Supporting Information

Enhanced carbon dioxide capture in indole-based microporous organic polymer via synergistic effects of indoles and their adjacent carbonyl groups

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Main materials and measurements

1,3,5-Benzenetricarbonyl trichloride was purchased from Sigma-Aldrich Chemicals. Indole 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 purification.

FT-IR spectra were recorded on a Nicolet 6700 FTIR spectrometer. ¹H NMR and ¹³C NMR spectra were recorded using Bruker AMX600 MHz NMR spectrometers in DMSO-d₆. Solidstate cross-polarization magicangle-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⁻¹ under a nitrogen atmosphere. The scanning electron microscopy (SEM) image 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 Quantachrome NOVA 3000. The samples were degassed for 10 hours at 120 °C, and the obtained adsorption-desorption

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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 using the nonlocal density functional theory (NLDFT) approach. The selectivity of the the prepared PKIN to separate CO₂ from $CO_2/N_2/CH_4$ mixtures was estimated by the ratio between the CO_2 , N₂ and CH₄ adsorption capacities at a selected pressure. The Clausius-Clapeyron equation was employed to calculate the enthalpies of adsorption for 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 the 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 $(In P)_n$ as a function of 1/T. The simulation method was presented in Supporting Information.

Synthesis and characterizations of KIN

To a solution of indole (363 mg, 3.1 mmol) in anhyd DCE (3.5 mL) taken in a round-bottom flask at 0 °C under nitrogen was added 1,3,5-Benzenetricarbonyl trichloride (265 mg, 1 mmol) in anhyd DCE (1.5 mL) by a syring under nitrogen. Zirconium tetrachloride (1049 mg, 4.5 mmol) was added under a flow of nitrogen. The reaction temperature was then

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gradually increased to 20 °C, and the reaction was continued at 20 °C. After completion of the reaction as indicated by TLC (4 h), the resultant mixture was quenched with water (10 mL) and extracted with EtOAc (3×30 mL). The combined organic layer was washed with water (2×10 mL), dried with anhyd Na₂SO₄, and concentrated under vacuum. The column chromatographic purification of crude mass on silica gel eluting with EtOAc-DCM provided light yellow powders (294mg, 58% yield). MS (ESI): m/z = 506 [M]⁺; Anal. Calcd for C₃₃H₂₁N₃O₃: C, 78.09; H, 4.17; N, 8.28; Found: C, 78.07; H, 4.15; N, 8.29. FT-IR spectrum (KBr pellet, cm⁻¹): 1607, 1428, 1177, 751, 635; ¹H NMR (400 MHz, DMSO-d₆): δ =12.01 (s, 3H), 8.29 (s, 6H), 8.10(s, 3H), 7.50(d, 3H), 7.25(s, 6H); ¹³C NMR (100 MHz, DMSO-d₆): δ =189.17, 141.20, 137.26, 136.76, 130.79, 126.63, 123.76, 122.56, 121.92, 115.30, 112.83 ppm.



Scheme. S1. Synthetic route of 1,3,5-Tris-(3-indolcarbonyl)benzene (KIN).



Figure S1. Characterizations of compound 1,3,5-Tris-(3-indolcarbonyl)benzene (KIN). (A) ¹H NMR, (B) ¹³C NMR, (C) FTIR.

Preparation of the PKIN

KIN (506mg, 1mmol) was dispersed in 50 mL of DCE under the nitrogen environment. To this solution, we added iron(III) chloride (1.407 mg, 8.7 mmol), and the mixture was stirred at room temperature for 24 h. The resulting mixture was transferred to 150 mL of methanol. The precipitates were collected by filtration and washed with methanol, dilute HCI, distilled water, and methanol, sequentially. After washing, the precipitates were collected and dried under vacuum at 60 °C for 36 h. Yield = 93%. Additionally, the PKIN weas also characterized by a FTIR spectrometer and ¹³C CP/MAS NMR spectrometer, and the satisfactory results were in good agreement with the proposed structures (Fig. S3). Furthermore, in order to further understand the structure of the resulting material, the elemental analysis was also investigated, and the result was listed as follows: Anal. Calcd for $C_{33}H_{18}N_3O_3$: C, 78.50; H, 3.57; N, 8.38; Found: C, 77.88; H, 3.61; N, 8.27.



