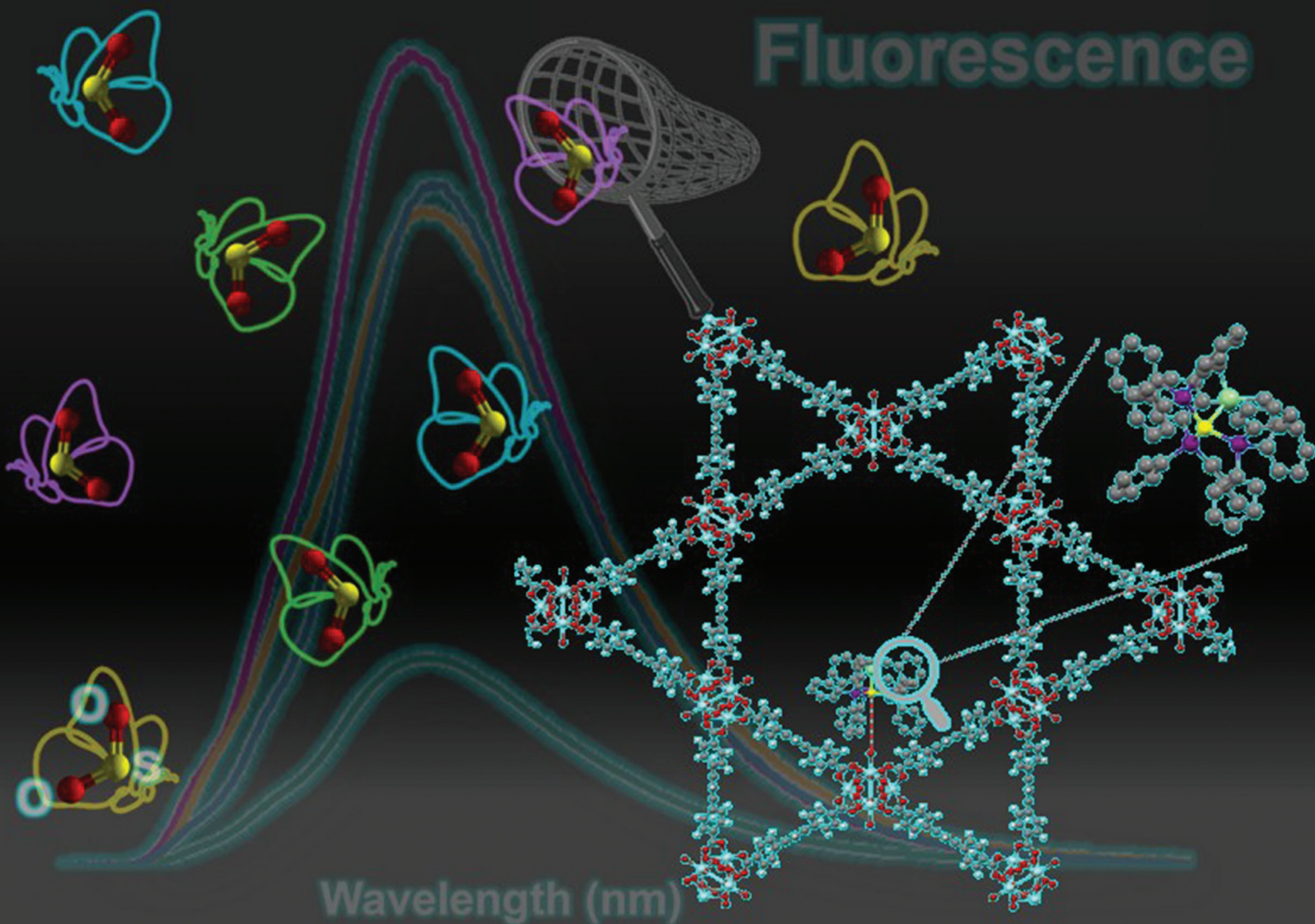


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**COMMUNICATION**

Elí Sánchez-González, Ilich A. Ibarra,  
Virginia Montiel-Palma *et al.*  
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## Selective detection of SO<sub>2</sub> in NU-1000 via organometallic nickel silylphosphine post-synthetic complex incorporation†

