Electronic Supplementary Information

Detection of SO_2 using a chemically stable Ni(II)-MOF

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S1. Materials and Methods

Chemicals and solvents were purchased from ReagentPlus, Aldrich, and used without further purification. Samples were synthesized and characterized at the Korea University, prior to SO_2 adsorption experiments and further characterization at Universidad Nacional Autónoma de México.

Ligand synthesis: H_4dobpdc was synthesized according to the literature.[S1] It was further washed with excess H_2O: acetone = 1:1 (v:v) solution with string, collected with filtration, and dried in a vacuum.

Powder X-ray diffraction (PXRD): PXRD patterns at Korea University were collected using a Rigaku Ultima III diffractometer (Cu Kα, λ = 1.5406 Å) with a scan speed of 5^{o}min^{-1} and a step size of 0.02^{o}. The tube voltage and current were 48 kV and 40 mA, respectively. PRXD patterns after SO_2 exposure were recorded at Universidad Nacional Autónoma de México on a Siemes Diffractometer, D5000 with a Cu-Kα1 radiation (λ = 1.5406 Å) using a nickel filter. Patterns were recorded in the 5–50° 2θ range with a step scan of 0.02° and a scan rate of 0.08° min^{-1}.

IR spectroscopy: Infrared spectroscopy measurements at Korea University were recorded with the attenuated total reflectance (ATR) module by using a Nicolet iS10 FTIR spectrometer. FT-IR spectra after SO_2 exposure were obtained on a Bruker Tensor 27 spectrometer with a Golden Gate Single Reflection diamond ATR cell at Universidad Nacional Autónoma de México.

TGA analyses: Thermogravimetric analyses (TGA) were performed at Korea University with a ramp rate of 2 °C min^{-1} up to 900 °C in an N_2 (99.999%) flow using a TA instruments Discovery TGA.

Gas Uptake: N_2 gas sorption measurements at 77 K and ammonia gas isotherm at 298 K were collected on a Micromeritics 3FLEX instrument up to 1 atm of gas pressure. N_2 gas used in measurements were highly pure (99.999%). Purity of ammonia gas used in measurement was 99.9995%. Before sorption analysis, the sample was activated under high vacuum at 250 °C for 24 hours.

SO_2 uptake: SO_2 adsorption experiments were carried out using a Dynamic Gravimetric Gas/Vapour Sorption Analyser, DVS vacuum (Surface Measurement Systems Ltd) at Universidad Nacional Autónoma de México. Ni_2(dobpdc) was degassed in a vacuum (1 x 10^{-6} Torr) at 473 K for 2 h. After cooling to 25°C, the isotherms were measured from 0.0007 to 100% P/P0 of SO_2 gas, followed by the desorption isotherm.

UV-vis spectroscopy: Absorption measurements were recorded at Universidad Nacional Autónoma de México using a Shimadzu spectrophotometer UV-2600 equipped with an ISR-2600Plus integrating sphere and a $BaSO_4$ blank.

Fluorescence: The fluorescence experiments were carried out in an Edinburgh Instruments FS5 Spectrofluorometer at Universidad Nacional Autónoma de México, coupled with the SC-10 solid-state sample holder. The samples were packed into quartz sample holders and positioned into the instrument. Both the activated and saturated samples were packed right after being taken out of the activation and saturation processes.

S2. Synthesis

Ni_2(dobpdc) was prepared according to the previous report with a modified procedure.[S2] Into a 32 mL pyrex cell, H4dobpdc (263.14 mg, 0.959 mmol, 1 eq), $NiCl_2$·6H2O (684.20 mg, 2.878 mmol, 3 eq) and 12 mL of solvent (DMF:EtOH = 1:1 (v:v)) were loaded and sonicated until clear solution obtained. The pyrex cell was sealed with a PTFE cap, and the solution was irradiated in a microwave reactor (CEM Discover) for 20 min at 383 K. The collected MOF solid was immersed in DMF and heated at 333 K overnight. The washed MOF solid was collected via filtration and reimmersed in methanol to exchange solvent for 3 days. In each day, the supernatant was decanted, and fresh methanol was added. Ni_2(dobpdc) was activated under high vacuum (1.4 x 10^{-3} torr) at 523 K for 12 h.

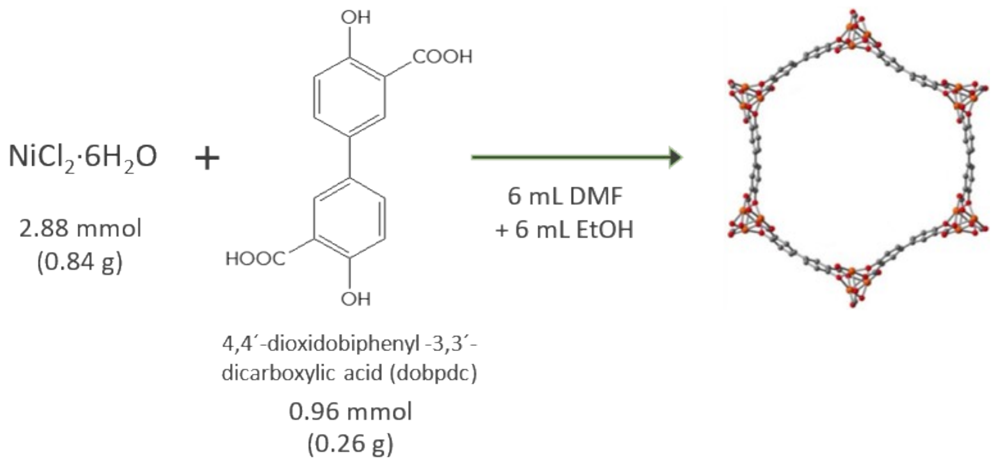

Fig. S1 Scheme of Ni_2(dobpdc) synthesis.

