

Supporting Information

Synthesis and Gas Separation Performance of Intrinsically Microporous Polyimides Derived from Sterically Hindered Binaphthalenetetracarboxylic Dianhydride

Xiaofan Hu,^a Hongliang Mu,^b Jie Miao,^{a,b} Yao Lu,^{a,b} Xianwei Wang,^a Xiangsheng Meng,^{*a} Zhen Wang^{*a} and Jingling Yan^{*a}

^a Ningbo Institute of Material Technology and Engineering, Chinese Academy of Science, Ningbo 315201, China.

^b Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China.

Email: mengxiangsheng@nimte.ac.cn, wz@nimte.ac.cn, Jingling, jyan@nimte.ac.cn

List of Contents for Supplementary Materials:

Experimental Section	SI-2
Figure S1. ¹ H NMR spectrum of BiphenMe ₂	SI-5
Figure S2. ¹³ C NMR spectrum of BiphenMe ₂	SI-5
Figure S3. ¹ H NMR spectrum of Br-BiphenMe ₂	SI-6
Figure S4. ¹³ C NMR spectrum of Br-BiphenMe ₂	SI-6
Figure S5. ¹ H NMR spectrum of TNTTA.....	SI-7
Figure S6. ¹³ C NMR spectrum of TNTTA.....	SI-7
Figure S7. ¹ H NMR spectrum of TNTDI.....	SI-8
Figure S8. ¹³ C NMR spectrum of TNTDI.....	SI-8
Figure S9. ¹ H NMR spectrum of MMBMA.....	SI-9
Figure S10. ¹³ C NMR spectrum of MMBMA.....	SI-9
Figure S11. ¹ H NMR spectrum of FDBMA.....	SI-10
Figure S12. ¹³ C NMR spectrum of FDBMA.....	SI-10
Figure S13. FTIR spectra of TNTDA-derived PIs.....	SI-11
Figure S14. TGA curves of TNTDA-derived PIs.....	SI-11
Table S1. Solubility of TNTDA-derived PIs in various organic solvents.....	SI-12
Table S2. Molecular weights and mechanical and thermal properties of TNTDA-derived PIs.....	SI-12

Experimental

Materials

2-*tert*-Butyl-4,5-dimethylphenol,¹ 3,3'-di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diol (H₂[Biphen]),² 2,8-diamino-4,10-dimethyl-6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine (TBDA1),³ 2,6-diaminotriptycene (DAT),⁴ 5,5'-(*m*-mesitylmethylene)bis(4-methylbenzene-1,2-diol) (MMBMD), and 5,5'-(9H-fluorene-9,9-diyl)bis(4-methylbenzene-1,2-diol) (FDBMD)⁵ were prepared according to literature methods. Anhydrous tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) were purified by distillation over Na and CaH₂, respectively. Carbon tetrachloride was dried over activated 4A molecular sieve. All other reagents were obtained from TCI (Tokyo Chemical Industry) and used without additional purification.

Monomer synthesis

3,3'-Di-*tert*-butyl-5,5',6,6'-tetramethyl-2,2'-dimethoxy-1,1'-biphenyl (BiphenMe₂) Sodium hydride (NaH, 0.90 g, 0.0375 mol) was slowly added into a flask containing H₂[Biphen] (5.0 g, 0.0141 mol) and anhydrous tetrahydrofuran (THF, 40 mL) at 0 °C. The suspension was stirred at ambient temperature for 2 h. Then, methyl iodide (3 mL) was added dropwise, and the reaction was stirred for 15 h. THF was depleted by distillation, and then diethyl ether (150 mL) was added. NaH was filtered out, and the filtrate was concentrated by rotatory evaporation to afford BiphenMe₂ (5.2 g, 96%). ¹H NMR (500 MHz, CDCl₃): δ 7.12 (s, 2H), 3.12 (s, 6H), 2.26 (s, 6H), 1.90 (s, 6H), 1.38 (s, 18H). ¹³C NMR (125 MHz, CDCl₃): δ 155.73, 139.55, 134.58, 132.52, 130.50, 127.19, 59.29, 34.60, 30.79, 20.47, 16.61.

2,2'-Bis(bromomethyl)-5,5'-di-*tert*-butyl-3,3'-bis(dibromomethyl)-6,6'-dimethoxy-1,1'-biphenyl (Br-BiphenMe₂) BiphenMe₂ (5.0 g, 0.0131 mol), *N*-bromosuccinimide (NBS, 23.3 g, 0.131 mol), 2,2'-azobis(2-methylpropionitrile) (AIBN, 1.07 g, 0.00655 mol), and anhydrous carbon tetrachloride (150 mL) were stirred in a flask at 90 °C for 14 h. The mixture was cooled and filtered, and the filtrate was concentrated by rotatory evaporation. The residual solid was washed by hexane (2×50 mL) and methanol (4×50 mL), and dried at 90 °C in vacuum to give Br-BiphenMe₂ (8.73 g, 78%). ¹H NMR (500 MHz, CDCl₃): δ 8.14 (s, 2H), 7.28 (s, 2H), 4.35–4.24 (m, 4H), 3.24 (s, 6H), 1.44 (s, 18H). ¹³C NMR (125 MHz, CDCl₃): δ 157.59, 145.64, 136.22, 130.69, 130.29, 128.73, 59.63, 38.19, 35.60, 30.36, 27.09.

3,3'-Di-*tert*-butyl-2,2'-dimethoxy-[1,1'-binaphthalene]-6,6',7,7'-tetracarboxylic acid (TNTTA) Br-BiphenMe₂ (6.42 g, 0.0075 mol), sodium iodide (15.0 g, 0.100 mol), and maleic anhydride (3.0 g, 0.030 mmol) were combined into a Schlenk flask under nitrogen. Then, anhydrous DMF (50 mL) was added with a syringe. After stirred at 90 °C for 30 h, the mixture was precipitated with 10 wt% sodium bisulfite aqueous solution. The solid was filtered, washed with DI water, dried under vacuum to yield the crude product. Afterwards, the crude product was dissolved in NaOH aqueous solution (10 wt%, 20 g), filtered to remove insoluble impurities, and neutralized with concentrated HCl (13.5 g). The precipitate was collected, washed three times with deionized water, and dried at 100 °C in vacuum for 16 h to afford TNTTA (1.62 g, 36%). ¹H NMR (500 MHz, DMSO-*d*₆): δ 12.96 (s, 4H), 8.41 (s, 2H), 8.25 (s, 2H), 7.43 (s, 2H), 3.08 (s, 3H), 1.51 (s, 18H). ¹³C NMR (125 MHz, DMSO-*d*₆): δ 169.17, 168.93, 159.08, 145.78, 132.45, 130.24, 130.15, 129.40, 128.07, 126.17, 123.91, 60.24, 36.00, 30.67.

