1H, 8-H), 8.60 (s,1H, O-*H*), 12.72 (s, 1H, N-*H*), Elemental Analysis (%) Found (Calcd.): C: 71.35(72.17), H: 4.68(5.30), N: 9.76(10.52)

4-(2'-5'-dimethyl-4'-hydroxyphenyl) (2*H*)phthalazin-1-one (1g)

White solid, yield based on two steps: 82%, mp: 288-289˚C. ^{1}H NMR (400 MHz, DMSO-d_6/TMS int, ppm) δ: 1.96(s, 3H, 2'-CH_3), 2.14(s, 3H, 5'-CH_3), 6.78(s, 1H, 3'-H), 7.00(s, 1H, 6'-H), 7.29(m, 1H, 5-H), 7.86(m, 2H, 6, 7-H), 8.32(dd, 1H, 8-H), 9.51(s, 1H, O-*H*), 12.72(s, 1H, N-*H*), Elemental Analysis (%) Found (Calcd.): C: 71.43(72.17), H: 4.79(5.30), N: 9.65(10.52)

4-(4'-hydroxynaphthalenyl) (2*H*)phthalazin-1-one (1h)

White solid, yield based on two steps: 65%, mp: 302-303˚C. ^{1}H NMR (400 MHz, DMSO-d_6/TMS int, ppm) δ: 7.02(d, 1H, 3'-H), 7.15(d, 1H, 5-H), 7.41(m, 3H, 2', 7', 8'-H), 7.49(m, 1H, 6'-H), 7.75(t, 1H, 6-H), 7.84(t, 1H, 7-H), 8.26(d, 1H, 5'-H), 8.37(d, 1H, 8-H), 10.55(s, 1H, O-*H*), 12.85(s, 1H, N-*H*), Elemental Analysis (%) Found (Calcd.): C: 73.95(74.99), H: 3.58(4.20), N: 8.74(9.72)

General procedure for synthesis of polymer 2a-2h

A typical example of direct polycondensation of **FPOx** and monomer **1a** for polymer **2a** was shown as follows. A mixture of **FPOx** (0.402 g, 1.0 mmol), **1a** (0.238g, 1.0 mmol), an excess of anhydrous KF (4.0 mmol) and 5 mL of DMAc, was stirring at 25˚C overnight. The obtained polymer solution was slowly poured into methanol (100 mL) with constant stirring, producing fibrous precipitate. The resultant polymer **2a** was washed thoroughly with hot water and then dissolved with chloroform and precipitated in methanol. The precipitate was collected and purified by re-dissolving in chloroform and re-precipitating in methanol for 3 times to obtain the polymer, and then dried at 100 ^{o}C under vacuum overnight.

2a, Yield: 96%, ^{1}H NMR (400 MHz, $CDCl_3$/TMS int, ppm) δ: 7.08-8.00(m, 7H, Ar-*H*), 8.63(m, 1H, 8-H), ^{19}F NMR (400 MHz, $CDCl_3$, ppm) δ: -135.58, -142.00, -151.30, Elemental Analysis (%) Found (Calcd.): C: 54.98(56.01), H: 1.12(1.34), N: 8.55(9.33)

2b, Yield: 97%, ^{1}H NMR (400 MHz, $CDCl_3$/TMS int, ppm) δ: 2.67(s, 3H, C*H*$_3$), 8.61(m, 1H, 8-H), 7.90-8.04(m, 3H, 5, 6, 7-H), 7.57(s, 1H, 2'-H), 7.41(d, 1H, 5'-H), 6.84(d, 1H, 6'-H), ^{19}F NMR (400 MHz, $CDCl_3$, ppm) δ: -135.66, -142.20, -152.46, Elemental Analysis (%) Found (Calcd.): C: 55.75(56.69), H: 1.33(1.64), N: 8.74(9.12)

