Monitoring the Electric Field in CdSe Quantum Dots Under Ultrafast Interfacial Electron Transfer via Coherent Phonon Dynamics

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SI1. Synthesis of CdSe Nanocrystals. The synthesis of CdSe particles stabilized by trioctylphosphine oxide (TOPO) is described as follows (Nordell et al. 2005) with some modifications (Nadtochenko et al. 2017). A stock solution of Se precursor was prepared by combining 0.79 g of Se, 8.65 mL of 1-octadecene and 5.2 mL of trioctylphosphine in a 20-mL flask in an argon atmosphere with stirring with a magnetic stirrer under warming until Se was dissolved. Cd precursor was made by adding 0.128 g of CdO, 1.26 mL of oleic acid and 12.7 mL of octadecene to a 50-mL round-bottom flask at 230 °C with magnetic stirring in argon. TOPO 2.5 g and pentadecane 6 ml were consistently added to CdO solution. The solution of Se precursor was injected into the mixture at 230 °C with magnetic stirring in an argon atmosphere. Samples of 6 mL were taken from the reaction solution at a time interval of 2 min. The products were washed three times with ethanol, followed by centrifugation. Waxy precipitates were obtained which were redispersed in toluene.

SI2. Diameter (d) and extinction coefficient (ε) of sensitized CdSe QDs was estimated using wavelength of the first exciton at 579,02 nm ($E_{1Se-1S3/2}$ = 2.1416 eV). Diameter d was estimated according formulas: a) $d = 1.6122 \cdot 10^{-9} \cdot \lambda^4 - 2.6575 \cdot 10^{-6} \cdot \lambda^3 + 1.6242 \cdot 10^{-3} \cdot \lambda^2 - 0.4277 \cdot \lambda + 41.57 = 3.7869$ nm, $\varepsilon = 5857 \cdot d^{2.65} = 1.9958 \cdot 10^5$ (M cm)$^{-1}$ (Yu et al. 2003); b) $d1 = 59.60816 - 0.54736 \cdot \lambda + 1.8873 \cdot 10^{-3} \cdot \lambda^2 - 2.85743 \cdot 10^{-6} \cdot \lambda^3 + 1.62974 \cdot 10^{-9} \cdot \lambda^4 = 3.9077$ nm, $\varepsilon =$

$155507 + 6.67054 \cdot 10^{13} \cdot exp(-E_{1Se-1S3/2} / 0.10551) = 2.5758 \cdot 10^5$ (M cm)$^{-1}$ (Jasieniak et al. 2009). The average value of QDs diameter is 3.85±0.06 nm. The average value of QDs extinction coefficient is $\varepsilon(QD) = 2.28 \pm 0.29 \cdot 10^5$ (M·cm)$^{-1}$.
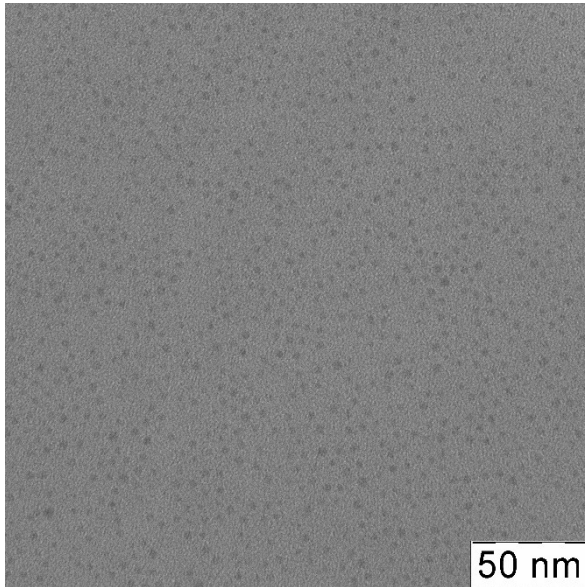
TEM image of CdSe NPs.

Polydispersity was estimated from the Gauss fit $A * exp\left[-\dfrac{(x-x_0)^2}{2\sigma^2} \right]$. The polydispersity is σ=±0.5 nm.

