Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Journal of
Materials Chemistry A

Materials for energy and sustainability
www.rsc.org/materialsA

Li⁺

ROYAL SOCIETY
OF CHEMISTRY

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/materialsA

TOC

A magnesium MOF as highly selective fluorescence sensor for CS$_2$ and nitroaromatic compounds

Zhao-Feng. Wu,[a,b] Bin Tan,[a,b] Mei-Ling Feng,[a] An-Jian Lan[a,]* and Xiao-Ying Huang[a,]*
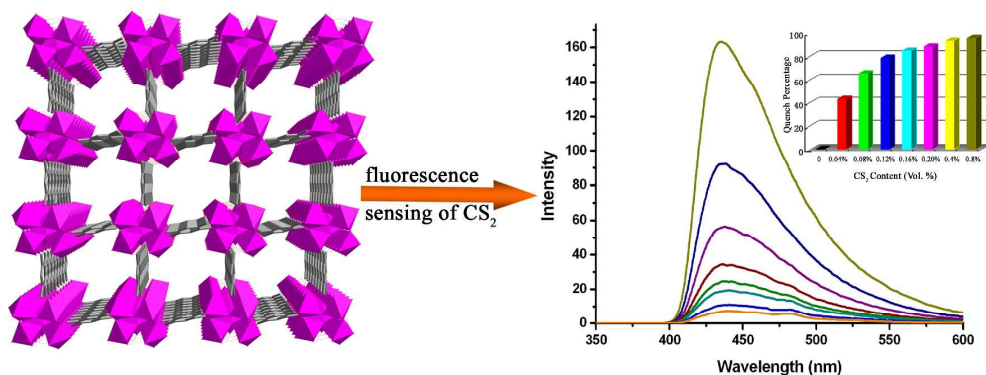
A magnesium MOF, namely Mg$_5$(OH)$_2$(BTEC)$_2$(H$_2$O)$_4$·11H$_2$O (**1**) (H$_4$BTEC = pyromellitic acid), has been synthesized and characterized, which reveals a highly selective fluorescence sensing for CS$_2$ and nitroaromatic compounds.

PAPER

A magnesium MOF as sensitive fluorescence sensor for CS$_2$ and nitroaromatic compounds

Zhao-Feng Wu,[a,b] **Bin Tan,**[a,b] **Mei-Ling Feng,**[a] **An-Jian Lan***[a] **and Xiao-Ying Huang***[a]

Presented here are the hydrothermal synthesis, structural characterization, and luminescent and gas adsorption properties of a magnesium metal-organic framework compound, namely Mg$_5$(OH)$_2$(BTEC)$_2$(H$_2$O)$_4$·11H$_2$O (**1**, H$_4$BTEC = 1,2,4,5-Benzenetetracarboxylic acid). The structure of **1** features a three-dimensional network constructed from the linkage of BTEC ligands and rare 10 pentanuclear magnesium clusters as secondary building units, giving rise to the 1D channels along the *a* axis. Luminescence studies revealed that compound **1** demonstrated high fluorescence sensing for carbon disulfide (CS$_2$) and nitroaromatic compounds, that is, the fluorescence intensities were almost completely quenched only at the concentrations of 0.8 vol% of CS$_2$ and 0.04 vol% of nitrobenzene.

Introduction

15 Metal-organic framework (MOF) compounds have attracted intensive scientific interests, not only driven by their highly tuneable structures,[1] but also motivated by their potential applications in the fields such as catalysis,[2] electronics,[3] gas storage and selective separation,[4] and fluorescence sensing.[5] 20 Many advances have been made in MOFs containing d- or f-block metal ions.[6] By contrast, the MOFs based on main-group light-metal ions,[7] especially the magnesium-based MOFs[8] have been relatively less explored, however they are widely regarded as promising competitive materials for gas 25 storage.

As an emerging class of fluorescent sensing materials, the MOFs based on transition metal and lanthanide ions for detection of volatile organic solvent molecules[9] and nitroaromatic explosives[10] have been reported recently. Carbon disulfide (CS$_2$), 30 a harmful volatile organic solvent, can be a neurotoxin when people expose to it at high levels. The development of atherosclerosis and coronary artery disease can also be triggered by prolonged exposure to CS$_2$.[11] Moreover, as an industrial chemical for the production of viscose rayon fibres, CS$_2$ can be 35 oxidized to carbonyl sulfide and sulfur dioxide as high hazard air pollutants.[12] On the other hand, nitroaromatic compounds such as nitrobenzene are also notorious environmental pollutants,[13] and those containing di or tri-nitro groups are known as high explosives that could cause serious safety problems. Now the 40 detection for CS$_2$ and nitroaromatic pollutants are mainly based on well-trained canines or sophisticated analytical instruments.[14] It is urgent to seek more convenient and quick sensing methods for these pollutants. With high surface area, fast response time, sensitive detection and convenient preparation, MOFs are 45 promising sensing materials for this detection purpose.

