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Detection of SO₂ using a chemically stable Ni(II)-MOF†

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The MOF-type Ni_2 (dobpdc) shows a high chemical stability towards SO_2 , high capacity for SO_2 capture at low pressure (4.3 mmol g^{-1} at 298 K and up to 0.05 bar), and exceptional cycling performance. Fluorescence experiments demonstrated the SO_2 detection properties of Ni_2 (dobpdc) with a remarkable SO_2 detection selectivity. Finally, time-resolved photoluminescence experiments provided a plausible mechanism of SO_2 detection by this Ni(n)-based MOF material.

Introduction

Sulphur dioxide (SO₂) is classified as one of the most toxic chemicals with a pungent odour. SO₂ is an irritant, colourless, irritating, and non-flammable gas easily absorbed by the respiratory system or dermal contact.¹ The presence of SO₂ is accountable for a direct rise in respiratory complications (*e.g.*, broncho-constriction in lung function) and even death (contact over 100 ppm of SO₂ in only a few minutes).² Although it is naturally formed by volcanic activity, the main source of SO₂ is the combustion of fossil fuels containing sulphur and metal extraction from ores.³ Moreover, SO₂ is a precursor of particulate matter (PM), another high threat to human health.⁴ In addition, SO₂ is one of the principal constituents of acid rain, which negatively impacts aquatic environments and causes loss of minerals and nutrients from

the soil, hampering the growth of forests and crop plants.⁵ Acid rain, in urban areas, drastically accelerates the corrosion of metallic structures and attacks the main constituents of buildings (*e.g.*, limestone, marble, and mortar).⁶ Thus, it becomes imperative to improve air quality, especially in urban areas, by reducing the emissions of SO₂ and identifying potentially polluted environments with SO₂.

Most of the technological efforts toward SO₂ have been concentrated on capturing this toxic gas. For this, the most used technology for SO₂ capture is based on scrubbers.⁷ However, this technology has demonstrated serious disadvantages such as low capture of SO₂, vast quantities of wastewater, corrosion of pipelines, and considerable cost of use and recovery.⁸ In addition, other solid-state materials (*e.g.*, zeolites⁹ and metal oxides¹⁰) have been investigated for the efficient capture of SO₂ with considerable drawbacks, such as high re-activation temperatures (above 250 °C) and a significant loss in porosity.¹¹ Unquestionably, the capture of SO₂ has shown to be a challenging task that requires new technological approaches.

A relatively new class of highly crystalline and porous materials known as metal–organic frameworks (MOFs) has been recently explored. ¹² Selected examples have demonstrated remarkable SO₂ capture results, ¹³ even under humid conditions. ¹⁴ However, one of the main criticisms of MOFs is the current high cost of production for the organic ligands, in combination with difficult scalability, which raises questions about the sustainable economics of capturing SO₂ using MOFs at the industrial scale.

Interestingly, more research needs to be dedicated to detecting SO₂ with MOFs.¹⁵ Conversely to SO₂ capture with MOFs, where large amounts of these materials are required, for the detection of SO₂, only small amounts of a particular MOF material are needed.¹⁶ Thus, detecting SO₂ is an extremely desirable characteristic for a MOF material to identify potentially polluted surroundings with this toxic gas. For example, if a chemically stable MOF material exhibits luminescence properties, the fluorescent response to SO₂ change would be the key to exploring such material as an effective SO₂ detector.

