

Supplementary information (SI) for

**Microporous polyimide networks constructed through a two-
step polymerization approach and their carbon dioxide
adsorption performance**

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A. Supplementary Method

1. Materials

4-Bromophenyl hydroquinone (BrPHQ) was synthesized according to the literature.¹ 1,3,5-Tris(4-aminophenyl)benzene, tris(4-aminophenyl)amine and tetrakis(4-aminophenyl)methane were synthesized according to the literature.^{2,3} Cesium carbonate (Cs_2CO_3), diphenyl sulfone and 4-nitrophthalonitrile were purchased from Energy chemical (China). Phenylacetylene was purchased from TCI chemical company. Bis(triphenylphosphine) palladium(II) chloride ($\text{PdCl}_2(\text{PPh}_3)_2$) was purchased from Sigma-Aldrich Co. LLC. Cuprous iodide (CuI), triphenylphosphine (PPh_3), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), isoquinoline and trimethylamine (TEA) were purchased from Aladdin Reagents Co., Ltd. (China). Acetic anhydride, acetic acid, acetonitrile and acetone were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd (China).

2. Synthesis of 2, 5-bis(3, 4-dicarboxyphenoxy) -4'-phenylethynyl biphenyl dianhydride (PEPHQDA)

(1) Synthesis of 2, 5-bis(3, 4-dicyanophenoxy)-4'-bromo-biphenyl (ii)

A mixture of BrPHQ (i) (15.91 g, 60 mmol), 4-nitrophthalonitrile (22.85 g, 132 mmol), Cs_2CO_3 (21.50 g, 66 mmol) were dissolved in DMF (130 mL) and stirred at room temperature for about 36 h. The resulting solution was poured into deionized water (1.5 L) to precipitate solid, which was collected and washed thoroughly with water. The crude product was recrystallized from acetonitrile to afford white powder. Yield: 83%. Mp: 243 °C (DSC in N_2). MALDI-TOF MS: $m/z=516.3$. IR (KBr): 2231 cm^{-1} ($\text{C}\equiv\text{N}$), 1009 cm^{-1} (C-Br). $^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$): δ 8.143-8.172 (d, $J=11.6\text{ Hz}$, 1H), 8.051-8.080 (d, $J=11.6\text{ Hz}$, 1H), 7.934-7.942 (d, $J=3.2\text{ Hz}$, 1H), 7.799-7.807 (d, $J=3.2\text{ Hz}$, 1H), 7.616-7.625 (d, $J=3.6\text{ Hz}$, 1H), 7.587-7.596 (m, 1H), 7.555-7.570 (m, 1H), 7.418-7.461 (m, 4H), 7.386 (s, 1H), 7.326-7.364 (m, 1H).

(2) Synthesis of 2, 5-bis(3, 4-dicyanophenoxy)-4'-phenylethynyl-biphenyl (iii)

In a 250 mL three-necked flask, the 2, 5-bis(3, 4-dicyanophenoxy)-4'-bromo-

biphenyl (ii) (10.35 g, 20 mmol) and triphenylphosphine (0.23 g, 0.86 mmol) were dissolved in 50 mL of DMAc under a nitrogen flow. To the solution phenyl acetylene (2.25 g, 22 mmol), PdCl₂(PPh₃)₂ (0.09 g, 0.12 mmol) and triethylamine (40 mL) were added. The mixture was slowly heated to 60 °C, and then CuI (0.06 g, 0.29 mmol) was added with 40 mL triethylamine. The reaction mixture was heated to 80 °C and maintained for 12 h. After cooling to room temperature, the reaction mixture was filtered to remove inorganic salts and evaporate the triethylamine. The concentrated product was poured into acidic water. The precipitated solid was filtered and recrystallized from acetonitrile and dried at 80 °C under vacuum to afford white powder. Yield: 87%. Mp: 140 °C (DSC in N₂). MALDI-TOF MS: m/z=537.3. IR (KBr): 2231 cm⁻¹ (C≡N). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.153-8.171 (d, J=7.2 Hz, 1H), 8.053-8.071 (d, J=7.2 Hz, 1H), 7.945-7.950 (d, J=2.0 Hz, 1H), 7.807-7.812 (d, J=2.0 Hz, 1H), 7.622-7.627 (d, J=2.0 Hz, 1H), 7.605-7.610 (d, J=2.0 Hz, 1H), 7.550 (m, 5H), 7.536-7.541 (d, J=2.0 Hz, 1H), 7.485-7.490 (d, J=2.0 Hz, 1H), 7.423-7.456 (m, 4H), 7.413 (s, 1H), 7.348-7.371 (m, 1H).

(3) Synthesis of 2, 5-bis(3, 4-dicarboxyphenoxy)-4'-phenylethynyl biphenyl (iv)
In a 250 mL flask, a mixture of 2, 5-bis(3, 4-dicyanophenoxy)-4'-phenylethynyl-biphenyl (iii) (8.10 g, 15 mmol) and potassium hydroxide (20.16 g, 360 mmol) were dissolved in 50% aqueous ethanol (140 mL) and stirred at a reflux temperature until no further ammonia was generated. The resulting clear solution was filtered hot to remove any insoluble impurities. After cooling to room temperature, the solution was acidified by concentrated hydrogen chloride to PH=2-3. The precipitated product was collected, washed for two or three times and dried at 60 °C under vacuum to give a white solid. Yield: 79%. Mp: 171 °C (DSC in N₂). MALDI-TOF MS: m/z=614.2. IR (KBr): 2500-3500 cm⁻¹ (O-H), 1705 cm⁻¹ (C=O), 1273 cm⁻¹ (C-O-C). ¹H NMR (400 MHz, DMSO-*d*₆): δ 12.5-14.5 (s, -COOH), 7.842-7.870 (d, J=11.2 Hz, 1H), 7.739-7.767 (d, J=11.2 Hz, 1H), 7.536-7.607 (m, 6H), 7.371-7.430 (m, 4H), 7.219-7.321 (m, 4H), 7.141 (s, 1H),

7.021-7.058 (m, 1H).

