Molecular Clusters of Binary and Ternary Mercury Chalcogenides: Colloidal Synthesis, Characterization, and Optical Spectra

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A series of binary (HgSe) and ternary (HgSe_{1-x}S_x) mercury chalcogenide clusters are synthesized utilizing a colloidal technique involving the phase separation of metal and chalcogen precursors in the presence of strong Hg(II) coordinating ligands. The clusters vary in size between 2 and 3 nm and possess the cubic zinc blende structure of the bulk. Energy-dispersive X-ray measurements show that the composition of the ternary material can be varied throughout the entire composition range from HgS to HgSe. In all cases, the linear absorption of these binary and ternary species is narrow with well-resolved transitions at both the band edge and at higher energies. Complementary band edge emission is also observed with no apparent deep trap emission. Size- and composition (x)-dependent optical properties of these clusters are investigated using photoluminescence (PL) and photoluminescence excitation (PLE) spectra. In the case of HgSe clusters, the size-dependent behavior of up to four excited states is followed. For HgSe_{1-x}S_x clusters, where x varies from 0 to 1, a size/composition-dependent progression of up to five excited states is observed.

Introduction

Over the last twenty years, a great deal of work has gone into understanding the properties of matter at the nanometer scale. One class of mesoscopic system receiving much attention are colloidal semiconductor quantum dots (QDs) or nanocrystals (NCs).¹ Progress in this area has benefited from the dynamic interplay between advances in synthesis, optical characterization, and theory.² Despite this synergy, a major bottleneck in the field has traditionally been the availability of high quality, crystalline samples with narrow size distributions, high photoluminescence efficiencies, and controlled surface chemistries. II–VI materials in particular have led to new opportunities for better understanding and utilizing the size-dependent optical and electrical behavior of QDs^{3,4} as a result of the discovery in the early 90's by Murray and others that one could make high-quality QDs through the thermolysis of pyrophoric organometallic reagents.^{5,6}

Prior to these advances, however, analogous examples of high quality II–VI nanocrystalline compounds could already be found in small clusters of zinc and cadmium chalcogenides of precise molecular weight. These clusters represent the molecular limit of QDs and are also some of the first examples of colloidal nanoparticles. They contain less than 100 atoms and typically lie in the size range between 1 and 2 nm. For example, in 1982 Dance and co-workers were able to isolate discrete clusters of CdS and ZnS of the stoichiometry $M_{10}S_{20}$ (M = Zn, Cd).⁷ The core of such Cd and Zn compounds was found to be congruent with the unit cell of the cubic sphalerite structure, making them nanometer-sized (tetrahedral) fragments of the bulk. Larger CdS clusters were subsequently isolated by Wang and Herron (Cd₃₂S₅₀)⁸ as well as by Weller and co-workers (Cd₁₇S₃₀,

 $Cd_{32}S_{50}$).⁹ This work was also extended to make ZnS, ZnSe, and ZnTe clusters^{10,11} as well as homologous CdSe clusters¹² (Cd₄Se₆, Cd₈Se₁₃, Cd₁₀Se₁₆, Cd₁₇Se₂₈, and Cd₃₂Se₅₀), providing further examples of the trailing molecular limit in these materials. Banin has since investigated the evolution of the CdSe band gap within this molecular limit and has also studied the nature of the emitting state, showing the importance of the surface in small semiconductor clusters.¹³

In the case of II-VI mercury chalcogenides, very little work exists to date on either clusters or QDs, although interest in these materials abounds. Bulk mercury chalcogenides are semimetals widely used in infrared sensing applications. Alloys of Hg compounds (Hg_{1-x}Cd_xTe, for example) are particularly important systems because of the wide range of tunable optical, electrical, and magnetic properties, achieved through compositional tuning (x) of this material, from pure semimetallic Hg-(S,Se,Te) to narrow gap $Hg_{1-x}Cd_x(S,Se,Te)$ and ultimately to wider gap semiconductor Cd(S,Se,Te). At the same time, such material tunability can also be explored by making QDs or clusters of these compounds, exploiting well-known quantum confinement effects that occur when the physical size of the NC is smaller than the bulk exciton Bohr radius. Furthermore, the ease of compositional tuning suggests that a similar parameter space can be investigated, not only through size, but also through composition, with the creation of ternary mercury chalcogenide QDs/clusters leading to tunable absorbing and emitting species spanning anywhere from the visible into the far-infrared. Such compounds have potential use as visible/ infrared fluorescent tags, lasing/amplifying elements at 1.3 and 1.55 μ m, and in remote sensing applications.¹⁴

While a great deal of work has been done to explore organometallic precursor routes to QD synthesis in other II– VI and III–V materials,^{15–21} analogous preparations for II–VI mercury chalcogenide QDs or clusters have not been reported. This likely stems from the toxicity and dangers associated with corresponding organometallic Hg(II) precursors in NC prepara-

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tions that involve the high-temperature decomposition of pyrophoric reagents in a mildly coordinating solvent. Furthermore, significant differences exist in the reactivity, as well as chemistry, of mercury relative to other group II elements,²² making such approaches potentially problematic. To illustrate, in the synthesis of mercury chalcogenide NCs, reactions between metal and chalcogen precursors are commonly observed to progress very quickly at room temperature, often bypassing the nanocrystal stage, to yield bulk or bulklike material. At best, NCs with broad size distributions and poorly resolved optical transitions are obtained. This has been seen previously²³ and more recently in our attempts to make mercury chalcogenide QDs.²⁴ By contrast, reactions of Cd and Zn compounds with corresponding chalcogen precursors are generally well controlled, even at temperatures >200 °C, as evidenced by a variety of routes now available for making high-quality zinc- and cadmium-based QDs.5,6,18-21

