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A new 2D Cu-MOF constructed from carboxylate ligands containing $C-H\cdots\pi$ interactions as a recyclable responsive luminescent sensor for VOCs⁺

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A new type of 2D metal-organic framework (MOF), namely Cu-MOF, was constructed from Cu(NO₃)₂·3H₂O and the novel ligand 1,4-bis(4-naphthoic acid)benzene. The C-H··· π interactions in the Cu-MOF effectively reduced aggregation-caused quenching (ACQ) due to restrictions in intramolecular motion (RIM), increased fluorescence, and controlled crystal packing properties, resulting in low dimensional parallelogram channels and a responsive "turn-on" fluorescence. The activated Cu-MOF exhibited excellent chemical sensing properties to various volatile organic compounds (VOCs) and showed excellent recyclability.

Metal-organic frameworks (MOFs) are hybrid materials containing extended, highly porous networks that are formed via self-assembly processes between organic ligands and metal centers.¹ Since MOF 5 was first reported in 1999,² it has been widely used in various research and commercial applications for gas separation and storage,³ catalysis,⁴ drug delivery,⁵ and chemical sensing.⁶ Compared with traditional micromolecular fluorescent materials that possess extended π -conjugated structures, luminescent MOFs offer unique advantages in molecular recognition and sensing because the rigid framework effectively prevents the formation of π -stacked aggregates with forbidden fluorescence and reduces aggregation-caused quenching (ACQ).⁷ The porosity of the framework provides enough room for interactions with guest molecules.8 Luminescent MOFs that exhibit tunable fluorescence are extensively used for temperature monitoring⁹ applications and for the production of medicines,¹⁰ explosives,¹¹ chemical weapons,¹² solvents,¹³ and small organic molecules¹⁰ due to

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their high sensitivity, extreme selectivity, and ease of use.¹⁴ Despite the obvious advantages of using luminescent MOFs to detect VOCs, there are glaring disadvantages that hinder their widespread application. Only a handful of luminescent MOFs have been used to detect VOC vapors,¹⁵ such as extremely rare ligand-based luminescent MOFs,^{16,17} due to the restrictions in intramolecular motion (RIM) that occur after their formation and the intrinsically poor fluorescence of the component ligands.¹⁸ Yet, these drawbacks do not mitigate the potential usefulness of ligand-based luminescent MOFs for detecting VOCs. This trait is attributed to the weaker molecular C-H $\cdots\pi$ interactions¹⁹ that occur between soft acids and soft bases. These interactions play significant roles in molecular conformation,²⁰ chiral recognition,²¹ and crystal packing.²² Indeed, the C-H··· π interaction-assisted alignment of organic conjugated systems significantly impacts the regulation of photophysical properties.²³ Unlike the conventional hydrogen bond and Coulomb forces, C-H... π interactions are nonpolar and effective in water due to their inherent stability, which is attributed to dispersion interactions and the electrostatic contributions that account for about 20% of the total interactions exhibited by these compounds.²⁴ In this study, Cu-MOF was successfully prepared using a carboxylate ligand possessing strong C-H··· π interactions that made the Cu-MOF product to exhibit intense fluorescence. Additionally, the newly synthesized Cu-MOF contained low-dimensional channels and dangling phenyl rings that enhanced the contact interaction between the framework and the guest molecules. The activated Cu-MOF showed responsive "turn-on" fluorescence in the presence of VOC vapors, high selectivity, and excellent recyclability.

The structure of this previously unreported carboxylate ligand, namely 1,4-bis(4-naphthoic acid)benzene, was determined *via* ¹H and ¹³C NMR spectroscopy and X-ray crystallography; here, the solvent molecules were removed for spectroscopic clarity. Details of the synthesis of this carboxylate ligand can be found in the ESI.† Theoretically, the two dangling phenyl rings that lacked carboxylate groups were able to



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vibrate, and the other benzene rings could rotate in extremely dilute solutions of the ligand. However, the spectroscopic analysis revealed that a molecule of the ligand was closely connected with six surrounding ligands, thereby forming a two-dimensional plane that restricted the intramolecular vibration and rotation of the ligand's crystals. The extensive $C-H\cdots\pi$ interactions also suppressed nonradiative decay through intramolecular motion restrictions (Fig. S3†).

