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Organization of Tetrahedral Chalcogenide Clusters Using a Tetrahedral Quadridentate Linker

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Using predesigned tetrahedral quadridentate linker tetrakis(4-pyridyloxymethylene)methane (TPOM) as the organic linker, tetrahedral P1 clusters ($[Cd_8S(SPh)_{16}]^{2-}$) and C1 clusters ($[Cd_{17}S_4(SPh)_{28}]^{2-}$) have been assembled into beltlike (MCOF-9) or chainlike (MCOF-10) configurations, as determined by single-crystal X-ray diffraction. The onset of optical absorptions of MCOF-9 and MCOF-10 is around 400 and 420 nm, respectively. The thermal analysis shows that both materials are stable up to 250 °C.

Metal chalcogenide chemistry has received increasing interest because of its relation to both semiconductor nanoparticles and crystalline porous materials.[1−4] Using organic ligands of various length, geometry, and rigidity to create spatially organized nanocluster−ligand composite structures through the synthetic design of either nanoclusters or cross-linkers represents a new direction in the approach to novel inorganic−organic hybrid materials. Because the properties of semiconducting nanocluster superlattices are dependent on individual clusters, organic linkers, and their spatial organization, the coassembly between semiconducting nanoclusters and organic linkers can lead to synergistic properties that have the potential to be utilized for new applications in areas such as electrochemical solar cells and sensors.[5−7] In addition, the assembly of chalcogenides with desired organic linkers can provide unprecedented crystalline porous semiconductors that integrate uniform porosity with semiconductivity. Such porous semiconductors could have applications that complement other porous materials (e.g., zeolites) that are usually insulators. Toward these goals, several interesting chalcogenide−organic hybrid materials have been reported through judicious choice of suitable building blocks.[8−10]

Recently, our group has become interested in the coassembly between chalcogenide nanoclusters and functional organic linkers.[11−14] Among various bifunctional ligands, commercially available bipyridines were selected to organize different cadmium or zinc chalcogenide clusters into inorganic−organic one- or two-dimensional superstructures. These results show that it is possible to create ordered nanocluster−spacer architectures through the synthetic design of either nanoclusters or bridging linkers of different lengths and rigidity, in addition to various patterns of joining them together.

However, one limitation in our previous studies is that only bipyridines were employed to cross-link chalcogenide clusters. The low connectivity (two-connected) of bipyridines could limit the range of topologies available. We anticipate that the synthetic and structural chemistry will be more diverse and interesting if more sophisticated organic ligands are used to organize chalcogenide nanoclusters. In particular, tetrahedral quadridentate linkers might provide richer op-

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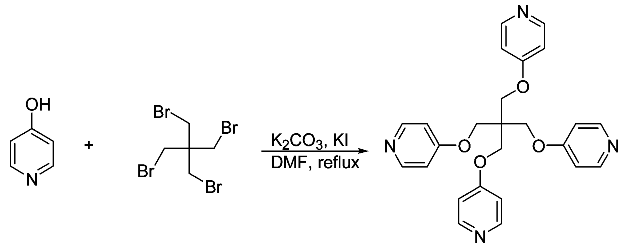
Scheme 1. Synthetic Route of TPOM



portunities for organizing chalcogenide nanoclusters into periodic arrays of various dimensions.

The work reported here represents our first step in the organization of chalcogenide clusters with ligands beyond commercially available bipyridines. Here, we examine how tetrahedral quadridentate linker tetrakis(4-pyridyloxymethylene)methane (TPOM; Scheme 1) and solvents affect the size of the clusters and their spatial organization. It is worth noting that TPOM is a rather uncommon ligand considering that no crystal structures containing TPOM are known in the current version of the Cambridge Structural Database. New composite superstructures reported here are denoted as MCOF-9 and MCOF-10, where MCOF denotes metal chalcogenide organic frameworks.

MCOF-9 (formula: $\{[Cd_8S(SPh)_{14}]_2TPOM\}_n$) and MCOF-10 (formula: $\{[Cd_{17}S_4(SPh)_{26}]TPOM\}_n$) were synthesized under solvothermal conditions at 85 °C.[15,16] Cd^{2+} and SPh^- came from the single-source precursor in the form of $Cd(SPh)_2$ synthesized according to the previously reported precedure.[17] Thiourea is used as the S^{2-} source. The S^{2-} source is essential for the growth of large clusters that require the presence of one or more core S^{2-} sites, which is the case for clusters reported here. In the absence of the S^{2-} source, the largest accessible tetrahedral cluster is only supertetrahedral T2 $Cd_4(SPh)_{10}{}^{2-}$.

