Synthesis and Characterization of Surface-Capped, Size-Quantized CdS Clusters. Chemical Control of Cluster Size

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Abstract: Clusters of CdS in the quantum confinement regime <50-Å diameter are prepared in a rational technique whereby the cluster size and its distribution are controlled by chemical means. Competitive reaction chemistry between CdS core cluster growth and surface capping by thiophenolate leads to clusters whose core is essentially sphalerite CdS but whose reactive surface has been passivated by covalently attached phenyl groups. Adjustment of the sulfide to thiophenol ratio during synthesis takes advantage of the competitive reaction rates of these species with Cd ions to control the eventual cluster size. The clusters remain soluble in several organic solvents but may be isolated as stable powders and subsequently redissolved. The Cd [113]NMR data for this series of capped clusters confirm the presence of sphalerite CdS as the cluster core and the increasing percentage of Cd involved in this core as the S/SPh ratio increases. Optical properties demonstrate well-behaved absorption edge and emission band shifts with development of exciton features as the clusters grow.

Colloidal semiconductor species are currently under intense investigation as examples of nonmolecular materials that demonstrate the effects of quantum confinement.[1] The enhanced photoreactivity and photocatalysis as well as the predicted effects on nonlinear optical properties of these species has led to a wide range of synthetic approaches to these materials.[2] The key to any synthetic investigation of this sort must be the careful control of semiconductor cluster size and, even more important, the control of the size distribution.

The relatively amorphous character of small clusters prepared in this way necessitates the use of structural probes that provide information even in the absence of long-range periodicity. While X-ray diffraction can offer information for particles in excess of 25 Å in crystalline dimensions, smaller particles are X-ray amorphous and larger sizes (>100 Å) can suffer from significant contributions to the line widths by strain broadening. Quantitative interpretation using X-ray diffraction alone is therefore difficult. Among the various techniques suitable for such problems, solid-state NMR has the distinct advantage of providing element-selective, inherently quantitative information about local coordination environments and symmetries. In addition, NMR chemical shifts are also expected to be sensitive to cluster sizes, since the size quantization effects present in small semiconductor clusters should lead to an increase in the average excitation energy parameter in the paramagnetic term of Ramsey's chemical shift theory. This has been recently verified by Duncan and co-workers in a liquid-state ^{77}Se NMR study of colloidal CdSe solution.[3]

We wish to describe a new synthetic approach to such colloids of CdS based on the competitive growth/termination of CdS species in the presence of thiophenol surface-capping agents. The reports by Steigerwald et al.[4] using a micellar approach to benzeneselenol-capped CdSe clusters and by Dance et al.[5] on the preparation of a molecular fragment of sphalerite CdS where a $Cd_{10}S_4$ core was capped by 16 SPh groups led us to investigate this approach to the rational control of CdS cluster size by capping of the cluster surface by thiophenol-like species. Systematic, detailed optical and NMR behaviors have been revealed. Our NMR data, in addition, complement previous wide-line NMR studies undertaken on bulk cadmium sulfide[6-8] and add to the extremely limited database presently available for non-oxide chalcogenide systems.

Experimental Section

Cadmium acetate, thiophenol, and sodium sulfide (anhydrous) were used as received from Alfa Chemical Co. Chemical analyses using

combustion (C + H) and atomic absorption were performed by Galbraith Co., Knoxville, TN. X-ray powder diffraction measurements were performed on a Scintag automated powder diffractometer using Cu Kα radiation. Solid-state [113]Cd NMR spectra were obtained at 66.69 MHz on a General Electric GN-300 spectrometer, equipped with a multinuclear MAS-NMR probe from Doty Scientific and an Explorer fast digitizer. Normal single-pulse acquisition was used, with 90° pulses of 7-μs length, at a spinning speed between 3.5 and 5.2 kHz. Recycle delays were typically on the order of 10-15 min, resulting in spectra free from saturation effects. Chemical shifts are reported with respect to a sample of liquid Me_2Cd.

