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Supporting information for:

Flexible polyolefin dielectric by strategic design of organic modules for harsh condition electrification

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Section 1. Material synthesis

1.1 Monomer Synthesis-

General Synthesis Procedure -

Two-neck round-bottomed flask (500 mL), equipped with a magnetic stirring bar, was flame-dried and purged with argon gas. The flask was charged with exo-3,6-Epoxy-1,2,3,6-tetrahydrophthalic anhydride [1] (1.0 equivalent), and anhydrous toluene (0.5M based on mole of the limiting reagent) was added to the flask via cannula. To the white suspension mixture, aniline derivative [2] (1.5 equivalent) was added dropwise via syringe. The white suspension was dissolved entirely and turned into a clear colorless solution after completion of aniline derivative addition. Then, the mixture was stirred at 50 °C for 6 hours. The reaction mixture formed a white precipitate and cooled to room temperature. The white solid was filtered and washed with pentane or hexane to remove the excess aniline and give a white powder, amic acid [3]. The product was used for the next step without further purification.

Amic acid (1.0 equivalent) and anhydrous sodium acetate (0.5 equivalent) were placed in a single neck round bottom flask with a magnetic stirring bar. Acetic anhydride (1.0 M based on the mole of the amic acid) was added to the flask and stirred at 70 °C for 8 hours. The reaction mixture turned dark brown solution. The mixture cooled down to room temperature and poured to a conical flask contains ice and magnetic stirrer. The flask placed in ice bath and stirred for 30 minutes. An off-white solid crashed out the dark brown solution and filtered under vacuum. The solid was washed with plenty of water and recrystallized in ethanol/hexane mixture (5:95%) to give a white crystal product, ONBA-N(Ar) [4].

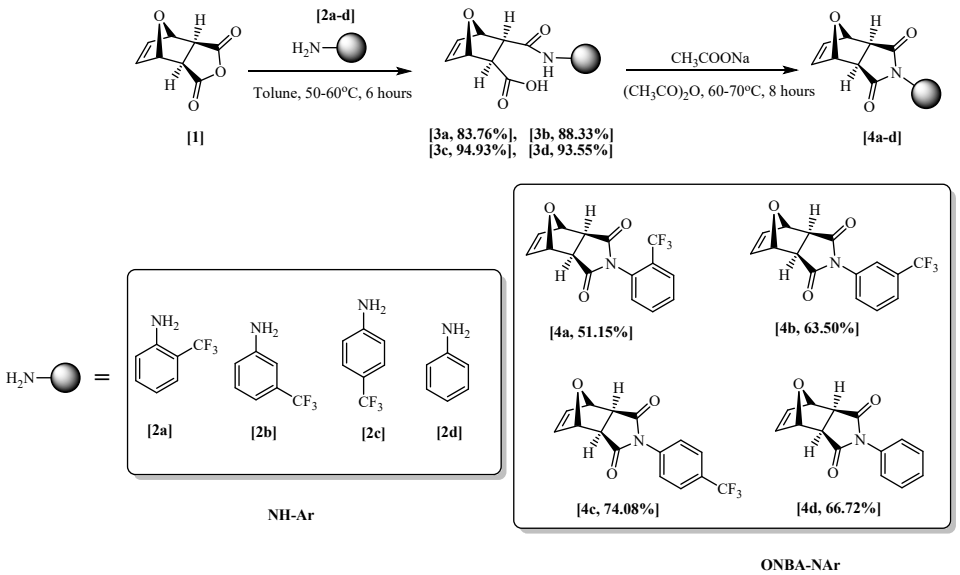
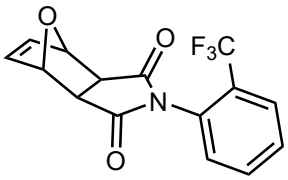


Figure S1. Schematic of Monomer Synthesis

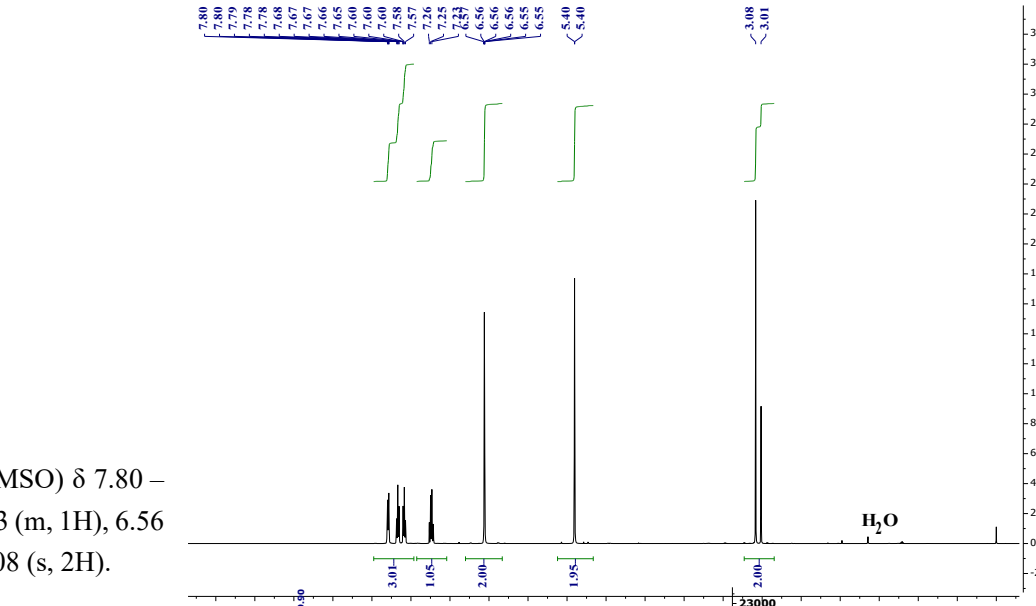
Compound [4a]: ONBA-NPh(o-CF3)

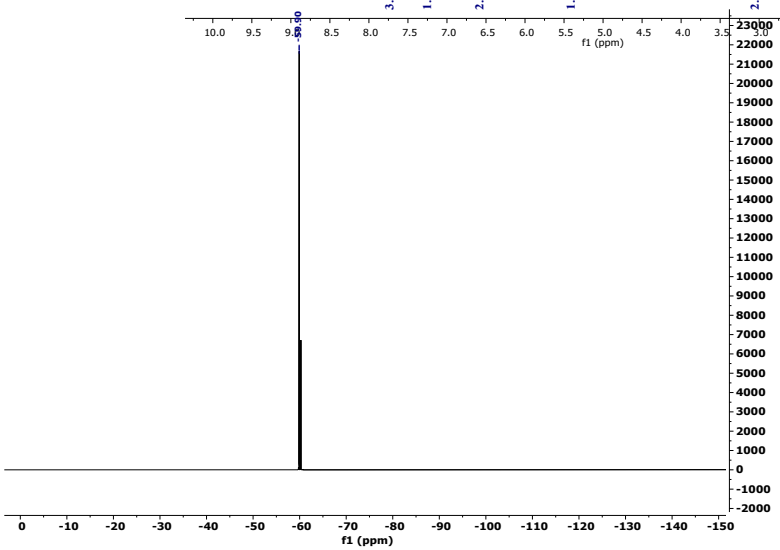
Exo-3,6-Epoxy-1,2,3,6-tetrahydrophthalic anhydride [1] (10.00 g, 60.19 mmol), 2-(Trifluoromethyl)aniline [2a] (14.55 g, 11.35 mL, and 90.29 mmol) reacted in anhydrous toluene (120 mL) to form a white solid product, amic acid [3a] (16.50 g, 83.76%). This product used for the next step without purification. The obtained amic acid (12.00 g, 36.67 mmol) was imidized in acetic anhydride (35 mL) in the presence of anhydrous sodium acetate (1.50 g, 18.33 mmol) and purified according to method described in the general synthesis procedure section of monomer synthesis to give a white crystal product, ONBA-NPh(o-CF3) [4a] (5.8 g, 51.15%).

o-OFNB Monomer NMR $CDCl_3$-



^{1}H NMR (500 MHz, DMSO) δ 7.80 – 7.57 (m, 3H), 7.26 – 7.23 (m, 1H), 6.56 (s, 2H), 5.40 (s, 2H), 3.08 (s, 2H).





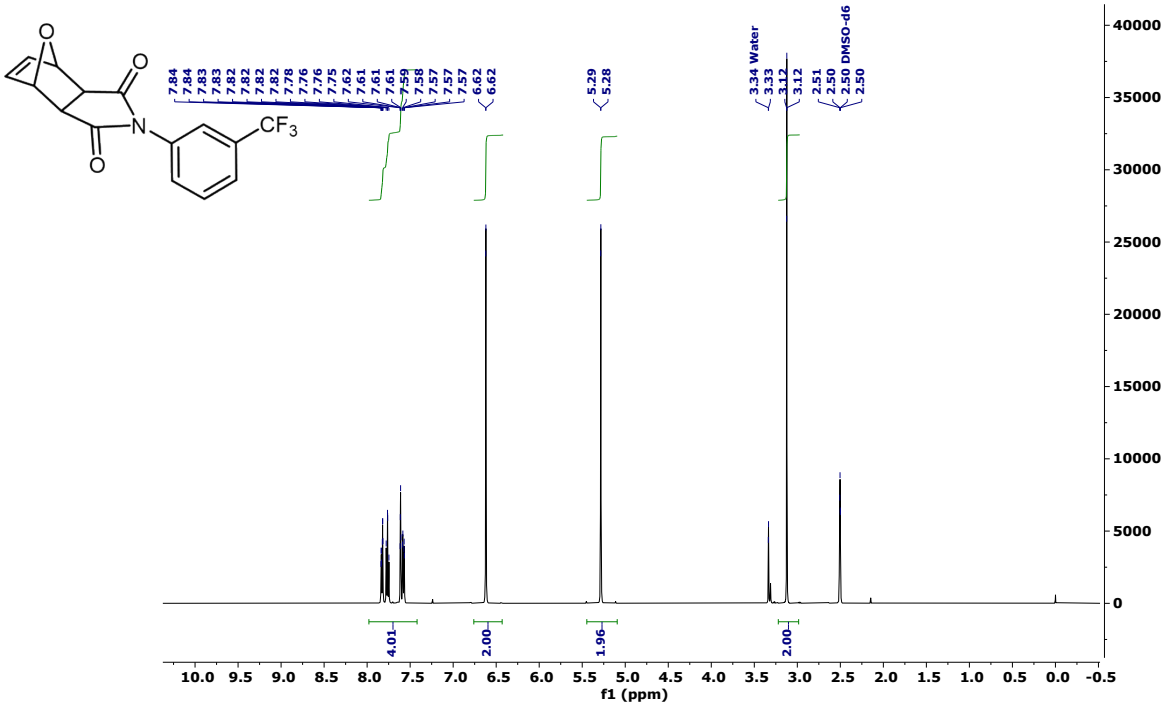
^{19}F NMR (500 MHz, DMSO, ppm): δ = -59.90 (s, 3F)

Figure S2. a, ^{1}H and b, ^{19}F NMR of *o*-OFNB monomer

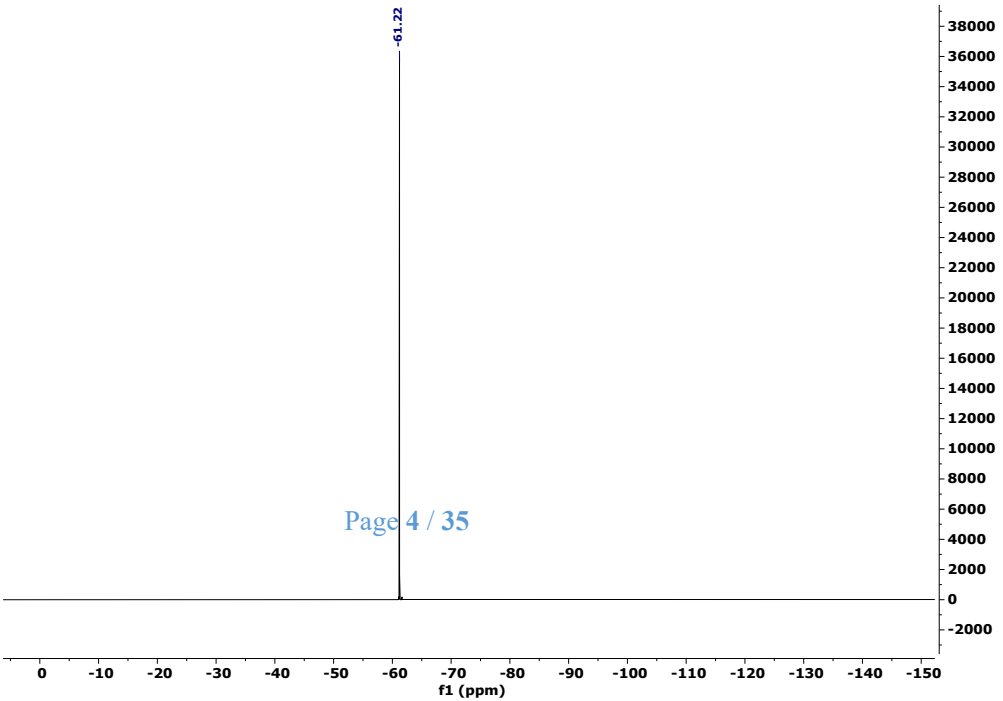
Compound [4b]: ONBA-NPh(m-CF3)

Exo-3,6-Epoxy-1,2,3,6-tetrahydrophthalic anhydride [1] (10.00 g, 60.19 mmol), 3-(Trifluoromethyl)aniline [2b] (14.55 g, 11.28 mL, and 90.29 mmol) reacted in anhydrous toluene (120 mL) to form an white solid product, amic acid [3b] (17.40 g, 88.33%). This product used for the next step without purification. The obtained amic acid (12.00 g, 36.67 mmol) was imidized in acetic anhydride (35 mL) in the presence of anhydrous sodium acetate (1.50 g, 18.33 mmol) and purified according to method described in the general synthesis procedure section to give a white crystal product, ONBA-NPh(m-CF3)[4b] (7.2 g, 63.50%).

m-OFNB NMR DMSO-



^{1}H NMR (500 MHz, DMSO) δ 7.84 – 7.57 (m, 4H), 6.62 (s, 2H), 5.28 (s, 2H), 3.12 (s, 2H).



