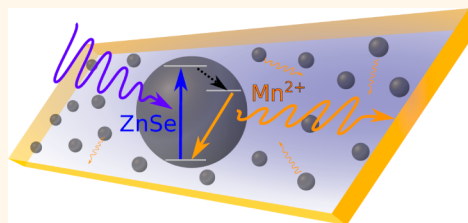


Zero-Reabsorption Doped-Nanocrystal Luminescent Solar Concentrators

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ABSTRACT Optical concentration can lower the cost of solar energy conversion by reducing photovoltaic cell area and increasing photovoltaic efficiency. Luminescent solar concentrators offer an attractive approach to combined spectral and spatial concentration of both specular and diffuse light without tracking, but they have been plagued by luminophore self-absorption losses when employed on practical size scales. Here, we introduce doped semiconductor nanocrystals as a new class of phosphors for use in luminescent solar concentrators. In proof-of-concept experiments, visibly transparent, ultraviolet-selective luminescent solar concentrators have been prepared using colloidal Mn²⁺-doped ZnSe nanocrystals that show no luminescence reabsorption. Optical quantum efficiencies of 37% are measured, yielding a maximum projected energy concentration of $\sim 6\times$ and flux gain for a-Si photovoltaics of 15.6 in the large-area limit, for the first time bounded not by luminophore self-absorption but by the transparency of the waveguide itself. Future directions in the use of colloidal doped nanocrystals as robust, processable spectrum-shifting phosphors for luminescent solar concentration on the large scales required for practical application of this technology are discussed.



KEYWORDS: solar energy · solar concentrators · doped nanocrystals · transparent solar collector

Luminescent solar concentrators (LSCs) are dye-containing waveguides used to collect and concentrate sunlight for energy conversion.^{1–3} Simultaneous spectral and spatial concentration is achieved without the use of focusing optics. Instead, sunlight absorbed by the dye is emitted into guided modes to travel by total internal reflection for collection at the perimeter (Figure 1). LSCs require no solar tracking, exhibit omnidirectional acceptance providing comparable performance under diffuse and specular illumination, and offer the potential for higher energy concentration ratios (CR) than designs based on mirrors or lenses.⁴ Their ability to deliver high-irradiance, narrow-bandwidth light by active wavelength shifting makes LSCs particularly suitable for driving photovoltaics and semiconductor-based photochemical processes where wavelength-to-bandgap matching can be exploited to improve efficiency and mitigate thermal rejection.⁵ Unlike lens- and mirror-based concentrators, LSCs selectively collect sunlight in a limited spectral band, established by the absorption range of the

luminophore. Other wavelengths are transmitted for use in secondary applications such as interior lighting, heat generation, or photovoltaic conversion, enabling high combined-cycle efficiencies. The LSC itself obeys the single-bandgap Shockley–Queisser efficiency limit,⁶ with maximum energy efficiencies of $E_{lim} \approx 3–5\%$ for UV-selective collection, increasing up to $\sim 30\%$ if absorption extends into the near-infrared. The thermodynamically limited energy concentration ratio depends on the effective luminescence Stokes shift, with values of $CR_{lim} \geq 100$ predicted at room temperature for a Stokes shift of ~ 0.1 eV.⁷ Attached photovoltaics receive high-irradiance, narrow-bandwidth light, resulting in a power density enhancement (referred to as the flux gain) up to several times larger than CR_{lim} when the photovoltaic's bandgap is matched to luminophore emission.⁸

Despite several decades of research,^{9,10} actual LSC performance levels remain far below these thermodynamic limits, primarily due to three main factors: (1) only a fraction of incident sunlight is absorbed,

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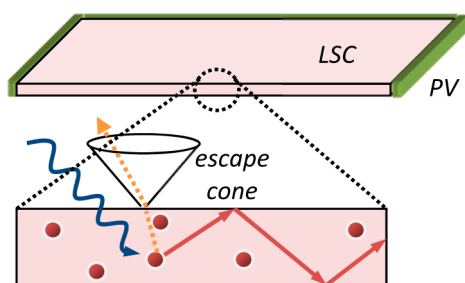


