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## ARTICLE

# Fluorescent Metal-organic Framework Based On PyreneChromophore For Sensing of Nitrobenzene

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A highly luminescent metal-organic framework (MOF) constructed by a rare dendritic multicarboxyl acid with a pyrenechromophore was synthesized successfully. The fluorescence intensity of the MOF in DMF is obviously stronger than that in other common solvents such as acetone, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, cyclohexane, toluene, pyridine and THF. This particular fluorescence response to DMF is significant in sensing DMF. In addition, this MOF can sense nitrobenzene effectively. Low detection limit and good reproducibility make this material promising for explosive substances detection.

## Introduction

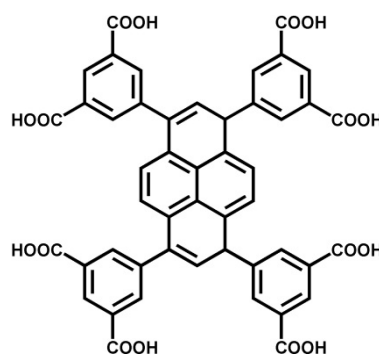
In the past few decades, metal-organic frameworks (MOFs) have gained great attention of so many crystal engineers from all over the world because of their delicate architectures,<sup>1</sup> topological diversity,<sup>2</sup> controllable channels,<sup>3</sup> and a great many potential applications such as gas storage and separation,<sup>4</sup> molecule sensing and recognizing,<sup>5</sup> catalysis,<sup>6</sup> optical and magnetism,<sup>7</sup> bioimaging<sup>8</sup> and so on. The tunable size and porosity of these materials are in favor of chemical sensing because high internal surface areas and large cavities can concentrate analytes to levels high above those in the surrounding atmosphere and can lead to much smaller detection levels. A fast and sensitive detection of explosive constituents is of great importance for environmental monitoring. Fluorescence quenching based sensing is a common strategy for its simplicity and sensitivity.<sup>9</sup> Till now, many reports about MOFs as sensors for nitroaromatic explosive sensing, which confirmed their potential application in sensor fields. However, designing and synthesizing a luminescent MOF with fast and sensitive fluorescence response is still challenging.

To get a luminescent MOF, a common method is to design and synthesize a fluorescent organic ligand. For this purpose, many aromatic rigid molecules such as benzene, naphthalene, anthracene, carbazole, triphenylamine were used for ligands synthesizing. However, ligands with a pyrenechromophore are very few because of their synthesizing complexities and poor solubilities. In the year of 2010, Rosseinsky *et al.* reported a InMOF constructed with the first

pyrene based ligand, tetrakis(*p*-benzoic acid)pyrene (TBAPy).<sup>10</sup> After that, a few MOFs based on this ligand had been reported by Rosseinsky and Hupp.<sup>11</sup> Recently, Zhu *et al.* reported a new MOF constructed by another pyrene based ligand, 1, 3, 6, 8-tetrakis (3, 5-isophthalic acid)pyrene (H<sub>8</sub>TIAPy).<sup>12</sup> All these pyrene based MOFs showed fascinating fluorescent properties.

Herein, we report another MgMOF (**1**) constructed with the ligand H<sub>8</sub>L. The crystals of **1** are strongly fluorescent when dispersed in DMF and show sensitive response to nitrobenzene through a fluorescence quenching mechanism. In addition, good repeatability and small detection level make this material promising for sensing application.

**Scheme 1.** Structure of H<sub>8</sub>L.



## Experimental section

### Chemicals and Materials

All solvents and reagents were bought from commercial sources as analytical grade and directly used without further purification. The ligand was synthesized according to a reported literature.<sup>12</sup> Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku DMAX 2550 diffractometer at 50 kV, 20 mA for Cu K $\alpha$  ( $\lambda$  = 1.5418 Å). Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer thermogravimetric analyzer with a heating rate of 5 °C per minute. Fluorescence measurement was conducted on FLUOROMAX-4 spectrometer.

