

RSC Advances



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. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this 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.

COMMUNICATION

Selective pyridine recognition by a imidazole dicarboxylate-based 3D cadmium(II) MOF[†]

Cite this: DOI: 10.1039/x0xx00000x

Zhifang Yue, Zhenna Chen, Minjie Yao, Haili Wang and Gang Li*

Received 00th May 2014,
Accepted 00th May 2014

DOI: 10.1039/x0xx00000x

www.rsc.org/

One new 3D coordination polymer (1) composed of left- and right-handed helices containing [Cd₈(*p*-ClPhHIDC)₁₂(4,4'-bipy)₆] cages shows selective pyridine recognition, with a visual colour change from pearl to pink under ultraviolet irradiation.

Luminescent MOFs have attracted an upsurge interest due to their highly sensitive response to small molecules and potential applications in chemical sensors.¹⁻⁴ Because some guest molecules within MOFs can emit and/or induce luminescence, the MOFs can be used to probe local environment, structure, and guest species.⁵⁻⁷ As a new type of sensing materials, the luminescent MOFs have a bright promise.⁸ Thus, the design of efficient fluorescence MOFs has become an important goal.

It is well known that the most practical and convenient sensor candidates are naked-eye colorimetric ones. So far, only a handful MOFs that exhibit guest-responsive naked-eye colorimetric properties after incorporating certain guest species (including cation, anion and neutral molecule) have been described.⁵⁻⁷ The most common form of signal transduction in luminescent MOFs is quenching, or enhancing occasionally.⁹⁻¹⁵ But in this paper, we report an extremely scarce case, guest molecule pyridine engender blue-shift of the MOF excitation and emission, which is inherently more attractive than luminescence quenching and enhancing because analyte uptake can be read out as an increase in the intensity of luminescence at the peak of the shifted emission band.¹⁶

Furthermore, there are only several examples of imidazole dicarboxylate-based complexes as anion or cation sensors.¹⁷⁻¹⁹ There is no example of imidazole dicarboxylate-based MOFs as small molecular sensor. Based on the above points, herein, we selected a newly designed imidazole dicarboxylate compound, 2-(4-chlorophenyl)-1*H*-imidazole-4,5-dicarboxylic acid (*p*-ClPhH₃IDC), to react with cadmium metal to prepare a new 3D MOF, {[Cd₂(*p*-ClPhHIDC)₂(4,4'-bipy)]·H₂O}_n (4,4'-bipy = 4,4'-bipyridine) (**1**). The coordination features of the *p*-ClPhH₃IDC ligand have been investigated by theoretical (supporting information, Scheme S1) and experimental methods. More important, polymer **1** not only shows

elaborate crystallographical structure, but also indicates interesting selectively recognizing for pyridine.

Colourless cubic blocks crystals of **1** were obtained via the solvothermal reaction of Cd(NO₃)₂ with *p*-ClPhH₃IDC and 4,4'-bipy ligands in the solution of EtOH/H₂O at 155°C for 96 h. It was formulated as {[Cd₂(*p*-ClPhHIDC)₂(4,4'-bipy)]·H₂O}_n based on IR, thermal gravimetric analysis (TGA) (see the supporting information, Fig. S1), elemental analysis and single-crystal X-ray diffraction studies, and the phase purity of bulk products was confirmed from powder X-ray diffraction (PXRD). The existence of the “Solvent Accessible VOIDS” in polymer **1** is owing to the unstable of the crystal. We guess that maybe the solvent molecule is escaping as the determining process. That is to say, at the beginning of the determination, some solvent may exist, but they are slowly escaping as the determination going. Indeed, we have not used the Squeeze. It should be noted that the free water molecule in compound **1** is confirmed by elemental and thermal analyses. That is to say, although the solvent water molecules are escaping as the determination going, the free water molecules can be determined by other methods, such as elemental and thermal analyses. The IR spectrum of **1** displays characteristic absorption bands for carboxylate, imidazole and phenyl units. The carboxyl can be observed from the absorption bands in the frequency range 1556 cm⁻¹ as a result of ν_{as}(COO⁻) and 1465 cm⁻¹ as ν_s(COO⁻) vibrations, respectively. Compound **1** also shows broad absorption band in the range of 3400–3500 cm⁻¹, which indicates the presence of the ν_{O-H} stretching frequencies of water molecules. TGA indicated that the framework of **1** was thermally stable up to 107.3 °C.

