SO₂ Capture Using Porous Organic Cages

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Abstract: We report the first experimental investigation of porous organic cages (POCs) for the demanding challenge of SO₂ capture. Three structurally related N-containing cage molecules were studied. An imine-functionalized POC (CC3) showed modest and reversible SO₂ capture, while a secondary-amine POC (RCC3) exhibited high but irreversible SO₂ capture. A tertiary amine POC (6FT-RCC3) demonstrated very high SO₂ capture (13.78 mmol g⁻¹; 16.4 SO₂ molecules per cage) combined with excellent reversibility for at least 50 adsorption–desorption cycles. The adsorption behavior was investigated by FTIR spectroscopy, ¹³C CP-MAS NMR experiments, and computational calculations.

Introduction

Modern society faces critical challenges related to controlling the release of toxic pollutants into the atmosphere. Air pollution reduction is a fundamental part of strategies to tackle climate change.[1] Air pollution produces a large variety of health problems (e.g., morbidity and premature death)[2] and it also accounts for decreases in biodiversity, water acidification and crop damage.[3] Sulphur dioxide (SO₂), is a colourless, irritating and non-flammable gas with a sharp odour, which can be absorbed through the respiratory system or by dermal contact.[4] SO₂ is highly toxic to humans, and exposures over 100 ppm can be deadly.[5] The frightening increase in SO₂ emissions by anthropogenic activities such as fossil fuel combustion[6] creates an urgent need for immediate environmental remediation action. In fact, the World Health Organization (WHO) has classified SO₂ as one of the most hazardous air pollutants with catastrophic health effects, correlated primarily to severe modifications of the respiratory system (e.g., broncho-constriction in lung function).[7] For example, if a healthy person is exposed to a SO₂ concentration of 1.5 ppm for just a few minutes, it can produce a temporary inability to breathe.[8] At slightly higher concentrations, SO₂ can cause laryngitis, chronic bronchitis and severe infections of the respiratory tract.[9] Air quality guidelines advise the maximum values for human exposure to SO₂ to be 500 μg m⁻³ (175 ppb) over 10 min and 20 μg m⁻³ (8 ppb) for daily averages.[10] To comply with these standards, significant quantities of SO₂ must be removed from our environment to ensure both human health protection and environment preservation, particularly in urban areas.

One of the first techniques to remove SO₂, spiral-tile packed tower, was developed in 1933.[11] Currently, the most common strategies for SO₂ removal from industrial combustion units are scrubbers. Typically, electricity power plants employ desulphuration methods based on aqueous alkaline solutions and/or wet-sulphuric-acid processes.[12] However, these methods create huge quantities of wastewater, corrosion of pipelines, substantial cost of use and recovery, and leave traces of SO₂ (approximately 400 ppm[13]), posing a foremost health risk according to the WHO.[14] As a result of these disadvantages, we need to explore more efficient and effective technologies for the capture of SO₂, and solid state materials show potential to overcome many of these pitfalls. For example, the removal of SO₂ has been investigated with

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The key to adsorbing large amounts of SO\textsubscript{2} under practical relevant conditions is the careful selection of functional groups that have a high affinity for this acidic gas, as demonstrated in other porous materials that contain -OH or -NH\textsubscript{2} groups.\cite{38} Furthermore, it has been demonstrated that the adsorption of SO\textsubscript{2} is preferred on surfaces with N-containing functional groups\cite{37} and its reversibility strongly depends on the basicity of the N species in the adsorbent.\cite{36} In fact, most of the materials used in industrial desulphurization technologies are amine solutions.\cite{39} Taking that into account, we decided to investigate a series of molecular cages as SO\textsubscript{2} adsorbents with three different N-containing functional groups: imine, CC3; secondary amine, RCC3; and tertiary amine functionalization, 6FT-RCC3 (Figure 1).\cite{23,27,41} As can be seen in Figure 1, it is possible to obtain high densities of nitrogen atoms (shown in blue) in these cage materials. It is worth noting that, the three cages are isostructural in crystalline form, with almost identical size, shape and packing mode in solid state (Figure 1).