All synthetic procedures and sample manipulations were carried out in an inert-atmosphere (nitrogen) drybox from Vacuum Atmospheres (<10 ppm oxygen, <10 ppm water). Solvents for synthetic procedures and optical spectroscopies were dried and deoxygenated by standard techniques. The compound $(NMe_4)_4(Cd_{10}S_4SPh_{16})$ was prepared in the glovebox by following the published procedure.[5]

Preparation of Clusters. The preparation of all of the cluster species discussed below was essentially identical—the only difference between preparations being in the relative ratio of sulfide to thiophenol used. All preparations were conducted so that $[Cd^{2+}] \times 2 = [S^{2-}] \times 2 + [PhSH]$. A typical procedure (S:SPh = 1:2) is as follows.

Three stock solutions were prepared in the glovebox: (A) 2.67 g of cadmium acetate in 100 mL of methanol, [Cd] = 0.1 M; (B) 0.8 g of sodium sulfide in 50 mL of water and 50 mL of methanol, $[S^{2-}]$ = 0.1 M; and (C) 2.2 mL of thiophenol in 100 mL of methanol, [PhSH] = 0.2 M. These stock solutions are mixed as follows: 50 mL of B and 50 mL of C are stirred well together, and with continuous stirring, 100 mL of solution A is added. This immediately results in a cloudy yellow solution. The solution is stirred for 15 min, then filtered, and suction dried by drawing dry nitrogen through the filter cake for 10 min to leave 3.0 g

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Table I. Analytical Results for CdS/SPh Clusters Isolated as Powders

S/SPh used	Cd, %	S, %	C, %	H, %	empirical formula	Cd:S:C$_6$H$_5$	S/SPh calc	X-ray diam, Å
0.33[a]	39.25	20.02	38.62	2.60	CdS$_{0.26}$(SPh)$_{1.48}$(HSPh)$_{0.06}$	1:1.80:1.54	0.17	<15
0.5[a]	42.29	9.90	35.53	2.52	CdS$_{0.34}$(SPh)$_{1.31}$(HSPh)$_{0.00}$	1:1.65:1.31	0.26	<15
0.75[a]	47.68	20.40	29.31	2.19	CdS$_{0.54}$(SPh)$_{0.92}$(HSPh)$_{0.04}$	1:1.50:0.96	0.56	~20
1.17[a]	58.92	21.23	18.06	1.43	CdS$_{0.78}$(SPh)$_{0.44}$(HSPh)$_{0.04}$	1:1.26:0.48	1.62	~25
2.0[a]	61.38	21.45	15.22	1.20	CdS$_{0.84}$(SPh)$_{0.32}$(HSPh)$_{0.07}$	1:1.23:0.39	2.15	~30
4.5[a]	66.45	22.18	9.68	0.85	CdS$_{0.92}$(SPh)$_{0.16}$(HSPh)$_{0.09}$	1:1.17:0.25	3.70	~35
0.5[b]	45.89	21.80	26.94	2.04	CdS$_{0.75}$(SPh)$_{0.50}$(HSPh)$_{0.42}$	1:1.67:0.92	0.81	<15
0.75[b]	50.65	23.03	24.04	1.97	CdS$_{0.86}$(SPh)$_{0.28}$(HSPh)$_{0.46}$	1:1.60:0.74	1.16	~20

[a] Materials prepared in methanol solvent. [b] Materials prepared in mixed solvent with acetonitrile.
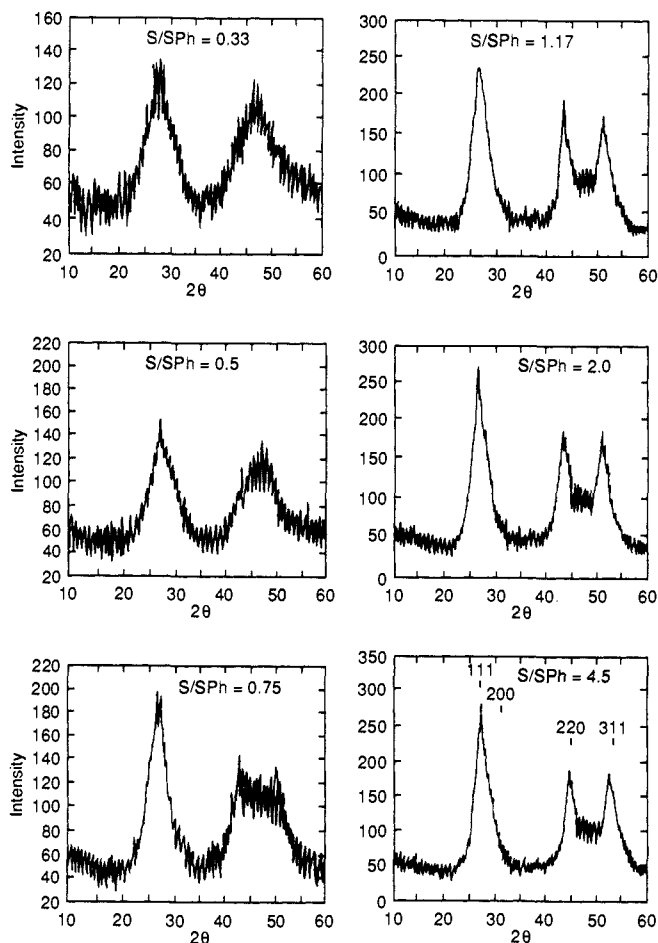

