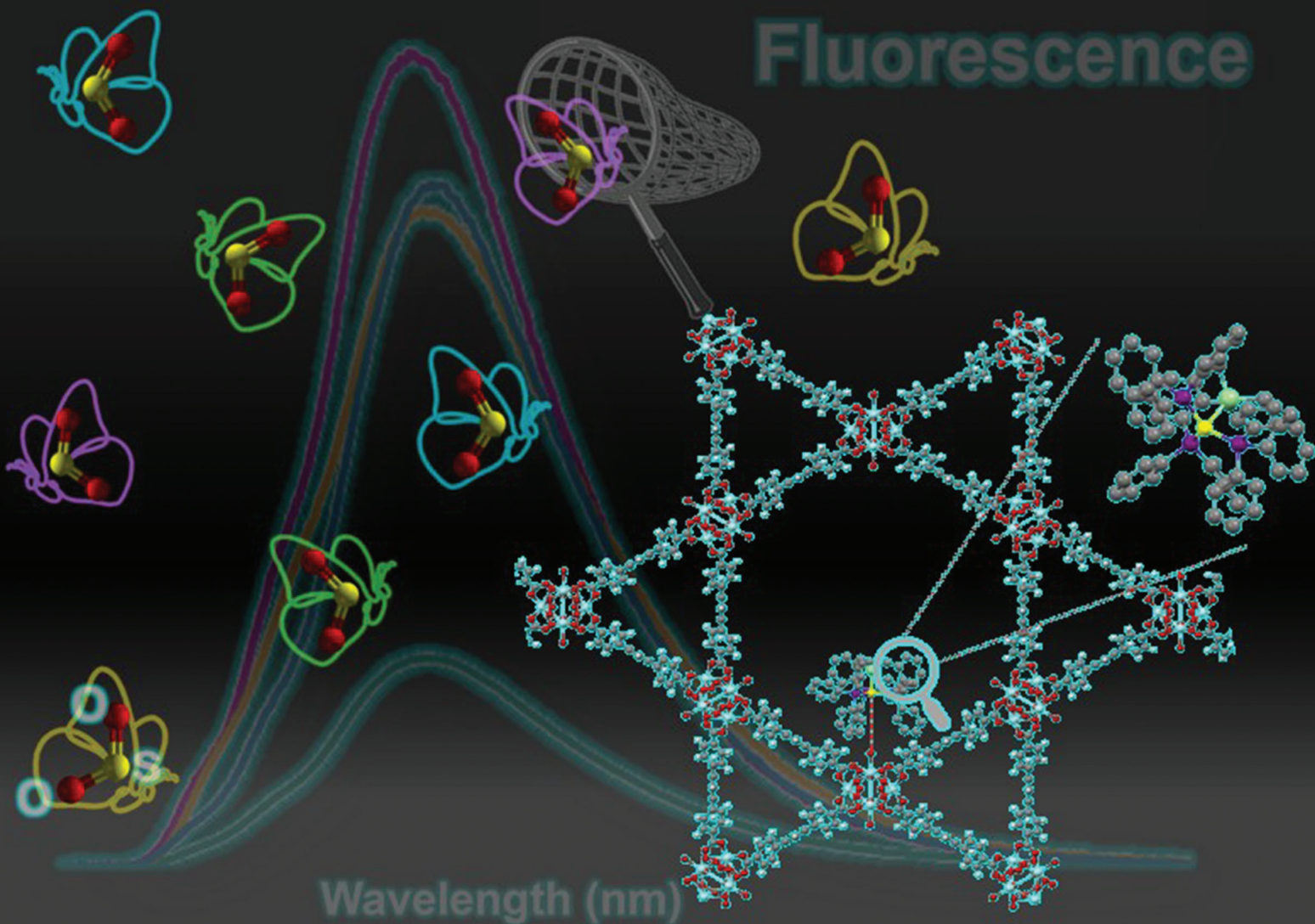


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Selective detection of SO₂ in NU-1000 via organometallic nickel silylphosphine post-synthetic complex incorporation†

