

## A surfactant-thermal method to prepare four new three-dimensional heterometal–organic frameworks†

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Junkuo Gao,<sup>a</sup> Mi He,<sup>b</sup> Zhi Yi Lee,<sup>a</sup> Wenfang Cao,<sup>a</sup> Wei-Wei Xiong,<sup>a</sup> Yongxin Li,<sup>b</sup> Rakesh Ganguly,<sup>b</sup> Tom Wu<sup>c</sup> and Qichun Zhang<sup>\*a</sup>

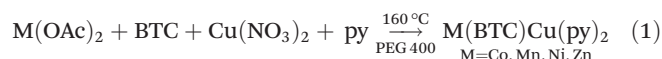
**Here, we report on a surfactant-thermal method to prepare four new 3-D crystalline heterometal–organic frameworks (HMOFs). The results indicate that our new strategy for growing crystalline materials in surfactant media has great potential for the synthesis of novel MOFs with various structures.**

Due to their unique properties and ‘designable’ structures, metal–organic frameworks (MOFs) have been receiving a lot of attention in the past two decades. In fact, MOFs have already been demonstrated to have a broad range of applications such as gas storage and separation,<sup>1</sup> catalysis,<sup>2</sup> magnetism<sup>3</sup> and sensors.<sup>4</sup> Generally, MOFs can be synthesized *via* hydrothermal and solvothermal methods.<sup>5</sup> However, the low boiling point and high vapour pressure of common solvents have posed a limitation on further exploring novel structures. Recently, ionic liquids (ILs) have been considered to be greener solvents to prepare MOF materials and other crystalline materials due to their lower vapour pressure and higher thermal stability.<sup>6</sup> Unfortunately, their high cost restricts their usage in large-scale synthesis of MOFs. Thus, new synthetic strategies are required for preparing crystalline MOFs with novel structures and interesting properties.

Surfactants have been widely applied in controlling the sizes and shapes of nanocrystals and the pore sizes and phases of porous materials.<sup>7</sup> Compared with organic solvents, surfactants are more thermally stable and more environmentally friendly. Meanwhile, the low or no vapour pressure of surfactants makes reactions under surfactant media available at

much higher temperatures.<sup>8</sup> In addition, surfactants possess more multifunctional properties than ILs, such as cationic, anionic, neutral, zwitterionic, acidic, basic *etc.*<sup>9</sup> More importantly, the low cost and industrial abundance of surfactants make them ideal reaction media in the fabrication of functional materials. Currently, most research groups employ surfactant media to prepare nano-materials, and it is noteworthy that using surfactants as reaction media to grow crystalline materials is unprecedented.<sup>10</sup> Recently, our group has developed a new strategy for growing crystalline materials: growing crystalline chalcogenide materials in surfactants (a surfactant-thermal method).<sup>2c,11</sup> Crystalline chalcogenides from zero-dimensional (0D) clusters to three-dimensional (3D) frameworks were successfully synthesized by using different surfactants as the reaction media. Wang *et al.* also demonstrated that surfactants could be used as templates in the synthesis of crystalline zeolite frameworks with nanosized channels.<sup>12</sup> The Janus characteristics of surfactants that contain both hydrophobic groups and hydrophilic groups may efficiently increase the solubility of metal ions and organic ligands,<sup>13</sup> making them perfect media for growing MOFs. To the best of our knowledge, reports on the synthesis of crystalline MOFs by using the surfactant-thermal method are still rare.

Heterometal–organic frameworks (HMOFs) that contain more than one kind of metal in the frameworks are widely studied in view of not only their impressive structural diversity but also their versatile applications in catalysis, sensors, luminescence and magnetism.<sup>14</sup> To date, only hydrothermal and solvothermal methods have been applied to the synthesis of HMOFs. Here, we report on the growth of crystalline HMOFs by using a surfactant-thermal method for the first time. Four new 3D crystalline HMOFs are synthesized and characterized. The magnetic properties of the HMOFs are studied in detail. In planning the synthesis, polyethylene glycol (PEG), which is widely applied in materials science and medicine and has low toxicity, biodegradability and tunable melting point, is used as the reaction solvent.<sup>15</sup>

