

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

One Non-interpenetrated Chiral Porous Multifunctional Metal–Organic Framework and Its Applications for Sensing Small Solvent Molecules and Adsorption

Ling Qin^{a,b}, Meng-Xi Zheng^a, Zi-Jian Guo^a, He-Gen Zheng^{a*}, Yan Xu^{c*}

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000

The obtained multifunctional compound is a promising fluorescent material that can give tunable fluorescence emissions by changing the solvent molecules. The fluorescence sensing behaviors are different for non-protonic and protonic solvents. No such a large response range of emission positions for fluorescent MOFs has been reported.

Research on metal-organic frameworks (MOFs) which self-assemble from organic ligands and metal ions or clusters is shifting more and more from a focus on structural aspects towards the implementation of function such as gas storage and separation,¹ catalysis,² sensors,³ light harvesting,⁴ medical and magnetic materials.^{5,6} Framework materials combined and integrated with two or more properties, such as conductivity, porosity, ferroelectric and piezoelectric properties have recently attracted intense interest because these so-called multifunctional materials offer the possible synergism of different functions and thus new potential applications.⁷

These applications hinge on two important properties of MOFs: porosity and stability. The augmentation of their channel sizes to meso-porous range still poses a great challenge. Ligand extension is a major option, but MOFs built from large ligands often exhibit framework interpenetration, which could drastically reduce the size of the pores. To avoid interpenetration, Yaghi described the possibility of constructing nanotubular MOFs by using infinite rod-shaped secondary building units (SBUs),⁸ which provide constructed MOFs with permanent porosity and rigid architectures. The key step in designing meso-porous MOFs is the judicious choice of organic ligands and inorganic rod-shaped SBUs.

The nanosized ligand N,N,N',N'-tetrakis (4-(4-pyridine)-phenyl) biphenyl-4,4'-diamine (TPPBDA)⁹ is our choice for constructing compound **1**, $\{[\text{Cd}_2(\text{TPPBDA})(\text{bpdc})_{3/2}(\text{H}_2\text{O})_2](\text{CO}_3)_{1/2}\}$.¹⁰ Compound **1** was prepared in a solvothermal reaction of Cd(NO₃)₂, TPPBDA and H₂bpdc in DMF/H₂O/CH₃CN at 85 °C. The product was isolated as yellow crystals (yield: 56%). The crystal structure determination reveals that compound **1** crystallizes in monoclinic crystal system of C₂. As shown in Fig. S1a, compound **1** consists

of bpdc ligands and half of lattice carbonate anion. Each Cd (II) is a distorted octahedral coordination sphere coordinated by two nitrogen atoms of TPPBDA, three carboxyl oxygen atoms and one water molecule. Two adjacent Cd cations are linked in sequence by carboxyl groups of bpdc²⁻ forming an infinite rod-shaped secondary building unit (SBU) (Fig. S1b). Each rod-shaped SBU links four adjacent SBUs through the TPPBDA molecules to generate a designable non-interpenetrated 3D framework (Figs. S1c and S1d). The effective free volume of **1** is calculated by PLATON analysis as being 55% of the crystal volume.

It is interesting that compound **1** is built by three types of 2₁ helices along c-axis. Among them, the first (P1) right-handed one is bridged by the bpdc²⁻ ligand using carboxylate end and nitrogen donors of the half of TPPBDA (mode AA' in Fig. S2) and between the rod-shaped SBUs with a pitch of 10.278Å; the second (P2) right-handed one is bridged by the bpdc²⁻ ligand using a carboxylate end and nitrogen donors of the half of TPPBPA (mode AB) and between the rod-shaped SBUs with a pitch of 10.279Å. Another (M1) left-handed one is bridged by the bpdc²⁻ ligand using a carboxylate end and a nitrogen donor of the half of TPPBPA (mode AA') and between the rod-shaped SBUs with a pitch of 20.557Å (Fig. 1).

