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Time-Evolving Self-Organization and Autonomous Structural Adaptation of Cobalt(II)–Organic Framework Materials with scu and pts Nets

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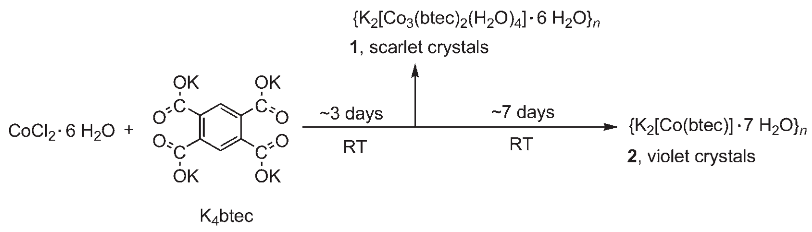
Self-organization is a process, in which an internal system spontaneously opens a new route to increase system complexity without being guided by an external source. The concept of self-organization is central to the understanding of living organisms, biominerals, and new supramolecular materials.[1–3] For chemistry, self-organizing equilibrium conditions can be controlled by changing a few critical factors (concentration, template, pH, temperature, solvent system, etc.) to generate desirable compounds.[4–6] However, these explorations seem not to be completely applied in a few particular supramolecular systems. Inspired by biology, to construct a high-order architecture from individual building components, various driving forces may competitively predominate at certain stages of the self-assembly process.[2,3] A subtle thermodynamic/kinetic balance may control and tune the materials growth delicately. Namely, self-organization processes can be operative if the building components are sufficient and in close proximity, under suitable conditions. If the supply of building units is depleted or reduced, the original equilibrium conditions will change, and a new self-organization process will take place. These intriguing phenomena of self-organization are triggered by an internal stimulus and seem to be easily understood in biology,[2d,e] but the phenomena has not been addressed in the synthesis system of metal–organic framework (MOF) materials.[6]

As part of our ongoing efforts in the design and synthesis of functional crystalline materials,[4k,7] we report herein on an intriguing supramolecular system that involves a distinct self-organization process, in which the product structures adapt to autonomous dynamic changes in the ratio of building components at ambient temperature. As shown in Scheme 1, two 3D metal–organic framework materials, of $\{K_2[Co_3(btec)_2(H_2O)_4]\cdot6H_2O\}_n$ (**1**, btec = benzene-1,2,4,5-tetracarboxylate) with a rare scu net and $\{K_2[Co(btec)]\cdot7H_2O\}_n$ (**2**) with a pts net, are formed in the simple one-pot reaction system. For the initially designed self-assembly system, a solution of $CoCl_2\cdot6H_2O$ (0.40 mmol) in ethanol (5 mL) was carefully layered on top of a bilayer solution comprised of a solution of K_4btec (0.20 mmol) in water (5 mL) on the bottom and a buffer solvent of THF on the top at room temperature. Scarlet crystals of **1** were generated about within the first three days, and, after the reaction system was allowed to stand for a few more days, violet crystals of **2** formed gradually. Surprisingly, although the reactant ratio



Scheme 1. Self-organization of **1** and **2** in a one-pot supramolecular synthesis system.

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was changed slightly, both products always appeared clearly in the system (details see the Supporting Information).

The most reasonable explanation for this unique adaption phenomenon is that the K^I/Co^{II} ratio can automatically and dynamically change during the self-assembly of **1** and **2** (Figure 1). The production of $\{K_2[Co_3(btec)_2(H_2O)_4]\cdot 6H_2O\}_n$ (**1**) consumes more Co^{II} atoms (3 units) than K^I atoms (2 units), thus, the K^I/Co^{II} ratio in the solution gradually increases as **1** is formed. At a distinct critical point, the self-organization direction autonomously changes in favor of the generation of $\{K_2[Co(btec)]\cdot 7H_2O\}_n$ (**2**), because less Co^{II} atoms (1 unit) are consumed than K^I atoms (2 units). Fortunately, the colors of **1** (scarlet) and **2** (violet) are so different that this intriguing phenomenon can be detected by the naked eye.