**Synthesis of 1.** H<sub>8</sub>L (5 mg, 0.0058 mmol), Mg(NO<sub>3</sub>)<sub>2</sub> (20 mg, 0.1351 mmol), DMF (3 ml), H<sub>2</sub>O (0.5 ml) were combined in a 20 mL glass vial, sealed and heated in a 85 °C oven for about 2 days, and then cooled to room temperature. Yellow block crystals were collected and air dried (yield: 70% based on H<sub>8</sub>TIAPy). Elemental and ICP analysis for Mg<sub>4</sub>(L)(DMF)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>(DMF)<sub>0.5</sub> = C<sub>61.5</sub>H<sub>60</sub>Mg<sub>4</sub>N<sub>4.5</sub>O<sub>25.5</sub>, calculated (%): C, 54.07; H, 4.40; O, 29.89; N, 4.61; Mg, 7.03. Found (%): C, 53.80; H, 4.80; O, 29.81; N, 4.45; Mg, 7.14.

**Single Crystal X-ray Crystallography.** Single crystal X-ray diffraction data were collected using a Bruker APEX II Smart CCD diffractometer (Mo K $\alpha$ ,  $\lambda$  = 0.71073 Å). Indexing was performed using APEX II. Data integration and reduction were performed using SaintPlus. Absorption correction was performed by multiscan method implemented in SADABS. Space group was determined using XPREP implemented in APEX II. Structure was solved using SHELXL-97 (full-matrix least squares on F<sup>2</sup>) with anisotropic displacement contained in APEX II program packages. Hydrogen atoms on carbon and nitrogen were calculated in ideal positions with isotropic placement parameters set to  $1.2 \times U_{eq}$  of the attached atoms.

## Results and discussion

### Structure and characterization

The ligand H<sub>8</sub>L was synthesized according to a reported literature. The reaction of the ligand with Mg(NO<sub>3</sub>)<sub>2</sub> in DMF at 85 °C for 2 days gave the yellow block crystals of **1** formulated as Mg<sub>4</sub>(L)(DMF)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>(DMF)<sub>0.5</sub> confirmed by single crystal X-ray diffraction and TG analysis with a good yield. Single crystal X-ray analysis reveals that **1** crystallized in the monoclinic space group *P* 2<sub>1</sub>/c with the lattice parameters *a* = 11.064 Å, *b* = 15.957 Å, *c* = 23.362 Å,  $\beta$  = 92.265° which was isomorphic with JUC-118 reported by N. Zhao *et al.*<sup>12</sup> However, the coordinating style and the terminal are different from JUC-118. Each ligand connects to eight Mg<sub>2</sub> clusters and each Mg<sub>2</sub> cluster connects to four ligands (Figure 1a). The two Mg atoms in the cluster are both six-coordinated. Mg1 is coordinated by three carboxyl oxygen atoms from the ligands, two oxygen atoms from terminal disordered DMF molecules and one oxygen atom from water which is also splitted. Mg2 is coordinated by five carboxyl oxygen atoms from the ligands among which one

takes the  $\mu_2$ -O style and one oxygen atom from water (Figure 1b). In addition, the conformation of the ligand was different from JUC-118. The torsion angles between the pyrene and the benzene were 42.59 and 49.78 degrees in **1** of this work and 44.59 and 52.88 degrees in JUC-118 and 54.69 and 60.78 degrees in JUC-118-1. (Figure S6)<sup>12</sup> The assemble of the clusters and ligands give a three dimensional (3D) porous framework (Figure 1c). The solvent accessible volume was 62.0% calculated by platon. Attempt for getting the BET surface was failed because of the rapid collapse of the framework upon activation in vacuum. The topology analysis of the framework was conducted by the TOPOS 4.0 program.<sup>13</sup> Each benzene ring in the ligand could be simplified as a three-connected node and the pyrene as a four-connected node and each Mg<sub>2</sub> cluster as a four-connected one. Thus, the whole framework of **1** could be simplified as a 3,3,4,4-net (Figure 1d), the point symbol for net was  $\{4 \cdot 6 \cdot 8\}2\{4 \cdot 6^2 \cdot 8^3\}2\{6^2 \cdot 8^2 \cdot 10 \cdot 12\}\{6^2 \cdot 8\}2$ .