Since the C–H··· π interactions were most effective in water/ solutions,²⁴ the ligand was configured as a dilute solution of 1.0×10^{-6} mg L⁻¹ using THF/H₂O mixed solutions of various volume ratios as the solvents during spectroscopic analysis. The fluorescence of the ligand first intensified after the initial dilution step, but this intensity eventually decreased, presumably due to ACQ. A subsequent increase in the emission was attributed to RIM caused by C–H··· π interactions and the emission maximum gradually red-shifted when the water ratio increased (Fig. S4†). The ligand's quantum yield was 14.52%, and the fluorescence lifetime was 68.5 ns, which indicated that the ligand is a good fluorescent material or a monomer in luminescent MOFs even in the solid or aggregated state.

Cu-MOF, which was isolated as green transparent individual crystals, was obtained via solvothermal reactions between the carboxylate ligand and Cu(NO₃)₂·3H₂O in DMF. Singlecrystal X-ray diffraction analysis revealed that the Cu(II) complex crystallized in the triclinic system with the $P\bar{1}$ space group and exhibited a 2D dinuclear copper-paddlewheel secondary building unit (SBU) in its structure. The ligand eliminated a proton in the copper-paddlewheel SBU, and each carboxylic moiety coordinated with two Cu(II) ions. Since the two Cu(II) ions formed a Cu-Cu bond with a distance of 2.6326(15) Å, the ions simultaneously coordinated with four oxygen atoms from four deprotonated ligands with two oxygen atoms from two DMF molecules. The asymmetric unit included two coordinated DMF molecules, two free DMF molecules, and two SBU-extended ligands (Fig. S5[†]). There are six types of benzene rings in Cu-MOF, forming three types of C–H··· π interactions. First, the two sides of the benzene ring at which C13 is located simultaneously accept the C-H··· π interactions from H28 or H31, resulting in their fixed positions. Each carbon atom on the benzene ring has only one possible position, the occupancy factor of which is 1. Second, one side of the benzene ring at which C10 is located accepts the C-H $\cdots\pi$ interaction from H22 or H39, which is simultaneously connected to the benzene ring at which C13 is located. Hence, some of the atoms are fixed in position, with occupancy factors of 1. There are two possible positions for another atom, the occupancy factors of which are 0.5. Finally, one side of the benzene ring at which C33 or C18 is located accepts the C-H… π interaction from H6 or H6A. Therefore, all the atoms have two possible positions, the occupancy factors of which are 0.5. The benzene rings of H28, H31, H22, H39, H6, and H6A are all providers and not acceptors of the C-H··· π interactions, because of which all atoms have two possible positions, the occupancy factors of which are 0.5. The detailed C–H $\cdots\pi$ interaction table is shown in the ESI (Table S1[†]). The activated Cu-MOF has a

responsive "turn-on" fluorescence character because the unfixed benzene rings are easily affected by the analytes in the pores.⁸ The individual crystals of Cu-MOF exhibited a 2D splitlevel lamellar structure with 1D parallelogram-shaped channels; Fig. S6† shows that some of these channels were occupied by the dangling benzene rings. The observed C-H… π interactions suspended the dangling benzene rings in the adjacent layers bound to the same channels, thereby resulting in Cu-MOF channels that were 10.30 Å in diameter (Fig. 1b).

The obtained Cu-MOF was soaked sequentially in MeOH and CH₂Cl₂ for 3 days each at room temperature before being vacuum-dried at 80 °C to give the activated Cu-MOF as green transparent lamellar crystals. Unfortunately, the crystals could not be subjected to X-ray crystallography; thus, the structure of the activated Cu-MOF was determined via powder X-ray diffraction (PXRD), thermogravimetric analysis, and surface area and pore size distribution measurements. As shown in Fig. S5,† Cu-MOF contained two kinds of solvent molecules, namely coordinated and free solvent molecules. Each of the aforementioned molecules accounted for 11.7% of the total molecular weight $(C_6N_2O_2H_{12})$. The thermogravimetric analysis (Fig. 2a) revealed that Cu-MOF had lost its free solvent molecules at 150 °C (~11.7 wt%), followed by its coordinated solvent molecules at 250 °C (~11.7 wt%). The onset of thermal stability at 320 °C prevented further losses in mass. However, the activated Cu-MOF did not undergo mass losses; instead, it violently decomposed at 320 °C, which indicated that the activated Cu-MOF had lost all solvent molecules. Thus, the deprotonated ligands were linked by Cu-Cu interactions in a solvent-free 2D split-level lamellar structure, as confirmed via PXRD (Fig. S7[†]).