Here we report on the synthesis, structure and properties of a magnesium MOF, namely Mg$_5$(OH)$_2$(BTEC)$_2$(H$_2$O)$_4$·11H$_2$O (**1**), (H$_4$BTEC = 1,2,4,5-Benzenetetracarboxylic acid). In particular, the luminescence studies revealed that **1** could highly selectively 50 detect CS$_2$ and nitrobenzene, as the luminescence intensities of **1** were almost completely quenched at the concentrations of 0.8 vol% (CS$_2$) and 0.04 vol% (nitrobenzene), respectively. Detections for 2,4-dinitraniline, p-nitraniline and o-nitraniline at a concentration of 10^{-3} mol/L demonstrated that **1** could also be a 55 luminescent probe for detecting nitroaromatic explosives. To our knowledge, there was only one report about the sensing for NH$_3$ with a Mg-MOF,[15] but the Mg-MOFs as sensors for CS$_2$ and nitroaromatic organics detection have not been investigated until now.

60 ## Experimental

All reagents and chemicals were purchased from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Miniflex II diffractometer using a CuKα radiation. Microprobe elemental 65 analyses were performed by using a field-emission scanning electron microscope (FESEM, JSM6700F) equipped with an

[a] Z.–F. Wu, B. Tan, A.–J. Lan and Prof. Dr. X.–Y. Huang
State Key Laboratory of Structural Chemistry
Fujian Institute of Research on the Structure of Matter
Chinese Academy of Sciences
Fuzhou, Fujian 350002, P. R. China.
Fax: (+86) 591-8379-3727
E-mail: laj@fjirsm.ac.cn, xyhuang@fjirsm.ac.cn

[b] Z.–F. Wu
University of Chinese Academy of Sciences
Beijing, 100049 (P. R. China)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.200xxxxx.((Please delete if not appropriate))

energy-dispersive X-ray spectroscope (EDXS, Oxford INCA). Elemental analyses for C, H were performed on a German Elementary Vario EL III instrument. Thermogravimetric analyses were carried out with a NETZSCH STA 449F3 unit at a heating
5 rate of 5 □/min under a nitrogen atmosphere. The UV/Vis diffuse reflectance spectra and absorption spectra were measured at room temperature using a PE Lambda 950 UV/Vis spectrophotometer. The spectrophotometer was calibrated against the surface of $BaSO_4$ for 100% reflectance over the wavelength range under
10 consideration in the UV/Vis diffuse reflectance spectra measurments. Emission and excitation spectra of the compounds were recorded on a PerkinElmer LS55 luminescence spectrometer. The photoluminescence lifetime measurements were carried out using laser pulses at 378 nm as the excitation
15 source and determined by a Varian Cary Eclipse and an Edinburgh FLS980 fluorescence spectrometer at room temperature. Gas adsorption measurement was performed in the ASAP (Accelerated Surface Area and Porosimetry) 2020 System.

Synthesis of $Mg_5(OH)_2(BTEC)_2(H_2O)_4 \cdot 11H_2O$ (1)

20 1 mmol $Mg(NO_3)_2 \cdot 6H_2O$ (0.256 g), 0.5 mmol H_4BTEC (0.127 g) and 2 mmol $NaHCO_3$ (0.168 g) were dissolved in 10 mL distilled water, and then the solution was sealed in a 20 mL Teflon-line stainless-steel autoclave and maintained at 170 °C for 4 days, followed by cooling to room temperature. The colorless
25 rod-crystals of **1** were isolated after filtered, washed with distilled water several times and dried at ambient temperature; yield 30.4% (0.075 g) based on Mg. Anal. calc. for **1**: C, 25.94%; H, 3.92%. Found: C, 25.56%; H, 3.75%.

Fluorescence measurements

30 The fluorescence of **1** was measured by dispersing 5 mg of **1** (the as-made crystalline sample of **1** was loaded into an agate mortar and was manually ground with the pestle to afford a fine powder) in 5 mL of CS_2, H_2O, CH_3OH, ethanol, CH_2Cl_2, acetone, 2-butanol, ethylene glycol, DMF (N,N-dimethylformamide),
35 NMF (N-methylformamide), THF (tetrahydrofuran), isopropanol, acetonitrile and ethyl ether, respectively. After ultrasonic treatment for a few minutes, the suspension was placed in a quartz cell of 1 cm width for fluorescence detection. Detailed detections for all titrants were carried out by gradually adding the
40 CS_2, nitrobenzene, 2,4-dinitraniline (1.0×10^{-3} mol/L ethanol solution), p-nitraniline (1.0×10^{-3} mol/L ethanol solution) and o-nitraniline (1.0×10^{-3} mol/L ethanol solution) solutions as quenchers in an incremental fashion. The fluorescence spectra of **1** were monitored, before and after exposing it to the equilibrated
45 vapors of nitrobenzene for varied periods of time/s. Their corresponding fluorescence emission spectra were recorded at 298 K. For all measurements, the dispersed solutions of **1** were excited at λ_{ex} = 322 nm (λ_{em} = 435nm) and the corresponding emission wavelengths were monitored from λ_{em} = 375 nm to 600
50 nm. The fluorescence efficiency was calculated by $[(I_0-I)/I_0] \times 100\%$, where I_0 is the initial fluorescence intensity.