The single-crystal X-ray diffraction result revealed that **1** crystallized in the tetragonal space group *I4₁/a*, and presented an exquisite mesomer 3D framework. The asymmetric unit of complex **1** consists of one Cd(II) cation, one *p*-ClPhHIDC²⁻ anion and one half of 4,4'-bipy ligands. Each Cd(II) ion has a distorted octahedron [CdO₃N₃] geometry, which is defined by three individual *p*-ClPhHIDC²⁻ and one 4,4'-bipy ligands (Fig. S2).

Each *p*-CIPhHIDC²⁻ ligand adopts a μ_3 -*kN*,*O*:*kO*:*kN'*,*O'* fashion (supporting information, Scheme S2), and bridges Cd(II) ions to form left- and right-handed helical chains along the *a*-axis. The intra-chain distance of two adjacent Cd(II) ions is 6.7042(3) Å. As shown in Fig. 1a, the carboxyl groups act as the linkers and combine two types of helical chains to be a mesochain with the distance of two adjacent Cd(II) ions in different types of helical chains is 3.8786(2) Å. Interestingly, *via* the further bridged by carboxyl groups and 4,4'-bipy among the helical chains, an exquisite mesomer 3D framework structure is revealed to us (Fig. S3). Interestingly, the irregular cage, [Cd₈(*p*-CIPhHIDC)₁₂(4,4'-bipy)₆], composed of eight Cd(II) ions, twelve *p*-CIPhHIDC²⁻ ligands and six 4,4'-bipy is emerged (Fig. 1b), and the eight Cd atoms are not in the same plane. The total accessible volume within the crystal is calculated as 28.5% by the program PLATON. Additionally, the intermolecular hydrogen bonds, [O(2)–H(2A)...O(1)] (Table S3), make a contribution to the stability of **1**.

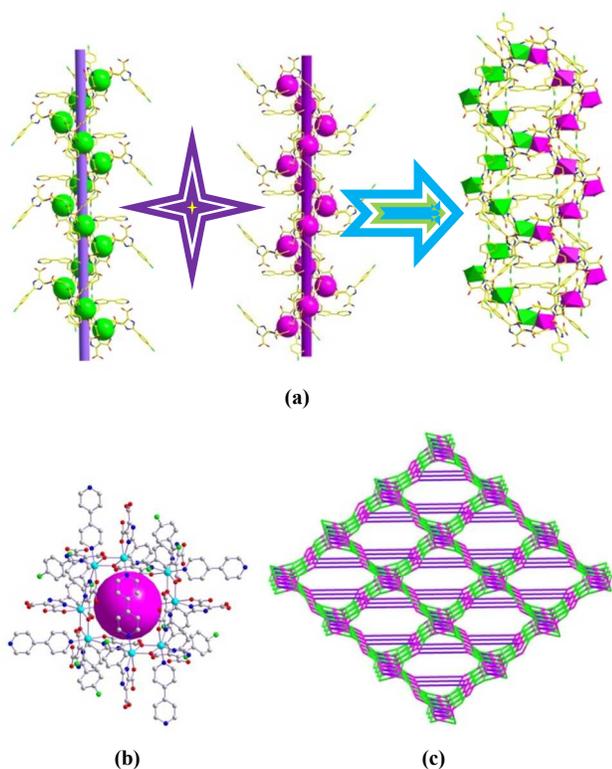


Fig. 1 (a) The double helical which is composed of the left-handed and right-handed helical chains along the *a*-axis. (Cd(II) in the left-handed helical chains, green; Cd(II) in the right-handed helical chains, violet). (b) View of the cage [Cd₈(*p*-CIPhHIDC)₁₂(4,4'-bipy)₆] in **1**. (c) The 3D topological net observed in **1** along the *b*-axis.

