A new luminescent Zn-MOF has been synthesized under hydrothermal condition using a semi-rigid ligand H₃cpoip (4-(2-carboxyphenoxy)isophthalic acid). The luminescence properties of 1 in methanol, ethanol, and water have been investigated respectively. Interestingly, compound 1 have a unique response to methanol molecule against ethanol and water. Moreover, 1 performs a turn-on switching property triggered by methanol solvent molecule and a high sensitivity towards methanol as low as 2×10⁻⁷ (volume concentration) in ethanol solution. The results indicate that the Zn-MOF has potential application as a sensor for detecting methanol in ethanol solution with excellent selectivity and highly sensitivity.

In the last two decades, porous metal-organic frameworks (MOFs) materials which constructed from metal ions/metal clusters as nodes and multitopic organic ligands as linkers have drawn widespread attention not only because of their intriguing varieties of architectures and topologies but also owing to a wide range of their potential applications in selective adsorption/separation, heterogeneous catalysis and light-emission diode (LED) etc. Among a plethora of porous frameworks investigated, a large number of luminescent MOFs have been reported in the literature. However, only a few of them, which have specific and detective change in luminescence when contacting an analyte, have potential application in chemical sensor.

Generally, luminescent MOFs are classified as transition-metal MOFs and lanthanide-MOFs (Ln-MOFs) according to the type of metal used. In Ln-MOFs system, intensity change of lanthanide luminescent signal caused by analyte-metal or analyte-ligand interaction occurs. By contrast, many luminescent transition-metal MOFs exhibit turn-on switching property triggered by analytes. Position of their responsive emission usually changes upon those interactions. Compared to common luminescence-enhancing/quenching method, detection occurs relative to a dark background is intrinsically more sensitive.

As a very important raw material, ethanol is widely used in many field like chemical industry, food industry etc. Methanol, a cheaper and more easily accessible analogue of ethanol, sometimes is mixed into ethanol to reduce the cost of ethanol producing, and sometimes it is even used in producing imitated spirits and wine. But, methanol is an alcohol toxic to mammals, overtake of the compound will cause headache, vomiting, blindness or even worse. That leads one of the highest risks to food safety worldwide. Therefore detection of methanol in ethanol and alcoholic beverages is of great significance and necessity. Actually, it’s hard to differentiate methanol and ethanol because of their similar chemical and physical properties. Generally, high performance liquid chromatography, gas chromatography, and Raman spectroscopy etc. are usually used for detecting methanol. But their high cost, inconvenience and inefficiency impede their wild application in daily life. Herein, we report a novel luminescent transition-metal MOF exhibiting efficient turn-on switching property triggered by solvent molecule, with fast response, excellent selectivity and highly sensitivity for methanol molecule. To the best of our knowledge, this is the first report of luminescent-MOF based sensor displaying such capability.
connectivity at Zn2 and Zn3 are quite similar and both of them contain tetrahedral Zn centers of which the apical are occupied by one nitrogen atom and three oxygen atoms which from three different carboxylate groups (Fig S2b, c). The bond lengths of Zn-O [1.921(2) - 2.048(2) Å] and Zn-N [2.027(2) - 2.043(2) Å] are all within the normal range. Meanwhile, two types of cpoip ligands denoted as L1 and L2 are also found in 1. All the three carboxylate groups of L1 exhibit a bis-monodentate coordination mode, and two O atoms from two different carboxylate groups bind to Zn(2) via chelate fashion. Therefore, L1 displays \( \eta^1: \eta^1: \eta^1: \eta^1: \eta^1 \) coordination mode to link five adjacent Zn atoms. Carboxylate groups from isophthalate moiety of L2 adopt monodentate mode (Fig.S3). 4,4′-bpy ligands here also adopt two coordination manner, one binds Zn3 as a terminal molecular. On the basis of the coordination mode of L1 and conformation of ligand cpoip\(^{3-}\), the adjacent Zn2 and Zn3 atoms are connected into a 1D zigzag chain along crystallographic b-axis (Fig. S2d). This 1D chain further interconnect with each other via isophthalate moiety of L2 along a-axis giving 2D layers as depicted in (Fig. S2e). Finally, the adjacent 2D layers are connected by Zn1 binuclear paddle-wheel unit and the bidentate 4,4′-bpy along c-axis to generate a 3D framework. The guest water molecules are found in the channel along a-axis which surrounded by L1, bidentate 4,4′-bpy and Zn atoms (Fig. 1). Intermolecular H-O⋯H hydrogen bonding interaction between guest water molecules and a carboxyl oxygen atoms (O3) (d(O15⋯O3) = 2.919 Å and \( \angle O15-H151⋯O3 = 126.19^\circ \)) is also found. Although there is a 1D channel in the framework, gas adsorption data can’t be obtained. Because the framework collapses once the guest water molecules removed. This phenomenon indicates that the guest water molecular plays a key role in stabilizing the pore structure.

