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Electronic Supporting Information (ESI) for the manuscript:

Post-Synthetic Approach Trigger Selective and Reversible Sulphur Dioxide Adsorption on a Metal-Organic Framework

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Experimental Section

<u>Chemicals</u>

All chemicals were of reagent grade quality. They were purchased from commercial sources and used as received. Compound $Ni^{II}_{2}{Ni^{II}_{4}[Cu^{II}_{2}-(Me_{3}mpba)_{2}]_{3}}\cdot54H_{2}O(1)$ was prepared as reported earlier.¹

Preparation of $[Ba^{II}(H_2O)_4]_{1.5}[Ba^{II}(H_2O)_5]_{0.5}[Ni^{II}_4[Cu^{II}_2(Me_3mpba)_2]_3] \cdot 57.5H_2O(2).$

Well-formed hexagonal green prisms of **2**, suitable for X-ray diffraction, were obtained by soaking crystals of **1** (*ca.* 51.8 mg, 0.015 mmol) in a saturated solution of Ba(NO₃)₂ for 48 hours in water. The cation-exchanged crystals (**2**) have the same size and shape as those of the ancestor material (**1**), ruling out a possible dissolution-recrystallization mechanism for this system and strongly suggesting a solid-state process.² The crystals were washed with an aqueous solution several times, isolated by filtration on paper and air-dried. Aiming at exploring possible industrial applications, a multigram-scale procedure was also carried out. So, a much higher amount of a polycrystalline sample of **1** (4.14 g, 1.2 mmol), was suspended in a saturated aqueous solution of Ba(NO₃)₂ for 48 hours under a mild stirring. Afterwards, the product was collected by filtration, washed with a H₂O/CH₃OH (1:1) solution and air-dried. Anal.: Calcd. for Ba₂Cu₆Ni₄C₇₈H₁₉₂N₁₂O₁₀₂ (3821.1): C, 24.52; H, 5.07; N, 4.40%. Found: C, 24.46; H, 4.98; N, 4.41%. IR (KBr): v = 1605 cm⁻¹ (C=O).

Physical Techniques

Elemental (C, H, N) analyses were performed at the Microanalytical Service of the Universitat de València. FT–IR spectra were recorded on a Perkin-Elmer 882 spectrophotometer as KBr pellets. The thermogravimetric analysis was performed on crystalline samples under a dry N₂ atmosphere with a Mettler Toledo TGA/STDA 851^e thermobalance operating at a heating rate of 10 °C min⁻¹. Scanning Electron Microscopy coupled with Energy Dispersive X-ray (SEM/EDX) was carried out with a XL 30 ESEM (PHILIPS) microscope equipped with a home-made EDX energy dispersive x-ray detector.

Static gas adsorption

The N_2 and CO_2 adsorption-desorption isotherms at 77 and 273 K, were carried out on a polycrystalline sample of **2** with a Micromeritics ASAP2020 instrument. Sample was evacuated at 348 K during 19 hours under 10^{-6} Torr prior to their analysis. The sample was weighted before and after

activation in order to estimate accurately the number of water molecules lost during the activation process.

X-ray Powder Diffraction Measurements

Polycrystalline sample of 2 was introduced into 0.5 mm borosilicate capillary prior to being mounted and aligned on a Empyrean PANalytical powder diffractometer, using Cu K α radiation ($\lambda = 1.54056$ Å). Five repeated measurements were collected at room temperature ($2\theta = 2-60^{\circ}$) and merged in a single diffractogram.

Breakthrough Experiments for Gas Separation

The chromatographic column, was prepared employing a stainless steel 10 cm-column (0.4 cm internal diameter) packed with *ca*. 0.5 g of the studied materials (**1**, **2**). The columns were activated under a pure He flow (20 mL min⁻¹) at 353 K overnight and for two hours between successive breakthrough cycles. The N₂/SO₂ (97.5: 2.5) gas mixture (20 mL min⁻¹) was prepared via mass flow controllers in order to simulate the emission of flue gas from a power plant. The breakthrough experiments were carried out, at 303 K, by step changes from He to N₂/SO₂ flow mixtures. A coadsorption experiment simulating a flue gas composition N₂/CO₂/SO₂ (82.5:15:2.5) gas mixture (20 mL min⁻¹) was used to evaluate the impact of CO₂ in SO₂ adsorption. The multiple breakthrough cycles were measured under a constant N₂/SO₂ (97.5:2.5) gas mixture (20 mL min⁻¹) with a temperature swing of 303-353 K. The relative amounts of gases passing through the column were monitored on a Mass Spectrometer Gas Analysis System (Pfeiffer Vacoon) detecting ion peaks at m/z 64 (SO₂), 28 (N₂) and 4 (He).