What mercury chalcogenide NC syntheses have been reported largely deal with solvothermal or solvent-based approaches to making these compounds. These approaches entail sonochemistry,²⁵ microwave-assisted heating,^{26,27} and the thermolysis of common mercury precursors.^{28,29} Other methods make use of metal ion impregnated Langmuir Blodgett films³⁰ or other restricted environments such as vesicles³¹ or sol gel networks³² to grow HgS QDs. Most, if not all, of these preparations lack the controlled growth kinetics and narrow size distributions characteristic of more developed organometallic syntheses such as those for CdSe, InP, and InAs.5,6,15-17 To date, the most successful syntheses for mercury chalcogenide nanomaterials appear to be those developed by Weller and Fenske for QDs and clusters, respectively. Weller et al. have synthesized HgTe nanocrystals using an aqueous preparation wherein mercury salts are exposed to hydrogen telluride gas bubbled through the reaction mixture.33 HgTe QDs between 3 and 6 nm diameter are obtained, emitting with high integrated yields broadly between 800 and 1400 nm. HgSe clusters (Hg₆Se₁₂, Hg₁₀Se₁₆, Hg₃₂Se₅₀) have been isolated by the Fenske group and in particular, the Hg₃₂Se₅₀ species was found to have a 2.4 nm edge length with structured absorption beginning at about 546 nm (2.27 eV).³⁴ Both preparations, however, suffer from the same problems which generally plague the mercury chalcogenides, namely, the instability, high reactivity, and tendency for uncontrolled reactions leading to the parent bulk, rather than nanocrystalline, material. For example, continued growth of HgTe QDs was observed, evidenced by a continuous red-shift of the absorption over a period of days.^{33a} Likewise, Hg₃₂Se₅₀ clusters in THF or toluene, when warmed to room temperature, undergo rapid growth leading to a black precipitate,^{34b} which is likely bulk HgSe or large NCs with broad size distributions, similar to those observed by Brennan.²³

As part of a search for new infrared emitting NCs, we have recently explored possible "ligand-mediated" routes to making mercury chalcogenide QDs using approaches recently brought to attention by Peng,^{35–37} Murray,³⁸ and others³⁹ for making high-quality CdS, CdSe, CdTe, and PbSe nanocrystals. In their studies, these groups have illustrated that through the choice of an appropriate metal binding ligand, such as long chain fatty acids or alkylphosphonic acids, crystal nucleation and growth can be controlled by the ligand, which modulates the concentration of reactive species in the immediate vicinity of the growing QD. Control over the particle growth rate is achieved by retarding the heterogeneous reaction rate to various degrees with more (or less) strongly binding metal ligands or by increasing (or decreasing) their steric hindrance. In such a manner, high-

quality QDs (5% size distributions, >10% quantum yields, highly crystalline) are produced, comparable to those obtained from more traditional organometallic methods. Such preparations represent alternative approaches to making high-quality NCs and possess distinct benefits over previous syntheses.^{5,6} Advantages include tunable reactivity achieved by varying the overall ligand concentration, use of cheaper and safer metal precursors, and, most importantly, the improved reproducibility of the preparations.^{35–37}

In this vein, we have explored the use of many Hg(II) coordinating ligands covering a vast range of stability constants (K).⁴⁰ Ligands with log K values between 1 and 50 were investigated. Those with stability constants less than 10¹⁷ such as fatty acids (log K 6–9) and amines (log K 10–18) resulted in uncontrolled reactions between Hg(II) and common chalcogen precursors, leading to the precipitation of bulk or bulklike material. At the other limit where very strongly coordinating ligands, such as thiols (log K > 30), phosphines (log K 30 to 37), or phosphine oxides (log K > 30), are used, crystal nucleation is severely retarded, requiring elevated temperatures to help dissociate the metal-ligand complex. Unfortunately, often associated with this combination of strong ligands and high temperatures is the reduction of Hg(II) to Hg(0), which competes with the desired reaction. Such dissociation pathways have been documented for Hg(II)-thiolate complexes⁴¹ and suggest that reduction is a favored decomposition pathway because of mercury's high reduction potential.⁴²

To circumvent these problems, we have found alternative routes for making high-quality mercury chalcogenide QDs by employing not only strong Hg(II) coordinating ligands, but also by segregating the metal and chalcogen precursors in different phases of the reaction mixture. In our previous work,²⁴ we have used a common micellar medium (bis(2-ethylhexyl)sulfosuccinate (AOT) in cyclohexane) to achieve this phase separation of both mercury and chalcogen precursors. The general micellar approach entails the use of a surfactant, which has both hydrophobic and hydrophilic regions and organizes in alkanes into water-bearing and water-excluding regions. Within the water-bearing regions, aqueous metal precursors can be sequestered, making the micelles a compartmentalized source of metal ions.⁴³ Using this approach, we have been able to make highquality HgS and HgSe QDs controllably in the presence of thioglycerol, a strong Hg(II) coordinating ligand. In the case of HgS, small QDs between 1 and 5 nm in diameter are obtained, which absorb and emit in the visible region of the spectrum. When passivated with Cd or Zn, the emission quantum yield (OY) increases dramatically and there is no further growth observed over a period of weeks.24

In this paper, we report a similar synthesis of small binary and ternary mercury chalcogenide clusters, which approach the molecular limit of these materials. The synthesis is a generalization of the above precursor phase separation and strong ligandmediated approach. Rather than traditional micellar media, however, a nonionic surfactant in an organic phosphine is used. Wide-angle X-ray diffraction studies of the resulting particles show that they possess the cubic zinc blende phase of the parent bulk material and range in size from 2 to 3 nm in diameter. Energy-dispersive X-ray measurements show that the stoichiometry of the ternary material (x, $HgSe_{1-x}S_x$) can be varied throughout the entire composition range from x = 0 to x = 1. Preliminary characterization of the surface of these particles is conducted through ¹H and ³¹P nuclear magnetic resonance (NMR) experiments. The optical properties of these clusters are subsequently investigated using photoluminescence (PL), photoluminescence excitation (PLE), and low-temperature timeresolved PL decay experiments. The evolution of states as a function of cluster size and/or composition is investigated. In the case of HgSe, the size-dependent behavior of up to four excited states is followed; whereas for HgSe_{1-x}S_x clusters, where x varies from 0 to 1, a size/composition-dependent progression of up to five excited states is observed.

