Self-Assembly

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The Designed Assembly of Augmented Diamond Networks From Predetermined Pentanuclear Tetrahedral Units**

Yue-Ling Bai, Jun Tao, Rong-Bin Huang, and Lan-Sun Zheng*

One of the most important goals in the synthesis of new materials is to achieve real "design" and to obtain tailor-made compounds with expected structures and properties starting from well-characterized inorganic and organic precursors. To this end, secondary building units (SBUs), which have the advantage of allowing the topologies of structures to be predicted,[1] are widely used to design and construct the extended frameworks that are attracting much interest in materials science, chemistry, and crystallography.[2] SBUs usually possess attributes, such as the necessary shape and geometry, metal coordination environments, and desired directionality, that offer the possibility to assemble predefined building units into network structures with expected topologies. For example, some solid materials based on SBUs (trimetallic octahedra with a common μ_3-O center[3] or polymeric clusters[4]) linked through polycarboxylate and polypyridyl ligands have been obtained. TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane) has attracted much attention as a polytopic bridge in recent years[5] as this redox-active ligand can act as a good electronic acceptor or donor depending on whether its valence is 0, −1, or −2. TCNQ-bridged complexes generally also display unusual electrical, optical, and magnetic properties.[5]

A large number of extended frameworks based on some specific SBUs have been designed and synthesized over the past two decades, although little attention has been focused on investigating the role of the SBU precursors and/or the reaction intermediates in the assembly of metal–organic frameworks. An EXAFS study by Férey et al. has provided direct evidence that Fe_3O building units remain intact during the crystallization of starting materials into products.[6] Similarly, electrospray ionization mass spectrometry (ESI-MS) has been used to identify intermediates in solutions prior to the formation of networks,[7] thereby providing an effective method of following the assembly process. Herein, we utilize two pentanuclear metal clusters with predetermined shapes, sizes, and geometries, namely $[M_5(btz)_6(NO_3)_4(H_2O)_4]$ (btz = benzotriazolate; M = Co (**1**), Ni (**2**)), as the SBUs and the radical anion $TCNQ^{\bullet-}$ as the organic linker to realize the step-by-step synthesis of two twofold interpenetrated three-dimensional diamond networks with formula $[M_5(btz)_6(TCNQ^{\bullet-})_4(H_2O)_4]\cdot n\,H_2O$ (**3**: M = Co, $n = 2$; **4**: M = Ni, $n = 3.5$).

Complex **1** (or **2**) was prepared from btz-CH_2OH and $Co(NO_3)_2\cdot 6\,H_2O$ (or $Ni(NO_3)_2\cdot 6\,H_2O$) in acetone solution. The CH_2OH group at the 2-position of btz is lost during the reaction. Single-crystal X-ray diffraction analysis revealed that **1** and **2** are isomorphous and crystallize in the space group $I\bar{4}$.[8] The structure of **1** is shown in Figure 1. The pentanuclear cluster is composed of a tetrahedral arrangement of four six-coordinate Co^{2+} ions centered on the fifth one. Each of the six μ_3-btz ligands straddles an edge of the tetrahedron and is bound to the central metal through the nitrogen atom in the 2-position. Six nitrogen atoms from six btz ligands therefore complete the coordination sphere of the central Co^{2+} ion, while each Co^{2+} ion on the apical positions is coordinated by three nitrogen atoms from three btz ligands and two oxygen atoms from a chelating nitrate group; the remaining position is occupied by a water molecule. The Co–$O_{nitrate}$ bonds [2.155(6) and 2.186(6) Å] are slightly longer than the Co–O_{water} bond [2.109(6) Å], thus suggesting the feasibility of substitution of the nitrate group. It should be mentioned that similar pentanuclear tetrahedral structures have been reported for the copper complexes $[Cu_5(btz)_6L_4]$

