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Cluster-based metal–organic framework as sensitive and selective luminescent probes for sensing nitro explosives

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One new cluster-based metal–organic frameworks, namely, $[\text{Cd}_{2.5}\text{Na}(\text{NTB})_2(\text{DMF})_4] \cdot 3\text{DMF}$ (**1**) ((NTB = 4,4',4''-nitrilotrisbenzoic acid; DMF = N, N-dimethylformamide) have been successfully obtained by employing a C₃ symmetric ligand. In **1**, the NTB links two different metal centers (single metal and Cd₃ cluster) to form two kinds of 1D chains, which linked through carboxylate O atom of the NTB ligand to give rise to a 3D framework. Moreover, desolved **1** can be well dispersed in different solvents, which demonstrate distinct solvent-dependent luminescent spectra with emission intensities significantly quenched toward nitrobenzene (NB) and 2,4,6-trinitrophenol (TNP). The results reveal that **1** could be applied as a fluorescence sensor for TNP with high sensitivity and selectivity.

Introduction

The design and synthesis of novel metal-organic frameworks (MOFs) have attracted considerable attention owing to their fascinating structural topologies, as well as the realization of their potential for use in magnetism, catalysis, gas storage, molecular recognition and optical properties, etc.^{1,2} Compared with single metal ions, the coordination geometry and positions of polynuclear clusters have more directionality and selectivity. Moreover, MOFs based on metal cluster as SBU are generally more robust because they can maintain the framework integrity after the removal of guest molecules. Therefore, the utilization of metal clusters as secondary building blocks (SBUs) has proved to be a feasible method to construct unusual coordination polymers with unique network topologies and desirable properties.^{3,4} More efforts have therefore been made on this field: for example, higher nuclearity clusters, octahedral $\text{Zn}_4(\mu_4\text{-O})(\text{CO}_2)_6$ clusters and cuboctahedral $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$ clusters, can be used as nodes by linking linear bridging organic ligands to form $[\text{Zn}_4(\mu_4\text{-O})(\text{bdc})_3]$ (MOF-5) and $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bdc})_{12}$ (UiO-66).⁵

In the past two decades, the detection of nitro compounds has drawn great interest due to its importance in homeland security and environmental safety.⁶ The most commonly nitro aromatics are nitrobenzene (NB), 1,3-dinitrobenzene (1,3-DNT), 2,4,6-Trinitrotoluene (TNT) and 2,4,6-trinitrophenol (TNP), and so on, and they are also categorized as plastic explosives.⁷ During commercial production and use, TNP is released into the environment, leading to the contamination of soil and aquatic systems. During mammalian metabolic processes, TNP transforms into picramic acid (2-amino-4,6-dinitrophenol), which has ten times more mutagenic activity than TNP.⁸ Detection of explosives by

fluorescence quenching methods employing suitable chemical sensors has been proven to be very effective. Metal organic frameworks (MOFs) have been shown to have high sensitivity and selectivity towards nitro explosives due to their high binding strength to the nitroaromatic compounds as electron donors.⁹ Considering the above, there is an urgent need to develop sensitive and reliable MOF sensors for nitro explosives, especially for TNP.

Following the above consideration, we report one new MOFs based on polynuclear cadmium cluster SBUs, namely, $[\text{Cd}_{2.5}\text{Na}(\text{NTB})_2(\text{DMF})_4] \cdot 3\text{DMF}$ (**1**), which is structurally characterized by single-crystal X-ray diffraction. In compound **1**, the NTB links two different metal centers (single metal and Cd₃ cluster) to form two 1D chains (A and B chain), which linked through O atom of the NTB, to give rise to a 3D framework. Considering metal-organic frameworks constructed from d¹⁰ metal ions and conjugated organic linkers are promising candidates for potential photoactive materials, luminescent properties of activated **1a** dispersed in different solvents have been investigated systematically. Notably, it exhibits high sensitivity for 2,4,6-trinitrophenol (TNP) with K_{sv} constant $2.8 \times 10^4 \text{ M}^{-1}$ through luminescence quenching experiments.