Tetrahedral quadridentate linker TPOM was synthesized by reacting pentaerythrityl tetrabromide with 4-hydroxylpyridine in *N*,*N'*-dimethylformamide (DMF) containing K_2CO_3 and KI at refluxing conditions (Scheme 1).[18] The structures of MCOF-9 and MCOF-10 were determined from single-crystal X-ray diffraction data collected at 150 K on an APEX II CCD diffractometer.[19]

Chalcogenide clusters (P1, $[Cd_8S(SPh)_{16}]^{2-}$, and C1, $[Cd_{17}S_4(SPh)_{28}]^{2-}$; Figure 1a,b) reported here are members of two separate series of tetrahedral chalcogenide clusters: pentasupertetrahedral clusters (denoted as P*n*) and capped supertetrahedral clusters (denoted as C*n*).[2] P1 cluster $[Cd_8S(SPh)_{16}]^{2-}$ found in MCOF-9 (Figure 1c) is the first member of the P*n* series. One key structural feature of the P1 cluster is the presence of a core Cd_4S antitetrahedron covered by four outer CdS_4 regular tetrahedra. The metal chalcogen core of P1 clusters is also known in other compositions, particularly II−IV (e.g., Zn−Sn) chalcogenides that contain no surface ligands.[3,4] The C1 cluster in MCOF-10 (Figure 1d), which is far less common than P1, is the first member of the C*n* series. One key structural feature of the C1 cluster is the presence of a core CdS_4 tetrahedron sharing its S sites with four corner Cd_4S_4 barrelanoid cages.

In the beltlike MCOF-9 structure, adjacent P1 clusters are assembled into a one-dimensional structure by TPOM linkers. In each P1 cluster, two corners are occupied by terminating SPh^- groups and the remaining two corners are replaced by N donors from organic linkers. As a result, the chalcogenide cluster is only two-connected while the organic ligand is four-connected. The replacement of two corner −SPh groups by neutral linkers decreases the charge on each P1 cluster from −2 to 0, which leads to neutral one-dimensional structures that are aligned in the same direction and packed together through noncovalent interactions.

If the solvent was changed from CH_3CN/CH_3OH to DMF/H_2O while keeping other reaction conditions unchanged, MCOF-10 containing a larger cluster C1 was obtained. Unlike MCOF-9, which uses all four pyridyl groups in TPOM for cross-linking, the tetrahedral TPOM in MCOF-10 only use two of its four pyridyl groups for cross-linking C1 clusters. Similarly, each chalcogenide cluster also uses its two corners for cross-linking. Such lower-than-expected connectivity of TPOM (two instead of four in MCOF-9) may be due to the much larger size of C1 clusters (as compared to P1), which makes it sterically unfavorable to crowd four C1 clusters around TPOM.

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(15) The detailed synthesis for MCOF-9 is as follows: 100 mg of $Cd(SPh)_2$, 50 mg of thiourea, and 50 mg of TPOM were mixed in a glass vial containing 6 g of CH_3CN/methanol (weight ratio = 2:1). After 30 min, the vial was sealed and heated at 85 °C for 3 weeks. Then, the vial was allowed to cool to room temperature. Clear crystals was filtered and washed with methanol three times. Yield: 35% (based on Cd). IR data (cm^{-1}): 3090, 2890, 1580, 1520, 1475, 1263, 1185, 983, 692, 620.

(16) The detailed synthesis for MCOF-10 is as follows: 100 mg of $Cd(SPh)_2$, 50 mg of thiourea, and 50 mg of TPOM were mixed in a glass vial containing 6 g of DMF/H_2O (weight ratio = 2:1). After 30 min, the vial was sealed and heated at 85 °C for 3 weeks. Then, the vial was allowed to cool to room temperature. Clear crystals was filtered and washed with methanol three times. Yield: 30% (based on Cd). IR data (cm^{-1}): 3060, 2920, 1579, 1518, 1475, 1270, 1180, 991, 785, 540.