SI 3. Femtosecond Laser Photolysis Setup. The regenerative amplifier system (Spitfire, Spectra-Physics, USA) intensify the output of a Ti:sapphire oscillator (800 nm, 80 MHz, 80 fs, Tsunami, Spectra-Physics, Santa Clara, CA, USA). The femtosecond gauss pump pulse of 25 nJ, 25 fs centered at 600 nm was used to excite the CdSe QDs were dispersed in toluene:methanol = 95:5. The pump pulse operation frequency was 60 Hz. The sample in 300 μm cell was refreshed between incident laser pulses by a pump. Probe pulse was light of supercontinuum generated in H_2O cell by focused 800 nm femtosecond pulses. Transient spectra of absorbance changes ΔA (t, λ) were recorded over the range of 380–800 nm. The pump and probe light spots had the diameters of 300 and 120 μm, respectively. The relative polarization of pump and probe pulses was oriented at 54.7° (magic angle), parallel or perpendicular. The experiments were carried out

at 278 K. The measured spectra were corrected for group delay dispersion of the supercontinuum using the procedure described previously in (Shelaev et al. 2008; Nadtochenko et al. 2017). The time window of the "coherence spike" seen during the pump-probe overlap was neglected.
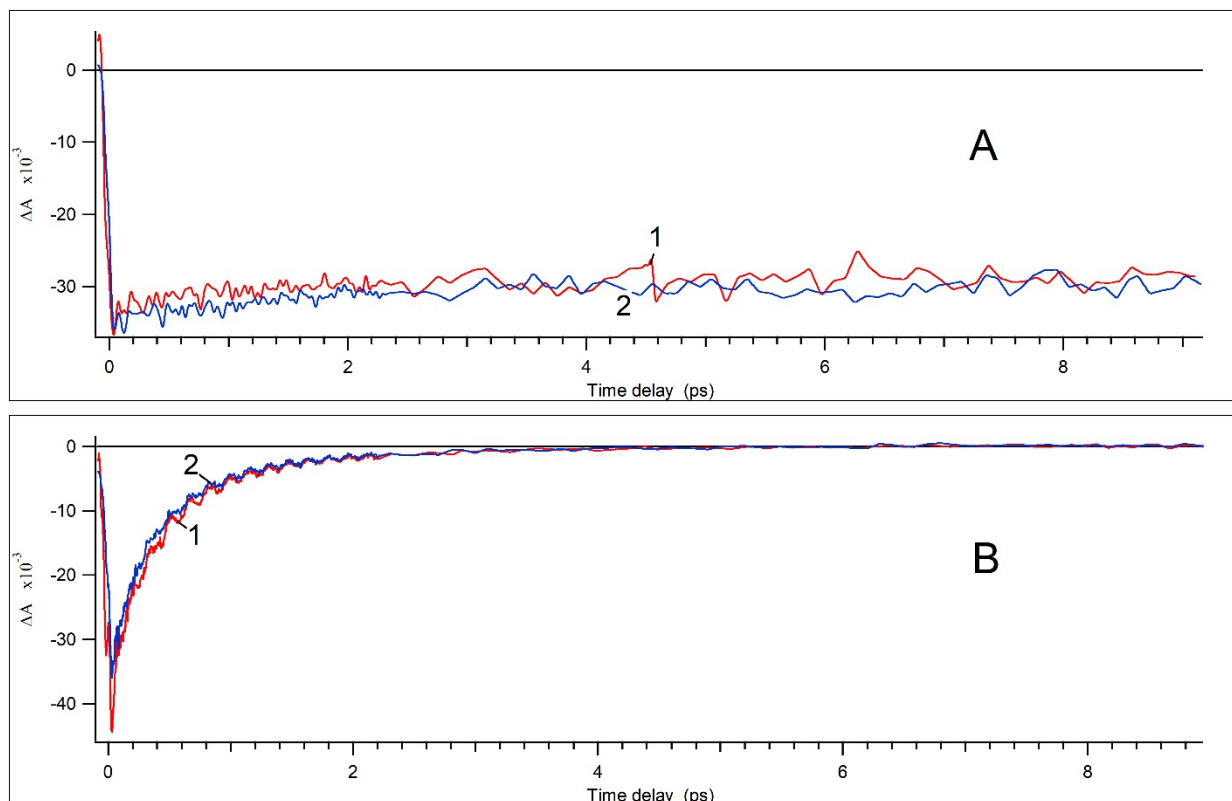

