

A luminescent cyclic binuclear zinc–pamoate complex for highly selective and sensitive sensing of 2,4,6-trinitrophenol



Limei Zhao, Junwei Ye, Wenbing Li, Raji Feyisa Bogale, Bin Wang, Weitao Gong, Guiling Ning*

State Key Laboratory of Fine Chemicals and School of Chemical Engineering, Faculty of Chemical, Environmental and Biological Science and Technology, Dalian University of Technology, 2 Linggong Road, Dalian 116024, PR China

ARTICLE INFO

Article history:

Received 22 April 2014

Accepted 30 May 2014

Available online 2 June 2014

Keywords:

Cyclic binuclear complex

Zinc–pamoate

Luminescent

2,4,6-Trinitrophenol

Chemosensor

ABSTRACT

A luminescent cyclic binuclear zinc–pamoate complex, $[\text{Zn}_2(\text{PAM})_2(1,3\text{-PDA})_2]$ (**1**), has been synthesized by self-assembly of Zn(II) ions, 4,4'-methylenebis(3-hydroxy-2-naphthalenecarboxylic acid) (H_2PAM) and 1,3-propanediamine (1,3-PDA) under hydrothermal condition and characterized by elemental analysis, infrared spectroscopy, powder X-ray diffraction and single-crystal X-ray diffraction analysis. In **1**, two Zn^{2+} ions are bridged by two PAM ligands to form a 24-membered ring binuclear structure. The emission of **1** could be quenched efficiently and selectively by 2,4,6-trinitrophenol (TNP), indicating that **1** can serve as a selective chemosensor for the detection of TNP via a fluorescence quenching mechanism.

© 2014 Elsevier B.V. All rights reserved.

Rapid and selective detection of high explosives is attracting increasing attention due to its importance in homeland security, environment and health-care issues [1]. Among the nitroaromatic explosives, 2,4,6-trinitrophenol (TNP) is the firstly synthesized explosive used militarily with strong explosion ability and low safety coefficient [2], and it is widely used in dyes, leather, fireworks, matches and pharmaceutical industry [3]. TNP extensively existing in the soil and ground water near military and industrial facilities may lead to serious environmental pollution [4]. Furthermore, TNP may cause skin irritation, liver or kidney damage, cyanosis and aplastic anemia when living organisms inhale, ingest or touch it, especially people [5]. Thus it is highly desired to develop some analytical methods for detecting and quantifying TNP.

In the past decades, fluorescence-based detection of explosives or metal ions by utilizing photoluminescent polymers, small organic molecules and nanomaterials has attracted much attention owing to its sensitivity, selectivity, portability, short response time and convenient visual detection [6]. Regrettably, less effort has been paid to detect TNP [7], although its explosive power is somewhat superior to other hazardous substances, such as 2,4,6-trinitrotoluene (TNT). Recently, Peng et al. described a fluorescent and colorimetric N-acylhydrazone receptor for specific recognition of TNP [8]. Su et al. reported a near-infrared fluorescent probe for the determination of TNP based on bovine serum albumin coated CuInS_2 quantum dot [9]. S.K. Ghosh and co-workers developed a fluorescent cadmium(II) metal–organic framework for selective detecting TNP [10]. In this context, considering highly

electron-deficient feature of TNP, we surmised that metal coordination complex constructed from rich electron–donor ligands can significantly enhance electron transfer from complex to TNP, which may lead to obvious fluorescence quenching of complex for detecting TNP sensitively. Based on this idea, we selected rigid-flexible ligand pamoic acid (H_2PAM , 4,4'-methylenebis(3-hydroxy-2-naphthalenecarboxylic acid)) to construct the luminescent d^{10} metal coordination complexes. Herein, we reported a fluorescent cyclic binuclear zinc–pamoate complex, $[\text{Zn}_2(\text{PAM})_2(1,3\text{-PDA})_2]$ (**1**), synthesized by self-assembly of Zn(II) ions, H_2PAM and 1,3-propanediamine (1,3-PDA), which can serve as a selective chemosensor for the detection of TNP via a fluorescence quenching mechanism.