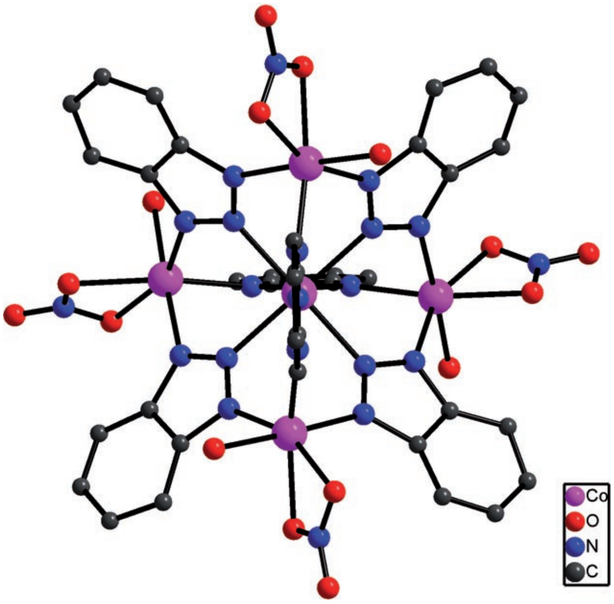

Figure 1. Perspective view of the molecular structure of **1**.

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[*] Y. L. Bai, Prof. J. Tao, Prof. R.-B. Huang, Prof. L.-S. Zheng
State Key Laboratory for Physical Chemistry of Solid Surfaces and Department of Chemistry, Xiamen University
Xiamen 361005 (P.R. China)
Fax: (+86) 592-218-3047
E-mail: taojun@xmu.edu.cn

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(L = tfpbd, trop, acac, ph/Me-pd, ph/ph-pd, C_4H_3S/CF_3-pd) (tfpbdH = 4,4,4-trifluoro-1-phenyl-1,3-butanedione; tropH = tropolone; acacH = acetylacetone; ph/Me-pdH = 1-phenyl-1,3-butanedione; ph/ph-pdH = 1,3-diphenyl-1,3-propanedione; C_4H_3S/CF_3-pdH = 4,4,4-trifluoro-1-(2-thienyl-1,3- butanedione)[9] and the nickel complex $[Ni_5(OH)(Rbtz)_5(acac)_4(H_2O)_4]$.[10]

In view of the structural feature of the pentanuclear tetrahedron as well as the four apical M^{2+} coordination sites, the nitrate groups and water molecules bonded to these apical sites might be replaceable by organic linkers that possess specific functionalities to give network structures with a desired shape, geometry, and rigidity. The pentanuclear clusters **1** and **2** also have the advantage of being readily soluble in common organic solvents such as methanol, ethanol, acetonitrile, and acetone. These facts inspired us to construct targeted networks based on these rigid and directional pentanuclear building units.

When an acetone solution of **1** or **2** was allowed to slowly diffuse into an aqueous solution of LiTCNQ the expected 3D complexes **3** or **4**, respectively, were obtained by substitution of the nitrate groups with the $TCNQ^{\bullet-}$ radical anion. The IR spectra of **1** and **2** (Figure S1 in the Supporting Information) show a strong peak at $\tilde{\nu} = 1384\ cm^{-1}$ due to the ν(NO) absorption of the nitrate group. This peak is no longer present in the spectra of **3** and **4** and a new, strong peak appears at $\tilde{\nu}$ = 2198 for **3** and 2201 cm^{-1} for **4**. As the $\nu(C{\equiv}N)$ absorption of Li(TCNQ) appears at 2197 cm^{-1} (2222 cm^{-1} for neutral TCNQ and 2164 and 2096 cm^{-1} for the $TCNQ^{2-}$ dianion in Na_2TCNQ)[5], the new absorptions of **3** and **4** were assigned to the $\nu(C{\equiv}N)$ mode of the mono-radical anion $TCNQ^{\bullet-}$. The charge on the TCNQ moiety was estimated from the empirical equation[11] $\rho = A[c/(b+d)] + B$. The values of A (−41.667) and B (19.833) were determined from neutral TCNQ ($\rho = 0$)[12] and RbTCNQ ($\rho = -1$),[13] respectively, and the values of b, c, and d from the bond lengths of TCNQ defined in Scheme S1 (Supporting Information). This equation give TCNQ charges of −1.08 and −1.04 for **3** and **4**, respectively, thus confirming the presence of monoanionic $TCNQ^{\bullet-}$ as suggested by the IR spectra.

