This paper is published as part of a *Dalton Transactions* themed issue entitled:

New Talent: Americas

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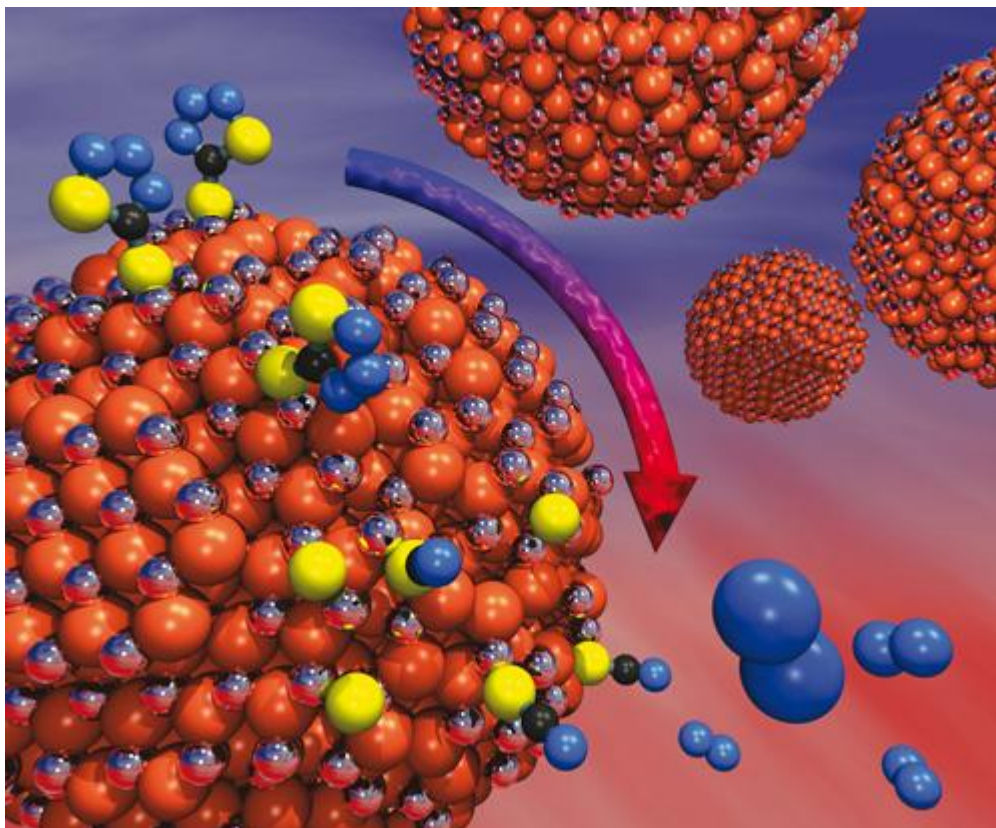Published in issue 26, 2012 of *Dalton Transactions*

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PAPER

Gas sorption and luminescence properties of a terbium(III)-phosphine oxide coordination material with two-dimensional pore topology†

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The structure, stability, gas sorption properties and luminescence behaviour of a new lanthanide-phosphine oxide coordination material are reported. The polymer PCM-15 is based on Tb(III) and tris(*p*-carboxylated) triphenylphosphine oxide and has a 5,5-connected net topology. It exhibits an infinite three-dimensional structure that incorporates an open, two-dimensional pore structure. The material is thermally robust and remains crystalline under high vacuum at 150 °C. When desolvated, the solid has a CO_2 BET surface area of 1187 m^2 g^{-1} and shows the highest reported uptake of both O_2 and H_2 at 77 K and 1 bar for a lanthanide-based coordination polymer. Isolated Tb(III) centres in the as-synthesized polymer exhibit moderate photoluminescence. However, upon removal of coordinated OH_2 ligands, the luminescence intensity was found to approximately double; this process was reversible. Thus, the Tb(III) centre was used as a probe to detect directly the desolvation and resolvation of the polymer.

Introduction

The development of porous coordination polymers that incorporate uncommon organic moieties has received recent attention as a means to functionalise internal pore surfaces for specific applications in selective sorption of small molecules.[1] Recent work has demonstrated that inclusion of polar organic substituents into a coordination polymer (*e.g.* amide,[2a,b] sulfonate,[2c] piperazine[2d]) can offer control over not only sorption selectivity, but also the spatial orientation and isosteric heat of adsorption of certain guest adsorbates.[2–4]