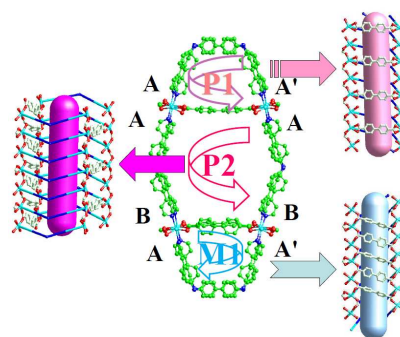


Fig. 1. A view of three types of helical chains (labeled by P1, P2, M1).

The fluorescent properties of compound **1** in the solid state and suspension in different organic solvents have been investigated systematically. The solid-state emission spectrum for the compound **1** exhibits a broad peak at 573 nm, which is more likely to be attributed to intraligand transition, since a broad emission (562 nm) is observed for TPPBDA (Fig. S5). A finely ground as-synthesized compound **1** (10 mg) was immersed in different organic solvents (20 mL), treated by ultrasonication for 2 hours. The interesting feature is that its fluorescent intensity is largely dependent on the solvent molecules with acetic acid > chloroform > dimethylformamide > dichloromethane > toluene > dimethylacetamide > acetonitrile > hexane > ethanol > methanol > water > acetone (Fig. S9), which is probably due to the chromophores in **1** have different interactions with solvents.¹¹ Evidently, the fluorescence intensities of **1** strongly depend on the solvent molecules, particularly in acetone, which exerted the most significant quenching effect; acetic acid quenching is the lowest. Further detailed experiments were undertaken to examine the ability of **1** to sense acetone. Compound **1** dispersed in chloroform was considered as the standard emulsion **1**-CHCl₃, and acetone was gradually increased to investigate the emission response. It was found that the fluorescence intensity of the **1**-CHCl₃ quickly decreased to with the addition of acetone.

As shown in Fig. 2, in the acetic acid, there is an emission with a maximum at 556 nm ($\lambda_{\text{ex}} = 385$ nm). In the hexane, there is an emission with a maximum at 405 nm ($\lambda_{\text{ex}} = 345$ nm, blue-shift of that in the acetic acid about 151 nm). The maximum emission peaks are also largely dependent on the solvent molecules, with acetic acid > dimethylformamide = dimethylacetamide > ethanol > acetonitrile > methanol > water > dichloromethane > chloroform > toluene > hexane. Although some fluorescent MOFs relying to guest molecules have been observed previously,¹² most examples are reflected in the intensity. Here we have presented a rare example of the tunable fluorescence emission centers. To our knowledge, such a large response range of emission positions for fluorescent MOFs has been not reported.

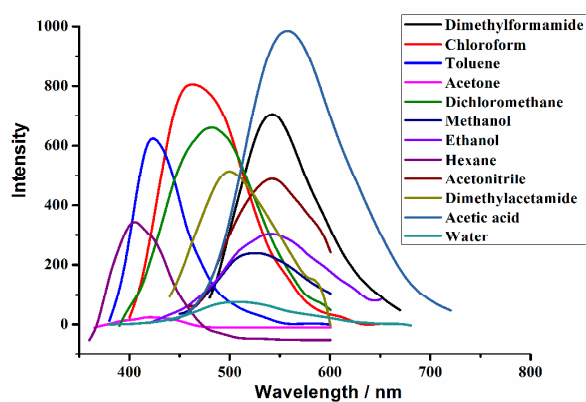


Fig. 2. The emission of compound **1** in suspension in various organic solvents under the same testing conditions.

The maximum emission peaks show certain correlation with the dielectric constant values of solvents. The dielectric constant values of the solvent-included compounds are incorporated in Table S1. The correlations are obtained by separately plotting non-protonic and protonic solvents as shown in Fig. 3. Such solvent dependence indicates that **1** can be powerful for sensing

these solvents. With the increasing of the dielectric constant of solvent guests, the maximum emission peaks are red-shifted showing a positive correlation effect for non-protonic solvents; and a negative correlation effect for protonic solvents. To make a deep discussion on the issues about the emission of compound **1** that is dependent on the solvent dielectric constant and the protonic property, we checked whether the TPPBDA ligand itself has the same solvent sensitivity. The results show that the emission position for TPPBDA ligand is not related with the dielectric constant of the solvent and whether it is protonic as shown in the Fig. S11.

