RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Luminescent sensing from a new Zn(II) metal-organic framework

Jian-Qiang Liu[a*], Jian Wu[b], Fu-Mei Li[a], Wei-Cong Liu[a], Bao-Hong Li[a], Jun Wang[c], Qin-Ling Li[a], Reena Yadav[d] and Abhinav Kumar[d*]

[a]*School of Pharmacy, Guangdong Medical University, Dongguan, 523808, P. R. China and Guangdong Key Laboratory for Research and Development of Natural Drugs, Guangdong Medical University, P. R. China*

[b]*Guangxi Key Laboratory of Chemistry and Engineering of Forest Products, Guangxi University for Nationalities, College of Chemistry and Chemical Engineering, Nanning, Guangxi 530006, China*

[c]*School of Chemistry and Pharmaceutical Engineering, Sichuan University of Science & Engineering, Zigong 643000, PR China*

[d]*Department of Chemistry, Faculty of Science, University of Lucknow, Lucknow 226 007,India*

Corresponding Authors: jianqiangliu2010@126.com and kumar_abhinav@lkouniv.ac.in, Tel/Fax: 86-769-22896560

Abstract

_____

A new metal–organic framework having formula $(NH_2(CH_3)_2[Zn_2(OAc)(L)]\cdot 0.5DMF$ (H_4L =2,5-di(3',5'-dicarboxylphenyl)pyridine) (**GDMU-3**) have been synthesized and characterized. The net of **GDMU-3** is uninodal and is closely related to the **lvt** net, which has the same Schläfli symbol of $4^2.8^4$. The **GDMU-3** displays selective properties in detection of nitrobenzene and Fe^{3+} ion. Remarkably, **GDMU-3** exhibits an excellent capability to adsorb methylene blue (MB) with high selectivity. The present work indicates that the **GDMU-3** could be taken as a potential candidate for developing novel luminescence sensors for the selective sensing of nitrobenzene which can be deployed in explosives, Fe^{3+} and organic dyes.

Introduction

The luminescent properties of metal–organic frameworks (MOFs) have attracted considerable attention for some time, naturally, these properties of luminescent MOFs (LMOFs) can potentially be used for real-world applications.[1-3] Recently, chemical sensors for fast and highly selective detection of high explosives and heavy metal ions have attracted increasing attention concerning environmental and humanitarian implications.[4-8] The advantages and challenges of LMOF based luminescent sensors

1

1 are well summarized by several previous review articles.[9-10] In principle, the

2 spectroscopic characteristics of LMOFs can potentially be used as a sensing signal.[11]

3 Out of the several spectroscopic characteristics the change in intensity of the

4 fluorescecent emission is the most commonly observed change.[11] It has been also

5 speculated that the electronic nature of the molecule may affect the electron transfer

6 or energy transfer between the guest molecules and the LMOFs.[13-15] The metal ions,

7 such as Mn^{2+}, Fe^{3+}, and Cu^{2+}, are also capable of quenching fluorescence since they

8 can induce ligand-metal charge transfer and relax the excitation energy through a

9 non-radiative pathway.[16-19] However, it is a significant and challenging task to

10 synthesize new materials for fluorescence detection of toxic solvents and heavy metal

11 ions.[20]

12 The selection of ligand plays a crucial role in design and construction of the stable

13 LMOFs for fluorescence detection.[21] We had selected

14 2,5-di(3',5'-dicarboxylphenyl)pyridine (H_4L) and Zn(II) to synthesize MOFs for

15 detection of explosives and heavy metal ions. The choice of the ligand and Zn(II)

16 stems because of the following reasons:[22-24] 1) Numerous explosives are comprising

17 of good electron acceptors having electron deficient -NO_2 groups, which are the

18 common chemical constituents of commercial explosives. 2) H_4L is a rigid

19 dicarboxylate ligand with aromatic rings and nitrogen atoms with lone-pair electrons,

20 so this N atom as a functional site is predicted to recognize metal ions. 3) In addition,

21 d^{10} metal ions, usually show high complexation affinity to carboxylate and do not

22 interfere with fluorescence, because they can display varied coordination numbers and

23 geometries, and exhibit outstanding luminescent properties.[24]

24 With these view-points herein, we report a new MOF of **GDMU-3** that exhibit a 3D

25 net with Schläfli symbol of $4^2.8^4$. The luminescence property investigations of

26 **GDMU-3** emulsions in different solvents and its selective sensing of Fe^{3+} ions and

27 MB are also demonstrated. Also, the efforts have been made to address the quenching

28 mechanism for nitrobenzene detection.