3,3'-Di-*tert*-butyl-2,2'-dimethoxy-[1,1'-binaphthalene]-6,6',7,7'-tetracarboxylic dianhydride (TNTDA) TNTTA (2.0 g, 0.0033 mol) was refluxed in acetic anhydride (20 g) for 9 h. After cooling, the precipitate was collected by filtration, washed with acetic anhydride (2×10 mL) and diethyl ether (3×10 mL), and dried at 180 °C under vacuum for 12 h to yield TNTDA (1.64 g, 87% yield). ¹H NMR (500 MHz, CDCl₃): δ 8.60 (s, 2H), 8.25 (s, 2H), 7.74 (s, 2H), 3.06 (s, 6H), 1.56 (s, 18H). ¹³C NMR (125 MHz, CDCl₃): δ 163.24, 162.60, 161.79, 149.09, 136.69, 133.08, 129.73, 128.35, 126.77, 124.98, 124.62, 123.74, 60.31, 36.29, 30.17. Elem. Anal. Calcd. for C₃₄H₃₀O₈: C, 72.07; H, 5.34; Found: C, 72.14; H, 5.26.

***N,N*-diphenyl-3,3'-di-*tert*-butyl-2,2'-dimethoxy-[1,1'-binaphthalene]-6,6',7,7'-tetracarboxydi-imide (TNTDI)** TNTDA (1.318 g, 0.00233 mol), aniline (0.455 g, 0.0049 mol), and *m*-cresol (9 g) were stirred in a three-necked flask at 100 °C for 1 h, then 180 °C for 10 h. After cooling, the solution was poured into ethanol (100 mL). The solid was collected by filtration, Soxhlet extracted with ethanol for 8 h, and dried at 100 °C in vacuum for 10 h to yield TNTDI (1.18 g, 71 %). The single crystal of TNTDI was prepared by slowly recrystallization from its DMF solution. ¹H NMR (500 MHz, DMSO-*d*₆): δ 8.81 (s, 2H), 8.55 (s, 2H), 7.73–7.33 (m, 12H), 3.09 (s, 6H), 1.55 (s, 18H). ¹³C NMR (125 MHz, DMSO-*d*₆): δ 167.09, 166.96, 160.40, 146.79, 135.49, 132.71, 132.49, 130.15, 129.24, 128.68, 128.57, 127.87, 126.88, 126.24, 125.43, 120.59, 60.58, 36.17, 30.61. Crystal data: C₄₆H₄₀N₂O₆, colorless, *fw* = 716.80; monoclinic, P 2/n; a = 12.5498(14)

\AA , $b = 9.3561(10) \text{\AA}$, $c = 20.332(2) \text{\AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 93.893(2)$; $V = 2381.8 (5) \text{\AA}^3$, $Z = 2$; $T = 293(2) \text{K}$, $R_1 [I > 2\sigma(I)] = 0.0540$, $\omega R_2 (\text{all data}) = 0.1669$; $\text{GOF} = 1.028$.

3,3'-(Mesitylmethylene)bis(2-methyl-8-nitrodibenzo[b,e][1,4]dioxine) (MMBMN) MMBMD (2.0 g 0.0053 mol), 3,4-difluoronitrobenzene (1.77 g, 0.0111 mol), K_2CO_3 (4.6 g 0.0333 mol), and DMF (30 mL) were stirred in a flask under nitrogen for 8 h at 80 °C. Afterwards, the mixture was poured into DI water, and the solid was collected by filtration, washed completely with DI water. The crude product was purified by silica-gel column chromatography with ethyl acetate/petroleum ether (1:3) as an eluent to yield MMBMN as a yellow solid (2.6 g, 79%). ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 7.90–7.79 (m, 2H), 7.77–7.57 (m, 2H), 7.22–7.13 (m, 1H), 7.05 (d, $J=8.8$ Hz, 1H), 6.99–6.75 (m, 4H), 6.24 (s, 2H), 5.46 (s, 1H), 2.21 (s, 3H), 2.13–1.74 (m, 12H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): δ 146.37, 142.57, 140.79, 137.80, 137.49, 135.86, 135.23, 133.76, 133.39, 132.99, 129.83, 119.85, 117.51, 116.35, 115.80, 111.29, 45.60, 25.77, 20.92, 19.74, 17.56.

7,7'-(Mesitylmethylene)bis(8-methyldibenzo[b,e][1,4]dioxin-2-amine) (MMBMA) Hydrazine hydrate (8 mL, 99%) was added dropwise into a 500 mL flask with MMBMN (2.5 g 0.0041 mol), Pd/C (0.37 g, 10% Pd), and ethanol (150 mL). After stirring at 90 °C for 8 h, the mixture was filtrated to remove the catalyst. The filtrate was concentrated by rotatory evaporation. The solid was washed with ethanol (3×10 mL), and dried at 100 °C under vacuum to yield MMBMA (1.87 g, 83%). ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 6.87–6.76 (m, 4H), 6.64 (d, $J=8.6$ Hz, 1H), 6.56 (d, $J=8.5$ Hz, 1H), 6.20–6.05 (m, 6H), 5.42 (s, 1H), 4.96 (s, 4H), 2.22 (s, 3H), 2.10–1.70 (m, 12H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): δ 144.96, 140.90, 139.06, 138.72, 135.83, 134.90, 134.37, 131.71, 131.17, 130.98, 129.74, 117.33, 115.86, 115.50, 108.21, 100.95, 45.56, 21.03, 19.74, 17.54. Anal. Calcd. for $\text{C}_{36}\text{H}_{32}\text{N}_2\text{O}_4$: C, 77.68; H, 5.79; N, 5.03; Found: C, 77.49; H, 5.82; N, 5.17.

3,3'-(9H-fluorene-9,9-diyl)bis(2-methyl-8-nitrodibenzo[b,e][1,4]dioxine) (FDBMN) FDBMN was synthesized using an analogous procedure to MMBMN, yield: 76%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 7.96 (d, $J=7.5$ Hz, 2H), 7.87–7.75 (m, $J=8.3$ Hz, 2H), 7.71–7.59 (m, $J=27.4$ Hz, 2H), 7.52–7.38 (m, 4H), 7.38–7.26 (m, $J=7.4$ Hz, 2H), 7.15–6.95 (m, $J=50.2, 8.0$ Hz, 2H), 6.86–6.71 (m, $J=19.9$ Hz, 2H), 6.29 (s, 2H), 2.56–2.49 (m, 1H), 1.94 (s, 5H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): δ 150.73, 147.19, 143.55, 141.65, 139.91, 139.53, 138.82, 138.24, 133.46, 128.69, 125.90, 121.26, 120.83, 120.47, 117.38, 112.29, 65.16, 26.80, 21.99.

7,7'-(9H-fluorene-9,9-diyl)bis(8-methyldibenzo[b,e][1,4]dioxin-2-amine) (FDBMA) FDBMA was synthesized using an analogous procedure to MMBMA, Yield: 80%. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 7.94 (d, $J=7.4$ Hz, 2H), 7.62–7.23 (m, 6H), 6.90–6.46 (m, 4H), 6.40–5.96 (m, 6H), 5.24–4.79 (m, 4H), 2.24–1.61 (m, 6H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): δ 150.33, 144.91, 140.71, 139.46, 138.79, 138.14, 137.71, 137.12, 130.83, 130.32, 127.70, 127.37, 124.88, 120.05, 119.25, 115.87, 113.61, 108.23, 100.88, 64.18, 20.84. Elem. Anal. Calcd. for $\text{C}_{39}\text{H}_{28}\text{N}_2\text{O}_4$: C, 79.57; H, 4.79; N, 4.76; Found: C, 79.48; H, 4.84; N, 4.72.

