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Short communication

# A two-fold interpenetrated metal-organic framework for the highly selective detection of explosive picric acid

Meng-Yao Sun [a], Di-Ming Chen [b,*], Huan Zhang [c,*]

[a] School of Computer and Communication Engineering, Zhengzhou University of Light Industry, Zhengzhou 450002, People's Republic of China
[b] Henan Provincial Key Laboratory of Surface & Interface Science, Zhengzhou University of Light Industry, Zhengzhou 450002, People's Republic of China
[c] College of Science, Tianjin University of Science and Technology, Tianjin 300457, People's Republic of China

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ABSTRACT

A two-fold interpenetrated metal-organic framework{[Zn(bpydb)($H_2O$)](DMF)$_{0.75}$} (**1**, DMF = *N*,*N*-dimethylformamide), involving the aromatic trigonal heterofunctional ligand 4,4′-(4,4′-bipyridine-2,6-diyl) dibenzoic acid ($bpydbH_2$) and Zn(II) metal center has been successfully synthesized under solvothermal condition. The structure of **1** was characterized by single-crystal X-ray diffraction, which shows a two-fold interpenetrated 3-connected framework with **$ThSi_2$**-type topology. The luminescent sensing of different nitro-explosives was investigated, and the results indicated that **1** could behave as an effective sensor for detecting picric acid (PA) with high selectivity and sensitivity. Furthermore, the quenching mechanism has also been investigated in detail.



The sensitive and selective detection of nitroaromatic explosives has received increasing attention in recent years because of their involvements in military applications, homeland security, forensic investigations, and mine-field analysis [1–3]. The 2,4,6-trinitrophenol (PA) is an even more powerful explosive than the well-known trinitrotoluene (TNT), which has also been widely used in the preparation of lethal weapons and in the manufacture of rocket fuels, dyes, fireworks and matches [4,5]. In addition, the wide use of PA has made it highly possible to leak into the living environment which further leads to serious environmental pollution and human health risks. Therefore, there is an urgent demand to develop novel and highly selective sensory materials for picric acid detection [6]. As a kind of promising solid crystalline materials, Metal-organic frameworks (MOFs) have gained considerable interest in the area of luminescent sensing for the simplicity, cost-effectiveness and short response time [7]. In particular, MOFs has inherent advantages in luminescence sensing because they effectively concentrate analyte molecules at higher levels to enhance the host–guest interactions to export an analytical response. Recent studies have revealed that MOFs could selectively detect trace amount of nitroaromatic explosives in solution though luminescent quenching [8]. Compared with detection of nitroaromatic explosives with other non-nitro compounds, the selective detection of PA among nitroaromatic explosives is more challengeable for their similarity in electronic character [9]. In this work, we have chosen a highly conjugated, aromatic trigonal heterofunctional linker 4,4′-(4,4′-bipyridine-2,6-diyl) dibenzoic acid ($bpydbH_2$) as the organic building block and Zn(II) ion as the metal ion, so was a new luminescent three-dimensional Zn-based MOF {[Zn(bpydb)($H_2O$)](DMF)$_{0.75}$} (**1**) with a two-fold interpenetrated framework and **$ThSi_2$**-type topology synthesized. This luminescent MOF exhibits highly selective responses towards picric acid comparing to other nitroaromatic explosives. Furthermore, the detection mechanism has also been investigated in detail.

Solvothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$ and $bpydbH_2$ in a DMF/$H_2O$ mixed solvent at 90 °C for two days afforded yellow single crystals of **1** with high quality. Single crystal X-ray diffraction analysis reveals that **1** belongs to the monoclinic system with a space group of C2/c (Table S1). The asymmetric unit consists of one crystallographically independent Zn(II) ion, one $bpydb^{2-}$ ligand and one coordinated water molecule. As shown in Fig. 1a, the Zn(II) ion is six-coordinated by four carboxylic O atoms from two different $bpydb^{2-}$ ligands, one N atom from another $bpydb^{2-}$ ligand and one water O atom, resulting in a pseudo-octahedral environment. The Zn—N bond distance is 2.066(8) Å, and the Zn—O bond lengths fall in the range of 2.037(1) to 2.372(1) Å, both of which are comparable to the reported distance values [10–14]. The $bpydb^{2-}$ ligand bridges to three Zn(II) ion, in which each nitrogen and each carboxylate group bridge to one Zn(II) ion. Such a connection mode leads to the formation of a three-dimensional network with a series of L-helix and R-helix channels whose ratio is 1:1 (Figs. 1b and S1). Although the single network possesses large hexagonal 1D channels with a diameter of 11.3 Å along the *b* axis, the whole framework is two-fold interpenetrated, which reduces the pore diameter to 4.6 Å as revealed by poreblazer_v3.0.2 (Fig. 1c) [15]. The effective free volume of **1** is 57.5% as calculated using PLATON,

* Corresponding authors.
*E-mail address:* cdm700@sina.com (D.-M. Chen).

