

In situ tetrazole ligand synthesis leading to a microporous cadmium–organic framework for selective ion sensing†

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***In situ* tetrazole ligand synthesis leads to a luminescent microporous cadmium–organic framework $\{[\text{Cd}(\mu_2\text{-Cl})(\mu_4\text{-5MT})]_n$ (5MT = 5-methyl-1*H*-tetrazole) that exhibits a high-sensitivity sensing function with respect to nitrite in both DMF and water.**

The network approach to the design and synthesis of crystalline solids has produced a wide range of novel and useful coordination polymers, also known sometimes as metal–organic frameworks (MOFs).^{1,2} The field of porous MOFs has witnessed remarkable progress, and many novel functionalities and potential applications have been discovered, such as gas storage,³ separation⁴ and sensing.⁵ All of these properties have been shown to be heavily reliant on the specific pore size and the nature of the pore surface. The entry of small molecules into a porous MOF, for example, is determined by both the shape of the molecules, and the structural and pore characteristics of the MOF. Thus, similar to active sites in proteins, MOFs can be used for molecular recognition. When combined with a suitable sensing mechanism, such as photoluminescence (or the quenching of it), one can obtain a molecular sensor for applications in, for example, biological and environmental systems. Recently, intriguing recognition and sensing functions of lanthanide-based porous MOFs with respect to small solvent molecules and ions have been reported.⁶ However, work on d¹⁰ metal-based MOFs as luminescent probes for the sensing of small molecules has been very limited.⁷

An effective strategy to synthesize robust porous MOFs is the use of multifunctional ligands, and many high-dimensional microporous materials have been isolated based on this strategy.^{3,10,11} Demko and Sharpless pioneered a facile approach to the synthesis of 5-substituted 1*H*-tetrazoles, namely through the [2 + 3]-cycloaddition reaction of an azide with

nitriles in water aided by a Lewis acid.⁸ A number of research groups have continued to work in this field, and have isolated numerous coordination frameworks with intriguing structural motifs and functional properties.⁹ Recently, we reported a high-symmetry cubic coordination framework that exhibits reversible shrinking and expansion in a crystal-to-crystal dehydration/rehydration process.¹⁰

In this Communication, we present another highly-symmetric tetragonal MOF prepared *via* the *in situ* synthesis of the ligand 5-methyl-1*H*-tetrazole (5MT),[†] namely $\{[\text{Cd}(\mu_2\text{-Cl})(\mu_4\text{-5MT})]_n$ (**1**). The compound is thermally stable, luminescence active, and exhibits the capacity to both store hydrogen gas and selectively sense nitrite ions.

As-synthesized, compound **1** (Fig. 1a) is insoluble in water and common organic solvents. It was prepared by a simple hydrothermal reaction of cadmium chloride with azide in an acetonitrile/water mixture at 150 °C, and was characterized by elemental microanalysis, IR spectroscopy and single-crystal X-ray diffraction; phase purity was confirmed by powder X-ray diffraction (PXRD) and thermal gravimetric analysis (TGA) (see the ESI, Fig. S3 and S4†). The presence of a peak at 1371 cm⁻¹ in its IR spectrum showed the formation of tetrazole groups. TGA indicated that the framework of **1** was thermally stable up to 390 °C. The PXRD pattern of an as-synthesized powder of **1** was almost identical to that calculated from the single-crystal structure.

Compound **1** crystallizes in the non-centrosymmetric tetragonal space group $I42m$ and displays a very complicated 3D network. There are three unique Cd atoms, four unique 5MT ligands and four unique Cl anions (Fig. 2a). Each Cd bonds to four 5MT ligands and two *cis*-Cl anions, while each 5MT ligand bonds to four metal ions (two of the unique 5MTs lie across mirror planes) and each Cl anion bridges two metal atoms. The ligands bridge the metal atoms in a complicated 3D network. Concentrating on just on the Cd-5MT network, it is best described in terms of 1D columns (ESI, Fig. S5a†) in which Cd₂(C1-5MT)₄ rings (C1-5MT is the 5MT ligand containing C1 (green in Fig. 2)) are bridged by pairs of Cd₁Cd₃(C3-5MT)₂ ‘struts’ to create open-ended cavities *ca.* 9.65 Å across, which stack in such a way that each cavity is orientated 90° with respect to its neighbours (the columns lie about a $\bar{4}$ axis). These columns are then interconnected (ESI, Fig. S5b†) by the 5MT ligands that lie on mirror planes (C5- and C7-5MT) such that each column is connected to six others to give an overall 3D network (Fig. 2b, where the columns are viewed end-on). This connectivity is simply reinforced by the chloride bridges (ESI, Fig. S6†).

