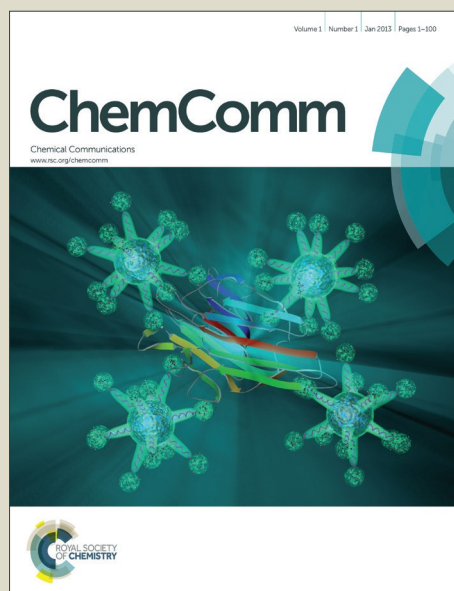


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ARTICLE TYPE

A rare three-coordinated zinc cluster-organic framework with two types of second building units

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A rare chiral 3D cluster-organic framework $\{[Zn_{17}O_5(NTB)_6(NDB)_3] \cdot 41H_2O\}_n$ (**1**) ($H_3NTB = 4,4',4''$ -nitrilotrisbenzoic acid and $H_2NDB = 4,4'$ -nitrilodibenzoic acid) was prepared and structurally characterized. Complex **1** contains two types of $[Zn_4(\mu_4-O)(COO)_6]$ and unreported $[Zn_9(\mu_3-O)_3(COO)_{12}]$ SBUs, which link bi- and tri-carboxylic acids and extend to an unprecedented (3, 6, 12)-connected framework. In addition, electronic structure calculations were performed to scrutinize the features of embedded clusters.

Metal carboxylate clusters coordination polymers, owing to their high thermostability and favouring the formation of noninterpenetrated frameworks, have been of intense interest due to their intriguing aesthetic structures and topological features,¹ as well as their promising applications in many important fields including photochemistry areas,² molecular magnetism,³ heterogeneous catalysis,⁴ and molecular sorption.⁵ As we all know, zinc carboxylate second building units (SBUs), such as di-, tri-, tetra- and pentanuclear zinc carboxylate clusters, have been widely used to build interesting networks and functional materials with multi-topic carboxylates as linkers.⁶ Usually, the expansion of the clusters favours highly-connected networks.⁷ However, the high-nuclear clusters, such as hexa-, hepta- and octanuclear zinc clusters, are rarely incorporated into infinite frameworks due to difficulties in the formation of such clusters,⁸ hence higher-connected networks are still scarce.

Recently, a great number of novel mixed-ligand metal-organic frameworks (MOFs) were reported,⁹ revealing that the combination of different ligands can result in greater tunability of structural frameworks than single ligands. Most of mixed-ligand polymers adopt N-containing ligands in metal-polycarboxylate systems, while the systems with two types of polycarboxylates are scarcely.¹⁰ The availability of different organic carboxylic acids linkers not only offer the potential for the construction of structurally diverse MOFs, but also offer the opportunity to create functionalized frameworks. We are interested in the development of MOFs constructed from semirigid carboxylic acids, which exhibit excellent coordination ability and can free rotate the arms to meet the requirement of coordination geometries in the assembly processing. Here, two semirigid carboxylic acids ($H_3NTB = 4,4',4''$ -nitrilotrisbenzoic acid and $H_2NDB = 4,4'$ -nitrilodibenzoic acid) are selected to construct a chiral (3, 6, 12)-connected functionalized MOF with novel SBUs $[Zn_4(\mu_4-O)(COO)_6]$ and $[Zn_9(\mu_3-O)_3(COO)_{12}]$.

