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Molecular Limit of a Bulk Semiconductor: Size Dependence of the "Band Gap" in CdSe Cluster Molecules

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A primary goal of cluster science is the study of the development of bulk properties from the molecular regime.[1] Here we report on the evolution of the optical "band gap" in a series of CdSe cluster molecules spanning a size range of 1−2 nm.[2−4] These clusters serve as a unique molecular model for the solid semiconductor in the sense that they exhibit its basic crystal structure motif and, as we clearly show here, also its basic electronic structure motif. The largest cluster molecule that we study overlaps in size with the smallest CdSe nanocrystals, where quantum confinement leads to a systematic blue shift of the band gap with reduced size, and to the development of discrete states.[5,6] Using absorption, photoluminescence (PL), and photoluminescence excitation (PLE) spectroscopy at room and low temperatures, we found that the systematic blue shift of the absorption onset persists down to the cluster molecule regime, in which the molecular composition and structure are precisely known.

Previous spectroscopic and theoretical studies on the electronic structure of II−VI semiconductor cluster molecules were focused primarily on CdS- and ZnS-based compounds. The absorption onset of two forms of $Cd_{32}S_{50}$ clusters[7,8] was found to be around 3.5 eV, considerably blue shifted from the band gap of bulk CdS. For a $Cd_{17}S_{30}$ cluster, the absorption is shifted further to the blue, to ∼4.1 eV.[9] Theoretical and experimental work on smaller CdS clusters did not reveal a systematic size-dependent behavior for the band gap.[10,11] This was also the case for a series of ZnS clusters with thiophenolate surfaces, where the absorption spectra showed strong features around 4.9 eV, assigned to transitions mainly localized on the bridging and terminal thiophenolates.[12]

CdSe-based cluster -molecules, capped by selenophenols, have only recently been successfully synthesized and characterized by single-crystal X-ray diffraction (XRD).[2−4] The electronic structure of the CdSe compounds is particularly interesting for two main reasons. First, the absorption onset of the cluster molecules of CdS and ZnS already falls into the region of intraligand electronic excitations, considerably affecting the nature of their lowest electronically allowed transition.[10,12] For CdSe, however, the bulk band gap is narrower than that of bulk CdS and ZnS ($E_g = 1.7$ eV compared with $E_g = 2.4$ and 3.6 eV, respectively), and is much smaller than the transition energies of selenophenol ligands ($\Delta E > 4.4$ eV).[13] Thus, for CdSe cluster molecules, a larger range of energetic shift is possible prior to mixing between the "band gap" transition and the intraligand transitions. Second, combining our data with the accumulated knowledge on CdSe nanocrystals may allow us to fully map the scaling law for the band gap transition from ∼10 atoms and up to the bulk semiconductor.

We investigated four cluster molecules in three compounds: $[Cd_{10}Se_4(SePh)_{12}(PPr_3)_4]$ (**1**,[3] shown in the inset of Figure 1), $\{[Cd_{17}Se_4(SePh)_{24}(PPh_2Pr)_4]^{2+}[Cd_8Se(SePh)_{12}Cl_4]^{2-}\}$(**2a**, **2b**),[4] and $[Cd_{32}Se_{14}(SePh)_{36}(PPh_3)_4]$ (**3**,[2] Ph = phenyl, Pr = *n*-propyl groups). The compounds were prepared using an organometallic synthetic route, crystallized from solution, and their structures were determined using single-crystal XRD.[14] All molecules display structures of the published CdSe cluster cages[2−4] although **1** and **2** are synthesized with a different phosphine ligand to obtain improved yield and purity. The room temperature absorption for the three compounds as a suspension in Nujol is shown in Figure 1.[15] With reduction of the cluster size, a blue shift of the absorption onset is clearly observed. The molar extinction coefficients, ϵ, for the cluster molecule compounds were determined in acetonitrile solutions. The values of ϵ at the first absorption feature were 57 000, 56 000, and 52 000 M^{-1} cm^{-1} for compounds **1**, **2a**, and **3**, respectively. The first transition is strongly allowed, and the similar values of the extinction coefficients for the different compounds indicates that there is a concentration of the oscillator strength per atom in the smaller cluster molecules. This follows the predicted behavior for concentration of oscillator strength in strongly quantum-confined semiconductor nanocrystals.[16]

