

Electronic Supporting Information (ESI)

Fluorometric detection of iodine by MIL-53(AI)-TDC

Mariana L. Díaz-Ramírez,^{‡a} Brenda Vargas,^{‡a} J. Raziel Álvarez,^a Bruno Landeros-Rivera,^b Marcos Rivera-Almazo,^b Carlos Ramos,^c J. Gabriel Flores,^a Eriseth Morales,^c Rubicelia Vargas,^b Jorge Garza,^b Eduardo González-Zamora,^b Ana Martínez,^{*c} Diego Solís-Ibarra^{*a} and Ilich A. Ibarra^{*a}

^a Laboratorio de Fisicoquímica y Reactividad de Superficies (LaFRoS), Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior s/n, CU, Del. Coyoacán, 04510, Ciudad de México, Mexico.

E-mail: dgo.solis@gmail.com

E-mail: argel@unam.mx

^b Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco 186, Col. Vicentina, Iztapalapa, C. P. 09340, Ciudad de México, Mexico.

^c Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior s/n, CU, Del. Coyoacán, 04510, Ciudad de México, Mexico.

E-mail: martina@unam.mx

‡ These authors contributed equally to this work

1. Experimental

Synthesis of MIL-53(Al)-TDC

The solvothermal synthesis of MIL-53(Al)-TDC was based on a method previously reported.¹ All materials, from Sigma-Aldrich, were used as received without further purification. A mixture of AlCl₃ (64 mg, 0.48 mmol) and 2,5-thiophenedicarboxylic acid (62 mg, 0.36 mmol) dissolved in 1.8 mL of DMF and 2.5 mL of H₂O was sealed in a pressure tube. This mixture was heated at 100 °C under autogenous pressure for 5 h, and then cooled down to room temperature. The product was filtered under vacuum and washed with 5 mL of DMF. To remove any unreacted starting material inside the MOF material, the as-synthesised product was mixed with DMF and heated to 150 °C for 1 h. Afterward, DMF molecules were removed via acetone-exchange before thermal activation at 200 °C for 4 h under vacuum.

PXRD experiments

Powder X-ray diffraction (PXRD) patterns were collected in Bragg–Brentano geometry with Cu-K_{α1} radiation ($\lambda = 1.540562 \text{ \AA}$) in a Rigaku ULTIMA IV with a nickel filter. The powder patterns were recorded from 5 to 40° (2 θ) in 0.01° steps and a scan rate of 0.319° min⁻¹.

Iodine adsorption measurements

For iodine uptake measurements, a fully activated MIL-53(Al)-TDC sample (180 °C for 2h under vacuum (1x10⁻⁴ bar)) was immediately transferred to a saturator chamber containing I₂ (PQM®, 99.9%, lot# 815302) equipped with a digital balance at room temperature. Different times of exposure were tested: the sample was removed from the saturator and weight at each time.

UV-Vis absorption measurements

Absorption measurements were recorded using a Shimadzu spectrophotometer UV-2600 equipped with an ISR-2600Plus integrating sphere and a BaSO₄ blank.

2. Iodine kinetic adsorption experiments

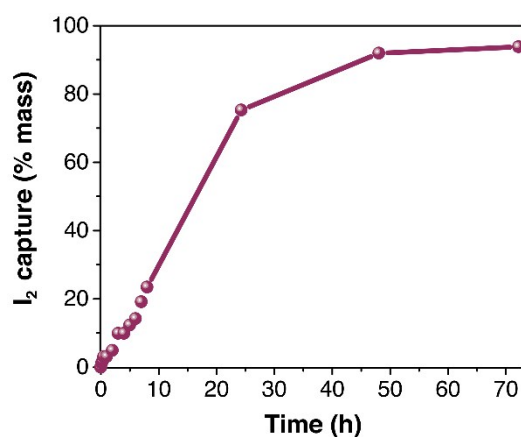


Fig. S1. I₂ vapour uptake curve on MIL-53(AI)-TDC at room temperature (25 °C). Solid circles were the actual experimental weight points and the solid lines represent the trend of the total I₂ capture.