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The adsorption and detection of SO₂ using Zr-based MOF, NU-1000 grafted with an organometallic nickel silylphosphine complex ([NiSi]@NU-1000) via post-synthetic modification are reported. [NiSi]@NU-1000 exhibits high stability under dry and wet SO₂, with a high cyclability performance. Moreover, fluorescence experiments postulate [NiSi]@NU-1000 as a promising SO₂ detector due to its high SO₂ selectivity over CO₂ and air, showing an evident quenching effect, especially at low SO₂ concentrations (0.1 bar of SO₂). Time-resolved photoluminescence experiments suggest that host–guest SO₂ interactions are associated with the turn-off effect.

Sulphur dioxide (SO₂) is an irritant, colourless gas at ambient temperature and pressure and is classified as a primary pollutant because it is released directly into the atmosphere.¹ It is naturally emitted by volcanic activity and fires (forest and agricultural).² However, the major source of this gas is anthropogenic from power plants, oil refineries, and smelters. Its emissions are of concern because of their adverse effects on human

health and the environment.³ Currently, most of the flue gas desulphurisation (FGD) technologies are based on the absorption of SO₂ in wet alkaline scrubbers. Despite their effectiveness, these systems have highly energetic regeneration conditions, and their by-products generate corrosion.⁴ Thereby, another alternative for capturing toxic gases is adsorption, which uses less energy and minimises waste.⁵

Most research efforts concerning SO₂ have concentrated on its capture. However, due to the danger it poses to human health, many industries need accurate detection methods for SO₂ to prevent it from reaching toxic levels.⁶ Currently, the detection of SO₂ in ambient air has been carried out by colourimetric,⁷ conductimetric,⁸ and fluorescent methods.⁹ Fluorescence-based chemical detectors stand out due to their simplicity, sensitivity, nontoxicity, and ease of operation.¹⁰ In this context, MOFs are a class of hybrid materials composed of metal clusters intertwined by organic linkers,¹¹ which have emerged as viable platforms to detect pollutants in water and air.⁶ Mainly, applying MOF materials as fluorescent detectors for small molecules or conjugated polymers is innovative. Moreover, MOFs display chemical tunability, resulting in efficient and specific recognition, and their structures are rich in π and n electrons, which are conducive to forming excellent and variable fluorescence signals.¹² MOF active site dispersion is suitable for an outstanding guest–host interaction, which can generate a turn-on or turn-off in the luminescence of the material due to the rearrangement of electrons within the MOFs.^{13,14} Therefore, it is crucial to have a relatively strong interaction between the gas and the material to obtain a fluorescence response. Interestingly, incorporating additional adsorption sites in a MOF can generate a higher energy transfer, causing a significant change in its fluorescence properties.¹⁵

As a ligand to transition metals, the SO₂ molecule exhibits three main coordination modes: planar η^1 -S and η^2 -S, O when it acts as a Lewis base, and a pyramidal η^1 -S mode when it acts as a Lewis acid, and since the energy barriers for interconversion

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are relatively small, a planar $\eta^1\text{-S}/\eta^2\text{-S}_2\text{O}$ isomerisation can readily occur.^{16–18} Accordingly, we have previously reported enhancement of the reversible SO_2 uptake in MOF material NU-1000 by incorporation of organometallic moieties of precious metals Ru¹⁹ and Ir.²⁰ Grafting of the organometallic fragment enhances the uptake of SO_2 by the MOF material due to the accessibility of additional coordination sites. In parallel, preservation of the porosity of the MOF material and recyclability for up to 10 adsorption/desorption cycles make those materials attractive.

Herein, we have now employed the grafted NU-1000 with an earth-abundant base metal complex derived from a silicon-substituted triphosphine ligand, $[\text{HNi}(\kappa^4(\text{Si},\text{P},\text{P},\text{P})\text{-Si}(o\text{-C}_6\text{H}_4\text{CH}_2\text{PPh}_2)_3)]$, herein entitled $[\text{NiSi}]\text{@NU-1000}$ (Fig. 1), for the adsorption and detection of SO_2 . The material exhibits outstanding fluorescence properties with high selectivity and remarkable cyclability.

