



A windmill-like Zn_3L_2 cage exhibiting conformational change imparted sensing for DMA and highly selective naked-eye detection of Co^{2+} ion by dynamic quenching

Kai Xing, Ruiqing Fan*, Xi Du, Yang Song, Wei Chen, Xuesong Zhou, Xubin Zheng, Ping Wang, Yulin Yang*

MIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, PR China

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ABSTRACT

A Zn_3L_2 -type metal organic aggregate featuring “six leaf windmill” shaped double cages constructed from a semi-rigid tripodal carboxyl acid ligand H_3TCPB (1,3,5-tri(4-carboxyphenoxy) benzene) exhibits sensitive luminescent response toward DMA with obvious intensity enhancement and red-shift. During the procedure, the host-guest interaction was supported by single-crystal-to-single-crystal transformation involving drastic conformational change of the molecular host upon μ_2 -bridging H_2O release and the sensing mechanism was also discussed through theoretical calculations from charge separation hypothesis perspective. The DMA post-modified result of crystal transforming reveals high selective and effective naked eye reversible recognition for Co^{2+} ions through the dynamic and static quenching mechanisms. Moreover, the visual luminescent test paper was realized for potential application in concerns of the biology and environment.

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1. Introduction

Metal ions pollution which can cause damage and disease in humans or other living organisms has become a serious environment issue [1,2]. Cobalt ion is one of the essential trace elements on account of its important role in the metabolism and some biological compounds [3–5], however, it also shows negative influence on the growth of crops and human health [6–8]. Besides, some serious health concerns are associated with volatile organic compounds like N,N-dimethylacetamide (DMA) both through skin contact and inhalation during the industrial production [9,10]. Therefore, it is of great importance to detect and monitor them. Compared with several well-developed methods for detecting these species, the intricate samples pretreatments, high handling cost and long response times are major bottle necks to restrict practical utilization [11]. To address the issues, the sensitive and economical naked-eye recognition by eco-friendly sensor is urgently desired, which could rely on the development of advanced materials.

As a represent, the coordination-driven supramolecular metal organic aggregates (MOA) with well-defined hollow structure (cage, polyhedra, capsule *etc.*) have stirred a great deal of interest due to their fascinating structures and intriguing applications [12,13]. The luminescent MOA which has been considered as one of the most promising technology for detection have developed rapidly due to diverse adjustability and modularity of constructing units [14]. It is well known that the quenching/enhancement of luminescent MOA are mainly attributed to the guest-host interaction. For crystalline MOA, the single-crystal-to-single-crystal (SC–SC) transformations raised considerable concern are usually regarded as effective methods in the study of structural changes, guest-host interaction and structure-property relationship [15]. Generally, coordinated terminal or bridging waters are served as potential active sites of SC–SC transformation [16,17]. During the active sites uptake and release, molecules in host will show the negligible structure rearrangement [18]. To date, the reported SC–SC transformation involving substitution of μ_2 -bridging H_2O [19] and drastic conformational change of the molecular host by external solvent molecule is really rare.

In this contribution, we successfully prepared a M_3L_2 -type cage-like MOA, $H[Zn_3(OH)(TCPB)_2(H_2O)_3] \cdot 3H_2O$ (1)

* Corresponding author at: School of Chemistry and Chemical Engineering, Harbin Institute of Technology Harbin 150001, PR China.

E-mail addresses: fanruiqing@hit.edu.cn (R. Fan), ylyang@hit.edu.cn (Y. Yang).

(H₃TCPB = 1,3,5-tri(4-carboxyphenoxy) benzene) by using a semi-rigid tripodal carboxyl acid ligand. Remarkably, **1** exhibits efficient luminescent enhancement towards N,N-dimethylacetamide (DMA) by a solvent-induced SC–SC transformation involving a drastic conformational change of the molecular host into H[Zn₃(OH)(TCPB)₂(DMA)]·DMA·4H₂O (**2**). The charge separation hypothesis supported by theoretical calculations gives a convinced explanation for diverse luminescent performance between **1** and **2** resulting from the subtle guest-host interaction. Furthermore, DMA post-modified **2** exhibits selective and effective recognition for Co²⁺ ions through naked eye and luminescent quenching effect caused *via* dynamic and static quenching mechanisms. Amusingly, the visual luminescent test paper was fabricated for practical application.

2. Experimental section

2.1. Synthesis of H[Zn₃(OH)(TCPB)₂(H₂O)₃]·3H₂O (**1**)

Zn(ClO₄)₂·6H₂O (74.4 mg, 0.20 mmol), H₃TCPB (24.3 mg, 0.05 mmol) were dissolved in DMA (4.0 mL) and H₂O (4.0 mL) mixture solvent and stirred by magnetic stirrer for 30 min. The resulting solution was further transferred to a 20.0 mL Teflon-lined stainless steel reaction vessel and heated at 85 °C for 120 h in an oven. Until cooled to the 25 °C for two days, colorless block-shaped crystals of **1** were harvested by filtration, washed by ethanol, and then dried in air (yield, 55%, based on H₃TCPB) Anal. Calcd. For C₅₄H₄₃O₂₅Zn₃ (Mr: 1288.05): C, 50.35; H, 3.36. Found: C, 50.31; H, 3.39. FT-IR (KBr pellet, cm⁻¹) for **1** (Fig. S7): 3475 (br, m), 1619 (s), 1604 (s), 1567 (s), 1384 (s), 1218 (s), 1124 (s), 960 (w), 833 (m), 767 (m), 663 (m), 590 (w), 482 (w).

