

Exceptional ammonia uptake by a covalent organic framework

Christian J. Doonan, David J. Tranchemontagne, T. Grant Glover, Joseph R. Hunt and Omar M. Yaghi*

Covalent organic frameworks (COFs) are porous crystalline materials composed of light elements linked by strong covalent bonds. A number of these materials contain a high density of Lewis acid boron sites that can strongly interact with Lewis basic guests, which makes them ideal for the storage of corrosive chemicals such as ammonia. We found that a member of the covalent organic framework family, COF-10, shows the highest uptake capacity (15 mol kg^{-1} , 298 K, 1 bar) of any porous material, including microporous 13X zeolite (9 mol kg^{-1}), Amberlyst 15 (11 mol kg^{-1}) and mesoporous silica, MCM-41 (7.9 mol kg^{-1}). Notably, ammonia can be removed from the pores of COF-10 by heating samples at 200°C under vacuum. In addition, repeated adsorption of ammonia into COF-10 causes a shift in the interlayer packing, which reduces its apparent surface area to nitrogen. However, owing to the strong Lewis acid-base interactions, the total uptake capacity of ammonia and the structural integrity of the COF are maintained after several cycles of adsorption/desorption.

Covalent organic frameworks (COFs) are porous crystalline materials constructed by linking light elements such as carbon, boron, oxygen and silicon through strong covalent bonds^{1–6}. An attractive feature of some COFs is the high density of Lewis acidic boron atoms, present in boroxine (B_3O_3) or boronate ester ($\text{C}_2\text{O}_2\text{B}$) rings, which are an integral component of their frameworks. These boron sites present a unique adsorbent surface ready for interaction with Lewis basic gases such as ammonia, in a manner similar to the classical ammonia–borane coordinative bond (Fig. 1a).

Ammonia is transported as a compressed liquid for use in a wide variety of industrial applications and is toxic, corrosive and difficult to handle; hence we sought to take advantage of the reversible formation of molecular ammonia–boranes⁷ and to examine the ability of COF materials to act as high-surface-area adsorbents for the uptake and release of ammonia. We therefore screened a series of two- and three-dimensional members of the COF family for their potential to reversibly uptake and release ammonia (Supplementary Figs S1, S2). We discovered that COF-10 (Fig. 1b) shows the highest capacity (15 mol kg^{-1}) for ammonia storage in a porous solid and, remarkably, ammonia can be released and re-adsorbed in a reversible manner although retaining its structural order.

Results and discussion

COF-10 was prepared according to previously published procedures³. Its structure comprises hexahydroxytriphenylene (HHTP) and biphenyldiboronic acid (BPDA) building units linked into porous hexagonal layers (Fig. 1b). These layers are stacked in an approximately eclipsed pattern to give a **bnn** (ref. 8) type structure with one-dimensional pores with diameters of 34 \AA . Each hexagonal ring contains 12 boron atoms as part of the five-membered boronate ester rings ($\text{C}_2\text{O}_2\text{B}$). An ammonia adsorption isotherm was measured on COF-10 at 25°C (Fig. 2). The isotherm profile is best described as Type IV, which is indicative of a mesoporous material⁹. Further evidence for this is provided by the low uptake at pressures below 150 torr, beyond which COF-10 shows exceptional uptake (15 mol kg^{-1}), significantly outperforming the state-of-the-art materials Zeolite 13X (9 mol kg^{-1}) and Amberlyst 15 (11 mol kg^{-1})¹⁰. The hysteresis observed for

COF-10 is attributed to the strong adsorption behaviour of ammonia⁹. However, 80% (12 mol kg^{-1}) of the adsorbed ammonia can be removed by applying vacuum (0.1 torr), and the remaining ammonia can be completely removed by heating to 200°C at that pressure. The ammonia isotherm of MCM-41 at 298 K was collected for comparison because of its similar pore dimensions to COF-10, and is also displayed in Fig. 2. In this pressure region, the MCM-41 ammonia isotherm most resembles a Type I profile, with a total ammonia uptake capacity of 7.9 mol kg^{-1} at 760 torr, approximately half that of COF-10. Additionally, only a relatively small hysteresis is observed compared to COF-10, which is attributable to capillary filling rather than strong surface/adsorbate interactions⁹.

A noteworthy feature of COF-10 is that repeated ammonia adsorption/desorption cycling does not result in any significant loss of ammonia uptake capacity. Figure 3a displays three successive ammonia isotherms collected for a COF-10 sample with a surface area of $1,200 \text{ m}^2 \text{ g}^{-1}$, subsequent to adsorption/desorption cycles, each cycle comprising ammonia adsorption followed by a regeneration step (200°C for 12 h at 0.1 torr). These data show that the total ammonia uptake decreases by only 4.5% between the first and third cycles. Each of the ammonia isotherms has a large desorption hysteresis that persists to the low-pressure region of the isotherm. Such behaviour has been observed for the adsorption of polar adsorbates in layered clay minerals and is attributed to intercalation of the adsorbate in the interlamellar region of the material¹¹. In the second and third ammonia adsorption cycles, strong hysteresis is also observed. However, a steeper ammonia uptake is observed in the low-pressure region (<450 torr) of these cycles. This is consistent with an increase in the micropore character of COF-10 (ref. 9). The changes in the ammonia adsorption isotherms are also consistent with the changes in the calculated pore size distributions (Supplementary Fig. S3).