Fig. S1 Transients decay in pure CdSe (A) and CdSe/MV^{2+} (B) colloids. Red line 1 is parallel polarization. Blue line 2 is perpendicular polarization. Probe wavelength is 587.7 nm.
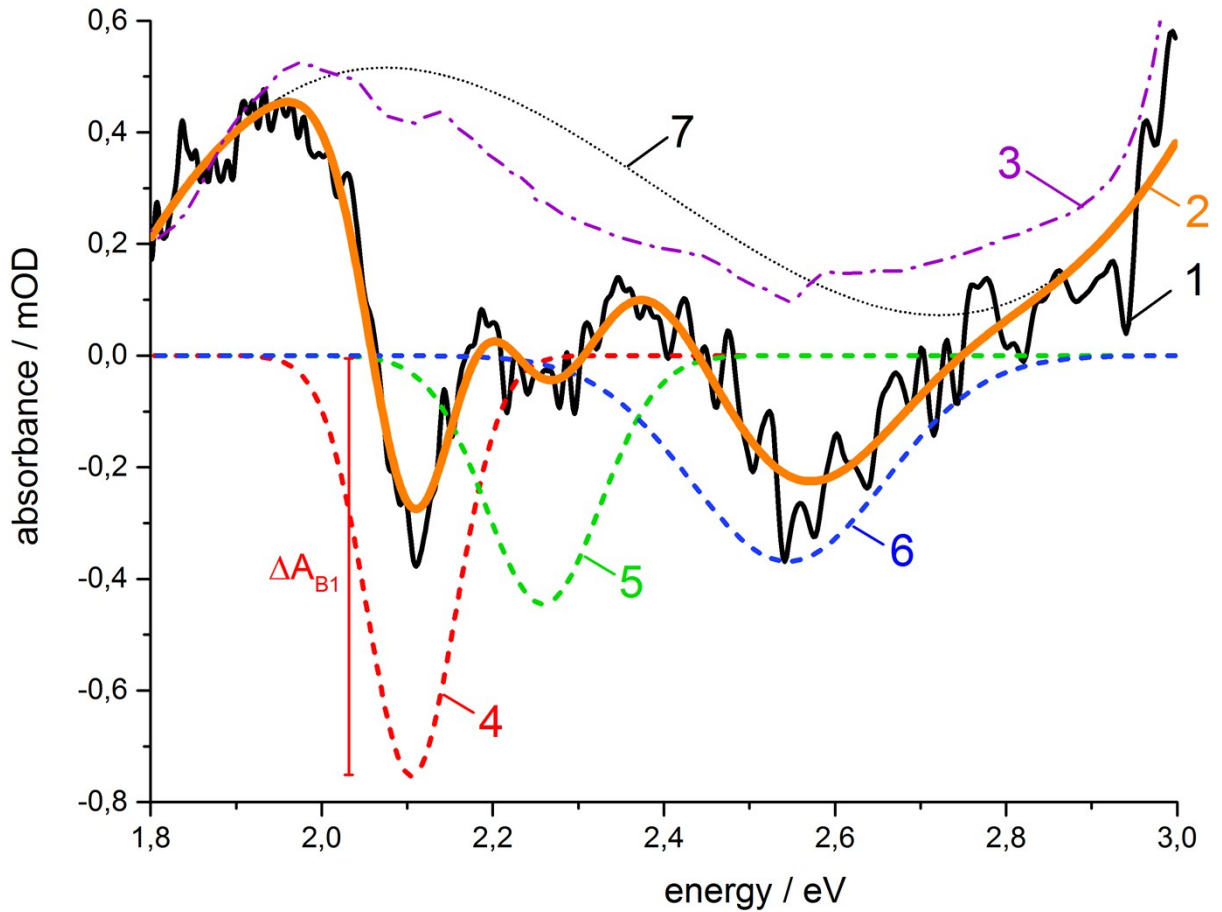
Fig. S2. Decomposition of the transient absorption spectrum of the coupled CdSe/MV^{2+} colloid at the 4ps delay $\Delta A(\omega_{probe}, t_d=4ps)$ into the three Gaussian bleaching components B1, B2 and B3. 