Supporting Information

Spectroelectrochemical Signatures of Surface Trap Passivation on CdTe Nanocrystals

Ward van der Stam,*[§] Indy du Fossé,[§] Gianluca Grimaldi, Julius O. V. Monchen, Nicholas

Kirkwood, and Arjan J. Houtepen*

Opto-Electronic Materials Section, Faculty of Applied Sciences, Delft University of Technology,

van der Maasweg 9, 2629 HZ Delft, The Netherlands

*a.j.houtepen@tudelft.nl and w.vanderstam@tudelft.nl

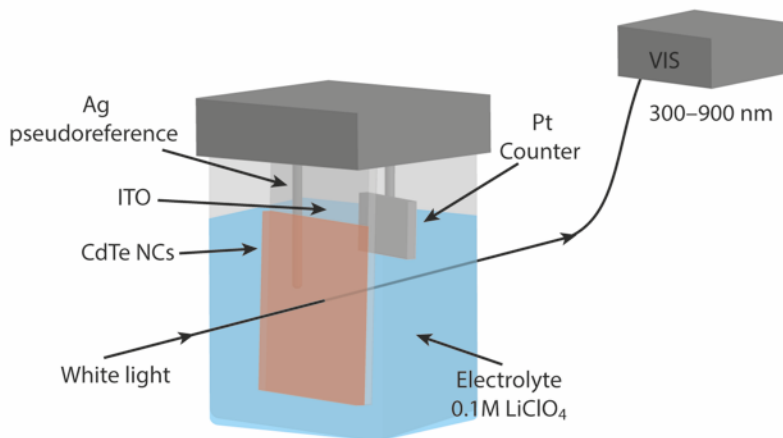§ These authors contributed equally to this work.

Figure S1. Schematic representation of the electrochemical cell.

1. Calibration of the Ag pseudo-reference electrode

The Ag pseudo-reference electrode used during the spectroelectrochemical experiments was calibrated with the ferrocene/ferrocenium couple. An example of a cyclic voltammogram is shown in Figure S2, for which the half-wave potential was determined to be +0.224 V via the equation

$$E_{1/2} = \frac{E_{p,o} + E_{p,r}}{2} = \frac{+0.491\ V - 0.044\ V}{2} = +0.224\ V$$

The potential of the Ag pseudo-electrode can then be calculated to be -4.92 eV versus vacuum *via* the equation

$$E_{vac} + E_{Ag} = -4.68\ (SCE\ vs\ vacuum) - 0.46\ (ferrocene\ vs\ SCE)$$
$$+ 0.224\ (ferrocene\ vs\ Ag) = -4.92\ eV$$

