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Title
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$\times$ 10^{-14} J. If this energy is converted completely into visible photons (energy $\sim$4 $\times$ 10^{-19} J), the total number of photons is 7 $\times$ 10^{-14}/4 $\times$ 10^{-19} $\sim$ 2 $\times$ 10^5. Taking account of the light collection efficiency ($\sim$0.004), the number of photons collected per diode array channel is $\sim$0.8, which could hardly be detected. Considering also the efficiency of energy conversion from discharge to emission, the energy consumed for the excitation of TSE should be several orders of magnitude higher than E estimated above. Namely, most of the electrical energy must be used in the internal discharge across the microcracks.

The rise and decay times and pulse width of V_{TSE} exhibit a pulse-to-pulse variation in synchronism with V_{PyE}. The fastest decay time of TSE ($\sim$20 μs) is shorter than the normal decay time ($\sim$0.7 ms) for PL.[14] These facts indicate that the excited state involved in TSE must have a much faster decay rate than that in PL. Generally the PL emission from $UO_2{}^{2+}$ shows no dependence on the excitation wavelength;[15] i.e., there is no possibility of emission from vibrationally excited $^3\Pi_u$ state. Therefore the shorter lifetime of TSE cannot be explained on this basis. The most plausible explanation for this would be that the $UO_2{}^{2+}$ ions near the crack surface are involved in TSE where the environment of the ions is different from that in the bulk and results in a faster nonradiative decay from the vibrationless $^3\Pi_u$ state. The blue shift of the TSE spectrum with respect to the PL spectrum should also be due to the unusual environment near the crack surfaces.

C. Summary. We have shown that TSE observed for a single crystal of UNH has the same spectroscopic origin as photoluminescence ($^3\Pi_u \rightarrow {}^1\Sigma_g^+$ transition in $UO_2{}^{2+}$) with a remarkable blue shift. Simultaneous time-resolved measurements of the TSE and PyE pulses have established the correlation between the luminescence and the electric charge separation. The piezoelectricity coupled with microcrack formation has been revealed to be the main cause for the temperature-induced charge separation. It has also been suggested that the charge neutralization across the microcrack is most probably responsible for the TSE excitation. This mechanism is essentially the same as that proposed so far for TL, except that the stress is not caused by an external force but caused internally by temperature change. We hope that the present investigation would reveal not only the mechanism of TSE and charge separation accompanied but also some further details of the TL phenomenon. We have also suggested the possibility of phase transition involved in the process. Further investigation on the crystal structure and thermal measurements would clarify this point.

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Surface Derivatization and Isolation of Semiconductor Cluster Molecules

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Abstract: We describe a synthesis of nanometer-sized clusters of CdSe using organometallic reagents in inverse micellar solution and chemical modification of the surface of these cluster compounds. In particular we show how the clusters grow in the presence of added reagents and how the surface may be terminated and passivated by the addition of organoselenides. Passivation of the surface allows for the removal of the cluster molecules from the reaction medium and the isolation of organometallic molecules which are zinc blende CdSe clusters terminated by covalently attached organic ligands. Preliminary cluster characterization via resonance Raman, infrared, and NMR spectroscopy, X-ray diffraction, transmission electron microscopy, and size-exclusion chromatography is reported.

Large inorganic cluster molecules are interesting as representatives of a state of matter intermediate between molecules and crystalline solids.[1] The differences are especially evident in molecules that are fragments of the lattice of infinite solid-state compounds.[2] Recent studies of bare semiconductor crystallites (stabilized as colloids) have described electronic properties that depend on the size of the colloidal particles[3] and have thereby yielded insight into the transition from the molecular regime to the solid state. It is important for further examination of this transition to be able to prepare and isolate true molecules of the semiconductor solid that are size-selected, having from 100 to 10^4 atoms, are soluble in convenient solvents, and are chemically protected from growth and aggregation into bulk solids.