2c, yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$/TMS int, ppm) δ: 1.40(t, 3H, C*H*$_3$), 2.90(q, 2H, C*H*$_2$), 6.80(d, 1H, 5'-H), 7.42(d, 1H, 6'-H), 7.58(s, 1H, 2'-H), 7.75-7.91(m, 3H, 5, 6, 7-H), 8.53(m, 1H, 8-H), ^{19}F NMR (400 MHz, $CDCl_3$,ppm) δ: -135.77, -142.20, -152.28, Elemental Analysis (%) Found (Calcd.): C: 56.29(57.34), H: 1.09(1.92), N: 7.54(8.92)

2d, yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$/TMS int, ppm) δ: 1.37(d, 6H, C*H*$_3$), 3.58(h, 1H, C*H*(CH_3)), 6.85(d, 1H, 5'-H), 7.42(d,1H, 6'-H), 7.62(s, 1H, 2'-H), 7.81-7.91(m, 3H, 5, 6, 7-H), 8.65(m, 1H, 8-H), ^{19}F NMR (400 MHz, $CDCl_3$, ppm) δ: -135.77, -142.17, -151.91, Elemental Analysis (%) Found (Calcd.): C: 56.91(57.95), H: 1.79(2.20), N: 7.74(8.72)

2e, yield: 96%. ^{1}H NMR (400 MHz, $CDCl_3$/TMS int, ppm) δ: 6.10-8.10(m, 11H, Ar-*H*), 8.60(m, 1H, 8-H), ^{19}F NMR (400 MHz, $CDCl_3$, ppm) δ: -135.87, -142.10, -152.25, Elemental Analysis (%) Found (Calcd.): C: 59.45(60.37), H:1.08 (1.79), N: 7.15(8.28)

2f, yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$/TMS int, ppm) δ: 2.35(s, 6H, C*H*$_3$), 7.48(s, 2H, 2'-6'-H), 7.92-8.10(m, 3H, 5, 6, 7-H), 8.61(m, 1H, 8-H), ^{19}F NMR (400 MHz, $CDCl_3$, ppm) δ: -135.95, -142.21, -156.79, Elemental Analysis (%) Found (Calcd.): C: 56.28(57.34), H:

1.21(1.92), N: 7.89(8.92)

2g, yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$/TMS int, ppm) δ: 2.16(s, 3H, C*H*$_3$), 2.46(s, 1H, C*H*$_3$), 6.91(s, 1H, 3'-H), 7.31(s, 1H, 5'-H), 7.45(m, 1H, 5-H), 7.91(m, 2H, 6, 7-H), 8.88(m, 1H, 8-H), ^{19}F NMR (400 MHz, $CDCl_3$, ppm) δ: -135.90, -141.60, -143.08, -152.23, Elemental Analysis (%) Found (Calcd.): C: 56.25(57.34), H: 1.10(1.92), N: 7.87(8.92)

2h, yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$/TMS int, ppm) δ: 6.85-7.89(m, 8H, Ar-H), 8.61(m, 1H, 7-H), 9.13(m, 1H, 8-H), ^{19}F NMR (400 MHz, $CDCl_3$, ppm) δ: -135.43, -141.86, -142.46, -151.65, Elemental Analysis (%) Found (Calcd.): C: 58.21(59.09), H: 1.04(1.55), N: 7.59(8.61)

Measurements

FTIR was recorded with KBr pellets on Nicolet Nexus 670 FTIR spectrometer. ^{1}1H and ^{19}F NMR spectra were recorded on Bruker AM-300 spectrometer instrument at room temperature using tetramethylsilane (TMS) and CF_3Cl as internal references, respectively. and dimethyl sulfoxide-d6 (DMSO-d_6) or chloroform ($CDCl_3$) as solvent. DSC and TGA were performed on a TA Instrument Q100. Elemental analysis was carried out on a EURO EA3000 system. Inherent viscosities of **2a-2h** were measured in $CHCl_3$ at 0.5g/dL concentration with an Ubbelohde viscometer at 30˚C. Gel permeation chromatograms (GPC) using polystyrene as a standard were obtained on a Waters 1515 instrument with tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min.