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Thus, with this specific target in mind, a robust and chemically stable Ni(II)-based MOF material entitled Ni₂(dobpdc) was selected to address SO₂ detection effectively. Ni₂(dobpdc) MOF is constructed from the coordination of Ni(II) ions and 4,4'dioxidobiphenyl-3,3'-dicarboxylate (dobpdc)4-(Fig. S1†).17 Each Ni(II) centre is hexa-coordinated to six O-donor atoms: in the equatorial plane, Ni(II) is coordinated to two trans-disposed bridgings (µ2) aryloxide O atoms from two different dobpdc ligands to one bridging (μ_2) carboxylate O atom and one nonbridging carboxylate O atom. Also, from the ligand, whereas, in the axial plane, the Ni(II) centre is coordinated to one bridging (μ_2) carboxylate O atom from the ligand and a methanol (MeOH) molecule, which is used as a solvent in the solvothermal synthesis. 18 Such coordination array forms hexagonal helical chains across the c-axis of the crystal with a pore size of approximately 17 Å (Fig. S1†). After an activation process at 523 K for 12 h under vacuum (1.7 \times 10⁻³ Torr), coordinated MeOH molecules to Ni(II) metal centres are fully removed, providing uncoordinated Ni²⁺ sites.

Herein, Ni₂(dobpdc) exhibited to be chemically stable to SO_2 , with a total SO_2 uptake of 12.5 mmol g^{-1} , at 298 K and 1 bar. Remarkably, solid-state fluorescence experiments demonstrated that Ni₂(dobpdc) has proven to be an effective selective detector of this toxic pollutant.

Powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA) confirmed the phase purity of Ni₂(dobpdc) (Fig. S2 and S3†). A sample of Ni₂(dobpdc) was activated at 523 K for 12 h under vacuum (1.4×10^{-3} torr). Then, an N₂ isotherm at 77 K (Fig. S4†) demonstrated a BET surface area of $3005 \text{ m}^2 \text{ g}^{-1}$ with a pore volume of 1.11 cm³ g⁻¹.

SO₂ adsorption-desorption isotherm using a Dynamic Gravimetric Gas/Vapour Sorption Analyser, DVS vacuum (Surface Measurement Systems Ltd), was carried out from 0 to 1 bar at 298 K on an activated sample of Ni₂(dobpdc). Fig. 1 shows the resulting isotherm obtained. A steep with fast SO₂

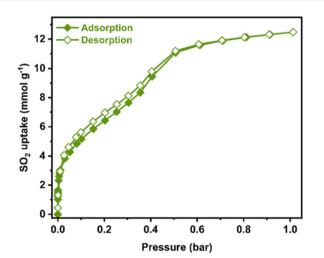


Fig. 1 Experimental SO₂ adsorption-desorption isotherm collected for a fully activated Ni₂(dobpdc) sample (filled green diamonds = adsorption; open green diamonds = desorption) at 298 K and up to 1 bar.

uptake from 0.0 to 0.05 bar is noted, accounting for a total uptake of approximately 4.3 mmol g⁻¹. From 0.05 to 0.4 bar, the SO₂ adsorption isotherm showed an approximate linear uptake with a total amount of ≈ 9.4 mmol g⁻¹. Finally, from 0.4 to 1.0 bar (end of the SO₂ adsorption experiment), a slow SO_2 uptake is observed. A total SO_2 uptake of 12.5 mmol g^{-1} was achieved. This fully SO2 uptake is comparable to representative chemically stable MOFs. 19 Furthermore, the desorption isotherm shows a slight hysteresis, suggesting a relatively high SO₂/MOF interaction energy.

Possibly, the most significant property of a chemically stable MOF material toward SO₂ detection is high SO₂ adsorption at low pressure (P < 0.1 bar). Considering that concentration ranges for SO₂ detection are at the ppm level, these can be naturally correlated to the SO₂ low-pressure range. Thus, the total SO₂ uptake (at ambient pressure) becomes irrelevant. For example, flue gas displays SO₂ concentrations up to 10 000 ppm, which is directly related to a pressure below 0.05 bar.20

Interestingly, at a very low pressure of only 0.002 bar, Ni_2 (dobpdc) captures 1.98 mmol g^{-1} of SO_2 (Fig. 2). In this case, only four MOF materials surpassed this value: Mg₂(dobpdc) (2.35 mmol g⁻¹),²¹ Ni-gallate (4.25 mmol g⁻¹),²² Mg-gallate (6.09 mmol g^{-1}), 22 and Co-gallate (6.13 mmol g⁻¹), ²² at 298 K. Thus, this SO₂ capture at such low pressure is highly relevant for detecting SO₂.

