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Solvo-thermal synthesis of a unique alkaline earth-transition Ba-Cd micro-porous coordination framework as hetero-metallic luminescent sensor for Cu²⁺ and real-time detection of benzaldehyde

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ABSTRACT

In this work a unique hetero-metallic alkaline earth-transition Ba-Cd luminescent micro-porous metal-organic framework {[BaCd(μ₆-tp)_{1.5}(μ₂-Cl)(H₂O)(DMF)₂·0.75H₂O]_n(H₂tp = terephthalic acid) (**1**) has been prepared under solvo-thermal conditions. In **1** infinite 1D {Ba-X-Cd} (X = O, Cl) inorganic chains are linked via these full de-protonated tp²⁻ ligands forming a unique 3D I¹O² type micro-porous coordination framework. PXRD patterns of **1** have been determined confirming pure phases of **1**. Luminescence investigations suggested that **1** exhibits highly selective and sensitive sensing for trace amounts of benzaldehyde in ethanol, which provides a facile method for real-time detection of benzaldehyde. Meanwhile **1** also exhibits highly selective and sensitive sensing for Cu²⁺ over other cations with high quenching efficiency K_{sv} value 1.15 × 10⁴ L·mol⁻¹. As far as we know, **1** represents the first example of alkaline earth-transition hetero-metallic Ba-Cd micro-porous coordination framework as bi-functional luminescent probes for Cu²⁺ and benzaldehyde.

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1. Introduction

In the past twenty years, metal-organic frameworks (MOFs), which are constructed from metal ions or metal clusters and different organic linkers, have received great attention due to their fascinating structural motifs and unique functional applications in separation, gas absorption, catalysis, magnetism and luminescence [1–4]. Among MOFs, luminescent MOFs have attracted great attention because these materials can be widely applied in highly sensitive detection of different analytes for human health, homeland security and environmental protection [5]. Luminescent MOFs has some advantages because they have the controllable porosity and size, high surface area and structural stability. Thus these materials are more competitive over other luminescent materials because more analytic objects can interact with surface of MOFs, which in turn can reduce the detection limit, increase the detection sensitivity and enhance the luminescent response rate [6–9]. On the other hand, nowadays design and syntheses of these inorganic-organic hybrid coordination frameworks, which combine the flexibility of organic part with

the rigidity of inorganic framework, is one of the most active research topics [10,11]. For these hybrid coordination frameworks, the symbol I^mOⁿ has been defined on the basis of the dimensionality (*m*, *n*) of inorganic (*I*) and organic (*O*) connectivities [12,13]. As for the inorganic dimensionality, coordination frameworks possessing the higher inorganic connectivity (I¹Oⁿ, I²Oⁿ, and especially I³Oⁿ) can be expected to have better chemical, thermal, and photo-luminescent/ magnetic properties because of the existence of Metal-Oxygen-Metal linkages and cooperative interactions between metallic centers through bridging oxygen atoms. For instance, Kitagawa et al. also report an alkaline earth I³O⁰ type MOFs: [Ba₂TMA(NO₃)(DMF)], which contains the unique 3D inorganic Ba-O-Ba connectivity [14].

In biological living systems, particularly in the human brain, Cu²⁺ is one of the most important and essential metal ions. The straightforward, efficient and simple detection of Cu²⁺ amounts is important to diagnose and treat these diseases induced by copper metabolism disorders [15]. On the other hand, with the development of modern industry, benzaldehyde has been widely employed as an important chemical raw material, which can be applied as a low temperature lubricant, a plasticizer, and a fragrance additive in cosmetics, soap, and food. It is also noted that recent investigation have revealed that benzaldehyde can generate mutagenic and genotoxic effects [16]. When the amount of

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benzaldehyde exceeds the normal amount in food, it not only can contaminate serious environment problem, but also affect the public's health [17]. Therefore, the development of a convenient method for the detection of benzaldehyde and Cu^{2+} is quite important in terms of biological safety and environmental protection.

Heterometallic organic frameworks (HMOFs) are one of the most active research topics in the crossover field of material and chemistry science [18–20]. In comparison with these widely investigated metal-organic frameworks (MOFs) based on single metal centers, the construction and application of heterometallic coordination frameworks is still less studied. Because both alkaline earth and transition metals have rich coordination numbers, versatile coordination geometries and unique functional properties, construction of these novel alkaline earth-transition hetero-metallic luminescent MOFs is still exciting and unexpected to obtain some unique functional materials. We are also interested in the preparation of these luminescent coordination frameworks possessing beautiful structural architectures and interesting functional properties [21–23]. In this work a unique hetero-metallic Alkaline-earth-transition Ba-Cd micro-porous coordination framework $\{[\text{BaCd}(\mu_6\text{-tp})_{1.5}(\mu_2\text{-Cl})(\text{H}_2\text{O})(\text{DMF})_2] \cdot 0.75\text{H}_2\text{O}\}_n$ (H_2tp = terephthalic acid) (**1**) has been prepared under solvo-thermal conditions. PXRD patterns of **1** have been determined confirming pure phases of **1**. Luminescence investigations suggested that **1** can exhibit highly selective and sensitive sensing for benzaldehyde, which allows **1** can be used as an excellent luminescent sensor for traces of benzaldehyde in ethanol. Meanwhile **1** also exhibits highly selective and sensitive sensing for Cu^{2+} over other cations with high quenching efficiency K_{sv} value $1.15 \times 10^4 \text{ L} \cdot \text{mol}^{-1}$. As far as we know, **1** also represents the first example of hetero-metallic Ba-Cd micro-porous coordination framework as bi-functional luminescent probes for Cu^{2+} and benzaldehyde.