The low-temperature spectroscopic data for the three compounds in the form of a suspension in Nujol are summarized in Figure 2.[15] Several peaks are resolved in the PLE spectra (solid lines) for each compound, and as seen for the room temperature absorption, a blue shift of the excitation onset is observed for the smaller clusters. For compound **2**, which contains cluster molecules **2a** and **2b**, two structured peaks separated by ∼0.7 eV are observed in the PLE spectrum. By monitoring the PLE spectra at various detection wavelengths, we established that there are two emitting species in this case, which we assign to cluster molecules **2a** (lower energy PLE features) and **2b (**higher energy PLE features).

Figure 3 displays the size dependence of the energies of the first transition extracted from our room temperature absorption and low-temperature PLE for all the studied cluster molecules, along with the band gaps reported for CdSe nanocrystals.[5,6] The equivalent spherical diameter for each cluster molecule was determined as the height of the tetrahedron with the center of the Cd−P bond taken as the tetrahedron apex. A considerable blue shift is observed from an onset at 3.3 eV for the largest cluster

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(14) The optical measurements required a high degree of purity of gram amounts of each compound, which was verified also by measuring the representative powder XRD pattern and comparing it with a pattern simulated from the single-crystal diffraction data.

(15) Crystalline powder of **1**, **2**, or **3** was ground in Nujol and placed between two quartz windows to give a homogeneous transparent film. The room temperature absorption was measured on a Perkin-Elmer Lambda 900 spectrometer, with an integrating sphere. Low-temperature spectral measurements were performed in a continuos flow He cryostat with use of a locally built fluorometer setup with lock-in detection.

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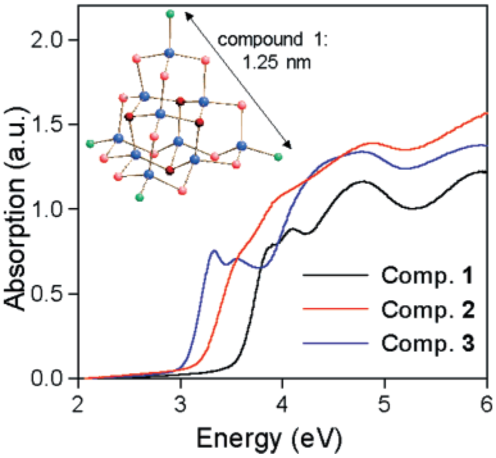

Figure 1. Absorption spectra of CdSe cluster molecule compounds as suspensions in Nujol at room temperature. Inset shows the structure of cluster molecule **1**: green spheres, PPr_3; blue spheres, Cd^{2+}; dark red spheres, Se^{2-}; and light red spheres, $SePh^-$.

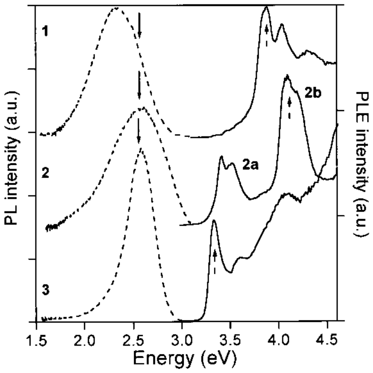

Figure 2. PL spectra (dashed lines, excitation energies denoted by dashed arrows) and PLE spectra (solid lines, detection energy denoted by solid arrows) for the cluster molecule compounds **1** (top traces), **2** (middle traces), and **3** (bottom traces) at $T = 20$ K.

