Supplementary Information (SI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2024

Supporting Information for:

UTSA-16(Zn) for SO_2 detection: elucidating the fluorescence mechanism

Valeria B. López-Cervantes,[a+] Marco L. Martínez,[a,b,+] Juan L. Obeso,[a,c,d] Celene García-Carvajal,[a,e] Nora S. Portillo-Vélez,[f] Ariel Guzmán-Vargas,[b] Ricardo A. Peralta,[f] Eduardo González-Zamora,[f] Ilich A. Ibarra,[a] Diego Solis-Ibarra,[a*] John Luke Woodliffe[g*], and Yoarhy A. Amador-Sánchez[a,f*]

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, México.*
b. *ESIQIE – Instituto Politécnico Nacional, Avenida IPN UPALM Edificio 7, Zacatenco, 07738 México D.F, Mexico.*
c. *Instituto Politécnico Nacional, CICATA U. Legaria, Laboratorio Nacional de Ciencia, Tecnología y Gestión Integrada del Agua (LNAgua), Legaria 694, Irrigación, 11500, Miguel Hidalgo, CDMX, México.*
d. *División de Ingeniería en Sistemas Automotrices, Tecnológico de Estudios Superiores del Oriente del Estado de México, Tecnológico Nacional de México, Estado de México 56400, Mexico*
e. *Laboratorio de Sólidos Porosos (LabSoP) – INFAP-CONICET, Universidad Nacional de San Luis, San Luis, Argentina.*
f. *Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, Av. Ferrocarril San Rafael Atlixco 186, Col. Leyes de Reforma 1A Sección, Iztapalapa, 09310, Ciudad de México, México*
g. *Advanced Materials Research Group, Faculty of Engineering, University of Nottingham, Nottingham NG7 2RD, UK.*

Table of contents

S1. Experimental details

S1.1. Materials

Chemicals and reagents were utilized as received without further treatment. Zinc acetate dihydrate (≥99.0%), citric acid monohydrate (≥99.0%), and potassium hydroxide (86.7%) were purchased from Sigma Aldrich. Ethanol (absolute, SpS grade) was obtained from Scientific Laboratory Supplies LTD and methanol (≥99.9%) from Fisher Scientific. All water was deionised.

S1.2. Synthesis

The synthetic method for UTSA-16(Zn) was the same as previously reported.[S1] Briefly, zinc acetate dihydrate (2 mmol), citric acid monohydrate (2 mmol) and potassium hydroxide (5.2 mmol) were dissolved in 5 mL H_2O in a 35 mL microwave vial. 5 mL ethanol was added and the mixture stirred for 10 minutes before the vial was sealed and irradiated by microwave at 300 W and 60 °C for 10 minutes. After cooling, the product was collected and washed with MeOH (3 x 30 mL) before drying in an oven (50 °C, >4 h), yielding a white powder of UTSA-16(Zn) (0.31 g, 77%).

S1.3. Analytical instruments

Powder X-Ray Diffraction Patterns (PXRD)

X-ray powder diffraction patterns (XRPD) were measured on a Siemens Diffractometer model D5000, with CuKa1 radiation (l=1.5406) using a nickel filter with a step scan of 0.02° and a scan rate of 0.08 $°min^{-1}$.

Fourier-transform infrared spectroscopy (FT-IR)

IR spectra were acquired using a FT-IR spectrometer by Thermo Fisher Scientific model Nicolet 6700 equipped with an ATR accessory. Measurements were made at 25 °C, from 4000 to 400 cm^{-1}.

Thermal gravimetric analysis (TGA)

Thermograms were collected using a PerkinElmer STA 6000 apparatus under a N_2 atmosphere, with a temperature range between 30-650 °C. The heating rate was 10 °C min^{-1} and the N_2 flow was 20 ml min^{-1}.

Solid-state ultraviolet-visible spectroscopy (UV-Vis)

Absorption measurements were performed from 200-800 nm using a Shimadzu spectrophotometer UV-2600 equipped with an ISR-2600Plus integrating sphere and a $BaSO_4$ blank.

X-ray Photoelectron Spectroscopy (XPS)

For the X-ray photoelectron spectroscopy (XPS) study of UTSA-16, a PHI VersaProbe II spectrometer by Physical Electronics was used. Both the pristine material, as well as saturated with SO_2 (after activation) data were acquired. The measurement was made without ion sputtering.

Fluorescence Spectroscopy

Fluorescence spectra were collected on a FS5 Edinburgh Instruments Spectrofluorometer using a continuous wave 150 W ozone-free xenon arc lamp at room temperature, coupled with the SC-10 Solid-state and SC-05 Standard Cuvette sample holder. The solid-state samples were packed into quartz sample holders and positioned into the instrument. Dispersed in THF samples were measured in quartz cuvettes. All spectra were acquired at ambient conditions (around 27 °C). Emission measurements were carried out using an excitation wavelength of 360 nm, with a LP-395 filter on the detector side to remove any remaining light from the excitation source. Emission spectra were collected with a step size of 1 nm and a dwell time of 0.1 s. The excitation bandwidth was set at 2.00 nm, and the emission bandwidth for the detector at 1.00 nm.

Time-resolved photoluminescence (TRPL)

TRPL spectra were measured in an Edinburgh Instruments FS5 Spectrofluorometer using a 375 nm laser, with an excitation bandwidth of 0.01 nm and an emission bandwidth of 1 nm, at an emission wavelength of 450 nm.

S1.4. Custom ex-situ SO_2 adsorption system

The system (Figure S1) contains two principal parts:

A. The gas generator, in which Fe_2S_3 is added to a two-neck ball flask [1], one of which is capped with a rubber stopper through which concentrated HCl is injected with a glass syringe [2], while the other port is connected to the 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].

To start the process, a sample of about 15 mg in a 1.5 mL glass vial was activated in a sand bath with N_2 flow at 120 °C under vacuum for 12 h. The vial was then placed in the saturation chamber, and the system was evacuated with a vacuum line. Next, H_2S gas was generated by dripping concentrated HCl over Fe_2S_3, the sample was left continuously exposed to the gas for 3 hours.

