Supporting Information for:

Impact of Ni(II) Coordinatively unsaturated sites and coordinated water molecules on SO₂ adsorption by a MOF with octanuclear metal clusters

Juan L. Obeso,^{a,c+} Karuppasamy Gopalsamy,^{b+} Mohammad Wahiduzzaman,^{b+} Eva Martínez-Ahumada,^c Dong Fan,^b Hugo A. Lara-García,^d Francisco J. Carmona^e, Guillaume Maurin,^{b*} Ilich A. Ibarra^{b,f*}and Jorge A. R. Navarro^{e*}

^aInstituto Politécnico Nacional, Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, Legaria 694, Col. Irrigación, Miguel Hidalgo, 11500, CDMX, México.

^bICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, 34293, France.

^cLaboratorio 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, México.

^dInstituto de Física, Universidad Nacional Autónoma de México, Circuito Exterior s/n, CU, Coyoacán, 04510, Ciudad de México, México.

^eDepartamento de Química Inorgánica, Universidad de Granada, Av. Fuentenueva S/N, Granada, 18071 Spain.

^fOn sabbatical as "Catedra Dr. Douglas Hugh Everett" at Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco 186, Col. Leyes de Reforma 1ra Seccion, Iztapalapa, C.P. 09310, Ciudad de México, Mexico.

⁺ These authors contributed equally to this manuscript.

Table of contents

S1. Experimental details	S3
S2. Results and Discussions	S4
S3. References	S15

S1. Experimental details

Chemicals

All the general reagents and solvents were commercially available and used as received.

Analytical instruments

Patterns were recorded with a Bruker Advance II diffractometer equipped with a $\theta/2\theta$ Bragg-Brentano geometry and Ni-filtered CuK α radiation (K α 1 = 1.5406 Å, K α 2 = 1.5444 Å, $K\alpha 1/K\alpha 2 = 0.5$). The tube voltage and current were 40 kV and 40 mA, respectively. Samples for PXRD were prepared by placing a thin layer of the appropriate material on a zerobackground silicon crystal plate. Patterns were measured on a Bruker D8 Advance X-ray diffractometer equipped with a LynxEye detector using CuK α radiation ($\lambda = 1.5406$ Å; monochromator: germanium) in a range 2-theta of $4-60^{\circ}$ with a step of 0.02° . The voltage and current were 35 kV and 35 mA, respectively. Fourier transform infrared (FTIR) spectroscopy was carried out using a Nicolet 6700 spectrometer. The spectrum was generated and collected 16 times and corrected for the background noise in the wavenumber ranging from 400 to 3400 cm⁻¹. Nitrogen adsorption-desorption isotherms were measured by a volumetric method using a Micromeritics ASAP 2020 gas sorption analyzer. The sample mass was 65.0 mg. Free space correction measurements were performed using ultra-high purity He gas (UHP grade 5, 99.999% pure). Nitrogen isotherms were measured using UHPgrade Nitrogen. All nitrogen analyses were performed using a liquid nitrogen bath at 77 K. Oil-free vacuum pumps were used to prevent contamination of the sample or feed gases. DRIFTS experiments were performed using an environmentally controlled PIKE DRIFTS cell with ZnSe windows coupled to a Thermo Scientific Nicolet iS50 spectrometer with an MCT/A detector. Absorbance spectra were obtained by collecting 64 scans at a 4 cm⁻¹ resolution. A sample of 0.020 g was pre-treated in situ under a He flow at 523.15 K for 4 h. After this treatment, the sample was cooled to room temperature, and then, a flow of carbon monoxide (CO: 30 mL min⁻¹; 5 % of CO diluted in He) was passed through the sample. Elemental analysis was performed in an elemental analyzer Thermo ScientificTM FLASH 2000. Nickel content was determined on the basis of Thermogravimetric analysis (TGA) carried out by a thermogravimetric analyser SHIMADZU mod. TGA-50H with a heating ramp of 20 °C/min in a synthetic air atmosphere. Electronic spectra were measured on diffuse reflectance mode on a polycrystalline sample of NiBDP on a VARIAN CARY-5E spectrometer.

S2. Results and Discussions

Characterization of NiBDP



Figure S1. Selection of the framework structure of NiBDP MOF obtained from the X-ray crystal structure data (CCDC number 931410). a) View of the unit cell showing the two types of cages in NiBDP, b) view of the tetrahedral cage. Color code: O = red, N = blue, Ni = green, C = yellow (tetrahedral cage), C = black (octahedral cage), H = white, H = magenta (inside tetrahedral cage).





