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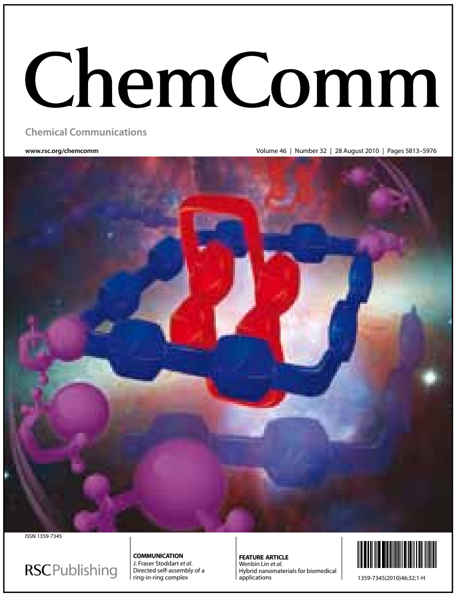

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ARTICLE TYPE

Cu(I)-MOF: naked-eye colorimetric sensor for humidity and formaldehyde in single-crystal-to-single-crystal fashion

Yang Yu, Xiao-Meng Zhang, Jian-Ping Ma, Qi-Kui Liu, Peng Wang, Yu-Bin Dong*

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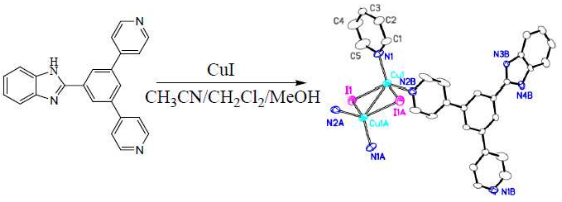
A porous Cu(I)-MOF is constructed from CuI and 1-benzimidazolyl-3,5-bis(4-pyridyl)benzene (L). This Cu(I)-MOF can be a highly sensitive naked-eye colorimetric sensor to successively detect water and formaldehyde species in a single-crystal-to-single-crystal fashion. The solid-state guest-responsive luminescence is also used to monitor the sensing process.

Porous metal-organic frameworks (MOFs),[1] consisting of both organic and inorganic components, are potential hybrid materials for sensing. The functionlization of the framework ligand with non-coordinated heteroatoms would enhances the interior surface interaction of host frameworks toward specific guest analytes and causes the changes in photo-, electrochemical or other properties. So far, only handful porous MOFs with guest sensing properties, generally luminescence-based (including emission wavelength and /or intensity) MOF sensors, have been described. Recent progress of luminescence-based MOF sensors is summarized recently by Hupp and Chen[2] et al in two review papers. As we know, the most practical and convenient sensor candidates are naked-eye colorimetric ones. Compared to the luminescent colorimetric MOF sensors, MOFs[3] exhibit guest-responsive naked-eye colorimetric property after incorporating certain guest species (including cationic, anionic and neutral species) are extremely rare.

Our research group has been exploring the reversible selective adsorption, separation and sensing properties of organic and inorganic guest species based on porous MOFs and discrete molecular containers.[4] Some of them do exhibit naked-eye and luminescent colorimetric sensing properties.[5] Motivated by our interest in this field, in this contribution, we report a new porous Cu(I)-MOF generated from a benzimidazolyl-attached bent organic ligand (**L**) (Scheme 1) with Cu(I) ion in solution. Furthermore, it can serves as a sensitive visual colorimetric sensor to successively apperceive humidity and formaldehyde in a single-crystal-to-single-crystal fashion.

The combination of **L** (Experimental section †) with CuI in a $CH_3CN/CH_2Cl_2/MeOH$ mixed-solvent system to afford **1** ($CH_3CN·MeOH·1.5H_2O⊂Cu_2(\mathbf{L})_2I_2$, experimental section, ESI†) as bright yellow crystals (Scheme 1). Single-crystal X-ray diffraction studies (ESI†) revealed that **1** crystallizes in the monoclinic C2/c space group. As shown in Scheme 1, each Cu(I) center in **1** lies in a tetrahedral $\{CuI_2N_2\}$ coordination sphere. Two Cu(I) nodes are bound together by two I^- anions to afford a bimetallic $\{Cu_2I_2\}$ cluster core ($d_{Cu\cdots Cu}$ = 2.7390(19 Å which is shorter than twice of van der Waals radius of Cu(I), i.e., less than 2.8 Å) which is further ligated by four terminal pyridyl groups on **L** into a porous 2D net (Fig. 1, Fig. S1†). These 2D nets interlock together to form a rhombus-like open channels (dimensions ~10 × 11 Å) running along the crystallographic *c* axis (Fig. S1†). As shown in Fig. 1, the channels contain disordered solvent molecules of CH_3CN, MeOH and H_2O, which were further confirmed by the ^1H NMR spectra and thermogravimetric analysis (TGA, Fig. S2†). Single-crystal analysis indicates that the organic molecules are fixed inside by hydrogen bonding interactions (Fig. S1†).