Experimental section

General information

All chemical materials were purchased from commercial sources and used without further purification. The FT-IR spectra were recorded from KBr pellets in the range 4000–400

cm^{-1} on a Mattson Alpha-Centauri spectrometer. XRPD patterns were recorded on a Siemens D5005 diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation in the range of $3\text{--}60^\circ$ at a rate of $5^\circ/\text{min}$. The C, H, and N elemental analyses were conducted on a Perkin-Elmer 2400CHN elemental analyzer. TG curves were performed on a Perkin-Elmer TG-7 analyzer heated from room temperature to 1000°C at a ramp rate of $5^\circ\text{C}/\text{min}$ under nitrogen. The photoluminescence spectra were measured on a Perkin-Elmer FLS-920 Edinburgh Fluorescence Spectrometer.

Crystal structure determination

Single-crystal X-ray diffraction data for **1** were collected on a Bruker Apex CCD II area-detector diffractometer with graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at $296(2) \text{ K}$. Absorption corrections were applied using multi-scan technique. Their structures were solved by the direct method of SHELXS-97 and refined by full-matrix least-square techniques with the SHELXL-97 program.¹⁰ The crystal data and structure refinement results of **1** are summarized in Table S1. CCDC 1056264 (**1**) contain the supplementary crystallographic data for this paper.

Synthesis of $[\text{Cd}_{2.5}\text{Na}(\text{NTB})_2(\text{DMF})_4]\cdot 3\text{DMF}$ (**1**)

The mixture of $\text{CdCl}_2\cdot 6\text{H}_2\text{O}$ (45 mg, 0.2 mmol), and NTB (18 mg, 0.05 mmol) in 3 mL of *N,N*-Dimethylformamide (DMF) and 2 drops of NaOH (2M) was sealed in a 15 mL vial and heated to 100°C for 3 days, and then cooled to room temperature. The light yellow crystals were obtained, washed with ethanol, and dried at room temperature (Yield: 60%). Anal. Calcd for $\text{C}_{63}\text{H}_{73}\text{N}_9\text{O}_{19}\text{NaCd}_{2.5}$: C 48.37; H 4.70; N 8.06. Found: C 48.01; H 4.48; N 7.72. IR (KBr, cm^{-1}): 3068.90 (w), 630.69 (w), 3421.78 (w), 436.82 (w), 2928.55 (w), 1014.44 (w), 714.57 (w), 536.11 (w), 675.89 (w), 1095.20 (m), 1174.04 (m), 857.49 (m), 783.34 (m), 1272.76 (m), 1506.10 (s), 1538.73 (s), 1671.14 (s), 1314.99 (s), 1592.78 (s), 1389.46 (s).

Activation of **1a**

The samples **1** were immersed in CH_2Cl_2 for 24 h, and the extracts were decanted. Fresh CH_2Cl_2 was subsequently added, and the crystals were allowed to stay for an additional 24 h to remove the nonvolatile dimethylformamide (DMF). After the removal of dichloromethane by decanting, the activated samples **1a** were obtained by drying under a dynamic vacuum at 80°C overnight.

The solvent sensing experiment

The solvent sensing experiment has been performed as follows: finely ground samples of **1a** was immersed in different organic solvents (3 mL), treated by ultrasonication for 30 minutes, and then aged to form stable emulsions before fluorescence was measured.