Colloids of II–VI crystallites small enough ($\leq$50 Å) to have incomplete band structure were first prepared by arrested precipitation in homogeneous solution.[3] Better size control and dispersion stability were achieved by arrested precipitation in structured media (zeolites, inverse micelles, polymer films, etc.).[4]

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Henglein and collaborators first isolated re-dispersible powders of colloidal clusters protected by polymeric sodium hexameta-phosphate.[5] This paper reports synthesis and isolation of a family of molecular CdSe fragments. Arrested precipitation in reverse micelles gives a bare semiconductor lattice, and in situ molecular modification of the cluster surface enables isolation of the molecular product with a variety of organic surface ligands.

Experimental Section

General. All manipulations involving silylselenium reagents were carried out with standard airless techniques. The surfactant bis(2-ethylhexyl) sulfosuccinate (Aerosol-OT; AOT) was used as purchased from Aldrich, as was LiHBEt. Metal salts were used as purchased from Alfa. Standard solutions of Cd^{2+} (1.0 M) were prepared from $Cd(ClO_4)_2 \cdot 6H_2O$ and deoxygenated water. Heptane, thf, and pyridine were anhydrous, purchased from Aldrich, and petroleum ether was 35–60 °C, purchased from Mallinckrodt. Water was routinely deoxygenated by ebullition with nitrogen. The silylselenium and silyltellurium reagents were prepared via literature methods[6] and stored at 0 °C in the drybox. Throughout the text $Se(TMS)_2$ stands for bis(trimethylsilyl)selenium, $PhSeTMS$ for phenyl(trimethylsilyl)selenium, and $Te(TBDMS)_2$ for bis(*tert*-butyldimethylsilyl)tellurium. The ratio *W* is defined as the molar ratio $[H_2O]/[AOT]$. Values of *W* are nominal, given by the ratio of water purposely added to initial soap. Corrections to account for hygroscopicity and/or water of hydration of the soap were not made and were found to be not important in this work.

Preparation of a Typical $AOT/H_2O/Heptane$ Microemulsion. The surfactant AOT (33.3 g, 75 mmol) is purified and degassed by dissolving the solid in petroleum ether, filtering to remove particles, and evaporating the filtrate to dryness. The dried surfactant is redissolved in heptane (1300 mL), and deoxygenated water (4.3 mL) is added. The mixture is stirred magnetically until the mixture becomes homogeneous. This preparation gives a microemulsion with $W = 3.2$.

Typical Preparation of Surfactant-Stabilized CdSe Particles. An aliquot (1.12 mL) of the standard Cd^{2+} solution is added to the above microemulsion. Stirring gives an optically homogeneous microemulsion with $W = 4.0$. A solution of $Se(TMS)_2$ (210 μL, 0.93 mmol) in heptane (50 mL) is added quickly to the microemulsion via syringe. A color develops throughout the homogeneous microemulsion as the semiconductor particles form. The absorption spectrum of the solution shifts to its final, persistent form over the time of seconds (for large *W*) to minutes (for small *W*). This surfactant-stabilized colloid can be treated in a number of ways subsequent to this preparation: (1) further surface chemical modification (see below); (2) evaporation to dryness; or (3) flocculation. Evaporation of the microemulsion to dryness yields colored solid surfactant in which the CdSe particles are embedded. This surfactant–particle composite may be redissolved in hydrocarbon to give an optically homogeneous solution. These solutions are stable indefinitely, showing little or no sensitivity to air and/or room light, although some deterioration has been noticed over the space of 8–10 months in solution samples that have been left unprotected from air and light.

If the CdSe-containing microemulsions are not evaporated to dryness (thereby removing the sequestered water), flocculation of the semiconductor particles occurs within hours. Flocculation occurs immediately if a large amount of water is added directly to the as-prepared microemulsion. The flocculated solid does not redissolve in any common organic or inorganic solvent.

