Supplementary Information

Post-synthetic Modification of Zirconium Metal-Organic Frameworks for Adsorption and Separation of Light Hydrocarbons

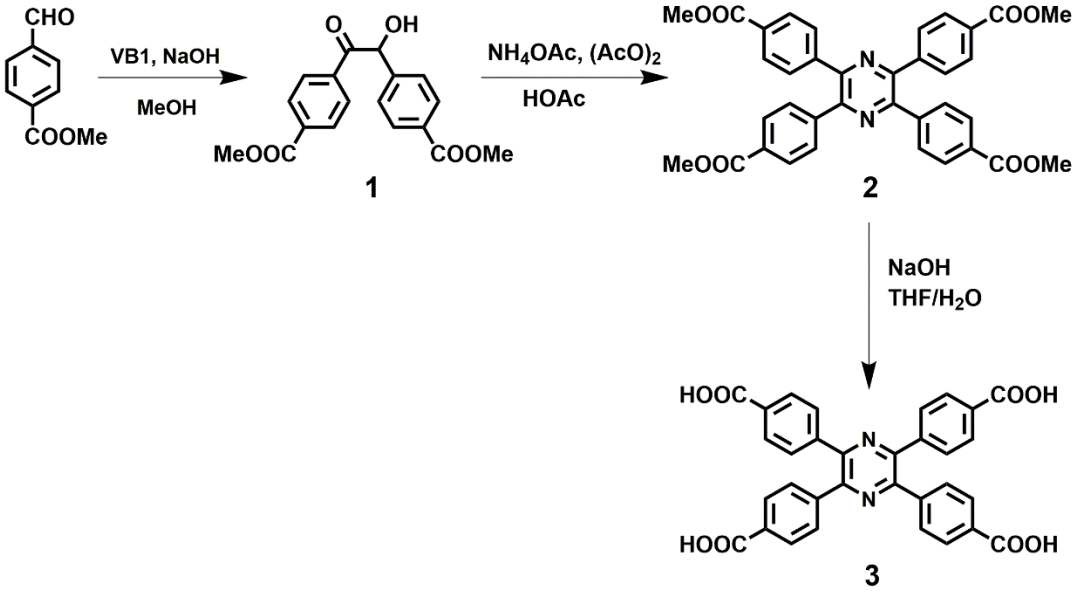
Huihui He[†,#], Bingbing Guo[‡,#], Yang Liu[†], Liangliang Zhang[†,] and Wei Huang[†]*

[†] Frontiers Science Center for Flexible Electronics (FSCFE), Shaanxi Institute of Flexible Electronics (SIFE) & Shaanxi Institute of Biomedical Materials and Engineering (SIBME), Northwestern Polytechnical University (NPU), 127 West Youyi Road, Xi'an 710072, China.

[‡] Key Laboratory of Unconventional Oil & Gas Development (China University of Petroleum (East China)), Ministry of Education, School of Materials Science and Engineering, China University of Petroleum (East China), Qingdao, Shandong 266580, People's Republic of China

Contents

Section 1. Synthesis of H_4TPTA and PCN-207-FA



Synthesis of Dimethyl 4,4'-(2-hydroxyacetyl) dibenzoate (1) In a 100 ml round-bottom flask, thiamine hydrochloride (3.6 g, 10.70 mmol) was dissolved in 40 mL of 1:3 water/methanol mixture and cooled down using an ice bath before 10 mL of a 2 M NaOH solution was added dropwise for a period of 20 min. To the resulting solution 4-formyl benzoate (29.8 g, 182 mmol) was added and then the mixture was heated to 60 °C for 20 min and afterward at reflux conditions for 2 h. The resulting suspension was cooled to room temperature and the white solid was filtered off, washed with water, methanol and ethyl ether, then was dried on air. Yield: 21.7 g (72.5%). ^{1}H NMR (300 MHz, DMSO-d_6) δ = 8.11 (d, 2H), 8.01 (d, 2H), 7.91 (d, 2H), 7.57 (d, 2H), 6.45 (s, 1H), 6.16 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H).

