Thiadiazole-functional porous metal–organic framework as luminescent probe for Cd$^{2+}$†

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The solvothermal reaction of 4,4′-(benzothiadiazole-4,7-diyl) dibenzoate and Zn(a) leads to the generation of an interdigitating three-dimensional (2D + 2D → 3D) porous metal–organic framework, which displays a highly selective fluorescent enhancement with Cd$^{2+}$ amongst other metal ions.

In recent years, functional metal–organic frameworks (MOFs) have been one of the most rapidly developing areas of chemical science, not only because of the exceptionally artistic architecture of these materials, but also because of their justifiably enormous potential for many practical applications such as gas adsorption and separation, catalysis and luminescence.¹ Organic carboxylate ligands have been widely used in synthesizing porous MOFs or magnetic materials with aesthetic topologies and unique properties because of the controllable length of ligand, the various coordination modes of the carboxyl group and functionalized site on the ligand, which can decorate the pore surfaces.² A number of luminescent materials sensing small molecules or metal ions are widely exploited in many areas, such as luminescent probes in biomedical assays and time-resolved microscopy, fluorescent lighting, luminescent probes for chemical species.³ In fact, the MOF chemosensors have caused considerable attention due to their intriguing photophysical properties including evident Stokes shifts, excitation in the visible range and relatively long lifetimes.⁴ Most probes are sensitive to certain metal ions, which follow the principle that there exists coordination sites in the structure to postsynthetically interact with the special metal ions, and then exert an affect on the luminescent intensity of the material.

So, the design and synthesis of the corresponding analogues with specific Lewis basic sites for sensing of metal ions and exhibiting special metal-sensitive fluorescence properties have attracted tremendous interest in coordination chemistry.

Cadmium is widely used in many areas such as industry and agriculture although it has been recognized as a highly toxic heavy metal. Chronic exposure to Cd$^{2+}$ sources can cause serious disease and increased Cd$^{2+}$ accumulation in the human body even resulted in certain cancers.⁵ To the best of our knowledge, the probes utilizing MOFs for Cd$^{2+}$ have not been previously documented, although several organic compound-based fluorescent probes for cadmium ions are reported.⁶

Over a very large number of previous studies, the facts evidence that the success of synthesizing functional MOFs relies on the systematic development of suitable secondary building units (SBUs) in which a structurally and functionally diverse class of novel materials might evolve.⁷ The special features or unique sites of organic ligands in the structure determine the chemical environment and function of the resulting void spaces of this material. Herein, we introduce a linear ditopic carboxylate ligand (btodb$^{2−}$) with athiadiazole-functional site (Fig. 1a), and its Zn(a) 3D interdigitating porous MOF, Zn(btodb)(DMA)·H₂O (1), which was obtained by solvothermal reaction of Zn(a) and H₂btodb in DMA media.† This MOF exhibits strong luminescence properties both in the solid state and in methanol suspension. Most interestingly, it can be a selective luminescent probe for Cd$^{2+}$. The synthesis and ¹H-NMR of the H₂btodb ligand are described in the ESI†.

Single-crystal X-ray analysis reveals that 1 crystallizes in chiral space group C222₁.§ and its asymmetric unit contains one crystallographically independent Zn(a) centre, one btodb ligand, one coordinated DMA and one lattice water molecule. It is an three-dimensional porous metal–organic framework interdigitated by two sets of two-dimensional grid sheets inclined with respect to each other (2D + 2D → 3D). The well-known zinc binuclear “paddlewheel” SBU is a structural component of the earliest porous MOFs.⁸ In the binuclear zinc...
[Zn₂(CO₃)₄] cluster, each Zn(II) centre is five-coordinate and surrounded by four carboxylate oxygen atoms of four individual btdb ligands, and one oxygen atom belongs to a DMA molecule (Fig. 1b), completing a square pyramidal coordination geometry. In this structure, the Zn(II) paddlewheel clusters as the 4-connect nodes are linked by four btdb ligands to form a 2D grid sheet (Fig. 2a). The terminal DMA molecules are located in the up or down of the 2D grid sheet. The 2D grid sheet is square with an interior angle of 90.74(2)° and 90.06(3)°, and a side length of 19.661(6) Å based on Zn⋯Zn separation. Due to the wide opening of the grid, benzothiazole rings have space to rotate freely, and allow another sheet to be inserted to form a 3D interdigitating architecture (2D + 2D → 3D). Along the diagonal of every square grid, two sets of parallel 2D grid layers interpenetrated into an interlocked structure of 3D networks (Fig. 2b), actually perpendicular each sheet passing through an inclined one just once along a line of intersection of the two planes. The rings around the pores point to different orientations, there exists 1D rhombic channels in the structure along the c-axis (Fig. 2c), entangled by two sets of parallel layers. The size of a channel is 12.481 × 8.529 Å². PLATON¹⁰ analysis revealed that the 3D framework was composed of voids of 940.5 Å³ which represent 18.3% per unit cell volume.

The thermal stability of 1 was examined by TGA from 30 to 900 °C (Fig. S4, ESI†) and the powder X-ray diffraction (PXRD) at room temperature, 110 and 150 °C (Fig. S5, ESI†). The results imply that 1 is stable up to 210 °C, and then begins to decompose upon further heating.

Previous studies have shown that coordination polymers containing zinc or benzo-[2,1,3]-based compounds exhibit photoluminescent properties.¹¹ So we investigated the luminescent properties of 1 in the solid state and in methanol suspension at room temperature. As expected, 1 exhibits an intense emission band at ca. 494 nm in the solid state upon excitation at 370 nm, as shown in Fig. 3a, and in methanol suspension, the fluorescent emission band at 491 nm is observed at room temperature upon excitation at 350 nm (Fig. 3b). It should be noted that there is a relatively weak emission at 512 nm for free H₂btdb ligand under the

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**Fig. 1** (a) H₂btdb ligand; (b) zinc paddlewheel SBU.