Results and discussion

Crystal structure description

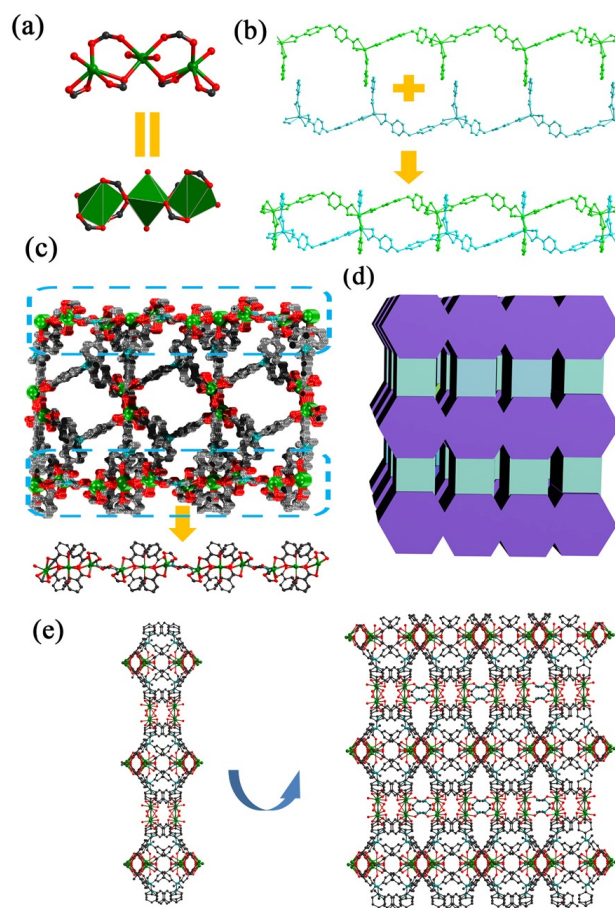


Fig. 1 (a) Polyhedral view of the coordination environment of the $\{\text{Cd}_3(\text{CO}_2)_6\}$ cluster. (b) The view of the square-shaped cavity formed by 1D A chains. (c) 3D framework in the sequential order of AAB along the *b* axis. (d) Schematic representations and (e) View of the 3D “vase” structure of **1** along the *c* axis.

Crystal structure of $[\text{Cd}_{2.5}\text{Na}(\text{NTB})_2(\text{DMF})_4]\cdot 3\text{DMF}$ (**1**)

Single-crystal X-ray determination reveals that compound **1** contains paddle-wheel trinuclear $\{\text{Cd}_3(\text{CO}_2)_6\}$ secondary building units, which are further connected via O atoms from NTB to result in a 3D coordination framework. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with the asymmetric unit consisting of two and a half Cd(II) ions, one Na ion and two NTB ligands and four coordinated DMF molecules. As shown in Fig. 1, the Cd(II) cations exhibit three different coordination geometries: Cd1 is six-coordinated by four oxygen atoms (O1, O6) from four individual NTB ligands, leaving the remaining coordination sites occupied by two DMF molecules ($\text{Cd-O} = 2.301(10)\text{--}2.283(11) \text{ \AA}$). Each of the two symmetry-related terminal Cd2 atoms is bound to five carboxylate O atoms (O1, O2, O3, O4, O5) from three NTB ligands, one oxygen atom (O02) from DMF to form a distorted octahedral geometry. The Cd-O bond distances range from $2.199(12)$ to $2.459(10) \text{ \AA}$. Cd3, different to other two Cd ions, six-coordinated by five carboxylate O atoms (O7, O9, O10, O11, O12) from three NTB ligands and one O atom from DMF molecule ($\text{Cd-O} = 2.263(11)\text{--}2.384(12) \text{ \AA}$). The three Cd

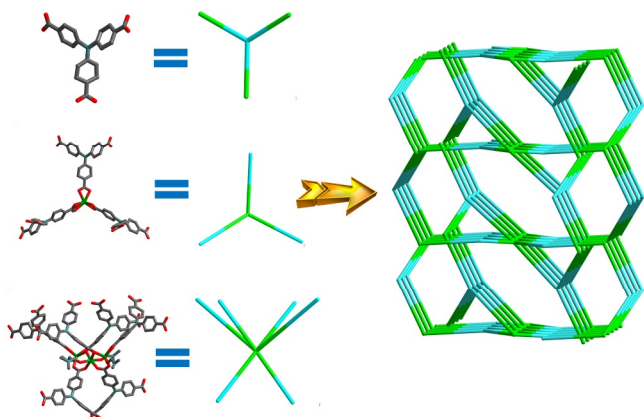


Fig. 2 The (3, 3, 3, 6)-connected network with the point symbol of $\{4.8^2\}_2\{4^2.8^5.10^8\}\{8^2.10\}_2\{8^3\}_2$.