(4) Synthesis of 2, 5-bis (3, 4-dicarboxyphenoxy) -4'-phenylethynyl biphenyl dianhydride

In a 100 mL flask, 2, 5-bis (3, 4-dicarboxyphenoxy) -4'-phenylethynyl biphenyl (iv) (5 g, 8 mmol) was suspended in mixed solvent of acetic anhydride (25 mL) and acetic acid (25 mL). The suspension was reflux for 3 h. After the solution was cooled to room temperature, the product was filtered and dried overnight at 150 °C under vacuum. The crude product was further purified by column chromatography (dichloromethane) to afford a milky powder. Yield: 85%. Mp: 158 °C (DSC in N₂). MALDI-TOF MS: m/z=577.5. IR (KBr): 2218 cm⁻¹ (C≡C), 1851, 1776 cm⁻¹ (C=O). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.107-8.137 (m, 1H), 8.003-8.033 (m, 1H), 7.679-7.717 (m, 2H), 7.629 (s, 1H), 7.556-7.601 (d, J=2 Hz, 2H), 7.479-7.539 (m, 6H), 7.401-7.436 (m, 4H), 7.342-7.381 (m, 1H).

3. Synthesis of TAPB-HBPI, TAPA-HBPI and TAPM-HBPI.

The hyperbranched polyimides bearing amino end-groups (TAPB-HBPI, TAPA-HBPI and TAPM-HBPI) were synthesized by the polycondensation reaction of PEPHQDA with 1,3,5-tris(4-aminophenyl)benzene (TAPB), tris(4-aminophenyl)amine (TAPA) and tetrakis(4-aminophenyl)methane (TAPM), respectively, by using 1:1 monomer molar ratio. A typical polycondensation procedure, illustrated by preparation of the TAPA-HBPI, can be described as follows. TAPA (0.4355 g, 1.50 mmol) was first dissolved in NMP (20 mL) in a 100 mL three-necked round-bottomed flask under a nitrogen flow. To the mixture was added dropwise a solution of 2, 5-bis (3, 4-dicarboxyphenoxy) -4'-phenylethynyl biphenyl dianhydride (PEPHQDA) (0.8678 g, 1.50 mmol) in NMP (20 mL) through a dropping funnel with a duration of 2 h under mechanical stirring at room temperature. After the mixture was stirred for overnight, isoquinoline (12 drops) was added, and further stirred for 3 h at 120 °C. Then the mixture was heated at 180 °C for 24 h. After cooling to room temperature, the resultant polymer solutions were poured into an excess of ethanol (400 mL). The

polymers were collected by filtration and washed with ethanol for several times then dried under vacuum at 100 °C for 24 h.

4. Synthesis of TAPB-HBPI-CR, TAPA-HBPI-CR and TAPM-HBPI-CR.

A typical crosslinking procedure, illustrated by preparation of the TAPA-HBPI-CR, can be described as follows. The TAPA-HBPI and diphenyl sulfone was added in a thoroughly dried 100 mL, three-necked flask under anitrogen flow. The reaction mixture was heated to 360 °C for 24 h. After cooling to 150 °C, the mixture was poured slowly into acetone. The polymers were collected by filtration. Finally, the polymer was purified in a Soxhlet apparatus with acetone and dried at 100 °C for 24 h.

5. Synthesis of TAPB-HBPI-GEL, TAPA-HBPI-GEL and TAPM-HBPI-GEL.

The hyperbranched polyimide gels (TAPB-HBPI-GEL, TAPA-HBPI-GEL and TAPM-HBPI-GEL) were synthesized from PEPHQDA with 1,3,5-tris(4-aminophenyl)benzene (TAPB), tris(4-aminophenyl)amine (TAPA) and tetrakis(4-aminophenyl)methane (TAPM), respectively, by using 1:1 functional group ratio via the traditional one-step polycondensation gel reaction. A typical polycondensation procedure, illustrated by preparation of the TAPA-HBPI-GEL, can be described as follows. To a solution of TAPA (0.3484 g, 1.20 mmol) in m-cresol (16 mL) was added PEPHQDA (1.0413 g, 1.80 mmol), and the mixture was stirred for 2 h at 0 °C until all of the solids were dissolved. Several drops of isoquinoline were added prior to removal of the ice bath. After the mixture had reached room temperature, it was stirred for overnight. The polymerization reaction was carried out at 80 °C for 4 h, 160 °C for 4 h, 200 °C for 8 h, and 220 °C for 4 h. The mixture was cooled to room temperature. The polymer was washed sequentially with DMF and ethanol. Finally, the polymer was purified in a Soxhlet apparatus with acetone and dried at 100 °C for 24 h.

