A Recyclable Metal-Organic Framework as a Dual Detector and Adsorbent for Ammonia


Abstract: Recyclable materials for simultaneous detection and uptake of ammonia (NH3) are of great interest due to the hazardous nature of NH3. The structural versatility and porous nature of metal-organic frameworks (MOFs) make them ideal candidates for NH3 capture. Herein, we report the synthesis of a water-stable and porous 3-dimensional Cu(II)-based MOF (SION-10) displaying a ship-in-a-bottle structure: the pores of the host SION-10 framework accommodate mononuclear Cu(II)-complexes. SION-10 spontaneously uptakes NH3 as a result of two concurrent mechanisms: chemisorption due to the presence of active Cu(II) sites and physical adsorption (bulk permanent porosity). The color of the material changes from green to blue upon NH3 capture, with the shifts of the absorption bands clearly seen at NH3 concentrations as low as 300 ppm. SION-10 can be recovered upon immersion of SION-10·2NH3 in liquid water and can be further reused for NH3 capture for at least three cycles.

Ammonia (NH3) is a corrosive and toxic gas with a strong odor that is widely produced and used in industries. In industrial settings, 25 ppm of NH3 is the exposure limit recommended by the US Occupational Safety and Health Administration,[1] and exposure to up to 300 ppm of NH3 can cause serious health issues.[2] Meanwhile, there is still a very high demand for NH3 at the industrial scale as reflected by its production of 145 million tons in 2014.[3] NH3 is an important raw material for the manufacturing of large numbers of chemicals including fertilizers, dyes, plastics, and pharmaceuticals,[4] and is considered as a potential carbon-free green fuel due to its high energy density and its lower cost of production, storage, and delivery compared to hydrogen.[5] Both the danger and usefulness of NH3 have motivated researchers to develop economical and responsive materials that can selectively detect and capture NH3; for example, NH3 sensors based on catalytic metals[6] and conducting polymers[7] have been reported, whilst porous materials such as activated carbons,[8] organic polymers,[9] and covalent organic frameworks,[10] and MOFs[11] are known as efficient NH3 sorbents.

MOFs are crystalline materials prepared by the self-assembly of metal ions or clusters with organic ligands to form porous extended structures.[12] MOFs are characterized by high porosity, with some of them possessing the highest volume and surface area, and lowest crystal density among all materials known to date.[13] The immense choice of metal ions or clusters and ligands offers vast opportunities to rationally design and synthesize MOFs with specific functionalities for targeted applications in areas of gas storage and separation,[14] catalysis,[15] sensing,[16] non-linear optics,[17] ferroelectricity,[18] magnetism,[19] and conductivity.[20] Recently, there is an increasing interest in developing porous and robust MOFs for the selective detection, capture and destruction of harmful molecules including toxic industrial chemicals (SO2 and NH3), and chemical warfare agents (sarin, sulfur mustard, and dimethyl methylphosphonate).[21]

Due to the high basicity and corrosivity of NH3, the most challenging task in the MOF research area is to develop sorbents and detectors that can efficiently capture and detect NH3, and can be recycled while retaining their structural integrity.[22] Recently, Dincă et al. have reported mesoporous and robust azolate-based MOFs exhibiting open Mn(II), Co(II), and Ni(II) sites which display high and reversible NH3 uptake.[11] The strategy of employing azolates to increase the stability of MOFs, initially addressed by Rosi et al.,[23] motivated us to synthesize SION-10 by employing adenine in the MOF structure. We chose to use Cu(II) in which, along with other d-element cations in MOFs, has the potential to introduce strong interactions with NH3.[22] SION-10 is a 3-dimensional MOF based on the earth abundant Cu(II) and readily available benzene-1,3,5-tricarboxylic acid and adenine ligands. It exhibits reversible NH3 uptake, and displays a visible and reversible color change upon adsorption and desorption of NH3.