Dielectric properties were acquired using an Agilent LCR meter (E4980A) with 1.0 V bias. Temperature and frequency dependent of dielectric properties were measured using a Hewlett Packard 4284A LCR meter in conjunction with a Delta Design oven model 2300. Dielectric breakdown strength measurements were performed using the electrostatic pull-down method, with a 500 V/s ramp. A ball-shape upper contact to the sample electrode was used to avoid any mechanical damage from needle-shape contact. The voltage power supply from Trek has a maximum output of 30 KV. To avoid air breakdown, the samples were immersed in silicone oil during the test.

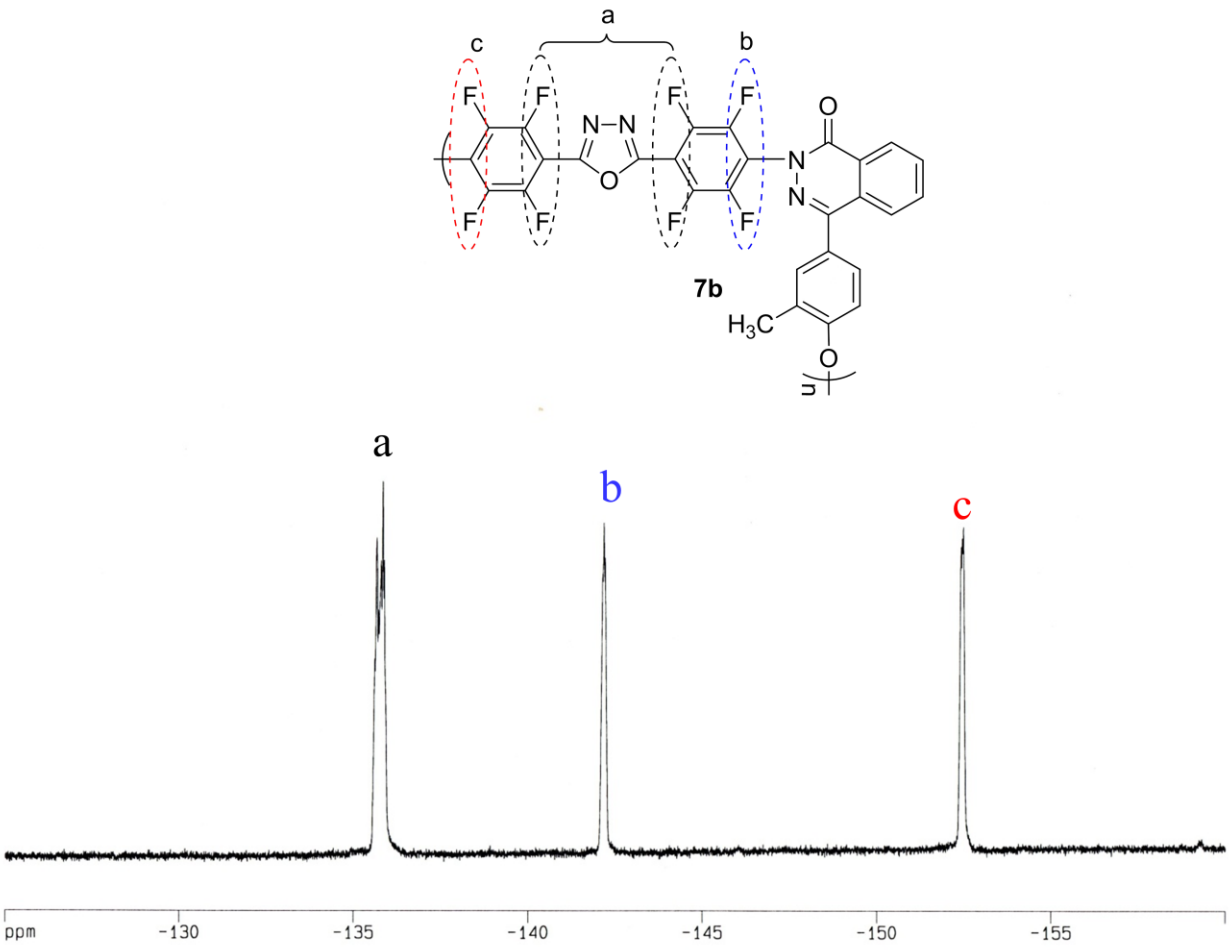


Figure S1. ^{19}F NMR spectrum of polymer **2b**.