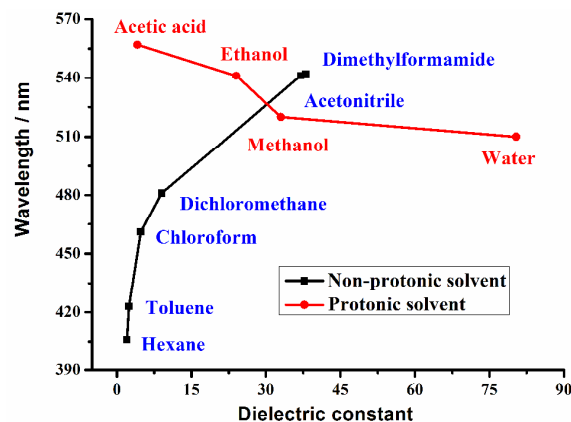


Fig. 3. The maximum emission peaks against dielectric constant values of solvents.

It is also interesting to find that the solvate-optical sensing behaviours can be fine-tuned, and the subtle distinctions indicate possible sensing selectivity of this activated fluorescent MOF material toward different solvent guests. The suspensions of **1**-DMF and **1**-CHCl₃ were prepared by dissolving 10mg compound **1** in 20mL dimethylformamide or chloroform, respectively. Different ratios of sample **1**-DMF and **1**-CHCl₃ were mixed to monitor mixed-solvent sensing selectivity tests, while the total volumes of the mixture are all constant. As shown in Fig. 4, the fluorescent emission peak of the emulsions significantly blue-shifted and approached to the emission peak of **1**-CHCl₃ with the increasing volumetric ratios of sample **1**-CHCl₃. To further prove the role of the solvent molecules, same amounts of sample **1**-CHCl₃ or fresh CHCl₃ solvent were added to the sample **1**-DMF. The main emission peaks and the emission intensities are almost identical (Fig. 5). Such phenomenon was also observed in other solvent systems (Fig. S10).

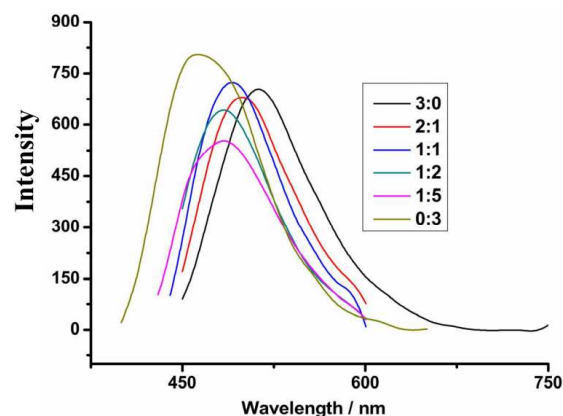


Fig. 4. The fluorescent emission spectra of the sample 1-DMF series immersed in sets of mixtures of solvents with increasing volumetric ratios of sample 1-CHCl₃.

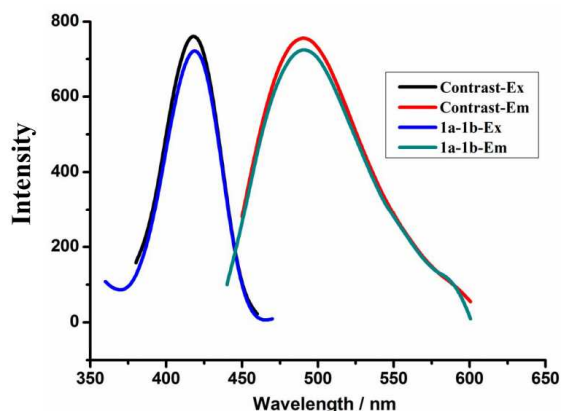


Fig. 5. Excitation and emission spectra of mixtures of 1-DMF / 1-CHCl₃ or contrast mixtures of 1-DMF fresh CHCl₃ solvent.