6. Measurements

FTIR spectra were measured on a Nicolet Impact 410 Fourier-transform infrared spectrometer. ¹H NMR spectra of the copolymers were measured on a

Bruker AVANCE NMR spectrometer (^1H , 300 MHz) using DMSO- d_6 as solvent and tetramethylsilane (TMS) as internal reference. Solid-state ^{13}C CP/MAS NMR measurements were recorded on a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 kHz and a CP contact time of 2 ms. All ^{13}C CP MAS chemical shifts are referenced to the resonances of an adamantane ($\text{C}_{10}\text{H}_{16}$) standard ($\delta \text{CH}_2 = 38.5$). Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC821e instrument at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from 100°C to 500°C under nitrogen. The thermal gravimetric analyses (TGA) were performed by a Perkin-Elmer TGA-1 thermo-gravimetric analyzer. The samples were evaluated in the range of $100\text{--}800\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen. Field emission scanning electron microscopy (FE-SEM) was performed on a SU8020 model HITACHI microscope. Transmission electron microscopy (TEM) was performed on a JEOL model JEM-2100 micro-scope. The sample was prepared by drop-casting an ethanol suspension of polymers onto a copper grid. The Atomistic calculation of crosslinked structure was conducted using Materials Studio software by successive geometry and molecular mechanics optimizing. Nitrogen sorption isotherms were measured at 77 K with a JW-BK 132F analyzer. Before measurement, the samples were degassed in a vacuum at $150\text{ }^\circ\text{C}$ for more than 10 h. The surface areas were calculated according to the Brunauer-Emmett-Teller (BET) model in the relative pressure (P/P_0) range from 0.10 to 0.20. To estimate pore size distributions of HBPI-CRs, nonlocal density functional theory (NLDFT) was applied to analyze the N_2 isotherm on the basis of the model of N_2 at 77 K on carbon with slit pores and the method of non-negative regularization. The particle sizes were measured by using Nano Measurer 1.2 software. The cross-linked structure was modeled using the Vienna ab initio simulation package (VASP) based on density functional theory (DFT). Projector augmented wave (PAW) potentials were adopted to simulate electron-ion interactions. Generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional was employed to approximate exchange and correlation effects for structural relaxation. In all calculations, the cut-off energy was set at 520 eV for the plane-

wave basis restriction. K-points were sampled under Monkhorst-Pack scheme for the Brillouin-zone integration. All atomic models were fully relaxed. In the atomic structure relaxation, self-consistency accuracy of 10^{-4} eV was reached for electronic loops. CO₂ adsorption isotherms were measured at 273 K and 298 K up to 1.0 bar.

B. Supplementary Figures

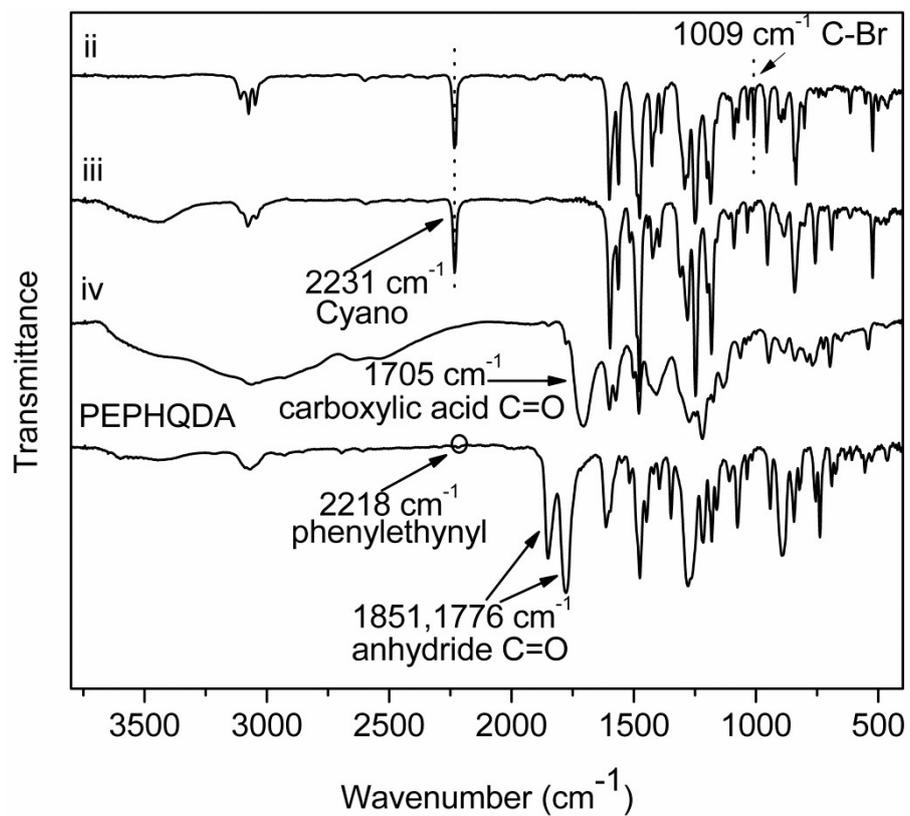


Figure S1. FTIR spectra of intermediate product (ii), (iii), (iv) and PEPHQDA.

