Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2016, **26**, 52–53

Mendeleev Communications

An unusual 2D → 3D polythreading framework based on (4)-c sql networks with arms: synthesis, structure and luminescence

Zhi-Guo Kong,* Sheng-Nan Guo, Xin-Yu Zhao and Xue An

Key Laboratory of Preparation and Applications of Environmental Friendly Materials, Ministry of Education,
College of Chemistry, Jilin Normal University, Siping 136000, P. R. China. Fax: +86 0434 329 1890;
e-mail: kongzhiguo1977@sohu.com

DOI: 10.1016/j.mencom.2016.01.020

An exceedingly rare 2D → 3D polythreading framework based on (4)-c sql networks with arms, $[Cd(L)(bipy)_2]_n$, has been prepared and characterized by X-ray diffraction analysis, and its solid state luminescence has been examined at room temperature.

The entangled coordination polymers are of interest because of their potential applications as functional materials and their aesthetic architectures and topologies.[1–3] Among the entangled systems, interpenetrating nets, as a main system of entanglements, have been well documented and discussed.[4–8] Along with the coordination polymers, other types of entangled topologies, such as polycatenation, interdigitated and polythreaded architectures, are also known.[9–12] Note that the rarely reported polythreaded and interdigitated architectures are completely different from the interpenetration and polycatenation structures. Their differences can be found *via* separating the individual nets forming the overall entangled motifs.[13–15] For the interpenetrated and polycatenated arrays, the individual motifs could be obtained through breaking chemical bonds.[16] In contrast, to separate the individual motifs it is not necessary to break chemical bonds for the interdigitated and polythreaded architectures. Thus far, only a very limited fascinating 0 → 1D and 1D → 2D polythreaded examples have been reported.[4–6] Especially, the assembly for 2D → 3D polythreaded framework remains exceedingly rare.[12–17]

The basic design element of the 2D → 3D polythreaded framework is the synthesis of a 2D network with arms and the insertion of arms through those grids of networks. The rigid ligand 4,4′-bipyridine (bipy) has a proven ability to give 2D networks involving grids. 3,5-Dinitrosalicylic acid (H_2L), as a rigid ligand, is a good candidate for an arm in the assembly. Thus, it may be possible to yield this new class of polythreaded frameworks through combining two types of different precursors. We report here a fascinating 2D (4)-c sql network structure with arms of $[Cd(L)(bipy)_2]_n$ **1**.[†] Strikingly, the long arms of the L anions thread into the square windows of the adjacent networks, furnishing an exceedingly rare 2D → 3D polythreaded framework. The solid-state luminescence of **1** was also studied.

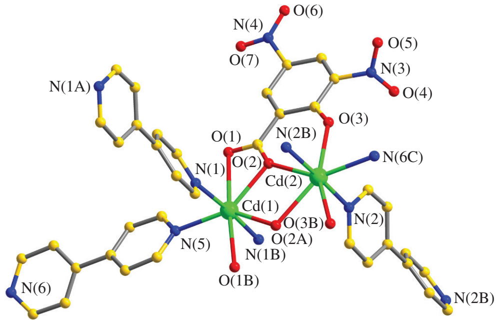

Figure 1 View of the coordination environments of the Cd^{II} cations in **1**.

X-ray crystallographic analysis reveals that the crystal of **1** is solved in monoclinic space group *P*2/*n*[‡] and exhibits an exceedingly rare 2D → 3D polythreaded framework. The asymmetric unit of **1** contains two halves of Cd^{II} cations [Cd(1) and Cd(2)] each situated on a twofold rotation axis, one L anion, and three halves of bipy ligands. Each Cd^{II} cation is seven-coordinated by three nitrogen atoms from three different bipy ligands, and four carboxylate oxygen atoms from two distinct L anions in a pentagonal bipyramidal CdN_3O_4 coordination sphere (Figure 1). Each L anion bridges two Cd^{II} cations in a tridentate coordination mode to furnish a $Cd_2(L)_2$ dimer with Cd–O distances from 2.281(2) to 2.615(3) Å. Note that each $Cd_2(L)_2$ dimer is linked by six bipy ligands into a 2D (4)-c sql network with Cd–N distances from 2.309(3) to 2.405(4) Å [Figure 2(*a*)]. The L anions as arms are alternately located on both sides of the network [Figure 2(*b*)]. Interestingly, each long arm of the L anion threads into the square windows of the adjacent networks, furnishing a 2D → 3D polythreaded framework (Figure 3). This

