

Electronic Supplementary information (ESI) for
**Construction and carbon dioxide capture of microporous
polymer networks with high surface area based on cross-
linkable linear polyimides**

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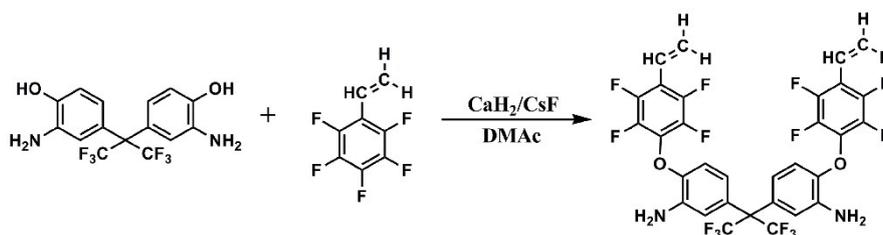
A. Supplementary Method

1. Materials

Acetone, acetonitrile, acetic anhydride and acetic acid were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd (China). Cesium carbonate (Cs_2CO_3), calcium hydride (CaH_2), cesium fluoride (CsF), 4-nitrophthalonitrile and diphenyl sulfone 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-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), isoquinoline, N-methyl-2-pyrrolidone (NMP) and trimethylamine (TEA) were purchased from Aladdin Reagents Co., Ltd. (China).

2. Synthesis of 2,2-Bis(3-amino-4-(2,3,5,6-tetrafluoro-4-vinylphenoxy)phenyl) hexafluoropropane (6FATFVP)

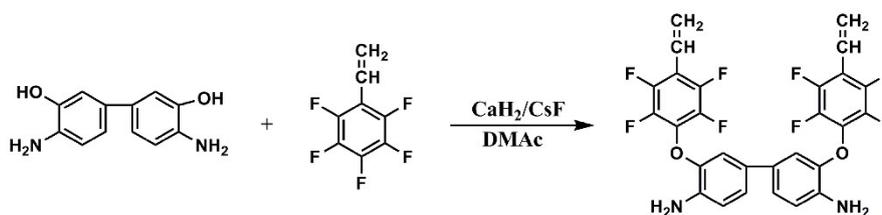
The diamine monomer 6FATFVP was synthesized using 2,3,4,5,6-pentafluorostyrene and 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane in our laboratory and the reaction procedure is depicted in Scheme S1. 2,2-Bis(3-amino-4-hydroxyphenyl) hexafluoropropane (1.4650 g, 4 mmol), 2, 3, 4, 5, 6-pentafluorostyrene (1.5696 g, 8 mmol), calcium hydride (0.6848 g, 16 mmol), and cesium fluoride (0.2431 g, 1.6 mmol) were added into a 50 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a water condenser. Then, 20 mL DMAc was added into the flask under the nitrogen atmosphere. The mixture was heated to 80°C with stirring under nitrogen 24 h. After cooled to room temperature, it was poured into 200 mL deionized water, washed with deionized water, extracted with ether, dried with anhydrous MgSO_4 , and then filtrated. The solvent was evaporated under vacuum, and the residue was purified by column chromatography (ethyl acetate/ petroleum ether) to afford the pure products. Yield: 82%. The structure of the target diamine monomer was confirmed by ^1H NMR spectroscopy, as shown in Fig. S1. The ^1H NMR results were consistent with the assigned structure of the 6FATFVP, indicative of the successful preparation of designed monomer. ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ : 5.48 (s, 4H, NH_2), 5.81-5.85 (d, $J=12$ Hz, 2 H), 6.04-6.10 (d, $J=18$ Hz, 2 H), 6.38-6.41 (d, $J=9$ Hz, 2 H), 6.67-6.74 (m, 2 H), 6.77-6.80 (d, $J=9$ Hz, 2 H), 6.83 (s, 2 H).



Scheme S1 The synthetic route used to prepare the 6FATFVP monomer.