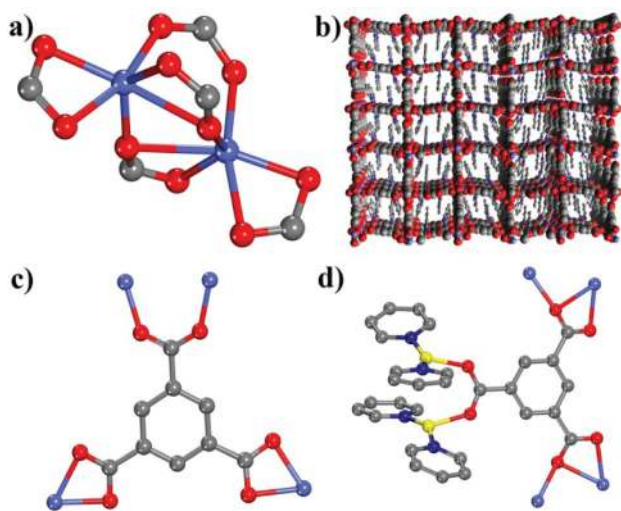


<sup>a</sup>School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore. E-mail: qczhang@ntu.edu.sg

<sup>b</sup>School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

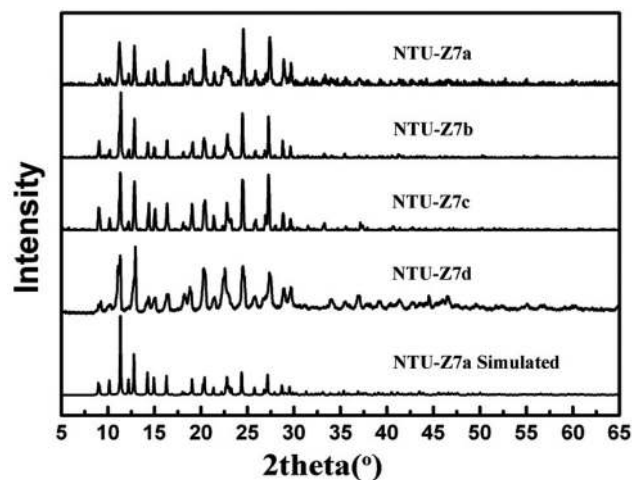
<sup>c</sup>Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, Thuwal, 23955-6900, Saudi Arabia

†Electronic supplementary information (ESI) available: Experimental details, a summary of the crystal structure and refinement details of NTU-Z7a and NTU-Z7c, IR spectra, EDX spectra and TGA spectra of HMOFs. CCDC 932108 and 932109. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51103k



**Fig. 1** (a) The bi-metal cobalt cluster and its coordination with carboxylate groups in **NTU-Z7a**. (b) The 1D channel formed in **NTU-Z7a** along the *a*-axis. (c) The coordination of BTC ligand with cobalt atoms in **NTU-Z7a**. (d) The coordination of BTC ligand with both cobalt and copper atoms in **NTU-Z7a**. C, N, O, Co and Cu atoms are shown in gray, blue, red, purple and yellow, respectively. H atoms were removed for clarity.

The reactions between metal acetate, copper nitrate, pyridine (py) and trimesic acid ( $H_3BTC$ ) in PEG 400 produced four 3D structures with the formula  $M(BTC)Cu(py)_2$  ( $M = Co$  for **NTU-Z7a**,  $Mn$  for **NTU-Z7b**,  $Ni$  for **NTU-Z7c** and  $Zn$  for **NTU-Z7d**). It is noteworthy that when PEG 400 was replaced by organic solvents such as methanol and *N,N*-dimethylformamide, no crystals were obtained for all the reaction systems.<sup>†</sup> Single crystal XRD analysis shows that **NTU-Z7a** crystallizes in the orthorhombic  $C222(1)$  space group. All the cobalt atoms displayed disordered octahedral coordinations with four carboxylate groups of BTC ligand as shown in Fig. 1a. The copper atom is three-coordinated with one oxygen atom from the carboxylate group and two pyridine molecules. The charge of Cu in **NTU-Z7a** is +1, which is derived from the charge balance of the crystals and its T-shaped trigonal coordination mode, indicating that an *in situ* reduction process occurred in the reaction. The bond distances of Cu–N and Cu–O are 1.921 Å and 2.099 Å respectively, which are quite consistent with the reported bond distances in the Cu(I) complex.<sup>16</sup> There are two crystalline independent BTC ligands in **NTU-Z7a**, one BTC is coordinated with cobalt atoms *via* all three carboxylate groups with  $\mu_2-\eta^1:\eta^1$  mode and chelating  $\eta^2$  mode (Fig. 1c), while the other BTC ligand is coordinated with cobalt atoms in  $\mu_2-\eta^2:\eta^1$  mode and connected with two  $Cu^{1+}$  atoms in  $\mu_2-\eta^1:\eta^1$  mode (Fig. 1d). The BTC ligands link the  $Co^{2+}$  atoms to form a 3D framework, where 1D channels with the dimensions of *ca.* 9.2 × 6.9 Å along the *a*-axis are observed (Fig. 1b). The py molecules coordinated with  $Cu^{1+}$  atoms fill in the 1D channels. The energy dispersive X-ray spectroscopy (EDX) analysis shows that the molar ratio of Co and Cu is about 1 : 1, which is quite consistent with the formula obtained from the crystal structure (Fig. S3<sup>†</sup>). Details of the crystal structure and refinement data