Theoretical calculations

A theoretical study on the interaction of SO₂ molecules with the framework of **2** was performed using Materials Studio 6.0 (MS6.0) software from Accelrys, Inc.³ The Adsorption Locator module in MS6.0 software was employed to construct the simulated systems diminishing the crystal symmetry to P1 and to perform the MC simulation. The used forcefield was COMPASS, the charge was forcefield assigned and the summation methods were group and atom based. Monte Carlo simulation yielded several conformations of SO₂ molecules in **2**. The results of the most stable conformation are presented in this work.

X-ray crystallographic data collection and structure refinement

A crystal of **2**, with *ca.* 0.18 x 0.18 x 0.22, mm as dimensions was selected and mounted on a MITIGEN holder in Paratone oil and very quickly placed on a liquid nitrogen stream cooled at 90 K to avoid the possible degradation upon dehydration. Diffraction data for **2** were collected on a Bruker-Nonius X8APEXII CCD area detector diffractometer using graphite-monochromated Mo-K_a radiation ($\lambda = 0.71073$ Å). The data were processed through SAINT⁴ reduction and SADABS⁵ multi–scan absorption software. The structure was solved with the SHELXS structure solution program, using the Patterson method. The model was refined with version 2013/4 of SHELXL against *F*² on all data by full–matrix least squares.^{6,7}

As reported in the main text, the robustness of the 3D network, allowed the resolution of the crystal structure of **2**, being their crystals suitable for X-ray diffraction, even after a single-crystal to single-crystal (SC to SC) solid-state PS process consisting of replacing Ni^{II} ions by Ba^{II} ones (see previous section, preparation of **2**). For these reasons it is reasonable to observe a diffraction pattern sometimes affected by expected internal imperfections of the crystals [likely at the origin of some Alert Level A for **2** in checkcif related to U(eq) value of some atoms] and thus a quite expected difficulty to perform a perfect correction of anisotropy, mainly affected by highly disordered water molecules within big pores of the MOF and even as terminal ligands of Ba^{II} ions (*vide infra*).

All non-hydrogen atoms of the MOF net, together with some coordinated water molecules, except the highly disordered ones, were refined anisotropically. The use of some C-C and C-O bond lengths restrains as well as thermal displacement restrains during the refinements, has been reasonable imposed and related to flexibility of Me₃mpba phenyl rings and coordinated water molecules that are dynamic components of the framework. Disordered sites (by symmetry) for atom O2W in refinement of **2** belongs to the Jahn-Teller elongated copper metal ion of the net whereas for O15W it is related to statistic disorder detected on Ba3 metal ion environment residing in square pores (see Figs. S2 and S4). As a consequence of such disorder alerts A and B in the checkcifs, are detected. Alerts of level A and B are also related for short intra $H \cdots H$ lengths of the thermal disordered methyl substituents of the Me₃mpba ligand.

The occupancy factors of Ba^{2+} ions have been defined in agreement with SEM and ICP–MS results [0.25 for both Ba1 and 0.125 for Ba2 and Ba3], as a consequence the occupancy factors of the coordinated water molecules have been defined accordingly. The lattice molecules were highly

disordered, even if not all the ones detected by TGA analysis and reported in the final formula, have been somehow modeled – some refined double positions are detected as Alerts A in the checkcif – the quite large channels featured by this MOF likely account for that [Alert of level A in checkcif for mismatch in given/expected molecular weight]. For this reason, only some of them have been somehow modelled. Thus, the contribution to the diffraction pattern for the highly disordered water molecules located in the voids was subtracted from the observed data through the SQUEEZE method, implemented in PLATON.^{8,9} The hydrogen atoms of the ligand were set in calculated positions and refined as riding atoms whereas for water molecules were neither found nor calculated.

The comments for the alerts are described in the CIFs using the validation reply form (vrf).

A summary of the crystallographic data and structure refinement for **2** is given in Table S2. CCDC reference number is CCDC- 1846740.

The final geometrical calculations on free voids and the graphical manipulations were carried out with PLATON^{8,9} implemented in WinGX,¹⁰ and CRYSTAL MAKER¹¹ programs, respectively.

Table S1. Selected data from the ICP–MS^{*a*} and SEM/EDX^{*b*} analyses for 2.

Metal	% mass ^a	Metal stoichiometry ^a	% mass ^b	Metal stoichiometry ^b
Cu	9.9312	6.0000	9.94	6.00
Ni	6.1154	4.0001	6.23	4.07
Ba	7.1423	1.9967	7.18	2.01

Solid samples were digested with 0.5 mL of HNO₃ 69% at 60°C for 4 hours followed by the addition of 0.5 mL of HCl 37% and digestion 80° C for 1 hour. Metal stoichiometric is given according to formula unit.