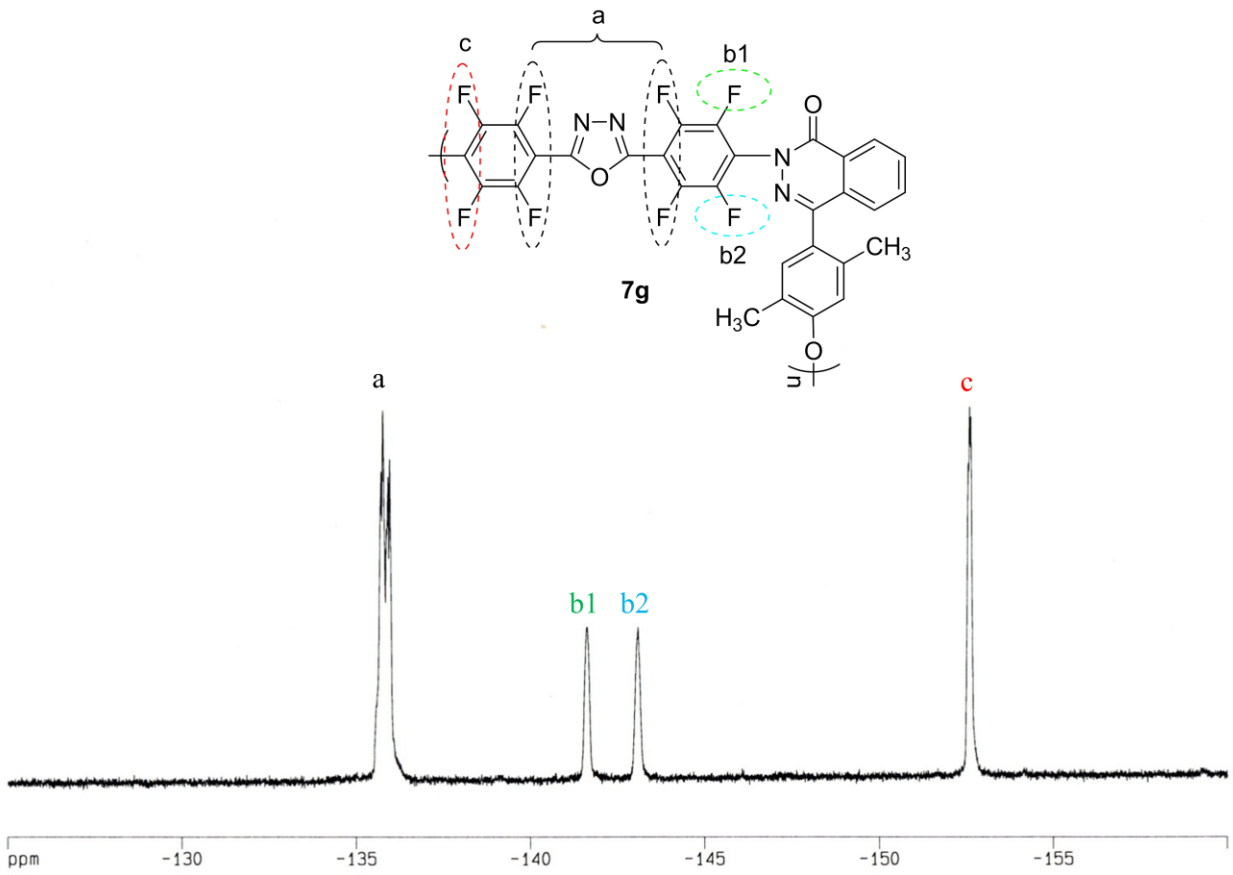


Figure S2. ^{19}F NMR spectrum of polymer **2g**.