The pore size distribution calculations clearly show the evolution of the mesoporous COF-10 structure to one that contains a broad range of pores of ~ 10 – 30 \AA . A plausible explanation for this is that the intercalating ammonia molecules push the COF-10 layers apart, thus disrupting the intermolecular stacking forces¹. Subsequent removal of the ammonia results in a turbostratic

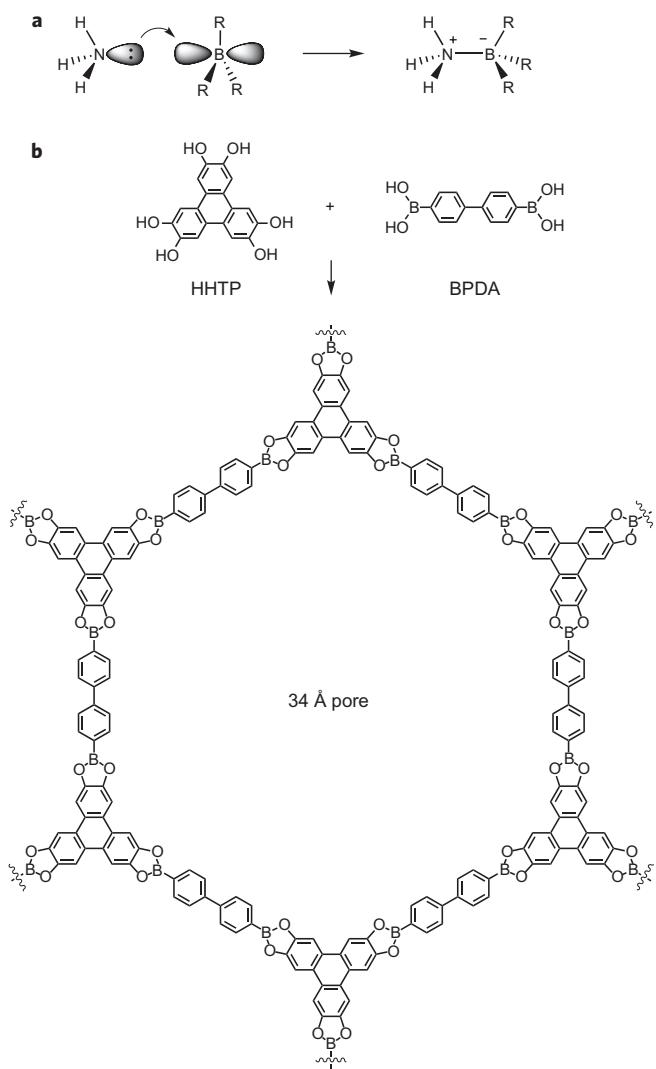


Figure 1 | Construction of COF-10 for ammonia storage. **a**, Ammonia–boron (Lewis acid–base) interactions present on the surface of COF-10. **b**, Schematic representation of a COF-10 pore showing its atom connectivity (bottom) and its organic building blocks (top).

repacking that obscures the mesoporous channels. Such structural changes are consistent with the nitrogen isotherms (Fig. 3b) collected subsequent to each ammonia run, which show decreasing total capacity but increasing micropore filling character⁹. The decrease in nitrogen uptake is not concomitant with that of ammonia as it lacks the strong Lewis acid–base interactions with boron and thus does not penetrate the interlamellar region. Additionally, given the smaller size of ammonia (2.56 Å) compared with nitrogen (3.64 Å)¹², a lower total uptake can be rationalized and has previously been documented for the adsorption of ammonia on graphite oxide¹³. Nevertheless, we note that a significantly higher uptake of ammonia in the lower-pressure region is observed for the second and third cycles than in the first, thus suggesting a rich structural chemistry resulting from the adsorption process.