29 **Materials and Method**

30 All chemicals were purchased from Jinan Henghua Sci. & Tec. Co. Ltd. without

1   further purification. Powder X-ray diffraction (PXRD) was collected on a Bruker D8

2   ADVANCE X-ray diffractometer with Cu-Kα radiation (λ=1.5418 Å) at 50 kV, 20

3   mA with a scanning rate of 6°/min and a step size of 0.02°. The simulated powder

4   patterns were calculated using Mercury 2.0. The purity and homogeneity of the bulk

5   products were determined by comparison of the simulated and experimental X-ray

6   powder diffraction patterns. Fourier transform infrared (FT-IR) spectra were

7   measured using a Nicolet Impact 750 FTIR spectrometer in the range of 400-4000

8   cm^{-1} and KBr pellet samples. Thermogravimetric analysis was performed under air

9   atmosphere from room temperature to 800 °C at a heating rate of 10 °C min^{-1}, using a

10   SDT Q600 thermogravimetric analyzer. Energy dispersive X-ray spectroscopy (EDS)

11   data were obtained on a Philips XL-30 scanning electron microscope.

12   **X-ray Crystallography**

13   Room-temperature single crystal X-ray diffraction data collection were

14   carried out on a Bruker SMART APEX diffractometer that was equipped with a

15   graphite monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å) by using an ω-scan

16   technique. The intensities were corrected absorption effects by using SADABS.

17   The structures were solved by using *SHELXL2014*.[25] Absorption corrections

18   were applied by using multi- Non-hydrogen atoms were refined anisotropically.

19   For **GDMU-3**, the unit cell exhibits large regions that are occupied by solvent

20   molecules; the solvent molecules could not be modeled. The SQUEEZE option

21   in *PLATON*[26] was used to produce a set of solvent-free diffraction intensities.

22   The nature and number of solvent molecules were established from CHN

23   elemental analyses and thermogravimetric analyses. Crystallographic details

24   and selected bond dimensions for **GDMU-3** are listed in Tables 1 and 2. **CCDC**

25   number: 1437346.

26   **Synthesis of $(NH_2(CH_3)_2)[Zn_2(OAc)(L)]\cdot0.5DMF$ (GDMU-3)**

27   A mixture of $Zn(OAc)_2\cdot2H_2O$ (0.220 g), H_4L (0.018 g) and DMF (4 mL) in a

28   screw-capped vial. After two drops of HNO_3 (63%, aq.) was added into the mixture.

29   The vial was capped and placed in an oven at 105 °C for 3 days. The resulting

30   colorless single crystals obtained were washed with absolute CH_3CH_2OH three times

1   to get **GDMU-3**. Anal. Calcd for $C_{26.5}H_{24.5}N_{2.5}O_{10.5}Zn_2$, C, 47.03; H, 3.65; N, 5.17.

2   Found C, 47.22.; H, 3.52; N, 5.20. IR (KBr, cm^{-1}) : 3402 (vs); 2918 (m); 1621 (vs);

3   1560 (v); 1415 (v); 1226 (m); 1042 (m); 720 (v); 530 (m). ^{13}C NMR (126 MHz,

4   DMSO-d_6) δ 166.33 (-COOH), 166.28(-COO$^-$), 153.12(-C_7), 147.23(-C_{11}),

5   138.14(-C_{13}), 137.32(-$C_{4,3,2}$), 136.98(-$C_{14,18}$), 133.79(-C_9), 132.34(-C_{10}),

6   132.09(-$C_{14,18}$), 131.60(-$C_{1,5}$), 131.35(-$C_{15,17}$), 130.68(-C_{16}), 129.69(-C_6), 121.42(-C_8),

7   40.02(DMSO), 39.95(-CH_3-N), 39.85(DMSO), 39.78(-CH_3- COO$^-$), 39.69(DMSO),

8   39.52(DMSO), 39.35(DMSO), 39.19(DMSO), 39.02(DMSO).

9   **Results and discussion**

10   The structure of **GDMU-3** contains Zn_2 units in which the two metals are

11   connected by carboxylates from two L ligands and a bridging acetate ligand (Fig. 1a).