atoms in the sequence of Cd2-Cd1-Cd2, are bridged by six carboxylate groups to form a trinuclear $\{Cd_3(CO_2)_6\}$ SBU with the paddle-wheel structure, and the adjacent Cd1-Cd2 distance is 3.95 Å. In **1**, the NTB ligands show two different coordination modes. L^a adopts $\mu^3-\eta^1:\eta^1:\eta^1:\eta^1:\eta^1$ chelating bidentate coordination mode to connect three Cd^{II} ions; meanwhile L^b adopts $\mu^5-\eta^1:\eta^2:\eta^1:\eta^1:\eta^1:\eta^0$ coordination mode to connect five Cd^{II} ions (Fig. S3). The NTB links single metal center Cd3 into a 1-D chain (A chain), two of which forming a square-shaped cavity (Fig. 1b). The Cd_3 cluster units are connected by carboxylate O of NTB to form a 1D chain that extends along the b axis (B chain). The B chains containing $\{Cd_3(CO_2)_6\}$ SBU are linked infinitely through O atom of the NTB (Fig. 1c), in the sequential order of AAB, which gives rise to a 3D “vase” framework (Fig. 1e). Meanwhile, the total solvent-accessible volume in this noninterpenetrated framework accounts for approximately 25.9 % of the whole crystal volume as estimated by PLATON.¹¹

From the viewpoint of structural topology, the NTB ligand linked with three $\{Cd_3(CO_2)_6\}$ SBUs as 3-connected node, and the trinuclear $\{Cd_3(CO_2)_6\}$ SBUs act as 6-connected nodes, the whole 3D structure exhibits a (3, 3, 3, 6)-connected net with the point symbol of $\{4.8^2\}_2\{4^2.8^5.10^8\}\{8^2.10\}_2\{8^3\}_2$ (Fig. 2).¹²

Powder XRD patterns and Thermal properties

In order to confirm the phase purity of **1**, we measured the powder X-ray diffraction at room temperature (Fig. S5). The experimental X-ray diffraction patterns compared to the corresponding simulated patterns calculated based on single crystal diffraction data, which indicates that all the samples were in a pure phase. To study the thermal stability of the compound, thermogravimetric analyses (TGA) were performed on polycrystalline samples under nitrogen atmosphere with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ (Fig. S6). The TGA curve of **1** reveals the first weight loss 14.0 % is from 25 to 263 °C and corresponds to the loss of three DMF molecules, then starts to decompose after 263 °C. The architectural stability and permanent porosity of **1a** were confirmed by measuring the N_2 adsorption experiments at 77 K, the N_2 adsorption amount

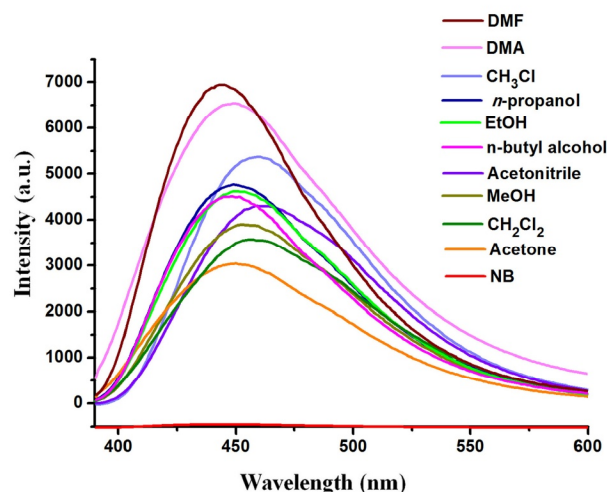


Fig. 3 Comparisons of the luminescence intensity of **1a**-solvent emulsions at room temperature (excited at 369 nm) (solvent = CH_3Cl , DMA, CH_2Cl_2 , DMF, n -propanol, EtOH, n -butyl alcohol, Acetonitrile, MeOH, Acetone and Nitrobenzene).

of **1a** at 1 bar was about $30.2\text{ cm}^3\text{g}^{-1}$ (Fig. S7).