$[\text{NiSi}]\text{@NU-1000}$ (Scheme S1†) was synthesised reported²¹ and obtained as a yellow powder; its crystalline structure was corroborated by PXRD (Fig. S6†). The presence of the $[\text{NiSi}]$ complex was ascertained by a variety of techniques, including FT-IR and ^1H NMR of the digested sample (Fig. S12 and S13†). XANES and SEM analyses are consistent with Ni in oxidation state of +2 and with the homogeneous distribution of the Ni complex through the material (Fig. S7 and S8†).

$[\text{NiSi}]\text{@NU-1000}$ displays moderate thermal stability up to 300 °C (Fig. S10†). The Ni and Zr contents were verified by ICP-MS as 0.6 wt% and 5.4 wt% respectively, corresponding to a Ni:Zr molar ratio of *ca.* 1:6, very close to the ideal one Ni atom per Zr_6 cluster unit of the NU-1000 material.²¹ The BET surface area decreased from 1970 $\text{m}^2 \text{g}^{-1}$ in the as-synthesised NU-1000 to 1354 $\text{m}^2 \text{g}^{-1}$ in $[\text{NiSi}]\text{@NU-1000}$ in accordance with grafting of the organometallic complex onto the MOF (Fig. S6†).²¹ We propose that upon grafting, the structure of the Ni silylphosphine complex is maintained, and the Ni centre binds to the zirconium node through a terminal hydroxyl group.²¹ Solid-state UV-Vis of $[\text{NiSi}]\text{@NU-1000}$ (Fig. S11†) exhibits a maximum adsorption peak at 420 nm.

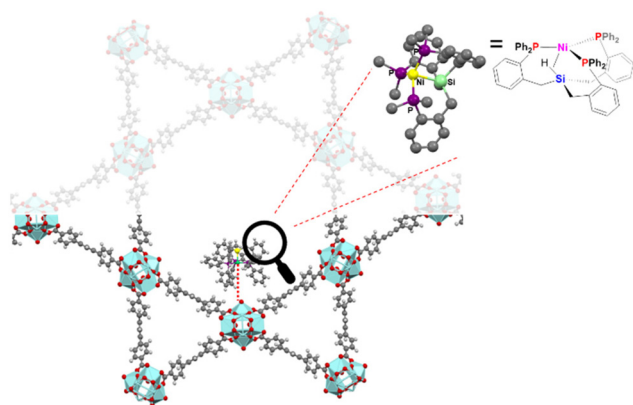


Fig. 1 Structure representation of NU-1000 post-synthetically grafted with a nickel phosphinosilyl complex. Atom label: light blue: Zr, yellow: Ni, dark grey: carbon, light grey: hydrogen, purple: P and green: Si.

Prior to adsorption experiments, $[\text{NiSi}]\text{@NU-1000}$ was activated at 120 °C under vacuum for 24 h to release the pores. Fig. 2 shows the SO_2 adsorption–desorption isotherm. First, rapid capture from 0 to 0.01 bar of 0.52 mmol g^{-1} is observed, followed by a linear capture with a total amount of 2.48 mmol g^{-1} at 0.5 bar. This performance has been observed for mesoporous materials because the saturation of the material is not achieved at the experimental conditions.^{19,20} The isotherm shows a desorption step with a slight hysteresis, indicating that SO_2 was completely released from the sample, and a relatively low SO_2 -MOF interaction can be inferred.²² Moreover, to explore its potential application in SO_2 detection, the adsorption in the low-pressure range was analysed. It is important to highlight that adsorption in the low-pressure range can be associated with low SO_2 concentrations (ppm levels).²³ At low pressures (<0.01 bar), the $[\text{NiSi}]\text{@NU-1000}$ material shows a higher adsorption uptake in comparison with the unmodified NU-1000 material (Fig. S14†). This could be due to the higher affinity of the organometallic moiety for SO_2 coordination.¹⁹ At higher pressures, the presence of the organometallic restricts access to the pores, resulting in a decrease in the adsorption capacity compared to the unmodified material (Fig. S14†). The $[\text{NiSi}]\text{@NU-1000}$ outperforms the SO_2 uptake at 0.002 bar (0.40 mmol g^{-1}) of NU-1000, $[\text{Ir}]\text{@NU-1000}$,²⁰ $[\text{RuGa}]\text{@NU-1000}$,¹⁹ DUT-67(Zr),²⁴ Zr-DMTDC, UiO-66, and MFM-133,²⁵ all of which contain Zr-based SBUs and have surface areas above 1000 $\text{m}^2 \text{g}^{-1}$ (Table S2†). Nonetheless, $[\text{NiSi}]\text{@NU-1000}$ falls short of the best-performing MOF, Mg-gallate, with an SO_2 uptake of 4.65 mmol g^{-1} at 0.002 bar.²⁶