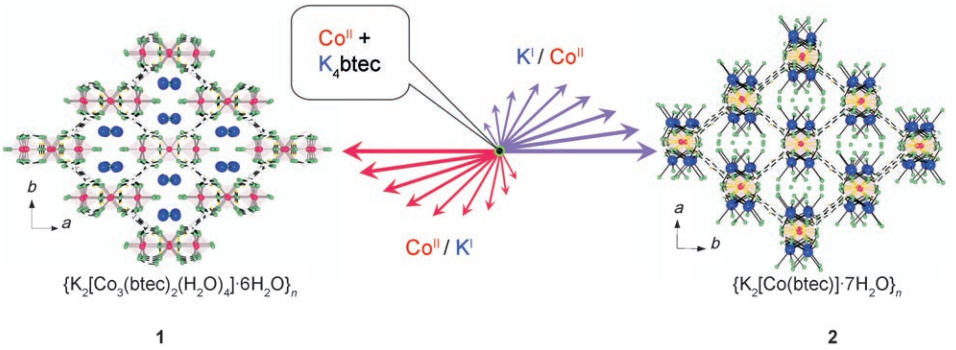

Figure 1. Structural adaptation of **1** (left) and **2** (right) upon the dynamic adjustment of the Co^{II}/K^I concentration ratio. For structures of **1** and **2**, Co = pink, C = white, O = sea-green, H = yellow, K = blue.

To identify the driving forces and controlling factors involved in the self-assembly process in detail, a series of experiments on the dynamic adjustment of the K^I/Co^{II} ratio to modify the equilibrium conditions in this system were performed (Table S1 in the Supporting Information). Different amounts of KCl were added to the self-assembly systems, while holding the $CoCl_2\cdot 6H_2O/K_4$btec ratio fixed, at ambient temperature. As expected, tuning the K^I/Co^{II} concentration ratio by adding KCl, resulted in a controllable structural self-adaptation in the cobalt(II)–organic frameworks. The yield of **2** increased with increasing amounts of added KCl and the yield of **1** decreased in a corresponding manner. That is, the higher the concentration of K^I ions, the stronger tendency to generate **2**, and the weaker probability of producing **1**. In an extreme case, when an especially high or low K^I/Co^{II} ratio was used, either **1** or **2** was formed exclusively. The generation of **1**, results in a higher K^I/Co^{II} ratio in the solution and a stronger tendency to form **2**. Conceptually, potassium ion seems to be silent in the preparation of MOF materials because of its weak coordination interactions. However, it is alive and plays a critical role now. To our knowledge, this kind of phenomenon concerning time-evolving self-organization and autonomous structural adaptation has scarcely been highlighted in the MOF synthesis system.[1–6]

A single-crystal X-ray diffraction analysis of **1** reveals that there are two crystallographic distinct Co^{II} centers. Both centers adopt a distorted *trans*-$Co(OCO)_4(OH_2)_2$ octahedral geometry; whereas, the btec ligand exists in a μ_6-bridging mode with two monodentate carboxylate groups at the *para*-positions and the other two carboxylate groups in a *syn,syn*-bridging bidentate mode (Figure S1). A trinuclear cluster with the formula $[Co_3(O_2CR)_8(H_2O)_4]$ is observed. In this cluster, the three Co ions are linear, and a total of eight carboxylate groups and two water molecules bridged the Co ions (Figure 2a). Each btec ligand acts as a four-connecting node in a distorted square planar geometry and coordinates to four tricobalt clusters that serve as eight-connecting cubical vertices. To understand the framework topology in **1**, the motif of the tricobalt cluster connected to eight btec linkers is represented by a box connected with four squares through eight simple bars (Figure 2a). The framework of **1** results in a rare (4,8)-connected net with the Schläfli symbol of $\{(4^4.6^2)_2(4^{16}.6^{12})\}$ and has the topology of a scu net (square planar and cubical vertices).[8]

