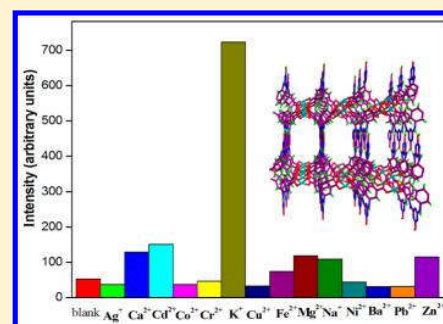


Functional Hydrogen-Bonded Supramolecular Framework for K⁺ Ion SensingZheng-Bo Han,^{*,†} Zi-Zhong Xiao,[†] Miao Hao,[†] Da-Qiang Yuan,^{*,‡} Lin Liu,[†] Na Wei,[†] Hui-Meng Yao,[†] and Ming Zhou^{*,§}[†]College of Chemistry, Liaoning University, Shenyang 110036, P. R. China[‡]State Key Lab Structural Chemistry, Fujian Institute Research on the Structure Matter, Chinese Academy of Sciences, Fuzhou 350002, P. R. China[§]Panjin Vocational and Technical College, Panjin 124010, P. R. China

Supporting Information

ABSTRACT: A luminescent metal–organic framework was assembled by using 3,3'-((6-hydroxy-1,3,5-triazine-2,4-diyl)bis(azanediyl))dibenzoic acid and Zn(II), which exhibits a 2D layer architecture, and the adjacent layers are further stacked via hydrogen-bonding and N⋯N van der Waals interactions to form a 3D supramolecular framework. This material can be used as fluorescent probe of K⁺ ion.



Crystal engineering of supramolecular polymers has attracted attention not only due to the easily predicted hydrogen-bonding supramolecular synthons^{1,2} but also due to their potential applications as functional materials, such as proton conduction, sensing, and catalysis.^{3–6} To achieve these kinds of functional materials, it is necessary to precisely position the synthons in the crystal lattice by means of appropriate noncovalent interactions between molecules. Hydroxyl and amides are two commonly used functional synthons in crystal engineering because they easily form robust architectures via O–H⋯N or N–H⋯O hydrogen-bonding.⁷ This approach can introduce new functions into the system of supramolecular polymers. For example, some luminescent supramolecular polymers containing hydrogen bonds in the structure are widely used as fluorescent materials sensing to chemical species, which include luminescent probes for metal ions, explosives, solvent molecules, etc. Furthermore, these materials are exploited as luminescent probes in biomedical assays.^{8–11} In fact, the chemosensors based on a new kind of supramolecular polymer or metal–organic framework (MOF) have reached hotspots due to the intriguing photophysical properties of the materials. Because of their existing active sites in the structure, which postsynthetically interact with the particular metal ions, as the result, most probes are sensitive to certain metal ions through enhancing or quenching the luminescent intensities of the compounds.^{12–14} Therefore, the design and synthesis of supramolecular polymers, which using specific functional sites in the structure to sense metal ions and then exhibiting special metal ion-selective sensitive luminescent properties, have attracted tremendous interest in the area of crystal engineering.

Potassium is indispensable element for the human body. The shortage or excess amounts of K⁺ in body fluids may cause a potentially fatal disease such as hypokalemia and hyperkalemia.^{15,16} Therefore, the detection of potassium is extremely important in medicine. However, to the best of our knowledge, the probe for the K⁺ ions utilizing MOFs has not been previously documented, although the sensing of K⁺ ions using crown molecules has been reported.¹⁷

The facts of plenty of previous studies evidence that systematic development of appropriate secondary building units (SBUs) will contribute to the successful synthesis of functional MOFs, in which structurally and functionally diverse class of novel materials might evolve.^{18–21} 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 supramolecular framework, [Zn(L)(DMA)]·2.5H₂O (**1**) constructed from nonrigid carboxylate ligand 3,3'-((6-hydroxy-1,3,5-triazine-2,4-diyl)bis(azanediyl))dibenzoic acid (H₂L) with imine functional sites (Figure 1a) and Zn(II) through coordination bond and hydrogen bonds. The systematic luminescent experiment to complex **1** was investigated and the result showed that **1** exhibits strong fluorescent emission both in the solid state and in methanol suspension. More notably, it exhibits a special

Received: August 24, 2014

Revised: December 19, 2014

Published: January 8, 2015

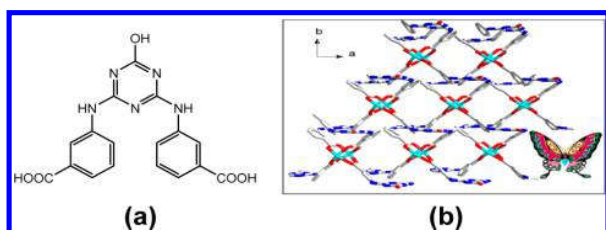


Figure 1. (a) H_2L ligand. (b) Butterfly-shaped unit, generating a 2D layer along the ab plane (H atoms and coordinated DMA molecules were omitted for clarity).

luminescent phenomenon with K^+ ion adding in, which can be used as a selective luminescent probe for K^+ .