Cycling SO_2 experiments were conducted at 0.05–0.1 bar and 298 K (Fig. 2, inset). Each regeneration process was per-

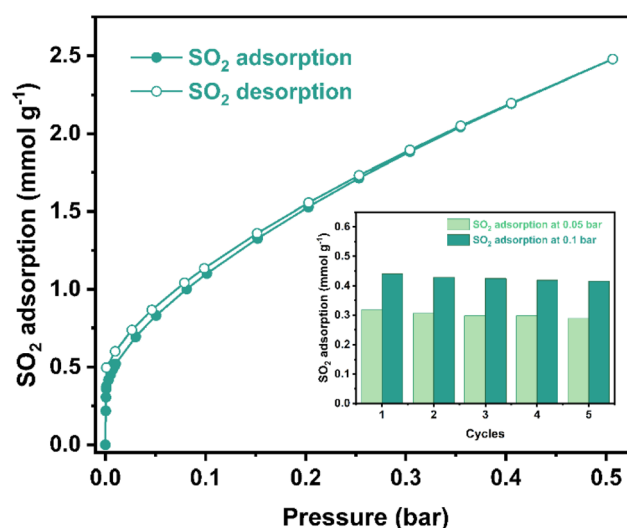


Fig. 2 Experimental SO_2 adsorption–desorption isotherm collected for a fully activated $[\text{NiSi}]\text{@NU-1000}$ sample (filled green diamonds = adsorption; open green diamonds = desorption) at 298 K and up to 0.5 bar. Inset: adsorption–desorption cycles for SO_2 in $[\text{NiSi}]\text{@NU-1000}$ at 0.05–0.1 bar and 298 K. The reactivation step was carried out only by applying vacuum (1.7×10^{-3} torr) for 45 minutes at room temperature (298 K).



formed under vacuum (1.7×10^{-3} Torr) for 45 minutes and 298 K. It was observed that even after five adsorption-desorption experiments, the SO₂ uptake was maintained at 0.05 and 0.1 bar. This confirms complete SO₂ release during the desorption cycles. PXRD measurements corroborated the retention of the crystallinity (Fig. S15†) and the material's stability after the SO₂ adsorption and cyclability test. Energy-dispersive X-ray spectroscopy (EDX) analyses showed no evidence of changes in the amount of Ni before and after the SO₂ experiments, highlighting the stability of the isolated metal complex within the MOF framework (Table S3†). Moreover, the presence of sulphur within the MOF was corroborated, revealing that the calculated amount is two times more than expected only from the incorporated metal complex and supporting that the uptake of SO₂ takes place in different parts of the MOF framework, and not exclusively in the Ni centre. Also, the stability of [NiSi]@NU-1000 under wet SO₂ was tested. An activated sample was exposed for 3 h to humid SO₂ (exposure at 60% relative humidity, RH), generated in a home-designed setup (Fig. S20†). It was observed by PXRD that the crystalline structure was maintained (Fig. S15†).

