

Supporting Information

Materials

1,4-bis (3,4-dicarboxyphenoxy) benzene dianhydride (HQDA) was purchased from Changchun Institute of Applied Chemistry Chinese Academy of Sciences and dried in vacuum oven at 160 °C for 4 hours. All other reagents and solvents were obtained from J&K Chemical Ltd such as 3,3',4,4'-biphenyltetracarboxylic dianhydride (s-BPDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene (DBC), etc., and used as received.

Trans- and cis-dinitrodibenzo-18-crown-6 (NDBC)

Both dinitrodibenzo-18-crown-6 (NDBC) and diaminodibenzo-18-crown-6 (AmDBC) were obtained by the method of Jagur-Grodzinski and M. Shporer.¹ The structure of NDBC and AmDBC is characterized by elemental analyses, ¹H NMR (shown in **Figure S1, S2**), FTIR (shown in **Figure S3**)

Trans-dinitrodibenzo-18-crown-6: m.p. 238-241 °C (lit. 247-252 °C²); IR (KBr, cm⁻¹): 2969, 2887(νC-H); 1589, 1343(νN-O); 1511, 1450, 1397(benzene skeleton vibration, stretching); 1234(νC-C); 1135, 993(νC-O); Anal. calcd for C₂₀H₂₂N₂O₁₀: C 53.7, H 5.00, N 6.29; found: C 53.33, H 4.93, N 6.22.

Cis-dinitrodibenzo-18-crown-6: m.p. 208-212 °C (lit. 206-232 °C²). IR (KBr, cm⁻¹): 2926, 2876(νC-H); 1589, 1343(νN-O); 1503, 1450, 1403(benzene skeleton vibration, stretching); 1253(νC-C); 1135, 993(νC-O); Anal. calcd for C₂₀H₂₂N₂O₁₀: C 53.4, H 5.10, N 6.31; found: C 53.33, H 4.93, N 6.22. ¹H NMR (400 MHz, DMSO-d₆) δ 3.86 (d, 8H, J=1.6 Hz), 4.22(m, 8H), 7.16 (d, 2H, J=8.8 Hz), 7.73 (d, 2H, J=2.8 Hz), 7.89 (dd, 2H, J=9, 2.6 Hz).

Cis- and trans-diaminodibenzo-18-crown-6 (AmDBC)

Cis-diaminodibenzo-18-crown-6: m.p. 185-188 °C (lit. 180-184 °C²). IR (KBr, cm⁻¹): 3322, 3223(νN-H); 2937, 2861(νC-H); 1590, 1511, 1447 (benzene skeleton vibration, stretching); 1268 (νC-C); 1280 (νAr-O-R), 1124 (νC-O-C); Anal. calcd for C₂₀H₂₆N₂O₆: C 61.48, H 6.58, N 7.26; found: C 61.51, H 6.72, N 7.17, yield 43%.

Trans-diaminodibenzo-18-crown-6: m.p. 198-203 °C (lit. 199-203 °C).² IR (KBr, cm⁻¹):

¹): 3417, 3353(ν N-H); 2937, 2861(ν C-H); 1590, 1511, 1447 (benzene skeleton vibration, stretching); 1268 (ν C-C); 1280 (ν Ar-O-R), 1124 (ν C-O-C); Anal. calcd for C₂₀H₂₆N₂O₆: C 61.63, H 6.84, N 7.20; found: C 61.51, H 6.72, N 7.17. ¹H NMR (400 MHz, DMSO-d₆) δ 3.77-3.82 (m, 8H), 3.92-3.97 (m, 8H), 4.63 (bs, 4H), 6.05 (dd, 2H, J=8.4, 2.4 Hz), 6.23 (d, 2H, J=2.4 Hz), 6.63 (d, 2H, J=8.4 Hz).

Crown ether-contained polyimides (PIs)

PIs containing crown ether units were propagated as shown in **Scheme 1**, which were obtained by the diamine (AmDBC) and dianhydride, 3,3,4,4'-biphenyltetracarboxylic dianhydride (s-BPDA), 3, 3', 4, 4'-benzophenonetetracarboxylic dianhydride (BTDA) and 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (HQDA) via a two-step method, and were denoted as PI-a, PI-b and PI-c, respectively. Typically, to prepare PI-a film, AmDBC (13.665g, 0.035mol) and s-BPDA (10.2977g, 0.035mol) were added to 60 g of N,N'-diethylacetamide (DMAC) in a round bottom flask, and the mixture was reacted at 0 °C for 24 h. The resulting polyamic acid (PAA) solution with 20 wt% was diluted into 15 wt% by DMAC and casted into PAA films. The imidization process of PAA films is as follows: (1) heating to 150 °C at a rate of 5 °C/min and annealing at 150 °C for 1 h to remove the residual solvent; (2) heating to 250 °C at a rate of 2 °C/min and annealing for 1 h; (3) heating to 300 °C a rate of 4 °C/min and annealing for 1 h to complete the imidization process.