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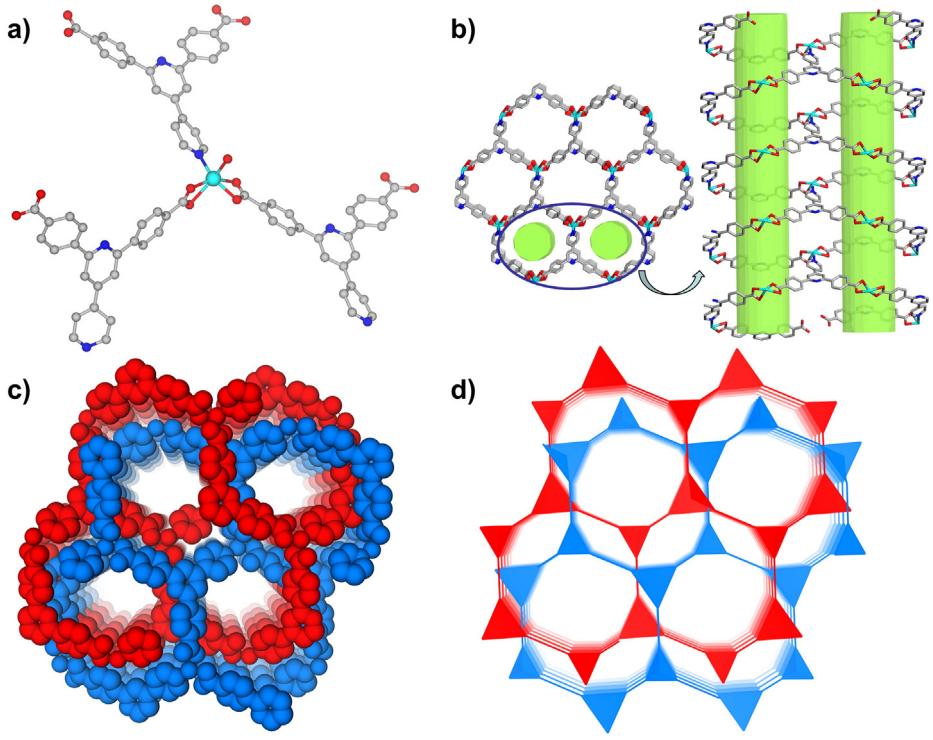


**Fig. 1.** Views of (a) The coordinating surrounding for Zn(II) ion in **1**, (b) the 1D helix channels in **1**, (c) space-filling representation of **1** viewed from *b* axis, and (d) the two-fold interpenetrated 3D net with 3-connected **ThSi$_2$** topology.

which is relatively high among the interpenetrated MOFs reported [16–19]. Topological analysis shows that the Zn(II) ion and the bpydb$^{2-}$ ligand could be judged as three connected nodes, so the whole framework of **1** could be simplified as a 3-connected 2-fold interpenetrated **ThSi$_2$** network with the point symbol of ($10^3$) (Figs. 1d and S2).

The purity of the bulk sample for the as-synthesized **1** was confirmed by the good match between the powder X-ray diffraction (PXRD) patterns of the as-synthesized sample and the simulated one from the crystallographic data (Fig. S3). The TGA curve of **1** shows a continuous 13.3% weight loss in the temperature range of 25–235 °C (Fig.

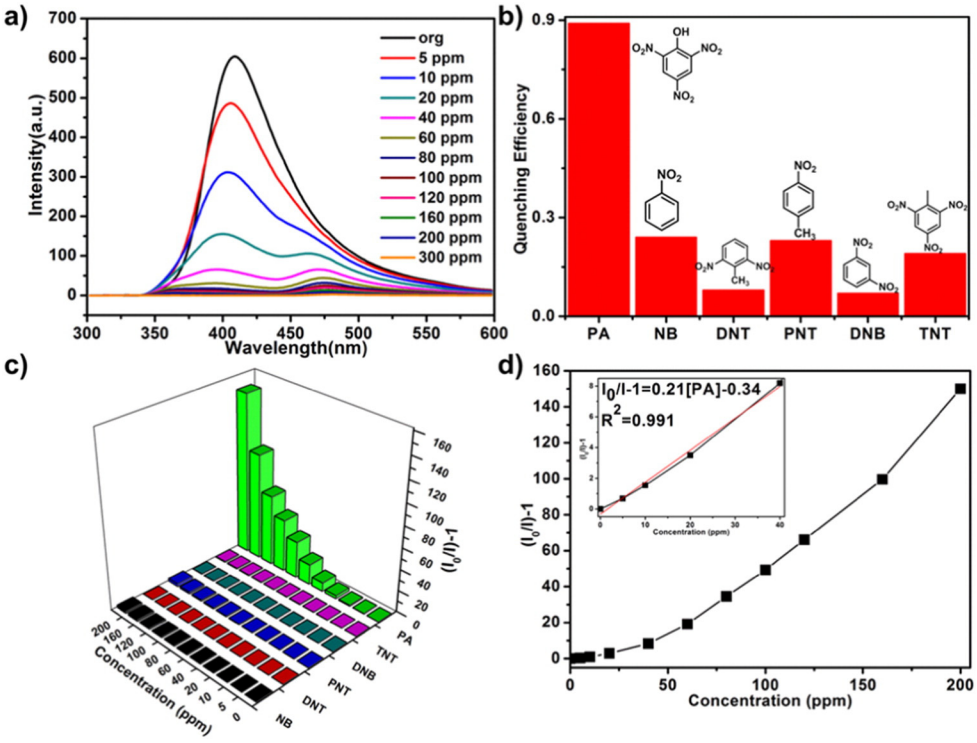


**Fig. 2.** (a) Fluorescence spectra of **1** upon the addition of various PA concentrations in DMF. (b) Fluorescence quenching efficiency obtained for **1** upon addition of 40 ppm of different nitroaromatic explosives. (c) Stern–Volmer plots of **1** with different nitro-explosives. (d) Nonlinear Stern–Volmer plot for PA by exponential quenching equation, inset shows the fitting curve of the linearity of the Stern–Volmer plot for PA of 0–40 ppm.