

A “Strongly” Self-Catenated Metal–Organic Framework with the Highest Topological Density among 3,4-Coordinated Nets

Huiqing Ma,[†] Di Sun,[†] Liangliang Zhang,[‡] Rongming Wang,[‡] Vladislav A. Blatov,^{*,§,||} Jie Guo,[†] and Daofeng Sun^{*,†,‡}

[†]Key Lab for Colloid and Interface Chemistry of Education Ministry, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, People’s Republic of China

[§]Department of Chemistry, Samara State University, Ac. Pavlov St. 1, Samara 443011, Russia

[‡]College of Science, China University of Petroleum (East China), Qingdao Shandong 266555, People’s Republic of China

^{||}Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

S Supporting Information

ABSTRACT: A new type of 3D “strongly” self-catenated metal–organic framework (SDU-9) has been constructed from $[\text{Cu}_2(\text{COO})_4]$ paddlewheel secondary building units and a tripodal carboxylate linker. SDU-9 ($[\text{Cu}_6(\text{H}_2\text{O})_6\text{L}_4] \cdot 24\text{H}_2\text{O}$, where $[\text{H}_3\text{L} = 4,4',4''\text{-(hydroxysilanetriyl)tris(triphenyl-4-carboxylic acid)}$), represents a rare example of a highly symmetrical coordination network and extremely tight self-catenation. To the best of our knowledge, SDU-9 has the highest topological density among all known 3,4-coordinated nets.

Metal–organic frameworks (MOFs) have caused an upsurge of interest not only for their potential applications in gas adsorption, catalysis, ion exchange, biomedical applications, etc.,^{1–6} but also for their intriguing variety of architectures and topologies.^{4a,7} The network topological approach proposed by Wells⁸ is an important and essential aspect of the analysis, comparison, and design of MOFs by reducing multidimensional structures to simple node-and-connection reference nets. In the past decade, many structural types and entanglement topological features unprecedented in the world of inorganic compounds and minerals have been unmasked in the MOF field.⁹ Recently, Yang and co-workers described a silver coordination polymer with a record 54 interpenetrating networks, which provide a new template for future highly interpenetrated or self-catenated structures.¹⁰

Among the different types of entanglements, such as interpenetration, polycatenation, polythreading, and self-catenation (other equivalent terms are self-penetration or polyknotting), interpenetrating networks are the most abundant and most comprehensively studied objects, as shown in the extensive reviews.¹¹ However, the study of self-catenated networks considered as extended periodic equivalents of molecular knots remains largely unexplored.^{11a} These structures are single networks with regions in which chains from the same net pass through smallest topological circuits in a fashion similar to that of interpenetrating systems. Recently, uninodal (with one kind of node) self-catenated coordination networks were reviewed by Ke et al.¹² According to the list given by Batten in a web site (<http://www.chem.monash.edu.au/staff/sbatten/interpen/examples7>.

html), a few examples of self-catenated networks with nodes of different connectivity such as 4,4,¹³ 3,5,¹⁴ 3,6,¹⁵ and 3,12-connections¹⁶ have been observed; however, reports on a self-catenated 3,4-coordinated network are quite rare. Mu et al. reported an unusual 3,4-coordinated self-catenated network that can be viewed as the cross-linking of a 2D + 2D → 3D inclined polycatenation.¹⁷ Similarly, most of the self-catenated networks can be represented as interweaved arrays of 2D or 3D individual equivalent components after breaking some edges,¹⁸ which we call the “weakly” self-catenated nets, in order to discriminate the net reported here. Generally, most reported self-catenated nets are constructed from flexible organic ligands; reports on rigid carboxylate ligands are somewhat rare. To construct such self-catenated nets, the conformation and linking mode of the organic ligand seem very important.