Luminescence behaviors and sensing properties

To examine the luminescence properties of MOFs, the photoluminescence spectra of **1** and the free ligand in the solid state were investigated. The NTB ligand presents blue luminescence with emission maxima at 450 nm ($\lambda_{ex} = 379\text{ nm}$), this may be assigned to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transition. Compounds **1** exhibits one broad band with the maximum emission peaks centered at ca. 445 nm ($\lambda_{ex} = 370\text{ nm}$) (Fig. S8). Such fluorescent emissions may be tentatively assigned to the intraligand $\pi^*-\pi$ emission, since similar emission at 448 nm ($\lambda_{ex} = 366\text{ nm}$) was observed for the free NTB ligand.

The luminescence property of **1a** in different solvent emulsions was investigated. The solvents used are CH_3Cl , CH_2Cl_2 , N, N-dimethylformamide (DMF), N, N-dimethylacetamide (DMA), acetonitrile, ethanol, methanol, acetone, n -propanol, n -butyl alcohol, and nitrobenzene (NB). The most interesting feature is that its PL spectrum is largely dependent on the solvent molecules. The intensity of **1a** in DMA/DMF is almost unchanged, and diminished in other solvents. Particularly in the case of nitrobenzene, the luminescence property exhibits the most significant quenching effects (Fig. 3). Such solvent-dependent luminescence properties are of interest for the sensing of nitrobenzene solvent molecules. To examine the sensitivity of fluorescence quenching by NB, a batch of emulsions of **1a** in DMF with gradually increased nitrobenzene concentration. As seen in Fig. 4, the luminescent intensity of the emulsions significantly decreased with increasing addition of nitrobenzene. The intensity of **1a** standard emulsion decreased to 43 % at 400 ppm and 17 % at 500 ppm, which allowed us to detect small amounts of nitrobenzene in solution. The possibility of quenching mechanism is assumed to originate from the electron-withdrawing property of the nitro groups in the analytes, which

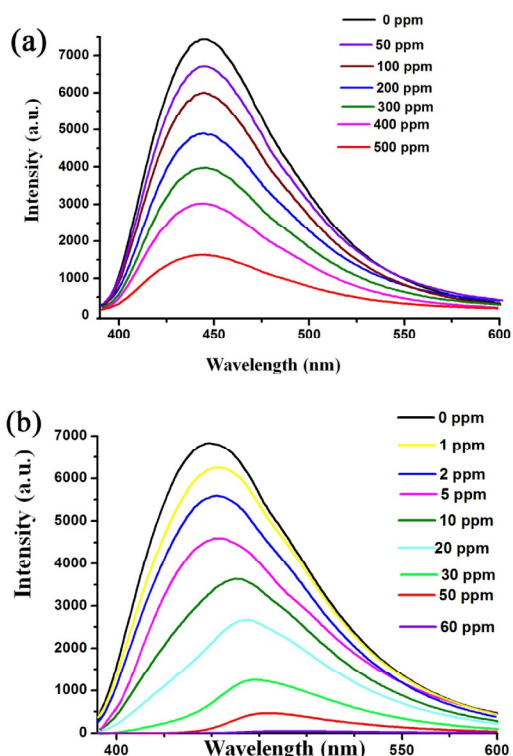


Fig. 4 (a) Emission spectra of **1a** at different nitrobenzene (NB) concentrations in DMF. (b) Emission spectra of **1a** dispersed in DMF upon incremental addition of a TNP (excited at 369 nm).

results in a significant donor–acceptor electron transfer from the ligands to the electron-donating MOF structures.¹³

To further investigate the sensing ability of **1** for TNP, the emission spectra are recorded by the gradual addition of TNP solution into a suspension of 0.3 mg of **1** dispersed in 3 mL of a DMF solution. As shown in Fig. 5, the fluorescent intensity clearly decreased with increasing TNP amount. The quenching efficiency was estimated to be 8.5% for 1 ppm of TNP, 51% for 10 ppm of TNP, and 93% for 50 ppm of TNP.

