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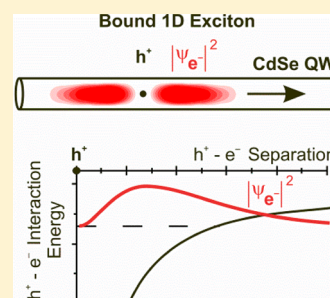
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S Supporting Information

ABSTRACT: Photogenerated electron–hole pairs are observed to be bound as 1D excitons in CdSe quantum wires (QWs) at room temperature. Microscopy experiments performed on dilute samples of CdSe QWs prepared on coverslips with patterned electrodes reveal that there is no change in either the overall photoluminescence (PL) intensity or the distribution of the PL intensity with the application of an external electric field. Changes in the PL intensity, and thus evidence for separate charge carriers within the QWs, are observed only for concentrated samples. In these concentrated samples, a thin film of other compounds, including trioctylphosphine oxide and a bismuth salt formed in the synthesis, is observed to encompass the QWs. The separate charge carriers that influence the PL intensity are attributed to the other compounds in the sample.

SECTION: Physical Processes in Nanomaterials and Nanostructures



Semiconductor quantum wires (QWs) have significant potential for practical applications due to their ease of synthesis,^{1–6} tunable band gap energies,^{2,7} large absorption cross sections, up to nearly 10× bigger per unit volume in comparison with quantum dots (QDs),^{8,9} and 1D shape that should permit efficient charge transport. With average lengths that can be on the order of tens of micrometers,^{2,3} these nanomaterials have nearly the same dimensionality as the absorbing medium in most photovoltaic and optoelectronic devices.¹⁰ Even with low photoluminescence (PL) quantum yields (Φ_{PL}), typically <0.2% for low excitation power densities,¹¹ which indicate poor overall physical and chemical properties and the presence of a high density of charge-trap sites, QWs have already been incorporated in electronic and photovoltaic devices to increase efficiencies.^{12–14} The dynamics of charge carriers in semiconductor QWs will ultimately dictate their utility.

The charge-carrier dynamics in QWs are quite sensitive to the surface of a QW, as incomplete surface passivation and varying chemical coverage can result in variations in the potential-energy landscape along the length of the QW.^{15–17} Evidence of this irregular landscape was observed in PL images of single CdSe QWs recorded at low temperatures, as the emission was preferentially observed at localized positions along the individual QWs.¹⁵ The synchronous PL intensity blinking spanning entire lengths of single QWs¹⁸ was also explained through the dynamic filling and emptying of carrier trap sites with time.¹⁹ These potential minima also give rise to increasing Φ_{PL} values with higher excitation power densities.^{11,18,19} The proposed mechanism here is that at lower power densities a large fraction of the photogenerated excitons and charge carriers becomes trapped in unoccupied trap sites. With increasing excitation fluence, a higher fraction of the trap

sites becomes filled, and additional photogenerated excitons are not under the influence of the trap sites. Even with these higher exciton densities and rates for Auger recombination, multiparticle relaxation does not effectively compete with radiative relaxation.²⁰ These charge–charge interactions depend on the dimensionality of nanostructures and will most likely dictate the utility of semiconductor QWs in devices.^{20–22}

Even at lower excitation power densities, the charge-carrier dynamics are influenced by electron–hole interactions. Following the absorption of a photon with an energy greater than the band gap of the QW, the photogenerated electron in the conduction band and the associated hole in the valence band interact through Coulombic forces and can be stabilized as a bound Wannier–Mott 1D exciton that may efficiently diffuse along the length of the QW as a boson with no net electron spin.^{23,24} This is in contrast with QDs, where the electron and hole are forced to occupy the same volume, the confinement energies are larger than the Coulombic interactions, and the electron–hole pairs behave as independent, uncorrelated particles.^{22,25} Nor do excitons tend to be bound in quantum wells at room temperature because the electron–hole binding energies are much lower with quantum confinement in only one dimension.²⁶

The wave functions used to define idealistic quantum-mechanical 1D excitons in QWs can be generically written as: $\Psi(x_e, y_e, x_h, y_h, z) = \Psi_e(x_e, y_e) \Psi_h(x_h, y_h) \phi(z) e^{\pm ik_z z}$.²⁷ The wave function includes components that make up the electron and hole wave functions in the radial dimensions, $\Psi_e(x_e, y_e)$ and $\Psi_h(x_h, y_h)$, the hydrogen-atom-like electron and hole inter-