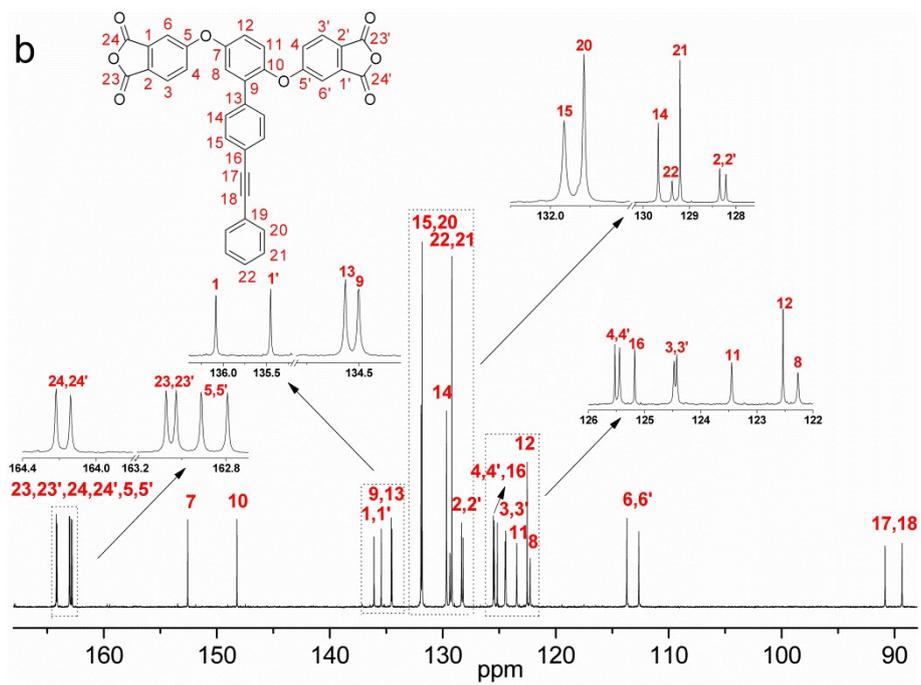
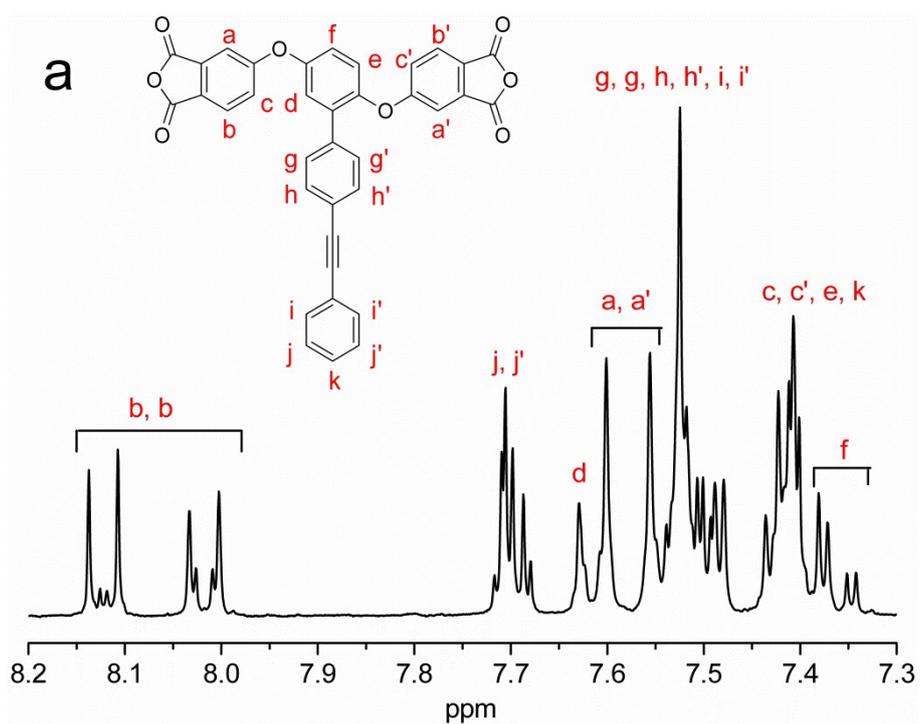


Figure S2. ^1H NMR and ^{13}C NMR spectra of PEPHQDA.