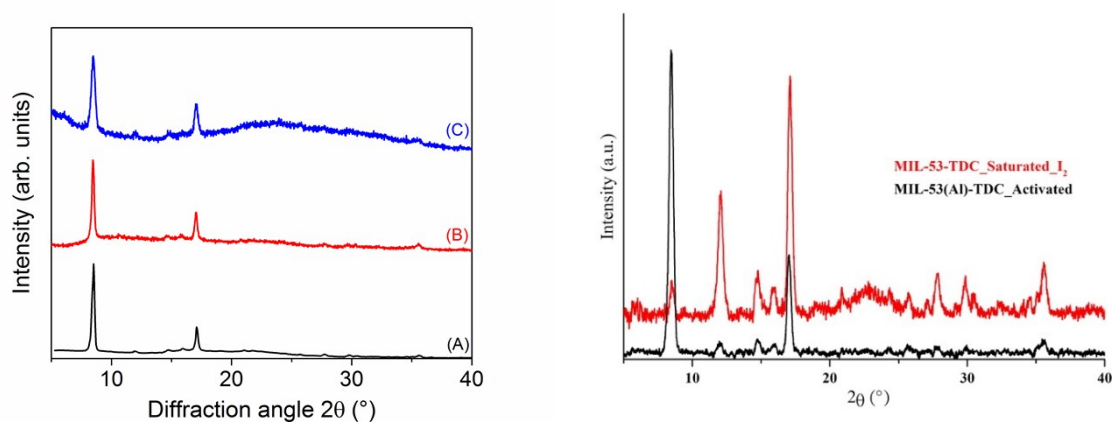


Fig. S2. (left) (A) PXRD pattern of reported¹ MIL-53(AI)-TDC, (B) PXRD pattern of the as-synthesised MIL-53(AI)-TDC (before the I₂ capture experiment) and (C) PXRD pattern of activated MIL-53(AI)-TDC (180 °C for 2 h under vacuum (1×10^{-4} bar); after the I₂ capture experiment); (right) PXRD patterns of activated (180 °C for 2 h under vacuum (1×10^{-4} bar) MIL-53(AI)-TDC (black) and saturated with I₂ (red). The change on the relative intensities of the diffraction peaks on MIL-53(AI)-TDC sample saturated with I₂, may correspond to I₂ confined within the micropores of the MOF material.

3. Iodine detection

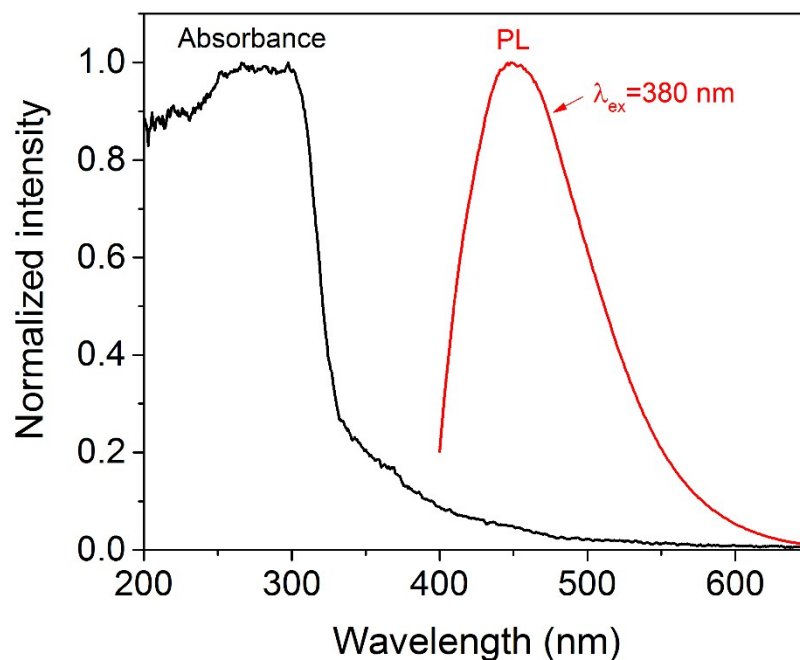


Fig. S3. Absorbance (black line) and photoluminescence (red line) spectra of MIL-53-(Al)-TDC before iodine absorption. The emission spectrum was obtained with an excitation wavelength of 380 nm.