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(18) The synthesis of TPOM: 2.6 g of pentaerythrityl tetrabromide, 3 g of 4-hydroxylpyridine, 20 g of K_2CO_3, and 100 mg of KI were mixed in 100 mL of DMF and refluxed for 3 days. After it was cooled, the mixture was poured into 1000 mL of water and stirred overnight. The white product was collected. Yield: 75%. MS (EI, *m/e*): 444. ^{1}H NMR (ppm, $CDCl_3$): 4.40 (s, 2), 6.80 (d, 2), 8.42 (d, 2). ^{13}C NMR (ppm, $CDCl_3$): 45.1, 66.0, 110.2, 152.2, 164.4.

(19) Crystal data: MCOF-9, $C_{193}H_{164}N_4O_4S_{30}Cd_{16}$, triclinic, space group $P\bar{1}$, $a = 24.7767(4)$ Å, $b = 29.0550(5)$ Å, $c = 29.9908(6)$ Å, $\alpha = 81.5090(10)°$, $\beta = 76.6240(10)°$, $\gamma = 89.4980(10)°$, $V = 20766.9(6)$ Å^3, $Z = 4$, $D_c = 1.715$ g/cm^3, $F_{000} = 10520$, Mo Kα radiation, $\lambda = 0.710\,73$ Å, $T = 150$ K, $2\theta_{max} = 40°$, final GOF = 1.145, R1 = 0.0563, wR2 = 0.1452, *R* indices based on 29 149 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1771 parameters; MCOF-10, $C_{181}H_{154}N_4O_4S_{30}Cd_{17}$, triclinic, space group $P\bar{1}$, $a = 19.1627(8)$ Å, $b = 23.6863(8)$ Å, $c = 24.0266(9)$ Å, $\alpha = 96.700(2)°$, $\beta = 92.453(2)°$, $\gamma = 112.115(2)°$, $V = 9989.5(7)$ Å^3, $Z = 2$, $D_c = 1.769$ g/cm^3, $F_{000} = 5192$, Mo Kα radiation, $\lambda = 0.710\,73$ Å, $T = 150$ K, $2\theta_{max} = 35°$, 12 600 reflections collected, final GOF = 1.024, R1 = 0.0985, wR2 = 0.2347, *R* indices based on 12 600 reflections with $I > 2\sigma(I)$ (refinement on F^2), 856 parameters. Structure solution *SHELXL-97*, full-matrix least squares based on F^2 using *SHELXL-97*. The high *R* factor for MCOF-10 is due to the low quality of the crystal that limits the diffraction angle to only 35° and an overall weak diffraction. This phenomenon is common in chalcogenide structures with large clusters, C1 in this case. Repeated syntheses and crystal data collection fail to improve the data quality.