Juan L. Obeso, <sup>‡a,b</sup> Luz J. Barrios-Vargas,<sup>‡c</sup> Valeria B. López-Cervantes, <sup>‡a</sup> Yoarhy A. Amador-Sánchez,<sup>a</sup> Nancy Martin-Guaregua,<sup>d</sup> Ricardo A. Peralta, <sup>d</sup> Ramon Munoz,<sup>e</sup> Ana Martínez, <sup>f</sup> Carolina Leyva, <sup>b</sup> Diego Solís-Ibarra, <sup>a</sup> Eli Sánchez-González, <sup>\*a</sup> Ilich A. Ibarra <sup>\*a</sup> and Virginia Montiel-Palma <sup>\*c</sup>

**The adsorption and detection of SO<sub>2</sub> 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 SO<sub>2</sub>, with a high cyclability performance. Moreover, fluorescence experiments postulate [NiSi]@NU-1000 as a promising SO<sub>2</sub> detector due to its high SO<sub>2</sub> selectivity over CO<sub>2</sub> and air, showing an evident quenching effect, especially at low SO<sub>2</sub> concentrations (0.1 bar of SO<sub>2</sub>). Time-resolved photoluminescence experiments suggest that host–guest SO<sub>2</sub> interactions are associated with the turn-off effect.**

Sulphur dioxide (SO<sub>2</sub>) 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.<sup>1</sup> It is naturally emitted by volcanic activity and fires (forest and agricultural).<sup>2</sup> 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.<sup>3</sup> Currently, most of the flue gas desulphurisation (FGD) technologies are based on the absorption of SO<sub>2</sub> in wet alkaline scrubbers. Despite their effectiveness, these systems have highly energetic regeneration conditions, and their by-products generate corrosion.<sup>4</sup> Thereby, another alternative for capturing toxic gases is adsorption, which uses less energy and minimises waste.<sup>5</sup>

Most research efforts concerning SO<sub>2</sub> have concentrated on its capture. However, due to the danger it poses to human health, many industries need accurate detection methods for SO<sub>2</sub> to prevent it from reaching toxic levels.<sup>6</sup> Currently, the detection of SO<sub>2</sub> in ambient air has been carried out by colourimetric,<sup>7</sup> conductimetric,<sup>8</sup> and fluorescent methods.<sup>9</sup> Fluorescence-based chemical detectors stand out due to their simplicity, sensitivity, nontoxicity, and ease of operation.<sup>10</sup> In this context, MOFs are a class of hybrid materials composed of metal clusters intertwined by organic linkers,<sup>11</sup> which have emerged as viable platforms to detect pollutants in water and air.<sup>6</sup> 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  $\pi$  and  $n$  electrons, which are conducive to forming excellent and variable fluorescence signals.<sup>12</sup> 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.<sup>13,14</sup> 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.<sup>15</sup>

As a ligand to transition metals, the SO<sub>2</sub> molecule exhibits three main coordination modes: planar  $\eta^1$ -S and  $\eta^2$ -S, O when it acts as a Lewis base, and a pyramidal  $\eta^1$ -S mode when it acts as a Lewis acid, and since the energy barriers for interconversion

<sup>a</sup>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, Mexico.

E-mail: argel@unam.mx, elisg@materiales.unam.mx

<sup>b</sup>Instituto Politécnico Nacional, CICATA U. Legaria, Laboratorio Nacional de Ciencia, Tecnología y Gestión Integrada del Agua, (LNAgua), Legaria 694 Irrigación, Miguel Hidalgo, CDMX, Mexico

<sup>c</sup>Department of Chemistry, Mississippi State University, Mississippi State, Mississippi 39762, USA. E-mail: vmontiel@chemistry.msstate.edu

<sup>d</sup>Departamento de Química, División de Ciencias Básicas e Ingeniería, Universidad Autónoma Metropolitana Unidad Iztapalapa (UAM-I), 09340, Mexico

<sup>e</sup>Mississippi School for Maths and Science, 1100 College St, Columbus, Mississippi 39701, USA

<sup>f</sup>Departamento de Materiales de Baja Dimensionalidad. Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior s/n, CU, Coyoacán, 04510 Ciudad de México, Mexico