Except for a couple of inorganic salt,[9a,b] such as $PoCl_2$, metal–organic complexes with the scu-net topology are extremely rare.[9c] Remarkably, like the rare (4,8)-connected metal–organic replicas of fluorite with the flu net which contain tetrahedral and cubical vertices,[10] compound **1** represents the first extended metal–organic replicate of $PoCl_2$ with the scu net containing an eight-connecting polynuclear cluster and a large four-connecting organic ligand to date. Furthermore, this unique tricobalt cluster is stabilized by strong hydrogen-bonding interactions between the hydrogen atoms of bridging water molecules and the noncoordinated carboxylate oxygen atoms ($H\cdots O = 1.919(2)$, $O\cdots O = 2.624(2)$ Å, $O{-}H\cdots O = 153.87(1)°$). The 3D network contains rhombic channels, with diagonal dimensions of 11.90×15.74 Å^2 along the *c* axis, where the potassium ions and guest water molecules reside to form a K^I-water rod of $\{(H_2O)_4(K_2(H_2O)_4)\}_n$ (Figure S5a).

Compound **2** is an isostructure of a Zn species in our early papers, but the similar dynamic self-organization process was not observed owing to coordinating natures of different metal centers.[7c] The btec ligand also serves as an expanded square planar node that connected to four Co^{II} centers. Each Co^{II} center is bound to four monodentate carboxylate groups in a distorted tetrahedral geometry. The overall 3D porous framework of **2** adopts a (4,4)-connected net with the Schläfli symbol $\{4^2.8^4\}$ and has the topology of a pts net (Figure 2b).[11] This network contained rhombic channels with a Co-to-Co cross section of 11.33×15.36 Å^2 along the *c*

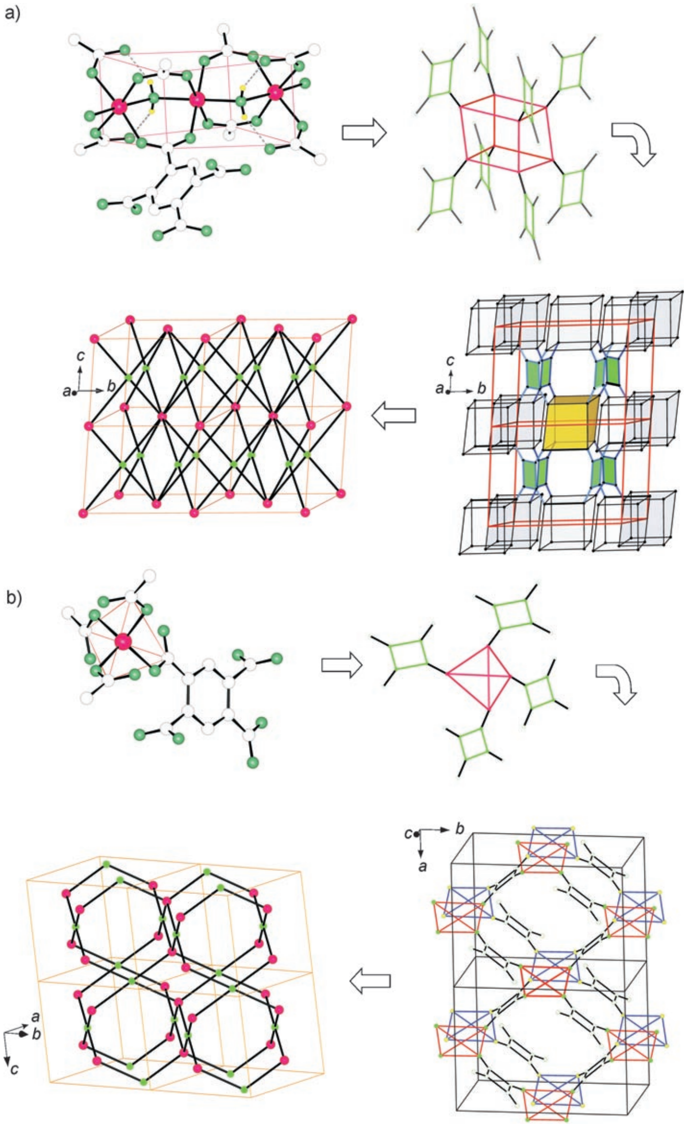

Figure 2. Schematic representations of a) an eight-connecting cubical unit and a four-connecting square-planar btec node in **1** (Co = pink, C = white, O = sea-green, H = yellow), and a view of the scu net. b) a four-connecting tetrahedral unit and a four-connecting btec node in **2**, and a view of the pts net.

axis, in which potassium ions and guest water molecules reside (Figure S5b).

