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

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Abstract: A novel porous anionic MOF \([\text{Mg}_3(\text{ndc})_2\text{HCO}_2\text{H}_2\text{O}]\text{[NH}_3\text{Me}_2\text{H}_2\text{O}\text{DMF]}(\text{I})\) having exchangeable dimethyl amine cations in 1D channels has been synthesized and characterized. Through cation exchange, \text{I} manifests bimodal functionality, being a turn-off sensor of Cu\textsuperscript{II} on one hand, and a selective sensitizer for Eu\textsuperscript{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 cations\textsuperscript{1}. 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 functionalities\textsuperscript{2}. The efficiency of MOFs in gas storage and separation\textsuperscript{3}, catalysis, drug delivery and optoelectronic devices are well documented\textsuperscript{4-5}. However, unlike zeolites, ion exchange is infrequent in MOFs\textsuperscript{6}, which are generally neutral in nature. Applying proper synthetic strategies, it is possible to get anionic MOFs (AMOFs)\textsuperscript{7}, 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\textsuperscript{8}, drug delivery\textsuperscript{9}, tunable adsorption\textsuperscript{10} and catalysis\textsuperscript{11}. However the chemical affinity of the coordination spaces determines the selective capture of a specific metal ion, therefore proper functionalization of pore surface is crucial\textsuperscript{12}. 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\textsuperscript{II} ion by such AMOFs would be particularly interesting as this strategy would ensue a novel route for Cu\textsuperscript{II} sensing\textsuperscript{13}, which is of paramount importance for biological applications. The study of prognosis of copper imbalance related diseases, e.g., Menkes, Wilson and Alzheimer’s diseases, prion disorders, and amyotrophic lateral sclerosis demand effective sensing and removal of copper\textsuperscript{14} 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\textsuperscript{III} cations to furnish novel Ln-doped luminescent materials and new Ln sensors has been studied previously\textsuperscript{15}. However, selective Eu\textsuperscript{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 labelling\textsuperscript{16}.

In this communication, we report the synthesis and structural characterization of a 3D anionic MOF, \([\text{Mg}_3(\text{ndc})_2\text{HCO}_2\text{H}_2\text{O}]\text{[NH}_3\text{Me}_2\text{H}_2\text{O}\text{DMF]}(\text{I})\) [ndc: 1,4-naphthalenedicarboxylate] and its metal ion sequestration and sensing properties. The framework contains 1D channels occupied by the cationic guest \text{NH}_3\text{Me}_2\text{H}^+ [dimethyl ammonium (DMA)] which can be selectively replaced by Cu\textsuperscript{II} ions among other transition metal cations. Moreover the framework can encapsulate several lanthanide metal ions but selectively sensitize Eu\textsuperscript{III} resulting in a bright red luminescent framework (Scheme 1). To the best of our knowledge, such bimodal functionalities of specific sensing\textsuperscript{17} and removal of a transition metal (Cu\textsuperscript{II}) and selective sensitization of a lanthanide
metal (EuIII) based on luminescence quenching and enhancing respectively using a single framework system is yet to be reported.