The ferrocene/ferrocenium couple was measured several times and subsequently averaged, which eventually resulted in a potential of -4.90 ± 0.03 eV *versus* vacuum.
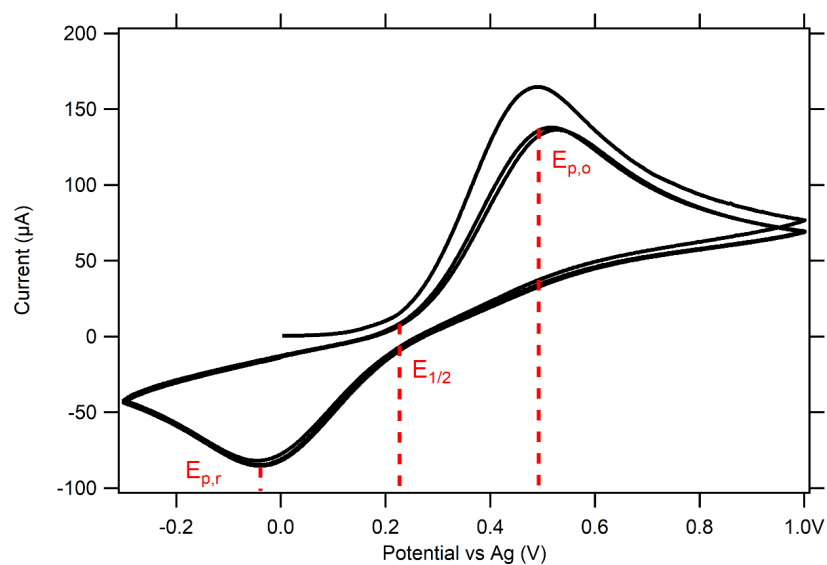
Figure S2. Example of a cyclic voltammogram of ferrocene in 0.1 M LiClO$_4$ in acetonitrile electrolyte solution, scanned at 50 mV/s. The oxidation and reduction peaks (E$_{p,o}$ and E$_{p,r}$ respectively) are shown, as well as the half-wave potential (E$_{1/2}$).
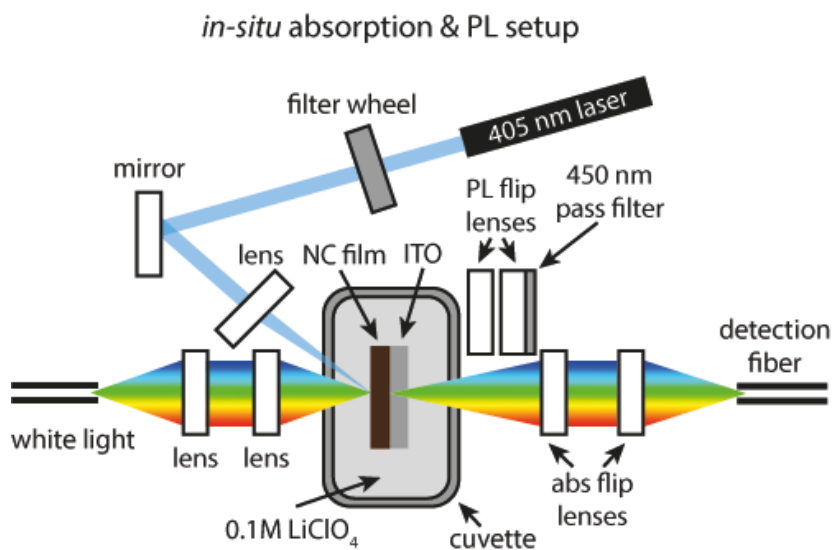

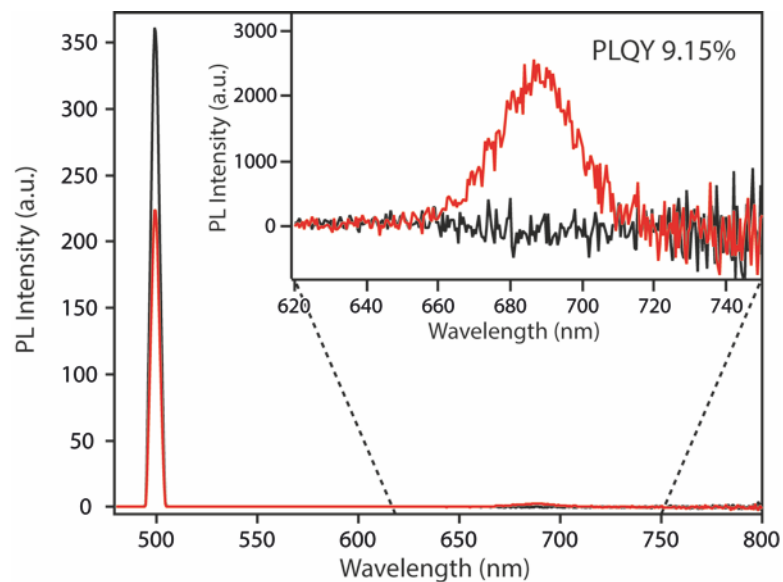**Figure S3.** Schematic representation of the *in-situ* photoluminescence and absorbance setup.