Polymer preparation

Polyimides in this study were synthesized *via* an ester-acid procedure devised by McKeown.⁶ A representative process is shown as below: TNTDA (1.5328 g, 0.0027 mol), triethylamine (1.64 g, 0.0162 mol), and ethanol (20 mL) were added to a flask equipped with a magnetic stirrer under nitrogen atmosphere. After refluxing at 90 °C for 2 h, ethanol and excessive triethylamine were depleted using a Dean-Stark trap. Then, TBDA1 (0.7585 g, 0.0027 mol) in anhydrous 1-methyl-2-pyrrolidinone (NMP 7 g) was added. After heated at 90 °C for 2 h and 190 °C for 8 h, the viscous solution was poured into methanol (100 mL). The polymer was collected, Soxhlet extracted using methanol for 48 h. Afterwards, the product was dissolved in CHCl_3 and then re-precipitated in ethanol, dried under vacuum at 130 °C for 10 h to yield polyimide TNTDA-TBDA1 (1.82g, 83%).

Membrane fabrication

Polyimides solution in CHCl_3 (3wt%) was filtering onto glass plates using 0.45 μm PTFE filters. The solvent was removed by evaporation at room temperature for 72 h. The membrane was peeled off and dried at 120 °C for 10 h under vacuum to deplete any residual solvent. Afterwards, the membrane was immersed in methanol for 24 h, and dried at 120 °C under vacuum for 24 h before characterizations.

Characterization

X-ray crystallographic data were obtained using a Bruker SMART APEX diffractometer with a CCD area detector and a graphite monochromated Mo K α radiation ($\lambda=0.71073 \text{ \AA}$). Fourier transform infrared (FT-IR) spectra were collected by using a Bio-Rad Digilab Division FTS-80 spectrometer. ^1H NMR and ^{13}C NMR spectra were carried out on a Bruker DPX 500 (500 MHz) instruments. Elemental analysis was performed using the MOD-1106 elemental analyzer (Carl Erba, Italy). Gel permeation chromatography (GPC) was recorded on a Waters 1500 GPC instrument with a Waters 2414 differential refractive-index detector. DMF was used as the eluent with a flowrate of 1.0 mL min^{-1} . Tensile properties were measured using an Instron material testing system (Model 5982) with a constant displacement rate of 5.0 mm min^{-1} . Thermogravimetric analysis was performed using a TGA Q50 system (TA Instruments) at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ under nitrogen. N_2 sorption isotherms at 77 K and CO_2 sorption measurements at 273 K were measured using a Micromeritics ASAP 2020 HD88 surface area analyzer. Wide-angle X-ray diffraction (WAXD) was performed on a Nano-inXider system (Xenocs, France) equipped with a semiconductor detector (Pilatus 100 K, DECTRIS, Swiss) attached to a multilayer focused Cu K α X-ray source. Film density (ρ) was determined by using a density balance (FA2104J, Shanghai) at an accuracy of 0.1 mg. FFV was calculated by the following equation:

$$FFV = 1 - \frac{1.3\rho V_w}{M}$$

where M is the molar mass (g mol^{-1}) of the repeat unit, V_w represents the van der Waals volume calculated by a literature method.^{7,8}

Pure gas permeability (P) was measured using a PERME VAC-2 permeation system at 1 atm and $25 \text{ }^\circ\text{C}$ by the constant-volume/variable-pressure method. P was calculated by the following equation:

$$P = D \times S = \frac{V_d l}{AT p_{up} \times 0.278} \times \frac{dp}{dt} \times 10^{10}$$

where P is permeability, p_{up} is the upstream pressure (cmHg), dp/dt is the increase rate of pressure in the steady state, V_d is the calibrated permeate volume, l is the thickness, A is the effective area, and T is the temperature. Diffusion coefficient (D) was calculated from $D = l^2/6\theta$, where θ is the time lag of the permeability measurement. Solubility coefficient (S) was calculated from $S = P/D$.

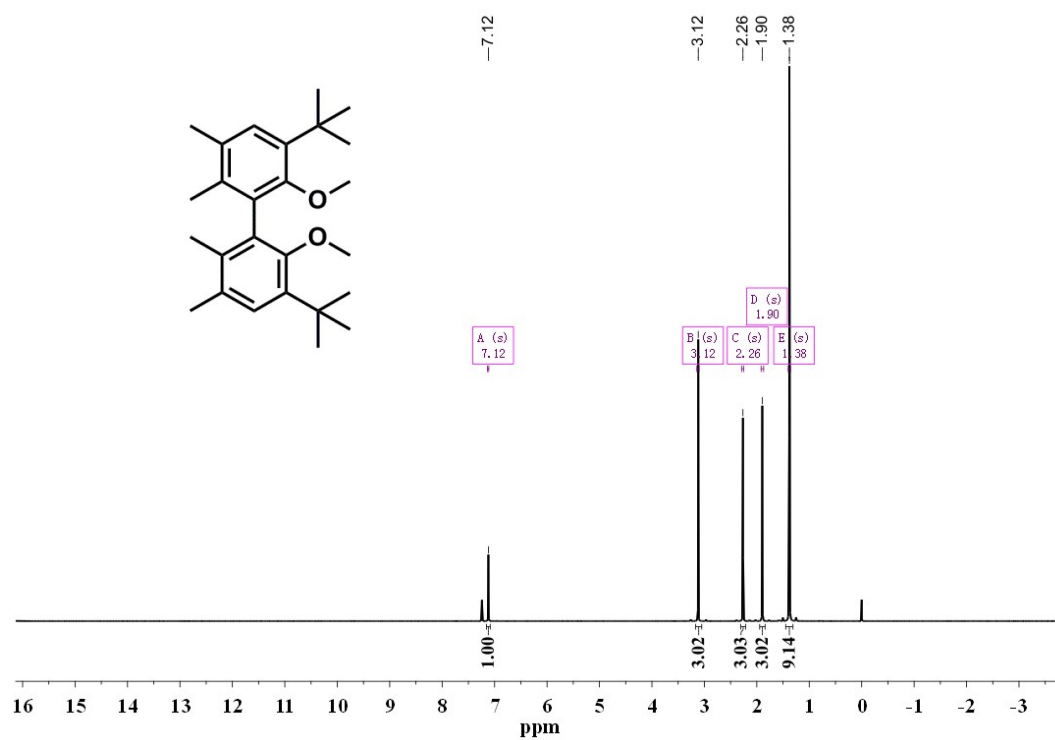


Figure S1. ¹H NMR spectrum of BiphenMe₂.