The first molecular cage studied was CC3, this structure contains 12 imine groups per molecular cage (Figure 1a). CC3 showed a SO\textsubscript{2} uptake of 2.78 mmol g\textsuperscript{-1} at 1 bar and 298 K; the isotherm is shown in Figure 2. The SO\textsubscript{2} adsorption capacity agrees (approximately) with the grand canonical Monte Carlo simulations carried out by W. Li and J. Zhang, where the adsorption of different acidic gases in CC3 was studied computationally.\cite{41} The simulated isotherm for SO\textsubscript{2} shows an approximate total adsorption of 3.6 mmol g\textsuperscript{-1} at 1 bar and 275 K, and an atypical type-I shape, associated to Coulomb interaction for SO\textsubscript{2}···SO\textsubscript{2} complexes.\cite{41} In our case, the experimental adsorption follows a characteristic type-I isotherm without hysteresis that it is associated with the reversibility of the process; that is, physisorption of the gas molecule inside the cages. Somewhat surprisingly given its imine bonding, retention of crystallinity was observed by PXRD after the exposure to SO\textsubscript{2} (ESI Figures S1a). We also carried out an SO\textsubscript{2} adsorption experiment at 308 K to calculate the heat of adsorption (see Table 1 and ESI Figure S2a). The resultant $Q_{st}$ was equal to 38.46 kJ mol\textsuperscript{-1}, which is characteristic for a physisorption rather than a chemisorption processes.\cite{42} The SO\textsubscript{2} adsorption capacity for CC3 does not compete well with various stable MOFs. The linear uptake portion of the isotherm also implies poor adsorption kinetics and lack of equilibration.

The next material analyzed was a secondary amine-cage RCC3 (Figure 1b). RCC3 showed a much higher SO\textsubscript{2} uptake capacity of 12.34 mmol g\textsuperscript{-1} at 298 K up to 1 bar, comparable to the current best performing MOF materials for this applica-

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**Figure 1.** Crystal structures (top) and chemical structures (bottom) for porous cage CC3 (a), RCC3 (b), and FT-RCC3 (c). Carbon and nitrogen atoms are shown in grey and blue, respectively. Hydrogen atoms are omitted for clarity, except in at the secondary amine group of RCC3, where hydrogen is shown in whitepink.\cite{38}
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cycles as confirmed by solution NMR experiments (ESI, Figure S10 and S11).

PXRD analyses of RCC3 and 6FT-RCC3 after SO2 exposure confirm a significant loss in crystallinity. We believe that for RCC3, the high heat of adsorption for SO2 and the lack of recyclability of the material indicates a chemical transformation of the structure (chemical bonding, N—SO2), which may collapse the structure. Conversely, the loss of crystallinity for 6FT-RCC3 can be attributed to the flexibility of the material and the relatively strong interaction with SO2 molecules, as demonstrated by the heat of adsorption and high sorption cyclability (see Figure 3). We speculate that SO2 molecules might be accommodated into the pore structure of 6FT-RCC3 as result of the high affinity, even after all the voids in the structure of the crystalline phase have been filled, and eventually disrupt the regular packing. We note that amorphous POCs of this type can be more porous than their crystalline analogues in some cases, and hence loss of crystallinity is not necessarily a disadvantage—a key distinguishing feature between these inherently molecular solids and frameworks such as MOFs and COFs, which typically lose their porosity when they become amorphous. This may be particularly beneficial for separations that involve strongly interacting and chemically reactive guests such as SO2.

FTIR spectroscopy experiments were performed on the as-synthesised, after SO2 exposure, and fully re-activated materials to corroborate the preferential binding sites of the SO2 molecule in the cages (see ESI Figure S7). The fundamental vibrational frequencies of the SO2 molecule are the symmetric stretch ($\nu_1$), asymmetric stretch ($\nu_2$), and bending motion ($\nu_3$) located at 1153 cm$^{-1}$, 1368 cm$^{-1}$, and 508 cm$^{-1}$, respectively. The interaction of SO2 and amine-based materials can be often be defined, as the formation of a charge-transfer complex, from the N: lone pair of electrons to the antibonding SO2 orbital (N—SO2). This interaction causes the appearance of new SO2 vibrational bands, as reported for several amines where the formation of charge-transfer is verified. As shown in Figure 4a, the strongest vibrational frequencies are assigned to C= N, CH2, C—N, and C— H stretching modes at 1654 cm$^{-1}$, 1448 cm$^{-1}$, 1160 cm$^{-1}$ and 690 cm$^{-1}$, respectively. The CC3 spectra before and after SO2 adsorption showed no changes, and these results are in good agreement with the adsorption isotherm (vide supra), demonstrating the weak SO2 interaction with the CC3 structure. By contrast, the FTIR spectrum for the RCC3 cage shows new bands after SO2 adsorption (Figure 4b, green line). These bands at 1382 cm$^{-1}$ and 649 cm$^{-1}$ are in the range reported for asymmetric stretching and bending for SO2 gas, while the vibrational frequencies at 1226 cm$^{-1}$, 1033 cm$^{-1}$ and 540 cm$^{-1}$ are associated to the N-S interaction and have been reported for NH2-SO2. These results suggest that the adsorption of SO2 occurs mainly at the amino groups, while some free SO2 interacts as a dimer. Additionally, the molecular cage with tertiary amine functionalisation, 6FT-RCC3, showed four vibrational frequencies at 1178 cm$^{-1}$, 1083 cm$^{-1}$, 611 cm$^{-1}$ and 520 cm$^{-1}$, which are also related to the formation of an N—SO2 complex, see Figure 3.