Figure 1. A luminescent solar concentrator. Sunlight (blue) is absorbed by luminophores and emitted into a planar waveguide (red), traveling to the edge of the collector to concentrate light for conversion by PV cells. A fraction of light is lost to nonunity LQY or out the escape cone (dashed orange) with each successive reabsorption/re-emission event.

determined by the integrated overlap of luminophore absorption and solar spectra; (2) only a fraction of absorbed light is re-emitted, depending on the luminophore's luminescence quantum yield (LQY); (3) only a fraction of this emitted light is captured in guided modes ($\sim 75\%$ in an LSC waveguide with refractive index $n \sim 1.5$), with the remainder ($\sim 25\%$) lost out the top or bottom escape cone defined by Snell's Law.¹¹ Most problematic of all is that losses from mechanisms (2) and (3) occur repetitively, because photons traveling within the waveguide may be absorbed and re-emitted by other luminophores multiple times before reaching an edge. In practical LSC implementations, for example, optical path lengths may easily reach a meter or more, and even small overlap between absorption and emission spectra results in catastrophic self-absorption losses. Concentrator efficiencies thus fall exponentially with the number of reabsorption/re-emission events, which is in turn determined by the overlap of luminophore absorption and emission spectra and by the device dimensions.

Efforts to improve LSC performance by reducing luminophore self-absorption or mitigating its effects have included the use of dichroic mirrors and other photonic structures to reduce escape-cone losses,^{12–15} controlling luminophore orientation to capture a greater proportion of emitted photons in guided modes,^{16–20} and use of large Stokes shift luminophores.²¹ Regarding the latter, a wide range of materials and strategies have been investigated, including organometallic and sensitized lanthanide phosphors,²² Stokes shift enhancement by solid-state solvation,²³ and other concepts.^{24–26} Various types of semiconductor nanocrystals (quantum dots, or QDs) have also been investigated, including those with both Type I and Type II heterointerfaces.^{27,28} Despite these efforts, it has proven difficult to identify phosphors that simultaneously absorb strongly, are photostable, are solution processable, and generate sufficiently large Stokes shifts without sacrificing LQYs.

Here, we demonstrate a new class of LSCs based on impurity-doped QDs as the active phosphor material.

Incorporation of small amounts (0.1–1 atom %) of a luminescence activator ion within a QD introduces new localized excited states within the bandgap that can be efficiently excited *via* exchange-mediated energy transfer from the photoexcited host semiconductor.²⁹ Emission from these states can be downshifted substantially relative to the semiconductor absorption so that, by choosing an activator whose extinction coefficient is sufficiently small, self-absorption can be effectively eliminated. The same mechanism is employed by classic sensitized inorganic phosphors commonly used in lighting or display applications.³⁰ Importantly, the small dimensions of colloidal doped QDs eliminates scattering effects typical of classic inorganic phosphor microcrystal powders.

In addition to minimal self-absorption and scattering, doped QDs possess several other characteristics useful for LSC applications. The semiconductor host provides a large extinction coefficient along with broadband absorption that is in principle tunable over a wide spectral range through composition and size control. Doped QDs also exhibit minimal concentration quenching and higher resistance to photo-oxidation than most organic dyes or undoped nanocrystals (due to rapid energy localization at the buried luminescence activator).³¹ Depending on the semiconductor, they can be made from low cost, nontoxic, Earth-abundant starting materials, and they are compatible with a variety of economical solution-based synthesis and processing techniques advantageous for integration into polymer or glass waveguides. While doped QDs have been investigated extensively as phosphors^{32–35} and for their unusual magneto-optical and magnetoelectronic properties,^{36–39} to our knowledge this class of materials has not previously been used in LSCs.

As proof of concept, we have prepared and studied LSCs based on Mn^{2+} -doped ZnSe/ZnS core–shell quantum dots. The results presented here identify doped QDs as promising candidates for addressing the major challenges confronting the development of efficient LSCs. Although these challenges are not all fully overcome in the present study, our findings point to specific modifications of the doped QD compositions that could offer major improvements in device efficiency. Moreover, the specific doped QD materials described here may be of practical interest for unique applications ranging from window layers in stacked photovoltaics to transparent building-integrated energy-harnessing smart windows.