Typical Preparation of "Phenyl-Capped" CdSe Molecular Particles. A sample of surfactant-stabilized CdSe particles is prepared as above. The surface of the particles is coated with Cd^{2+} by the addition of 0.5 mL of the stock $Cd(ClO_4)_2$ solution. After the emulsion becomes optically homogeneous once more, PhSeTMS (350 μL (1.5 mmol) in 50 mL of heptane) is added via syringe. The mixture becomes cloudy, and a colored precipitate is collected either by centrifugation or filtration. Exhaustive washing with petroleum ether followed by air-drying gives a free-flowing powder.

The yield from the above sequence is 260 mg. This is 53% of the total combined mass of Cd, Se, and Ph added to the reaction mixture. The capping reagent (PhSeTMS) is added in excess, and any unused PhSeTMS and any possible byproducts such as Ph_2Se_2 are removed during the purification process. Similarly, a deficiency of $Se(TMS)_2$ is used in the first step. Therefore, in a sense, Cd^{2+} is also in excess at points along the preparation. These two points make the interpretation of the percent yield a bit vague. If it is assumed, based on overall

stoichiometry, that Cd is the limiting reagent, the yield from the above reaction is 67%. The average yield from our preparations ($0 < W < 10$, absolute mass of reagents within an order of magnitude of those cited above) has been ~55% based on total input mass, or ~75% based on Cd as the limiting reagent.

Samples prepared according to the given prescription dissolve completely in pyridine. Addition of petroleum ether causes reprecipitation of the semiconductor material. This sequence can be used to remove any truly flocculated colloid material from the molecular particles, since the flocculated material does not dissolve in pyridine. Precipitation of insoluble, flocculated material has been indicative of incomplete surface passivation and can generally be avoided.

Preparation of Powders of II–VI Materials with Silylchalcogenide Reagents. We have prepared CdSe, HgSe, and CdTe using $Se(TMS)_2$ and $Te(TBDMS)_2$ and the corresponding metal salts ($Cd(ClO_4)_2$ or $HgCl_2$). The procedure is the same for all three cases; we describe the preparation of HgSe.

A solution of $Se(TMS)_2$ in thf (ca. 0.3 M) is prepared, starting with 0.53 g (6.7 mg-atom) of selenium powder, 13 mL (13 mmol) of $LiHBEt_3$ in thf, and 1.45 g (13 mmol) of $(CH_3)_3SiCl$. Subsequent to formation, this material is transferred via canula to $HgCl_2$ (1.82 g, 13 mmol) in 10 mL of thf. Immediately on addition a jet-black precipitate forms. After complete addition the mixture is filtered (in air) to give a black solid that is washed (H_2O, acetone, then Et_2O) and dried in air to give 1.67 g of black solid whose X-ray powder pattern shows only HgSe. This gives 92% yield of HgSe, based on $HgCl_2$.

The preparations of CdSe and CdTe are identical except that the X-ray powder patterns of the precipitated powders showed no peaks (neither starting materials, products, nor byproducts), using our routine instrument. Annealing the powders (temperatures from 250 to 500 °C) gave powders whose patterns showed only CdSe and CdTe, respectively. We rationalize this based on the lower diffusivity of Cd, which requires higher temperatures for crystallization of the Cd materials than the corresponding Hg compounds.

At no point during any of the preparations of bulk HgSe, CdSe, or CdTe was there any evidence for the formation of any other phase. Specifically, no elemental chalcogen was ever observed.

Results and Discussion

Arrested precipitation from inorganic aqueous ions has proven to be quite useful in preparing semiconductor colloids. We became interested in extending this methodology and were led to bis-(trimethylsilyl)chalcogenides by several reports in the literature which describe these compounds as organometallic equivalents of chalcogenide dianions.[1b,c,7]

We initially observed that treatment of $Cd(ClO_4)_2 \cdot 6H_2O$ with an equimolar amount of $Se(TMS)_2$ in THF at room temperature gave immediate precipitation of a red-brown solid whose X-ray powder pattern showed no reflections. Subsequent annealing of this solid gave hexagonal CdSe as the only observed solid-state compound. This preparative scheme was extended to HgSe (by using $HgCl_2$ in place of $Cd(ClO_4)_2 \cdot 6H_2O$) and to CdTe (by using $Te(Si(CH_3)_2(C(CH_3)_3))_2(Te(TBDMS)_2)$ in place of $Se(TMS)_2$). In each case the II–VI compound of interest is the only solid-state product observed in the X-ray analysis.