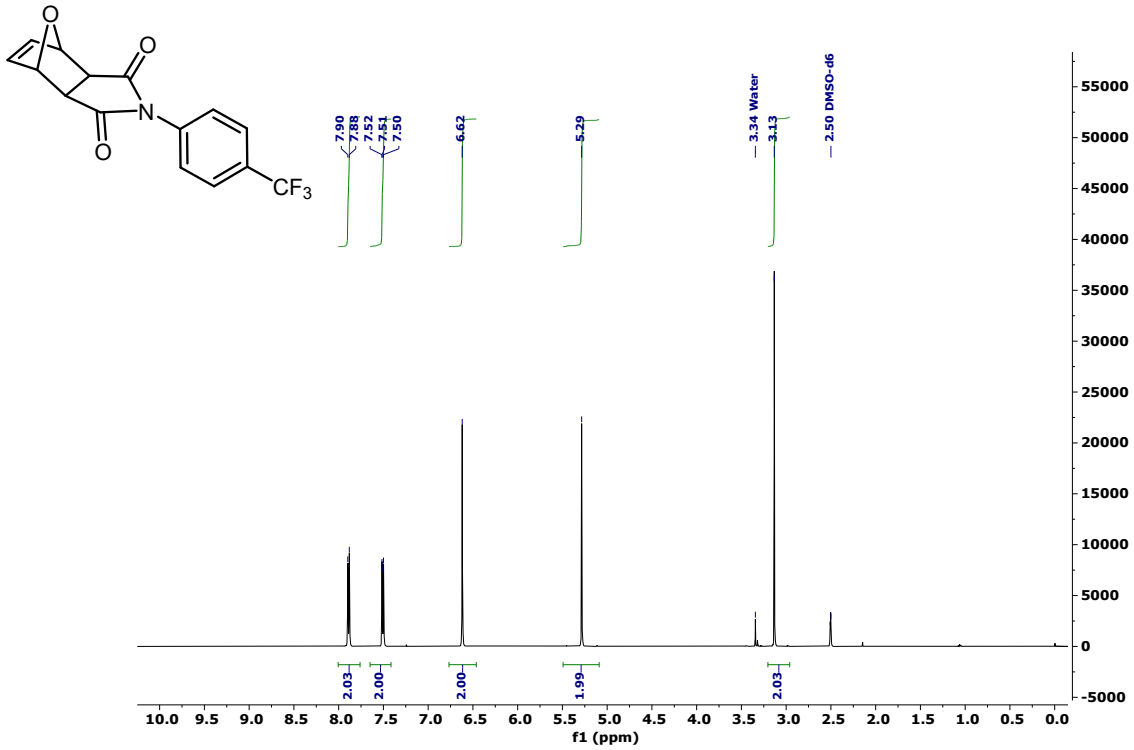
^{19}F NMR (500 MHz, DMSO, ppm): δ = -61.22 (s, 3F)

Figure S3. a, ^{1}H and b, ^{19}F NMR of *m*-OFNB monomer

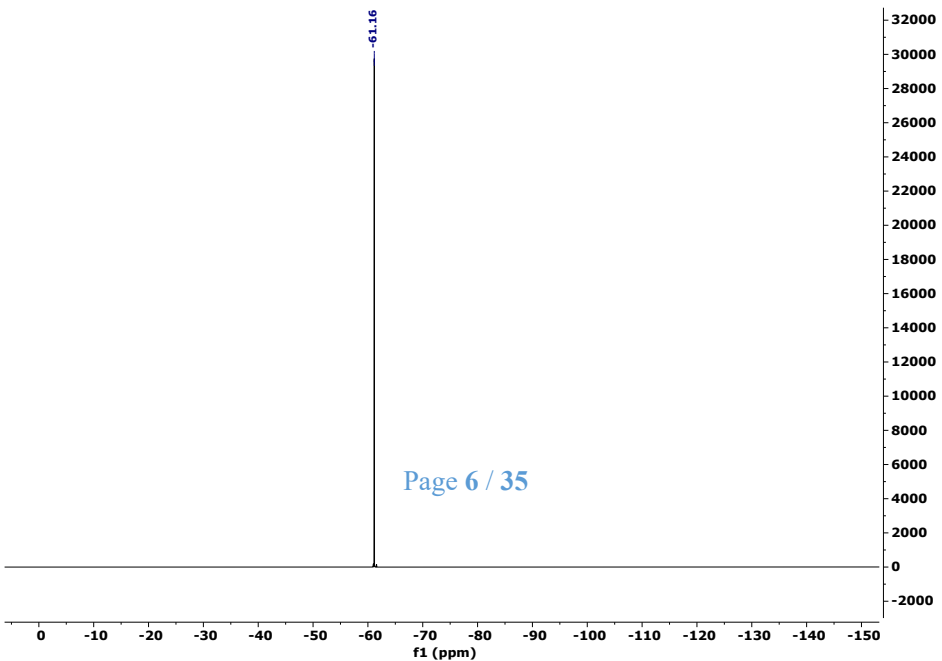
Compound [4c]: ONBA-NPh(p-CF3)

Exo-3,6-Epoxy-1,2,3,6-tetrahydrophthalic anhydride [1] (10.00 g, 60.19 mmol), 4-(Trifluoromethyl)aniline [2c] (14.55 g, 11.34 mL, and 90.29 mmol) reacted in anhydrous toluene (120 mL) to form an white solid product, amic acid [3c] (18.70 g, 94.93%). This product used for the next step without purification. The obtained amic acid (12.00 g, 36.67 mmol) was imidized in acetic anhydride (35 mL) in the presence of anhydrous sodium acetate (1.50 g, 18.33 mmol) and purified according to method described in the general synthesis procedure section to give a white crystal product, ONBA-NPh(p-CF3)[4c] (8.4 g, 74.08%).

p-POFNB NMR DMSO-



^{1}H NMR (500 MHz, DMSO) δ 7.89 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.8 Hz, 2H), 6.62 (s, 2H), 5.29 (s, 2H), 3.13 (s, 2H).



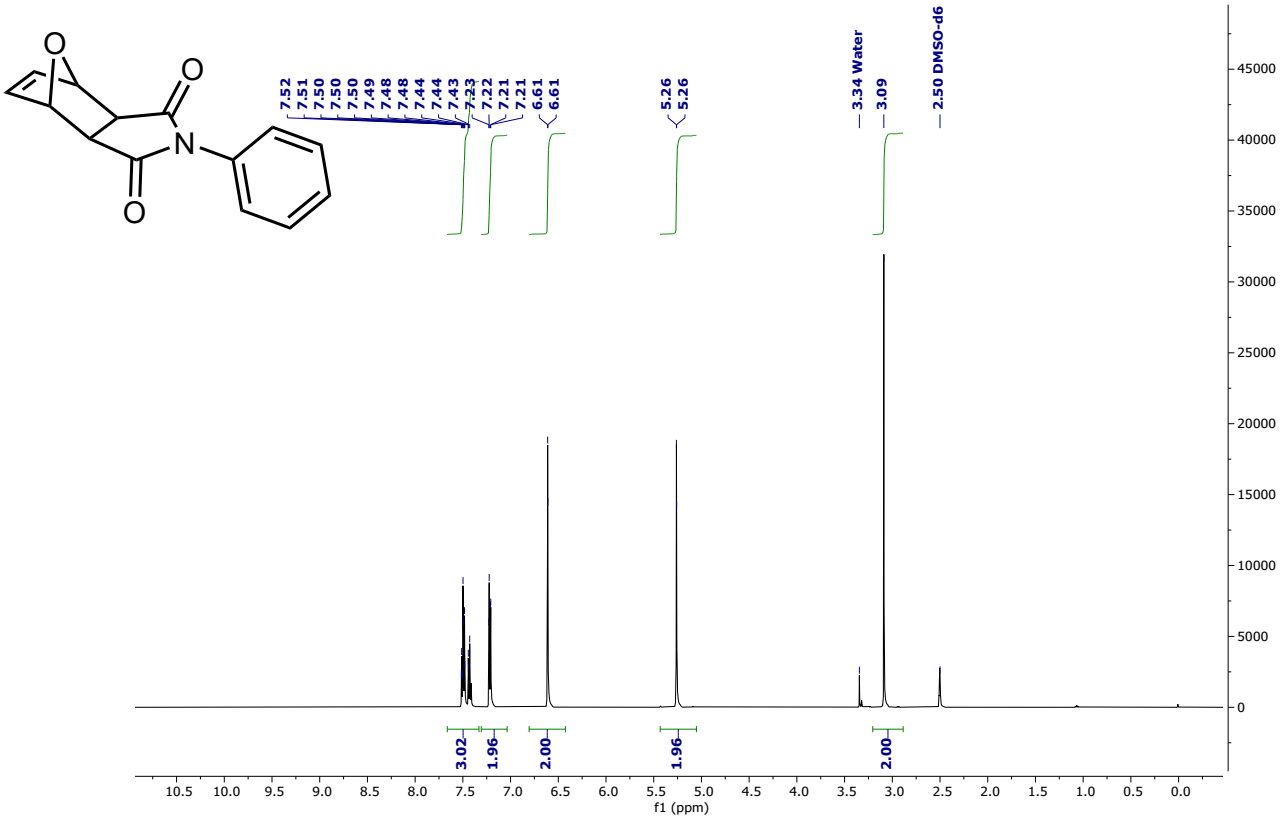
^{19}F NMR (500 MHz, DMSO, ppm): δ = -61.16 (s, 3F)

Figure S4. a, ^{1}H and b, ^{19}F NMR of *p*-OFNB monomer

Compound [4d]: ONBA-NPh

Exo-3,6-Epoxy-1,2,3,6-tetrahydrophthalic anhydride [1] (10.00 g, 60.19 mmol), aniline [2d] (8.41 g, 8.23 mL, and 90.29 mmol) reacted in anhydrous toluene (120 mL) to form a white solid product, amic acid [3d] (14.60 g, 93.55%). This product used for the next step without purification. The obtained amic acid (12.00 g, 46.29 mmol) was imidized in acetic anhydride (45.0 mL) and purified according to method described in the general synthesis procedure section in the presence of anhydrous sodium acetate (1.90 g, 23.14 mmol) to give a white crystal product,

ONB Monomer – DMSO-



ONBA-NPh [4a] (7.45 g, 66.72%). ^{1}H NMR (500 MHz, DMSO) δ 7.52 – 7.21 (m, 5H), 6.61 (s, 2H), 5.26 (s, 2H), 3.09 (s, 2H).

