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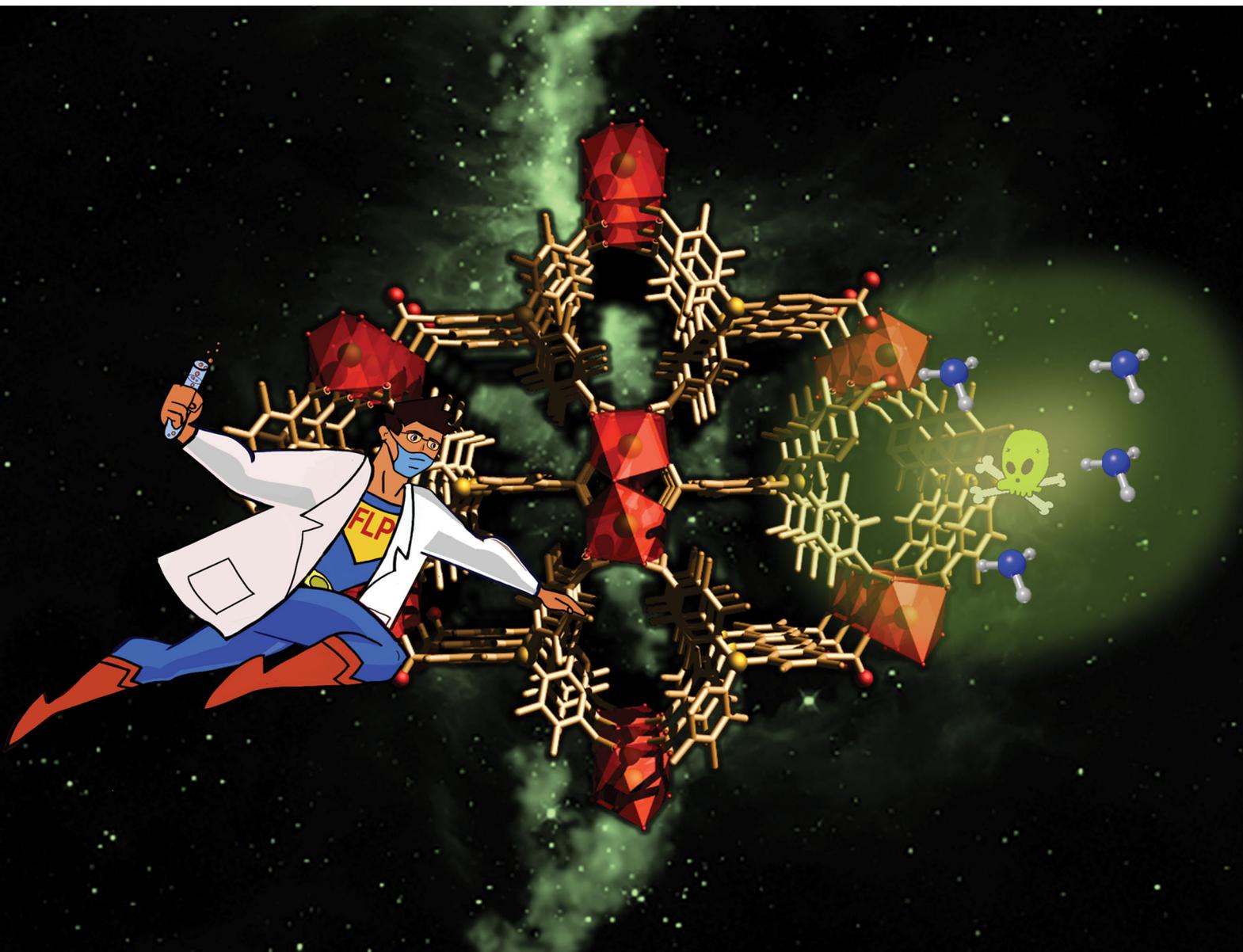
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A recyclable metal–organic framework for ammonia vapour adsorption†

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Herein, we present a new strategy to design metal–organic frameworks (MOFs) as adsorbents for ammonia (NH_3) vapour. The linking ligand is functionalized with a sterically hindered Lewis acidic boron (B) centre, allowing efficient capture of NH_3 and easy recycling of the MOF by simply heating at low temperature. The recycled MOF material can be used for NH_3 capture for at least 5 cycles without losing its crystallinity or its luminescence properties.