Fig. 1 (a) The C–H··· π interactions of Cu-MOF, represented as dotted lines, measured between H and the adjacent phenyl ring centroids. (b) The crystal structure of Cu-MOF viewed along the [010] direction. Here, red and blue represent two neighboring layers, whereas the yellow capsules represent 1D channels with a diameter of 10.30 Å. The solvent molecules have been removed for clarity. (c) The crystal structure of Cu-MOF viewed along the [100] direction. The solvent molecules have been removed for clarity.



Fig. 2 (a) Thermogravimetric curves of Cu-MOF and activated Cu-MOF. (b) Nitrogen adsorption–desorption isotherm of the activated Cu-MOF. Inset: NLDFT pore size distribution of the activated Cu-MOF.

Based on the obtained adsorption and desorption isotherms of N₂, the surface area measurements of Cu-MOF gave a typical type I sorption isotherm, indicating the presence of homogeneous micropores inside (Fig. 2b). The existence of significant hysteresis loops between the adsorption and desorption branches suggests wide channels and/or dynamic structural alteration, such as double bonds, $\pi \cdots \pi$ interactions, or C-H··· π interactions. According to previous reports,^{6,8} MOFs with such structures may be used in detection and separation. Its Langmuir surface area is 312 m² g⁻¹, which is equivalent to the value of the reported 2D MOFs with 1D channels and indicates^{25,26} that the framework retains some porosity after the removal of the solvent. The NLDFT pore size distribution shows that the micropore diameter mainly ranges from 1.2 to 1.4 nm, which is in good agreement with the crystal structure.

The solid-state fluorescence of the ligands was determined before the Cu-MOF was used to conduct fluorescence sensing experiments. Here, we noted that the fluorescence lifetime of Cu-MOF was 99.5 ns, and the associated quantum yield was 2.21%, whereas those of the ligand were 68.5 ns and 14.52%, respectively. It was theorized that the low quantum yield was due to the dangling phenyl rings in Cu-MOF that were unaffected by the C-H··· π interactions, which, in turn, encouraged nonradiative decay processes. Fig. 3a shows that the emission maximum of Cu-MOF was observed at 431 nm, which exhibited a clear blue-shift relative to the emission maximum of the activated Cu-MOF (*i.e.*, at 444 nm). Additionally, the observed intensity of fluorescence was lower, indicating that the fluorescence character of the Cu-



Fig. 3 (a) Fluorescence emission spectrum of the activated Cu-MOF \supset guest. The side entrance slits were 3 nm (solid line) and 0.5 nm (dotted line). Inset: Changes in the intensity of fluorescence as a function of the emission maximum. (b) "On/off" cycles of the activated Cu-MOF *via* alternating treatment with methanol vapor and under vacuum.

MOF was heavily influenced by the attached guest molecules. This relationship between the guest molecule and the Cu-MOF could be exploited to produce fluorescent molecular sensors.

Chemosensing studies were performed by exposing the activated Cu-MOF to various solvent vapors (as discussed in the ESI†). As illustrated in Fig. 3a, the subsequent photoluminescence tests showed that the spectral intensities changed with peak shifts (see the inset). The emission maximum of the respective appropriately-sized guest molecules was preferentially adsorbed into the pores. This means that the observed emission maximum values of the activated Cu-MOF \supset guest molecules were significantly influenced by the size of the guest molecule and followed the order: cyclohexane > benzene > toluene > DMF > acetone > methanol.