Experimental Section

The following chemicals were purchased from Aldrich and were used without further purification: mercury(II) acetate (HgAc₂), bis(2-ethylhexyl)sulfosuccinate (AOT), thioglycerol, and polyoxyethylene 4-lauryl ether (Brij30). Bis(trimethylsilyl)sulfide ((TMS)₂S) and bis(trimethylsilyl)selenide ((TMS)₂Se) were purchased from Acros and used as received. Technical grade trioctylphosphine (TOP) and tributylphosphine (TBP) were purchased from Fluka and likewise used without further purification. Deionized water was obtained from a Millipore MilliQ unit. Care should be exercised to avoid exposure to mercury compounds. In addition, TBP is pyrophoric, and prolonged exposure to air should be avoided.

A stock solution of the mercury precursor is prepared by dissolving 100 mg of HgAc₂ (3×10^{-4} mol) in 3 mL of deionized water, and then adding 27 μ L (3×10^{-4} mol) of thioglycerol. Thioglycerol should be added last, because it reacts immediately with HgAc₂ to produce an insoluble black precipitate. The stock solution keeps for several weeks with eventual discoloration and precipitation of a gray/black powder determined to be HgS from energy-dispersive X-ray spectroscopy (EDXS). In the current synthesis, the equimolar amount of thioglycerol prevents the hydrolysis of Hg(II) and eventual precipitation of HgO that normally occurs in aqueous solutions. It should be noted that polar solvents other than water can also be used to create the above mercury stock solution. For example, dimethylformamide (DMF) works equally well with no obvious difference in the overall behavior of the synthesis.

Chalcogen stock solutions are prepared by dissolving 2 μ L (1 × 10⁻⁵ mol) of (TMS)₂S in 10 mL hexanes and likewise 2.6 μ L (1 × 10⁻⁵ mol) of (TMS)₂Se into 10 mL of hexanes. In either case, the actual amount of hexane used does not appear to be critical and only serves to dilute the stock solution sufficiently such that subsequent reactions between the metal and chalcogen are controlled. To prepare binary HgSe clusters, only the above (TMS)₂Se solution is used in the synthesis. For the preparation of ternary compounds, appropriate amounts of each chalcogen solution are combined to achieve an effective S/Se solution with the desired sulfur content (*x*, HgSe_{1-x}S_x). For example, to target *x* = 0.3, 3 mL of the (TMS)₂Se stock solution.

In a typical preparation, 8 mL of TOP is mixed with 2 mL of Brij30 in a three-neck flask. Once clear, $0.11 \text{ mL} (1 \times 10^{-5} \text{ mol Hg})$ of the mercury stock solution is introduced. The solution is stirred until clear. The actual amount of TOP used does not appear to be critical to the synthesis, provided it remains in excess. Likewise, the actual amount of Brij30 also does not appear to be critical, but amounts greater than 1 mL should be used to better solubilize the aqueous Hg(II) solution. In addition, Brij30 can also be replaced by 3.4 g (0.01 mol) of AOT. However, we found this to be inconvenient as moderately high temperatures (~100 °C) were needed in order to solubilize AOT in TOP. In all cases, when the Hg(II)-containing micro emulsion is clear, the chalcogen solution is brought out of the glovebox and is introduced into the flask at a rate of ~1 mL/min using a syringe pump. All preparations are conducted at

To isolate $HgSe_{1-x}S_x$ clusters, excess acetone is added to the growth solution. The amount of acetone required to remove most (all) of the material from solution depends on the sulfur content (x); samples having more sulfur require more acetone to precipitate from solution. In practice, 30-40 mL of acetone is sufficient to recover nearly all the material in a given preparation. The suspensions are then centrifuged and a colored precipitate is recovered. This precipitate can then be re-dispersed in toluene or chloroform, yielding a strongly colored solution and residual insoluble material. Solutions can subsequently be centrifuged or passed through glass wool to yield a homogeneous solution. Samples with x < 0.4 are much less soluble in toluene than their counterparts with x > 0.5. It should also be noted that samples washed more than once with acetone or methanol or those initially exposed to too much acetone generally become insoluble in any solvent.

NMR samples are prepared by precipitating the clusters with acetone, centrifuging the suspension to recover the precipitate and immediately redissolving the recovered material in deuterated toluene. Proton (¹H) and phosphorus (³¹P) NMR spectra are acquired on a Bruker AC300 spectrometer (300 MHz ¹H; 121 MHz ³¹P) equipped with a multinuclear probe. EDXS samples are prepared by washing the recovered precipitate multiple times with methanol (or acetone) to remove any excess surfactant. The precipitate is then dried under vacuum and dispersed onto conductive carbon tape mounted to a scanning electron microscope (SEM) sample holder. EDXS measurements are performed with an EDAX energy-dispersive X-ray spectrometer attached to a Leo 1550 SEM operating at an accelerating voltage of 10 kV. Wide-angle X-ray (WAXS) samples are prepared in the same manner and are occasionally sonicated during the washing procedure to assist in removing any excess surfactant. Diffraction experiments are conducted using Cu Ka radiation derived from a 12 kW rotating anode generator (Rigaku) on samples mounted to silicon (001) substrates. Peak positions and their full width at half-maximum were obtained using a commercial peak fitting program.

Linear absorption experiments are carried out with a diode array UV-visible spectrometer (Hewlett-Packard, HP 8453), while photoluminescence (PL) and photoluminescence excitation (PLE) experiments are conducted at room temperature using a Spex Fluorolog fluorimeter. During PL experiments, samples are typically excited at 410 nm (\sim 3 eV) with light from a 400 W Xe arc lamp passed through a double monochromator. Emitted light is detected with a second double monochromator and a Hammamatsu R928 photomultiplier tube. A long pass colored glass filter is often used to suppress unwanted solvent Raman contributions to the emission spectra. PLE experiments are conducted by monitoring the intensity of the room temperature emission at three fixed wavelengths, generally at positions red of the emission maximum, at 2/3 height, 1/2 height, and on the shoulder of a second feature accompanying the main emission peak, while scanning the excitation wavelength to the blue of this position.

Time-dependent fluorescence lifetimes are measured using a time-correlated single-photon counting (TCSPC) apparatus. The excitation source for TCSPC measurements is a modelocked Nd:YLF laser, operating at 100 MHz. The second harmonic (527 nm) of the Nd:YLF synchronously pumps a cavity-dumped dye laser using Rhodamine 590 as the lasing medium. A single plate birefringent filter is inserted within the dye laser to generate laser oscillation at 600 nm. The variable repetition rate (20–30 kHz) cavity-dumped output is then frequency-doubled (300 nm; 4.13 eV) using a 3 mm KDP crystal. Samples are inserted into a He flow through cryostat (Janis) and cooled to 20 K. Emission from the sample is spectrally filtered with a monochromator and detected with a Hamamatsu R2809U-11, water-cooled, micro channel plate. The instrument response is measured by detecting scatter off of a 1 cm path length cell and has a full width at half-maximum of ~100 ps.