Figure S2. PXRD patterns of NiBDP as-synthesized (black trace) and after SO₂ adsorptiondesorption experiment (red trace).

Nitrogen sorption



Figure S3. N₂ sorption isotherm of NiBDP as-synthesised. Adsorption (black circles) and desorption (open circles).

Thermogravimetric analysis



Figure S4. Thermogravimetric analysis trace in air atmosphere for NiBDP.

Diffuse reflectance electronic spectra



Figure S5. Electronic spectra of a polycrystalline sample of NiBDP material.

SO₂ sorption measurements in NiBDP

Experimental Heat of Adsorption of SO₂.

The heat of adsorption of NiBDP was calculated according to the reported literature,¹ using a virial-type equation (Eq. S1) to fit the low coverage region of two adsorption isotherms at 298 and 308 K.

$$Ln (n/p) = A_0 + A_1\eta + A_2\eta^2 + \cdots$$
 Eq. S1

Where p is the pressure in kPa, n is the amount adsorbed and A_0 , A_1 , ... are the virial coefficients. The plot *Ln (P) vs. n* can fit both isotherms simultaneously (Figure S4). From the linear fittings, the virial coefficients are used to estimate the enthalpy of adsorption.



Figure S6. Virial fit plot for the SO₂ adsorption at low surface coverage in NiBDP at 298 and 308 K.

FTIR spectroscopy



Figure S7. FTIR spectra of NiBDP before and after SO₂ exposure from 3700 to 450 cm⁻¹.

In situ DRIFTS



Figure S8. DRIFT spectra of CO adsorption on NiBDP from v 4000 to 600 cm⁻¹ at two different activation temperatures.

Computational methodology

Table S1. Calculated partial atomic charges of NiBDP-nH₂O (n = 0, 1, 2) framework atoms.

	NiBDP-0H ₂ C)		NiBDP-1H ₂ C)		NiBDP-2H ₂ C)
Atom	Description	q(e)	Atom	Description	q(e)	Atom	Description	q(e)
Types			Types			Types		
Ni1	CUS site	0.7153	Ni1	CUS site	0.7469	Ni1	CUS site	0.7592
01	O of OH	-0.8016	01	O of OH	-0.8004	01	O of OH	-0.7996
H1	H of OH	0.4026	O2	O of H ₂ O	-0.7285	O2	O of H ₂ O	-0.7274
H2	H of linkers	0.0939	H1	H of OH	0.3852	H1	H of OH	0.3864
C1	Cafbanzana	0.0809	H2	H of H ₂ O	0.3785	H2	H of H ₂ O	0.3804
C2	C of benzene	-0.0390	H3	H of linkers	0.0959	H3	H of linkers	0.0951
C3	C of diazole	-0.1320	C1	C of benzene	0.0813	C1	C of benzene	0.0807

C4		-0.0417	C2		0.1072	C2		-0.0429
N1	N of diazole	-0.2070	C3		-0.1327	C3		-0.1328
			C4	C of diazole	-0.0427	C4	C of diazole	-0.0429
			N1	N of diazole	-0.2169	N1	N of diazole	-0.2205

Calculation of Texture Properties

Texture properties of the three investigated NiBDP MOFs were determined utilizing the Zeo++ software package.² The accessible surface area was calculated employing a N₂ probe with a radius of 1.82 Å and a trial number set to 2000. The pore volume of the MOF structures was assessed using a probe radius of 0 Å, with the trial number set to 50000. The '-ha' tag was employed throughout all texture property calculations to ensure high-accuracy results. Detailed input comments are provided below.