Figure 1. X-ray powder diffractograms of CdS/SPh clusters (S/SPh ratio given) isolated from methanol solvent. Peak assignments are based on sphalerite CdS. Estimated particle sizes are listed in the table.

Figure 2. Absorption coefficients of ~30-Å CdS/SPh cluster solid. Also shown is the coefficient of bulk CdS in a medium of dielectric constant 30, calculated with the Lorentz–Mie formula.

of a dry yellow powder. Chemical analysis of the resulting powder indicates only Cd, S, C, and H with no inclusion of Na, which is presumably washed away in the methanol as sodium acetate (see Table I). It is these powders which were used for NMR investigations.

Powders prepared in this manner tend to be only moderately soluble (up to ~2 × 10^{-2} M in [Cd]) in polar organic solvents and so we have also developed a second technique for synthesis in mixed solvents as follows that produces a material with much higher solubility.

Three stock solutions were again prepared: (A) 0.1 M cadmium acetate in 80% methanol, 20% acetonitrile; (B) 0.1 M sodium sulfide in 50% water, 50% methanol; and (C) 0.2 M thiophenol in acetonitrile. Mixing these solutions as described above gives a cloudy yellow solution, which may be evaporated to dryness in vacuum. Extraction of the yellow solid into acetonitrile and filtration gives a deep yellow clear solution and leaves behind a pale cream solid of sodium acetate. This technique will work well for S/SPh ratios of <1.0, higher ratios giving yellow insoluble materials, much as in the technique above. The yellow filtrate may be evaporated to dryness giving a bright yellow solid, which has excellent solubility in DMF, DMSO, CH$_3$CN, acetone, or THF but not in methanol or water. Indeed, solutions may be prepared that are >1 M in Cd ion in DMF and are clear and nonscattering. The chemical analysis of powders prepared by this route are also listed in the table.
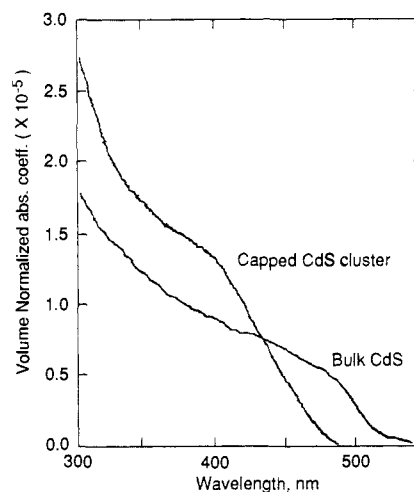
Results and Discussion

The X-ray diffractograms of the isolated powders show very broad peaks associated with CdS in the sphalerite structure with calculated particle sizes as noted in the table and illustrated in Figure 1. Preliminary electron micrographs of the powders dispersed in DMF have shown extremely small cluster sizes consistent with the size estimated from the X-ray patterns. Strictly speaking, the observation of crystalline CdS diffraction peaks only indicates that the sample contains reasonable amounts of CdS since for such small clusters X-ray diffraction is not a quantitative tool. To establish that CdS is present quantitatively, one needs a combination of the chemical analysis (table) and absorption coefficient measurements. The volume-normalized coefficient of the ~30-Å cluster is shown in Figure 2. Also shown is the bulk CdS coefficient in acetonitrile, calculated by using the Lorentz–Mie formula in the dipolar limit. The agreement in magnitude between the two implies that the solid sample is quantitatively composed of CdS-like clusters.