Coordination materials that contain available Lewis base sites are of particular interest because they are convenient for direct post-synthetic modification. For example, *via* post-synthetic attachment of catalytic metal species.[5] The use of triarylphosphines as Lewis base ligands is well known in coordination chemistry. However, there remain few examples of their application in the design and synthesis of functional coordination polymers.[6] Phosphine ligands are ideal candidates for the construction of new functional coordination materials for several additional reasons that include the broad range of P(III) → P(V) chemistry which provides access to polar (*e.g.* R_3PE (E = O, S, NR, $BX_3…$)) or ionic substituents (*e.g.* $[R_3PR']^+$).[7] Moreover, phosphine ligands that have three acid-functionalized aryl rings show a trigonal geometry at P, which provides an organic building block that greatly favours the formation of 3-dimensional

coordination polymers over lower dimensional (layered) solids. Recent studies using tris(carboxylated) triphenylphosphine,[8] the corresponding oxide[9] and also methylphosphonium derivates[8a,10] have provided the first examples of phosphine coordination materials (PCMs). The chemistry is somewhat flexible. For example, it is possible to incorporate polar groups such as P═O into coordination polymers by pre-, per- or post-synthetic methods: oxidation of the phosphine can be achieved in the molecular building block, in a direct, one-pot synthesis route, or by selective oxidation in the already formed coordination polymer (Scheme 1).

A recent extension of this work has focused on the incorporation of lanthanides into PCM materials. In comparison to the multitude of *d*-block-based coordination polymers that now exist, examples based on Ln cations remain few in number. This may be due to the greater variation in coordination numbers and geometries that are exhibited by *f*-block ions, which complicate the crystallisation of high symmetry frameworks.[11] However, higher overall metal–ligand connectivity, coupled with a greater degree of ionic character (as commonly observed in Ln(III) coordination chemistry) may be advantageous in the generation of thermally more stable and less dense materials. Moreover, reaction of M(III) cations with tris(*p*-carboxylated) triphenylphosphines should form coordination polymers with simple (1 : 1) metal–ligand stoichiometries.[12] In contrast, previous work using relatively more common M(II) cations with phosphine-based trianions has required the incorporation of metal hydroxide nodes to achieve overall charge neutrality (*e.g.* $Zn_3(OH)$,[8a] $Mg_4(OH)_2$[9b]).

Somewhat surprisingly, studies of the gas adsorption properties of homometallic *f*-block coordination polymer materials have received limited attention.[12–22] The majority of previously reported examples have focused on the solid-state magnetic[23]

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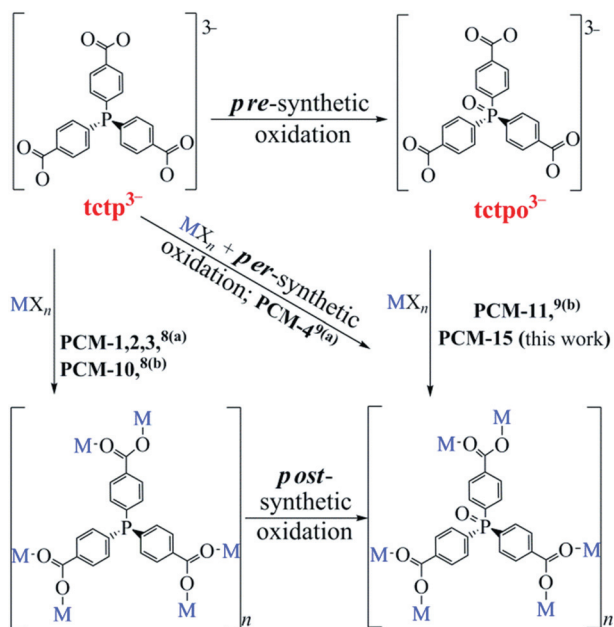
Scheme 1 Incorporation of the polar group P=O into coordination polymers by pre-, per- or post-synthetic methods.
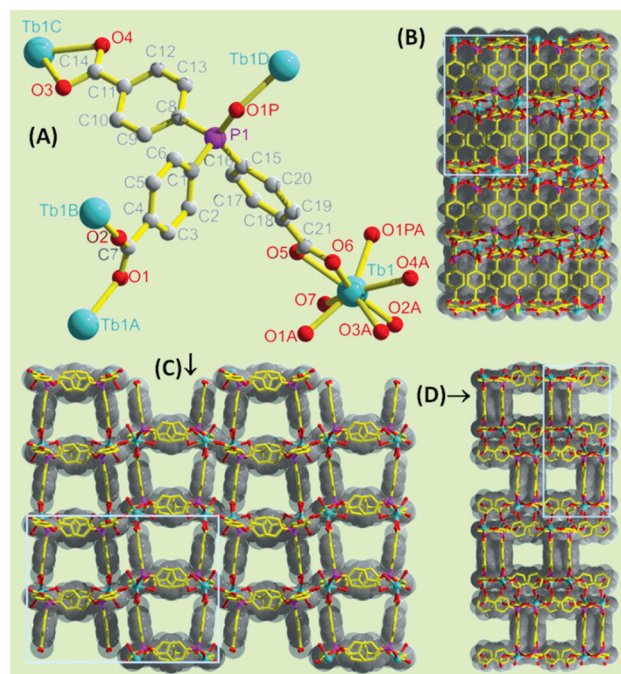