**Fig. 2** The experimental powder XRD patterns for **NTU-Z7a**, **NTU-Z7b**, **NTU-Z7c** and **NTU-Z7d**, and the simulated powder XRD patterns for **NTU-Z7a**.

are provided in ESI (Table S1<sup>†</sup>). The experimental powder XRD pattern for **NTU-Z7a** matches very well with the simulated ones that are generated on the basis of single crystal structure analysis, which confirmed the phase purity of the bulk materials (Fig. 2). The HMOFs **NTU-Z7b**, **NTU-Z7c** and **NTU-Z7d** are isostructures of **NTU-Z7a**, which can be confirmed from the similar single crystal unit cell parameters (Table 1) and the match of powder XRD patterns with **NTU-Z7a** (Fig. 2). Due to the similar crystal structures of the HMOFs as shown in Table 1, only the crystal data of **NTU-Z7a** and **NTU-Z7c** were collected and refined (Table S1<sup>†</sup>). The EDX spectra further confirmed that M ( $M = Mn$  for **NTU-Z7b**,  $Ni$  for **NTU-Z7c** and  $Zn$  for **NTU-Z7d**) and Cu (Fig. S4–S6<sup>†</sup>) have the same ratio. TGA analysis indicates that all of the HMOFs **NTU-Z7(a,b,c,d)** show quite good thermal stability (up to 230 °C, Fig. S7<sup>†</sup>).

The magnetic susceptibilities ( $\chi_M$ ) of the HMOFs **NTU-Z7a**, **NTU-Z7b** and **NTU-Z7c** were measured in the temperature range of 2–300 K. As shown in Fig. 3, the  $\chi_M$  of **NTU-Z7a**, **NTU-Z7b** and **NTU-Z7c** obeys the Curie–Weiss law over the whole temperature range. The calculated Curie constant (*C*) and Weiss constant ( $\theta$ ) for **NTU-Z7a**, **NTU-Z7b** and **NTU-Z7c** are 1.99  $cm^3 K mol^{-1}$  and  $-0.45 K$ , 1.81  $cm^3 K mol^{-1}$  and  $-4.92 K$ , and 1.51  $cm^3 K mol^{-1}$  and  $-2.95 K$ , respectively. The results indicate weak antiferromagnetic interactions between the nearest magnetic  $Co^{2+}$  ions,  $Mn^{2+}$  ions and  $Ni^{2+}$  ions in the HMOFs **NTU-Z7a**, **NTU-Z7b** and **NTU-Z7c**, respectively.

**Table 1** Cell parameters of the isostructures of the HMOF **NTU-Z7**

	<b>NTU-Z7a</b>	<b>NTU-Z7b</b>	<b>NTU-Z7c</b>	<b>NTU-Z7d</b>
<i>a</i> (Å)	12.39	12.38	12.42	12.39
<i>b</i> (Å)	15.74	15.79	15.58	15.83
<i>c</i> (Å)	19.53	19.47	19.68	19.50
<i>V</i> (Å <sup>3</sup> )	3810	3805	3808	3822
Data collection	Yes	No	Yes	No

