Electronic Supplementary Information

Confined benzene within InOF-1: contrasting CO_2 and SO_2 capture behaviours

Luz J. Barrios-Vargas,[†a] José G. Ruiz-Montoya,[†b] Bruno Landeros-Rivera,[c] J. Raziel Álvarez,[a] Daniel Alvarado-Alvarado,[a] Rubicelia Vargas,*[c] Ana Martínez,[d] Eduardo González-Zamora,[c] Ludy M. Cáceres,[e] Juan C. Morales*[e,b] and Ilich A. Ibarra*[a]

a.Laboratorio de Fisicoquímica y Reactividad de Superficies (LaFReS), Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior s/n, CU, Coyoacán, 04510 Ciudad de México, Mexico. E-mail: argel@unam.mx

b. Laboratorio de Investigación de Electroquímica Aplicada, Facultad de Ciencias, Universidad Nacional de Ingeniería, Av. Túpac Amaru 210, Rímac, Lima, Perú.

c. Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco 185, Col. Vicentina, Iztapalapa, C. P. 09340 Ciudad de México. E-mail: brunolanderos@hotmail.com; ruvf@xanum.uam.mx

d. Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior S/N, CU, Del. Coyoacán, 04510, Ciudad de México, México.

e. Facultad de Ingeniería y Arquitectura, Universidad de Lima, Avenida Javier Prado Este 4600, Santiago de Surco, Lima 1503, Perú. E-mail: jcmorale@ulima.edu.pe

* Corresponding Authors
E-mail: argel@unam.mx, jcmorale@ulima.edu.pe and ruvf@xanum.uam.mx

† These authors contributed equally to this work.

1. Crystal Structure of InOF-1

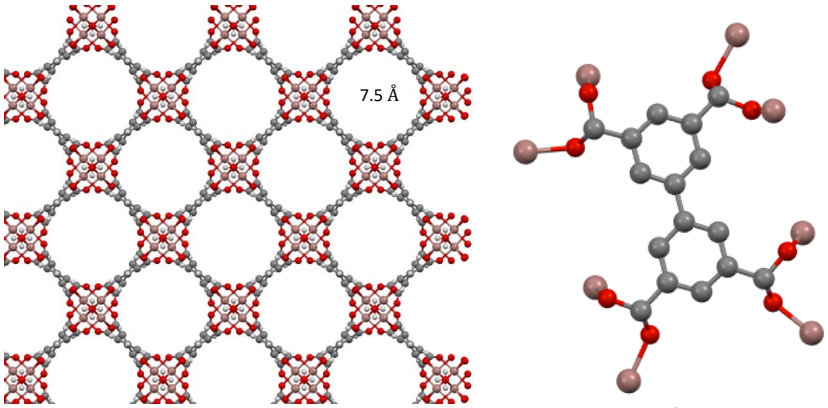

Fig. S1. (left) crystal structure of InOF-1 along the *c* axis showing 7.5 Å channels; and right (view) of the coordination at In(III) in InOF-1, showing $[BPTC]^{4-}$ and the μ_2-OH group.

2. Experimental Details

Chemicals

Indium nitrate ($In(NO_3)_3$), biphenyl-3,3',5,5'-tetracarboxylic acid (H_4BPTC), *N,N*-dimethylformamide (DMF), acetonitrile (CH_3CN), 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 ($In_2(OH)_2(BPTC)]\cdot 6H_2O$) was synthesized according to previously reported procedure: [2] $In(NO_3)_3$ (156 mg, 0.40 mmol) and H_4BPTC (33 mg, 0.10 mmol) were dissolved in CH_3CN (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 $K\alpha_1$ (λ= 1.5406 Å). The IR spectrums were taken on a Thermo Scientific™ Nicolet™ iS™5 FT-IR Spectrometer with a resolution of 4 cm^{-1} and 16 scans, as initial parameters.