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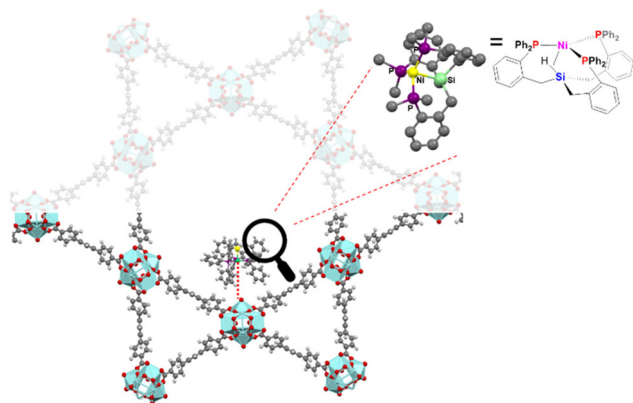
‡ These authors contributed equally to this manuscript.

are relatively small, a planar  $\eta^1\text{-S}/\eta^2\text{-S}_2\text{O}$  isomerisation can readily occur.<sup>16–18</sup> Accordingly, we have previously reported enhancement of the reversible  $\text{SO}_2$  uptake in MOF material NU-1000 by incorporation of organometallic moieties of precious metals Ru<sup>19</sup> and Ir.<sup>20</sup> Grafting of the organometallic fragment enhances the uptake of  $\text{SO}_2$  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,  $[\text{HNi}(\kappa^4(\text{Si},\text{P},\text{P},\text{P})\text{-Si}(\text{o-C}_6\text{H}_4\text{CH}_2\text{PPh}_2)_3)]$ , herein entitled  $[\text{NiSi}]\text{@NU-1000}$  (Fig. 1), for the adsorption and detection of  $\text{SO}_2$ . The material exhibits outstanding fluorescence properties with high selectivity and remarkable cyclability.

$[\text{NiSi}]\text{@NU-1000}$  (Scheme S1†) was synthesised reported<sup>21</sup> 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  $^1\text{H}$  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†).

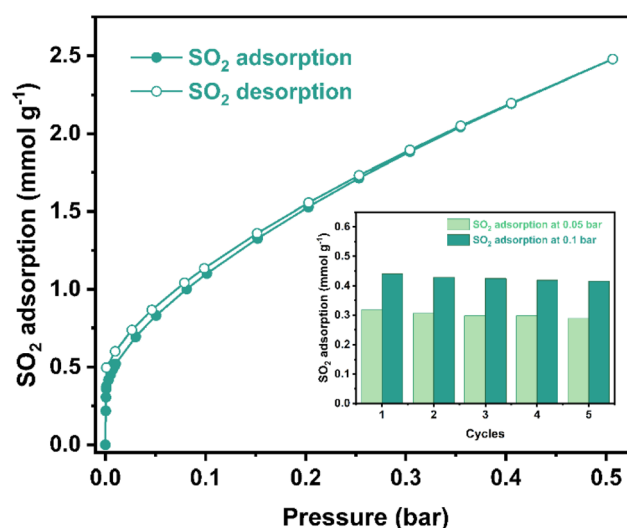
$[\text{NiSi}]\text{@NU-1000}$  displays moderate thermal stability up to 300 °C (Fig. S10†). The Ni and Zr contents were verified by ICP-MS as 0.6 wt% and 5.4 wt% respectively, corresponding to a Ni:Zr molar ratio of *ca.* 1:6, very close to the ideal one Ni atom per  $\text{Zr}_6$  cluster unit of the NU-1000 material.<sup>21</sup> 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†).<sup>21</sup> 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.<sup>21</sup> 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  $\text{SO}_2$  adsorption–desorption isotherm. First, rapid capture from 0 to 0.01 bar of 0.52  $\text{mmol g}^{-1}$  is observed, followed by a linear capture with a total amount of 2.48  $\text{mmol g}^{-1}$  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.<sup>19,20</sup> The isotherm shows a desorption step with a slight hysteresis, indicating that  $\text{SO}_2$  was completely released from the sample, and a relatively low  $\text{SO}_2$ -MOF interaction can be inferred.<sup>22</sup> Moreover, to explore its potential application in  $\text{SO}_2$  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  $\text{SO}_2$  concentrations (ppm levels).<sup>23</sup> 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  $\text{SO}_2$  coordination.<sup>19</sup> 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  $\text{SO}_2$  uptake at 0.002 bar (0.40  $\text{mmol g}^{-1}$ ) of NU-1000,  $[\text{Ir}]\text{@NU-1000}$ ,<sup>20</sup>  $[\text{RuGa}]\text{@NU-1000}$ ,<sup>19</sup> DUT-67(Zr),<sup>24</sup> Zr-DMTDC, UiO-66, and MFM-133,<sup>25</sup> 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  $\text{SO}_2$  uptake of 4.65  $\text{mmol g}^{-1}$  at 0.002 bar.<sup>26</sup>

