

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

A bimodal anionic MOF: Turn-off sensing for Cu^{II} and specific sensitization of Eu^{III}

Cite this: DOI: 10.1039/x0xx00000x

Sohini Bhattacharyya^a, Anindita Chakraborty^a, Kolleboyina Jayaramulu^a, Arpan Hazra^a, and Tapas Kumar Maji^a *

Received 00th January 2012,

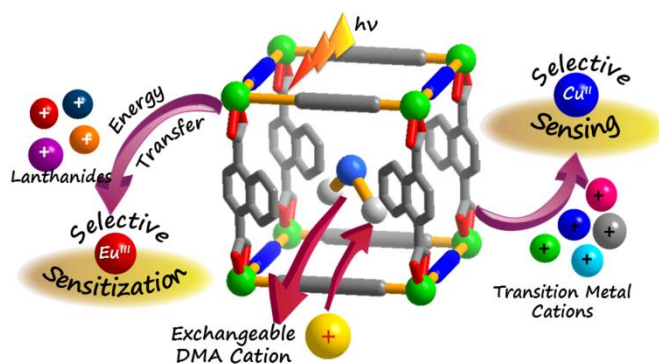
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Abstract: A novel porous anionic MOF {[Mg₃(ndc)_{2.5}(HCO₂)₂(H₂O)][NH₂Me₂].2H₂O.DMF}(1) having exchangeable dimethyl amine cations in 1D channels has been synthesized and characterized. Through cation exchange, 1 manifests bimodal functionality, being a turn-off sensor of Cu^{II} on one hand, and a selective sensitizer for Eu^{III} emitting intense pure red emission on the other.

Zeolites, the much studied microporous aluminosilicates, are established ion exchangers owing to the presence of extra framework cations¹. However, zeolites do not allow the functionalization of pore surfaces and thus selective sequestration and read-out signalling of a specific metal cation is not possible. This drawback has been overcome in metal-organic frameworks (MOFs), which are tunable porous materials with modifiable pore surfaces and functionalities². The efficiency of MOFs in gas storage and separation³, catalysis, drug delivery and optoelectronic devices are well documented⁴. However, unlike zeolites, ion exchange is infrequent in MOFs⁴, which are generally neutral in nature. Applying proper synthetic strategies, it is possible to get anionic MOFs (AMOFs)⁵, where the cationic guest molecules can undergo facile exchange with other exogenous cationic species. Such post-synthetically modified AMOFs have already shown potential in second harmonic generation^{5a, 5c}, drug delivery^{5d}, tunable adsorption^{5g} and catalysis^{5b, 5e}. However the chemical affinity of the coordination spaces determines the selective capture of a specific metal ion, therefore proper functionalization of pore surface is crucial⁶. Furthermore flexible cation exchangeable nano-spaces constructed from chromophoric linkers would provide a fast fluorescence read-out of the recognition process through change in emission intensity for a particular metal ion leading to sensory MOFs. Hence, it should have correct pore window dimensions and proper stabilization environment, preferably the presence of Lewis basic sites for better interaction with the specific metal cation. Selective uptake of Cu^{II} ion by such AMOFs would be particularly interesting as this strategy would ensue a novel route for Cu^{II} sensing⁷, which is of paramount importance for biological applications. The study of prognosis of copper imbalance related



Scheme 1 Schematic representation of the bimodal functionalities in 1 through cation exchange.

diseases, e.g., Menkes, Wilson and Alzheimer's diseases, prion disorders, and amyotrophic lateral sclerosis demand effective sensing and removal of copper⁸ in biological systems. Also, by exploiting the cation exchange in AMOFs, new luminescent materials can be designed by inclusion of lanthanide (Ln) ions. The role of the AMOF as a light harvesting antenna for sensitizing Ln^{III} cations to furnish novel Ln-doped luminescent materials and new Ln sensors has been studied previously⁹. However, selective Eu^{III} sensitization by an AMOF is very unusual and finds its application in low-energy driven pure red emitters in optoelectronic devices and also for biological labelling¹⁰.