12   The tetrahedral geometry of each Zn(II) is then completed by L carboxylate in

13   momnodentate manner, indicating that each dinuclear complex is coordinated by four

14   different L ligands. Each L is, in turn, coordinated to four clusters, meaning that both

15   the clusters and the ligands act as 4-connecting nodes. Such connectivity modes give

16   rise to a 3D structure packed along the *ab*-plane (Fig.1b). The overall 4-connected net

17   is shown in Figure 1c. The net is uninodal and is closely related to the **lvt** net,[27] which

18   has the same Schläfli symbol of $4^2.8^4$. Both nets contains channels of eclipsed

19   4-membered rings which share edges with helical channels. The **lvt** net is non-centric

20   and channels on opposite sides of the 4-membered rings have the same handedness

21   (those on adjoining sides have the opposite handedness). The net defined by

22   **GDMU-3** is centrosymmetric and thus those on opposite sides of the 4-membered

23   ring are of opposite handedness, while each side adjoins one of the same handedness

24   and one of the opposite handedness. There exist two types of pores having dimensions

25   5.8 ×3.8 Å along the *b* axis and 10.2 ×20.5 Å along the *c* axis, respectively. These

26   pores are filled with the terminal acetate, dimethylammonium and DMF molecules

27   (Fig. S1). As a consequence, the solvent-accessible voids, as calculated by using

28   PLATON[26] for **GDMU-3** without the contribution of disordered DMF and

29   dimethylammonium, amounts to a volume of 2026.3 $Å^3$ and represent 44.7% of the

30   total volume of the structure. More importantly, the dimethylammonium anions are

1   derived from the decomposition of DMF molecules and were used to balance the full

2   charge of **GDMU-3**. It was also confirmed by the ^{13}C NMR. As shown in Figure S2.

3   **Thermogravimetric Analysis**

4   The thermogravimetric analysis (TGA) of **GDMU-3** indicated two weight loss

5   steps (Fig. S3). The first weight loss begins at 25°C and is completed at 127°C. The

6   observed weight loss of 4.6% corresponds to the loss of the free DMF molecules

7   (calcd 5.3%). The second weight loss can be attributed to the elimination of

8    $[NH_2(CH_3)_2]^+$ cations and organic ligands. The final residual mass of 25.8% is

9   roughly consistent with the formation of ZnO (calcd 24.1%).

10   **Photoluminescence Measurements**

11   Since the **GDMU-3** is assembled by the luminescent rigid ligand and the Zn^{II} center

12   having configuration d^{10},[28] it shows strong luminescence with emission peaks at 428

13   nm (λ_{ex}=320 nm). This emission band can be assigned to H$_4$L ligand-centered

14   emission, because the emission for the free H$_4$L was observed at 375 nm (λ_{ex}=312 nm)

15   (Figure S4). The enhancement in the emission intensity of **GDMU-3** may arise from

16   the aggregation induced emission, where the coordination of the ligand and the metal

17   ions can reduce the freedom of the ligands and their non-radiative transitions.[29-30] This

18   interaction shifts the energy levels for H$_4$L, as confirmed by the UV-Vis-NIR

19   absorption spectrum for **GDMU-3** (Fig. S5).

20   In addition, the fluorescence properties of **GDMU-3** in different solvent emulsions

21   were investigated (Figure 2). It has been reported that the photoluminescence (PL)

22   intensities are largely dependent on the solvent molecules, particularly in the case of

23   nitrobenzene (NB),[31-35] which exhibits significant quenching behavior. The physical

24   interaction of the solute and solvent plays pivotal role in such fluorescence behavior.

25   To explore the sensing sensitivity of **GDMU-3** towards NB in more detail, the

26   suspensions of **GDMU-3** with gradually increasing concentration of NB in DMF were

27   prepared to monitor the emissive response (Figure 3). The finely grounded powder of

28   **GDMU-3** was dispersed in the solution (Fig. S3). This enables NB to be closely

29   adhered to the surface of the MOF particles and facilitates possible host–guest

30   interactions as a result electron transfer from the electron-donating framework to the

5

1 highly electron-deficient NB molecule can take place upon excitation, resulting in

2 fluorescence quenching.[36-37] The luminescence intensity decreased to 50% at 75 ppm,

3 and complete quenching was observed at 175 ppm. The emission in nitrobenzene

4 exhibited the quenching effect. The observed quenching may be due to an inner filter

5 effect as NB can absorb the excitation light. On the other hand, the $-NO_2$ group

6 attached to the aromatic ring makes it electron deficient in nature.[38-40] Amongst the

7 different solvents used in the investigation, NB shows a strong absorbing range from

8 260 to 410 nm, while other solvents have no significant absorption band in this range.

