Supplementary Information

Enhancing Electrical Energy Storage using Polar Polyimides with Nitrile Groups Directly Attached to the Main Chain

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I. Syntheses of monomers and polymers

Materials. Tetracarboxylic dianhydrides used in this work, pyromellitic dianhydride (PMDA), 4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-oxydiphthalic dianhydride (ODPA) and 2,2'-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA), are all commercial products (Chriskev Co., <u>www.chriskev.com</u> and Akron Polymer Systems, <u>www.akronpolysys.com</u>) and were purified by sublimation. All other reagents and solvents were purchased from Aldrich Chemical Co. and used as received.



Scheme S1. Synthesis of *p*,*p*-, *m*,*m*- and *p*,*m*-diamine monomers containing three nitrile groups.

Instrumentation. Transmittance Infrared (IR) spectra were recorded on a Nicolet Nexus 470 Fourier transform IR spectrophotometer. Attenuated total reflection IR (ATR-IR) was measured on a Bruker Alpha-R spectrometer. Proton (¹H) and carbon (¹³C) nuclear magnetic resonance (NMR) spectra were recorded at 300 MHz on a Bruker AVANCE 300 spectrometer.

Synthesis of 2,6-bis[3-(4-aminophenoxy)-2-cyanophenoxy]benzonitrile (p,p-3BCN, VIb). Into a 100 mL round bottom flask equipped with stir bar, condenser, and nitrogen inlet was charged 2,6-bis(2-cyano-3-fluorophenoxy)benzonitrile (IV, 2.00 g, 5.4 mmol), 4-aminophenol (Vb, 1.29 g, 11.8 mmol), potassium carbonate (1.78 g, 12.9 mmol), and N-methyl-1-pyrrolidone (NMP, 32 mL). The mixture was stirred at 100 °C for 24 h until GC/MS showed no remaining reactant. It was filtered and then the filtrate was poured into about 500 mL of saturated NaCl aqueous solution and was extracted with ethyl acetate (3×200 mL). The organic layer was combined and washed with distilled water (3 \times 200 mL). It was then dried over sodium sulfate and filtered. Carbon black was added to the solution, which was then stirred at 65 °C for 30 min. It was passed through a Celite filter to remove carbon and the solvent was removed by a rotary evaporator. A small amount of NMP residue in the product was removed by refluxing it in ethanol (75 mL). Product was collected by filtration and dried overnight at 80 °C in a vacuum oven to afford 1.52 g (51.5%) of beige solid, m.p.: 242.6-243.8 °C (dec.). ¹H NMR (DMSO-d₆): 5.18 (s, 4H, Ar-H), 6.57-6.65 (m, 6H, Ar-H), 6.88-6.92 (m, 2H, Ar-H), 7.58-7.61 (t, 2H, Ar-H), 7.77-7.80 (t, 1H, Ar-H). ¹³C NMR (DMSO-d₆): 94.08, 96.90, 110.97, 111.18, 111.53, 111.81, 112.62, 114, 80, 121.29, 136.02, 136.69, 143.57, 146.84, 157.72, 158.05, 162.56. FT-IR (cm⁻¹): 3366 (NH₂), 3045, 2229 (C=N), 1601, 1568, 1506, 1450, 1238, 1198, 1057, 833, 780. Anal. Calcd. for C₃₃H₂₁N₅O₄: C, 71.86%; H, 3.84%; N, 12.70%. Found: C, 71.40%; H, 4.00%; N, 12.33%.



Fig. S1 ¹H NMR spectrum of *p*,*p*-3BCN diamine.





Fig. S3 FT-IR spectrum of *p*,*p*-3BCN diamine.



Scheme S2 Synthesis of polyimides containing 3BCN groups.