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actions as a function of separation between them along the length of the QW, $\phi(z)$, and the motion of the bound 1D exciton along the length of the QW, $e^{\pm ikz}$.^{27–29} The small diameters of QWs give rise to quantum-confinement effects of the radial wave functions and increasing band gap energies with decreasing diameter. The dimensionality also gives rise to enhanced electron–hole interactions due to dielectric confinement associated with the lower dielectric constant of the surrounding medium in comparison with that of the semiconductor. Calculations of electron–hole binding energies as large as 257 meV have been predicted for 4.0 nm diameter CdSe QWs embedded in a chrysotile asbestos insulator.³⁰ Even for core-only CdSe quantum rods (QRs) binding energies for ground-state excitons have been calculated to be >150 meV.²³

There are conflicting results in the literature, however, regarding experimental evidence of the existence of bound 1D excitons in CdSe QWs at room temperature. First, for high Φ_{PL} values to be achieved, values higher than 20%,^{11,18} it is unlikely that separate charge carriers are formed with excitation above the band gap; the propensity for geminate radiative recombination would be low for separate charge carriers, and nonradiative Auger rates that compete with radiative recombination would become high with increasing charge-carrier density. Second, the observation of synchronous PL intensity blinking spanning entire CdSe QWs¹⁸ suggests that once nonradiative trap sites are filled, a more ideal QW is achieved, and the 1D nature of excitons is observed as evidenced by nearly equal PL intensity along the length of the entire QW.

Contradicting these conclusions are the results of Schäfer et al.,³¹ who performed simultaneous electrostatic force microscopy (EFM) and optical microscopy to measure charging in individual CdSe QWs. They found that localized irradiation near one end of a QW gives rise to separate charge carriers with a preference for accumulation of positive charge near the excitation region and the diffusion of negative charges to the opposite end of the QW. Additional results from the Mews group,³² however, suggest that there is no charging with continuous irradiation. Specifically, they found that individual CdSe QWs remained neutral after a photoenhancing period. More recently, the Mews group reported that charge separation does occur at CdSe/CdTe junctions in single heteronano-wires.³³

Protasenko et al.³⁴ reported that the PL intensity along the length of single CdSe QWs with diameters between 5 and 12 nm could be altered with the application of an external electric field. In that work, they found that the total PL intensity of a single QW increased and that the spatial distribution of the PL intensity changed with the application of an external electric field; the PL intensity increased at the end of a QW closest to the positive electrode and decreased at the opposite end. The strength of the electric field was varied from 0 to 33 kV/cm in these experiments, and the PL-intensity enhancement and steering were always observed. The authors concluded that the PL intensity changes were due to the motion of separate charge carriers induced by the electric field and varying charge-carrier relaxation dynamics that resulted. The observations also suggested that under most conditions the mobile charge carriers were electrons and that some were permanent within the QWs and others were photogenerated. Under most conditions, there was no evidence of mobile photogenerated holes within the QWs.

The Mews group discovered a correlation between the charge on a QW and the measured PL intensity.³² They

measured a quenching of the PL intensity detected from a single CdSe QW immediately after injection of positive charge carriers into the QW using an EFM tip. In contrast, an enhancement in the PL intensity was observed with the addition of a small number of electrons. These trends are fully consistent with the findings in the electric-field measurements of Protasenko et al.,³⁴ where enhancements of the PL intensity were observed at the ends of QWs with excess electrons and decreases were measured at the other ends.

It is not clear, however, what is the source of the separate charge carriers on the QWs in the experiments of Protasenko et al.³⁴ Spectroscopic evidence from the Kuno group suggests that excitons should be bound at room temperature in CdSe QWs with diameters as large as 10 nm.⁹ They found that it was necessary to include an exciton-binding energy when fitting extinction spectra of single CdSe QWs. They concluded that the exciton-binding energies range from 100 to 300 meV, increasing with decreasing QW diameter. Furthermore, the electric-field strengths used by Protasenko et al.³⁴ should not be sufficient to dissociate the electron–hole pairs.^{35,36}

