A new 2D→3D polythreaded framework constructed on an N-centered tripodal linker and copper(I)

Jin-Song Hu,*[a,b] Zhang Lei,[a] Cheng-Ling Pan[a] and Jie He*[a]

[a] *School of Chemical Engineering, Laboratory of Multiscale Materials and Molecular Catalysis, Anhui University of Science and Technology, Huainan 232001, P. R. China. E-mail: jshu@aust.edu.cn*
[b] *State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China*

A new copper(I) coordination polymer [(tppa)(CuBr)]$_n$·⊃solvents with a rare 2D→3D polythreaded framework was synthesized in a diffusion process by employing the triangular N-containing ligand tris[4-(4-pyridyl)phenyl]amine (tppa).

The rationally designed construction of coordination polymers from multidentate molecular building blocks is of interest not only due to their structural diversity[1,2] but also because of their applications in the fields of photochemistry,[3,4] gas adsorption and separation,[5,6] molecular magnetism[7,8] and heterogeneous catalysis.[9,10] Interpenetrated systems are an extremely active subject of coordination chemistry[11,12] owing to their esthetic architectures and topologies. Polythreading as an important branch of interpenetrated systems has attracted more and more attention, and various polythreaded nets have been reported.[13–16] The polythreaded structure depends upon not only the metal coordination geometry but also the shapes of special ligands. Polythreading is commonly assembled from lower dimensional motifs with side arms (0D→1D or 2D; 1D→2D or 3D).[17]

Recently, many polythreaded structures with mixed ligands have been reported,[18–21] however, the design of the polythreaded frameworks with single ligand is still challenging. Based on our previous works on interpenetration,[22] we tried to explore new polythreaded frameworks such as a new 2D→3D polythreaded framework [(tppa)(CuBr)]$_n$·⊃solvents **1** based on an N-centered tripodal linker and copper(I).[†]

X-ray analysis revealed that **1** crystallized in monoclinic space group *P*2$_1$/*n*.[‡] As shown in Figure 1, the crystallographically independent Cu(I) is linked by two bromine atoms from two CuBr molecules and two nitrogen atoms from two tppa in a slightly distorted tetrahedral geometry. The Cu–Br length is 2.7036(8) Å, and the Cu–N lengths are 2.022 and 2.042 Å, which are all similar to the values found in other Cu(I) complexes. The N(1)–Cu–N(4) and Br(1)–Cu–Br(1) angles are 114.99(14)° and 118.28(2)°, respectively.

In complex **1**, two CuBr linked each other to form a binuclear [CuBr]$_2$ cluster, four tppa ligands connect four [CuBr]$_2$ clusters
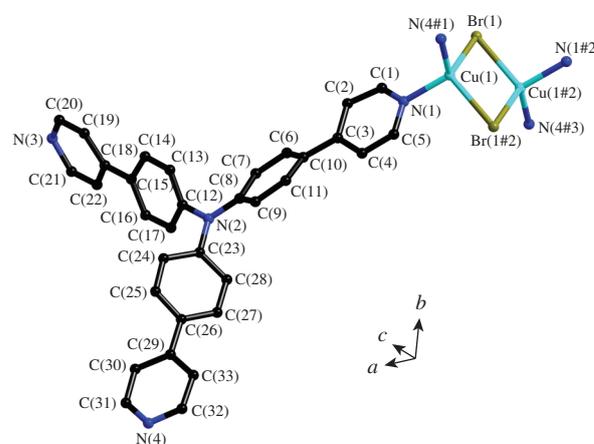

Figure 1 Coordination environment of Cu(I) in **1**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = 1.5 – *x*, 0.5 + *y*, 0.5 – *z*; #2 = = –*x*, 2 – *y*, –*z*; #3 = –1.5 + *x*, 1.5 – *y*, –0.5 + *z*. Selected bond lengths (Å) and angles (°): Cu(1)–N(4#1) 2.022(4), Cu(1)–N(1) 2.042(3), Cu(1)–Br(1) 2.7036(8); N(4#1)–Cu(1)–N(1) 114.99(14), N(4#1)–Cu(1)–Br(1) 106.24(11), N(1)–Cu(1)–Br(1#2) 108.23(13), N(4#1)–Cu(1)–Br(1#2) 103.24(10), N(1)–Cu(1)–Br(1) 106.18(11), Br(1#2)–Cu(1)–Br(1) 118.28(2).