SION-10 was synthesized hydrothermally after mixing CuCO3 with 1,3,5-benzenetricarboxylic acid (H3btc) and adenine (9Hade) (see SI Section 1 for the synthesis details) in pure water for 48 hours at 100 °C. The crystals obtained were characterized by single-crystal X-ray diffraction (SCXRD). SION-10 with the formula of [Cu(btc)2(s)(ade)(Hade)(μ2-\(\mu\))-OH)(H2O)]·0.4[Cu(ade)(H2O)]·10.5(H2O) crystallizes in the triclinic space group \(P\bar{1}\) (SI Section 3), and comprises three components: i. a 3-dimensional host framework - [Cu(btc)2(s)(ade)(Hade)(μ2-\(\mu\))-OH)(H2O)]·0.4[Cu(ade)(H2O)]·10.5(H2O), ii. guest mononuclear complexes that are partially occupying the void channels within the host SION-10 - 0.4[Cu(ade)(H2O)]·10.5(H2O), and iii. highly disordered guest H2O solvent molecules. The host framework of SION-10 is based on Cu-paddlewheel units, in which two Cu1
atoms are bridged by two deprotonated ade$^{-}$ ligands via an $\eta^1$-$\eta^1$ binding mode through their N3 and N9 atoms (ade$^{-}$ colored in green – Figure 1a). The neutral 1Hade ligand is coordinated via N7 to the axial sites of the Cu-paddlewheel (1Hade colored in orange – Figure 1a). The coordination of the paddlewheel is completed by the two bridging carboxylates from two crystallographically equivalent btc$^{2-}$ ligands. The Cu-paddlewheel units are connected to each other via a tetranuclear Cu-cluster, Cu$_4$(µ$_2$-OH)$_2$ (Figure 1b), constructed from four Cu(II) centers (two Cu2 and two Cu3) linked by two µ$_2$-hydroxo groups.$^{[20]}$ All Cu2 and Cu3 display a square pyramidal coordination geometry. The apical positions of these pyramids are occupied by H$_2$O molecules coordinated to Cu(II) through considerably long bonds (Cu2–O2 2.431(6) Å, Cu3–O3 2.424(6) Å). A single Cu4 atom, also with a square pyramidal coordination geometry, bonds to two btc$^{2-}$ ligands (monodentate – yellow and bidentate – pink), one ade$^{-}$ and one H$_2$O molecule (Cu4–O4 2.211(0) Å - Figure 1c), and acts as a link between Cu-paddlewheel units and tetranuclear Cu-clusters. The host framework of SION-10 displays an accessible volume of 37.9%, as determined by PLATON.$^{[26]}$

The cavities of the host SION-10 framework are occupied by mononuclear complexes with the formula of [Cu(ade)$_2$(H$_2$O)$_4$]$^-$ present with 80% partial occupancy (Figures 1d, and S3). The octahedrally coordinated Cu5 of the complex displays a Jahn–Teller distortion with two long Cu–N(ade) bonds (2.226(17) Å), two long Cu–O$_2$ bonds (2.24(2) Å), and two short Cu–OH$_2$ bonds (1.941(14) Å) (Figure 1d). The complex displays $\pi$-$\pi$ stacking interactions between the pyrimidine ring of the ade$^{-}$ group and the phenyl ring of the btc$^{2-}$ ligand with a distance of about 3.7 Å (Figure S4), and is involved in an array of hydrogen bonds that stabilize its position within the framework cavities (Figure S5). Our attempts to wash the Cu(II)-complexes out were not successful, confirming that they cannot be removed from the host SION-10 framework. Interestingly, molecular crystals of Cu(ade)$_2$(H$_2$O)$_4$, are not known, and the theoretically predicted structure of this complex$^{[27]}$ is markedly different from the one reported in this work. Thus, SION-10 represents a typical example of a ship-in-a-bottle material. It is worth noting here that although the encapsulation of molecular species in the pores of a MOF is known,$^{[28]}$ the direct observation of them as a part of a refined crystal structure is rather rare.$^{[29]}$ The accessible volume of SION-10 (with the complexes present within the channels) was found to be 20.3%,$^{[26]}$ revealing that the complexes occupy nearly half of the accessible volume of the host-framework voids.

The phase purity of SION-10 was confirmed by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) and elemental analysis (EA), whereas the thermogravimetric (TGA) profile coupled with the variable-temperature (VT) PXRD study revealed the thermal stability of SION-10. The PXRD pattern of SION-10 (Figure 2a) can be indexed to unit-cell parameters consistent with the parameters obtained from SCXRD (SI Section 5). SEM images reveal only one type of crystal morphology (Figure S14). Elemental and inductively coupled plasma (ICP) analyses confirm that the [Cu(ade)$_2$(H$_2$O)$_4$] complex is not 100% present within the pores as the composition of SION-10 can fit to the formula derived from the SCXRD data (SI Section 5c). FTIR spectra show characteristic features originating from both

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Figure 1. The structure of SION-10 consists of: a. Cu1-paddlewheel units which are linked to b. Cu2Cu3 tetranuclear clusters Cu$_4$(µ$_2$-OH)$_2$ and c. mononuclear Cu4 to extend the structure in 3-dimensions. d and e. The pores of the host SION-10 accommodate guest mononuclear Cu5-complexes generating a material with ship-in-a-bottle structure. Atom color code: C gray, H pale yellow, N blue, O red, Cu cyan.

Figure 2. Le Bail fits of a. SION-10 and b. SION-10′ collected at 288 K using the Cu Kα. The blue plots represent the experimental data, the red dots show the refined Le Bail profiles while the green plots represent the difference between them. SION-10′ is porous to: c. N$_2$ at 77 K and 900 mbar and d. CO$_2$. 

