

Controlling the Trap State Landscape of Colloidal CdSe Nanocrystals with Cadmium Halide Ligands

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Detailed Experimental.

General Considerations. The following chemicals were used as received without further purification. Tetradecanoic acid (> 99.0%, Sigma-Aldrich), sodium hydroxide (pellets, 97%, Sigma-Aldrich), Cd(NO₃)₂•4 H₂O (98.0 %, Sigma-Aldrich), Cd(CH₃CO₂)₂ hydrate (>99.99%, Sigma-Aldrich), selenium dioxide (≥99.9%, Sigma-Aldrich), oleic acid (technical grade, 90%, Sigma-Aldrich), 1-octadecene (technical grade, 90%, Sigma-Aldrich), methanol (production grade, VWR), CdCl₂•H₂O (99.99%, Alfa Aesar), CdBr₂ (98%, Alfa Aesar), CdI₂ (99.5 %, Alfa Aesar), butylamine (Acros), Na₂S hydrate (>60%, Lancaster), sulfur (precipitated, 99.5%, Alfa Aesar).

CdSe Nanocrystal Synthesis. The cadmium myristate precursor was prepared according to a previously published procedure.¹ In a 1-L flask equipped with a 2" magnetic stir bar and fitted with two rubber septa and a 14" condenser, Cd(C₁₄H₂₇O₂)₂ (10.0 g, 17.6 mmol) was added followed by SeO₂ (2.67 g, 22.0 mmol) and Cd(C₂H₃O₂)₂ (0.45 g, 1.8 mmol). The mixture was suspended in 1-octadecene (ODE, 250 mL), and the flask was fitted a nitrogen-connected condenser and two rubber septa, one of which was used to fix a stainless steel thermocouple in the reaction suspension in order to monitor the internal temperature over the entire reaction course. An initial period of 1-2 h under vacuum at 130 °C was found to be necessary to obtain monodisperse nanocrystal size distributions. After the initial heating step, the reaction was vented to nitrogen and ramped to 240 °C (6-7 °C min⁻¹). Aliquots were taken every 30 s, and nanocrystal nucleation was first observed around 200 °C, as evidenced by the appearance of excitonic features in the

absorption spectra. The reaction was quenched by removal from heat, cooling in a room temperature oil bath, and injection of a 1:1 vol/vol oleic acid:ODE (60 mL) mixture. After cooling to room temperature, the crude reaction mixture was purified by flocculation with acetone and redispersion in toluene. This flocculation/redispersion cycle was repeated 4 additional times before filtering the final toluene dispersion of CdSe(NL) nanocrystals through a 0.45 μm syringe filter. The final product was stable in the dark for several months at concentrations up to 150 mg mL^{-1} CdSe(NL).

Thin Film Deposition. Nanocrystal thin films were deposited by spin-casting (1000 rpm, 60 s) onto pre-cleaned glass or ITO substrates (Thin Film Devices, Inc., $\rho = 20\text{-}30 \Omega \text{sq}^{-1}$) under a nitrogen atmosphere. After spin-casting, films were placed into a nitrogen filled cabinet for 20-30 min to complete the drying process before being used for experiments. CdSe(NL) nanocrystals were cast from toluene suspensions, whereas all other nanocrystal films were cast from chlorobenzene suspensions.

Material Characterization. TGA data were collected using a TA Instruments TGA Q50 instrument, using a sample size of 5-10 mg in an alumina crucible under flowing nitrogen. Samples for TGA were prepared by drying the colloid in a vial under flowing nitrogen at 50-60 $^{\circ}\text{C}$ for 30 min, then crushed and transferred into the crucible.

FT-IR spectra were acquired from pressed pellets on a Bruker Vertex 80. To obtain quantitative information, an internal standard, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ was pre-mixed into a KBr matrix, and exactly 200.0 mg of this pre-mixed standard FT-IR matrix was used with exactly 3.5 mg of ground nanocrystal sample to press sample pellets. For FT-IR measurements involving annealed nanocrystal samples, nanocrystal powders were heat treated at 250 $^{\circ}\text{C}$ in a tube furnace under nitrogen flow before being mixed with the KBr/internal standard matrix and pressed into pellets.

Optical absorption spectra were obtained using a Perkin Elmer Lambda 950 equipped with a 150 mm integrating sphere. All nanocrystal films were mounted inside of the integrating sphere at a 7 $^{\circ}$ angle relative to the incident light beam to ensure collection of all scattered as well as specularly or diffusely reflected light. This experimental configuration ensured that all observed red (or blue)-shifts in the spectral data were intrinsic to the nanocrystal sample and not due to experimental artifacts.

STEM-EDX maps for CdSe(CdI₂) nanocrystal samples were acquired using an FEI Titan Themis microscope at an operating voltage of 80 kV. All other TEM and EDX data presented were acquired with a JEOL-2100F microscope at an operating voltage of 200 kV, equipped with a Gatan Orius CD camera and an EDAX Apollo silicon drift detector.