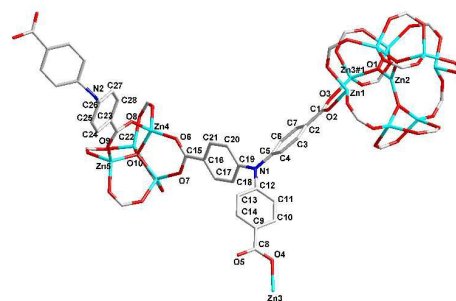
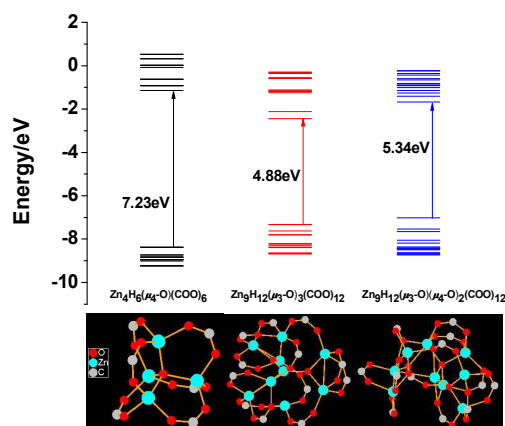


Fig. 1. Coordination environment of the Zn(II) ions in **1**, which contains $[Zn_4(\mu_4-O)(COO)_6]$ and $[Zn_9(\mu_3-O)_3(COO)_{12}]$ SBUs.

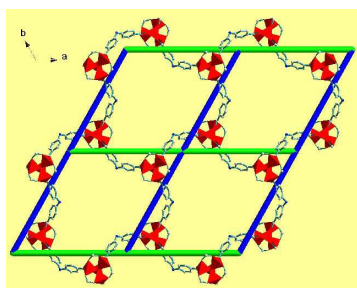
Solvothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$ with H_3NTB and H_2NDB in H_2O medium afforded a metal-organic framework $\{[Zn_{17}O_5(NTB)_6(NDB)_3] \cdot 41H_2O\}_n$ (**1**). Complex **1** crystallizes in the chiral space group $R\bar{3}2$, the asymmetric unit consists of five crystallographically independent Zn(II) ions, one NTB^{3-} , a half NDB^{2-} , two oxygen anions, and lattice H_2O molecules (Fig. 1). Interestingly, there are two types of clusters $[Zn_4(\mu_4-O)(COO)_6]$ (SBU1) and $[Zn_9(\mu_3-O)_3(COO)_{12}]$ (SBU2) in complex **1**, SBU1 is built by Zn_4 and Zn_5 connecting μ_4-O and six carboxylate groups, which is always reported in zinc carboxylate frameworks. SBU2 is constructed by Zn_1 , Zn_2 and Zn_3 linking μ_3-O and twelve carboxylate groups. Interestingly, there are two types of three-coordinated Zn environments in SBU2, Zn_2 center is connected by three μ_3-O atoms to form a $[Zn(\mu_3-O)_3]$ plane ($Zn_2-O1 = 1.740 \text{ \AA}$). Zn_1 has a similar coordination environment to Zn_2 , which is coordinated by three carboxylate oxygen atoms forming a triangle pyramid ($Zn_1-O2 = 1.948 \text{ \AA}$). As far as we know from CCDC database, three-coordinated Zn environments are quite rare in zinc coordination polymers, only two examples with three coordinated $[ZnO_3]$ plane have been reported previously,¹¹ while no examples with triangle pyramid coordination mode have been reported. Two types of three-coordinated Zn environments in one SBU is rather unique, the formation may be attribute to the unique configuration of $[Zn_9(\mu_3-O)_3(COO)_{12}]$. While Zn_3 is coordinated by three carboxylate oxygen atoms ($Zn_3-O3 = 1.922$, $Zn_3-O4 = 1.914$, $Zn_3-O5 = 1.973 \text{ \AA}$) from three NTB^{3-} , one oxygen atom ($Zn_3-O1 = 1.892 \text{ \AA}$) from a μ_3-O to form tetrahedral geometry. Although all the Zn-O bond lengths are comparable to those documented values in the previous literatures, the average Zn_2-O1 bond length is obviously shorter than those of Zn_1-O2 and Zn_3-O . Zn_1 , Zn_2 and Zn_3 connect each other via three μ_3-O and twelve carboxylate groups forming an unique unreported

nonnuclear $[\text{Zn}_9(\mu_3\text{-O})_3(\text{COO})_{12}]$ cluster. It is notable that the $\text{Zn}_2 \cdots \text{Zn}_1 \cdots \text{Zn}_2$ are almost in line and the distance between adjacent Zn atoms is 3.139 Å, which may be the one reason that why Zn2 and Zn1 are three coordination.