In this letter, we present results from single-QW PL microscopy measurements performed in a similar manner as reported by the Kuno group.³⁴ Two sets of experiments are performed, one with the QWs highly diluted in toluene (*dil*-QWs) and the other with more concentrated samples (*conc*-QWs) that have a significant concentration of other compounds, including trioctylphosphine oxide (TOPO), reagents used in the synthesis, and species formed during the synthesis. The CdSe QWs used in these studies have diameters of ~ 7 nm and typical lengths of 7–10 μm . It is possible that the optical measurements were performed on bundles of QWs, but the AFM data suggest that there are usually single QWs prepared on the coverslip, especially for the dilute-QW samples. The findings indicate there are no, or at least no detectable, separate charge carriers, permanent or photogenerated, in the CdSe QWs. Steering of the PL intensity along a single QW, and thus evidence of separate charge carriers, is observed only in the *conc*-QW samples for which the QWs are found to be embedded within a thin film.

The PL-intensity images of a single CdSe QW (diameter ~ 7 nm) prepared from a *dil*-QW sample are included in Figure 1 for no applied electric field (a) with the electric-field vector oriented up (b) and down (c). The applied average electric field (3.2 kV/cm with a 0.2 Hz square-wave) is plotted in Figure 1d, and the images in panels b and c were obtained at times with electric-field vectors pointing up and down, respectively. The temporal dependence of the PL intensity integrated over the entire QW is shown in Figure 1e. The data recorded over the first five seconds shown were collected with no electric field to provide measures of the baseline PL intensity level and the magnitude of the PL intensity fluctuations. There is no noticeable change in the total integrated PL intensity of the entire QW or correlation of the PL intensity with the varying direction of the field with time after turning on the electric field. Instead, the PL remains fairly constant with small fluctuations, as are often observed for CdSe QWs.³⁷

To monitor possible steering of the PL intensity along the CdSe QW with electric field direction, we show the integrated intensities of the bottom third (blue) and top third (red) of the QW in Figure 1f. The PL intensity profile along the QW does not noticeably change with the application of the external electric field. No PL-intensity steering was observed using

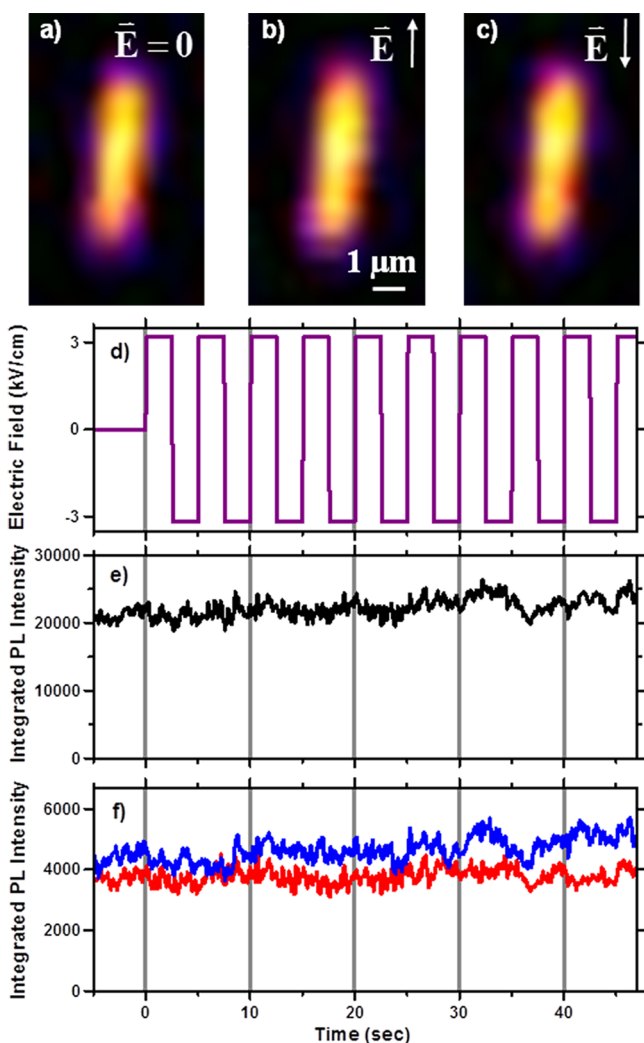


Figure 1. PL intensity data of a single ~ 7 nm diameter CdSe QW prepared from a *dil*-QW sample obtained with a power density of ~ 100 W/cm 2 . Wide-field PL microscopy images of a single QW with no electric field, with the electric-field vector pointing up, and with the electric-field vector pointing down are shown in panels a–c, respectively. The average electric field applied, a 0.2 Hz square-wave with a magnitude of 3.2 kV/cm, is plotted in panel d. The integrated PL intensity of the entire QW is shown in panel e, whereas the integrated PL intensity for the top (red) and bottom (blue) region of the QW is shown in panel f.