9 As shown in Fig. S11, the strong absorption band of L is located at ~260 nm, which is

10 largely overlapped by the electronic absorption band of NB. Upon excitation, there

11 may be a competition of the absorption of the light source energy between NB and L.

12 Combined with the electronic absorption and luminescent spectra, it may be suggested

13 that the energy absorbed by the L is transferred to the NB molecules, thereby resulting

14 in the decrease in luminescence intensity, even quenching, of **GDMU-3**. The

15 quenching mechanism is in agreement with that of the previously proposed

16 reports.[32,40]

17 The luminescence spectra of **GDMU-3** dispersed in DMF solutions (3 mL) of metal

18 ions are also studied (Fig 4). Fig. 4a indicates that metal ions with saturated electron

19 configurations doesn't lead to a significant change in the luminescent intensity; in

20 contrast, the other metal cations, especially Fe^{3+},[41] can bring essentially complete

21 quenching of the emission intensity. These results demonstrate that compound

22 **GDMU-3** can be highly effective and selective luminescent sensors for Fe^{3+} ions. As

23 illustrated in Fig. 4b, the luminescence intensity of **GDMU-3** is almost completely

24 quenched at a $Fe(NO_3)_3$ concentration of 10^{-2} M. According to the Stern–Volmer

25 equation: $I_0/I = 1 + K_{sv}[M]$,[42] the quenching coefficient K_{sv} of 4926 M^{-1} is obtained

26 from the luminescent data. The decreases in intensity caused by Fe^{3+} ions induces

27 LMCT and provide a non-radiative pathway for the excitation energy to come to the

28 ground state. As reported by Zheng,[43] Fe^{3+} shows strong absorption from 320 nm to

29 400 nm, which exhibit a wide overlap with the emission spectra of **GDMU-3**,

30 indicating the existence of energy transfer. As confirmed by the powder X-ray

6

1　　diffraction patterns (see Fig. S6), the crystal structures of **GDMU-3** immersed in

2　　metal ion solutions remain unchanged. The framework integrity of the

3　　metal-incorporated **GDMU-3** samples was confirmed by PXRD patterns (Fig. S6) and

4　　Energy Dispersive X-ray spectra (EDS) on **GDMU-3**-Fe^{3+} indicated that the sample

5　　has a Fe: Zn ratio of 0.5 (Fig. S7). We speculate that the recognition of Fe^{3+} ions

6　　might be related to the interaction between the Fe^{3+} ions and the N atoms of pyridyl

7　　rings in **GDMU-3**. These observations are similar to previously reported MOFs.[19,23]

8　　To elucidate the possible mechanism for such luminescence quenching by metal

9　　cations, N1s X-ray photoelectron spectroscopy (XPS) studies were carried out on

10　**GDMU-3** and **GDMU-3**@Fe^{3+}. The N1s peak from free pyridyl nitrogen atoms at

11　401.6 eV in **GDMU-3** is shifted to 402.4 eV on the addition of Fe^{3+} (Figure S8),

12　indicating the weak binding of pyridyl nitrogen atoms to Fe^{3+} in **GDMU-3**@Fe^{3+}.

13　　The removal of dyes from effluents before discharge into natural bodies is

14　extremely important from an environmental point of view.[44] To investigate whether

15　compound **GDMU-3** has the ability to adsorb dye molecules, we used it to capture

16　dyes from DMF solutions. Dye molecules with different charges (see Figure S9) were

17　selected. The samples of **GDMU-3** were soaked in DMF solutions containing two

18　dyes of the methylene blue (MB) and solvent yellow 2. It was observed that the

19　methylene blue (MB) dye molecules could be efficiently adsorbed over a period of

20　time (2h) and the colorless crystals of **GDMU-3** gradually became colored, while the

21　solvent yellow 2 could not be incorporated efficiently (Fig. 5). The capability of

22　**GDMU-3** to adsorb dyes from DMF solution was evaluated through UV/Vis

23　spectroscopy. Spectroscopic investigations of the supernatants showed that **GDMU-3**

24　can effectively incorporate cationic dyes into their networks, whereas neutral dyes