Cycling  $\text{SO}_2$  experiments were conducted at 0.05–0.1 bar and 298 K (Fig. 2, inset). Each regeneration process was per-



**Fig. 2** Experimental  $\text{SO}_2$  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  $\text{SO}_2$  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 ( $1.7 \times 10^{-3}$  torr) for 45 minutes at room temperature (298 K).





formed under vacuum ( $1.7 \times 10^{-3}$  Torr) for 45 minutes and 298 K. It was observed that even after five adsorption-desorption experiments, the  $\text{SO}_2$  uptake was maintained at 0.05 and 0.1 bar. This confirms complete  $\text{SO}_2$  release during the desorption cycles. PXRD measurements corroborated the retention of the crystallinity (Fig. S15†) and the material's stability after the  $\text{SO}_2$  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  $\text{SO}_2$  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  $\text{SO}_2$  takes place in different parts of the MOF framework, and not exclusively in the Ni centre. Also, the stability of  $[\text{NiSi}]\text{@NU-1000}$  under wet  $\text{SO}_2$  was tested. An activated sample was exposed for 3 h to humid  $\text{SO}_2$  (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  $\text{SO}_2$  and  $[\text{NiSi}]\text{@NU-1000}$  was elucidated by calculating the isosteric enthalpy of adsorption ( $\Delta H_{\text{ads}}$ ) for  $\text{SO}_2$  at low coverage for a fully activated sample using the virial method (Fig. S19†).<sup>27</sup> The calculated  $\Delta H_{\text{ads}}$  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  $[\text{NiSi}]\text{@NU-1000}$  compared to the pristine NU-1000 ( $-50.8 \text{ kJ mol}^{-1}$ ),<sup>20</sup> could be attributed to both the high metal content (1 : 1, Ni per  $\text{Zr}_6$  cluster) and the steric bulk of the silicon-substituted triphosphine ligand in the  $[\text{NiSi}]$  complex. These values of enthalpies of adsorption are in agreement with the formation of hydrogen bonds between  $\text{SO}_2$  and the bare  $[\text{Zr}_6(\mu_3\text{-OH})_8(\text{OH})_8]$  cluster as well as the establishment of electrostatic interactions between the  $\text{SO}_2$  and the grafted  $[\text{NiSi}]$  complex (Fig. S25†). The pristine NU-1000 material only exhibits hydrogen bond interactions with the  $\text{SO}_2$ . In contrast, the  $[\text{NiSi}]\text{@NU-1000}$  material additionally has lower energy  $\text{SO}_2$  electrostatic interactions with the  $[\text{NiSi}]$  complex, accounting for the decrease in the overall enthalpy of adsorption. This weak interaction was confirmed by the FTIR spectrum of an  $\text{SO}_2$ -loaded sample, which showed some weak bands at 1336 and  $1144 \text{ cm}^{-1}$  (Fig. S18†); these correspond to adsorbed  $\text{SO}_2$ , which is slightly redshifted compared to free  $\text{SO}_2$  (1362 and  $1151 \text{ cm}^{-1}$ ).<sup>41</sup> In comparison, the previously studied  $[\text{Ir}]\text{@NU-1000}$  material, an organometallic iridium bis(silyl)phosphine complex grafted onto NU-1000 in a molar ratio 1 : 11 ( $\text{Ir}:\text{Zr}_6$ ), exhibited a higher enthalpy of adsorption towards  $\text{SO}_2$  ( $-89.8 \text{ kJ mol}^{-1}$ ), where chemisorption occurred upon  $\text{SO}_2$  bonding with the metal center.<sup>20</sup>