Results and Discussion

As described in the Introduction, previous attempts to synthesize mercury chalcogenide nanocrystals have suffered from problems associated with the high reactivity of Hg(II) and ensuing reactions to produce nanocrystals have tended toward broad size distributions and/or bulklike material. Our previous work has focused on exploring possible ligand-mediated preparations for HgX (X = S, Se) NCs and has led to the development of small HgS and HgSe QDs emitting in the visible region of the spectrum. The strategy used to make such QDs entails not only strong Hg(II)-coordinating ligands but also the phase separation of both metal and chalcogen precursors. In this manner, reactions between Hg(II) and S^{2-}/Se^{2-} are controlled, allowing the synthesis of mercury chalcogenide QDs with improved size distributions. Here we describe a generalization of the above approach using a surfactant in trialkylphosphine mixture to make small binary and ternary mercury chalcogenide NCs or clusters, which also absorb and emit in the visible region of the spectrum.

In this preparation, Hg(II) ions passivated by thioglycerol are phase-segregated into water-bearing regions of a polyoxyethylene ether surfactant (Brij30; alternatively called C₁₂E₄ where $E = OCH_2CH_2$). The remainder of the growth solution consists of either trioctylphosphine (TOP) or tributylphosphine (TBP), which acts as a coordinating solvent for the growing mercury chalcogenide clusters. To initiate growth, common chalcogen precursors ((TMS)₂S, (TMS)₂Se) are introduced into the organic phosphine phase with a syringe pump. Upon introduction of the selenium precursor, slow color changes occur over the course of minutes, with a gradual evolution of the solution's color from light yellow to burgundy. When mixtures of sulfur and selenium precursors are added to make ternary clusters, very little of this color progression is evident. Instead the optical density of the reaction solution increases with only a small spectral shift of the sample absorption spectrum. The reaction to make binary/ ternary mercury chalcogenide clusters likely stems from the decomposition of (TMS)₂S and (TMS)₂Se into corresponding S^{2-} and Se^{2-} ions, which then migrate through the phase barrier to react with sequestered Hg(II) ions. Both the phase barrier and Hg(II) coordinating species, TOP (or TBP) and thioglycerol, modulate subsequent reactions leading to the controlled growth of both HgSe and HgSe_{1-x}S_x clusters.

Evidence for the vastly improved growth kinetics can be seen in the UV-visible absorption spectra of the resulting particles. Figure 1 shows both the band edge absorption and emission of ternary HgSe_{1-x}S _x clusters, isolated from the growth solution with acetone and re-dispersed in toluene. The stoichiometry of the introduced chalcogen solution is varied to achieve values of x between 0.1 and 0.8, spanning nearly the entire composition range of the alloy. Sharp structured absorption is observed in each case with a clearly resolved band edge transition followed by a weaker "second" state and finally a prominent shoulder consisting of unresolved transitions at higher energies. The



Figure 1. Linear absorption (solid line) and complementary band edge emission (dashed line) of $HgSe_{1-x}S_x$ clusters with 0.1 < x < 0.8.

reported spectra are for the equilibrium structure of each $HgSe_{1-x}S_x$ cluster, taken after the complete, stoichiometric addition of both chalcogen precursors. Prior to this, the absorption spectrum of each sample is nearly identical but less intense, suggesting a smaller concentration of the final equilibrium species. Although it is possible that the species formed at nonstoichiometric chalcogen additions have different sizes, the small (1-2 nm) shift of the absorption, which occurs during addition, and the much more dramatic rise of the sample optical density suggest an increase in concentration rather than particle growth.

The emission of these ternary species is weak at room temperature and is red-shifted relative to the band edge absorption. It is often obscured by solvent Raman contributions, making it necessary to measure the spectrum under concentrated conditions, achieved by isolating the sample from the growth solution and re-dispersing it in toluene.44 The band edge emission has an asymmetric shape with a shoulder suggesting either a phonon progression toward lower energies or emission from a surface-related trap state. In Figure 1, the energy difference or "global" Stokes shift between the peak of the band edge absorption and band edge emission appears to be composition (x)-dependent, becoming smaller with decreasing overall sulfur content. Values of the global shift in Figure 1 range from 100 to 220 meV (x = 0.19 to x = 0.74) and represent an upper limit to the true shift given the potential influence of emission reabsorption.

Figure 2a shows the absorption and emission of HgSe clusters made in the same manner. As with $HgSe_{1-x}S_x$ clusters, the band edge absorption is well-resolved with structure at higher energies. In particular, one sees a second state followed by a shoulder to the blue, consisting of several unresolved transitions. The complementary band edge emission is also narrow and red-shifted relative to the absorption. A value of the global Stokes shift is 87 meV and is again an upper limit due to potential reabsorption effects.

The spectra in Figure 2a are for stable HgSe clusters with a band edge absorption maximum at 595 nm (2.08 eV). This 2.08 eV species is unusually stable, and evidence for its thermodynamic stability lies in the observation that no further growth is



Figure 2. (a) Linear absorption (solid line) and complementary band edge emission (dashed line) of stable 2.08 eV HgSe clusters. (b) Progression of HgSe cluster linear absorption during growth, numbered from bottom to top.

observed beyond this "magic" size. Addition of more mercury and/or chalcogen precursor only increases the concentration of the 2.08 eV species. Similarly, rapid injection of (TMS)₂Se, rather than its slow addition through a syringe pump, simply results in the immediate formation of this stable compound. Temperature jumps such as heating the reaction mixture from room temperature up to 100 °C may be used to partially overcome this bottleneck, and push the growth to a second "magic" size with a band edge absorption close to 628 nm (1.97 eV). This is generally accompanied by a dramatic color change of the solution from red to green. Growth to the 1.97 eV species, however, is not complete and a bimodal absorption spectrum is typically observed with a fraction of clusters at 1.97 eV and the rest at 2.08 eV. Alternatively, injection of the chalcogen precursor into the reaction mixture at elevated temperatures (<100 °C) promotes growth beyond 2.08 eV, but again with the same apparent bimodal distribution of resulting species. In addition, increasing the temperature of the reaction mixture often causes mercury chalcogenide clusters to precipitate from solution, as do repeated precipitation/resuspension steps, making it problematic to push the growth beyond 2.08 eV in this manner.