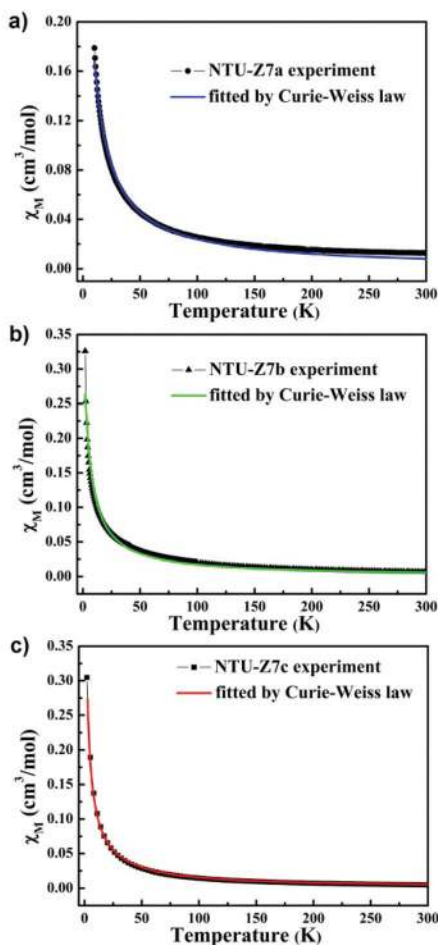


Fig. 3 Temperature dependence of magnetic susceptibility of NTU-Z7a, NTU-Z7b and NTU-Z7c.

## Conclusions

In conclusion, four new 3D crystalline HMOFs have been successfully synthesized and characterized *via* a surfactant-thermal method. Magnetic studies of HMOFs show that there are weak antiferromagnetic interactions between the nearest magnetic  $\text{Co}^{2+}$  ions,  $\text{Mn}^{2+}$  ions and  $\text{Ni}^{2+}$  ions in NTU-Z7a, NTU-Z7b and NTU-Z7c, respectively. The results indicated that our new strategy for growing crystalline materials by using a surfactant-thermal method has great potential for the synthesis of novel MOFs with various structures.

## Acknowledgements

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## Notes and references

† Data collection of crystals was carried out on a Bruker APEX II CCD diffractometer equipped with a graphite-monochromatized Mo-K $\alpha$  radiation source ( $\lambda =$

0.71073 Å). Empirical absorption was performed, and the structure was solved by direct methods and refined with the aid of a SHELXTL program package. All hydrogen atoms were calculated and refined using a riding model. The CCDC numbers for NTU-Z7a and NTU-Z7c are 932108 and 932109, respectively.