Single-crystal structure determination

Single-crystal X-ray diffraction data of the compound **1** were collected on a Xcalibur E Oxford diffractometer with graphite
55 monochrochromated Mo$K\alpha$ radiation (λ = 0.71073 Å) at room temperature. The absorption corrections were applied using

multi-scan technique. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXL-97 program.[16] Non-hydrogen atoms were refined with
60 anisotropic displacement parameters, and the hydrogen atoms bonded to C and N atoms were positioned with idealized geometry. The empirical formula was confirmed by thermogravimetric analyses and element analyses results. The detailed crystallographic data and structure-refinement
65 parameters for compound **1** are summarized in Table 1.

Results and discussion
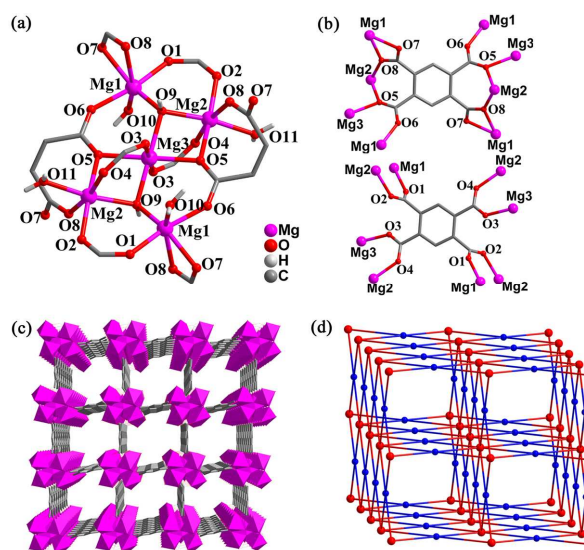
Description of crystal structure

Fig. 1 (a) The pentanuclear cluster as SBU in **1**. (b) coordination modes
70 of the ligand. (c) 3D framework of **1** viewed along the *a* axis (lattice water molecules in channels are omitted for clarity). (d) topology of **1**.

Single crystal X-ray analysis revealed that compound **1** crystallized in the triclinic space group *P*-1. The crystallographically asymmetric unit of **1** consists of two and a
75 half Mg^{2+} ions, two halves of BTEC ligands, two coordinated water molecules, one coordinated hydroxyl group and five and a half lattice water molecules (see the supporting information, Fig. S1). Its structure features a three-dimenaional (3D) open-framework based on a pentanuclear magnesium cluster as
80 secondary building unit (SBU, Fig. 1a). All the three independent Mg^{2+} sites adopt an octahedral coordination geometry, however, they connect to oxygen atoms from different BTEC ligands, hydroxyl groups and/or water molecules, with the Mg–O bond lengths varying from 2.0195(15) to 2.2604(15) Å (Table S1).
85 Both the independent half BTEC ligands are fully deprotonated and have different coordination modes (Fig. 1b). The hydroxyl group O(9)H(9) is a tridentate linker connecting one Mg(1), Mg(2) and Mg(3) ions to form a trinuclear magnesium cluster. Then two such trinuclear clusters share one Mg(3)$^{2+}$ ion in an
90 inversion centre to form a pentanuclear cluster as SBU for the structure. It is noteworthy that in the reported Mg-MOFs the SBUs are commonly linear tri-magnesium units,[17] whereas the SBU for **1** is unprecedented. The SBUs are bridged by carboxylate groups from the BTEC ligands to result in a 1D
95 ribbon along the *a* axis. Finally, the 1D ribbons are further

weaved by the BTEC ligands to give rise to a 3D network with the 1D channels along the *a* axis, which are filled with the lattice water molecules (Fig. 1c). The solvent accessible volume is 33.4% if all the water molecules are removed according to the calculation performed by *PLATON* analysis. Topology analysis with *TOPOS* software[18] suggests that the 3D framework displays an (4,8)-connected $\{4^4.6^2\}_2\{4^{16}.6^{12}\}$ topology with each pentanuclear magnesium cluster serving as a 8-connected square planar node, and H$_4$BTEC ligand as equivalent 4-connected nodes (Fig. 1d).

Luminescent detection properties

The luminescent spectra of compound **1** in the solid state exhibited blue-purple light emission (λ_{ex}= 328 nm) at room temperature and showed emission bands at 425 nm (Fig. S3). Compared to the free ligand of H$_4$BTEC (Figure S3), the compound **1** showed red-shift emission which could be assigned to the emissions of ligand-to-metal charge transfer (LMCT).[19] Compound **1** has 11.22 Å×12.17 Å pore sizes with 33.4% accessible volume, and the robustness and micropore features provide sufficient conditions to contact with small solvent molecules that may cause different luminescent responses of **1**. In order to detect whether **1** has the luminescent response for volatile organic molecules, **1** was dispersed in 14 kinds of different solvents. As shown in Fig. 2, the luminescent intensities of **1** were heavily dependent on the identities of the organic solvent molecules.
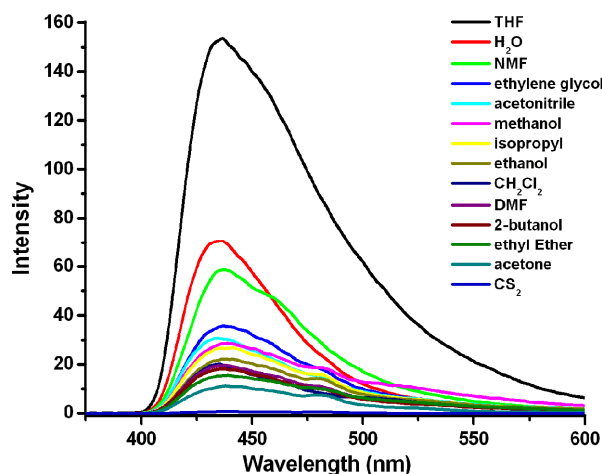

Fig. 2 Emission spectra of 1 dispersed in different solvents.