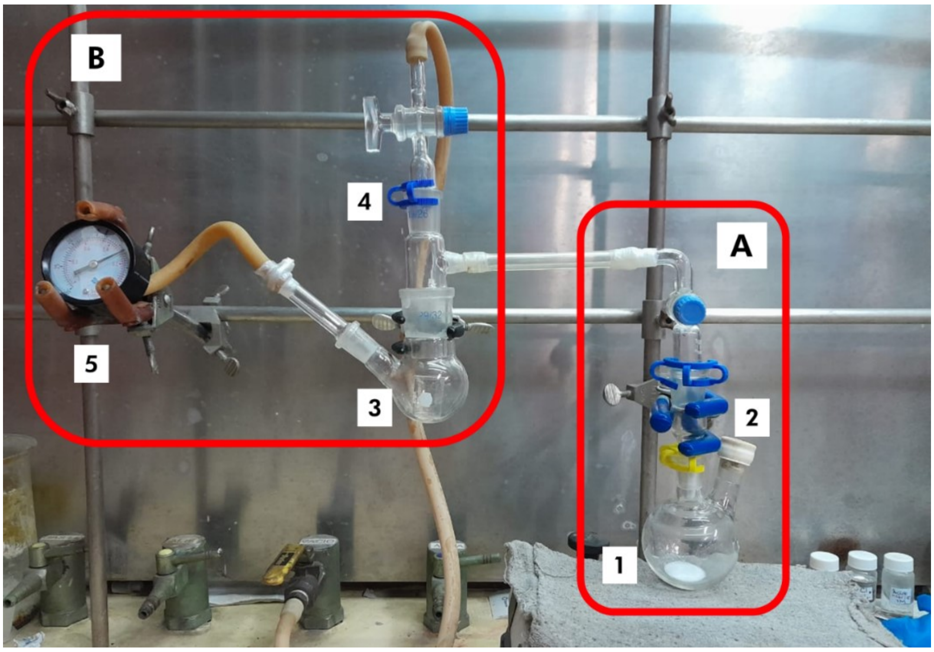

Figure S1. Ex-situ SO_2 generator homemade system.

S2. Results and Discussion

S2.1. SO_2 adsorption in UTSA-16(Zn) before and after SO_2 exposure

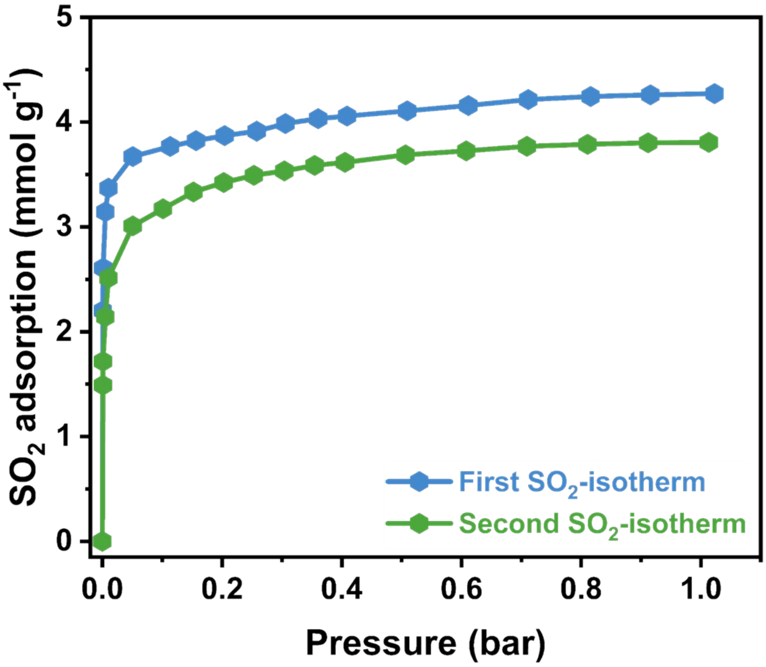

Figure S2. Comparison of SO_2 adsorption performance on a pristine sample (blue) and a sample previously exposed to SO_2 (green) at 25°C and from 0 to 1 bar.

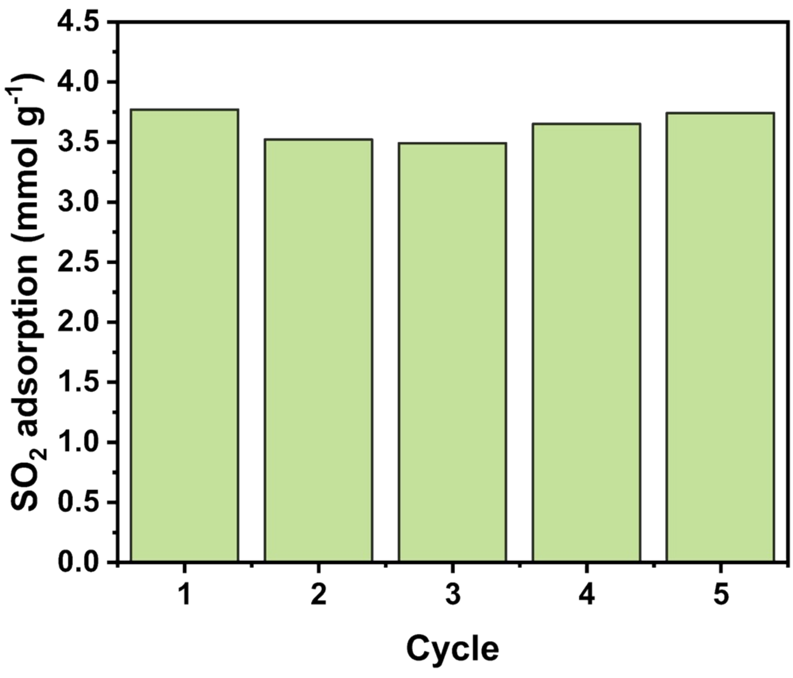

Figure S3. UTSA-16 adsorption-desorption cycles at 0.1 bar SO_2. Average uptake at 0.1 bar SO_2: 3.63 mmol g^{-1}.