excitation power densities ranging from 5 to 500 W/cm 2 . The power densities were typically kept on the lower end of this power range to avoid the observation of PL-intensity blinking along the QW that would complicate the monitoring of any PL changes induced by the electric field. These and similar data recorded on many other QWs prepared from three different *dil*-QW samples indicate that there are no detectable separate charge carriers, either initially existing or photogenerated within the CdSe QWs. These results contradict those of Protasenko et al.³⁴

Similar microscopy experiments were performed on *conc*-QW samples to investigate if other compounds within the samples may influence the PL intensity behavior with the electric field applied. Steering of the PL intensity is usually observed for the *conc*-QW samples, and the results obtained are similar to those previously reported by Protasenko et al.³⁴ The PL intensity images of a single QW from a *conc*-QW sample are

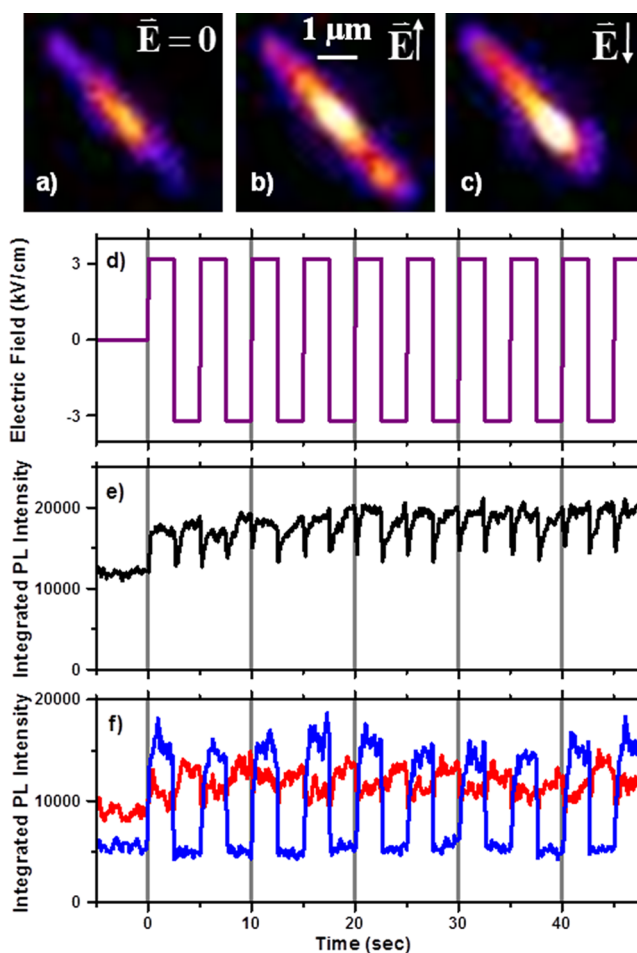


Figure 2. PL intensity data of a single ~ 7 nm diameter CdSe QW prepared from a *conc*-QW sample obtained with a power density of ~ 100 W/cm 2 . Wide-field PL microscopy images of a single QW with no electric field, with the electric-field vector pointing up, and with the electric-field vector pointing down are shown in panels a–c, respectively. The average electric field applied as a function of time is plotted in panel d. The integrated PL intensity of the entire QW is shown in panel e, whereas the integrated PL intensity for the top (red) and bottom (blue) region of the QW is shown in panel f.

included in Figure 2a–c for no external electric field applied, for the electric-field vector pointing up and down, respectively. There is an overall increase in the PL intensity of the entire QW observed with the application of an external electric field, 0.2 Hz square-wave with a magnitude of 3.2 kV/cm. Note, that this increase in PL intensity is nearly the same with no dependence on field direction, Figure 2e. As the electric-field vector changes direction, the PL intensity quickly returns to the baseline intensity and then grows back to the enhanced value. With the electric field on, the PL intensity increases at the end of the QW closest to the positive electrode, Figure 2f. The changes induced by the electric field are more clearly observed at the bottom of this specific QW, but the trends are the same at both ends. This emission steering continued until the electric field was turned off, at which point the PL intensity redistributed itself along the entire QW, and the intensity distribution returned to approximately the same as was observed prior to the application of the electric field. Most of the QWs from *conc*-QW samples exhibit similar behavior. Nearly the same trends and changes in the PL intensity were observed for electric-field strengths in the range of 0.5 to 3.2

kV/cm. It seems improbable that the electric fields incorporated in our studies are sufficiently strong to dissociate the bound electron–hole pairs into separate charge carriers. Further evidence of this conclusion may be gleaned from PL spectra of the individual CdSe QWs.