S3. Characterization

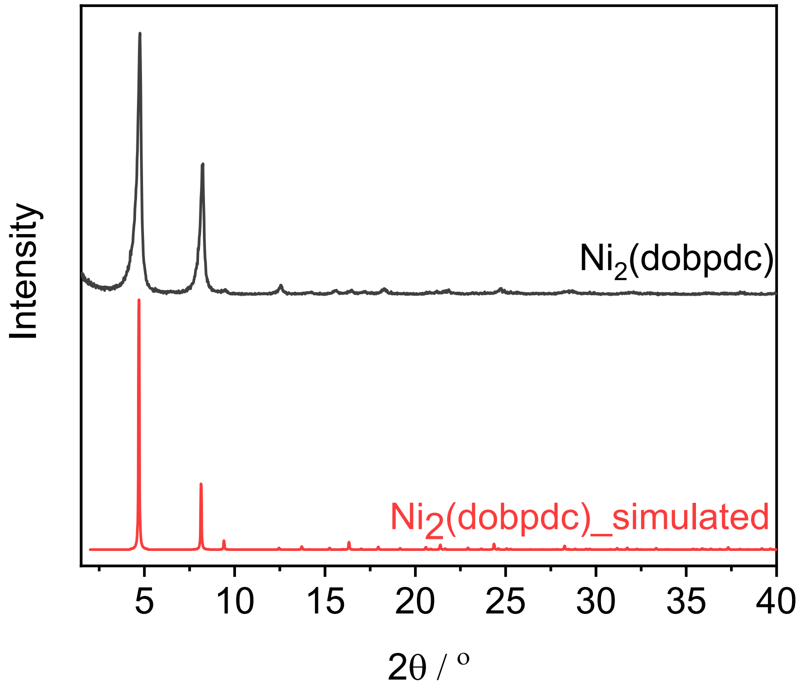

Fig. S2 Ni_2(dobpdc) as-synthesized PXRD pattern.

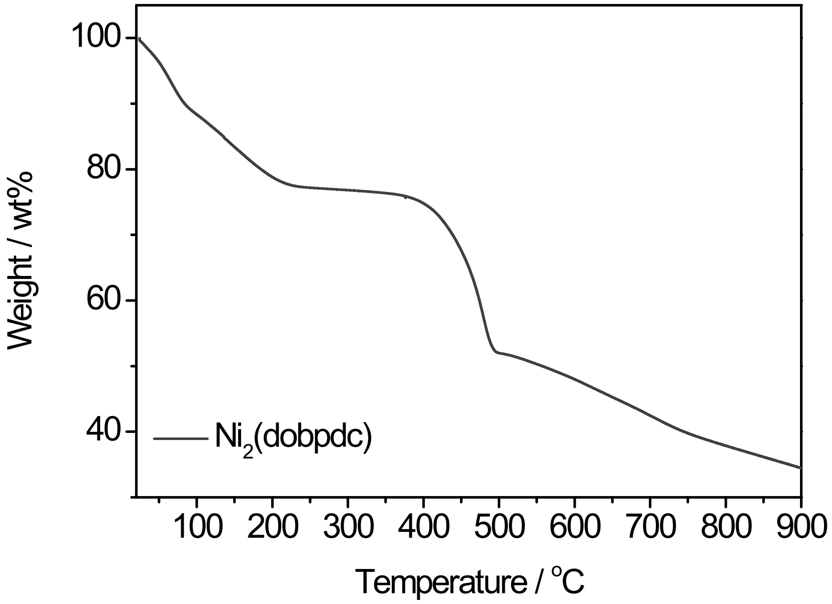

Fig. S3 Ni_2(dobpdc) as-synthesized TGA analysis.