To understand the crystal structure well, each 4,4'-bipy in **1** can be regarded as a two-connected linker, each *p*-CIPhHIDC²⁻ ligand linking three Cd atoms can be represented by a 3-connected unit and each Cd atom is surrounded by three *p*-CIPhHIDC²⁻ and one 4,4'-bipy ligands, which can be represented by a 4-connected unit. Therefore, compound **1** can be simplified as a (3, 4)-connected topology with a point symbol of (4.7⁴.10)(4.7²) (Fig. 1c).

As mentioned in the above descriptions, **1** has two remarkable

structural features: being a 3D Cd(II) MOF and containing [Cd₈(*p*-CIPhHIDC)₁₂(4,4'-bipy)₆] cages. The two features showed that its luminescence properties can be explored as small molecule recognition. Therefore, we selected the small molecular organic solvents as guest species to detect its sensing properties.

As depicted in Fig. S4, polymer **1** shows luminescence with the emission maximum at 468 nm by selective excitation at 367 nm, which is attributed to the ligand-centered π - π^* transitions, since the Cd²⁺ ion is difficult to oxidize or to reduce due to its d¹⁰ configuration, as reported for other similar complexes with N-donor ligands.²²⁻²⁴

Upon immersing the crystalline samples of **1** into these solvents for 10 h, for example, methanol, ether, acetone, THF, acetonitrile, DMF and pyridine, it is interesting to find that **1** shows selective recognition to pyridine, with a visual color change from pearl to pink, under the excitation of a standard laboratory UV lamp at 254 nm (Fig. 2a), while other solvents fail to induce obvious color change discerned by naked eyes. In the spectra there is about 111 nm blue-shift of the emission band induced by pyridine, which is the largest shift in response to these solvents. Also, the luminescence intensity is largely enhanced, while other solvent molecules have no distinct effect to **1** (Fig. 2b). The similar case can be observed from the excitation spectra (Fig. 2c). That is to say, after interacted with pyridine, the excitation and emission spectra of **1** are strongly affected.

In order to elucidate the possible mechanism for such photoluminescence changing by the pyridine molecule of **1**, PXRD was employed to monitor the structure changes during different solvent treatment. As shown in Fig. 2d, the measured patterns of polymer **1** incorporated with different organic solvents are in good agreement with the simulated pattern from the single-crystal data except pyridine. XRPD studies clearly indicated that pyridine has been immobilized into polymer **1**, coincided with above. Furthermore, the EA, TGA and IR analyses of **1** immersed in pyridine have been investigated (see the supporting information, Figs. S1 and S7). Based on the TGA and EA analyses, we suspect that the formula of **1** immersed in pyridine is {[Cd₂(*p*-CIPhHIDC)₂(4,4'-bipy)]·2py·H₂O}_n (py = pyridine). The IR analyses of **1** (before and after immersed in pyridine) indicated that the location of peaks changed on certain degree. Importantly, the most prominent variation is the peak at 1684 cm⁻¹ disappeared. We speculate that in polymer **1**, the -COOH groups of the *p*-CIPhHIDC²⁻ ligand expressed some sort of nature of C=O, so the peak located 1684 cm⁻¹ arises. After soaking in pyridine, pyridine molecule may seize the H atom of -COOH group, and made the -COO⁻ group to form a symmetric conjugated system, and thus the peak at 1684 cm⁻¹ disappeared. That is to say, because pyridine has suitable size and N donor, which could be introduced in the polymeric system, and interacted with the -COOH groups of the imidazole dicarboxylate ligand, and further change the crystal structure of **1**. Consequently, intramolecular charge transfer (ICT) have taken place,²⁵ which makes the changes of the excitation and emission spectra of **1** after soaked in pyridine. Unfortunately, when crystallographic **1** immersed in pyridine, the crystal became opacity, so we could not

acquire its crystal structure by the single-crystal X-ray diffraction method.