2.2. Synthesis of H[Zn₃(OH)(TCPB)₂(DMA)]·DMA·4H₂O (**2**)

After the rhombus crystals of **1** were immersed in DMA for over 60 h, rectangle crystals of **2** were obtained and harvested by filtration, which are demonstrated by single-crystal X-ray diffraction. Anal. Calcd. For C₆₂H₅₇N₂O₂₅Zn₃ (Mr: 1426.26): C, 52.21; H, 4.02; N, 1.96. Found: C, 52.18; H, 4.05; N, 1.94. FT-IR (KBr pellet, cm⁻¹) for **2** (Fig. S7): 3475 (br, m), 3014 (w), 2937 (w), 2876 (w), 1603 (s), 1567 (s), 1384 (s), 1222 (s), 1124 (m), 960 (w), 832 (m), 769 (m), 664 (w), 591 (w), 478 (w).

3. Results and discussion

3.1. Crystal structure of **1**

The self-assembled structure of **1** crystallizes in the monoclinic space group *P2₁/n* featuring discrete “six leaf windmill” shaped cage. As shown in Fig. S1, the asymmetric unit of **1** constitutes two TCPB³⁻ ligand, three Zn(II), and three coordinated and three free water molecules. Each seven-coordinated Zn²⁺ is bounded by four O donors from two TCPB³⁻ ligand and three oxygens from two μ₂-H₂O molecules and one μ₃-OH moiety. Three Zn²⁺ ions connected with each other by μ₃-OH group to form a [Zn₃(OH)(H₂O)(CO₂)₆] cluster (Fig. S2), which capped by two TCPB³⁻ ligands to generate a cage-like metal organic aggregate. For each Zn₃L₂ cage, the two central phenyl rings are nearly parallel to each other with distance of 9.070 Å, which is far longer than π–π stacking, suggesting that the formation of the dimeric structure can be attributed to metal-ligand-directed coordination. Interestingly, according to the twist direction of ether linkage, two conformations named type I and type II simultaneously exist in one cage and adjacent cages show the clockwise and anticlockwise twist forms along *a* axis, resulting a 1D chain *via* 3.486 Å π–π stacking (Fig. 1). Further connect-

ing through C–H···π interactions, 3D supermolecular framework with 26.1% porosity calculated using the PLATON routine was constructed [20,21].

3.2. Luminescence properties

Since **1** is constructed with d¹⁰ electron Zn²⁺ ions and luminescent semi-rigid H₃TCPB ligand, the solid luminescence spectra of H₃TCPB ligand and **1** were evaluated at room temperature. As shown in Fig. S10, the free H₃TCPB displays luminescent emission at 433 nm excited by 365 nm UV light. Upon coordinated with Zn²⁺ ions, the luminescent emission band of **1** locates at around 435 nm upon the same excitation, correspondingly, the Commission Internationale d'Eclairage (CIE) coordinates code is (0.18, 0.17). The similarity in the emission between ligand and **1** indicates that the emission of **1** can be tentatively ascribed to the intraligand π* → π transition [22]. As for the phenomenon that luminescent intensity was enhanced after formation of MOA (by 2.3 times) compared with free ligand, aggregation-induced emission (AIE) may be responsible for that, namely, the coordination to metal ions restricted the deformation of the ligand and the induced nonradiative relaxation [23].

3.3. Small organic molecules sensing ability

Considering the intrinsic structural property of multi water molecules around the trinuclear cluster, it is reasonable to expect that the water molecules replacement process induced by other common organic molecules. From this perspective, to investigate the potential sensing ability towards organic molecules, the luminescent emissions of **1** in different solvents (formaldehyde, CH₂Cl₂, CH₃OH, CH₃CN, pyridine, NMP, benzene, cyclohexane, DMF, DMA and DMSO) were recorded. As shown in Fig. 2, it was found that the luminescent emissions of **1** have solvent dependence in peak position and intensity. Comparing to other organic molecules, amide type solvent molecules showed the increased effect, particularly, **1** suspended in DMA exhibited the largest red-shift and the most enhancing behavior. The strong emission of **1** in DMA shows the potential application for luminescent sensing and DMA capture from waste water. The stability of **1** in solvents was ensured by the similarity to the simulated in PXRD patterns (Fig. S11). The difference between **1** and **1**-DMA indicated the possibility of structure transformation.

To examine sensing sensitivity toward DMA quantitatively, the suspensions of **1** dispersed in water with gradually increasing DMA contents were prepared to monitor the sensing property. A gradual increase of the luminescence intensity was observed upon the addition of DMA to the water suspension of **1** (Fig. S12) and the luminescence intensities kept constant in higher concentration region. The relationship between enhancing efficiency ($I/I_0 - 1$) and DMA concentration is almost linear (slope = 7439 vol%⁻¹, R² = 0.997) in the concentration range of 0–0.17 vol%, and the limit of detection of **1** for DMA molecules is calculated as 0.0028 vol%, which is comparable with those obtained by other sensors for DMA (Table S4). Generally, the binding interaction between framework and solvent makes a huge contribution to the luminescence increasing phenomena [24]. To ascertain the binding stoichiometric ratio between **1** and DMA, the Job's plot method was applied here. As shown in Fig. S13a, the intensity of **1**-DMA nearly reaches a maximum when the proportion of DMA is 0.5, implying the stoichiometric ratio of **1** and DMA is 1:1. Based on 1:1 stoichiometric ratio, the calculated binding constant is 0.79 × 10³ M⁻¹ for **1**-DMA according to the Benesi–Hildebrand equation (Fig. S13b). Subsequently, the time-response characteristic of **1** towards DMA was also investigated. Fig. S14a shows that with interaction time increasing, the luminescence intensity is continuously increased.

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