Both **3** and **4** crystallize in the tetragonal space group $I4_1/acd$.[14] All metal ions in the pentanuclear units of **3** and **4** still adopt an octahedral coordination geometry, although the two oxygen atoms from one nitrate group on the apical metal coordination sites in **1** and **2** have been replaced by two nitrogen atoms from two $TCNQ^{\bullet-}$ ligands and the coordinated water molecules in the equatorial planes of the metal ions in **1** and **2** appear in the axial positions in **3** and **4**. The $Co{-}N_{TCNQ}$ bonds [2.137(5) and 2.142(5) Å] are slightly shorter than the respective $Co{-}O_{nitrate}$ bonds, and the M−N−C angles [164.2(5)° and 172.7(4)° for **3**; 166.0(4)° and 172.5(3)° for **4**] indicate that the μ_2-TCNQ linkers are nonplanar. As shown in Figure 2a, each tetrahedral unit can be viewed as a four-connected uninode surrounded by $TCNQ^{\bullet-}$ ligands, which adopt a *trans-anti* coordination mode to connect four adjacent tetrahedral units into a 3D diamondoid network (Figure 2b) containing large 1D rectangular channels ($20.096 \times 23.294\ Å^2$; Figure S2 in the Supporting Information). It is well-established that diamondoid networks tend to interpenetrate to fill the voids generated within a single diamond net[15] and, indeed, complexes **3** and **4** also adopt interpenetrated structures to avoid the formation of very large open cavities (Figure 2c). Furthermore, because of this structural interpenetration, significant π–π interactions between neighboring TCNQ radical ions from the two identical frameworks are found, with TCNQ–TCNQ π-stacking distances of 3.331 and 3.348 Å in **3** and **4**, respectively. It is worth noting that this interpenetrating feature of **3**

