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A channel-equipped metal-organic framework, resulted from pyrolysis of \( [(\text{CH}_3)_2\text{NH}_2]@\text{Eu}_2\text{L}_3\{\text{HCOO}\} ] \), showed the preferable absorption of \( \text{CO}_2 \) and the Eu(III)-based emission quenched by aromatics.
Pyrolytic cavitation, selective adsorption and molecular recognition of a porous Eu(III) MOF

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ABSTRACT: A channel-equipped metal-organic framework (1-pyr), resulted from pyrolysis of [(CH$_3$)$_2$NH$_2$]@[Eu$_2$L$_3$(HCOO)] (1) (L$^{2-}$ = isophthalate), showed the preferable absorption of CO$_2$ and the Eu(III)-based emission quenched by aromatics.

In recent decades, porous metal-organic frameworks (PMOFs) allowing residence of small molecules have captured an intense attention of coordination chemistry because of their potential applications in such as gas storage and separation, molecular recognition, and controlled medicine releasing, etc. Structurally the frameworks are made of metal ions and linking ligands, but, they are not doomed to produce directly from the reactions of these reagents because the open structures usually permit the occupation of neutral molecules or counter ions to sustain their long-span vacancy and therefore the PMOFs with permanent porosity are often prepared by thermally removing the existing guests, a step so called post-synthesis. But, it is of note that, in the documented cases, the removed species are limited to included molecules, instead, a desertion of guest accompanied by a loss of anionic coordinating part of MOF has never been exemplified.

Herein, as illustration of the unprecedented cavitation and dual function of a PMOF in selective absorption and molecular recognition, we report the porosity-based property of a Eu(III) PMOF resulted from pyrolysis of a host-guest adduct (CH$_3$)$_2$NH$_2$@[Eu$_2$L$_3$(HCOO)] (L = isophthalate).

The single crystal of 1 for X-ray determination was harvested from heating the mix of Eu$_2$O$_3$ and H$_2$L in a DMF/CH$_3$OH/H$_2$O solvent at 160°C for 3 days, followed by slowly cooling to room temperature, whose structure has been determined by LUO et al, to be a host-guest adduct showing the channels occupied by protonated dimethylamines (Fig. 1). It is of note that excessive isophthalic acid is needed for getting the single crystal of 1 most likely due to the requirement of protonation of dimethylamine. The guess is confirmed by the isolation of the single crystals of Gd(III) and Sm(III) analogues (denoted as 2 and 3 respectively) under parallel conditions (See the Supporting Information).

Fig. 1 The structure of 1 (left) and expected structure of 1-pyr (right).

Expectably, the channels of 1 can be emptied by thermolysis since the charged [(CH$_3$)$_2$NH$_2$]$^+$ and [HCOO]$^-$
groups produced from hydrolysis of DMF are decomposable. Thermogravimetric analysis of 1 agrees the assumption by giving first a weight loss of ca 10.45% at 350°C, corresponding to the ratio sum of these groups (Fig. S1). More supportively, the solid FT-IR spectrum of pyrolyzed 1 (denoted as 1-pyr) shows no absorption band in the range of 2400 - 3200 cm\(^{-1}\) for [(CH\(_3\)_3NH\(_2\)] and HCOO (Fig. S2), and the elemental analysis indicates its formula as [Eu\(_2\)L\(_2\)] (C% 36.18, calcd. 36.16, H% 1.46, calcd. 1.51). Moreover, the powder x-ray diffraction spectrum verify its crystallinity (Fig. S3).

The accessible void of 1-pyr is calculated by PLATON\(^9\) for 1471.8 Å\(^3\) per unit cell (21.6 % of the total volume). Its openness is proved by the \(N_2\) and \(H_2\) adsorption isotherms at 77K, from which the Brunauer–Emmett–Teller and Langmuir surfaces are determined as 124 m\(^2\)/g and 192 m\(^2\)/g, respectively (Fig. 2). The absorption capacities of 1-pyr (76 cm\(^3\)/g for \(N_2\) and 35 cm\(^3\)/g for \(H_2\)), in comparison with those of synthesized 1 (6.3 cm\(^3\)/g for \(N_2\), 0.3 cm\(^3\)/g for \(H_2\)) are significantly higher (Fig. S4), so suggesting that the channels of 1-pyr are effectively evacuated by pyrolysis and so illustrating a pyrolytic cavitation of PMOF by removing both a cationic guest species and an anionic unit of MOF.