Measurements

Proton nuclear magnetic resonance spectra (¹H NMR) were obtained with Bruker Avance-400 spectrometers at 400 MHz. Fourier transform infrared spectroscopy (FTIR) spectra were measured by a Perkin–Elmer SP one FTIR. Elemental analyses were determined on a Perkin–Elmer model 2400 CHN analyses. Thermal gravimetric analysis (TGA) was measured with 4~10 mg film samples with a Perkin–Elmer Pyris1 TGA at a heating rate of 10 °C/min in nitrogen. The glass transition temperatures were identified using a Perkin–Elmer Diamond DMA instrument at a heating rate of 10 °C/min in nitrogen. A SANS CMT8012 (Shenzhen, China) instrument was used to performer the tensile tests of polymer films at 5 mm/min on strips. The dielectric properties were tested on an HP4276A LCR electrometer at

different frequencies.

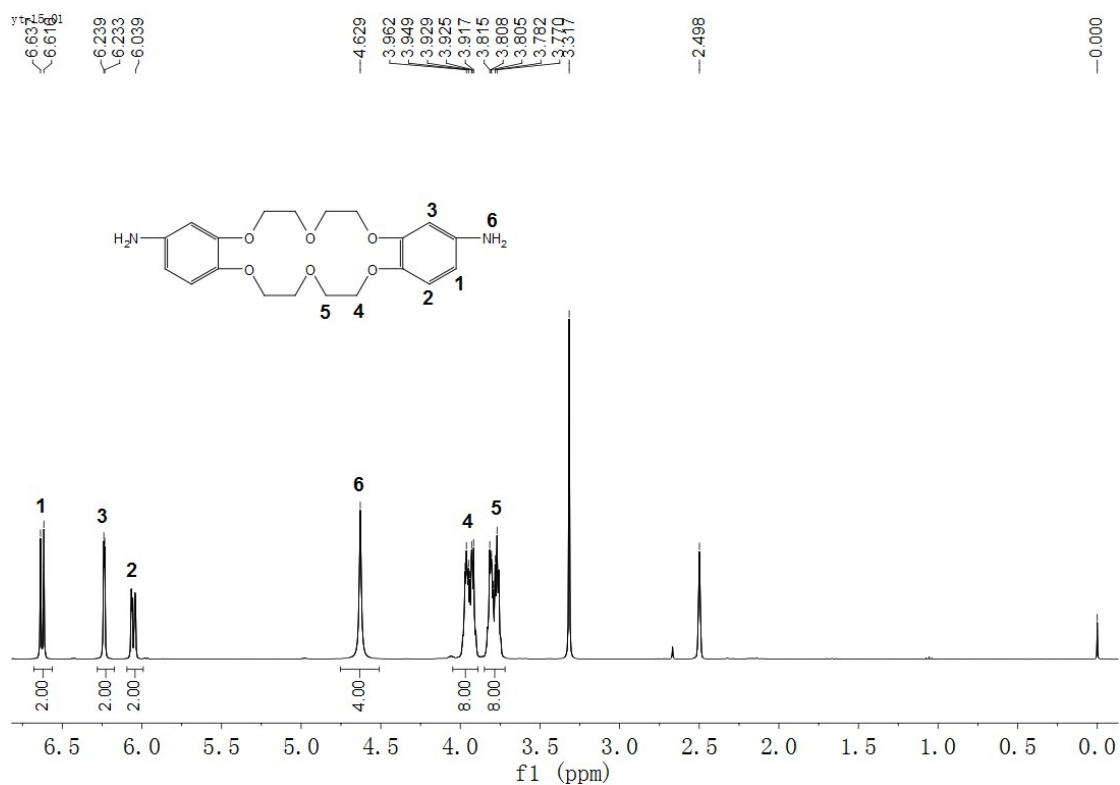


Figure S1. ¹H NMR of AmDBC in DMSO-d₆.

