Electronic Supplemental Information for:

Carbonization of Covalent Triazine-based Frameworks via Ionic Liquid Induction

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1. Materials and Methods:

All reagents were obtained from commercial sources unless otherwise noted. Powder X-ray diffraction patterns were collected on a PANanalytical X'Pert PRO MPD X-ray diffractometer at 45 kV, 40 mA for CuKα (λ = 1.5418 Å) with a scan speed of 2°/min. High-resolution dynamic thermogravimetric analysis (TGA) was performed under a continuous O_2 flow and recorded on a TA Instruments Hi-Res TGA Q500 Thermogravimetric Analyzer with a heating rate of 1 °C/minute. Fourier-transform infrared (FT-IR) data (4000–650 cm^{-1}) were collected in the solid state on a Nicolet 700 FT-IR spectrometer. Low-pressure gas adsorption measurements were performed on a fully automated Autosorb-1C gas adsorption analyzer (Quantachrome Instruments) and 3-Flex Surface Characterization Analyzer (Micromeritics). The SEM images were collected on a Nova Nano 600 and Quanta 600 FEG scanning electron microscope. ^{1}H NMR spectrum was recorded on a Bruker Avance III 400 MHz instrument. Chemical shifts for ^{1}H NMR spectrum are reported in ppm (δ, relative to TMS) using DMSO residual peak (δ = 7.26 and 2.50 ppm) in CDCl$_3$ and DMSO-d$_6$ as an internal standard. Solid state NMR spectrum was recorded on a Bruker Avance III 400 MHz spectrometer by conventional double-resonance 4 mm CPMAS probe at 12 kHz MAS and 298 K with sample packed into 4-mm MAS zirconia rotor.

2. Synthesis of Monomer and the POPs
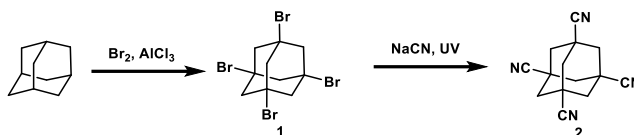
Scheme 1. Monomer synthesis

Synthesis of 1,3,5,7-Tetrabromoadamantane (1)

In a 100 mL round flask, 40 g anhydrous AlCl$_3$ (29 mmol) was suspended in 20 mL (36 mmol) Br$_2$ and the mixture was cooled to 0 °C. 10 g adamantine (7.3 mmol) was slowly added to the mixture. After finishing the addition, the reaction was heated at 70 °C for 8 h. After cooled to room temperature, saturated bisulfite solution was added to the flask to reduce excess Br$_2$. The obtained solution was extracted with CH$_2$Cl$_2$ and the organic layer was washed with water for three times. The organic layer was evaporated, and the crude product was recrystallized by acetone to get desired product as a white crystals of 20 g (81%). ^{1}H NMR (CDCl$_3$): δ 2.71 (s, 12 H).

Synthesis of 1,3,5,7-Tetracyanoadamantane (TCA)

1 (5.0 g, 35 mmol) and sodium cyanide (8.6 g, 0.21 mol) were dissolved in a 200 mL quartz reactor with 180 mL DMSO. The solution was irradiated with 254 nm light for 6 h in a Rayonet reactor. After cooling to room temperature, DMSO was distilled, and 500 mL water was added to get precipitation. The mixture was filtrated, and residue sodium cyanide was decomposed by a commercial beach. The solid was recrystallized from acetone and water to get pale yellow **2** (TCA) of 1.5 g (53%). ^{1}H NMR (d$_6$-DMSO): δ 2.38 (s, 12 H).

Synthesis of KPOP-6a

200 mg monomer TCA and 100 mg anhydrous ZnCl$_2$ were mixed in a pyrex tube measuring o.d × i.d. = 20 × 18 mm^2. The tube was evacuated to an internal pressure of 0.15 mmHg and flame sealed. The tube was introduced in a muffle furnace and heated at 400 °C (heating rate of 0.2 °C/min). After a period of 72 h, the reaction was spontaneously cooled down to room temperature. The black polymer obtained was soaked in 3M HCl for one day and exchanged with water for three times to remove ZnCl$_2$. The solid was continually soaked in acetone for one day during which the activation solvent was decanted and freshly replenished for three times. After that, the sample was evacuated at 200 °C for 10 h to afford the desired POP material. The synthesis procedure of **KPOP-6b**, **KPOP-6c**, **KPOP-6d**, and **KPOP-6e** were same with **KPOP-6a** except using different ZnCl$_2$ amounts of 200, 400, 600, and 1000 mg, respectively.