In this communication, we report the synthesis and structural characterization of a 3D anionic MOF, {[Mg₃(ndc)_{2.5}(HCO₂)₂(H₂O)][NH₂Me₂].2H₂O.DMF} (1) [ndc: 1,4-naphthalenedicarboxylate] and its metal ion sequestration and sensing properties. The framework contains 1D channels occupied by the cationic guest NH₂Me₂⁺ [dimethyl ammonium (DMA)] which can be selectively replaced by Cu^{II} ions among other transition metal cations. Moreover the framework can encapsulate several lanthanide metal ions but selectively sensitize Eu^{III} resulting in a bright red luminescent framework (Scheme 1). To the best of our knowledge, such bimodal functionalities of specific sensing¹¹ and removal of a transition metal (Cu^{II}) and selective sensitization of a lanthanide

metal (Eu^{III}) based on luminescence quenching and enhancing respectively using a single framework system is yet to be reported.

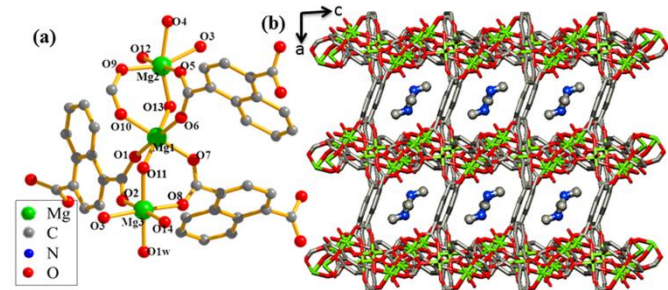


Fig. 1 (a) Coordination environment of Mg^{II} centers in **1**. (b) View of 3D framework of **1** along *b* axis showing DMA cations in the pore.

Single crystal X-ray diffraction analysis reveals that compound **1** crystallizes in monoclinic $P2_1/c$ space group. Each asymmetric unit contains three crystallographically independent hexa-coordinated Mg^{II} centers, all of which are distorted from perfectly octahedral geometry (Fig. 1(a))¹². The hexa-coordination of Mg1 is fulfilled by oxygen atoms (O1, O6, O7 and O10) from three different ndc ligands and two oxygen atoms (O11 and O13) from two different formate ligands. Mg2 adopts a similar coordination environment with O3, O4, O5 and O9 atoms from ndc and O12 and O13 from formate ligands. Mg3, three oxygens from three different ndc moieties (O2, O3, and O8), two oxygen atoms (O11 and O14) from formate and one coordinated water molecule (O1w) ligate to fulfill the hexa-coordination. Mg1 and Mg3 centers are bridged to each other through two ndc and one formate ligands. Mg1 and Mg2 centers are also connected similarly. Thus three Mg^{II} centers are arranged to form a 1D chain along *c* direction¹². These 1D chains are further connected with each other through ndc_a molecules to generate a 2D network in the crystallographic *ac* plane¹². These 2D sheets are further cross-linked by ndc_b and ndc_c and repeat themselves along *b* direction to generate the 3D framework¹² with 1D channels occupied by the guest H_2O , DMF and extra framework DMA cations (Fig. 1(b)). The formate and DMA cations are formed *in situ* from DMF under solvothermal conditions^{5d, 5e}. The solvent accessible void space of the desolvated framework (**1'**) is 28% including the cation. TGA of **1** shows initial loss of ~6% up to 100°C that corresponds to two guest and one coordinated water molecules and a subsequent loss of ~8% till 170°C correlating to a guest DMF¹². The desolvated framework decomposes continuously after that. **1** maintains its structural integrity after desolvation as evident from the powder X-ray diffraction (PXRD) pattern of **1'**. **1'** shows type-I CO_2 adsorption isotherm at 195 K, while N_2 adsorption reveals only surface adsorption (Fig. 2(a))¹². The typical type I adsorption profile clearly indicates that **1** is microporous in nature. The preferential interaction of CO_2 with **1'** could be attributed to the presence of polar carboxylate groups and unsaturated Mg^{II} sites in **1'**, which can interact well with the quadrupole moment of CO_2 .¹³

