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Toward a Facile One-Step Construction of Quantum Dots Containing Zn_8S Cores

Jingli Xie*

School of Chemistry and Bio21 Molecular Science and Biotechnology Institute, The University of Melbourne, Parkville, Victoria 3010, Australia

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Three neutral nanoclusters $Zn_8S(SC_6H_5)_{14}L_2$ [L = 3-aminopyridine (**1**), 4-(dimethylamino)pyridine (**2**), 4-methylpyridine (**3**)] featuring a wurtzite-like core have been assembled by a controlled one-step hydrothermal reaction. Their detailed photoluminescence properties depend upon the ligand substituents. Cluster **1** exhibited a narrow, symmetric emission spectrum and has a potential application as a fluorescence quantum dot.

Semiconductor nanocrystals (quantum dots or QDs) have significant potential in photocatalysis[1] and in biolabeling, -imaging, and -sensing.[2] Core−shell QDs based upon II−VI chalcogenides (CdSe−ZnS) have received particular attention because their high photostability and narrow symmetric emission properties established them as the most popular optical material for bioconjugation. Compared with colloidal dots, stoichiometric crystalline chalcogenide nanoclusters with ordered arrangements are very appealing because of their well-defined size and composition.[3]

Concentrating on cadmium sulfide clusters, Li et al. used the supertetrahedral T5 cluster $[M_{35}S_{56}]$ to build QDs with an open-framework structure,[4] while Feng and co-workers have observed numerous nanocrystalline superlattices consisting of single-sized QDs.[5] Zinc sulfide clusters are an important subclass with potential versatile conformations based upon sphalerite (cubic ZnS) and wurtzite (hexagonal ZnS) phases plus related centers observed in metallothionein proteins.[6] Dance and Vahrenkamp have explored metal thiolate cluster anions such as $[Zn_8Cl(SC_6H_5)_{16}]^-$,[7a] $[Zn_{10}S_4(SC_6H_5)_{16}]^{4-}$,[7b,c] $[Zn_8S(SCH_2C_6H_5)_{16}]^{2-}$,[7d] and neutral $[Zn_4(SC_6H_5)_8(ROH)]$ (R = alkyl) one-dimensional polymers.[8]

Discrete neutral clusters have been restricted to $Zn_{10}(SC_2H_5)_{10}(C_2H_5)_{10}$ (wurtzite-like core; formed via insertion of sulfur into Zn−C bonds)[9] and $Zn_{10}S_4(SC_2H_5)_{12}L_4$ (L = 3,5-lutidine),[10] plus some multinuclear benzylthiolate clusters linked by organic ligands.[11]

The current work has generated a set of neutral zinc sulfide clusters based upon a wurtzite-like core. These appear to provide a convenient entry point for extension of the study of quantum-confinement effects and have the potential for application as fluorescent QDs.

Three new crystalline materials $Zn_8S(SC_6H_5)_{14}L_2$ [L = 3-aminopyridine (**1**), 4-(dimethylamino)pyridine (**2**), 4-methylpyridine (**3**)] were obtained by controlled one-step hydrothermal reactions. They feature wurtzite-core compositions in which $Zn_8S_{15}N_2$ clusters are stacked in an ABABAB pattern (Figure 1).

$Zn(CH_3COO)_2 \cdot 2H_2O$ (0.878 g, 4.0 mmol), thiourea (0.038 g, 0.5 mmol), and 3-aminopyridine (0.094 g, 1.0 mmol) were dissolved in H_2O (15 mL) in a Teflon-lined stainless steel

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* To whom correspondence should be addressed. E-mail: xij@unimelb.edu.au.

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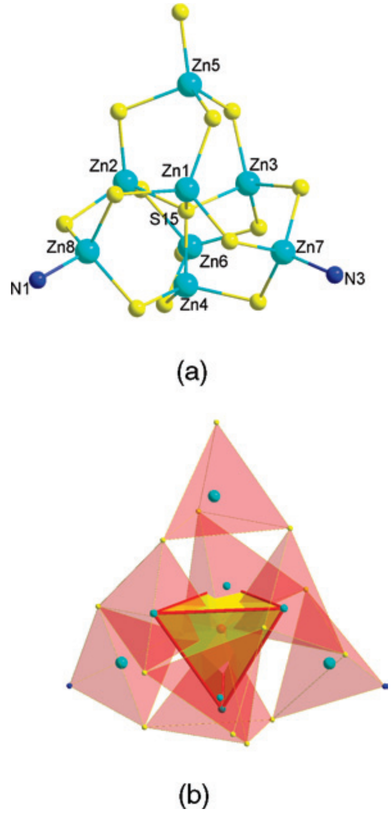