Figure 2b shows the absorption spectrum of binary HgSe clusters during addition of the chalcogen precursor. Unlike $HgSe_{1-x}S_x$ clusters, an evolution of the absorption spectrum (numbered from bottom to top) is observed as they converge to the 2.08 eV magic size and complete (1:1) addition of the selenium precursor. At the earliest measured time (Spectrum 1 in Figure 2b), the absorption spectrum shows three well-resolved transitions. The energy of these three states (2.23, 2.40, and 2.61 eV) nearly coincide with those seen in the absorption spectrum of Hg₃₂Se₅₀ clusters (2.27 eV, 2.48 eV, and \sim 2.68 eV).34 However, the third state (2.61 eV) is markedly pronounced whereas in the Hg₃₂Se₅₀ absorption spectrum it is weak and rapidly evolves into a continuum of states toward higher Kuno et al.



Figure 3. Wide-angle X-ray diffraction spectra of $HgSe_{1-x}S_x$ clusters. (a) HgSe_{0.7}S_{0.3}, (b) HgSe_{0.4}S_{0.6}. Stick spectra for bulk HgSe and β -HgS are provided both above and below the experimental patterns for comparison purposes.

energies. As more chalcogen is added, both the second and third states diminish in intensity while the first state gains strength, becoming the dominant feature in the spectrum. The similarity of spectrum 1 (Figure 2b) to the absorption spectrum of Hg₃₂-Se₅₀ clusters³⁴ as well as their joint dissimilarity to the 2.08 eV species (Figure 2a) supports the notion that different sized HgSe clusters are being generated during the nonstoichiometric phase of the current synthesis.

Mercury chalcogenide clusters can be isolated from the growth solution by adding excess acetone. They can subsequently be re-dispersed in a suitable solvent such as toluene or chloroform. In the case of $HgSe_{1-x}S_x$ clusters, samples in toluene or chloroform without excess TOP show evidence of continued growth over the course of several days to a week with eventual darkening of the solution and precipitation of a black/brown residue. In the case of HgSe clusters, only the stable 2.08 eV clusters species can be isolated from solution with acetone and re-dispersed in toluene or choloroform. They exhibit comparable instability toward growth over long periods of time in the absence of excess TOP. Smaller HgSe clusters that are seen at nonstoichiometric chalcogen additions (Spectra 2-8, Figure 2b) cannot be isolated in this fashion, however. Although the addition of large amounts of acetone does cause partial precipitation of the smaller species, what is often recovered has generally evolved into the 2.08 eV species. The inability to isolate small HgSe clusters therefore represents a problem for studying their photophysics because their room-temperature emission is weak and often obscured by the overwhelming Raman signal of TOP.44

Wide-angle X-ray scattering (WAXS) spectra of isolated $HgSe_{1-x}S_x$ clusters confirm the presence of a ternary solid solution, showing a single pattern for the alloy rather than two discrete, superimposed, patterns for HgS and HgSe. Slow precursor addition rates and high chalcogen dilutions likely compensate for any major differences in reactivity of (TMS)2S or (TMS)₂Se toward Hg(II) that would otherwise allow the nucleation and growth of two compositionally distinct cluster species. Figure 3 shows WAXS patterns for $HgSe_{1-x}S_x$ samples with predicted x values of approximately (a) 0.3 and (b) 0.6(see EDXS discussion below). Three distinct peaks with Miller indices of (111), (220), and (311) are identified for each sample. Based on the positions of the three assigned reflections, extracted lattice parameters are $a = 6.0142 \pm 0.0255$ Å (Figure 3a) and $a = 5.9461 \pm 0.0115$ Å (Figure 3b). For comparison, the lattice parameters for β -HgS and HgSe are 5.8517 and 6.085 Å,



Figure 4. Composition of $HgSe_{1-x}S_x$ clusters as determined by energydispersive X-ray and WAXS measurements. The solid black line is the theoretical 1:1 line representing uniform introduction of the added sulfur. WAXS results are shown by the asterisks.

respectively. By interpolating between the lattice parameters of either binary compound (β -HgS or HgSe), the ternary composition is estimated to be (a) HgSe_{0.7}S_{0.3} and (b) HgSe_{0.4}S_{0.6} using Vegard's Law, consistent with the composition measured via EDXS as described below. An average crystallite size is determined to be 3 and 2.5 nm, respectively, using the Scherrer equation, indicating relatively small changes in cluster size with large changes in composition.

To confirm the composition of $HgSe_{1-x}S_x$ and HgSe clusters, energy-dispersive X-ray (EDXS) measurements were conducted on a series of particles. Samples were probed at multiple locations to generate an average stoichiometry for the ensemble. Figure 4 shows the results of the measurements for $HgSe_{1-x}S_x$ samples with values of x between 0 and 1. Results obtained from WAXS experiments described in Figure 3 are denoted by asterisks, indicating good agreement between both techniques. In the figure, the solid black line represents the ideal 1:1 sulfur added/incorporated case. The composition of the ternary clusters is sulfur-rich over most reaction conditions, particularly for situations with low overall sulfur content (x < 0.5). This suggests that S^{2-} competes more aggressively than Se^{2-} in reactions with Hg(II). Still, the entire composition range of the $HgSe_{1-x}S_x$ solid solution can be spanned using the above synthesis. In the case of HgSe clusters, EDXS analysis shows the stoichiometry of the samples to be nearly 1:1 in good agreement with the initial concentration of Hg(II) and Se²⁻ precursors.