Conclusions

In summary, we have successfully presented a non-interpenetrated 3D chiral porous framework by introducing rod-shaped SBUs constructed by connections of carboxylate and tetratopic pyridyl ligands to metal centers. The compound is built by three types of 2₁ helices along c-axis, which are right-handed ones (P1, P2) and left-handed one (M1). Besides it can be sensing for small molecules. The fluorescence intensity and maximum emission peaks both greatly depend on the different interactions with solvents. The sensing behaviors are different for non-protonic and protonic solvents. Deeper mechanism is to be studied further.

This work was supported by grants from the Natural Science Foundation of China (Nos. 21371092; 91022011), National Basic Research Program of China (2010CB923303).

Notes and references

^a State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, P.R. China. Fax: 86-25-83314502; E-mail: zhenghg@nju.edu.cn;

^b Xuancheng Campus, Hefei University of Technology, Xuancheng, 242000, Anhui, P. R. China

^c College of Chemistry and Chemical Engineering, State Key Laboratory of Materials-oriented Chemical Engineering, Nanjing Tech University Nanjing 210009, P.R. China

† Electronic Supplementary Information (ESI) available: experimental section, crystal data, XRD, TG data, IR, UV-vis, bond lengths (Å) and angles (deg). CCDC-1021084 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

- 1 R. T. Woodward, L. A. Stevens, R. Dawson, M. Vijayaraghavan, T. Hasell, I. P. Silverwood, A. V. Ewing, T. Ratvijitvech, J. D. Exley, S. Y. Chong, F. Blanc, D. J. Adams, S. G. Kazarian, C. E. Snape, T. C. Drage and A. I. Cooper, *J. Am. Chem. Soc.*, 2014, **136**, 9028-9035; J. Teufel, H. Oh, M. Hirscher, M. Wahiduzzaman, L. Zhechkov, A. Kuc, T. Heine, D. Denysenko and D. Volkmer, *Adv. Mater.*, 2013, **25**, 635-639.
- 2 C. Wang, J. L. Wang and W. Lin, *J. Am. Chem. Soc.*, 2012, **134**, 19895-19908; S. H. Shinpei Hasegawa, Ryotaro Matsuda, Shuhei Furukawa, and Y. K. Katsunori Mochizuki, and Susumu Kitagawa, *J. Am. Chem. Soc.*, 2007 **129**, 2607-2614; Y. Liu, W. Xuan and Y. Cui, *Adv. Mater.*,

