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Molecular sensing and discrimination by a luminescent terbium–phosphine oxide coordination material†

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PCM-15 is a robust and recyclable sensor for the effective discrimination of a wide range of small molecules. Sensing is achieved by direct attenuation of the luminescence intensity of Tb(III) ions within the material. A competition study involving trace amounts of NH_3 in H_2 gas shows that PCM-15 can be used to quantitatively detect trace analytes.

Porous coordination polymer (PCP) materials attract wide-spread attention, particularly for small molecule storage and separation.[1] PCPs are thermally and chemically robust, while the physical properties such as size, shape and chemical composition of the pores can be tailored towards selective adsorption of a wide range of guest molecules.[2] Chemical sensing by PCPs is an intriguing application that has been suggested, but remains much less extensively studied.[3] A useful PCP-based sensor would exhibit a measurable and reversible change, induced by host–guest chemical interactions inside the pores, and would be reversible over many cycles.[4] The inherently high surface areas exhibited by PCPs should also allow for very small amounts of material to provide a sufficient sensor response in implemented devices.

The vast majority of known PCP materials contain coordinatively-saturated metal cations and therefore do not offer a convenient spectroscopic handle for guest adsorbate sensing. PCP sensors might be prepared by: (i) incorporation of metal ions that show a measurable response to external stimulus (*e.g.*, light,[5] magnetism,[6] temperature[7]); (ii) direct, or post-synthetic incorporation of guest-responsive organic moieties;[8] and, (iii) exploitation of bulk guest-induced properties of PCP single crystals (*e.g.*, vapochromism).[9] Route (i) has attracted the most significant attention, primarily because a number of metals that are photoluminescent can be directly incorporated into PCPs as the framework cations.[10,11] The photoluminescence of Ln(III)-based materials is known to be sensitive to the coordination environment of the metal ion.[12] However, in reported examples of luminescent Ln(III)-based PCPs where the metal sites are coordinated exclusively to organic ligand anions, the absorption and emission wavelengths/intensities do not vary significantly due to guest species adsorbed in the pores. Vibrationally-coupled luminescence quenching is a short-range phenomenon that diminishes as a function of R^6 (R = donor–acceptor separation).[13] So, in order to utilize relative luminescence in a PCP as a sensor to identify and discriminate between adsorbed species, it is necessary to incorporate labile ligands on the metal centres. Post-synthetic removal thus generates vacant coordination sites and allows guest molecules to interact closely with the luminescent metal sites, thus facilitating quantifiable luminescence quenching.

We recently reported a Tb(III)-based phosphine oxide coordination material, $[Tb(tctpo)(OH_2)]\cdot 2dmf\cdot H_2O$ (PCM-15; tctpo = $P(=O)(C_6H_4-CO_2)_3$), which is a highly robust three-dimensional coordination material with a two-dimensional pore network.[14] The largest pore windows in PCM-15 measure 14.2 Å (diagonal distance Tb–P; Fig. S1, ESI†), permitting interior access to a broad range of small molecules. In addition to seven ligand-based donors, each Tb(III) ion has an eighth coordination site that is occupied by a terminal OH_2 ligand, which can be removed by heating at 423 K at 1×10^{-8} Torr for 1 h to obtain the 'activated' form of the material (Scheme 1). Each OH_2 ligand projects into the pore, so the resulting vacant coordination sites that are generated upon activation are accessible to guests. We previously showed that the photoluminescence intensity of Tb(III) sites in PCM-15 underwent a reversible two-fold increase upon dehydration of the crystalline material, thus acting as an efficient and direct probe for the hydration state of individual Tb(III) sites.[14] In the present work, we have studied in detail the luminescence quenching due to adsorption of fifteen different small molecule adsorbates, and have successfully performed competition experiments that demonstrate the ability of PCM-15 to sense low-level impurities.

Crystalline samples of PCM-15 were prepared in gram quantities by a low-temperature (358 K) reaction of $Tb(NO_3)_3$ and $tctpoH_3$ in DMF–THF–OH_2 solvent.[14] Thermogravimetric analyses (TGA; Fig. S2–S5, ESI†) and bulk powder X-ray diffraction (PXRD; Fig. S6 and S7, ESI†) patterns of as-synthesized, desolvated and resolvated PCM-15 samples confirmed that the material consistently retained its structural integrity upon

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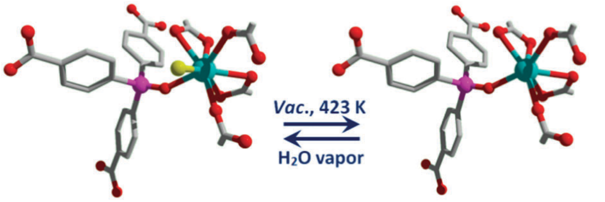

Scheme 1 Left: expanded view of the asymmetric unit in as-synthesized PCM-15; right: after removal of the single OH_2 ligand from the Tb(III) coordination sphere. Tb = cyan; P = magenta; OH_2 = yellow.

