Electronic Supplementary Information

Confined benzene within InOF-1: contrasting CO$_2$ and SO$_2$ capture behaviours

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1. Crystal Structure of InOF-1

Fig. S1. (left) crystal structure of InOF-1 along the c axis showing 7.5 Å channels; and right (view) of the coordination at In(III) in InOF-1, showing [BPTC]$^4^-$ and the $\mu_2$-OH group.

2. Experimental Details

Chemicals

Indium nitrate (In(NO$_3$)$_3$), diphenyl-3,3’,5,5’-tetracarboxylic acid (H$_4$BPTC), N,N-dimethylformamide (DMF), acetonitrile (CH$_3$CN), nitric acid (65%, HNO$_3$), anhydrous ethanol (<0.005% water) and ethanol (reagent grade alcohol, 95%) were purchased from Sigma-Aldrich and used as received.

Synthesis of InOF-1

InOF-1 (In$_2$(OH)$_3$(BPTC)]·6H$_2$O) was synthesized according to previously reported procedure: In(NO$_3$)$_3$ (156 mg, 0.40 mmol) and H$_4$BPTC (33 mg, 0.10 mmol) were dissolved in CH$_3$CN (5 ml), DMF (5 ml) and HNO$_3$ (65%, 0.2 mmol) and sealed in a pressure tube. The clear solution was heated at 85 ºC in an oil bath for 72 h. The tube was cooled to room temperature over a period of 12 h and the colourless crystalline product was separated by filtration, washed with DMF (5 ml) and dried in air. Yield: 72% (based on ligand).

Measurements

Powder X-ray diffraction (PXRD) data were collected under ambient conditions on a Rigaku ULTIMA IV diffractometer operated at 160 W (40 kV, 40 mA) for Cu K$_\alpha_1$ ($\lambda=1.5406$ Å). The IR spectrums were taken on a Thermo Scientific™ Nicolet™ iST™5 FT-IR Spectrometer with a resolution of 4 cm$^{-1}$ and 16 scans, as initial parameters.
3. PXRD of InOF-1

Fig. S2. Calculated PXRD pattern for InOF-1 (green), the as-synthesized (experimental) pattern (orange) for InOF-1, the pattern of InOF-1 after the benzene uptake (blue) and the pattern after SO₂ experiments (purple).

4. FT-IR spectrum of InOF-1

Fig. S3. IR spectrums, before and after the preadsorption of benzene. Comparison of InOF-1 structure.
5. Determination of the isosteric enthalpy of adsorption for benzene

The enthalpy of adsorption, $\Delta H_{ads}$, was calculated from the analysis of benzene adsorption isotherms using the isosteric method by fitting a virial-type equation to both temperatures, 298 K and 308 K (Fig. S4). The virial-type equation used to fit the both isotherms is:  

$$ln \left( \frac{n}{p} \right) = A_0 + A_1 n + A_2 n^2 \ldots$$  

where $p$ is the pressure, $n$ is adsorbed amount on InOF-1 and, $A_0$, $A_1$, etc. are virial coefficients. $A_2$ and higher-order terms can be ignored.

Fig. S4. Benzene ($C_6H_6$) adsorption-desorption isotherms at 298 K (left) and 308 K (right) of InOF-1 from $%P/P_0 = 0$ to 85. Solid circles represent adsorption, and open circles show desorption.

A plot of $ln \left( \frac{n}{p} \right) \text{ vs } n$ should give a straight line at low surface coverage (Fig. S5).

Fig. S5. Virial fitting plots for the adsorption of benzene on InOF-1 at 298 K (violet) and 308 K (orange).
Once obtained the plots, $\Delta H_{ads}$, was calculated with the help of the Clausius-Clapeyron equation, obtaining a value of -25.1 kJ mol$^{-1}$:

$$\Delta H_{ads} = R \left( \frac{T_1 \times T_2}{T_1 - T_2} \right) \ln \left( \frac{P_1}{P_2} \right)$$

*Ec. (2)*

**Fig. S6.** Variation of adsorption enthalpy at low benzene loading for InOF-1.

Negative slope is indicative of homogeneous interactions due to, possibly, cooperative adsorptive-adsorptive interactions (via $\pi - \pi$ stacking) rising with pressure increase.\(^3\)

### 6. Uptake benzene on InOF-1 with H$_2$O pre-adsorption

Fig. S7 shows that adsorption-desorption isotherm with a small amount of confined water (1.5 wt%) within InOF-1 structure (red curve) has the same form as the isotherm of InOF-1 fully activated (blue curve). However, in the desorption branch, the confinement of water enhanced the benzene that was retained by the InOF-1 by more 5.84 wt%. This phenomenon is most likely due to the interactions between benzene and water molecules. These molecules can interact with each other to form small complexes\(^7\), where the benzene can act as hydrogen bond donor and acceptor. The formation of water-benzene clusters can explain the observed differences in the desorption behaviour.
Fig. S7. Comparison of adsorption-desorption isotherms performed in InOF-1 (blue curve) and H$_2$O@InOF-1 (red curve) at 298 K from P/P$_0$ = 0 to 85.

7. Computational calculations

Fig. S8. Molecular graph of the Bz@InOF.1 system. The bond critical points and bond paths are depicted by orange points and lines, respectively. Benzene molecule is shown in blue.
**Fig. S9.** Molecular graphs of $\text{CO}_2\cdots\text{InOF-1a}$ (left) and $\text{CO}_2\cdots\text{InOF-1b}$ (right). The bond critical points and bond paths are depicted by orange points and lines, respectively. $\text{CO}_2$ molecule is shown in green.

**Fig. S10.** Molecular graphs of $\text{SO}_2\cdots\text{InOF-1a}$ (left) and $\text{SO}_2\cdots\text{InOF-1b}$ (right). The bond critical points and bond paths are depicted by orange points and lines, respectively.

**Fig. S11.** Molecular graphs of $\text{CO}_2\cdots\text{Bz@InOF-1b}$ (left) and $\text{SO}_2\cdots\text{Bz@InOF-1b}$ (right). The bond critical points and bond paths are depicted by orange points and lines, respectively. Benzene and $\text{CO}_2$ molecules are shown in blue and green, correspondingly.
References