^1H NMR spectra were collected on a Varian 500 spectrometer (500 MHz in ^1H) with chemical shifts represented in units of ppm. All spectra are normalized relative to the residual benzene solvent peak at 7.16 ppm for the purpose of enabling semi-quantitative comparison between different samples. NMR sample preparation and analyses were conducted according to previously published procedures for nanocrystal ligand analysis.²⁻

⁴ Briefly, samples were prepared by digesting dried nanocrystal solids (50 mg) in half-

concentrated aqua regia (7 mL), and then the organics were extracted using d_6 -benzene (2 mL). The solvent was then dried with MgSO_4 and filtered before ^1H NMR analysis. 32 scans were taken for each sample, and the data are presented as averages of those scans.

Powder X-ray diffraction data was collected using a Rigaku Ultima IV diffractometer in parallel beam geometry (2 mm beam width) using $\text{Cu } K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Samples were prepared by drop-casting onto Si wafers.

XPS spectra were acquired using a Kratos Axis Ultra X-ray photoelectron spectrometer with the analyzer lens in hybrid mode. High resolution scans were performed using a monochromatic aluminum anode with an operating current of 5 mA and voltage of 10 kV using a step size of 0.1 eV, a pass energy of 20 eV, and a pressure range between $1\text{--}3 \times 10^{-8}$ torr. The binding energies for all spectra were referenced to the C1s core level at 284.6 eV.

SEM images were acquired using a JEOL JSM-7001F SEM. Nanocrystal samples were spun-cast onto ITO coated glass slides and treated accordingly prior to imaging.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed on each nanocrystal sample for analysis of cadmium and selenium using a Thermo Scientific iCAP 7000 series ICP-OES. Nanocrystal samples were prepared by drying out a minimum of 10 mg of solid, digesting in 1 mL of 12 M HNO_3 with the aid of bath sonication, and diluting with *ca.* 99 mL 2% HNO_3 . All samples were filtered prior to analysis.

Photoelectrochemistry. Photoelectrochemical response was performed using a BASi Epsilon-EC potentiostat. A quartz cuvette was used with a Pt-wire counter electrode and an Ag-wire pseudo-reference electrode. The working electrode was a CdSe nanocrystal film on ITO-coated glass. The redox couple and experimental parameters were chosen based on previously published work involving photoelectrochemical characterization of CdSe nanocrystal films.^{5,6} An aqueous 0.050 M Na_2S / 0.005 M S electrolyte was made from nitrogen-sparged deionized water, and care was taken to avoid exposure of the electrolyte solution to oxygen throughout the course of the experiments. For photoelectrochemical experiments, two 472 nm LEDs mounted *ca.* 6 cm from either side of the sample were used to illuminate the working electrode. The illumination intensity was measured using a Newport model 818-ST photodiode connected to a Newport 2832-C dual-channel power meter. Measurements were taken for both illumination directions and summed, giving a result of 4.9 mW cm^{-2} . The total illuminate area of the CdSe working electrode was 1.7 cm^2 .

Thin Film Photoluminescence. Spectra were collected on a Horiba Jobin Yvon Nanolog spectrofluorometer equipped with a 450 W Xe short-arc excitation source and an Si photodiode detector using 0.1 s integrating time, and were then corrected for the Si detector response function.

Photoluminescence Lifetime Studies. Films were placed in the sample chamber of a ST-100 Janis cryostat. TCSPC measurements (30 ps time resolution) were performed using a R3809U-50 Hamamatsu PMT with a B&H SPC-630 module. Samples were excited with the 400 nm frequency-doubled output of a Ti:sapphire regenerative amplifier operating at 250 kHz (Coherent RegA 9050). Laser pulses were focused onto the sample using a 15 cm focal lens, with illumination powers between 20 μ W and 10 mW, depending on the strength of the photoluminescence signal (*i.e.*, depending on the ligands and on the temperature), so that excitation resulted in less than one excited electron-hole pair per nanocrystal.^{7,8} Emission was collected at the emission peak of the nanocrystals at perpendicular polarization relative to the 400 nm excitation. The emission was collimated and then focused into a monochromator with a 10 cm lens. The monochromator was a CVI CMSP112 double spectrograph with a 1/8 m total path length in negative dispersive mode with a 600 g mm⁻¹ grating blazed at 600 nm. The slit widths were 2.4 mm, resulting in a 9-nm resolution at 600 nm.

Estimation of the Ligand-induced Trap Density and Depth. In order to estimate the ligand-induced trap density and depth, we developed a model to fit the long time bleach recovery between 100 ps and 1200 ps. As shown in Scheme S1, we consider that the ground state recovers by two mechanisms: (i) a ligand-independent relaxation to the ground state with rate k_1 and (ii) a ligand-dependent relaxation with rate k_2 . For simplicity, we assume that these mechanisms are independent, *i.e.* we assumed that all the trapping from the excited state is over by 100 ps and that detrapped charges cannot be trapped again.

We assume that the total number of excitations N is constant; excitations reside either in the ground state N_{GS} , or in the excited state N_{ES} or finally in the trap state N_T . We further assume that the excitations reside either on the excited state or on the trap state at 100 ps – $N_{ES}(t = 100 \text{ ps}) + N_T(t = 100 \text{ ps}) = N$. Finally, the native ligand CdSe(NL) nanocrystals posses no trap states in this model and therefore $N_T(t) = 0$ for the this sample.