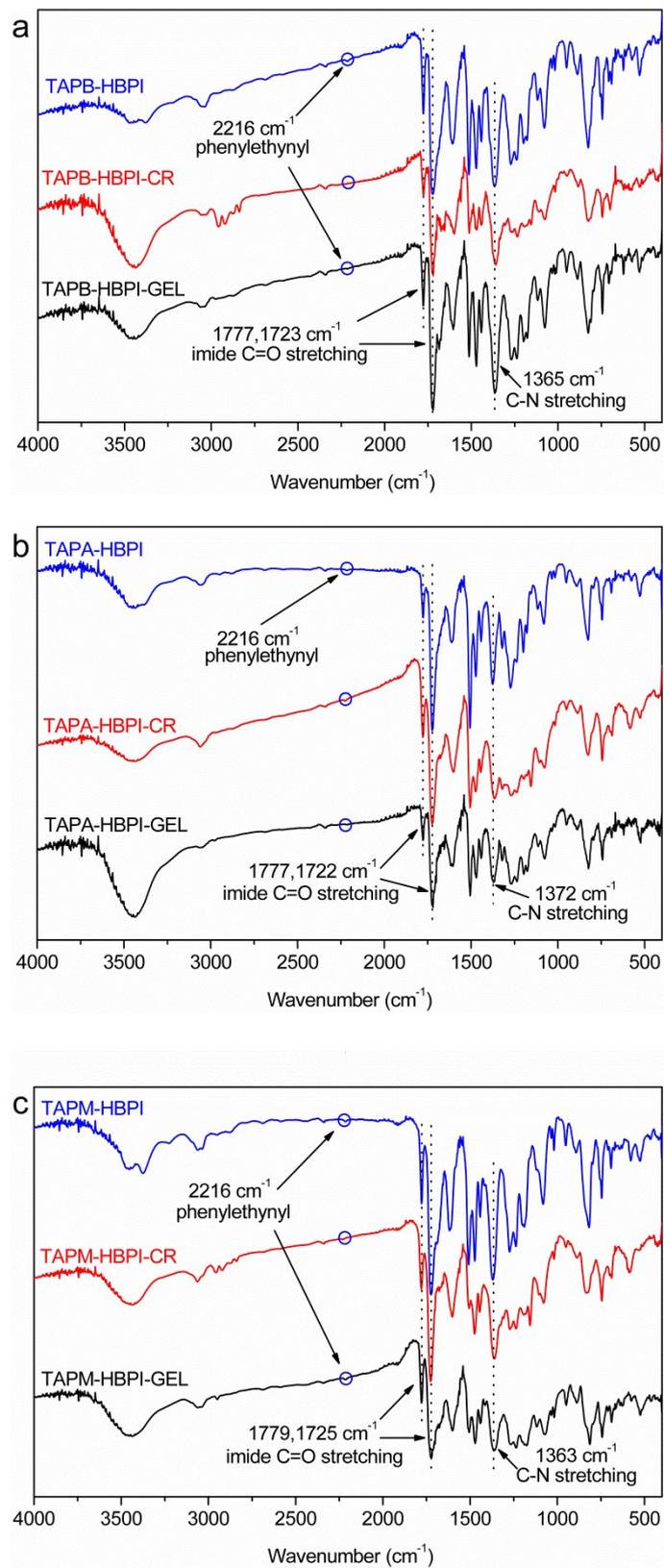


Figure S3. FT-IR spectra of (a) TAPB-HBPIs, (b) TAPA-HBPIs and (c) TAPM-HBPIs.

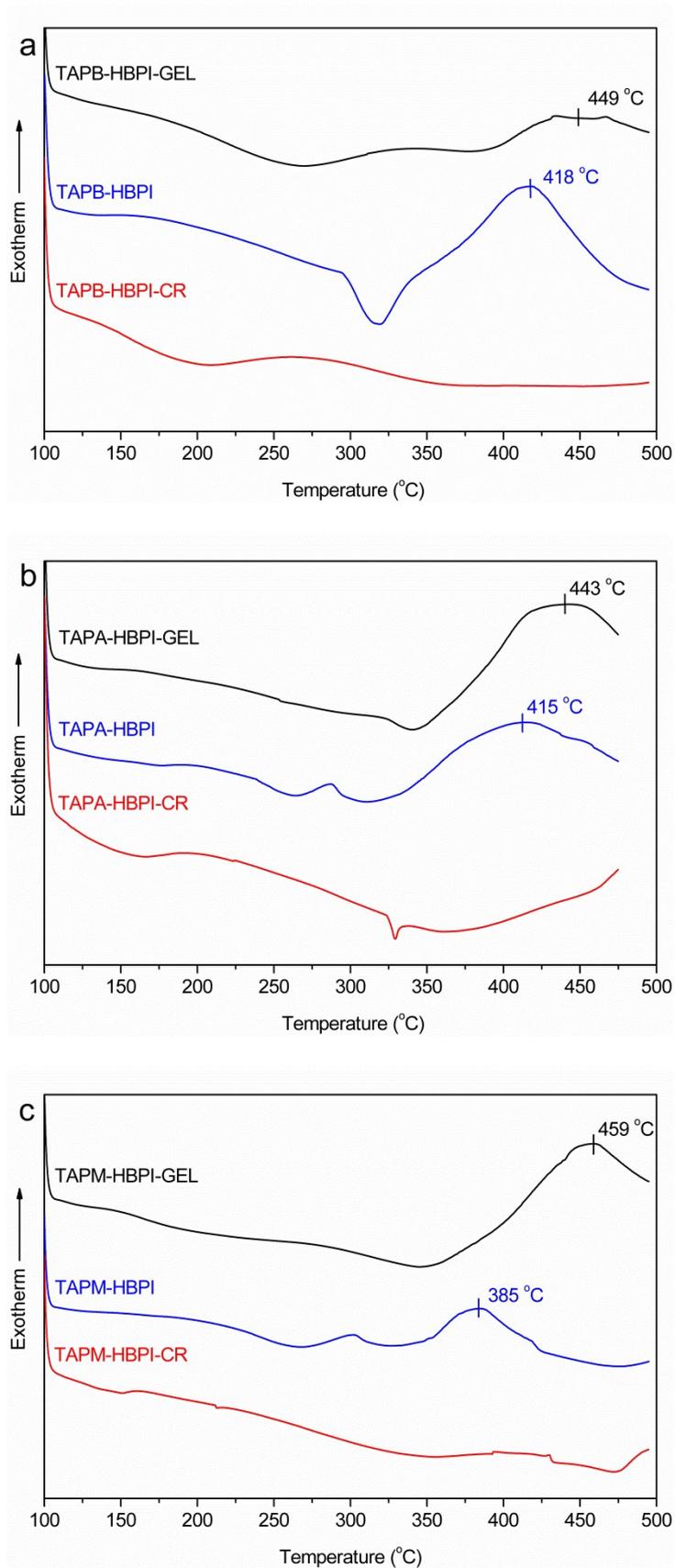


Figure S4. DSC curves of (a) TAPB-HBPIs, (b) TAPA-HBPIs and (c) TAPM-HBPIs.