3. Elemental Analysis, PXRD, TGA Plots and SEM Images

Table S1. Elemental Analysis of the POPs

Name	Monomer /ZnCl$_2$ weight ratio	Found (%)					Calculated (%)				
		C	N	H	C/N	C/H	C	N	H	C/N	C/H
KPOP-6a	2/1	57.83	12.92	4.92	5.2	0.97	71.17	23.71	5.12	3.5	1.16
KPOP-6b	1/1	56.80	11.09	5.09	5.9	0.92	71.17	23.71	5.12	3.5	1.16
KPOP-6c	1/2	72.25	7.49	3.73	11.2	1.6	71.17	23.71	5.12	3.5	1.16
KPOP-6d	1/3	69.82	6.64	3.01	12.2	1.9	71.17	23.71	5.12	3.5	1.16
KPOP-6e	1/5	69.12	5.39	2.58	14.9	2.2	71.17	23.71	5.12	3.5	1.16

Note that the residual mass observed in all cases is higher than the residues detected by TGA measurements which is also reported by other triazine POPs. The incomplete combustion of the samples is probalblely responsible for deviations from the calculated values. The actived sample which will adsorb water from the air may be another reason. During the N$_2$ purging stage of the TGA test at room temperature, weight loss was found.
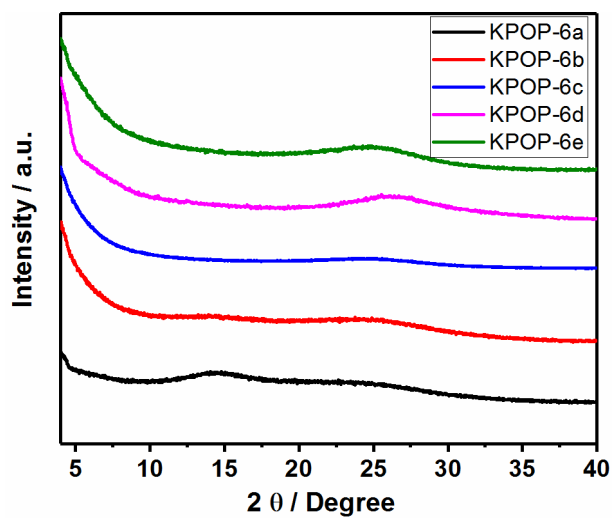
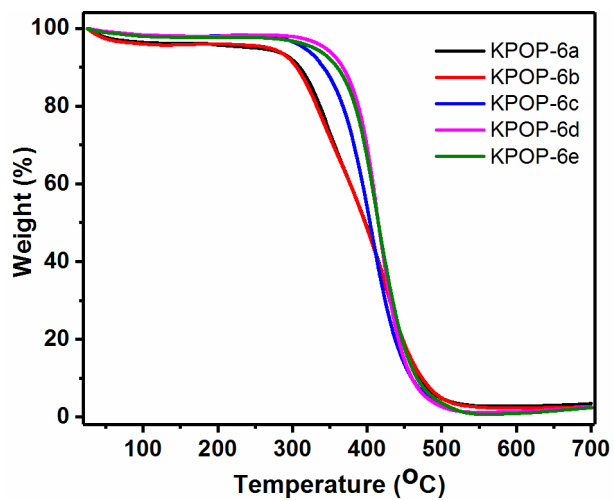**Fig. S1.** Powder XRD patterns of the POPs.