- 5 $[\text{Zn}_9(\mu_3\text{-O})_3(\text{COO})_{12}]$ (SBU2) as an unique cluster arouses our great interests. In order to scrutinize the nature of SBUs, electronic structure calculations were performed for model clusters $\text{Zn}_4\text{H}_6(\mu_4\text{-O})(\text{COO})_6$ and $\text{Zn}_9\text{H}_{12}(\mu_3\text{-O})_3(\text{COO})_{12}$ (see ref. S3-S5 of ESI). Some important informations are obtained: (1) Natural electron configurations (NEC) and NBO charges reveal that Zn ($3d^{9.89-9.93}4s^{0.27-0.32}$ and 1.7e) in the zinc carboxylate clusters tend to display the oxidation state of +2 and μ -oxygen ($2s^{1.9}2p^{5.8}$ and $\sim -1.8e$) display more negative oxidation state than oxygen ($2s^{1.7}2p^{5.1}$ and $-0.9e$) in the carboxylate groups (-2 versus -1). (2) Frequency calculations disclose that the cluster $\text{Zn}_4\text{H}_6(\mu_4\text{-O})(\text{COO})_6$ is a minimum. To our surprise, $\text{Zn}_9\text{H}_{12}(\mu_3\text{-O})_3(\text{COO})_{12}$ belongs to a high order saddle point (-59.1i, -59.1i, -30.0i, -30.0i, -16.6i), destabilized by 56 kcal/mol relative to another configuration $\text{Zn}_9\text{H}_{12}(\mu_3\text{-O})(\mu_4\text{-O})_2(\text{COO})_{12}$. It indicates that the configurations $[\text{Zn}_9(\mu_3\text{-O})_3(\text{COO})_{12}]$ are greatly stabilized by linkers or dynamically stable in the MOFs. In such a special configuration, a smaller HOMO-LUMO energy gap (Fig. 2) will favorably influence optical properties of the MOFs.



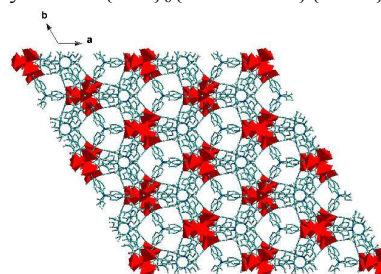
- 25 **Fig. 2.** Calculated energy diagram for clusters $\text{Zn}_4\text{H}_6(\mu_4\text{-O})(\text{COO})_6$, $\text{Zn}_9\text{H}_{12}(\mu_3\text{-O})_3(\text{COO})_{12}$, and $\text{Zn}_9\text{H}_{12}(\mu_3\text{-O})(\mu_4\text{-O})_2(\text{COO})_{12}$ by the B3LYP/6-311++G(d,p) (For clarity, hydrogen atoms are omitted.)



- 30 **Fig. 3.** A view of 2D sheet constructed by $\text{Zn}_4(\mu_4\text{-O})(\text{COO})_6$ cluster and H_2NDB , which contains 1D left-helical chains.

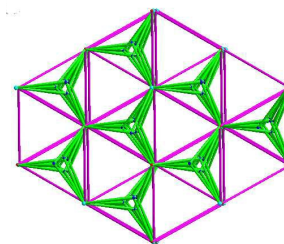
There are many left-helically chiral channels along the c axis with effective diameter of ~ 6.0 Å (Fig. 3), formed by $[\text{Zn}_4(\mu_4\text{-O})]$ core and NDB^{2-} anion, these channels are perpendicular each other. NTB^{3-} anions link $[\text{Zn}_9(\mu_3\text{-O})_3]$ and $[\text{Zn}_4(\mu_4\text{-O})]$ cores to form a 3D framework with hexagon channel. NDB^{2-} anions filled into the hexagon channels by linking $[\text{Zn}_4(\mu_4\text{-O})]$ cores (Fig. 4), and the ratio of SBU1 versus SBU2 is 2/1. From the topological

point of view, $[\text{Zn}_9(\mu_3\text{-O})_3(\text{COO})_{12}]$ cluster can be defined as a 12-connected node, $[\text{Zn}_4(\mu_4\text{-O})(\text{COO})_6]$ cluster can be defined as a 6-connected node, and NTB^{3-} as 3-connected linker. Thus, the overall framework is a (3, 6, 12)-connected 3D framework with the Schläfli symbol of $\{4.6^2\}_6\{4^6.6^{24}.7^{27}.8^9\}\{6^{12}.7^3\}_2$ (Fig. 5).



