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An Unprecedented 8-Fold Interpenetrating Diamondoid-like Coordination Polymer Containing a $Cu^{+}_{4}(RCO_2)_4$ Cluster as Connecting Node

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The reaction of $Cu(I)(CH_3CN)_4BF_4$ with 4-pyridylacrylic acid (4-HPYA) affords an unprecedented 8-fold interpenetrating diamondoid-like coordination polymer network $[Cu(I)_3(4\text{-}PYA)_2(H_2O)(BF_4)]$ (**1**) with a $Cu^{+}_{4}(CO_2)_4$ cluster as connecting node. The interpenetration in metal coordination polymers is the highest degree ever found within diamondoid nets containing a cluster as connecting note. Its fluorescent property was also reported.

Synthetic organic chemistry[1] and inorganic−organic hybrid supramolecular chemistry systems[2] widely involve interpenetrating (or catenation) phenomena, even including DNA in biological systems.[3] Usually, interpenetration is widely believed to have a negative impact on the size and accessibility of pores in microporous materials.[4] More recently, the Yaghi group made use of the strategy for the design of a highly porous and structurally stable coordination polymer in which a pair of interwoven metal−organic frameworks are mutually reinforced.[5] As Robson et al.[6] addressed in their review paper, there are a number of diamondoid-like networks involved in interpenetrating phenomena while the fold-interpenetrating number ranges from 2 to 9, to date. More recently, Ciani et al. report that the self-assembly of 1,12-dodecanedinitrile with various silver salts afforded a coordination polymer network with 10-fold diamondoid-like interpenetration which is the highest degree of interpenetration ever found within diamondoid nets exclusively based upon coordination bonds.[6b] However, it is noteworthy that the largest fold-interpenetrating number of a diamondoid-like network containing a cluster as connecting node is, to our knowledge, 3 to date.[6,7] To our surprise, the reaction of $Cu(I)(CH_3CN)_4BF_4$ with 4-pyridylacrylic acid (4-HPYA) affords an unprecedented 8-fold interpenetrating diamondoid-like coordination polymer with a $Cu^{+}_{4}(CO_2)_4$ cluster as connecting node, $Cu(I)_3(4\text{-}PYA)_2(H_2O)(BF_4)$ (**1**) (Scheme 1). To the best of our knowledge, the $Cu^{+}_{4}(CO_2)_4$ cluster as

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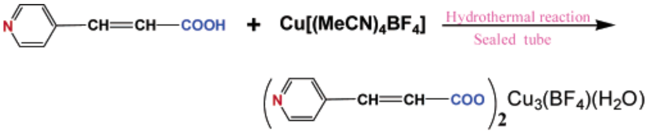
Scheme 1



connecting node is the first example in the supramolecular chemistry field although there are some excellent examples to use a Cu(II) paddle-wheel dimer as connecting node (secondary building block unit, SBBU) to construct three-dimensional coordination polymers.[8] Here, we would like to report its synthesis, crystal structure, and luminescent property.

Pale yellow crystals of **1** were obtained by treating 4-HPYA and $Cu(MeCN)_4(BF_4)$ under the solvothermal reaction conditions.[9] The IR spectrum of complex **1** shows a strong and broad peak at 1082 cm^{-1}, indicating the existence of a typical BF_4^- anion. Two peaks at 1620 cm^{-1} (s) and 1550 cm^{-1} (m) combined with a strong peak at 1405 cm^{-1}(s) suggest that the carboxylic acid group of 4-HPYA in **1** is deprotonated.[10] A peak at 3400 cm^{-1} indicates there may be coordinated water molecules persisting in **1**. This respect was further confirmed by thermogravimetric analysis (TGA) which was performed on the polycrystalline sample, indicating that one clean weight loss step occurred at 118 °C (2.91% loss), corresponding to the removal of one water molecule per formula unit (3.04% calculated). The dehydrated framework is stable between the temperatures of 118 and about 220 °C. The dehydrated framework decomposes beyond 220 °C. EPR results also show that the Cu atom oxidation state in **1** is +1.