General procedure for polyimide (PI) synthesis and fabrication of PI films via one-step thermal imidization

PMDA-ppDAm(CN)₃ (3a). Into a 50 mL round bottom flask equipped with stir bar and nitrogen inlet was charged 2,6-bis[3-(4-aminophenoxy)-2-cyanophenoxy]benzonitrile (*p*,*p*-3BCN, **VIb**, 1.00 g, 1.81 mmol) and DMAc (8.00 g). After **VIb** was dissolved, pyromellitic dianhydride (PMDA, **VIId**, 0.3955 g, 1.81 mmol) was added and the mixture was stirred for 24 h. The solution became increasingly viscous with progressive molecular weight build-up as the reaction proceeded. The viscous poly(amic acid) solution (**PAA**, **VIII**) was diluted with DMAc (4.00 g) and the poured onto 6 separate 2 in. \times 2 in. glass plates (2 \times 0.52 g of solution, 2 \times 1.39 g, and 2 \times 2.72 g). The plates were manipulated by tilting and rotating until the entire surface was covered by PAA solution. Once completed, all plates were placed in a vacuum oven, which was maintained at

50 °C and reduced pressure overnight. The oven pressure was released under nitrogen and the temperature was ramped to 300 °C on hourly intervals (100, 150, 175, 200, 250, and 300 °C). They were allowed to cool down and the resulting PI films (20-40 μ m) were removed from the plates by submerging them in water overnight. Films were tough, creasable, and transparent.



Fig. S4 FT-IR spectrum of PMDA-ppDAm(CN)₃ polyimide (3a).



Fig. S5 Transmission- and reflection-mode X-ray diffraction profiles for various polar polyimides containing 1 or 3 nitrile groups.

III. Details of calculation III.1. Repeat unit density (m⁻³)

 $N = \frac{\rho}{M_{RU}} N_A$, where ρ is the density of the polymer, M_{RU} the molar mass of a repeat unit, and N_A the Avogadro number.

III.2. Repeat unit dipole moment (D)

 $\mu_{RU} = \mu_{DAm} - \mu_{DAn}$, where μ_{DAm} is the dipole moment of the diamine part and μ_{DAn} is the dipole moment of the dianhydride part of the polyimide. The two dipole moments need to be subtracted because they are assumed to point in the opposite directions.

III.3. Predicted dipolar polarization (C/m²) $P_{dip} = N\mu_{RU} \left(\coth u - \frac{1}{u} \right), \text{ here } u = \frac{\mu_{RU}E}{k_{B}T}, \text{ where N is the repeat unit density, } \mu_{RU} \text{ the}$

dipole moment of a repeat unit, E the applied electric field (100 MV/m for all samples), k_B the Boltzmann constant, and T the absolute temperature (463.15 K). The function in the parenthesis is also known as the Langevin function.

III.4. Polarization only due to dipolar motion

 $P_{dip} = P_{DE} - P_{BDS} = P_{DE} - (\varepsilon_{BDS} - 1)\varepsilon_0 E$, where P_{DE} is the polarization from a D-E loop measured at 100 MV/m, 190 °C, and 1 kHz, and P_{BDS} is the polarization calculated from the permittivity ε_{BDS} measured with broadband dielectric spectroscopy at -150 °C, 100 kHz, and under an applied voltage of 1 V_{rms}. ε_{BDS} , since measured at a very low temperature and high frequency, is assumed to only contain contributions from electronic and vibrational polarizations. E is the electric field used in the D-E loop measurements and is equal to 100 MV/m.

III.5. Calculating permittivity from molar refraction

From the Lorentz-Lorenz relation $R_M = \frac{\varepsilon_{r,e}-1}{\varepsilon_{r,e}+2} \frac{M_{RU}}{\rho}$, we can express $\varepsilon_{r,e}$ from electronic polarization as: $\varepsilon_{r,e} = \frac{2R_M\rho + M_{RU}}{M_{RU} - R_M\rho}$, where R_M is the molar refraction of the repeat unit. The molar refraction values are obtained by adding up the refractions of bonds that make up the repeat unit. The bond refraction values are obtained from literature. To account for the vibrational polarization, which is approximately 20% of that of the electronic polarization, the R_M value in the above equation will be multiplied by 1.2 in order to obtain the ε_r from both electronic and vibrational polarizations.

IV. BDS data for sample 2a



Fig. S6 ϵ_r' and ϵ_r'' as a function of temperature for sample 2a.