2. Experimental

2.1. General

All the chemical agents are commercially available and employed without further purification. Deionized water can be employed as solvent in this work. D/Max-2500 X-ray diffractometer (Cu-K α radiation) has been used to determine Powder X-ray diffraction analysis. TGA experiments were performed using a NETZSCH TG 209 apparatus (heating rate is $10^\circ\text{C min}^{-1}$). C, N, and H elemental analysis were determined using a Perkin-Elmer 240 elemental apparatus. Photo-luminescent experiments have been determined on a Cary Eclipse Fluorescence spectrophotometer apparatus (Agilent Technologies) equipped with a quartz cell (1 cm \times 1 cm) and a plotter unit. KQ-100E instrument (nominal power of 100 W, Kunshan, China) with a frequency of 40 kHz was used as ultrasonic device. Photo-luminescent emission spectra were recorded in the 300–500 nm wavelength range upon excitation at 260 nm. The voltage of photomultiplier tube (PMT) has been set at 650 V. The emission and excitation slit width has been set as 5 nm and 5 nm, respectively.

2.2. Synthesis of $\{[\text{BaCd}(\mu_6\text{-tp})_{1.5}(\mu_2\text{-Cl})(\text{H}_2\text{O})(\text{DMF})_2] \cdot 0.75\text{H}_2\text{O}\}_n$ (**1**)

A mixture of $\text{Ba}(\text{NO}_3)_2$ (26.14 mg, 0.1 mmol), CdCl_2 (18.33 mg, 0.1 mmol) and H_2tp (24.91 mg, 0.15 mmol) has been mixed and stirred for 1 h in water (5 mL) and DMF (7.5 mL). Then the resulting mixtures were putted into a Teflon vessel in a steel autoclave, heated at 160°C for 12 h and then slowly cooled down to ambient conditions during the time of 48 h. The obtained colorless block-shaped crystals were washed a couple of times by diethyl ether and water. Yield: 21% based on H_2tp . Elemental analysis calcd (%) for $\text{C}_{18}\text{H}_{22.5}\text{BaCdClN}_2\text{O}_{9.75}$: C 3.20%, H 30.53%, N 3.96%; found: C 3.57%, H 30.69%, N 4.13%. FT-IR data (cm^{-1}): 3450 (m), 3080 (w), 1565 (s), 1460 (w), 1392 (vs), 1263 (m), 1142 (m), 1060 (w), 950 (m), 863 (m), 830(m), 753(m), 513 (m).

2.3. X-ray Crystallography

Bruker SMART 1000 CCD diffractometer (graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$)) is used to determine the crystal structure of **1**. X-ray crystal diffraction intensities for **1** have been determined through using ω - ϕ scan method. Lorentz polarization and Absorption corrections have been used. The structure has been solved through the direct methods and refined using the full-matrix least-squares method by SHELXL-97 and SHELXS-97 software [24,25]. Analytical expressions of neutral-atom scattering factors have been incorporated, and anomalous dispersion corrections were used. Organic hydrogen atoms have been geometrically generated; hydrogen atoms of these aqua molecules can be defined from difference maps and further refined with isotropic temperature factors. Anisotropic thermal parameters have been assigned to all non-hydrogen atoms. Hydrogen atoms on the aromatic rings have been geometrically placed with isotropic thermal parameters 1.2 times of those of the attached carbon atoms. CCDC-1523120 (**1**) contains the crystallographic data of **1** for this work. Crystallographic data can also be downloaded free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystallographic data and details of refinements for **1** are summarized in Table 1. Selected bond angles and bond lengths are summarized in Table S1. Bond lengths and angles of these intermolecular hydrogen bonds are summarized in Table S2.

3. Results and Discussion

3.1. Preparation of Coordination Polymer **1**

Single-crystal diffraction analysis shows that coordination complex **1** lies in the monoclinic crystal system ($P2_1/c$ space group). The asymmetric structural unit of **1** has one crystallographically independent Ba^{II} ion (Ba1), one crystallographically independent Cd^{II} ion (Cd1), 1.5 full de-protonated tp^{2-} ligands, one bridging chloride atom (Cl1), two

Table 1
Crystal data and structure refinement information for complex **1**.

Complex	1
Empirical formula	$\text{C}_{18}\text{H}_{22.5}\text{BaCdClN}_2\text{O}_{9.75}$
Formula weight	708.07
Crystal system	Monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	11.8657(6)
$b/\text{\AA}$	15.9283(6)
$c/\text{\AA}$	14.1337(7)
$\alpha/^\circ$	90
$\beta/^\circ$	114.491(6)
$\gamma/^\circ$	90
$V/\text{\AA}^3$	2430.9(2)
Z	4
$D/\text{g} \cdot \text{cm}^{-3}$	1.935
μ/mm^{-1}	21.010
$F(000)$	1374
Crystal size/ mm^3	$0.22 \times 0.20 \times 0.18$
θ range for data collection/ $^\circ$	$13.77\text{--}134.124$
Limiting indices	$-14 \leq h \leq 13$ $-13 \leq k \leq 13$ $-14 \leq l \leq 17$ $-19 \leq m \leq 15$ $-16 \leq n \leq 16$
Reflections collected/unique (R_{int})	11,086/4324 (0.0449)
Completeness	99.73%
Max. and min. transmission	1.00000 and 0.8561
Data/restraints/parameters	4324/21/311
Goodness-of-fit on F^2	1.109
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0361$, $wR_2 = 0.0696^a$
R indices (all data)	$R_1 = 0.0480$, $wR_2 = 0.0804$
	$wR_2 = 0.2069$
Largest diff. peak and hole/ $e \cdot \text{\AA}^{-3}$	1.09/−0.81

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

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