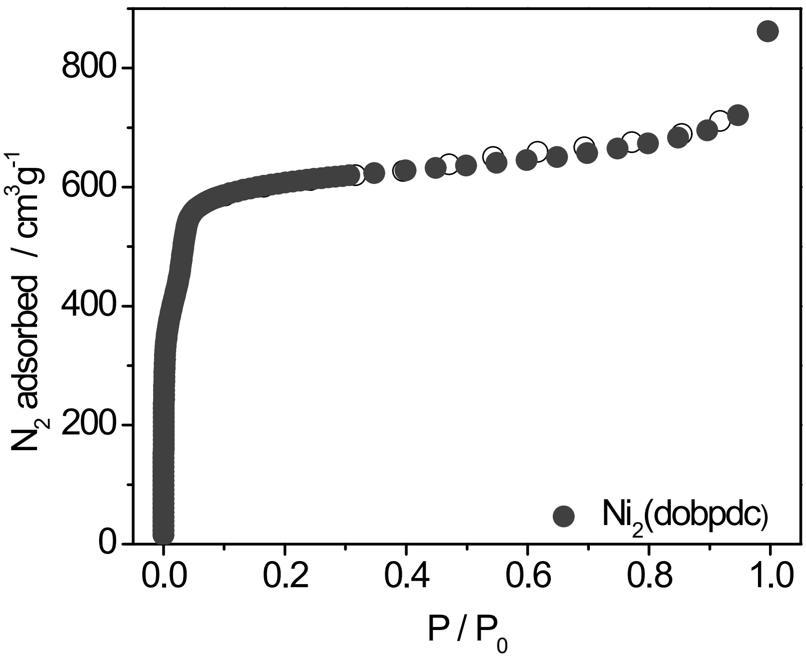

Fig. S4 Ni$_2$(dobpdc) N_2 isotherm at 77 K.

S4. Stability after SO_2 exposure

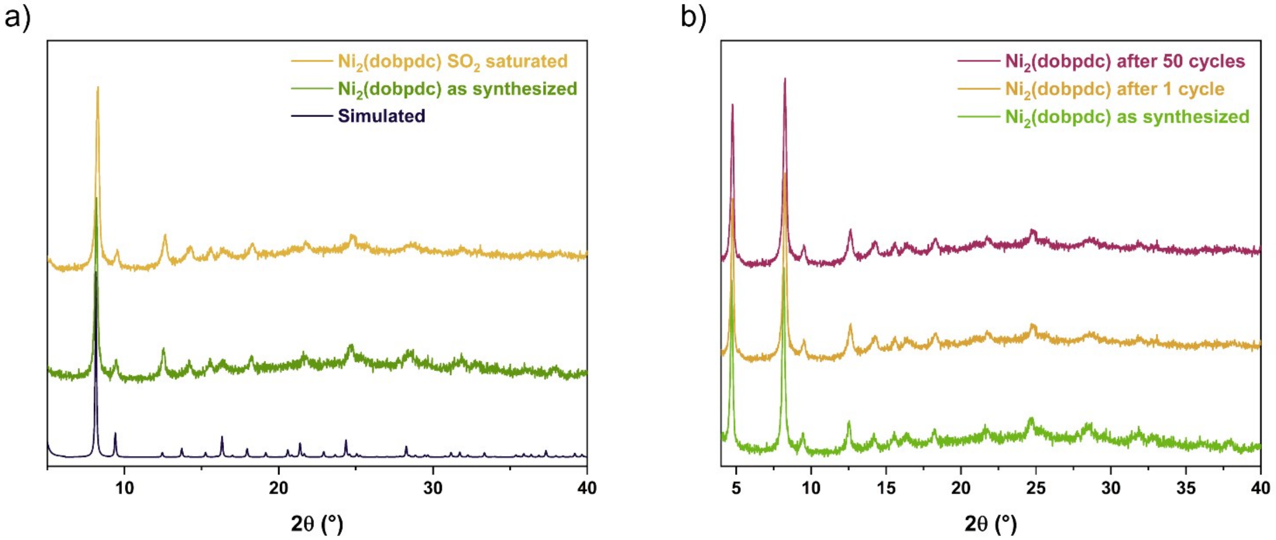

Fig. S5 Comparison of the PXRD patterns of a) simulated (black), synthesized and washed (green) and exposed to SO_2 (yellow) $Ni_2(dobpdc)$ material, and b) after 50 SO_2 adsorption-desorption cycles.