Toxic gases, such as NH_3, CO, or H_2S, cause an immediate danger to life even at ppm concentrations.[1] For example, the exposure limit of NH_3 in industrial settings recommended by the US Occupational Safety and Health Administration is 25 ppm.[2] Therefore, developing adsorption materials capable of capturing these gases could offer a strategy of great importance for the protection of the environment, workplace safety and public health.

Porous materials with relatively high surface areas such as zeolites and activated carbons have been the traditional adsorbents for toxic gases.[3] During the last decade, metal–organic frameworks (MOFs) and covalent-organic frameworks (COFs), which often possess high porosity and pore-surface tunability, have emerged as adsorbents that are superior to zeolites and activated carbons.[4] It is well known that the sole reliance on the materials' porosity is not sufficient for effective capture of gas/vapour.[5,6] The adsorption rate and capacity for gas molecules can be increased when the pore surface incorporates sites for coordination, acid–base interactions, electrostatic interactions, π–π stacking, or H-bonding. The incorporation of these sites either on the pore surface or at the nodes within the scaffold of MOFs and COFs has been widely examined. A large number of MOFs and COFs have integrated Brønsted and Lewis acidic groups, *e.g.* –COOH, –SO_3H, –PO_3H_2, –OH, open metal sites, or boroxine rings[7] have been reported as promising NH_3 sorbent due to the strong acid–base interaction.[8a–g]

Strong interactions of the gas molecules with the metal nodes or organic linkers of the MOF and COF adsorbents could cause collapse of the materials' frameworks[9] or difficulties in recycling the adsorbents.[10] For example, in the case of the boronic acid-based COF-10, adsorbed NH_3 can only completely be removed by heating at 200 °C for 12 hours at 0.1 Torr,[8a] presumably a result of strong B-NH_3 binding.

An ideal porous material for recyclable NH_3 adsorption should provide interactions that are neither too strong nor too weak, allowing both capture and release. In molecular chemistry, such reversible interactions have been achieved for Lewis acid–base adducts *via* the introduction of steric demands, affording so-called "frustrated Lewis pairs".[11] Applying this strategy to MOFs for NH_3 capture, bulky Lewis acidic B centers were introduced into a MOF. While this enhances the electrophilicity of the pores, the steric demanding environment about B deters strong dative binding thus facilitating subsequent release and thus a recyclable adsorbent.

Targeting recyclable NH_3 binding, the highly stable MOF, **SION105-Eu** with the chemical formula of ($[Eu(tctb)_3(H_2O)]$) (Fig. 1, left) was selected. This MOF contains the linking ligand $tctb^{3-}$ with a central sterically hindered Lewis acidic B centre (Fig. 1, right) and has been shown to adsorb CO_2, with an uptake capacity of ~1.9 mmol g^{-1} at 195 K and 1 bar, and a BET surface area of 216 m^2 g^{-1} (Fig. S4, ESI†), and has been utilized for fluoride ion detection in drinking water, and as a catalyst for CO_2 transformation.[12] Herein, we demonstrate this MOF also captures NH_3 vapour but at the same time, releases it upon heating, affording a stable, recyclable MOF for NH_3 adsorption.

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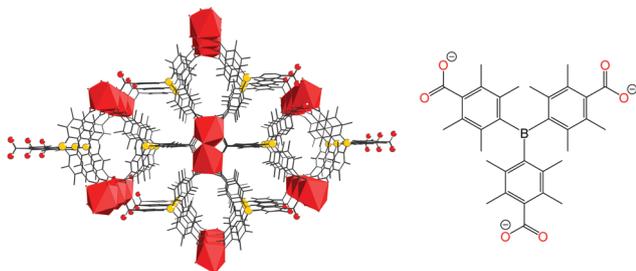
Fig. 1 (left) Structure of **SION105-Eu**, with Eu ions shown as red polyhedra and H atoms omitted for clarity; (right) ligand tctb^{3-}.

