Electronic Supplementary Information (ESI)

Rational Construction of Microporous Imide-Bridged Covalent-Organic

Polytriazines for High-enthalpy Small Gas Absorption

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1. Materials

1,2,4,5-Benzenetetracarboxylic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, and 3,4,9,10-perylenetetracarboxylic dianhydride were purchased from Alfa Aesar Chemical Inc. and used as received. 3-Methylphenol, 4-aminobenzonitrile (PABN), and isoquinoline were purchased from Aladdin Chemical Inc. and used as received. ZnCl₂ was refluxed over SOCl₂ and filtered prior to use. All other solvents and reagents were purchased from Energy Inc. and used as received.

2. Methods

FT-IR spectra were collected on a VARIAN 1000 FT-IR (scimitar series) spectrometer in the 400-4000 cm^{-1} region. Samples were prepared by dispersing the complexes in KBr and compressing the mixtures to form disks. Thermo-gravimetric analysis (TGA) was performed at a heating rate of 10 K/min under N2 and air atmosphere using a PERKIN ELMER TGA7. CHN analysis was performed on a Vario ELIII CHNOS Elementaranalysator from Elementaranalysesyteme GmbH. NMR measurements were carried out on a Bruker 400MHz spectrometer at 25 °C, using tetramethylsilane as an internal reference. Solid-state ¹³C CP/MAS (cross-polarization with magic angle spinning) spectra were measured on a Bruker Avance III 400 NMR spectrometer at 100.61 MHz at an MAS rate of 5.0 kHz using zirconia rotors 4 mm in diameter using a contact time of 3.0 ms and a relaxation delay of 2.0 s. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF/MS) analyses were performed on a Micromass GC-TOF CA 156 MALDITOF/MS. All the adsorption and desorption measurements for N2, H2, CO2 and CH4 were performed on an Autosorb-iQ (Quantachrome) analyzer at selected temperatures. Low pressure N₂ adsorption and desorption isotherms were measured at 77 and 273 K. The cumulative apparent surfaces areas for N2 were calculated using the Brunauer-Emmett-Teller (BET) model range from 0.01 to 0.1 bar for all samples. Microporous volumes were calculated using the t-plot method, while the total porous volumes were obtained from the N₂ isotherm at P/P₀= 0.99. Pore size distributions were derived from the N₂ adsorption isotherms using NLDFT methods. H2 adsorption isotherms were measured at 77 K up to 1.0 bar. CO₂ adsorption isotherms were measured at 273 and 298K up to

1.0 bar. CH₄ adsorption isotherms were measured at 298K up to 22.0 bar. High purity gas (99.999 %) was used for the adsorption experiments. Prior to the measurements, the samples were degassed at 150 $^{\circ}$ C under high vacuum for 12 h. Inductive coupled plasma atom emission spectrometer (ICP-AES) were performed with PerkinElmer Optima 5300 DV.

3. Synthesis of the monomers

m₁: 1,2,4,5-Benzenetetracarboxylic dianhydride (2.18 g, 1 mmol), 4-aminobenzonitrile (2.36 g, 2 mmol) and isoquinoline (1 mL) were mixed in a 100 mL flask, and then 40 mL 3-methylphenol was added. The mixture was heated to 180 °C for 8 h. The yellow solid was collected by filtration, washed with ethanol several times, and dried to give m1 (3.82 g, 91.3%). ¹H NMR (DMSO-d₆): σ = 8.49 (s, 2 H), σ = 8.11 (d, 4 H), σ = 7.78 (d, 4 H). IR (KBr, cm⁻¹): 3117 (Ar-H), 2235(C=N), 1721(C=O). MALDI-TOF/MS (M+ Calcd. as C₂₄H₁₀N₄O₄, 418.0702) m/z: 418.0765 (M+).