Synthesis of Tetramethyl(4,4',4'',4'''-(pyrazine-2,3,5,6-tetrayl))tetrabenzoate (2) Into a 50 mL round bottom flask was added 4.5 g (13.5 mmol) of **3**, 3.12 g (40.5 mmol) of ammonium acetate, 2 mL (20.25 mmol) of acetic anhydride, and 11 mL of acetic acid. After refluxing for 4 h, the mixture was cooled down to room temperature, filtered, and then washed with hot acetic acid. Light-yellow powder was obtained in 54.4% yield. ^{1}H NMR (300 MHz $CDCl_3$): δ = 8.01 (d, 8H), 7.69 (d, 8H).

Synthesis of H_4TPTA (3). Compound 2 (5.1 g, 8.3 mmol) was suspended in 150 mL THF/H_2O (v: v = 1: 1). 60.0 mL of 10 % NaOH solution was added to the suspension and stirred overnight. The pH was adjusted to approximately 3 using hydrochloric acid. The resulting brown precipitate was collected by centrifuge, washed with water, and dried under vacuum to yield H_4TPTA (3.9 g, 78 %). ^{1} H NMR (300 MHz, DMSO-d_6): δ = 7.94 (d, 8H), 7.67 (d, 8H).

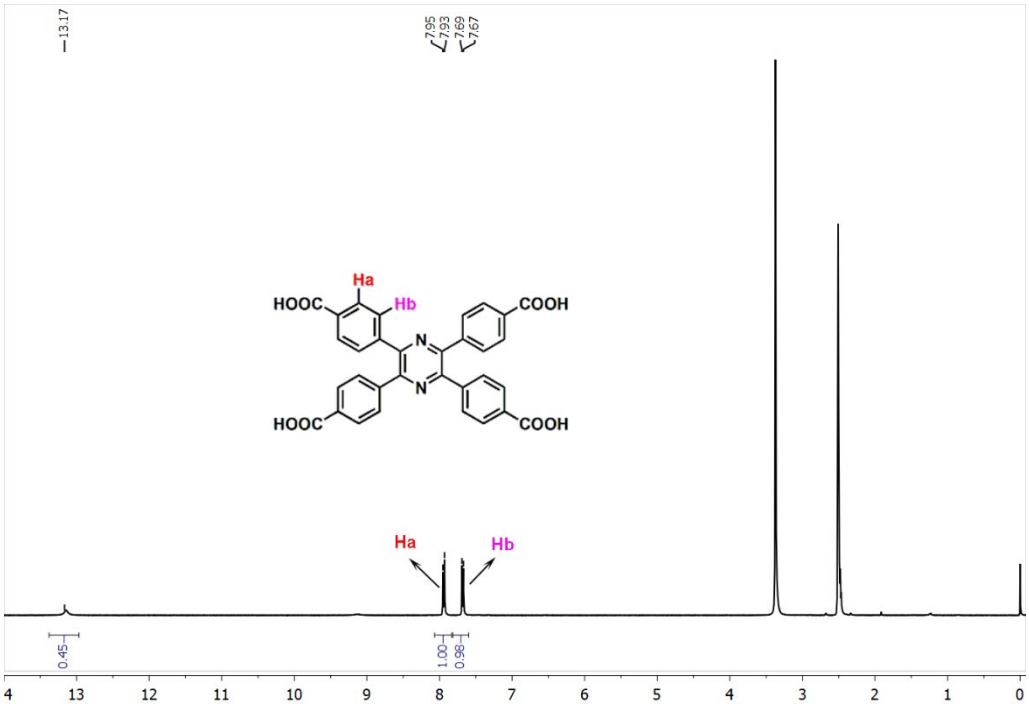


Figure S1. ^{1}H NMR spectrum of H_4TPTA (300 MHz, DMSO-d^6).

Synthesis of PCN-207

$ZrCl_4$ (20 mg, 29 mM), H_4TPTA (10 mg, 6 mM), and benzoic acid (600 mg, 1.85 M) in DMF were charged in a Pyrex vial. The mixture (3 mL) was heated in a 120 ºC oven for 24 h. After cooling down to room temperature, the mixture was washed by DMF for three times and a colorless crystalline **PCN-207** was harvested.