Figure S4. Photoluminescence quantum yield (PLQY) measurement on CdTe NCs in toluene, yielding a PLQY of 9.15%.
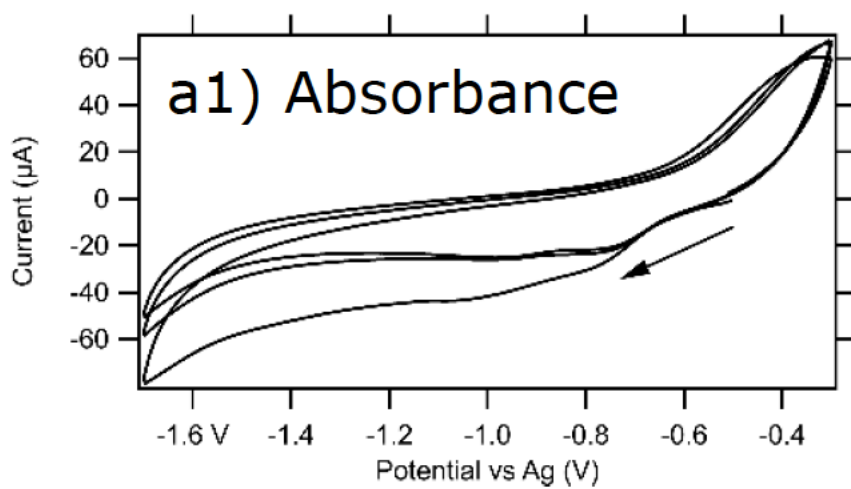

Figure S5. Cyclic voltammogram for a CdTe NC film during *in-situ* absorbance measurements.
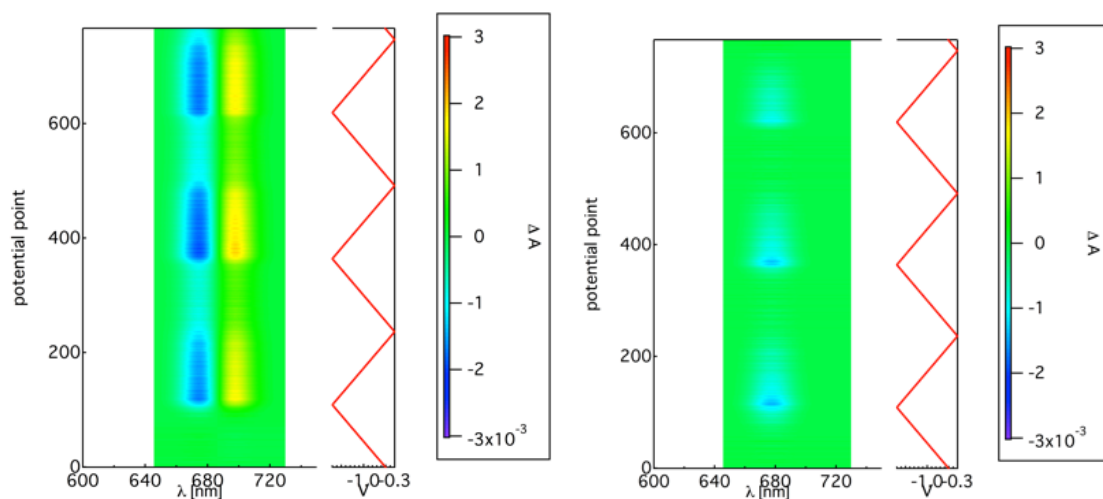
Figure S6. (a) Stark shift correction for untreated CdTe NC films. (b) Effective band edge bleach after Stark shift correction.
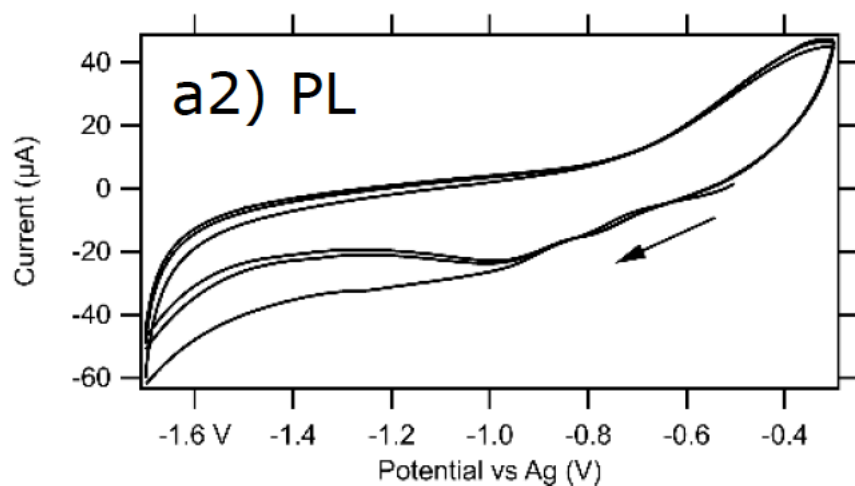