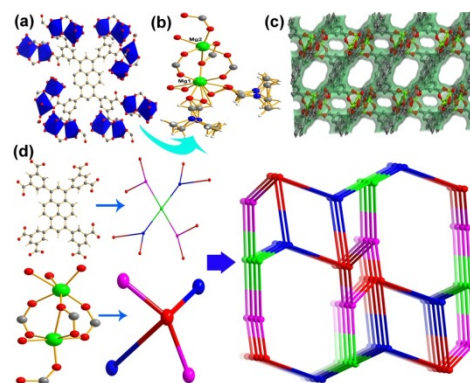


Figure 1. (a) the coordination style of the ligand. (b) the dinuclear Mg<sub>2</sub> cluster. (c) the 3D structure of **1**. (d) topology simplification strategy.

The similarity between the simulated and experimental powder X-ray diffraction (PXRD) confirmed the phase purity (Figure S5). TG analysis showed that **1** started to decompose around 400 °C and the weight loss before 350 °C could be mainly attributed to the isolated guest molecules in the channels and coordinated solvent molecules (Figure S2).

### Fluorescence Property and Sensing of Organic Solvent Molecules

As the pyrene is a strong fluorescent chromophore, the ligand and **1** are both luminescent. The maximum emission of the ligand is at about 540 nm, while the maximum emission of **1** is at about 490 nm (Figure S3). The blue fluorescence shift of **1** relative to the ligand might be caused by metal-to-ligand charge transfer (MLCT). In order to research the fluorescence of **1** further, we had soaked the same amount crystals of **1** in different common solvents (DMF, acetone, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, cyclohexane, toluene, pyridine and THF), treated with ultrasonication, and then aged to form stable emulsions prior to fluorescence measurements. As shown in Figure 3, the fluorescence intensity of **1** in DMF was obvious stronger which was almost twice than that in other solvents. The particular fluorescence

response to DMF was of significant interest in the sensing of DMF, which is very harmful to human health.

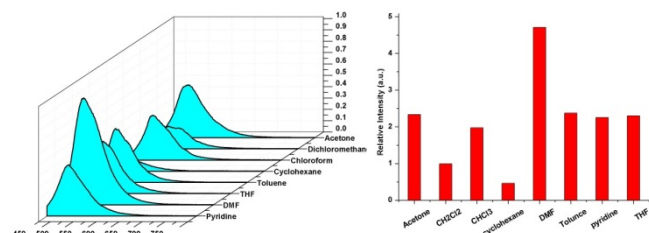


Figure 3. The fluorescence intensity of **1** in some common solvents (left) and their relative intensity.

### Sensing of Nitrobenzene

Nitrobenzene is a common solvent in organic synthesis, but it is extremely poisonous to human beings. **1** was highly luminescent and can easily sense nitrobenzene by a fluorescence quenching mechanism. 5 mg crystals of **1** were added to 3 ml DMF and sonicated for about 10 minutes to get a good disperse. And then different amounts of nitrobenzene were added to this suspension. The fluorescence intensities were recorded, respectively. As shown in Figure 4, when the concentration of the nitrobenzene was 80 ppm, the fluorescence began to have an obvious quenching, and when the concentration of nitrobenzene was about 800 ppm, the fluorescence was almost quenched completely. According to the Stern-Volmer equation:  $I_0/I = 1 + K_{SV}[M]$ , among which  $[M]$  means the concentration of the quenching agent, we got the Stern-Volmer curve of **1** and the  $I_0/I$  had an approximate linear relationship with the nitrobenzene. In addition, this MOF could be regenerated and reused for a significant number of cycles by centrifuging the dispersed solution after nitrobenzene detection and washing several times with fresh DMF. It is noteworthy that almost regaining the initial fluorescence intensity and high quenching efficiency over repeated cycles implied a high photostability of this material (Figure 5). The low detection level and good repeatability of the MOF made it promising for nitrobenzene detection application.