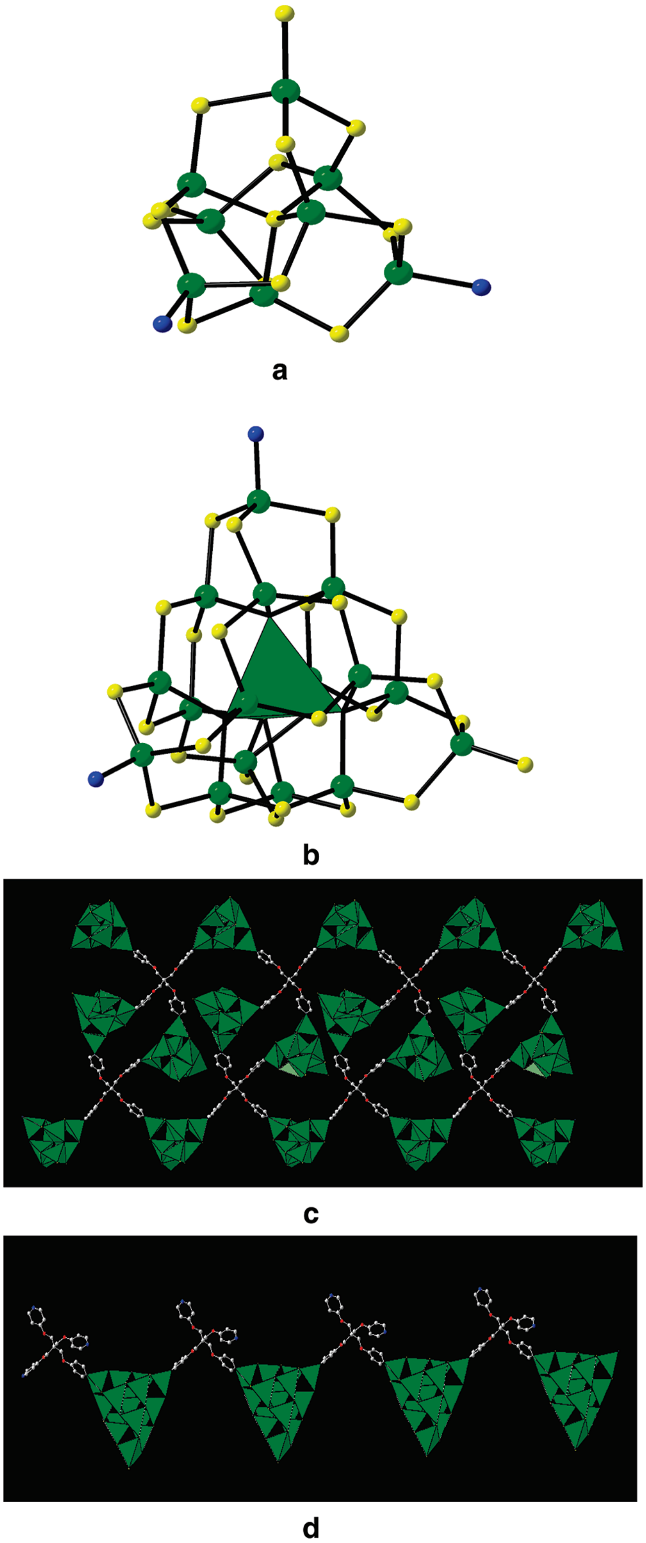

Figure 1. (a) P1 cluster in MCOF-9. (b) C1 cluster in MCOF-10. (c) Structure of MCOF-9. (d) Structure of MCOF-10. CdS_4: green tetrahedral. Cd: green ball. S: yellow ball. N: blue ball. The surface ligands are omitted for clarity.

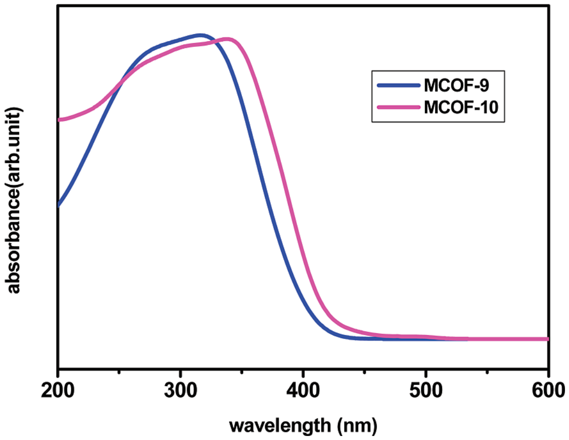

Figure 2. UV−vis absorption spectra of MCOF-9 and MCOF-10.

While TPOM behaves differently in MCOF-9 and MCOF-10, P1 and C1 clusters share one common feature because only two corners of the P1 or C1 clusters are replaced by pyridyl groups. This is because both P1 and C1 clusters carry −2 charges; further replacement of the cluster corners (−SPh) by neutral pyridyl ligands would result in positively charged clusters that are not known to be stable under solvothermal conditions. If synthetic conditions that favor C2 clusters can be found (i.e., $[Cd_{32}S_{14}(SPh)_{40}]^{4-}$), all four corners of the C2 cluster could be replaced, which represents one possible route toward higher-dimensional and high-porosity structures.

Prior to this work, no examples of the covalent coassembly between tetrahedral chalcogenide clusters and tetrahedral quadridentate linkers are known. The successful coassembly between tetrahedral sulfide clusters and organic polydentate linkers reported here demonstrates a promising approach that may eventually be extended for the synthesis of higher-dimensional structures, three-dimensional porous solids in particular.

The diffuse-reflectance spectra of MCOF-9 and MCOF-10 were studied on a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer using $BaSO_4$ powder as a 100% reflectance reference. As shown in Figure 2, MCOF-9 and MCOF-10 have absorption onsets at about 400 and 420 nm, respectively, indicating that MCOF-9 and MCOF-10 are wide-gap semiconductors with band gaps of 3.10 and 2.95 eV. The simultaneous thermogravimetric−differential scanning calorimetry analysis performed under a flowing N_2 atmosphere shows that both materials are stable up to 250 °C.

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Supporting Information Available: Crystallographic data including positional parameters, thermal parameters, and bond distances and angles (CIF), thermogravimetric analysis, IR spectra, and X-ray powder patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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