The presence of guest DMA cations and several carboxylate oxygens on the pore surface prompted us to study the exchange properties of **1** with different transition metal cations by immersing **1'** in 0.01M solutions of different metal chlorides¹². Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis of the exchanging solution showed the absence of Mg^{II} ions, implying that only the guest DMA cations are exchanged. Also ICP analysis of resulting samples showed that 88% of the DMA guests are exchanged with Cu^{II} ions, while the extent of exchange for Mn^{II} , Co^{II} , Ni^{II} and Zn^{II} are 0, 4, 12 and 0% respectively¹². This high percentage of exchange for Cu^{II} is evident as a green solution of Cu^{II} in ethanol becomes colourless on

immersing **1'** in it, while the white solid **1'** yields bright green $\text{Cu}^{\text{II}}@1'$ (Fig. 2(b)). The decrease in the absorbance intensity of the UV spectra of the supernatant solution indicates that 84.5% DMA are exchanged with Cu^{II} ¹². Due to d-d transition, a new band appears in the UV spectra of $\text{Cu}^{\text{II}}@1'$ at ~720 nm in addition to the band at ~317 nm as observed in **1**. This further supports the coordination of Cu^{II} with the carboxylate oxygens of **1'**¹². Due to structural reorganization after encapsulation of Cu^{II} , there are some changes in the PXRD pattern of $\text{Cu}^{\text{II}}@1'$ as well as the appearance of a few new peaks.¹² The inclusion of Cu^{II} into the pore of **1** was further confirmed from the CO_2 adsorption isotherm (Fig. 2(a)) of $\text{Cu}^{\text{II}}@1'$ at 195 K, which shows a 48% decrease in CO_2 uptake compared to that of **1**. This decrease in uptake may be attributed to the fact that Cu^{II} ions occupy the pores of **1** randomly, thus inhibiting the diffusion of CO_2 . Furthermore, the Cu^{II} selectivity of **1** was studied by immersing **1'** in an equimolar solution of a mixture of Mn^{II} , Cu^{II} , Co^{II} , Ni^{II} and Zn^{II} ions. ICP-OES analysis confirmed the exchange of 85% of the DMA cations with Cu^{II} , which is much higher compared to the other metal ions (Fig. 2(c))¹². This selective capture of Cu^{II} may be explained based on the flexible geometry of Cu^{II} owing to which it can be accommodated in a variety of coordination environments, unlike other transition metal ions. Furthermore, **1** shows ndc linker based emission maximum at ~410 nm when excited at 317 nm¹² in solid state. We anticipated that the emission intensities would be affected by the incorporation of Cu^{II} and this was validated by the significant quenching of emission in $\text{Cu}^{\text{II}}@1'$. The quenching of emission can be attributed to the ligand field splitting of d-orbitals of Cu^{II} resulting in reabsorption of emission energy by the framework. In order to check the sensing efficiency, **1** was immersed in 10^{-3} , 10^{-4} , 10^{-5} , 10^{-6} and 10^{-9} M solutions of Cu^{II} and emission is quenched gradually as the concentration of the Cu^{II}