Given these results, we then attempted to control the crystallite growth by performing the reaction in $AOT/H_2O/heptane$ reversed micelle solutions. Several groups have shown that the ratio $W = [H_2O]/[AOT]$ controls the size of colloidal crystallites formed from ionic reagents.[4a–e] We observe that the organometallic reactions described above readily occur in reverse micelle solution. After Cd^{2+} was dissolved in the water pools of $AOT/H_2O/heptane$ solutions (at a concentration of approximately one ion per pool) the resulting solution was treated with a heptane solution of $Se(TMS)_2$. This immediately produces intense color. A UV–vis spectrum characteristic of CdSe cluster crystallites[8] is observed. The crystallite absorption threshold shifts red with increasing *W*, as expected for increasing crystallite size (Figure 1). Transmission electron microscopy directly images CdSe crystallites in thin AOT soap films made by colloid evaporation (Figure 2). These internal

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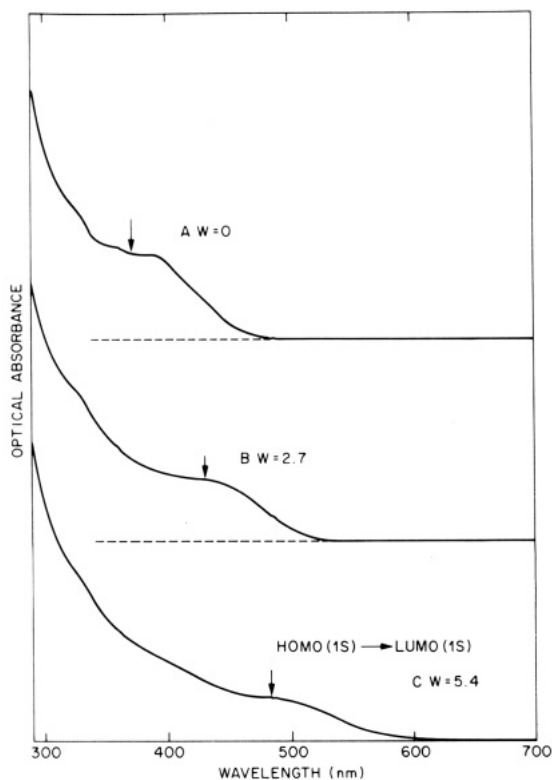
Figure 1. Optical absorption spectra (25 °C) of CdSe clusters synthesized and stabilized in microemulsion media. Synthesis conditions: [AOT] = 0.05 M, [Cd(ClO$_4$)$_2$] = 7.5 × 10^{-4} M, [Se(TMS)$_2$] = 5 × 10^{-4} M; (A) W = 0; (B) W = 2.7, (C) W = 5.4. The lowest, size dependent HOMO → LUMO transition is marked with an arrow in each case. The curves are offset vertically for clarity.

lattice images allow analysis of the size, shape, and internal unit cell of crystallites. Crystallites with ⟨111⟩ axes in the micrograph plane show alternating light and dark lines representing planes of atoms. The clusters show a narrow size distribution for smaller sizes made at low W. The clusters corresponding to Figure 1a ($W \simeq 0$) have a mean cross sectional dimension of 17 (3) by 19 (5) Å (where the numbers in parentheses are one standard deviation). As the repeat distance along ⟨111⟩ is 3.51 Å, these particles vary in diameter by only one CdSe layer. Larger W preparations yield larger crystallites; a lowest discrete state at ≈530 nm corresponds to ~45 Å diameter with a 25% standard deviation.