Nuclear magnetic resonance (NMR) experiments are conducted to investigate the surface of these clusters and in particular to determine the identity of the passivating ligands. For ternary clusters, both proton (¹H) and phosphorus (³¹P) NMR spectra are shown in Figure 5a,b. While thioglycerol may act to passivate resulting HgSe_{1-x}S_x clusters, both TOP and Brij30 are in excess by factors greater than 10³ and 10², respectively, suggesting that these latter two compounds are the dominant surface coordinating agents. It should be noted that TOP oxidizes to trioctylphosphine oxide (TOPO) under ambient conditions and this must also be considered as a (potential) passivating agent. Furthermore, technical grade TOP (90%) contains a number of impurities, which may act to passivate the clusters as well.

Proton NMR spectra of isolated $HgSe_{1-x}S_x$ clusters in deuterated toluene show the presence of Brij30 as a multiplet at 3.4 ppm, which is assigned to the ethylene protons in the repeat unit of the polyoxyethylene ether. Identification of Brij30 through protons further upfield (multiplets at 1.52, 1.28, and



Figure 5. (a) ¹H and (b) ³¹P NMR data of $HgSe_{1-x}S_x$ clusters in deuterated toluene. The inset in (b) is the proton decoupled spectrum of the doublet.

0.92 ppm relative to TMS) is problematic due to the overlapping contributions from TOP/TOPO/TOP impurities. The Brij30 contribution to these overlapping multiplets, however, can be estimated through its downfield (3.4 ppm) component. Using this, we quantify its contribution to the experimental HgSe_{1-x}S_x ¹H spectrum and determine that the ratio of phosphines/ phosphine oxides to Brij30 is 15:1. This shows that TOP, TOPO, and/or TOP impurities are in excess by at least an order of magnitude, suggesting that these phosphine/phosphine oxide species predominantly passivate the surface of these clusters.

To further identify these ligands, ³¹P NMR experiments are performed on solutions of $HgSe_{1-x}S_x$ clusters. Chemical shifts are measured relative to an internal standard of H₃PO₄ (0 PPM), and spectra are acquired with and without broadband proton decoupling. The phosphorus spectrum in Figure 5b shows the presence of a number of peaks both upfield and downfield relative to H_3PO_4 . In particular, a peak at -32 ppm can be identified as free, unbound TOP. Likewise, a peak at 45 ppm can be assigned to free, unbound TOPO with a peak at 55 ppm arising from an impurity in the technical grade TOP. Of special relevance are the two peaks at 33 and 29 ppm of nearly equal intensity. To see whether the peaks are actually a doublet, ³¹P NMR spectra were proton decoupled. The results of broadband proton decoupling show that the two peaks do indeed converge into a single peak centered at 31 ppm (inset) and the extracted coupling constant is 440 Hz, in excellent agreement with reported values for ${}^{1}J_{PH}$.⁴⁵ This, along with the appearance of the same proton-coupled doublet in the ³¹P NMR of technical grade TOP (described below), provides direct evidence that at least one of the impurities in TOP has a phosphorus-hydrogen bond. Possible species include primary or secondary phosphines (R₂PH, RPH₂) or phosphinic acids.

This proton-coupled species exists as a minority impurity in technical grade TOP with a ³¹P resonance at 29 ppm. Majority impurities exhibit peaks at 54 and 133 ppm. In the ³¹P NMR of $HgSe_{1-r}S_r$ clusters, however, the doublet is shifted slightly downfield to 31 ppm and, most significantly, appears as a sizable contribution to the overall spectrum. This enhancement can be rationalized if primary or secondary phosphines or phosphinic acids have significantly stronger binding affinities to $HgSe_{1-x}S_x$ clusters than TOP, causing the ³¹P spectrum of isolated clusters to be enriched in this proton-coupled impurity. The slight downfield shift can be explained by an increase in nuclear shielding upon coordination with mercury. It should be pointed out that phosphine-based impurites have been shown to be critical ingredients in mediating the synthesis of CdSe QDs,^{35–37} and has led to the recent development of ligand-mediated nanocrystal syntheses.

No broad phosphorus resonance are seen in Figure 5b, unlike similar experiments conducted on TOP/TOPO passivated CdSe QDs.⁴⁶ All ³¹P NMR transitions for the mercury chalcogenide clusters are narrow and have chemical shifts similar to that observed for each compound free in solution. This suggests that all passivating ligands are weakly bound to the surface of the clusters, exchanging readily with the solution such that the net chemical environment is relatively homogeneous. This hypothesis is supported by the high sensitivity of the cluster solubility to repeated washings as well as by the observation of longterm instability in cluster suspensions, which do not contain excess TOP/TOPO or TOP impurity. An alternative explanation for the narrow NMR transitions is the presence of well-defined binding sites on the surface of the small clusters, unlike the inhomogeneous surface of larger 2-6 nm diameter CdSe QDs. However, there do not appear to be significant differences in the chemical shifts for each ligand, particularly for the impurity doublet, "free" versus "bound" positions, making this scenario unlikely.

A primary goal of the current investigation is to learn more about the optical properties of mercury chalcogenide clusters and/or QDs. To this end, photoluminescence excitation (PLE) experiments are conducted on binary and ternary mercury chalcogenide clusters. This technique is a "size-selective" optical method in the sense that a small fraction of the size-broadened distribution of emitting states is probed; it has previously been used to reveal states in the linear absorption of various NCs, which were otherwise obscured by the inhomogeneous size distribution present in most samples. Figure 6 shows the resulting PLE spectra of four HgSe_{1-x}S_x samples with x varying from 0.19 to 0.58. In all cases, PLE spectra of each sample were taken by monitoring the emission intensity at three different energies (denoted by vertical lines in the accompanying emission spectrum) while scanning the excitation wavelength to the blue of this position. These energies generally correspond to locations at 2/3 height, 1/2 height, and on the broad, low-energy shoulder of the main peak, effectively sampling the entire spectral profile of the emission.