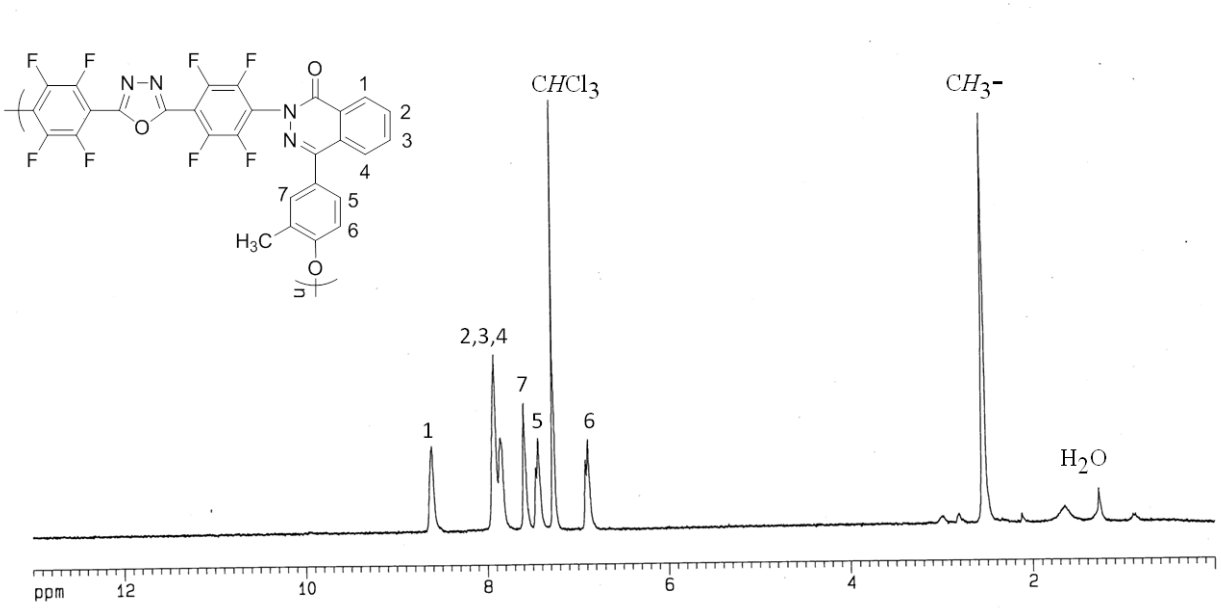


Figure S3. ^{1}H NMR spectrum of polymer **2b**.

