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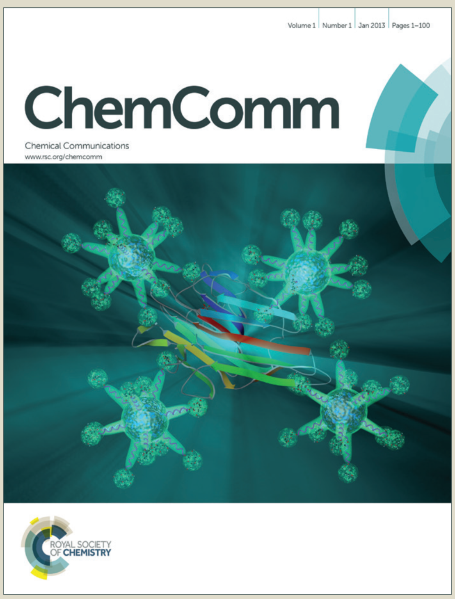

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COMMUNICATION

Towards multifunctional lanthanide-based metal-organic frameworks

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We report the synthesis, structure and physicochemical attributes of a new holmium(III)-based metal-organic framework whose 3D network structure gives rise to porosity; the reported structure-type can be varied using a range of different lanthanide ions to tune the photophysical properties and produce ligand-sensitised near-infrared (N-IR) and visible light emitters.

Metal-organic frameworks (MOFs) are fascinating metallo-supramolecular systems in which metal ions or polynuclear complexes are linked through organic ligands.[1] Synthetic approaches to MOFs which consider the topological characteristics of these organic and inorganic secondary building units (SBUs) to rationally construct 'default' structures, have attracted significant scientific interest over the last decades.[2] Under this purview, the use of extended rigid organic linkers in combination with selected inorganic SBUs led for instance to highly augmented structures with surface areas exceeding 7000 m^2/g,[3a] unprecedented gas storage capabilities or new heterogeneous catalysts with promising reactivity, turnover numbers/frequencies or shape/size selective properties.[3,4] Lanthanide(Ln)-based MOFs are a particularly interesting subclass of MOFs as the intrinsic attributes of the heavy transition metal ions can lead to multi-functional materials which combine porosity, or other structural characteristics, with molecular magnetic, electronic, photo-physical attributes.[5,6] The lanthanides are a unique family of homologous elements that resemble each other remarkably in their chemical attributes. The electronic configuration and associated energy levels of individual lanthanide ions within the homologous series facilitate the population of their excited states and minimized non-radiative deactivation pathways giving rise to characteristic narrow-line emission properties. These features promote their applications in self-assembly formations, as lamp phosphors, materials in biological assays and sensing, and as medical imaging systems or electroluminescent materials in optical fibres and LEDs.[7]

However, rational strategies to porous Ln-based MOFs are hampered by rather large, irregular and partially solvated coordination environments often leading to dense hybrid materials or structures whose 3D framework topologies lose their integrity and cannot maintain their open topologies after de-solvation. Thus, the number of reported porous Ln-Based MOFs is limited in comparison to other, lighter transition metal containing MOFs. Exemplarily, the use of Gd^{III}-MOFs as MRI contrast agents was demonstrated by Lin *et al.*[6a] A cyclam-based Eu^{III}-MOF was successfully applied as a sensor material for the detection of selective transition and main-group metal ions.[6b] Lobkovsky *et al.* efficiently detected F^- anions using MOF-76b, Tb(BTC)·MeOH taking advantage of H-bonding effects to modulate N-H and O-H oscillators, which provide efficient non-radiative decay mechanisms of excited Tb states.[6c] A similar sensing-principle for the isostructural Eu^{III} derivative which contains an exposed metal centre after the removal of a coordinated water molecule was successfully applied to a series of solvent molecules.[6d] NIR emitting Ln materials are particularly