RESULTS AND DISCUSSION

ZnSe is a direct bandgap semiconductor with a bulk bandgap of ~ 3.1 eV, meaning it selectively absorbs UV light. In the weak tetrahedral field provided by the ZnSe lattice, substitutional Mn^{2+} impurity ions possess

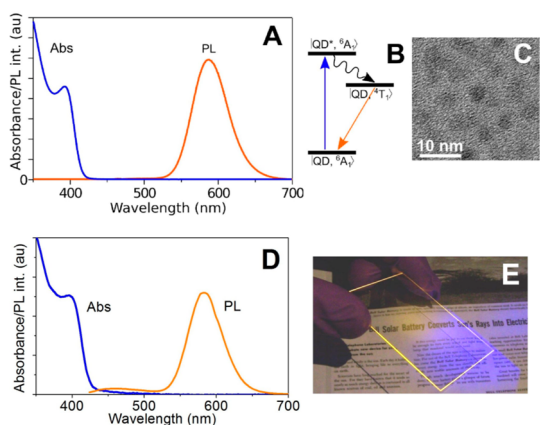


Figure 2. (A) Absorption and photoluminescence spectra of colloidal Mn^{2+} -doped ZnSe/ZnS QDs in toluene. (B) Schematic description of luminescence sensitization in Mn^{2+} -doped QDs. Photon absorption by the doped quantum dot in its ground state ($|\text{QD}, {}^6\text{A}_1\rangle$) gives the excited quantum dot ($|\text{QD}^*, {}^6\text{A}_1\rangle$). Energy rapidly localizes to excite Mn^{2+} within the QD ($|\text{QD}, {}^4\text{T}_1\rangle$), which then emits with a high quantum yield. Radiative processes are indicated as straight lines and nonradiative processes as wavy lines. (C) TEM image of representative Mn^{2+} -doped ZnSe/ZnS QDs. (D) Absorbance and photoluminescence spectra of Mn^{2+} -ZnSe/ZnS QDs in an LSC device. (E) A device seen under UV illumination.

a ${}^6\text{A}_1$ ground state and show luminescence associated with a ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ $d-d$ transition at an energy of ~ 2.1 eV (Figure 2A).²⁹ This Mn^{2+} luminescence is efficiently sensitized by the host ZnSe nanocrystal (Figure 2B). The luminescence sensitization scheme active in our colloidal Mn^{2+} -doped ZnSe nanocrystals is very similar to that of bulk Mn^{2+} -doped ZnSe, but the colloids show greater sensitization efficiencies because of longer excitonic lifetimes and faster energy transfer. At room temperature, the rate of energy transfer from the photoexcited nanocrystal to Mn^{2+} (\sim ps) greatly exceeds that of exciton recombination (\sim ns),^{40,41} making quantitative energy capture by Mn^{2+} possible. The excited Mn^{2+} then relaxes to its ground state with a high room-temperature LQY. The corresponding ${}^6\text{A}_1 \rightarrow {}^4\text{T}_1$ absorption transition is spin-forbidden, with a maximum extinction coefficient of only $\sim 1 \text{ M}^{-1} \text{ cm}^{-1}$, about 5 orders of magnitude smaller than that of the host nanocrystal. This difference in absorptivity yields a large effective Stokes shift of as much as ~ 1 eV, precluding self-absorption of Mn^{2+} emission and thereby overcoming a key challenge in LSC phosphor design. Although the long (\sim ms) lifetime of the ${}^4\text{T}_1$ excited state can lead to luminescence quenching *via* a multiphoton process,^{41,42} the threshold photon flux for this effect greatly exceeds solar irradiance.⁵⁷

Mn^{2+} -doped ZnSe/ZnS nanocrystals (Figure 2C) were synthesized by methods adapted from those described previously^{41,43,44} and incorporated into polymer films by dispersing a toluene suspension of nanocrystals into a mixture of laurylmethacrylate, trioctyl phosphine, and ethylene glycol dimethacrylate, containing a photoinitiator (Methods). Devices were