1 - the transient spectrum $\Delta A(\omega_{probe}, t_d=4ps)$; 2 – the fitting function that includes the bleach Gaussian components and a third degree polynomial; 3 – the spectrum of MV$^{+\bullet}$ ion-radical in water shifted to red by 8 nm; 4-6 – the bleach components B1, B2 and B3, respectively, with the parameters determined from the CdSe absorption spectrum in Scheme 1; 7 – the third degree polynomial (the base line for Gaussian decomposition). The amplitude of the bleach band B1 at the 4 ps delay ΔA_{B1} is 4.6% of the initial bleach amplitude. Because the quantum yield of MV$^{+\bullet}$ formation is 0.4, the attenuation factor for the absorption transition in the charge-separated state [h$^{+}_{v\_conf}$...MV$^{+\bullet}$] is $\alpha = 0.115$.
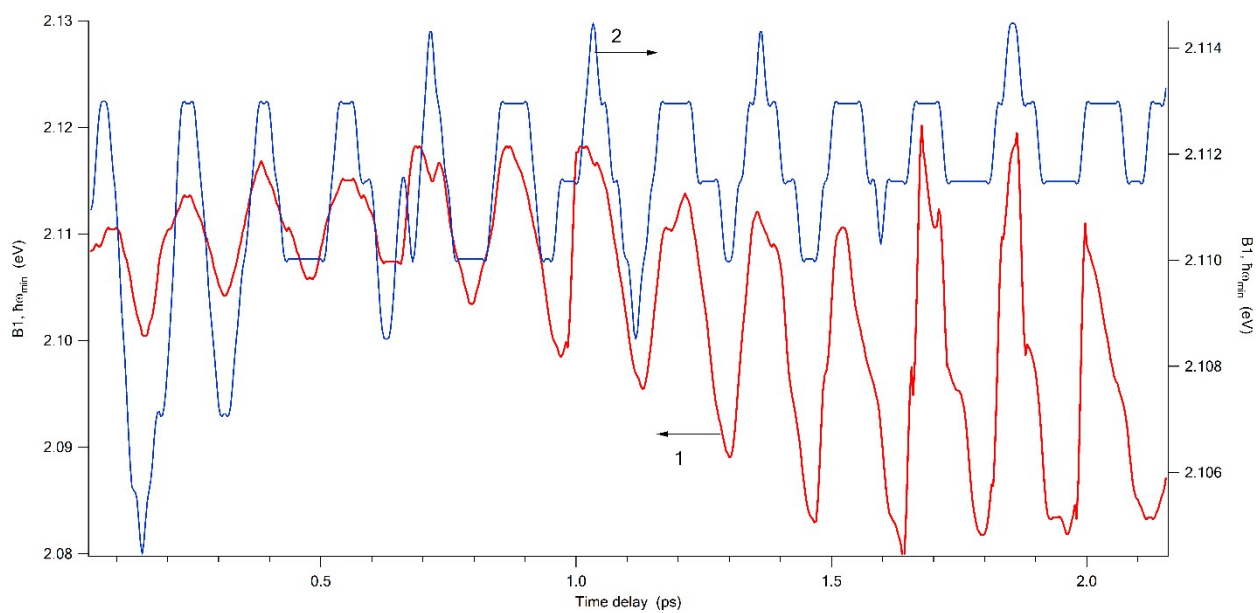
Fig. S3. Comparison of $\hbar\omega_{min}(t_d)$ traces for CdSe/MV^{2+} (1, red line) and pure CdSe(2, blue line).
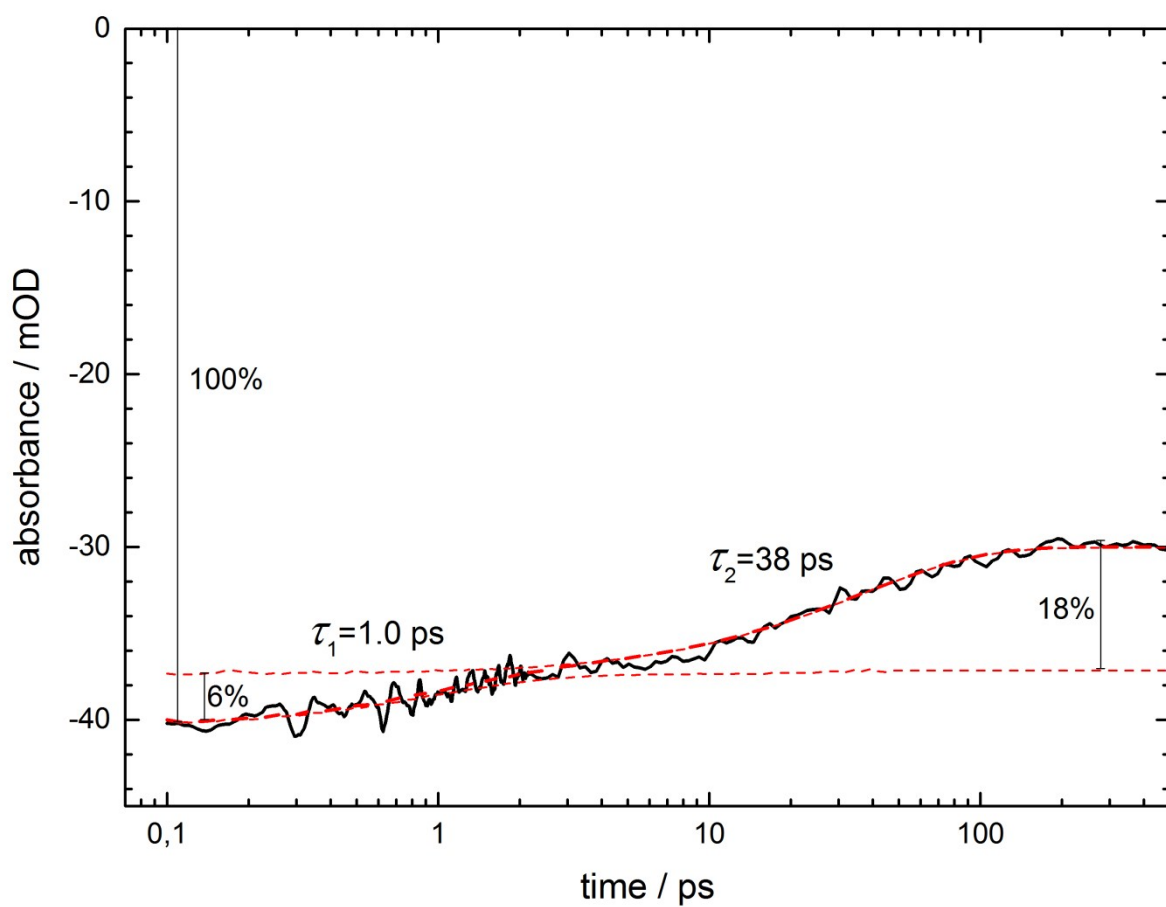

