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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

Supporting Information

ABSTRACT: A new type of 3D "strongly" self-catenated metal−organic framework (**SDU-9**) has been constructed from $[Cu_2(COO)_4]$ paddlewheel secondary building units and a tripodal carboxylate linker. **SDU-9** ($[Cu_6(H_2O)_6\mathbf{L}_4]\cdot 24H_2O$, where $[H_3\mathbf{L}$ = 4,4′,4″-(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 Wells[8] 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-connections[16] 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) ($H_3\mathbf{L}$). Surprisingly, the solvothermal assembly of $H_3\mathbf{L}$ and copper paddlewheel secondary building units (SBUs) resulted in the formation of a novel "strongly" self-catenated MOF ($[Cu_6(H_2O)_6\mathbf{L}_4]\cdot 24H_2O$, which is quite different from other MOFs based on tripodal carboxylate ligands and paddlewheel SBUs.

The solvothermal reaction of $Cu(NO_3)_2\cdot 6H_2O$ with $H_3\mathbf{L}$ (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 $[Cu_2(COO)_4]$ 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

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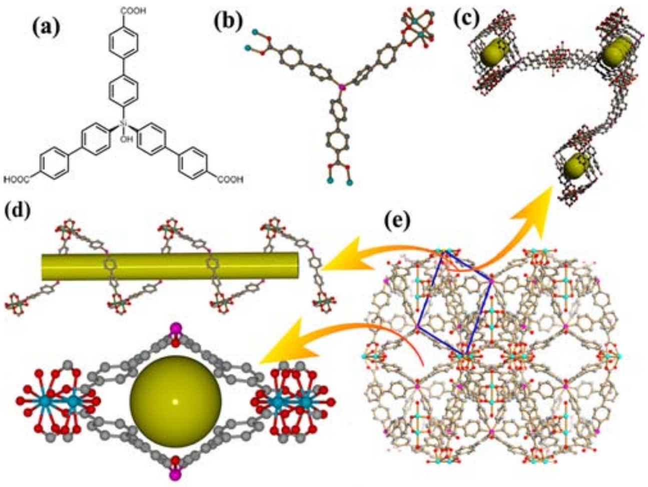

Figure 1. (a) Organic ligand used in this work. (b) Coordination environment of $\mathrm{Cu^{II}}$ ions in **SDU-9** with thermal ellipsoids at the 50% probability level. Hydrogen atoms were omitted for clarity. (c) Connection type between the helical chains (viewed along the [0,1,−1] direction). (d) 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 $[\mathrm{Cu_2(COO)_4}]$ 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 $\mathrm{Cu_2}$-SBU as a 4-coordinated node (Figure 2) and 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 symbol[21] 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 $\mathrm{Cu_2}$-SBUs that are connected by six halves of organic ligands.

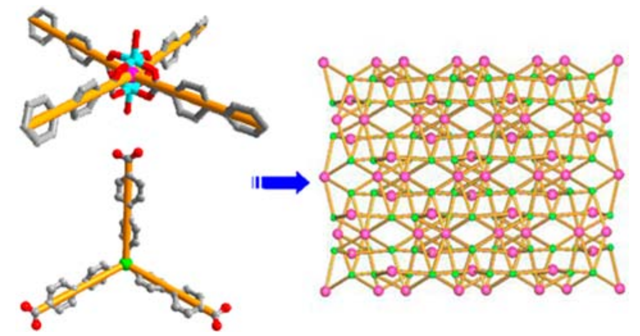

Figure 2. Schematic representation of the 3D framework of **SDU-9**, where the purple balls are the simplified paddlewheel units.

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 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 density[23] of the net, $\mathrm{TD_{10}} = 3245$; 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.

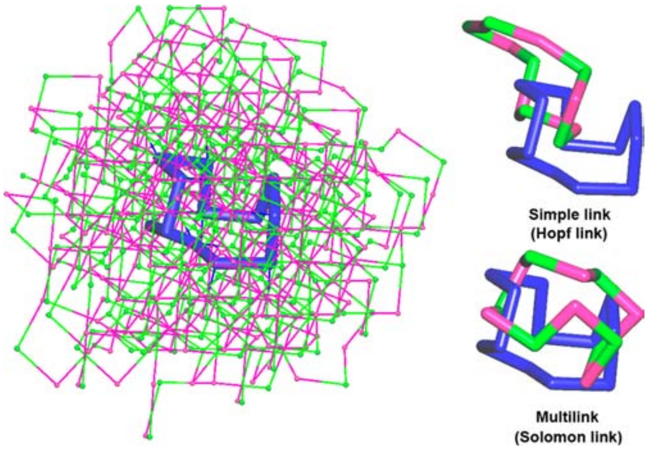

Figure 3. (left) One of the 12-rings (12b, in blue) catenated by 176 other 12-rings in the underlying net **sdf1** of **SDU-9**. (right) One of the 174 simple links between the 12-rings and one of two multilinks.

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 $\mathrm{Cu^{II}}$ 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

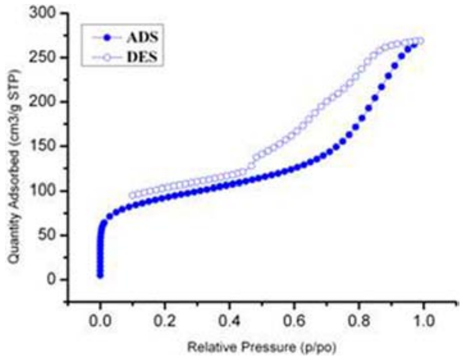

Figure 4. $\mathrm{N_2}$ sorption isotherms at 77 K (solid circles, adsorption; open circles, desorption).

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 m^2 g^{-1} calculated from these data.

In summary, a 3D $(12^3)_4(12^6)_3$ coordination network with high topological density and extremely tight self-catenation of 12-rings has been obtained based on $[Cu_2(COO)_4]$ 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.

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Notes

The authors declare no competing financial interest.

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