$^{13}$C CP MAS NMR experiments (Figure 4 bottom) showed a good correlation with the FT-IR for the solid materials. Figure 5a shows a similar spectrum for the CC3 sample both before and after the SO2 adsorption. Both spectra show narrow NMR signals due to aliphatic carbons at 22.8, 32.4 and 73.5 ppm. Three further peaks assigned to aromatic carbons are observed at 130.0, 136.8 and 159.6 ppm. These resonances are similar in breadth and position before and after SO2 adsorption, in line with a weak interaction between SO2 and CC3. The spectra of RCC3 (Figure 4b) are composed by peaks assigned to aliphatic carbons at 24.8, 31.1, 50.6 and 61.9 ppm, and by peaks due to aromatic carbons at 125.6 and 140.5 ppm. In contrast with CC3, the NMR peaks corresponding to RCC3 are broad, in keeping with a more flexible molecular solid structure that has less long-range order. After the SO2 adsorption, the mobility and chemical environment of carbons, from the primary units, are significantly modified corroborating a strong interaction with the SO2 molecule. However, the isotropic signals are unmodified suggesting that the structure, at least the primary units of this POC, are unchanged. Finally, the spectra corresponding to the 6FT-RCC3 sample (Figure 4c) show NMR signals of aliphatic carbons at 23.2, 29.4, 58.9, 67.7 and 78.1 ppm and peaks due to aromatic carbons at 122.6 and 139.1 ppm. The peaks before the SO2 adsorption are narrow suggesting an ordered crystalline solid but after the SO2 adsorption the peaks became very broad. Signals are observed but the peaks are not sharp or strong enough resolved. It seems that the SO2 interaction is strong in this material and that the number of molecules inside the pores significantly modifies the structure and the relaxation of NMR signals.

To better understand of the SO2 adsorption mechanism, we carried out theoretical calculations using density functional theory methods and employing the Gaussian 16 software package. Calculations used the PBE density functional approximation with Ahlrich’s def2-TZVP basis set of a polarized triple-$\xi$ quality. Dispersion was considered with Grimme’s D3 dispersion corrections in conjunction with the Becke-Johnson damping parameters. Geometries were optimized and vibrational frequencies computed to confirm structures were minima on the potential energy surface. All

![Figure 3](image-url) Fifty adsorption-desorption cycles for SO2 in 6FT-RCC3 at 298 K. SO2 was fully desorbed under dynamic vacuum at 353 K between cycles. No loss of uptake capacity was observed.
SO₂ binding energies are reported with zero-point vibrational energy corrections.

The SO₂ binding energies were calculated as the difference between the unbound POC moiety and SO₂ from that of the complex. The structures of the moieties, SO₂ binding energies, and shortest N-S distances are shown in Table 2. The SO₂ binding energies follow the trend of the experimental heats of adsorption, increasing from CC3 (49.7 kJ mol⁻¹) to 6FT-RCC3 (68.6 kJ mol⁻¹) to RCC3 (86.4 kJ mol⁻¹). These binding energies are greater than for imidazole (39.1 kJ mol⁻¹), and a range of imidazole derivatives reported by Shannon et al.⁶¹ The results are again consistent with the notion that binding strength increases with the degree of substitution, since the electron-donating alkyl groups enhance the nucleophilic character of the N atoms resulting in a greater SO₂ affinity.

Binding was investigated beyond one SO₂ molecule for the 6FT-RCC3 moiety and shows that 2 SO₂ molecules bind per moiety with a negligible change to the binding energy, and (Table 3). This result supports the experimental result of 1:1 binding of SO₂ to N atoms in the structure.

Figure 4. a–c) FT-IR spectra of as-synthesised, SO₂-loaded, and regenerated a) CC3, b) RCC3, and c) 6FT-RCC3, split into 1800–400 cm⁻¹ wavelength region. Dashed lines in (a) shows the strongest vibrational frequencies assigned to C=N, CH₂,C=N, and C–H stretching modes. Dashed lines in (b) and (c) are a visual guide to the new bands observed after SO₂ exposure. d–f)¹³C CP MAS NMR spectra of as-synthesised (black line) and SO₂-loaded (red line) of d) CC3, e) RCC3, and f) 6FT-RCC3 porous organic cages. * Indicates spinning side bands (6 kHz).