S2.2. Characterization of UTSA-16(Zn) before and after SO_2 exposure

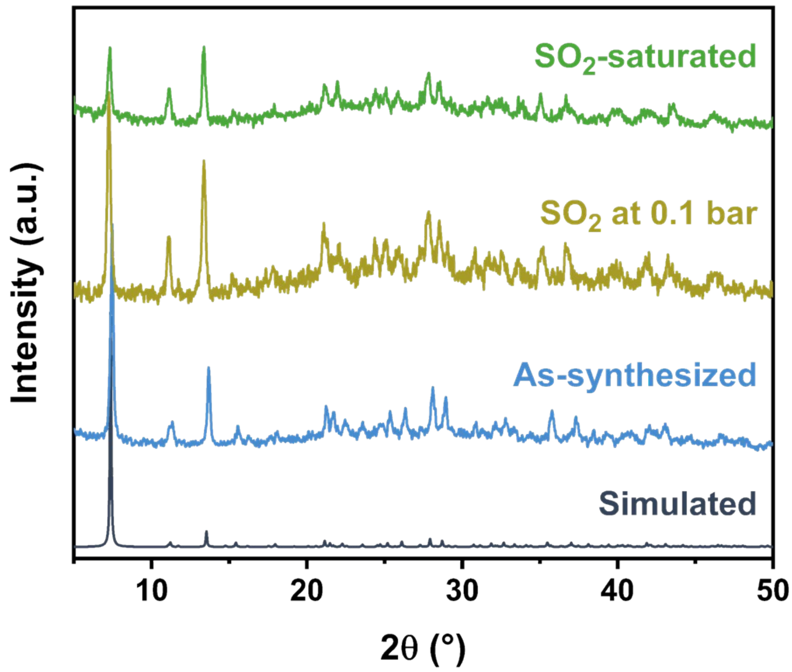

Figure S4. PXRD patterns of UTSA-16(Zn) material: simulated (grey), as-synthesized (blue), exposed to 0.1 bar SO_2 (yellow) and saturated with SO_2 (green).

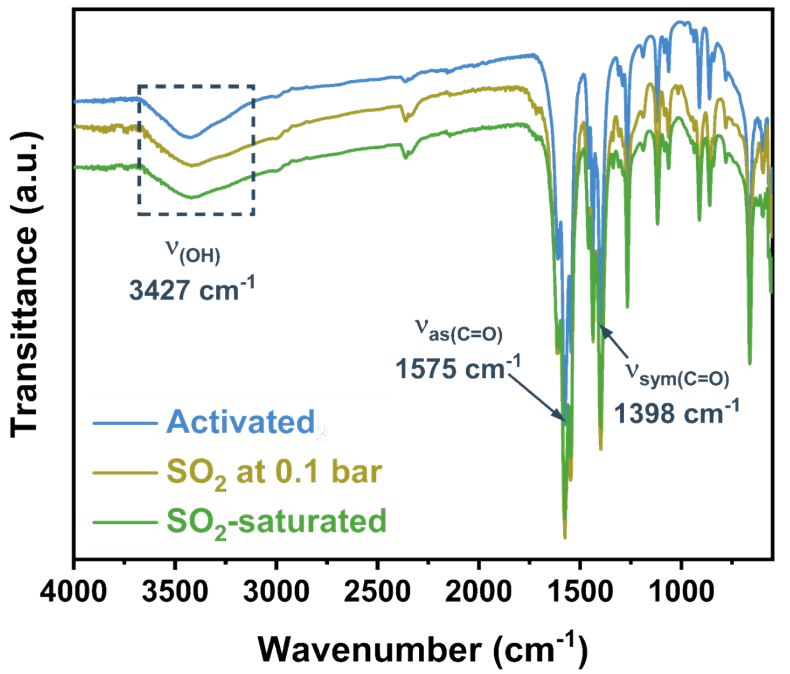

Figure S5. FTIR spectra of UTSA-16(Zn) material: activated (blue), exposed to 0.1 bar SO_2 (yellow) and saturated with SO_2 (green).

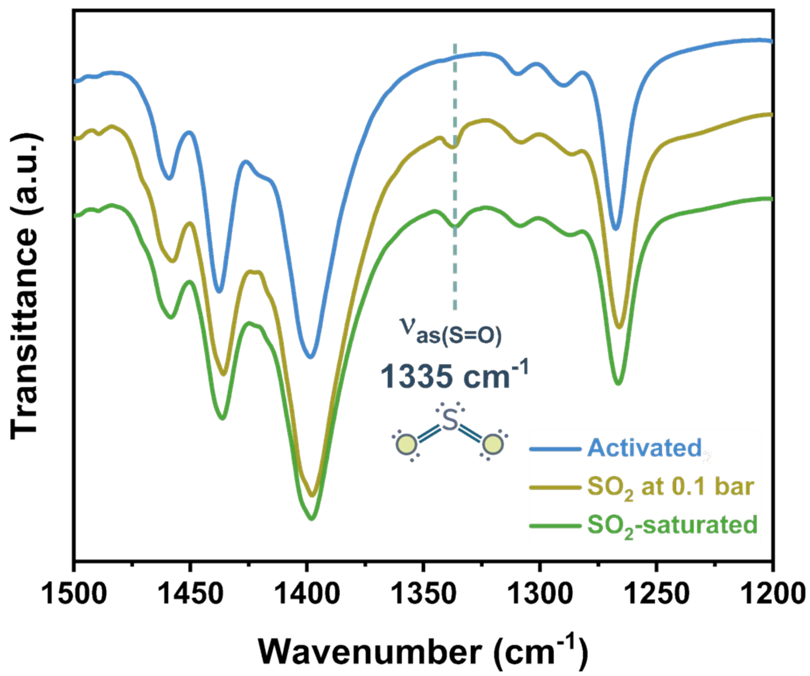

Figure S6. FTIR spectra at 1335 cm^{-1} of UTSA-16(Zn) material: activated (blue), exposed to 0.1 bar SO_2 (yellow) and saturated with SO_2 (green).