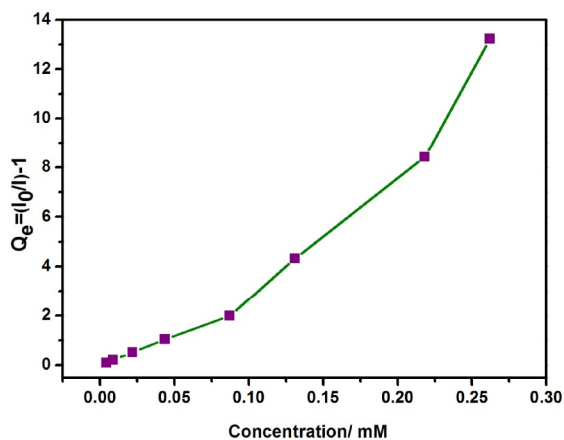


Fig. 6 The Stern-Volmer plot for TNP.

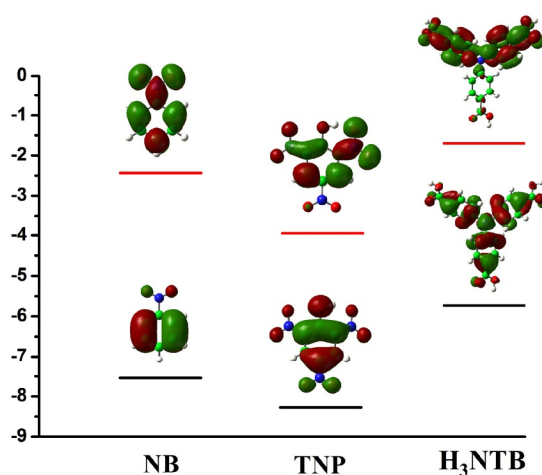


Fig. 7 Shapes of HOMO and LUMO of the molecular orbitals considered and the relative energy level investigated by the B3LYP/6-31G* method.

The fluorescence quenching efficiency was further analyzed using the Stern–Volmer (SV) equation: $(I_0/I) = K_{sv}[A] + 1$, in which I_0 is the initial fluorescence intensity without analyte, I represents the fluorescence intensity with added analyte of the molar concentration $[A]$, and K_{sv} is the quenching constant (M^{-1}).¹⁴ The SV plot for TNP was nearly linear at low concentrations and subsequently deviated from linearity, bending upwards at higher concentrations. The nonlinear nature of the SV plot of TNP may be ascribed to a self-absorption or energy transfer process.¹⁵ The quenching constant (K_{sv}) of **1** for TNP is $2.8 \times 10^4 M^{-1}$ (Fig. 6). These observations clearly demonstrate the potential of **1** as a highly selective sensor for TNP.

The luminescence quenching may be due to the photoinduced electron-transfer (PET) mechanism. The electron-transfer progress can be interpreted by inductive effect. The nitrobenzene/2,4,6-trinitrophenol with electron-deficient property can obtain an electron from excited ligand,¹⁶ which has been confirmed by molecular orbital theory.¹⁷ The frontier molecular orbitals of nitrobenzene, TNP and the ligand are calculated by density functional theory at the level of B3LYP/6-31G*.¹⁷ The LUMO of analytes (nitrobenzene and 2,4,6-trinitrophenol) are low-lying π^* -type orbital stabilized by the $-NO_2$ through conjugation, so it is lower than LUMO of ligand (Fig. 7). Therefore, the excited state electrons can transfer from MOF to nitrobenzene, which leads to luminescence quenching.

Conclusions

One new cadmium metal–organic frameworks constructed from C_3 symmetric NTB ligand have been successfully obtained under solvothermal conditions. Compounds **1** display diverse structural features including a (3, 3, 3, 6)-connected net with the point symbol of $\{4.8^2\}_2\{4^2.8^5.10^8\}\{8^2.10\}_2\{8^3\}_2$ constructed from $\{Cd_3(CO_2)_6\}$ SBU. Especially, **1** can display distinct solvent-dependent PL emissions and detect TNP with high selectivity and sensitivity. The fluorescence quenching mechanism is in consequence of photoinduced electron transfer

from electron-rich MOF framework to electron-withdrawing 2,4,6-trinitrophenol.¹⁸ This work provides a new perspective into the design of highly sensitive sensor with multifunction applications.