Both the scu and pts nets belong to the recently identified 28 three-periodic nets with two kinds of vertices and one kind of link.[12] These edge-transitive binodal networks are of great interest and have been attracting increasing attention relative to the design and synthesis of metal–organic materials owing to their unique geometric and functional properties.[9b] However, 3D networks with mixed connectivities, such (3,6)-, (4,6)-, and (4,8)-connected frameworks, are still considered hard to achieve because of their greater geometric limitations.[13] To fulfill the net topologies, the design strategies used in this study focused on the selection of a rigid organic ligand with four connectivities, as they provide a suitable geometry that permits synthesis of the target structures. As a result of the nature of cobalt ions, the formation of the tricobalt cluster can be transformed toward the monocobalt node (from eight- to four-connected nodes).

In conclusion, we demonstrate herein an unique supramolecular system and the successful synthesis of two metal–organic frameworks which possess a rare (4,8)-connected scu net and a (4,4)-connected pts net, respectively. The former contains eight-connecting trinuclear cobalt-carboxylate clusters and square planar organic building units, the latter has four-connecting tetrahedral metal nodes and square planar organic linkers. The spontaneous self-adjustment of the K^I/Co^{II} concentration ratio offers a strong driving force that determines the self-assembled frameworks. We believe that the autonomous structural adaptation of a self-organizing process may occur in other supramolecular systems in response to a self-dynamic change in the ratio of building units under mild conditions. However, such an internal stimulus is often ignored. Our results highlight an important concept and help get a better understanding of a few unique and ambiguous problems with the self-assembly of MOF materials.

Experimental Section

MOFs 1 and 2: A solution of $CoCl_2{\cdot}6H_2O$ (0.40 mmol) in ethanol (5 mL) was carefully layered on top of a bilayer solution comprised of a solution of K_4btec (0.20 mmol) in water (5 mL) on the bottom and a buffer solvent of THF on the top. It was then allowed to stand at room temperature for three days, whereupon scarlet needle-like crystals of **1** were form in 80% yield (based on K_4btec). After allowing the solution to stand for further seven days, violet rod-like crystals of **2** appeared in about 1% (based on K_4btec). The solid product was washed with deionized water and ethanol, and dried in air. Elemental analysis calcd (%) for **1**, $C_{20}H_{24}Co_3K_2O_{26}$: C 25.68, H 2.59; found: C 25.24, H, 2.58; for **2**, calcd for $C_{10}H_{16}CoK_2O_{15}$: C 23.40, H 3.14; found: C 23.42, H, 3.35.

Following a similar procedure, but with a different concentration of $CoCl_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$ (0.16 mmol) and K_4btec (0.20 mmol) were introduced into the reaction system. The scarlet crystals of **1** were formed in the first several days, and then the violet crystals of **2** generated. Because this supramolecular system is not always totally homogeneous, both compounds **1** and **2** can be forming for a further period of time. Yield of **1**: 46%, **2**: 47% (based on $CoCl_2{\cdot}6H_2O$). Crystal data for **1**: $C_{20}H_{24}Co_3K_2O_{26}$, $M_r = 935.38$, monoclinic, $C2/m$, $a = 15.737(2)$, $b = 11.901(1)$, $c = 9.467(1)$ Å, $\beta = 113.29(1)°$, $V = 1628.5(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.908$ g cm^{-3}, $R_1 = 0.0458$, $wR_2 = 0.1349$, GOF = 1.160. Crystal data for **2**: $C_{10}H_{16}CoK_2O_{15}$, $M_r = 513.36$, monoclinic, $C2/c$, $a = 11.335(1)$, $b = 15.368(3)$, $c = 11.167(2)$ Å, $\beta = 90.95(1)°$, $V = 1945.0(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.753$ g cm^{-3}, $R_1 = 0.0441$, $wR_2 = 0.1264$, GOF = 1.076. CCDC 688763 (**1**) and 688764 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Experimental details on dynamic self-assembly of **1** and **2**, crystal structure determination and other physical measurement studies are given in the Supporting Information.

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