Figure 3 illustrates the effect of increasing S^{2-}/SPh$^-$ ratio on the ^{113}Cd resonances. At low ratios a peak near −78 ppm ("resonance a") signifies Cd^{2+} ions whose bonding environment is dominated by thiophenolate ligands; this peak persists up to an S^{2-}/SPh$^-$ ratio of 0.75. The chemical shift is identical with that observed for Cd(SPh)$_2$, although the X-ray data show no evidence for a bulk Cd(SPh)$_2$ phase being present. The shift is also very close to the values observed in solution for Cd(SPh)$_4$$^{2-}$ and Cd$_4$(SPh)$_{10}$$^{2-}$ complexes,[9-11] as well as the four Cd^{2+} ions in [S$_4$Cd$_{10}$(SPh)$_{16}$]$^{4-}$ that are entirely coordinated to SPh$^-$.[12] On this basis we assign resonance a to Cd^{2+} ions whose bonding environments are dominated by thiophenolate ligands, i.e., Cd^{2+} on the cluster surfaces. In addition, all samples containing both

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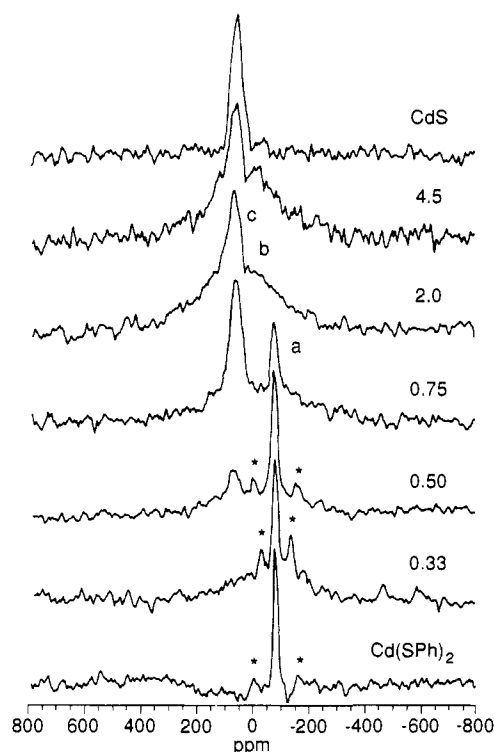(12) Dance, I. G. *Aust. J. Chem.* **1985**, *38*, 1745.

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Figure 3. Solid-state (66.69 MHz) ^{113}Cd MAS-NMR spectra of a series of CdS/SPh solids isolated from methanol with the indicated (idealized) S/SPh ratios (see table for empirical formulas). The three different types of signal observed are labeled a, b, and c (see Discussion in text). Spinning side bands are indicated by asterisks. Reference, Me$_2$Cd.

Figure 4. Absorption spectra of CdS/SPh clusters in acetonitrile solution with [Cd] = 4 × 10^{-3} M in 1 mm path-length cells. (1) Cluster with idealized S/SPh ratio (see table) of 0.75, (2) solution 1 with additional 4 × 10^{-3} M Na$_2$S.

S^{2-} and SPh$^-$ ligands show an extremely broad absorption ("resonance b") whose fractional area increases with increasing S^{2-}/SPh$^-$ ratio. The signal is, however, notably absent in any samples not containing SPh$^-$ species; (for example, see the top trace of Figure 3). A third, better defined peak ("resonance c") near 60 ± 5 ppm emerges at S^{2-}/SPh$^-$ ratios in excess of 0.5, becoming the exclusive resonance at the stoichiometric CdS composition. On this basis, we assign resonance c to Cd^{2+} ions in an exclusive sulfide environment. The moderately large MAS peak width (50–60 ppm) most likely arises from a distribution of isotropic chemical shifts. In view of the limited particle size this might reflect a continuous structural perturbation of the CdS$_{4/2}$ environments when going from the core toward the outer surface of the particles. Nevertheless, the NMR results clearly distinguish this material from wurtzite–CdS, which resonates at 42.3 ppm, i.e., almost 20 ppm upfield.