The ground state signal then writes $S \propto -(1 - N_T(t = 100 \text{ ps}))e^{-k_1 t} - N_T(t = 100 \text{ ps})e^{-k_2 t}$.

Finally, the CdX_2 halide-dependent relaxation is thermally activated: $k_2 = A e^{-\Delta E_{\text{lig}} / kT}$. We assume that the halide dependence is solely carried by ΔE_{lig} (*i.e.*, the prefactor A does not depend on the halide ligands). The measured data d_{obs} is the ground state bleach recovery of the $1S_e$ - $2S_{3/2}$ transition normalized at $t = 100$ ps.

We first determined k_1 by fitting the decays of the CdSe(NL) nanocrystals at 77 K and 298 K simultaneously. Then, we determined ΔE and N_T by fitting the decays of the halide-treated samples at 77 K and 298 K. Figure S14 shows the data and the fits.

The fits were obtained with a Bayesian analysis: 20,000 parameter sets (k_1 , ΔE , N_T) were randomly generated and for each parameter set, the model prediction was calculated: $d_{\text{pred}} \propto -(1 - N_T(t = 100 \text{ ps}))e^{-k_1 t} - N_T(t = 100 \text{ ps})e^{-k_2 t}$ and normalized at $t = 100$ ps. Each prediction was then compared to the measured data d_{obs} and the corresponding parameter set was attributed a likelihood depending on the match between d_{pred} and d_{obs} . The parameter set with the maximal likelihood is called the most likely parameter set. The uncertainty of the fit procedure due to experimental noise is

accessible and is given by the width of the distribution of the likelihood of each parameter. In other words, error bars here described how much the data can actually constrain the extraction of parameters. In Figure S14 we give the experimental data d_{obs} (circles) and a number of predictions d_{pred} (lines) computed for parameters sets that are within the likelihood distribution. Table S1 gives the resulting most likely parameters and the corresponding spread. In conclusion, our fits indicate that the detrapping activation energy DE increased for heavier halide CdX_2 ligands and that the fraction of excitations that are trapped at 100 ps $N_{\text{T}}(t = 100 \text{ ps})$ correspondingly increases for heavier halide ligands.

Supplementary Figures

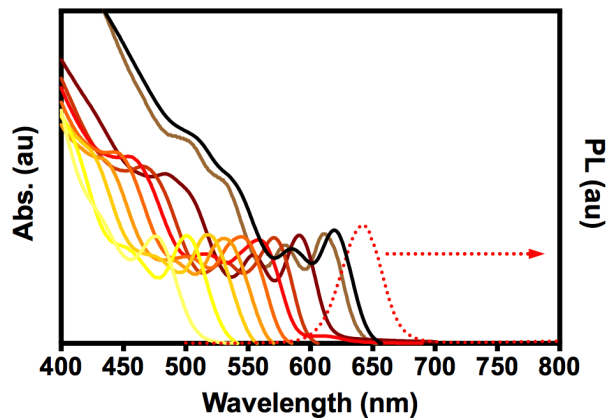


Figure S1. Optical absorption spectra of aliquots (in 1-octadecene) taken over the course of the reaction representing CdSe nanocrystal growth, as evidenced by a continually red-shifting first exciton peak. The emission spectrum is shown for the final aliquot taken.

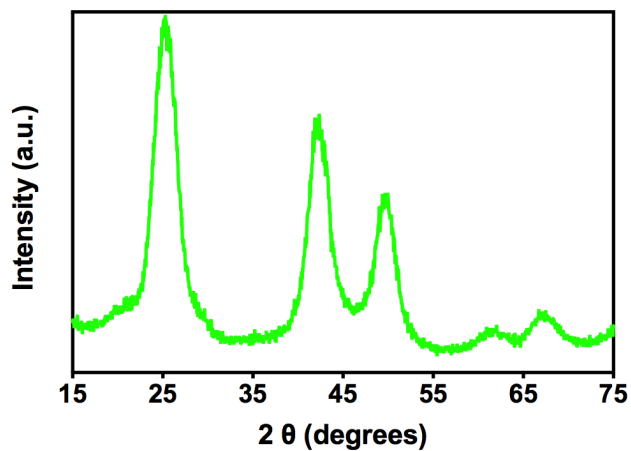


Figure S2. XRD pattern for a CdSe(native ligand) nanocrystal film on silicon.