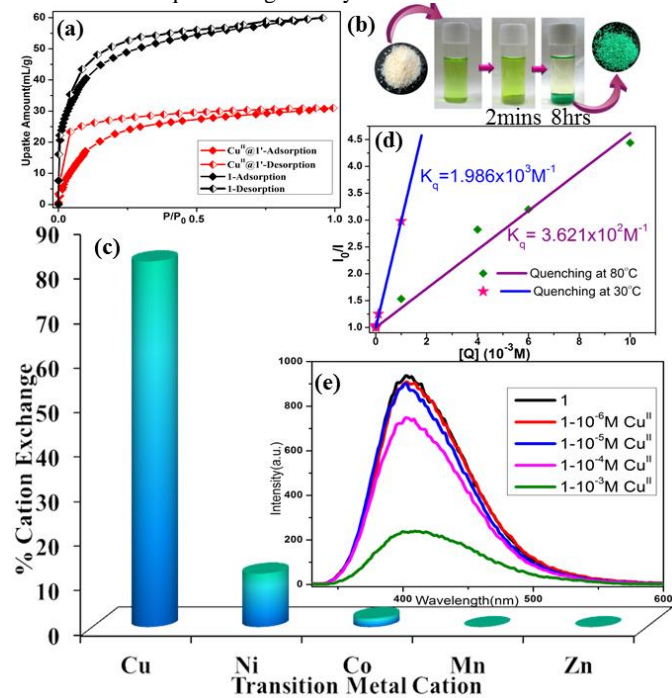


Fig. 2 (a) CO_2 adsorption isotherms of **1** and $\text{Cu}^{\text{II}}@1'$ at 195K. (b) Cu^{II} exchange in **1'** in ethanol medium. (c) Uptake of different cations by **1'** from an equimolar mixture of all the cations. (d) Stern Volmer plot for quenching by Cu^{II} at 30°C and 80°C. (e) Characteristic emission of **1** quenched by different concentration of Cu^{II} solutions.

solution increases (Fig. 2(e)). To determine the efficiency of **1** as a

Cu^{II} sensor, the Stern-Volmer plot at room temperature (~30°C) was constructed and the quenching constant was found to be $1.986 \times 10^3 \text{ M}^{-1}$ (Fig. 2(d)), which decreased to $3.621 \times 10^2 \text{ M}^{-1}$ on repeating the experiment at 80°C¹². This suggests that the quenching follows a static mechanism, presumably by the complexation of Cu^{II} with **1'**. Increase in temperature decreases this complexation promoting the decrease in the quenching constant. The new band in the UV spectra at ~720 nm is also an evidence of the static quenching.

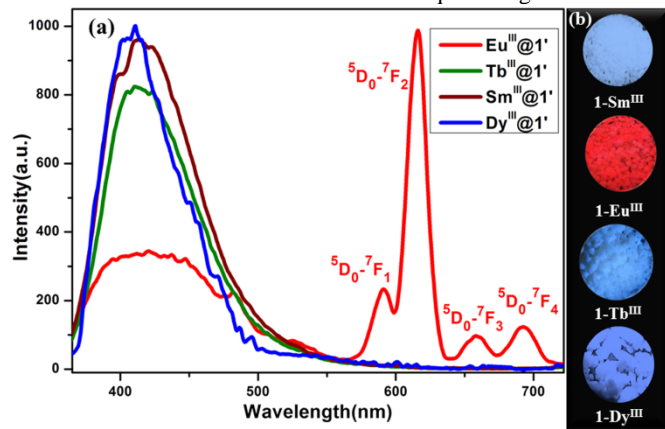


Fig. 3(a) Emission spectra of Eu^{III}@**1'**, Tb^{III}@**1'**, Sm^{III}@**1'** and Dy^{III}@**1'**. (b) Photographs of the respective samples under UV lamp.