Recently, we reported a series of porous 3,24-coordinated *rht*-type MOFs based on C_{3v} -symmetry silicon-based hexatopic carboxylate linkers.¹⁹ According to the *TOPOS TTD* collection,^{11b} in total there are 20 examples of *rht*-type coordination networks, the first of which were synthesized in 2008. Developing our previous results, in this work, we have synthesized a new tripodal organic ligand, 4,4',4''-(hydroxysilanetriyl)tris(triphenyl-4-carboxylic acid) (H_3L). Surprisingly, the solvothermal assembly of H_3L and copper paddlewheel secondary building units (SBUs) resulted in the formation of a novel “strongly” self-catenated MOF ($[\text{Cu}_6(\text{H}_2\text{O})_6\text{L}_4] \cdot 24\text{H}_2\text{O}$, which is quite different from other MOFs based on tripodal carboxylate ligands and paddlewheel SBUs.

The solvothermal reaction of $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with H_3L (Figure 1a) in *N,N*-dimethylformamide/ethanol/water [1:1:1 (v/v/v), 10 mL] at 75 °C for 2000 min yields cubic green crystals of SDU-9. Single-crystal X-ray diffraction analysis reveals that SDU-9 crystallizes in the chiral cubic space group *F*432. Two copper ions are bridged by four carboxylates to form the well-known paddlewheel $[\text{Cu}_2(\text{COO})_4]$ SBU (Figure 1b). Each SBU connects four organic ligands, and each ligand binds three SBUs to form a 3D 3,4-coordinated self-catenated MOF containing right-handed helices along the [1,0,1] direction (Figure 1d). The

Received: July 23, 2013

Published: September 23, 2013

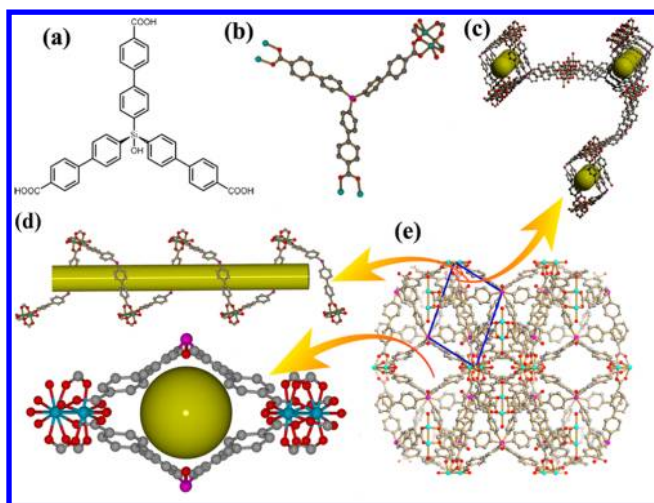


Figure 1. (a) Organic ligand used in this work. (b) Coordination environment of Cu^{II} ions in **SDU-9** with thermal ellipsoids at the 50% probability level. Hydrogen atoms were omitted for clarity. (c) Connection type between the helical chains (viewed along the $[0,1,-1]$ direction). (d) Perspective view of the helical chain along the $[1,0,1]$ direction in **SDU-9** (top) and the 1D channel (bottom). (e) 3D packing of **SDU-9** along $[1,0,0]$ direction.

connection type between the helices is different (Figure 1c): one is connected through the $[\text{Cu}_2(\text{COO})_4]$ SBU, and the other is linked through the silicon atom.

To perform topological analysis of the 3D architecture, we have used the *TOPOS* program package.²⁰ Topologically, by regarding each Cu_2 -SBU as a 4-coordinated node (Figure 2) and

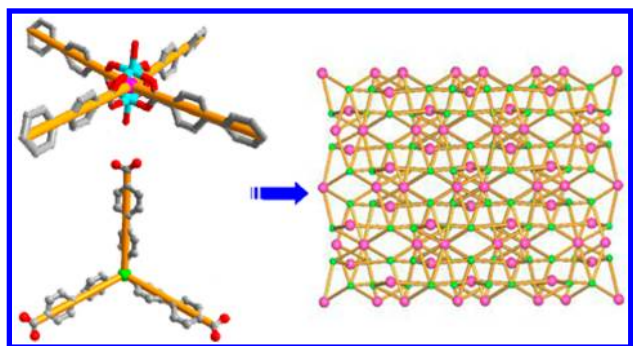


Figure 2. Schematic representation of the 3D framework of **SDU-9**, where the purple balls are the simplified paddlewheel units.