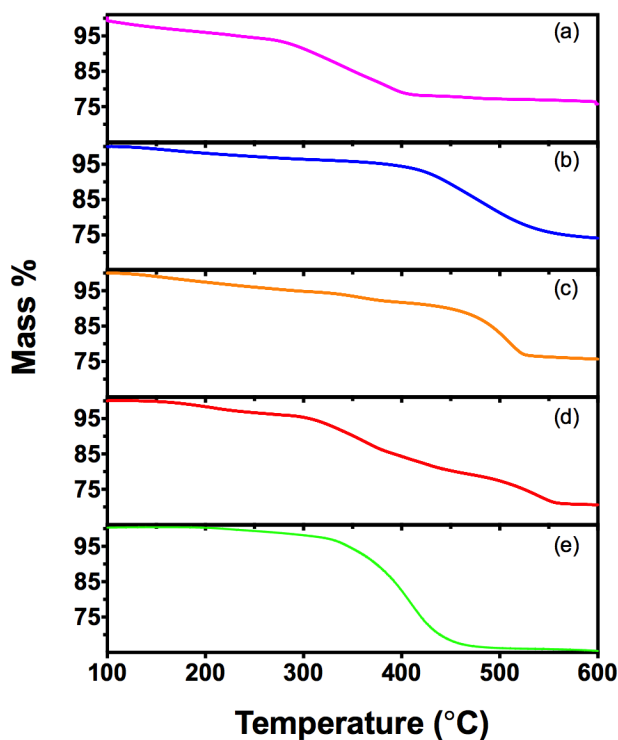


Figure S3. TGA thermograms of (a) CdSe(butylamine), (b) CdSe(CdI₂), (c) CdSe(CdBr₂), (d) CdSe(CdCl₂), and (e) CdSe(native ligand).

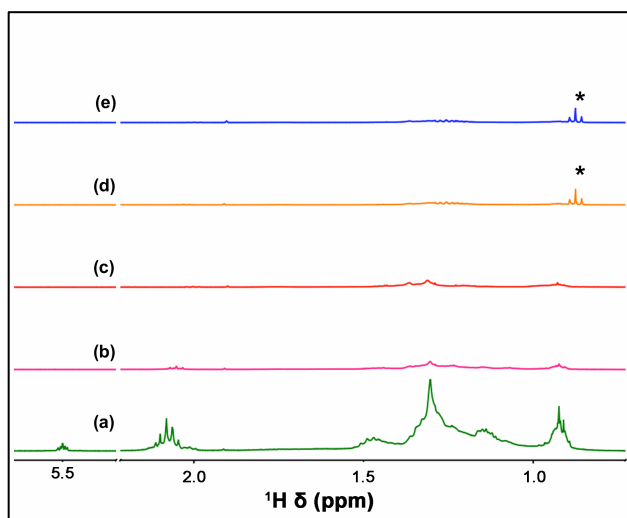


Figure S4. Normalized ¹H NMR spectra for (a) CdSe(native ligand), (b) CdSe(butylamine), (c) CdSe(CdCl₂), (d) CdSe(CdBr₂), and (e) CdSe(CdI₂) after digestion in aqua regia and extraction with *d*₆-benzene. The spectra demonstrate the removal of native ligand protons after ligand exchange as evidenced by the reduced aliphatic proton signal from 0.8-2.2 ppm. All spectra are normalized to the residual benzene solvent peak at 7.16 ppm (not shown for clarity). The remaining native ligands in the CdSe(butylamine) and CdSe(CdCl₂) nanocrystal samples are visible as small signals in

the aliphatic proton range. The aliphatic proton signals for the CdSe(CdBr₂) and CdSe(CdI₂) samples are almost completely gone, which supports our assessment of nearly quantitative CdX₂ ligand exchange. Proton signal from butylamine is not observable since amine protonation during the acid digestions prevents extraction into the organic *d*₆-benzene layer. The asterisked triplet around 0.7 ppm is from residual pentane, which was used as an anti-solvent for CdSe(CdBr₂) and CdSe(CdI₂) nanocrystals.

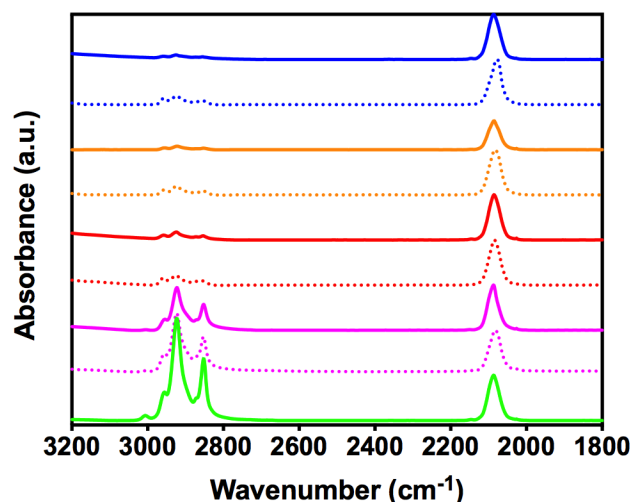


Figure S5. Quantitative FT-IR spectra of unannealed (dashed lines) and 250 °C annealed (solid lines) nanocrystal samples. From bottom to top: CdSe(native ligand) (green), CdSe(butylamine) (pink), CdSe(CdCl₂) (red), CdSe(CdBr₂) (orange), and CdSe(CdI₂) (blue). An internal standard, Fe₄[Fe(CN)₆]₃ with $\nu(\text{C}\equiv\text{N})$ at 2090 cm⁻¹, was mixed into a KBr matrix and used for pellet preparation so that spectra could be quantitatively compared. All thermal annealing steps were performed prior to mixing with the KBr/internal standard matrix. From integration of the $\nu(\text{C-H})$ signals between 2750-3050 cm⁻¹, it was found that thermal annealing at 250 °C reduces the $\nu(\text{C-H})$ intensity by 44.6, 74.3, and 51.6% for CdSe(CdCl₂), CdSe(CdBr₂), and CdSe(CdI₂), respectively.