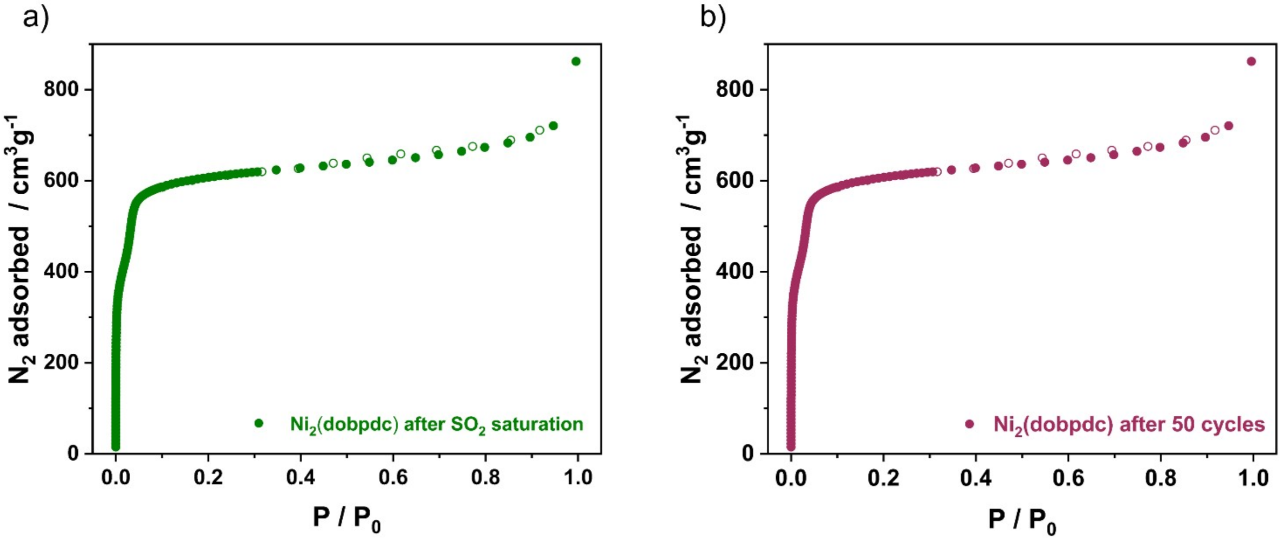

Fig. S6 Comparison of a) $Ni_2(dobpdc)$ N_2 isotherm at 77 K after SO_2 exposure b) after 50 SO_2 adsorption-desorption cycles.

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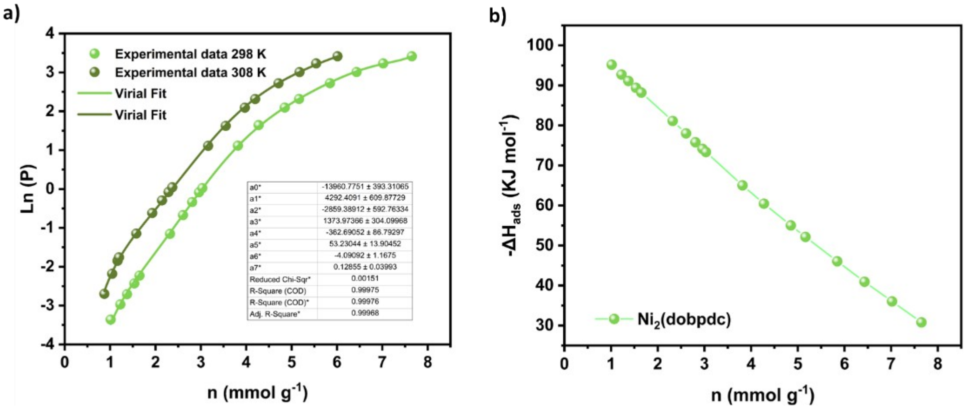
S5. Isosteric heat of adsorption for SO_2



a0*	-13960.7751 ± 393.31065
a1*	4292.4091 ± 609.87729
a2*	-2859.38912 ± 592.76334
a3*	1373.97366 ± 304.09968
a4*	-362.69052 ± 86.79297
a5*	53.23044 ± 13.90452
a6*	-4.09092 ± 1.1675
a7*	0.12855 ± 0.03993
Reduced Chi-Sqr*	0.00151
R-Square (COD)	0.99975
R-Square (COD)*	0.99976
Adj. R-Square*	0.99968

Fig. S7 a) Virial fitting for SO_2 adsorption isotherms at 298 and 308 K, b) Isosteric enthalpy of adsorption of SO_2 for Ni_2(dobpdc) from a virial fit at different coverage.

The isosteric enthalpy of SO_2 adsorption for Ni_2(dobpdc) was calculated and obtained a value of -95.2 kJ mol^{-1}. Calculations were carried out accordingly to the reported literature.[S3] A virial-type equation (Eq. S1) was used to fit the low coverage region of two adsorption isotherms at 273 and 298 K for the three materials.

$$\mathrm{Ln}(n/p) = A_0 + A_1\eta + A_2\eta^2 + \ldots \quad (\mathrm{Eq.}\ S1)$$

Where p is the pressure, n is the amount adsorbed, and A_0, A_1, … are the virial coefficients. The plot of Ln (n/p) gives a straight line at low surface coverage (Fig. S7). From the linear fittings (using the Clausius-Clapeyron equation), the virial coefficients are used to estimate the enthalpy of adsorption.

S6. Custom *in situ* SO_2 adsorption system

The system (Fig. S8) contains two principal parts:

A. The gas generator, in which Na_2SO_3 is added to a two-neck ball flask [1], one of which is capped with a rubber stopper through which Na_2SO_3 is injected with a syringe [2]. one of which is covered with a rubber stopper through which concentrated H_2SO_4 is injected with a glass syringe [2], while the other is covered with a rubber stopper [3]. concentrated H_2SO_4 [2] is injected through a glass syringe while the other port is connected to the saturation chamber. saturation chamber.

B. The saturation chamber, made of a round flask [3], is connected to a vacuum line [4] and a vacuum line [4]. vacuum line [4] and a pressure gauge [5].

