Electronic Supplementary Information

Pore Polarity Engineering in Hydrogen-bonded Organic

Frameworks for Enhanced lodine Capture

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Sorption experiments

Gaseous I₂ adsorption and release: The adsorption chamber (50 mL) consisted of a cylindrical weighing bottle equipped with a hermetically plug-style stopper, containing excess iodine. Activated adsorbent materials (20 mg) were uniformly distributed on a cylindrical weighing bottle, and inserted into the loading chamber, in a convection oven at 348 K. Iodine uptake was measured gravimetrically at different intervals. The iodine adsorption capacity, Q (g g⁻¹), was calculated using the following equation:

$$Q = \frac{m_e - m_0}{m_0}$$

where m_0 and m_e are the weights of sorbent materials before and after iodine capture. For the competitive adsorption experiments, additional saturated calcium chloride (CaCl₂) aqueous solution was placed in the adsorption chamber to keep a constant relative humidity (RH, 18%, 350 K). For recycling the adsorbents, iodine was released in methanol. Specifically, I₂@HOFs were dispersed in 50 mL of methanol at room temperature for 24 h. The resulting sample was collected by certification and washed with methanol three times. Before adsorption cycles, the material was activated under N₂ flow at room temperature after the solvent exchange with hexane.

Iodine capture from aqueous solution: A stock solution of 1000 ppm of iodine was made by dissolving 1 g of nonradioactive iodine and 1.96 g of KI in 1 L of water and stored in an amber volumetric flask. Lower concentrations were made through serial dilutions of the stock solution. The solution was stored in darkness, due to decomposition in the light.

Iodine sorption isotherms: To obtain the iodine adsorption isotherms, various adsorbents were added into 10 mL aqueous solutions with different concentrations. Sorbents were suspended fully by brief sonication and then the mixtures were stirred vigorously overnight, by which time it was assumed that adsorption equilibrium had been reached. The treated solutions were filtrated through a 0.45-µm membrane filter. The supernatant was analyzed using UV-vis analysis to determine the remaining iodine concentration. The adsorbed amount at equilibrium (q_e , mg g⁻¹) was calculated by

$$q_e = \frac{(C_i - C_e) \times V}{m}$$

where V is the volume of the treated solution (mL), m is the amount of used adsorbent (g), and C_i and C_e are the initial concentration and the final equilibrium concentration of iodine, respectively.

lodine sorption kinetics. Iodine aqueous solution (50 mL, 100 ppm), and adsorbents (10 mg) were added to an Erlenmeyer flask with a magnetic stir bar. The mixture was stirred at room temperature. At appropriate time intervals, the aliquots (1 mL) were taken from the mixture,

and the adsorbents were separated by a syringe filter (0.45-µm membrane filter). The iodine concentrations in the resulting solutions were analyzed by UV-vis or ICP-MS. The percentage removal of iodine was calculated using the following equation:

Removal percentage (%) =
$$\frac{C_0 - C_t}{C_0} \times 100$$

where C_0 and C_t are the initial and equilibrium concentrations of iodine, respectively.

Breakthrough tests: For column separation of iodine species from the aqueous solution, 200 mg of HOF-TAM-BPY was packed approximately 2 cm in length in a column made by a 10 mL syringe. 20 ppm of iodine aqueous solution was passed through the column at a speed of 1.0 mL h⁻¹ controlled by a syringe pump. Approximately 200 mL of iodine aqueous solution was passed through the column, and the effluent was collected at 20 mL intervals and analyzed by ICP-MS to determine the concentration changes of iodine.

Characterization

Powder X-ray diffraction (PXRD) data were collected on a Bruker AXS D8 Advance A25 Powder X-ray diffractometer (40 kV, 40 mA) using Cu K α (λ =1.5406 Å) radiation. Raman spectra were recorded on a Renishaw inVia model confocal microscopy. TGA was carried out on a Q50 thermogravimetric analyzer under N₂ atmosphere. Raman spectrometer equipped with a germanium CCD camera detector using UV radiation from a He/Ne laser for excitation and a resolution of 4 cm⁻¹. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) spectra were performed on a Thermo ESCALAB 250 with AI K α irradiation at θ =90° for X-ray sources, and the binding energies were calibrated using the C1s peak at 284.9 eV. UV-vis spectra were recorded on a SHIMADZU UV-2600 spectrometer. EPR spectrum was recorded on the Bruker ELEXSYS-II E500 CW.