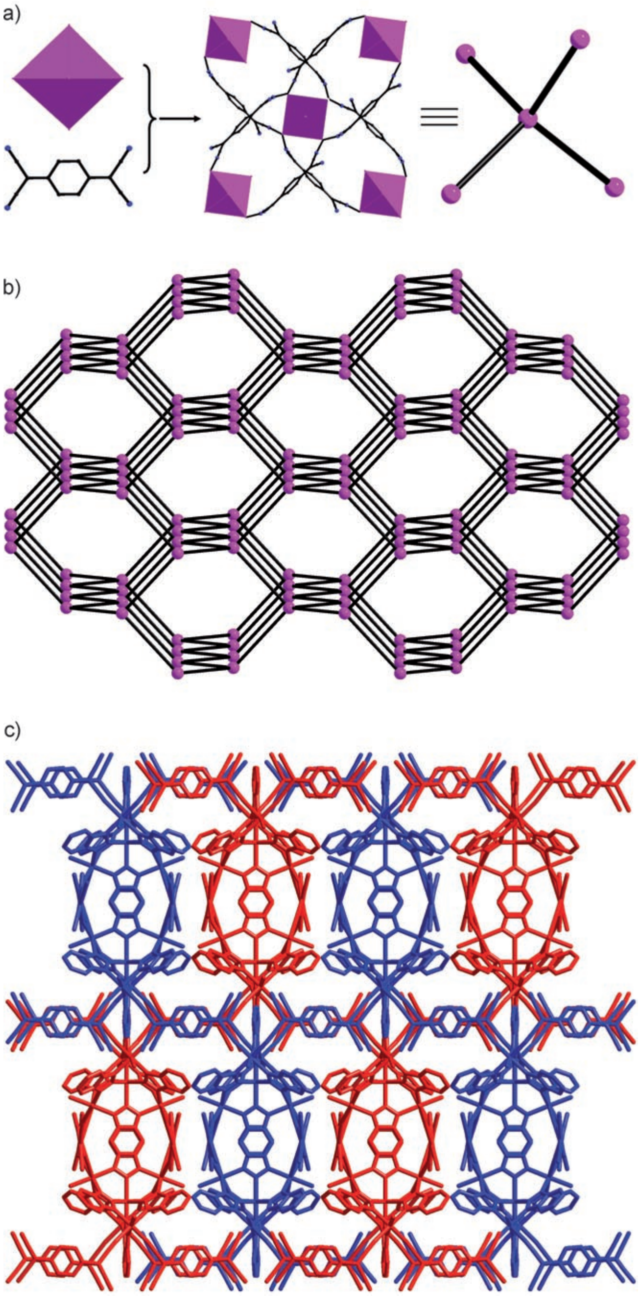

Figure 2. Structures of **3** and **4**. a) Pentanuclear clusters as SBUs with four adjacent clusters connected by μ_2-TCNQ linkers. b) The 3D diamondoid framework viewed along the *a* axis (balls and sticks represent pentanuclear tetrahedral units and $TCNQ^{\bullet-}$ ligands, respectively). c) The twofold (color-separated in blue and red) interpenetrated 3D frameworks of **3** and **4**.

or **4**, which contain tetrahedral clusters, is seldom found in extended frameworks.[16]

ESI-MS experiments were conducted with acetone solutions of **1** and **2** in order to gain further insight into the assembly process. As shown in Figures 3 a (**1**) and 3 b (**2**), the main ion peaks observed have a weight of 10 less than the molecular weight as a result of the clusters losing four coordinated water molecules and capturing a nitrate ion to form $[M_5(btz)_6(NO_3)_5]^-$. The weak ion peaks with a weight 37 less than the molecular weight correspond to the clusters losing two coordinated water molecules and one hydrogen atom to form $[M_5(btz)_6(NO_3)_4(H_2O)(OH)]^-$ in the anionic mode of the ESI source.[17] All the mass peaks for **2** were isotopically resolved and agree very well with the theoretical distributions (Figure 3 c and d). These results indicate that the tetrahedral structures of **1** and **2** remain stable while assembling into three-dimensional frameworks in solution.