Later, a structural stability test of Ni₂(dobpdc) after the SO₂ adsorption-desorption experiment was conducted. PXRD analysis confirmed the retention of the crystallinity (Fig. S5†) after the first SO₂ sorption experiment. Moreover, an N₂ adsorption isotherm at 77 K demonstrated that the porosity is not modified (BET area $\approx 3005 \text{ m}^2 \text{ g}^{-1}$, Fig. S6†).

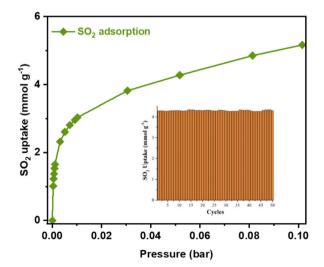


Fig. 2 Experimental SO₂ adsorption isotherm collected for a fully activated Ni₂(dobpdc) sample at 298 K and up to 0.1 bar. Inset: Adsorptiondesorption cycles for SO₂ in Ni₂(dobpdc) at 0.05 bar and 298 K. The reactivation of the sample was performed by only operating under a vacuum (1.7 \times 10⁻³ torr) for 45 minutes at room temperature (298 K).

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Moreover, the host-guest interaction (SO₂-Ni₂(dobpdc)) was quantified by calculating the isosteric heat of adsorption (ΔH) for SO₂ at low coverage for a fully activated sample of Ni₂(dobpdc) (two adsorption isotherms at 298 and 308 K were fitted to a Clausius-Clapeyron equation, Fig. S7†). Then, the calculated $\Delta H = -95.2 \text{ kJ mol}^{-1}$ was demonstrated to be relatively high, suggesting a relatively strong interaction between SO₂ and the walls of the MOF material. This ΔH value is also consistent with the hysteresis shown in Fig. 1. It is characteristic of SO₂ and open metal site systems (e.g., Mg₂(dobpdc), ²¹ $\Delta H = -90.0 \text{ kJ mol}^{-1}$). Also, it is observed a decrease in ΔH (Fig. S7†) when the SO₂ loading is increased. Thus, open metal sites are first occupied by SO₂ (higher energy binding sites), and then, at higher loadings, the SO2 molecule interacts through intermolecular forces with the pore walls of the MOF.

Therefore, cycling SO₂ experiments at 298 K and 0.05 bar were further investigated in order to evaluate the stability of the SO₂ adsorption-desorption performance and the regeneration capacity of Ni₂(dobpdc) by simply applying vacuum (1.7 × 10⁻³ Torr) for 45 minutes and 298 K. Thus, it was shown that the SO₂ capture capacity, at very low pressure, constantly continued for 50 adsorption-desorption cycles (4.31 \pm 0.10 mmol g^{-1} , Fig. 2, inset). This shows that SO_2 is fully released during the subsequent desorption cycles. Also, PXRD analyses of the material after 50 adsorption/desorption cycles confirmed the retention of the crystal structure (Fig. S5†). At the same time, N₂ adsorption isotherm at 77 K evidenced that the porosity was not modified (BET area $\approx 3005 \text{ m}^2 \text{ g}^{-1}$, Fig. S6†). This result exhibits that SO2 can be fully released when SO2 cycle experiments are carried out without modifying the crystal structure of Ni₂(dobpdc).

Up to this point, the SO₂ capture by Ni₂(dobpdc), particularly at very low pressure (0.002 bar), has been demonstrated. This is a fundamental requirement for SO₂ detection. Ni₂(dobpdc) also showed high SO₂ cyclability and extraordinary chemical stability to SO₂, desirable characteristics for SO₂ detection.

Thus, another fundamental aspect of any detector is selectivity.²³ A CO₂ single-component adsorption isotherm was collected at 298 K and 1 bar (Fig. S9†). The SO₂ adsorbed amount in Ni₂(dobpdc) was higher than the CO₂ in the whole pressure range. Then, we calculated the selectivity of SO₂ over CO₂ at different compositions (SO₂/CO₂) using the Python package (Table S1†), pyIAST,24 corroborating a remarkable SO2/CO2 selectivity by Ni₂(dobpdc).

