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An Unprecedented Densely Self-Catenated Metal–Organic Framework Containing Inclined Catenated Honeycomb-like Units with the Highest Topological Density among 4-Coordinated Nets

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A 3D 4-coordinated self-catenated metal-organic framework 10 {[Co(bibp)(1,4-chdc)] \cdot 2H₂O}_n (1) (bibp 4,4'-bis(1-imidazolyl)biphenyl, 1,4-H₂chdc 1,4-cyclohexanedicarboxylic acid) has been synthesized under hydrothermal reaction and its structure has been determined. This framework buries an unprecedented 4-coordinated 15 self-catenated net that can be represented as an array honeycomb-like units catenated in an inclined mode, with the highest topological density among the 4-coordinated nets that occurred in crystal structures. Additionally, the thermogravimetric, photo-catalytic and electrochemical 20 behaviors have been investigated.

The rational design and syntheses of metal-organic frameworks (MOFs) have attracted particular interest due to their fascinating structural complexity and potential application in electrochemistry, catalysis, gas sorption and magnetism.¹ In the ²⁵ realm of MOFs, topology control is fundamental for determining the properties and applications of the crystalline materials.² Therefore, the structural investigation of intricate entangled structures for coordination frameworks, such as the most familiar interpenetrating nets, self-penetrating nets, polyrotaxane ³⁰ structures etc. has attracted great attention. Self-catenated framework structures are a subclass of entanglements with fascinating topological properties.³ These species are single nets, but have the peculiarity that the smallest topological rings are catenated by the other smallest rings belonging to the same

³⁵ network. However, the study of self-catenated networks, being considered as extended periodic equivalents of molecular knots, remains largely unexplored.^{3a}

From both zeolite chemistry and crystal engineering points of

view, the topological nets built from 4-coordinated (4-c) nets 40 draw much attention both thanks to their practical significance (all zeolites are 4-c nets) and from a theoretical point of view: many 4-c nets have been deduced and summarized, firstly by Wells,⁴ followed by several comprehensive discussions.⁵ Two known examples of 4-coordinated self-penetrating nets are the natural structures of ice IV and coesite, and the latter has been mimicked in [Ag(2-ethpyz)₂][SbF₆] (2-ethpyz=2-ethylpyrazine).⁶ Recently, Gong et al. reported two metal-organic frameworks built by an amide derivative and organodicarboxyl co-ligands, exhibiting 3-fold interpenetration of $6^5.8$ -mok nets, which are ⁵⁰ 4-coordinated self-catenated.⁷ As has been proved, by using the co-ligands of an exo-bidentate N-heterocycle and dicarboxylate ligands, together with the suited transition metal ions, it is possible to synthesize the self-catenated MOFs.⁸ As our continuing efforts, we herein report a new 3D 4-coordinated $\{[Co(bibp)(1,4-chdc)] \cdot 2H_2O\}_n$ 55 self-catenated MOF (1) $(1,4-H_2chdc = 1,4-cyclohexanedicarboxylic acid; bibp =$ 4,4'-bis(1-imidazolyl)biphenyl), which is an unprecedented "strongly" self-catenated MOF and provides the highest topological density for the 4-coordinated nets that occurred in 60 crystal structures up to now.⁹ The bibp ligand was prepared according to the previously reported synthetic procedure.¹⁰

Compound 1 was prepared by hydrothermal reaction, performed in a 25 mL Teflon-lined stainless steel vessel at 140 °C for 72 h.‡ Single-crystal X-ray diffraction analysis 65 reveals that compound 1§ is a 3D coordination polymer, which crystallized in the monoclinic space group C2/c. The asymmetric unit consists of one Co(II) ion, two distinct half molecules of the bibp ligand, two different half ligands of the 1,4-chdc²⁻ anion, e.e-trans-conformation and e,e-cis-conformation, with 70 respectively, as well as two lattice water molecules. As depicted in Figure 1a, the Co(II) center is tetra-coordinated and shows a distorted [CoN2O2] tetrahedral geometry, ligated by two carboxylato oxygen atoms (O2, O3) from two different 1,4-chdc²⁻ ligands and two nitrogen atoms (N1, N3) from two 75 distinct trans-coordinated bibp ligands with Co-N distances of 2.018(4) Å and 2.050(4) Å. The Co1-O bond lengths are 1.990(4) Å and 2.016(4) Å, respectively, and the coordination angles around Co1 hold within the range of 90.89(16)-122.41(18)°, which is in accord with previously reported values for Co(II) 80 complexes.¹¹