In spectroscopic investigations of GaAs/AlGaAs quantum wells, Miller et al.³⁵ reported shifts in the first exciton peak to lower energy with increasing strength of an externally applied electric field when approaching the exciton-binding energy and dissociation of the electron–hole pairs. Field strengths of $\sim 10^2$ kV/cm were needed to observe spectral shifts of the first-exciton feature and thus dissociate excitons in GaAs/AlGaAs quantum wells for which the electron–hole binding energies are ~ 10 meV.³⁵

We recorded PL spectra in the presence of external electric fields to determine if the field strengths utilized were sufficient to generate shifts of the band gap emission to lower energies that would be indicative of the dissociation of the 1D excitons in ~ 7 nm CdSe QWs. No changes were observed in the PL spectra recorded from individual CdSe QWs from *dil*-QW samples, Figure S3c in the Supporting Information. Only slight changes in the PL spectra were observed for QWs from the *conc*-QW samples. The PL spectra acquired with and without the 3.2 kV/cm electric field across single QWs from a *conc*-QW sample (Figure S3a,b in the Supporting Information) are very similar with the same peak energy. The overall spectral intensity is slightly higher with the electric field on, as suggested by the data in Figure 2. There is a small increase in the PL intensity on the high-energy side of the PL feature with the electric field present in comparison with the spectrum without the electric field, as was previously reported for CdSe QWs.³⁴ The lack of a spectral shift to lower energy of the PL spectra induced by the electric field further suggests that the observed steering of the PL intensity for the *conc*-QW samples is not a result of producing separate charge carriers through dissociation of 1D excitons.

Alternatively, we propose that the electric field induces an interaction with the environment of the QW, which results in the accumulation of mobile charge carriers in the QWs and the observed PL-intensity changes and steering trends in the *conc*-QW samples. This is consistent with the CdSe QW experiments of Schäfer et al.,³² where increases (decreases) in PL intensity were observed with the injection of negative (positive) charges. In addition, Rothenberg et al.³⁸ observed reversible electric-field-induced on/off switching of the emission collected from single CdSe QRs. In that study, the PL intensity from some of the QRs switched off with an external electric field, whereas the PL from other QRs switched on with the application of an electric field. This unpredictable switching behavior was attributed to differences in the specific local-field conditions of each of the CdSe QRs.³⁸ Many factors may dictate the affects of local fields on specific QRs or QWs within a sample as well as along single QWs, including solvents used, surface defects on the nanostructure, surface ligands and coverage, and interactions with the coverslip.

Inspection of the *conc*-QW samples prepared on coverslips reveals an opaque film that is associated with regions containing the QW sample. Weak PL with a maximum in the PL spectrum near 2.30 eV (532 nm) is often observed in these spatial regions. This emission quickly bleaches with irradiation time and is not attributed to emission from CdSe QWs or nanoparticles. Similar spectral signals are also observed for CdSe QWs suspended predominantly in TOPO, but this

emission is more resilient to bleaching, Figure S4 in Supporting Information.

Separate PL spectroscopy measurements performed on combinations of the multiple reagents used in the synthesis of the CdSe QWs and possible byproducts that could be formed during the synthesis indicate that a Bi^{3+} -containing compound is most likely associated with this emission. A brief summary of these results is included in the Supporting Information. Acids, such as tetradecylphosphonic acid (TDPA), oleic acid (OA), and dioctylphosphinic acid (DOPA) used in the SLS synthesis of the CdSe QWs, can form coordinating polymers with metal ions, and the presence of TOPO and TOP may offer additional complexity to the compounds remaining in the samples as they may influence the PL intensity and dynamics of charge carriers within or on the CdSe QWs.