Fig. 1 (A) Asymmetric unit of PCM-15 with solvent molecules omitted for clarity; all unique atoms have their coordination spheres drawn completed. (B) View of the dense and non-porous walls in the bc-plane. (C) The ac-plane. (D) Corresponding view in the ab-plane; the unit cell is shown in light blue.

and photoluminescence properties.[24] The highly defined absorption–emission properties of Ln(III) ions has led to important recent applications in the field of low-energy light emitting materials. Thus, the luminescence behaviour of non-interacting Ln(III) sites embedded within infinite three-dimensional crystalline lattices are of interest.[25] Ln(III)-containing coordination polymer materials provide a unique opportunity to study the luminescence quantum yield as a direct function of the local coordination environment around the ion, in a way that is not easily achieved with molecular species. Specifically, 'guest' solvent molecules (that may act as luminescence quenching agents, *e.g.* H_2O) can be selectively added or removed from Ln(III) sites in the 'host' framework. The inherent rigidity of the host framework may perturb further substantial changes in the coordination geometry around the metal ion. As such, Ln(III) sites in a coordination network may exhibit guest-dependent luminescence.[26] Here, we report on the synthesis of a new material, PCM-15, based on Tb(III) and $R_3P(=O)$, which is a highly robust three-dimensional coordination material with two-dimensional pore network. The material displays noteworthy luminescence and gas adsorption properties.

Results and discussion

Synthesis and structure of PCM-15

Reaction of $Tb(NO_3)_3 \cdot xH_2O$ with tris(p-carboxylato) triphenyl-phosphine oxide $\{P(=O)(C_6H_4CO_2H)_3\}$,[27] (tctpoH$_3$) in a slightly acidified 3 : 4 : 1 solvent mixture of N,N-dimethylforma-mide–tetrahydrofuran–water at 85 °C afforded reproducibly large quantities of crystalline rods. Initial X-ray diffraction studies of a single crystal provided its structure and composition as, Tb(tctpo)(OH$_2$)·2dmf·H$_2$O, hereafter referred to as PCM-15. The material was found to inhabit the centrosymmetric orthorhombic

space group *Pccn* with $Z = 8$, such that the asymmetric unit contains one complete formula unit (Fig. 1A).‡ All atoms reside on general positions in this cell setting.

The metal centre Tb1 has a distorted eight-coordinate environment with bond angles in the range 53.8(2)–153.3(3)° and an average Tb1–O bond distance of 2.39(1) Å. Seven of the donor groups are provided by ligand-based carboxylates and are comprised of: two monodentate carboxylate contacts (O1, *syn*; O2, *anti*); two pairs of chelated carboxylates (O3/O4 & O5/O6); and, a P=O group (P1–O1P–Tb1 = 150.3(5)°). The remaining ligand is provided by a coordinated OH$_2$ molecule (O7). The metal acts as a 5-connected node in the polymer. Examination of the completed coordination sphere of a single tctpo^{3-} ligand shows that it also acts as a 5-connected ligand node with respect to P1.

The resulting convoluted 5,5-connected net structure on which PCM-15 is based (see ESI Fig. S1†) gives rise to an intricate porous network with square pore windows that are accessible from two of the three crystallographic planes (ac & bc; Fig. 1C & 1D respectively). The largest of these openings has a corner-to-corner accessible opening of approximately 10.9 Å. However, when viewed in the crystallographic bc-plane, dense packing of aromatic moieties precludes any pore openings or void spaces

‡ Crystal data for PCM-15: $C_{24}H_{25}NO_{10}PTb$; MW = 671.29, orthorhombic, space group *Pccn*, $a = 27.185(5)$, $b = 12.100(2)$, $c = 20.605(4)$ Å, $V = 6778(2)$ Å^3, $Z = 8$, $\rho = 1.316$ g cm^{-3}, μ(Mo Kα) = 2.177 mm^{-1}, $R_1 = 0.080$ (0.091), 60 180 measured reflections, (5944 independent reflections, $I > 2s(I)$), wR_2 (all data) = 0.189 (0.218), $R_{int} = 0.185$ (0.213), GoF = 1.059 (1.050), $\pm\Delta e^- = 1.310$ (1.433) e$^-$ Å^{-3} (data before the application of SQUEEZE).