Thus this reaction yields micelle-encapsulated colloidal CdSe crystallites, in a fashion analogous to the previously reported syntheses of CdS in reverse micelles.[4a-e] In order to understand the mechanism of size control in these preparations, we performed the growth experiment summarized in Figure 3. To 120 mL of heptane solution containing AOT (3.3 g; 0.06 M), water (420 μL, 0.22 M), and Cd^{2+} (as the perchlorate, 0.06 mmol; 5 × 10^{-4} M) was added Se(TMS)$_2$ (0.044 mmol in 7 mmol of heptane). This gave small crystallites of CdSe as shown by UV–vis spectroscopy (trace a in Figure 3). Subsequent to this seed formation, alternate aliquots of Cd^{2+} and Se(TMS)$_2$ were added. After each addition the UV–vis spectrum was recorded (traces b and c in the figure). These data show no change on addition of excess Cd^{2+} (since the system is already Cd-rich) and a shift of the onset of absorption to longer wavelength upon addition of Se(TMS)$_2$. *The shift shows that rather than forming more particles of the same size as the original ones, the new cadmium and selenium reagents add to the original CdSe crystallites, giving larger particles.* In this sense the colloidal crystallites are inorganic living polymers: the crystallites are stable in the reverse micelles, yet their surfaces are reactive. Although this experiment is not conclusive, it does suggest a growth mechanism for arrested precipitation in micelles. We propose that particle growth occurs by addition of atoms (or ions) one at a time, by exchange of Cd^{2+} between water pools, and by an organometallic reaction at the interface. The micelle prevents contact between two large (growing) crystallites, and the
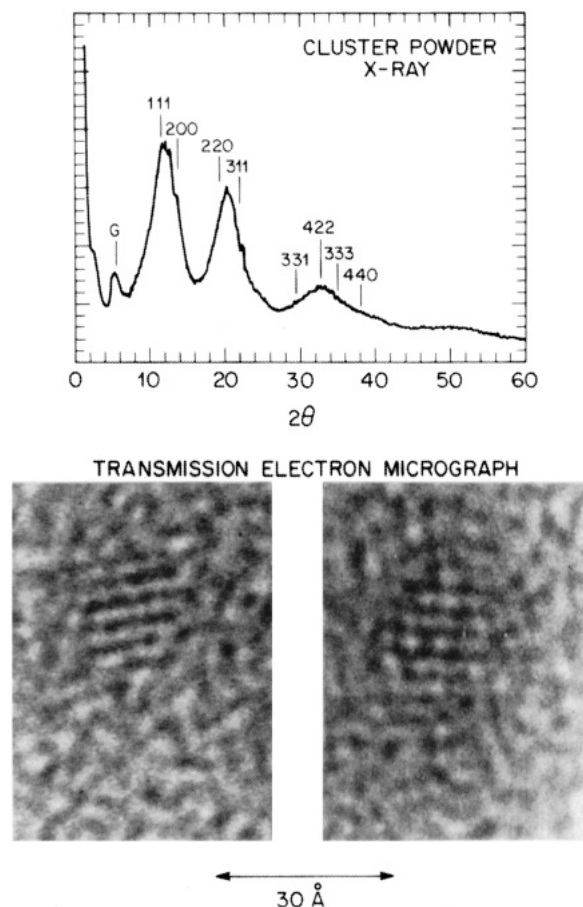