Interestingly, we found that **1** exhibited significant quenching of the luminescence intensity when dispersed in CS$_2$. Then the sensing sensitivity towards CS$_2$ was examined in detail through gradually increasing CS$_2$ contents into emulsions of **1** dispersed in THF to monitor the emissive response. As shown in Fig. 3a, the luminescence intensity of **1** decreased to 66% only at CS$_2$ content of 0.08 vol% and was almost completely quenched at a concentration of 0.8 vol%, indicating that **1** was a benign candidate for selective sensing of CS$_2$. Compared to the former reports detected for acetone based on MOFs luminescence intensity,[9a,b] the quenched concentration of CS$_2$ is very low which indicates more sensitive detection limit. Quantitatively, this quenching effect can be rationalized by the Stern–Volmer

equation (SV plot): $I_0/I = 1 + K_{sv} \times$ [M], where I_0 and I are the suspension luminescence intensity of compound **1** without and with addition of quencher, respectively, and [M] is the molarity of quencher and K_{sv} is the quenching constant.[19a, b] The SV plot in Fig. 3b displays a good linear behavior. According to the former reports, K_{sv} (diffusion) = $k_q \times \tau$, where k_q is the quenching rate constant and τ is the excited-state lifetime without added quencher. The apparent quenching rate constant calculated from the experimental data is 2.26×10^5 L·mol^{-1}. Given the SV relationship in the above equation, the quenching rate constant is $kq = 6.4 \times 10^{13}$ M^{-1} S^{-1} (τ = 3.51 ns, Fig. S4). This value is more than 2 orders of magnitude higher than the diffusion-controlled limit under these conditions, ruling out diffusional quenching.[19] As depicted in Fig. S5, the absorption band of H$_4$BTEC ligand and that of compound **1** are located between 280 and 350 nm that well overlapped with the absorption band of CS$_2$,[20] thus the excitation energy absorbed by the organic ligands of the MOFs could be transferred to CS$_2$,[21d,e] resulting in a decrease in the luminescence intensity.[21]
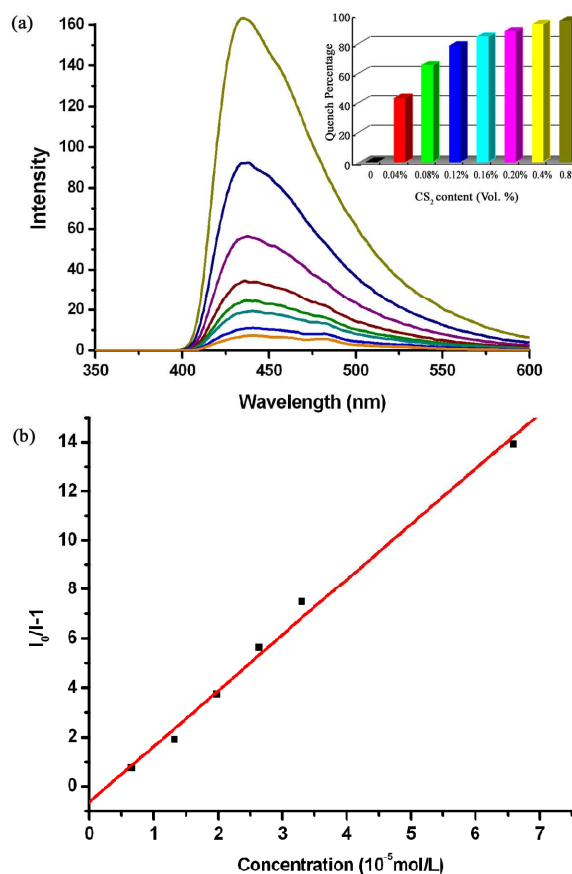

Fig. 3 (a) Emission spectra of **1** dispersed in THF with various contents of CS$_2$. (b) The SV plot for the quenching of **1** by CS$_2$.