Single-crystal X-ray analysis reveals that **1** crystallizes in space group $C2$ and its asymmetric unit contains one L ligand, one crystallographically independent Zn(II) center, one coordinated DMA ligand, and 2.5 lattice water molecules. In the binuclear zinc cluster $[Zn_2(CO_2)_4]$, each Zn(II) is five-coordinate and surrounded by four oxygen atoms rooted from four carboxylate oxygen atoms of L ligands, and one oxygen atom belongs to an aqua ligand, completing a square pyramidal coordination geometry. In this structure, the Zn(II) paddlewheel clusters as the 4-connect nodes are linked by four L ligands to form a butterfly-shaped unit and then generating a two-dimensional (2D) wave-like layer along the ab plane (Figure 1b). The adjacent layers are further stacked together through hydrogen bonding interactions and $N\cdots N$ van der Waals interactions viewed along the a axis, forming a three-dimensional (3D) supramolecular structure (Figure 2a) with a pore size of $10.53 \times 10.19 \text{ \AA}^2$. Interestingly, there exists the

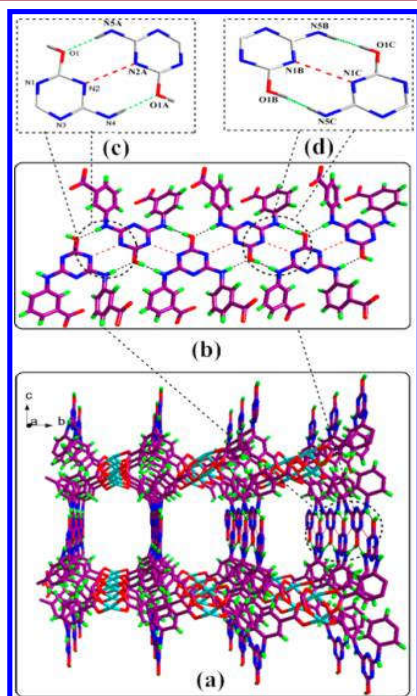


Figure 2. (a) Three-dimensional structure of **1** along the c -axis. (b) Ribbon-like supramolecular structure formed by L ligands viewed along the b axis. (c,d) Hydrogen-bonded supramolecular synthons with graph sets $R_2^2(12)$ patterns. Symmetry code: A, $-x + 1, y, -z + 1$; B, $x - 1, y, z$; C, $x - 2, y, z$.

hydrogen bond interactions, both $N-H\cdots O$ and $O-H\cdots N$ hydrogen-bonded synthons have graph sets that match motifs patterns $R_2^2(12)$ (Figure 2b).²² Especially, in the synthon, N4, N5, and O1 atoms were used as both donor and acceptor, simultaneously (Figure 2c,d). PLATON analysis^{23,24} revealed that the 3D framework was composed of voids of 1235.7 \AA^3 , which represent 43.9% per unit cell volume.

Previous studies have shown that d^{10} metal organic coordination polymers containing zinc may exhibit excellent photoluminescence properties.^{25–28} So, the luminescent properties of **1** were investigated.

As expected, **1** exhibits extraordinary photoluminescence behavior both in the solid state and suspending in methanol solution. In the solid state, as shown in Figure S2a, Supporting Information, strong fluorescent emission band at 405 nm is observed at room temperature, excited at 330 nm, and in methanol suspension, the fluorescent emission band at 378 nm is observed at room temperature, excited at 305 nm (Figure 3a). It should be noted that the free ligand H_2L exhibits an