m₂: 1,4,5,8-Naphthalenetetracarboxylic dianhydride (2.68 g, 1 mmol), 4-aminobenzon- itrile(2.36 g, 2 mmol) and isoquinoline (1 mL) were mixed in a 100mL flask, and then 40 mL 3-Methylphenol was added. The mixture was heated to 180 °C for 8 h. The brown solid was collected by filtration, washed with water and ethanol several times, and dried to give m2 (3.77 g, 80.5%).¹H NMR (DMSO-d₆): σ =8.76 (d, 4H), σ =8.09 (d, 4H), σ =7.75 (d, 4H).IR (KBr, cm⁻¹): 3089 (Ar-H), 2235 (C=N), 1721 (C=O). MALDI-TOF/MS (M+ Calcd. as C₂₈H₁₂N₄O₄, 468.0859) m/z: 468.0235 (M+).

m₃: 3,4,9,10-Perylenetetracarboxylic dianhydride (1.96 g, 0.5 mmol), 4-aminobenzonitrile (PABN) (1.18 g, 1 mmol) were mixed in a 100 mL flask. Subsequently 30 mL NMP and 20 mL acetic anhydride was added. The mixture was heated to 180 °C for 16 h. The dark red solid was collected by filtration, washed with water and ethanol several times, and dried to give m3 (1.84 g, 62.1%). IR (KBr, cm⁻¹): 3081 (Ar-H), 2229 (C=N), 1715 (C=O). MALDI-TOF/MS (M+ Calcd. as C₃₈H₁₆N₄O₄, 592.1172) m/z: 592.0859 (M+).

4. Temperature program

To prevent monomers from being broken down, the consolidated ionothermal strategy¹ was adopted, instead of traditional one-step procedure. After these three monomers were heated at 400 °C for 20 h in this strategy, we obtained TPI-1@IC from m1 with a BET surface area of 1053 m² g⁻¹, but no polymers were gained from m2 or m3 when washing the reaction mixture with solvents. The apparent surface area of 403 m² g⁻¹ was observed for TPI-2@IC prepared at 500 °C, while a negligible surface area was shown for polymer synthesized from monomer m3 (TPI-3@IC-500°C) at this temperature (Figure.S2). As compared to TPI-3@IC-500°C, increasing the reaction temperature to 600 °C endows TPI-3@IC with a remarkable BET surface area of 963 m² g⁻¹.

monomer	heating program	polymer	Yield	BET
				(m^2/g)
m1	200 °C/5 h, 300 °C /5 h, 400 °C/20 h	TPI-1@IC	94	1053
m2	200 °C/5 h, 300 °C /5 h, 400 °C/20 h	Soluble product	89	-
m3	200 °C/5 h, 300 °C /5 h, 400 °C/20 h	Soluble product	92	-
m2	200 °C/5 h, 300 °C/5 h, 400 °C/10 h, 450 °C/10 h, 500 °C/20 h	TPI-2@IC	91	814
m3	200 °C/5 h, 300 °C/5 h, 400 °C/10 h, 450 °C/10 h, 500 °C/20 h	TPI-3@IC-500°C	92	18
m3	200 °C/5 h, 300 °C/5 h, 400 °C/10 h, 450 °C/10 h, 500 °C/10 h, 600 °C/20 h	TPI-3@IC	90	963

Table S1.	multipl	v-heating	programs
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5. Infrared spectroscopy



6. ¹³C CP-MAS NMR Spectrum of TPI-2@IC



7. Elemental analysis and ICP of TPIs@IC.

Dolumous	Calculated (%)					Found (%)							
Polymers	С	Н	0	Ν	C/O	C/N	С	Н	0	Ν	C/O	C/N	Zn
TPI-1@IC	68.90	2.41	15.30	13.39	4.50	5.15	65.08	2.24	7.43	7.09	8.75	9.18	6.7
TPI-2@IC	71.79	2.58	13.66	11.96	5.26	6.00	67.87	2.38	7.12	6.75	9.53	10.05	6.1
TPI-3@IC	76.71	2.76	10.95	9.58	7.01	8.01	72.46	2.45	6.26	5.88	11.58	12.32	5.9

Table S2. Elemental analysis data of TPIs@IC and Zinc contents determined by ICP.