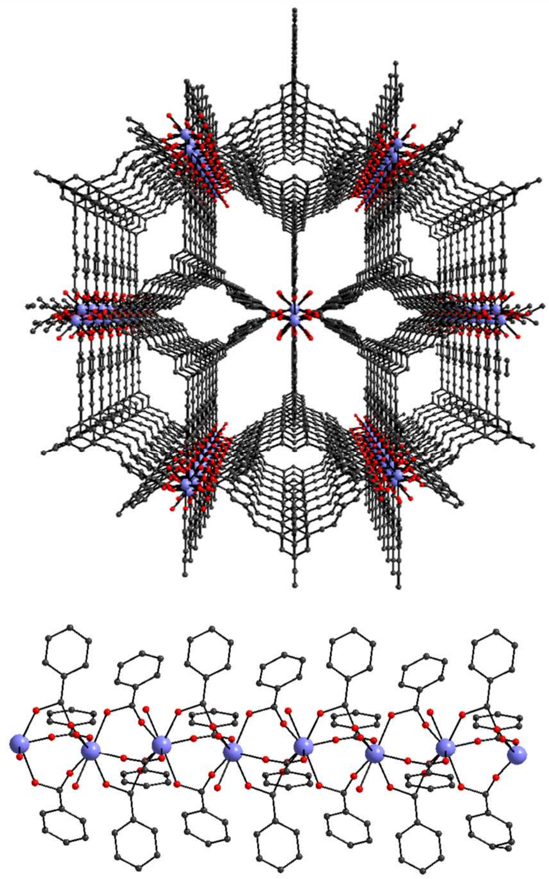

Fig. 1. Crystal structure of $[Ho(BTEB)(H_2O)_2]$ **TCM-9-Ho**; *Top*: extended network structure with view in the direction of the crystallographic c-axis; *Below:* Carboxylate-bridged Ho(III) ions forming 1D chain motifs that extend in the [001] direction.

appealing to the telecommunication industry, yet the number of reported NIR emitting Ln-MOFs remains low. The first example of a NIR emitting Ln-based MOF was reported by Rosi and co-workers using the Yb-PVDC-1 MOF, where PVDC= 4, 4'-[(2, 5-dimethoxy-1, 4-phenylene)di-2, 1-ethenediyl]bis-benzoic acid.[6e] Er_xYb_{1-x}-PVDC-1 further allowed the design of near-infrared (NIR) barcodes with potential applications in bio-analytical assays.[6f]

Herein we report a synthetic approach to highly augmented lanthanide-based MOFs that give rise to porosity. The resulting structures can be regarded as multifunctional materials whereby their photophysical and magnetic properties can be tuned by the nature of the used lanthanide ion producing ligand-sensitised visible and near-infrared (N-IR) emitters. The results complement our expertise in the areas of MOFs, molecular magnetism and luminescent materials.[8]

Pale pink, needle-like crystals of the archetype MOF [Ho(BTEB)(H_2O)$_2$].sov, **TCM-9-Ho**, form upon reacting Ho(NO_3)•5H_2O with two mole equivalents of 1,3,5-benzene-trisethynylbenzoic acid (BTEB) in DMF at 100 °C. Despite the very small size of rather weakly-diffracting crystals, single-crystal X-ray studies provided us with a molecular model of the compound. The compound was refined in the orthorhombic space group *I*ma/2 and the phase-purity of the bulk material was confirmed using powder XRD experiments. The asymmetric unit of **TCM-9-Ho** is composed of one symmetry independent Ho^{III} ion, one water molecule and half of a deprotonated BTEB ligand. The individual Ho^{III} ion is highly distorted 8-coordinated. Six O donor atoms arise from separate carboxylate functionalities from six BTEB ligands and further two O donor atoms are provided by two *cis*-coordinating water molecules. The carboxylate functionalities in **TCM-9-Ho** adopt bidentate *μ*-bridging modes, linking neighbouring Ho^{III} ions in 1D chains which extend parallel to the crystallographic *c*-axis (Ho(1)···Ho(1') *ca.* 4.2 Å). These chains may be envisaged as infinite 2-fold helical rod-like [Ho(CO_2)$_3$]$_n$ SBUs. Each deprotonated, tri-functional BTEB ligand in turn coordinates to six separate Ho^{III} ions, connecting the individual 1D chains involving symmetry operations in the crystallographic *b*- and *c*- directions to generate a neutral 3D, non-interpenetrated framework structure. The mean planes of the three outer phenyl rings of the BTEB ligands adopt almost perpendicular orientations to the central phenyl ring (torsion angle of *ca.* 84°). The ligand binding and arrangement in **TCM-9-Ho** results in two distinct channels with rhombic topology, containing solvent DMF molecules and which extend parallel to the crystallographic *c*-axis. The larger channels are characterised by a cross sectional diameter of *ca.* 9 Å; the smaller channels by diameters of approximately 5 Å. Upon removal of the DMF molecules, the total solvent accessible void volume was calculated to be *ca.* 60% of the unit cell volume (approx. 3547 $Å^3$ of 5882 $Å^3$). Thermogravimetric analyses of **TCM-9-Ho** in an air atmosphere reveal an initial weight loss of *ca*. 36.5% between *ca*. 25 and 300°C corresponding to the loss of DMF solvent molecules and coordination water molecules upon which the compound loses its crystallinity. This degradation is followed by the oxidation of the organic ligands between *ca*. 400 and 515 °C. Nitrogen sorption studies confirmed the permanent porosity of the thermally treated samples of **TCM-9-Ho** whereby activation methods involving solvent-exchange and freeze-drying using supercritical CO_2 led to similar results: type I N_2 adsorption isotherms and BET surface areas varying between 765 $m^2 g^{-1}$ and 720 $m^2 g^{-1}$. The resulting porous materials are stable and a close match between the IR spectra of de-solvated, porous materials and pristine crystals of **TCM-9-Ho**, confirm a close structural