Noticeable differences and improvements in the PLE spectra of all samples are apparent relative to the absorption spectra in Figure 1. Most prominently, the third shoulder in Figure 1, consisting of several overlapping transitions, is clearly resolved into at least two distinct transitions shown by the states centered near 3.5 eV in Figure 6a,b. Furthermore, in HgSe_{1-x}S_x samples with x > 0.5 (Figure 6c,d), a small state immediately to the



Figure 6. Photoluminescence (dashed line) and photoluminescence excitation spectra (solid line) of $HgSe_{1-x}S_x$ clusters where (a) x = 0.19, (b) x = 0.35, (c) x = 0.51, and (d) x = 0.58. In all cases, the emission intensity as a function of excitation energy was monitored at the positions denoted by the vertical lines. Spectra are offset for clarity.

blue of the first transition is resolved. This state can also be seen in samples with x < 0.5 and in Figure 6a,b appears as a small shoulder on the blue edge of the first peak. The spectra in Figure 6 are representative of all samples investigated and, in particular, those in Figure 6a,b (Figure 6c,d) are characteristic of the line shapes/intensities seen in samples with x < 0.5 (x > 0.5).

Apart from improving the spectral resolution, the PLE spectra in Figure 6 establish that the observed luminescence is directly related to $HgSe_{1-x}S_x$ clusters rather than to other extrinsic sources of emission. Previous PLE experiments on CdSe clusters¹³ have shown that emission from such particles is occasionally complicated by an admixture of discrete sizes, for example $Cd_{17}Se_{30}$ and Cd_8Se_{13} , within the same sample. In the case of ternary mercury chalcogenide clusters, such mixtures could arise from the presence of compositionally distinct species (e.g., HgS or HgSe) and/or distinct sizes within a given sample. However, no substantial intensity changes occur when the emission energy being monitored is altered, suggesting that a single $HgSe_{1-x}S_x$ species is the source of the emission. This is corroborated by the WAXS data, which indicate the successful preparation of the ternary alloy.

PLE experiments were also conducted on stable 2.08 eV HgSe clusters. Figure 7 shows data taken by monitoring the emission intensity at three energies corresponding to positions at 2/3 height, 1/2 height, and on the shoulder of a second feature accompanying the main emission band. Figure 7 shows subtle improvements over the ensemble absorption spectrum (Figure 2a) similar to that observed for $HgSe_{1-x}S_x$ clusters, although



Figure 7. Photoluminescence (dashed line) and photoluminescence excitation spectra (solid line) of stable 2.08 eV HgSe clusters. In all cases, the emission intensity as a function of excitation energy was monitored at positions denoted by the solid vertical black lines. A small sharp feature immediately to the blue of the first excited state is a solvent Raman artifact. Spectra are offset for clarity.

the effect is less dramatic. In particular, the region near 3.4 eV, which was present as an unresolved shoulder in the absorption data, is now better resolved. The PLE data also indicate that the observed emission originates from stable 2.08 eV HgSe clusters. As with $HgSe_{1-x}S_x$ clusters, no dramatic intensity changes occur in any of the PLE spectra when the observation energy is tuned over the entire emission profile, suggesting that different size fractions do not exist in HgSe samples.

To analyze PLE experiments conducted on $\text{HgSe}_{1-x}S_x$ clusters with *x* between 0.1 and 0.8, spectra were fit using a nonlinear least squares Levenberg–Marquardt algorithm. In all cases, experimental PLE data were fit to a sum of Gaussians from which peak positions of underlying states could be determined. The results of such a fitting procedure for two representative $\text{HgSe}_{1-x}S_x$ samples with low (x = 0.19) and high (x = 0.58) sulfur content are shown in Figure 8a,b. The fit (dotted line) and experimental spectrum (solid line) are superimposed and offset from the fitting results. In certain cases a polynomial or Gaussian background function is used to improve the quality of the fits and is shown by the broad dashed lines in Figure 8a,b.

Up to five excited states are identified by the fitting procedure. These states are labeled by Greek letters in order of their progression from lower to higher energies. Because of the broad background used to account for unresolved transitions, no oscillator strengths are reported. An interesting observation, immediately apparent from this analysis, is the behavior of the two lowest excited states (denoted α and β). In Figure 8b, β is resolved whereas in Figure 8a it has merged with α to create a single asymmetric peak. The gradual evolution of the spacing between α and β appears to be a function of *x* and/or size. This observation, that up to two states coexist under what appears to be a single peak, explains why in the ensemble absorption spectrum of ternary clusters (Figure 1), the first peak appears broad in samples with large values of *x* and progressively narrows with decreasing sulfur content.



Figure 8. Fitting results to PLE and absorption spectra of $HgSe_{1-s}S_x$ and HgSe clusters. Experimental data (solid line) and fit (dotted line) are superimposed and offset from the extracted states, which are shown below and labeled by Greek letters. (a) $HgSe_{0.81}S_{0.19}$, (b) $HgSe_{0.42}S_{0.58}$, (c) small HgSe clusters, and (d) stable 2.08 eV HgSe clusters.

Because intermediate HgSe clusters other than the 2.08 eV species cannot be isolated, we are currently unable to conduct PLE experiments on these compounds. However, the evolution of their ensemble absorption spectrum (Spectra 1–9, Figure 2b) can be studied using the same nonlinear least-squares fitting procedure. Results of the analysis for "small" (Spectrum 1, Figure 2b) and "large" (Spectrum 9, Figure 2b) HgSe clusters are shown in Figure 8c,d. As before, the fit (dotted line) and experimental data (solid line) are superimposed and offset from the fitting results. Up to four excited states are identified and denoted by primed Greek letters in ascending order, from lower to higher energies. A broad Gaussian or polynomial background function representing unresolved transitions is also occasionally used to improve the fit, and consequently, no oscillator strengths for the various transitions are reported. Furthermore, the absorption spectrum of the stable 2.08 eV HgSe species (Spectrum 9, Figure 2b) closely matches the PLE data (Figure 7), showing the self-consistency of the data and the approach.

Figure 9a,b summarizes the results of the fitting procedure for both $HgSe_{1-x}S_x$ and HgSe clusters. Positions of extracted states are denoted by energy offsets relative to the ground excited state. In the case of $HgSe_{1-x}S_x$ clusters, the progression of up to five excited states is seen (denoted by alternating open and closed symbols in the figure). Solid lines are a linear fit through the data and also serve as a guide to the eye. Whether the trends seen in Figure 9a arise solely from changes in composition (*x*) or from differences in size (or both) is difficult



Figure 9. Summary of excited-state energies in (a) $HgSe_{1-x}S_x$ and (b) HgSe clusters. In both cases, energies are denoted as offsets relative to the ground excited-state energy. Extracted states from the fitting procedure are labeled by lowercase Greek letters in ascending order, from lower to higher energies.

to ascertain due to complications in systematically sizing the ternary clusters. However, the preliminary WAXS data indicate that the size variation is small over the composition range, suggesting that stoichiometry (*x*) is primarily responsible for the progression of excited states. What is clear, though, is that with increasing *x* (or size), the spacing between α and β decreases while γ appears to be independent of either. States labeled δ and ϵ (where resolvable) also diverge with decreasing *x* and energy of the first excited state.