Figure 2. Top: X-ray powder pattern of phenyl-capped CdSe cluster powder. Positions of CdSe bulk zinc blende lines are marked. G stands for silicone grease used as a powder support. Bottom: Bright field transmission electron micrographs showing faint images of CdSe cluster internal lattice structure. A crystallite ⟨111⟩ axis lies in the plane of the supporting substrate producing the pattern of alternating light and dark lines. The amorphous carbon substrate produces an underlying speckle pattern. At this large magnification, the crystallite shape and edges become diffuse.
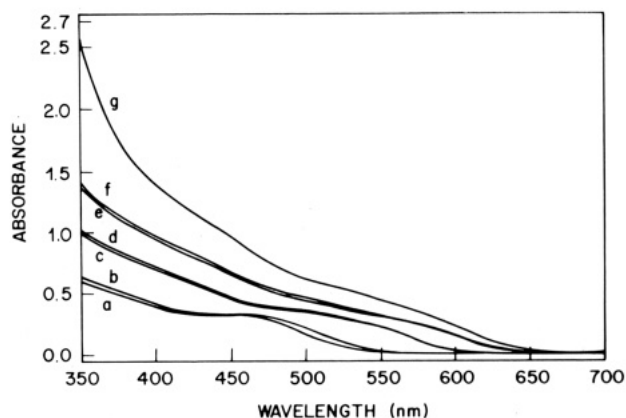
Figure 3. UV–visible spectra of the CdSe growth experiment. Traces a through f are in the heptane/AOT/H$_2$O reaction medium, with the starting cadmium-containing solution as the reference. Trace g is in pyridine with pure pyridine as reference. After addition of (a) 44 μmol of Se(TMS)$_2$ to the initial Cd^{2+} solution (see text); (b) 30 μmol of Cd^{2+}(as a micellar solution); (c) 20 μmol of Se(TMS)$_2$; (d) 30 μmol of Cd^{2+}; (e) 30 μmol of Se(TMS)$_2$; (f) 60 μmol of Cd^{2+}. (g) Spectrum of capped CdSe molecular particles after isolation, washing, and redissolution in pyridine.

crystallites grow until the supply of feedstock Cd and Se is exhausted. In this way size control is statistical (only a very small fraction of the micelles are eventual hosts to a CdSe particle) and kinetic (once a growth atom (ion) is attached to a growing
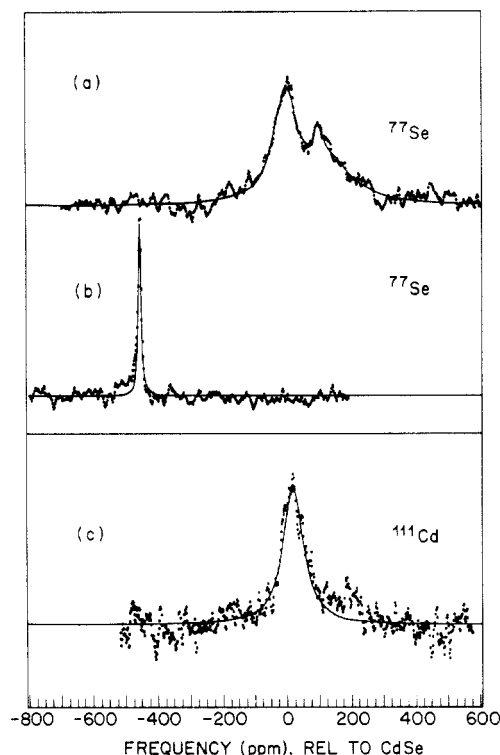
Figure 4. ^{77}Se and ^{111}Cd NMR spectra of capped semiconductor clusters dissolved in pyridine. Spectra are plotted on the σ scale (negative shifts corresponding to lower field) with solid lines through the data to guide the eye. Selective incorporation of ^{77}Se isotopic labels in the clusters aids interpretation of the peaks. (a) A broad line near the shift of bulk CdSe is observed for interior labeled clusters. The major component of this line (at $\sim$0 ppm) increases with increasing particle size. A sharp line in spectrum b is observed for clusters isotopically labeled in the selenium bonded to the organic ligands. This sharp resonance appears approximately midway between the shifts of CdSe and the neat organoselenide materials. In spectrum c, the ^{111}Cd spectrum of the cluster also shows a broad line characteristic of the interior of the cluster. If present, an organocadmium signal would lie upfield from zero ppm.

crystallite it does not redissolve on a competitive time scale). Experimentally there is no change in optical spectra if W is increased after growth is complete, showing that dissolution does not occur.