3. Synthesis of 3,3'-bis(2,3,5,6-tetrafluoro-4-vinylphenoxy) -4,4'-biphenyldiamine (TFVBPA)

The synthetic route of diamine monomer TFVBPA is similar to the 6FATFVP and is depicted in Scheme S2. The structure of the target diamine monomer was confirmed by ^1H NMR spectroscopy, as shown in Fig. S2. The ^1H NMR results were consistent with the assigned structure of the TFVBPA, indicative of the successful preparation of designed monomer. ^1H NMR (300 MHz, DMSO- d_6) δ : 5.22 (s, 4H, NH_2), 5.79-5.83 (d, $J=12$ Hz, 2 H), 6.02-6.08 (d, $J=18$ Hz, 2 H), 6.65-6.71 (m, 2 H), 6.74-6.77 (m, 2 H), 6.81 (s, 2 H), 7.00-7.04 (dd, 2 H).



Scheme S2 The synthetic route used to prepare the TFVBPA monomer.

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

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

A mixture of BrPHQ (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). ^1H NMR (400 MHz, DMSO- d_6): δ 8.143-8.172 (d, $J=11.6$ Hz, 1H), 8.051-8.080 (d, $J=11.6$ Hz, 1H), 7.934-7.942 (d, $J=3.2$ Hz, 1H), 7.799-7.807 (d, $J=3.2$ Hz, 1H), 7.616-7.625 (d, $J=3.6$ 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

In a 250 mL three-necked flask, the 2, 5-bis(3, 4-dicyanophenoxy)-4'-bromo-biphenyl (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), $\text{PdCl}_2(\text{PPh}_3)_2$ (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:

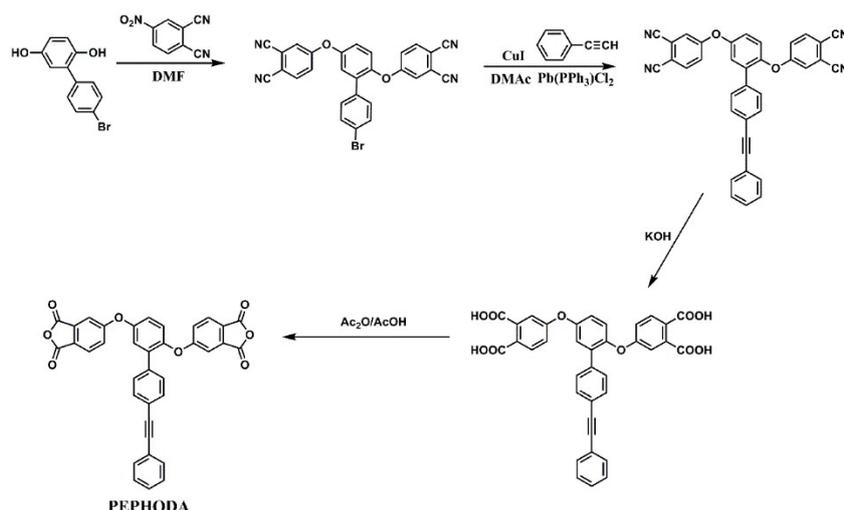
140°C (DSC in N₂). MALDI-TOF MS: $m/z=537.3$. IR (KBr): 2231 cm⁻¹ (C≡N). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.153-8.171 (d, J=7.2 Hz, 1H), 8.053-8.071 (d, J=7.2 Hz, 1H), 7.945-7.950 (d, J=2.0 Hz, 1H), 7.807-7.812 (d, J=2.0 Hz, 1H), 7.622-7.627 (d, J=2.0 Hz, 1H), 7.605-7.610 (d, J=2.0 Hz, 1H), 7.550 (m, 5H), 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

In a 250 mL flask, a mixture of 2, 5-bis(3, 4-dicyanophenoxy)-4'-phenylethynylbiphenyl (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 (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 8.108-8.148 (m, 1H), 8.002-8.046 (m, 1H), 7.680-7.728 (m, 2H), 7.632 (s, 1H), 7.555-7.615 (d, 2H), 7.480-7.545 (m, 6H), 7.402-7.450 (m, 4H), 7.346-7.394 (m, 1H).