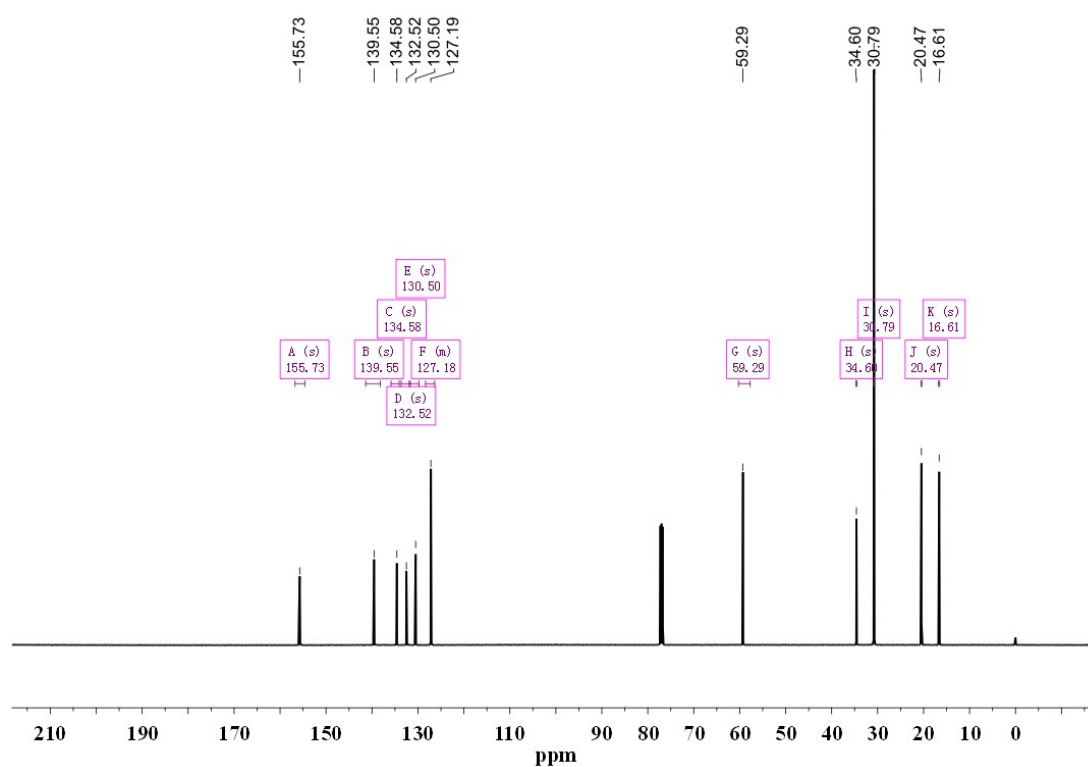


Figure S2. ¹³C NMR spectrum of BiphenMe₂.

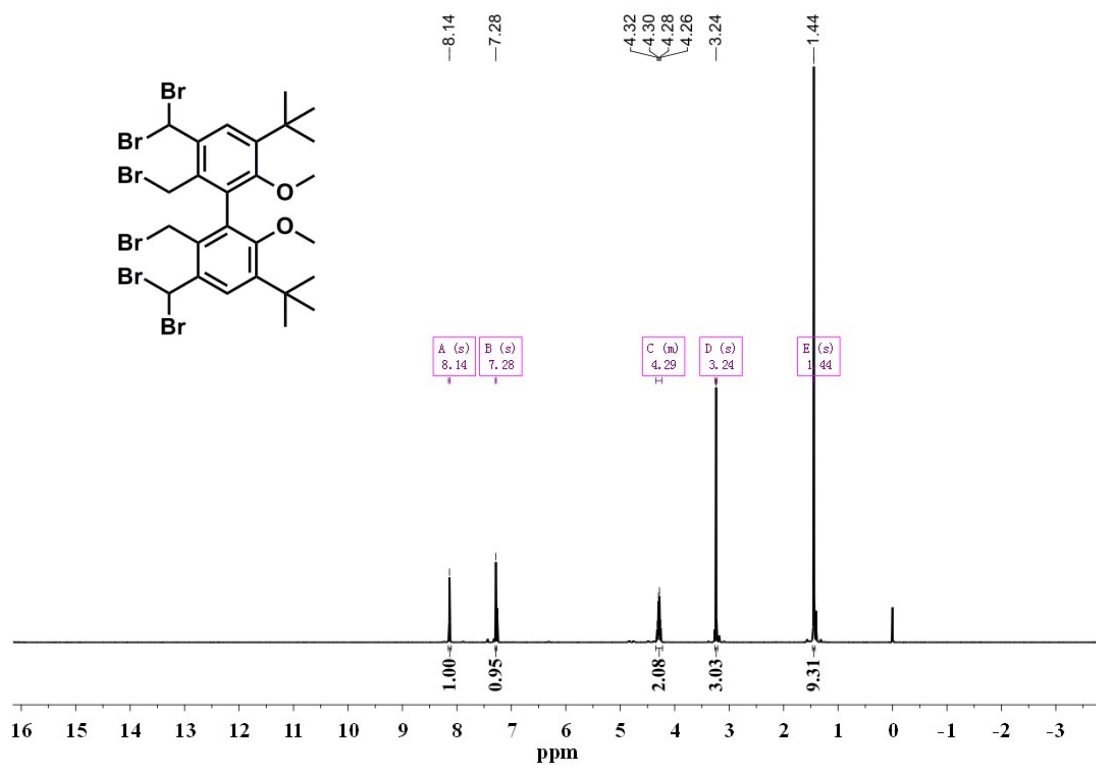


Figure S3. ^1H NMR spectrum of Br-BiphenMe₂.

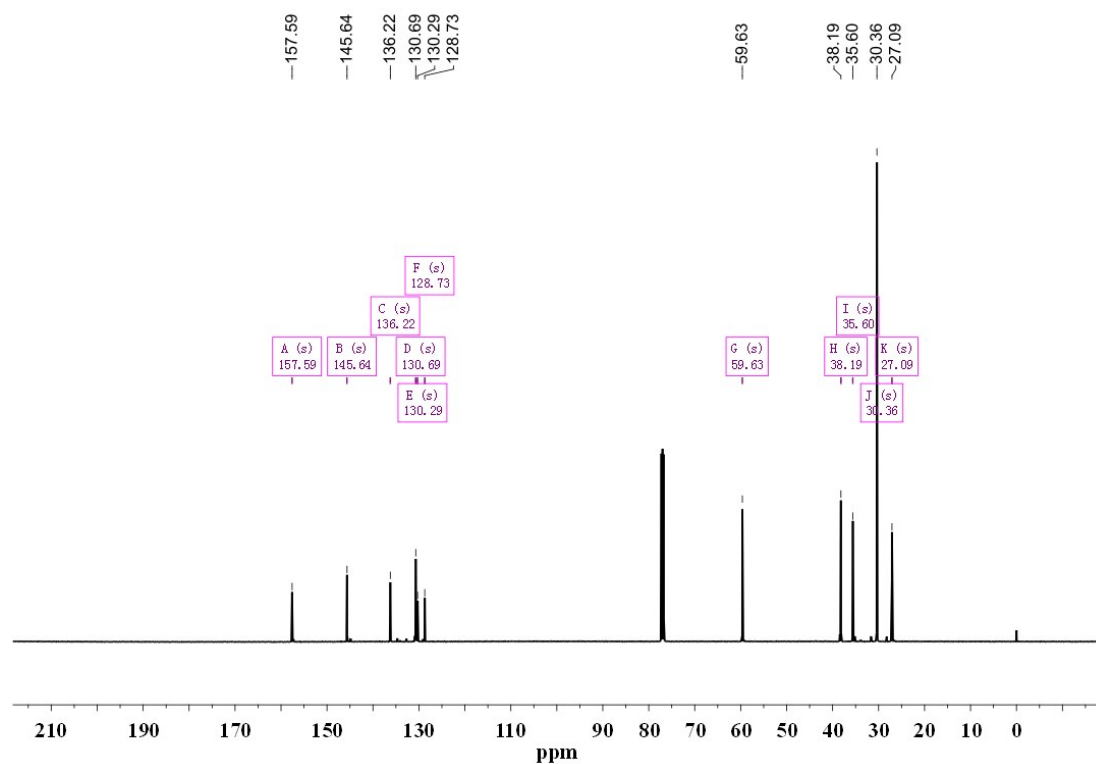


Figure S4. ^{13}C NMR spectrum of Br-BiphenMe₂.