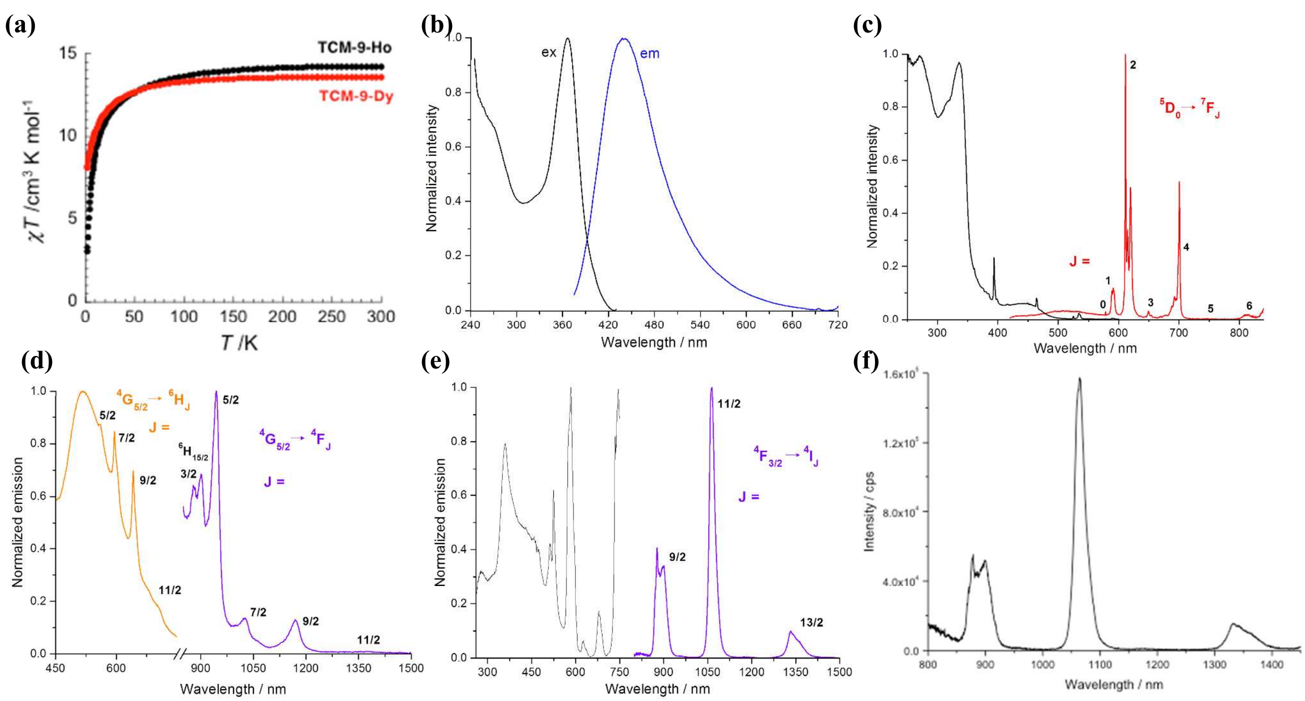

Fig. 2. Physicochemical characterisation of lanthanide-based MOFs. **(a)** Temperature dependence of χT product at 1000 Oe (where χ is the molar magnetic susceptibility equal to the ratio between the magnetization and the applied magnetic field, *M/H*, per mole of Ln(III) complex) between 1.85 and 300 K for a polycrystalline sample of **TCM-9-Ho** and **TCM-9-Dy**; **(b)** Normalised ligand-centred emission and excitation spectra of BTEB (λ_{ex} = 365 nm, λ_{an} = 440 nm); **(c)** Emission (red) (λ_{ex} = 340 nm) and excitation (black) (λ_{an} = 612 nm) spectra of **TCM-9-Eu**; **(d)**; Visible (yellow) and near-infrared (purple) emission spectra of **TCM-9-Sm** (λ_{ex} = 340 nm); **(e)** Emission (λ_{ex} = 360 nm) and excitation (λ_{an} = 1065 nm) spectra of **TCM-9-Nd**; (f) NIR-to-NIR down-conversion photoluminescence of **TCM-9-Nd** in the solid state (λ_{ex} = 745 nm; (λ_{em} [850-1450nm]).

relationship. However, it should be noted that **TCM-9-Ho** indeed undergoes a structural/morphological transition as suggested by the results of PXRD experiments and the BET analyses. The observed surface areas compare to that of MIL-103, which contains the related, but less extend, ligand BTB (1,3,5-benzentrisbenzoic acid). MIL-103, $[Tb(BTB)(H_2O)] \cdot 2(C_6H_{12}O)$, is a 3D porous framework composed of chains of corner-sharing $\{TbO_9\}$ polyhedra, linked through BTB ligands, to generate a framework with hexagonal channels of *ca.* 10 Å in diameter and which are comparable to those found in **TCM-9-Ho**.[5r] The experimentally determined surface area of desolvated **TCM-9-Ho** is relatively high in comparison to other previously published Ln-MOFs, as lanthanide-based framework structures have a propensity to collapse upon removal of solvent molecules, due to structural rearrangement or instability of the lanthanide coordination environment that often contains coordinated solvent molecules. Thus, porous LnMOFs are relatively rare when compared to transition metal based frameworks.