- 2010, **22**, 4112-4135.
- 3 M. Zhang, G. Feng, Z. Song, Y. P. Zhou, H. Y. Chao, D. Yuan, T. T. Tan, Z. Guo, Z. Hu, B. Z. Tang, B. Liu and D. Zhao, *J. Am. Chem. Soc.*, 2014, **136**, 7241-7244; J. J. Gassensmith, J. Y. Kim, J. M. Holcroft, O. K. Farha, J. F. Stoddart, J. T. Hupp and N. C. Jeong, *J. Am. Chem. Soc.*, 2014, **136**, 8277-8282; L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105-1125.
- 4 H. J. Son, S. Jin, S. Patwardhan, A. S. Roy, S. Manirul Islam and S. Kumar, *Chem. Eur. J.* 2013, **19**, 16607-16614; S. Dang, X. Min, W. Yang, F. Y. Yi, H. You and Z. M. Sun, *Chem. Eur. J.* 2013, **19**, 17172-17179; P. F. Shi, B. Zhao, G. Xiong, Y. L. Hou and P. Cheng, *Chem. Commun.*, 2012, **48**, 8231-8233; X. Q. Zhao, P. Cui, B. Zhao, W. Shi and P. Cheng, *Dalton Trans.* 2011, **40**, 805-819; B. Zhao, X. Y. Chen, Z. Chen, W. Shi, P. Cheng, S. P. Yan and D. Z. Liao *Chem. Commun.*, 2009, 3113-3115.
- 5 P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Ferey, R. E. Morris and C. Serre, *Chem. Rev.*, 2012, **112**, 1232-1268; D. Liu, R. C. Huxford and W. Lin, *Angew. Chem. Int. Ed. Engl.*, 2011, **50**, 3696-3700.
- 6 N. F. Sciortino, K. R. Scherl-Gruenwald, G. Chastanet, G. J. Halder, K. W. Chapman, J. F. Letard and C. J. Kepert, *Angew. Chem. Int. Ed.*, 2012, **51**, 10154-10158.
- 7 R. Saha, B. Joarder, A. S. Roy, S. Manirul Islam and S. Kumar, *Chem. Eur. J.* 2013, **19**, 16607-16614; S. Dang, X. Min, W. Yang, F. Y. Yi, H. You and Z. M. Sun, *Chem. Eur. J.* 2013, **19**, 17172-17179; P. F. Shi, B. Zhao, G. Xiong, Y. L. Hou and P. Cheng, *Chem. Commun.*, 2012, **48**, 8231-8233; X. Q. Zhao, P. Cui, B. Zhao, W. Shi and P. Cheng, *Dalton Trans.* 2011, **40**, 805-819; B. Zhao, X. Y. Chen, Z. Chen, W. Shi, P. Cheng, S. P. Yan and D. Z. Liao *Chem. Commun.*, 2009, 3113-3115.
- 8 N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 1504-1518.
- 9 L. Qin, Z. M. Ju, Z. J. Wang, F. D. Meng, H. G. Zheng and J. X. Chen, *Cryst. Growth Des.*, 2014, **14**, 2742-2746; L. Qin, M. D. Zhang, Q. X. Yang, Y. Z. Li and H. G. Zheng, *Cryst. Growth Des.*, 2013, **13**, 5045-5049.
- 10 Z. W. Mao, F. W. Heinemann, G. Liehr and R. Eldik, *J. Chem. Soc., Dalton Trans.* 2001, 3652-3662; J. P. Naskar, M. G. B. Drew, A. Hulme, D. A. Tocher and D. Datta, *CrystEngComm* 2005, **7**, 67-70. D. F. Sun, Y. X. Ke, D. J. Collins, G. A. Lorigan and H. C. Zhou, *Inorg. Chem.*, 2007, **46**, 2725-2734.
- 11 C. A. Bauer, T. V. Timofeeva, T. B. Settersten, B. D. Patterson, V. H. Liu, B. A. Simmons and M. D. Allendorf, *J. Am. Chem. Soc.*, 2007, **129**, 7136-7144.
- 12 J. H. Wang, M. Li and D. Li, *Chem. Sci.*, 2013, **4**, 1793-1801; S. Gao, N. Koshizaki, H. Tokuhisa, E. Koyama, T. Sasaki, J. K. Kim, J. Ryu, D. S. Kim and Y. Shimizu, *Adv. Funct. Mater.*, 2010, **20**, 78-86; M. A. Rawashdeh-Omary, M. D. Rashdan, S. Dharanipathi, O. Elbjairami, P. Ramesh and H. V. Dias, *Chem. Commun.*, 2011, **47**, 1160-1162; J. Pang, E. J. P. Marcotte, C. Seward, R. S. Brown and S. Wang, *Angew. Chem.*, 2001, **113**, 4166-4169; S. Das and P. K. Bharadwaj, *Inorg. Chem.*, 2006, **45**, 5257-5259; E. Cariati, X. Bu and P. C. Ford, *Chem. Mater.*, 2000, **12**, 3385-3391; F. Sun, Z. Yin, Q. Q. Wang, D. Sun, M. H. Zeng and M. Kurmoo, *Angew. Chem., Int. Ed.* 2013, **52**, 4538-4543; M. H. Zeng, Y. X. Tan, Y. P. He, Z. Yin, Q. Chen and M. Kurmoo, *Inorg. Chem.*, 2013, **52**, 2353-2360.