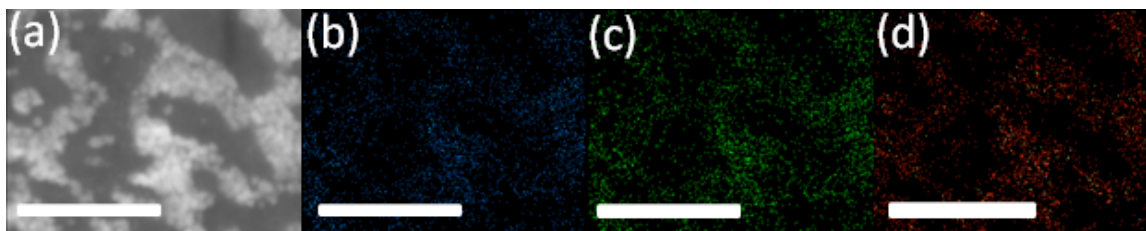


Figure S6. STEM-EDX maps of CdSe(CdCl₂) nanocrystal ensemble demonstrating a uniform distribution of chloride throughout the nanocrystals. (a) STEM field of view; (b) Cl (*K*-line); (c) Se (*K*-line); (d) Cd (*L*-line). The scale bars are 50 nm.

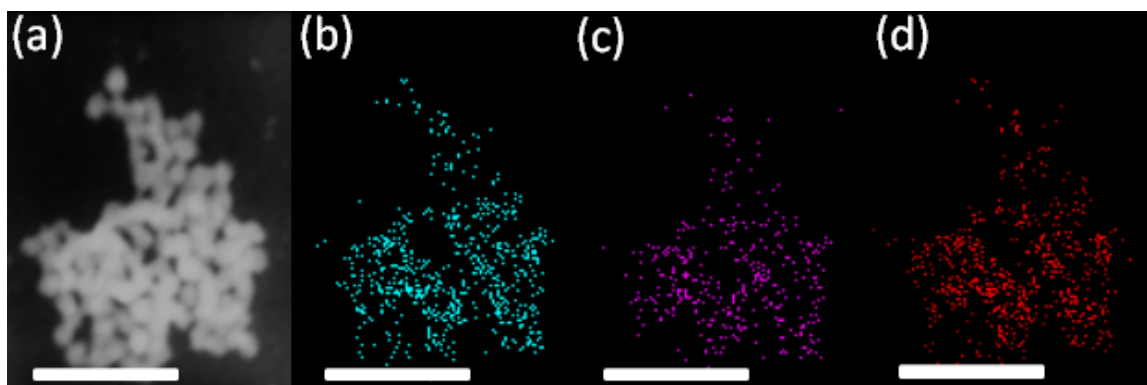


Figure S7. STEM-EDX maps of CdSe(CdBr₂) nanocrystal ensemble demonstrating a uniform distribution of bromide throughout the nanocrystals. (a) STEM field of view; (b) Se (*K*-line); (c) Br (*K*-line); (d) Cd (*L*-line). The scale bars are 35 nm.

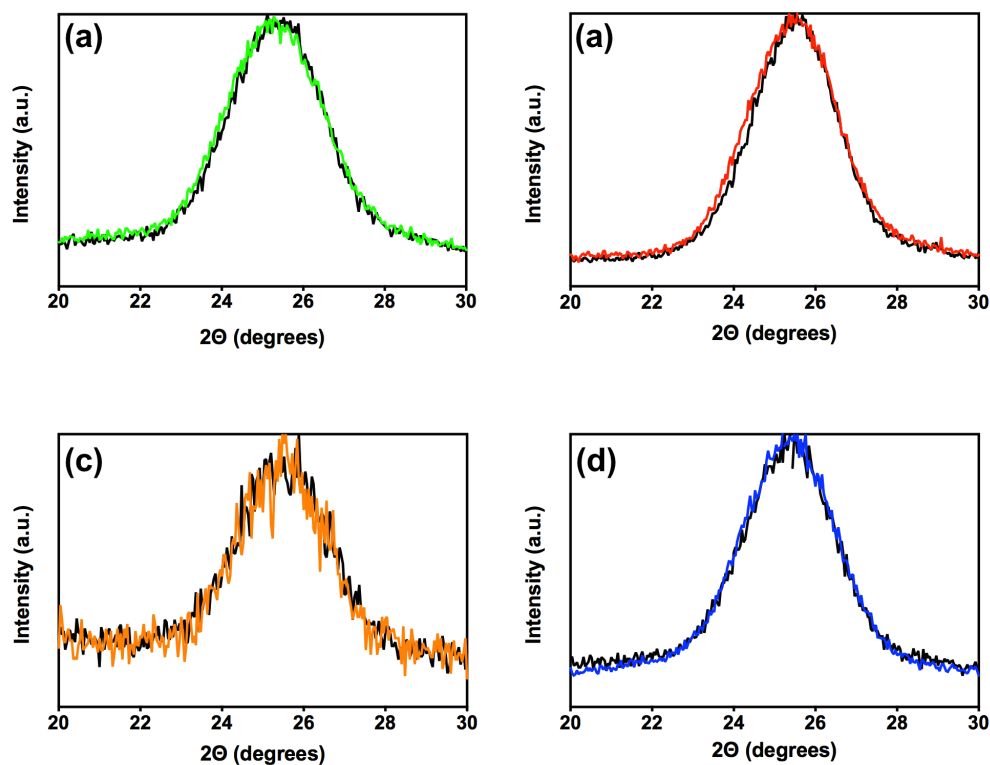


Figure S8. XRD patterns of CdSe nanocrystal thin films comparing the (111) peak before (color) and after (black) 250 °C annealing. From top left to bottom right: (a) CdSe(native ligand), (b) CdSe(CdCl₂), (c) CdSe(CdBr₂), and (d) CdSe(CdI₂).