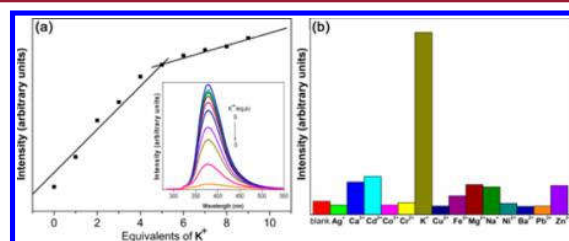


Figure 3. (a) Luminescence emission spectra of the complex **1** (10^{-4} M) in methanol suspension at room temperature in the presence of 0 to 9 equiv of K^+ ions with respect to **1**. Orange, no addition; excited at 305 nm, with emission monitored at approximately 378 nm. (b) Room-temperature luminescent intensity of **1** at 378 nm in methanol suspension upon the addition of various metal ions (4 equiv, excited at 305 nm).

emission band at 403 nm upon excitation at 321 nm (Figure S2b, Supporting Information). Thus, the fluorescent emissions of **1** may be assigned to the ligand-centered $\pi-\pi^*$ transition because the fluorescent emission bands are very similar to that of the free ligand.²⁹ The metal ions in the structure may change intraligand transitions.³⁰

Attributing to the characteristic structure of L ligand, the N atoms can conduct as coordination sites to coordinate with the additional metal ions. So, we investigated the effects of the metal ions such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Cr^{3+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , Ag^+ , and Pb^{2+} ions on the fluorescent intensity of **1** in methanol suspension at room temperature. The counteranion is Cl^- for K^+ , Ca^{2+} , Na^+ , Mg^{2+} , Ba^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , and NO_3^- for Cr^{3+} , Zn^{2+} , Cd^{2+} , Ag^+ , and Pb^{2+} . The as-synthesized samples were ground and suspended in methanol solution (10^{-4} M) containing the 0–4 equiv of metal ions (Ag^+ , Ca^{2+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Cu^+ , Fe^{3+} , Mg^{2+} , Na^+ , Ni^{2+} , Ba^{2+} , Pb^{2+} , and Zn^{2+}) and 0–9 equiv of K^+ for 5 min. Then, the luminescence spectra of **1** were investigated with a Hitachi F-4500 fluorescence spectrophotometer. For detailed experimental process, see the Supporting Information.

Upon the K^+ ions being added in, the emission intensity of **1** enhanced remarkably. More interestingly, with the increasing of the concentration of K^+ ion, the fluorescent intensities of **1** enhanced pronouncedly accordingly. The emission intensity increased gradually upon the addition of 0 to 9 equiv of K^+ , as

shown in Figure 3a. The emission intensity of **1** enhanced by 19 times when 9 equiv of K^+ doped-in; however, when other metal ions were added in, even 4 equiv of Ba^{2+} , Cr^{3+} , Co^{2+} , Ni^{2+} , Ag^+ , and Pb^{2+} cause the fluorescence intensities of **1** to be weakened or quenched by varying degrees, and the remaining ions had no obvious impact on the luminescence intensity of **1** (Figure 3b).

Taking the above discussion into account, **1** can selectively sense the exoteric K^+ through luminescent emission enhancement. The results indicate that the energy transfer process become more effective with the addition of K^+ because of its matched ionic size and charge number. In this contribution, the enhancement of emission intensity may account for more effective intramolecular energy transfer from Zn^{2+} to the L ligand.^{31–33}

In conclusion, a luminescent functional hydrogen-bonded 3D supramolecular framework has been successfully synthesized, which displays a highly selective luminescent sensitive to K^+ ion among other metal ions through self-luminescent emission intensity enhancement. In the future work, we will continue to explore other coordination polymers constructed by functional ligands in order to seek for practical applications in the area of sensor for chemical species.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental details of synthesis, luminescence, and additional characterizations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: ceshzb@lnu.edu.cn.

*E-mail: ydq@fjirsm.ac.cn.

*E-mail: zhouminglab@163.com.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was granted financial support from NNSF of China (20871063, 21271096, and 21271172).

■ REFERENCES

- (1) Desiraju, G. R. *Angew. Chem., Int. Ed.* **1995**, *34*, 2311–2327.
- (2) Nangia, A.; Desiraju, G. R. *Top. Curr. Chem.* **1998**, *198*, 57–95.
- (3) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705–714.
- (4) Zhang, J. P.; Zhang, Y. B.; Lin, J. B.; Chen, X. M. *Chem. Rev.* **2012**, *112*, 1001–1033.
- (5) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450–1459.
- (6) Yoon, M.; Suh, K.; Natarajan, S.; Kim, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 2688–2700.
- (7) Sadakiyo, M.; Yamada, T.; Honda, K.; Matsui, H.; Kitagawa, H. J. *Am. Chem. Soc.* **2011**, *133*, 7701–7707.
- (8) Young, V. G.; Quiring, H. L.; Sykes, A. G. *J. Am. Chem. Soc.* **1997**, *119*, 12477–12480.
- (9) Chu, T. S.; Liu, H. P.; Yang, Y. Y.; Wang, H. M.; Hu, Y. S.; Wang, Y.; Yu, M. H.; Ng, S. W. *J. Photochem. Photobiol. A: Chem.* **2014**, *294*, 38–43.
- (10) Zhang, X.; Wang, W.; Hu, Zhang J.; Wang, G.; Uvdal, K. *Coord. Chem. Rev.* **2015**, *284*, 206–235.
- (11) Cui, J.; Lu, Z.; Li, Y.; Guo, Z.; Zheng, H. *Chem. Commun.* **2012**, *48*, 7967–7969.