- 45 **Fig. 4.** A perspective of the 3D framework along the c axis.

Recently, only few of high nuclear zinc carboxylate frameworks have been reported. Trikalitis has reported two hexanuclear $[\text{Zn}_6(\mu_3\text{-OH})(\mu_4\text{-O})(\text{H}_2\text{O})_2(\text{CO}_2)_5]$ and heptanuclear $[\text{Zn}_7(\mu_3\text{-OH})_3(\text{CO}_2)_6]^-$ clusters-based MOF.¹² Bu group has reported a 10-connected self-penetrating framework based on pentanuclear $[\text{Zn}_5(\mu_3\text{-O})_2(\text{COO})_8]$ unit,¹³ a 14-connected framework based on heptanuclear $[\text{Zn}_7(\text{OH})_2(\text{HOME})_2(\text{OCO})_{12}]$ unit,¹⁴ and other novel clusters-based MOFs.¹⁵ As far as we know, $[\text{Zn}_9(\mu_3\text{-O})_3(\text{COO})_{12}]$ is the first examples of 12-connected nonanuclear zinc-based SBU. These high nuclear zinc carboxylate clusters could help us deeply understand the nature of clusters-based MOFs and design porous crystalline functional materials.



- 60 **Fig. 5.** Schematic representation of a (3, 6, 12)-connected $\{4.6^2\}_6\{4^6.6^{24}.7^{27}.8^9\}\{6^{12}.7^3\}_2$ 3D framework.

In order to evaluate the spontaneous resolution process, the solid-state CD spectrum in KCl matrix is determined by using bulk crystals. As seen in Fig. S1, the CD spectrum exhibits positive CD signal, revealing the formation of enantiomeric excess in crystals (Fig. S1 of ESI). X-ray powder diffraction patterns of simulated and experimental are in good agreement with each other, demonstrating the phase purity of the product (Fig. S2 of ESI). The TGA curve of **1** shows that the weight loss takes place at 35–95°C, which corresponds to the loss of free water molecules (17.05%). From then on, no weight loss is observed until 400 °C. The decomposition process ended at about 550 °C. The TAG analysis shows that complex **1** has excellent thermal stability (Fig. S3 of ESI).

75 Considering that complex **1** crystallizes in the chiral space group $R32$, the second harmonic generation (SHG) efficiency was studied. Preliminary examinations indicate that the SHG efficiency is approximately 0.5 times that of urea (an efficiency of 12 times that of KDP and an efficiency of 200 times that of quartz). The luminescent properties of H_3NTB and H_2NDB as well as complex **1** in the solid state were studied at room temperature (Fig. S4 of ESI). Emissions of the free H_3NTB and H_2NDB are observed with emission peaks at 412 nm and 411 nm, which are attributed to the $\pi^*-\pi$ or π^*-n transitions. The emission

peaks of complex **1** at 465 nm and 525 nm ($\lambda_{\text{ex}} = 370$ nm) show larger red shifts than that of H_3NTB and H_2NDB , which may be attributed to metal-to-ligand charge transfer (MLCT) or cluster-to-ligand charge transfer.¹⁶ While the high emission intensity of **1** is due to the enhanced conjugation in the ligands upon metal coordination. Furthermore, the emission decay lifetime of complex **1** was monitored and the curve is best fitted by bi-exponentials in solid.¹⁷ The emission decay lifetimes of complex **1** are: $\tau_1 = 0.97$ ns and $\tau_2 = 3.84$ ns ($\chi^2 = 1.258$) at 450 nm and $\tau_1 = 9.56$ ns and $\tau_2 = 2.56$ ns ($\chi^2 = 1.273$) at 520 nm, (Fig. S5 of ESI).