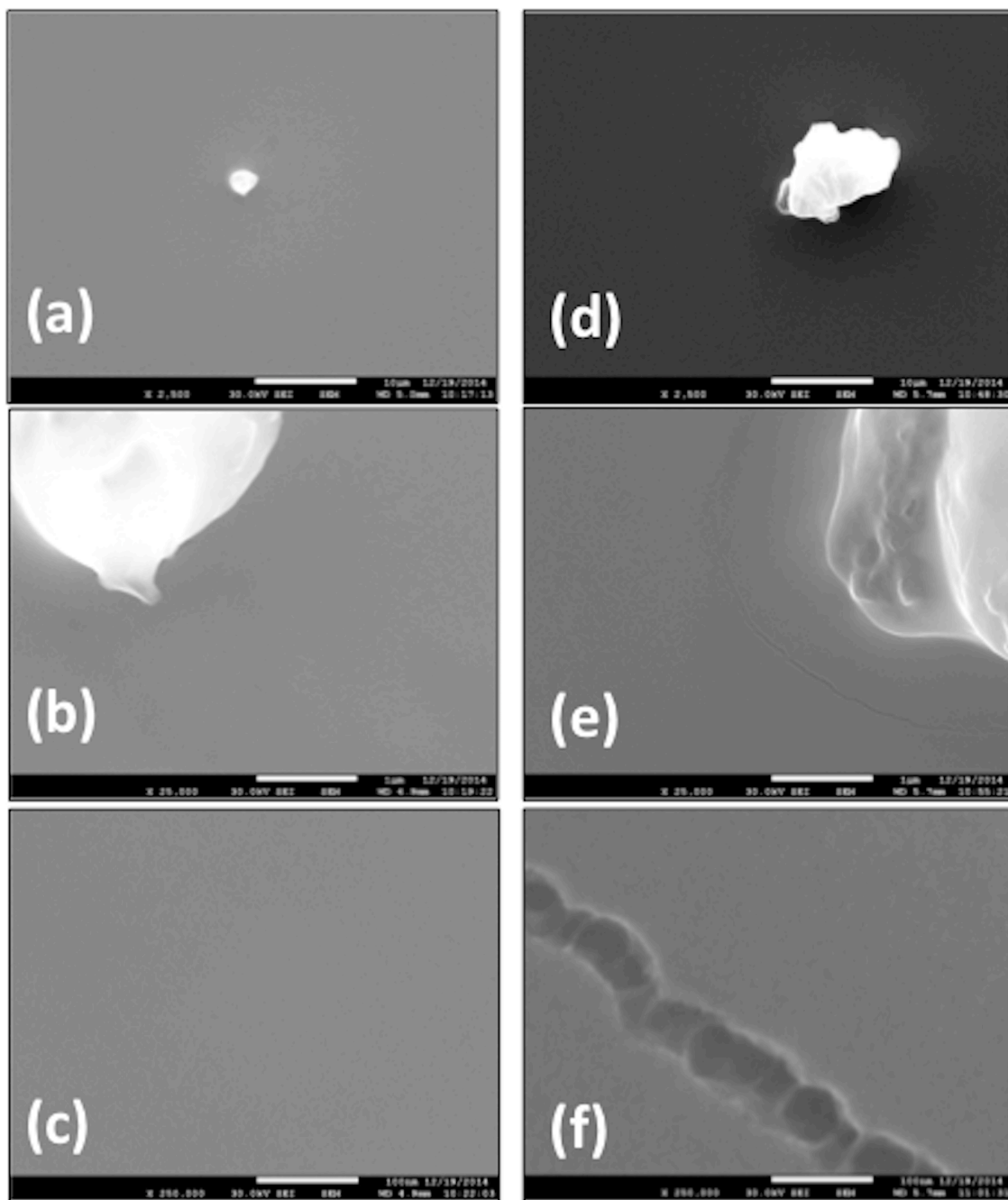


Figure S9. SEM top-down images of CdSe(CdCl₂) nanocrystal films before (left side) and after (right side) 250 °C annealing. The images are shown at magnifications of 2,500× in (a) and (d), 25,000× in (b) and (e), and 250,000× in (c) and (f). A contaminant particle is shown in the lower magnification panels to demonstrate proper focus. The images show no obvious grain growth upon heat treatment, although the appearance of a crack is seen after thermal annealing.