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[†]Electronic Supplementary Information (ESI) available: Electrochemical experiment, Catalysis Experiments, the topology of 1, selected bonds and angles, FTIR, TGA, XRPD, UV/Vis absorption spectrum of 1, and the absorption spectra of the MO solution. See http://dx.doi.org/10.1039/b000000x/

In 1, the bibp ligands adopt a bis-monodendate bridging mode, linking the adjacent Co atoms together, and further assemble into an infinite 1D [Co(bibp)]_n zigzag chain with Co···Co distances of 17.691 Å and 18.035 Å, respectively, and a Co···Co···Co angle 5 of the infinite 1D chain of 79.637° (Figure 1b). The 1D [Co(bibp)]_n chains are further linked through *e,e-trans*-chdc²⁻ ligands, acting in a $\mu_2-\eta^1:\eta^1$ coordination mode to result in the formation of a 2D 6³-hcb network (Figure 1c). There are 78-membered macrocycles in the 2D sheet, formed by four bibp 10 and two *e,e-trans*-chdc²⁻ ligands together with six Co(II) atoms. Furthermore, such 2D layers are extended by *e,e-cis*-chdc²⁻ ligands with a Co···Co distance of 10.8196(11) Å to complete the complicated 3D framework structure¹² (Figure 1d).



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Fig. 1 (a) Coordination environment around the Co(II) centers in the complex 1. Hydrogen atoms are omitted for clarity. Symmetry codes: A: -x+1/2, -y-1/2, -z; B: -x, -y, -z+1; C: -x, -y+1, -z; D: -x+1, y, -z+1/2; (b) A view of the 1D zigzag chain by bibp ligands and Co(II) centers; (c) The 2D 6³-hcb layer network of **1**. (d) 3D packing of **1** constructed from bibp, 1,4-chdc²⁻ ligands and Co(II) ions.

The coordination network was simplified and analyzed with ¹⁵ the ToposPro program package.¹³ We have used the standard simplification mode, with the Co(II) atoms and organic ligands were treated as the nodes of the underlying net. Since all the ligands are bridging they were transformed to edges of the simplified net, which became uninodal, i.e. only the metal centers

- ²⁰ remained as nodes. Each metal center is connected to four ligands, i.e. the resulting underlying topology is 4-coordinated. It has the point symbol $\{6^3.10^3\}$ and vertex symbol $(6.10_{12}.6.10_{12}.6.10_{12})$ and has never occurred before in any crystal structure according to the TOPOS TTD Collection.¹³ Furthermore, there are no other
- 25 4-coordinated nets that are even locally similar to this net by the method of mutual connection of the rings. We have deposited this topology under the name cgh5. A close inspection of the network showed that it is strongly catenated; all 6- and 10-membered rings of the nodes are crossed by other rings (Figure 2). Moreover,
- ³⁰ the strong self-catenation provides an extremely high topological density: $TD_{10} = 5035$, which is the number of nodes within the first 10 coordination spheres of a given node. Up to now this is the highest value for the 4-coordinated nets that occur in crystal structures; according to the RCSR database¹⁰ the leaders are the ³⁵ elv net ($TD_{10} = 21922$) and the ten net ($TD_{10} = 6747$), but both of

³⁵ elv net (TD₁₀ = 21922) and the **ten** net (TD₁₀ = 6747), but both c them were discovered in modeled structures.^{3c}



Fig. 2 A fragment of the underlying net cgh5. The fragments formed by 6- and 10-membered rings are highlighted by different colors.