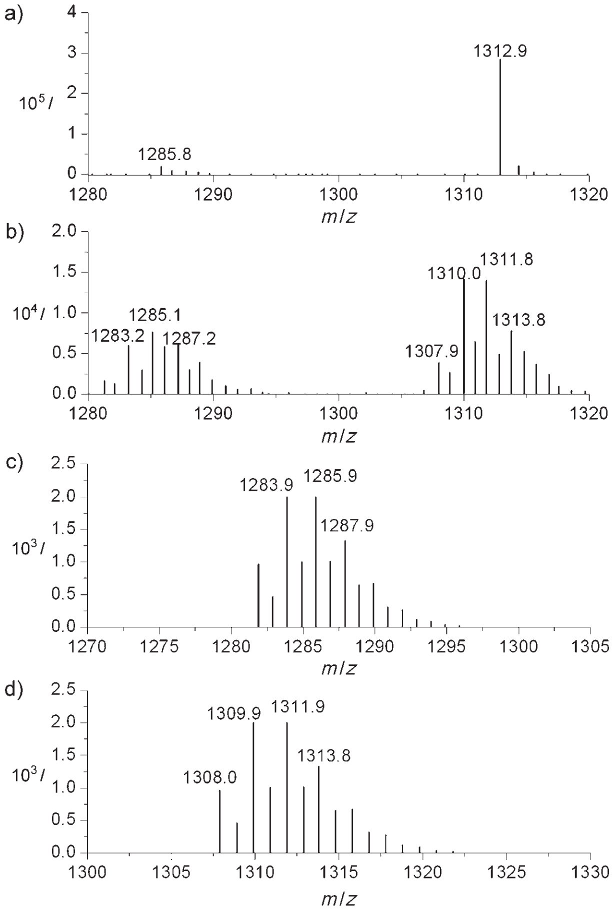

Figure 3. ESI mass spectra of **1** (a) and **2** (b) in acetone solution, and the simulated isotopic distributions of m/z 1285 for $[Ni_5(btz)_6(NO_3)_4(H_2O)(OH)]^-$ (c) and m/z 1311 for $[Ni_5(btz)_6(NO_3)_5]^-$ (d).

The magnetic susceptibilities of **1**–**4** are shown in Figure 4. The $\chi_M T$ values observed at room temperature are 9.28 and 9.23 $cm^3\,K\,mol^{-1}$ for **1** and **3** and 4.06 and 4.52 $cm^3\,K\,mol^{-1}$ for **2** and **4**, respectively. These values are lower than the theoretical values of 9.375 $cm^3\,K\,mol^{-1}$ for five spin-only Co^{2+} ($S=3/2$) ions for **1** and **3** and 5.0 $cm^3\,K\,mol^{-1}$ for five uncoupled Ni^{2+} ($S=1$) ions for **2** and **4**. There is clearly no significant contribution to the $\chi_M T$ values from the $S=1/2$ $TCNQ^{\bullet -}$ radical anions in **3** or **4**. This is because π-stacked $TCNQ^{\bullet -}$ ions (as in **3** or **4**) are diamagnetic (magnetically dimerized) and/or strongly antiferromagnetically coupled, which results in nearly zero magnetic contributions at high temperature.[18] The $\chi_M T$ value of **1** gradually decreases upon lowering the temperature, reaching a minimum of 3.59 $cm^3\,K\,mol^{-1}$ at around 5 K then increasing to 3.71 $cm^3\,K\,mol^{-1}$ at 2 K. The $\chi_M T$ values of **2**–**4** decrease continuously in the whole temperature range, thereby indicating dominant antiferromagnetic interactions in **1**–**4** even though the χ vs. T plots (Figure S5 in the Supporting Information) do not show a maximum. As **1** shows no bifurcation in the FCM and ZFCM plots (Figure S6 a in the Supporting Information), the increase of $\chi_M T$ for **1** at low temperature is not due to long-range ordering. The magnetic moment of this compound between 2 and 25 K in various fields (Figure S6 b in the Supporting Information) varies in a manner similar to that of a Co–dca (dca = dicyanamide) network complex[15b] and is due to the effect of spin–orbit coupling and low-symmetry ligand-field splittings on single-ion $^4T_{1g}$ states combined with weak ferromagnetic coupling between such ions.

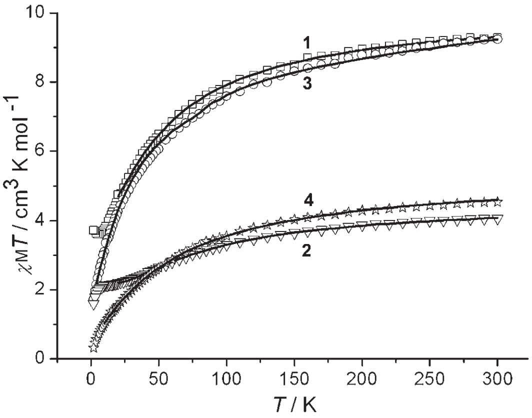

Figure 4. Magnetic susceptibilities of **1**–**4** in the temperature range 2–300 K in an applied field of 1 KOe. These plots were fitted with a highly symmetric model.[9]