(Fig. 1B). Thus, while PCM-15 is an infinite three-dimensional network, the internal pore network is actually two-dimensional. From the single crystal structure of the as-synthesized material at 120 K, one dmf molecule and two H_2O molecules (the latter refined with $\frac{1}{2}$ site occupancies) were also located in the void spaces. The estimated total void space in PCM-15 is 1070 $Å^3$ per unit cell (calculated using the SQUEEZE[28] utility in PLATON[29]). An additional 308 e^- of disordered residual electron density were removed from the void spaces by SQUEEZE; this corresponds to 38.5 e^- per formula unit and is equivalent to a single dmf molecule. This assumption is supported by TGA and elemental analyses, of the as-synthesized and desolvated PCM-15, *vide infra*.

Solid-state characterization

Thermogravimetric analysis (TGA) of an as-synthesized sample of PCM-15 under He carrier gas showed a continuous mass loss of approximately 24.1% over the temperature range 25–170 °C (see ESI Fig. S2†). This corresponds to the loss of two dmf molecules and two H_2O molecules per formula unit (calc. 24.3%) to yield the fully desolvated solid, Tb(tctpo). Between 170–410 °C, there is only a further 7.3% loss in mass. Above 410 °C, the onset of irreversible structural degradation is observed.

To study in more detail the thermal stability of PCM-15 the bulk X-ray powder diffraction (XRPD) pattern of a crystalline sample was monitored upon incremental heating under high vacuum (Fig. 2). In this experiment, the as-synthesized crystalline PCM-15 was heated in a borosilicate tube to a given temperature and held at that temperature under vacuum for 10 min. Then, the XRPD was recorded under an atmosphere of dry He. The as-synthesized XRPD for a bulk sample (Fig. 2, red solid line) is in good agreement with the predicted pattern generated from the single crystal data (Fig. 2, black solid line). Upon activation under vacuum at 50 °C the crystallinity is entirely
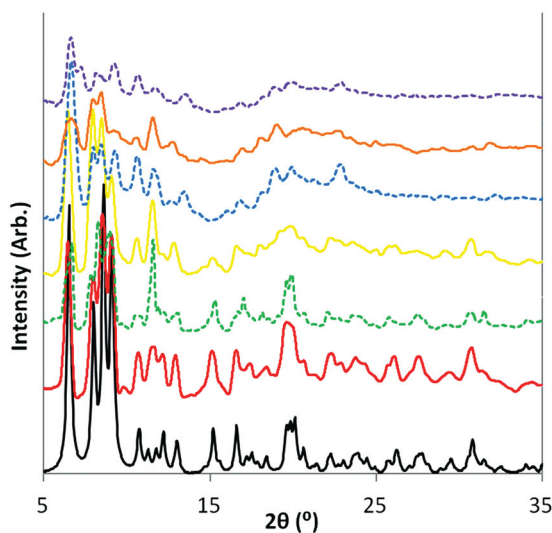
maintained, albeit with the loss of a number of peaks due to removal of solvent from the voids (Fig. 2, green broken line). The XRPD pattern remains largely unchanged up to 150 °C and the most intense peaks are still observed above 250 °C and at 1×10^{-10} bar. At temperatures higher than 300 °C, new peaks were observed at high angle, probably due to the formation of Tb_2O_3 and related oxidation products (not shown).

Gas sorption studies

Initial estimation of the net surface area of activated (meaning evacuated at 150 °C and 1×10^{-10} bar for 12 h) crystalline PCM-15 was performed using both N_2 and CO_2 probe gases. The estimated mean pore size distribution was 11.0 Å (BJH method; CO_2 sorption), which is in excellent agreement with the value determined from the single crystal structure. Application of the standard Brauner–Emmett–Teller (BET) model to adsorption data in the range $p/p_0 = 0.05$–0.3 gave measured surface areas of 674 and 1187 $m^2 g^{-1}$ for N_2 and CO_2 respectively, with corresponding estimated micropore volumes of 0.13 and 0.62 mL g^{-1} (Fig. 3).