each L as a 3-coordinated node (Figure 2), the overall 3D net can be rationalized as a binodal 3,4-coordinated edge-transitive (with one kind of edge) underlying net (i.e., the net of centroids of structural groups) with the point symbol²¹ of $(12^3)_4(12^6)_3$ (Figure 2). It is striking that this net has collisions; i.e., some of its vertices have coordinates that are the average of the coordinates of their neighbors.^{11c,d} This feature is quite rare for the underlying nets.^{11c} Topological classification with the *TOPOS TTD* collection revealed that such a net has never been found in crystals; we have deposited it into the *TTD* collection under the name **sdf1**. Further analysis showed that there are four kinds of 12-rings in this 3D framework (Figure S4 in the Supporting Information). Each ring consists of six Cu_2 -SBUs that are connected by six halves of organic ligands.

The most fascinating and peculiar structural feature of **SDU-9** is that all of the rings are catenated together, coming to a

complete framework. Because the underlying net is edge-transitive (all edges are equivalent by symmetry), it cannot be naturally split into separate interpenetrating 2D or 3D nets; after breaking any edge, one obtains an unconnected structure. Hence, we call such self-catenation “strong”. The self-catenation is extremely tight: each 12-ring is crossed by more than 100 other 12-rings. Figure 3 demonstrates the unprecedented complexity

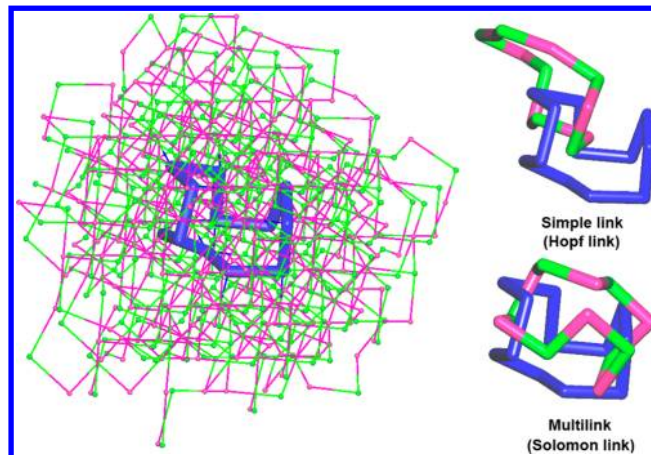


Figure 3. (left) One of the 12-rings (12b, in blue) catenated by 176 other 12-rings in the underlying net **sdf1** of **SDU-9**. (right) One of the 174 simple links between the 12-rings and one of two multilinks.

of self-catenation: all depicted nodes of the underlying net belong to the 176 12-rings that catenate the same (blue) 12-ring. Besides simple (Hopf-type) links between 12-rings, there are a few multilinks (also known as Solomon links)²² that are rare in self-catenated coordination networks (Figure 3). This tight self-catenation causes a high topological density²³ of the net, $\text{TD}_{10} = 3245$; according to the *RCSR* database,²⁴ to the best of our knowledge, this is the highest topological density among all known 3,4-coordinated nets.

On the basis of the calculation from the *PLATON/VOID* routine,²⁵ the total solvent-accessible volume for the desolvated framework after removal of guest solvents and coordinated water molecules is estimated to be 35.9%. To check the permanent porosities of **SDU-9**, the freshly prepared samples were soaked in methanol and dichloromethane to exchange the less volatile solvent molecules. A color change from bright-blue to blue-green, indicating that open Cu^{II} sites similar to those observed for other frameworks have been generated.¹⁸ As shown in Figure 4, desolvated crystal **SDU-9** displays a typical type IV adsorption

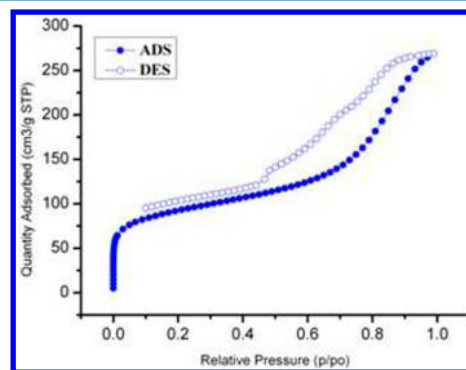


Figure 4. N_2 sorption isotherms at 77 K (solid circles, adsorption; open circles, desorption).

isotherm. This may derive from the flexibility of the self-catenated net, which causes dislocation moves of the framework upon an increase of the pressure, as found in other soft porous MOFs.²⁶ The Brunauer–Emmett–Teller surface area of SDU-9 is 332.8 m² g⁻¹ calculated from these data.