SION105-Eu was synthesized based on a solvothermally synthetic procedure, by heating Eu(NO$_3$)$_3$·6H$_2$O (1 equivalent) and tris(p-carboxylic acid)tridurylborane (H$_3$tctb) (1 equivalent) in a 2 : 1 mixture of DMF : H$_2$O at 120 °C for 72 hours.[12a] The crystalline powder was filtered, soaked in MeOH for three days, filtered again, and then dried in oven at 120 °C. The purity of the sample was confirmed by PXRD, in which the experimental pattern matched well with the simulation based on the single-crystal structure (Fig. S1, ESI†). The MOF powder is expected to be hydrophobic due to the presence of a large number of –CH$_3$ groups on the ligand, which was confirmed by the measurement of the contact angle (119.86°) with a water drop (Fig. S2, ESI†). The MOF floats in water (Fig. S3, ESI†), and the exposure to water left the crystallinity of the sample unaltered as confirmed by PXRD (Fig. S1, ESI†).

The activated sample of **SION105-Eu** was first subjected to NH$_3$ gas adsorption under dry conditions, with the isotherms measured at 303 and 313 K (Fig. S5, ESI†). At ~1 bar and 303 K, the MOF adsorbs 5.7 mmol g^{-1} NH$_3$. The isosteric heat of NH$_3$ adsorption calculated based on the Clausius–Clapeyron relation is −28.7 kJ mol^{-1} for the coverage of 1.5 mmol g^{-1} and slightly decreases at higher adsorption amounts (Fig. S6, ESI†), suggesting a good interaction between NH$_3$ and the MOF.

The ability of the material to capture of NH$_3$ vapour from an aqueous NH$_3$ solution was tested at room temperature (Fig. S7, ESI†). 100 mg of the powder in a 2 mL vial was placed inside a 50 mL vessel. A second vial containing 3.0 mL of aqueous NH$_3$ solution (28 wt%) was also placed into the larger vessel. With the cap loose, the capture of NH$_3$ by the MOF was assessed at ambient pressure while higher pressures were achieved with the cap tightly closed. The amount of NH$_3$ vapour adsorbed by the sample was gravimetrically recorded as a function of time (Fig. 2). The MOF adsorbs up to ~10 wt% after 6 hours, and ~36 wt% after 66 hours when the vessel is tightly closed. Adsorption is slower and reaches saturation of ~10 wt% after 12 hours when the cap is loose. These findings are consistent with the adsorption of NH$_3$ being pressure dependent. The thermal gravimetric analysis (TGA) of the sample collected after 6 hours of NH$_3$ adsorption in a closed vessel (NH$_3$@**SION105-Eu**) shown in Fig. S8 (ESI†) also illustrates the weight loss of around 10 wt% at below 100 °C, corresponding to the release of NH$_3$. As the MOF unit molecular weight is 709.43 g mol^{-1}, 10 wt% (5.9 mmol g^{-1}) is similar to the value obtained with dry NH$_3$ gas, and indicates an average molar ratio of NH$_3$: B of *ca.* 4 : 1.
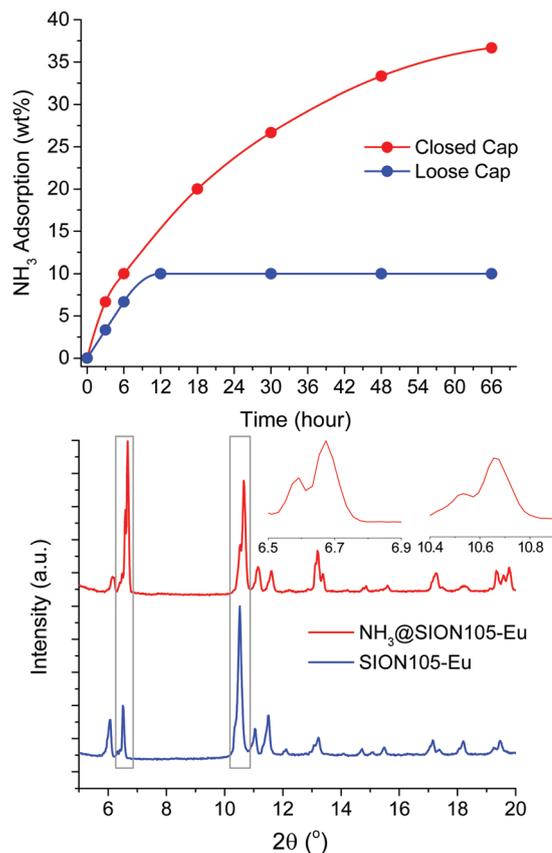

Fig. 2 (top) NH$_3$ adsorption curve for **SION105-Eu** as a function of time; (bottom) PXRD pattern of the **SION105-Eu** sample after 6 hour of NH$_3$ vapour adsorption in comparison to the as-made sample. Inset: The appearance of new peaks within the selected regions.