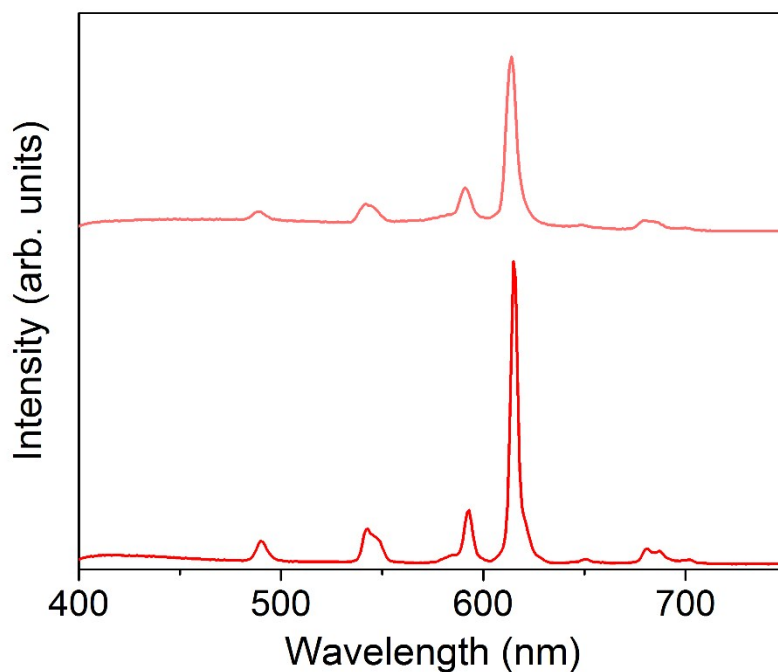


Fig. S4. Emission of the I_2 @ MIL-53-(Al)-TDC freshly prepared sample (red line) and after 30 days exposure to air and moisture (red light line). Emission spectra were obtained with an excitation wavelength of $\lambda_{ex}=380\text{ nm}$.

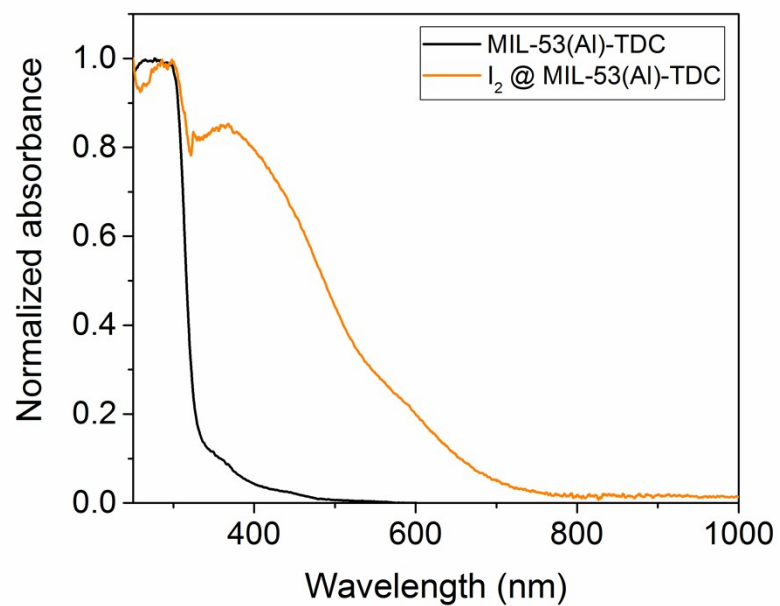


Fig. S5. Absorbance spectra of MIL-53-(Al)-TDC before iodine adsorption (black line) and after iodine adsorption (orange line).