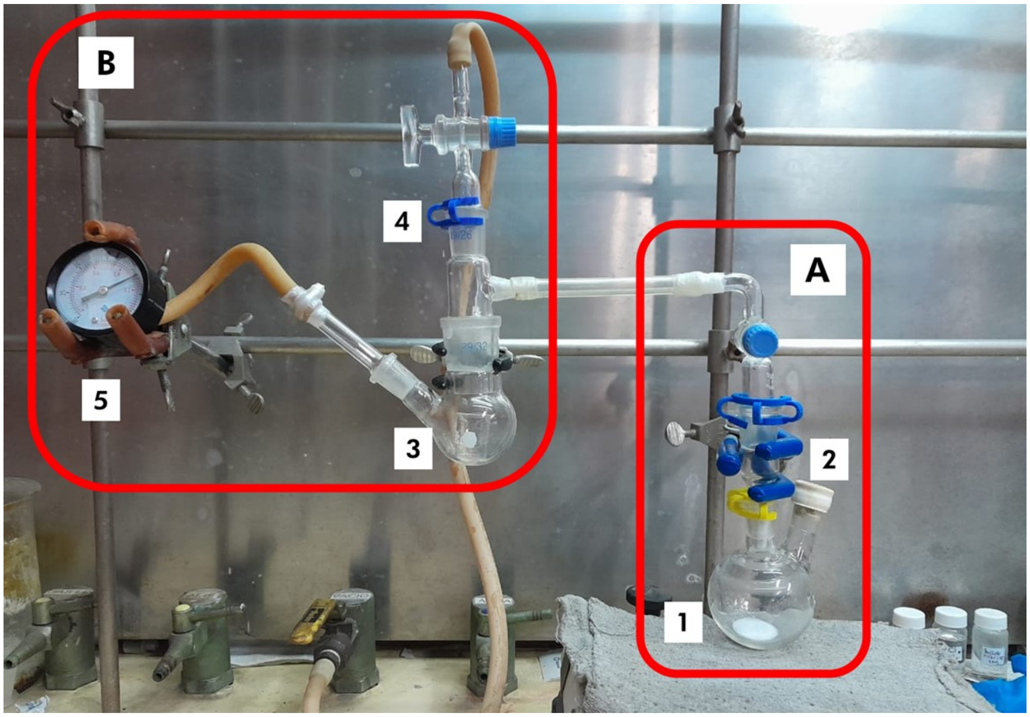


Fig. S8 In situ SO_2 homemade system.

To start the process, a sample of about 20 mg in a 1.5 mL glass vial was activated in a sand bath at 523 K under vacuum for 24 h. The sample was then placed in the saturation chamber, and the system was evacuated with a vacuum line. The vial was then placed in the saturation chamber, and the system was evacuated with a vacuum line. Next, 1 bar of SO_2 gas was generated by dripping 1.2 mL of concentrated H_2SO_4 over 2 g of Na_2SO_3, the sample was left continuously exposed to the gas for 3 hours. For the sample exposed to 0.1 bar SO_2, the sample was activated in the same way, and 0.12 mL of concentrated H_2SO_4 was dripped onto 0.2 g of Na_2SO_3. The sample was left continuously exposed to the gas for 3 hours.

S7. Ideal Adsorbed Solution Theory (IAST)

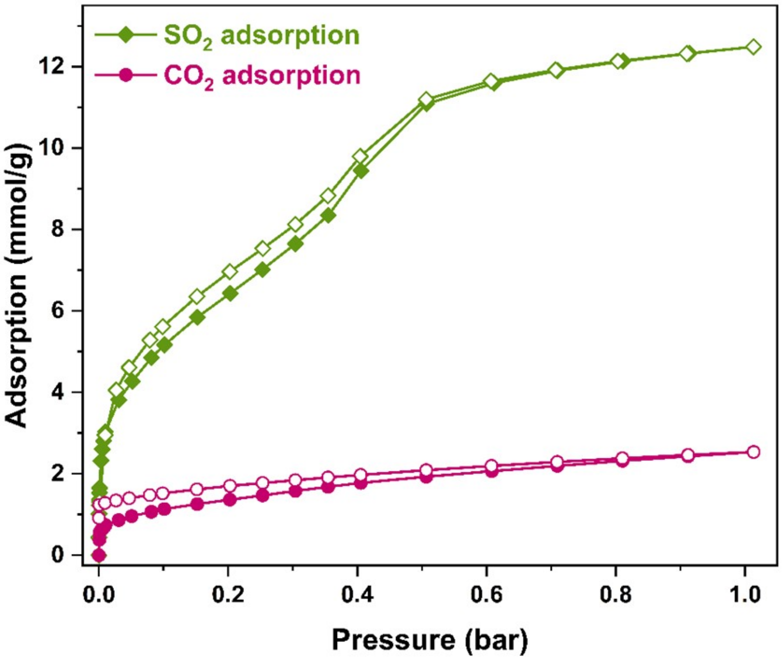


Fig. S9 Comparison of monocomponent SO_2 (green) and CO_2 (pink) adsorption isotherms Ni_2(dobpdc).

Predictions of the coadsorption of SO_2:CO_2 mixtures on Ni_2(dobpdc) were performed assuming the Ideal Adsorbed Solution Theory (IAST) assumptions as valid and using the Python package pyIAST.[S4]

None of the analytical models available in pyIAST fitted both experimental SO_2 and CO_2 isotherms of Ni_2(dobpdc). Therefore, these adsorption data were linearly interpolated, and the distributed pressures were calculated by numerical quadrature implemented in pyIAST (Fig. S14). Therefore, the adsorption selectivity was calculated as:

$$S_{SO_2/CO_2} = \frac{x_{SO_2} y_{CO2}}{x_{CO_2} y_{SO2}}$$

where x_i and y_i are the mole fraction of components i = SO_2 and CO_2 in adsorbed and gas phase, respectively.