Figure S7. Cyclic voltammograms for a CdTe NC film during *in-situ* photoluminescence measurements.
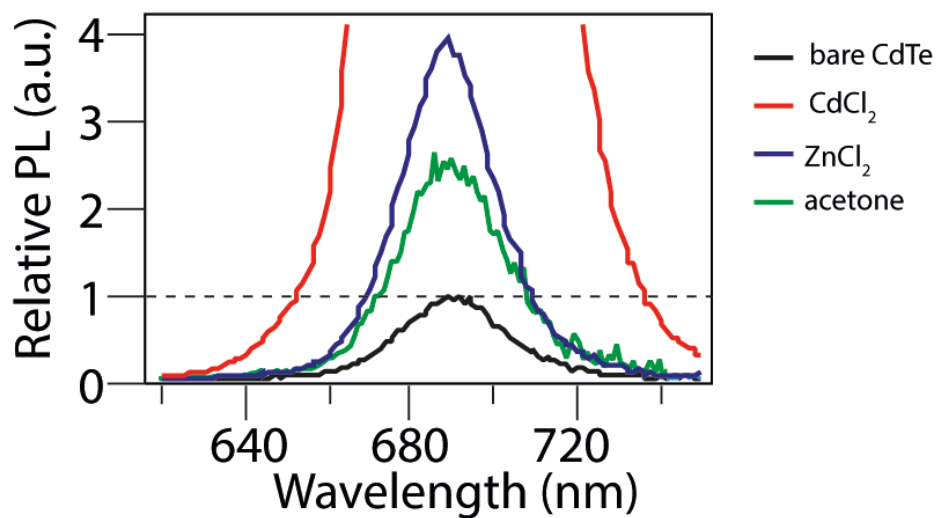
Figure S8. PL spectra of CdTe NC films before and after acetone only treatment (black and green line, respectively), compared to $ZnCl_2$ and $CdCl_2$ treatment (blue and red line, respectively).
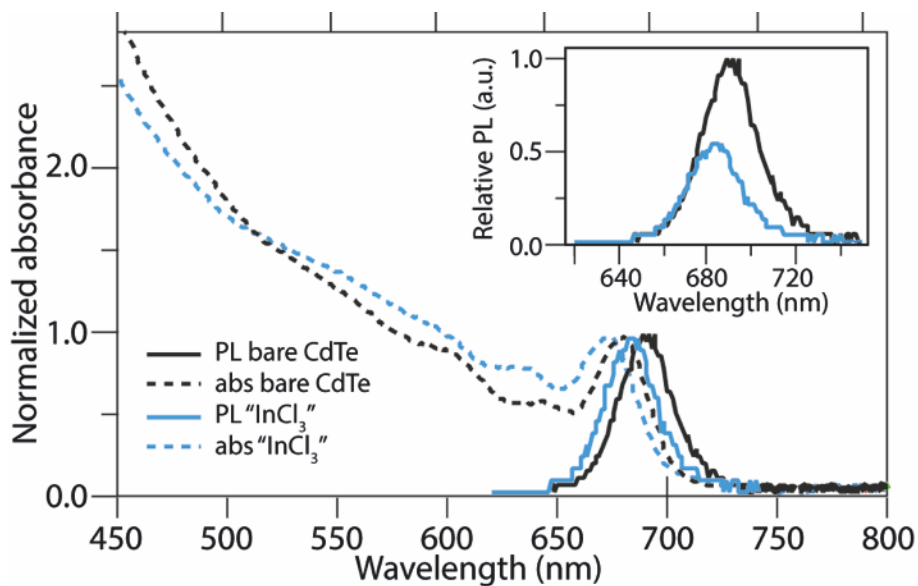