The selective sensing property for CS$_2$ encouraged us to further investigate whether **1** could be used for detection of nitroaromatic compounds. Indeed, the luminescence quench of **1** was 83% with the content of nitrobenzene at 0.04 vol% using the similar detection method as that for CS$_2$ (Fig. 4), corresponding to the low quencher concentrations of 1.56×10^{-5} mol·L^{-1}. The K_{sv} value is 1.52×10^6 L·mol^{-1} for nitrobenzene from the linear

region of plots, indicating a more sensitive detection limit than CS_2. In order to further detect the sensitivity of **1** in detail, we put **1** into the vapor of nitrobenzene and the luminescence intensity of **1** in solid state was quenched to 50% only in 60s (Fig. 5). The detection is much more convenient and sensitive which indicates compound **1** may be used as luminescence sensors for detect nitrobenzene vapor based on healthy and safety.
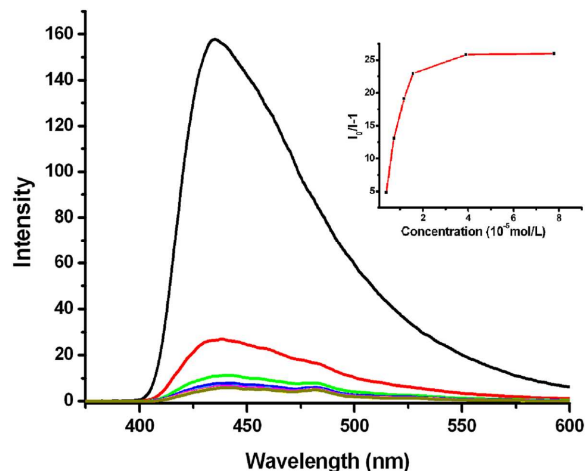

Fig. 4 Emission spectra of **1** dispersed in THF with various contents of nitrobenzene. The inset is the SV plot for the quenching of **1** by nitrobenzene.
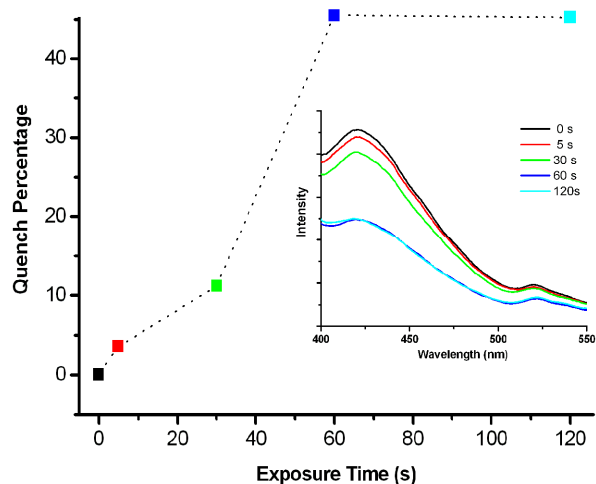

Fig. 5 Time-dependent fluorescence quenching by nitrobenzene vapor.

Then the other nitroaromatics such as 2,4-nitraniline, p-nitraniline and o-nitraniline were chosen to study the luminescence response. The nitroaromatics are dissolved in anhydrous ethanol to get the 10^{-3} mol/L concentration solutions, then the solutions as quenchers were added to the dispersed solution of **1** in THF and the luminescence response was recorded. As seen in Fig. 6a, the luminescence intensity decreases to 63% after 200 uL 2,4-dinitraniline was added. The steady-state emission SV plot shows a good linear behavior as detection for CS_2 and K_{sv} value is 2.35×10^4 L·mol^{-1}. The decreasing percentages for p-nitraniline and o-nitraniline are 38% and 32%, respectively (Fig. S6 and S7). The above results indicated that compound **1** showed sensitive response for the nitroaromatics at

very low concentrations and may be applied for nitroaromatic explosives detection.

The maximum absorption of nitroaromatics used as quencher here are located around 360 nm (Fig. S3) showing nearly no overlap with the 425 nm emission region of compound **1**, indicating little energy transfer between **1** and the nitroaromatics. Thus, upon excitation by photons, compound **1** with conjugated aromatic ring acts as electron donors and excited electrons will be transferred to the analyte with electron withdrawing nitro groups, which facilitates fluorescence quenching. This may be the main mechanism of fluorescence detection for the nitroaromatics reported here which is consistent with the recently reported.[22] However, there still exists small overlapped region between the absorption spectra of nitroaromatics and emission spectrum of compound **1**, especially for o-nitraniline, so energy transfer can not be excluded totally during fluorescence quenching process.[23] Further investigation is still required to explore the mechanism of fluorescence quenching in compound **1**.

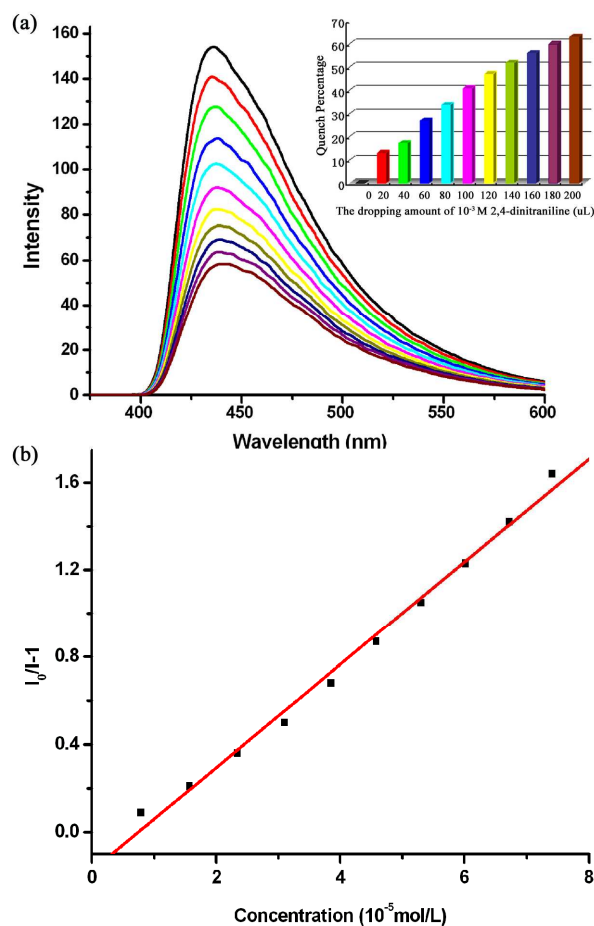**Fig. 6** (a) Emission spectra of **1** dispersed in THF by gradual addition of 10^{-3} M solutions of 2,4-dinitraniline in ethanol. (b) The SV plot for the quenching of **1** by 2,4-dinitraniline.

