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Solvent-dependent luminescence behavior of a new charge-transfer Cu(I)-MOF: An experimental and theoretical investigation

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ABSTRACT

Herein we report the first charge-transfer metal–organic framework with open Cu(I)-sites, which exhibits intriguing solvent-dependent luminescence behaviors. An extended analysis of experimental and computational result indicates that strong metal–solvent bonding interaction plays a dominant role in the sensing of various solvents.

Recently, the investigation of metal–organic frameworks (MOFs), particularly luminescent MOFs, has become an increasing interest due to their effective application used as a new class of solid-state crystalline materials in diverse fields that include gas storage, separations, catalysis, adsorption, sensing, and so on [1]. In addition, owing to the various host–guest interactions, such as coordination-bond, hydrogen-bond, electrostatic force and van der Waals (vdW) interaction, the luminescent MOFs containing functional sites can be easily altered their luminescence behavior via changing their around environment, which shows that they can be used as sensing luminescent materials [2]. To date, the sensing luminescent MOF materials as detection devices of various small molecules, volatile organic compounds and explosives have been extensively exhibited due to their significant advantages, including single detection, low cost, high signal out and reliability [3]. A further significant challenging task for them is still to obtain a shift of an existing emission band or the production of a new emission band because of a lack of satisfactory chemical selectivity and sensitivity for most MOF sensors reported, which only exhibits the emission signal "turn-off" via fluorescence quenching [4]. Moreover, owing to the limit of the pore-size of MOFs, the sensing luminescent MOFs can only be used as excellent detection devices for small molecules, so much further work for luminescent MOFs should also be done in the sensing topic of macromolecules. With this mind, based on the continuation of our previous studies on the luminescent MOFs and chemical sensors [5], we design and assembly a new charge-transfer Cu(I)-MOF, $Cu_2(CN)_2(PymNH_2)$ (**1**), ($PymNH_2$ = 2-aminopyrimidine), which exhibits open Cu(I)-site feature in the solid surface, high thermal stability and intriguing solvent-dependent luminescent properties.

The yellow block crystals of **1** were readily obtained via the solvothermal reaction of CuCN, $K_4[Fe(CN)_6]\cdot 3H_2O$, and $PymNH_2$ ligand in a $MeOH/H_2O$ (1:2) mixture at 160 °C for three days. Single-crystal X-ray diffraction study presents that it crystallizes in a monoclinic space group *C*2/*c*. Complex **1** displays a new three-dimensional pillared-layer metal–organic framework via Cu···Cu bonding interactions with the classical *dia* topology. The asymmetric unit of **1** contains only one fragment consisted of two independent cuprous centers, two cyanide groups, and one $PymNH_2$ ligand (Fig. S1a). The cuprous atoms are all three-coordinated and assume distorted triangular pyramid geometry configuration. Each cuprous atom is coordinated to one carbon atom from one cyanide group and two nitrogen atoms from other cyanide group and one $PymNH_2$ ligand, respectively. The bond lengths and angles around the two cuprous atoms vary within the range of 1.883(3)–2.105(2) Å and 100.46(9)–129.49(10)°, respectively. Each μ_2-cyanide group bridges adjacent two cuprous atoms to produce infinite one-dimensional *meso*-helical CuCN chains in the *c*-axis direction with a pitch of 14.7359(6) Å (Fig. S1b). These *meso*-helical chains are further bridged in a unique way via the μ_2-$PymNH_2$ ligand through the Cu1 and Cu2 atoms constructing a distinct wave-like two-dimensional (6, 3) topology grid layer parallel to the *bc* plane (Fig. S1b). Interestingly, the Cu1 and Cu2 atoms in the two-dimensional layer distribute in two different parallel planes, respectively, with a separated distance of 1.0157 Å between the (Cu1)n and (Cu2)n planes. These wave-like layers are stacked in parallel positions in an –A–B–A–B– model along the *a*-axis, causing packing of the two-dimensional layers via the interconnections of adjacent Cu···Cu bonding interactions, Cu1···Cu1 = 2.6295(6) Å and Cu2···Cu2 = 2.6972(6) Å. The Cu···Cu interactions as pillars joined the adjacent two-dimensional layers to form a three-dimensional pillared-layer metal–organic framework, with the interlayer distance of 2.0332 Å, (Cu1)