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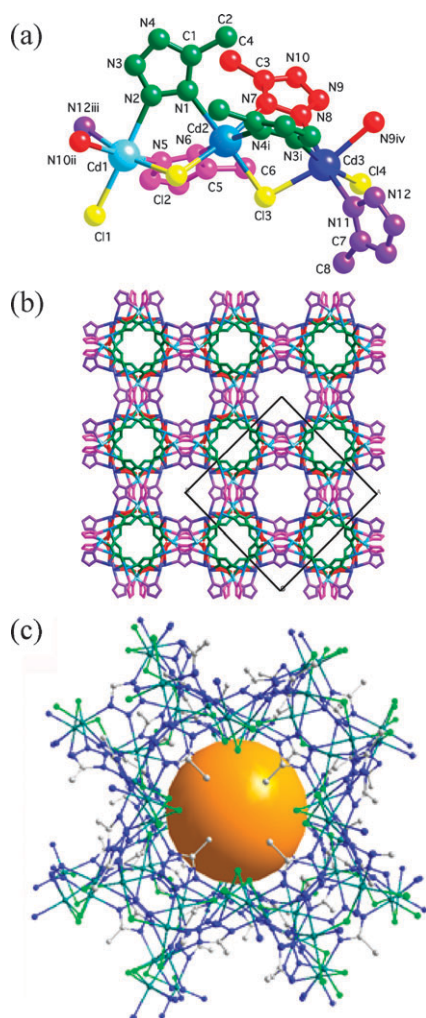


Fig. 1 (a) The asymmetric unit of **1**, (b) the 3D microporous framework viewed along the *c*-axis (methyl groups and chloride anions omitted for clarity) and (c) part of its microporous framework showing one of the large voids. Each crystallographically-unique Cd and 5MT moiety is coloured differently, and colours are consistent between (a) and (b). Symmetry codes: (i) $0.5 - x, 0.5 + y, 0.5 - z$; (ii) $0.5 - x, 0.5 - y, 0.5 + z$; (iii) $-0.5 + x, 0.5 - y, 0.5 - z$; (iv) $x, 1 - y, -z$.

A consequence of this packing arrangement is that further larger cavities are created between these columns (*ca.* $13.0 \times 14.7 \times 18.4 \text{ \AA}$ diameter; ESI, Fig. S7†). These large voids can be reversibly filled with small solvent molecules, as shown by the X-ray analysis of single crystals immersed in water for 1 d. The positions of individual water molecules were ill-defined, with no apparent order. However, analysis of the residual electron density¹¹ indicated that the voids were completely and densely filled with water molecules (*ca.* one water molecule per 33 \AA^3 , see the ESI for details†). The free water in the voids was largely removed upon drying at $80 \text{ }^\circ\text{C}$ overnight without collapse of the structure or detrimental effects on the single crystals. The size of the voids created by the removal of the water molecules was about 2994 \AA^3 , which is 32.5% of the unit cell volume.¹¹

Examination of the sorption properties of **1** for N_2 and H_2 suggested little N_2 sorption at 77 K . However, H_2 adsorption isotherms at this temperature indicated type I adsorption,

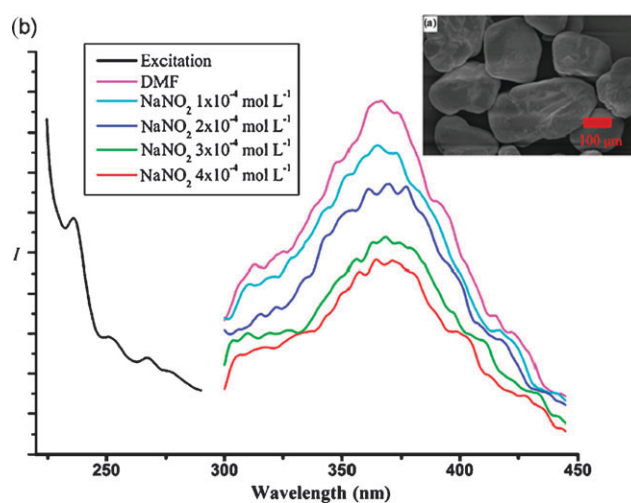


Fig. 2 (a) SEM view of as-prepared **1**. (b) Excitation and photoluminescence spectra of **1** in the solid state, and PL spectra of **1** after being treated in DMF solutions of NaNO_2 at different concentrations (excited and monitored at 236 nm and 370 nm , respectively).

characteristic of a microporous material (ESI, Fig. S1 and S2†). The H_2 uptake ($0.67 \text{ wt}\%$) of **1** at 77 K and 1 atm is comparable to that of the most favorable zeolite, ZSM-5 ($0.7 \text{ wt}\%$).