Differential scanning calorimetry (DSC) (Fig. S4) curve presents an endothermal peak between 70 and 140 °C, meanwhile the thermogravimetric analysis (TGA) curve shows 1.8% weight loss (calculated: 1.6%) in this temperature range, which reveals release of the guest water molecules. An abrupt weight loss in TGA curve and two obvious exothermic peaks in DSC curve were observed in the range of 370 and 480 °C, indicating collapse of the whole framework. Powder XRD patterns were used to examine the structural homogeneity of bulk powder samples of 1. The peak positions of experimental patterns match well with those of simulated ones from single-crystal X-ray diffraction data (Fig. S5), which indicates the homogeneous phase of final products of 1.

To investigate the luminescence properties of 1, the luminescence spectrum of 1 in solid state has been firstly studied. The complex displays a blue emission band with an intense peak maximum at 448 nm upon excitation at 377 nm, (Fig. S7). According to the previous reports, the emission of 1 can be attributed to the Zn-O inorganic cluster which closely resembles ZnO oxide nanostructure in MOF structure. It’s also found that the emission of Zn-O inorganic cluster in MOF can be strongly influenced by guest molecules. Encouraged by the result above, the luminescence response behavior of 1 in methanol, ethanol and water emulsion was further investigated, respectively. As shown in Fig 2, 1 exhibits different luminescent properties when dispersed in different solvent. When exited at 377 nm, 1 in ethanol and water emulsion displays the similar emission spectra with that of 1 in solid state. But in methanol, no responsive emission is observed. Instead, an obvious blue-shift emission at 404 nm is observed upon excitation at 304 nm. These results indicate that 1 may have a unique response to methanol molecule against ethanol and water. Considering the pore size along the H bond direction (4.60 Å) is bigger than the size of water and methanol molecules, 2.55 and 3.84 Å, respectively, but smaller than that of ethanol (5.07 Å), we speculate the selectivity of methanol and ethanol for 1 is mainly dependence on the size effect of the pore and the analytes. (Fig S8)

![Luminescence spectra of 1 in methanol (red solid); water (green dash); ethanol (blue dot).](image)

**Fig. 2** Luminescence spectra of 1 in methanol (red solid); water (green dash); ethanol (blue dot).

![Emissive response spectra of 1 for methanol in ethanol solution with different methanol volume concentration. Plot of Lg value of luminescence intensity (Y) versus the Lg value of methanol volume concentration (inset).](image)

**Fig. 3** Emissive response spectra of 1 for methanol in ethanol solution with different methanol volume concentration. Plot of \( L_g \) value of luminescence intensity (Y) versus the \( L_g \) value of methanol volume concentration (inset).

Inspired by such solvent dependent luminescent properties, more detail studies were carried out in methanol/ethanol binary system. 1 was dispersed in ethanol as the standard emulsion, while the methanol solvent was gradually increased to monitor the emissive response. As shown in Figure 3, the standard emulsion without methanol shows no detectable luminescent response signal when exited at 304 nm. With increasing methanol concentration, the
The relationship of the increasing trend of luminescence intensity versus the volume ratio of methanol was further studied. The results revealed that there was a good linear relationship ($R^2 > 0.99$) between $\log I$ and $\log C$ ($\log I = \log C + I = \text{luminescence intensity of 1 emulsion with different methanol concentration, } C = \text{methanol volume concentration}$). That means that the methanol content in ethanol solution could be quantified in the linear range of 0 to 0.01. The equation calculated is $I = 0.2914X + 4.35134$.

In summary, a novel 3D Zn-MOF (1) based on semi-rigid ligand H$_2$poip has been successfully synthesized under hydrothermal condition. The luminescence properties of 1 in different solvent have been investigated. Experimental results indicate that 1 perform a turn-on switching property trigged by methanol solvent molecule and a high sensitivity towards methanol as low as $2 \times 10^{-7}$ (volume concentration) in ethanol solution. Furthermore, the concentration of methanol in the methanol/ethanol mixture can be quantified according to the fluorescence intensity in the range of 0–0.01. Compound 1 was also proved to be an excellent candidate sensor for detecting trace amount methanol in alcoholic beverages. It is the first report about MOF-based sensor in such application area. And we believe it could play an essential role on food safety in the future.

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Notes and references

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