As the pore surface of **1** is studded with hard oxygen donors, we anticipated the framework to be a potential candidate for encapsulating different hard acid Ln^{III} cations. The Ln^{III} ions are capable of expanding the coordination spheres based on their flexible geometry. Ln^{III}@**1'** samples were prepared by immersing **1** in 0.01M solutions of nitrate salts of Eu^{III}, Tb^{III}, Sm^{III} and Dy^{III}¹². ICP-OES data suggests that the exchange is about 62% with Sm^{III}, 68% with Eu^{III}, 75% with Tb^{III} and 77% with Dy^{III} in the respective exchanged compounds. The emission properties of Ln^{III}@**1'** were studied since typically non emissive Ln^{III} ions were expected to furnish new luminescent materials through the antenna effect¹⁴ when captured in the pores of **1'**. However, to our surprise, **1** fails to sensitize Dy^{III}, Sm^{III} or Tb^{III} which is evident from the absence of the characteristic peaks of Dy^{III}, Sm^{III} or Tb^{III} from emission spectra of the respective exchanged compounds when excited at 317 nm (Fig. 3(a)). Rather Ln^{III}@**1'** [Ln=Dy, Sm, Tb] samples show a blue emission similar to as-synthesized **1** which is observed under UV lamp (Fig. 3(b)). The emission spectrum of Eu^{III}@**1'** is rather remarkable, showing the appearance of characteristic emission bands of the Eu^{III} ion centred at 591, 615, 659, 693nm which can be attributed to the ⁵D₀→⁷F₁₋₄ transitions. This is accompanied with concomitant decrease in the emission intensity of the AMOF at ~410 nm (Fig. 3(a)). The spectrum is dominated by the ⁵D₀→⁷F₂ intense band and it is responsible for the brilliant red emission of the Eu^{III}@**1'** hybrid. This confirms that **1** acts as an antenna and selectively sensitizes Eu^{III}, although it takes up other Ln^{III} cations¹². Probably this unprecedented selective sensitization of Eu^{III} is realized due to the facile energy transfer to the excited ⁵D₀ state of Eu^{III} from the singlet excited states of **1**, which is not favourable in case of the other lanthanides.

Conclusions

In conclusion, we have synthesized a new Mg based AMOF (**1**) with 1D cation exchangeable channels that has been exploited for selective sequestration for Cu^{II} ions. This can be realized through fluorescence read out by the turn-off of emission. The AMOF can also encapsulate several hard lanthanide metal ions through preferential binding with the hard oxygen centers. The Ln^{III} exchanged framework exhibits unprecedented specific sensitization

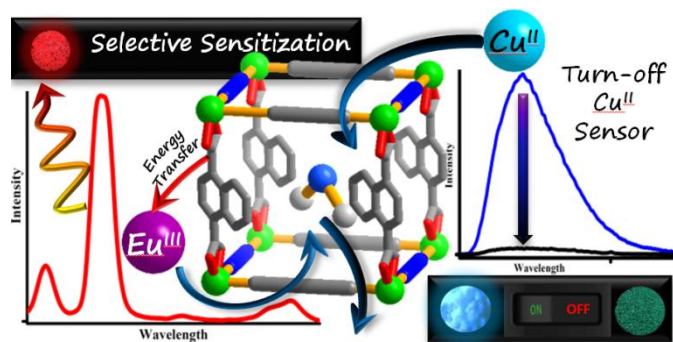
for Eu^{III} resulting in a red luminescent material through Post Synthetic Modification. Such bimodal functionalities are accomplished through proper size and functionalities of the cation exchangeable channels in **1**. Inclusion of specific cationic groups in such AMOFs would also facilitate targeted fabrication of smart materials with versatile properties like catalytic activity, adsorption, magnetism, nonlinear optical response etc., which is currently being explored in our laboratory.

Notes and references

^a Molecular Materials Laboratory, Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064, India

[†] Electronic Supplementary Information (ESI) available: X-ray crystallographic details in CIF format, detailed experimental procedures, excitation and emission spectra, PXRD patterns, adsorption isotherms and TGA profiles.

