In response to ever-increasing energy demands and subsequent costs, a tremendous emphasis is being placed on energy saving, solid state lighting devices in the form of light emitting diodes, or LED’s. Specifically, a need exists for pure white-light LED’s as a more efficient replacement for conventional lighting sources. Switching to solid state lighting would reduce global electricity use by 50% and reduce power consumption by 760 GW in the United States alone over a 20 year period. The complications associated with design and fabrication of such devices have generated great interest in developing white-light phosphors that do not depend on complex doping schemes or combinations of materials. One proposed solution is to use a mixture of semiconductor nanocrystals as the intrinsic emitting layer for an LED device. Semiconductor nanocrystals exhibit high fluorescence quantum efficiencies and large molar absorptivities. However, they still suffer from the problem that simply mixing the traditional red, green, and blue colors to achieve white light results in a loss in total device efficiency due to self absorption for a device of more than a few monolayers. In this communication, we demonstrate white-light emission from ultra-small cadmium selenide (CdSe) nanocrystals. This raises the intriguing possibility of using these nanocrystals as a white-light phosphor. These ultra-small nanocrystals exhibit broadband emission (420–710 nm) throughout most of the visible light spectrum while not suffering from self absorption. This is the direct result of the extremely narrow size distribution and an unusually large (40–50 nm) Stokes shift (Figure 1), making them ideal materials for devices currently under development and also an ideal platform to study the molecule-to-nanocrystal transition.

Figure 1 shows the absorption and emission properties of a sample of magic-sized CdSe nanocrystals prepared by the methods of Peng et al. with modifications (see Supporting Information). The first absorption feature is at 414 nm, which has been assigned as a thermodynamically determined “magic size”, on the order of 15 Å, for CdSe. The emission spectrum shows a band edge transition (Figure 1), making them ideal materials for devices currently under development and also an ideal platform to study the molecule-to-nanocrystal transition.

Our pyrolytically grown magic-sized nanocrystals do not typically exhibit the strong band edge emission feature that is observed in CdSe nanocrystals, but do exhibit strong band edge absorption features indicative of high quality CdSe nanocrystals. We attribute the broad emission to charge recombination from surface midgap states that arise from the presence of noncoordinated surface selenium sites. While band edge emission occurs by direct recombination of the electron and hole within the nanocrystal, deep trap emission occurs when a photogenerated hole, trapped in a midgap state, encounters an electron before it can relax nonradiatively to the ground state.

This phenomenon of hole trapping to the selenium surface sites has been studied by ultrafast fluorescence upconversion spectroscopy. These studies indicate that as nanocrystal size decreases, the amount of hole trapping increases. This is due not only to the reduced physical distance the hole must travel to reach the surface but also to an increased surface-to-volume ratio resulting in more available surface sites. It is not unreasonable to infer that as the nanocrystal size continues to decrease, an even larger population of photoexcited excitons would be funneled toward the hole-trapping decay pathway, ultimately making it the dominant mode of radiative relaxation. Magic-sized nanocrystals are so small that the electron wave function has significant overlap with the selenium surface sites. Therefore, any hole trapped on the surface would likely encounter the electron before nonradiatively relaxing to the ground state. Compounding this situation, the nanocrystal growth time is so short (10–20 s normally) that surface reconstruction and high temperature annealing have little time to occur. This results in a surface that is likely defect-ridden. Furthermore, unlike larger nanocrystals, the diameter of the magic-sized nanocrystal and the length of the ligand are quite comparable. Coupling of vibrational modes of the ligand to surface atoms, as well as collisional...
A quantum well is pumped by laser emission, generating electrons. One example developed by Klimov et al. utilizes core/shell nanocrystals deposited onto an InGaN quantum well. The emission can be tuned by simply controlling the nanocrystal size. Nanocrystal-based LED's have been demonstrated showing colored-light state lighting. Unlike commercial phosphors, their emission colors would bias the white-light emission toward a particular color, typically to a single wavelength. This bias occurs because they are optimized for specific colors and lack the ability to cover the entire visible spectrum. Consequently, these magic-sized nanocrystals provide the ideal platform to study the nanocrystal—molecule transition. Further, the combination of their intrinsic properties makes them an ideal material for solid state lighting applications. Study of the fundamental properties of this material could lead to the development of more economical and environmentally friendly materials with similar properties, eventually leading to the next generation of solid state lighting technologies.

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Supporting Information Available: A comparison of magic-sized CdSe nanocrystal emission to conventional light sources as well as a complete author list for ref 13, and the synthetic scheme used in this work is available. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA055470D

Figure 2. White-light emission from magic-sized CdSe. (a) Thin film of magic-sized CdSe in polyurethane excited by a frequency doubled titanium:sapphire laser (400 nm) with white light clearly seen reflecting off the table surface. (b) A 5 mm commercial UV LED (400 nm) illuminating a thin coating of magic-sized CdSe in polyurethane.