Synthesis of PCN-207-FA

50 mg PCN-207, FA (20 mg, 172 mM) in 5 ml DMF were charged in a Pyrex vial. The mixture was heated in a 120 ºC oven for 24 h. After cooling down to room temperature, the mixture was washed by DMF for three times and a colorless crystalline **PCN-207-FA** was harvested.

Section 2. The SEM and Crystal data for PCN-207, PCN-207-FA and PCN-207-BDC

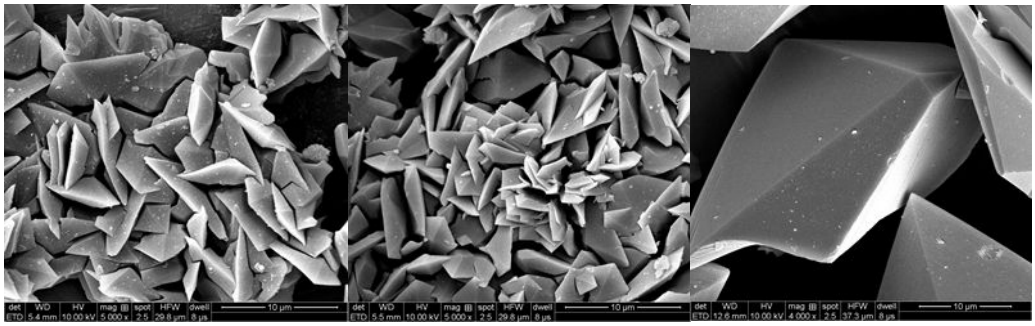


Figure S2. The SEM of (a) PCN-207, (b) PCN-207-FA, (c) PCN-207-BDC

Table S1. Crystal data of PCN-207-FA, PCN-207-BDC and PCN-207

	a(Å)	b(Å)	c(Å)	a/b	Rotation of Ph 1	Rotation of Ph 2
PCN-207-FA	12.7331	29.7668	31.3904	0.4278	38.11 º	38.11 º
PCN-207-BDC	14.588	29.712	30.803	0.4910	67.48 º ,	114.39 º
PCN-207	14.1135	30.892	29.961	0.9699	66.05 º	115.12 º ,

Section 3. thermal and chemical stability

Materials and methods

All the materials were purchased and used without further purification. NMR data were collected on a Mercury 300 spectrometer. Thermo-gravimetric analysis (TGA) experiments were carried out on a Mettler Toledo TGA instrument with a heating rate of 10 C min1 in the range of 25–800 C under a N_2 atmosphere. The powder XRD data were obtained on an X-Pert PRO MPD diffractometer with Cu-Ka radiation. Gas-sorption isotherms were carried out on a Micrometritics ASAP 2020 system.

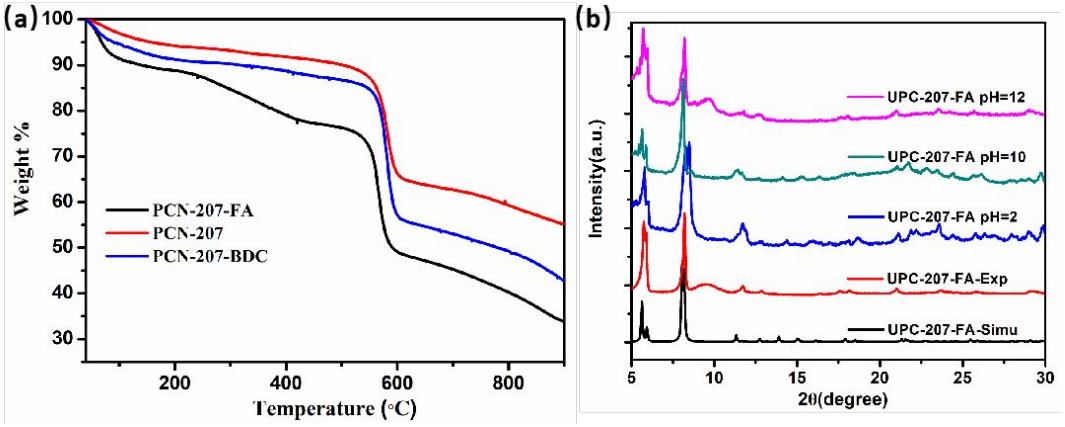


Figure S3. (a) Thermogravimetric analysis (TGA) of PCN-207, PCN-207-FA and PCN-207-BDC. (b) Chemistry stability analysis of PCN-207-FA in different pH value.