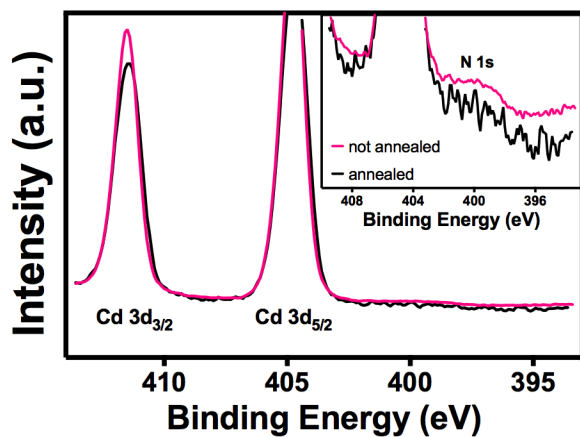


Figure S10. XPS spectrum for annealed CdSe(butylamine) showing a reduction in the N 1s peak near 399 eV after thermal annealing.

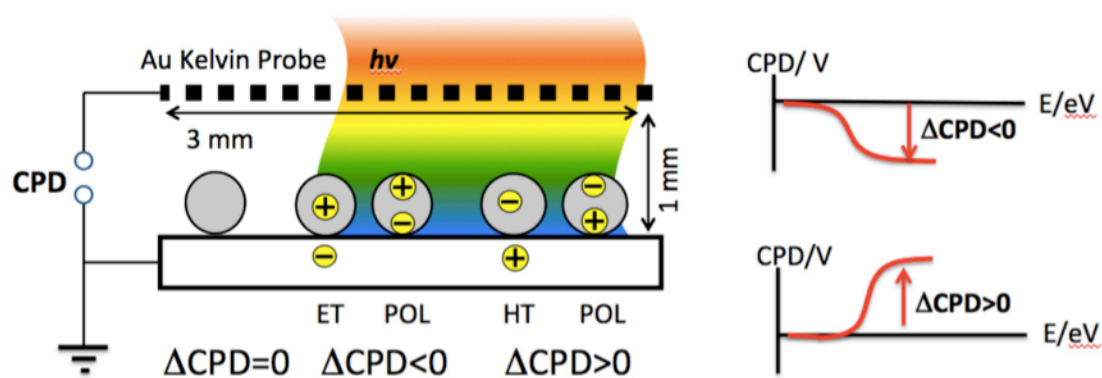


Figure S11. Measurement configuration for SPV and sample spectra.