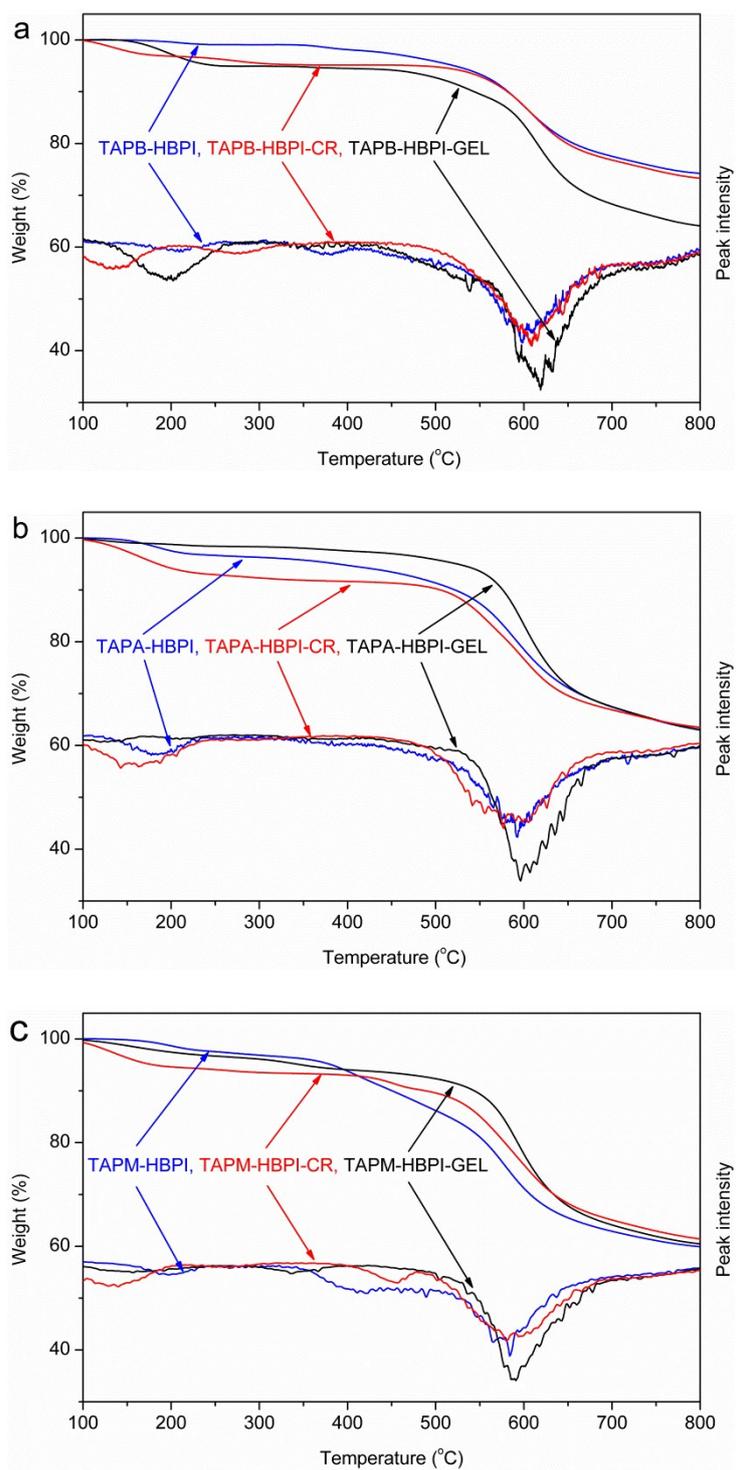


Figure S5. TGA curves of (a) TAPB-HBPIs, (b) TAPA-HBPIs and (c) TAPM-HBPIs.