Scheme S3 The synthetic route used to prepare the PEPHQDA monomer.

3. Synthesis of TF-PI and 6FA-PI

The linear polyimides bearing cross-linkable groups (TF-PI and 6FA-PI) were synthesized by the polycondensation reaction of TFVBPA and 6FATFVP with PEPHQDA respectively, by using 1:1 monomer molar ratio. A typical polycondensation procedure, illustrated by preparation of the TF-PI, can be described as follows. 3,3'-bis(2,3,5,6-tetrafluoro-4-vinylphenoxy) -4,4'-biphenyldiamine (TFVBPA) (1.1429 g, 1 mmol) and PEPHQDA (0.5785 g, 1 mmol) were first dissolved in NMP (12 mL), then the mixture was added into a 50 mL three-necked round-bottomed flask under a nitrogen flow. After the mixture was stirred for 30 min at room temperature, a catalytic amount of 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. The polymers were collected by filtration and extracted by Soxhlet's apparatus in ethanol to completely remove NMP then dried under vacuum at 100°C for 24 h.

4. Synthesis of TF-PI-CL and 6FA-PI-CL

A typical crosslinking procedure, illustrated by preparation of the TF-PI-CL can be described as follows. The TF-PI and diphenyl sulfone was added in a dried 100 mL three-necked flask under a nitrogen 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 120°C for 24 h.

5. Measurements

FTIR spectra were measured on a Bruker VERTEX 80V Fourier-transform infrared spectrometer. ¹H NMR spectra of the monomers were measured on a Bruker AVANCE NMR spectrometer (¹H, 300 MHz) using DMSO-*d*₆ as solvent and tetramethylsilane (TMS) as internal reference. The thermal gravimetric analyses

(TGA) were performed by a Perkin-Elmer TGA-1 thermo-gravimetric analyzer. The samples were evaluated in the range of 100-800°C at a heating rate of 10°C min⁻¹ under nitrogen. Solid-state ¹³C 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 ¹³C CP MAS chemical shifts are referenced to the resonances of an adamantane (C₁₀H₁₆) standard (δ CH₂= 38.5). Elemental analyses were determined with an vario MICRO elemental analyzer. 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-2100F micro-scope. The sample was prepared by drop-casting an ethanol suspension of polymers onto a copper grid. Adsorption and desorption measurements for all the gases and vapors were conducted on JW-BK 132F analyzer. Prior to measurements, the samples were degassed at 200 °C under vacuum overnight. Adsorption and desorption isotherms of nitrogen were measured at 77 K. The surface areas were calculated according to the Brunauer-Emmett-Teller (BET) model in the relative pressure (P/P₀) range from 0.10 to 0.25. CO₂ adsorption–desorption isotherms were measured at 273 and 298 K up to 1.0 bar. N₂ adsorption isotherms at 273 K were measured in order to evaluate the adsorption CO₂/N₂ selectivity.

B. Supplementary Figures

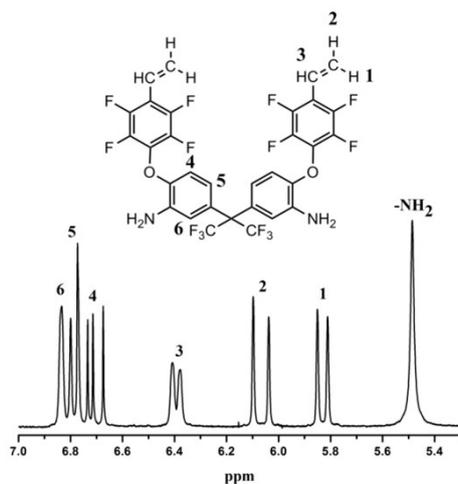


Figure S1. ^1H NMR spectra of 6FATFVP.