---

[†] Crystals of **1** were prepared by a hydrothermal reaction: a mixture of $CdSO_4 \cdot 2.5H_2O$ (0.154 g, 0.2 mmol), H_2L (0.068 g 0.3 mmol), bipy (0.016 g, 0.1 mmol), NaOH (0.018 g, 0.45 mmol) and 10 ml of distilled water was stirred at room temperature for 1 h. Then, the mixture was transferred and sealed in a 25-ml Teflon-lined stainless steel container and heated at 438 K for four days. After cooling the mixture to room temperature at a rate of 5 K h^{-1}, yellow crystals of **1** were obtained in 23% yield (based on Cd). IR (ν/cm^{-1}): 3441 (w), 1605 (s), 1568 (w), 1414 (m), 1352 (w), 1291 (w), 1219 (w), 1137 (s), 1075 (w), 1012 (w), 953 (w), 804 (w), 705 (w), 628 (m), 537 (s), 516 (w). Found (%): C, 45.44; H, 2.31; N, 11.74. Calc. for $C_{22}H_{14}N_5O_7Cd$ (%): C, 46.13; H, 2.46; N, 12.23.

[‡] *Crystal data for* **1**: crystals of $C_{22}H_{14}CdN_5O_7$ (M = 572.78) are monoclinic, space group *P*2/*n*, at 293 K: a = 11.707(5), b = 15.674(6) and c = 13.001(5) Å, β = 112.855(16)°, V = 2198.3(14) Å^3, Z = 4, d_{calc} = = 1.731 g cm^{-3}, μ(MoKα) = 1.049 mm^{-1}, F(000) = 1140. 20547 reflections were measured and 5025 independent reflections (R_{int} = 0.0543) were used in a further refinement. The refinement converged to wR_2 = = 0.0976 and GOF = 1.068 for all independent reflections [R_1 = 0.0360 was calculated against F^2 for 3964 observed reflections with $I > 2\sigma(I)$]. The measurements were performed on a Rigaku RAXIS-RAPID diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 293 K. The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedure based on F^2.[20] The hydrogen atom positions on carbon atoms were fixed geometrically at calculated distances and allowed them to ride on the parent atoms.

CCDC 1049503 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

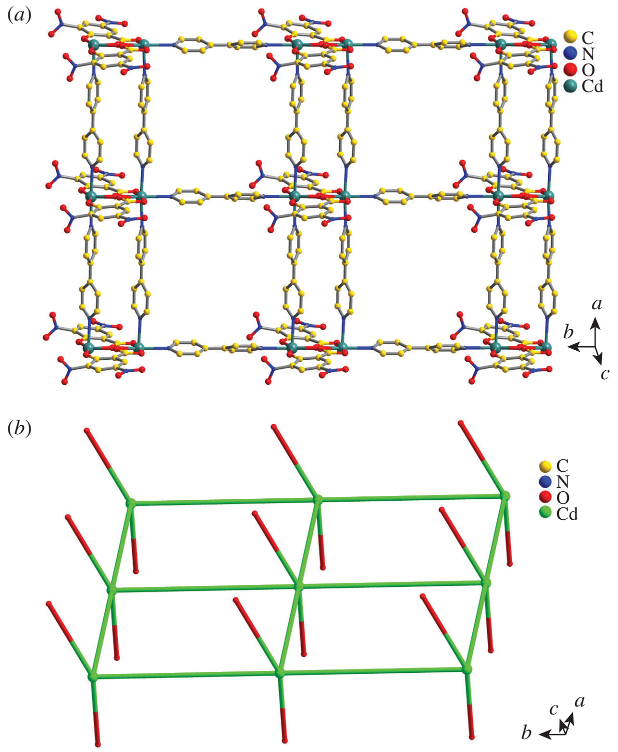

Figure 2 (*a*) View of the 2D (4)-c sql network of **1**. (*b*) Schematic representation of the (4)-c sql network with long arms.

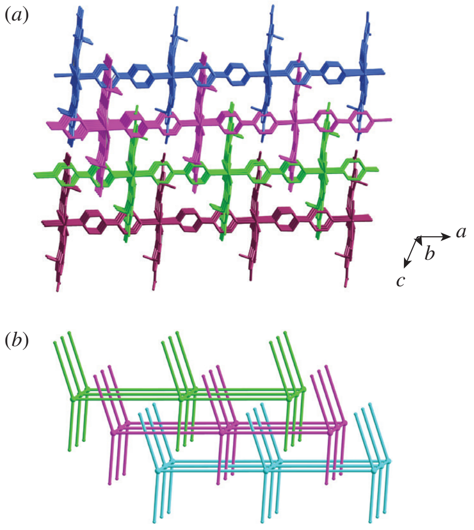

Figure 3 (*a*) View of 2D → 3D polythreaded framework of **1**. (*b*) Schematic representation of the 2D → 3D polythreaded framework of **1**.