25　were left in the supernatants. The absorptivity of **GDMU-3** is 0.35 mg/g for

26　methylene blue and is 0.08 mg/g for solvent yellow 2. The selectivity of **GDMU-3** for

27　dyes could be attributed to the anionic framework, in which the $[(CH_3)_2NH_2]^+$ cations

28　can be exchanged with cationic dyes. Preliminary investigations suggest that

29　**GDMU-3** may have potential application in removal of dyes from effluents.[44-46] To

30　confirm that selective absorption is due to ionic interaction of dye with the anionic

7

framework, dye releasing experiment was performed in DMF and a saturated solution of NaCl in DMF measured by UV/Vis spectroscopy. This showed that, under the action of NaCl, the dye MB molecules in **GDMU-3** can be gradually released (see Figure S10), while in DMF without NaCl the dye molecules are hardly released. Hence, we can safely conclude that selective absorption is due to ionic interaction of dyes with the anionic framework.[47-50]

Summary and Conclusions

In summary, a new net of **GDMU-3** is uninodal and is closely related to the **lvt** net. The compound is a potential candidate for developing novel luminescence sensors for the selective sensing of nitrobenzene which can be deployed in explosives, Fe^{3+} and organic dyes. These remarkable preliminary results provides us impetus to develop new metal–organic framework materials which finds important and multifarious application for selective adsorption of cations and dyes and there separation.

Acknowledgments

References:

1. S. R. Zhang, D. Y. Du, J. S. Qin, S. J. Bao, S. L. Li, W. W. He, Y. Q. Lan, P. Shen and Z. M. Su, *Chem. Eur. J.* 2014, **20**, 3589.

2. Z. C. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.,* 2014, **43**, 5815.

3. D. Zacher, O. Shekhah, C. Woll and R. A. Fischer, *Chem. Soc. Rev.*, 2009, **38**, 1418.

4. O. Shekhah, J. Liu, R. A. Fischer and C. Woll, *Chem. Soc. Rev.*, 2011, **40**, 1081.

5. Y. Q. Xiao, Y. Cui, Q. Zheng, S. C. Xiang, G. D. Qian, B. L. Chen, *Chem. Commun.*, 2010, **46**, 5503.

6. B. Chen, L. B. Wang, Y. Q. Xiao, F. R. Fronczek, M. Xue, Y. J. Cui and G. D. Qian, *Angew.*

1   *Chem., Int. Ed*., 2009, **48**, 500.

2   7. S. W. Thomas, G. D. Joly and T. M. Swager, *Chem. Rev*., 2007, **107**, 1339.

3   8. A. Lan, K. Li, H. Wu, D. H. Olson, T. J. Emge, W. Ki, M. Hong and J. Li, *Angew. Chem., Int.*

4   *Ed*., 2009, **48**, 2334.

5   9. Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev*., 2012, **112**, 1126.

6   10. L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem.*

7   *Rev*., 2012, **112**, 1105.

8   11. J. He, M. Zha, J. Cui, M. Zeller, A. D. Hunter, S.-M. Yiu, S.-T. Lee and Z. Xu, J.

9   Am. Chem. Soc., 2013, 135, 7807–7810.

10   12. Q. Tang, S. Liu, Y. Liu, J. Miao, S. Li, L. Zhang, Z. Shi and Z. Zheng, *Inorg. Chem*., 2013, **52**,

11   2799.

12   13. S. Yoon, E. W. Miller, Q. He, P. H. Do and C. J. Chang. *Angew. Chem. Int. Ed.*

13   2007, **46**, 6658.

14   14. G. G. Shan, H. B. Li, H. Z. Sun, D. X. Zhu, H. T. Cao and Z. M. Su, *J. Mater. Chem. C* 2013,

15   **1**, 1440.

16   15. P. Wu, J. Wang, C. He, X. Zhang, Y. Wang, T. Liu and C. Duan, *Adv. Funct. Mater*., 2012, **22**,

17   1698.

18   16. S. R. Zhang, D. Y. Du, K. Tan, J. S. Qin, H. Q. Dong, S. L. Li, W. W. He, Y. Q. Lan, P. Shen

19   and Z. M. Su, *Chem. Eur. J.* 2013, **19**, 11279.

20   17. K. Jayaramulu, R. P. Narayanan, S. J. George and T. K. Maji, *Inorg. Chem*., 2012, **51**, 10089.