Scheme. S2. Synthetic of carbonyl functionalized indole-based microporous polymer (PKIN).



Figure S2. Characterizations of PKIN. (A) FT-IR, (B) ¹³C CP/MAS NMR spectrum.

Thermal behaviors of the PKIN



Figure S3. Thermogravimetric (TG) analysis of PKIN in nitrogen.

Gas selectivities of the PKIN



Figure S4. Gas selectivities of the PKIN at different conditions.



Figure S5. CO₂ adsorption capacity at different temperatures (1 bar).

CO₂ multi-cycle sorption isotherms for PINAA



Figure S6. CO₂ multi-cycle sorption isotherms for PKIN at 273K.

Heat of adsorption of the PKIN



Figure S7. Heat of adsorption of the PKIN and PINK, the Q_{st} was calculated from the CO₂ adsorption isotherms at 273 and 298 K using the Clausius–Clapeyron equation.



Figure S8. Plots of In P vs 1=T to determine CO₂ heat of adsorption in PKIN.

Samples	CO ₂ capacity (1.0 bar, 273 K)	CO ₂ /N ₂ (1.0 bar, 273 K)	CO ₂ /CH ₄ (1.0 bar, 273 K)	$\begin{array}{c} Q_{st} \\ (kJ \cdot mol^{-1}) \end{array}$
PKIN-This work	6.12 mmol/g	76	20	35.2
PINK ¹	~4.0 mmol/g	15	32	28.9
N-PEINK ²	~5.2 mmol/g	97	18	31.3
PINAA ³	5.83 mmol/g	83	22	33.1

Table S1. Gas uptake and Q_{st} of different indole-based materials.

 Table S2. Elemental analysis of different indole-based materials.

Samples	Repeat unit	N content (calculated value)	N content (tested value)	Comparison of indole content [#]
PKIN-This work	$C_{33}H_{18}N_3O_3$	8.4%	8.3%	1
PINK ¹	C _{52.5} H ₃₆ N ₃ O ₃	5.5%	5.3%	0.64
N-PEINK ²	C _{37.5} H ₂₁ N ₃ O _{4.5}	7.2%	6.6%	0.40
PINAA ³	$C_{34}H_{22}N_4O_4S$	9.6%	9.0%	0.54

[#] In this work, we define that the content of indole in PKIN is 1, and the others are relative values.

Fully optimized geometries of model compound-CO₂ interactions



Figure S9. Fully optimized geometries of model compound- CO_2 interactions calculated using density functional theory (DFT).



Figure S10. CO₂ adsorption enthalpy for different indole-carbonyl distances.

Simulation method

To illustrate the molecular mechanism, we used density functional theory (DFT)^{4,5} to investigate the interaction of indole, carbonyl with CO₂ and to track the CO₂ capture process. They were calculated at the M06-2X level with the aug-cc-pVDZ basis set and the resolution-of-identity spin-component-scaling Möller-Plesset second-order perturbation theory (RI-scs-MP2) level with the aug-cc-pVTZ basis set.⁶⁻⁸ The geometries were fully optimized without symmetry constraints at each calculation level. The M06-2X functional (hybrid-meta GGA with dispersion correction) has shown good performance in the investigation of the dispersion interaction as well as the electrostatic interaction (H-bonding, H- π interaction, π -

π interaction, additional electrostatic and induction energies of neutral and charged dimeric systems).^{9,10} Single point calculations using the RI-coupled cluster theory with single, double and perturbative triple excitations (RI-CCSD(T)) were performed by employing the aVTZ and aug-cc-pVQZ (aVQZ) basis sets at the RI-scs-MP2/aVTZ geometries. The CO₂-BEs were calculated at the complete basis set (CBS) limit at the RI-CCSD(T) level with the aVTZ and aVQZ basis sets by employing the extrapolation approximation.^{11,12} The complete basis set energies were estimated with the extrapolation scheme utilizing the electron correlation error proportional to N⁻³ for the aug-cc-pVNZ basis set (N=3:T, N=4:Q). It is generally known that the zero-point-energy (ZPE)-uncorrected BE(- ΔE_e) is closer to the experimental CO₂-adsorption enthalpy (ΔH_{ads}) than the ZPE-corrected BE(- ΔE_0).^{3,13,14} Therefore, the values of - ΔE_e are reported as the CO₂-BEs.

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