The broad resonance b is attributed in part to cadmium species with mixed S^{2-}/SPh$^-$ ligand environments. This assignment is confirmed by the solution-state ^{113}Cd NMR chemical shift of the six Cd^{2+} ions in [S$_4$Cd$_{10}$(SPh)$_{16}$]$^{4-}$ complexes that are coordinated to two S^{2-} and SPh$^-$ ligands.[8,12] However, in samples with low SPh$^-$ contents this signal is much stronger than expected, indicating that other cadmium species also contribute to it. We suggest that at least part of resonance b arises from Cd atoms that have four sulfide neighbors, but are closer to the surface and/or belong to very small particles showing strong size-quantization effects. While the center of gravity for resonance b cannot be measured precisely because of the large width, Figure 3 clearly shows that it is upfield of the signal attributed to bulk CdS species. Similar upfield shifts have been previously observed in ^{77}Se and ^{31}P NMR studies of size-quantized CdSe[3,4] and GaP species,[13] respectively. The upfield shift can be understood in terms of a decrease in the paramagnetic chemical shielding contribution, caused by an increase of the average excitation energy parameter in Ramsey's theory of chemical shielding.[14] Since the average excitation energy
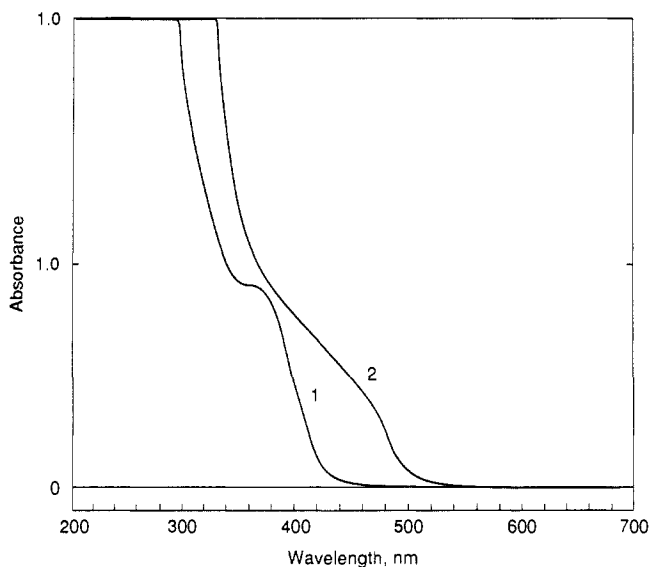
is related to the band gap (which is tuned here via the cluster size), one might expect that a direct correlation exists between the magnitude of this upfield shift and the cluster size. This prediction is difficult to verify for the present system due to the excessively large line widths and the interfering effect of mixed-ligand cadmium species. Nevertheless, the results of this study illustrate the suitability of solid-state NMR in monitoring the structural evolution as a function of the S^{2-}/SPh$^-$ ratio of these phenyl-capped, size-quantized CdS semiconductors.

The difference between the preparations of clusters in methanol/water and in methanol/water/acetonitrile solvents is curious. In both preparative procedures the clusters become insoluble (in CH$_3$CN, acetone, THF, DMF, DMSO) above a ratio of S/SPh > 2.0. However, as indicated in the table, the chemical analyses of materials isolated from methanol/water solvents, and which are relatively less soluble, tend to show a lower than expected S/SPh ratio, i.e., they are thiophenol rich and also have exactly the amount of S + SPh ions to balance the charge of the Cd ions. The materials are therefore nominally neutral in net charge, and this may explain the poor solubility in polar solvents. The clusters prepared in acetonitrile solvents and isolated from neat acetonitrile, in which they are extremely soluble, have higher than expected S/SPh ratios and also have more S + SPh ions than are necessary to charge compensate the Cd. This results in a net anion charge for the cluster—presumably compensated by protons since no other elements are present in the chemical analysis. The anionic nature is supported by the migration behavior of the clusters in microelectrophoresis, where the clusters, in DMF or CH$_3$CN solution, migrate toward the anode in silica capillaries using sodium trifluoroacetate as supporting electrolyte. This dramatic effect of subtle changes in the solvent character is typical of many preparations of colloidal semiconductor species.[2] The soluble materials represent one of the few examples of a bottlable "reagent" consisting of a controlled-size quantum-confined semiconductor.