The magnetic susceptibilities of **1**–**4** were fitted with a highly symmetric model (Scheme S2 in the Supporting Information)[9] to give $J_1=-1.09$, $J_2=-3.07\,cm^{-1}$, and $g=2.08$ for **1**; $J_1=-2.46$, $J_2=-8.39\,cm^{-1}$, and $g=1.92$ for **2**; $J_1=-0.94$, $J_2=-1.99\,cm^{-1}$, and $g=1.96$ for **3**; and $J_1=-2.98$, $J_2=-6.11\,cm^{-1}$, and $g=2.07$ for **4**, thereby indicating that the intracluster interactions in **3** and **4** are weaker than those in **1** and **2** and that the interactions between nickel ions are stronger than those between cobalt ions. The intercluster coupling constants of -0.05 and $-1.60\,cm^{-1}$ for **3** and **4**, respectively, show antiferromagnetic interactions between clusters through the $TCNQ^-$ bridges, as supported by the *M*-*H* plots shown in Figure S7 (c and d; see the Supporting Information).

In summary, two pentanuclear clusters have been synthesized as building units for the construction of three-dimen-

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sional, diamondlike networks by taking advantage of their predetermined shapes, sizes, geometries, substitutable sites, and solubility. The ESI-MS results reported herein reveal that the pentanuclear units maintain their structural integrity before condensing into frameworks, thereby allowing a successful step-by-step assembly. To the best of our knowledge, this is the first example of a compound that contains interpenetrating 3D nets constructed from pentanuclear building units and TCNQ radical ions. The magnetic results indicate the presence of distinct antiferromagnetic interactions between pentanuclear clusters through TCNQ$^{\bullet-}$ linkers. We are currently aiming to synthesize new, stable, multidimensional coordination polymers based on these pentanuclear building units and other anionic/neutral organic linkers and hope to be able to prevent their interpenetration.

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[8] Crystal data for **1**: $C_{36}H_{32}Co_5N_{22}O_{16}$, f.w. = 1323.49 g mol^{-1}, tetragonal, space group $I\bar{4}$, $Z = 2$, 298(2) K, $a = 13.3156(6)$, $c = 19.1355(3)$ Å, $V = 3392.8(2)$ Å^3, $\rho_{\text{cald}} = 1.295$ g cm^{-3}, $R_1 = 0.0691$, $wR_2 = 0.2012$, $\mu = 1.264$ mm^{-1}, $S = 1.089$. Crystal data for **2**: $C_{36}H_{32}N_{22}Ni_5O_{16}$, f.w. = 1322.39 g mol^{-1}, tetragonal, space group $I\bar{4}$, $Z = 2$, 298(2) K, $a = 12.9950(14)$, $c = 18.922(4)$ Å, $V = 3195.4(8)$ Å^3, $\rho_{\text{cald}} = 1.374$ g cm^{-3}, $R_1 = 0.0409$, $wR_2 = 0.1115$, $\mu = 1.517$ mm^{-1}, $S = 1.112$. CCDC-675502 to 675505 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.

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[14] Crystal data for **3**: $C_{84}H_{52}Co_5N_{34}O_6$, f.w. = 1928.25 g mol^{-1}, tetragonal, space group $I4_1/acd$, $Z = 8$, 223(2) K, $a = 23.1690(2)$, $c = 42.7980(10)$ Å, $V = 22\,974.1(6)$ Å^3, $\rho_{\text{cald}} = 1.115$ g cm^{-3}, $R_1 = 0.0648$, $wR_2 = 0.2226$, $\mu = 0.763$ mm^{-1}, $S = 1.119$. Crystal data for **4**: $C_{84}H_{55}N_{34}Ni_5O_{7.5}$, f.w. = 1954.17 g mol^{-1}, tetragonal, space group $I4_1/acd$, $Z = 8$, 223(2) K, $a = 23.0807(10)$, $c = 42.2528(4)$ Å, $V = 22\,508.9(3)$ Å^3, $\rho_{\text{cald}} = 1.153$ g cm^{-3}, $R_1 = 0.0746$, $wR_2 = 0.2388$, $\mu = 1.406$ mm^{-1}, $S = 1.091$.

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