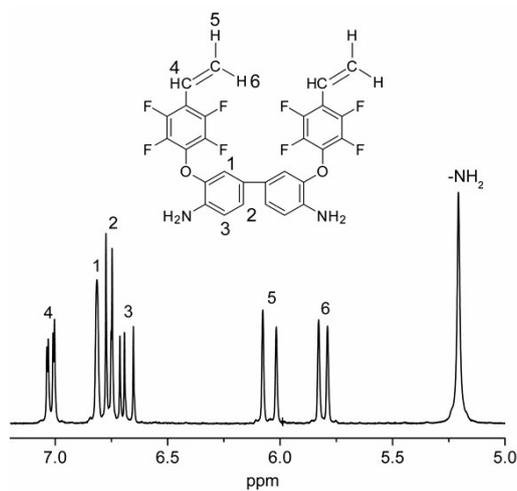


Figure S2. ^1H NMR spectra of TFVBPA.

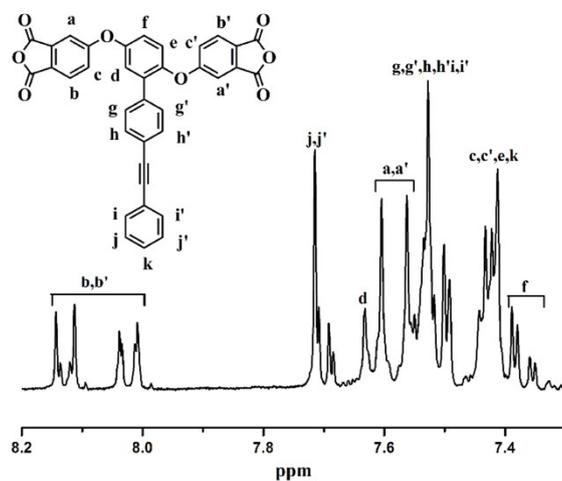


Figure S3. ^1H NMR spectra of PEPHQDA.

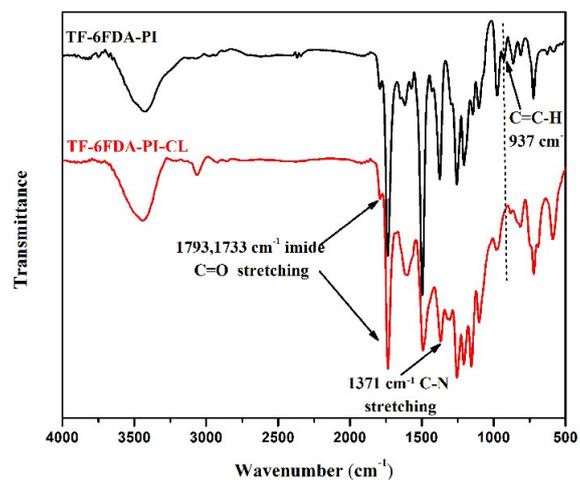


Figure S4. FTIR spectra of the TF-6FDA-PI and TF-6FDA-PI-CL.

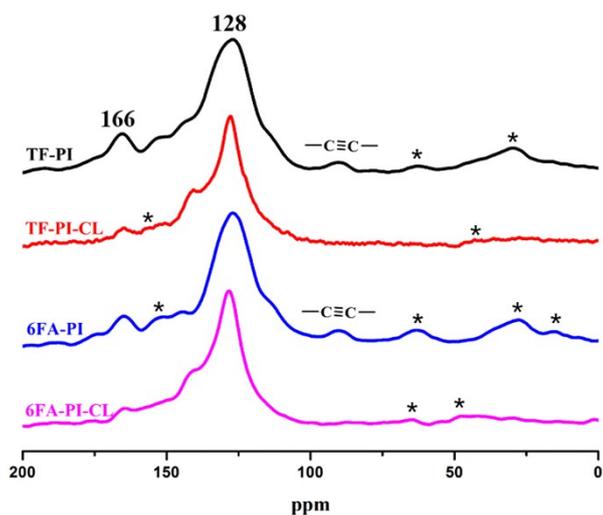


Figure S5. ^{13}C CP/MAS NMR spectra of the TF-PI, TF-PI-CL, 6FA-PI, and 6FA-PI-CL (asterisks indicate peaks arising from spinning side bands).