The disparity in the values obtained using the different probe analytes suggests that PCM-15 has a greater affinity for CO_2 adsorption, which is similar to what has been previously observed for other porous *f*-block coordination polymers. In comparison with recent leading examples of porous lanthanide coordination polymers, the micropore volume for PCM-15 measured with either N_2 or CO_2 is larger than those reported for: Tb(bdc)(NO_3) (bdc = 1,4-benzenedicarboxylate; 0.032 $cm^3 g^{-1}$ by CO_2);[13] Er_2(pda)$_3$ (pda = 1,4-phenylendiacetate; 0.027 $cm^3 g^{-1}$ by CO_2);[14] or, Tb(btc)(OH_2)$_{1.5}$·dmf (btc = 1,3,5-benzenetricarboxylate; 0.121 $cm^3 g^{-1}$ by N_2).[15] The CO_2 surface area of PCM-15 appears to be the highest reported to-date for lanthanide-based coordination polymers. Meanwhile, its N_2 BET surface area is comparable with other leading recent examples of lanthanide-based porous coordination polymers, such as: Tb(btc)(OH_2)$_{1.5}$·dmf (334 $m^2 g^{-1}$ using the Langmuir method);[15] Er(pdc)$_3$(dmf)$_2$, (pdc = pyridine-3,5-dicarboxylate; 427 $m^2 g^{-1}$);[18] Tb(btc), (678 $m^2 g^{-1}$);[19] Ln(btb)(OH_2)·*x*(solv),

Fig. 2 XRPD patterns for PCM-15 as a function of activation temperature under high vacuum: simulated pattern from single crystal data (black, solid); as-synthesized bulk sample (red, solid); post-activated samples at 50 °C (green, broken), 100 °C (yellow, solid), 150 °C (blue, broken), 200 °C (orange, solid), and 250 °C (purple, broken).
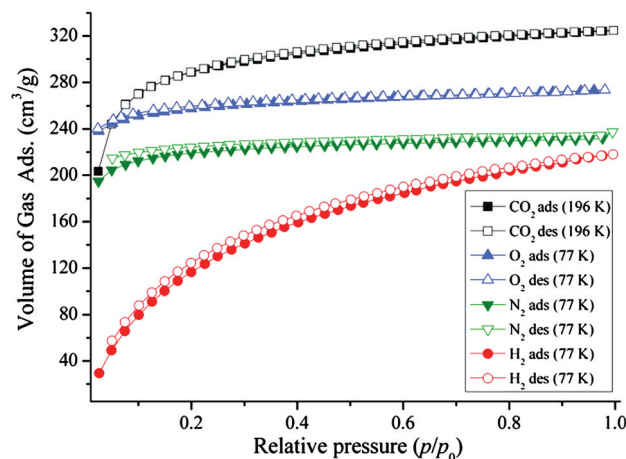

Fig. 3 Observed type-I adsorption/desorption isotherms for PCM-15 using various probe gases.

(denoted MIL-103 where Ln = La to Ho; btb = 1,3,5-benzene-trisbenzoate; ~700 m^2 g^{-1});[17] and, Tb(btb)(OH$_2$)·2(C$_6$H$_{12}$O); 930 m^2 g^{-1}.[16] The N$_2$ surface area is also similar to those reported by Zhou and co-workers for the PCN-17 series (Er, 606; Dy, 738; Yb, 820 m^2 g^{-1}).[21,22] Hong and co-workers recently reported a porous lanthanide-based coordination polymer, using the tctpo^{3-} ligand with early Ln(III) ions, (Ln = Nd, Sm, Eu, Gd).[12] These polymers showed lower CO$_2$ BET surface areas and total pore volumes of 793–1079 m^2 g^{-1} and 0.344–0.487 cm^3 g^{-1} respectively.

After confirming the permanent porosity of PCM-15, H$_2$ adsorption experiments were performed on a desolvated sample using the established activation conditions. The H$_2$ isotherm showed rapid uptake kinetics and complete reversibility, without hysteresis (Fig. 3, red circles). The total H$_2$ uptake for PCM-15 was 1.96 wt% at 77 K and p/p_0 = 1.0 (218.09 cm^3 g^{-1}, 19.63 mg g^{-1}). This uptake is approximately triple that of Er (pdc)$_3$(dmf)$_2$, (6.75 mg g^{-1})[18] and is higher than the previous highest H$_2$ uptake for a lanthanide-based coordination polymer (1.82 wt%).[12]

Additional O$_2$ adsorption experiments were also performed on PCM-15, which showed a total O$_2$ uptake of 274 cm^3 g^{-1} (1 bar, 77 K; Fig. 3, blue triangles). This value represents the highest measured O$_2$ uptake for a lanthanide-based coordination polymer, and compares to the previously reported (PCN-17(Dy), 258 cm^3 g^{-1} at 1 bar and 77 K).[22]

Due to the apparent preference of PCM-15 to adsorb CO$_2$ over N$_2$, it was decided to attempt a measurement of the isosteric heat of adsorption for this analyte. An activated sample of PCM-15 confirmed a total CO$_2$ uptake of 44 cm^3 g^{-1} at 298 K, and 63 cm^3 g^{-1} at 278 K (both p/p_0 = 1.0 bar; Fig. 4). The enthalpy for CO$_2$ adsorption was then determined by fitting both isotherms to a virial-type equation;[30] the isosteric heat of adsorption of CO$_2$ in PCM-15 was thus estimated as 18.40 kJ mol^{-1} (Fig. 4) Kaneko *et al.* previously reported the only other similar measurement, which yielded a value of 30.10 kJ mol^{-1} for Er$_2$(pda)$_3$.[14] This value is considerably higher than that for PCM-15, which is unsurprising since the effective pore window of Er$_2$(pda)$_3$ is relatively small (~3.3 Å *cf.* 10.9 Å in PCM-15).