L **1**

Scheme 1. Synthesis of **1**.

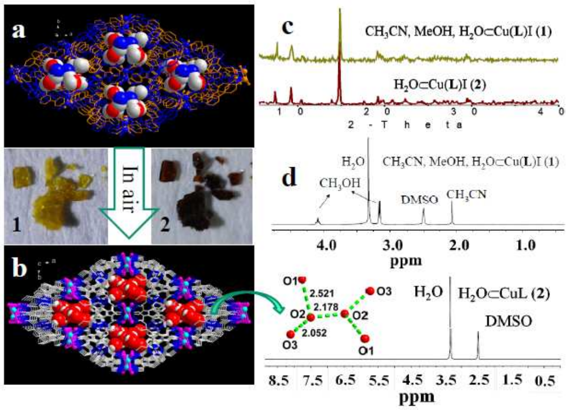


Fig. 1 a) Single-crystal structure of **1** (two sets of frameworks are shown in different colors). b) Single-crystal structure of **2**. c) XRPD patterns of **1** and **2**. d) ^1H NMR (DMSO-d^6) spectra of **1** and **2**. The sample pictures of **1-2** are inserted. The solid-state UV-vis spectra of **1** and **2** further confirmed this color change (Fig. S5†).

Interestingly, when the yellow crystals of **1** were allowed to stand at room temperature for a while, the crystal color gradually changed from bright yellow to deep red brown with retention of their single-crystal nature (Fig. 1b). The single-crystal analysis

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revealed that the compounds **1-2** are identical and no phase transition occurred. In **2**, the encapsulated organic molecules CH_3CN and MeOH escaped and the water molecules in air came into the cavities to generate a new host-guest system of $4H_2O\subset Cu_2(\mathbf{L})_2I_2$ (**2**). Such guest-exchange is further supported by ^1H NMR spectrum (Fig. 1d) and TGA (Fig. S2 †). The trapped water molecules are bound together through hydrogen bonding interactions into a H_2O-cluster (Fig. 1b), and no obvious interactions between water cluster and framework are found (Fig. S3†). Closer examination of **1** and **2**, some structural parameter changes in Cu_2I_2 cluster were observed. Compared to **1**, the Cu···Cu distance (2.7601(19) Å) in **2** increased by 0.02 Å, while the Cu-I bond lengths in **2** increased by 0.02 and 0.018 Å, respectively. The XRPD pattern indicates that the bulk sample of **1** remains intact upon removal of organic solvent molecules (Fig. 1c). Therefore, the color change from **1** to **2** is certainly caused by the different guest species encapsulation. Inspired by this, we wondered if **1** could be a visual colorimetric humidity sensor.

To explore the possibility, the bright yellow crystals of **1** were put in closed glass chambers (1L) which can respectively provide different constant relative humidity (RH) of 5%, 33%, 43%, 57%, and 75.8% in 24 h (ESI†).[6] As indicated in Fig. 3, no obvious color change of **1** was observed within 5 h in dry air (RH 5%). Notably, the color of **1,** however, immediately changed in the atmospheres with RH above 33%. At moderate RH of 33-57 %, the color of **1** changed to red-brown (**2**) after 2-4 h, respectively. At high RH of 78.5 %, the color change from **1** to **2** took only 1.5 h (Fig. 2).

In addition, the sensing process was monitored by solid-state emission spectra. The emission spectra on different water-loaded samples obtained from different RH atmospheres also reflect the humidity change at ambient temperature. As indicated in Fig. 2, the maximum emission of **1** is 607 nm upon excitation at 418 nm. The emission might be assigned to be cluster-centered (CC∗) transition having mixed halide-to-metal charge transfer (XMCT), $d\rightarrow(s, p)$ character.[7] The emission of **1**, however, is strongly quenched by the encapsulated water molecules. Fig. 2 shows that the emission intensity of **1** decreased by degrees as time progressed. At RH 33, 43, 57, 78.5%, the emission intensity of **1** was strongly quenched by water after 4, 3, 2 and 1.5h, respectively. As mention above, the water guests are suspensed in the cavities and not bound to the framework. So the observed emission quenching could be attributed to non-rediative energy transition.[8] In addition, the emission maximum is slightly red-shifted to 613 nm from **1** to **2**, which might be caused by the slight variation of the bond distances within Cu_2I_2 cluster core.