Compound	2	
Formula	Ba2Cu6Ni4C78H194N12O103	
$M (\mathrm{g} \mathrm{mol}^{-1})$	3839.20	
λ (Å)	0.71073	
Crystal system	Orthorhombic	
Space group	P4/mmm	
a (Å)	36.209(3)	
<i>c</i> (Å)	15.2135(15)	
$V(Å^3)$	19946(4)	
Ζ	4	
$ ho_{ m calc} ({ m g}{ m cm}^{-3})$	1.278	
$\mu \text{ (mm}^{-1}\text{)}$	1.469	
<i>T</i> (K)	90	
θ range for data collection (°)	0.795-25.24	
Completeness to $\theta = 25.0$	100 %	
Measured reflections	233826	
Unique reflections (Rint)	9683 (0.1228)	
Observed reflections $[I > 2\sigma(I)]$	6812	
Goof	1.622	
$R^{a}[I > 2\sigma(I)]$ (all data)	0.1826 (0.2245)	
$wR^b[I > 2\sigma(I)]$ (all data)	0.4736 (0.4992)	
${}^{a}R = \sum (Fo - Fc) / \sum Fo . {}^{b}wR = \sum$	$\sum w(Fo - Fc)^2 / \sum w Fo ^2]^{1/2}.$	

 Table S2. Summary of Crystallographic Data for 2.



Fig. S1. View along *c* crystallographic axis of crystal structures of **2** showing Ba^{2+} ions confined in hydrophilic octagonal and square pores, respectively. Hydrogen atoms have been omitted for clarity. Copper(II) and nickel(II) cations from the coordination network are represented by cyan and blue spheres, respectively, whereas the ligands are depicted as gray sticks. Barium(II) cations and water molecules hosted in the channels are represented by gold and red spheres, respectively. Orange-Red lines represent ionic interactions between the Ba^{2+} ions with the network and the water molecules. Free water molecules are omitted for clarity.



Fig. S2. Perspective view of a single hydrophilic pore hosting Ba^{2+} ions in crystal structure of **2**. Copper(II) and nickel(II) cations from the coordination network are represented by cyan and blue spheres, respectively, whereas the ligands are depicted as gray sticks. Barium(II) cations and water molecules hosted in the channels are represented by gold and red spheres, respectively. Orange-Red lines represent ionic interactions between the Ba^{2+} ions with the network and the water molecules. Free water molecules are omitted for clarity. Circle underlines statistical disorder of O2W molecule coordinated to copper metal ions of the network.



Fig. S3. View along *a* crystallographic axis of crystal structures of **2** showing Ba^{2+} ions confined in hydrophilic octagonal and square pores, respectively. Hydrogen atoms have been omitted for clarity. Copper(II) and nickel(II) cations from the coordination network are represented by cyan and blue spheres, respectively, whereas the ligands are depicted as gray sticks. Barium(II) cations and water molecules hosted in the channels are represented by gold and red spheres, respectively. Orange-red lines represent ionic interactions between the Ba^{2+} ions with the network and the water molecules. Free water molecules are omitted for clarity.



Fig. S4. Details of host-guest interactions in **2** related to the three crystallographically distinct Ba^{2+} ions. (a) Direct visualization by crystallography of Ba^{2+} ions detailed environments comprising carbonyl-oxygen atoms from the coordination network and water molecules for Ba1 (a,b), Ba2 (c,d) and Ba3 (e,f).



Fig. S5. Calculated (a) and experimental (b) PXRD pattern profiles of 2 in the 2θ range 2.0–60.0.





Fig. S7. N_2 (77 K) adsorption isotherms for the activated compounds 1 (red) and 2 (blue). Filled and empty symbols indicate the adsorption and desorption isotherms, respectively. The samples were activated at 348 K under reduced pressure for 19 h prior to carry out the sorption measurements.



Fig. S8. CO_2 (273 K) adsorption isotherms for the activated compounds 1 (red) and 2 (blue). Filled and empty symbols indicate the adsorption and desorption isotherms, respectively. The samples were activated at 348 K under reduced pressure for 19 h prior to carry out the sorption measurements.



Fig. S9. Theoretical (bottom) and experimental (top) PXRD pattern profile of 2 in the 2θ range 2.0–60.0 after the N₂/SO₂ breakthrough experiments.



Fig. S10. $N_2/CO_2/SO_2$ separation breakthrough curves at 303 K for 2 using 20 mL min⁻¹ flow of $N_2/CO_2/SO_2$ (82.5/15/2.5) gas mixture at 303 K..

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