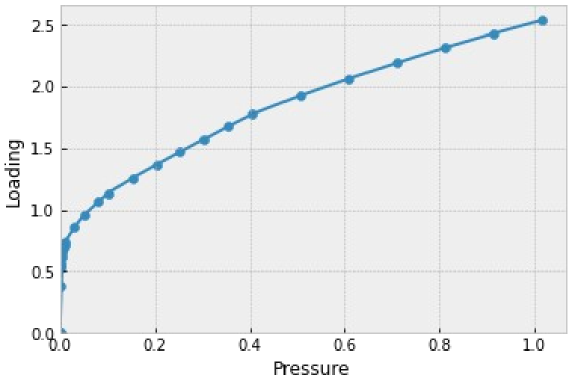


Fig. S10 Experimental CO_2 adsorption isotherm of Ni_2(dobpdc) at 298 K (full circles) and the interpolation model fit (continuous line). Loading in mmol/g and Pressure in bar.

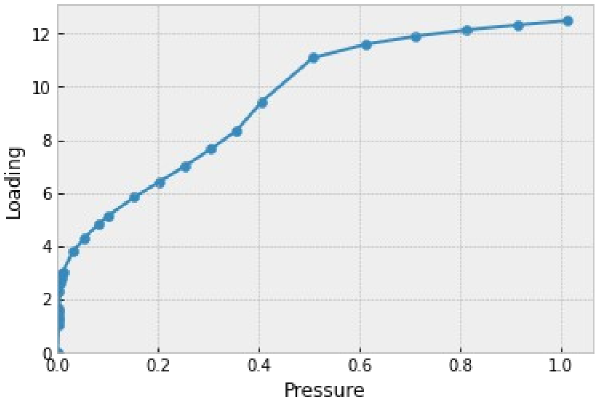


Fig. S11 Experimental SO_2 adsorption isotherm of Ni_2(dobpdc) at 298 K (full circles) and the interpolation model fit (continuous line). Loading is in mmol/g and Pressure in bar.

The selectivity of SO_2 versus CO_2 of different SO_2:CO_2 mole fractions at 1 bar pressure was calculated. The results are shown in Table S1.

Table S1. SO_2/CO_2 selectivity

SO_2/CO_2 composition (%)	Selectivity
0.07/99.93	s = 16.90
0.1/99.9	s = 12.18
0.3/99.7	s = 4.68
0.5/99.5	s = 3.08
1/99	s = 1.78
3/97	s = 0.74
5/95	s = 0.48

S8. UV-vis Spectroscopy

Before doing fluorescence experiments, a solid UV experiment was performed on Ni_2(dobpdc), to know their possible excitation wavelength, which was 320 nm.

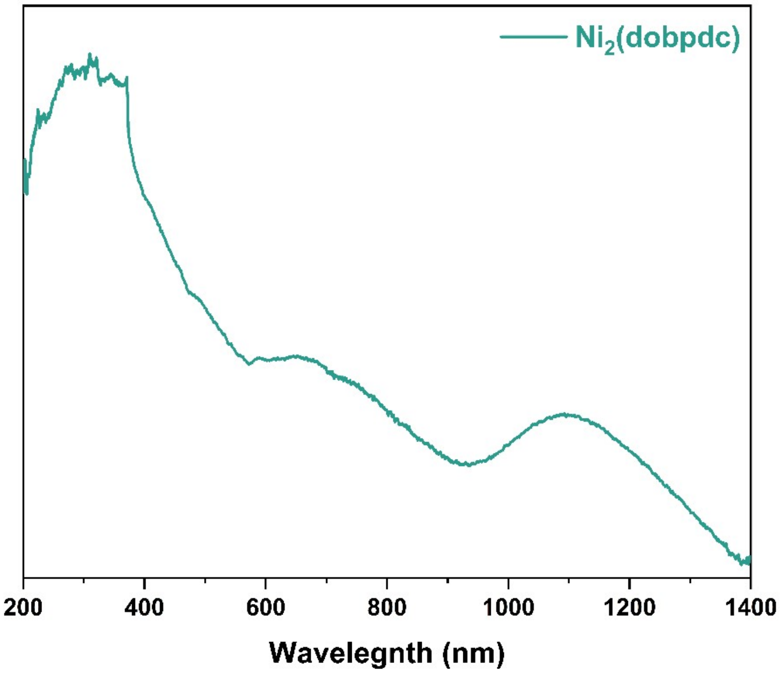


Fig. S12 Comparison of mono-component SO_2 (green) and CO_2 (pink) adsorption isotherms Ni_2(dobpdc).

S9. Time-resolved emission experiments

Time-resolved emission experiments were carried out on activated and SO_2-saturated Ni_2(dobpdc) samples with an EPLED-340 laser (λ_{ex} = 340 nm) at three different emission wavelengths: 405 nm which was the emission maximum of the SO_2-saturated sample, 450 nm which was the emission maximum of the activated sample and 425 nm because a signal was observed in both spectra. In all cases, a decrease in the fluorescence lifetime of the material exposed to SO_2 was observed. Three exponential decay components were considered to fit the data properly.