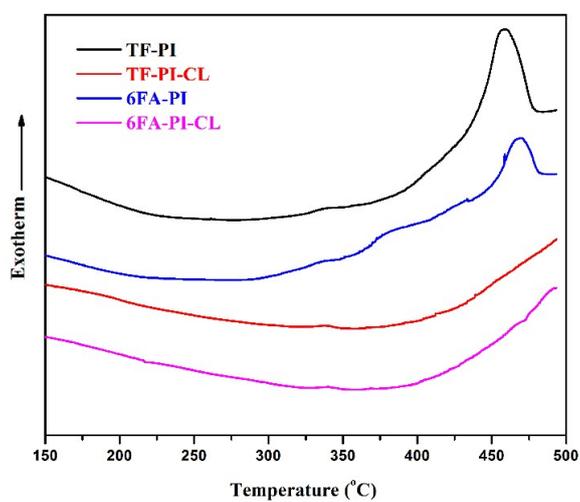


Figure S6. DSC curves of PIs and PI-CLs.

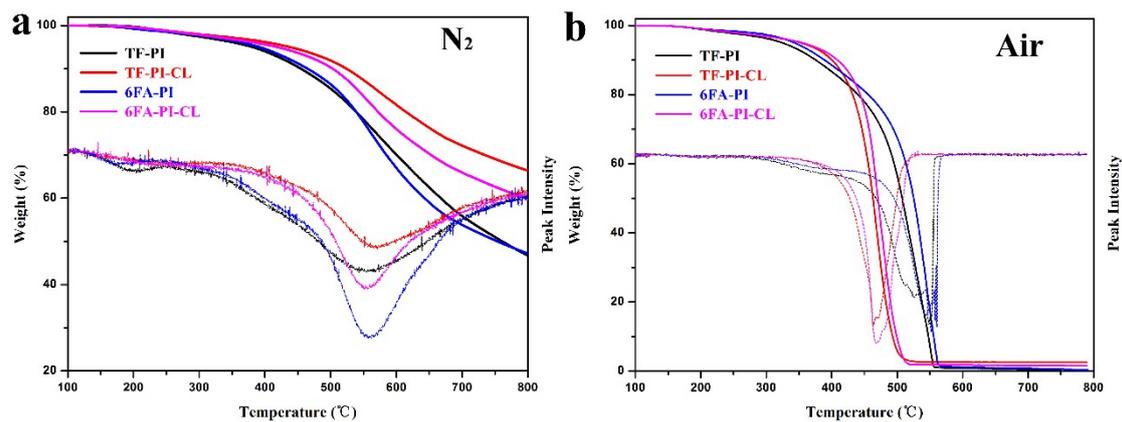


Figure S7. TGA curves of PIs and PI-CLs at (a) N_2 and (b) air.

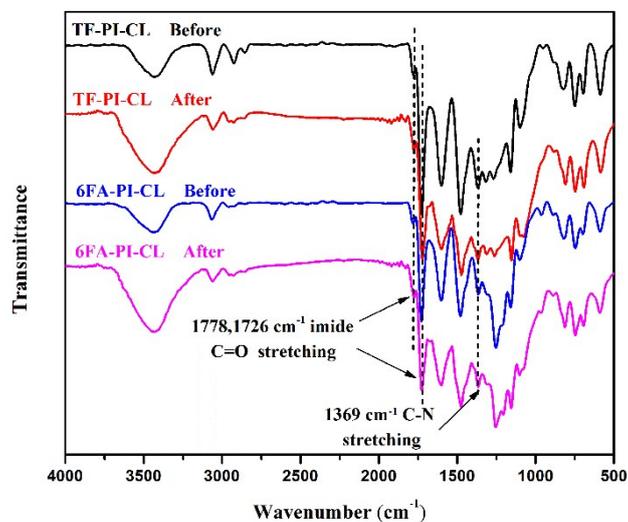


Figure S8. FT-IR spectra of the PI-CLs before and after boiled in water for 24 h.