Although the adsorption of ammonia disrupts the interlayer packing, it is evident from powder X-ray diffraction (PXRD) collected on samples of COF-10 after cycling of ammonia (Fig. 4) that complete turbostratic structural disorder does not occur. Careful analysis indicates that the low angle peaks, corresponding to the (100), (110) and (200) planes, broaden and decrease in intensity subsequent to each cycle, which is suggestive of increasing

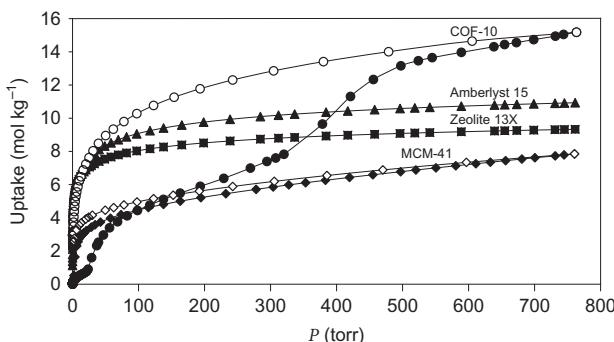


Figure 2 | Ammonia uptake in state-of-the-art materials and COF-10.

Comparison of total ammonia uptake capacities at 298 K and 760 torr of COF-10 (15 mol kg⁻¹, circles), Amberlyst 15 (11 mol kg⁻¹, triangles), Zeolite 13X (9 mol kg⁻¹, squares) and MCM-41 (7.9 mol kg⁻¹, diamonds). Adsorption and desorption points are represented by closed and open symbols, respectively.

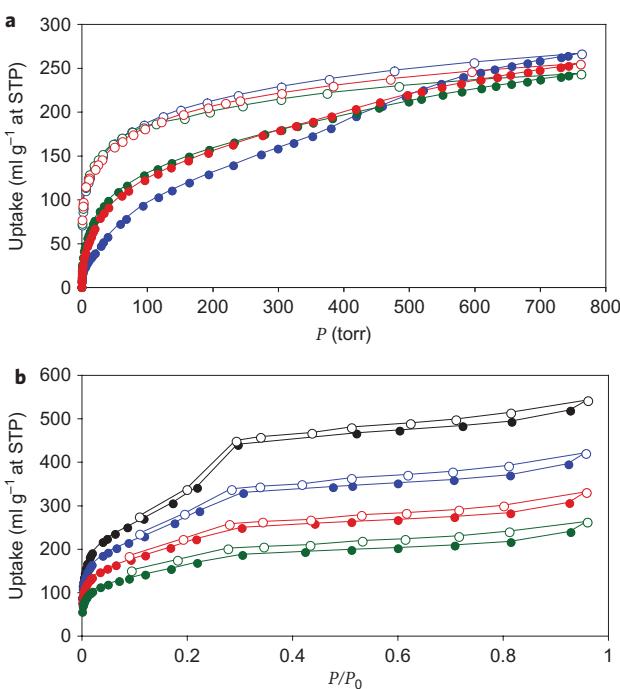


Figure 3 | Ammonia uptake and release in COF-10. **a**, First (blue), second (red) and third (green) successive ammonia 298 K adsorption isotherms of a sample of COF-10. Subsequent to each adsorption/desorption cycle, the sample was regenerated at 200 °C and 0.1 torr. **b**, Nitrogen gas adsorption isotherms (77 K) performed on the same COF-10 material (black), after one cycle (blue), two cycles (red) and three cycles (green) of ammonia adsorption/desorption. Adsorption and desorption points are represented by closed and open circles, respectively. Connecting lines are guides for the eyes.

disorder in packing between layers, consistent with the decreasing mesoporous character and lower total uptake capacity observed in the nitrogen isotherms. To ensure that the connectivity of the COF-10 framework was sustained subsequent to the cycling of ammonia, ¹³C cross-polarization magic angle spinning (CP/MAS) nuclear magnetic resonance (NMR) spectra were collected on as-synthesized COF-10 and on samples after the three ammonia adsorption/desorption cycles (Supplementary Fig. S4). Indeed, identical peak positions are observed in the two samples, indicating that the connectivity of the COF-10 framework is not disrupted,

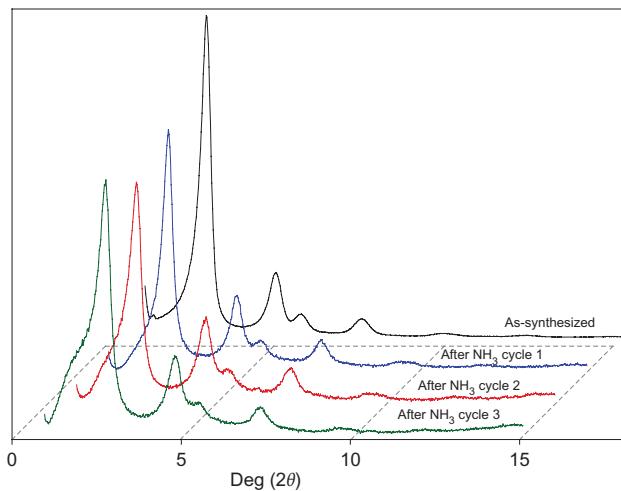


Figure 4 | Preservation of COF-10 structure during uptake and release cycles of ammonia. PXRD patterns, showing analogous peak positions of as-synthesized COF-10 material (black), after one cycle (blue), two cycles (red) and three cycles (green) of ammonia adsorption/desorption.

further supporting the notion that the reduction in the nitrogen capacity after ammonia cycling is the result of an increase in turbostratic disorder^{10,11}.