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n planes and 2.2403 Å, (Cu2)n planes, respectively (Fig. 1). In addition, the cuprous atoms can be assigned to the 4-connected node, and the cyanide groups, $PymNH_2$ ligands and Cu···Cu interactions can all be simplified to linear linkers. TOPOS analysis of this three-dimensional framework exhibits a classical 4-connected *dia* net (Fig. S1c). Most interestingly, the structure feature bearing open Cu(I)-sites in the solid-surface facilitates the coordination interaction between the cuprous centers and the incorporated analytes. Moreover, the analysis of molecular electrostatic surface potential (ESP) exhibits the presence of one maximum around each cuprous center with an ESP value of +38.25 (Cu1) or 35.82 kcal/mol (Cu2) on the vdW surface of the Cu atom (Fig. 2). Clearly, each cuprous center can readily accept an electron-donor. All above these are helpful for chemical sensing, which coincide with the following results of the experimental measurements and theoretical computations.

To test the robustness of **1**, thermalgravimetric analysis (TGA) was obtained via heating the crystalline sample in the temperature range of 25 to 800 °C in a N_2 atmosphere (Fig. S2). The result displays that the framework of **1** can be stable up to approximately 190 °C, and then started to abruptly chemically decompose. The first major weight loss of the $PymNH_2$ ligand occurred in the range of 190 to 415 °C by 33.5% weight (calc. 34.8%), and then the second weight loss of the cyanide group is observed. Until 800 °C, it did not completely decompose. The aforementioned result indicates that **1** should have high thermal stability, which was further corroborated by quantum chemistry calculations. The computational topological parameters at the bond critical points (BCPs) of the coordination bonds were given in Table S3. Comparing the electron density values ($\rho(r)$), the strength order of coordination bonds is Cu–C (cyanide) > Cu–N (cyanide) > Cu–N ($PymNH_2$), which is in agreement with the result of TGA analysis. The positive Laplacian ($\nabla^2\rho(r)$) indicates that they all qualify as closed-shell interactions. Additionally, the negative electronic energy density ($H(r)$) values and the $|V(r)|/G(r)$ ratio more than one illustrate that all coordination bonds are basically the intermediate types between covalent ones and ionic ones, and covalent dominant in **1** [6]. So the experimental and computational results present that the resulting **1** has high thermal stability, which makes us further explore its chemical sensing behavior.

In order to deeper explore the nature of the **1**–guest interactions, density functional calculations were performed on the representative dimer model, consisting of the fragment, $[Cu_2(CN)_2(HCN)_2PymNH_2]$ of **1**, and eight different small molecules. Fig. 2 presents the interaction energy curves for all eight **1**–guest complexes studied, which exhibits that the two fragments for each **1**–guest complex have attractive interactions and also presents that the stable complexes come into being between the **1** and eight small guest molecules at the minimum point of the interaction energy curves. The polar molecules like NH_3, DMF, CH_3OH, C_2H_5OH and H_2O possess considerably higher attractive interaction than no-polar (or less polar) residues, e.g., N_2, CO and CO_2. Moreover, Atom in Molecules (AIM) analysis indicates that there is metal–

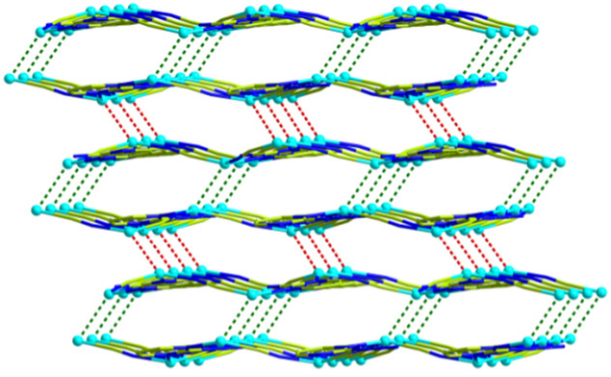

Fig. 1. The schematic representation of three-dimensional pillared-layer structure via Cu···Cu bond interactions in **1**.