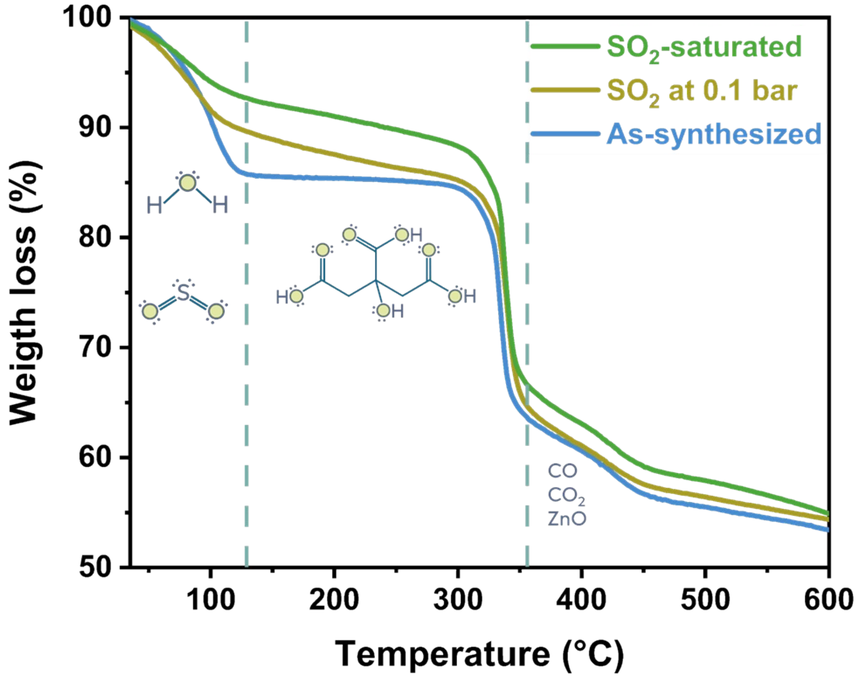

Figure S7. TG profile of UTSA-16(Zn) material: activated (blue), exposed to 0.1 bar SO_2 (yellow) and saturated with SO_2 (green).

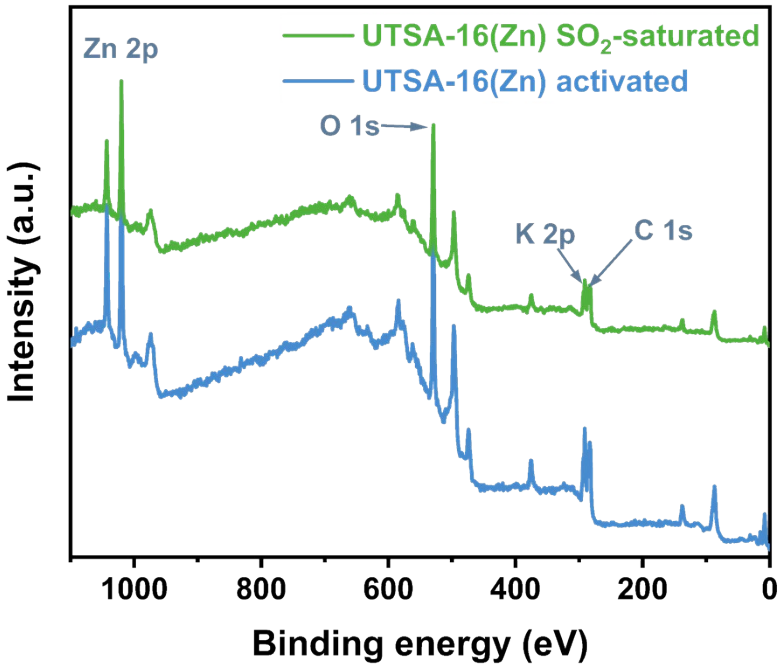

Figure S8. XPS survey plot of UTSA-16(Zn) material: activated (blue) and saturated with SO_2 (green).

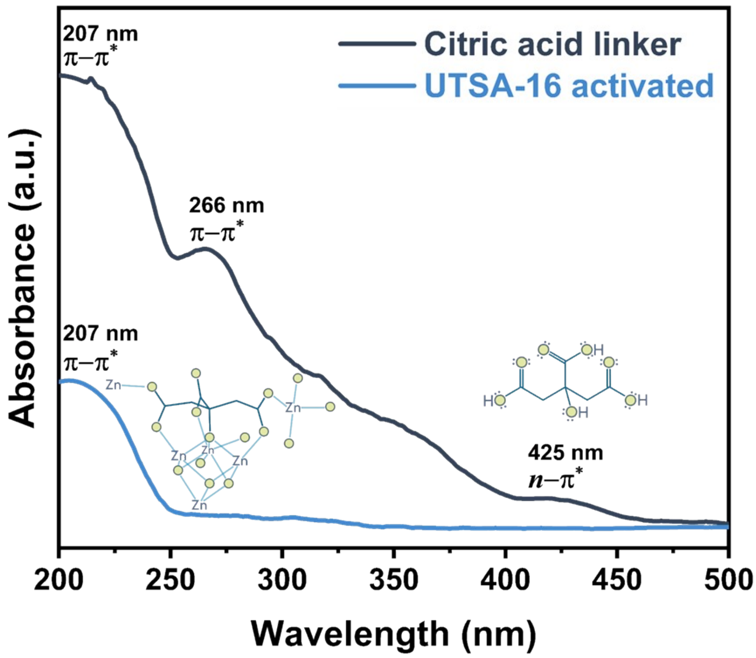

Figure S9. Solid-state UV-vis spectra of citric acid ligand (gray) and UTSA-16(Zn) (blue).