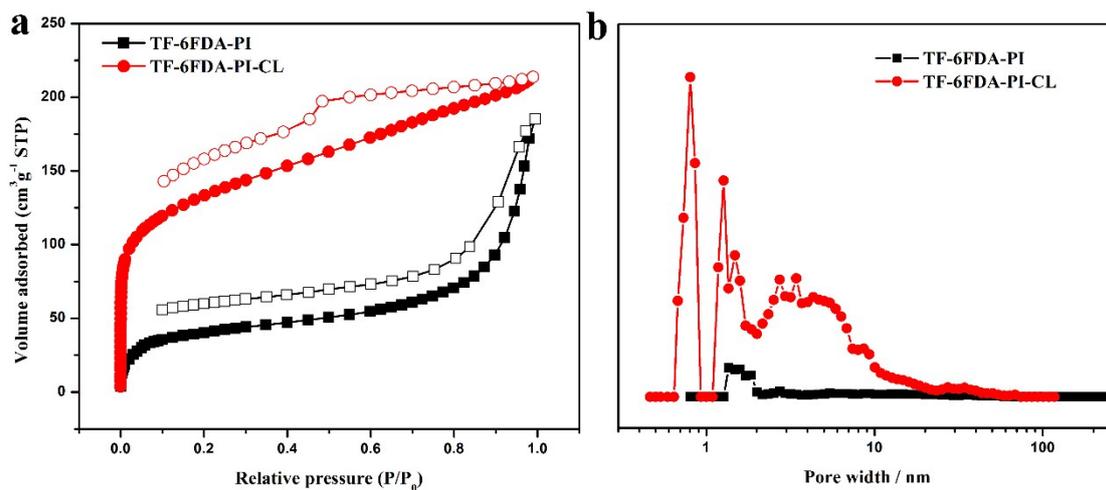


Figure S9. (a) Nitrogen adsorption (filled) and desorption (empty) isotherms of the TF-6FDA-PI and TF-6FDA-PI-CL at 77 K; (b) pore size distribution of the TF-6FDA-PI and TF-6FDA-PI-CL as determined by the NLDFT method.