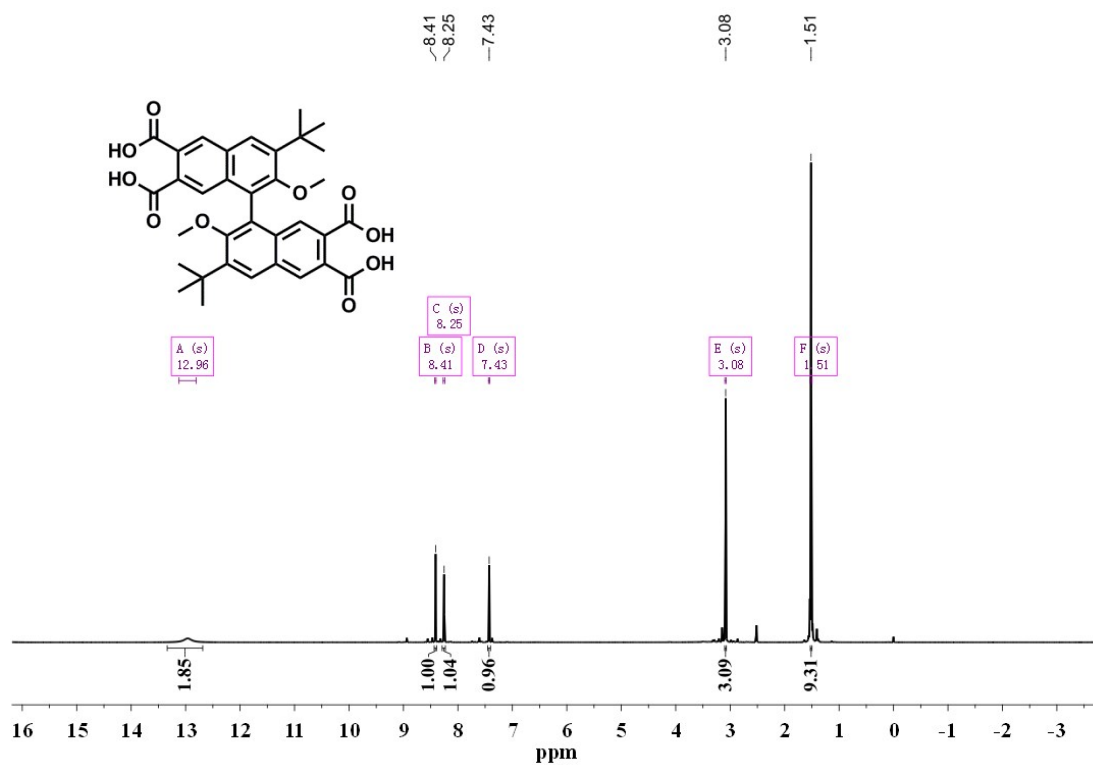


Figure S5. ^1H NMR spectrum of TNTTA.

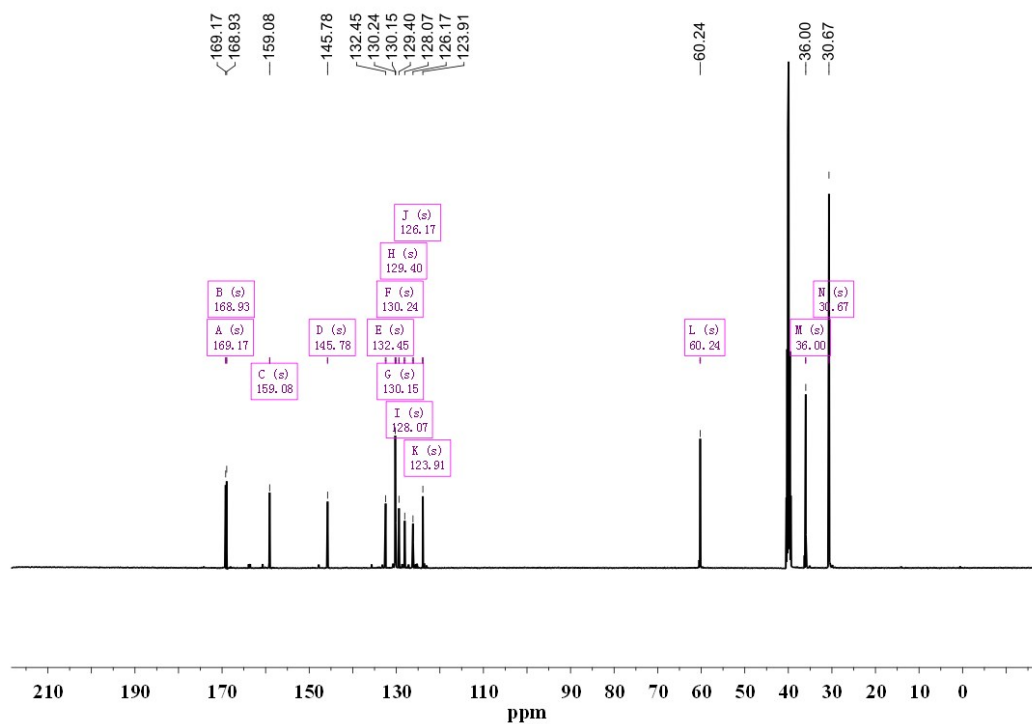


Figure S6. ^{13}C NMR spectrum of TNTTA.