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Notes and references

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Electronic Supplementary Information (ESI) available: Experimental details, XRPD, TG, IR, solid photoluminescence (PL) spectra and additional figures. CCDC 1056264 (1). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

- 1 (a) G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray and J. D. Cashion, *Science*, 2002, **298**, 1762; (b) Z. Wang, G. Chen and K. Ding, *Chem. Rev.*, 2009, **109**, 322; (c) N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2005, **38**, 176; (d) S. Kitagawa and R. Matsuda, *Coord. Chem. Rev.*, 2007, **251**, 2490; (e) X. L. Hu, C. Y. Sun, C. Qin, X. L. Wang, H. N. Wang, E. L. Zhou, W. E. Li and Z. M. Su, *Chem Commun.*, 2013, **49**, 3564; (f) A. Y. Robin and K. M. Fromm, *Coord. Chem. Rev.*, 2006, **250**, 2127; (g) M. P. Suh, Y. E. Cheon and E. Y. Lee, *Coord. Chem. Rev.*, 2008, **252**, 1007; (h) X. L. Hu, F. H. Liu, H. N. Wang, C. Qin, C. Y. Sun, Z. M. Su and F. C. Liu, *J. Mater. Chem. A.*, 2014, **2**, 14827.
- 2 (a) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. V. Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105; (b) X. L. Wang, C. Qin, S. X. Wu, K. Z. Shao, Y. Q. Lan, S. Wang, D. X. Zhu, Z. M. Su and E. B. Wang, *Angew. Chem.*, 2009, **121**, 5395; *Angew. Chem., Int. Ed.*, 2009, **48**, 5291.
- 3 (a) U. Schubert, *Chem. Soc. Rev.*, 2011, **40**, 575; (b) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705; (c) D. J. Tranchemontagne, J. L. Mendoza-Cortés, M. O'Keeffe and O. M. Yaghi, *Chem. Soc. Rev.*, 2009, **38**, 1257; (d) J. J. Perry IV, J. A. Perman and M. J. Zaworotko, *Chem. Soc. Rev.*, 2009, **38**, 1400.
- 4 (a) Q. Chen, W. Xue, B. Y. Wang, M. H. Zeng and X. M. Chen, *CrystEngComm.*, 2012, **14**, 2009; (b) M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4900.e
- 5 (a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science*, 2002, **295**, 469; (b) J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850.
- 6 (a) M. E. Germain and M. J. Knapp, *Chem. Soc. Rev.*, 2009, **38**, 2543; (b) Y. Salinas, R. Martinez-Manez, M. D. Marcos, F. Sancenon, A. M. Costero, M. Parra and S. Gil, *Chem. Soc. Rev.*, 2012, **41**, 1261; (c) S. Pramanik, C. Zheng, X. Zhang, T. J. Emge and J. Li, *J. Am. Chem. Soc.*, 2011, **133**, 4153; (d) B. Liu, *J. Mater. Chem.*, 2012, **22**, 10094.
- 7 (a) c) S. J. Toal, W. C. Trogler, *J. Mater. Chem.*, 2006, **16**, 2871; (b) Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815; (c) H. Wang, W. Yang and Z.-M. Sun, *Chem.-Asian J.*, 2013, **8**, 982; (d) Z. Hao, X. Song, M. Zhu, X. Meng, S. Zhao, S. Su, W. Yang, S. Song and H. Zhang, *J. Mater. Chem. A.*, 2013, **1**, 11043.
- 8 a) G. He, H. Peng, T. Liu, M. Yang, Y. Zhang and Y. Fang, *J. Mater. Chem.*, 2009, **19**, 7347; (b) P. G. Thorne and T. F. Jenkins, *Field Anal. Chem. Technol.*, 1997, **1**, 165; (c) K. M. Wollin and H. H. Dieter, *Arch. Environ. Contam. Toxicol.*, 2005, **49**, 18.