The three-dimensional polymeric structure of **1** was revealed by an X-ray single-crystal diffraction study in which there are three different Cu(I) centers, as shown in Figure 1.[11] Cu(1) has a linear coordination environment with an angle of 168.3° and binds to two oxygen atoms from two different PYA^- ligands while Cu(2) is three-coordinated from three oxygen atoms (one from water and two from PYA^- ligand), resulting in the formation of T-shaped local coordination geometry. Like the Cu(1) center, Cu(3) only connects two nitrogen atoms from two PYA^- moieties to form a nearly linear geometry with an angle of 179.5°. Thus, each PYA^- ligand acts as tridentate chelating agent to bridge three Cu(I) centers, resulting in the formation of a 3-D coordination polymer. Furthermore, it is noteworthy that two PYA^- ligands are connected together by the Cu(3) atom and act as a pseudotetradentate bridging ligand to link four Cu(I) centers, or the pseudotetradentate ligand can be considered as a dicarboxylate tetradentate ligand if two pyridylvinyl groups connected together by linear coordination Cu(3) are treated as a straight line. Thus, overall each $Cu^+_4(CO_2)_4$ cluster is coordinated by four bi-PYA^- pseudotetradentate ligands (or a pseudo-dicarboxylate bridging ligand, secondary building block unit, SBBU) in a distorted tetrahedral environment. If the $Cu^+_4(CO_2)_4$ cluster can be treated as one connecting node, a diamondoid-like network clearly formed, as shown in Figure 2. Due to each net being larger (21.877Å, the proximate distance of a $Cu^+_4(CO_2)_4$ cluster to another $Cu^+_4(CO_2)_4$ cluster in a diamond net), to stabilize this network, there is a need for another seven nets to interpenetrate each other, as shown in Figure 3. For the same reason, there is a need for an anion to fill this space to stabilize this network and reach charge balance. It is also woth noting that the distance between adjacent two Cu(I) atoms is about 2.770 Å, while the distance between two diagonal Cu(I) atoms is about 3.042 Å, suggesting there is a weak interaction between two Cu(I) centers. Thus, as we are aware, **1** represents the first example of an 8-fold interpenetrating diamondoid-like network containing a $Cu^+_4(CO_2)_4$ cluster as connecting node.

The diffuse reflectance UV−vis spectrum of **1** shows a high energy band at about 200 nm and a relatively low energy

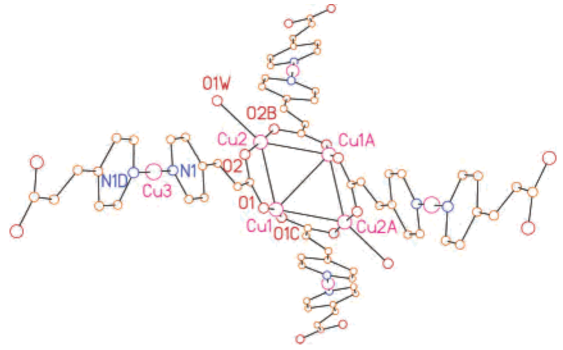


Figure 1. $Cu^+_4(CO_2)_4$ cluster as pseudotetrahedron connecting node in **1**, anion BF_4^- is omitted for clarity.

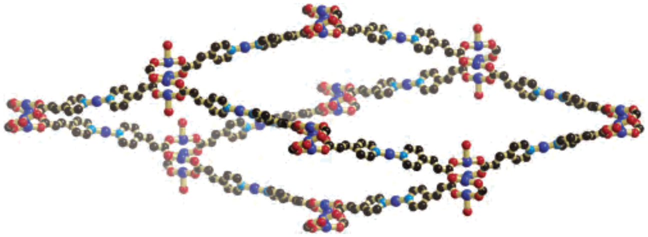


Figure 2. Diamondoid-like net containing $Cu^+_4(CO_2)_4$ cluster as node, anion BF_4^- is omitted for clarity.

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(9) Synthesis of **1**: A heavy-walled Pyrex tube containing a mixture of $Cu(MeCN)_4(BF_4)$ (0.2 mmol), the ligand HPYA (0.2 mmol), and H_2O (0.8 mL) as well as EtOH (1.2 mL) was frozen in liquid nitrogen, sealed under vacuum, and placed inside of an oven at 110 °C. The pale yellow block crystals were harvested after heating 24 h, with a yield of 41% based on HPYA. (Found: C, 32.34; H, 2.27; N, 4.56. Calcd: C, 32.45; H, 2.37; N, 4.73%.) IR (KBr, cm^{-1}): 3400(m), 1620(s), 1550(s), 1405(m), 1216(w), 1080(vs), 860(w), 826(m), 744-(m), 650(w), 520(w), 480(w).

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(11) Crystal data for **1**: $C_{16}H_{14}BCu_3F_4N_2O_5$, $M_r = 591.72$, tetragonal, $P4/nnc$, $a = 13.6036(5)$ Å, $b = 13.6036(5)$ Å, $c = 20.5614(7)$ Å, $V = 3805.1(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 2.066$ g cm^{-3}, $\mu = 3.395$ mm^{-1}, R1 = 0.0725, wR2 = 0.2082 for 1360 observed reflections from 2384, GOF = 1.023.