Conclusions

In summary, a Mg-MOF, namely $Mg_5(OH)_2(BTEC)_2(H_2O)_4·11H_2O$, has been synthesized and structurally characterized, which showed highly sensitive luminescent response for CS_2 and nitroaromatic compounds such

as nitrobenzene, 2-nitraniline, 4-nitraniline and 2,4- nitraniline at low concentrations. Future work will be focused on the construction of more porous Mg-MOFs and exploring their fluorescent sensing properties for detection of harmful organic molecules and selective gas adsorption properties.

Notes and references

ᵃ State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, the Chinese Academy of Sciences, Fuzhou, Fujian 350002, P.R. China. Fax: (+86) 591-83793727; Tel: (+86) 591-83793727; E-mail: xyhuang@fjirsm.ac.cn.
ᵇ University of the Chinese Academy of Sciences, Beijing 100049, P.R. China.

† Electronic Supplementary Information (ESI) available: Crystallographic data in CIF format, detailed synthetic procedures, more structural details, PXRD, TGA curves, elemental analysis. CCDC no. 965518. See DOI: 10.1039/b000000x/.

1   (a) Y. P. He, Y. X. Tan and J. Zhang, *CrystEngComm*, 2012, **14**, 6359; (b) S. M. Chen, J. Zhang and C. Z. Lu, *CrystEngComm*, 2007, **9**, 390; (c) Y. P. He, Y. X. Tan and J. Zhang, *Inorg. Chem.*, 2012, **51**, 1995. (d) H. M. Zhang, J. Yang, Y. C. He and J. F. Ma, *Chem. Asian J.*, 2013, **8**, 2787; (e) J. K. Sun, Q. X. Yao, Z. F. Ju and J. Zhang, *CrystEngComm*, 2010, **12**, 1709; (f) J. K. Sun, Q. X. Yao,Y. Y. Tian, L. Wu, G. S. Zhu, R. P. Chen and J Zhang, *Chem. Eur. J.*, 2012, **18**, 1924.

2   (a) D. Y. Hong, Y. K. Hwang, C. Serre, G. Férey and J. S. Chang, *Adv. Funct. Mater.*, 2009, **19**, 1537; (b) Y. K. Hwang, D. Y. Hong, J. S. Chang, S. H. Jhung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre and G. Férey, *Angew. Chem., Int. Ed.*, 2008, **47**, 4144; (c) M. Meilikhov, K. Yusenko and R. A. Fischer, *J. Am. Chem. Soc.*, 2009, **131**, 9644; (d) L. Q. Ma, J. M. Falkowski, C. Abney and W. B. Lin, *Nat. Chem.*, 2010, **2**, 838.

3   (a) S. Bureekaew, S. Horike, M. Higuchi, M. Mizuno, T. Kawamura, D. Tanaka, N. Yanai and S. Kitagawa, *Nat. Mater.*, 2009, **8**, 831; (b) G. de Combarieu, M. Morcrette, F. Millange, N. Guillou, J. Cabana, C. P. Grey, I. Margiolaki, G. Férey and J. M. Tarascon, *Chem. Mater.*, 2009, **21**, 1602.

4   (a) M. Dincă and J. R. Long, *Angew. Chem., Int. Ed.*, 2008, **47**, 6766; (b) N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 2003, **300**, 11270; (c) J. L. C. Rowsell and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2005, **44**, 4670; (d) C. Volkringer, T. Loiseau, N. Haouas, F. Taulelle, D. Popov, M. Burghammer, C. Riekel, C. Zlotea, F. Cuevas, M. Latroche, D. Phanon, C. Knofelv, P. L. Llewellyn and G. Ferey, *Chem. Mater.*, 2009, **21**, 5783; (e) S. Vaesen, V. Guillerm, Q. Y. Yang, A. D. Wiersum, B. Marszalek, B. Gil, A. Vimont, M. Daturi, T. Devic, P. L. Llewellyn, C. Serre, G. Maurin and G. D. Weireld, , *Chem. Commun.*, 2013, **49**, 10082.

5   (a) Y. H. Zhang, X. Li and S. Song, *Chem. Commun.*, 2013, **49**, 10397; (b) D. Li, J. Song, P. C. Yin, S. Simotwo, A. J. Bassler, Y. Y. Aung, J. E. Roberts, K. I. Hardcastle, C. L. Hill and T. B. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 14010.