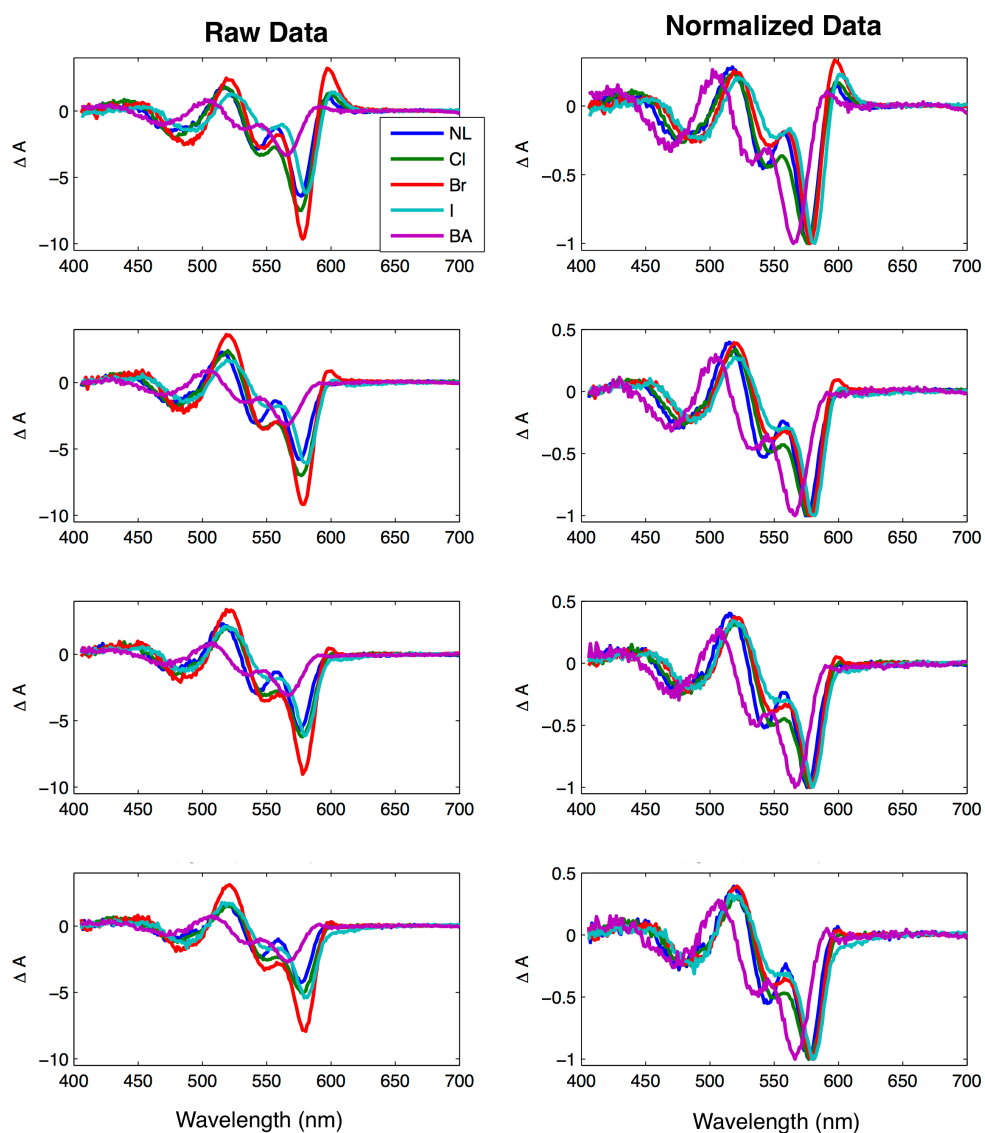


Figure S12. TA difference spectra for nanocrystal films at 77 K for different probe times after excitation at 400 nm. Spectra are color coded: CdSe(native ligand) (green), CdSe(butylamine) (pink), CdSe(CdCl₂) (red), CdSe(CdBr₂) (orange), and CdSe(CdI₂) (blue). Left side depicts raw difference spectra, and the right side shows normalized spectra.

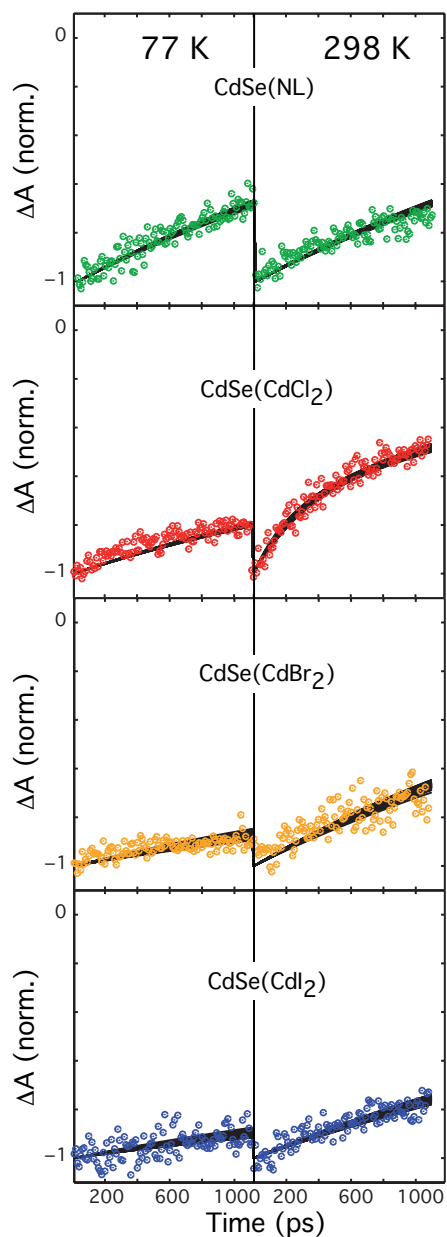


Figure S13. Experimental $2S_{3/2}-1S_e$ bleach decay d_{obs} for the CdSe(native ligand) and CdSe(CdX₂) nanocrystal films (circles) and a number of predictions d_{pred} given our simplified model (black lines). See the text for details.

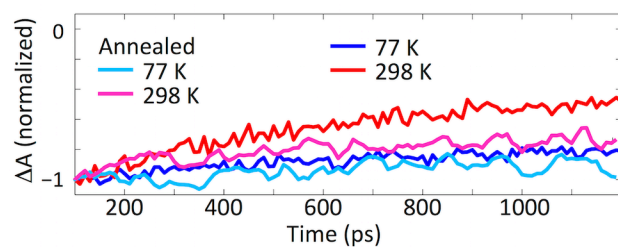
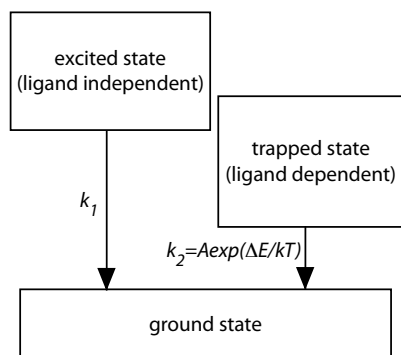


Figure S14. TA dynamics of the bleach of the $2S_{3/2}-1S_e$ transition (at 540 nm) for the annealed CdSe(CdCl₂) nanocrystal film at 77 K (black traces) and 298 K (colored traces).



Scheme S1. Simplified kinetic model used to estimate the parameters of the halide induced trap states: trap depths and relative populations.

Table S1. Average fit parameters for the decays shown in Figure S11.

	k_1 (ps ⁻¹)	$N_T(t = 100 \text{ ps})$ (fraction of the total population)	DE (eV)
CdSe(NL)	$3.54 \pm 0.007 \times 10^{-4}$	Fixed at 0	n/a
CdSe(CdCl ₂)	Fixed at $3.54 \pm 0.007 \times 10^{-4}$	0.37 ± 0.01	0.141 ± 0.003
CdSe(CdBr ₂)	Fixed at $3.54 \pm 0.007 \times 10^{-4}$	0.59 ± 0.03	0.200 ± 0.001
CdSe(CdI ₂)	Fixed at $3.54 \pm 0.007 \times 10^{-4}$	0.68 ± 0.02	0.212 ± 0.002

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