framework of **1** is completely different from the recently reported 2D → 3D polythreaded framework of [Cd(HL)(biim-3)]·5H_2O [H_3L = 5-(2-carboxybenzyloxy)isophthalic acid, biim-3 = = 1,1′-(1,3-propanediyl)bis(imidazole)], where each hexagonal mesh is threaded by two arms from the adjacent layers.[18] Therefore, compound **1** represents an exceedingly rare example of a 2D → 3D polythreaded framework.[19]

Coordination polymers with Zn^{II} and Cd^{II} are excellent candidates for photoactive materials.[18] We studied the luminescent properties of free organic ligands and compound **1** in a solid state at room temperature (Figure 4). The free H_2L and bipy show emission peaks at 453 and 502 nm, and 557 nm, respectively (λ_{ex} = 325 nm), which may be assigned to the π*–n or π*–π transition as previously reported.[18] The emission peak of compound **1** occurs at 550 nm (λ_{ex} = 325 nm). Since the Cd^{II} ion is difficult to oxidize or to reduce due to the d^{10} configuration, the emission of compound **1** is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT).[18] For compound **1**, the emission (λ_{em} = 550 nm) can be attributed to intraligand transitions of the H_2L ligand since a similar emission was observed for the free H_2L ligand (λ_{em} = 557 nm).

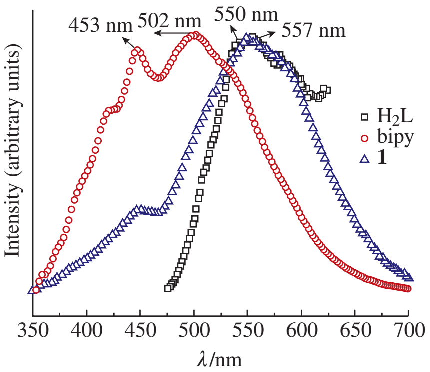

Figure 4 Solid-state emission spectra of H_2L, bipy and **1** at room temperature.

In conclusion, a new coordination polymer based on bipy ligand and L anion has been prepared under hydrothermal conditions. Remarkably, it exhibits an exceedingly rare 2D → 3D polythreading structure based on (4)-c sql networks with arms and shows strong solid-state luminescence at room temperature.

This work was supported by the Key Laboratory of Preparation and Applications of Environmental Friendly Materials and the Science and Technology Research Projects of the Education Committee of Jilin Province (no. 2013206).

References

1 D. M. Proserpio, R. Hoffman and P. J. Preuss, *J. Am. Chem. Soc.*, 1994, **116**, 9634.
2 J. Yang, J.-F. Ma, S. R. Batten and Z.-M. Su, *Chem. Commun.*, 2008, 2233.
3 Y. Zhao, X.-H. Chang, G.-Z. Liu, L.-F. Ma and L.-Y. Wang, *Cryst. Growth Des.*, 2015, **15**, 966.
4 J. Yang, J. F. Ma and S. R. Batten, *Chem. Commun.*, 2012, **48**, 7899.
5 S. R. Batten and R. Robson, *Angew. Chem. Int. Ed.*, 1998, **37**, 1460.
6 S. R. Batten, *CrystEngComm*, 2001, **3**, 67.
7 J.-S. Hu, Z. Lei, C.-L. Pan and J. He, *Mendeleev Commun.*, 2014, **24**, 290.
8 J.-S. Hu, Z. Lei, H.-L. Xing, X.-M. Zhang, J.-J. Shi and J. He, *Mendeleev Commun.*, 2013, **23**, 229.
9 Z.-G. Kong, X.-Y. Wang and L. Carlucci, *Inorg. Chem. Commun.*, 2009, **12**, 691.
10 J.-S. Hu, C.-L. Zhu, X.-M. Song and J. He, *Mendeleev Commun.*, 2012, **22**, 220.
11 H. Wu, H. Y. Liu, Y. Y. Liu, J. Yang, B. Liu and J. F. Ma, *Chem. Commun.*, 2011, **47**, 1818.
12 J.-S. Hu, X.-M. Zhang, H.-L. Xing, J. He and J.-J. Shi, *Mendeleev Commun.*, 2013, **23**, 231.
13 V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2004, **6**, 378.
14 L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247.
15 L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2003, **5**, 269.
16 X. L. Wang, C. Qin, E. B. Wang, Y. G. Li, Z. M. Su, L. Xu and L. Carlucci, *Angew. Chem. Int. Ed.*, 2005, **44**, 5824.
17 S. R. Batten, B. F. Hoskins and R. Robson, *Chem.-Eur. J.*, 2000, **6**, 156.
18 W. Q. Kan, J. F. Ma, Y. Y. Liu and J. Yang, *CrystEngComm*, 2012, **14**, 2316.
19 J.-S. Hu, C.-H. Zhou, Y.-M. Wang, K.-P. Xu and Y.-W. Li, *Mendeleev Commun.*, 2015, **25**, 211.
20 G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

Received: 23rd March 2015; Com. 15/4587