- 9 (a) B. Gole, S. Shanmugaraju, A. K. Bar and P. S. Mukherjee, *Chem. Commun.*, 2011, **47**, 10046; (b) D. Tian, Y. Li, R.-Y. Chen, Z. Chang, G.-Y. Wang and X.-H. Bu, *J. Mater. Chem. A.*, 2014, **2**, 1465; (b) A. K. Chaudhari, S. S. Nagarkar, B. Joarder and S. K. Ghosh, *Cryst. Growth Des.*, 2013, **13**, 3716.
- 10 G. M. Sheldrick, SHELXS 97, *Program for Crystal Structure Analysis*, University of Göttingen, Germany, 1997.
- 11 A. L. Spek, PLATON, A multipurpose crystallographic tool Utrecht University, The Netherlands, 2003.
- 12 (a) V. A. Blatov and A. P. Shevchenko, *TOPOS-Version 4.0 Professional (Beta Evaluation)*, Samara State University, Samara, Russia, 2006; (b) V. A. Blatov, A. P. Shevchenko and V. N. Serezhkin, *J. Appl. Crystallogr.*, 2000, **33**, 1193. (c) V. A. Blatov, *Struct. Chem.*, 2012, **23**, 955; (d) E. V. Alexandrov, V. A. Blatov, A. V. Kochetkov and D. M. Proserpio, *CrystEngComm.*, 2011, **13**, 3947.
- 13 (a) Q. Zhang, A. Geng, H. Zhang, F. Hu, Z.-H. Lu, D. Sun, X. Wei and C. Ma, *Chem. Eur. J.*, 2014, **20**, 4885; (b) K. S. Asha, K. Bhattacharyya and S. Mandal, *J. Mater. Chem. C.*, 2014, **2**, 10073.
- 14 (a) J. C. Sanchez and W. C. Trogler, *J. Mater. Chem.*, 2008, **18**, 3143; (b) J. C. Sanchez, S. A. Urbas, S. J. Toal, A. G. DiPasquale, A. L. Rheingold and W. C. Trogler, *Macromolecules*, 2008, **41**, 1237; (c) C. Zhang, L. Sun, Y. Yan, J. Li, X. Song, Y. Liu and Z. Liang, *Dalton Trans.*, 2015, **44**, 230.
- 15 (a) H. Sohn, M. J. Sailor, D. Magde and W. C. Trogler, *J. Am. Chem. Soc.*, 2003, **125**, 3821; (b) Y. Salinas, R. Martinez-Manez, M. D. Marcos, F. Sancenon, A. M. Costero, M. Parra and S. Gil, *Chem. Soc. Rev.*, 2012, **41**, 1261; (c) S. R. Zhang, D. Y. Du, J. S. Qin, S. L. Li, W. W. He, Y. Q. Lan and Z. M. Su, *Inorg. Chem.*, 2014, **53**, 8105.
- 16 (a) H. Wang, W. Yang and Z. M. Sun, *Chem.-Asian J.*, 2013, **8**, 982; (b) D. Ma, B. Li, X. Zhou, Q. Zhou, K. Liu, G. Zeng, G. Li, Z. Shi and S. Feng, *Chem. Commun.*, 2013, **49**, 8964; (c) B. Gole, A. K. Bar and P. S. Mukherjee, *Chem. Commun.*, 2011, **47**, 12137.
- 17 (a) G. Y. Wang, C. Song, D.-M. Kong, W.-J. Ruan, Z. Chang and Y. Li, *J. Mater. Chem. A.*, 2014, **2**, 2213; (b) Y. C. He, H. M. Zhang, Y. Y. Liu, Q. Y. Zhai, Q. T. Shen, S. Y. Song and J. F. Ma, *Cryst. Growth Des.*, 2014, **14**, 3174.
- 18 (a) Y.-N. Gong, L. Jiang and T.-B. Lu, *Chem. Commun.*, 2013, **49**, 11113; (b) M. Guo and Z. M. Sun, *J. Mater. Chem.*, 2012, **22**, 15939; (c) S. S. Nagarkar, A. V. Desai and S. K. Ghosh, *Chem. Commun.*, 2014, **50**, 8915; (d) B. Gole, A. K. Bar, and P. S. Mukherjee, *Chem. Eur. J.*, 2014, **20**, 13321; (e) I. H. Park, R. Medishetty, J. Y. Kim, S. S. Lee and J. J. Vittal, *Angew. Chem. Int. Ed.*, 2014, **53**, 5591.