21   18. J.X. Ma, X.F. Huang, X.Q. Song and W.S. Liu, *Chem.–Eur. J.*, 2013, **19**, 3590.

22   19. J. C. Jin, L. Y. Pang, G. P. Yang, L. Hou and Y. Y. Wang, *Dalton Trans*., 2015, **44**, 17222.

23   20. Y. Salinas, R. Martinez-Manez, M. D. Marcos, F. Sancenon, A. M. Castero, M. Parra, S. Gil,

24   *Chem. Soc. Rev*., 2012, **41**, 1261.

25   21. J. X. Ma, X. F. Huang, X. Q. Song and W. S. Liu, *Chem. –Eur. J.*, 2013, **19**, 3590.

26   22. S. Pramanik, C. Zheng, X. Zhang, T. J. Emge, J. Li, *J. Am. Chem. Soc*., 2011, **133**, 4153.

27   23. B. Liu, W. P. Wu, L. Hou and Y. Y. Wang, *Chem. Commun.*, 2014, **50**, 8731.

28   24. F. Y. Yi, W. T. Yang, Z. M. Sun, *J. Mater. Chem*. 2012, **22**, 23201.

29   25. G.M. Sheldrick,. *Acta Cryst.* 2008, A64, 112.

30   26. A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

31   27. M. O'Keeffe, M.A. Peskov, S. Ramsden and O.M. Yaghi, *Acc. Chem. Res.* 2008, **41**, 1782

32   28. M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, Chem. Soc. Rev., 2009, **38**,

33   1330.

34   29. P. Alama, G. Kaurb, C. Climentc, S. Pashaa, D. Casanovad, P. Alemanyc, A. R. Choudhuryb

35   and I. R. Laskar, *Dalton Trans*., 2014, **43**, 16431.

36   30. A. Singh, T. Raj, T. Aree and N. Singh, *Inorg. Chem*., 2013, **52**, 13830.

37   31. K. Jayaramulu, R. P. Narayanan, S. J. George and T. K. Maji, *Inorg. Chem*., 2012, **51**, 10089.

38   32. Z.M. Hao, X. Z. Song, M. Zhu, X. Meng, S. N. Zhao, S. Q. Su, W. T. Yang, S. Y. Song and H.

39   J. Zhang, *J. Mater . Chem. A*., 2013, **1**, 11043.

40   33. W. Liu, T. Jiao, Y. Li, Q. Liu, M. Tan, H. Wang and L. Wang, *J. Am. Chem. Soc*., 2004, **126**,

41   2280.

42   34. L. E. Kreno, M. Allendorf and J. T. Hupp, *Chem. Rev*., 2012, **112**, 1105.

43   35. Z. Y. Guo, H. Xu, S. Q. Su, J. F. Cai, S. Dang, S. C. Xiang, G. D. Qian, H. J. Zhang, M.

44   O'Keeffe and B. L. Chen, *Chem. Commun*., 2011, **47**, 5551.

1   36. J. X. Ma, X. F. Huang, X. Q. Song and W. S. Liu, *Chem. –Eur. J.*, 2013, **19**, 3590.

2   37. S. Horike, S. Bureekaew and S. Kitagawa, *Chem. Commun.*, 2008, 471.

3   38. G. Y. Wang, C. Song, D. M. Kong, W. J. Ruan, Z. Chang and Y. J. Li, *J. Mater. Chem. A.*,

4   2014, **2**, 2213.

5   39. H. Wang, W. Yang and Z. M. Sun, *Chem.-Asian J.* 2013, **8**, 982.

6   40. (a) B. Gole, A. K. Bar and P. S. Mukherjee, *Chem. Commun.* 2011, **47**, 12137; (b) S. Dang, E.

7   Ma, Z. S. Sun and H. J. Zhang, *J. Mater. Chem.*, 2012, **22**, 16920; (c) W. T. Yang, J. Feng and H.

8   J. Zhang, *J. Mater. Chem.*, 2012, **22**, 6819; (d) W. T. Yang, J. Feng, S. Y. Song and H. J. Zhang,

9   *ChemPhysChem*, 2012, **13**, 2734; (e) Y. Q. Xiao, L. B. Wang, Y. J. Cui, B. L. Chen, F. Zapata and

10   G. D. Qian, *J. Alloys Compd.*, 2009, **484**, 601.

11   41. Q. R. Fang, D. Q. Yuan, J. L. Sculley, J. R. Li, Z. B. Han and H. C. Zhou, *Inorg. Chem.*, 2010,

12   **49**, 11637.