It is expected that narrow pores enhance the CO$_2$ binding energy in porous materials at low loading pressure.[31]

Photoluminescence properties

The solid-state photoluminescence spectrum of PCM-15 was recorded at room temperature and displayed the characteristic emission pattern of the Tb(III) ion. The strong emission lines at 490, 544, 584, and 620 nm are assigned to transitions between the first excited state, $^5D_4$, and the ground state multiplet ^7F_J (J = 6, 5, 4, 3). The notable Stark splitting of the most intense transition in the spectrum is indicative of the low site symmetry of the Tb(III) ion in the solid-state structure, which results in the observation of the degeneracies of the $^7F_5$ levels ($2J + 1$) of the ground state manifold.[32] The absolute quantum yield of emission of the solid-state material was determined as 22 ± 7% using an integrating sphere detector. This value is comparable to other reported Tb(III)-containing coordination polymers which range from 38 to 90%.[33] The solid-state photoluminescence behaviour of PCM-15 was found to display a marked response to the activation conditions, which underlines the potential use of lanthanide sites within coordination polymers as reporters of local chemical environments in the material.[34] Freshly prepared PCM-15 contains isolated Tb(III) centres that are seven-coordinate with respect to the lattice, and are also singly solvated by an OH$_2$ ligand (Fig. 1A). It is well-established that OH$_2$ species act to quench lanthanide luminescence because these ligands facilitate non-radiative decay pathways of the excited ion through vibrational resonance.[35] The measured photoluminescence spectrum of an as synthesized (Fig. 5, black line) sample of PCM-15 was obtained with an excitation wavelength of 330 nm, thus utilizing the tctpo^{3-} ligand to sensitize the Tb(III) ion emission. However, upon activation of the same sample at 150 °C for 1 h under vacuum (to ensure removal of both coordinated water molecules and uncoordinated solvent in line with the TGA and XRPD studies) the photoluminescence was found to increase by a factor of approximately two (Fig. 5, red line). The large increase in the luminescence intensity offers strong supporting

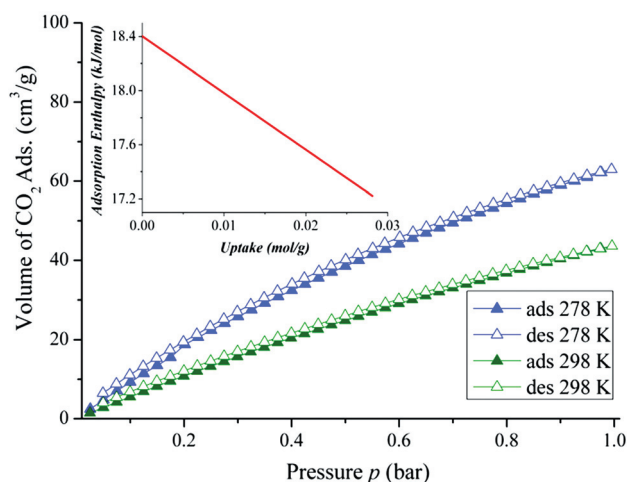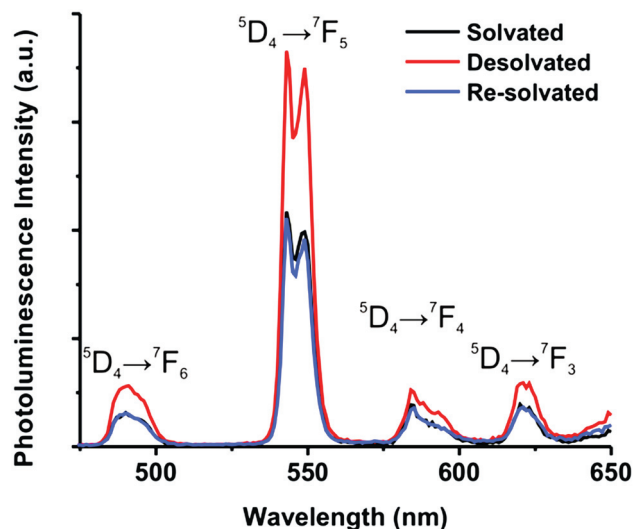**Fig. 4** High temperature CO$_2$ adsorption/desorption in PCM-15 with isosteric enthalpy of adsorption plot (inset; see ESI† for details).