Yellow block-shaped crystals of compound **1** were synthesized by hydrothermal reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6(\text{H}_2\text{O})$, H_2PAM and 1,3-PDA in H_2O at 120 °C for 72 h [11]. Single-crystal X-ray diffraction [12,13] (Tables S1 and S2) reveals that **1** is a cyclic binuclear structure crystallizing in the monoclinic space group $P2_1/c$, with one Zn(II) ion, one PAM ligand and one 1,3-PDA ligand in the asymmetric unit. As shown in Fig. 1a, the Zn1 center is coordinated in the slightly distorted tetrahedral geometry with two carboxylate oxygen atoms [$\text{Zn}(1)\text{-O}(1) = 1.954(2)$ Å, $\text{Zn}(1)\text{-O}(4A) = 1.947(2)$ Å] from two PAM ligands and two nitrogen atoms [$\text{Zn}(1)\text{-N}(1) = 2.006(3)$ Å, $\text{Zn}(1)\text{-N}(2) = 2.042(2)$ Å] from one 1,3-PDA. Two Zn^{2+} ions are bridged by two PAM ligands to form a 24 membered ring binuclear structure with the Zn–Zn distance of 10.728 Å (Fig. 1b and c). PAM ligand adopts bis-monodentate bridging coordination modes. As a terminal ligand, 1,3-PDA adopts chelating coordination mode with N–Zn–N angles 99.69(11)°. Both intra and intermolecular hydrogen bonds are observed in **1** (Figs. 1d, S1 and

* Corresponding author.

E-mail address: ninggl@dlut.edu.cn (G. Ning).

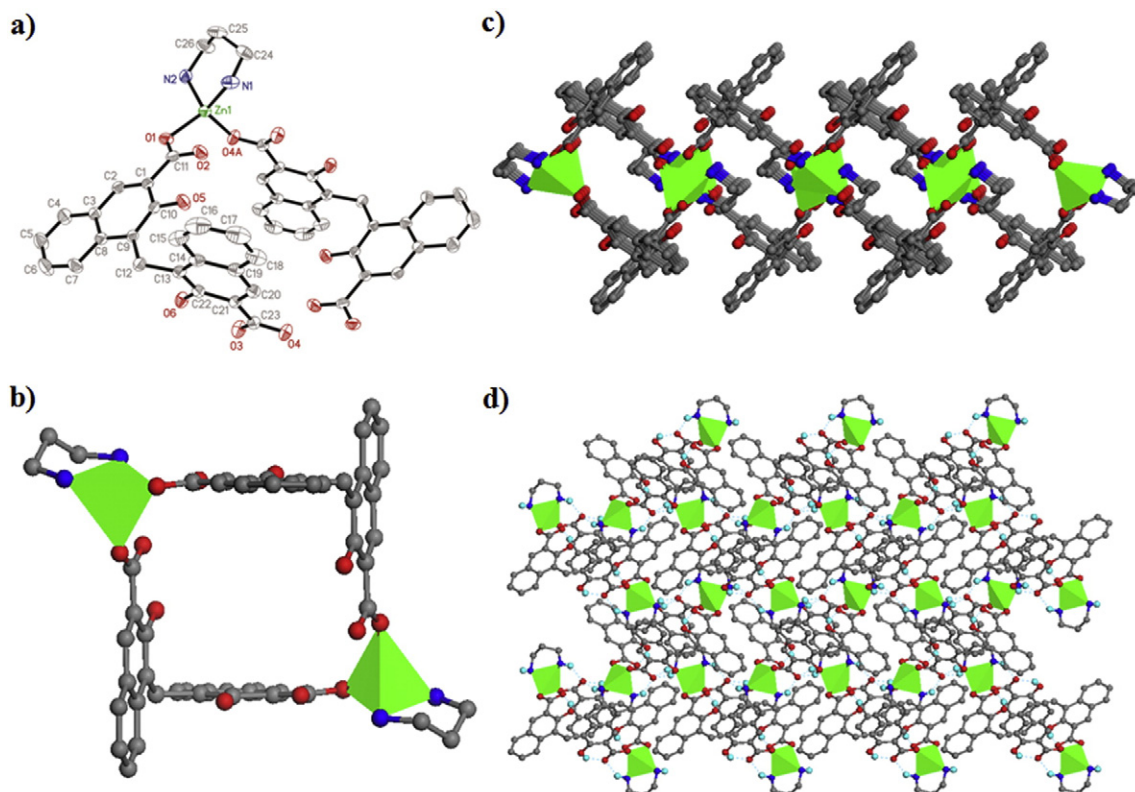


Fig. 1. (a) View of coordination environments of Zn²⁺ center. (b and c) Cyclic binuclear structure; (d) two-dimensional supramolecular network. Color code: Zn, green; O, red; N, blue; C, gray; H, cyan.