Density-functional theory calculations

First-principles density functional theory (DFT) calculations were performed using the Quantum-Espresso package.^{S1} A semi-empirical addition of dispersive forces to conventional DFT was included in the calculation to account for van der Waals interactions.^{S2} Vanderbilt-type ultrasoft pseudopotentials and generalized gradient approximation with Perdew-Burke-Ernzerhof (PBE) exchange correlation were used. Cutoff energy of 544 eV and 2×2×2 k-point mesh (generated using the Monkhorst-Pack scheme) were found to be enough for the total energy to converge within 0.01 meV atom⁻¹. Considering that the conventional cell contains a large number of atoms and the guest molecular is large, we first built a 1×1×1 supercell based on the primitive cell and optimized the cell framework structure. Guest I₂ molecules were then introduced to various locations of the channel pore. The static binding energy (T = 0 K) was then calculated using:

$E_B = E(HOF + I_2 \text{ molecules}) - E(HOF) - E(I_2 \text{ molecule})$

 Table S1. lodine sorption performance of representative adsorbents in the literature.

Adsorbents	Gaseous I ₂	Saturation time (h) ^[a]	I_2 in the liquid phase		
COFs					
TPT-DHBDX COFs ^[1]	543 wt %	50			
TPB-DMTP COF ^[2]	620 wt %	100			
iCOF-AB-50 ^[3]	1021 wt%	70 h			
SCU-COF-2 ^[4]	600 wt%	96 h			
TPB-DMTP-COF films ^[5]	637 wt%	240 min			
TAPA-PDA COF ^[6]	509 wt%	10 h			
JUC-561 ^[7]	819 wt%	21 h			
COGF ^[8]	140 wt%	22 h			
TJNU-201 ^[9]	563 wt%	96 h			
MOFs					
MOF-808 ^[10]	218 wt %	40			
MOF@polymer composite beads ^[11]			53.8 wt %		
MIL-101-NH ₂ ^[12]		50 h	31.1 wt %		
IL@PCN-333(AI) ^[13]	735 wt%	50 h	340 wt %		
{[Zn3(DLlac)			101 wt %		
2(pybz)2] · 2.5DMF}n ^[14]					
MFM-300(Sc) ^[15]	154 wt%				
AIOC-27-NC ^[16]		150 min	50.3 wt %		
Amorphous porous polymers					
HCMP-3 ^[17]	336 wt %	1.6			
SCMP ^[18]	222 wt %	4	18.4 wt %		
NRPP-2 ^[19]	222 wt %	5			
CMP-4 ^[20]	208 wt%	20			
PHF-1-Ct ^[21]	405 wt%	24 h	13.3 wt %		
PTIBBL ^[22]			66.7 wt %		
NiP-CMP ^[23]	202 wt%	24 h	32.6 wt %		
C-poly- 1 5 ^[24]	574 wt%		320 wt %		
BDP-CPP-1 ^[25]	283 wt%				
TBIM ^[26]	943 wt%	80 h			
Supramolecular materials	-	-			
G-TP5 ^[27]			67 wt %		
MeBID[3] ^[28]	512 wt%	24 h			
Zeolite					
Ag@Zeolite Mordenites ^[29]	27.5 wt%				
HOFs					
ENTDAT ^[30]	180 wt%	4 h			

This work			
HOF-TAM-BDA	441 wt%	30 h	67.1 wt%
HOF-TAM-PNA	678 wt%	20 h	89.1 wt%
HOF-TAM-BPY	783 wt%	15 h	112 wt%

^[a]Time required for the adsorbents to reach saturation for gaseous I₂.

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Figure S1. TG curves of HOF-TAM-BDA and I₂@HOF-TAM-BDA.



Figure S2. TG curves of HOF-TAM-PNA and I₂@HOF-TAM-PNA.



Figure S3. TG curves of HOF-TAM-BPY and I₂@HOF-TAM-BPY.



Figure S4. N₂ sorption isotherms of the active HOF-TAM-BPY (dark blue) and the regenerated one after the release of the captured iodine species (light blue).



Figure S5. IR spectra of the as-synthesized HOF-TAM-BDA, I_2 @HOF-TAM-BDA, and regenerated I_2 @HOF-TAM-BDA after I_2 release.



Figure S6. IR spectra of the as-synthesized HOF-TAM-PNA, I_2 @HOF-TAM-PNA, and regenerated I_2 @HOF-TAM-PNA after I_2 release.



Figure S7. IR spectra of the as-synthesized HOF-TAM-BPY, I_2 @HOF-TAM-BPY, and regenerated I_2 @HOF-TAM-BPY after I_2 release.



Figure S8. XRD patterns of the as-synthesized HOF-TAM-BPY, I_2 @HOF-TAM-BPY, and regenerated I_2 @HOF-TAM-BPY after I_2 release.



Figure S9. EPR patterns of HOF-TAM-BDA and I_2 @HOF-TAM-BDA.



Figure S10. EPR patterns of HOF-TAM-PNA and I_2 @HOF-TAM-PNA.



Figure S11. DFT optimized structures of I_2 @HOFs.



Figure S12. Linear regression by fitting the equilibrium data with the Langmuir adsorption model shown in Figure 5a of the main text. (a) HOF-TAM-BDA, (b) HOF-TAM-PNA, and (c) HOF-TAM-BPY, respectively.

Supporting reference

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