In summary, a 3D (12³)₄(12⁶)₃ coordination network with high topological density and extremely tight self-catenation of 12-rings has been obtained based on [Cu₂(COO)₄] paddlewheel SBUs and a tripodal carboxylate linker. The self-catenation is “strong”; i.e., the network cannot be transformed into an array of interpenetrating nets by breaking any chemical bond.

■ ASSOCIATED CONTENT

■ Supporting Information

X-ray crystallographic data in CIF format, detailed synthetic procedures, IR and TGA for the compounds, and additional graphics. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: blatov@samsu.ru.

*E-mail: dfsun@sdu.edu.cn.

Funding

This work was supported by the NSFC (Grants 21001115 and 21271117), NCET-11-0309 and the Shandong Natural Science Fund for Distinguished Young Scholars (JQ201003), and the Fundamental Research Funds for the Central Universities (Grants 13CX05010A and 13CX02006A).

Notes

The authors declare no competing financial interest.

■ REFERENCES

- (a) Zhou, H. C.; Long, J. R.; Yaghi, O. M. *Chem. Rev.* **2012**, *112*, 673. (b) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D.-W. *Chem. Rev.* **2012**, *112*, 782. (c) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724. (d) Getman, R. B.; Bae, Y.-S.; Wilmer, C. E.; Snurr, R. Q. *Chem. Rev.* **2012**, *112*, 703.
- (a) Farha, O. K.; Özgür Yazaydın, A.; Eryazici, I.; Malliakas, C. D.; Hauser, B. G.; Kanatzidis, M. G.; Nguyen, S. T.; Snurr, R. Q.; Hupp, J. T. *Nat. Chem.* **2010**, *2*, 944. (b) Lu, G.; Li, S.; Guo, Z.; Farha, O. K.; Hauser, B. G.; Qi, X.; Wang, Y.; Wang, X.; Han, S.; Liu, X.; DuChene, J. S.; Zhang, H.; Zhang, Q.; Chen, X.; Ma, J.; Loo, S. C.; Wei, W. D.; Yang, Y.; Hupp, J. T.; Huo, F. *Nat. Chem.* **2012**, *4*, 310. (c) McKinlay, R. M.; Cave, G. W. V.; Atwood, J. L. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 5944.
- (a) Long, J. R.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1213. (b) Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Férey, G.; Morris, R. E.; Serre, C. *Chem. Rev.* **2012**, *112*, 1232. (c) Corma, A.; Garcia, H.; Xamena, F. X. L. *Chem. Rev.* **2010**, *110*, 4606. (d) Cui, Y. J.; Yue, Y. F.; Qian, G. D.; Chen, B. L. *Chem. Rev.* **2012**, *112*, 1126. (e) Yoon, M.; Srirambalaji, R.; Kim, K. *Chem. Rev.* **2012**, *112*, 1196.
- (a) Yaghi, O. M.; O’Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (b) Müller, U.; Schubert, M.; Teich, F.; Puetter, H.; Schierle-Arndt, K.; Pastre, J. J. *Mater. Chem.* **2006**, *16*, 626. (c) Dinca, M.; Long, J. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 6766. (d) Czaja, A. U.; Trukhan, N.; Müller, U. *Chem. Soc. Rev.* **2009**, *38*, 1284.
- (a) Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* **2009**, *38*, 1248. (b) Czaja, A. U.; Trukhan, N.; Müller, U. *Chem. Soc. Rev.* **2009**, *38*, 1284. (c) Allendorf, M. D.; Bauer, C. A.; Bhakta, R. K.; Houk, R. J. T. *Chem. Soc. Rev.* **2009**, *38*, 1330.