The interactions of **1** with different salt solutions containing the anions ClO_4^- , NO_3^- , NO_2^- , Cl^- and I^- in DMF were investigated by photoluminescence at room temperature. Fig. 3 shows the photoluminescence of **1** upon excitation at 236 nm . Compared with previous reports,^{7,10} the emission at around 370 nm is more likely to be due to intraligand transitions than to ligand-to-metal charge transfer (LMCT).¹² The luminescence intensity of **1** decreased continuously upon adding nitrite, while there was only a negligible effect on the luminescence intensity for other anions. Furthermore, a water suspension of **1** also exhibited the same luminescence response as the DMF suspensions (ESI, Fig. S9 and S10†). **1** can therefore be seen as a candidate for the selective sensing of nitrite.

The original framework could be regenerated from the solid containing intercalated nitrites after sensing tests by immersion in pure DMF or water suspension for 1 d. The

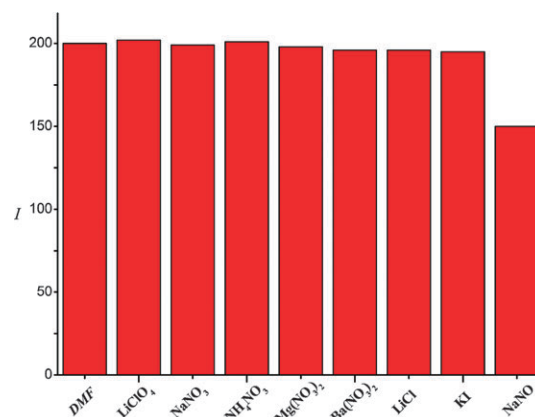


Fig. 3 Comparison of the luminescence intensity of **1** interacting with different ions in $1 \times 10^{-4} \text{ mol L}^{-1}$ DMF solutions of selected salts.

nitrite quenching effect remained in the regenerated solid. Hence, the permanent cavities show excellent reversibility for nitrite inclusion (see ESI, Fig. S8†).

A possible reason for the selective quenching of luminescence by nitrite may be that the size and shape of the cavities only allows the diffusion of the smaller nitrite anion into the framework and not those of the other oxoacid anions. X-Ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) clearly confirmed the incorporation of nitrite into the open framework. A peak from the intercalated solid at 46 mass units, not present in as-prepared **1**, is attributed to the NO₂⁻ fragment (ESI, Fig. S11†), indicating the capture of nitrite in the microporous framework. A peak at around 1080 eV in the Na 1s XPS spectra is ascribed to free Na⁺ ions (ESI, Fig. S12†). The intensity enhancement is not dependent on the cation (*i.e.* Li⁺, Na⁺) as no signal increase was observed with the corresponding LiClO₄ and NaNO₃ solutions. We believe that the luminescence quenching by nitrite can be ascribed to energy transfer through C–H···O hydrogen bonding interactions between methyl groups and the nitrite ions.¹³

In summary, we have prepared a new tetrazole-based microporous MOF *via* a facile *in situ* tetrazole ligand synthesis that is expected to play a crucial role in the recognition and selective sensing of anions based on its specific pore size and pore surface characteristics. The results confirm that further efforts should be concentrated on the rational design and construction of microporous luminescent MOFs with tuned pore sizes and surface properties in order to achieve highly selective recognition with respect to different ions in the near future.

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Notes and references

† Synthesis of {[Cd(μ₂-Cl)(μ₄-5MT)]_n: A mixture of CdCl₂·2H₂O (0.219 g, 0.5 mmol), NaN₃ (0.032 g, 0.5 mmol), pyridine-4-sulfonic acid (0.080 g, 0.5 mmol), CH₃CN (3 mL) and H₂O (7 mL) was sealed in a 20 mL Teflon-lined reactor. This was then heated in an oven to 150 °C for 50 h, then cooled to room temperature at a rate of 5 °C h⁻¹. Colorless block crystals were obtained in 65% yield based on Cd. Elemental analysis calc. for **1** (C₆H₉Cd₃Cl₃N₁₂): C, 10.40; H, 1.31; N, 24.26. Found: C, 10.43; H, 1.34, N, 24.24%. Main IR frequencies (KBr/cm⁻¹): 3450, 2923, 1630, 1493, 1371, 1263, 1161, 1055 and 694. **Warning: sodium azide is potentially explosive under hydrothermal reaction conditions.**

All crystallographic measurements were made on a Bruker SMART APEX II CCD area detector with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) operated at 2000 W power (50 kV, 30 mA). The structure was solved by direct methods and subsequent difference Fourier syntheses using the SHELXTL software suite. All non-hydrogen atoms were refined anisotropically. Crystallographic data for **1**: tetragonal *I*42m, *a* = 22.2338(1), *c* = 18.6223(2) Å, *V* = 9205.78(11) Å³, *Z* = 16, μ(Mo-K_α) = 3.108 mm⁻¹, ρ = 1.999 g cm⁻³,

T = 296 K, reflection numbers collected = 48 756, unique reflections (*R*_{int}) = 4955 (0.0539), *R*₁ [*I* > 2σ(*I*)] = 0.0319, w*R*₂ (all data) = 0.0743, GOF = 1.055.†

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