- (a) P. Vanelderen, J. Vancauwenbergh, B. F. Sels and R. A. Schoonheydt, *Coord. Chem. Rev.*, 2013, **257**, 483-494; (b) J. Jiang, J. Yu and A. Corma, *Angew. Chem. Int. Ed.*, 2010, **49**, 3120-3145.
- (a) R. Haldar and T. K. Maji, *CrystEngComm*, 2013, **15**, 9276-9295; (b) Themed Issue: Metal-organic Frameworks, *Chem. Rev.*, 2012, **112**, 673-1268.
- Z. Zhang, Z.-Z. Yao, S. Xiang and B. Chen, *Energy Environ. Sci.*, 2014, **7**, 2868-2899.
- S. Y. Vyasamudri and T. K. Maji, *Chem. Phys. Lett.*, 2009, **473**, 312-316.
- (a) Y. Liu, G. Li, X. Li and Y. Cui, *Angew. Chem.*, 2007, **119**, 6417-6420; (b) E. Quartapelle Procopio, F. Linares, C. Montoro, V. Colombo, A. Maspero, E. Barea and J. A. R. Navarro, *Angew. Chem. Int. Ed.*, 2010, **49**, 7308-7311; (c) J. Yu, Y. Cui, C. Wu, Y. Yang, Z. Wang, M. O'Keeffe, B. Chen and G. Qian, *Angew. Chem. Int. Ed.*, 2012, **51**, 10542-10545; (d) J. An, S. J. Geib and N. L. Rosi, *J. Am. Chem. Soc.*, 2009, **131**, 8376-8377; (e) D. T. Genna, A. G. Wong-Foy, A. J. Matzger and M. S. Sanford, *J. Am. Chem. Soc.*, 2013, **135**, 10586-10589; (f) J. Tian, L. V. Saraf, B. Schwenzer, S. M. Taylor, E. K. Brechin, J. Liu, S. J. Dalgarno and P. K. Thallapally, *J. Am. Chem. Soc.*, 2012, **134**, 9581-9584; (g) S. Yang, X. Lin, A. J. Blake, G. S. Walker, P. Hubberstey, N. R. Champness and M. Schröder, *Nat Chem*, 2009, **1**, 487-493.
- S. Yang, G. S. B. Martin, J. J. Titman, A. J. Blake, D. R. Allan, N. R. Champness and M. Schröder, *Inorg. Chem.*, 2011, **50**, 9374-9384.
- K. Jayaramulu, R. P. Narayanan, S. J. George and T. K. Maji, *Inorg. Chem.*, 2012, **51**, 10089-10091.
- T. Hirayama, G. C. Van de Bittner, L. W. Gray, S. Lutsenko and C. J. Chang, *Proc. Natl. Acad. Sci.*, 2012, **109**, 2228-2233.
- (a) J.-S. Qin, S.-J. Bao, P. Li, W. Xie, D.-Y. Du, L. Zhao, Y.-Q. Lan and Z.-M. Su, *Chem. Asian J.*, 2014, **9**, 749-753; (b) J.-S. Qin, S.-R. Zhang, D.-Y. Du, P. Shen, S.-J. Bao, Y.-Q. Lan and Z.-M. Su, *Chem. Eur. J.*, 2014, **20**, 5625-5630.
- C. Yang, L.-M. Fu, Y. Wang, J.-P. Zhang, W.-T. Wong, X.-C. Ai, Y.-F. Qiao, B.-S. Zou and L.-L. Gui, *Angew. Chem. Int. Ed.*, 2004, **43**, 5010-5013.
- (a) Y.-Q. Chen, G.-R. Li, Z. Chang, Y.-K. Qu, Y.-H. Zhang and X.-H. Bu, *Chem. Sci.*, 2013, **4**, 3678-3682; (b) S. Liu, J. Li and F. Luo, *Inorg. Chem. Commun.*, 2010, **13**, 870-872; (c) Y.-W. Li, J.-R. Li, L.-F. Wang, B.-Y. Zhou, Q. Chen and X.-H. Bu, *J. Mater. Chem. A*, 2013, **1**, 495-499.
- See Supporting Information.
- J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477-1504.
- (a) Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2011, **112**, 1126-1162; (b) S. Roy, A. Chakraborty and T. K. Maji, *Coord. Chem. Rev.*, 2014, **273-274**, 139-164; (c) S. Mohapatra, S. Adhikari, H. Rijju and T. K. Maji, *Inorg. Chem.*, 2012, **51**, 4891-4893; (d) B. Chen, L. Wang, Y. Xiao, F. R. Fronczek, M. Xue, Y. Cui and G. Qian, *Angew. Chem. Int. Ed.*, 2009, **48**, 500-503.



A bimodal anionic MOF is reported which acts as a turn-off Cu^{II} sensor as well as specific Eu^{III} sensitizer via cation exchange.