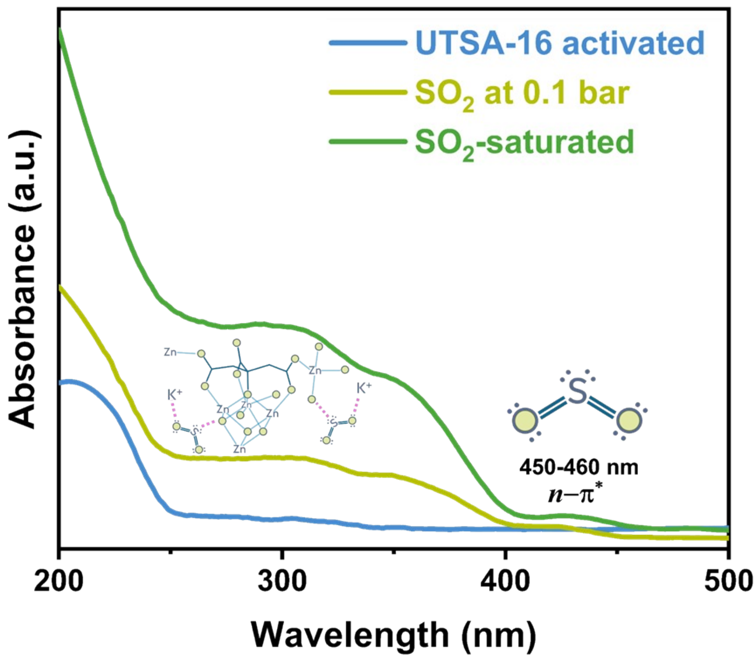

Figure S10. Solid-state UV-vis spectra of UTSA-16(Zn) material: activated (blue), exposed to 0.1 bar SO_2 (yellow) and saturated with SO_2 (green).

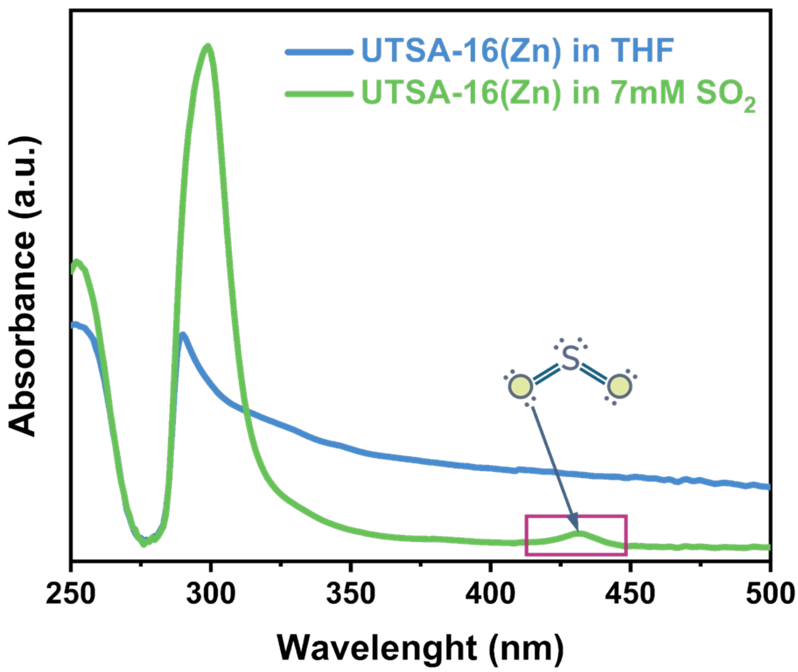

Figure S11. UV-vis spectra of dispersed in THF UTSA-16(Zn) material: pristine (blue) and exposed to a 7 mM SO_2 solution (green).

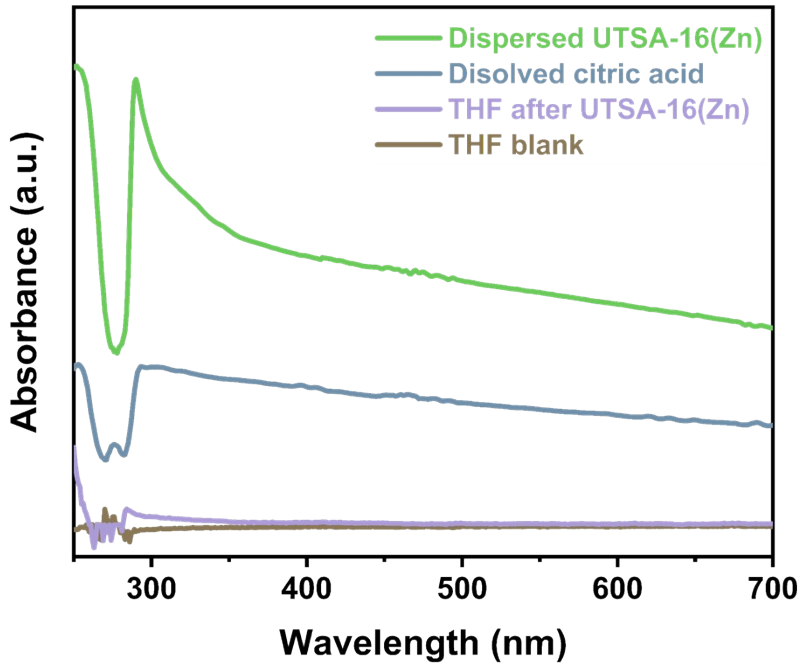

Figure S12. Comparison of UV-vis spectra of UTSA-16(Zn) material dispersed in THF (green), citric acid dissolved in THF (blue) and THF solution after filtration of UTSA-16(Zn) (purple).

S2.2. Tauc plots for the determination of the energies between HOMO-LUMO orbitals by direct and indirect method

The determination of the energy between the HOMO-LUMO orbitals of the linker, as well as of the activated UTSA-16(Zn) material, exposed to 0.1 bar SO_2 and saturated with SO_2, were performed by constructing Tauc plots using solid-state UV-visible spectroscopy data.[S2] Tauc plots in Figure S10, allow the assessment of the type of electronic transition present, either a direct or indirect transition, based on the analysis of the optical absorption of the material.