to achieve a 76-membered [(CuBr)$_8$(Tppa)$_4$] metallocyclic ring exhibiting a maximum dimension of (corresponding to the two pairs of Cu···Cu distances) 25.458×27.079 Å. Each two N atoms of one tppa coordinated to two [CuBr]$_2$ clusters, forming a 2D wave-like sheet; a noteworthy feature of this network is the presence of a pair of left-handed and right-handed 1D helical channels alternately arranged; the Cu···Cu distance is 18.484 Å (Figure 2).
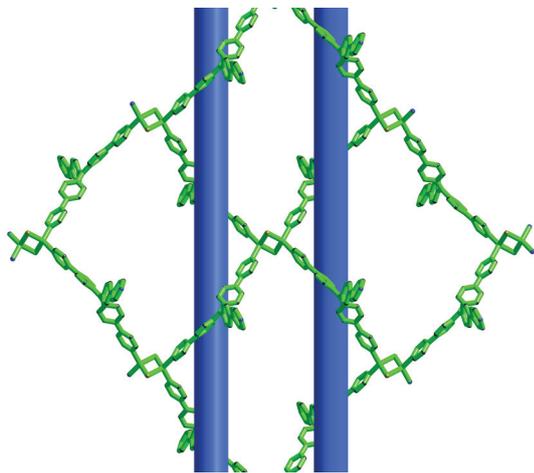

Figure 2 Wavelike 2D sheet of tppa and [CuBr]$_2$, which contains left-handed and right-handed helical channels alternately arranged.
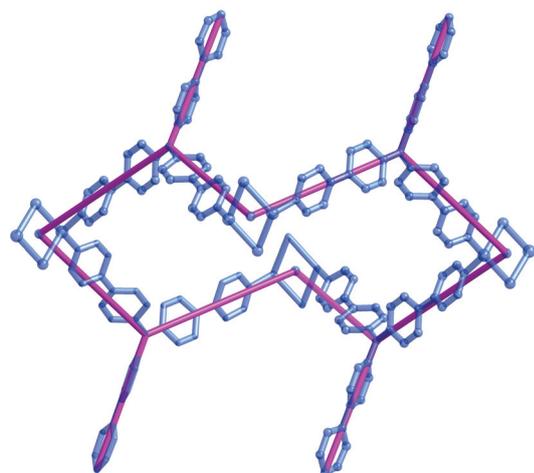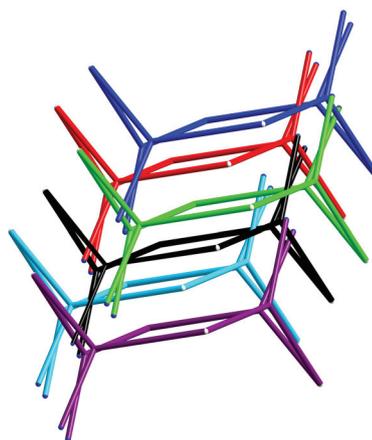

Figure 4 Multiarmed layers stacked parallel in the ABCABC mode, the uncoordinated pyridyl groups extend into the windows of adjacent layers in a mutual relationship.
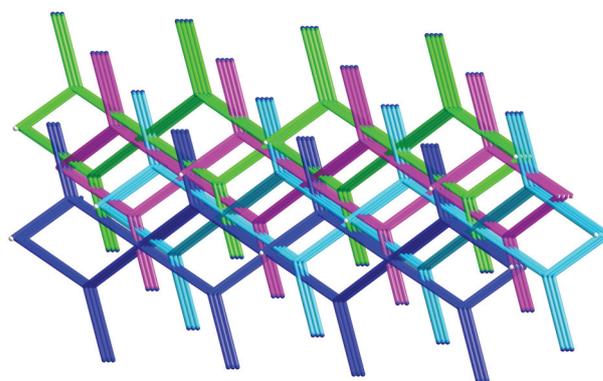

Figure 3 Four tppa ligands connect four [CuBr]$_2$ clusters to achieve a 76-membered window.

Figure 5 2D→3D polythreaded network.