In conclusion, we have prepared and characterized a rare (3, 6, 12)-connected framework based on nonanuclear and tetranuclear zinc carboxylate clusters. The electronic structure calculations were performed to understand the nature of embedded clusters. This work demonstrates that polynuclear cluster entities as SBUs is an effective and powerful synthetic strategy in constructing high-connected MOFs, also provides a rational design of metal clusters and appropriate choices of semirigid organic linkers for constructing new MOFs in the near future. Subsequent works will be focused on the structures and properties of various metal-organic frameworks constructed by these ligands with other polynuclear metal clusters.

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Notes and references

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† Electronic Supplementary Information (ESI) available: XRD, TG data, IR, bond lengths (Å) and angles (deg) and photoluminescent data of **1** as well as computational details, calculated cartesian coordinates and summary of natural population analyses for embedded clusters. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

‡ Crystal data: for **1**: $[\text{C}_{168}\text{H}_{96}\text{N}_9\text{O}_{53}\text{Zn}_{17}]$, $M_r = 4200.17$, Trigonal, space group $R\bar{3}2$, $a = b = 23.2738(11)$ Å, $c = 33.9318(14)$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$, $V = 15917.4(13)$ Å³, $Z = 3$, $D_c = 1.314$ g·cm⁻³, $\mu(\text{Mo-K}\alpha) = 1.951$ mm⁻¹, $T = 291(2)$ K, 6967 reflections measured, 373 independent reflections ($R_{\text{int}} = 0.0493$), final $R_1 = 0.055$ ($I > 2\sigma(I)$) and final $wR(F_2) = 0.1205$. CCDC: 1036604.

1 (a) R. Sen, D. Saha, S. Koner, *Chem. Eur. J.*, 2012, **18**, 5979. (b) M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.*, 2012, **112**, 1196. (c) S. T. Zheng, T. Wu, C. Chou, A. Fuhr, P. Y. Feng, X. H. Bu, *J. Am. Chem. Soc.*, 2012, **134**, 4517. (d) H. X. Deng, S. Grunder, K. E. Cordova, C. Valenta, H. Furukawa, M. Hmadeh, F. Gandara, A. C. Whalley, Z. Liu, S. Asasina, H. Kazumori, M. O. Keeffe, J. F. Stoddart, O. M. Yaghi, *Science*, 2012, **336**, 1018.

2 (a) N. B. Shustova, A. F. Cozzolino, M. Dincă, *J. Am. Chem. Soc.*, 2012, **134**, 19596. (b) S. Hou, Q. K. Liu, J. P. Ma, Y. B. Dong, *Inorg. Chem.*, 2013, **52**, 3255.

3 (a) Y. F. Bi, X. T. Wang, B. W. Wang, W. P. Liao, X. F. Wang, H. J. Zhang, S. Gao, D. Q. Lia, *Dalton Trans.*, 2009, 2250. (b)

P. F. Shi, G. Xiong, B. Zhao, Z. Y. Zhang, P. Cheng, *Chem. Commun.*, 2013, **49**, 2338.

4 (a) P. Y. Wu, C. He, J. Wang, X. J. Peng, X. Z. Li, Y. L. An, C. Y. Duan, *J. Am. Chem. Soc.*, 2012, **134**, 14991. (b) C. F. Zhu, G. Z. Yuan, X. Chen, Z. W. Yang, Y. Cui, *J. Am. Chem. Soc.*, 2012, **134**, 8058. (c) M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.*, 2012, **112**, 1196.

5 (a) Z. Z. Lu, R. Zhang, Y. Z. Li, Z. J. Guo, H. G. Zheng, *J. Am. Chem. Soc.*, 2011, **133**, 4172. (b) C. R. Murdock, D. M. Jenkins, *J. Am. Chem. Soc.*, 2014, **136**, 10983.

6 (a) P. V. Dau, K. K. Tanabe, S. M. Cohen, *Chem. Commun.*, 2012, **48**, 9370. (b) H. Yang, F. Wang, Y. Kang, T. H. Li, J. Zhang, *Chem. Commun.*, 2012, **48**, 9424. (c) S. Henke, A. Schneemann, A. Wutscher, R. A. Fischer, *J. Am. Chem. Soc.*, 2012, **134**, 9464. (d) L. Chen, K. Tan, Y. Q. Lan, S. L. Li, K. Z. Shao, Z. M. Su, *Chem. Commun.*, 2012, **48**, 5919.