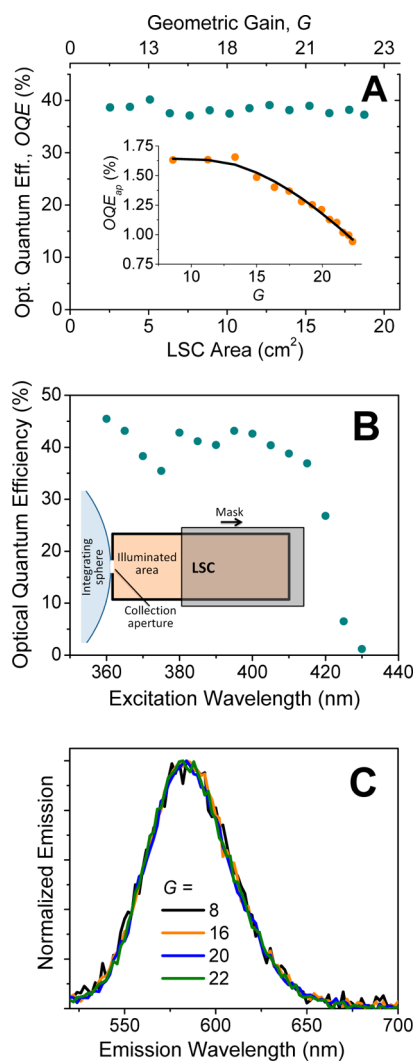


Figure 3. (A) The dependence of optical quantum efficiency on doped-nanocrystal LSC area and geometric gain for full perimeter, index-matched collection (OQE), and as measured through the collection aperture (OQE_{ap}, inset). Solid line results from fitting the model described in the text and SI. (B) Dependence of the OQE on excitation wavelength. OQE is independent of excitation wavelength above the bandgap. Inset: A monochromatic excitation source positioned above the device provides uniform light over the unmasked area, with edge-emitted light collected through an aperture into an integrating sphere. (C) Normalized edge emission spectra. (A) and (C) were obtained by excitation at 400 nm.

largely transparent to visible light (Figure 2E), with an optical density up to 0.30 at the first exciton absorption maximum, depending on the concentration of doped QDs used. Despite this transparency, waveguided luminescence is still clearly visible by eye when exposed to diffuse sunlight on a cloudy day (see Supporting Information (SI)). Overall concentrator dimensions were $25 \times 75 \times 0.42$ mm, corresponding to a geometric gain, defined as the ratio of facial to edge area, $G = 22$.

LSC absorbance and facial emission spectra are shown in Figure 2D. The peak exciton absorption occurs at 396 nm and is size-tunable over the range 350–450 nm for this composition. The small

absorption tail extending from the band edge is likely caused by scattering. With above-bandgap excitation (400 nm), luminescence is dominated by the $\text{Mn}^{2+} \text{}^4\text{T}_1 \rightarrow \text{}^6\text{A}_1$ transition centered at 582 nm. A second broad emission feature is observed at ~ 435 nm that can be attributed to weak fluorescence from the waveguide polymer. This feature was also present in control devices containing no doped QDs, and it was not present in the toluene suspension of doped QDs.

Unlike other concentrator designs, wavelengths not collected by an LSC are transmitted and hence available for use by a secondary process, such as for interior lighting. Accordingly, LSC performance is expressed in terms of the fraction of solar photons harvested by the concentrator, or optical quantum efficiency (OQE), defined as the fraction of absorbed photons concentrated at device edges. OQE was measured as a function of geometric gain under uniform diffuse illumination by collecting edge-emitted light through an aperture into an integrating sphere connected to a fluorometer. The remaining device perimeter was blackened with ink to eliminate reflections. Successively larger illuminated areas were measured using a movable mask (inset, Figure 3B) and the full perimeter OQE was computed, correcting for the finite size of the edge collection aperture and reflection losses at the aperture arising from the use of a non-index-matched detector (for details, see SI). Figure 3A shows the results of these measurements under illumination near the first excitonic absorption peak (400 nm). OQE_{ap} , shown in the inset, is the non-index-matched collection efficiency through the

small measurement aperture; the main figure shows the full perimeter OQE for an index-matched detector. The difference in curvature between the two plots stems from the decreasing solid angle occupied by the aperture as G increases. At $G = 22$, corresponding to full area illumination, $\text{OQE} = 37\%$, with efficiency being independent of excitation energy above the bandgap (Figure 3B). As shown in Figure 3C, the spectral distribution of edge-emitted light shows negligible variation with increasing G , contrasting with the behavior of previously studied LSC luminophores where self-absorption produces a strong bathochromic shift in edge-emitted light with increasing G .⁴⁵ This result highlights the lack of self-absorption in doped nanocrystal LSCs.