This uptake is similar to that seen for Zn(INA)2 (~6 mmol g^{-1}),[8b] and Al-PMOF (~7.6 mmol g^{-1}) at room temperature and 1 bar.[8g] In the present case, this suggests the presence of the Lewis acidic B centres prompts non-stoichiometric capture of NH$_3$ molecules, presumably facilitated by hydrogen bonding interactions among NH$_3$ molecules. In contrast, exposure of **SION105-Eu** to pure water showed negligible adsorption, suggesting that capture of more basic NH$_3$ is enhanced by the electrophilic nature of the MOF.

A suspension containing ~2 mg of the ground MOF powder in 200 μL of THF was deposited onto a filter-paper plate and allowed to dry (Fig. S9, ESI†). The luminescence emission measurements of this sample were made in the presence and absence of NH$_3$ vapour. After 20 minutes of exposure to NH$_3$ vapour, the luminescence peak at ~615 nm, characteristic for the transition $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+}, decreased in intensity by ~30% (Fig. S10, ESI†). Since lanthanide luminescence emission is induced by the antenna effect,[13] this partial quenching is consistent with a rather weak electrostatic interaction between the B centre of the antenna ligand tctb^{3-} and NH$_3$.

The PXRD pattern of the MOF sample collected after 6 hours of NH$_3$ adsorption (NH$_3$@**SION105-Eu**) showed the preservation of crystallinity, although the two original peaks in the regions of $2\theta = 6.5$–$6.9°$ and 10.4–$10.9°$ were split, and their intensities were altered (Fig. 2, bottom). This also suggests only weak electrostatic

or van der Waals interactions between the MOF and NH_3 as the formation of the B-NH_3 adduct would be expected to lead to quaternization of B and a drastic perturbation of the PXRD pattern. It is noteworthy that van der Waals interactions have detected for frustrated Lewis acidic boron–olefin interactions.[14] The B environment in trimesitylborane (Mes_3B) is similar to that in **SION105-Eu** and indeed, exposure of Mes_3B to NH_3 showed no evidence of adduct formation by ^{11}B-NMR spectra (Fig. S15, ESI†).[15]

The FTIR spectrum of the NH_3@**SION105-Eu** (Fig. S16, ESI†) shows the appearance of N–H stretching bands at 3300–3500 cm^{-1}, confirming the retention of NH_3 within the MOF. In contrast, the MOF MIL103-Eu which is highly porous, but does not contain B shows no evidence of NH_3 adsorption in the FTIR spectrum (Fig. S18, ESI†). This further supports the notion that the electrophilic pores in **SION105-Eu** facilitates NH_3 adsorption.

To assess the stability of **SION105-Eu** over the course of adsorption, the powdered MOF was exposed to NH_3 vapour (generated by an aqueous NH_3 solution (28 wt%) in a tightly closed vessel) for 6, 12, and 66 hours. The samples were subsequently heated at 75 °C in an oven for 30 min. In each case, the original mass of the sample was retrieved. PXRD measurements showed that the crystallinity was unaltered after 6 hours, slightly decreased after 12 hours and fully degraded after 66 hours of exposure to NH_3 (Fig. S19, ESI†). Similar experiments with the well-known MOFs, HKUST-1 (Cu) and MOF-5 (Zn) showed that these MOFs completely lost crystallinity in less than 1 hour of exposure to aqueous NH_3 (Fig. S20 and S21, ESI†). Indeed, while a number of transition metal-based MOFs[8b] are reported to be stable in the presence of dry NH_3 gas, they decomposed in "wet" NH_3 vapour, thus precluding recycling.[9] The present data demonstrate that **SION105-Eu** offers superior stability in this regard.

SION105-Eu was subjected to adsorption of NH_3 for 6 hours in a closed cap vessel and the NH_3 subsequently liberated by heating at 75 °C for 30 min; this process was repeated 5 times. The NH_3 adsorption capacity remains unchanged. The PXRD pattern, FTIR spectrum and luminescence emission of the MOF were unaltered after the 5th cycle of NH_3 capture, being essentially the same as those derived from the original material (Fig. 3). These observations affirm that **SION105-Eu** is recyclable for NH_3 capture.