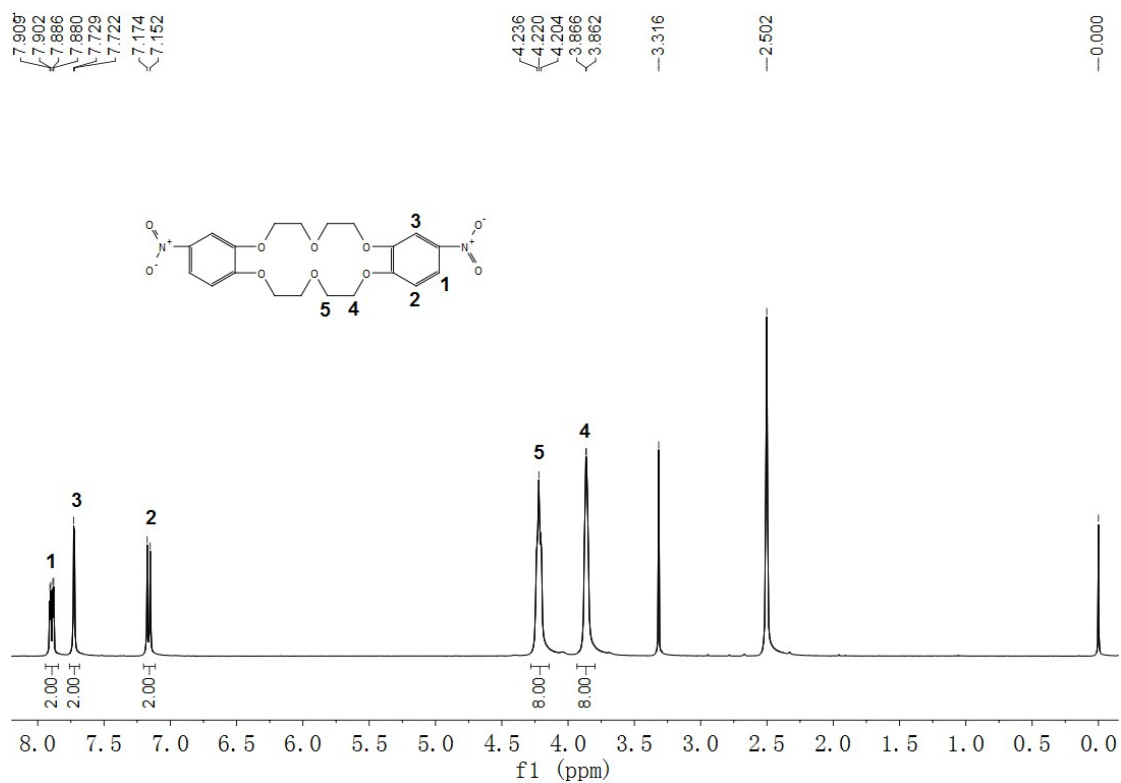


Figure S2. ¹H NMR of NDBC in DMSO-d₆.

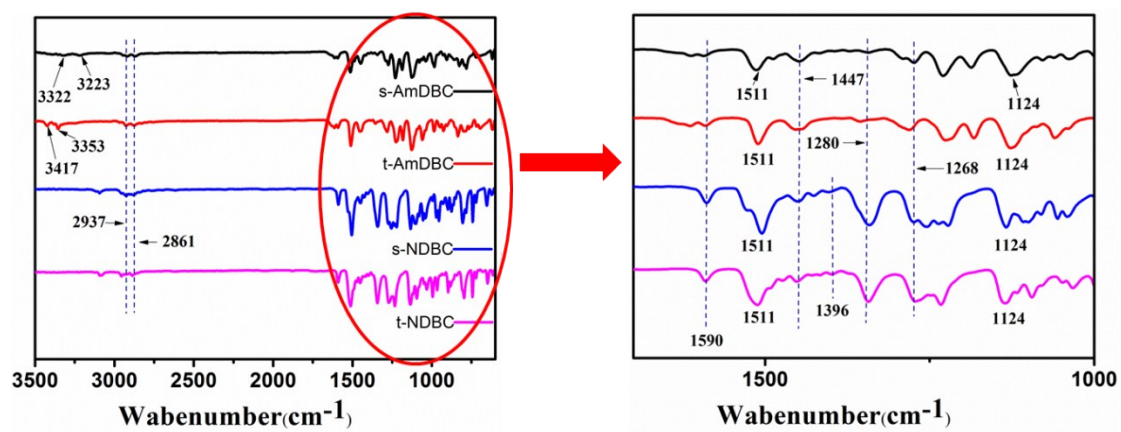


Figure S3. FTIR spectra of NDBC and AmDBC.

References

1. E. Shchori, J. Jagur-Grodzinski and M. Shporer, *Journal of the American Chemical Society*, 1973, **95**, 3842-3846.
2. W. M. Feigenbaum and R. H. Michel, *Journal of Polymer Science Part A-1: Polymer Chemistry*, 1971, **9**, 817-820.