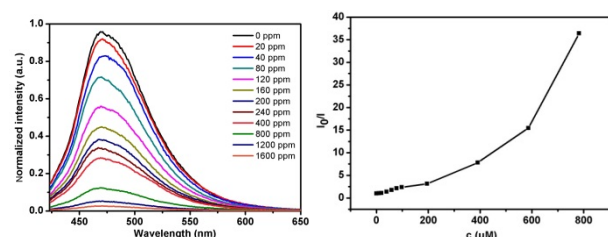


Figure 4. The normalized fluorescence intensities of **1** in DMF with different concentrations of nitrobenzene (left) and the Stern-Volmer curve (right).

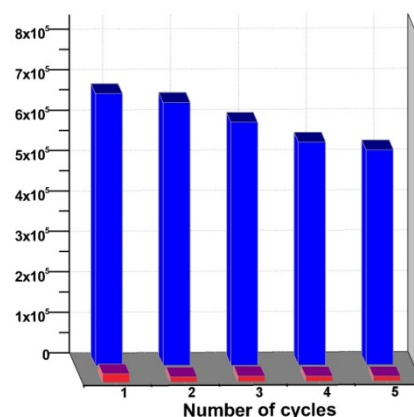


Figure 5. Reproducibility of the quenching ability of **1** dispersed in DMF to nitrobenzene solution.

### Conclusions

A strong fluorescent MgMOF has been synthesized constructed by a rare dendritic multicarboxylic ligand with a pyrenechromophore. The dispersed solution of **1** in DMF exhibits much stronger fluorescence emission in DMF than in other solvents. In addition, the fluorescence of **1** could be effectively quenched by nitrobenzene with a low concentration. Low detection level and good repeatability make this material very promising for explosives detection.

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### Notes and references

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† Electronic Supplementary Information (ESI) available: Supplementary figures, TG, fluorescence spectrum, UV adsorption spectrum. CCDC reference number 1023832. Crystallographic data can be found in CIF or other electronic format. See DOI: 10.1039/b000000x/.

- (a) M. O'Keeffe, M. A. Peskov, S. J. Ramsden, O. M. Yaghi, *Acc. Chem. Res.* 2008, **41**, 1782-1789. (b) L. Peng, J. L. Zhang, Z. M. Xue, B. X. Han, X. X. Sang, C. C. Liu, G. Y. Yang, *Nat. Commun.* 2014, **5**, 1678. (c) Q. L. Zhu, Q. Xu, *Chem. Soc. Rev.* 2014, **43**, 5468-5512.
- (a) P. J. Ma, Y. H. Li, L. Qin, G. H. Cui, *Bull. Korean Chem. Soc.* 2013, **34**, 3843-3846. (b) Z. J. Xiahou, Y. L. Wang, Q. Y. Liu, J. J. Wei, L. L. Chen, *Inorg. Chem. Commun.* 2013, **38**, 62-64.
- (a) Y. Cheng, H. Kajiro, H. Noguchi, A. Kondo, T. Ohba, Y. Hattori, K. Kaneko, H. Kanoh, *Langmuir* 2011, **27**, 6905-6909. (b) Q. Chen, Z. Chang, W. C. Song, H. Song, H. B. Song, T. L. Hu, X. H. Bu, *Angew. Chem.* 2013, **52**, 11550-11553.