The following relationships were used for this assessment:

- Direct transitions: $(\alpha h\upsilon)^2 \propto (h\upsilon - E_{gap})$
- Indirect transitions: $(\alpha h\upsilon)^{\frac{1}{2}} \propto (h\upsilon - E_{gap})$

Where α is the absorption coefficient, *hv* is the photon energy, and E_{gap} represents the HOMO-LUMO energy gap. By extrapolating the linear region of the Tauc plot to α=0, the E_{gap} value for each transition type is obtained.

The values obtained for the direct and indirect transitions are shown in Table S1.

Table S1. HOMO-LUMO energy values considering direct and indirect transitions calculated from the Tauc method for the citric acid ligand, and the activated, exposed to 0.1 bar and SO_2-saturated UTSA-16 samples.

Sample	Direct (eV)	Indirect (eV)
Citric acid ligand	3.52	2.63
UTSA-16(Zn) activated	5.15	4.91
SO_2 at 0.1 bar	3.16	2.72
SO_2 saturated	2.72	2.44

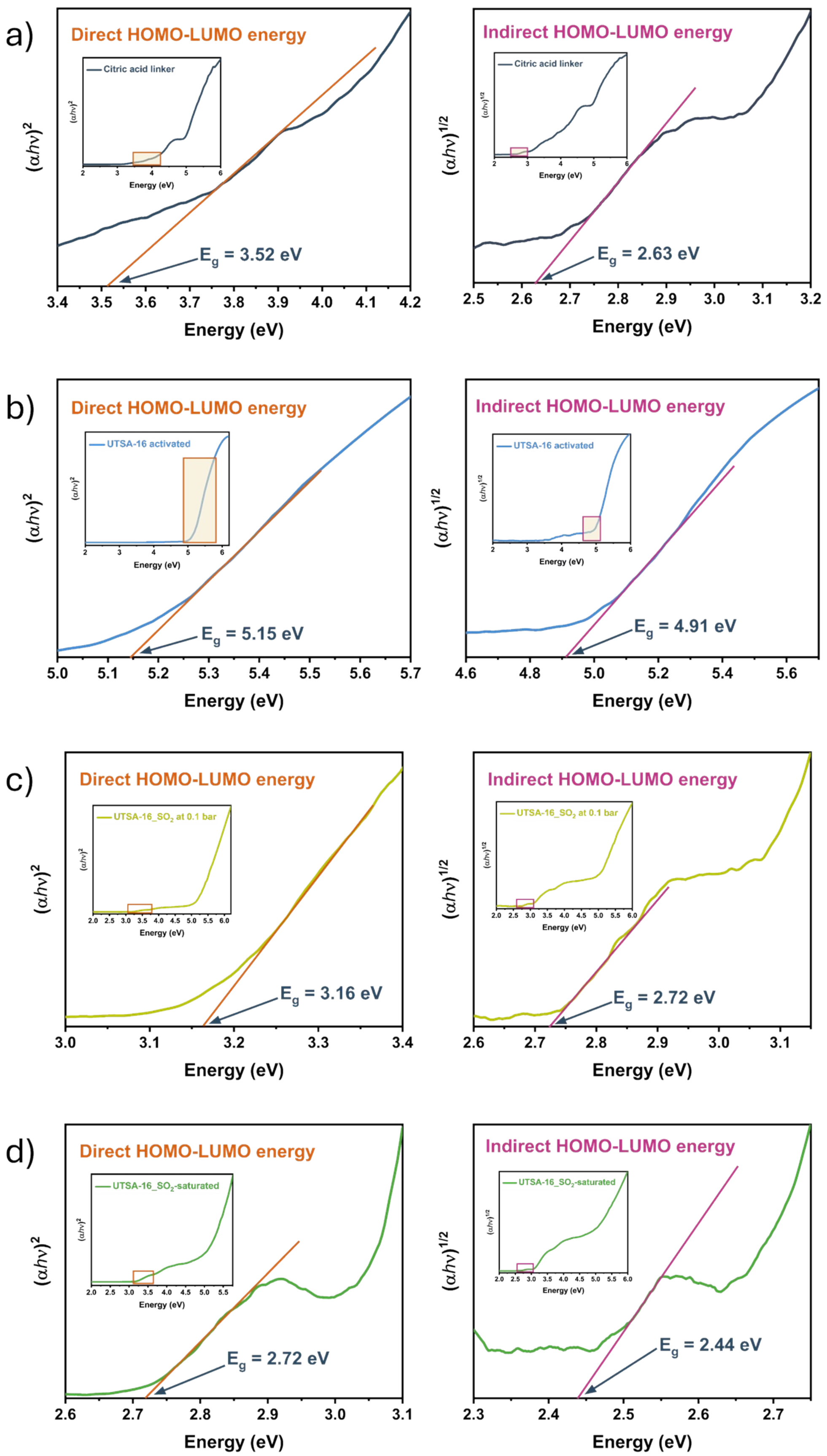

Figure S13. Tauc plots considering direct and indirect transitions for (a) and (b) citric acid (grey), (c) and (d) activated UTSA-16(Zn) (blue), (e) and (f) exposed to 0.1 bar (yellow), and (g) and (h) saturated with SO_2 (green). The insets show the normalised absorbances of the corresponding solid-state UV-vis spectra.