Figure 1. $Zn_8S_{15}N_2$ cluster structure with (a) a ball-and-stick model and (b) a polyhedral model.

autoclave (23 mL). Thiophenol (0.770 g, 7.0 mmol) was added to the clear solution, and the mixture was stirred efficiently for 30 min, leading to the formation of a white sticky suspension. The sealed vessel was then heated at 165 °C for 7 days. After cooling to room temperature, colorless block crystals of **1** (suitable for X-ray analysis) were obtained (weight, 0.740 g; yield, 65%). Analogous procedures led to **2** and **3**.[12] Crystals for compounds **2** and **3** were found to be twinned, and this has resulted in elevated R values for these structures. Preliminary observations demonstrated that the reaction temperature and duration were crucial to the products: (1) the temperature should be kept from 150 to 180 °C, and good quality crystals with high yield were obtained at 165 °C; (2) 3 days were necessary for the synthesis.[13] The molar ratio of raw materials used (8:1:14:2 for zinc precursor, thiourea, thiophenol, and pyridine ligand) match well with the composition $Zn_8S(SC_6H_5)_{14}L_2$. A change in the molar ratio to 5:2:6:2 in an attempt to produce the sphalerite-core stoichiometry of $Zn_{10}S_4(SC_6H_5)_{12}L_4$ still leads to the wurtzite phase, suggesting that the latter is the most thermodynamically stable cluster under the hydrothermal conditions.[9,13] This observation is consistent with molecular dynamic simulations for ZnS nanoparticles.[14]

X-ray structural analysis of **1** reveals a central S^{2-} (S15) ion coordinated to four Zn atoms (Zn1−Zn4), which are attached to three μ_2-thiophenolato ligands (Figures 1a and S1a in the Supporting Information). The central SZn_4 unit is capped on four faces by two ZnS_4 units and two ZnS_3N units; the coordinated sulfur atoms surrounding Zn5 and Zn6 define regular ZnS_4 tetrahedral units, while the remaining Zn7 and Zn8 atoms feature ZnS_3N coordination spheres incorporating 3-aminopyridine ligands. The Zn−S and Zn−N distances are within the ranges 2.261(4)−2.402(3) and 2.011(9)−2.022(8) Å, respectively, similar to the values reported in one-dimensional coordination polymers containing Zn−S nanoclusters and linear dipyridyl ligands.[11a] The role of the two terminal 3-aminopyridine ligands in maintaining an overall charge of zero on the clusters is reminiscent of the role of 3,5-lutidine in the neutral sphalerite-core $Zn_{10}S_4(SC_2H_5)_{12}L_4$ cluster.[10] The use of thiourea as the source of the central sulfide allowed the stoichiometric control necessary for assembly of the target structure.[5a,15]

Powder X-ray diffraction (PXRD) data were collected on a PW 1800 X-ray diffractometer (Philips) with Cu Kα radiation (λ = 1.5418 Å). The pattern of **1** matches well with the simulated curve based on the single-crystal structural analysis (Figure 2), confirming the high crystallinity of the

