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Self-Assembly of Novel Dye Molecules and $[Cd_8(SPh)_{12}]^{4+}$ Cubic Clusters into Three-Dimensional Photoluminescent Superlattice

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Nanocrystal superlattices represent a new family of materials that are different from either individual nanoclusters or bulk materials.[1] In the past two decades, examples of nanocrystal superlattices based on single-sized nanoclusters such as $Cd_{32}S_{14}(SPh)_{36}$·4DMF and $[Cd_{17}S_4(SCH_2CH_2OH)_{26}]$ have been prepared.[2−4] These nanoclusters can be considered as lower limits of colloidal nanoclusters. Some properties characteristic of nanoparticles such as size-dependence of band gap have been demonstrated in some of these relatively small clusters.[5]

We are interested in the use of multifunctional ligands to organize chalcogenide nanoclusters into covalent superlattices. This approach has the potential to create porous materials with tunable pore sizes in both micro- and meso- regimes. Few studies have been done in this area although organic ligands have been widely used to link metal cations or their oxygen-containing clusters.[6−11] The combination of molecular linkers and nanoclusters is expected to produce synergetic effects. For example, luminescent properties of nanoclusters can be enhanced if organic linker molecules serve to absorb photon energies and transfer them to inorganic clusters.

Here we report a three-dimensional photoluminescent superlattice (denoted as UCR-9) formed by linking $[Cd_8(SPh)_{12}]^{4+}$ clusters with tetradentate dye molecules.[12] Crystals of UCR-9 can be synthesized by the following procedure. The salt $[N(CH_3)_4]_4[Cd_{10}S_4(SPh)_{16}]$ was synthesized by the literature method.[13] A light yellow intermediate with the composition $Cd_{10}S_4(SPh)_{12}$ was obtained by heating $[N(CH_3)_4]_4[Cd_{10}S_4(SPh)_{16}]$ at 250 °C for 3 h.[14] To prepare crystals of UCR-9, 0.083 g of the light yellow precursor, 0.1150 g of 4,4′-trimethylenedipyridine, 0.0673 g of Na_2SO_4, and 2.1770 g of water were mixed in a 23 mL Teflon-lined stainless steel autoclave, and the mixture was stirred for 5 min. The vessel was then sealed and heated at 190 °C for 3 d. After the mixture was cooled to room temperature, brown yellow cubelike crystals (i.e., UCR-9) were recovered. The thermogravimetric analysis under nitrogen atmosphere showed that UCR-9 underwent an abrupt weight loss at about 300 °C.

A prominent structural feature in UCR-9 is the presence of a novel cadmium thiophenolate cluster (Figure 1). In the $[Cd_8(SPh)_{12}]^{4+}$ cluster, eight cadmium ions are arranged at corners of a cube, while 12 −SPh groups are distributed slightly off the center of each cubic edge. A sulfate group is located at the center of each cluster. For single-sized cadmium chalcogenide clusters with eight or more metal ions, few types are known, including $Cd_{32}S_{14}(SPh)_{36}$·4DMF, $[Cd_{17}S_4(SPh)_{28}]^{2-}$, $[Cd_{10}S_4(SPh)_{16}]^{4-}$, and $[Cd_8Se(SePh)_{12}Cl_4]^{2-}$.[5] Therefore, the $[Cd_8(SPh)_{12}]^{4+}$ cluster reported here is a valuable addition to this family.

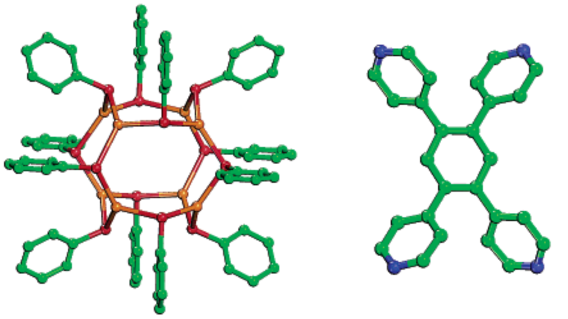
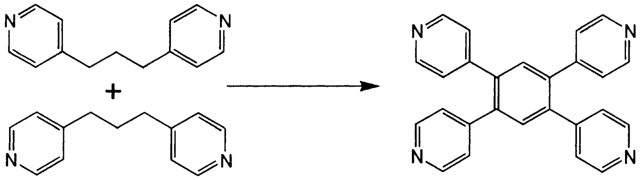


Figure 1. The $[Cd_8(SPh)_{12}]^{4+}$ cubic unit and the 1,2,4,5-tetra(4-pyridyl)benzene molecule in UCR-9.

Scheme 1



The structure of the $[Cd_8(SPh)_{12}]^{4+}$ cluster resembles the double four-ring unit in zeolites. The double four-ring unit such as $(Al_4Si_4O_{16})^{4-}$ is among the most important structural building units in zeolites.[15] There has been a significant amount of interest in synthesizing these types of structural units, because they could subsequently be linked into various topologies.[16]

Another interesting discovery is the in situ hydrothermal synthesis of a tetradentate dye molecule by oxidative coupling of two 4,4′-trimethylenedipyridine molecules (Scheme 1). The oxidative coupling between two 4,4′-trimethylenedipyridine units is essential in establishing the three-dimensional framework in UCR-9. UCR-9 can be considered as layers of $[Cd_8(SPh)_{12}]^{4+}$ clusters stacked along the *c*-axis. Within each layer, $[Cd_8(SPh)_{12}]^{4+}$ clusters are joined into a square pattern encircling large square pores formed by four $[Cd_8(SPh)_{12}]^{4+}$ clusters. The linkage between adjacent layers is provided by benzene rings formed between two 4,4′-trimethylenedipyridine units (Figure 2).