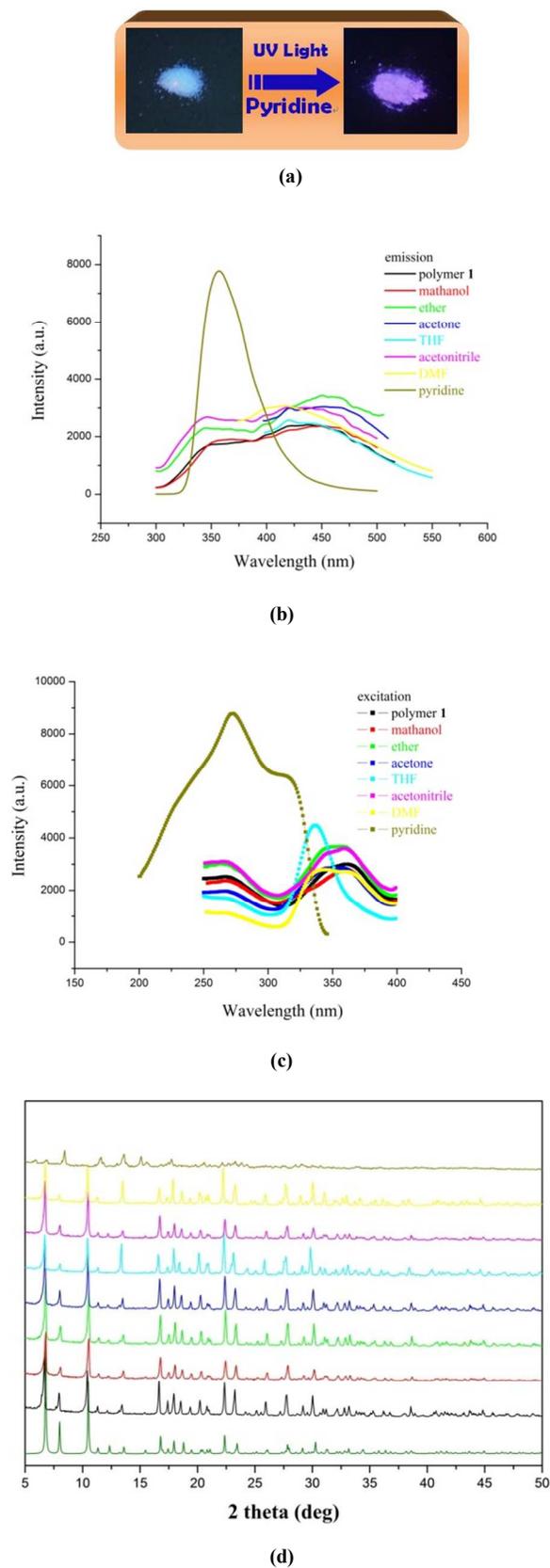


Fig. 2 (a) The color change of soaking **1** in pyridine. (b) Normalized solid-state emission and (c) excitation spectra of **1** immersed in different solvents. (d) The structural variations for **1** revealed by powder X-ray diffraction. Simulated data (olive), original sample (black), methanol (red), ether (green), acetone (blue), THF (cyan), acetonitrile (magenta), DMF (yellow) and pyridine (dark yellow). (e) The solid-state UV-Vis spectra of **1** immersed in different solvents at room temperature.

For further evidence, their solid-state ultraviolet absorption spectra have been investigated at room temperature. As shown in Fig. 2e, the absorption spectra are similar as the polymer **1** except pyridine; each of which shows a maximal absorption at around 253 nm, which can be assigned to $\pi-\pi^*$ excitations of *p*-ClPhH₃IDC. Polymer **1** immersed in pyridine also has an extra absorption peak at 311 nm, meanwhile, the absorption peak intensity receded significantly. This is to say, when soaked **1** in pyridine, it produced a new conjugated absorption band. Obviously, this is may be due to the existence of pyridine in polymer **1**.