In the absence of self-absorption, the relationship between OQE, luminophore LQY, and waveguide propagation and escape cone losses is

$$\text{OQE} = \text{LQY} \epsilon_{\text{ec}} \epsilon_{\text{wg}}(G) \quad (1)$$

where the escape cone loss term is given by Snell's Law, $\epsilon_{\text{ec}} = 1 - (1 - 1/n^2)^{1/2} \approx 0.75$, based on isotropic emission, and a waveguide refractive index $n = 1.5$. $\epsilon_{\text{wg}}(G)$ represents losses due to waveguide scattering and absorption, whose combined effects are expressed through a waveguide attenuation coefficient α_{dB} , defined such that the fraction of photons lost per unit distance l is $e^{-4.34l\alpha_{\text{dB}}}$.⁴⁶ Given ϵ_{ec} , eq 1 allows determination of the other two loss mechanisms in an LSC, LQY and waveguide losses, from measurements of OQE vs G . For a uniformly illuminated rectangular LSC measuring $L \times W$, the proportion of emitted light surviving to reach an edge, subject to waveguide losses, is

$$\epsilon_{\text{wg}}(G) = \frac{1}{4\pi WL} \int_0^W \int_0^L \int_0^{2\pi} 2 \int_{\theta_{\text{ec}}}^{\pi/2} e^{-4.34\alpha_{\text{dB}}l(x,y,\theta,\varphi)} \sin\theta \, d\theta \, d\varphi \, dy \, dx \quad (2)$$

where $\theta_{\text{ec}} = \sin^{-1}(1/n)$ is the escape cone angle, and $l(x, y, \theta, \varphi)$ is the distance a photon travels to the edge when emitted from (x, y) with directional spherical coordinates (θ, φ) . Combining eqs 1 and 2 and solving numerically, we fit the measured $\text{OQE}_{\text{ap}}(G)$ (inset Figure 3A) to find $\text{LQY} = 53\%$ and $\alpha_{\text{dB}} = 0.085$ dB/cm (see SI for details). For the sample in Figure 3, the doped QD LQY measured in toluene was 50%, close to the fitted value. This result indicates that the doped QD LQY is preserved upon incorporation into the polymer device.

The flux gain,

$$F \approx \text{CR}(\eta_{\text{PV}}^{\text{em}} / \eta_{\text{PV}}^{\text{AM1.5}}) \quad (3)$$

is the power produced from edge-attached photovoltaic cells relative to that produced from the same photovoltaic cells under direct AM1.5 exposure. Here $\eta_{\text{PV}}^{\text{em}}$ and $\eta_{\text{PV}}^{\text{AM1.5}}$ are the photovoltaic conversion

efficiencies at the peak LSC emission energy and under broadband AM1.5 illumination, respectively, and the energy concentration ratio $\text{CR} = \text{OQE} \times GN_{\text{abs}}e_{\text{em}}$, where N_{abs} is the number of solar photons absorbed by the LSC per unit area per second, found by integrating the AM1.5 solar spectrum over the doped QD absorption range (300–420 nm, Figure 3B), and $e_{\text{em}} = 2.12$ eV is the energy per luminescent photon. Figure 4 shows the size-dependent energy concentration ratio for a square LSC based on the LQY and α_{dB} for the experimental device in Figure 3, as well as the flux gain predicted for attached a-Si photovoltaic cells (see SI for details). The maximum concentration ratio and power density enhancement are projected to reach $\text{CR}_{\text{max}} = 6\times$ and $F_{\text{max}} = 15.6\times$ in the large- G limit, among the highest yet reported.^{20,23,47–49} Projected maximum flux gains for other benchmark photovoltaic technologies are given in Table S1 (SI); several