One feature offered by these chemically stable soluble species is the potential for the separation and isolation of unique cluster sizes by microelectrophoresis or size exclusion chromatography. Our preliminary efforts along these lines have shown that separations by both techniques are feasible and optimization of the process and collection of isolable fractions is ongoing research.

The mechanism of cluster formation appears to mimic an inorganic version of polymerization. Small CdS units are produced in an initiation step by mixing Cd ions and the S/SPh solution, and these units then rapidly aggregate in a cluster growth or

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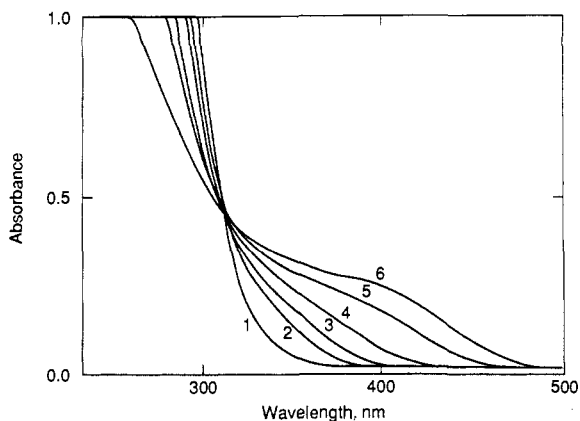(14) Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 669.

Figure 5. Absorption spectra of CdS/SPh clusters in acetonitrile solution with [Cd] = 4 × 10^{-3} M in 1 mm path-length cells. (1) $(NMe_4)_4$-$(Cd_{10}S_4SPh_{16})$; (2) idealized (see table) S/SPh ratio used in preparation, 0.33; (3) 0.5; (4) 0.75; (5) 1.17; (6) 2.0.
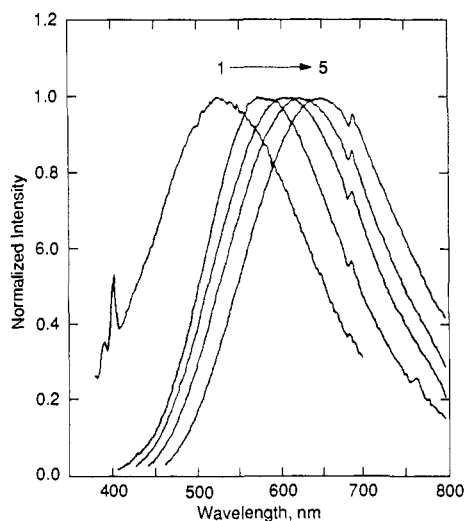

Figure 6. Photoluminescence spectra of various CdS/SPh clusters (1) $(Cd_{10}S_4SPh_{16})^{4-}$; (2) idealized (see table) S/SPh ratio used in preparation, 0.5; (3) 0.75; (4) 1.17; (5) 2.0.

propagation step in competition with surface capping by thiophenol species in a growth termination step. Surface thiophenol groups, while being covalently attached, may be displaced by additional sulfide ion and the clusters will continue to grow to a size that would be predicted on the basis of the new S/SPh ratio (Figure 4). The reverse is not true, however; additional thiophenol added to a cluster solution does not cause any perceptible change in absorption spectra and so the clusters do not shrink in proportion to the new S/SPh ratio. These observations indicate that the clusters are not in true dynamic equilibrium but rather that the observed species are those trapped kinetically by synthesis conditions. Clearly the cluster size is being determined by the relative rates of the propagation/termination reactions and in turn by the relative concentrations of the initiating (sulfide) and terminating (thiophenol) species in the polymerizing solution. This mechanism and kinetic scheme is still under investigation.

The optical properties of these clusters have all been measured by use of the less soluble methanol-derived clusters and are illustrated in Figures 5–9. Beautiful isosbestic behavior at 312 nm is noted in the absorption spectra of these cluster solutions in acetonitrile with a steady bathochromic shift as the S/SPh ratio increases (clusters grow). Concurrently with this shift, an excitonic feature develops at the band edge. It is satisfying to note that the spectra observed are a smooth extension of the spectrum of the $[Cd_{10}S_4(SPh)_{16}]^{4-}$ molecules prepared by Dance et al. (Figure 5).