3. PXRD of InOF-1

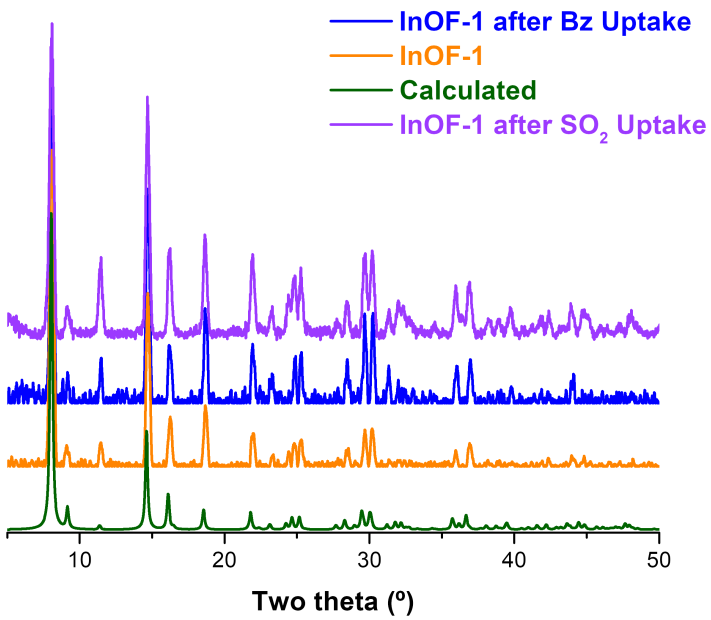

Fig. S2. Calculated PXRD pattern for InOF-1 (green), the as-synthesized (experimental) pattern (orange) for InOF-1, the pattern of InOF-1 after the benzene uptake (blue) and the pattern after SO_2 experiments (purple).

4. FT-IR spectrum of InOF-1

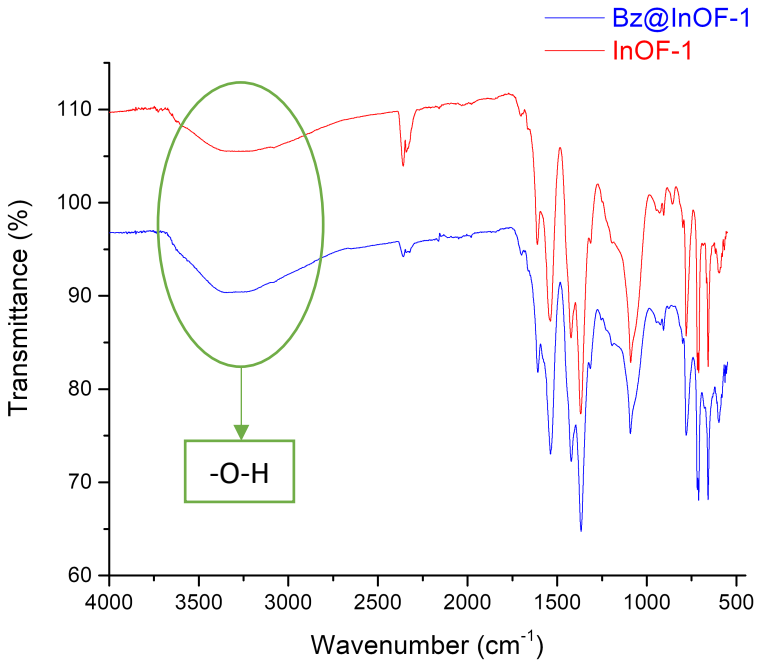

Fig. S3. IR spectrums, before and after the preadsorption of benzene. Comparison of InOF-1 structure.

5. Determination of the isosteric enthalpy of adsorption for benzene

The enthalpy of adsorption, ΔH_{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).[3] The virial-type equation used to fit the both isotherms is:[4]

$$ln\,(n/p) = A_0 + A_1 n + A_2 n^2 \ldots \qquad Ec.\ (1)$$

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.