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(12) **$Zn_8S(SC_6H_5)_{14}[H_2NC_5H_4N]_2$ (1)**. In a Teflon-lined stainless steel autoclave (23 mL), $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.878 g, 4.0 mmol), thiourea (0.038 g, 0.5 mmol), and 3-aminopyridine (0.094 g, 1.0 mmol) were dissolved in 15 mL of H_2O, resulting in a clear solution. Thiophenol (0.770 g, 7.0 mmol) was added, and the mixture was stirred for 30 min; a white sticky suspension was present. The sealed vessel was heated at 165 °C for 7 days. After cooling to room temperature, colorless block crystals suitable for X-ray analysis were obtained (weight, 0.740 g; yield, 65%). Anal. Calcd for $C_{94}H_{82}N_4S_{15}Zn_8$ (2271.50): C, 49.70; H, 3.64; N, 2.47%. Found: C, 46.92; H, 3.80; N, 2.92%. $\epsilon_{270} = 1.67 \times 10^4$ M^{-1} cm^{-1}. FTIR data (cm^{-1}): 3373 (m, $\nu(NH_2)$), 3047 (m, $\nu(NH_2)$), 1619 (s, δ(C=C)), 1577 (vs, δ(C=C)), 1475 (vs, δ(C=C)), 1436 (s, δ(C=C)), 1082 (s, ν(C−S)), 1023 (vs, ν(C−S)), 797 (m, δ(=CH)), 736 (vs, δ(=CH)), 688 (vs, δ(=CH)). ^1H NMR (400 MHz, $(CD_3)_2SO$, 25 °C): δ 5.27 (s, $2NH_2$, 4H), 6.83 (t, J = 7.2 Hz, 14CH, 14H), 6.95 (m, $14C(CH)_2$, 28H), 7.27 (m, $14C(CH)_2$, 28H), 7.35 (s, 2CH, 2H), 7.46 (s, 2CH, 2H), 7.66 (s, 2CH, 2H), 7.87 (d, J = 2.4 Hz, 2CH, 2H). **$Zn_8S(SC_6H_5)_{14}[(CH_3)_2NC_5H_4N]_2$ (2)**. The procedure was similar to that above using 4-(dimethylamino)pyridine, with colorless block crystals being obtained. Yield: 68%. Anal. Calcd for $C_{98}H_{90}N_4S_{15}Zn_8$ (2327.60): C, 50.57; H, 3.89; N, 2.40%. Found: C, 47.57; H, 3.38; N, 2.26%. $\epsilon_{270} = 1.53 \times 10^4$ M^{-1} cm^{-1}. FTIR data (cm^{-1}): 3052 (m, ν(=CH)), 1625 (s, δ(C=C)), 1577 (vs, δ(C=C)), 1547 (s, δ(C=C)), 1476 (vs, δ(C=C)), 1436 (s, δ(C=C)), 1395 (s, $\nu(CH_3)$), 1231 (vs, ν(C−S)), 1083 (s, ν(C−S)), 1067 (vs, ν(C−S)), 1018 (vs, ν(C−S)), 737 (vs, δ(=CH)), 687 (vs, δ(=CH)). ^1H NMR (400 MHz, $(CD_3)_2SO$, 25 °C): δ 2.28 (s, $2(CH_3)_2$, 12H), 6.81 (t, J = 5.7 Hz, 14CH, 14H), 6.94 (m, $14C(CH)_2$, 28H), 7.26 (m, $14C(CH)_2$, 28H), 8.34 (d, J = 6.2 Hz, $2(CH)_4$, 8H). **$Zn_8S(SC_6H_5)_{14}[CH_3C_5H_4N]_2$ (3)**. The procedure was similar to that above using 4-methylpyridine, with colorless platelike crystals being obtained. Yield: 72%. Anal. Calcd for $C_{96}H_{84}N_2S_{15}Zn_8$ (2269.51): C, 50.81; H, 3.73; N, 1.23%. Found: C, 53.31; H, 4.04; N, 1.73%. $\epsilon_{270} = 1.67 \times 10^4$ M^{-1} cm^{-1}. FTIR data (cm^{-1}): 3058 (m, ν(=CH)), 1623 (s, δ(C=C)), 1577 (vs, δ(C=C)), 1476 (vs, δ(C=C)), 1436 (vs, δ(C=C)), 1380 (m, $\nu(CH_3)$), 1082 (s, ν(C−S)), 1068 (s, ν(C−S)), 1023 (vs, ν(C−S)), 736 (vs, δ(=CH)), 686 (vs, δ(=CH)). ^1H NMR (400 MHz, $(CD_3)_2SO$, 25 °C): δ 2.28 (s, $2CH_3$, 6H), 6.80 (t, J = 5.6 Hz, 14CH, 14H), 6.93 (m, $14C(CH)_2$, 28H), 7.26 (m, $14C(CH)_2$, 28H), 8.36 (d, J = 6.0 Hz, $2(CH)_4$, 8H). **Notes**: There are discrepancies between the experimental elemental analyses and theoretical values. This is not unusual for this class of Zn−S cluster compounds (see, e.g., ref 10). Importantly, the PXRD data of the bulk samples matched well with simulations based on the single-crystal structural analyses (Figures 2 and S2 and S3 in the Supporting Information), consistent with the presence of a single-crystalline phase in each case.

