Design and synthesis of multifunctional porous N-rich polymer containing *s*triazine and Tröger's base for CO₂ adsorption, catalysis and sensing

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Experimental Details

Synthesis of 2,4,6-tris(4-aminophenyl)-s-triazine (TAPT)

TAPT was synthesized according to the literature. In a typical synthesis, 10 mL trifluoromethanesulfonic acid was added into a three-necked round bottom flask maintained at 0 °C under N₂ atmosphere. The solution was stirred for 0.5 h. Separately, 4-aminobenzonitrile (590.0 mg, 5 mmol) was added to the trifluoromethanesulfonic acid solution at 0 °C under N₂ atmosphere. The reaction mixture was warmed up to room temperature and was allowed to stir under N₂ for 24 h. The contents were neutralized by adding about 250 mL of 2 M NaOH solution. Upon neutralization, a pale-yellow precipitate (487.3 mg) was obtained, which was filtered and washed with copious amounts of distilled water. Yield: 82.6%. ¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm): 8.4-8.3 (d, 6H, Ar–H), 6.71-6.67 (d, 6H, Ar–H), 5.92 (s, 6H, Ar–NH₂). ¹³C NMR (75 MHz, DMSO-*d*₆) δ (ppm): 169.6, 152.9, 130.1, 123.0, 113.1.

Characterization



Fig. S1 TG analysis of porous N-rich polymer.



Fig. S2 Experimental powder X-ray diffraction PXRD pattern of porous N-rich polymer.



Fig. S3 Size distribution of porous N-rich polymer in EtOH (0.1 mg/mL) determined by DLS Analysis.



Fig. S4 SEM images of porous N-rich polymer.



Fig. S5 TEM images of porous N-rich polymer.

Heat of CO₂/CH₄ Adsorption Calculation

The isosteric heats (Q_{st}) of adsorption for porous N-rich polymer were calculated by fitting the CO₂ adsorption isotherms measured at 273 K, 283 K and 298 K to the Virial equation.

The isosteric heats (Q_{st}) of adsorption for porous N-rich polymer were calculated by fitting the CH_4 adsorption isotherms measured at 273 K and 298 K to the Virial equation.

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N_i + \sum_{i=0}^{n} b_j N_i$$

$$Q_{st} = -R \sum_{i=0}^{m} a_i N_i$$

- N: amount adsorbed (mg/g);P: pressure (mmHg);
- *T*: temperature (K);
- a_i, b_j : constants;
- *R*: 8.314 J·mol⁻¹·K⁻¹



Fig. S6 Virial fitting for CO₂ isotherms of porous N-rich polymer.



Fig. S7 The isosteric heat of adsorption for CO_2 .



Fig. S8 CH₄ adsorption isotherms at 273 K and 298 K for porous N-rich polymer.



Fig. S9 Virial fitting for CH₄ isotherms of porous N-rich polymer.



Fig. S10 Isosteric heat of adsorption for CH₄.

Prediction of adsorption of binary mixture by IAST theory

In order to perform the IAST calculations, the single-component isotherm was fitted by the single-site Langmuir-Freundlich (SSLF) adsorption model to correlate the pure-component equilibrium data and further predict the adsorption of mixtures. The SSLF model is described as:

$$N^{0}(f) = \frac{N_{1}k_{1}f}{1+k_{1}f}$$

Where f is the fugacity of bulk gas at equilibrium with adsorbed phase, N is the model parameter of the maximum adsorption amount, and k is the affinity constant.

Based on the above model parameters of pure gas adsorption, we used the IAST model, which was proposed by Myer and Prausnitz in 1965 to predict the multicomponent adsorption. Analogous to Raoult's law for vapor-liquid equilibrium, the IAST assumes that the adsorbed solutions are ideal and all activity coefficients in the adsorbed phase are unity. Thus, the adsorption equilibrium between adsorbed and gas phases will lead to the following equation

$$Py_i\varphi_i = x_i f_i^0(\pi)$$

Where f_i^0 is the fugacity of the equilibrium gas phase corresponding to the spreading pressure π for the adsorption of pure gas *i*, φ_i is the gas fugacity coefficient of component *i* calculated by *PR* equation of state, and x_i and y_i are the molar fraction of component *i* at the adsorbed and bulk phases, respectively. The binary gas mixing process is carried out at constant spreading pressure π and indicated by

$$\int_{0}^{f_{1}^{0}} N_{1}^{0}(f_{1}) dln(f_{1}) = \int_{0}^{f_{2}^{0}} N_{2}^{0}(f_{2}) dln(f_{2})$$