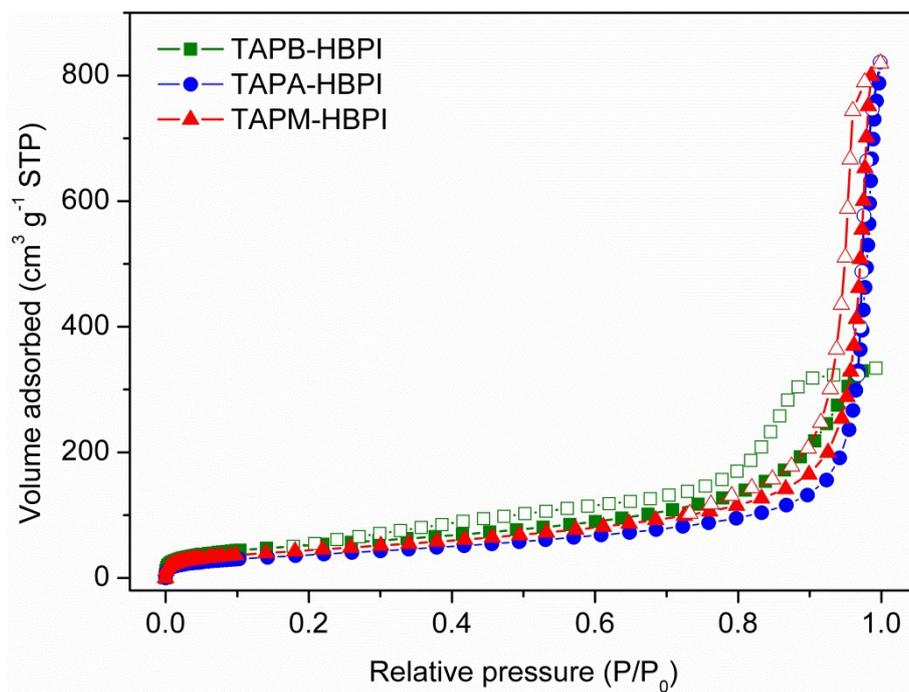


Figure S6. Nitrogen sorption isotherms of TAPB-HBPI, TAPA-HBPI and TAPM-HBPI.

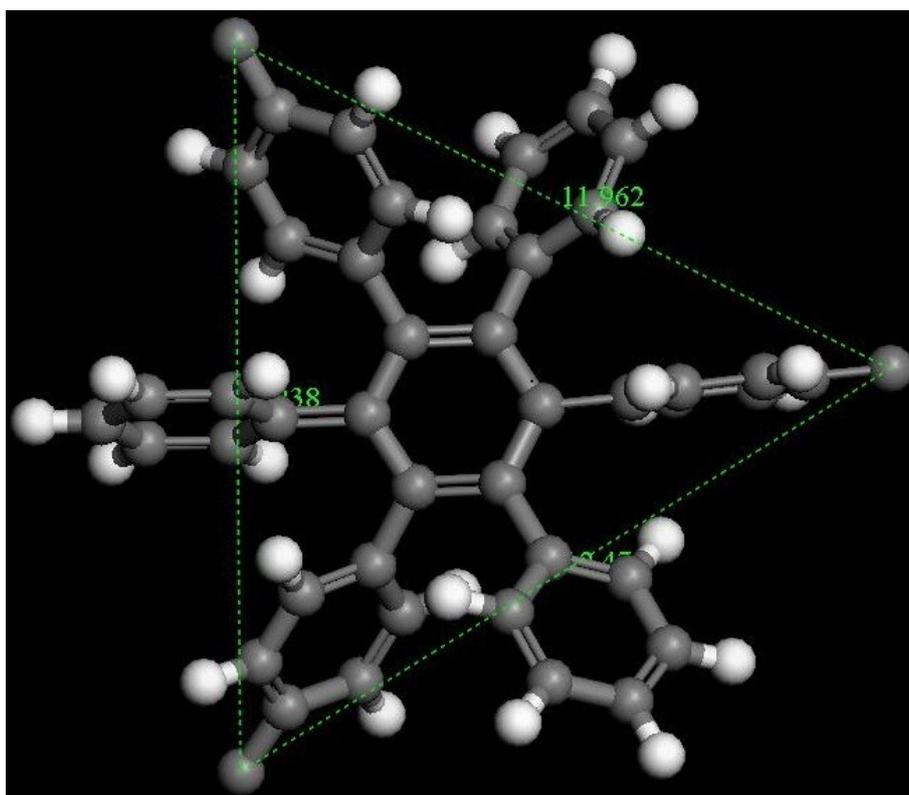


Figure S7. Atomistic calculation for possible cross-linked structure in HBPI-CRs using Materials Studio software.