Once it was comprehensively established that the SO₂ adsorption characteristics of Ni₂(dobpdc) as a promising SO₂ detector, the possibility of using this MOF material as a fluorescent SO2 detector was investigated, first, under UV light irradiation at λ_{ex} = 350 nm (Fig. S12†), an activated sample of Ni₂(dobpdc) showed a broad photoluminescence peak centred at λ_{max} = 450 nm, as it is observed in Fig. 3. This is attributed to the dobpdc fragment as previously reported for Mg₂(dobpdc).²¹ Then, another activated sample of Ni₂(dobpdc) was exposed (saturated) to SO2 in our homemade in situ adsorption system (Fig. S8†) to measure its photoluminescence

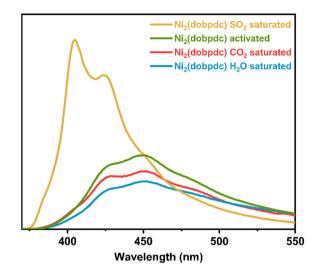


Fig. 3 Solid-state emission spectra of activated Ni₂(dobpdc) (green) and after exposure to SO₂ (yellow), CO₂ (red), and H₂O (blue).

absorption properties of it later. Interestingly, the photoluminescence shifts to 405 nm and an increase of approximately 61 % in emission intensity was observed.

These photoluminescence changes in position and intensity can be attributed to the electronic effect that SO₂ applies on the framework when coordinated to the Ni-centres, which is successively transferred to the dobpdc ligand. A control experiment was conducted further to test the selectivity of Ni₂(dobpdc). The fluorescence of Ni₂(dobpdc) upon exposure to H₂O and CO₂ was measured (Fig. 3). Importantly, none of these molecules generated significant changes in the shape or intensity of the photoluminescence compared to the spectrum of activated Ni₂(dobpdc).

Thus, since none of these conditions (exposure to H2O and CO₂) significantly altered the shape or intensity of the emission, corroborated the selectivity of Ni₂(dobpdc) to SO₂, indicating that the change in fluorescence is exclusively due to SO₂ adsorption-coordination and not due to other molecules. Later, five independent experiments were measured. An acti-Ni₂(dobpdc) sample was saturated with SO₂. Consistently, it was found that the same absorption spectrum shifted to 405 nm, with an approximate 61 % increase in emission intensity.

Once it was demonstrated the SO₂ detection selectivity for Ni₂(dobpdc), over H₂O and CO₂, and the reproducibility of the detection of saturated samples Ni2(dobpdc) with SO2, the detection properties of this Ni(II)-based material at low SO₂ pressure: non-saturated Ni₂(dobpdc) with SO₂ was investigated. Since Ni₂(dobpdc) demonstrated a relatively high SO₂ uptake at low pressure (P = 0.1 bar), vide supra, and this low pressure can be correlated to SO2 detection at low SO2 concentrations, it becomes crucial to investigate photoluminescence response at lower SO₂ pressures (in this case, 0.1 bar).

Thus, an activated sample of Ni₂(dobpdc) was exposed to 0.1 bar of SO₂ (Fig. S8†). The emission spectrum was measured

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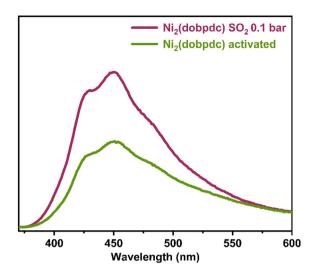


Fig. 4 Comparison of solid-state emission spectra of Ni₂(dobpdc) samples activated (green) and exposed to SO₂ at 0.1 bar (pink).