Moreover, to evaluate the capability of 1-pyr to separate \(CO_2\) from \(N_2\) under ambient conditions, the gas adsorption isotherms were tested at 273 K (Fig. S6) and 298 K and so gave the agreement with single-site Langmuir (SSL) model (Fig. S7 and Table S3). Ideal Adsorbed Solution Theory\(^13\) (IAST) has been widely used to predict absorption of mixed gases in PMOFs\(^6, 14\), and gives good agreement with the adsorption experiments\(^15\). The predicted selectivity of \(CO_2/N_2\) by IAST for 1-pyr at 273 K and 298 K are shown in Fig. 4, from which it is seen that the selectivity increases with the increases of loading amount (Fig. 4) and percentage of \(CO_2\) (Fig. S8). It is noticed that, as temperature changes from 273 K to 298 K, the selectivity of 1-pyr for a mix of \(CO_2/N_2\) in a ratio of 15:85, close to the gas composition from a power plant, increases from 40.4 to 72.5. Compared with the reported PMOFs based on \(m\)-benzenedicarboxylate\(^16\) (Table
S2). **1-pyr** shows an excellence in selectivity though it has the smallest BET surface and therefore it is a promising material for separating CO$_2$ from N$_2$ in a postcombustion gas mix$^{17}$.

Quantitatively detecting the toxic and explosive chemicals, nitrobenzene (NB), dinitrotoluene (DNB) and trinitrotoluene, (TNB), is an imperative mission of chemistry. For this purpose, a continuous effort has focused on developing the new probers capable of sensing the aromatics. As a kind of the candidates, PMOF shows a superiority in high sensitivity, easy preparation and cavity controllability$^{18}$.

Inspired by the work and considering the openness of **1-pyr**, we explored its responses to different solvents by examining the changes of Eu(III)-based $^5$D$_0$$\rightarrow$$^7$F$_j$ emission (620 nm, Fig. S9a). Fig. 5 presents the relations of emission intensities to solvents, showing that the bands of **1-pyr** dispersed in aliphatic solvents are almost identical to that as solids, while those in aromatics, especially in nitroaromatics, are remarkably quenched (Fig. S10). The fact suggests that the PMOF can recognize the aromatics, especially the nitroaromatics through being quenched by the aromatics. In light of the structure of **1-pyr**, the effect of aromatics can be assigned to a $\pi$$\cdot$$\pi$ interaction of their phenyl moieties with those in **1-pyr** since the supramolecular contact enables the host-guest communication. This is supported by the UV-Vis spectra of aromatics (Fig. S11), all showing a absorption at 290 nm (as excitation wavelength of various emulsions) with intensities proportional to their quenching efficiencies. Moreover, as seen in Fig. 5, the quenching effects of nitroaromatics are subject to the number of nitro groups, meaning that the quenching ability of aromatics is subject to the electron-withdrawing ability of substitution, and so suggest that the explosives play acceptors in the host-guest interactions. In such a sense, the quenching effect of aromatics is proposed via drawing electron from **1-pyr** through $\pi$$\cdot$$\pi$ communication$^{19}$.

**Conclusions**

In summary, the pyrolytic cavitation of **1-pyr** illustrates a new way to make a PMOF from a host-guest adduct by removing both a guest and a component of MOF. The cavitation leads to not only an enlarged inner surface of PMOF, but also the open metal sites serving as acidic centers to interact with polarized molecule. The cavity of **1-pyr** is selective, preferably absorbing CO$_2$ from N$_2$ and so promising a use in gas separation. Besides, the PMOF is photoluminescent, whose emission is quenched by aromatics, and thus can be used for molecular recognition.

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Notes and references
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