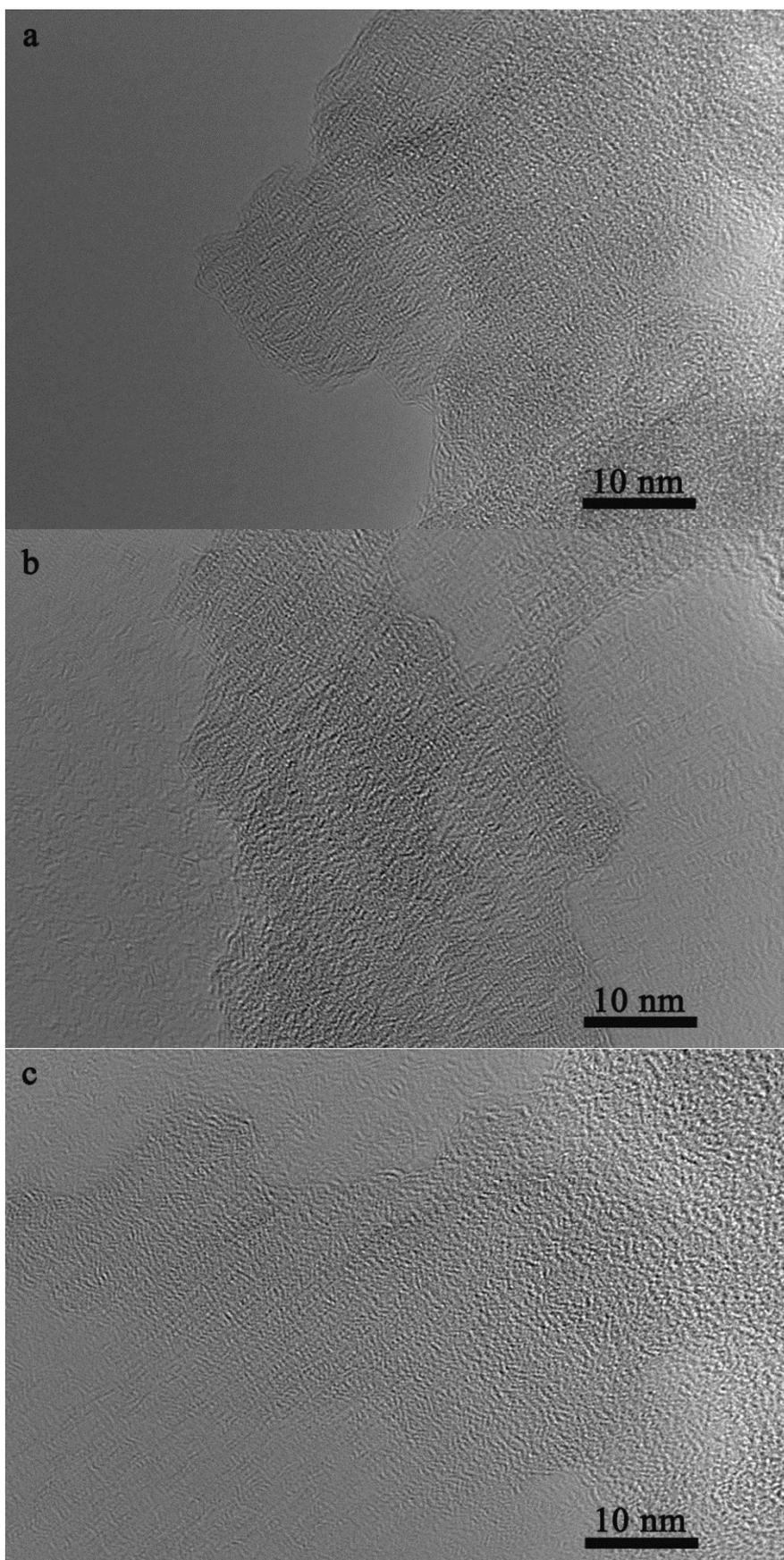


Figure S8. HR-TEM images of TAPB-HBPI-CR, TAPA-HBPI-CR and TAPM-HBPI-CR.

C. Supplementary Tables

Table S1. Porosity parameters of the HBPIs, HBPI-GELs and HBPI-CRs.

Polymers	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{Langmuir} ($\text{m}^2 \text{g}^{-1}$)	V_{total} ($\text{m}^3 \text{g}^{-1}$)	V_{micro} ($\text{m}^3 \text{g}^{-1}$)	Pore size (nm)
TAPB-HBPI-GEL	8	10	0.04	0.000	19.10 ^a
TAPA-HBPI-GEL	13	17	0.08	0.000	23.6 ^a
TAPM-HBPI-GEL	13	17	0.08	0.000	5.24 ^a
TAPB-HBPI	182	205	0.52	0.004	11.44 ^a
TAPA-HBPI	126	142	1.27	0.000	40.69 ^a
TAPM-HBPI	152	170	1.27	0.000	33.74 ^a
TAPB-HBPI-CR	385	521	0.19	0.089	0.68,1.27
TAPA-HBPI-CR	497	673	0.24	0.115	0.68,1.27
TAPM-HBPI-CR	492	676	0.25	0.096	0.59,1.27

^a The pore size of HBPI-GELs and HBPIs are the average pore size.

Table S2. Summary of porosity parameter for various porous polyimides

Dianhydride	Multiple amine	S _{BET} (m ² g ⁻¹) ^a	Pore size (nm)	Ref ^d
	TAPM	1407;1454	0.78;0.59	41,45
	TAPA(adamantane)	868	1.06,1.34	48
PMDA	TAPA(amine)	818;814	- ^c ;0.52	43,45
	TAPB	570;586	- ^c ;0.55	43,45
	TAPT	809 ^b	- ^c	47
	Melamine	660, 636	- ^c	42,45
	TATP	4	- ^c	53
	TAPM	690~810;732;721	0.35,0.52,0.82;-;0.60	40,41,46
	TAPA	232;291;567	- ^c ;0.59;- ^c	43,46,51
NTDA	TAPB	390;373	- ^c ;0.57,2.07	43,46
	TAPT	796 ^b	- ^c	47
	Melamine	366	- ^c	42
	TATP	541	- ^c	53
	TAPM	2213	1.08,0.54	44
PDA	TAPA	400	1.08,0.54, - ^c	44
	TAPT	40 ^b	- ^c	47
	TAPM	210	- ^c	51
	TAPA	130	- ^c	51
BTDA	TAPT	245 ^b	- ^c	47
	TAPM	490;443 ^b	0.53;- ^c	55,56
BNTDA	TAPM	574	0.6,1.4	49
BPDA	Melamine	265	- ^c	42
	TATP	378	- ^c	53
	TAPM	677	0.53	55
ODPA	TAPT	201 ^b	- ^c	47
	TAPM	644 ^b	- ^c	56

6FDA	TAPT	510 ^b	- ^c	47
	TAPM	781;921 ^b	0.48,- ^c	55,56
	TAPA(adamantane)	752	0.53	55
BSDA	TAPT	<10 ^b	- ^c	47
	TAPM	206 ^b	- ^c	56

^a The Brunauer–Emmett–Teller surface area of polymers were obtained by physical sorption of Nitrogen. ^b The Brunauer–Emmett–Teller surface area of polymers were obtained by physical sorption of Argon. ^c The pore size distribution is broad or not showed in the literatures. ^d The references are listed in the paper.

D. Supplementary References

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