4. Crystal structure

MIL-53(Al)-TDC, an Al-based MOF with the formula $[\text{Al}(\mu\text{-OH})(\text{TDC})]$,¹ is constructed using 2,5-thiophenedicarboxylate (TDC) ligands and Al(III)-oxygen octahedra $[\text{AlO}_4\text{trans-}(\mu\text{-OH})_2]$ and crystallises in the $Pmna$ space group ($a = 14.628$ Å, $b = 6.557$ Å and $c = 14.725$). Each Al(III) centre is coordinated by six oxygen atoms from four different TDC ligands and two hydroxyl ($\mu\text{-OH}$) groups. The overall framework structure of MIL-53(Al)-TDC shows square shape channels with a diameter of approximately 9.2×8.9 Å. The crystal structure of MIL-53(Al)-TDC was constructed from the cell parameters and atomic positions reported by Stock *et al.*¹ Channel dimensions were estimated using the van der Waals radii of the atoms using the software CrystalMaker.²

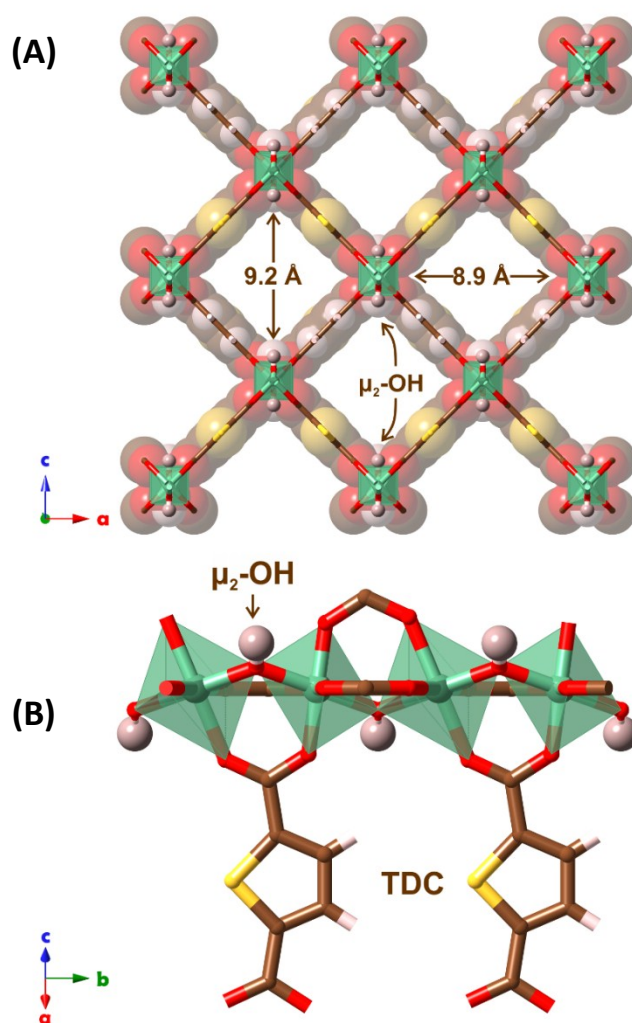


Fig S6. (A) view of the crystal structure of MIL-53(Al)-TDC along b axis showing 8.9×9.2 Å channels; (B) binuclear building block of two Al(III) metal ions oxygen-octahedra bridged by a μ_2 -hydroxyl group, and the TDC²⁻ ligand, through $\langle 101 \rangle$.