Figure S9. Absorbance and PL spectra of CdTe NC films after $InCl_3$ treatment.
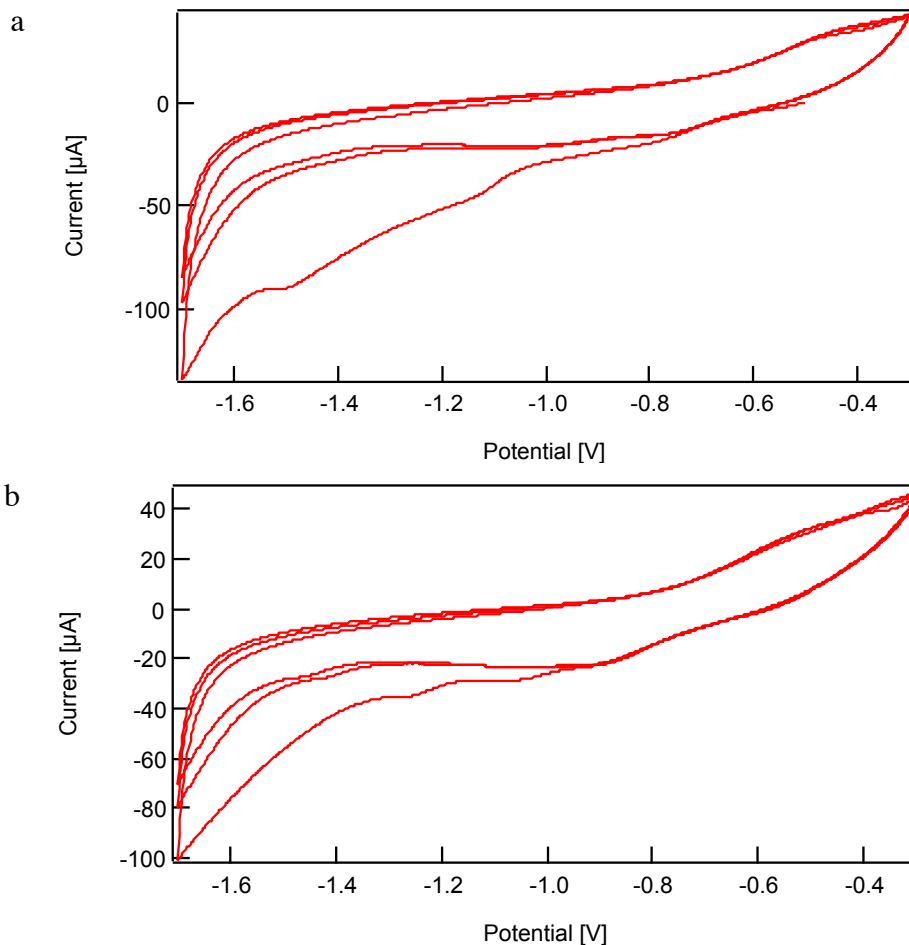
Figure S10. Cyclic voltammograms (CVs) after passivation with (a) CdCl$_2$ and (b) ZnCl$_2$.

2. Fit of the Stark shift feature in spectroelectrochemical measurements

A Stark shift of the 1S$_e$ absorption shifts the energy of the transition, changing its wavelength by λ_{shift}. The differential absorbance of a Stark-shifted 1S$_e$ feature, i.e. the difference between the absorbance at the currently applied potential and the absorbance at open-circuit potential in the presence of a Stark-shift, is obtained by a difference of two Gaussians:

$$F_2(\lambda) = A_2 * \left(e^{-\frac{(\lambda-\lambda_0-\lambda_{shift})^2}{2\sigma^2}} - e^{-\frac{(\lambda-\lambda_0)^2}{2\sigma^2}} \right)$$

where λ_0 and σ are respectively the central wavelength and the standard deviation of the unshifted 1S$_e$ feature. The parameter A_2 is the magnitude of the fitted function, related to the fraction of Stark-shifted QDs by the relation:

$$A_2 = A_0 f_{shift}$$

where A_0 is the steady state absorbance of the transition.