The host-guest interaction between SO₂ and [NiSi]@NU-1000 was elucidated by calculating the isosteric enthalpy of adsorption (ΔH_{ads}) for SO₂ at low coverage for a fully activated sample using the virial method (Fig. S19†).²⁷ The calculated ΔH_{ads} at low coverage was $-42.7 \text{ kJ mol}^{-1}$; such value corresponds to a physisorption, in line with the reversible adsorption/desorption cycles and easy desorption step, only with vacuum. The decrease in the enthalpy of adsorption of [NiSi]@NU-1000 compared to the pristine NU-1000 ($-50.8 \text{ kJ mol}^{-1}$),²⁰ could be attributed to both the high metal content (1 : 1, Ni per Zr₆ cluster) and the steric bulk of the silicon-substituted triphosphine ligand in the [NiSi] complex. These values of enthalpies of adsorption are in agreement with the formation of hydrogen bonds between SO₂ and the bare [Zr₆(μ_3 -OH)₈(OH)₈] cluster as well as the establishment of electrostatic interactions between the SO₂ and the grafted [NiSi] complex (Fig. S25†). The pristine NU-1000 material only exhibits hydrogen bond interactions with the SO₂. In contrast, the [NiSi]@NU-1000 material additionally has lower energy SO₂ electrostatic interactions with the [NiSi] complex, accounting for the decrease in the overall enthalpy of adsorption. This weak interaction was confirmed by the FTIR spectrum of an SO₂-loaded sample, which showed some weak bands at 1336 and 1144 cm^{-1} (Fig. S18†); these correspond to adsorbed SO₂, which is slightly redshifted compared to free SO₂ (1362 and 1151 cm^{-1}).⁴¹ In comparison, the previously studied [Ir]@NU-1000 material, an organometallic iridium bis(silyl)phosphine complex grafted onto NU-1000 in a molar ratio 1 : 11 (Ir : Zr₆), exhibited a higher enthalpy of adsorption towards SO₂ ($-89.8 \text{ kJ mol}^{-1}$), where chemisorption occurred upon SO₂ bonding with the metal center.²⁰

Several properties of MOF materials have been widely employed for the detection of SO₂ gas. SO₂ detection was conducted in Ni₃BTC₂ based on the change in its electrochemical behavior.²⁸ Also, the detection of SO₂ can be achieved using

the change in the magnetic properties related to the spin-crossover transition.²⁹ However, SO₂ detection using the change in the luminescence properties is an attractive technique for the simplicity of the experiment. Indeed, modifications in the fluorescence performance of several MOF materials including MOF-303, DNA-Tb-MOF and M₂(dobpdc) (M = Ni²⁺ and Mg²⁺) were investigated using this approach.^{9,30–32}

It has been reported that NU-1000 displays photoluminescence properties based on the highly conjugated TBAPy linker, which remains unchanged after coordination with Zr⁴⁺.³³ NU-100 has been evaluated to detect pesticides, explosive compounds, and metabolites in aqueous matrices by measuring the “turn-off” effect of these analytes.^{34–37} Also, the Ni complex incorporation in NU-1000 displays similar photoluminescence properties. Then, the pore confinement effect improves the detection effectiveness in this material at low pressures. Based on this and the SO₂ adsorption properties of NU-1000 and [NiSi]@NU-1000, the materials were evaluated as fluorescent SO₂ detectors for low pressure.

The fluorescence emission at different excitation wavelengths indicates that the appropriate excitation wavelength for [NiSi]@NU-1000 is 350 nm (Fig. S21†). The solid-state emission spectra of [NiSi]@NU-1000 are shown in Fig. 3a. The activated [NiSi]@NU-1000 sample displays a peak at 497 nm. Then, an activated [NiSi]@NU-1000 sample was exposed to 0.1 bar of SO₂. Interestingly, a “turn-off” effect is observed with a 3.65-decreased fold in emission intensity compared to the activated sample. In order to corroborate the stability in the emission of [NiSi]@NU-1000, a cycling test was performed (Fig. S22†).