7 (a) D. W. Lim, J. W. Yoon, K. Y. Ryu, M. P. Suh, *Angew. Chem., Int. Ed.*, 2012, **51**, 9814. (b) S. Sen, N. N. Nair, T. Yamada, H. Kitagawa, P. K. Bharadwaj, *J. Am. Chem. Soc.*, 2012, **134**, 19432. (c) N. Shustova, A. F. Cozzolino, M. Dinca, *J. Am. Chem. Soc.*, 2012, **134**, 19596. (d) S. S. Mondal, A. Bhunia, A. Kelling, U. Schilde, C. Janiak, H. J. Joldt, *J. Am. Chem. Soc.*, 2014, **136**, 44.

8 (a) W. R. Lee, D. W. Ryu, W. J. Phang, J. H. Park, C. S. Hong, *Chem. Commun.*, 2012, **48**, 10847. (b) S. B. Choi, H. Furukawa, H. J. Nam, D. Y. Jung, Y. H. Jhon, A. Walton, D. Book, M. O. Keeffe, O. M. Yaghi, J. Kim, *Angew. Chem., Int. Ed.*, 2012, **51**, 8791. (c) Y. Ling, M. L. Deng, Z. X. Chen, B. Xia, X. F. Liu, Y. T. Yang, Y. M. Zhou, L. H. Weng, *Chem. Commun.*, 2013, **49**, 78. (d) J. H. Cui, Y. Z. Li, Z. J. Guo, H. G. Zheng, *Chem. Commun.*, 2013, **49**, 555.

9 (a) H. Sato, R. Matsuda, M. H. Mir, S. Kitagawa, *Chem. Commun.*, 2012, **48**, 7919. (b) D. H. Hong, M. P. Suh, *Chem. Commun.*, 2012, **48**, 9168. (c) W. Y. Cao, W. M. Yan, R. Cao, K. Williams, A. Salas, L. Wojtas, X. D. Shi, S. Q. Ma, *Chem. Commun.*, 2012, **48**, 8898.

10 (a) k. Koh, A. G. Wong-Foy, A. J. Matzger, *J. Am. Chem. Soc.*, 2011, **133**, 15005. (b) M. Higuchi, K. Nakamura, S. Horike, Y. Hijikata, N. Yanai, T. Fukushima, J. Kim, K. Kato, M. Takata, D. Watanabe, S. Oshima, S. Kitagawa, *Angew. Chem., Int. Ed.*, 2012, **51**, 8369. (c) D. Kim, M. S. Lah, *CrystEngComm.*, 2013, **15**, 9491.

11 (a) M. Kunert, M. Brauer, O. Klobes, H. Górls, E. Dinjus, E. Anders, *Eur. J. Inorg. Chem.*, 2000, 1803. (b) J. S. Lum, P. E. Chen, A. L. Rheingold, L. H. Doerr, *polyhedron*, 2013, **58**, 218.

12 E. Neofotistou, C. D. Malliakas, P. N. Trikalitis, *Chem. Eur. J.*, 2009, **15**, 4523.

13 K. H. He, W. C. Song, Y. W. Li, Y. Q. Chen, X. H. Bu, *Cryst. Growth Des.*, 2012, **12**, 1064.

14 K. H. He, Y. W. Li, Y. Q. Chen, W. C. Song, X. H. Bu, *Cryst. Growth Des.*, 2012, **12**, 2730.

15 (a) D. Tian, Q. Chen, Y. Li, Y. H. Zhang, Z. Chang, X. H. Bu, *Angew. Chem. Int. Ed.*, 2014, **53**, 837. (b) Q. Chen, Z. Chang, W. C. Song, H. Song, H. B. Song, T. L. Hu, X. H. Bu, *Angew. Chem. Int. Ed.*, 2013, **52**, 11550.

16 E. Y. Lee, S. Y. Jang, M. P. Suh, *J. Am. Chem. Soc.*, 2004, **127**, 6374.

17 X. Li, H. L. Sun, X. S. Wu, X. Qiu, M. Du, *Inorg. Chem.*, 2010, **49**, 1865.