6   (a) D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim and K. Kim, *J. Am. Chem. Soc.*, 2004, **126**, 32; (b) L. Pan, H. M. Liu, X. G. Lei, X. Y. Huang, D. H. Olson, N. J. Turro and J. Li, *Angew. Chem., Int. Ed.*, 2003, **42**, 542; (c) J. He, M. Zeller, A. D. Hunter and Z. T. Xu, *J. Am. Chem. Soc.*, 2012, **134**, 1553; (d) H. M. Zhang, J. Yang, Y. C. He and J. F. Ma, *Chem. Asian J.*, 2013, **8**, 2787; (e) D. F. Sava, L. E. S. Rohwer, M. A. Rodriguez and T. M. Nenoff, *J. Am. Chem. Soc.*, 2012, **134**, 3983; (f) Y. Liu, M. Pan, Q. Y. Yang, L. Fu, K. Li, S. C. Wei and C. Y. Su, *Chem. Mater.*, 2012, **24**, 1954; (g) 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 and Z. M. Su, *Chem. Eur. J.*, 2013, **19**, 11279; (h) Z. F. Liu, M. F. Wu, S. H. Wang, F. K. Zheng, G. E. Wang, J Chen, Y. Xiao, A. Q. Wu, G. C. Guo and J. S. Huang, *J. Mater. Chem. C*, 2013, **1**, 4634.

7   (a) E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J.R. Long, O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 14382; (b) A. Mallick, S. Saha, P. Pachfule, S. Roy and R. Banerjee, *J. Mater. Chem.*, 2010, **20**, 9073; (c) D. Himsl, D. Wallacher and M. Hartmann, *Angew. Chem., Int. Ed.*, 2009, **48**, 4639.

8   (a) M. Majumder, P. Sheath, J. I. Mardel, T. G. Harvey, A. W. Thornton, A. Gonzago, D. F. Kennedy, I. Madsen, J. W. Taylor, D. R. Turner, and M. R. Hill, *Chem. Mater.*, 2012, **24**, 4647; (b) I. Senkovska and S. Kaskel, *Eur. J. Inorg. Chem.*, 2006, **22**, 4564.

9   (a) F. Y. Yi, W. T. Yang and Z. M. Sun, *J. Mater. Chem.*, 2012, **22**, 23201; (b) H. Yang, F. Wang, Y. X. Tan, Y. Kang, T. H. Li and J. Zhang, *Chem. Asian J.*, 2012, **7**, 1069; (c) A. M. Marti, S. D. Perera, L. D. McBeath and K. J. B. Jr, *Langmuir*, 2013, **29**, 5927; (d) A. M. Marti, N. Nijem, Y. J. Chabal and K. J. B. Jr, *Micro. Meso. Mater.*, 2013, **174**, 100.

10   (a) A. J. Lan, K. H. Li, H. H. Wu, D. H. Olson, T. J. Emge, W. Ki, M. C. Hong and J. Li, *Angew. Chem., Int. Ed.*, 2009, **48**, 2334; (b) B. Gole, A. K. Bar and P. S. Mukherjee, *Chem. Commun.*, 2011, **47**, 12137; (c) T. K. Kim, J. H. Lee, D. Moon and H. R. Moon, *Inorg. Chem.*, 2013, **52**, 589; (d) Y. P. Yuan, W, Wang, L. G. Qiu, F. M. Peng, X. Jiang, A. J. Xie, Y. H. Shen, X. Y. Tian and L. D. Zhang, *Mat. Chem. Phy.*, 2011, **131**, 358; (e) S. B. Ding, W. Wang, L. G. Qiu, Y. P. Yuan, F. M. Peng, X. Jiang, A. J. Xie, Y. H. Shen and J. F. Zhu, *Mater. Lett.*, 2011, **65**, 1385; (f) Y.X. Xu, Y. Q. Wen, W. Zhu, Y. N. Wu, C. X. Lin and G. T. Li, *Mater. Lett.*, 2012, **87**, 20.

11   M. Phillips, Int. Arch. Occup. *Environ. Health*, 1992, **64**, 119.

12   (a) B. M. R. Jones, R. A. Cox and S. A. Parkett, *J. Atmos. Chem.*, 1983, **1**, 65; (b) M. A. K. Khalil and R. A. Rasmussen, *Atmos. Environ.*, 1984, **18**, 1805.

13   P. S. Majumder and S. K. Gupta, *Water Res.*, 2003, **37**, 4331.

14   (a) L. Ciaffoni, R. Peverall and G. A. D. Ritchie, *J. Breath Res.*, 2011, **5**, 037101; (b) K. G. Furton, L. J. Myers, *Talanta*, 2001, **54**, 487; (c) A. G. Davies, A. D. Burnett, W. H. Fan, E. H. Linfield, J. E. Cunningham, *Mater. Today*, 2008, **11**, 18.