Interestingly, the encapsulated water molecules in **2** can be further replaced by formaldehyde molecules under ambient conditions. Again, compound **2** retains its single crystallinity after exchange of formaldehyde. When the crystals of **2** were exposed to formaldehyde vapour for around 24 h at room temperature (Experimental section†), the X-ray single-crystal analysis indicated that the three of four encapsulated water molecules per formula had been replaced by two formaldehyde molecules to generate $Cu_2(\mathbf{L})_2I_2\cdot2(HCHO)(H_2O)$ (**3**) (Fig. 3a). The incursive formaldehyde molecules are hydrogen-bonded to the framework via O···H-C and O···H-N bonds (Fig. S3†). Again, no phase-transition was found during the color change process. Compared to **2**, the Cu···Cu contact in **3** decreased only by 0.004 Å, and the corresponding Cu-I bond lengths decreased by 0.02 and 0.03 Å, respectively (Table S5-7†). Meanwhile, the crystal color changed from red-brown to orange (Fig. 3b). The XRPD pattern shows that the solvent-exchange reaction is clean (Fig. 3b). The included solvent amount and type are well supported by the TGA and ^1H NMR measurements (Fig. 3c and 3d). The emission

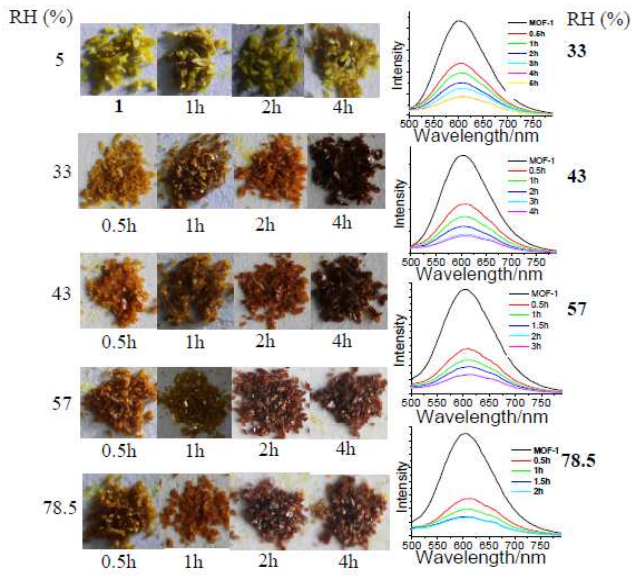

Fig. 2 Left: Photographs showing the color change of the bulk crystal samples of **1** in different atmospheres with different RH. The single crystal nature was kept during the color change process. Right: The corresponding solid-state emission spectra of **1** in different atmospheres with different RH (33-78.5%).

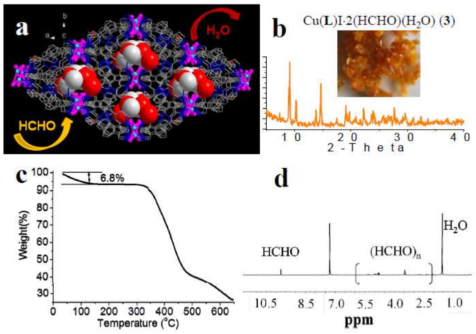

Fig. 3 a) Crystal structure of **3**. b) XRPD pattern of **3** and its sample picture. c) TGA trace of **3**. The observed solvent mass loss is 6.8% (calculated 6.8%). d) ^1H NMR spectrum of the $CDCl_3$ extract of **3**. Tiny amount of paraformaldehyde species, which might be formed during the solid-liquid extraction process, was detected (Fig. S6†).

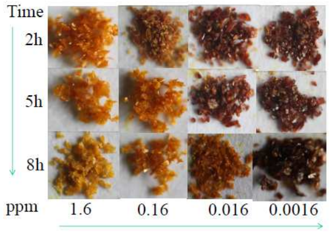

Fig. 4 Photographs showing the color change of the bulk samples of **2** in formaldehyde vapour with different vapor concentrations. The single crystal nature was kept during the color change process.