Fig. S2. TGA plots of the POPs. There are still small amount of residues noncombustible which might come from the partially oxidation of $ZnCl_2$ which was trapped inside the POP materials.
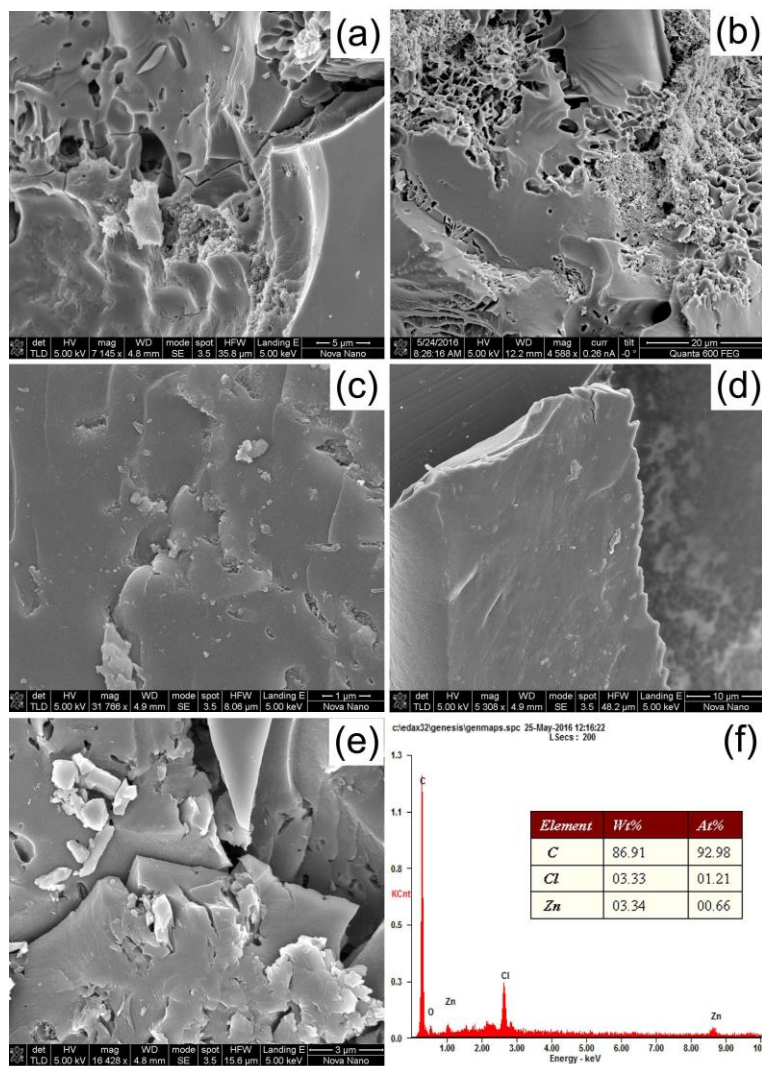
Fig. S3. SEM images of KPOP-6a (a), KPOP-6b (b), KPOP-6c (c), KPOP-6d (d), KPOP-6e (e) and EDS of KPOP-6b (f).
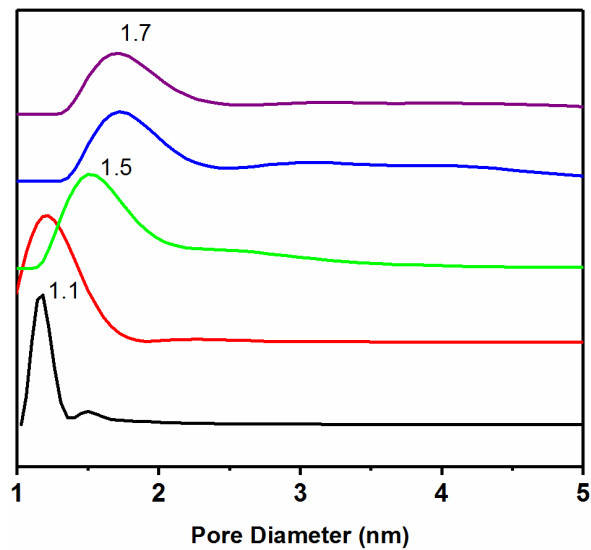
4. Low-Pressure Gas Adsorption Measurements

Fig. S4a. Pore size distribution of KPOP-6a (black), KPOP-6b (red), KPOP-6c (blue), KPOP-6d (green) and KPOP-6e (purple).
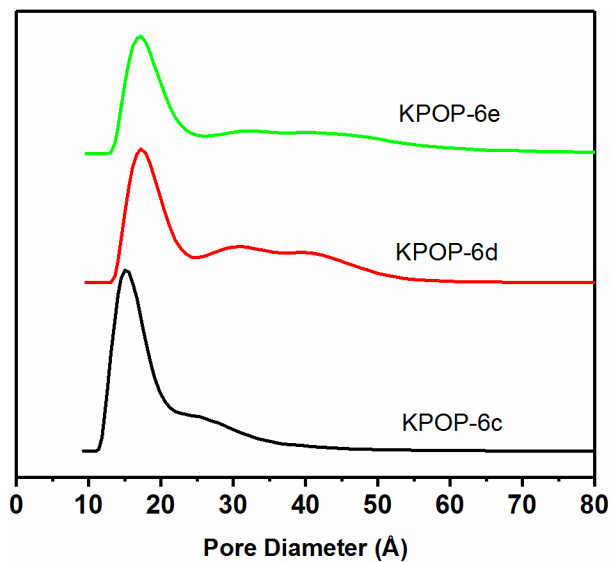