Compared with those values calculated, lower nitrogen and oxygen contents and higher C/O and C/N ratios were given by elemental analysis. This could be attributed to the incomplete combustion and trapped adsorbates including gases and water vapour, which were also discussed in other publications (P. Kuhn, A. Forget, D.-S. Su, A. Thomas and M. Antonietti, *J. Am. Chem. Soc.*, 2008, **130**, 13333-13337; A. Bhunia, I. Boldog, A. Moller and C. Janiak, *J. Mater. Chem. A.*, 2013, **1**, 14990-14999; A. Bhunia, V. Vasylyeva and C. Janiak, *Chem. Commun.*, 2013, **49**, 3961-3963; Y. Liu, S.-F. Wu, G. Wang, G.-P. Yu, J. G. Guan, C.-Y Pan and Z.-G Wang, *J. Mater. Chem. A.*, 2014, **2**, 7795-7801.).

8. Morphology analysis by SEM



Fig.S3 Scanning electron micrographs of TPI-1@IC



Fig.S4 Scanning electron micrographs of TPI-2@IC



Fig.S5 Scanning electron micrographs of TPI-3@IC

9. Morphology analysis by TEM



Fig.S6 TEM micrograph of TPI-1@IC



Fig.S7 TEM micrograph of TPI-2@IC



Fig.S8 TEM micrograph of TPI-3@IC

10.Powder X-Ray Diffraction



Fig.S9 Powder X-Ray Diffraction of TPI-1@IC



Fig.S10 Powder X-Ray Diffraction of TPI-2@IC



Fig.S11 Powder X-Ray Diffraction of TPI-3@IC

11.Thermo-gravimetric analysis of TPI-1@IC and TPI-2@IC



Fig.S12 TGA of TPI-1@IC and TPI-2@IC

12.Adsorption selectivity of CO_2 over N_2 for TPIs@IC at 273 K imitated by ideal adsorbed solution theory (IAST) model.



Fig.S13 CO2 isotherm of TPI-1@IC fitted by single-site Langmuir equation



Fig.S14 N₂ isotherm of TPI-1@IC fitted by single-site Langmuir equation



Fig.S15 CO₂ isotherm of TPI-2@IC fitted by single-site Langmuir equation



Fig.S16 N2 isotherm of TPI-2@IC fitted by single-site Langmuir equation



Fig.S17 CO₂ isotherm of TPI-3@IC fitted by single-site Langmuir equation



Fig.S18 N2 isotherm of TPI-3@IC fitted by single-site Langmuir equation

13.Adsorption selectivity of CO_2 over N_2 for TPIs@IC at 273 K based on initial slope calculations.



Fig.S19 Initial slope selectivity study of TPI-1@IC at 273 K (CO₂ over N_2)



Fig.S20 Initial slope selectivity study of TPI-2@IC at 273 K (CO₂ over N₂)



Fig.S21 Initial slope selectivity study of TPI-3@IC at 273 K (CO₂ over N₂)

14.Adsorption selectivity of CO₂ over CH₄ for TPIs@IC at 298K based on initial slope calculations.



Fig.S22 Initial slope selectivity study of TPI-1@IC at 298 K (CO₂ over CH₄)



Fig.S23 Initial slope selectivity study of TPI-2@IC at 298 K (CO₂ over CH₄)



Fig.S24 Initial slope selectivity study of TPI-3@IC at 298 K (CO₂ over CH₄)

References

1 S.-F. Wu, Y. Liu, G.-P. Yu, J.-G. Guan, C.-Y. Pan, Y. Du, X. Xiong and Z.-G. Wang, *Macromolecules*, 2014, **47**, 2875-2882.