The three-dimensional arrangement of $[Cd_8(SPh)_{12}]^{4+}$ clusters in UCR-9 is very close to that of the primitive tetragonal packing with cluster−cluster distances of 18.9, 18.9, and 13.3 Å along three orthogonal directions. The stacking of layers is eclipsed, leading to channels with large square pores along the *c*-axis (Figure 3). The crystal volume occupied by disordered extraframework species is as high as 47% as calculated by the program PLATON.[17]

The photoluminescent properties of UCR-9 reflect both inorganic and organic compositions and their synergetic effects. One prominent emission peak occurs at 580 nm (fwhm ≈ 100 nm), and its

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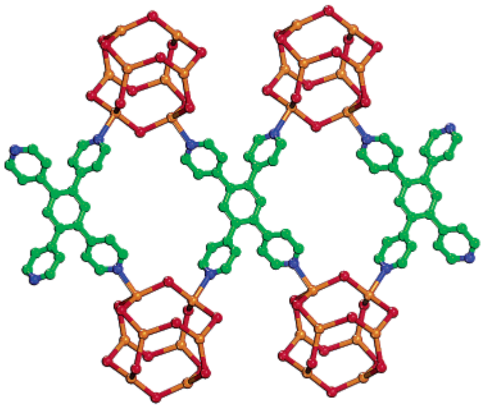

Figure 2. $[Cd_8(SPh)_{12}]^{4+}$ cubic units are joined together with 1,2,4,5-tetra-(4-pyridyl)benzene molecules in UCR-9.

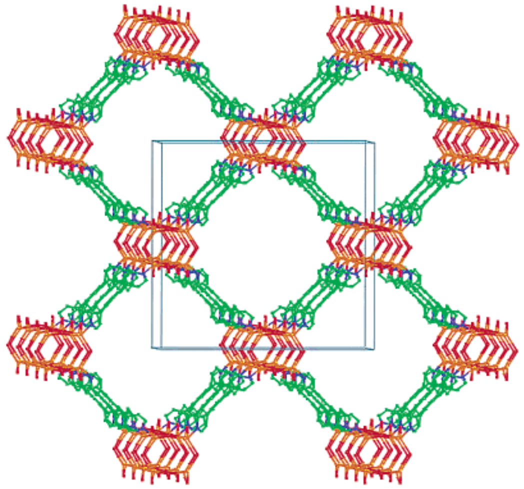

Figure 3. A view of the three-dimensional framework down the *c*-axis.

excitation spectrum shows a maximum absorption at 490 nm. This process is likely due to the S^{2-} to Cd^{2+} charge transfer, similar to that observed for the bulk CdS. The emission disappears upon dissolving UCR-9 in dilute nitric acid.

UCR-9 also displays a strong doublet at 415 and 440 nm. This doublet is likely to be from dye molecules because it is observable even after UCR-9 is dissolved in the nitric acid. The 580 nm emission and the doublet have about the same intensity when excited at 370 nm. Below 370 nm, the doublet is stronger, and above 370 nm, the 580 nm peak becomes more intense. The weak emission of UCR-9 at 360 nm when excited at 300 nm likely originates from the framework because it disappears after UCR-9 is dissolved in the nitric acid. One reason for its low intensity is that its emission maximum corresponds to the absorption maximum of the dye molecule.

The emission at 580 nm can be excited by a wide spectral range down to at least 350 nm. This property is desirable in applications such as photovoltaics where a broad absorption of the solar spectrum is advantageous. In UCR-9, the large absorption range is likely due to the effect of combining dye molecules and inorganic clusters together. Because the emission from dye molecules at about 440 nm is close to the absorption maximum (i.e., 490 nm) needed to produce emission at 580 nm, the absorption of the dye molecule and the subsequent energy transfer can enhance luminescent properties of the inorganic cluster.

In conclusion, this work describes the in situ formation of a novel dye molecule and an interesting cubic cluster. The self-assembly of inorganic and organic components leads to a novel open framework material with large pore size and interesting luminescent behavior. This work is our first step toward the organization of chalcogenide cluster units with molecular linkers and demonstrates the synergetic effect of creating inorganic−organic composite materials.

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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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(12) Crystal data for UCR-9: $[Cd_8(SC_6H_5)_{12}L_2 \cdot SO_4](HSO_4)_2(H_2O)_4$ where L = 1,2,4,5-tetra(4-pyridyl)benzene, $C_6H_2(C_5H_4N)_4$, $C2/m$, $Z = 2$, $T = 150$ K, Mo Kα, $2\theta_{max} = 50°$, $a = 27.156(3)$ Å, $b = 26.242(3)$ Å, $c = 13.2949(16)$ Å; $\beta = 90.570(3)°$, $V = 9474(2)$ Å^3, 8549 independent reflections, refinement on F^2, $R(F) = 7.40\%$ for 409 parameters and 5575 unique reflections with $I > 2.0\sigma(I)$. The elemental analysis (in wt %): 44.26 (calc. 44.53) for C, 3.18 (calc. 3.19) for H, 2.77 (calc. 3.35) for N, 14.73 (calc. 14.38) for S.
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