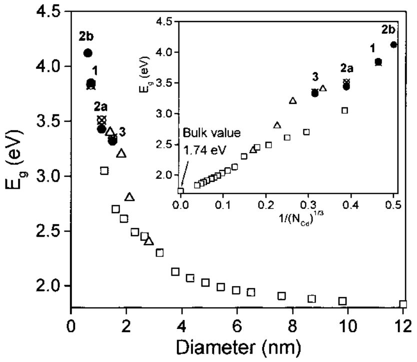

Figure 3. Size dependence of the band gap for CdSe from the molecular regime to the bulk. Filled (crossed) circles represent the band gap of cluster -molecules extracted from the low-temperature PLE data (room temperature absorption). For **2b**, only the low-temperature value is shown due to the uncertainty in its position from the room temperature absorption. Squares and triangles represent the band gap values for CdSe nanocrystals from refs 5 and 6, respectively. The inset represents the same data versus $1/(N_{Cd})^{1/3}$. For the data from refs 5 and 6, N_{Cd} was calculated assuming a spherical shape for the nanocrystals, and using the density of bulk CdSe.

molecule **1**, which overlaps with the smallest CdSe nanocrystals, to 4.2 eV for the smallest cluster molecule **2b**. Overall, an energetic shift of 2.4 eV is observed, spanning a remarkable range of sizes from nearly bulklike nanocrystals with a diameter of 10 nm, containing 15 000 Cd atoms, to the smallest cluster molecule **2b**, which contains merely 8 Cd atoms, and has an equivalent spherical diameter of 0.7 nm.

The PL from all the cluster molecules is red-shifted substantially, by at least 0.7 eV, from the absorption onset (Figure 2). Similar behavior was reported for the CdS cluster molecules.[7] We could not detect any PL at room temperature, indicating that efficient nonradiative decay processes are present for the electronically excited cluster molecules. At low temperature, the nonradiative processes slow down, allowing for observation of radiative decay. This, along with the fact that no absorption can be detected in the spectral region of the PL, clearly indicates that the emission electronic transition is forbidden.

In the assignment of the PL, we consider the behavior of semiconductor nanocrystals, where two types of emission bands can be detected: the "band gap" PL[17] and the "deep trap" PL.[18] The band gap PL is narrow (width determined by the size distribution), and is only slightly red shifted from the absorption onset (up to 0.1 eV for a CdSe nanocrystal, 2 nm in diameter). The deep trap PL is broad and is substantially red shifted from the absorption onset (typically by 0.5 eV). It has been associated with radiative recombination of localized surface trapped charge carriers, and because of its long lifetime, its intensity relative to the band gap PL is enhanced at low temperatures. The broad width, large red shift, and the enhancement at low temperature of the cluster molecule PL are fully consistent with the characteristics of the deep trapped emission in the nanocrystals. The PL is thus assigned to transitions involving the cluster molecule surface. This is consistent with calculations of the density of states for thiophenol-capped ZnS clusters, which showed that the LUMO is associated with the Ph-based π^* orbitals.[12] Thus, a distinction should be made between the "HOMO-LUMO" gap, and the "band gap" for the cluster molecules. The HOMO-LUMO gap involves forbidden transitions of surface states, which can only be detected in the emission and are not resolved in the absorption. The band gap, on the other hand, is the first electronically allowed transition, and it involves the metal and chalcogen atoms. The energetic value of this transition evolves systematically to the semiconductor bulk band gap value (Figure 3).

The nature of the band gap transition is a charge transfer from the valence band, which derives from the Se 4p atomic orbital, to the conduction band, which derives from the Cd 5s atomic orbital.[19] In the inset of Figure 3, we display the dependence of E_g on $1/(N_{Cd})^{1/3}$, with N_{Cd} the number of Cd atoms. This plot accentuates the dependence on size of E_g for our cluster molecules. In nanocrystals, the size dependence of the band gap is governed by competing terms: the confinement energy, which scales as $1/r^2$, and a coulomb attraction term that scales as $1/r$.[16] The variation in the dielectric constant with size also affects the size dependence of the gap. For the cluster molecules studied here, we observe that the dependence lies between $1/r$ and $1/r^2$. A precise determination of the scaling law is problematic due to the discontinuity in stable sizes which is an inherent property in the cluster molecule regime. However, this plot helps to identify two limits for the band gap. Its intercept represents E_g for the bulk semiconductor. On the other hand, the "Atomic limit" may be identified as the value of E_g for a hypothetical Cd_1Se_1 molecule. We have thus successfully mapped the size dependence of the semiconducting band gap in the truly molecular regime.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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