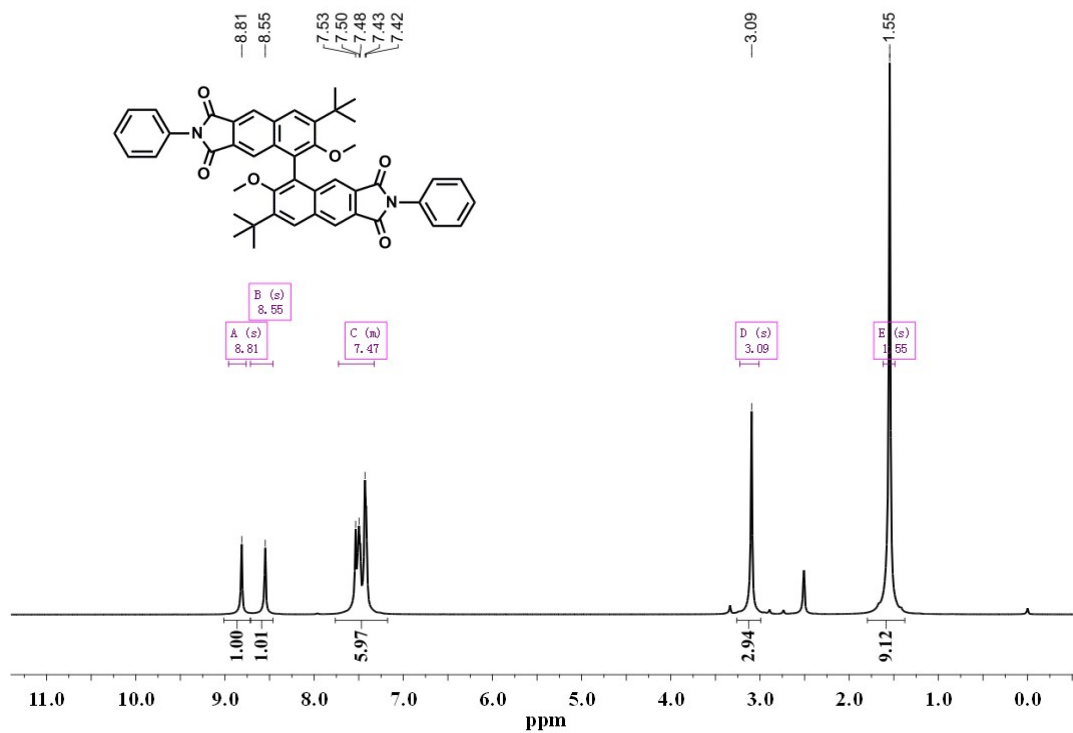


Figure S7. ^1H NMR spectrum of TNTDI.

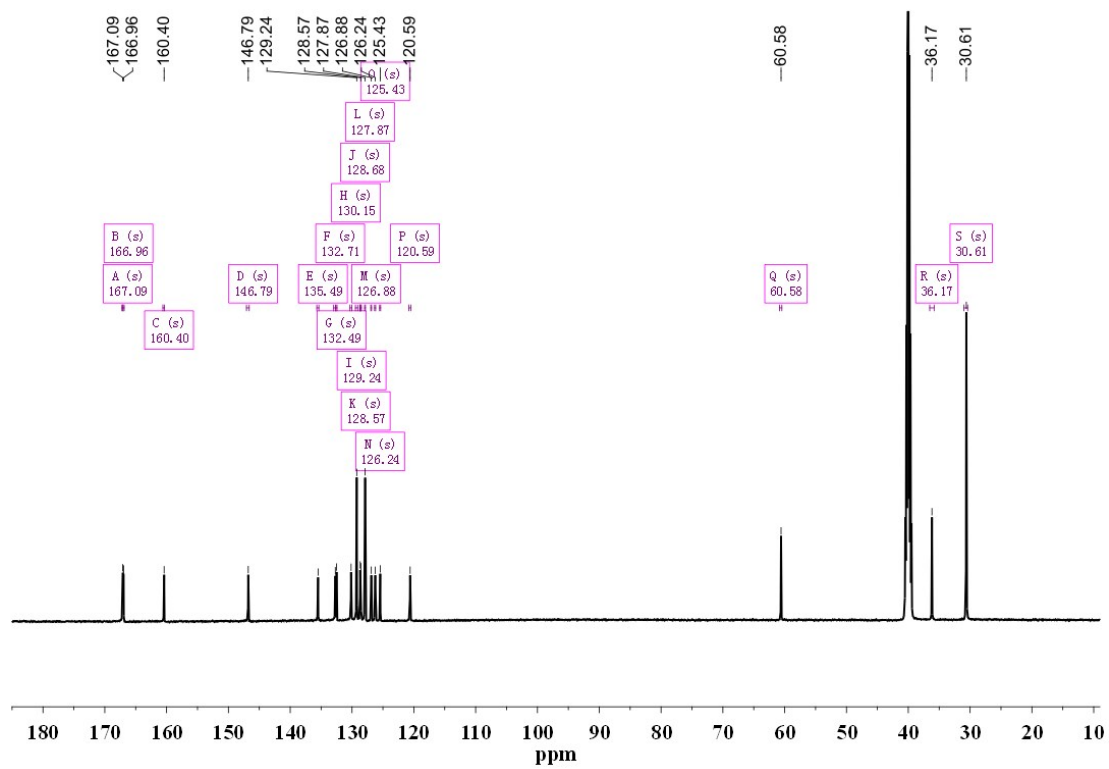


Figure S8. ^{13}C NMR spectrum of TNTDI.

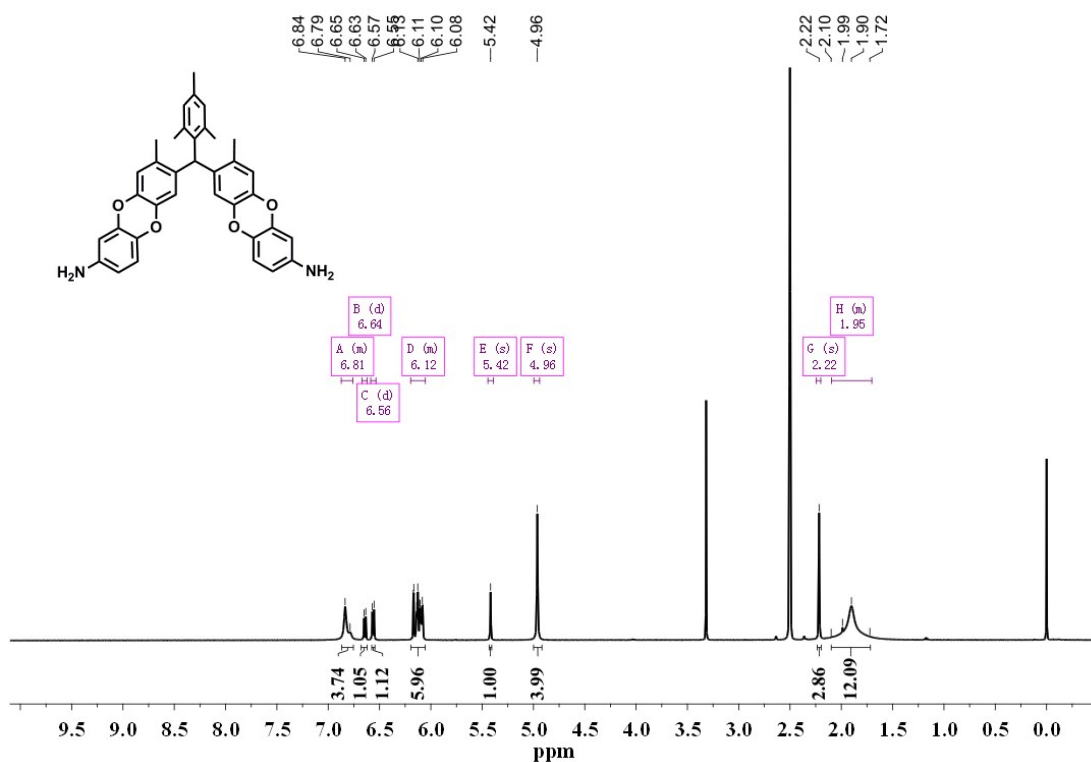


Figure S9. ¹H NMR spectrum of MMBMA.