Photoluminescence spectra of thiophenolate-capped CdS clusters are shown in Figure 6. Also displayed in the same figure is the
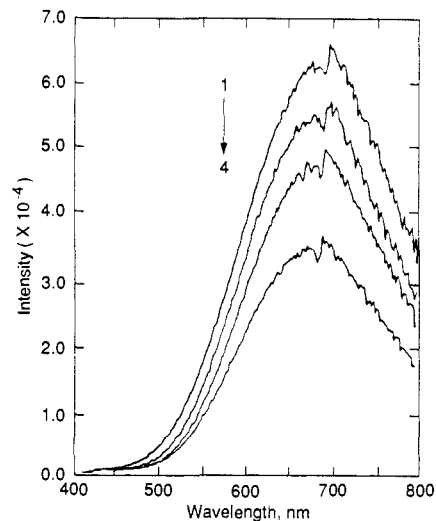

Figure 7. Quenching of luminescence intensity of the 30-Å CdS/SPh clusters ([Cd] = 2.14 × 10^{-3} M) in acetonitrile using excess added thiophenol. [thiophenol]: (1) 0.0, (2) 2.14 × 10^{-3} M, (3) 8.57 × 10^{-3} M, (4) 1.93 × 10^{-2} M.
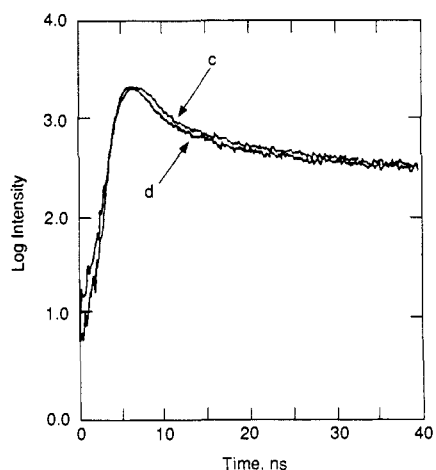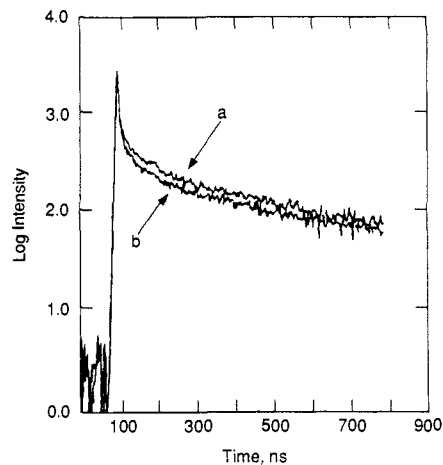

Figure 8. Luminescence decay of the 30-Å CdS/SPh clusters ([Cd] = 2.14 × 10^{-4} M) in acetonitrile in the presence of added thiophenol. [Thiophenol]: (a and d) 1.93 × 10^{-2} M, (b and c) 8.6 × 10^{-4} M.

luminescence spectrum of the reference compound, $[Cd_{10}S_4$-$(SPh)_{16}]^{4-}$. We note that all the luminescence spectra are Stokes-shifted from the absorption spectra, and there is no band-edge luminescence. In the case of the reference compound, which is essentially a molecular cluster, the Stokes-shifted emission indicates a large Franck–Condon displacement in the excited states. In the cases of the larger CdS clusters, the Stokes-shifted luminescences are attributed to midgap states. These results indicate that thiophenolate, unlike ammonia[15] and amines,[16] is