S2.3. Fluorescence and TRPL experiments

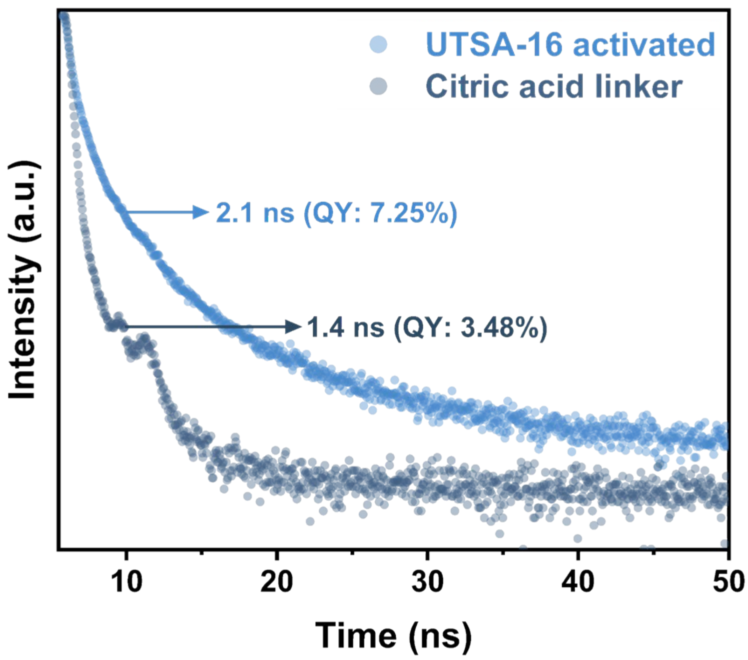

Figure S14. Solid-state emission spectra of activated UTSA-16(Zn) at different excitation wavelengths.

Table S2. Lifetimes of the activated and saturated samples.

Sample	Citric acid ligand	UTSA-16(Zn) activated	SO_2 at 0.1 bar	SO_2 saturated
τ_1 (ns)	0.0913	0.1292	0.0914	0.0950
a_1	0.7288	0.3163	0.5079	0.6292
τ_2 (ns)	0.5122	0.8918	0.8798	0.9943
a_2	0.1899	0.3191	0.2080	0.1708
τ_3 (ns)	2.2584	2.5934	2.8055	3.0075
a_3	0.0700	0.2362	0.2003	0.1260
τ_4 (ns)	15.3417	9.0222	10.2121	11.0128
a_4	0.0113	0.1284	0.0837	0.0741
Lifetime (ns)	**0.5213**	**2.0965**	**1.6461**	**1.4246**

Fluorescence lifetimes were determined from the TPRL spectra. The data obtained from the decay spectra were fitted in Fluoracle software, using a multi-exponential equation (Equation 1) to describe the fluorescence emission decay curve:[S3]

$$R(t) = B_1 e^{\left(\frac{-t}{\tau_1}\right)} + B_2 e^{\left(\frac{-t}{\tau_2}\right)} + B_3 e^{\left(\frac{t}{\tau_3}\right)} + B_4 e^{\left(\frac{-t}{\tau_4}\right)}$$

where R(t) represents the fluorescence intensity as a function of time, B_1, B_2, B_3 and B_4 are the amplitudes of the respective decay components, and τ_1, τ_2, τ_3 and τ_4 are the lifetimes of the different components.

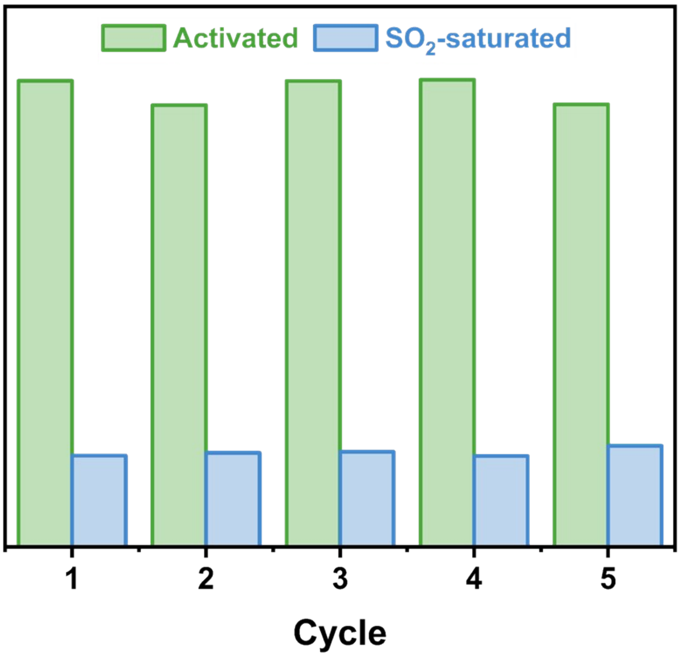

Figure S15. Fluorescence intensity during five cycles of activation (green) and SO_2-saturation (blue).

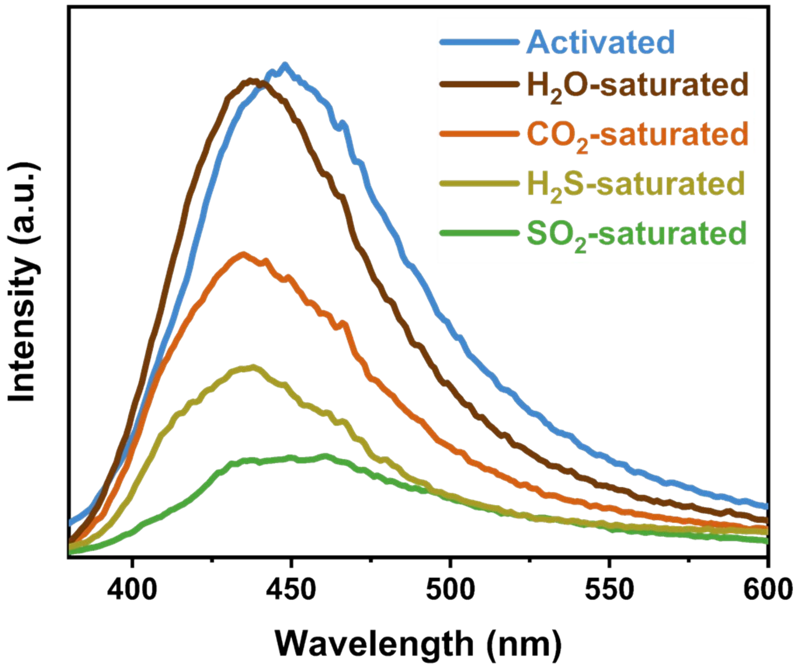

Figure S16. Comparison of solid-state emission spectra of UTSA-16(Zn) saturated with H_2O (brown), CO_2 (orange), H_2S (yellow) and SO_2 (green).