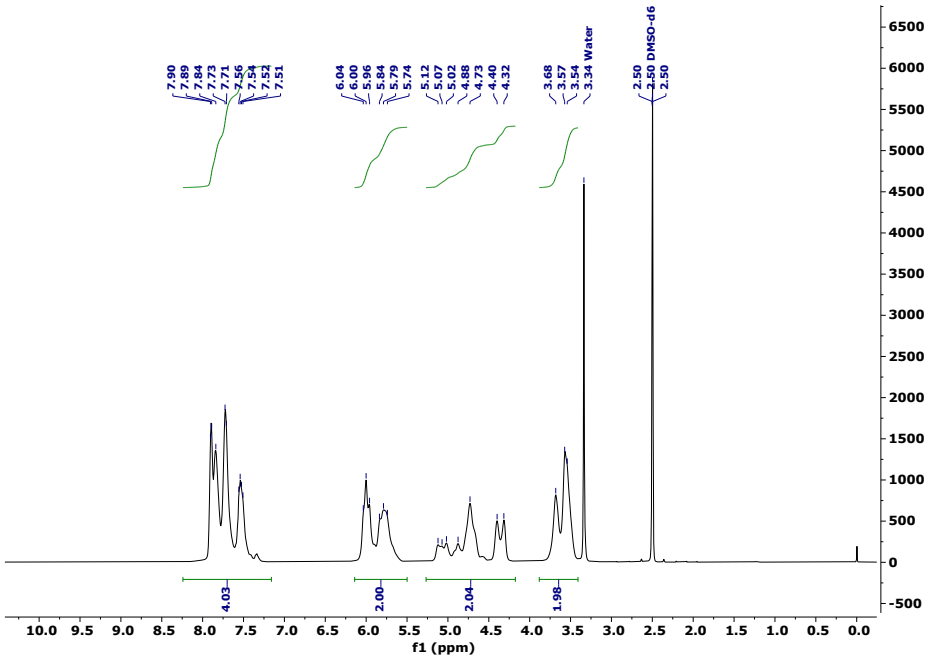
Figure S5. a, ^{1}H NMR of ONB monomer

1.2 Polymer synthesis

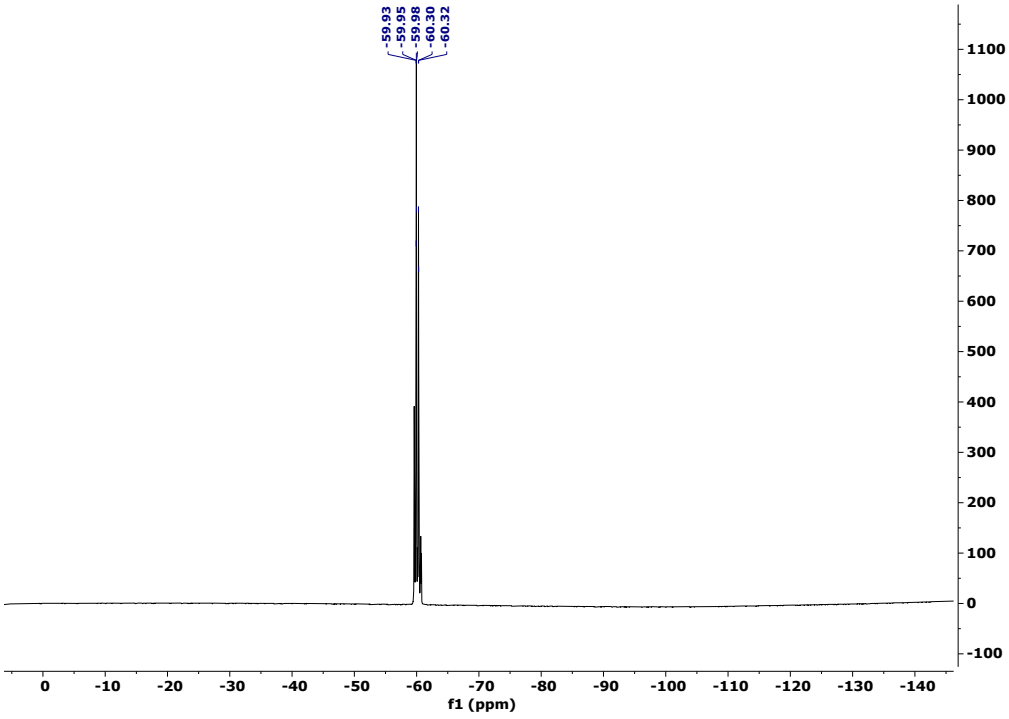
Polymers were synthesized by ring opening metathesis polymerization technique using Grubbs generation 2 catalyst in a clean and flame dried round bottom flask. For example, for synthesis of *o*-POFNB polymer, 2.5 g *o*-OFNB monomer was dissolved in around 25 ml of dichloromethane (DCM) in a round bottom flask under argon atmosphere. To this monomer solution, 0.028 g of Grubbs generation 2 catalyst dissolved in 5 ml of DCM was added in a one shot. Then the reaction is allowed to continue for 2 hours. After 2 hours, reaction was terminated using excess of ethyl vinyl ether. Then polymer is obtained by precipitating the polymer solution in excess of methanol. The obtained polymer is again dissolved in tetrahydrofuran (THF) and precipitated back in excess methanol. Polymer is then filtered to separate it from solvent and dried under vacuum at 60 – 70 °C for 48 hours. The dried and purified polymers then characterized using NMR analysis.

Similarly, *m*-POFNB, *p*-POFNB and PONB polymers were synthesized using same monomer to catalyst ratio. Polymers were synthesized using respective monomers. For PONB, polymer was dissolved in chloroform instead of THF for second precipitation as PONB polymer is not soluble in THF. The details of the NMR spectra of each polymer are given below.

o-POFNB NMR in DMSO



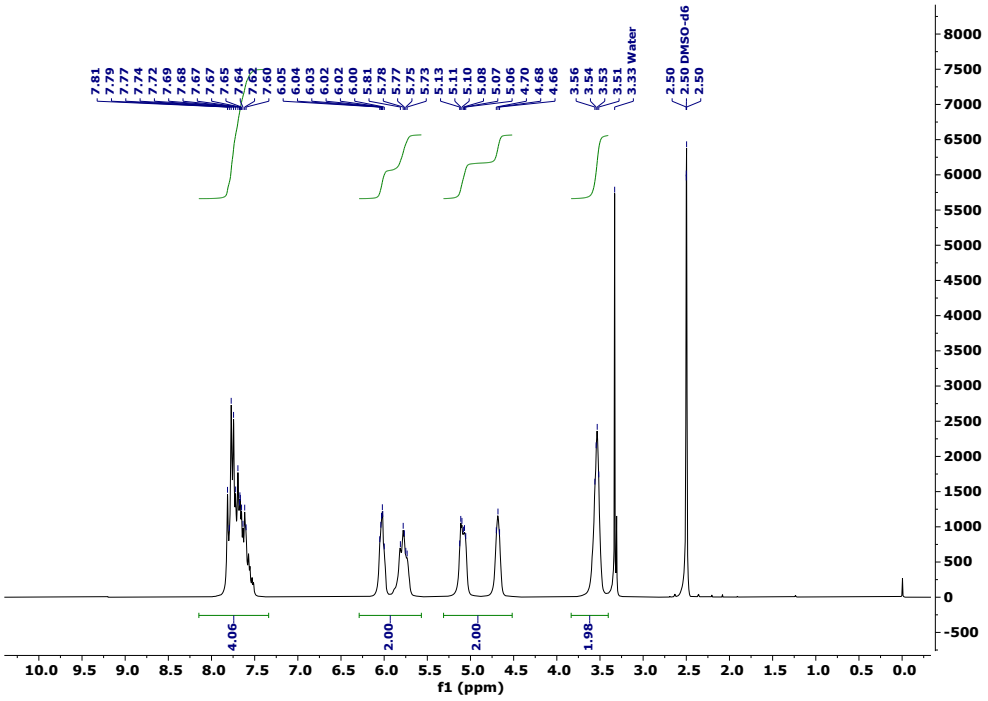
^{1}H NMR (500 MHz, DMSO, ppm): δ = 7.90 – 7.51 (m, 4H), δ = 6.04 – 5.96 (m, 2H, trans), δ = 5.84 – 5.74 (m, 2H, cis), δ = 5.12 - 4.32 (m, 2H), δ = 3.68 – 3.54 (m, 2H)



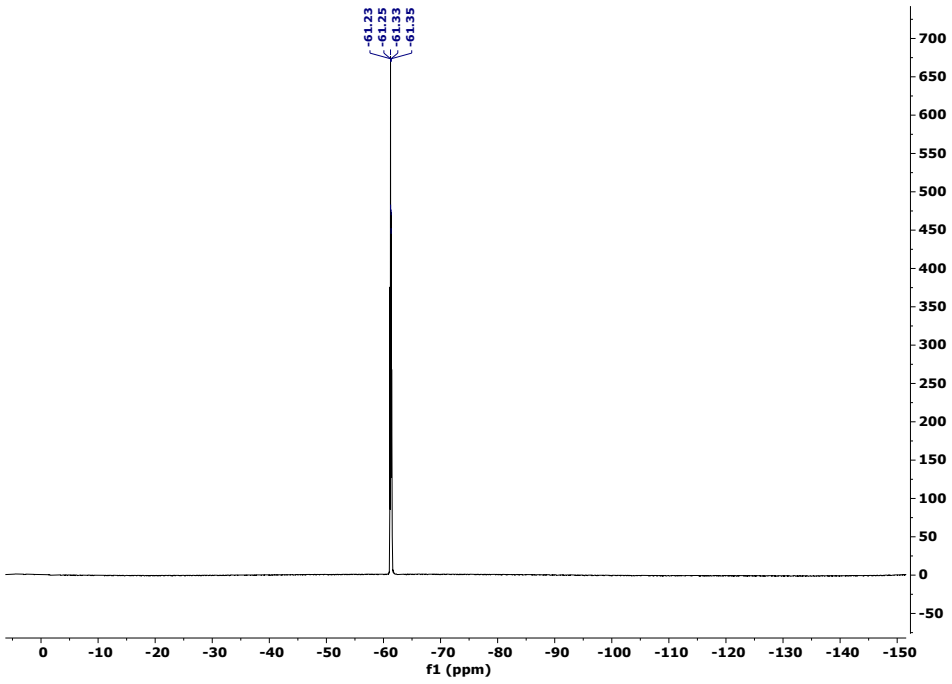
^{19}F NMR (500 MHz, DMSO, ppm): δ = -59.93 – -60.32 (m, 3F)

Figure S6. a, ^{1}H and b, ^{19}F NMR of *o*-POFNB Polymer

m-POFNB in DMSO



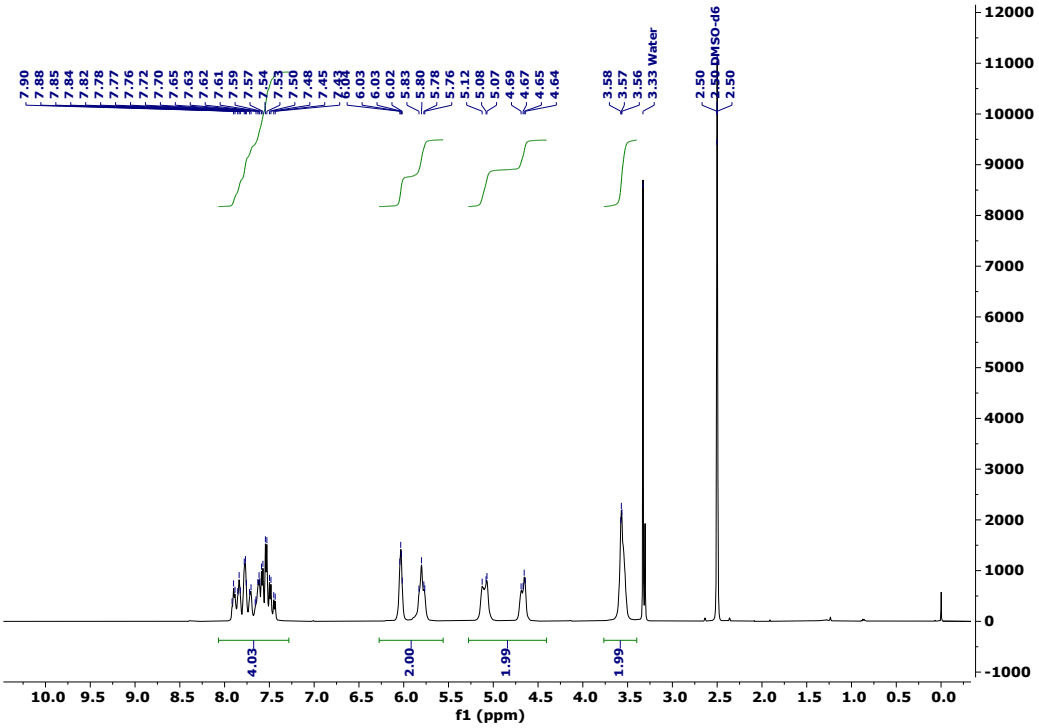
^{1}H NMR (500 MHz, DMSO, ppm): δ = 7.81 – 7.60 (m, 4H), δ = 6.05 – 5.81 (m, 2H, trans), δ = 5.78 – 5.73 (m, 2H, cis), δ = 5.13 - 4.66 (m, 2H), δ = 3.56 – 3.51 (m, 2H)



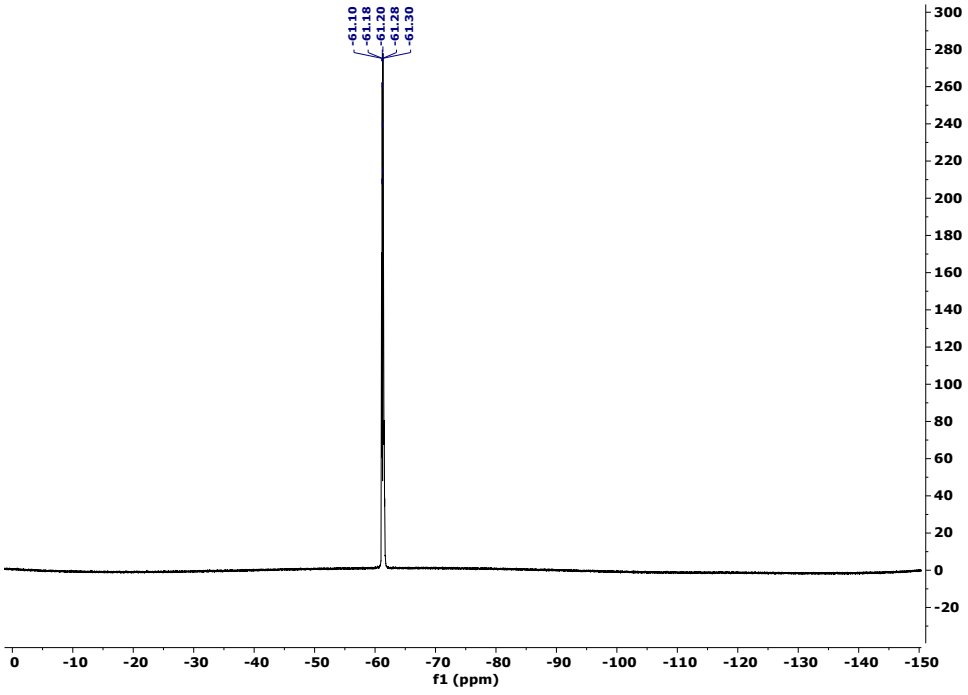
^{19}F NMR (500 MHz, DMSO, ppm): δ = -61.23 – -61.35 (m, 3F)