Section 4. Gas storage and separation characteristics

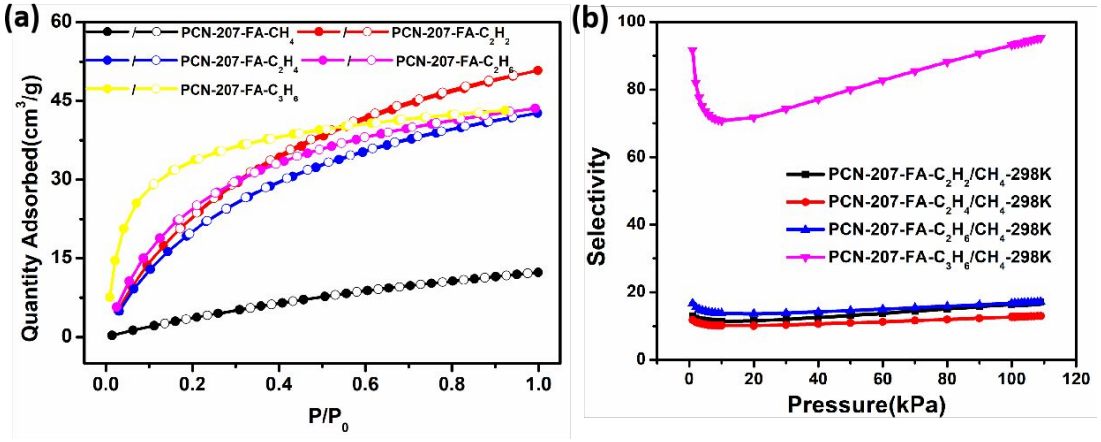


Figure S3. (a) Adsorption isotherms of hydrocarbonsa. (b) Selectivity of C2/C1 and C3/C1 (0.5:0.5) gas mixtures at 298 K.

Table S2. Comparison of the adsorption capacity of PCN-207-FA, PCN-207 and PCN-BDC for light hydrocarbons at 273 K (298K is in italics) and 1 bar

	CH_4(cm^3/g)	C_2H_2(cm^3/g)	C_2H_4(cm^3/g)	C_2H_6(cm^3/g)	C_3H_6(cm^3/g)
PCN-207-FA	18.28/*12.32*	68.90/*50.79*	50.93/*42.69*	53.24/*43.57*	48.69/*43.18*
PCN-207-BDC	9.97/*7.86*	54.74/*39.94*	42.64/*27.63*	43.05/*36.31*	44.44/*38.26*
PCN-207	12.53/*7.46*	63.97/*45.74*	49.45/*40.01*	49.75/*42.28*	48.86/*42.86*

Table S3. Comparison of the selectivity of PCN-207-FA, PCN-207 and PCN-BDC for light hydrocarbons at 273 K (298K is in italics) and 1 bar

	CH_4(cm^3/g)	C_2H_2(cm^3/g)	C_2H_4(cm^3/g)	C_2H_6(cm^3/g)
PCN-207-FA	47.04/*17.08*	18.81/*13.02*	39.76/*17.14*	329.27/*95.28*
PCN-207-BDC	76.71/*20.12*	43.42/*27.46*	92.64/*32.51*	1575.36/*244.00*
PCN-207	21.67/*15.97*	17.*05*/*15.12*	24.40/*21.79*	68.79/*54.32*

Table S4. Comparison of the adsorption enthalpy of PCN-207-FA, PCN-207 and PCN-BDC for light hydrocarbons at 1 bar

	Q_{CH4}(KJ/mol)	Q_{C2H2}(KJ/mol)	Q_{C2H4}(KJ/mol)	Q_{C2H6}(KJ/mol)	Q_{C3H6}(KJ/mol)
PCN-207-FA	19.72	32.47	25.01	29.95	61.29
PCN-207	11.62	28.86	32.95	28.12	50.43
PCN-207-BDC	16.46	28.85	26.19	27.85	48.33