(12) Liu, W.; Jiao, T.; Li, Y.; Liu, Q.; Tan, M.; Wang, H.; Wang, L. J. *Am. Chem. Soc.* **2004**, *126*, 2280–2281.

(13) Gole, B.; Bar, A. K.; Mukherjee, P. S. *Chem. Commun.* **2011**, *47*, 12137–12139.

(14) Wei, N.; Zhang, M. Y.; Zhang, X. N.; Li, G. M.; Zhang, X. D.; Han, Z. B. *Cryst. Growth Des.* **2014**, *14*, 3002–3009.

(15) Frolov, R. V.; Berim, I. G.; Singh, S. J. *Biol. Chem.* **2008**, *283*, 1518–1524.

(16) Bartter, F. C.; Pronove, P.; Gill, J. R.; MacCardle, R. C. *Am. J. Med.* **1962**, *33*, 811–828.

(17) Ast, S.; Schwarze, T.; Muller, H.; Sukhanov, A.; Michaelis, S.; Wegener, J.; Wolfbeis, O. S.; Korzdorfer, T.; Durkop, A.; Holdt, H. J. *Chem.—Eur. J.* **2013**, *19*, 14911–14917.

(18) Tranchemontagne, D. J.; Mendoza-Cortés, J. L.; O'Keeffe, M.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1257–1283.

(19) Li, J.-R.; Yu, J.; Lu, W.; Sun, L.-B.; Sculley, J.; Balbuena, P. B.; Zhou, H.-C. *Nat. Commun.* **2013**, *4*, 1538–1545.

(20) Zeng, M.-H.; Yin, Z.; Tan, Y.-X.; Zhang, W.-X.; He, Y.-P.; Kurmoo, M. *J. Am. Chem. Soc.* **2014**, *136*, 4680–4688.

(21) Sun, F.; Yin, Z.; Wang, Q.-Q.; Sun, D.; Zeng, M.-H.; Kurmoo, M. *Angew. Chem., Int. Ed.* **2013**, *125*, 4636–4641.

(22) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120–126.

(23) Spek, A. L. *Acta Crystallogr., Sect. D: Biol. Crystallogr.* **2009**, *65*, 148–155.

(24) Spek, A. J. *Appl. Crystallogr.* **2003**, *36*, 7–13.

(25) Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Hou, R. J. T. *Chem. Soc. Rev.* **2009**, *38*, 1330–1352.

(26) Zhang, X.; Gorohmaru, H.; Kadowaki, M.; Kobayashi, T.; Ishi-i, T.; Thiemann, T.; Mataka, S. J. *Mater. Chem.* **2004**, *14*, 1901–1904.

(27) Wang, S.-N. *Coord. Chem. Rev.* **2001**, *215*, 79–98.

(28) Yu, G.; Yin, S.; Liu, Y.; Shuai, Z.; Zhu, D. *J. Am. Chem. Soc.* **2003**, *125*, 14816–14824.

(29) Song, J.-L.; Zhao, H.-H.; Mao, J.-G.; Dunbar, K. R. *Chem. Mater.* **2004**, *16*, 1884–1889.

(30) Gong, Y.; Tang, W.; Hou, W.; Zha, Z.; Hu, C. *Inorg. Chem.* **2006**, *45*, 4987–4995.

(31) Chen, Z.; Sun, Y.; Zhang, L.; Sun, D.; Liu, F.; Meng, Q.; Wang, R.; Sun, D. *Chem. Commun.* **2013**, *49*, 11557–11559.

(32) Zhao, B.; Chen, X.-Y.; Cheng, P.; Liao, D.-Z.; Yan, S.-P.; Jiang, Z.-H. *J. Am. Chem. Soc.* **2004**, *126*, 15394–15395.

(33) Wei, N.; Zhang, Y. R.; Han, Z. B. *CrystEngComm* **2013**, *15*, 8883–8886.