Figure S7. a, ^{1}H and b, ^{19}F NMR of *m*-POFNB Polymer

p-POFNB in DMSO



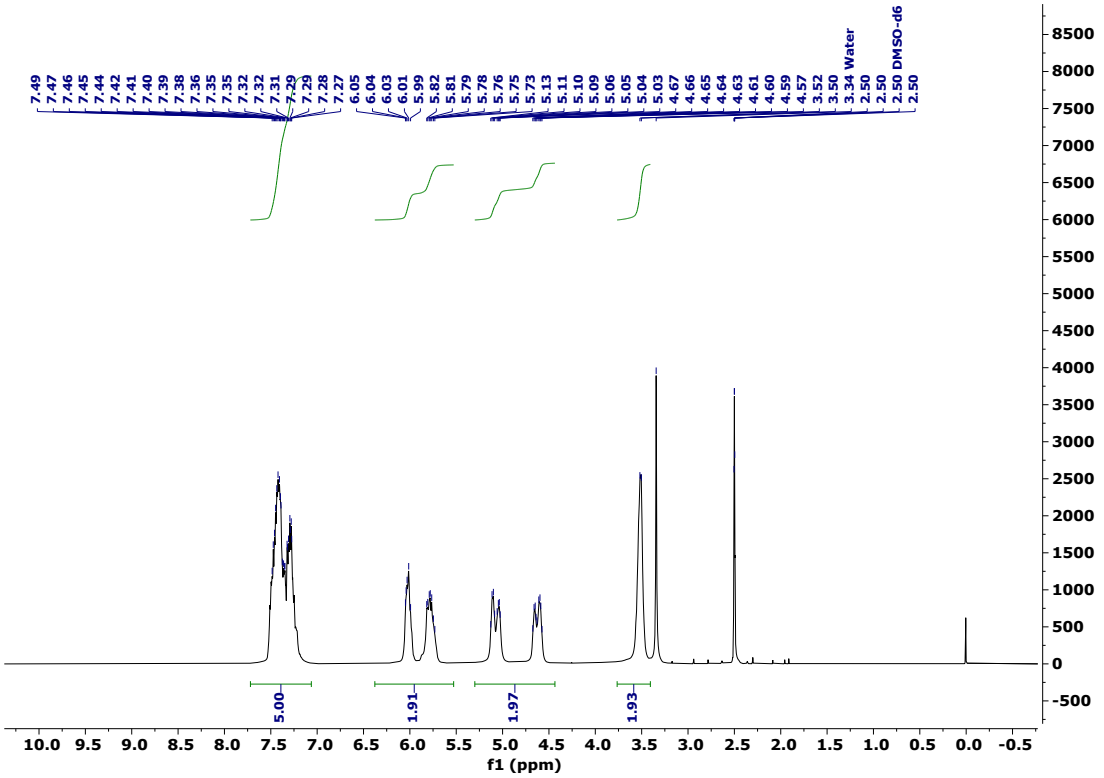
^{1}H NMR (500 MHz, DMSO, ppm): δ = 7.90 – 7.43 (m, 4H), δ = 6.04 – 6.02 (m, 2H, trans), δ = 5.83 – 5.76 (m, 2H, cis), δ = 5.12 – 4.64 (m, 2H), δ = 3.58 – 3.56 (m, 2H)



^{19}F NMR (500 MHz, DMSO, ppm): δ = -61.10 – -61.30 (m, 3F)

Figure S8. a, ^{1}H and b, ^{19}F NMR of *p*-POFNB Polymer

PONB NMR in DMSO



^{1}H NMR (500 MHz, DMSO, ppm): δ = 7.49 – 7.27 (m, 4H), δ = 6.05 – 5.99 (m, 2H, trans), δ = 5.82 – 5.73 (m, 2H, cis), δ = 5.13 – 4.57 (m, 2H), δ = 3.52 – 3.50 (d, 2H)

Figure S9. a, ^{1}H NMR of PONB Polymer

1.3 Polymer Film Processing-

For measurement of polymer dielectric properties, polymers were processed into flexible free standing films using solution casting method. For film processing, polymers were dissolved in anhydrous THF at 8 – 10 % concentration. This solution is then used to make film on a glass plate using blade applicator at room temperature. Film is then allowed to dry for overnight on the glass plate at 25 °C. After overnight drying, film is removed from the glass plate using DI water to give free standing film. This free-standing film is then dried under vacuum at 60 – 70 °C for 48 hours. The obtained free-standing flexible polymer films have thickness around 10 – 12 microns. The digital and SEM images of the *o*-POFNB film were shown in Figure S10.

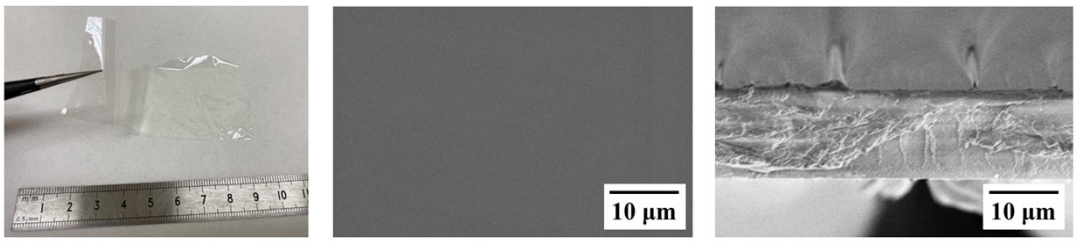


Figure S10. (a) Photograph of the flexible freestanding *o*-POFNB film. SEM images of (b)

surface and (c) cross section of the o-POFNB film.

Section 2. Characterization

2.1 Gel Permeation Chromatography

The molecular weight for synthesized polymers is obtained using gel permeation chromatography (GPC). The GPC characterization was done using Waters GPC with dimethylacetamide (DMAc) as a mobile phase and polystyrene as a standard with refractive index (RI) detector. The molecular weight results obtained are as shown below-

Polymer	Number Average Molecular Weight (M_n)	Weight Average Molecular Weight (M_w)
o-POFNB	122,210 Da	219,760 Da
m-POFNB	158,210 Da	299,950 Da
p-POFNB	182,960 Da	434,680 Da

Table S1. Molecular weight determination of synthesized polymers

2.2 Differential Scanning calorimetry

The glass transition temperatures of polymers were determined using differential scanning calorimeter. For determination of T_g, polymer samples were heated and cooled down at 10 °C/ min. Heating-Cooling-Heating cycle was used and T_g was obtained from the third heating cycle.

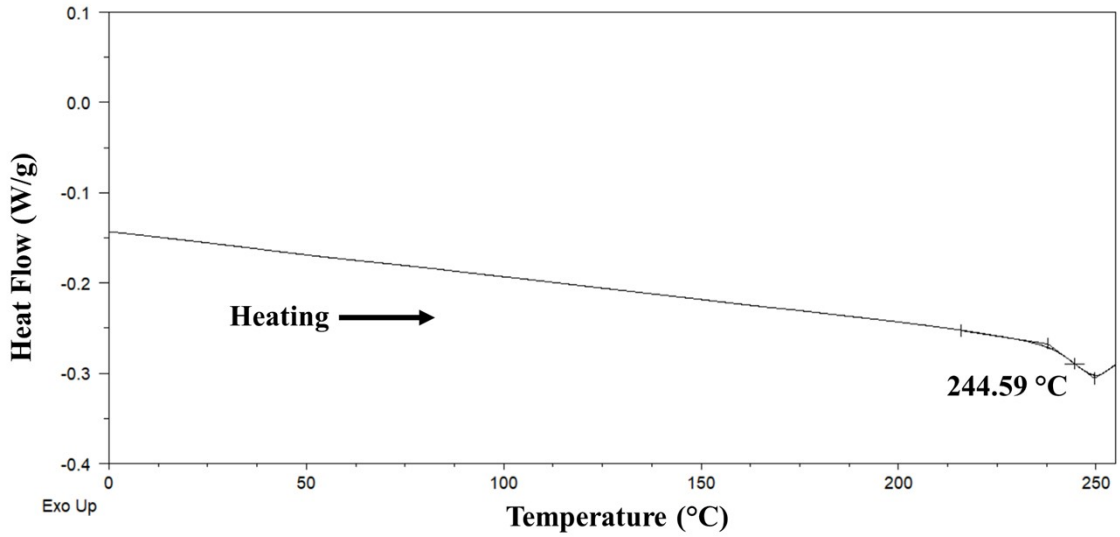


Figure S11. Differential Scanning Calorimetry of *o*-POFNB

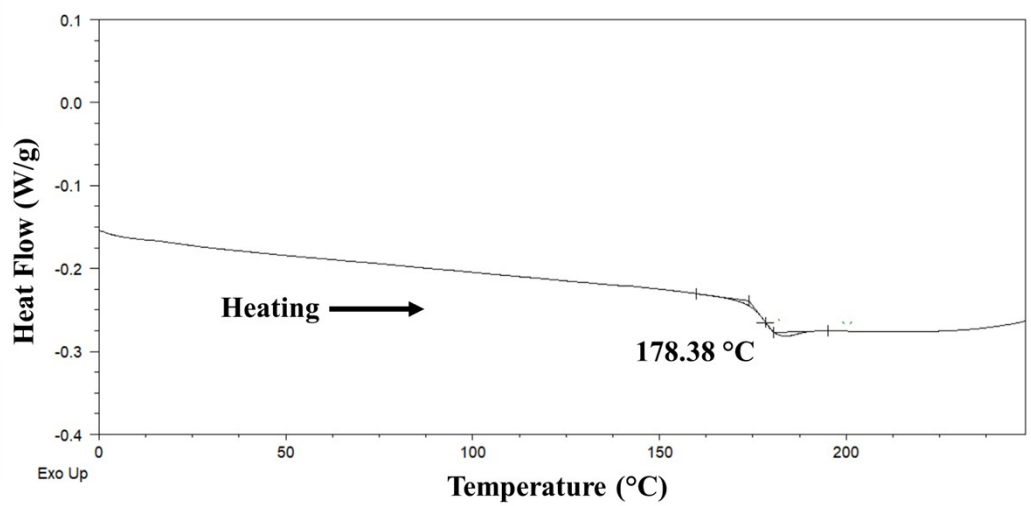


Figure S12. Differential Scanning Calorimetry of *m*-POFNB

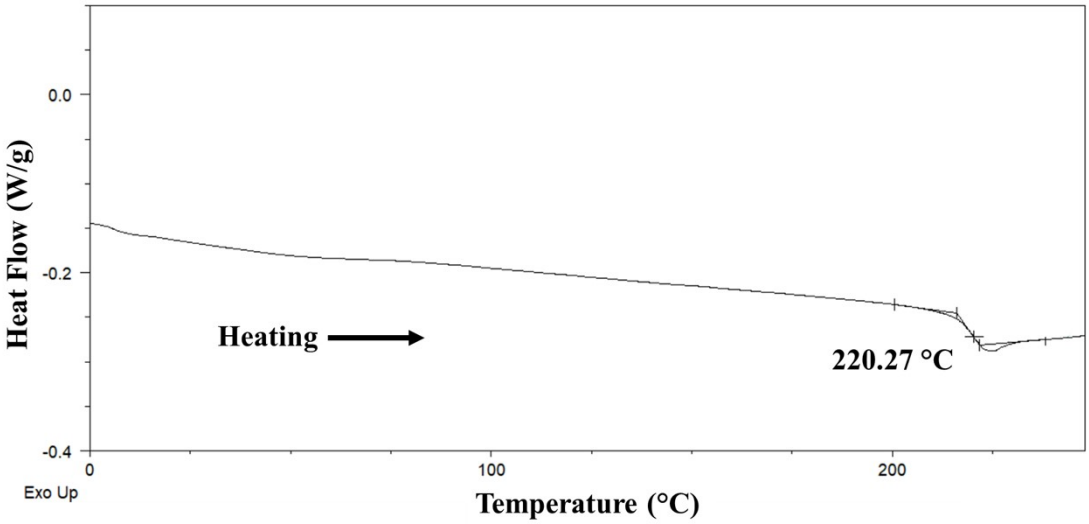


Figure S13. Differential Scanning Calorimetry of *p*-POFNB

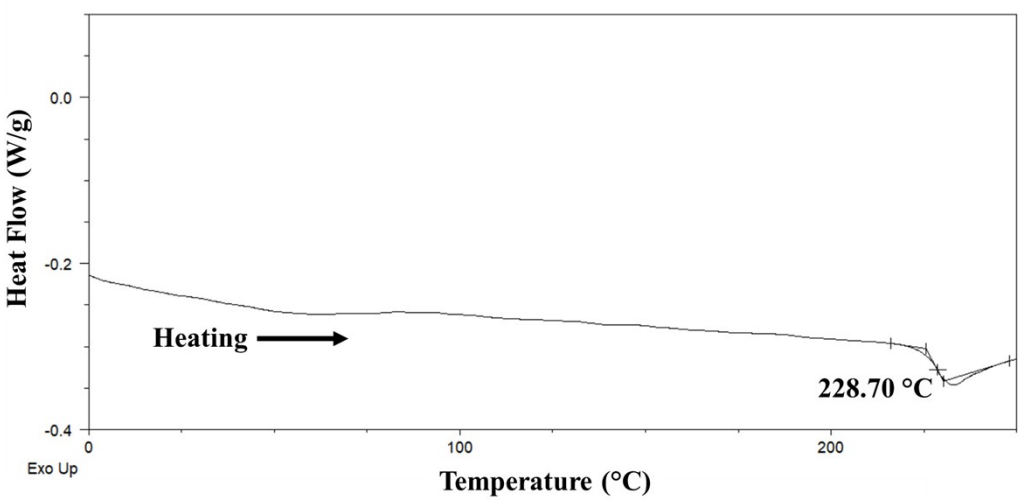


Figure S14. Differential Scanning Calorimetry of PONB

2.3 Degradation temperature

Thermogravimetric analysis was used for recording the polymer degradation temperature. Polymer sample was heated to 700 °C at 10 °C/min under nitrogen atmosphere. The temperature is recorded where 5% weight loss polymer is observed.