Tabelle 2: Structure of the POC moieties, the corresponding SO₂ binding energies, and shortest N-S distance to the SO₂ molecule for each system. All binding is exergonic.

| Parent POC | CC3    | RCC3   | 6FT-RCC3 |
|------------|--------|--------|----------|
| BE [kJ mol⁻¹] | 49.7   | 86.4   | 68.6     |
| r(N-S) [Å]  | 2.430  | 2.390  | 2.415    |

Figure 5. Three types of SO₂ adsorption behaviours of porous organic cages.
Based on the combined experimental and computational results, these three structurally related cages have quite distinct SO2 adsorption behaviors, which result from their different functional groups as well as their packing modes in the solid state (Figure 5). CC3 adsorbs SO2 molecules like a typical crystalline physisorptive porous solid, where SO2 molecules are accommodated in its pore structure without significant adsorbate-adsorbent interactions. The pore structure of CC3 is unchanged during the SO2 adsorption-desorption cycles.

The amine groups of RCC3 provide very strong binding sites for SO2 molecules drawing more gas molecules into the rather flexible pore structure of RCC3. However, those SO2 molecules are then hard to desorb from RCC3 structure, because of the high bind affinity between SO2 and RCC3 (82.78 kJ mol\(^{-1}\)). By contrast, the imidazolidine rings on 6FT-RCC3 seem have on ideal affinity for SO2 at 43.03 kJ mol\(^{-1}\); they can attract a large amount of SO2 into the pore structure, but the adsorbed gas can still be easily removed under dynamic vacuum at 80°C.

### Conclusion

In summary, we present the first experimental study of porous organic cages for gaseous SO2 capture. Three structurally related cage materials were studied, differing only in their functional groups (amines, CC3; secondary amines, RCC3; tertiary amines, 6FT-RCC3). The three cages have distinct SO2 adsorption behaviors, which stems from their very different SO2-adsorbent affinities, as confirmed by adsorption isotherms, FTIR spectroscopy, and \(^{13}\)C CP MAS NMR experiments. 6FT-RCC3 showed a remarkable SO2 uptake at 13.78 mmol g\(^{-1}\) (1 bar, room temperature), rivaling the best performing MOF materials and polymers for this application, as well as showing exceptional stability and cyclability. In particular, high uptake at low partial pressures indicates the potential of 6FT-RCC3 for trace SO2 capture.

The most prevalent technology for SO2 today is alkaline scrubbers, but as discussed above, these have numerous disadvantages. Effectively, we have removed the need for an aqueous solvent here by developing a porous organic base. We believe that the modest surface area of these materials is an advantage because their relatively high density means that the volumetric SO2 storage capacity is very high. For example, at 298 K/1 bar, 6FT-CC3 adsorbs 13.78 mmol g\(^{-1}\) SO2, which equates to 16.4 SO2 molecules per cage, on average; that is, one per amine group plus 4.4 others. Since these cages pack a large number of amine groups into a small, compact volume (Figure 1), this equates to an exceptional SO2 storage density, in principle allowing for reductions in scale of adsorbers based on these materials. 6FT-CC3 shows excellent cyclability over at least 50 sorption/desorption cycles (Figure 3) and, unlike many MOFs and other frameworks, loss of crystallinity does not necessarily equate to reduction in porosity for these cage materials.[32] Coupled with good processibility options and, recently, proven synthetic scalability,[42] we believe that POCs such as 6FT-RCC3 have strong promise for real-life SO2 capture.

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### Conflict of interest

The authors declare the following competing financial interest(s): A.I.C. and M.L. have a financial interest in the commercialize porous organic cages.

### Stichwörter:
- adsorption
- chemical stability
- porous organic cages
- SO2

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**Table 3**: Binding energies per SO2 molecule to the 6FT-RCC3 derived moiety, and shortest N-S distances for each SO2 molecule in the system.

| No. of SO2 | BE per SO2 [kJ mol\(^{-1}\)] | R(N-S) [Å] | Min. | Max. | Average |
|------------|----------------------------|------------|------|------|---------|
| 1          | 68.6                       | –          | –    | 2.415|
| 2          | 65.0                       | 2.389      | 2.395| 2.392|
| 3          | 54.7                       | 2.331      | 4.770| 3.166|
| 4          | 49.8                       | 2.330      | 4.854| 3.567|

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[62] POCS such as CC3 and RCC3 can now be synthesised on kilogram scale per batch in jacketed reactors. A typical synthesis procedure is described in the Supporting Information.

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Porous organic cages (POCs) were investigated for the first time for the capture of SO₂. A tertiary amine cage (6FT-RCC3) demonstrated remarkably high SO₂ capture that was perfectly reversible for at least 50 adsorption–desorption cycles.