Density functional theory (DFT) calculations were performed to confirm the electrostatic mechanism of **SION105-Eu** (see details in ESI†). It was revealed that no covalent bonds were formed between NH_3 molecules and the MOF scaffold as expected, and the computed heat of NH_3 adsorption was determined to be -40.9 kJ mol^{-1} at zero coverage, which is close to the value of -28.7 kJ mol^{-1} derived from the Clausius–Clapeyron equation. Notably, most works reported MOFs for NH_3 adsorption do not include the isosteric heat. Both the experimental and computed values for **SION105-Eu** are much lower than the value reported for the $[SrOOC]_{17}$-COF (-91.2 kJ mol^{-1}) due to the presence of the open Sr-sites in the latter that strongly interact with NH_3.[8f]

The above results demonstrate that the MOF **SION105-Eu** has several key features that may be further exploited in the design of stable and recyclable materials for toxic gas capture. Firstly, the use of lanthanide ions in the +3 oxidation state provides hard Lewis acids that associate strongly with hard donor atoms such as O from carboxylate ligands, providing stability in the presence of substrate molecules, in the present case, NH_3. Similarly, the incorporation of the bulky duryl groups on the Lewis acidic B centre within tctb^{3-} ligand precludes strong acid–base B–N interactions, again making the MOF structure robust in the
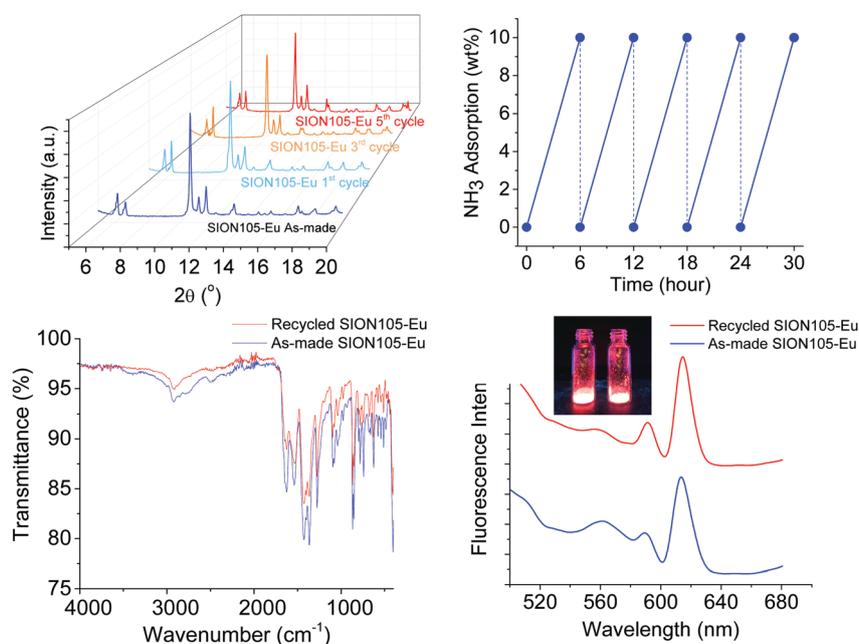

Fig. 3 (top left) PXRD patterns of **SION105-Eu** after recycling cycles; (top right) the NH_3 vapour adsorption capacity of the MOF remains the same after 5 cycles; (bottom) FTIR spectra and luminescence emission (λ_{ex} = 360 nm) of the as-made and recycled **SION105-Eu**. The inset shows the red emission under UV radiation of the as-made (left) and recycled (right) materials.

presence of NH_3. However, the presence of the B on the linkers also makes the pores electrophilic, prompting electrostatic attraction of NH_3 and thus its capture.

In conclusion, this work demonstrates a strategy for the design of materials for toxic gas adsorption based on the incorporation of sterically encumbered, electrophilic B sites in **SION105-Eu**. The resulting highly stable MOF is shown to capture NH_3 vapour. Moreover, this binding is reversible with simple heating to 75 °C, affording a recyclable material for NH_3 capture. Efforts to tune the Lewis acidity of the boron centers for improved uptake capacity and recyclability of related MOFs will be undertaken. In addition, practical applications of such materials are also being targeted *via* the shaping of the MOF powder[16] into pellets or beads.

Conflicts of interest

There are no conflicts to declare.

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