Importantly, this experiment suggests that a general "surface" chemistry may be performed on these colloidal crystallites. It has been reported that silylorganoselenides (e.g., RSeSiMe$_3$, R = organic moiety) react quickly with metal salts to form metal–selenium covalent bonds.[9] We now report that micelle stabilized CdSe crystallites having Cd-rich surfaces similarly react with PhSeTMS to give larger CdSe crystallites covered covalently with phenyl ligands (eq 1). The solution resulting from the stepwise
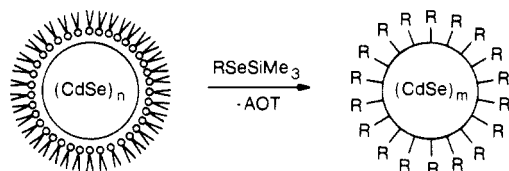
synthesis described above was treated first with an additional 0.06 mmol of Cd^{2+} to cover the crystallite surface with cadmium (trace f). After a few seconds PhSeTMS (0.25 mmol in 16 mL of heptane) was added. This gave the precipitation of a red solid from the initially optically homogeneous, red colloid. The solid was separated from the supernatant by filtration (the filtrate being colorless) and washed exhaustively with petroleum ether and dried in air. The solid subsequently dissolved completely in pyridine,
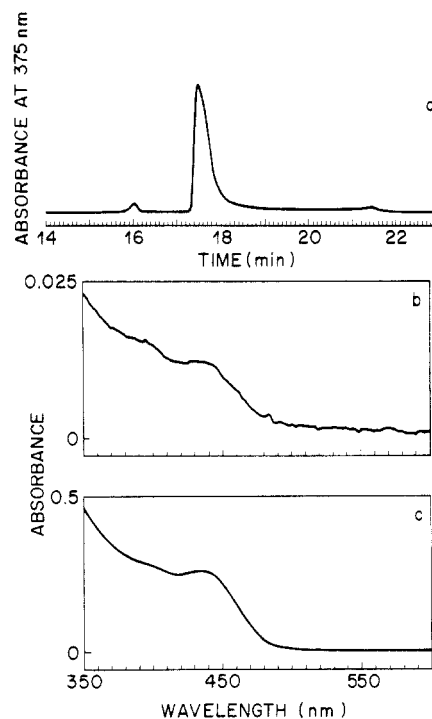
Figure 5. Size-exclusion chromatogram of "capped" CdSe clusters (W = 0.9). (a) Chromatographic trace (PL gel 500 column, pyridine mobile phase, 40 °C) showing absorbance of the eluant at 375 nm versus retention time. The bulk of the material elutes as a single peak at 17.5 min. The small peak at t = 16 min represents CdSe cluster dimers, and the small peak at 21.5 min is Ph$_2$Se$_2$. (b) UV–visible spectrum of the peak at 16.0 min. (c) UV–visible spectrum of the peak at 17.5 min.

giving a solution whose UV–vis spectrum is shown as trace g in Figure 3.

We propose that the solid is composed of CdSe crystallites with surfaces protected with phenyl ligands, based on the following evidence: (1) Electron micrographs of this "capped" material reprecipitated from pyridine are identical in structure with those of the surfactant-stabilized uncapped samples, showing crystallites of cubic CdSe. (2) The X-ray diffraction powder pattern (Figure 2) of the solid shows only broad peaks due to small zinc blende particles of CdSe. (3) ^{111}Cd NMR shows a broad peak (ca. 50 ppm upfield from bulk CdSe), and ^{77}Se NMR shows two nonoverlapping regions of absorption: a sharp resonance (ca. 440 ppm downfield from CdSe) assigned to Se–Ph, and a broad resonance with partially resolved structure (ca. 50–100 ppm upfield from CdSe) assigned to Se atoms in small CdSe crystallites (Figure 4). (4) Far-infrared absorption spectra of a sample dissolved in a polystyrene film show a $\simeq$190-cm^{-1} peak characteristic of the dipolar longitudinal optical mode of a spherical crystallite, and resonance Raman spectra show a $\simeq$206-cm^{-1} peak characteristic of an internal longitudinal optical mode. Analyses of NMR[10] and vibrational spectra are involved and will be reported separately. (5) Pyrolysis of a sample of the "capped" cluster yields bulk cubic CdSe as the only observed solid-state product, and Ph$_2$Se$_2$ as the primary organic products. (6) Size-exclusion chromatography of this material shows one major peak, and the UV–vis spectrum of the eluted peak is the same as that of the injected sample, this observation showing that there is essentially only one type of species in solution (Figure 5). All this evidence supports our conclusion that the solid is composed of surface-derivatized CdSe crystallites. The NMR evidence and our mechanistic discussion suggest that the phenyl group is bonded to a surface Se atom that is part of the sp^3 cluster network. We presently have no further evidence on surface reconstruction or bonding.