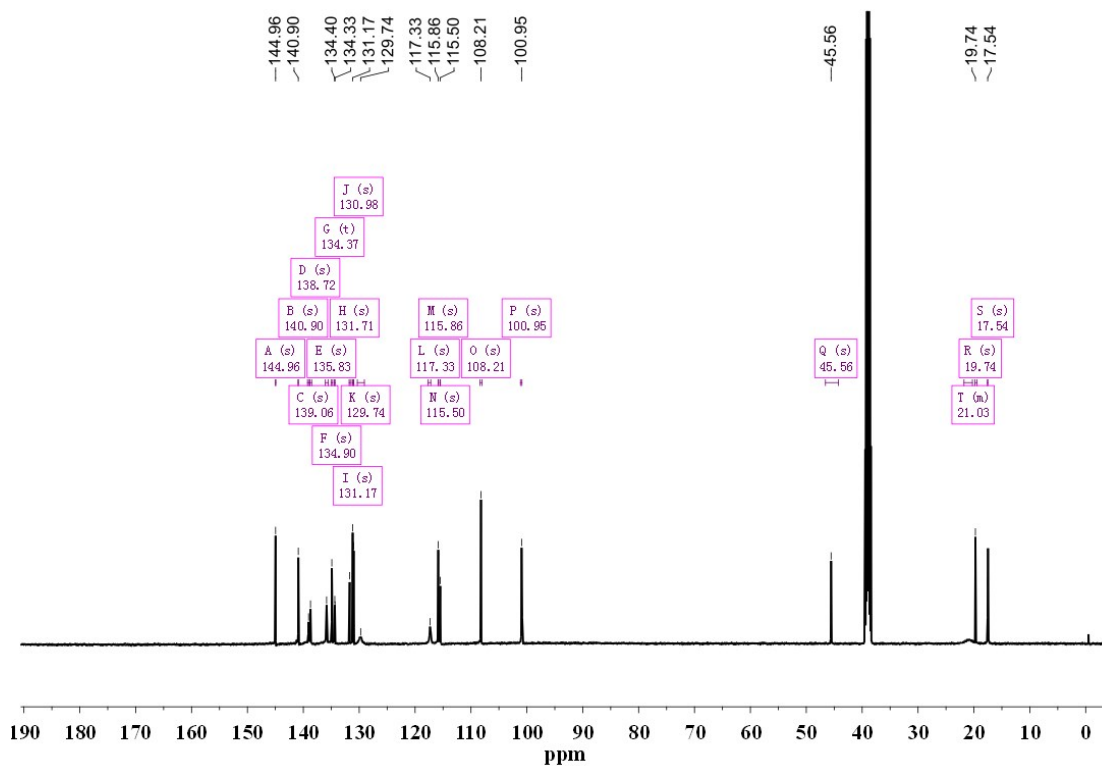


Figure S10. ¹³C NMR spectrum of MMBMA.

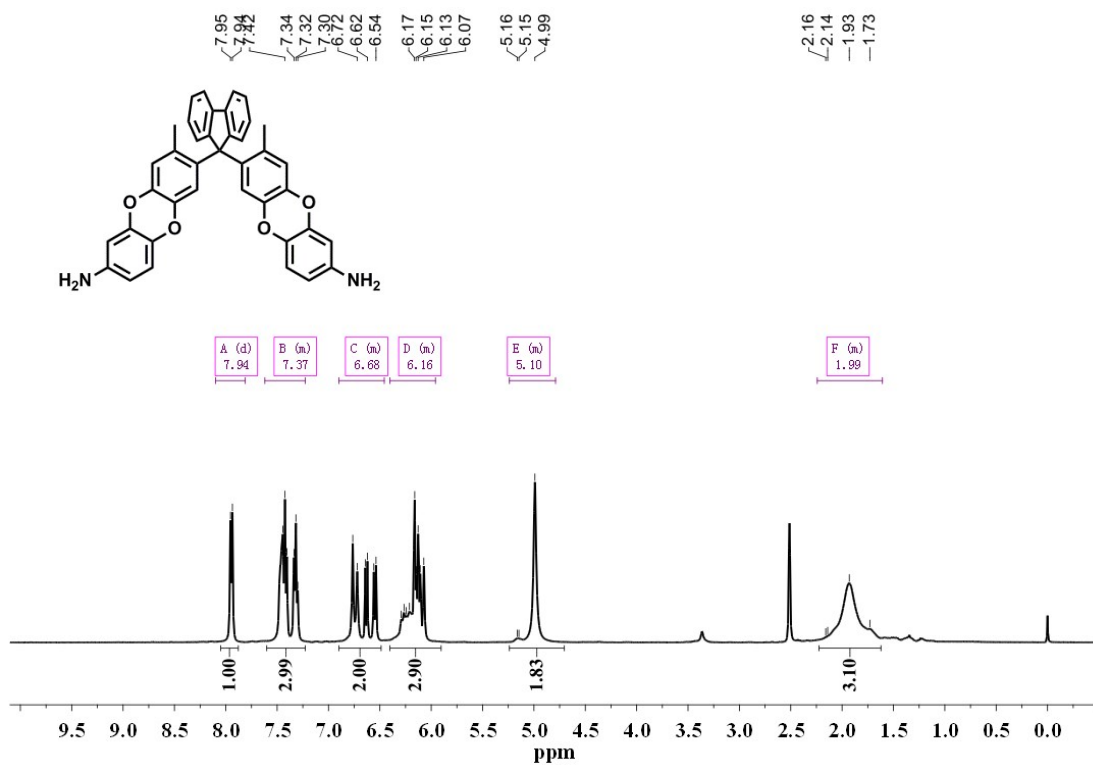


Figure S11. ^1H NMR spectrum of FDBMA.

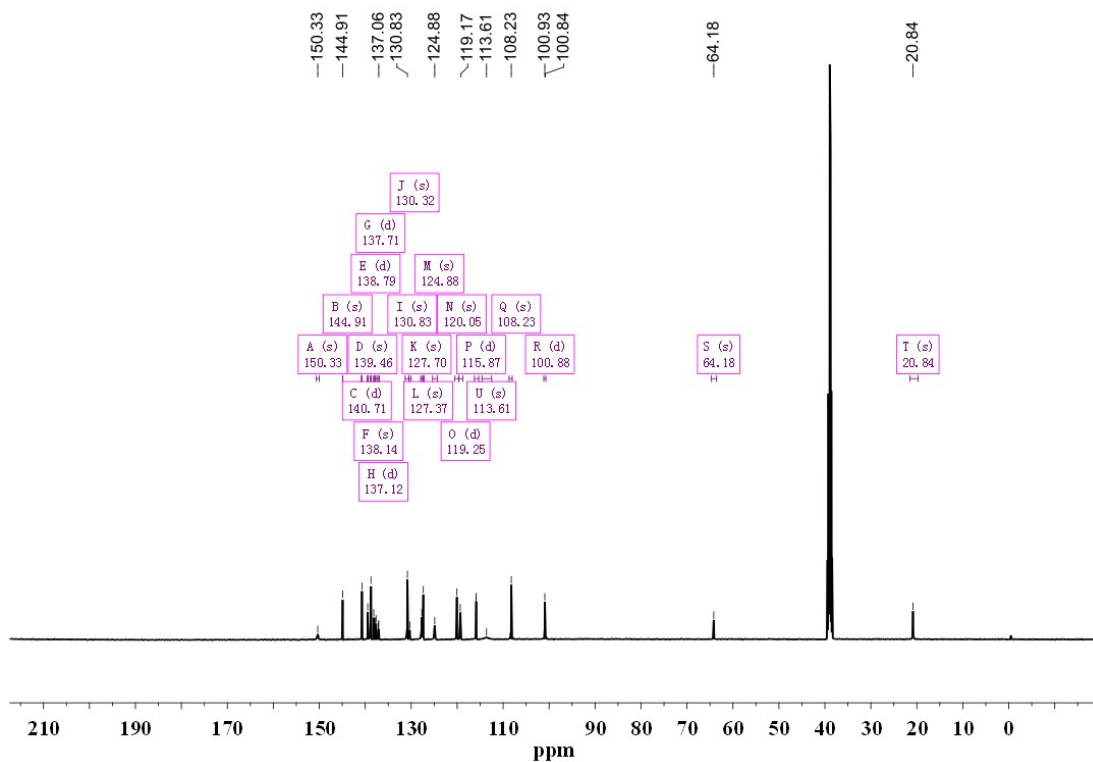


Figure S12. ^{13}C NMR spectrum of FDBMA.