Fig. S4b. Pore size distribution of KPOP-6c, 6d and 6e by cylinder pore model. The fitting error for KPOP-6c, 6d and 6e are 0.576 %, 0.699 %, and 0.636 %, respectively.
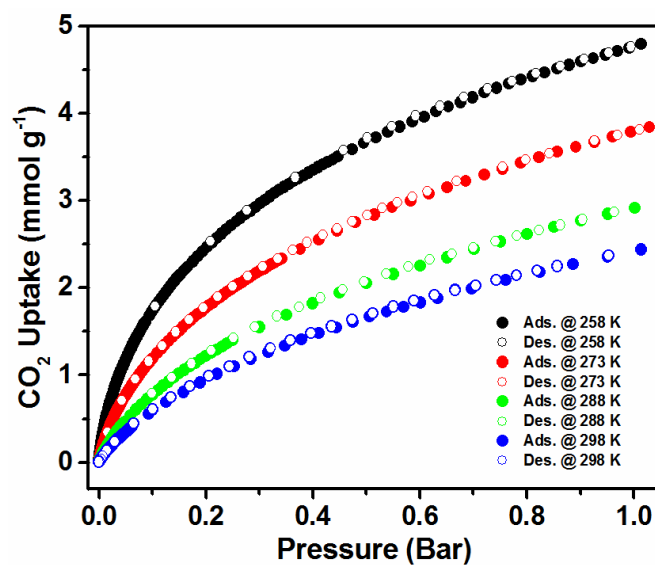
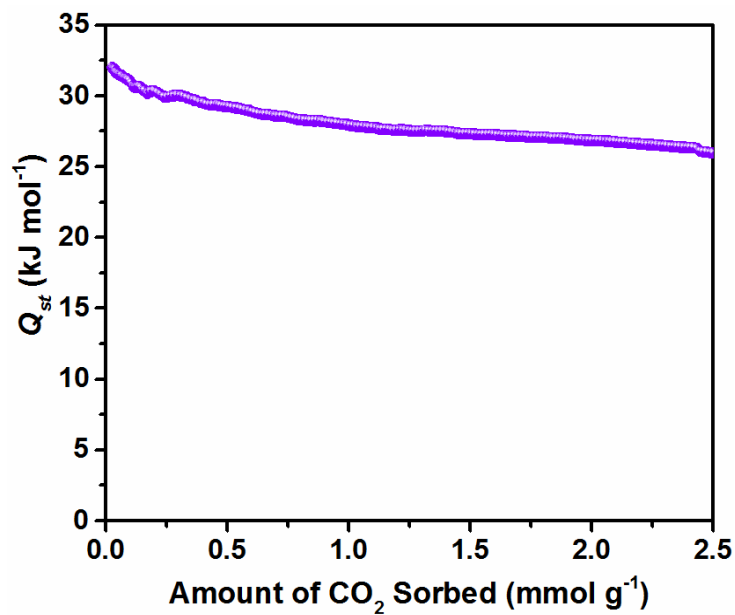**Fig. S5.** CO_2 adsorption/desorption isotherms of KPOP-6b.

Fig. S6. CO_2 adsorption heat curve of KPOP-6b.

5. Prediction of multicomponent gas adsorption Ideal Adsorption Solution Theory (IAST):

The Ideal Adsorption Solution Theory (IAST) proposed by Mayer and Prausnitz (1965)[1] uses pure gas adsorption isotherms to predict the mixture adsorption equilibrium at the temperature of interest. For IAST application, the main condition to be fulfilled is the availability of (i) good quality single component adsorption data of different gases, and (ii) an excellent curve fitting model for such data (Chen and Sholl, 2007; [2] Bae et al., 2008[3]). In the current work, Toth model was used to fit the pure gas isotherms.

The most important equations used in the IAST calculation are listed hereafter:

$$f_i = x_i f_i^0(\pi) \quad (1)$$

$$\frac{\pi A}{RT} = \int_0^{f_i^0} n_i d \ln f_i \quad (2)$$

$$\frac{1}{n_t} = \sum_i \frac{x_i}{n_i^0} \quad (3)$$

$$S_{CO_2-i} = \frac{x_{CO_2} / x_i}{y_{CO_2} / y_i} \quad (4)$$

where f_i is the fugacity of component i in the gas phase; f_i^0 is the standard-state fugacity (i.e., the fugacity of pure component i at the equilibrium spreading pressure of the mixture, π); x_i and y_i are the mole fractions of component i in the adsorbed and gas phase, respectively; A is the surface area of the adsorbent; n_i is the number of moles adsorbed of pure component i (i.e., the pure-component isotherm); and n_i^0 is the number of moles adsorbed of pure component i at the standard-state pressure.