Five cycle experiments were conducted, observing that the emission in both cases was maintained. The SO₂-exposed [NiSi]@NU-1000 shows a constant “turn-off” effect with an average 3.65 ± 0.03 -fold decrease in emission intensity. Furthermore, the fluorescence of [NiSi]@NU-1000 upon exposure to air (which contains ~78%) and CO₂ was investigated to determine the selectivity (Fig. 3a). By comparison, a slight change in the fluorescence intensity is observed. However, higher selectivity is clearly observed for SO₂ molecules. This can be attributed to the non-polar character of the CO₂ and N₂ molecules, which makes their interaction with the adsorption sites of the material unfavourable, whereas SO₂, being a polar molecule, can establish specific interactions with the material, resulting in a quenching effect on the fluorescence.

This high selectivity of [NiSi]@NU-1000 for SO₂ can be related to improved host-guest interactions due to the grafting of the organometallic species. As a comparison, the fluorescence performances for NU-1000 and [NiSi]@NU-1000 before and after SO₂ were tested (Fig. S23†). A slight shift in the emission maxima (5 nm) for the grafted material was observed compared to the pristine material, indicating the photoluminescent properties are mainly due to the pyrene core linker. A turn-off phenomenon was observed for both materials. It is evident, however, that grafted [NiSi]@NU-1000



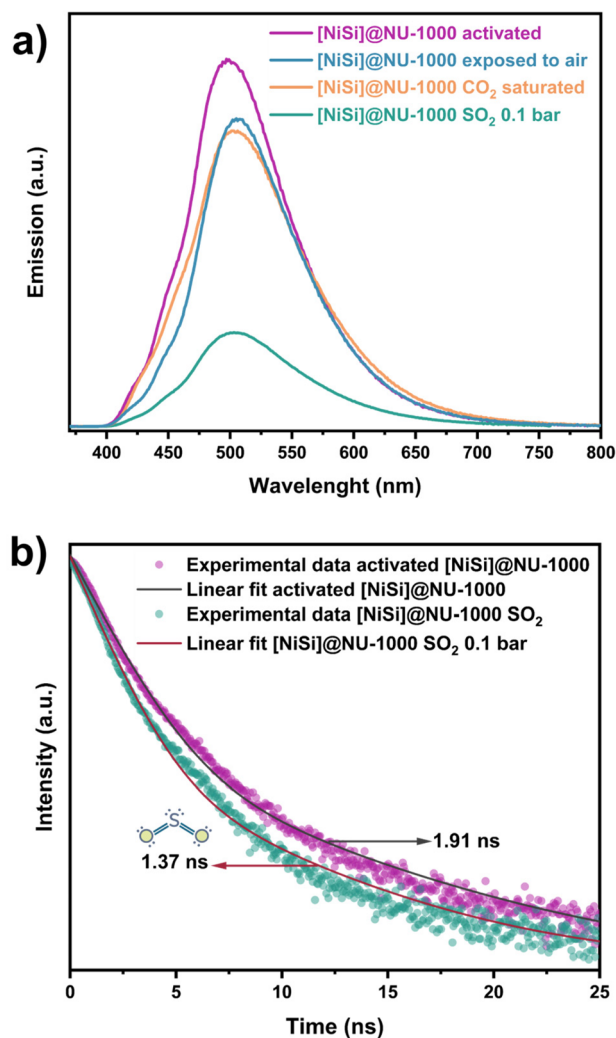


Fig. 3 (a) Solid-state emission spectra of activated [NiSi]@NU-1000 (purple line), and after exposure to 0.1 bar of SO₂ (green line), CO₂ (orange line), and air (blue line). The excitation wavelength was set at 350 nm, (b) time-resolved photoluminescence decay spectra of activated [NiSi]@NU-1000, and after exposure to 0.1 bar of SO₂ measured at 335.6 nm excitation and at 500 nm emission.

considerably improves the fluorescence response by turning off the response by almost 75%.