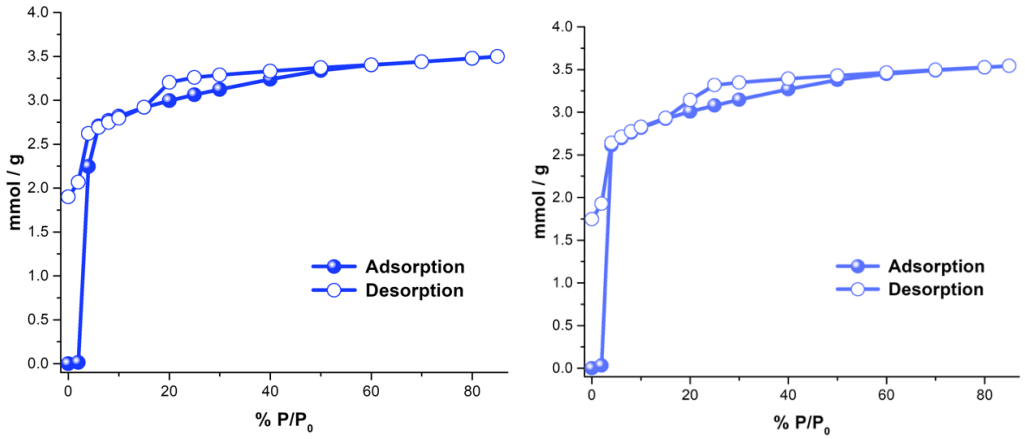

Fig. S4. Benzene (C_6H_6) adsorption-desorption isotherms at 298 K (left) and 308 K (right) of InOF-1 from %P/P$_0$ = 0 to 85. Solid circles represent adsorption, and open circles show desorption.

A plot of $ln\,(n/p)$ vs n should give a straight line at low surface coverage (Fig. S5).[5]

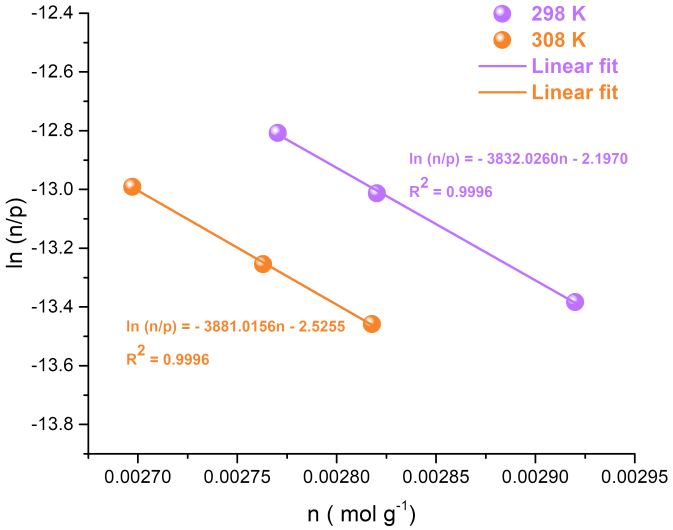

Fig. S5. Virial fitting plots for the adsorption of benzene on InOF-1 at 298 K (violet) and 308 K (orange).

Once obtained the plots, ΔH_{ads}, was calculated with the help of the Clausius-Clapeyron equation, [6] obtaining a value of -25.1 kJ mol^{-1}:

$$\Delta H_{ads} = R\left(\frac{T_1 * T_2}{T_1 - T_2}\right) ln\left(\frac{P_1}{P_2}\right) \qquad \textit{Ec. (2)}$$