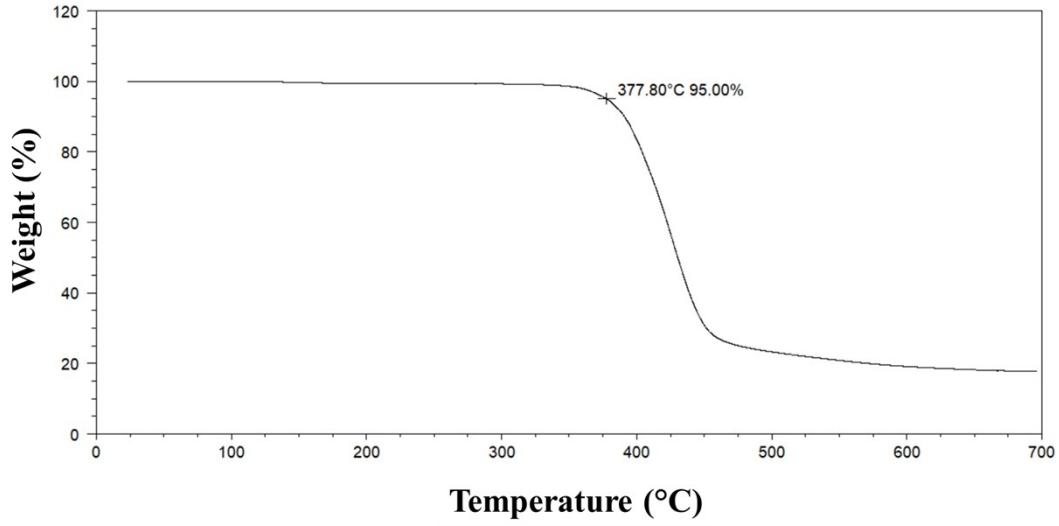


Figure S15. TGA analysis of *o*-POFNB

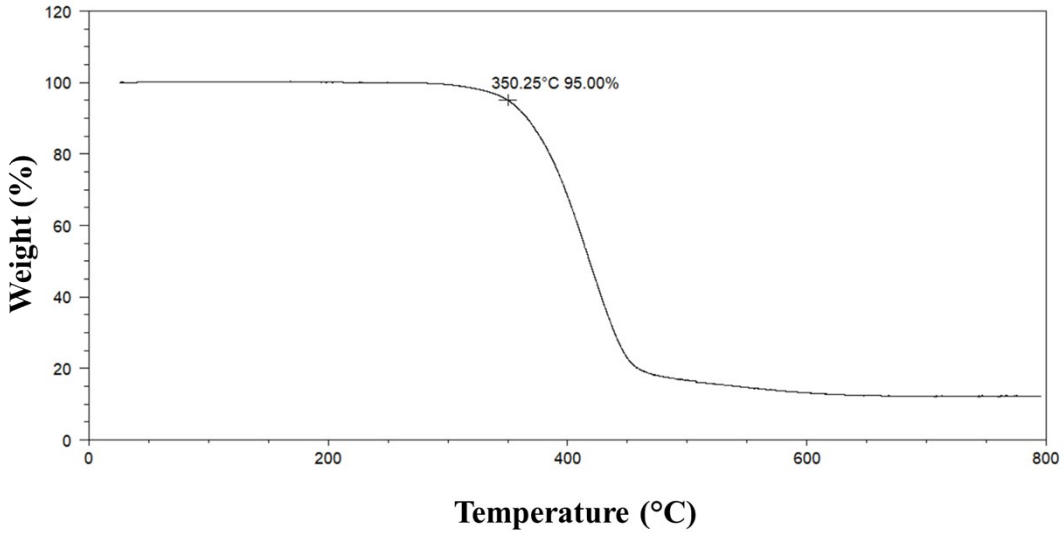


Figure S16. TGA analysis of *m*-POFNB

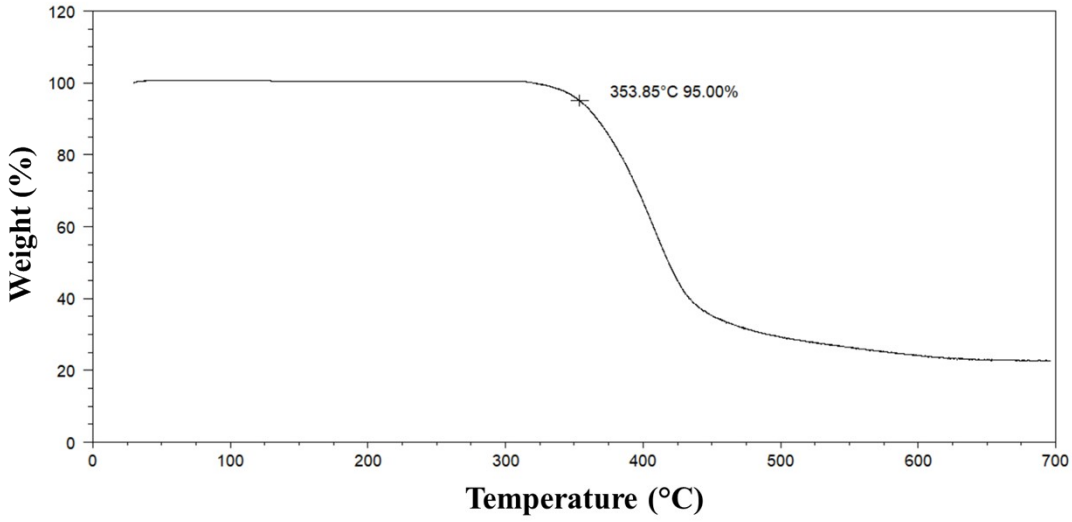


Figure S17. TGA analysis of *p*-POFNB

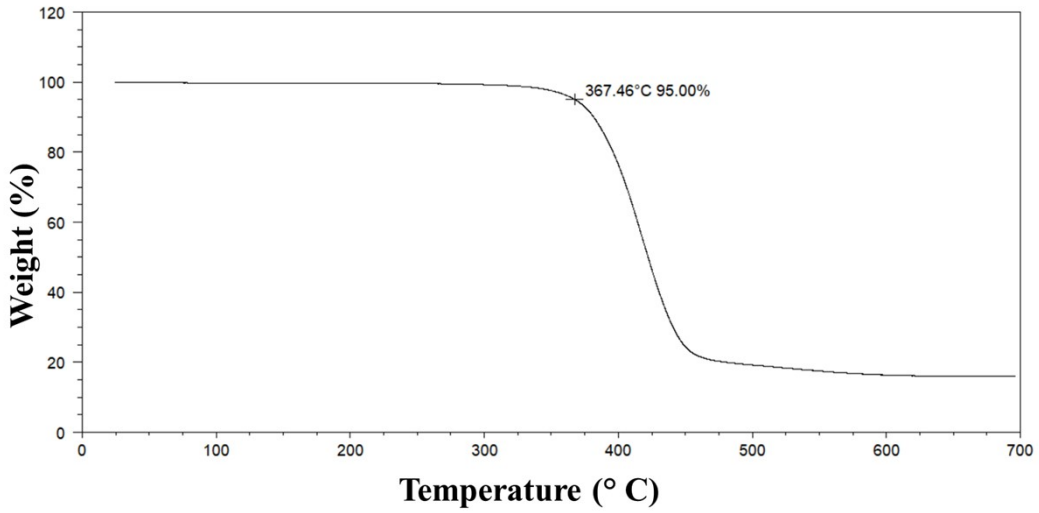
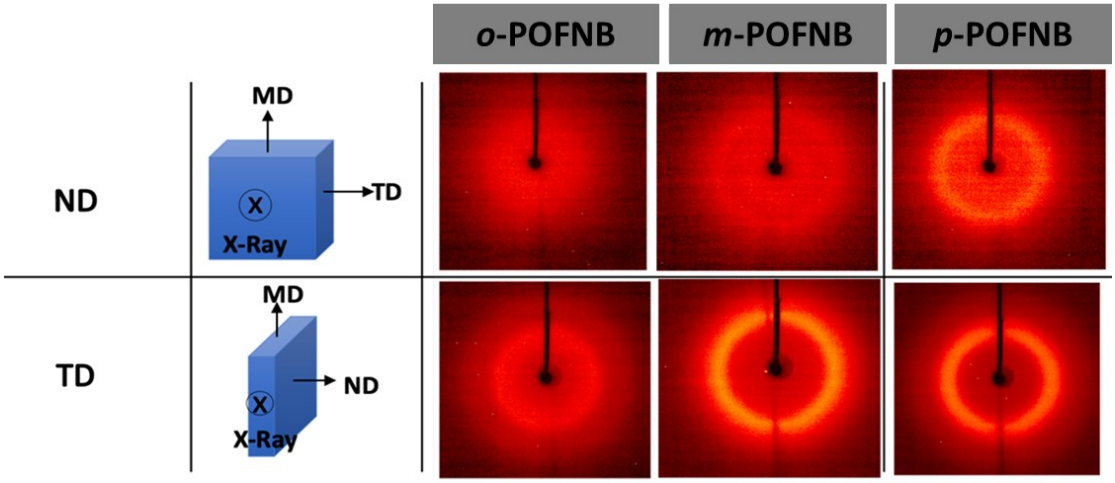


Figure S18. TGA analysis of PONB

2.4 Wide Angle X-Ray Diffraction (WAXS)-

Structures of different POFNB samples were characterized by using Bruker D8 Quest Single Crystal Diffractometer with Cu micro source (1.542 Å). It was equipped with a Photon-II detector (10 cm x 14 cm) to acquire 2D WAXS patterns. For all experiments samples were exposed to X-ray in their as-cast (dried) forms with the beam directed both along the thickness (normal) and the width (transverse) direction to evaluate the super structural order in the polymer. Exposure time was 2 hours for normal (ND) and 1 hour for transverse direction (TD). Figure S18 shows WAXS patterns of different chemistries. Figure S19 represents intensity-2theta graphs.