13   42. S. C. Xiang, Y. B. He, Z. J. Zhang, H. Wu, W. Zhou, R. Krishna and B. L. Chen, *Nat.*

14   *Commun.*, 2012, **3**, 954.

15   43. Q. Tang, S. X. Liu, Y. W. Liu, J. Miao, S. J. Li, L. Zhang, Z. Shi and Z. P. Zheng, *Inorg.*

16   *Chem.*, 2013, **52**, 2799.

17   44. C. Y. Sun, X. L. Wang, C. Qin, J. L. Jin, Z. M. Su, P. Huang and K. Z. Shao, *Chem. Eur. J.*

18   2013, **19**, 3639.

19   45. B. Adhikari, G. Palui and A. Banerjee, *Soft Matter.*, 2009, **5**, 3452.

20   46. J. T. Jia, F. X. Sun, T. Borjigin, H. Ren, T. T. Zhang, Z. Bian, L. X. Gao and G. S. Zhu, *Chem.*

21   *Commun.* 2012, **48**, 6010.

22   47. F. Pu, X. Liu, B. L. Xu, J. S. Ren and X. G. Qu, *Chem. Eur. J.* 2012, **18**, 4322.

23   48. H. L. Jiang, Y. Tatsu, Z. H. Lu and Q. Xu, *J. Am. Chem. Soc.* 2010, **132**, 5586.

24   49. J. A. Greathouse, N. W. Ockwig, L. J. Criscenti, T. R. Guilinger, P. Pohl and M. D. Allendorf,

25   *Phys. Chem. Chem. Phys.* 2010, **12**, 12621.

26   50. C. M. Doherty, Y. Gao, B. Marmiroli, H. Amenitsch, F. Lisi, L. Malfatti, K. Okada, M.

27   Takahashi, A. J. Hill, P. Innocenzi and P. Falcaro, *J. Mater. Chem.* 2012, **22**, 16191.

28

29

30

31

32

33

34

35

36

37

38

39

40

41

42
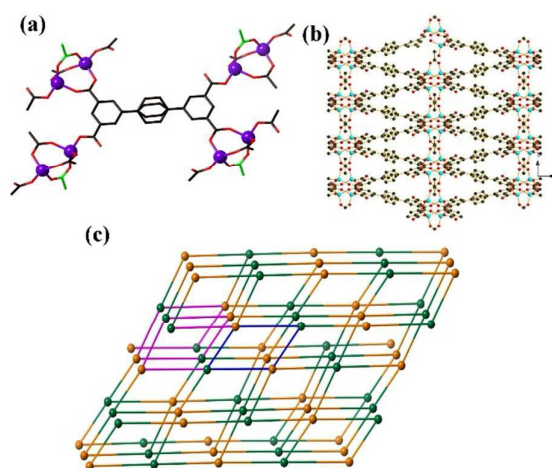
43   **Figure 1**   (a) Local coordination geometries of the ligands and Zn_2 clusters in the structure of

44   **GDMU-3**. The central ring of the L ligand is disordered over two positions, and the acetate ligand

of the cluster is highlighted in green (all other carboxylates belong to L ligands); (b) view of the 3D net along the ab-plane and (c) The underlying $4^2.8^4$ net in the structure of **GDMU-3**. Green nodes represent the 4-connecting ligands, while orange nodes represent the 4-connected Zn_2 clusters. A 4-membered ring is highlighted in blue, while an adjoining helical channel is highlighted in pink.
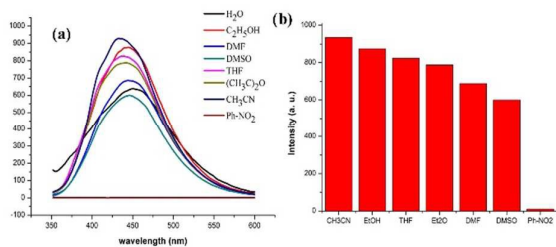