5. Theoretical results

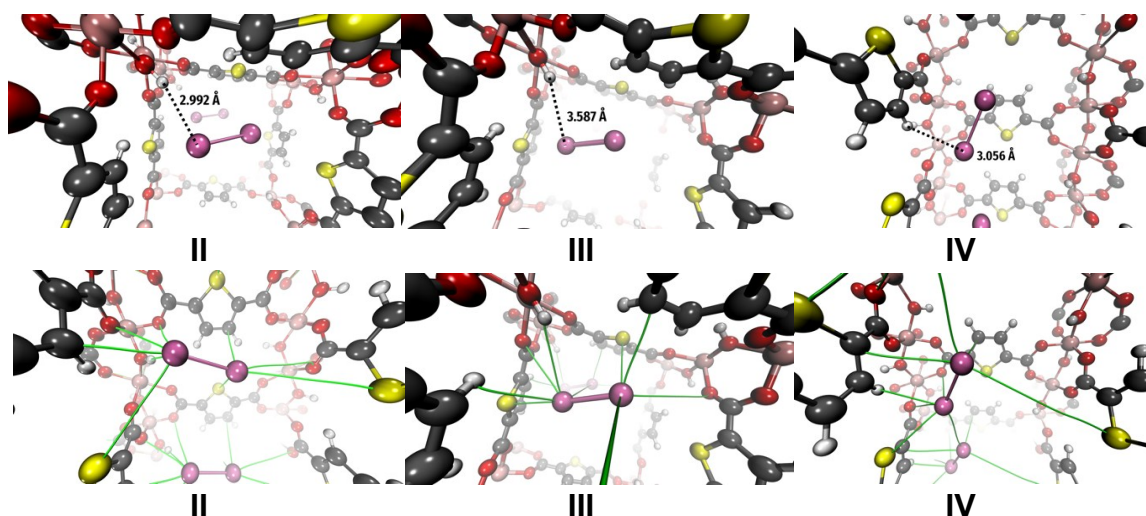


Fig. S7. Close-up view (top) and molecular graph (bottom) of configurations II, III and IV (first, second and third columns, respectively). Purple, yellow, pink, red, gray and white colors represent iodine, sulfur, aluminum, oxygen, carbon and hydrogen atoms, correspondingly. The hydrogen bond distances are depicted in black (Å). Green lines represent bond paths.

Table S1. Relative energy between the four configurations considered for the MIL-53(Al)-TDC \cdots I₂ system.

Configuration	ΔE (kcal/mol)
I	0.0
II	1.8
III	3.4
IV	3.4

Table S2. The electron density value at the bond critical point (ρ_{BCP}), the laplacian ($\nabla^2\rho_{\text{BCP}}$), interaction energy (E_{int}) and the number of equivalent contacts (N) for each BCP found between the iodine molecule and its surroundings in the four MIL-53(Al)-TDC \cdots I₂ configurations (I, II, III and IV).

Interatomic contact	ρ_{BCP} (a.u.)	$\nabla^2\rho_{\text{BCP}}$ (a.u.)	E_{int} (kcal/mol)	N
Configuration I				
O-H \cdots I	0.0192	0.0466	-3.7	1
C \cdots I	0.0060	0.0195	-0.9	2
O \cdots I	0.0056	0.0169	-0.8	2
C-H \cdots I	0.0054	0.0162	-0.7	2
I \cdots I	0.0046	0.0115	-0.5	2
S \cdots I	0.0032	0.0111	-0.4	2
Configuration II				
C \cdots I	0.0148	0.0346	-2.5	1
O-H \cdots I	0.0076	0.0185	-1.0	1
C \cdots I	0.0073	0.0213	-1.0	1
O \cdots I	0.0059	0.0183	-0.8	1
S \cdots I	0.0051	0.0163	-0.7	1
O \cdots I	0.0041	0.0127	-0.5	1
S \cdots I	0.0009	0.0038	-0.1	1
S \cdots I	0.0002	0.0011	0.0	1
O \cdots I	0.0002	0.0011	0.0	1
Configuration III				
S \cdots I	0.0219	0.0596	-4.7	1
C \cdots I	0.0095	0.0252	-1.4	1
C-H \cdots I	0.0063	0.0184	-0.9	1
O \cdots I	0.0054	0.0154	-0.7	1
S \cdots I	0.0031	0.0106	-0.4	1
O-H \cdots I	0.0024	0.0068	-0.3	1
I \cdots I	0.0002	0.0014	0.0	1
O \cdots I	0.0000	0.0003	0.0	1
Configuration IV				
C-H \cdots I	0.0094	0.0257	-1.4	1
O \cdots I	0.0072	0.0206	-1.0	1
S \cdots I	0.0072	0.0216	-1.0	1
C \cdots I	0.0066	0.0199	-0.9	1
O \cdots I	0.0057	0.0163	-0.7	1
C \cdots I	0.0052	0.0179	-0.8	1
I \cdots I	0.0049	0.0119	-0.6	1

References

- 1 C. B. L. Tschense, N. Reimer, C. W. Hsu, H. Reinsch, R. Siegel, W. J. Chen, C. H. Lin, A. Cadiou, C. Serre, J. Senker and N. Stock, *Zeitschrift für Anorg. und Allg. Chemie*, 2017, **643**, 1600–1608.
- 2 CrystalMaker (Version 9.0.0), CrystalMaker Software Ltd., UK 2014.