Fig. 5 Photoluminescence spectra for solvated, desolvated and re-hydrated PCM-15.

evidence for the generation of a majority of anhydrous seven-coordinate Tb(III) sites in the polymer. To confirm this assumption, the same sample was then treated with N_2 that had been bubbled through H_2O and the luminescence returned to its original level (Fig. 5, blue line). This behaviour is significant because previous reports of similar materials exhibit a decrease or complete loss of crystallinity upon dehydration with a concomitant change in luminescence signature.[34a] In the case of the title material, PCM-15, the crystalline porous network remains completely intact after the removal of coordinated water molecules, which results in an activated luminescent coordination material that possesses an open coordination site. PCM-15 therefore shows promise as a luminescent sensor material, because the luminescence intensity should be sensitive to selective binding of small molecules at this site.

Conclusions

The tctpo^{3-} ligand provides a useful tetrahedral organic building block for the formation of stable, porous coordination materials; this includes the use of higher-coordinate f-block metals, such as Tb(III), as demonstrated here. The high degree of metal–ligand connectivity in PCM-15 resulted in a very stable material that exhibits a large storage capacity for a range of small guest molecules. The photoluminescence intensity of Tb(III) sites in PCM-15 was observed to dramatically (and reversibly) increase upon dehydration of the material *in situ*, thus acting as an efficient and direct probe for the hydration state of metal sites in the polymer. It has been possible to prepare similar PCMs with other late Ln(III) ions, which will be reported upon in due course.

Experimental

Reagents and instrumentation

1,4-Dibromobenzene and PCl_3 (Aldrich), $Tb(NO_3)_3\cdot6H_2O$ (Alfa Aesar) HCl and H_2O_2 (Fisher Scientific) were used as received. Tetrahydrofuran, N,N-dimethylformamide, diethyl ether, chloroform and dichloromethane (Fisher Scientific) were purified prior to use by degassing followed by column distillation on an Innovative Technologies Inc. PureSolv system, and stored on molecular sieves under dry N_2 prior to use. PCM-15 was synthesized by heating mixtures in 40 capped scintillation vials using graphite thermal baths, with the vials submerged below the internal solvent level. Infrared spectra were collected on crystalline analyte using a Nicolet Avatar 330 FT-IR spectrometer fitted with attenuated total reflectance apparatus. Thermogravimetric analysis (TGA) was performed under He atmosphere at a scan rate of 2 °C min^{-1} in the range 25–800 °C using a TA instruments Q50 analyser. NMR analyses ^{1}H and ^{31}P were recorded in-house using a 300 MHz Oxford Instruments Cryomagnetic Systems spectrometer. Elemental analyses were performed by Intertek QTI, Whitehouse, NJ.

Synthesis

Trilithium salt of tris(p-carboxylato)triphenylphosphine ({P(C$_6$H$_4$-p-CO$_2$Li)$_3$}; tctpLi$_3$). This ligand was prepared using the reported method,[8a] which is a modified version of the original procedure reported by Amengual et al.[27] that directly provides the trilithium salt. The salt was dried under vacuum to afford a pale yellow solid that was stored under N_2 (yield 68% based on the tris(p-bromo)triphenylphosphine intermediate). ^{1}H NMR (D$_2$O; 300 MHz): δ = 7.38 (t, 6H); 7.70 ppm (dd, 6H); ^{31}P NMR (D$_2$O; 162 MHz): δ = −6.66 ppm.

Tris(p-carboxylic)triphenylphosphine oxide ({P(=O)(C$_6$H$_4$-p-CO$_2$H)$_3$}; tctpoH$_3$). TctpLi$_3$ (100 mg, 2.4 mmol) was dissolved into H_2O (10 mL) in a round-bottomed glass reactor tube fitted with magnetic stirred bar and heavy-duty Teflon-sealed screw cap. H_2O_2 (5 mL, 30%) was added and the mixture was vigorously stirred for 24 h. The resulting mixture was then cooled in an ice bath and acidified with ice cold HCl solution (1.0 M) to yield a white precipitate of potbcH$_3$ that was isolated by vacuum filtration, washed with ether and dried under vacuum (yield: 614 mg, 63%). Anal. found: C, 56.8; H, 3.94%. C$_{21}$H$_{15}$O$_7$P·2H$_2$O requires: C, 56.5; H, 4.29%. ν_{max} (solid/cm^{-1}): 2929 w, 1699 m br, 1652 m, 1565 w, 1395 m, 1262 m br, 1161 m, 1103 s, 1017 m, 962 s, 933 s, 894 br s, 704 m; ^{1}H NMR (DMSO; 300 MHz): δ = 7.92 (d, 6H), 8.15 (d, 6H) ppm; ^{31}P NMR (DMSO; 300 MHz): δ = 26 ppm.