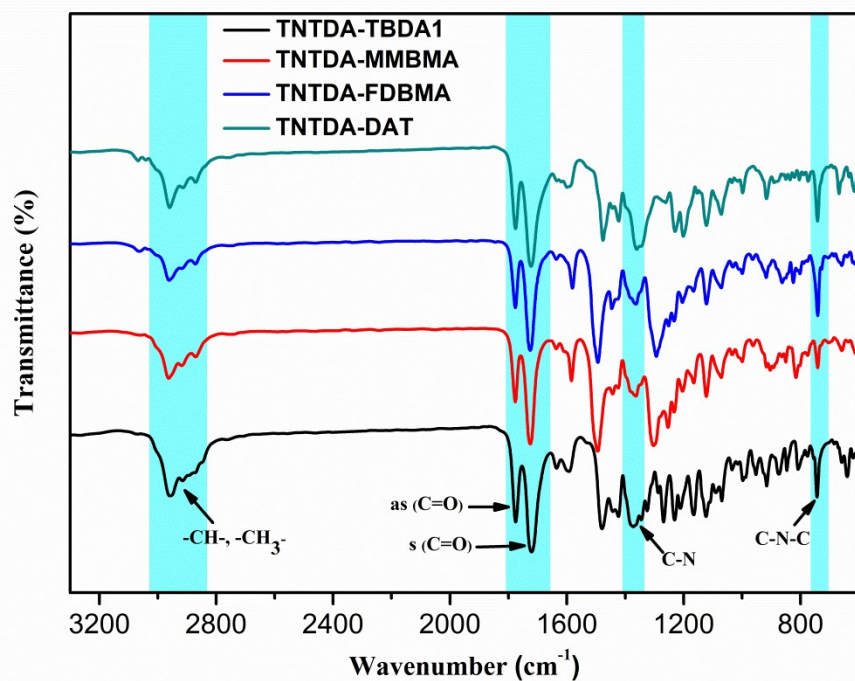


Figure S13. FTIR spectra of TNTDA-derived PIM-PIs.

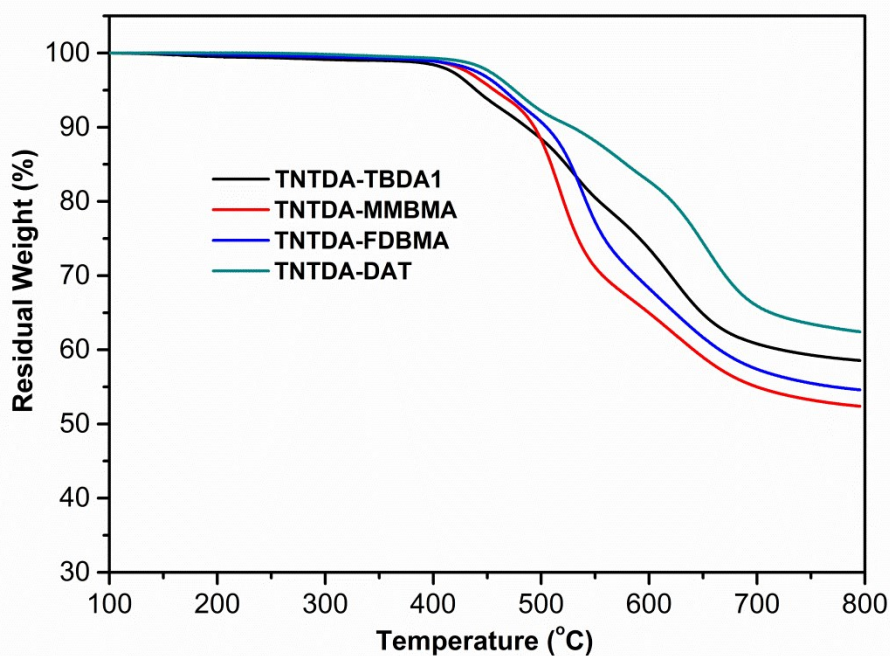


Figure S14. TGA curves of TNTDA-derived PIM-PIs.

Table S1. Solubility of TNTDA-based PIM-PIs

Polyimide	<i>m</i> -Cresol	NMP	DMAc	DMSO	CHCl ₃	CHCl ₂	THF
TNTDA-TBDA1	+	+	+	+	+	+	+
TNTDA-MMBMA	+	+	+	+	+	+	+
TNTDA-FDBMA	+	+	+	+	+	+	+
TNTDA-DAT	+	+	+	+	+	+	+

+: Soluble at room temperature; NMP: 1-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMSO: dimethylsulfoxide; CHCl₃: chloroform; CH₂Cl₂: dichloromethane; THF: tetrahydrofuran.

Table S2. Molecular weights, and mechanical and thermal properties of TNTDA-based PIM-PIs

Polyimides	M_n (kg mol ⁻¹)	M_w (kg mol ⁻¹)	Polydispersity $\frac{M_w}{M_n}$	Tensile strength (MPa)	Modulus (GPa)	Elongation at break (%)	$T_d^{5\%}$ (°C)
TNTDA-TBDA1	74	135	1.83	70	1.6	5.2	440
TNTDA-MMBMA	61	128	2.10	74	1.5	6.7	457
TNTDA-FDBMA	58	112	1.94	77	1.6	5.6	466
TNTDA-DAT	64	131	2.05	66	1.5	4.8	475

References

- S1. R. Martin and P. Demerseman, *Synthesis*, 1989, **1989**, 25-28.
- S2. J. B. Alexander, R. R. Schrock, W. M. Davis, K. C. Hultsch, A. H. Hoveyda and J. H. Houser, *Organometallics*, 2000, **19**, 3700-3715.
- S3. Z. Wang, D. Wang, F. Zhang and J. Jin, *ACS Macro Lett.*, 2014, **3**, 597-601.
- S4. C. Zhang, L. Fu, Z. Tian, B. Cao and P. Li, *J. Membr. Sci.*, 2018, **556**, 277-284.
- S5. S. Zhao and M. M. Abu-Omar, *Macromolecules*, 2017, **50**, 3573-3581.
- S6. M. Lee, C. G. Bezzu, M. Carta, P. Bernardo, G. Clarizia, J. C. Jansen and N. B. McKeown, *Macromolecules*, 2016, **49**, 4147-4154.
- S7. A. Bondi, *J. Phy. Chem.*, 1964, **68**, 441-451.
- S8. W. M. Lee, *Polym. Eng. Sci.*, 1980, **20**, 65-69.