Using the synthetic strategy employed to produce **TCM-9-Ho**, a series of structurally closely related lanthanide-based (Dy^{III}, Er^{III}, Eu^{III}, Tb^{III} , Yb^{III} and Nd^{III} and Sm^{III}) MOFs can be synthesised. Detailed structural analysis of the compounds proofed difficult as the compounds generally form small crystal sizes and readily desolvate loosing crystallinity. However, the close structural relationship of the resulting complexes with **TCM-9-Ho** was confirmed using a combination of analytical techniques including PXRD, FT-IR, thermogravimetric and elemental analyses (ESI).

Further evidence for the close structural relationship between **TCM-9-Ho** and **TCM-9-Dy** is exemplified by their closely related magnetic properties corresponding to typical lanthanide based paramagnetism (Fig. 2a and ESI). **TCM-9-Ho** and **TCM-9-Dy** have room temperature χT values of 14.2 and 13.6 cm^3 K mol^{-1} which are close to the expected values of 14.1 cm^3 K mol^{-1} and 14.2 cm^3 K mol^{-1} for one Ho^{III} (S = 2, L = 6, g = 5/4, $^5I_8$) or Dy^{III} ion (S = 5/2, L = 5, g = 4/3, $^6H_{15/2}$). Upon lowering the temperature, the χT product of the two complexes decreases to reach *ca.* 3 cm^3 K mol^{-1} for **TCM-9-Ho** and *ca.* 8 cm^3 K mol^{-1} for **TCM-9-Dy** at 1.8 K and 1000 Oe. For these complexes, their magnetic properties are mainly dominated by the thermal depopulation of the sublevels of the lanthanide ground state that result from spin-orbit coupling and a low symmetry crystal field. Therefore it is impossible to determine the relative contributions of this intrinsic lanthanide paramagnetism and weak magnetic interactions likely present in these systems. As expected in presence of a significant spin-orbit coupling, both systems show typical field- and temperature-dependences of the magnetisations below 8 K with an absence of saturation even at 1.8 K and 7 T together with a non-superposition of the *M vs. H/T* data.