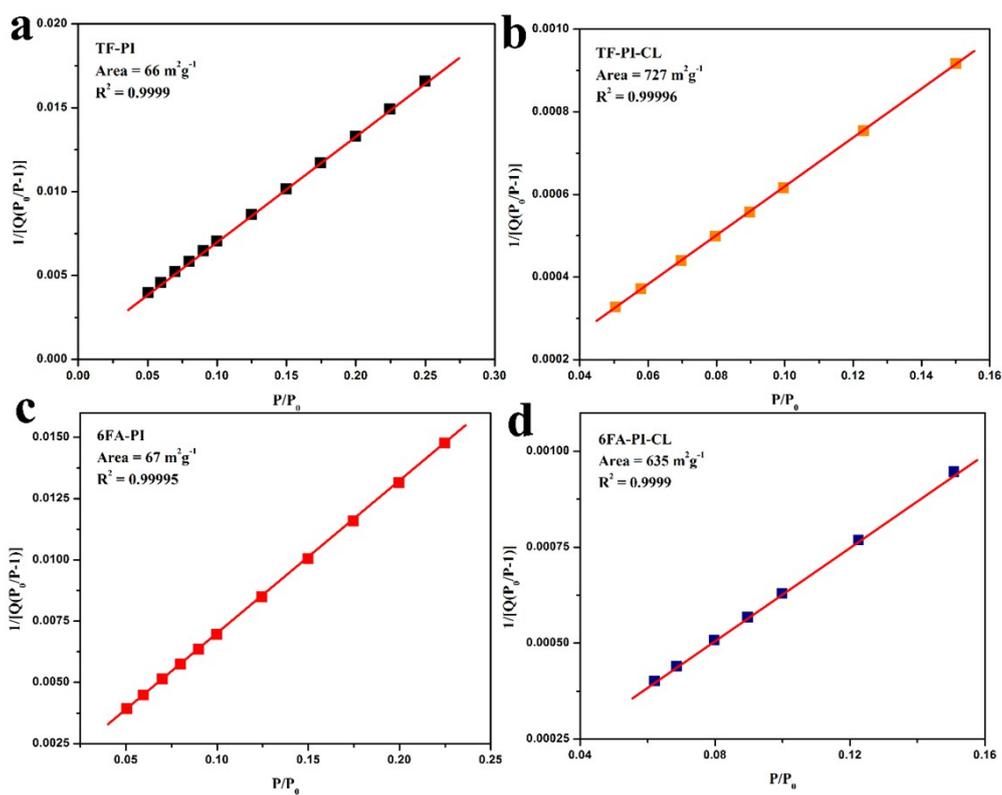


Figure S10. BET-plots for TF-PI, TF-PI -CL, 6FA-PI and 6FA-PI-CL calculated from the corresponding nitrogen adsorption isotherms at 77 K. The calculation was performed in the relative pressure region $P/P_0 = 0.04$ - 0.25 . The specific BET surface area and the correlation coefficient R are displayed.

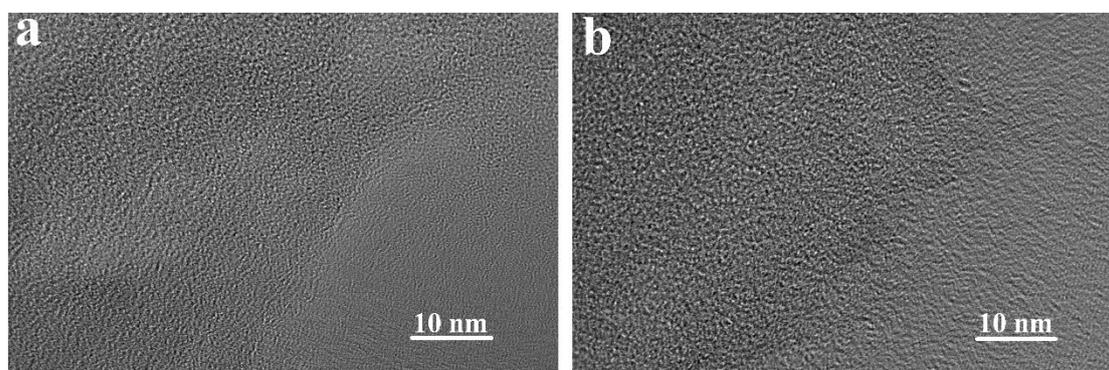


Figure S11. HR-TEM images of (a) TF-PI-CL and (b) 6FA-PI-CL.

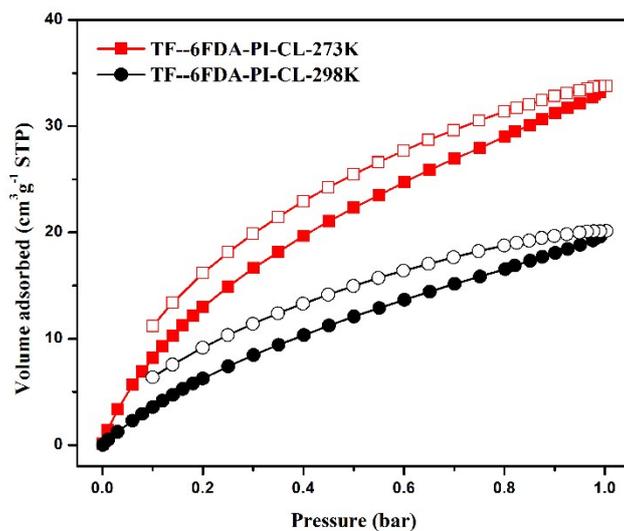


Figure S12. CO₂ adsorption (filled) and desorption (empty) isotherms for the TF-6FDA-PI-CL.