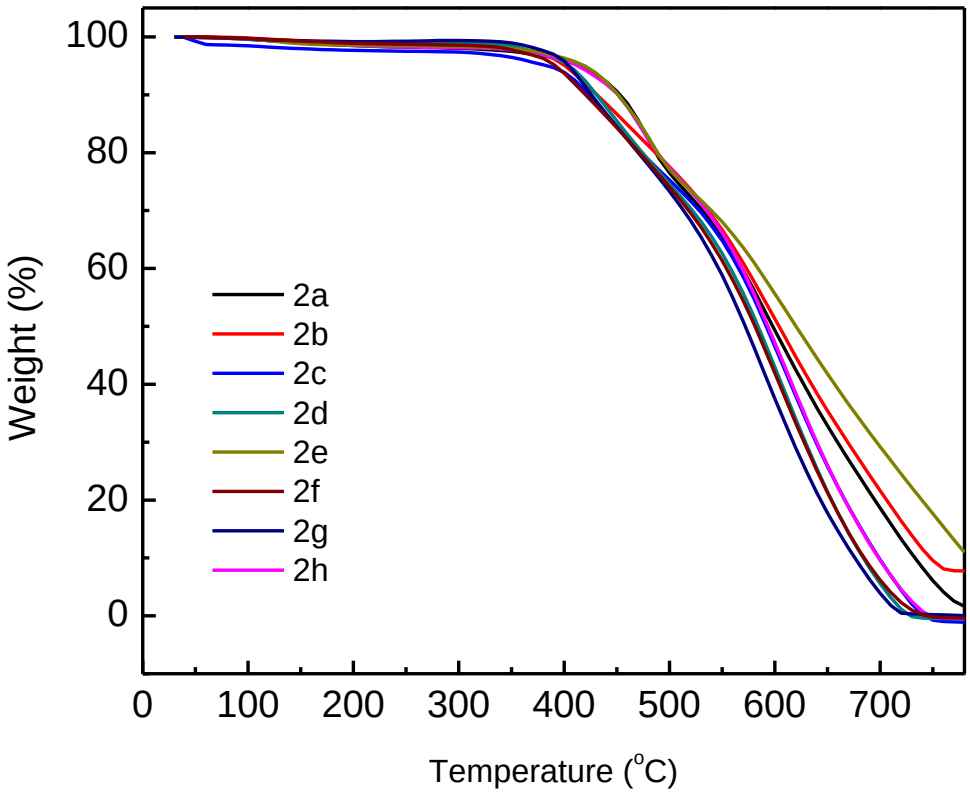
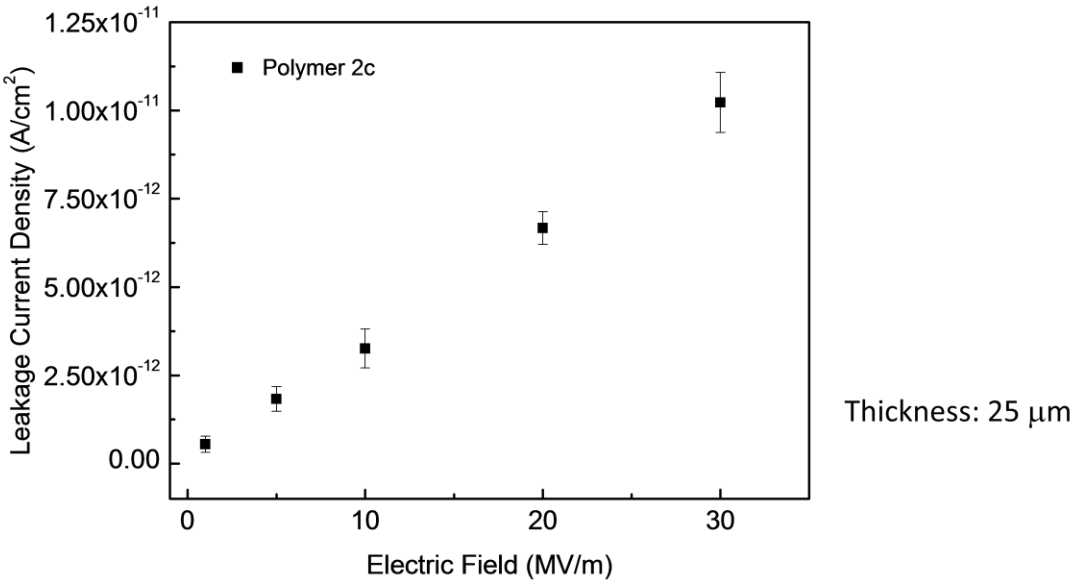


Figure S4. TGA curves of the polymers.



Voltage (V)	25	125	250	500	750
Leakage Current Density (10^{-13} A/cm^2)	5.5±2.3	18.3±3.5	32.6±5.5	66.7±4.6	102.3±8.5

Figure S5. Leakage current density of polymer **2c** at different fields.

Table S1. Molecular weights, intrinsic viscosities and thermal properties of the polymers.

Polymer	η_{inh} (dL/g)	M_n (10^4)	M_w/M_n	T_g (°C)	T_d (°C)
2a	0.69	3.2	1.95	306	452
2b	0.34	2.8	1.83	302	431
2c	0.41	2.9	1.71	314	423
2d	0.80	7.8	1.34	274	431
2e	0.53	1.2	1.53	271	451
2f	0.55	1.4	1.85	319	420
2g	0.79	3.4	2.04	288	426
2h	0.57	1.4	1.46	296	451

Table S2. Dielectric permittivity of the polymers.

Polymer	ε' (@1KHz)
2a	2.74
2b	3.19
2c	3.08
2d	3.09
2e	3.17
2f	2.97
2g	3.15
2h	3.04