S2), which play an important role in the formation of molecular packing structure. In **1**, the strong intramolecular O–H···O hydrogen bonds (O5···O2 and O6···O3 distances of 2.543(3) Å and 2.582(3) Å, respectively) between the hydroxyl and uncoordinated carboxylate O atom in the PAM ligand, and N–H···O hydrogen bond with N···O distance of 3.021(4) Å between the amino group of 1,3-PDA and uncoordinated carboxylate O atom of PAM ligand are formed (Fig. S1). Furthermore, there are two types of intermolecular hydrogen bonds between adjacent dimers. One type is N–H···O hydrogen bond with N···O distance of 3.046(4) Å between the amino group of 1,3-PDA and the uncoordinated carboxylate O atom of PAM ligand. Another type is O–H···O hydrogen bond with O···O distance of 3.143(3) Å formed by coordinated carboxylate O atom and the hydroxyl O atom of PAM ligand (Fig. S2). These cyclic binuclear units are connected by hydrogen bonds forming an extended two-dimensional supramolecular network (Figs. 1d and S3).

The powder X-ray diffraction (XRD) pattern of **1** was investigated. Fig. 2 shows the simulated and experimental XRD patterns of **1** which indicated the phase purity of the products. The most peak positions of experimental patterns were in good agreement with simulated those generated from single-crystal structure analysis result. The thermal stability of **1** was examined by thermal gravimetric analysis (TGA) (Fig. S4). The experiment was performed under air atmosphere with a heating rate of 10 °C/min. The TGA result indicates that **1** begins to decompose at 272 °C and displays almost one stage of weight loss which is ascribed to the loss of ligands.

The photoluminescence (PL) spectrum of **1** in dimethyl sulfoxide (DMSO) exhibits strong emission peak at 501 nm upon excitation at 371 nm at room temperature (Fig. 3), while in solid state, **1** exhibits a broad emission band at 548 nm (Fig. S5). To explore the ability of **1** to sense TNP, fluorescence-quenching titrations were performed by gradual addition of TNP (1 mM, DMSO) to solution of **1** in DMSO (1×10^{-5} mol/L, 3 mL). Immense fluorescence quenching was observed upon incremental addition of TNP (Fig. 3). The quenching efficiencies were estimated using the formula $(I_0 - I)/I_0 \times 100\%$, where I_0 is the maximum fluorescence

intensity of **1** before TNP added and I is the intensity of **1** containing TNP solution. The initial fluorescence intensity of **1** was decreased by 98.4% when only 13 ppm TNP was present, even fluorescence quenching phenomenon could be easily detected at low concentration (10 ppm). Good linear dependencies ($R^2 = 0.9980$) of $(I - I_{\min}) / (I_{\max} - I_{\min})$ on the TNP concentration were obtained as shown in Fig. S6. It is noticeable that the calibration curve plot of **1** toward TNP showed detection limit of 1.271×10^{-8} g/L. To the best of our knowledge, this is a rare case of MOF materials which can quantitatively detect the concentration of TNP [14].

To compare the sensing selectivity of **1** toward TNP, the emission spectra of **1** were also recorded upon addition of other NACs including 4-nitrophenol (4-NP), 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT), nitrobenzene (NB), 1,3-dinitrobenzene

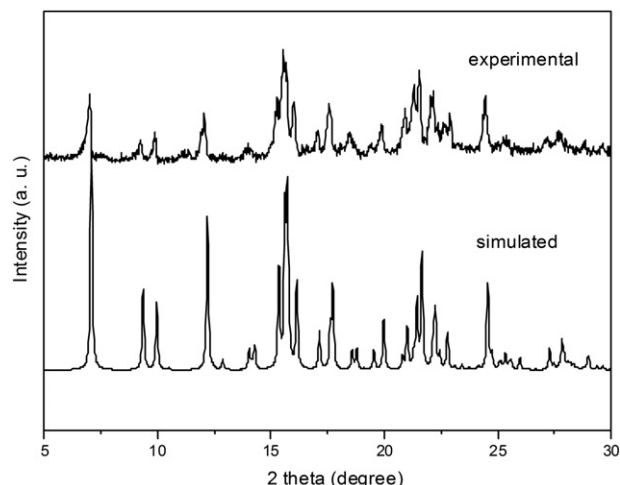


Fig. 2. The simulated and experimental XRD patterns of **1**.

Download English Version:

<https://daneshyari.com/en/article/1303596>

Download Persian Version:

<https://daneshyari.com/article/1303596>

[Daneshyari.com](https://daneshyari.com)