Several properties of MOF materials have been widely employed for the detection of  $\text{SO}_2$  gas.  $\text{SO}_2$  detection was conducted in  $\text{Ni}_3\text{BTC}_2$  based on the change in its electrochemical behavior.<sup>28</sup> Also, the detection of  $\text{SO}_2$  can be achieved using

the change in the magnetic properties related to the spin-crossover transition.<sup>29</sup> However,  $\text{SO}_2$  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  $\text{M}_2(\text{dobpdc})$  ( $\text{M} = \text{Ni}^{2+}$  and  $\text{Mg}^{2+}$ ) were investigated using this approach.<sup>9,30–32</sup>

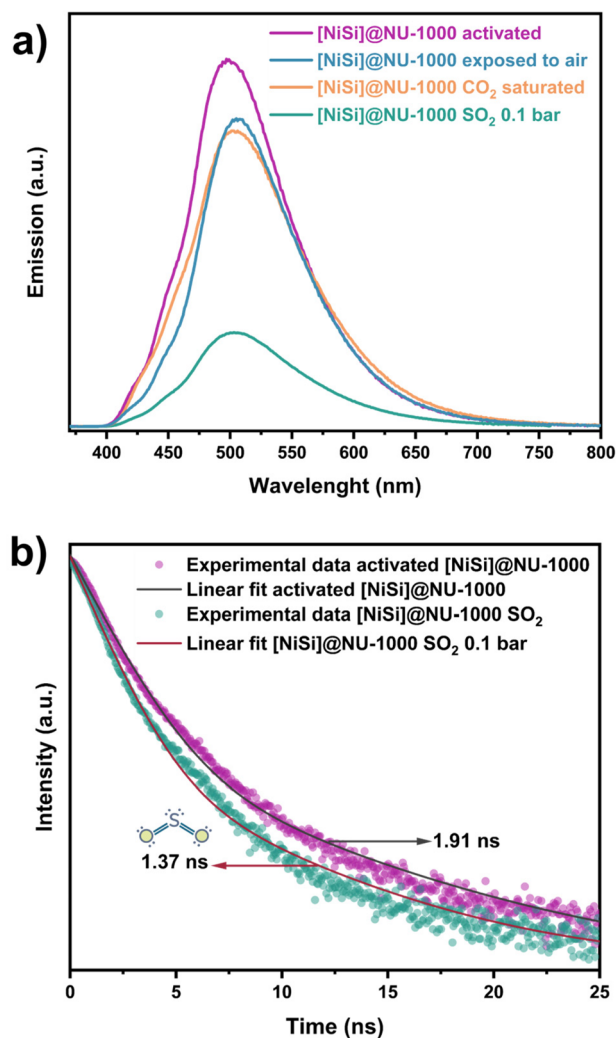
It has been reported that NU-1000 displays photoluminescence properties based on the highly conjugated TBAPy linker, which remains unchanged after coordination with  $\text{Zr}^{4+}$ .<sup>33</sup> NU-100 has been evaluated to detect pesticides, explosive compounds, and metabolites in aqueous matrices by measuring the “turn-off” effect of these analytes.<sup>34–37</sup> 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  $\text{SO}_2$  adsorption properties of NU-1000 and  $[\text{NiSi}]\text{@NU-1000}$ , the materials were evaluated as fluorescent  $\text{SO}_2$  detectors for low pressure.

The fluorescence emission at different excitation wavelengths indicates that the appropriate excitation wavelength for  $[\text{NiSi}]\text{@NU-1000}$  is 350 nm (Fig. S21†). The solid-state emission spectra of  $[\text{NiSi}]\text{@NU-1000}$  are shown in Fig. 3a. The activated  $[\text{NiSi}]\text{@NU-1000}$  sample displays a peak at 497 nm. Then, an activated  $[\text{NiSi}]\text{@NU-1000}$  sample was exposed to 0.1 bar of  $\text{SO}_2$ . 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  $[\text{NiSi}]\text{@NU-1000}$ , a cycling test was performed (Fig. S22†).