15   N. B. Shustova, A. F. Cozzolino, S. Reineke, M. Baldo and M. Dincă, *J. Am. Chem. Soc.*, 2013, **135**, 13326.

16   G. M. Sheldrick, *SHELXS97 and SHELXL97*, University of Göttingen, Germany, 1997.

17   (a) Z. F. Wu, M. L. Feng, B. Hu, B. Tan and X. Y. Huang, *Inorg. Chem. Commun.*, 2012, **24**, 166; (b) I. Senkovska and S. Kaskel, Eur. J. *Inorg. Chem.*, 2006, 4564.

18   V. A. Blatov, A. P. Shevchenko and V. N. Serezhkin, *J. ppl. Crystallogr.*, 2000, **33**, 1193. TOPOS software is available for download at .

19   (a) C. A. Kent, D. M. Liu, T. J. Meyer and W. B. Lin, *J. Am. Chem. Soc.*, 2012, **134**, 3991; (b) C. A. Kent, D. M. Liu, L. Q. Ma, J. M. Papanikolas, T. J. Meyer and W. B. Lin, *J. Am. Chem. Soc.*, 2011, **133**, 12940; (c) C. Wang and W. B. Lin, *J. Am. Chem. Soc.*, 2011, **133**, 4232; (d) J. D. Xiao, L. G. Qiu, F. Ke, Y. P. Yuan, G. S. Xu, Y. M. Wang and X. Jiang, *J. Mater. Chem. A*, 2013, **1**, 8745.

20   C. H. Hearn, J. A.Joens, *J. Quant. Spectrosc. Radiat. Transfer.*, 1991, **45**, 69.

21   (a) M. M. Wanderley, C. Wang, C. D. Wu and W. B. Lin, *J. Am. Chem. Soc.*, 2012, **134**, 9050; (b) G. Y. Wang, L. L. Yang, Y. Li, H. Song, W. J. Ruan, Z. Chang and X. H. Bu, *Dalton Trans.*, 2013, **42**, 12865; (c) W. T. Yang, J. Feng and H. J. Zhang, *J. Mater. Chem.*, 2012, **22**, 6819; (d) Z. M. Hao, G. C. Yang, X. Z. Song, M. Zhu, X. Meng, S. Zhao, S. Y. Song and H. J. Zhang, *J. Mater. Chem. A*, 2014, **2**, 237; (e) Y. Li, S. S. Zhang and D. T. Song, *Angew. Chem., Int. Ed.*, 2013, **52**, 710.

22   (a) S. Pramanik, Z. C. Hu, X. Zhang, C. Zheng, S. Kelly and J. Li, *Chem. Eur. J.*, 2013, **19**, 15964; (b) D. Tian, Y. Li, R. Y. Chen, Z. Chang, G. Y. Wang and X. H. Bu, *J. Mater. Chem. A*, 2014, **2**, 1465; (c) D. Banerjee, Z. C. Hu, S. Pramanik, X. Zhang, H. Wang and J. Li, *CrystEngComm*, 2013, **15**, 9745; (d) Y. N. Gong, L. Jiang and T. B. Lu, *Chem. Commun.*, 2013, **49**, 11113; (e) L. Li, S. Q. Zhang, L. j. Xu, L. Han, Z. N. Chen and I. H. Luo, *Inorg. Chem.*, 2013, **52**, 12323; (f) D. X. Ma, B. Y. Li, X. J. Zhou, Q. Zhou, K. Liu, G. Zeng, G. H. Li, Z. Shi and S. H. Feng, *Chem. Commun.*, 2013, **49**, 8964.

23   (a) Y. S. Zhao, H. B. Fu, F. Q. Hu, A. D. Peng, W. S. Yang and J. N.

Yao, *Adv. Mater.*, 2008, **20**, 79; (b) Y. L. Chang, Y. Song, Z. B. Wang, M. G. Helander, J. Qiu, L. Chai, Z. W. Liu, G. D. Scholes and Z. H. Lu, *Adv. Funct. Mater.*, 2013, **23**, 705.

5

Table 1. Summary of data collection and structure refinement for crystal **1**.

Empirical formula	$C_{20}H_{36}Mg_5O_{33}$
Crystal Size (mm)	0.28×0.22×0.12
Crystal system	Triclinic
Space group	*P* -1
a (Å)	7.3742(3)
b (Å)	11.4011(6)
c (Å)	11.6706(6)
α (°)	89.666(4)
β (°)	76.813(4)
γ (°)	74.971(4)
V (Å^3)	921.16(7)
Z	1
μ (mm^{-1})	0.233
λ(MoKα) (Å)	0.71073
F(000)	480
θ range (°)	2.51 to 26.75
Reflections measured	7769
Independent reflections	3872
Observed Reflection [$I>2\sigma(I)$]	3149
Temperature (K)	293
ρ_{calc}/g cm^{-3}	1.669
Parameter	313
R_{int}	0.0196
R_1, wR_2 [$I>2\sigma(I)$]^a	0.0366, 0.0760
R_1, wR_2 [all data]	0.0454, 0.0779
GOF	1.001
Largest diff. Peak and hole/e Å^{-3}	0.346, -0.478

$^a R_1 = \sum||Fo|-|Fc||/\sum|Fo|$, $wR_2 = \{\sum w[(Fo)^2 -(Fc)^2]^2/\sum w[(Fo)^2]^2\}^{1/2}$