To verify the selective recognition to pyridine, 2-methylpyridine, 2-acetylpyridine and benzene have been chosen to justify the selectivity. Performing the same step that the crystalline sample of **1** was immersed into these three different solvents for 10 h, the results show a apparent difference between these three solvents and pyridine in solid-state luminescent emission and excitation spectra (see the supporting information, Fig. S5).

In conclusion, an interesting 3D Cd(II) MOF, $\{[Cd_2(p\text{-ClPhHIDC})_2(4,4'\text{-bipy})\cdot H_2O]\}_n$, has been successfully synthesized and structurally characterized. In this compound, the left- and right-handed helical chains are linked into a 3D charming framework. Immersing the samples into different organic solvents, polymer **1** shows selective recognition to pyridine based on its specific pore size and pore surface characteristics, with a visual color change from pearl to pink, which is a rare instance. This result suggests that the imidazole dicarboxylate plays an important role in the photoluminescence variations of the title complex in response to guest pyridine. It is to be expected that more related microporous Cd-MOFs need to prepare to explore their sensing properties.

We gratefully acknowledge the financial support by the National Natural Science Foundation of China (21341002, 21071127 and J1210060), and Program for New Century Excellent Talents in University (NCET-10-0139) and the Natural Science Foundation of Henan Education Department (13A150655).

Notes and references

College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, Henan, P. R. China. Fax: 0086-371-67781764; E-mail: gangli@zzu.edu.cn.

† Electronic Supplementary Information (ESI) available: [Crystallographic data for **1** in CIF formats. Details of synthetic procedures, selected bond distances and angles.]. See DOI: 10.1039/b000000x/. CCDC no. 982162 for complex **1**.

‡ *Crystallographic data:* For **1**: C₁₆H₉CdClN₃O₄, *M* = 455.11, Tetragonal, space group *I*₄/a, *a* = 22.0734(10) Å, *b* = 22.0734(10) Å, *c* = 16.1233(14) Å, $\alpha = 90.00^\circ$, $\beta = 90.00^\circ$, $\gamma = 90.00^\circ$, *V* = 7855.8(8) Å³, *Z* = 16, $\mu = 1.270 \text{ mm}^{-1}$, *D*_c = 1.539 Mg m⁻³, *F*(000) = 3568, 4508 unique (*R*_{int} = 0.0414), *R*₁ = 0.0467, *wR*₂ = 0.1275 [*I* > 2σ(*I*)], GOF = 1.111. The intensity data were collected on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. All absorption corrections were performed by using the SADABS program. The structure was solved by direct methods, and all non-H atoms were subjected to anisotropic refinement by full-matrix least squares on *F*² using the SHELXTL program.