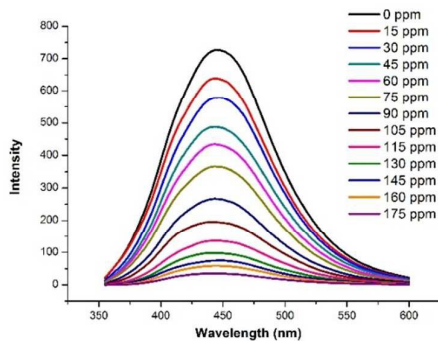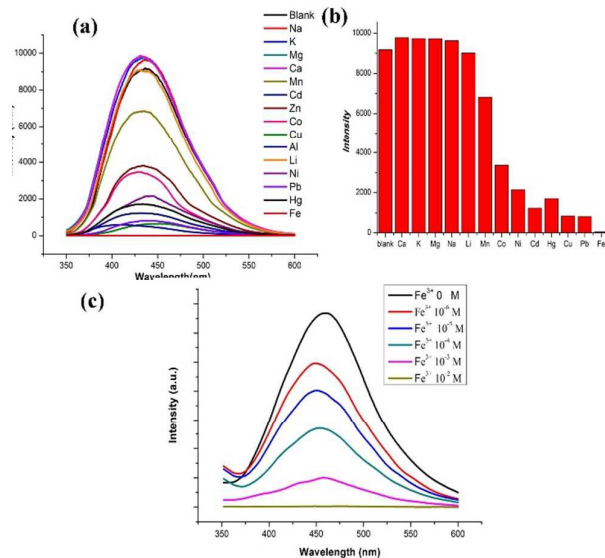Figure 2. (a) Emission spectra of **GDM-3** at different solvents. (b) Emission intensity at different solvents (λ_{ex} =320 nm).

Figure 3. Emission spectra of **GDMU-3** at different nitrobenzene concentrations (λ_{ex} =320 nm).

1   Fig. 4 (a) Emission spectra of **GDM-3** at different metal ions. (b) Emission intensity at different

2   metal ions; and (c) Emission spectra of **GDM-3** at different Fe^{3+} ions concertation (λ_{ex} =320 nm).
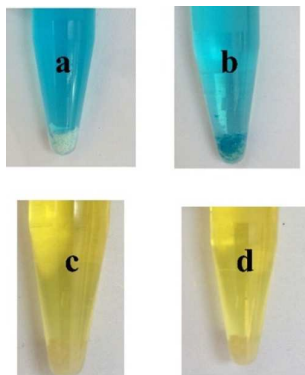
3

4   Fig. 5. Dye-selective adsorption of **GDMU-3**. Photographs of dye solutions before (a, c) and after

5   (b, d) interacting with materials.

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

31

32

33

34

1
2
3

4   **Table 1.** Crystal data and structure refinement information for compound **GDMU-3**

5

Formula weight	1033
Crystal system	Monoclinic
Space group	*C2/c*
Crystal color	colorless
a, Å	33.109(2)
b, Å	7.9520(5)
c, Å	18.4662(12)
β,^{o}	111.0306(10)
V, Å^3	4538.0(5)
Z	4
ρ_{calcd}, g/cm^3	1.416
μ, mm^{-1}	0.991
F(000)	1380
θ Range, deg	2.25-25.98
Reflection collected	11624
Independent reflections (R_{int})	0.0555
Reflections with $I > 2\sigma(I)$	4432
R_1, wR_2 ($I > 2\sigma(I)$)[*]	0.0348, 0.0934
R_1, wR_2 (all data)[**]	0.0451, 0.0981

6   * $R = \sum(F_o - F_c)/\sum(F_o)$, ** $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum(F_o^2)^2\}^{1/2}$.

7
8
9
10
11
12
13
14

Table 2. Selected bond distances (Å) and angles (deg) of structure **GDMU-3**

GDMU-3			
Zn1- O3	1.938(2)	Zn1-O2	1.961(2)
Zn1-O5	1.963(2)	Zn1-O1	1.988(2)
O3 -Zn1-O2	115.17(8)	O3- Zn1- O5	112.50(9)
O2- Zn1- O5	112.19(9)	O3- Zn1- O1	95.04(7)
O2 -Zn1- O1	111.43(8)	O5 -Zn1- O1	109.20(9)

14

Luminescent sensing from a new Zn(II) metal-organic framework

Jian-Qiang Liu[a*], Jian Wu[b], Fu-Mei Li[a], Wei-Cong Liu[a], Bao-Hong Li[a], Jun Wang[c], Qin-Ling Li[a], Reena Yadav[d] and Abhinav Kumar[d*]

The title compound is a potential candidate for developing novel luminescence sensors for the selective sensing of nitrobenzene which can be deployed in explosives, Fe^{3+} and organic dyes.