Table S2. Fluorescence lifetimes of Ni_2(dobpdc) activated and SO_2 saturated at different emission wavelengths.

Ni_2(dobpdc) activated					**Ni_2(dobpdc) SO_2 saturated**				
Emission (nm)	**τ_1 (ns)**	**τ_2 (ns)**	**τ_3 (ns)**	**Fluorescence lifetime (ns)**	**Emission (nm)**	**τ_1 (ns)**	**τ_2 (ns)**	**τ_3 (ns)**	**Fluorescence lifetime (ns)**
450	0.7567	2.7457	9.4713	**3.03773**	450	1.1867	2.8847	7.3995	3.16526
425	0.9669	2.4722	7.8039	2.30124	425	0.8940	2.2912	6.2680	2.65510
405	0.0564	1.5464	4.8198	2.14008	**405**	0.2065	1.7036	4.7748	**2.46850**

Comparisons of the time-resolved spectra obtained are shown below:

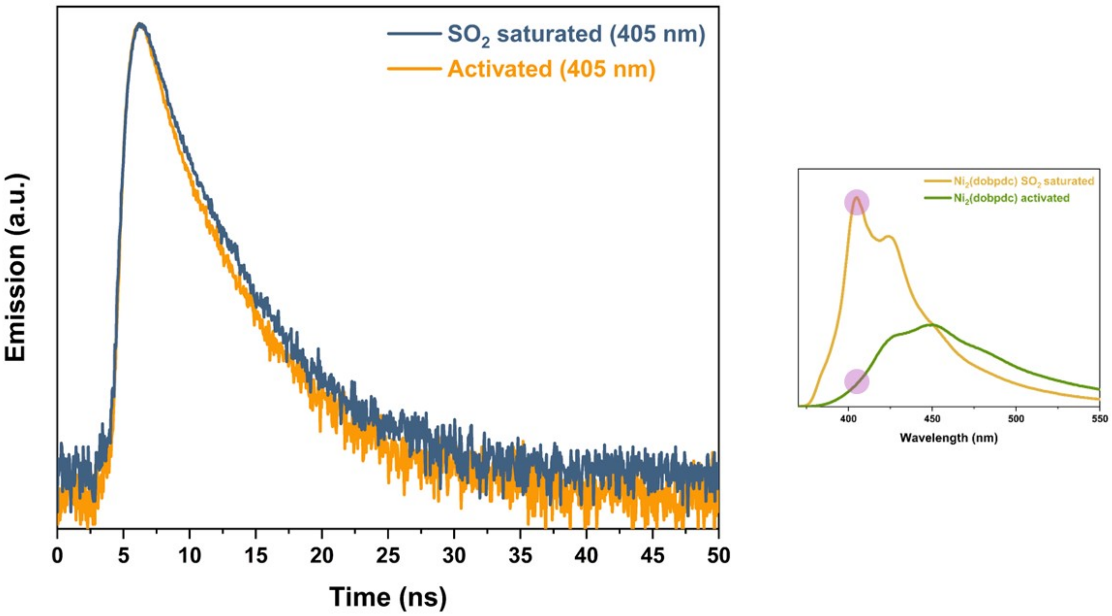


Fig. S13 Time-resolved spectra at 405 nm for Ni_2(dobpdc) activated (yellow) and SO_2 saturated (blue).

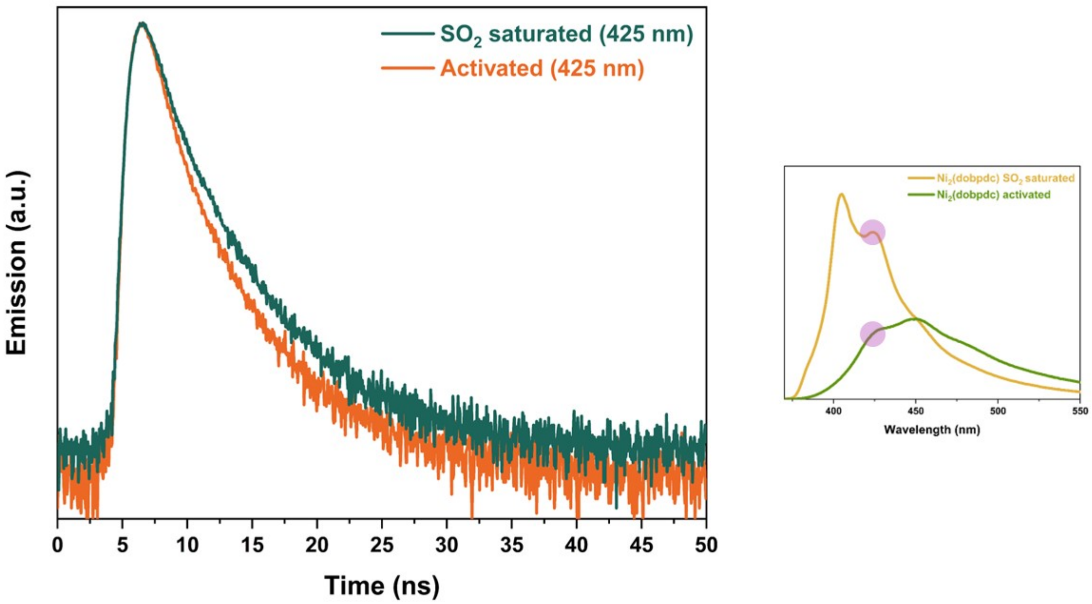


Fig. S14 Time-resolved spectra at 425 nm for Ni_2(dobpdc) activated (orange) and SO_2 saturated (green).