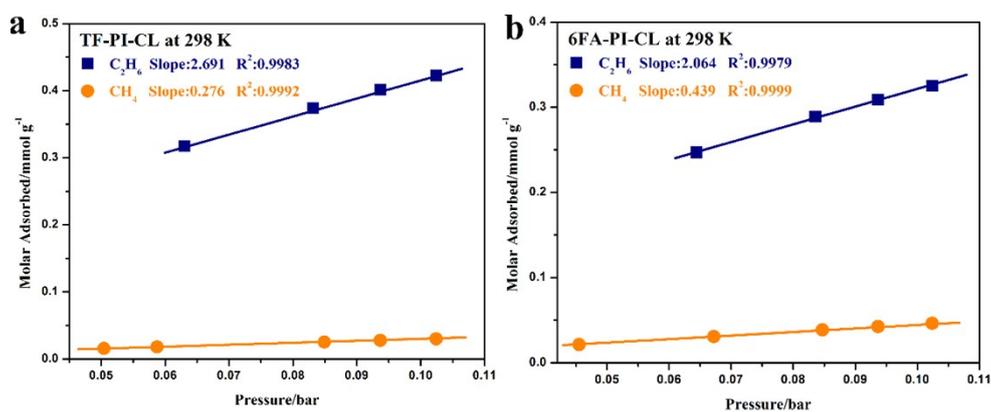


Figure S13. Adsorption selectivity of C₂H₆/CH₄ calculated by employing Henry's law initial slope method at 298 K for (a) TF-PI-CL and (b) 6FA-PI-CL.

C. Supplementary Tables

Table S1 Solubility of the PIs and PI-CLs in organic solvents.

Polymers	Solvent ^a							
	NMP	DMAc	DMF	DMSO	THF	CHCl ₃	Acetone	Ethanol
TF-PI	++	++	++	++	+	++	-	-
6FA-PI	++	++	++	++	+	++	-	-
TF-PI-CL	-	-	-	-	-	-	-	-
6FA-PI-CL	-	-	-	-	-	-	-	-

Qualitative solubility was determined with as 10 mg of polymer in 1 mL of solvent.

++: Soluble at room temperature; +: Partly soluble at room temperature; -: Insoluble on heating.

^a NMP: N-methyl-2-pyrrolidone; DMAc: N,N-dimethylacetamide; DMF: N,N-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran; CHCl₃: chloroform.

Table S2 Elemental analysis data of the monomers and PI networks

Polymers	Element composition (%)				C/N ratio	C/H ratio
	C	N	H	S		
TFVBPA	61.04	5.14	2.843	-	11.8755	21.4703
6FATFVB	49.44	3.65	2.607	-	13.5452	18.9643
PEPHQDA	75.35	-	3.100	-	-	24.3065
TF-PI	68.16	4.78	3.437	-	14.2594	19.8313
TF-PI-CL	73.42	3.85	3.481	0.50	19.0701	21.0916
6FA-PI	63.81	4.20	3.206	-	15.1929	19.9033
6FA-PI-CL	71.01	4.11	3.253	0.41	17.2774	21.8291

Table S3 K_H , A_o and Q_o values of CO₂ adsorption in PI-CL networks

polymer	T	K_H	A_o	Q_o
	K	mol g ⁻¹ Pa ⁻¹	ln(mol g ⁻¹ Pa ⁻¹)	kJ mol ⁻¹
TF-PI-CL	273	1.0094×10 ⁻⁴	-9.201	32.0
	298	3.0923×10 ⁻⁵	-10.384	
6FA-PI-CL	273	8.3305×10 ⁻⁵	-9.393	31.9
	298	2.5598×10 ⁻⁵	-10.573	