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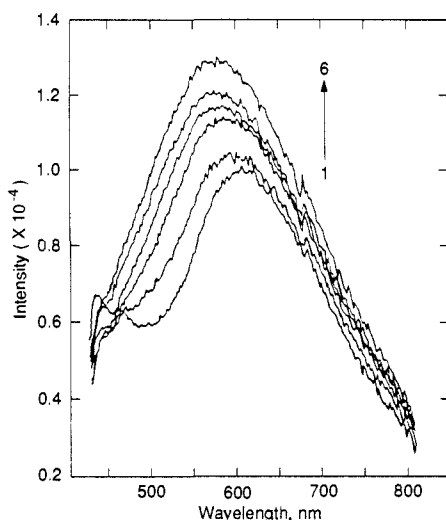
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Figure 9. Luminescence intensity of very small CdS/SPh clusters prepared with an idealized S/SPh ratio of 0.33 ([Cd] = 1.25×10^{-2} M) as a function of added thiophenol concentration. [Thiophenol]: (1) 0.0 M, (2) 1.25×10^{-2} M, (3) 2.5×10^{-2} M, (4) 3.75×10^{-2} M, (5) 5×10^{-2} M, (6) 6.75×10^{-2} M.

not an effective passivating agent for removing surface defects of CdS.

As the sizes of the clusters decrease the luminescence peak moves to higher energy, following that of the absorption spectra (Figures 5 and 6), and converges toward the luminescent peak of the reference compound, $[Cd_{10}S_4(SPh)_{16}]^{4-}$. This size-dependent shift of the luminescence spectrum has been observed before.[17,18] No definitive explanation has been provided, but it has been speculated that the luminescence is due to recombination emission from electrons trapped in the shallow defects and holes trapped in the deep defects, and shallowly trapped electrons still possess small effective masses and therefore exhibit the quantum-size effect. However, as we will show in the following, the nature of the emitting states can change as the size of the cluster changes.

We studied the effects of excess thiophenol on the luminescence spectrum and lifetime of these CdS clusters in both the large and small size limits. For the larger clusters, the luminescence peak is located at ~700 nm (Figure 6). This luminescence band is also commonly observed for CdS clusters without thiophenolate capping groups and is usually attributed to sulfur anion vacancies. Consistent with this view, we observed that the addition of thiophenol to the solution causes the quenching of the luminescence intensity (Figure 7), but not the lifetime (Figure 8). The reduction of the luminescence intensity is interpreted as due to the removal

of sulfur anion vacancies by the thiophenolate capping agents. Different behavior was observed for the smaller CdS clusters, which show a luminescence peak at ~600 nm. The addition of thiophenol induces a slight blue-shift of the luminescence peak and enhancement in intensity (Figure 9), yet only a slight effect on the absorption spectra. The fact that the luminescences intensity increase in the presence of thiophenol and its spectral peak converges toward that of the reference compound $[Cd_{10}S_4-(SPh)_{16}]^{4-}$ (which has the highest thiophenol to sulfide ratio) suggests that the nature of the luminescent states is thiophenolate-related. The observation, that the nature of the emitting states changes as the cluster size decreases, manifested here by their different responses to the addition of thiophenol, is really not surprising. As the cluster size decreases, the HOMO–LUMO gap opens up, which makes certain defect states energetically accessible. This has also been observed for CdS superclusters in different zeolites[19] and in principle can be quite general. Furthermore, these results indicate that the surfaces of these CdS clusters, especially the larger ones, are not totally covered by thiophenolate and the bonding between thiophenolate and CdS is reversible. This conclusion is strikingly demonstrated by the data in Figure 4.

Conclusions

We present a new method for preparing thiophenolate-capped CdS clusters. The method mimics organic polymerization reactions and is based on the competitive reactions between thiophenolate and sulfide with Cd^{2+}. The size of these clusters can be conveniently controlled by adjusting the relative concentrations of thiophenolate and sulfide. They can be collected as stable solids and redissolved in solution to obtain the original clusters. X-ray diffraction, Cd NMR, chemical analyses, and absorption coefficient measurements establish that these solids contain thiophenolate-capped CdS clusters quantitatively. Photoluminescence experiments show that thiophenolate capping is not effective for removing the surface defects of CdS clusters and the bonding between thiophenolate and CdS is reversible.

The synthetic approach we have described is under continued investigation for this and other semiconductor systems where the use of chemistry to control both cluster size and surface properties offers many potential benefits for the continued elucidation of these optically fascinating species. For example, the extremely high solubility of the acetonitrile-derived clusters has already allowed observation of relatively efficient nonresonant third harmonic generation using these clusters and this is the subject of a communication.[20]

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