Atomic force microscopy (AFM) experiments also identified the presence of a film spanning the *conc*-QW samples prepared on coverslips. The CdSe QWs in the *conc*-QW samples are covered by an unevenly distributed film, and most of the QWs observed optically are not even discernible in the AFM image. An AFM image obtained for a *conc*-QW sample spin-cast on a coverslip is included in Figure 3b. Only a few QWs project

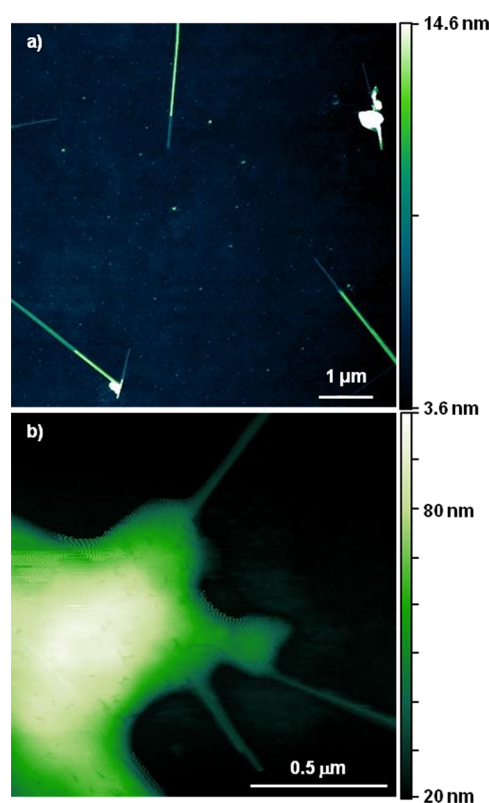


Figure 3. AFM images of ~ 7 nm diameter CdSe QWs prepared from a *dil*-QW (a) and a *conc*-QW (b) spin-cast onto coverslips. The color scales used for height are different for the two panels and are shown on the right of each image.

from the film, but even the protruding QWs are encased in a coating, as indicated by diameters that are significantly larger than observed in TEM images acquired for the same sample. In contrast, the AFM images of the *dil*-QW samples, Figure 3a, contain a low density of uncoated, single QWs with diameters commensurate with those measured using TEM. Once again,

PL-intensity changes and steering are observed only for QWs embedded in the film. We propose the separate charge carriers present in or on individual CdSe QWs that give rise to the changing PL intensity levels detected with the application of an external electric originate from compounds, including the bismuth salt, that are present within the film.

From the results presented in this letter, we draw the following conclusions. First, CdSe QWs are not permanently charged, they are neutral. This conclusion is drawn from the observation that for isolated QWs there is no detectable change in the overall PL intensity of the QW or the spatial distribution of the PL intensity along the length of the QW with the application of an external electric field. Second, because there is no change in the PL intensity or steering behavior with continued irradiation of dilute CdSe QW samples, separate charge carriers are not photogenerated within the QWs. PL-intensity steering induced by an electric field is observed only for QWs within concentrated samples that contain other compounds, including Bi salts, presumably $\text{Bi}^{3+}(\text{TOP})_n(\text{TOPO})_m$, which can inject separate charge carriers into the QWs. Third, the lack of PL-intensity steering for the *dil*-QW samples indicates that following the absorption of a photon with energy significantly greater than the band gap, 1D excitons are formed that may radiatively recombine, even at room temperature. This suggests that the electron–hole binding energy in these CdSe QWs is at least 26 meV. Experiments aimed at characterizing the delocalization of these 1D excitons along the length of single CdSe QWs are ongoing and will be published in due course.

■ EXPERIMENTAL SECTION

CdSe QWs were synthesized using an adapted SLS-synthetic method,^{1–5} which is described in the Supporting Information. The average diameter of the CdSe QWs was ~ 7 nm on the basis of high-resolution, transmission electron microscopy images. The *dil*-QW samples are obtained by diluting the *conc*-QW samples by 10–20 \times in toluene. The details of the microscopy and electric-field measurements are provided in the Supporting Information.

■ ASSOCIATED CONTENT

■ Supporting Information

Details of the CdSe-QW synthesis, sample preparation, PL spectra for a single CdSe QW obtained with the electric field on and off, PL spectra, and MALDI and mass spectrometry data identifying $\text{Bi}^{3+}(\text{TOP})_n(\text{TOPO})_m$ in the *conc*-QW samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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