The phenyl capping reaction effectively changes the crystallite surface from hydrophilic to hydrophobic. The crystallites leave

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the water pools and then precipitate. The surfactant, excess reagents, and other reaction products are easily removed as described. The hydrophobic cluster molecules obtained are somewhat soluble in DMF, DMSO, or toluene/PEt₃, and completely soluble in pyridine.

Conclusion

In this paper we have described two of our extensions of known semiconductor colloid chemistry. The first is the use of bis(silyl)chalcogenide reagents in the arrested precipitation reaction. This has allowed for the fairly safe and convenient preparation of the chalcogenides (both as colloids and in bulk form) with liquid reagents. The second modification is more crucial. Using the controlled-growth ("living-polymer") process, culminating with the use of (organo)(silyl)selenides, we have been able to passivate

the growing particle of the semiconductor solid and thereby isolate *molecular* particles of the solid-state infinite lattice. These particles are molecular in both size (10–100 Å) and solubility.

The solubility of these materials has been critical to our study of them. Since the compounds are quite stable and since they dissolve so readily we have been able to begin their detailed characterization using many of the analytical techniques of solution-phase chemistry.

MC–SCF Study of the Diels–Alder Reaction between Ethylene and Butadiene

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Abstract: In this paper we describe the results obtained in an MC–SCF STO-3G and 4-31G study of the cycloaddition reaction between butadiene (cis and trans) and ethylene. For this reaction it is possible to envisage three different mechanisms: a synchronous concerted approach, a nonsynchronous concerted approach, and a two-step process. At the STO-3G level we have found that the attack of ethylene on *cis*- or *trans*-butadiene involves three fragmentation transition states of diradicaloid nature associated with the syn–gauche, the trans, and the anti–gauche approach, which lead to three minima, again of diradicaloid nature, interconnected by two transition states of conformational origin. The attack on *cis*-butadiene involves also a fragmentation transition state of C_s symmetry associated with the concerted synchronous attack, which, however, is disfavored on energy basis, and the preferred paths are those associated with the nonsynchronous approaches. The 4-31G results provide a completely different mechanism, which agrees well with the experimental evidence. The main differences are (i) the three fragmentation transition states seem to disappear, so that the region of the potential energy surface associated with the gauche and trans approaches becomes very flat, and (ii) the C_s transition state is located at a slightly lower energy than the syn–gauche minimum. Therefore it appears that both synchronous and nonsynchronous paths exist and that the synchronous path is favored by ∼2 kcal/mol.

1. Introduction

The Diels–Alder (DA) reaction is of great significance in the history of organic chemistry, from both an experimental and a theoretical point of view. However, despite the large number of experimental[7–9] and theoretical[2–6,9–22] studies, the mechanism of

this reaction, even in the simple case of the reaction between butadiene and ethylene, is still in controversy. It is possible, in fact, to envisage three different mechanisms:[2–6] (i) a synchronous concerted approach, involving a cyclic aromatic transition state (TS) with the two new C–C bonds formed to equal extent; (ii) a two-stage asynchronous concerted mechanism in which there are two distinct stages to changes in the bonding, some mainly between the reactants and the single TS and the others mainly between the TS and products; (iii) a two-step process, which occurs in two kinetically distinct steps via a stable diradical intermediate.

In this paper we limit our attention only to the simple Diels–Alder reaction between butadiene and ethylene. Experimentally,

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