Fig. S4. Dynamics of the B1 band bleaching $\Delta A_{min}(t_d)$ in the CdSe colloid on the long time scale.
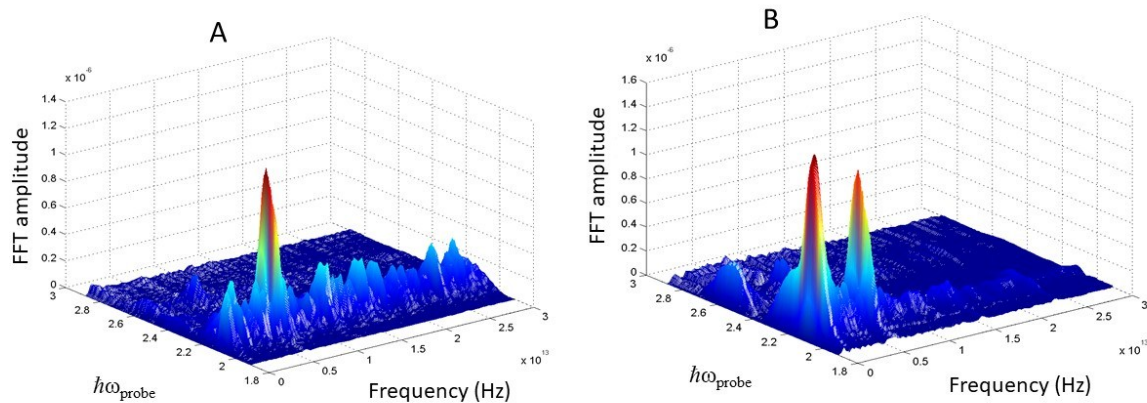
Fig. S5 FFT power spectra of oscillating residuals calculated by biexponential fitting of transient traces $\Delta A(\omega_{probe}, t_d)$. A. CdSe colloid. B. CdSe/MV^{2+} colloid.
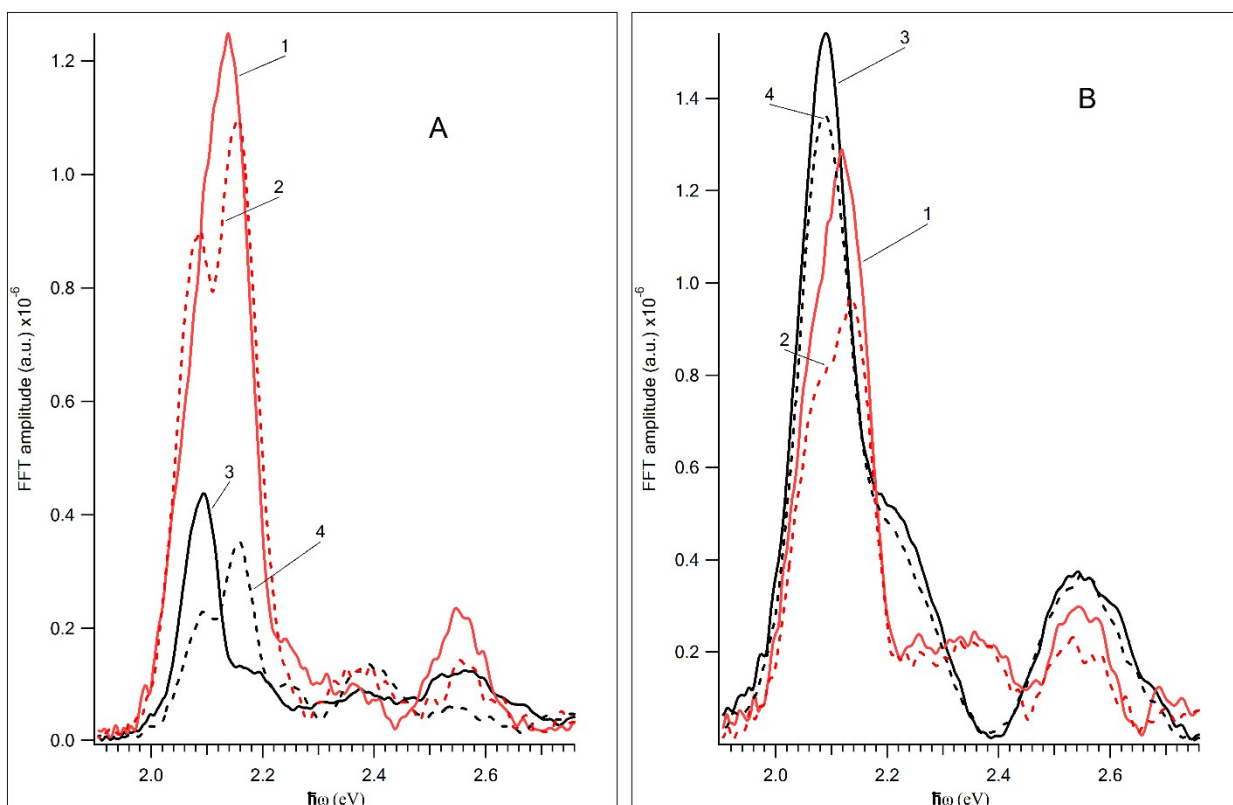