- (a) H. C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673; (b) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724; (c) M. P. Suh, H. J. Park, T. K. Prasad and D. W. Lim, *Chem. Rev.*, 2012, **112**, 782; (d) J. R. Li, J. Sculley and H. C. Zhou, *Chem. Rev.*, 2012, **112**, 869; (e) Q. P. Lin, T. Wu, S. T. Zheng, X. H. Bu and P. Y. Feng, *J. Am. Chem. Soc.*, 2012, **134**, 784.
- (a) M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.*, 2012, **112**, 1196; (b) J.-L. Wang, C. Wang and W. Lin, *ACS Catal.*, 2012, **2**, 2630; (c) G. Lu, S. Z. Li, Z. Guo, O. K. Farha, B. G. Hauser, X. Y. Qi, Y. Wang, X. Wang, S. Y. Han, X. G. Liu, J. S. DuChene, H. Zhang, Q. C. Zhang, X. D. Chen, J. Ma, S. C. J. Loo, W. D. Wei, Y. H. Yang, J. T. Hupp and F. W. Huo, *Nat. Chem.*, 2012, **4**, 310; (d) Y. X. Tan, Y. P. He and J. Zhang, *Chem. Mater.*, 2012, **24**, 4711; (e) A. Corma, H. Garcia and F. X. L. Xamena, *Chem. Rev.*, 2010, **110**, 4606.
- (a) R. X. Yao, X. Xu and X. M. Zhang, *Chem. Mater.*, 2012, **24**, 303; (b) C. M. Nagaraja, R. Haldar, T. K. Maji and C. N. R. Rao, *Cryst. Growth Des.*, 2012, **12**, 975; (c) Z. M. Wang, K. L. Hu, S. Gao and H. Kobayashi, *Adv. Mater.*, 2010, **22**, 1526; (d) M. Kurmoo, *Chem. Soc. Rev.*, 2009, **38**, 1353.
- (a) Y. J. Cui, Y. F. Yue, G. D. Qian and B. L. Chen, *Chem. Rev.*, 2012, **112**, 1126; (b) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2012, **112**, 1105; (c) H. Xu, X. T. Rao, J. K. Gao, J. C. Yu, Z. Q. Wang, Z. S. Dou, Y. J. Cui, Y. Yang, B. L. Chen and G. D. Qian, *Chem. Commun.*, 2012, **48**, 7377; (d) Y. J. Cui, H. Xu, Y. F. Yue, Z. Y. Guo, J. C. Yu, Z. X. Chen, J. K. Gao, Y. Yang, G. D. Qian and B. L. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 3979; (e) H. Yang, F. Wang, Y. X. Tan, Y. Kang, T. H. Li and J. Zhang, *Chem.-Asian J.*, 2012, **7**, 1069; (f) Y. Kang, F. Wang, J. Zhang and X. H. Bu, *J. Am. Chem. Soc.*, 2012, **134**, 17881.
- (a) F. A. A. Paz, J. Klinowski, S. M. F. Vilela, J. P. C. Tome, J. A. S. Cavaleiro and J. Rocha, *Chem. Soc. Rev.*, 2012, **41**, 1088; (b) N. Stock and S. Biswas, *Chem. Rev.*, 2011, **112**, 933; (c) S. T. Zheng, T. Wu, C. T. Chou, A. Fuhr, P. Y. Feng and X. H. Bu, *J. Am. Chem. Soc.*, 2012, **134**, 4517; (d) C.-P. Li and M. Du, *Chem. Commun.*, 2011, **47**, 5958; (e) S. T. Zheng, J. J. Bu, T. Wu, C. T. Chou, P. Y. Feng and X. H. Bu, *Angew. Chem., Int. Ed.*, 2011, **50**, 8858; (f) Y. Liu, M. J. W. Tan, F. Wei, Y. Tian, T. Wu, C. Kloc, F. Huo, Q. Yan, H. H. Hng, J. Ma and Q. Zhang, *CrystEngComm*, 2012, **14**, 75; (g) Y. Liu, L.-M. Yu, S. C. J. Loo, R. G. Blair and Q. Zhang, *J. Solid State Chem.*, 2012, **191**, 283; (h) Q. Zhang, X. Bu, Z. Lin, T. Wu and P. Feng, *Inorg. Chem.*, 2008, **47**, 9724.
- (a) H. Fu, C. Qin, Y. Lu, Z.-M. Zhang, Y.-G. Li, Z.-M. Su, W.-L. Li and E.-B. Wang, *Angew. Chem., Int. Ed.*, 2012, **51**,