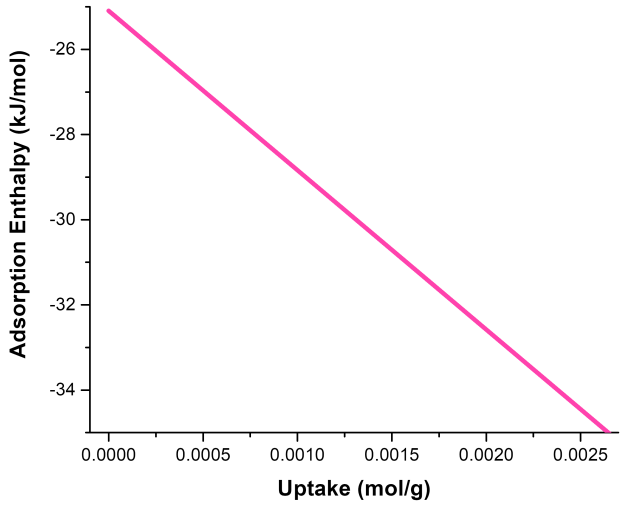

Fig. S6. Variation of adsorption enthalpy at low benzene loading for InOF-1.

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_2O 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.

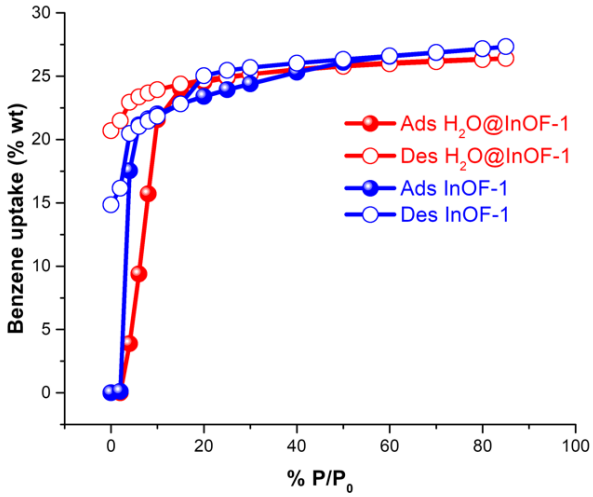

Fig. S7. Comparison of adsorption-desorption isotherms performed in InOF-1 (blue curve) and H_2O@InOF-1 (red curve) at 298 K from P/P_0 = 0 to 85.

7. Computational calculations

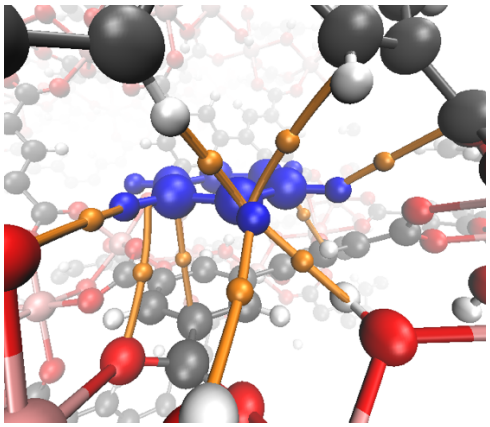

Fig. S8. Molecular graph of the Bz@InOF.1 system. The bond critical points and bond paths are depicted by orange points and lines, respectively. Benzene molecule is shown in blue.

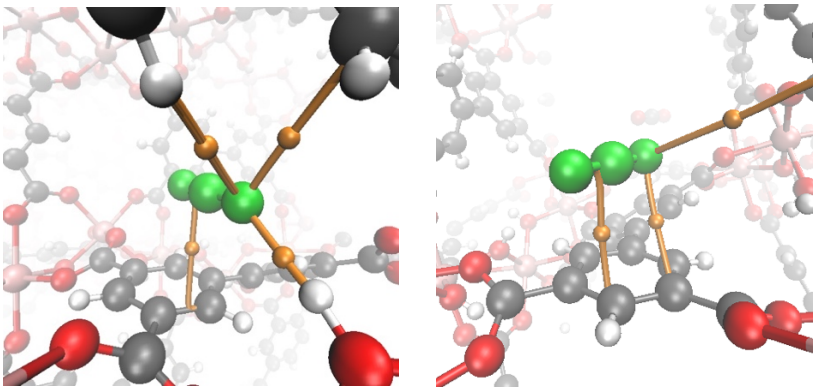

Fig. S9. Molecular graphs of **CO_2···InOF-1a** (left) and **CO_2···InOF-1b** (right). The bond critical points and bond paths are depicted by orange points and lines, respectively. CO_2 molecule is shown in green.