(Fig. 4). Interestingly, the broad photoluminescence peak remained centred at λ_{max} = 450 nm. An increase in emission intensity of approximately 62 % was observed. Also, the reproducibility of this experiment was evaluated with 5 independent experiments (re-activation of the sample and re-exposure to 0.1 bar of SO2). It was found that an increase of approximately 62 % in emission intensity. It is worth mentioning that only the SO₂ detection by Ni₂(dobpdc) at 0.1 bar was performed. At this point, it cannot be translated to SO₂ sensing. Although we consistently found an increase in the emission intensity when re-exposing to SO_2 and re-activating the sample of Ni_2 (dobpdc) at 0.1 bar SO_2 . Nevertheless, it is not possible to quantify the precise amount of SO₂ by photoluminescence. However, achieving a consistent and reproducible response is very promising when this Ni(II)-based MOF material is exposed to 0.1 or 1 bar of SO₂.

Finally, in order to investigate the plausible mechanism of SO₂ detection by Ni₂(dobpdc), a time-resolved photoluminescence (TRPL) experiment was performed using a 340 nm picosecond-pulsed LED as the excitation source (Fig. 5). TRPL experiments were carried out on an activated sample of Ni₂(dobpdc) and an SO₂-saturated sample. The photoluminescence decay was measured at three different emission wavelengths: 405 nm, which was the emission maximum of the SO₂-saturated sample; 450 nm, corresponding to the emission maximum of the activated sample and 425 nm since this signal was observed in both spectra (Fig. S13-S16†). For all three emission wavelengths, it was observed that the average decay lifetimes increased upon SO₂ exposure (Table S2†). Thus, the average fluorescence lifetime of the activated sample (at $\lambda_{\text{emission}} = 405 \text{ nm}$) was 2.14 ns, while the lifetime of the SO_2 -saturated sample (at $\lambda_{emission}$ = 405 nm) was 2.47 ns (Fig. 5). These results suggest that the coordination of SO2 molecules to the Ni(II) metal centres rigidify the molecular motions of the organic ligand (dobpdc). Subsequently, it hinders non-radiative decay pathways of the photoexcited state, causing the fluorescence lifetime to slow

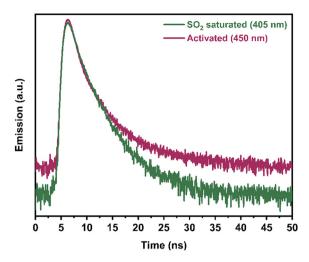


Fig. 5 Time-resolved photoluminescence decay spectra of activated Ni₂(dobpdc), and after exposure to SO₂ measured at 405 nm at 340 nm excitation.

down. Thus, it increases the number of radiatively decaying excited species, leading to an improvement in the fluorescence intensity.25

One of the reasons why the wavelength shifts, is the change in energy due to the electronic transitions, where intermolecular interactions can considerably influence. It was previously reported that a strong interaction could considerably impact the excited state of some materials.26 Thus, this can indicate that the coordination of SO₂ to all the Ni(II) centres is strong enough to increase the energy difference between the basal and excited states, causing the fully SO2-coordinated Ni₂(dobpdc) to emit light at higher energies. In other words, a shift in the spectrum can be observed at higher energies, i.e., at shorter wavelengths.

To summarise, the SO₂ adsorption and detection properties of a structurally stable MOF material entitled Ni₂(dobpdc) were investigated. Ni₂(dobpdc) demonstrated a high SO₂ uptake at low pressure (4.3 mmol g⁻¹ at 298 K and 0.05 bar), in combination with an excellent cyclability performance with a facile SO₂ regeneration at room temperature. Fluorescence studies exhibited a significant change in the emission spectra after SO₂ adsorption, with a clear SO₂ detection selectivity, over H₂O and CO₂ and reproducible SO₂ response when this Ni(II)-based MOF material was exposed to only 0.1 or 1 bar of SO₂. Finally, time-resolved photoluminescence experiments suggested that the coordination of SO₂ molecules to the Ni(II) metal centres rigidify the molecular motions of the organic ligand (dobpdc), leading to an increase in fluorescence intensity. Overall, this study postulates Ni₂(dobpdc) as a promising candidate for SO₂ detection.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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