Supporting Information

A nitrogen-rich azaindole-based microporous organic network: Synergistic effect of local dipole- π and dipolequadrupole interactions on carbon dioxide uptake

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Table of contents

1.	Main materials and measurements	S3-4
2.	Preparation and characterization of PEINK	
	6	
3.	Preparation and characterization of N-PEINK	S6-
	7	
4.	Solubility of the N-PEINK	S8
5.	Micro structures of PEINK	S8
6.	Three-dimensional structures of microporous N-PEINK and PEINK	S9-10
7.	Nitrogen adsorption-desorption isotherms of microporous PEINK	S10
8.	BET specific surface area plots of N-PEINK and PEINK	S11
9.	Thermal behaviors of microporous N-PEINK and PEINK	S12-13
10.	Gas adsorption isotherms of N-PEINK and PEINK	S14
11.	Water effect on gas adsorption	S14
12.	Isosteric heat of gas adsorption for the networks	
13.	Simulation method	S16
14.	References	S17

1. Main materials and measurements

1,3,5-tris-(4-fluorobenzoyl)benzene and 4-hydroxyindole were synthesized in our laboratoryicals. 4-hydroxy-7-azaindole was purchased from J & K Technology Co., Ltd., and was purified by recrystallization from alcohol twice before use. The rest of the materials and reagents were obtained from different commercial sources and used without further purification.

FT-IR spectrum was recorded on a Nicolet 6700 FTIR spectrometer. Solid-state cross-polarization magic-angle-spinning (CP/MAS) NMR spectra were recorded on a Bruker Avance III 400 NMR spectrometer. The elemental analysis characterization technique was performed using a Vario EL III apparatus. Mass spectra were recorded with a Microflex LRF MALDI-TOF mass spectrometer. Thermogravimetric analysis (TGA) was performed on a Setarma TG-92 at a heating rate of 10 °C/min under nitrogen atmosphere. Scanning electron microscopy (SEM) was recorded on an S-4800 (Hitachi Ltd) field emission scanning electron microscope. Morphological observation was performed with a Tecnai G2 F20 S-TWIN (FEI Company) transmission electron microscope. Gas adsorption isotherms were measured by a volumetric method using a Micromeritics AR-JW-BK112 instrument. The samples were degassed 10 hours at 120 °C, and the obtained adsorption-desorption isotherms were evaluated to obtain the pore parameters, including Brunauer-Emmett-Teller (BET) specific surface area, pore size, and pore volume. The pore size distribution (PSD) was calculated from the adsorption branch with the nonlocal density functional theory (NLDFT) approach. The selectivity of the prepared N-PEINK to separate CO₂ from CO₂/N₂/CH₄ mixtures was estimated by the ratio between the CO₂, N₂ and CH₄ adsorption capacities at a selected pressure. The Clausius-Clapeyron equation was employed to calculate the enthalpies of adsorption for H₂ and CO₂ on the networks. In each case, the data were fit using the equation: $(\ln P)_n = -(Q_{st}/R)(1/T) + C$, where *P* is the pressure, *n* is thxe amount adsorbed, *T* is the temperature, *R* is the universal gas constant and *C* is a constant. The isosteric heat of adsorption Q_{st} was subsequently obtained from the slope of plots of $(\ln P)_n$ as a function of 1/T. The simulation method was presented in Supporting Information.

2. Preparation and characterization of PEINK

To a two-necked flask equipped with magnetic stirrer, an argon outlet, inlet, and water-cooled condenser, 1,3,5-tris-(4-fluorobenzoyl)benzene (2.0 mmol), 4-hydroxyindole (3.0 mmol), K₂CO₃ (6 mmol), and NMP (20.0 mL) were added. The reaction mixture was evacuated and flushed with high-purity nitrogen. This procedure was repeated three times. The reaction mixture was heated to 160 °C under stirring for 2h, and then the temperature was subsequently brought to 180 °C and maintained at this temperature for 4h. The resulting polymer solution was allowed to slowly cool to room temperature, and subsequently poured into cold water, filtered, washed with water and methanol. After extraction with methanol in

a soxhlet extractor for 24 h, the desired PEINK was collected and dried overnight in a vacuum oven at 120 °C (yield 98%).



Fig. S1. FT-IR and ¹³C CP/MAS NMR spectra of PEINK

The resulting microporous PEINK was characterized at molecular levels by a FTIR spectrometer and ¹³C CP/MAS NMR spectrometer. The FTIR spectrum for the porous polymer is shown in **Fig. S1a**, in which the weak absorption peak at about 3430 cm⁻¹ correspond to the handful of tail end group (NH and OH in the 4-hydroxyindole units). The peaks at about 1604, 1490 and 1445 cm⁻¹ are attributed to the vibrations of the aromatic ring skeleton. In addition, we noticed the broad absorption peak at about 1661 cm⁻¹, which correspond to the structure of -C=O in the PEINK networks. The structural information of the prepared PEINK was also obtained by ¹³C CP/MAS NMR spectroscopy (**Fig. S1b**). There are two broad peaks at ~191 and 150-90 ppm. The peak at about 191 ppm is ascribed to the

carbonyl group carbons (**Fig. S1b**, **3**), the broad peaks at 150-90 ppm are ascribed to the indole group and other aromatic carbons (**Fig. S1b**, **1,2**, **4-15**).