1



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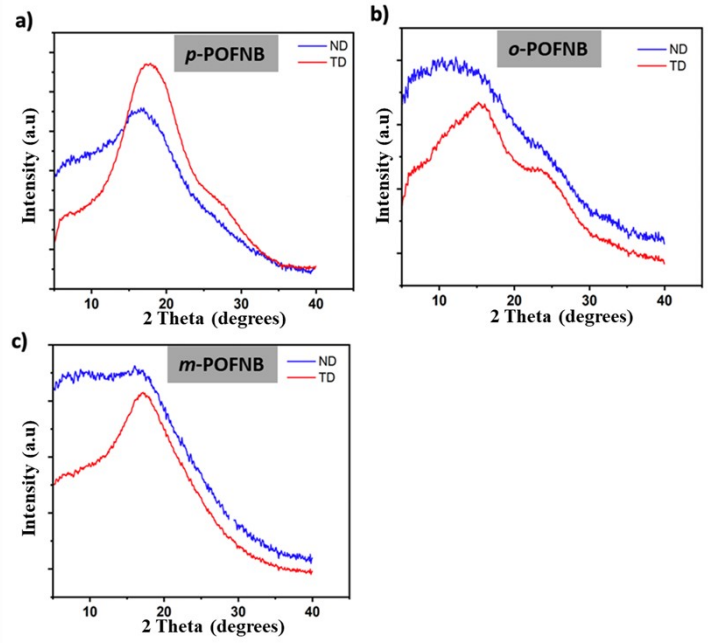
3

4 **Figure S19. 2D WAXS patterns of different POFNB samples**



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6

7 **Figure S20. 1D WAXS graphs of a) *p*-POFNB b) *o*-POFNB c) *m*-POFNB**

Section 3. Band-gap

UV-Visible spectroscopy was used for determination of bandgap of polymer films. Free-standing and dried polymer films obtained from solution casting were used for determination of bandgap. The bandgap was determined using the following equation, where wavelength at onset of the increase in the absorbance values was used for the bandgap calculations.

$$Eg\ (eV) = \frac{1240}{\lambda onset} \quad (1)$$

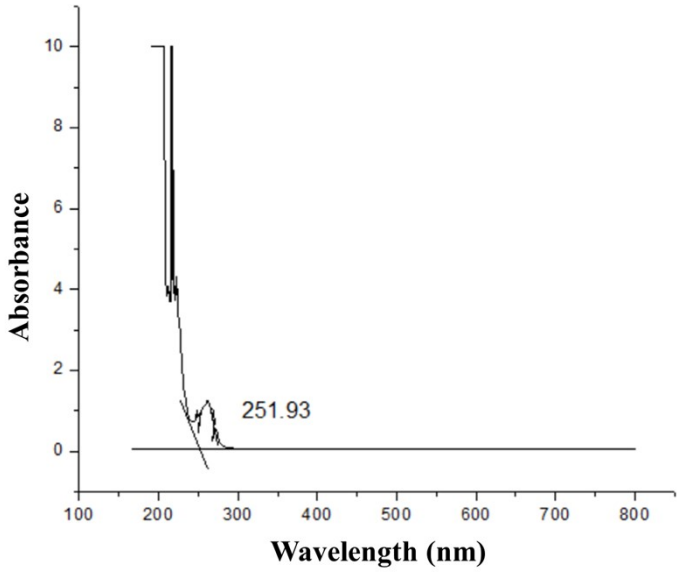


Figure S21. UV-Visible spectroscopy of *o*-POFNB

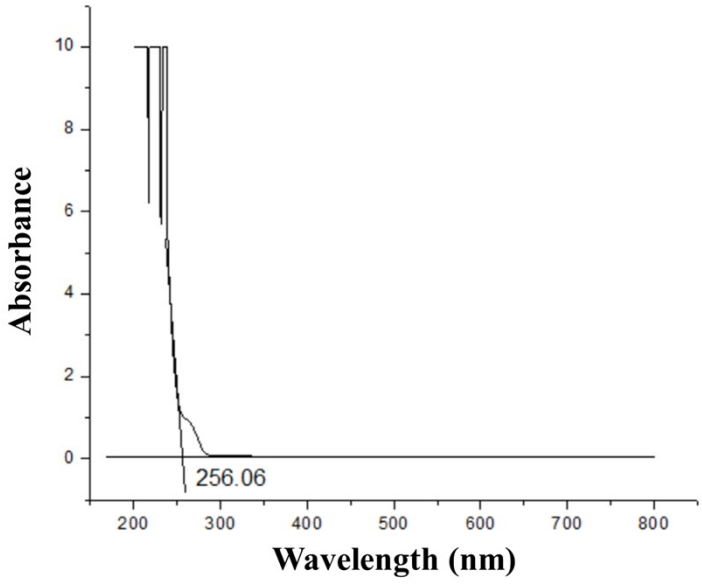


Figure S22. UV-Visible spectroscopy of *m*-POFNB

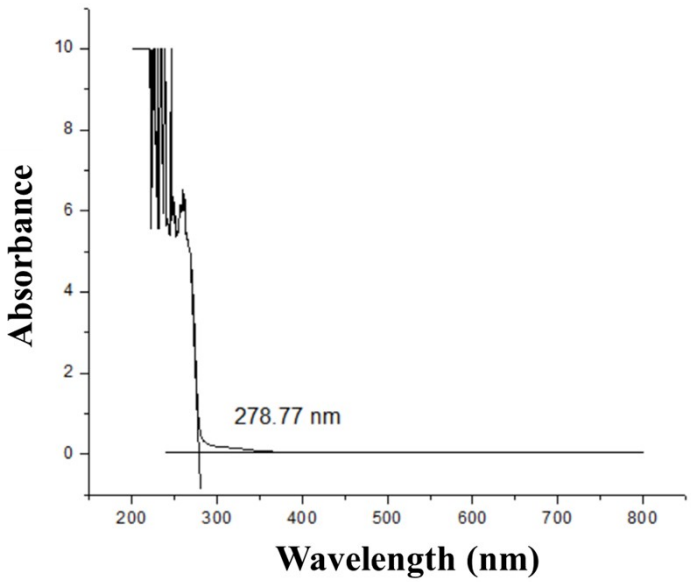
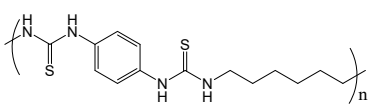
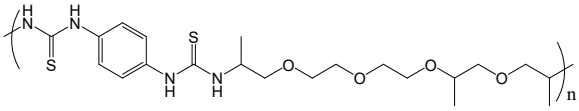


Figure S23. UV-Visible spectroscopy of *p*-POFNB

(a) Polythioureas:

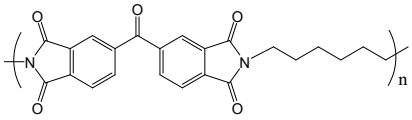


PDTC-HAD

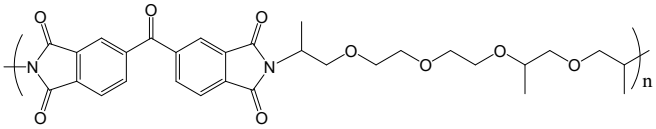


PDTC-HK511

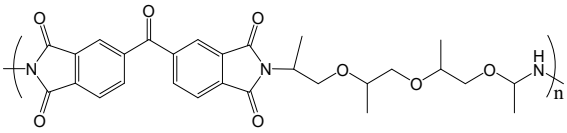
(b) Polyimides:



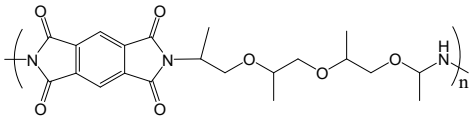
BTDA-HAD



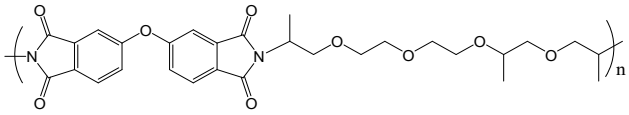
BTDA-HK511



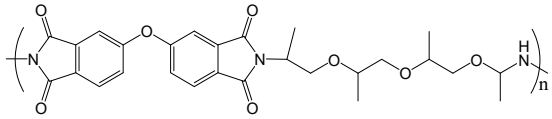
BTDA-D230



PMDA-D230



ODPA-HK511



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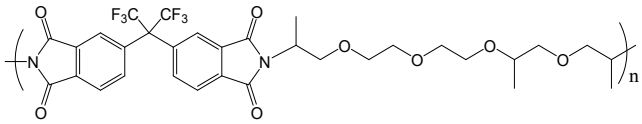
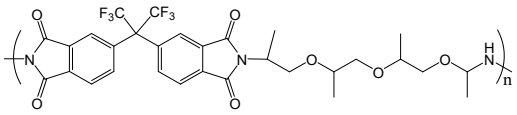


6FDA-HK511



6FDA-D230

Figure S24. Chemical structures of high-temperature materials presented in Figure 1c[14, 35].

Section 4. Electrical properties

4.1 Dielectric constants and dissipation factors

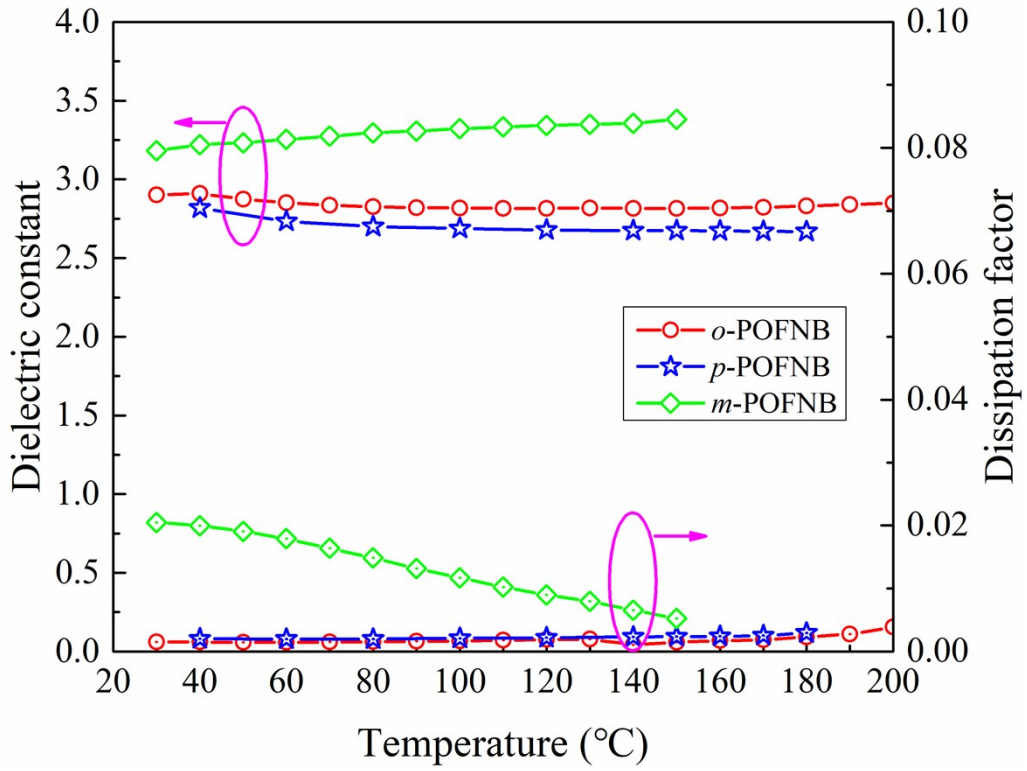


Figure S25. Dielectric constants and dielectric loss at 1k Hz for *o*-POFNB, *p*-POFNB and *m*-POFNB as a function of the temperature.

4.2 Schematic of DE loop

The energy density of dielectric material is described by equation (2). As presented in Figure S23, the charged energy density is the total area of region I and region II in DE loop curves. The discharged energy density is the area of region I.

$$U_e = \int EdD = A_I \tag{2}$$

$$U_{loss} = A_{II} \tag{3}$$

$$\eta = \frac{A_{II}}{A_I + A_{II}} \times 100\% \tag{4}$$

where,

U_e: Discharged energy density

U_{loss}: Energy density of loss

E: Electric field

D: Electric displacement

A_I: Area of region I in Figure S23

A_{II}: Area of region II in Figure S23

η: efficiency

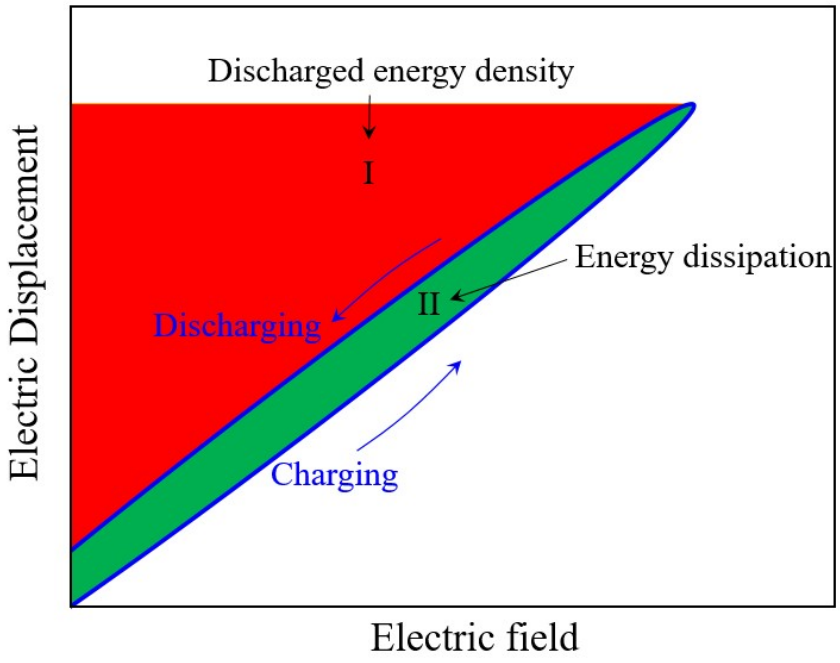
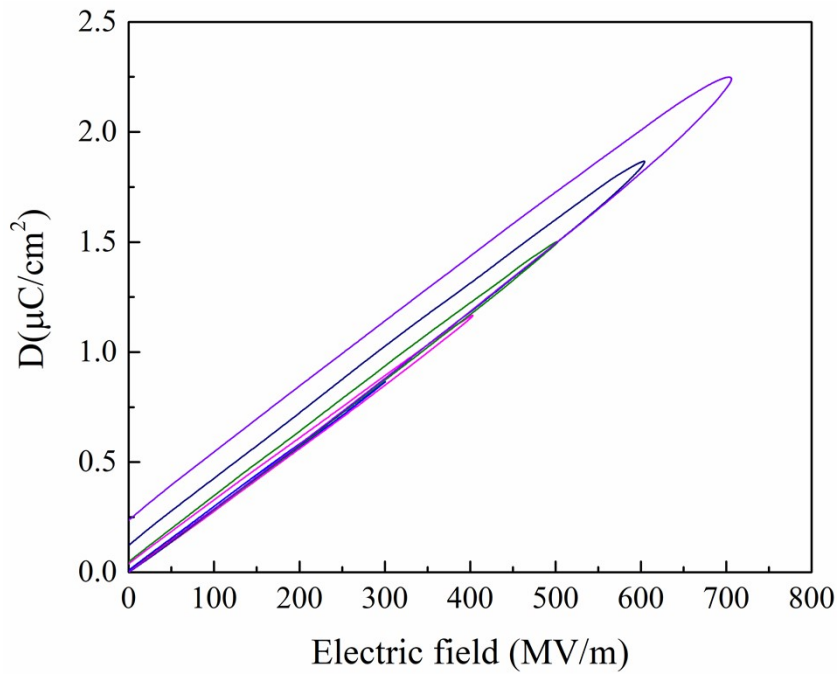


Figure S26. Schematic of regions in DE loop corresponding to the energy density.