**Fig. 2** (a) 2D grid sheet formed by btdb ligands and zinc paddlewheel SBUs; (b) interdigitation of two sets of parallel 2D grid sheets (2D + 2D → 3D); (c) two kinds of 1D rhombic channels resulting from entanglement viewed along the c-axis. (d) Space-filling model of 1D channels along the c-axis.

**Fig. 3** (a) Luminescence excitation (at 494 nm) and emission (at 370 nm) spectra of 1 in the solid state at room temperature. (b) Luminescence emission spectra of 1 in methanol at room temperature in the presence of 0–3 equiv of Cd²⁺ ions with respect to 1, respectively: black, no addition; red, 1 equiv; green, 2 equiv; blue, 3 equiv, excited at 350 nm, with emission monitored at approximately 491 nm.
same experimental conditions (Fig. S6, ESI†). Thus the fluorescent emissions of 1 may be attributed to the strong electronic coupling between the neighbouring ligands through Zn(II).\(^{10,12}\)

Owing to the special structure of btdb ligand, the N atoms in the thiadiazole ring can act as coordination sites coordinating to the added metal ions. So, we investigated the effects of the metal ions such as K\(^{+}\), Ca\(^{2+}\), Ba\(^{2+}\), Fe\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Cd\(^{2+}\), Ag\(^{+}\) and Hg\(^{2+}\) on the fluorescent intensity of 1 in methanol at room temperature. The emission intensity of 1 enhanced distinctly with Cd\(^{2+}\) doping (Fig. 3b). More remarkably, with increasing Cd\(^{2+}\) concentration, the luminescent intensities of 1 showed a pronounced enhancement. As shown in Fig. 3b, the emission intensity increased gradually upon addition of 1–3 equiv of Cd\(^{2+}\). The emission intensity of 1 increased by 3.5 times when adding 3 equiv of Cd\(^{2+}\), whereas adding other metal ions, such as 1–3 equiv of Ca\(^{2+}\), Ba\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\), Ag\(^{+}\) and Hg\(^{2+}\) cause the fluorescence intensity of 1 to be weakened or even quenched, and others had no evident effect on the emission intensity of 1 (Fig. 4). It should be noted that 3 equiv of Pd\(^{2+}\) and Au\(^{3+}\) addition induce a blue-shift of emission from 491 to 475 nm and 473 nm, but the Pd\(^{2+}\) and Au\(^{3+}\) only enhance the luminescent intensity to quite a small extent (Fig. S7, ESI†). The luminescent spectra of 1 after heating at 210 °C (Fig. S8, ESI†) also showed a strong luminescent band at 491 nm, which is similar to that of 1. With the increase of Cd\(^{2+}\) concentration, the emission intensity of 1 was clearly enhanced.

As mentioned above, the exoteric Cd\(^{2+}\) can sensitize the luminescence of 1. The results indicate that the energy transfer process is more effective with the addition of Cd\(^{2+}\).

In conclusion, a 3D-functional interdigiting porous framework via a 2D grid sheet (2D + 2D → 3D) was synthesized by using 4,4’-(benzothiazole-4,7-diyi) dibenzoate (btdb) and Zn(II). The ring of the btdb ligand can interact with metal ions. The luminescent intensities of 1 were enhanced in a pronounced manner upon addition of 1–3 equiv of Cd\(^{2+}\), which could be utilized as a probe for sensing Cd\(^{2+}\). In future work, we will continue to explore other MOFs with functional ligands for practical applications with respect to sensors for chemical species.

![Fig. 4](image)

**Fig. 4** Room-temperature luminescent intensity of 1 at 491 nm in methanol upon addition of various metal ions (excited at 350 nm).

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**Notes and references**

† Synthesis of 1: A reaction mixture of Zn(NO\(_3\))\(_2\)_6H\(_2\)O (0.015 g, 0.05 mmol), H\(_2\)btdb (0.005 g, 0.013 mmol) and N\(_2\)N-dimethylacetamide (1.5 mL) into sealed glass vial was stirred for 20 min in air, then was heated in an oven to 378 K for 72 h. The resulting pure yellow block crystals were filtered and dried in air (yield: ca. 32%). Elemental analysis calc’d (%) for 1C\(_{2}\)H\(_{14}\)N\(_{2}\)O\(_{6}\)Zn: C, 52.90; H, 3.88; N, 7.71. Found: C, 52.91; H, 3.86; N, 7.69. 1 is insoluble in water and common organic solvents, such as DMF, DMSO, CH\(_3\)CN and acetone.

‡ Crystal data for 1: Orthorhombic space group C\(_2\)\(_2\)_2\(_2\)\(_2\); \(M_r = 544.9, a = 18.768(6)\) Å; \(b = 28.890(14)\) Å; \(c = 9.479(5)\) Å; \(V = 5140(4)\) Å\(^3\); \(Z = 8; D_c = 1.048\) g cm\(^{-3}\); \(F(000) = 2240; \mu = 1.979\) mm\(^{-1}\); 15482 reflections measured; 5040 unique (R\(_{int} = 0.0586)\). Final \(R_1 = 0.0956; wR_2 = 0.2530. \) X = 1.306 for all data. Flack parameter \(x = 0.18(4)\). The structure was solved by direct methods and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on \(F^2\) using SHELXTL program.\(^{11}\)


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