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 MgII centers, all of which are distorted from perfectly octahedral geometry (Fig. 1(a))\textsuperscript{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. In case of 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 MgII centers are arranged to form a 1D chain along $c$ direction\textsuperscript{12}. These 1D chains are further connected with each other through ndc_b and ndc_c and repeat themselves along $b$ direction to generate the 3D framework\textsuperscript{12} with 1D channels occupied by the guest H2O, DMF and extra framework DMA cations (Fig. 1(b)). The formate and DMA cations are formed in situ from DMF under solvothermal conditions\textsuperscript{3d, 5c}. 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 DMF\textsuperscript{12}. 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))\textsuperscript{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 MgII sites in 1', which can interact well with the quadrupole moment of CO$_2$\textsuperscript{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 chlorides\textsuperscript{12}. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis of the exchanging solution showed the absence of MgII 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 CuII ions, while the extent of exchange for MnII, CoII, NiII and ZnII are 0, 4, 12 and 0% respectively\textsuperscript{12}. This high percentage of exchange for CuII is evident as a green solution of CuII in ethanol becomes colourless on immersing 1' in it, while the white solid 1' yields bright green CuII@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 CuII\textsuperscript{12}. Due to d-d transition, a new band appears in the UV spectra of CuII@1' at ~720 nm in addition to the band at ~317 nm as observed in 1. This further supports the coordination of CuII with the carboxylate oxygens of 1\textsuperscript{12}. Due to structural reorganization after encapsulation of CuII, there are some changes in the PXRD pattern of CuII@1' as well as the appearance of a few new peaks\textsuperscript{12}. The inclusion of CuII into the pore of 1 was further confirmed from the CO$_2$ adsorption isotherm (Fig. 2(a)) of CuII@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 CuII ions occupy the pores of 1 randomly, thus inhibiting the diffusion of CO$_2$. Furthermore, the CuII selectivity of 1 was studied by immersing 1' in an equimolar solution of a mixture of MnII, CuII, CoII, NiII and ZnII ions. ICP-OES analysis confirms the exchange of 85% of the DMA cations with CuII, which is much higher compared to the other metal ions (Fig. 2(c))\textsuperscript{12}. This selective capture of CuII may be explained based on the flexible geometry of CuII 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 nm\textsuperscript{12} in solid state. We anticipated that the emission intensities would be affected by the incorporation of CuII and this was validated by the significant quenching of emission in CuII@1'. The quenching of emission can be attributed to the ligand field splitting of d-orbitals of CuII 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$^{-5}$ and 10$^{-6}$ M solutions of CuII and emission is quenched gradually as the concentration of the CuII solution increases (Fig. 2(e)). To determine the efficiency of 1 as a
CuII sensor, the Stern-Volmer plot at room temperature (~30°C) was constructed and the quenching constant was found to be 1.986 × 10^3 M−1 (Fig. 2(d)), which decreased to 3.621 × 10^2 M−1 on repeating the experiment at 80°C. This suggests that the quenching follows a static mechanism, presumably by the complexation of CuII with I−. 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 EuIII@I−, TbIII@I−, SmIII@I− and DyIII@I−. (b) Photographs of the respective samples under UV lamp.

As the pore surface of I− is studded with hard oxygen donors, we anticipated the framework to be a potential candidate for encapsulating different hard acid LnIII cations. The LnIII ions are capable of expanding the coordination spheres based on their flexible geometry. LnIII@I− samples were prepared by immersing I− in 0.01M solutions of nitrate salts of EuIII, TbIII, SmIII and DyIII. ICP-OES data suggests that the exchange is about 62% with SmIII, 68% with EuIII, 75% with TbIII and 77% with DyIII in the respective exchanged compounds. The emission properties of LnIII@I− were studied since typically non emissive LnIII ions were expected to furnish new luminescent materials through the antenna effect when captured in the pores of I−. However, to our surprise, I− fails to sensitize DyIII, SmIII or TbIII which is evident from the absence of the characteristic peaks of DyIII, SmIII or TbIII from emission spectra of the respective exchanged compounds when excited at 317 nm (Fig. 3(a)). Rather LnIII@I− [Ln=Dy, Sm, Tb] samples show a blue emission similar to as-synthesized I− which is observed under UV lamp (Fig. 3(b)). The emission spectrum of EuIII@I− is rather remarkable, showing the appearance of characteristic emission bands of the EuIII ion centred at 591, 615, 659, 693nm which can be attributed to the 5D0→5F1,4 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→5D4 intense band and it is responsible for the brilliant red emission of the EuIII@I− hybrid. This confirms that I− acts as an antenna and selectively sensitizes EuIII, although it takes up other LnIII cations1−2. Probably this unprecedented selective sensitization of EuIII is realized due to the facile energy transfer to the excited 5D0 state of EuIII from the singlet excited states of I−, which is not favourable in case of the other lanthanides.

Conclusions

In conclusion, we have synthesized a new Mg based AMOF (I) with 1D cation exchangeable channels that has been exploited for selective sequestration for CuII 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 LnIII exchanged framework exhibits unprecedented specific sensitization for EuIII 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 I. 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

12. See Supporting Information.
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.