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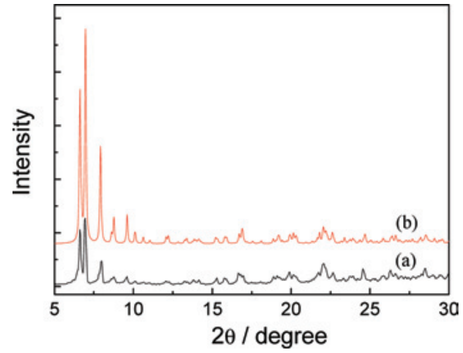
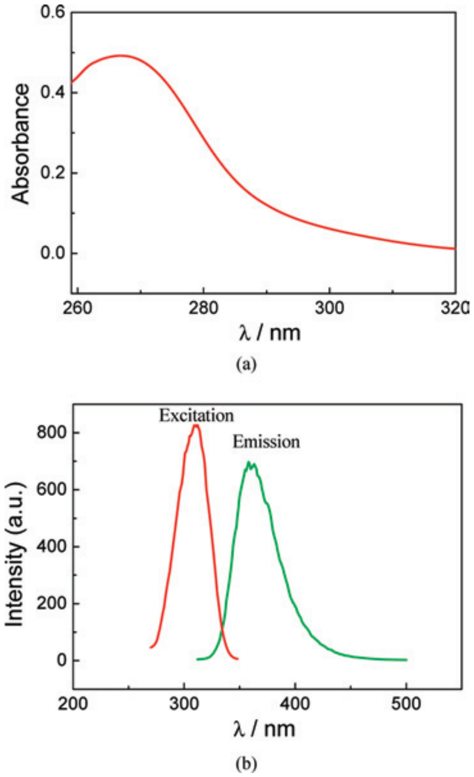


Figure 2. Experimental (a) and simulated (b) PXRD patterns for **1**.



(a)

(b)

Figure 3. (a) UV−vis absorption spectrum of cluster **1** in DMSO ($c = 3.0 \times 10^{-5}$ M). (b) Excitation spectrum (red) and room temperature emission spectrum (green) of **1** in DMSO ($c = 3.0 \times 10^{-5}$ M).

sample. Figures S2 and S3 in the Supporting Information demonstrated the corresponding patterns of complexes **2** and **3**.

The UV−vis absorption spectrum of **1** dissolved in dimethyl sulfoxide (DMSO) showed a maximum around 270 nm (Figure 3a), assigned to transitions having intraligand charge-transfer character involving terminal thiophenolates.[11a,16,17] The excitation spectrum of **1** (Figure 3b, red curve) showed a peak at 310 nm with an emission maximum (green curve) around 360 nm. The latter is narrow and symmetric, indicating the potential of **1** as a fluorescence QD. On the other hand, complexes **2** and **3** exhibited broad emission envelopes (Figure S5 in the Supporting Information), suggesting that the optical properties of the clusters are tunable by variation of ligand substituents. Future work will determine the solvent dependency and the aggregation state in solution.

Crystalline **1** is slightly soluble in toluene, allowing examination by high-resolution transmission electron microscopy (HR-TEM). A saturated solution was spread onto a strong carbon film on 300 mesh copper. After evaporation of the solvent, the resulting thin film was examined. The representative image shown in Figure S6 in the Supporting Information clearly reveals the presence of isolated spherical particles of a well-defined size distribution, revealing the purity of the wurtzite-like phase.[18,19]

In summary, neutral zinc sulfide clusters with wurtzite-like cores are reported that are exceptionally stable under hydrothermal conditions. A preliminary study suggests that their optical properties depend upon ligand substituents. Cluster **1** has potential as a QD. The next step is to increase the solubility by ligand modification, with further possibilities including dendritic ligands.[20]

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Supporting Information Available: Materials and general procedures, table of crystal data, structure solution and refinement, molecular structures of **1**−**3**, experimental and simulated PXRD patterns of **2** and **3**, IR spectra, PL spectra of **2** and **3**, HR-TEM image of **1**, and an X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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