PCM-15 ([Tb(tctpo)(OH$_2$)]·2dmf·H$_2$O). TctpoH$_3$ (20 mg, 48 μmol) and terbium nitrate (80 mg, 184 μmol) were mixed in dmf (3.0 mL), thf (4.0 mL), H_2O (1.0 mL) and HCl (36.5%, 1 drop). The resultant slurry was stirred until complete dissolution occurred. The solution was then heated in a scintillation vial at 85 °C for 4 days to yield colourless rods of the target material, which were isolated by decanting away any residual amorphous solid with the mother liquor (yield 23 mg, 64%). After treatment of as-synthesized PCM-15 in vacuum at 150 °C to remove solvent, found: C, 42.5; H, 2.28; N, 0.17%. C$_{21}$H$_{12}$O$_7$PTb requires: C, 44.5; H, 2.14; N, 0%. ν_{max} (solid/cm^{-1}): 3692 w, 3585 m, 2899 s, 2764 m, 2462 m, 2313 m, 1719 br m, 1465 w, 1387 s, 1256 m, 1166 s, 1059 s, 867 w, 756 m, 713 s.

Single crystal X-ray diffraction

Crystals were mounted on thin fibre loops using perfluoropolyether oil, which was frozen *in situ* by a nitrogen gas Cryostream flow. Data for PCM-15 was collected on a Rigaku AFC-12 diffractometer fitted with a Saturn 724 + CCD detector, using monochromated Mo Kα radiation (λ = 0.71075 Å). Cell refinement and data reduction was performed using the Crystal-Clear[36] utility. Absorption corrections were made based on multiple ω-scans using the SADABS[37] program. Structures were solved using direct methods and refined on F^2 using the program SIR-97[38] and then refined using SHELXTL-97[39] software. All non-hydrogen atoms were refined anisotropically for all atoms in the framework of PCM-15; uncoordinated dmf and H_2O solvent molecules were refined with isotropic displacement parameters. The dmf molecule was refined with geometric restraints in order to stabilize the refinement process and free variables were initially applied to determine the site occupancies of all solvent atoms, which were set to 1.0 or 0.5 in the final refinement cycle. PLATON[29] SQUEEZE[28] was applied to the solution post-refinement in order to remove residual peaks due to remaining

disordered solvent. This resulted in only small improvements to the final statistics (see CIF). All hydrogen atoms were fixed based on idealized coordinates and refined with U_{iso} values set to 1.5 times that of the carrier atom. Solvent H_2O H-atoms were not directly located in the peak difference map; compensatory alterations were made to final structural formulae in the CIF as required. See ESI† for full data in CIF format.

X-ray powder diffraction

The phase purity and thermal stability of PCM-15 were confirmed by analysis of powdered crystalline samples that were sealed inside borosilicate capillary tubes under inert atmosphere conditions and spun *in situ* to prevent preferential orientation of the crystallites. Spectra were recorded on a Rigaku Spider diffractometer equipped with an image plate detector, operating in Debye–Scherrer geometry using Cu Kα radiation (1.5412 Å). The 2-dimensional image plate data was converted to give a 1-dimensional spectrum using Rigaku Corp. 2DP software.[40] Reflection data in the range 5.0–35.0° 2θ was extracted from the entire dataset. The XRPD patterns were then compared directly to their corresponding simulated patterns that were generated using the *SimPowPatt* facility in PLATON[29] using *hkl* reflection data obtained from the single crystal experiment.

Gas sorption isotherms

CO_2, N_2, O_2 and H_2 isotherms were recorded on a Quantachrome Autosorb-1 system. Samples were pre-treated under ultra high vacuum in a clean system with a diaphragm and turbo pumping system. All analyte gases (Praxair) were ultra-high purity (99.9995%). The surface area of PCM-15 was calculated using the Brauner–Emmett–Teller method for N_2 and CO_2 based on adsorption datapoints in the range, $p/p_0 = 0.05$–0.30 (see ESI† for further details).

Photoluminescence measurements

All spectroscopic data was obtained in the solid-state unless otherwise noted. Luminescent measurements were recorded on a Photon Technology International QM 4 spectrophotometer equipped with a 6-inch diameter K Sphere-B integrating sphere. For quantum yield measurements, the integrating sphere was used. Quantum yield was calculated by dividing the area under the emission peaks of the complex by the difference between the area under the excitation peak of the sample from that of a blank solution ($A_{em(sample)}/(A_{ex(blank)} - A_{ex(sample)})$, where A = area under peak).[41]

Acknowledgements

Notes and references

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