3. Preparation and characterization of N-PEINK

To a two-necked flask equipped with magnetic stirrer, an argon outlet, inlet, and water-cooled condenser, 1,3,5-tris-(4-fluorobenzoyl)benzene (2.0 mmol), 4hydroxy-7-azaindole (3.0 mmol), K_2CO_3 (6 mmol), and NMP (20.0 mL) were added. The reaction mixture was evacuated and flushed with high-purity nitrogen. This procedure was repeated three times. The reaction mixture was heated to 160 oC under stirring for 2h, and then the temperature was subsequently brought to 180 °C and maintained at this temperature for 4h. The resulting polymer solution was allowed to slowly cool to room temperature, and subsequently poured into cold water, filtered, washed with water and methanol. After extraction with methanol in a soxhlet extractor for 24 h, the desired N-PEINK was collected and dried overnight in a vacuum oven at 120 °C (yield 97%).

In order to confirm the successful formation of the resulting microporous polymer, N-PEINK was characterized at molecular levels by a FTIR spectrometer and ¹³C CP/MAS NMR spectrometer. The FTIR spectrum for the porous polymer is shown in **Fig. S2a**, in which the weak absorption peak at about 3434 cm⁻¹ correspond to the handful of tail end group (NH and OH in the 4-hydroxy-7-azaindole group). The peaks at about 1633 and 1422 cm⁻¹ are attributed to the

S6

vibrations of the aromatic ring skeleton. In addition, we noticed the broad absorption peak at about 1677 cm⁻¹, which correspond to the structure of -C=O in the hypercrosslinked networks. The structural information of the prepared N-PEINK was also obtained by ¹³C CP/MAS NMR spectroscopy (**Fig. S2b**). There are two broad peaks at ~193 and 160-90 ppm. The peak at about 193 ppm is ascribed to the carbonyl group carbons (**Fig. S2b**, **3**), the broad peaks at 160-90 ppm are ascribed to the indole group and other aromatic carbons (**Fig. S2b**, **1,2, 4-13**).



Fig. S2. FT-IR and ¹³C CP/MAS NMR spectra of N-PEINK

4. Solubility of the N-PEINK

Solubility of the N-PEINK polymer was qualitatively determined by the dissolution of 5 mg of solid material in 1 mL of organic solvents at 50 °C, and the test data was summarized in Table S1.

Polymer Code	DMAc	DMSO	DMF	NMP	CHCl ₃
N-PEINK					
PEINK					

Table S1. Solubility of the N-PEINK

--: Solid polymer was not dissolved at 50 °C

5. Micro structures of PEINK

The morphologies of microporous polymer (PEINK) was investigated by scanning electron microscopy (SEM) image and high-resolution transmission electron microscopy (TEM) (**Fig. S3**). The TEM image (inset in **Fig. S3**) is indicative of porous structures of the material. SEM analysis of PEINK displays that the polymer consists of aggregated particles with submicrometer sizes.



Fig. S3. SEM and TEM (inset) of microporous PEINK.

6. Three-dimensional structures of microporous N-PEINK and PEINK



Fig. S4. The Three-dimensional pore structures of N-PEINK.





Fig. S5. The Three-dimensional pore structures of PEINK.

7. Nitrogen adsorption-desorption isotherms of microporous PEINK



Fig. S6. Nitrogen adsorption-desorption isotherms and the pore size distribution (inset) of microporous PEINK



8. BET specific surface area plots of N-PEINK and PEINK





Fig. S8. BET specific surface area plots of PEINK

9. Thermal behaviors of microporous N-PEINK and PEINK



Fig. S9. TG curve of N-PEINK in nitrogen.



Fig. S10. TG curve of PEINK in nitrogen.



Fig. S11. Glass transition curve of N-PEINK in nitrogen.



Fig. S12. Glass transition curve of PEINK in nitrogen.



10. Gas adsorption isotherms of N-PEINK and PEINK

Fig. S13. Gas adsorption isotherms of the resulting networks: (a), N-PEINK at 291 K; (b), N-PEINK at 308 K; (c), PEINK at 291 K; (d), PEINK at 308 K.

11. Water effect on gas adsorption



Fig. S14. Water effect on gas adsorption at 273 K.



12. Isosteric heat of gas adsorption for the networks

Fig. S15. Isosteric heat of CO₂ adsorption for N-PEINK and PEINK.



Fig. S16. Isosteric heat of H₂ adsorption for N-PEINK.

13. Simulation method

In this article, molecular models were performed on the Amorphous Cell module of the Materials Studio program (MS,^[1] version 4.4, Accelrys Software Inc., USA). The "Dreiding force field" was used. A single parent chain with 18 repeat units was generated originally. Although the system size of 18 repeat units is not enough to represent conformations of a real branched polymers, previous researchers have reported reasonable results when they used 10-15 repeat units for rigid polymer simulation.^[2] Then, periodic boundary conditions were imposed and an initial density of 0.6 g/cm³ was used to simulate the bulk aggregation structure for model N-PEINK and PEINK polymers, respectively. Each initial structure was optimized by a molecular mechanics (MM) technique using the conjugate gradient method. Because this optimized structure might, however, be still in a local energy minimum state, it was relaxed through NVT molecular dynamics (MD) (In the canonical ensemble, mole (M), volume (V), and temperature (T) are conserved), the time evolution of chain conformations up to 1000 ps with time steps of 0.0002 ps at 800 K. This high-temperature relaxation procedure was suggested by Lee et al.^[3] To obtain a suitable structure for further MD simulation, we built and relaxed 10 different initial structures for each system according to the procedure mentioned previously.^[4] Only one structure with the lowest energy for each system was selected as the sample structure for the further research.

14. References

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