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ligands present in the structure of SION-10 (Figure S11). The TGA profile of SION-10 shows that the coordinated and guest H$_2$O molecules can be removed in the temperature range of 30–265 °C with the total loss of 20.8% (Figure S9). The weight loss observed in TGA is in good agreement with the weight loss calculated from the EA (20.0%). Above 250 °C a substantial decrease in crystallinity is observed from the VT PXRD study (Figure S6) and the decomposition of SION-10 starts at 295 °C. As confirmed by PXRD (Figure S8) SION-10 is stable in liquid water as well as in acidic and basic aqueous solutions, thus confirming its hydrolytic stability.

The activated SION-10 was generated by heating the as-synthesized SION-10 at 120 °C under vacuum (10$^{-3}$ mbar). The weight loss of 19.8 % is consistent with the weight loss observed by TGA and EA. The PXRD pattern of SION-10′ (Figure 2b) shows the retention of crystallinity and Le Bail fits revealed that the unit cell is contracted by 3.5% compared to the cell parameters of SION-10 (SI Section 5a). When SION-10′ is exposed to the atmosphere for 1-2 hours or is immersed in liquid H$_2$O (10 mins), SION-10 can be recovered. This suggests that SION-10′ with open Cu(II) sites has high affinity for H$_2$O, and thus the re-coordination of H$_2$O molecules to Cu(II) leads in the generation of the ordered SION-10 structure. SION-10′ is permanently porous to N$_2$ at 77 K and 1 bar, exhibiting a reversible type I sorption behavior characteristic for microporous materials (Figure 2c). Application of the Brunauer–Emmett–Teller (BET) model in the relative pressure p/p$_0$ range of 0.02–0.22 results in a surface area of ~300 m$^2$/g. The calculated pore volume of SION-10′ is 0.138 cm$^3$/g, which is in good agreement with the pore volume derived from the single crystal data of the static structure of SION-10 (0.132 cm$^3$/g).

SION-10′ is porous to CO$_2$ and CH$_4$ at 273 and 298 K (type I isotherms, Figure 2d) and the isosteric heat of adsorption Q$_s$ at zero coverage derived from the virial-type expression are 30.8 kJ/mol for CO$_2$ and 21.3 kJ/mol for CH$_4$.

Since the complexes do not block the porosity in SION-10′ where open Cu(II) are present, and both polar and non-polar molecules can diffuse in the accessible voids, we subjected SION-10′ to NH$_3$ adsorption, with the NH$_3$ vapor generated by evaporation of a 25% ammonial solution at room temperature. Upon exposing the green powder of SION-10′ to NH$_3$ vapor, a color change was immediately noticed and the green color changed to blue, whilst its shade deepened over a loading period of 30 mins (Figure 3c, inset). The formula of SION-10′$\cdot$NH$_3$ (30 mins loading) corresponds to [Cu$_2$(btc)$_2$][ade](11Hade)$_2$(μ$_1$-OH)(NH$_3$)$_2$]$_{0.4}$[Cu(ade)$_2$(NH$_3$)$_4$] 4(NH$_3$)$\cdot$6.5(H$_2$O), revealing that the amount of chemisorbed NH$_3$ was 6.37 mmol/g (SI Section 5c and Figure S10). NH$_3$ molecules displace all H$_2$O ligands previously coordinated to Cu(II), and a part of non-coordinated H$_2$O guest molecules. In order to further evaluate the capability of SION-10′ to selectively capture NH$_3$, we have performed a breakthrough experiment using a 10mL min$^{-1}$ flow of N$_2$/NH$_3$ (9:1) gas mixture at 303 K (Figure 3a). At the NH$_3$ partial pressure of 0.1 bar SION-10′ exhibited the adsorption capacity of 27.3 mmol/g. In a separate experiment, the adsorption capacity of SION-10′ at the N$_2$ partial pressure of 0.9 bar and at 303 K was investigated (Figure S13). The amount of N$_2$ adsorbed (0.170 mmol/g) was significantly lower than that of NH$_3$, resulting in a NH$_3$/N$_2$ selectivity factor of 1440. This result is indicative of a selective and strong interaction of NH$_3$ molecules with SION-10′ due to chemisorption (presence of active Cu(II) centers) and physisorption (narrow pores of SION-10′), and places SION-10′ among materials with the highest NH$_3$ capacity reported up to date.