Given the high capacity of COF-10 for ammonia at 1 bar, one possible application for it is the transportation of ammonia as an adsorbed phase instead of a compressed liquid. This would provide a significantly safer means of transporting and using ammonia. Recent work has highlighted the possibility of using ammonia as a means of storing and transporting hydrogen^{7,14,15}. COF materials may provide a novel means of safely transporting and storing ammonia and for hydrogen fuel applications.

To investigate the potential for such applications, a binder-free tablet of pure COF-10 crystals was made using a conventional press at 2,000 psi. The nitrogen and ammonia adsorption capacity of the tablet was only slightly less than that of the pure COF-10 crystalline powder (Fig. 5). The loss of the mesoporous step at $P/P_0 \approx 0.4$ results from the mechanical disruption of the walls of the framework, leading to the material no longer providing the appropriate adsorbate-adsorbent wall interactions that produce rapid pore filling en route to condensation. Such behaviour is consistent with that observed for compressed samples of MCM-41 (refs 16,17). These results illustrate that COF materials not only have an exceptionally high capacity for ammonia, but also are sufficiently structurally robust to be compressed into tablets and pellets, which are the typical forms applied in industry when using adsorbent materials. Furthermore, the structural stability of COF tablets provides a means of taking advantage of this class of ultra-low-density crystals in a more compact volume.

This work presents the exceptionally high uptake of ammonia by COF-10 compared with state-of-the-art materials. The layered morphology of COF-10 seems to be disrupted during the adsorption cycles of ammonia, but atom connectivity and periodicity are maintained. We also show the full adsorption isotherms subsequent to the second and third cycles of ammonia and the remarkable result that, given that the handling and regeneration conditions are not optimized, only 4.5% of total uptake capacity is lost. It is noteworthy that the slight reduction in total uptake capacity is accompanied by a larger uptake at low pressure. The rich adsorption chemistry revealed in this work suggests that COF-10 may be a potentially viable material for the uptake and release of ammonia. Furthermore, we anticipate that analogous COF materials may be optimized for the capture and storage of other Lewis bases by

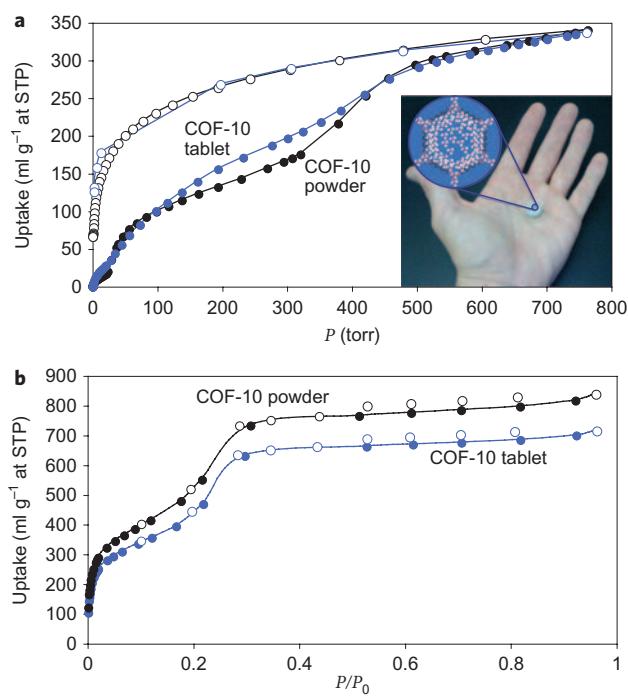


Figure 5 | COF-10 as a solid adsorbent for ammonia. **a**, Ammonia uptake at 298 K for COF-10 (black) and COF-10 tablet (blue). Inset, pressed tablet of COF-10 loaded with ammonia. **b**, Nitrogen gas adsorption isotherms (77 K) performed on the same COF-10 material (black) and COF-10 tablet (blue). Adsorption and desorption points are represented by closed and open circles, respectively. Connecting lines are guides for the eyes.

taking advantage of the interlayer adsorption interactions induced by their Lewis acidic surfaces.

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Author contributions

C.J.D and O.M.Y conceived and designed the experiments. All authors contributed significantly and collaboratively to performing the experiments, analysing the data and writing the paper.

Additional information

The authors declare no competing financial interests. Supplementary information accompanies this paper at www.nature.com/naturechemistry. Reprints and permission information is available online at <http://npg.nature.com/reprintsandpermissions/>. Correspondence and requests for materials should be addressed to O.M.Y.