The luminescent properties of **TCM-9-Eu**, **TCM-9-Nd** and **TCM-9-Sm**, measured in the solid state, demonstrate that the BTEB ligand can act as a suitable antenna for the sensitization of visible and/or near-infrared emitting lanthanide ions. BTEB itself displays a broad emission band between 375 and 700 nm, with a maximum occurring in the blue region at 440 nm (Fig. 2b). The emission spectrum of **TCM-9-Eu** displays predominantly the characteristic Eu^{III} $^5D_0 \rightarrow {}^7F_J$ (J = 0-6) transitions in the 570-840 nm range (Fig. 2c). However, some weak ligand-centred fluorescence is still observed, which is indicative of an incomplete energy transfer from BTEB to the lanthanide ions. Compared to BTEB itself, the residual ligand-centred fluorescence in **TCM-9-Eu** is red-shifted by *ca.* 70 nm upon complexation to Eu^{III}, with a maximum observed at 510 nm. The excitation spectrum obtained by monitoring the Eu^{III} $^5D_0 \rightarrow {}^7F_2$ transition presents a band in the 300-400 nm range similar to the one observed for the BTEB ligand itself, which demonstrates that the BTEB ligand is able to act as an antenna and sensitise the Eu^{III} emission in **TCM-9-Eu**. The excitation spectrum also displays the characteristic Eu^{III} transitions, such as the $^5L_6 \leftarrow {}^7F_0$ and $^5D_2 \leftarrow {}^7F_0$ transitions at 394 and 464 nm, respectively, as well as an additional band centred at *ca.* 450 nm, which can be attributed to a ligand-to-metal charge transfer (LMCT) state. The width of the LMCT band of *ca.* 8150-8200 cm^{-1} is consistent with typical values of lanthanide CT bands, *i.e.* between 5000 and 10000 cm^{-1}.[9] The existence of such a LMCT state as a result of the BTEB- Eu^{III} interaction which was further confirmed by recording the excitation spectrum of **TCM-9-Eu** at 510 nm, which shows both the 365 nm band already observed for BTEB itself and the charge transfer band that is not observed in the absence of the lanthanide ion (Fig. S18, ESI). While the LMCT band does not appear to affect the Eu^{III} emission, it is likely to be responsible for the poor sensitisation of the Sm^{III} emission. Indeed, the emission spectrum of **TCM-9-Sm** consists mainly of ligand-centred fluorescence with the additional weak contribution of Sm^{III} $^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2 and 11/2) transitions at 561, 595, 642 and 700 nm, respectively (Fig. 2d). Interestingly, **TCM-9-Sm** does not solely emit in the visible, but also in the near-infrared (NIR) range as a result of the $^4G_{5/2} \rightarrow {}^6F_J$, $^6H_{15/2}$ transitions. The BTEB ligand further enables the sensitisation of the NIR emission of **TCM-9-Nd**. Upon ligand excitation at 360 nm, its emission spectrum displays bands that are characteristic of the Nd^{III} $^4F_{3/2} \rightarrow {}^4I_J$ transitions (J=9/2, 11/2 and 13/2) at 880, 1065 and 1330 nm, respectively (Fig. 2e). A significant feature of **TCM-9-Nd** is that the Nd^{III} NIR emission can be obtained by indirect (or ligand) excitation at 360 nm, but also by direct excitation through the Nd^{III} transitions at 679 or 745 nm (Fig. 2f), thus achieving NIR-to-NIR down-conversion photoluminescence particularly interesting for biomedical imaging.[10]

In conclusion, we report a new Ho^{III}-based MOF whose 3D open-framework structure gives rise to porosity after desolvation. We demonstrate that the observed carboxylate-stabilised 1D chain motif can generally be used as a versatile SBU for MOFs that are stabilised by highly augmented, rigid tritopic linkers such as the 1,3,5-benzene-trisethynylbenzoic acid (BTEB**)** ligand. Further, the observed structure-type and employed preparation method allows the substitution of Ho^{III} ions by various other homologous lanthanide ions allowing a systematic variation of the photophysical properties whereby the BTEB ligand functions as an intramolecular sensitizer. Remarkable are the luminescence characteristics of **TCM-9-Eu** and the near-IR emission properties of **TCM-9-Nd** and **TCM-9-Sm.** Future activities will aim to exploit these MOFs for liquid and gas-phase sensing applications.

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Graphical Abstract:

The structure-type of a Ho(III)-based MOF can be varied using a range of different lanthanide ions to tune the photophysical properties and produce ligand-sensitised near-infrared and visible light emitters.