4.3 DE loops and energy storage parameters of POFNBs

a,



b,

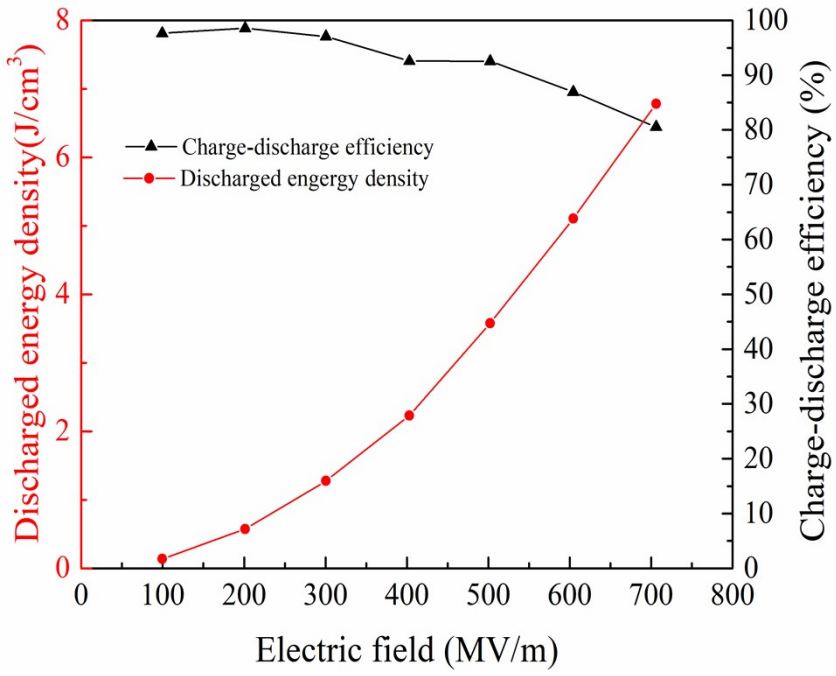
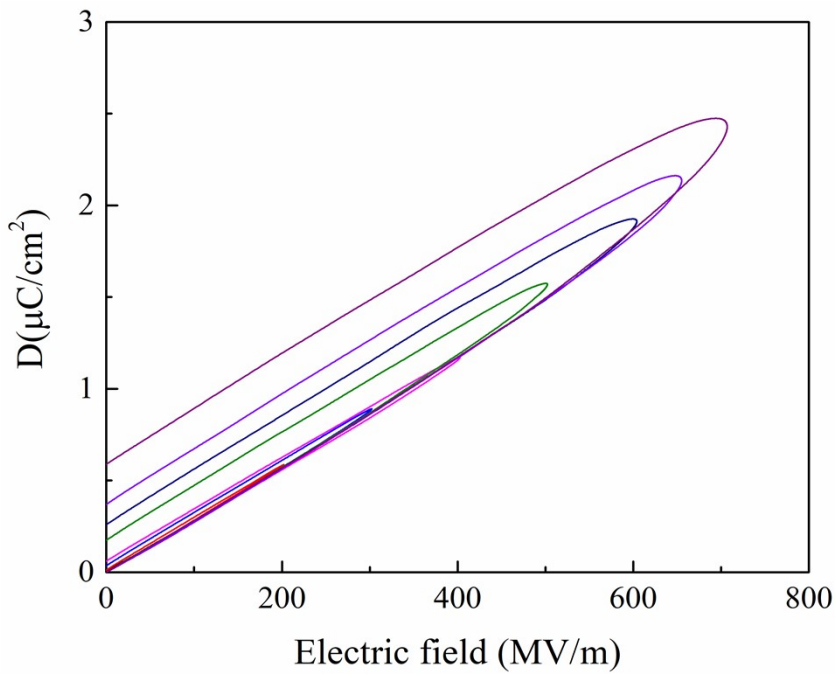


Figure S27. DE loop (a), and energy storage parameters (b), of p-POFNB at RT

a,



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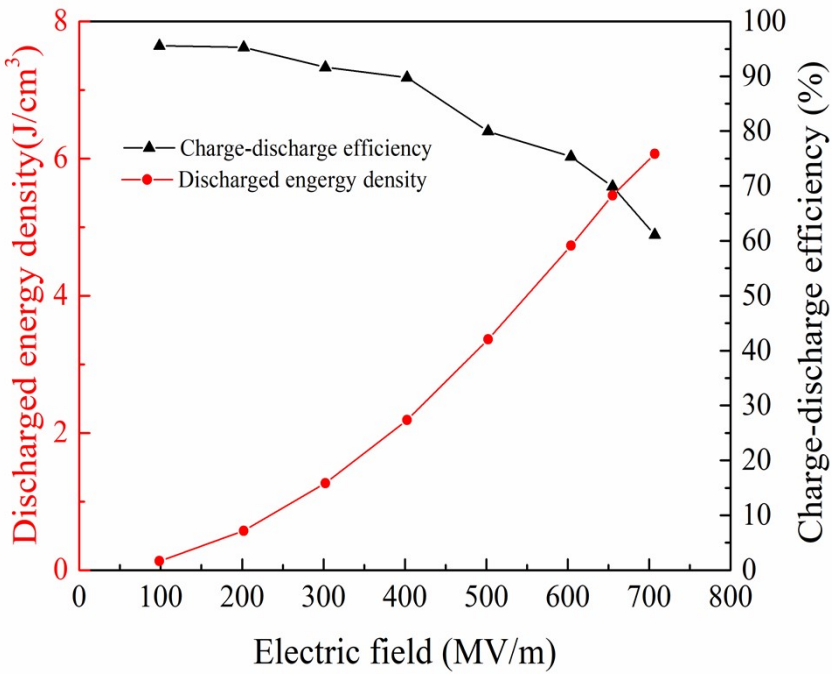
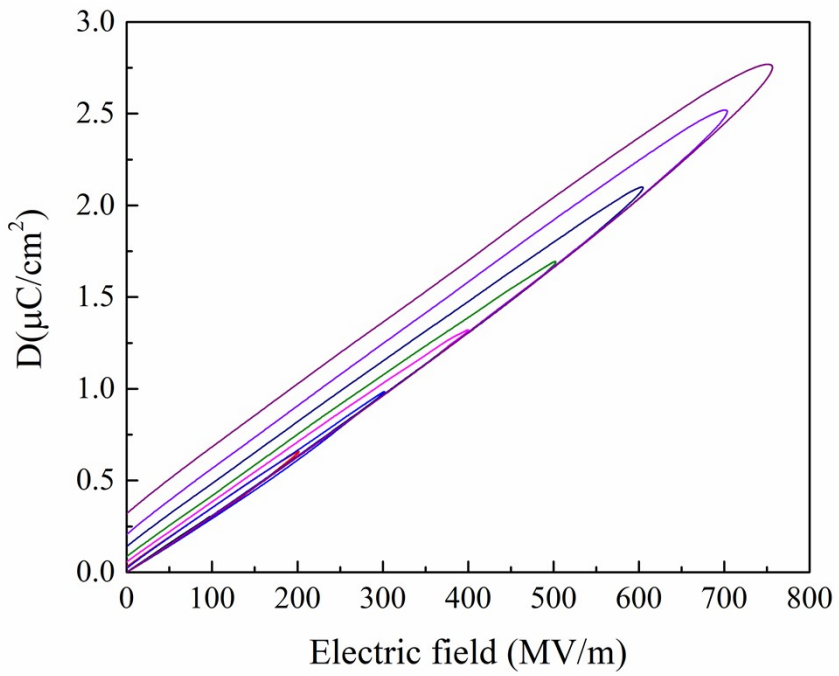


Figure S28. DE loop (a), and energy storage parameters (b), of p-POFNB at 150 °C

a,



b,

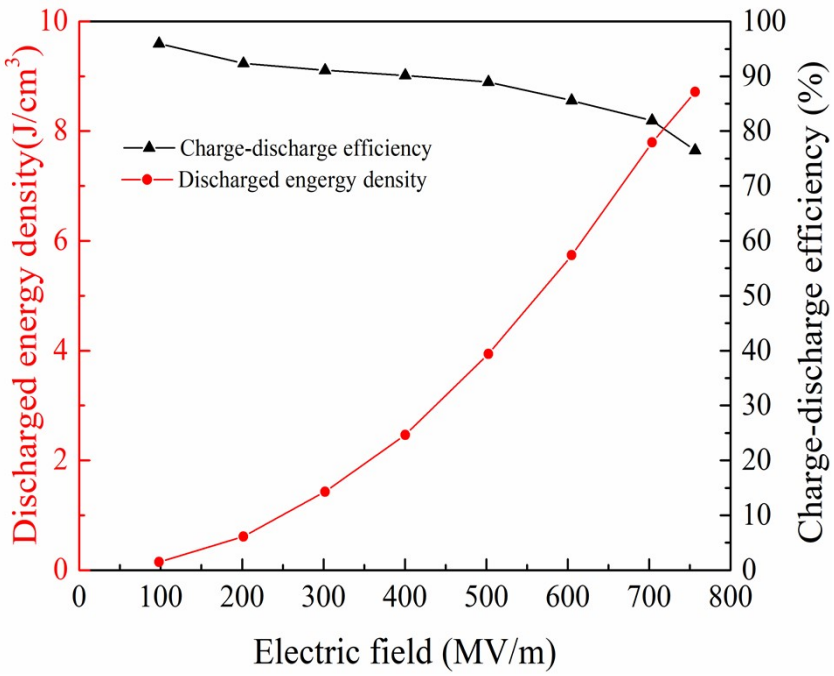
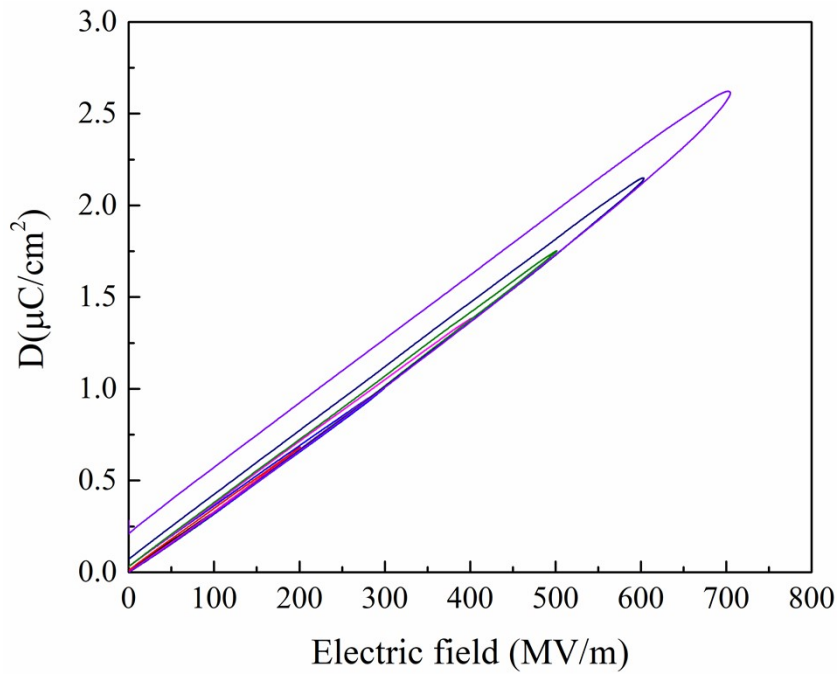