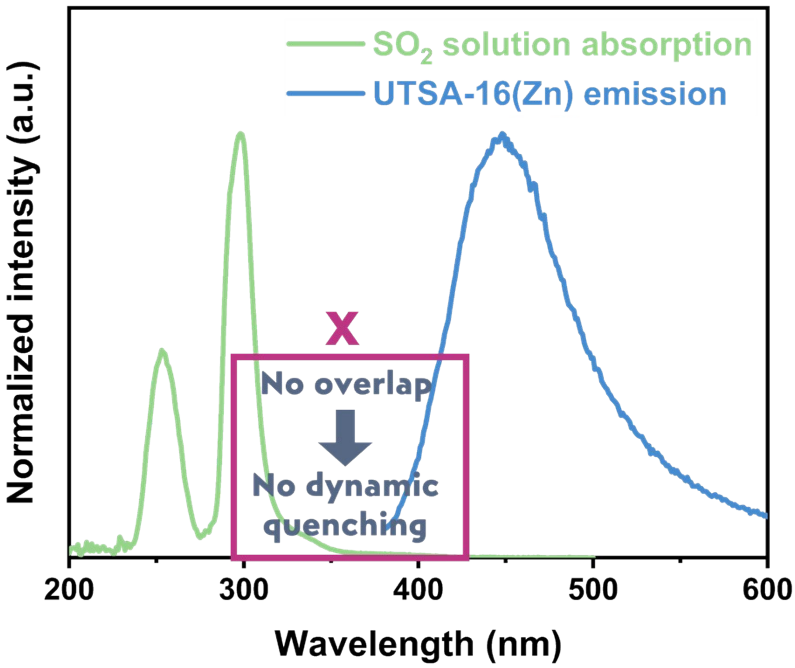

Figure S17. Comparison of SO_2 solution UV-vis (green) and pristine UTSA-16(Zn) dispersed in THF emission spectra.

S2.4. Determination of the limit of detection (LOD)

Detection limit was calculated using the following formula:[S4]

$$Detection\ limit\ = \frac{-3\sigma}{m}$$

Where σ is the standard deviation of blank readings and m is the slope of fluorescence intensity vs. SO_2 concentration plot.

The slope of the fluorescence intensity was determined by a linear fit of fluorescence intensity versus SO_2 concentration (Figure 2d in main text). Obtaining a line equation of:

$$y = -80066.2851\ x + 1927527.25526$$

With a good correlation of $R^2 = 0.9725$.

To obtain the standard deviation (σ) of the pristine material reading, 5 aliquots of a 12 mg suspension of UTSA-16(Zn) in 25 mL THF were taken and their emission spectra were measured (Figure S14). The standard deviation (σ) was calculated using the intensities of those 5 blank readings.

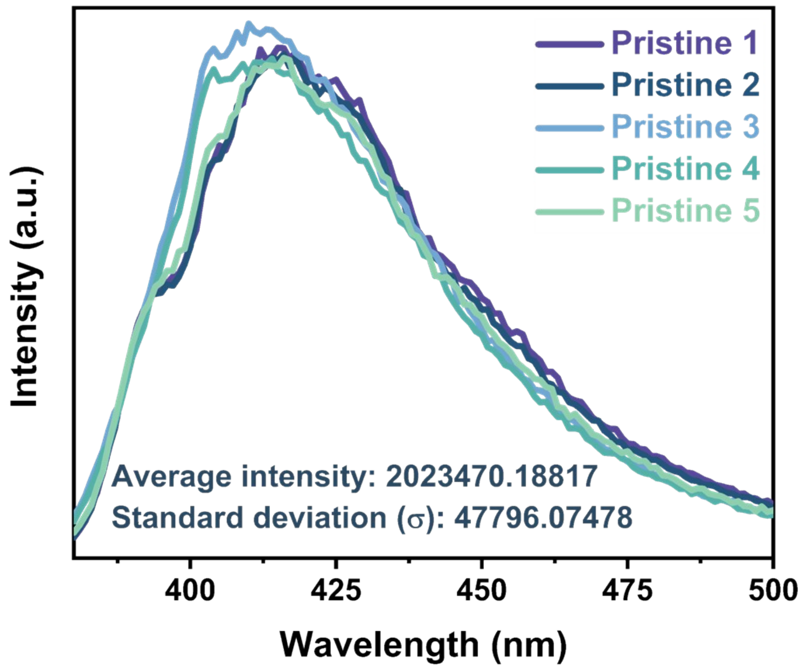

Figure S18. Emission spectra for five pristine UTSA-16(Zn) samples dispersed in THF.

Thus, the LOD was determined with the above data:

$$Detection\ limit\ = \frac{-3\sigma}{m} = -\frac{-3(47796.07478)}{-80066.2851} = 1.79\ mM\ (\sim 115\ ppm)$$

S3. References

1. J. L. Woodliffe, A.-L. Johnston, M. Fay, R. Ferrari, R. L. Gomes, E. Lester, I. Ahmed and A. Laybourn, *Mater Adv*, 2023, **4**, 5838–5849.
2. P. H. M. Andrade, C. Volkringer, T. Loiseau, A. Tejeda, M. Hureau and A. Moissette, *Appl. Mater. Today*, 2024, **37**, 102094.
3. U. Noomnarm and R. M. Clegg, *Photosynth. Res.*, 2009, **101**, 181–194.
4. A. Sharma, D. Kim, J. H. Park, S. Rakshit, J. Seong, G. H. Jeong, O. H. Kwon and M. S. Lah, *Commun. Chem*, 2019, **2**, 1–8.