A similar behavior is observed with HgSe clusters. The second state labeled β' converges toward α' with decreasing energy of the first excited state. The offset of the third state, γ' , however, is nearly constant, which is analogous to the behavior seen for γ in HgSe_{1-x}S_x clusters. Although δ' in Figure 9b can only be extracted in three samples, it also shows a similar trend as δ (Figure 9a) diverging with decreasing energy of the first excited state.

A compelling issue is the remarkable similarity in the progression of excited states for both HgSe and HgSe_{1-x}S_x clusters. Despite their differences in composition and oscillator strength (compare Figure 1 to Figure 2), the spacings between states not only follow the same divergent or convergent trends relative to the lowest excited state, but also have energy offsets of nearly equal magnitude. It is not yet understood whether such trends are expected nor is it yet possible to assign the various interband transitions. Furthermore, the divergent trend of δ (δ') and ϵ (ϵ') with decreasing energy of the first excited state is opposite to trends typically observed in other quantum dot systems.^{47,48} Another point of interest is the relative contribution of each valence band to the different transitions, whether the lowest excited-state involves an excitation from Γ_8 or Γ_6 to the conduction band or, more interestingly, if and when a reversal of Γ_8 and Γ_6 (from an inverted band structure to a more typical zinc blende ordering) occurs and how this affects the observed transitions.49

Low-temperature fluorescence decay experiments were conducted on $HgSe_{1-x}S_x$ clusters to provide a lower limit for their radiative lifetime. Isolated clusters in toluene were cooled to 20 K using a He flow-through cryostat and were subsequently



Figure 10. Time-resolved emission decay of $HgSe_{1-x}S_x$ clusters taken at 20 K. Fluorescence decays at four emission wavelengths were monitored.

excited at 4.13 eV (300 nm) using the doubled output of a dye laser. Emission decays were collected at four energies, at the peak and to the red or blue of the main emission band. Figure 10 shows $HgSe_{1-x}S_x$ fluorescence lifetime plots taken at four different emission wavelengths. Each curve can be fit by a sum of three exponentials, using similar parameters. In particular, a long, microsecond component of the data is apparent with an average (standard error) lifetime of 1.7 (4) μ s. This microsecond component accounts for 40 (10)% of the decay and suggests that the emission from $HgSe_{1-x}S_x$ clusters is forbidden. The fastest component has an average (standard error) lifetime of 110 (30) ns, accounting for 7 (4)% of the decay. The remaining intermediate component has an average lifetime of 500 (100) ns and accounts for 50 (10)% of the decay. Such long decays have previously been seen in CdSe clusters, where emission was argued to be surface mediated.¹³ In HgSe_{1-x}S_x clusters, this may also be the case but further work is needed to verify this and to exclude any recombination through internal core states. We additionally note that no significant changes of the decay profile occur over the range of energies investigated, which encompasses the broad, low-energy shoulder of the emission (Figure 1). This suggests that rather than multiple sources of emission (that is, from some combination of core states, deep trap states, or "shallow" surface states), only one type of emitting state is present.

Conclusion

The work presented herein describes the synthesis, characterization, and preliminary optical studies of binary and ternary mercury chalcogenide clusters. The synthesis used to create such clusters is a generalization of a strong Hg(II) ligand and precursor phase separation scheme that we have found necessary to control the high reactivity of Hg(II). It has the novelty of using a water/trialkylphosphine mixture as the growth medium, bridging previous work on NC synthesis using micellar media and more recent ligand-mediated and/or organometallic preparations conducted in both coordinating and noncoordinating solvents.

Characterization with WAXS and EDXS shows that both binary (HgSe) and ternary (HgSe_{1-x}S_x) mercury chalcogenide clusters can be made. In particular, EDXS results reveal that the entire compositional range of the ternary solid solution can be spanned with the above synthesis. Such clusters appear to be passivated by TOP/TOPO, and NMR experiments further indicate that an important role is played by proton-coupled impurities in technical grade TOP. Preliminary optical experiments to investigate the linear absorption of HgSe and HgSe_{1-x}S_x clusters reveal an interesting progression of states dependent on size in the case of HgSe and on a combination of size and composition for the ternary compounds. Time-resolved emission experiments at low temperatures complement work on the linear absorption by probing the emitting state and show that the emission, despite being weak with significant nonradiative channels, is relatively slow. Decays are multiexponential and occur over the course of hundreds of nanoseconds to several microseconds, suggesting that the emission is forbidden in nature. However, whether it occurs through internal triplet-like core states or through surface-related states is not yet established.

The current success in the development of high-quality mercury chalcogenide clusters, brings to light a number of compelling issues which will benefit from further study. From a synthetic perspective, better management of the high reactivity of Hg(II) and improved stabilization of larger clusters or QDs is necessary to push the growth beyond 2.08 eV and out of the visible region of the spectrum. One possible means of doing this is to use 2.08 eV HgSe clusters as "seeds" for growth in a more suitable medium, as described in recent work by Strouse.¹⁹ In addition, the present work presents a challenge for the development of a theoretical construct which can explain the unusual similarity between excited-state energy spacings of HgSe and HgSe_{1-x}S_x clusters, their dissimilarity in oscillator strengths, the identity of long-lived emitting states in these materials, as well as predict the precise point where a semimetalto-semiconductor transition occurs. Similarly, ab initio structural calculations, which can help determine the precise stoichiometry and shape of stable mercury chalcogenide clusters, such as the 2.08 eV HgSe species, are needed to better understand these materials.

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Supporting Information Available: Energy dispersive X-ray spectra of binary (HgSe) and ternary (HgSe_{1-x}S_x) mercury chalcogenide NCs. This material is available free of charge via the Internet at http://pubs.acs.org.

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