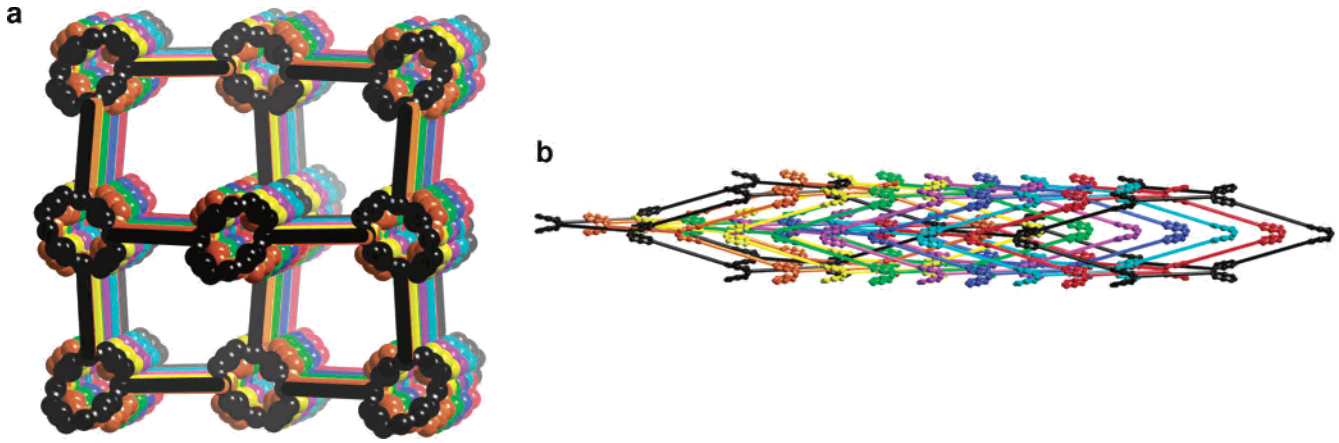

Figure 3. (a) Diamond net (dark line) containing seven diamond nets. (b) 8-Fold diamond interpenetrating relationship.

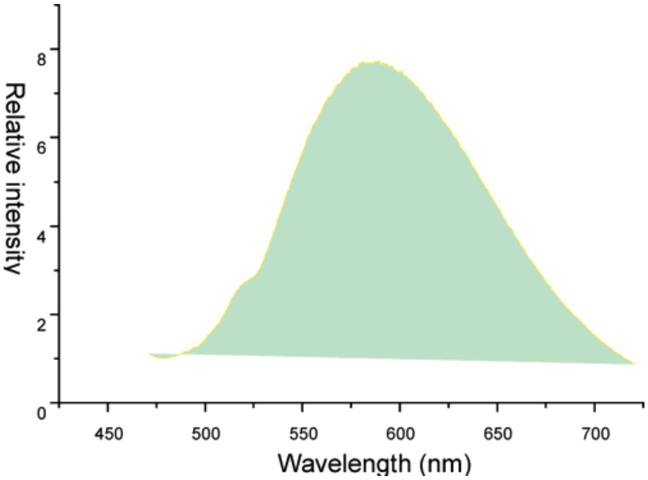

Figure 4. Fluorescent spectrum of **1** in the solid state at room temperature.

band about 265 nm, respectively; the former may be assigned to the intraligand transition of the free ligand due to the HPYA having a similar wavelength band at 198 nm.[12,13d] With reference to previous spectroscopic work on related systems, the low-energy band can tentatively be assigned to a metal-to-ligand charge transfer (MLCT). However, the metal center d-to-s orbital transition is also not ruled out.[12,13d] The strong yellow green fluorescent emission spectrum of **1** in the solid state at room temperature, shown in Figure 4, has a maximum at about 580 nm, very similar to those found in $Cu_4I_4(Py)_4$(pyridine)[13] and $[(3,4'\text{-bpy})(Br)Cu^{I}]n$[13] with λ_{max} 580 nm at room temperature.

In conclusion, the smart combination of linear coordinate copper(I) and two multidentate PYA ligands affords a larger SBBU (PYA−Cu(I)−PYA) to result in the formation of huge cantenation diamondoid-like network with a $Cu^{+}{}_4(CO_2)_4$ cluster as connecting node. The SBBU is a very useful strategy for construction of novel supramolecular aggregates.

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Supporting Information Available: X-ray CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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