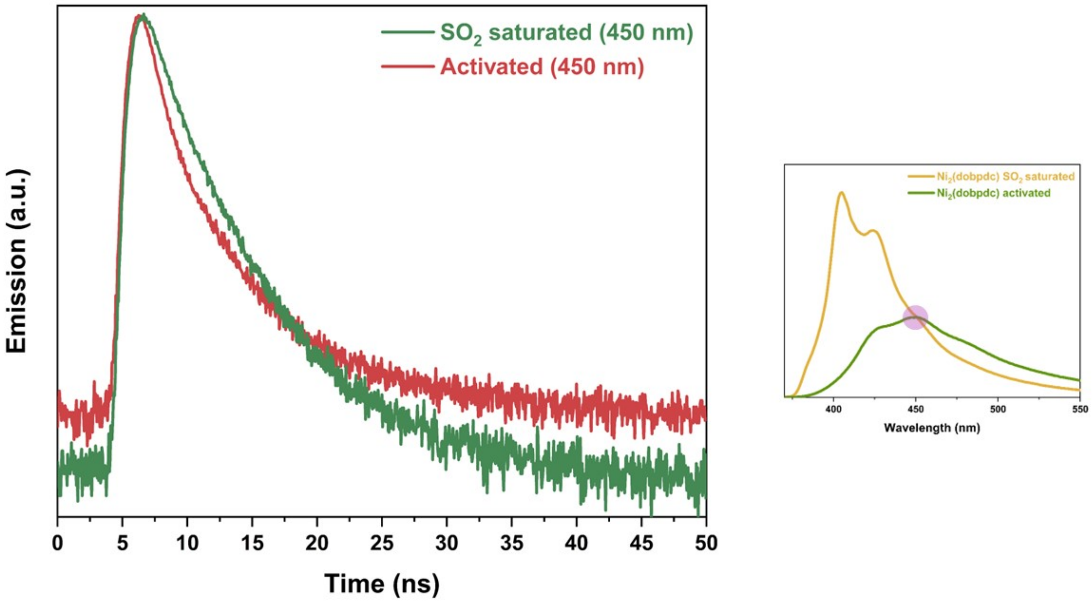


Fig. S15 Time-resolved spectra at 450 nm for Ni_2(dobpdc) activated (red) and SO_2 saturated (green).

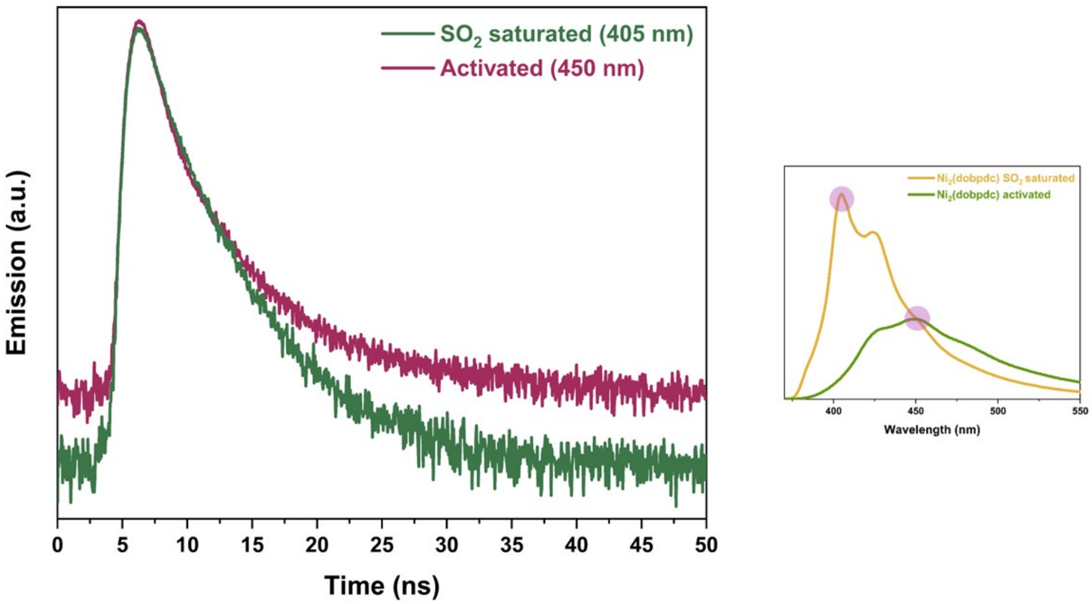


Fig. S16 Time-resolved spectra at the emission maximum for Ni_2(dobpdc) activated (pink) and SO_2 saturated (green).

S10. References

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