It has been reported that in NU-1000 materials, hydrogen bonding and π - π interactions could generate a quenching effect.³⁶ One possible explanation is that the presence of the [NiSi] complex within NU-1000 reversibly bonding SO₂ brings about a higher amount of SO₂ molecules into the MOF pore walls, triggering SO₂ packing and increasing π -SO₂ interactions in the vicinity of the pyrene linkers thus turning off the fluorescence response. The proposed hydrogen-bond interactions of SO₂ with [NiSi]@NU-1000 are illustrated in Fig. S24.†

Furthermore, a time-resolved photoluminescence (TRPL) experiment was performed using a 340 nm picosecond-pulsed LED as the excitation source (Fig. 3b) to investigate the possible SO₂ detection. TRPL experiments were conducted on an

activated [NiSi]@NU-1000 and an SO₂-exposed sample. It was observed that the average decay lifetimes (Table S4†) slightly decreased from 1.91 to 1.37 ns from activated [NiSi]@NU-1000 and an SO₂-exposed, respectively (a decrease of 28% in the fluorescence lifetime). This decrease can be explained by analysing the individual lifetime components (τ_n) and their contributions (a_n). Table S3† shows that, in all cases, τ_1 is the shortest lifetime component, which can be associated with fast non-radiative relaxation processes, which occur in orders of less than nanoseconds,³⁸ or very effective interactions. After SO₂ adsorption, the relative contribution (a_1) of this short component increases slightly, from 0.24 to 0.32, indicating that fast relaxation processes become slightly more relevant, coinciding with the observed decrease in fluorescence intensity. On the other hand, τ_3 , the longest lifetime component, is associated with slower phenomena, such as radiative mechanisms that occur on the order of nanoseconds.³⁹ This component decreases both in its value, from 5.4 to 4.3 ns, as its relative contribution, from 0.21 to 0.17, after SO₂ adsorption. This suggests that the interaction with SO₂ induces non-radiative relaxation processes in species with longer lifetimes. This pathway could be associated with an electron transfer phenomenon related to the direct interaction between SO₂ and the surface of the grafted [NiSi] complex, which deactivates the excited states in a non-radiative manner.^{14,40}

To further support this analysis, we performed TRPL experiments for the NU-1000 material, comparing it with its modified analogue, [NiSi]@NU-1000. The data (Table S4†) reveal that, in NU-1000, the fluorescence lifetime decreases from 2.23 to 1.75 ns after SO₂ adsorption, corresponding to a reduction of 21.5%. In comparison, [NiSi]@NU-1000 shows a more pronounced decrease of 28%. Similarly, the relative contributions of the lifetime components show more pronounced changes in [NiSi]@NU-1000. This indicates that the [NiSi] complex intensifies the non-radiative dissipation pathways, enhancing the sensitivity of the material to SO₂ adsorption. Regarding the possible influence of absorption on fluorescence quenching, we collected solid-state UV-Vis diffuse reflectance spectra for the activated, SO₂-exposed, and desorbed [NiSi]@NU-1000 samples (Fig. S11†). The spectra show that the absorption region of the material, as well as the relative intensity at the excitation wavelength (~340 nm), do not change significantly after SO₂ adsorption. This suggests that the decrease in fluorescence intensity is not related to a reduction in absorption at the excitation wavelength but to non-radiative processes associated with direct electronic interactions between SO₂ and the active sites of the material.

This study investigated the SO₂ adsorption and detection properties of a nickel silylphosphine organometallic complex post-synthetic grafted to a Zr-based MOF ([NiSi]@NU-1000). The material shows high stability to wet and dry SO₂. Furthermore, high cyclability at the low-pressure range was achieved with a facile SO₂ regeneration at room temperature. Fluorescence studies display a remarkable change in the intensity from the emission spectra after the SO₂ interactions with the material and high selectivity over CO₂ and air, and an



evident SO₂ quenching effect is observed even at low concentrations (0.1 bar of SO₂). Finally, time-resolved photoluminescence experiments suggest that the turn-off effect is associated with relatively strong host–guest SO₂ interactions.

Data availability

All data is available in the main text and in the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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