The self-catenation can be conceived with the procedure of the network decomposition, which we have already used for other self-catenated structures.¹⁴ The procedure consists in a ⁴⁰ subsequent breaking of independent edges (links) of the network, until it is split into motifs that are not self-catenated. In case of *cgh5*, this procedure gives the only way of such kind of splitting: breaking bonds with one of the dicarboxylate ligands leads to two sets of honeycomb-like layers (311) and (311) that cross each ⁴⁵ other in an inclined fashion and form a polycatenated 3D array (Figure **3**). Recently, we have already obtained a 4-coordinated self-catenated net that also contains catenated honeycomb layers, but in a parallel mode.^{14a} Probably, the inclined catenation of the layers, which favors their close arrangement, is the reason of the ⁵⁰ high topological density of the net.



Fig. 3 Representation of the *cgh5* underlying net as an inclined polycatenation of two sets of honeycomb-like layers (311) and ($3\overline{1}1$). The links between the layers are shown as dashed lines.

The IR spectrum between 400 and 4000 cm⁻¹ (Figure **S1**[†]) exhibits two characteristic bands at 1592 and 1381 cm⁻¹ attributed to the v_{COO} asymmetric and symmetric stretching vibration. The O-H stretching broad band of the crystalline water is observed at 35 3416 cm⁻¹. The characteristic bands for the bibp ligand are at 1513, 1305 and 1066 cm⁻¹, which can be assigned to the $v_{C=C}$, $v_{C=N}$ stretching vibration.

The thermal gravimetric curve of complex **1** exhibits two steps of weight loss (Figure **S2**[†]). In the first region of 72–116 °C, it ⁶⁰ has lost all lattice water molecules (6.40 % obsd; 6.52 % calcd). From 118 to 355 °C, the TGA curve of complex **1** passes through a plateau region, after which the material undergoes a rapid decomposition. The second step with a mass loss of 80.19 % occurs in the temperature region of 355–592 °C, corresponding Published on 07 January 2016. Downloaded by Gazi Universitesi on 11/01/2016 08:55:45.

to the burning of the organic ligands (79.89 % calcd). The remaining weight corresponds to the formation of CoO (13.41 % obsd; 13.59 % calcd). Therefore, this material displays rather high thermal stability after removal of the water solvates and that 5 might be attributed to the high self-catenation.

The electrochemical behavior of the 1-modified carbon paste electrode (1-CPE) in 1.0 M H₂SO₄ aqueous solution under different scan rates was investigated. Before the experiments, the phase purity of the sample was confirmed by a comparison of 10 experimental and simulated powder X-ray diffraction. The diffraction peaks of the experimental and simulated patterns are well matched in key positions, indicating phase purity of the bulk samples (Figure $S3^{\dagger}$). It can be seen from Figure 4 that in the potential range from 600 to -400 mV, there is no redox peak at 15 the bare CPE. Nevertheless, a redox couple was observed at the modified 1-CPE, which should be attributed to the redox of $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$.¹⁵ The mean peak potential $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$ is 31mV (100 mVs⁻¹). It is well-known that the scan rate has a remarkable influence on the electrochemical property. With the scan rates 20 increasing in the range from 20 to 250 mVs⁻¹, the reduction peak potentials shifted to the negative direction and the relevant oxidation peak potentials shifted to the positive direction. The redox peak currents are proportional to the scan rates, which demonstrate that the redox of 1-CPE is a surface-confined 25 process.¹⁶



Fig. 4 Cyclic voltammograms of the 1-CPE in 1.0 M $\rm H_2SO_4$ aqueous solution at different scan rates (from inner to outer: the bare CPE, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 250 mV s⁻¹). The inset shows the plots of the anodic and cathodic peak currents against scan rates.