Figure S29. DE loop (a), and energy storage parameters (b), of m-POFNB at RT

a,



b,

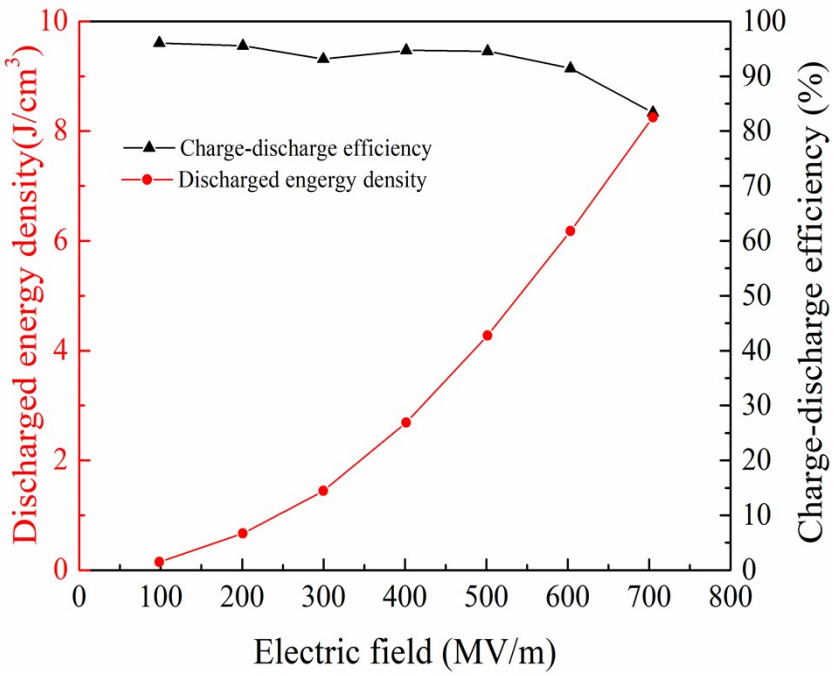
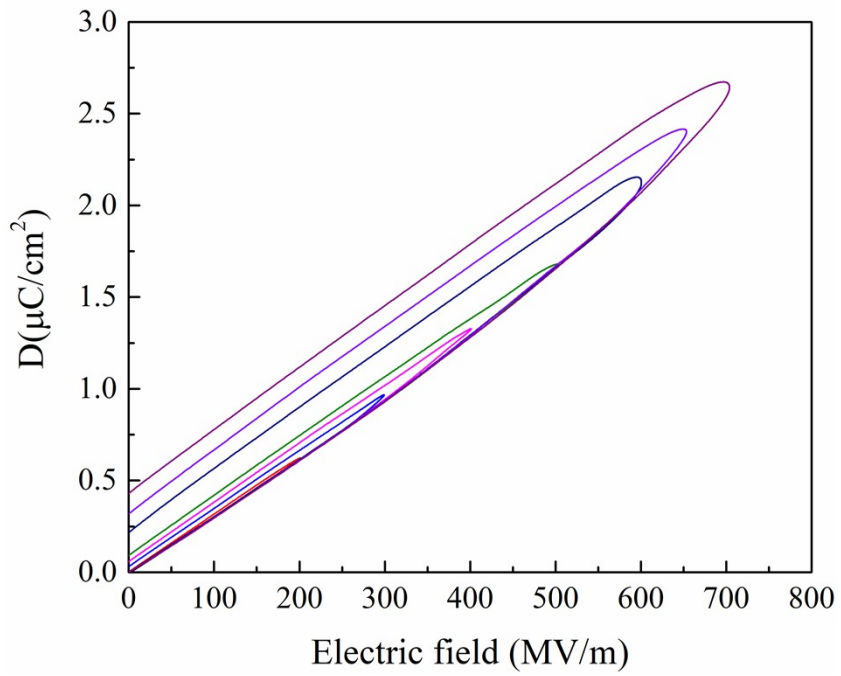


Figure S30. DE loop (a), and energy storage parameters (b), of m-POFNB at 100°C

a,



b,

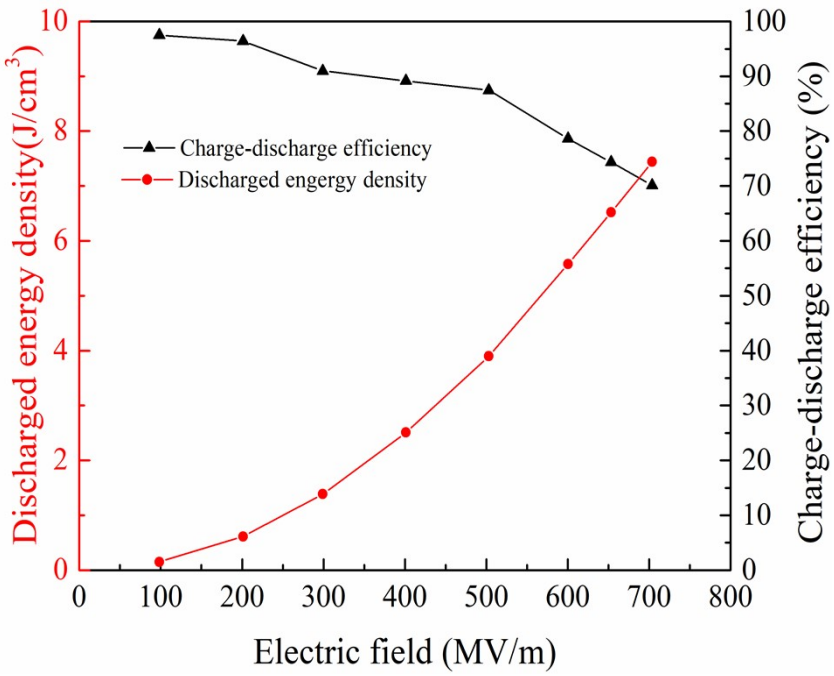
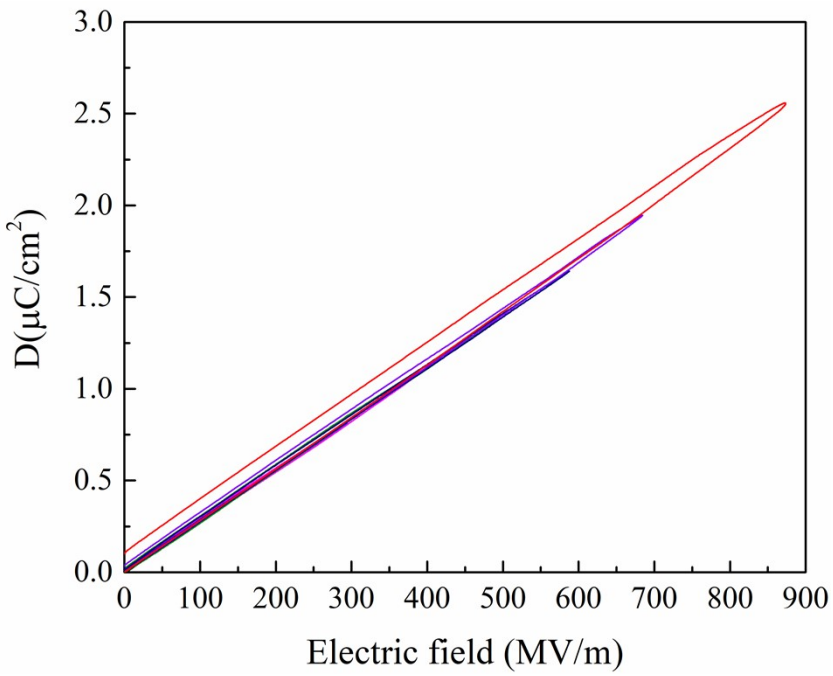


Figure S31. DE loop (a), and energy storage parameters (b), of m-POFNB at 150°C

a,



b,

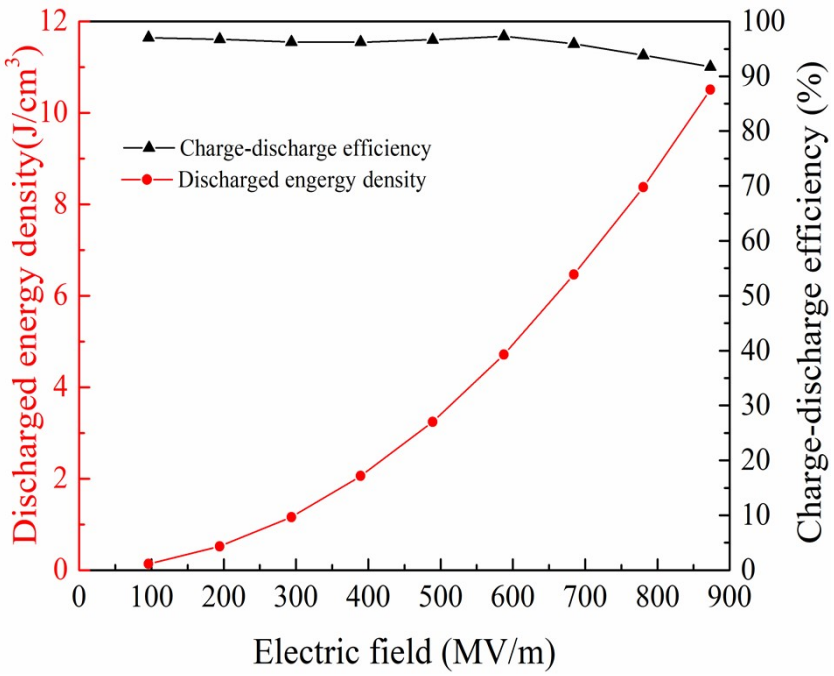
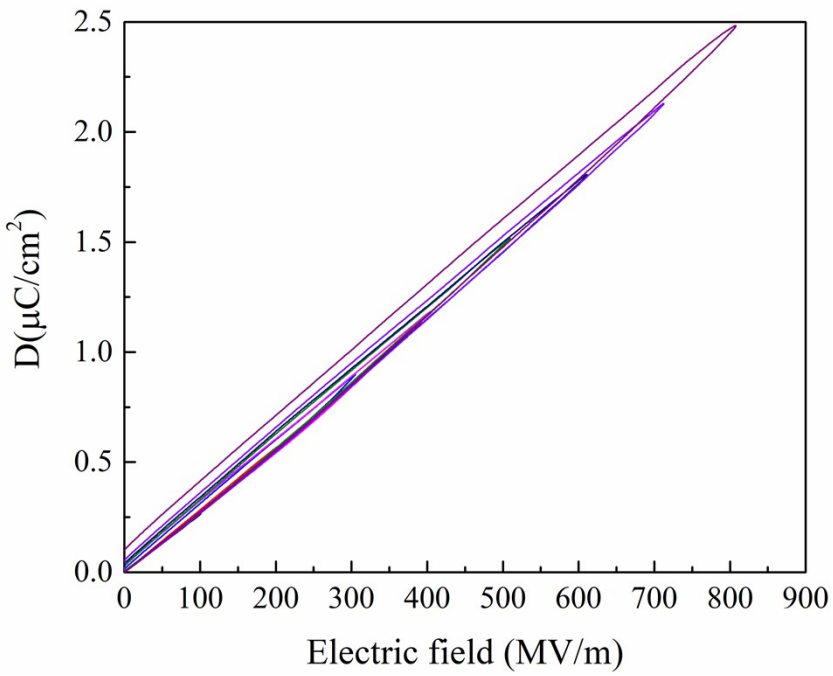


Figure S32. DE loop (a), and energy storage parameters (b), of *o*-POFNB at RT

a,



b,

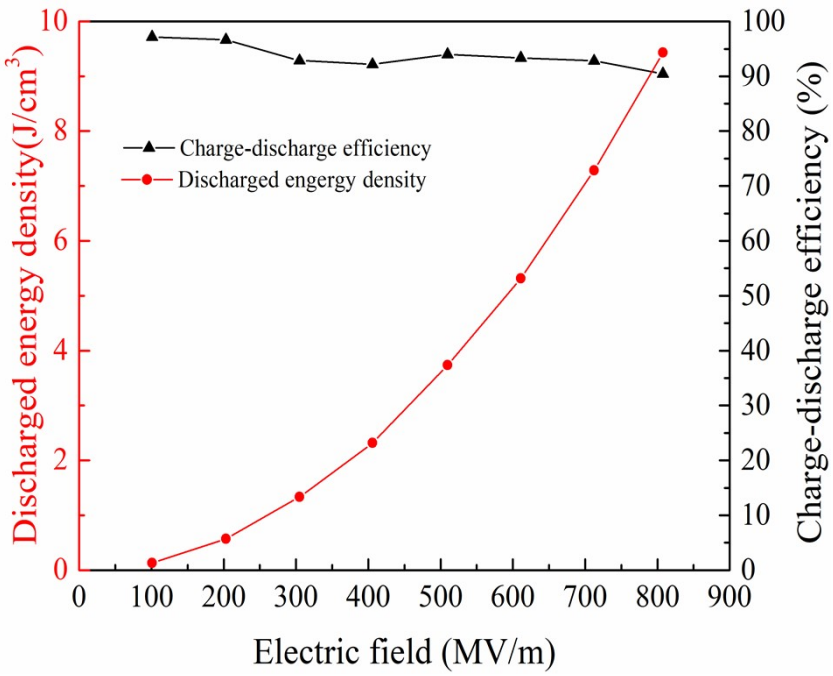


Figure S33. DE loop (a), and energy storage parameters (b), of *o*-POFNB at 100 °C

Section 5. Computations

Contribution of functional groups to the dielectric constants

The GNN model is trained to predict the dielectric constant for a polymer, where the training data for the high-frequency dielectric constant of the PNB polymers are computed via ab-initio molecular dynamics (MD) simulation. Atoms are colored based on their local feature values at the last GNN layer[1]. High/low values imply the significance of different fragments/atoms in determining the dielectric constants.

References

1. Ankit Mishra, Pankaj Rajak, Ekin Dogus Cubuk, Ken-ichi Nomura, Rajiv Kalia, Aiichiro Nakano, Ajinkya Deshmukh, Lihua Chen, Greg Sotzing, Yang Cao, Ramamurthy Ramprasad, Priya Vashishta. Accelerated Discovery of Dielectric Polymer Materials Using Graph Convolutional Neural Networks. Bulletin of the American Physical Society, Volume 65, Number 1, 2021.