In complex **1**, only two N atoms of each tppa coordinate to Cu(I); thus, the [CuBr]$_2$ unit acts as a 4-connector and tppa acts as a linker; the network is 4-connected (4, 4) sheet (Figure 3). The uncoordinated pyridyl groups perpendicularly decorated the sheet upwards and downwards, exhibiting an overall multiarmed sheet pattern. The large windows within the sheets and the dangling arms provide the possibility for the ultimate realization of a polythreaded framework. The multiarmed sheets stacked parallel in the ABCABC mode, and the uncoordinated pyridyl groups extend into the windows of adjacent sheets in a mutual relationship (Figure 4). The effective length from an N-center to the terminal uncoordinated nitrogen atom of the tppa is about 8.634 Å (longer than the stacking distance of sheets) contributable to the formation of threading. Each window is pierced by four uncoordinated pyridyl groups that belong to four adjacent layers resulting in a 2D→3D polythreaded network (Figure 5). The interpenetrated mode and the formation of the helices benefit not only from the shape of the bridging ligands but also from the large windows.

Up to now, the polythread is commonly assembled from lower dimensional motifs, such as 0D rings with side arms giving 1D or 2D arrays,[23,24] molecular ladders with dangling arms resulting in (1D→2D) or (1D→3D) polythreaded arrays,[19,25] 1D chains of alternating rings and rods (1D→1D),[26,27] 1D chains and 2D sheets (1D+2D→2D) or (1D+2D→3D),[15,28] 1D chains and 3D framework (1D+3D→3D).[29] So far, only a few 2D→3D polythreaded networks have been reported.[30] In polythreaded networks, almost all of which are mixed-ligand coordinated polymers, as far as

we know, only rare examples of polythreaded networks were constructed by a single ligand. One example of 1D→2D polythreaded bi-dimensional layers [Ag$_2$(bpethy)$_5$](BF$_4$)$_2$ was reported on 1,2-bis(4-pyridyl)ethyne(bpethy) ligand by Carlucci *et al.*[19] Meanwhile, in this work, a new 2D→3D polythreaded framework was constructed by a single tripodal ligand. In addition, most of dangling arms penetrate through the two neighboring sheets in polythreaded arrays, but the uncoordinated pyridyl groups in complex **1** extend into four neighboring sheets.

In summary, a new 2D→3D polythreaded coordination polymer [(tppa)(CuBr)]$_n$·⊃solvents **1** has been synthesized, which is constructed in such a way that the tppa ligand with free nitrogen cap in one sheet penetrated through the neighboring four sheets, forming a 2D→3D polythreaded network.

References

1 H. Eshtiagh-Hosseini and M. Mirzaei, *Mendeleev Commun.*, 2012, **22**, 323.
2 S. K. Chawla, M. Arora, K. Nättinen and K. Rissanen, *Mendeleev Commun.*, 2006, 88.
3 L. Rajput, D. Kim and M. S. Lah, *CrystEngComm*, 2013, **15**, 259.
4 P. K. Thallapally, J. Tian, M. R. Kishan, C. A. Fernandez, S. J. Dalgarno, P. B. McGrail, J. E. Warren and J. L. Atwood, *J. Am. Chem. Soc.*, 2008, **130**, 16842.
5 C. R. Tan, S. H. Yang, N. R. Champness, X. Lin, A. J. Blake, W. Lewis and M. Schröder, *Chem. Commun.*, 2011, **47**, 4487.
6 J. R. Li and H. C. Zhou, *Nat. Chem.*, 2010, **2**, 893.
7 R. A. Agarwal, A. Aijaz, C. Sañudo, Q. Xu and P. K. Bharadwaj, *Cryst. Growth Des.*, 2013, **13**, 1238.
8 D. W. Ryu, W. R. Lee, J. W. Lee, J. H. Yoon, H. C. Kim, E. K. Koh and C. S. Hong, *Chem. Commun.*, 2010, **46**, 8779.
9 A. Corma, H. García and F. X. Llabrés i Xamena, *Chem. Rev.*, 2010, **110**, 4606.