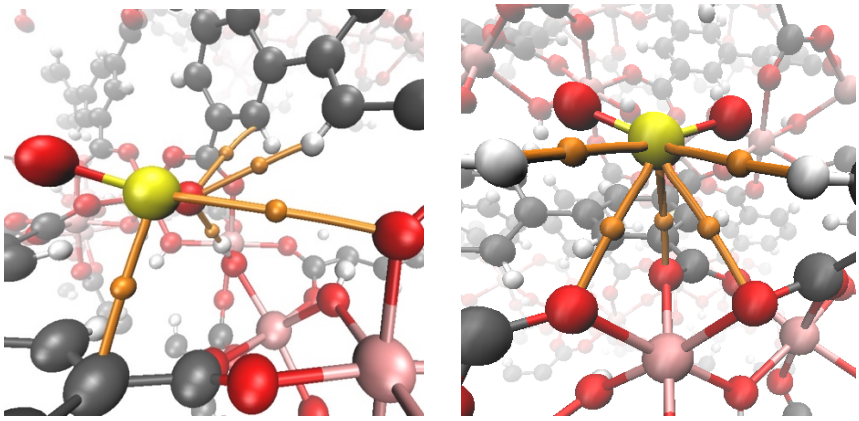

Fig. S10. Molecular graphs of **SO_2···InOF-1a** (left) and **SO_2···InOF-1b** (right). The bond critical points and bond paths are depicted by orange points and lines, respectively.

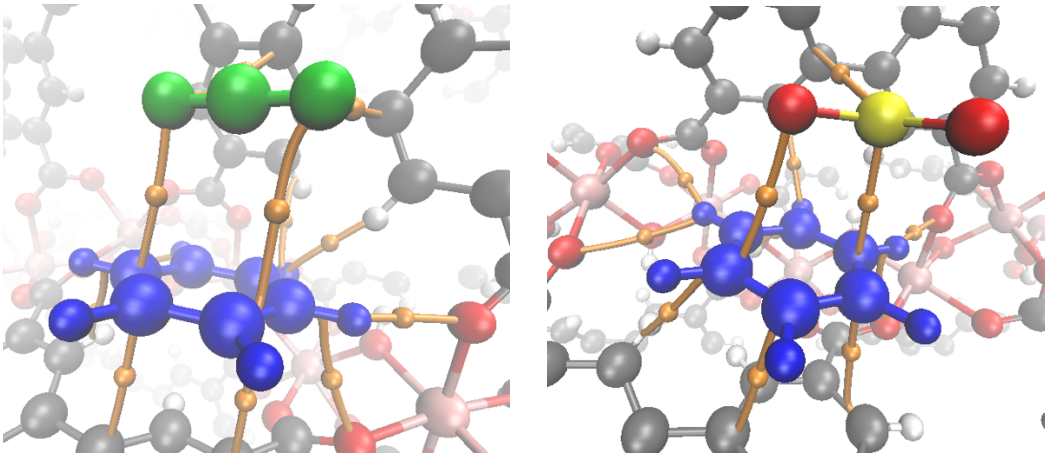

Fig. S11. Molecular graphs of CO_2···Bz@InOF-1b (left) and SO_2···Bz@InOF-1b (right). The bond critical points and bond paths are depicted by orange points and lines, respectively. Benzene and CO_2 molecules are shown in blue and green, correspondingly.

References

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