Three-Dimensional Superlattices Built from (M₄In₁₆S₃₅)ⁿ⁻ (M = Mn, Co, Zn, Cd)

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Semiconducting nanoparticles have been undergoing rapid development because of the feasibility for property engineering based on the particle size. These nanoparticles have properties intermediate between bulk materials and individual molecules and can serve as artificial atoms for constructing a variety of functional materials.

Nanoparticles can crystallize into colloidal or molecular crystals in which they are generally held together via weak van der Waals interactions. In molecular crystals, nanoclusters have well-defined chemical compositions and are free from size dispersion. ² These materials may therefore be useful for size-dependent property measurements that are free from the ambiguity due to size dispersion or surface irregularity.

For some applications (e.g., as porous hosts), a covalent network of nanoclusters is preferable. ³ By variation of the cluster dispersion or surface irregularity, measurements that are free from the ambiguity due to size dispersion or surface irregularity may therefore be useful for size-dependent property measurements that are free from the ambiguity due to size dispersion or surface irregularity.

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Figure 1. Structural diagram of a T₄ cluster, CdIn₁₆S₃₅, in UCR-1CdInS. The framework formula is CdIn₁₆S₃₅ because each terminal S²⁻ is shared between two clusters.

For example, from T₃ clusters, open-framework sulfides based on a network of nanoclusters is preferable. ³ By variation of the cluster dispersion or surface irregularity, measurements that are free from the ambiguity due to size dispersion or surface irregularity may therefore be useful for size-dependent property measurements that are free from the ambiguity due to size dispersion or surface irregularity.

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To prepare crystals of UCR-1CdInS, indium metal (85 mg), sulfur (68 mg), CdCl₂·2.5H₂O (46 mg) and 4.4′-trimethylene-dipiperidine (TMMDP) (608 mg) were mixed in a 23 mL Teflon-lined stainless steel autoclave. After addition of distilled water (4.231 g), the mixture was stirred for 10 min. The vessel was then sealed and heated at 190 °C for 10 d. The autoclave was subsequently allowed to cool to room temperature. Light-yellow prismatic crystals were obtained in 79% yield. UCR-1CdInS can also be synthesized under similar conditions with ethylene glycol as a cosolvent (up to 80 wt %). Crystals of other phases (Table 1) were synthesized under similar conditions. Starting materials included Zn(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, and Mn(CH₃COO)₂·4H₂O.

Crystal structures were solved from single-crystal data collected at room temperature on a SMART CCD diffractometer (Table 1). While all framework atoms can be determined, the guest molecules are disordered inside large cavities. In UCR-1, one-half of the T₄ cluster is crystallographically unique because it is located on a two-fold rotation axis. Using UCR-1CdInS as an example, the dimensions of six edges of the T₄ cluster are 15.47 Å(×2), 15.66 Å, 15.71 Å(×2), and 16.06 Å. Taking into account of van der Waals radius of the sulfur atom (1.8 Å), each edge of the supertetrahedron is about 20 Å long.

In UCR-1CdInS, each T₄ cluster is connected by S²⁻ to four other T₄ clusters with a center-to-center distance of 15.84 Å, comparable to the dimension of the supertetrahedral edge (Figure 2). A four-connected three-dimensional net is obtained by considering each T₄ cluster as an artificial tetrahedral atom (T-atom). This net consists of only four- and eight-rings. Each T-atom

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In UCR-1CdInS, Cd\(^{2+}\) and In\(^{3+}\) sites could not be distinguished from single-crystal structure refinement because Cd\(^{2+}\) and In\(^{3+}\) are isoelectronic. The Cd\(^{2+}\) sites are assigned to four metal sites (only two are unique in UCR-1) surrounding the tetrahedral S\(^{2-}\) site according to the Brown’s bond valence model.\(^{(15)}\) Valence sums for two Cd\(^{2+}\) sites are 2.23 and 2.27, respectively, whereas valence sums for eight In\(^{3+}\) sites range from 2.92 to 3.06.

To obtain more direct information about the distribution of divalent and trivalent cations in a T4 cluster, we prepared a series of structures in which the first-row transition metals are incorporated into [MnIn\(_{16}S_{33}\)]\(^{10^-}\) clusters. In these clusters, both the electron density and the bond distance indicate that four metal sites surrounding the tetrahedral sulfur atom are predominantly occupied by divalent cations such as Zn\(^{2+}\) or Mn\(^{2+}\) (Table 1).

Fluorescent spectra of UCR-1CdInS showed a broad emission centered at 521 nm. The excitation spectra showed an absorption onset of 350 nm and the maximum absorption at 401 nm. \(^{(15)}\) The fit to a triexponential equation gives \(\tau = 1.1, 4.6,\) and 23.2 ns. In comparison, open framework oxides were previously found to display photoluminescence with the emission maximum between 400 and 430 nm. \(^{(16)}\) It appears that by varying the composition of open-framework materials, it is possible to develop a family of inorganic–organic phosphors with a broad range of emission characteristics.