- (a) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W. S.; Withersby, M. A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117. (b) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (c) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638.
- Hill, R. J.; Long, D. L.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Acc. Chem. Res.* **2005**, *38*, 335.
- Wells, A. F. *Three-dimensional Nets and Polyhedra*; Wiley-Interscience, New York, 1977.
- (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. (b) Batten, S. R. *CrystEngComm* **2001**, *3*, 67.
- Wu, H.; Yang, J.; Su, Z. M.; Batten, S. R.; Ma, J. F. *J. Am. Chem. Soc.* **2011**, *133*, 11406.
- (a) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Coord. Chem. Rev.* **2003**, *246*, 247. (b) Alexandrov, E. V.; Blatov, V. A.; Kochetkov, A. V.; Proserpio, D. M. *CrystEngComm* **2011**, *13*, 3947. (c) Delgado-Friedrichs, O.; Foster, M. D.; O’Keeffe, M.; Proserpio, D. M.; Treacy, M. M. J.; Yaghi, O. M. *J. Solid State Chem.* **2005**, *178*, 2533. (d) Delgado-Friedrichs, O.; O’Keeffe, M. *Acta Crystallogr., Sect. A* **2003**, *59*, 351.
- Ke, X. J.; Li, D. S.; Du, M. *Inorg. Chem. Commun.* **2011**, *14*, 788 and references cited therein.
- Eckhardt, R. H.; Heidl, H.; Fischer, R. D. *Chem.—Eur. J.* **2003**, *9*, 1795.
- Sava, D. F.; Rohwer, L.; Rodriguez, E. S.; Nenoff, M. A. *J. Am. Chem. Soc.* **2012**, *134*, 3983.
- Schareina, T.; Schick, C.; Abrahams, B. F.; Kempe, Z. R. *Anorg. Allg. Chem.* **2001**, *627*, 1711.
- Li, D. S.; Zhang, P.; Zhao, J.; Fang, Z. F.; Du, M.; Zou, K.; Mu, Y. Q. *Cryst. Growth Des.* **2012**, *12*, 1697.
- Carlucci, L.; Ciani, G.; Moret, M.; Proserpio, D. M.; Rizzato, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1506.
- Sun, D.; Ma, S.; Ke, Y.; Collins, D. J.; Zhou, H. C. *J. Am. Chem. Soc.* **2006**, *128*, 3896.
- Zhao, X. L.; Sun, D.; Yuan, S. A.; Feng, S. Y.; Cao, R.; Yuan, D. Q.; Wang, S. N.; Dou, J. M.; Sun, D. F. *Inorg. Chem.* **2012**, *51*, 10350.
- Blatov, V. A. *Struct. Chem.* **2012**, *23*, 955; see also <http://www.topos.samsu.ru>.
- Blatov, V. A.; O’Keeffe, M.; Proserpio, D. M. *CrystEngComm* **2010**, *12*, 44.
- Forgan, R. S.; Sauvage, J.-P.; Stoddart, J. F. *Chem. Rev.* **2011**, *111*, 5434.
- O’Keeffe, M. Z. *Kristallogr.* **1991**, *196*, 21.
- O’Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M. *Acc. Chem. Res.* **2008**, *41*, 1782; see also <http://rcsr.anu.edu.au/>.
- Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.
- (a) Maji, T.; Matsuda, K. R.; Kitagawa, S. *Nat. Mater.* **2007**, *6*, 142. (b) Mulfort, K. L.; Farha, O. K.; Malliakas, C. D.; Kanatzidis, M. G.; Hupp, J. T. *Chem.—Eur. J.* **2010**, *16*, 276. (c) Yang, S. H.; Lin, X.; Lewis, W.; Suyetin, M.; Bichoutskaia, E.; Parker, J. E.; Tang, C. C.; Allan, D. R.; Rizkallah, P. J.; Hubberstey, P.; Champness, N. R.; Thomas, K. M.; Blake, A. J.; Schröder, S. M. *Nat. Mater.* **2012**, *11*, 710.