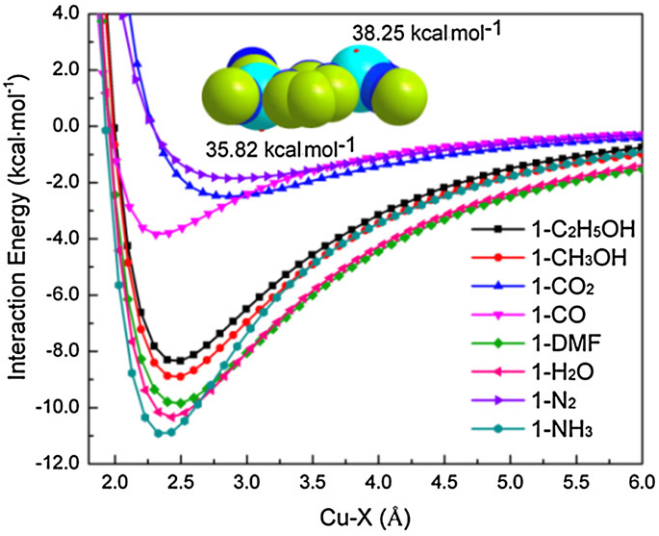

Fig. 2. Computed electrostatic surface potential on the vdW surface of Cu(I) of **1** as inset, and interaction energy curves obtained at the B3LYP/6-311G(d,p)/LanL2DZ level for the eight **1**–guest absorption models (X, donor-atoms of the various guest molecules).

guest bond interaction between the open Cu(I)-site and the selected eight small molecules. The topological parameter values at the BCPs for all eight **1**–guest complexes are given in Table S4. The topological characteristics of the $\nabla^2\rho(r) > 0$, $H(r) \rightarrow 0$ and $|V(r)|/G(r) \rightarrow 0$ illustrate that all the metal–guest interactions are basically intermediate types between electrostatic ones and covalent ones, and qualify as closed-shell interactions in the eight **1**–guest complexes studied. The aforementioned results indicate that **1** possesses good sensibility due to the strong coordination bond interaction between the open Cu(I)-sites and solvent molecules, which coincides with the following luminescent experimental result.

The luminescent cuprous complexes bearing the closed d^{10} shell feature have been fantabulous and potential candidates for their rich luminescent materials [7]. Herein we explored the luminescent properties of **1** at ambient temperature. As shown in Fig. 3, **1** exhibits an intense low-energy green emission with a peak maximum at 568 nm and a weak high-energy emission at 519 nm upon excitation at 290 nm. The reported solid free $PymNH_2$ ligand has an intense fluorescent emission band centered at 422 nm (excitation at 344 nm), which can be

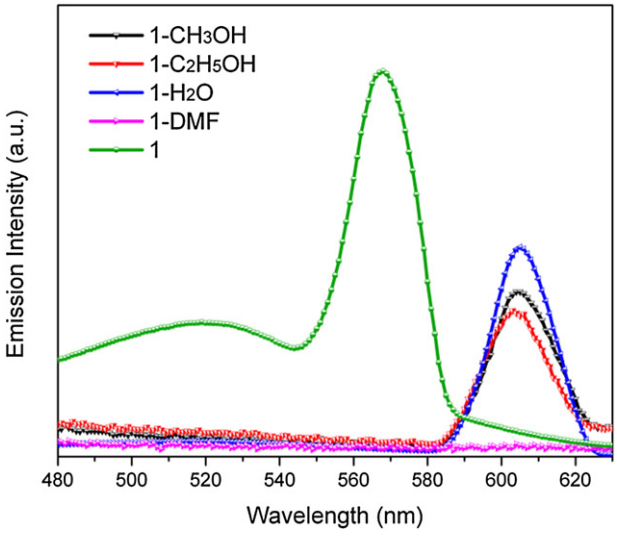

Fig. 3. The emission spectra of **1** in solid-state (exited at 290 nm) and dispersed various solvents as the suspension (exited at 300 nm) at room temperature, respectively.