It was theorized that the fluorescence of Cu-MOF was caused by the attached ligands and that the responsive "turnon" fluorescence of the activated Cu-MOF was derived from the intrinsically strong fluorescent ligands that exhibited incomplete RIM. The guest molecules filled the pores of the activated Cu-MOF, thereby restricting the vibration and rotation of the dangling benzene ring in the framework; the accompanying fluorescence of the compound is shown in the inset of Fig. 3a. It is worth noting that when benzene was used as the guest molecule, the intensity of fluorescence was extremely low. We theorized that dynamic vapor adsorption (VTI) processes between the activated Cu-MOF and benzene encouraged adsorption, even when benzene's vapor pressure was low (*i.e.*, only 10% of the saturated vapor pressure of the system). When benzene's vapor pressure was 25% of the total saturated vapor pressure of the system, the absorbance value was 4.9% of its own weight; generally, the absorbance values of the system increased continuously under higher vapor pressures. Since Cu-MOF contained free DMF molecules (11.7%) and the fluorescence of the activated $Cu-MOF \supset$ benzene was lower than that of Cu-MOF and its activated analog, there were few incidents of adsorption. This was because the perpendicular conformation of benzene tended to weaken the C-H··· π interactions, thereby encouraging the coplanar conformation in the system which easily transitioned to ACQ via π -stacked aggregation. As noted in the inset of Fig. 3b, the absorbance values increased with time at first, but as the reaction progressed, very little change was noted even when subjected to the same vapor pressure. However, once the vapor pressure inevitably increased, again the absorbance values continued to increase. In other words, even though the benzene vapor continued to flow and there were still vacancies in the metallic center, the associated MOF did not continue to absorb more benzene until the vapor pressure increased despite being subjected to the same vapor pressure. These findings confirmed the theory of the previous speculations, which stated that the fluorescence of the Cu-MOF was caused by the ligand. In the case of toluene, the methyl group limits its π - π stacking with the benzene ring in the MOF. However, in the case of cyclohexanes, such π - π stacking is almost nonexistent because of their noncoplanar structure and higher H content.27,28 Methanol, DMF, and acetone, which contain O or N in their structures, can easily form weak interactions with the ligands or the copper-paddlewheel SBU of the MOF, restricting the intramolecular movement of the benzene ring that is not fixed in the MOF, thereby enhancing its fluorescence intensity.^{29,30}

Since the emission maximum of the activated Cu- $MOF \supset$ methanol was significantly different from the numerical value associated with the activated Cu-MOF, methanol was used as the guest in cyclic experiments. Before this, the timedependent intensity quenching experiment was conducted with the result shown in Fig. S10.† The activated Cu-MOF was exposed to methanol vapor. When the vapor of the guest molecules gradually entered the channels of the MOF, the fluorescence intensity increased and the emission maximum blue shifted and reached the extreme value after adsorption saturation (24 h). To ensure sufficient contact, the activated Cu-MOF was placed in methanol vapor for 2 days when performing cyclic experiments. The emission spectrum was obtained after heating the activated Cu-MOF \supset methanol to 80 °C under vacuum for 3 h. Emission spectra were obtained after subsequent exposure to methanol vapor for 48 h at 40 °C. No obvious changes were noted in the resulting emission maximum and the PXRD data, even after the process was repeated six times (Fig. S7[†]). After the cyclic experiments, the Langmuir surface area of the MOF was 248 m² g⁻¹; furthermore, the adsorption and desorption measurements of N₂ still showed a typical type I sorption isotherm (Fig. S15[†]). This observation confirmed the new compound's excellent repeatability and recyclability (Fig. 3b).

Conclusions

By judiciously designing the ligand and conducting crystal engineering, a new type of 2D split-level fluorescent MOF exhibiting parallelogram 1D channels was synthesized using Cu $(NO_3)_2 \cdot 3H_2O$ and the previously unreported carboxylate ligand 1,4-bis(4-naphthoic acid)benzene, which contained C-H··· π interactions. The strong fluorescence character of the solidstate Cu-MOF was due to extensive C-H $\cdots\pi$ interactions that restricted the intramolecular vibration and rotation, thereby controlling the crystal packing. Its activated analog in the solid state exhibited responsive "turn-on" fluorescence toward VOC vapors and excellent recyclability. The size of guest molecules significantly influenced the emission maximum of the activated Cu-MOF \supset guest molecules, and the associated intensity of fluorescence showed the relationship between the ligands and the guest molecules. This finding presents a successful strategy for constructing MOFs with strongly fluorescent ligands containing C-H··· π interactions. This new method minimized the ACQ formation, which was different from traditional aggregation-induced emission (AIE), thereby providing a new direction for designing functional fluorescent molecules and preparing fluorophore-containing MOFs in the future.

Author contributions

C. X. Liu designed the material and performed the experiments; C. X. Liu and Y. F. Wang wrote the paper; J. Cui and M. J. Zhang contributed to the supervision and editing; all authors contributed to the general discussion.

Conflicts of interest

The authors declare no competing financial interest.

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