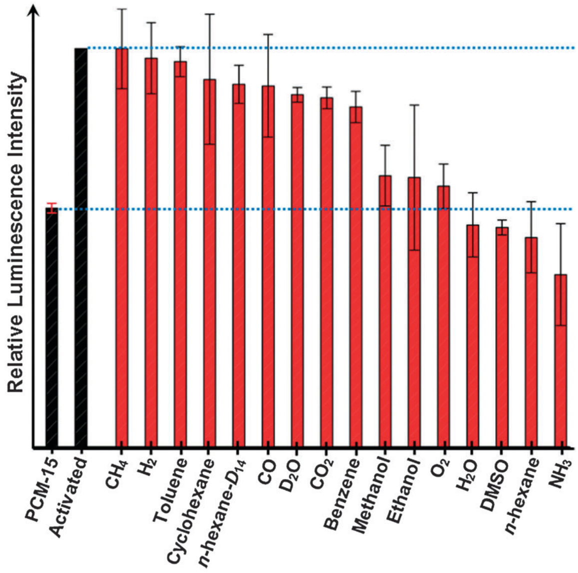

Fig. 1 Summary of the measured luminescence intensities and associated errors for activated PCM-15 in the presence of atmospheric pressures of various molecular adsorbates. All data is normalized *versus* the activated luminescence intensity.

exposure to a range of gas and vapour adsorbates, and after reactivation *in vacuo*.

PCM-15 has a bulk surface area of 1187 m^2 g^{-1} (BET method; CO_2). A custom cell (Fig. S8, ESI†) designed to be directly interchangeable between the gas adsorption analyser apparatus and the spectrophotometer cavity was employed, which allowed each sample of PCM-15 to be activated under vacuum, directly exposed to adsorbates *in situ*, and studied spectrophotometrically over many cycles without physical manipulation or exposure to air. In each study, a freshly-synthesized batch of PCM-15 (30–50 mg) was activated as described above and the luminescence quantum yield was measured to verify complete dehydration of the Tb(III) centres. Next, activated samples were exposed to 1 atm of each guest for 30 min. For gaseous adsorbates, the sample chamber was purged with ultra-high purity (UHP) gas; alternatively, anhydrous, degassed liquid adsorbates were vaporized with flowing UHP N_2 using an in-line bubbler. The resulting total luminescence quantum yields were then recorded and used to calculate the emissive lifetimes for each of fifteen different adsorbates; the data is summarized in Fig. 1 and Table S1 (ESI†). Each measurement was repeated three or more times using freshly-prepared samples of PCM-15 to provide error ranges as shown. It was possible to reactivate samples and recover the original luminescence behaviour using the standard activation conditions for all of the adsorbates studied.

Guest molecules that become adsorbed inside the pores of pre-activated PCM-15 could act as quenching agents, provided that: (i) they gain close proximity to the unsaturated Tb(III) centres in the pore walls (either *via* formal dative coordination to Tb, or *via* favourable dipolar interactions; see Scheme 1); or, (ii) there is sufficient Frank–Condon overlap between the corresponding overtone of the vibrational oscillator and the excited state of the Tb(III) ions. To confirm this hypothesis, the luminescence quenching ability of a broad range of guest adsorbates was studied in PCM-15 (Fig. 1). Perhaps the most immediately striking trend is the large variation of total luminescence quenching that was observed, in which only three of the fifteen adsorbates studied resulted in more quenching than the fully solvated parent material (Fig. 1, blue dotted line). The q_{corr} value for H_2O deactivation of the Tb(III) excited state in this system was determined to be 1.65 by the method of Beeby *et al.*[15a] This is consistent with the structural and TGA data used to determine that there are two water molecules per asymmetric unit in PCM-15 (a single bound water molecule and a second solvate H_2O closely associated with each Tb(III) site). As a control study, an activated PCM-15 sample was exposed to an atmosphere of D_2O in N_2 gas. The resulting luminescence intensity was only found to be partially reduced since the vibrational frequency of O–D bonds are lower (Fig. 1).[15b] The H_2O–D_2O data yield a quenching constant for water (q_{corr} = 1.20) which is internally consistent with the activation studies (*vide supra*) and the structural and TGA analyses.

Of the other fourteen adsorbates studied in this work, only NH_3, dimethylsulfoxide (DMSO) and *n*-hexane were found to be more effective quenching agents than H_2O. The quenching effectiveness of NH_3 is much higher than that observed in molecular systems, where it has been shown that each N–H oscillator is 52% as effective at quenching Tb(III) emission when compared to O–H oscillators.[16] N–H and O–H oscillators were observed to be equally effective quenchers with the difference in measured intensity coming from the increased number of oscillators per NH_3 molecule bound to the Tb(III) ions. The absolute uptake of a single equivalent of NH_3 per Tb in activated PCM-15 was confirmed by elemental analysis. The highly effective nature of NH_3 as a quenching guest can be emphasized by calculating the apparent number of N–H oscillators using the method developed by Wang *et al.*[16] This predicts a quenching due to the presence of ≈30 N–H oscillators based on comparison to molecular species in solution. This is consistent with the presence of a completely open coordination site per Tb with no requirement for competitive ligand exchange. DMSO is also a favourable ligand for Ln(III) ions *via* $(H_3C)_2S{=}O$–Tb coordination and the higher quanta of the C–H and S=O stretching vibrations can promote effective luminescence quenching.[15a]