The UV-assisted photocatalytic experiments for degrading methyl orange (MO) were carried out and the detailed photo-Fenton-like process is given in the supporting information.¹⁷ The diffuse-reflectance UV-vis spectrum of **1** ³⁰ reveals the absorption features in the UV region (Figure **S4**†). As shown in Figure **S5**†, the absorption peak of MO decreased obviously with increasing reaction time for **1** under UV irradiation. It can be clearly seen that the rapid degradation ensues and degradation efficiency can reach 76.1% for **1** within

³⁵ 30 min; after which methyl orange oxidation proceeds at a reduced rate, reaching up to 92.8% for 1 in 120 min in the photo-Fenton-like process (Figure 5). The color of the solution

changed obviously, from red to light pink or even colorless. The complex can catalyze persulfate to produce more strongly 40 oxidizing sulfate radicals (SO₄) and further increase the efficiency of the pollutant degradation significantly in the photo-Fenton-like process. For the sake of comparison, the total catalytic degradation efficiency of the control experiment without catalyst and equimolar amount of CoCl₂·6H₂O as catalyst only reached 14.21% and 21.40%, respectively, which indicated that there is almost no reaction going on between the persulfate and methyl orange. Additionally, after successive cycles for degradation experiments under the same conditions, the photo-catalytic activity of residual amount of catalyst (1) was 50 slightly decreasing due to leaching of metal ion, however it still can be well considered that the residual catalyst of 1 and the crystals used for powder X-ray diffraction are homogeneous (Figure S3[†]). Therefore, the complex exhibits higher stability and reproducibility for the degradation of methyl orange in the 55 photo-Fenton-like process.



Fig. 5 Experimental results of the catalytic degradation of methyl orange.

In summary, a 3D 4-connected coordination network with unusual $\{6^3.10^3\}$ cgh5 topology has been synthesized and topologically analyzed. This coordination framework shows a strongly self-catenated structure, containing inclined catenated b honeycomb-like units with the highest topological density for 4-coordinated nets that occur in crystal structures. Additionally, this coordination polymer displays higher thermal stability and favorable photo-catalytic capacities, as well as the electrochemical activity.

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Notes and references

⁺Synthesis of 1: The mixture of CoCl₂·6H₂O (0.2 mmol, 47.6 mg), 1,4-H₂chdc (0.20 mmol, 33.6 mg), bibp (0.10 mmol, 28.6 mg), NaOH (0.40 mmol, 16.0 mg) and distilled water (10mL) was stirred under ⁷⁵ ambient conditions until it was homogeneous, and was then sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 140 °C for 72 h. After slowly cooling to room temperature, purple block crystals of **1** were collected in 16% yield (based on bibp). Anal. Calcd. for $C_{26}H_{28}CON_4O_6$: C, 56.63; H, 5.12; N, 10.16. Found: C, 56.45; H, 5.06; N, 10.01.

- §Crystal data for 1: C₂₆H₂₈CoN₄O₆, M = 551.45, Monoclinic C2/c, a = 517.7012(7) Å, b = 16.3885(5) Å, c = 18.0629(8) Å, $\alpha = 90^{\circ}$, $\beta = 99.316(4)^{\circ}$, $\gamma = 90^{\circ}$, V = 5170.9(3) Å³, $\rho = 1.417$ g cm⁻³. Final R₁ = 0.0632, $wR_2 = 0.1565$ (for $I > 2\sigma$), GOF = 1.086, and Z = 8. CCDC 1420840. For crystallographic data in CIF or other electronic format see DOI: 10.1039/*******.
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Graphical Abstract

An Unprecedented Densely Self-Catenated Metal–Organic Framework Containing Inclined Catenated Honeycomb-like Units with the Highest Topological Density among 4-Coordinated Nets

⁵ Ju-Meng Hu^a, Vladislav A. Blatov^b, Baoyi Yu^c, Kristof Van Hecke^c, Guang-Hua Cui^{a,*}

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