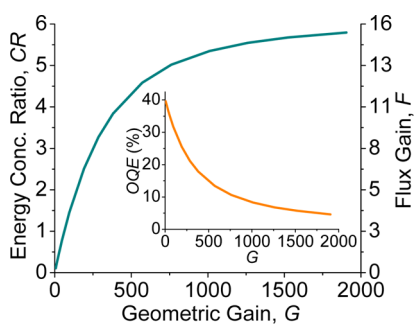


Figure 4. Predicted energy concentration ratio and flux gain for a-Si PVs as a function of geometric gain for square Mn^{2+} -doped ZnSe/ZnS nanocrystal LSCs ($\alpha_{\text{dB}} = 0.085$ dB/cm, LQY = 0.53). F and CR asymptotically approach $15.6\times$ and $6\times$ in the large area limit, respectively. Inset: optical quantum efficiency becomes limited by parasitic waveguide losses at large G . For our device thickness, $G = 2000$ corresponds to an LSC edge length of 3.36 m. See SI for details.

exceed $10\times$. These findings demonstrate the potential to achieve substantial reductions in photovoltaic area through optical concentration using doped nanocrystal LSCs. CR_{max} and F_{max} in doped QD LSCs are limited by parasitic waveguide losses (α_{dB}), which become the dominant loss mechanism for large G (inset, Figure 4). Such losses affect all LSCs, but heretofore have generally been negligible compared to self-absorption related losses. This result suggests that significant further improvements in large-area doped QD concentrator performance should be possible using more transparent polymer waveguide materials, for example, optical polysiloxanes or cyclic perfluoropolymers, which have intrinsic attenuation coefficients 1–3 orders of magnitude lower than polyacrylates at visible and near-IR wavelengths.^{50,51} Importantly, the fact that competitive F_{max} values can be achieved by pairing Si photovoltaics with a phosphor that absorbs little of the solar spectrum illustrates the pivotal importance of eliminating reabsorption losses.

CONCLUSIONS

In summary, colloidal doped nanocrystals are demonstrated as a promising new class of zero-reabsorption luminophores for LSC applications. Using Mn^{2+} -doped ZnSe/ZnS nanocrystals as the active phosphor material, concentrating polymer films capable of selectively absorbing solar UV light and producing intensified emission with optical quantum efficiencies approaching 40% have been demonstrated. These concentrators are largely transparent to visible light, making them attractive for application as transparent window coatings or in multijunction concentrator/PV configurations. As the first report of this approach, we anticipate further major improvements in LSC efficiencies using doped semiconductor nanocrystals. For the Mn^{2+} -doped ZnSe/ZnS-based LSCs described here, the nanocrystal LQYs can be increased by optimizing QD surface

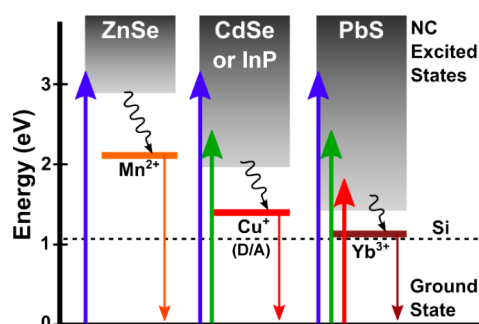


Figure 5. Potential dopant/semiconductor materials combinations for doped-nanocrystal-based LSCs. Cu^+ -doped CdSe or InP nanocrystals show donor/acceptor recombination luminescence that is red-shifted from the semiconductor absorption edge. Yb^{3+} -doped PbS is anticipated to show sharp sensitized Yb^{3+} f - f luminescence. These and related doped nanocrystals would improve LSC performance by harvesting a broader portion of the solar spectrum and providing better luminescence matching with Si photovoltaics, while retaining the small reabsorption losses displayed by Mn^{2+} -doped ZnSe nanocrystals.

passivation, and the energy gap can be narrowed by alloying with a small amount of Cd^{2+} . Waveguide losses, currently the limiting factor in our devices, can be reduced by improved processing and use of more transparent polymers. As such, the Mn^{2+} -doped nanocrystal LSCs described here hold promise for practical window-layer applications where transparency is desired. Restricting absorption to UV wavelengths limits the collectable fraction of sunlight to less than 10% of total irradiance, so transparent concentrators based on these materials would produce less power per unit area than many conventional PV panels. More generally, even higher LSC limiting efficiencies, concentration ratios, and flux gains can be expected from the use of related doped nanocrystals that absorb and emit at lower energies.