The observed quenching effect of anhydrous *n*-hexane was more surprising since hydrocarbon solvents do not usually quench Ln(III) luminescence. Sorption–desorption isotherms were collected for *n*-hexane in activated PCM-15 which revealed reversible type-I sorption behavior and a capacity of 10.2 wt% (p/p_0 = 0.94) or 0.67 *n*-hexane molecules per PCM-15 formula unit (Fig. S8, ESI†). The confirmation that *n*-hexane was adsorbed into the pores of PCM-15 led us to believe that quenching was being observed, presumably *via* C–H vibrational modes of alkanes in close proximity of unsaturated Tb(III) sites. In support of this assumption, sorption of anhydrous d_{14}-hexane resulted in only minimal quenching (Fig. 1). By comparison, the *n*-hexane and d_{14}-hexane rate constants for depopulation of

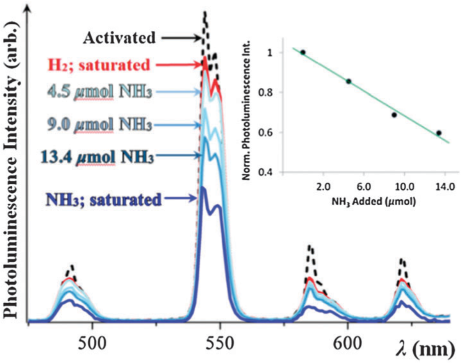

Fig. 2 Relative luminescence quenching observed as a function of NH_3 concentration in an H_2-saturated sample of PCM-15; inset: calibration curve showing linear response ($R^2 = 0.99$).

the Tb(III) excited states gave a Δk of 0.762 ms^{-1}, which is within the range of previous values of Ln(III) quenching observed for C–H oscillators (0.15–1.11 ms^{-1}).[15a]

Apolar adsorbates including CH_4, H_2, toluene and cyclohexane were not found to induce any significant quenching of the Tb(III) emission. CH_4 and H_2 adsorption isotherms for activated PCM-15 showed that both gases were fully adsorbed inside the pores, with modest total uptakes at 1.0 bar. It was also possible to confirm that the larger aromatic and aliphatic cyclic hydrocarbons were adsorbed inside PCM-15 (Fig. S8, ESI†). The total uptake of both toluene and cyclohexane at 0.95 bar (0.83 and 0.79 molecules per formula unit, respectively) and the observation of marked hysteresis in the desorption step confirmed that these were preferentially adsorbed inside the pores of PCM-15. However, neither facilitated luminescence quenching. Adsorption of methanol or ethanol into activated PCM-15 resulted in significant quenching, similar to that observed by H_2O. This is perhaps not surprising, as alcohols should be able to form weakly dative interactions to the Tb(III) centre, bringing O–H oscillators into close proximity. The adsorption–desorption profile of ethanol had a defined hysteresis, as observed in other PCPs (Fig. S8, ESI†).[17]

The potential application of PCM-15 as a sensor for the detection of small quantities of impurities was proven in a model study, in which trace amounts of a strong quencher (NH_3) were dosed into a non-quenching gas (H_2). A pre-activated sample was initially purged with H_2 gas at 298 K and the resulting photoluminescence intensity was recorded (Fig. 2, red line). Small aliquots of NH_3 (4.5 μmol) were then injected *in situ* and after each injection the relative change in luminescence intensity was recorded. As shown in Fig. 2, a clear decrease in the luminescence intensity was observed up to 13.4 μmol of NH_3 (corresponding to 0.25 equivalents of NH_3 per Tb(III)), significantly below saturation). The calibration curve obtained by integration of normalized photoluminescence intensity *versus* amount of added NH_3 confirmed a linear response in the region $NH_3/Tb \leq 0.25$ (Fig. 2, inset). The preferential and irreversible binding of NH_3 in H_2-loaded PCM-15 was also confirmed by treating an NH_3-loaded sample with H_2 gas, which did not result in NH_3 displacement (Fig. S9, ESI†). This study illustrates how PCM-15 may be utilized to quantitatively detect impurity levels in certain gas or vapour mixtures.

In summary, the Tb(III)–phosphine oxide coordination material PCM-15 can be utilized as an effective sensor for discrimination of a broad range of small molecule guest species, determined by relative luminescence quenching of Tb(III) sites. The measured quenching was shown to be directly proportional to amount of guest analyte within the pores. Due to the high density of Tb(III) sites in PCM-15, the luminescence intensity was easily detectable using only milligram quantities of sample; so, it could function as an effective sensor when incorporated into devices in dilute form (*e.g.*, impregnation into an inert matrix or membrane). The authors thank Dr V. M. Lynch (X-ray; Austin), the Welch Foundation (F-1738 & F-1631), The NSF (CHE-0847763; B.J.H.), and the Institutional Research Program (ISTK, SK-1210 and KK-1301-F0; J.W.Y. & J.-S.C.) for funding.

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