PLD and LCD zeo++-0.3/network -ha -res Filename.cif ASA zeo++-0.3/network -ha -sa 1.82 1.82 2000 Filename.cif PV

```
zeo++-0.3/network -ha -vol 0 0 50000 Filename.cif
```

Table S2. DFT-optimized NiBDP-nH ₂ O	(n = 0, 1, 2)) texture properties
---	---------------	----------------------

MOFs	Surface area m ² g ⁻¹	Pore Volume cm ³ g ⁻¹	LCD Å	PLD Å
NiBDP_0H ₂ O	2650	0.38	14.8	5.1
NiBDP_1H ₂ O	2502	0.35	14.4	5.0
NiBDP_2H ₂ O	2484	0.35	14.6	5.0

Table S3. Intermolecular LJ-potential parameters for the SO₂ molecule taken from Ketko *et al.*³

Atom Type	σ (Å)	ε/k _B (K)	q
$S(SO_2)$	3.39	73.80	0.590
$O(SO_2)$	3.05	79.00	-0.295

Table S4. LJ Potential parameters for the NiBDP- nH_2O (n = 0, 1, 2) framework atoms adopted from UFF.⁴

MOF Atom Type	σ (Å)	$\epsilon/k_{B}(K)$
Н	2.571	22.142
С	3.431	52.839
Ν	3.260	34.720
Ο	3.118	30.193

Ni	2.520	7.550

Table S5. DFT derived Morse potential parameters for the SO₂-Ni(II) CUS site interactions.

Atom Pairs	D (K)	α	r_{θ} (Å)
S(SO ₂)-Ni(II)	232.0905	25.6679	3.5825
$O(SO_2)$ -Ni(II)	1915.7443	10.5800	2.3000

The *D*, α , and r_0 parameters derived using the General Utility Lattice Program (GULP)⁵ by minimizing the difference between the DFT-calculated binding energy curve and the analytical function given in eq 1 (see Figure S7).

$$E(r_{ij}) = \sum_{i,j} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \sum_{i,j} D \left[\left(1 - e^{-\alpha * (r_{ij} - r_0)} \right)^2 - 1 \right] + \frac{q_i q_j}{4\pi\varepsilon_o r_{ij}}$$
(1)

i, j: all MOF atoms except Ni(II) *i*: Ni(II) and *j*: all SO₂ atoms *i, j*: all MOF and SO₂ atoms Lennard-Jones term Morse term SO₂ atoms Coulombic term

where r_{ij} is the distance between the interacting atoms *i* and *j*, ε_{ij} and σ_{ij} are the associated LJ interatomic potential parameters, ε_0 is the permittivity of vacuum while, *D*, α and r_0 are the Morse potential parameters for the interactions between Ni(II) and SO₂.



Figure S9. Comparison of the DFT calculated binding energy curve of SO₂–NiBDP-0H₂O framework interaction and the corresponding interaction energies obtained from the fitted force field parameters.



Figure S10. DFT optimized equilibrium adsorption configuration of SO_2 in NiBDP-OH₂O, illustrating dominant close contacts of SO_2 molecule with the framework atoms.



Figure S11. Intermolecular radial pair distribution functions of NiBDP-1H₂O MOF atoms and adsorbed SO₂ molecules were calculated at P = 0.10 bar (a-b), and guest SO₂-SO₂ (c) was calculated at P = 0.50 bar.



Figure S12. Intermolecular radial pair distribution functions of NiBDP-2H₂O MOF atoms and adsorbed SO₂ molecules were calculated at P = 0.10 bar (a-b), and guest SO₂-SO₂ (c) was calculated at P = 0.50 bar.



Figure S13. Snapshots of GCMC simulated adsorption sequence for SO_2 in NiBDP-1H₂O at 298 K and at different pressure levels. SO_2 atom color codes: Red (O), Yellow (S). MOF atom color codes: Red (O), Gray (C), Blue (N), White (H), Purple (Ni).



Figure S14. Snapshots of GCMC simulated adsorption sequence for SO_2 in NiBDP-2H₂O at 298 K and at different pressure levels. SO_2 atom color codes: Red (O), Yellow (S). MOF atom color codes: Red (O), Gray (C), Blue (N), White (H), Purple (Ni).

S3. References

- 1. A. Nuhnen and C. Janiak, Dalt. Trans., 2020, 49, 10295–10307.
- T. F. Willems, C. H. Rycroft, M. Kazi, J. C. Meza and M. Haranczyk, *Microporous Mesoporous Mater.*, 2012, 149, 134–141.

- 3. M. H. Ketko, G. Kamath and J. J. Potoff, J. Phys. Chem. B, 2011, 115, 4949–4954.
- A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard and W. M. Skiff, J. Am. Chem. Soc., 1992, 114, 10024–10035.
- 5. J. D. Gale and A. L. Rohl, Mol. Simul., 2003, **29**, 291–341.