Although it is not yet clear which doped nanocrystals will perform best in aggregate, two specific targets are proposed on the basis of their anticipated absorption and luminescence properties (Figure 5). First, replacing ZnSe with CdSe or InP would allow extension of the nanocrystal absorption down to as low as the ~ 1.3 eV InP bulk bandgap (~ 950 nm). Doping semiconductor nanocrystals with Cu^+ typically gives rise to donor–acceptor luminescence whose maximum is shifted by ~ 0.5 eV from the first absorption maximum, with little reabsorption. Both Cu^+ -doped CdSe and Cu^+ -doped InP nanocrystals have been synthesized previously,^{52,53} but they have not yet been thoroughly explored, and in particular they have not yet been examined as phosphors for LSCs. Even further improvement could be achieved by doping PbS nanocrystals with Yb^{3+} ions, which should show sharp f - f luminescence centered at ~ 1.2 eV (~ 1000 nm), well matched with the Si energy gap. Yb^{3+} -doped PbS nanocrystals of appropriate diameter could absorb near this energy, again with negligible reabsorption

losses. Colloidal Yb³⁺-doped PbS nanocrystals have not been made, and in fact represent a major synthetic challenge,^{54–56} but the experimental LSC results

presented here indicate they are worthy targets. Efforts to develop these and related doped nanocrystals for application in LSCs are presently underway.

METHODS

Doped QD Synthesis. Mn²⁺-doped ZnSe core nanocrystals were prepared by lyothermal degradation of [Zn₄(SePh)₁₀](Me₄N)₂ in the presence of MnCl₂. ZnS shells were grown by successive ionic layer adsorption and reaction (SILAR) deposition from Zn(oleate)₂ and tri-*n*-octyl phosphine sulfide (TOP-S). In a typical synthesis, 200 mg of [Zn₄(SePh)₁₀](Me₄N)₂ and 10 mg of Se were added anaerobically to a degassed mixture of 5.4 g of hexadecylamine and 5 mg of MnCl₂ in a three-necked round-bottom flask, and the temperature was raised to 275 °C. After 20–60 min at 275 °C, the mixture was cooled and nanocrystals precipitated by addition of ethanol. The nanocrystals were then resuspended in toluene, where they were purified by repeated precipitation with ethanol, isolation by centrifuging, and resuspension in toluene. Following purification, ZnS shells were grown by alternating slow addition of approximately monolayer equivalents of Zn(oleate)₂ and TOP-S to a degassed mixture containing the isolated nanocrystals, 1.5 g of oleylamine, and 1.5 g of octadecene, held at 225 °C. Each addition was allowed to react for 30 min before the subsequent addition. After shell growth, the mixture was cooled and purified in the same manner as described above. Electronic absorption spectra of toluene suspensions were collected using a Cary 500 spectrometer. Photoluminescence spectra were collected using 405 nm excitation and an Ocean Optics USB2000 spectrometer for detection. Transmission electron microscopy (TEM) images were collected using a FEI Tecnai G2 F20.

Device Fabrication. Nanocrystals were incorporated into polymer films by dispersing a toluene suspension into a 5:1:1 by weight mixture of laurylmethacrylate, trioctyl phosphine, and ethylene glycol dimethacrylate, containing <1 wt % of Irgacure 651 photoinitiator (CIBA). Several droplets of the resulting mixture were placed onto a clean borosilicate glass coverslip, which was then covered by a second coverslip, and the resulting glass/solution/glass samples were photopolymerized with UV light under nitrogen for 1–3 h to form a solid film with a thickness of approximately 100 μm. Except at the collection aperture, all device edges were blackened with a marker.

Device Characterization. Absorbance measurements were performed with a Jasco UV–vis spectrophotometer. Edge emission measurements were performed using a Horiba Fluorolog model FL3-21 fluorometer connected via fiber optic cable to an integrating sphere. Further details are provided in the text and SI.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Derivation of the computation of full-perimeter OQE from measurements over a small aperture, projected maximum flux gains for benchmark photovoltaic technologies, photograph of a doped QD LSC in sunlight. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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