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energy mainly affected by the Cu(I)-halide core structural feature in the ground state molecular structure has been described by many previous reports.[9] Single-crystal analysis and XRPD patterns revealed that the structures of quenched samples obtained from different RH atmospheres are the same as **2**, and the TGA on the quenched samples demonstrated that the water loss is comparable to that of **2**.

Further study demonstrated that compound **2** is very sensitive to formaldehyde vapor even at very low concentration, which is reflected by the clear color change in the solid state. As we know, formaldehyde is widely used in the manufacture of construction and decoration materials.[10] Formaldehyde is very harmful to human health as an indoor pollutant. OSHA (World Health Organization) has set the immediately dangerous to life or health limit at 20 ppm.[11] Therefore, the development of formaldehyde sensor, especially direct and convenient formaldehyde detector is very significant.[12] As shown in Fig. 4, the color of **2** changed to orange, deep-orange and light brown in 1.6, 0.16 and 0.016 ppm formaldehyde vapors, respectively. No obvious naked-eye detected color change was observed in 0.0016 ppm formaldehyde vapor. Besides X-ray single-crystal analysis, the ^{1}H NMR measurement on these samples provided direct evidence for formaldehyde enrichment (Fig. S7†).

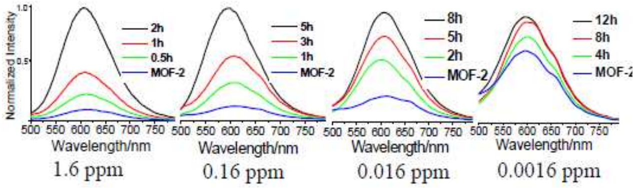

Fig. 5 The corresponding solid-state emission spectra of **2** in different atmospheres with different formaldehyde concentrations. The emission intensity of the sample in 0.0016 ppm formaldehyde vapor was not dramatically enhanced, which matches the naked-eye observation and ^{1}H NMR measurement. The tiny amount of encapsulated formaldehyde species, however, did cause the emission intensity enhancement as the time going on. At this point, Cu(I)-MOF is a really highly sensitive sensor for formaldehyde analyte.

Besides naked-eye detection, the HCHO encapsulation also caused the dramatically change in their emission spectra. As shown in Fig. 5, compared to **2**, the emission intensities of the HCHO-loaded samples are much enhanced with the increase of the amount of formaldehyde, which might be contributed to the structural rigidity enhancement imposed by the host-guest interactions. In addition, the structural variations of the Cu_2I_2 core led to the emission slightly blue-shifted (from 613 to 598 nm).[9] As we know, many prior formaldehyde sensors cannot exactly detect the formaldehyde analyte because of the ineluctable influence from water molecule in air,[12] which largely limits the sensor applications in real-world. Fortunately, compound **2** herein is able to detect formaldehyde in the presence of water molecules. Moreover, the temperature changes (from r.t. to ~75°C) cannot affect the color response. So Cu(I)-MOF could be a potential candidate for the portable sensing device toward to formaldehyde pollutant in real world.

In conclusion, we have prepared a new porous Cu(I)-MOF which can be a keen naked-eye colorimetric sensor to successively detect water and formaldehyde at very low concentrations. In addition, the guest-exchange processes are reversible (Reversible guest-exchange, ESI†) and single-crystallinity of the Cu(I)-MOF is maintained during the sensing process. Such a property is definitely important for certain devices. Work is in progress to obtain new naked-eye or luminescent colorimetric MOF-sensors based on other bent ligands and transition metals.

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Notes and references

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† Electronic supplementary information (ESI) available: Synthesis and characterization data for all compounds, including figures for ORTEP, hydrogen bonding interaction and CIF files, UV-vis spectra and crystal data. See DOI: 10.1039/b000000x/

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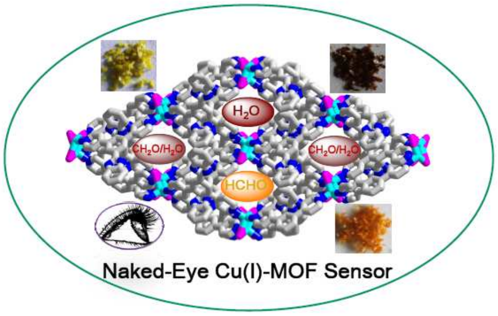

A highly sensitive visual Cu(I)-MOF sensor which is able to successively detect water and formaldehyde species in a single-crystal-to-single-crystal fashion is reported.