10 D. Bradshaw, A. Garai and J. Huo, *Chem. Soc. Rev.*, 2012, **41**, 2344.
11 J. H. He, D. R. Xiao, H.Y. Chen, S. W. Yan, D. Z. Sun, X. Wang, J. Yang, R. Yuan and E. B. Wang, *Inorg. Chim. Acta*, 2012, **385**, 170.
12 Z. Z. Lu, R. Zhang, Y. Z. Li, Z. J. Guo and H. G. Zheng, *J. Am. Chem. Soc.*, 2011, **133**, 4172.
13 J. Cui, K. Alramadan, D. S. Li and J. Y. Lu, *Inorg. Chem. Commun.*, 2013, **35**, 318.
14 X. Zhu, Q. Chen, Z. Yang, B. L. Li and H. Y. Li, *CrystEngComm*, 2013, **15**, 471.
15 M. Du, X. J. Jiang and X. J. Zhao, *Chem. Commun.*, 2005, 5521.
16 Y. L. Gai, F. L. Jiang, L. Chen, Y. Bu, M. Y. Wu, K. Zhou, J. Pan and M. C. Hong, *Dalton Trans.*, 2013, **42**, 9954.
17 L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247.
18 C. C. Wang, W. C. Chung, H. W. Lin, S. C. Dai, J. S. Shiu, G. H. Lee, H. S. Sheu and W. Lee, *CrystEngComm*, 2011, **13**, 2130.
19 L. Carlucci, G. Ciani and D. M. Proserpio, *Chem. Commun.*, 1999, 449.
20 J. Wang, X. Zhu, Y. F. Cui, B. L. Li and H. Y. Li, *CrystEngComm*, 2011, **13**, 3342.
21 G. L. Wen, Y. Y. Wang, Y. N. Zhang, G. P. Yang, A. Y. Fu and Q. Z. Shi, *CrystEngComm*, 2009, **11**, 1519.
22 J. S. Hu, X. H. Liu, J. J. Shi and J. He, *Mendeleev Commun.*, 2012, **22**, 310.
23 S. Banfi, L. Carlucci, E. Caruso, G. Ciani and D. M. Proserpio, *J. Chem. Soc., Dalton Trans.*, 2002, 2714.
24 G. F. Liu, B. H. Ye, Y. H. Ling and X. M. Chen, *Chem. Commun.*, 2002, 1442.
25 L. Carlucci, G. Ciani and D. M. Proserpio, *J. Chem. Soc., Dalton Trans.*, 1999, 1799.
26 C. S. A. Fraser, M. C. Jennings and R. J. Puddephatt, *Chem. Commun.*, 2001, 1310.
27 M. B. Zaman, M. D. Smith and H. C. Z. Loye, *Chem. Commun.*, 2001, 2256.
28 L. Carlucci, G. Ciani, M. Moret, D. M. Proserpio and S. Rizzato, *Angew. Chem. Int. Ed.*, 2000, **39**, 1506.
29 Y. F. Cui, X. Qian, Q. Chen, B. L. Li and H. Y. Li, *CrystEngComm*, 2012, **14**, 1201.
30 (*a*) B. Zheng and J. F. Bai, *CrystEngComm*, 2009, **11**, 271; (*b*) X. L. Wang, C. Qin, E. B. Wang, G. Y. Li, Z. M. Su, L. Xu and L. Carlucci, *Angew. Chem. Int. Ed.*, 2005, **44**, 5824; (*c*) B. Xu, J. Lü and R. Cao, *Cryst. Growth Des.*, 2009, **9**, 3003; (*d*) L. Y. Qiao, J. Zhang, Z. J. Li, Y. Y. Qin, P. X. Yin, J. K. Cheng and Y. G. Yao, *J. Mol. Struct.*, 2011, **994**, 1; (*e*) Y. Yang, P. Du, J. F. Ma, W. Q. Kan, B. Liu, J. Yang, *Cryst. Growth Des.*, 2011, **11**, 5540; (*f*) J. Guo, J. F. Ma, B. Liu, W. Q. Kan and J. Yang, *Cryst. Growth Des.*, 2011, **11**, 3609; (*g*) F. H. Zhao, Y. X. Che and J. M. Zheng, *CrystEngComm*, 2012, **14**, 6397; (*h*) Y. F. Cui, P. P. Sun, Q. Chen, B. L. Li and H. Y. Li, *CrystEngComm*, 2012, **14**, 4161; (*i*) J. H. Qin, L. F. Ma, Y. Hu and L. Y. Wang, *CrystEngComm*, 2012, **14**, 2891; (*j*) M. Du, Z. H. Zhang, X. G. Wang, L. F. Tang and X. J. Zhao, *CrystEngComm*, 2008, **10**, 1855; (*k*) X. Y. Wang, Y. He, L. N. Zhao and Z. G. Kong, *Inorg. Chem. Commun.*, 2011, **14**, 1186.
31 *SMART (Version 5.0), SAINT-plus (Version 6), SHELXTL (Version 6.1), and SADABS (Version 2.03)*, Bruker AXS Inc., Madison, WI, 2000.
32 A. L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, 194.