Five cycle experiments were conducted, observing that the emission in both cases was maintained. The  $\text{SO}_2$ -exposed  $[\text{NiSi}]\text{@NU-1000}$  shows a constant “turn-off” effect with an average  $3.65 \pm 0.03$ -fold decrease in emission intensity. Furthermore, the fluorescence of  $[\text{NiSi}]\text{@NU-1000}$  upon exposure to air (which contains  $\sim 78\%$ ) and  $\text{CO}_2$  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  $\text{SO}_2$  molecules. This can be attributed to the non-polar character of the  $\text{CO}_2$  and  $\text{N}_2$  molecules, which makes their interaction with the adsorption sites of the material unfavourable, whereas  $\text{SO}_2$ , being a polar molecule, can establish specific interactions with the material, resulting in a quenching effect on the fluorescence.

This high selectivity of  $[\text{NiSi}]\text{@NU-1000}$  for  $\text{SO}_2$  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  $[\text{NiSi}]\text{@NU-1000}$  before and after  $\text{SO}_2$  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  $[\text{NiSi}]\text{@NU-1000}$





**Fig. 3** (a) Solid-state emission spectra of activated [NiSi]@NU-1000 (purple line), and after exposure to 0.1 bar of SO<sub>2</sub> (green line), CO<sub>2</sub> (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 SO<sub>2</sub> 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  $\pi$ - $\pi$  interactions could generate a quenching effect.<sup>36</sup> One possible explanation is that the presence of the [NiSi] complex within NU-1000 reversibly bonding SO<sub>2</sub> brings about a higher amount of SO<sub>2</sub> molecules into the MOF pore walls, triggering SO<sub>2</sub> packing and increasing  $\pi$ -SO<sub>2</sub> interactions in the vicinity of the pyrene linkers thus turning off the fluorescence response. The proposed hydrogen-bond interactions of SO<sub>2</sub> 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 SO<sub>2</sub> detection. TRPL experiments were conducted on an

activated [NiSi]@NU-1000 and an SO<sub>2</sub>-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 SO<sub>2</sub>-exposed, respectively (a decrease of 28% in the fluorescence lifetime). This decrease can be explained by analysing the individual lifetime components ( $\tau_n$ ) and their contributions ( $a_n$ ). Table S3† shows that, in all cases,  $\tau_1$  is the shortest lifetime component, which can be associated with fast non-radiative relaxation processes, which occur in orders of less than nanoseconds,<sup>38</sup> or very effective interactions. After SO<sub>2</sub> 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,  $\tau_3$ , the longest lifetime component, is associated with slower phenomena, such as radiative mechanisms that occur on the order of nanoseconds.<sup>39</sup> 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 SO<sub>2</sub> adsorption. This suggests that the interaction with SO<sub>2</sub> 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 SO<sub>2</sub> and the surface of the grafted [NiSi] complex, which deactivates the excited states in a non-radiative manner.<sup>14,40</sup>

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 SO<sub>2</sub> 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 SO<sub>2</sub> adsorption. Regarding the possible influence of absorption on fluorescence quenching, we collected solid-state UV-Vis diffuse reflectance spectra for the activated, SO<sub>2</sub>-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 ( $\sim$ 340 nm), do not change significantly after SO<sub>2</sub> 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 SO<sub>2</sub> and the active sites of the material.

This study investigated the SO<sub>2</sub> 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 SO<sub>2</sub>. Furthermore, high cyclability at the low-pressure range was achieved with a facile SO<sub>2</sub> regeneration at room temperature. Fluorescence studies display a remarkable change in the intensity from the emission spectra after the SO<sub>2</sub> interactions with the material and high selectivity over CO<sub>2</sub> and air, and an



evident SO<sub>2</sub> quenching effect is observed even at low concentrations (0.1 bar of SO<sub>2</sub>). Finally, time-resolved photoluminescence experiments suggest that the turn-off effect is associated with relatively strong host–guest SO<sub>2</sub> interactions.

## Data availability

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

## Conflicts of interest

There are no conflicts to declare.

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