Where the single-component adsorption amount and selectivity are further obtained from the above equation by numerical integration and root exploration. To investigate the separation of binary mixtures, the adsorption selectivity is defined by

$$S_{ij} = \frac{\frac{x_i}{x_j}}{\frac{y_i}{y_j}}$$

Where the selectivity refers to the first component over the second one, and the x_i , x_j and y_i , y_j , denote the molar fractions of species *i*, *j* in the adsorbed and bulk phases, respectively.



Fig. S11 CO₂ adsorption isotherms at 273 K and 298 K for porous N-rich polymer.



Fig. S12 Nitrogen adsorption isotherms at 273 K of porous N-rich polymer.



Fig. S13 CH₄ adsorption isotherms at 273 K and 298 K for porous N-rich polymer.



Fig. S14 IAST selectivities for CO_2/CH_4 at 273 K and 298 K for 50:50 mixtures of porous N-rich polymer.



Fig. S15 IAST selectivities for CO_2/CH_4 at 273 K and 298 K for 5:95 mixtures of porous N-rich polymer.



Fig. S16 IAST selectivities for CO_2/N_2 at 273 K for 15:85 mixtures of porous N-rich polymer.



Fig. S17 IAST selectivities for CO_2/N_2 at 273 K for 50:50 mixtures of porous N-rich polymer.

The concentration of hydrochloric acid vapor was determined according to the following definitions:

$$ppm = \frac{c \times V_{HCl} \times V_m}{V}$$

Where *c* is the molar concentration of the hydrochloric acid, V_{HCl} is the volume of the hydrochloric acid, V_m is the molar volume of gas, and *V* is the volume of the glass solution bottle.



Fig. S18 UV-Vis diffusive reflectance spectra of the polymer by hydrochloric acid vapor at different concentrations within 10 s.



Fig. S19 UV-Vis diffusive reflectance spectra of the polymer by hydrochloric acid vapor (1345 ppm) at different times.



Fig. S20 UV-Vis diffusive reflectance spectra of the polymer in several hydrochloric acid / ammonia cycles within 15 s.



Fig. S21 Reusability of the porous N-rich polymer catalysts in the syntheses between benzaldehyde and malononitrile.



Fig. S22 Reusability of the porous N-rich polymer catalysts in the syntheses between 4-bromobenzaldehyde and malononitrile.



Fig. S23 ¹H NMR spectrum of benzylidenemalononitrile.



Fig. S24 ¹H NMR spectrum of 4-bromobenzylidenemalononitrile.



Fig. S25 ¹H NMR spectrum of 4-methylbenzylidenemalononitrile.



Fig. S26 ¹H NMR spectrum of 4-chlorobenzylidenemalonodinitrile.



Fig. S27 ¹H NMR spectrum of 4-cyanobenzylidenemalononitrile.



Fig. S28 ¹H NMR spectrum of 4-nitrobenzylidenemalononitrile.

Table S1. Elemental analysis of porous N-rich polymer.

Element	N-rich Polymer	Calculated
C [%]	67.71	74.98
H [%]	4.973	4.44
N [%]	18.44	20.58
C/N ratio	3.67	3.64

Table S2. The values of selectivity calculated by the IAST method

 CO_2/N_2	CO ₂ /CH ₄

Compound	Selectivity	Selectivity	Reference
this porous polymer	55.3	9.2	this work
MOPI-I	65.3	16	1
ALP-3	44	8	2
TNP3	48	9	3
PIN1	31	12	4
MPI-6FA	53.5	11.9	5
CTF-FL	48	5	6
Azo-COP-10	165.2		7
PCTF-4	56	20	8
Ni-Por-3	19.1	4.22	9
JLU-SOF1-R	31.2	3.7	10
JLU-Liu20		5.5	11

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