UCR-1CdInS can undergo a partial ion exchange. In one experiment, about 0.08 g of crystals of UCR-1CdInS was added to a KCl solution (50.09 g, 1.09M). After standing at room temperature for 24 h, the mixture was filtered, washed with ethanol, and dried at 110°C for 12 h. The crystallinity of the sample was confirmed by X-ray powder diffraction before and after the ion-exchange. The elemental analysis shows a significant decrease in the C, H, and N content.

Acknowledgment. Dedicated to Professor Galen D. Stucky on the occasion of his 65th birthday. We are grateful for the support of this work by UC Riverside, UC Energy Institute, and the donors of the Petroleum Research Fund (administered by the ACS).

Supporting Information Available: Crystallographic data including positional parameters, thermal parameters, and bond distances and angles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Fluorescent spectra were measured on a SPEX Fluorolog-3 Tau3 system equipped with a 450 W xenon lamp.
(17) Results of the elemental analysis (in wt %) for UCR-1CdInS are 16.84 (calc 16.82) for C, 3.09 (calcd 3.61) for H, and 2.11 (calc 3.02) for N before the ion exchange and 12.88 for C, 2.11 for H, and 2.12 for N after the exchange. The calculated values are based on the formula [Cd\(_{4}\)In\(_{16}\)S\(_{33}\)]\(^{10^-}\) (C\(_{13}\)H\(_{20}\)N\(_{18}\)O\(_{3}\)), \(x = 13\).

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**Table 1.** A Summary of Crystallographic Data for New T4 Framework Structures Synthesized in This Study

<table>
<thead>
<tr>
<th>name</th>
<th>T4 cluster</th>
<th>amine(^a)</th>
<th>sp. gr.</th>
<th>(a (\text{Å}))</th>
<th>(c (\text{Å}))</th>
<th>(R(F))</th>
<th>2(q_{\text{max}})</th>
<th>M–S (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCR-1CdInS</td>
<td>[Cd(<em>{4})In(</em>{16})S(_{33})](^{10^-})</td>
<td>TMDP</td>
<td>I-42d</td>
<td>42.105(3)</td>
<td>16.700(2)</td>
<td>6.72</td>
<td>45</td>
<td>2.503(6)</td>
</tr>
<tr>
<td>UCR-1ZnInS</td>
<td>[Zn(<em>{4})In(</em>{16})S(_{33})](^{10^-})</td>
<td>BAPP</td>
<td>I-42d</td>
<td>41.811(8)</td>
<td>16.685(4)</td>
<td>7.93</td>
<td>45</td>
<td>2.384(6)</td>
</tr>
<tr>
<td>UCR-1MnInS</td>
<td>[Mn(<em>{4})In(</em>{16})S(_{33})](^{10^-})</td>
<td>AEPP</td>
<td>I-42d</td>
<td>41.974(5)</td>
<td>16.727(3)</td>
<td>6.52</td>
<td>45</td>
<td>2.417(6)</td>
</tr>
<tr>
<td>UCR-1CoInS</td>
<td>[Co(<em>{4})In(</em>{16})S(_{33})](^{10^-})</td>
<td>BAPP</td>
<td>I-42d</td>
<td>41.698(8)</td>
<td>16.673(5)</td>
<td>8.32</td>
<td>45</td>
<td>2.344(7)</td>
</tr>
<tr>
<td>UCR-5ZnInS-1</td>
<td>[Zn(<em>{4})In(</em>{16})S(_{33})](^{10^-})</td>
<td>ATMP</td>
<td>I-42d</td>
<td>23.580(8)</td>
<td>43.92(1)</td>
<td>8.51</td>
<td>40</td>
<td>2.401(3)</td>
</tr>
<tr>
<td>UCR-5ZnInS-2</td>
<td>[Zn(<em>{4})In(</em>{16})S(_{33})](^{10^-})</td>
<td>ATMP</td>
<td>I-42d</td>
<td>23.396(8)</td>
<td>43.44(2)</td>
<td>9.87</td>
<td>40</td>
<td>2.381(4)</td>
</tr>
<tr>
<td>UCR-5ZnInS-3</td>
<td>[Zn(<em>{4})In(</em>{16})S(_{33})](^{10^-})</td>
<td>ATMP</td>
<td>I-42d</td>
<td>23.88(2)</td>
<td>43.69(2)</td>
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<tr>
<td>UCR-5ZnInS-4</td>
<td>[Zn(<em>{4})In(</em>{16})S(_{33})](^{10^-})</td>
<td>ATMP</td>
<td>I-42d</td>
<td>23.45(2)</td>
<td>43.60(5)</td>
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<tr>
<td>UCR-5ZnInS-5</td>
<td>[Zn(<em>{4})In(</em>{16})S(_{33})](^{10^-})</td>
<td>ATMP</td>
<td>I-42d</td>
<td>23.29(4)</td>
<td>43.44(6)</td>
<td></td>
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</tr>
</tbody>
</table>

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\(^{a}\) TMDP = 4,4′-trimethylenedipiperidine; BAPP = 1,4-bis(3-aminopropyl)piperazine; AEPP = 1-(2-aminoethyl)piperazine; ATMP = 4-amino-2,2,6,6-tetramethylpiperidine.

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