- 7985; (b) E. Ahmed and M. Ruck, *Angew. Chem., Int. Ed.*, 2012, **51**, 308; (c) Y. Zhao, J. Zhang, B. Han, J. Song, J. Li and Q. Wang, *Angew. Chem., Int. Ed.*, 2011, **50**, 636; (d) R. E. Morris, *Chem. Commun.*, 2009, 2990; (e) J. Zhang, S. M. Chen and X. H. Bu, *Angew. Chem., Int. Ed.*, 2008, **47**, 5434; (f) Z. J. Lin, D. S. Wragg, J. E. Warren and R. E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 10334; (g) Z. J. Lin, A. M. Z. Slawin and R. E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 4880; (h) Q. Zhang, I. Chung, J. I. Jang, J. B. Ketterson and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2009, **131**, 9896; (i) K. Biswas, Q. Zhang, I. Chung, J.-H. Song, J. Androulakis, A. Freeman and M. Kanatzidis, *J. Am. Chem. Soc.*, 2010, **132**, 14760.
- 7 (a) L. Peng, J. Zhang, J. Li, B. Han, Z. Xue and G. Yang, *Chem. Commun.*, 2012, **48**, 8688; (b) L. B. Sun, J. R. Li, J. Park and H. C. Zhou, *J. Am. Chem. Soc.*, 2012, **134**, 126; (c) J. Wei, Q. Yue, Z. K. Sun, Y. H. Deng and D. Y. Zhao, *Angew. Chem., Int. Ed.*, 2012, **51**, 6149; (d) H. Xu, F. Liu, Y. J. Cui, B. L. Chen and G. D. Qian, *Chem. Commun.*, 2011, **47**, 3153.
- 8 S. Mourdikoudis and L. M. Liz-Marzán, *Chem. Mater.*, 2013, **25**, 1465.
- 9 (a) Y. Y. Luk and N. L. Abbott, *Curr. Opin. Colloid Interface Sci.*, 2002, **7**, 267; (b) S. Paria, C. Manohar and K. C. Khilar, *Ind. Eng. Chem. Res.*, 2005, **44**, 3091; (c) K. D. Danov, S. D. Kralchevska, P. A. Kralchevsky, K. P. Ananthapadmanabhan and A. Lips, *Langmuir*, 2004, **20**, 5445; (d) M. Mishra, P. Muthuprasanna, K. S. Prabha, P. S. Rani, A. S. Babu, I. S. Chandiran, G. Arunachalam and S. Shalini, *Int. J. PharmTech Res.*, 2009, **1**, 1354.
- 10 (a) Y. Liu, J. Goebel and Y. Yin, *Chem. Soc. Rev.*, 2013, **42**, 2610; (b) Y. Yin and A. P. Alivisatos, *Nature*, 2005, **437**, 664.
- 11 (a) W.-W. Xiong, E. U. Athresh, Y. T. Ng, J. Ding, T. Wu and Q. Zhang, *J. Am. Chem. Soc.*, 2013, **135**, 1256; (b) W.-W. Xiong, P.-Z. Li, T.-H. Zhou, A. I. Y. Tok, R. Xu, Y. Zhao and Q. Zhang, *Inorg. Chem.*, 2013, **52**, 4148.
- 12 (a) H. Y. Lin, C. Y. Chin, H. L. Huang, W. Y. Huang, M. J. Sie, L. H. Huang, Y. H. Lee, C. H. Lin, K. H. Lii, X. H. Bu and S. L. Wang, *Science*, 2013, **339**, 811; (b) Y. Liu, F. Boey, L. L. Lao, H. Zhang, Xi. Liu and Q. Zhang, *Chem.-Asian J.*, 2011, **6**, 1004–1006.
- 13 (a) N. Carrasco, R. Kretschmar, M. L. Pesch and S. M. Kraemer, *Environ. Sci. Technol.*, 2007, **41**, 3633; (b) N. Carrasco, R. Kretschmar, M. L. Pesch and S. M. Kraemer, *J. Colloid Interface Sci.*, 2008, **321**, 279.
- 14 (a) Z. G. Gu, H. C. Fang, P. Y. Yin, L. Tong, Y. Ying, S. J. Hu, W. S. Li and Y. P. Cai, *Cryst. Growth Des.*, 2011, **11**, 2220; (b) L. Liang, G. Peng, L. Ma, L. Sun, H. Deng, H. Li and W. S. Li, *Cryst. Growth Des.*, 2012, **12**, 1151; (c) P. F. Shi, B. Zhao, G. Xiong, Y. L. Hou and P. Cheng, *Chem. Commun.*, 2012, **48**, 8231; (d) B. Zhao, X. Y. Chen, Z. Chen, W. Shi, P. Cheng, S. P. Yan and D. Z. Liao, *Chem. Commun.*, 2009, 3113; (e) X. Q. Zhao, B. Zhao, S. Wei and P. Cheng, *Inorg. Chem.*, 2009, **48**, 11048; (f) X. Q. Zhao, Y. Zuo, D. L. Gao, B. Zhao, W. Shi and P. Cheng, *Cryst. Growth Des.*, 2009, **9**, 3948; (g) X.-J. Kong, H. Zhang, H.-X. Zhao, Y.-P. Ren, L.-S. Long, Z. Zheng, G. S. Nichol, R.-B. Huang and L.-S. Zheng, *Chem.-Eur. J.*, 2010, **16**, 5292.
- 15 (a) C. Morelli, P. Maris, D. Sisci, E. Perrotta, E. Brunelli, I. Perrotta, M. L. Panno, A. Tagarelli, C. Versace, M. F. Casula, F. Testa, S. Ando, J. B. Nagy and L. Pasqua, *Nanoscale*, 2011, **3**, 3198; (b) A. Dumas, C. D. Spicer, Z. Gao, T. Takehana, Y. A. Lin, T. Yasukohchi and B. G. Davis, *Angew. Chem., Int. Ed.*, 2013, **52**, 3916.
- 16 J. Tao, Y. Zhang, M. L. Tong, X. M. Chen, T. Yuen, C. L. Lin, X. Y. Huang and J. Li, *Chem. Commun.*, 2002, 1342.