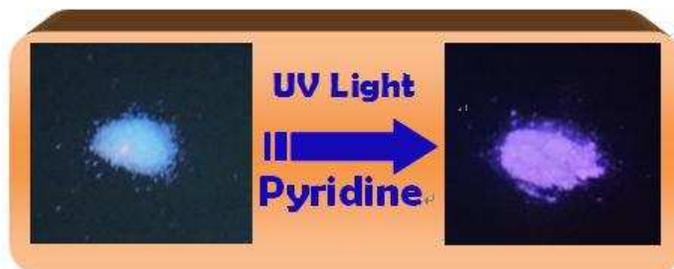
- M. D. Allendorf, C. A. Bauer, R. K. Bhaktaa and R. J. T. Houka, *Chem. Soc. Rev.* 2009, **38**, 1330.
- Y. J. Cui, Y. F. Yue, G. D. Qian and B. L. Chen, *Chem. Rev.* 2012, **112**, 1126.
- L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. V. Duyne and J. T. Hupp, *Chem. Rev.* 2012, **112**, 1105.
- C. Wang, D. M. Liu and W. B. Lin, *J. Am. Chem. Soc.* 2013, **135**, 13222.
- B. Liu, *J. Mater. Chem.* 2012, **22**, 10094.
- J. P. Ma, Y. Yu and Y. B. Dong, *Chem. Commun.* 2012, **48**, 2946.
- Y. Yu, J. P. Ma and Y. B. Dong, *CrystEngComm.* 2012, **14**, 7157.
- J. H. Cui, Z. Z. Lu, Y. Z. Li, Z. J. Guo and H. G. Zheng, *Chem. Commun.* 2012, **48**, 7967.
- Z. C. Hu, B. J. Deiberta and J. Li, *Chem. Soc. Rev.* 2014, Advance Article DOI: 10.1039/C4CS00010B.
- X. Liu, Q. Lin, T. B. Wei and Y. M. Zhang, *New J. Chem.* 2014, **38**, 1418.
- Y. J. Cui, H. Xu, Y. F. Yue, Z. Y. Guo, J. C. Yu, Z. X. Chen, J. K. Guo, Y. Yang, G. D. Qiao and B. L. Chen, *J. Am. Chem. Soc.* 2012, **134**, 3979.
- J. Wahsner and M. Seitz, *Inorg. Chem.* 2013, **52**, 13301.
- Z. Y. Guo, H. Xu, S. Q. Su, J. F. Cai, S. Dang, S. C. Xiang, G. D. Qian, H. J. Zhang, O. Michael and B. L. Chen, *Chem. Commun.* 2011, **47**, 5551.
- D. Shyamal, S. Debasish, B. Chanchal, D. Supriya and B. Sujoy, *Dalton Trans.* 2010, **39**, 4162.
- H. Xu, F. Liu, Y. J. Cui, B. L. Chen and G. D. Qian, *Chem. Commun.* 2011, **47**, 3153.
- L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.* 2012, **112**, 1105.
- Y. H. Zheng, C. L. Tan, Q. M. Wang and C. C. Zhang, *Solid State Sci.* 2011, **13**, 1687.
- S. Das, D. Saha, C. Bhaumik, S. Dutta and S. Baitalik, *Dalton Trans.* 2010, **39**, 17.
- S. L. Cai, S. R. Zheng, J. Fan, T. T. Xiao, J. B. Tan and W. G. Zhang, *Inorg. Chem. Commun.* 2011, **14**, 937.
- M. W. Guo, N. Chen, Z. F. Yue, Y. Zhang and G. Li, *CryEngComm.* 2012, **14**, 4955.
- C. J. Wang, T. Wang, L. Li, B. B. Guo, Y. Zhang, Z. F. Xiong and G. Li, *Dalton Trans.* 2013, **42**, 1715.
- Y. J. Mu, J. H. Fu, Y. J. Song, Z. Li, H. W. Hou and Y. T. Fan, *Cryst. Growth Des.* 2011, **11**, 2183.
- L. F. Ma, M. L. Han, J. H. Qin, L. Y. Wang and M. Du, *Inorg. Chem.*, 2012, **51**, 9431.
- L. Qin, J. S. Hu, Y. Z. Li and H. G. Zheng, *Cryst. Growth Des.* 2012, **12**, 403.
- J. K. Sun, X. H. Jin, L. X. Cai and J. Zhang, *J. Mater. Chem.* 2011, **21**, 17667.

Illustration

Selective pyridine recognition by a imidazole dicarboxylate-based 3D cadmium(II) MOF†

Zhifang Yue, Zhenna Chen, Minjie Yao, Haili Wang and Gang Li*

A graphical contents entry



One fresh 3D polymer (**1**) composed of left- and right-handed helices containing $[\text{Cd}_8(\text{p-CIPhHIDC})_{12}(4,4'\text{-bipy})_6]$ cages shows selective pyridine recognition, with a visual colour change from pearl to pink under ultraviolet irradiation.