Fig. S6 Dependence of FFT spectral power of LO and LA phonons on the probe phonon energy. A, pure CdSe: 1, LO(ν=6.1 THz), parallel polarization; 2, LO(ν=6.1 THz), perpendicular polarization; 3, LA (ν=0.56 THz), parallel polarization; 4, LA (ν=0.56 THz), perpendicular

polarization. B, CdSe/MV^{2+}: 1, LO(v=6.15 THz), parallel polarization; 2, LO(v=6.1 THz), perpendicular polarization; 3, LA (v=0.56 THz), parallel polarization; 4, LA (v=0.56 THz), perpendicular polarization.

### SI 6. Electric Field in the Spherical CdSe Nanoparticle

The analytical solution to the electrostatic problem in spherical coordinate system (r, θ, ϕ) for a point charge in a sphere of radius R with the dielectric permittivity ε_1 immersed in the infinite dielectric with the permittivity ε_2 can be obtained by the Kirkwood expansion (Kirkwood 1934):

$$\Psi_1(\mathbf{r}) = \frac{q}{\varepsilon_1 |\mathbf{r} - \mathbf{r}_s|} + \frac{q(\varepsilon_1 - \varepsilon_2)}{\varepsilon_1 R} \sum_{n=0}^{\infty} \frac{n+1}{\varepsilon_1 n + \varepsilon_2 (n+1)} \left(\frac{rr_s}{R^2} \right)^n P_n(\cos\theta)$$

Here $\mathbf{r} = (r, \theta, \phi)$ is the observation point, $\mathbf{r}_s$ is the point of charge q location, r_K is the Kirkwood parameter $r_K = R^2/r_s$, and $P_n(x)$ is the Legendre polynomial.

The dielectric permittivity of the CdSe particles of the radius 1.9 nm is $\varepsilon_1 = 5.6$ (Wang and Zunger 1996) and that of toluene $\varepsilon_1 = 2.38$.
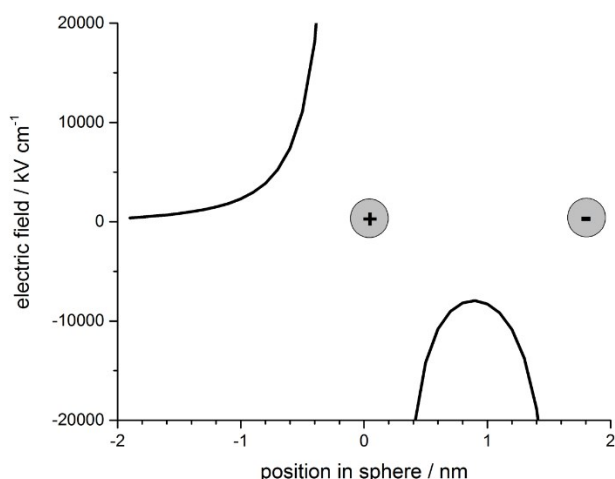
A.
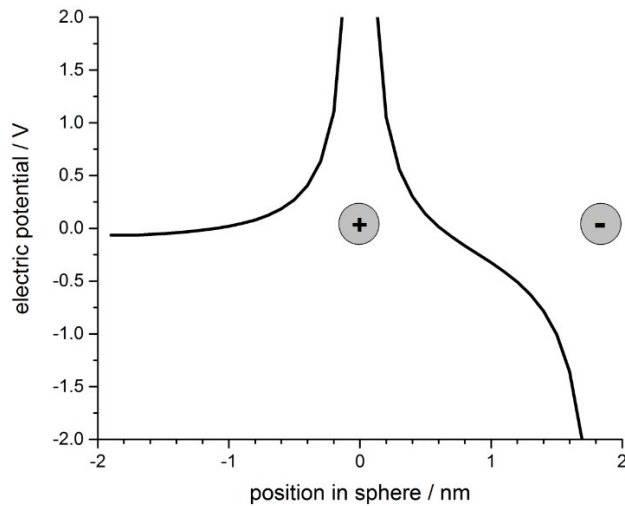
B.

Fig.S7. A. The electric potential along the axis connecting the cation-anion pair [$h^+_{v\_conf...}MV^{+\bullet}$] in the CdSe QD of the 3.8 nm diameter. B. The electric field $\boldsymbol{F}$ near the cation-anion pair [$h^+_{v\_conf...}MV^{+\bullet}$] in the CdSe QD of the 3.8 nm diameter.

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