Equation 3 is the central equation of IAST, specifying the equality of the chemical potential of component i in the gas and the adsorbed phase (which is assumed to be ideal in the sense of Raoult's law). Equation 4 allows the calculation of the spreading pressure from the pure-component adsorption isotherm. The total amount adsorbed of the mixture, n_t, and the selectivity of CO_2 with respect to i, S_{CO_2-i}, are given by equations 3 and 4, respectively. The selectivity, S_{CO_2-i}, reflects the efficiency of CO_2 separation.

Toth Model for single gas adsorption fitting

In the current work, the Toth model was used to fit the pure gas isotherms and its simple formulation as expressed by equation 7 (Toth, 2002)[4]

$$n = n_s \frac{KP}{(1 + (KP)^m)^{1/m}} \quad (7)$$

where n is the amount adsorbed, n_s is the amount adsorbed at saturation, P is the equilibrium pressure, K is the equilibrium constant, and m is a parameter indicating the heterogeneity of the adsorbent.

Table S2: Toth parameters for adsorption on KPOP-6b.

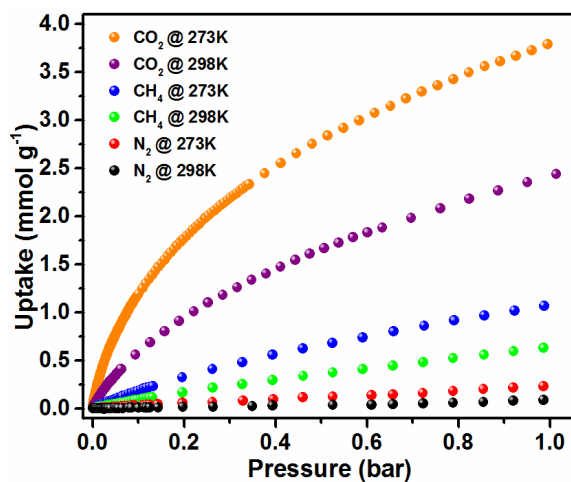|	Parameters	Gases		
		CH_4	CO_2	N_2
298 K	n_s	7.50	7.4	11.7
	K	**0.147**	**1.37**	**0.007**
	m	0.54	0.54	1
273K	n_s	12.2	16.5	11.7
	K	**0.22**	**3.05**	**0.029**
	m	0.45	0.35	0.45

Fig. S7. CO_2, CH_4 and N_2 adsorption isotherms of KPOP-6b.
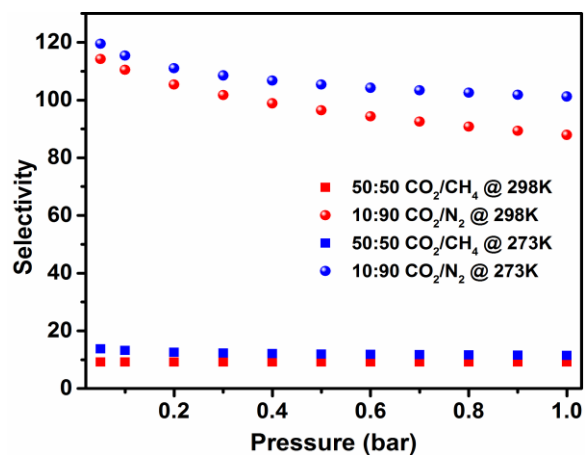
Fig. S8. IAST selectivities of KPOP-6b for 50:50 CO_2/CH_4 (squares) and 10:90 CO_2/N_2 (circles) binary mixtures predicted at 298 K (red) and 273 K (blue).

6. Reference

1) Myers, A.L.; Prausnitz, J.M. *AIChE J.* 1965, **11**, 121-127.
2) Chen, H.; Sholl, D.S., *Langmuir* 2007, **23**, 6431-6437.
3) Bae, Y.-S.; Mulfort, K.L.; Frost, H.; Ryan, P.; Punatahnam, S.; Braodbelt, L. J.; Hupp, J. T.; Snurr, Q.R. *Langmuir* 2008, **24**, 8592-8598.
4) Toth, J., 2002. Adsorption. Theory, modeling and analysis, Marcel Dekker, New York.