- 4 (a) L. J. Murray, M. Dinca, J. R. Long, *Chem.Soc.Rev.* 2009, **38**, 1294-1314. (b) Z. Zhao, X. Ma, A. Kasik, Z. Li, Y. S. Lin, *Ind.Eng. Chem. Res.* 2013, **52**, 1102-1108. (c) S. Van der Perre, T. Van Assche, B. Bozbiyik, J. Lannoeye, D. E. De Vos, G. V. Baron, J. F. M. Denayer, *Langmuir* 2014, **30**, 8416-8424.
- 5 (a) Y. Yu, X. M. Zhang, J. P. Ma, Q. K. Liu, P. Wang, Y. B. Dong, *Chem.Comm.* 2014, **50**, 1444-1446. (b) X. M. Lin, G. M. Gao, L. Y. Zheng, Y. W. Chi, G. N. Chen, *Anal. Chem.* 2014, **86**, 1223-1228. (c) W. Zhu, C. Wang, W. N. Li, C. A. Tao, J. C. Cui, H. W. Yang, Y. Jiang, G. T. Li, *J. Mater. Chem. A* 2013, **1**, 11741-11747. (d) J. H. Wang, M. Li, D. Li, *Chem. Sci.* 2013, **4**, 1793-1801. (e) D. X. Ma, B. Y. Li, X. J. Zhou, Q. Zhou, K. Liu, G. Zeng, G. H. Li, Z. Shi, S. H. Feng, *Chem.Comm.* 2013, **49**, 8964-8966. (f) Y. Li, S. S. Zhang, D. T. Song, *Angew. Chem. Int. Ed.* 2013, **52**, 710-713.
- 6 (a) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem.Soc.Rev.* 2009, **38**, 1450-1459. (b) K. K. Tanabe, S. M. Cohen, *Inorg. Chem.* 2010, **49**, 6766-6774.
- 7 (a) M. D. Allendorf, C. A. Bauer, R. K. Bhakta, R. J. Houk, *Chem.Soc.Rev.* 2009, **38**, 1330-1352. (b) M. Kurmoo, *Chem.Soc.Rev.* 2009, **38**, 1353-1379.
- 8 W. Morris, W. E. Briley, E. Auyeung, M. D. Cabezas, C. A. Mirkin, *J. Am. Chem. Soc.* 2014, **136**, 7261-7264.
- 9 (a) B. Gole, A. K. Bar, P. S. Mukherjee, *Chem.Comm.* 2011, **47**, 12137-12139. (b) Y.C. He, H.M. Zhang, Y.Y. Liu, Q.Y. Zhai, Q.T. Shen, S.Y. Song, J.F. Ma, *Cryst. Growth Des.* 2014, **14**, 3174-3178.
- 10 K. C. Stylianou, R. Heck, S. Y. Chong, J. Bacsá, J. T. A. Jones, Y. Z. Khimyak, D. Bradshaw, M. J. Rosseinsky, *J. Am. Chem. Soc.* 2010, **132**, 4119-4130.
- 11 (a) K. C. Stylianou, J. Rabone, S. Y. Chong, R. Heck, J. Armstrong, P. V. Wiper, K. E. Jelfs, S. Zlatogorsky, J. Bacsá, A. G. McLennan, C. P. Ireland, Y. Z. Khimyak, K. M. Thomas, D. Bradshaw, M. J. Rosseinsky, *J. Am. Chem. Soc.* 2012, **134**, 20466-20478. (b) J. E. Mondloch, W. Bury, D. Fairen-Jimenez, S. Kwon, E. J. DeMarco, M. H. Weston, A. A. Sarjeant, S. T. Nguyen, P. C. Stair, R. Q. Snurr, O. K. Farha, J. T. Hupp, *J. Am. Chem. Soc.* 2013, **135**, 10294-10297. (c) P. Deria, J. E. Mondloch, E. Tylianakis, P. Ghosh, W. Bury, R. Q. Snurr, J. T. Hupp, O. K. Farha, *J. Am. Chem. Soc.* 2013, **135**, 16801-16804. (d) C. W. Kung, T. C. Wang, J. E. Mondloch, D. Fairen-Jimenez, D. M. Gardner, W. Bury, J. M. Klingsporn, J. C. Barnes, R. Van Duyne, J. F. Stoddart, M. R. Wasielewski, O. K. Farha, J. T. Hupp, *Chem. Mater.* 2013, **25**, 5012-5017. (e) P. Deria, W. Bury, J. T. Hupp, O. K. Farha, *Chem.Comm.* 2014, **50**, 1965-1968.
- 12 N. Zhao, F. Sun, H. He, J. Jia, G. Zhu, *Cryst. Growth Des.* 2014, **14**, 1738-1743.
- 13 (a) V. A. Blatov, *Struct. Chem.* 2012, **23**, 955-963. (b) E. V. Alexandrov, V. A. Blatov, A. V. Kochetkov, D. M. Proserpio, *CrystEngComm*, 2011, **13**, 3947-3958.