Interestingly, the color change experienced by the NH$_3$ loaded SION-10′ was also observed when the as-made SION-10 was exposed to NH$_3$ vapors. The immersion of the blue SION-10$\cdot$NH$_3$ in liquid water resulted in the isolation of a green material suggesting that SION-10 could potentially be recovered. The PXRD patterns show that although the crystallinity of SION-10$\cdot$NH$_3$ is reduced to a significant degree, the recovered material displays the same pattern as with SION-10, confirming the regeneration of SION-10 (Figure S7). The FTIR spectrum of SION-10$\cdot$NH$_3$ (Figure S3b) shows a nearly identical pattern with that of SION-10 with characteristic bands at 3400–3300 cm$^{-1}$.
and 1640 cm\(^{-1}\), corresponding to the N–H, O–H, and C=O stretching bands of the ade\(^{2}\), the OH\(^+\) bridge/H\(_2\)O molecule, and the C=O of the btc\(^{3}\) ligand, suggesting that despite the low crystallinity it has the same structural fingerprint as SION-10. To further investigate the impact of NH\(_3\) uptake by SION-10 and its regeneration, the UV/Vis diffuse reflectance spectra were collected (Figure 3c). The UV/Vis spectra revealed a blue-shift of –70 nm of the Cu(II) d–d transition band of SION-10–NH\(_3\) compared to SION-10, suggesting the formation of new Cu–NH\(_3\) bonds that are formed after the stronger-field NH\(_3\) ligands substitute the weak-field H\(_2\)O ligands bound to Cu(II) centers. The recovered SION-10 displayed a comparable absorption band compared to the pristine SION-10, indicating that SION-10 could be recycled, and we successfully performed three NH\(_3\) adsorption-desorption NH\(_3\) cycles (Figure 3c). Previous studies demonstrated that the presence of open metal sites within MOFs are key factors for the capture of NH\(_3\). However, MOFs endowed with open metal sites were shown to reduce their porosity and crystallinity to a considerable extent when loaded with NH\(_3\) vapor.\(^{[22]}\) For SION-10, we strongly believe that the combination of narrow pores generated from the presence of the complexes, and the presence of active Cu(II) sites are the key factors for the efficient capture of NH\(_3\).

The substantial green-to-blue color change was not observed with other gases (such as CO\(_2\), N\(_2\), and CH\(_4\)) suggesting that SION-10 can also act as a selective detector for NH\(_3\) vapor. When 5 mg of SION-10 were exposed to controlled atmospheres of NH\(_3\) with concentrations of 300 and 600 ppm, the shifts of the absorption bands were clearly observed (Figure S12), indicating the relatively high sensitivity of SION-10 toward NH\(_3\). In addition, the fast response time, i.e., immediate color changes, ensures that SION-10 can quickly detect the presence of NH\(_3\) in the atmosphere. The high thermal sensitivity and hydrolytic stability together with the uptake of NH\(_3\), and its recyclability confirm that SION-10 can be potentially used as a dual detector and adsorbent for NH\(_3\).

In conclusion, we report the synthesis of a ship-in-a-bottle SION-10 material that is stable in water, and upon activation it is porous to N\(_2\), CO\(_2\), and CH\(_4\). The presence of the mononuclear Cu(II) complexes decorate the pores of the host SION-10 with active Cu(II) sites that allow NH\(_3\) to be chemisorbed. SION-10 adsorbs up to a paramount value of 27.3 mmol of NH\(_3\) per gram (chemisorption and physisorption) which is one of the highest NH\(_3\) uptake reported to date. The high sensitivity and selectivity of SION-10 toward NH\(_3\) makes SION-10 the first MOF that can quickly uptake NH\(_3\), easily regenerated and reused. In addition, it can detect NH\(_3\) at concentrations as low as 300 ppm. This work demonstrates a step forward toward the discovery of versatile, easily prepared and recyclable MOFs acting as dual detectors and adsorbents for NH\(_3\) and further synthetic efforts in developing novel porous and water stable MOFs sensitive to NH\(_3\) concentrations lower than 300 ppm are in progress.

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Keywords: metal-organic framework • ammonia • recyclability • ship-in-a-bottle • capture • detection


[25] The presence of the $\mu_3$-OH groups was confirmed by the bond valence sum calculation: $s = \sum(s_{ij}) = \sum(\exp(R_{ij}-d_{ij})/b)$, where $R_{ij}$ = 1.649 for Cu(II)-O, $d_{ij}$ is the Cu(II)-O bond distances, $b$ = 0.37. The value obtained was 1.23. For O, a value of 0-0.4 indicates $H_2O$, 1-1.4 indicates OH, and 1.8-2.2 indicates $O_2$.


Response to Ammonia. SION-10, a water stable and porous ship-in-a-bottle structure, uptakes NH$_3$ spontaneously and displays high sensitivity toward this hazardous gas. The SION-10$\supset$NH$_3$ can be easily regenerated and recycled for at least three times.