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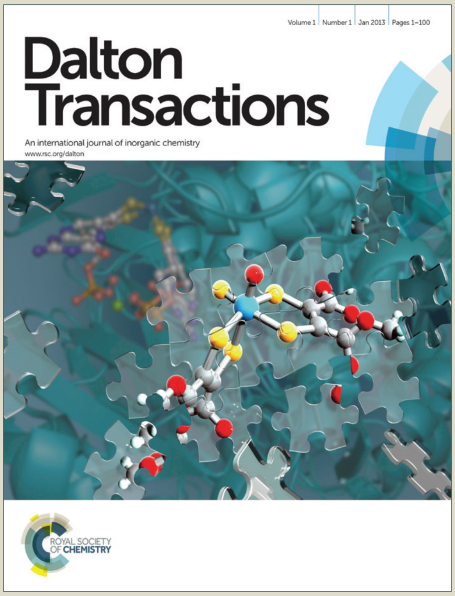

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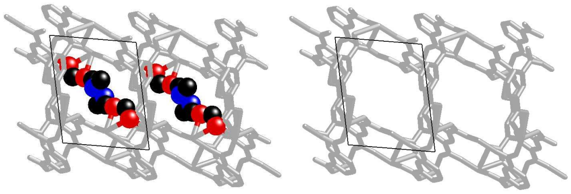

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Pyrolytic cavitation, selective adsorption and molecular recognition of a porous Eu(III) MOF

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ABSTRACT: A channel-equipped metal-organic framework (1-pyr), resulted from pyrolysis of $[(CH_3)_2NH_2]@[Eu_2L_3(HCOO)]$ (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[1] and separation[2], molecular recognition[3], and controlled medicine releasing[4], 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[5] and therefore the PMOFs with permanent porosity are often prepared by thermally removing the existing guests, a step so called post-synthesis[6, 7]. 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 $(CH_3)_2NH_2@[Eu_2L_3(HCOO)]$ (L = isophthalate).

The single crystal of **1** for X-ray determination was harvested from heating the mix of Eu_2O_3 and H_2L in a $DMF/CH_3OH/H_2O$ solvent at 160℃ for 3 days, followed by slowly cooling to room temperature, whose structure has been determined by LUO[8], 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).

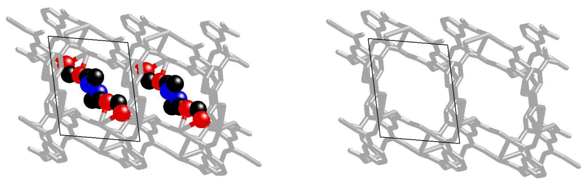

Fig. 1 The structure of **1** (left) and expected structure of **1-pyr** (right).

Expectably, the channels of **1** can be emptied by thermolysis since the charged $[(CH_3)_2NH_2]^+$ 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 $[(CH_3)_2NH_2]^+$ and $HCOO^-$ (Fig. S2), and the elemental analysis indicates its formula as $[Eu_2L_3]$ (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.

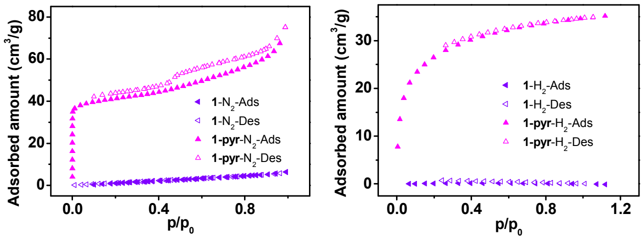

Fig.2 The N_2 (left) and H_2 (right) adsorption and desorption isotherms of **1** and **1-pyr** at 77K.

The adsorption isotherm of **1-pyr** at 298 K belong to type-I (Fig. 3) in accord with the behavior of a rigid MOF and show a preferable absorption of CO_2. The preferred absorption of CO_2 is clearly not size influenced because the dynamic diameter of CO_2 (3.30 Å) is even larger than that of H_2 (2.89 Å) but smaller than N_2 (3.64 Å). In the case, we ascribe the favor of **1-pyr** to CO_2 to an electrostatic interaction of the quadrupolar molecule[10] with acidic Eu(III) sites[11]. The excuse accounts for not only the absorption selectivity of **1-pyr**, but also a hysteresis of desorption. Besides, the much higher N_2 and H_2 absorptions of **1-pyr** at 77 K than those at 298 K reveal a noncovalent property of the interaction and a linear symmetry of the aperture of **1-pyr**. Such being the case, we conclude that the pyrolysis not only enlarges the inner surface of **1-pyr**, but also provides the open electrophilic Eu(III) centers. Calculating from initial slopes[12] of the isotherms (Fig. S5), the PMOF gives an selectivity of CO_2/N_2 for 57.4 at 298 K.

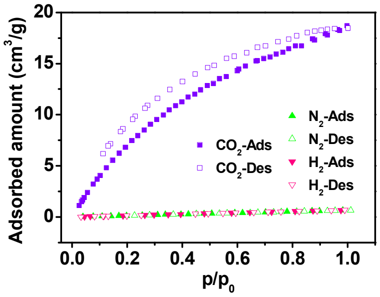

Fig. 3 Adsorption and desorption isotherms of **1-pyr** on CO_2, N_2 and H_2 at 298K.

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].

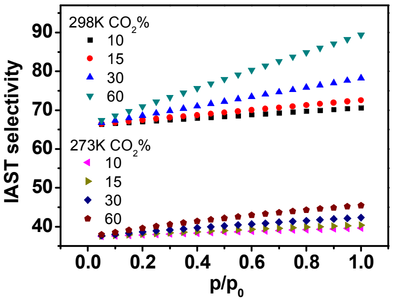

Fig. 4 The predicted IAST selectivitys of CO_2/N_2 at various CO_2 ratios for **1-pyr** at 273 K and 298 K.

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 sensoring 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 $^5D_0 \rightarrow {}^7F_J$ 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 π-π 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 π-π communication[19].

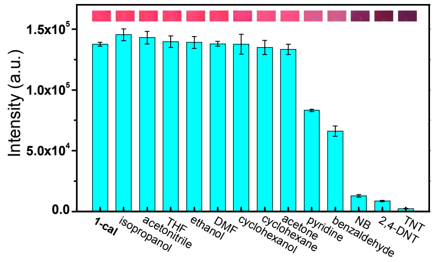

Fig. 5 The 620 nm emission intensities of **1-pyr** at as solids and suspensions in different solvents (Inset: Their photographs under UV light in dark excited at 290 nm).

Conclusions

In summary, the pyrolytic cavitation of **1-pyr** illustrates a new way to make a PMOF from a host-gust 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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