For small values of λ_{shift}/σ, F_2 can be approximated by the linear term of the Maclaurin expansion with respect to λ_{shift}/σ:

$$F_2(\lambda) \approx A_2\,\lambda_{shift} * e^{-\frac{(\lambda-\lambda_0)^2}{2\sigma^2}}\left(\frac{\lambda-\lambda_0}{\sigma^2}\right)$$

It is evident that for small values of λ_{shift}, a change in λ_{shift} and a change in A_2 produce the same variation of F_2, thus hampering extraction of reliable estimates of the two parameters from the fit (an increase in one can be compensated by a decrease in the other with negligible changes in the fitted function). It is rather their product, $A^* = A_2\,\lambda_{shift}$, whose best values is determined from a fit to the data.

If we assume that the amount of Stark shift is proportional to the average number of charges interacting with the Stark-shifted portion of the QD population, we obtain:

$$\lambda_{shift} = k_{shift}N_{charge}$$

$$A^* = k_{shift}N_{charge}A_0f_{shift} = k_{shift}A_0N_{traps}$$

where $N_{traps} = N_{charge}f_{shift}$ is the average number of trapped charges per QD. Thus, obtaining the potential dependence of A^* determines, within a proportionality factor, the potential dependence of the charged trap population.

In the fit to the spectroelectrochemical measurements, λ_{shift} was kept fixed and A_2 only was allowed to vary. Thus, the value of A_2 determined from the fit, $A_{2,fit}$, can be realted to the charged trap population per QD via:

$$A_{2,fit} = \frac{A^*}{\lambda_{shift}} = \frac{k_{shift}A_0}{\lambda_{shift}}N_{traps}$$

Thus, the fitted magnitude of the Stark shift feature is proportional to the number of trapped charges per QD, meaning the latter can then be determined within a proportionality factor from fit of the experimental data.
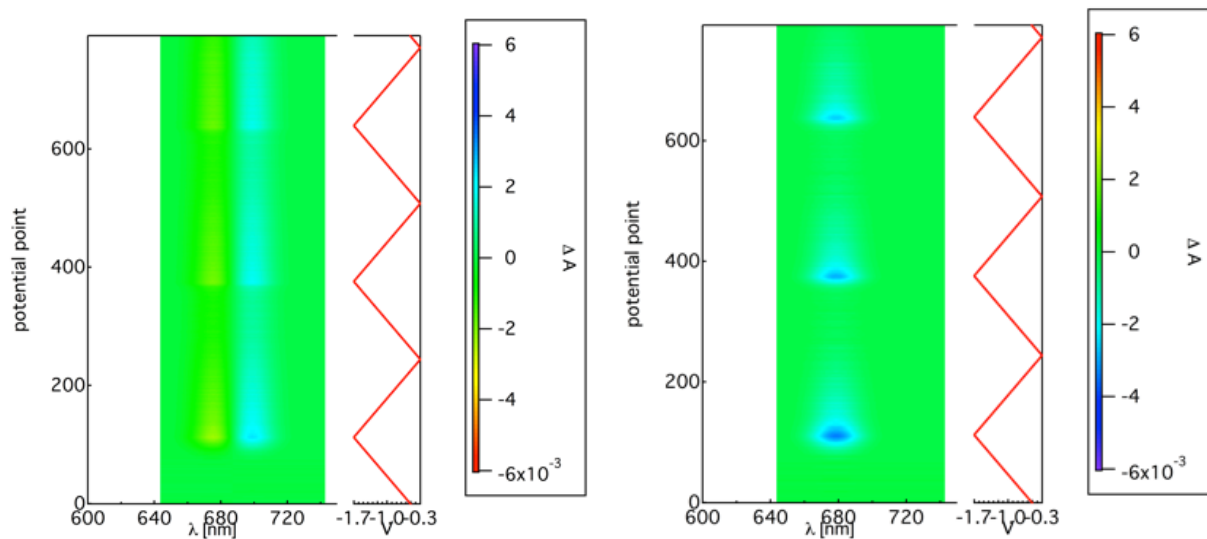
Figure S11. (a) Stark shift correction for ZnCl₂ treated CdTe NC films. (b) Effective bleach after correction.
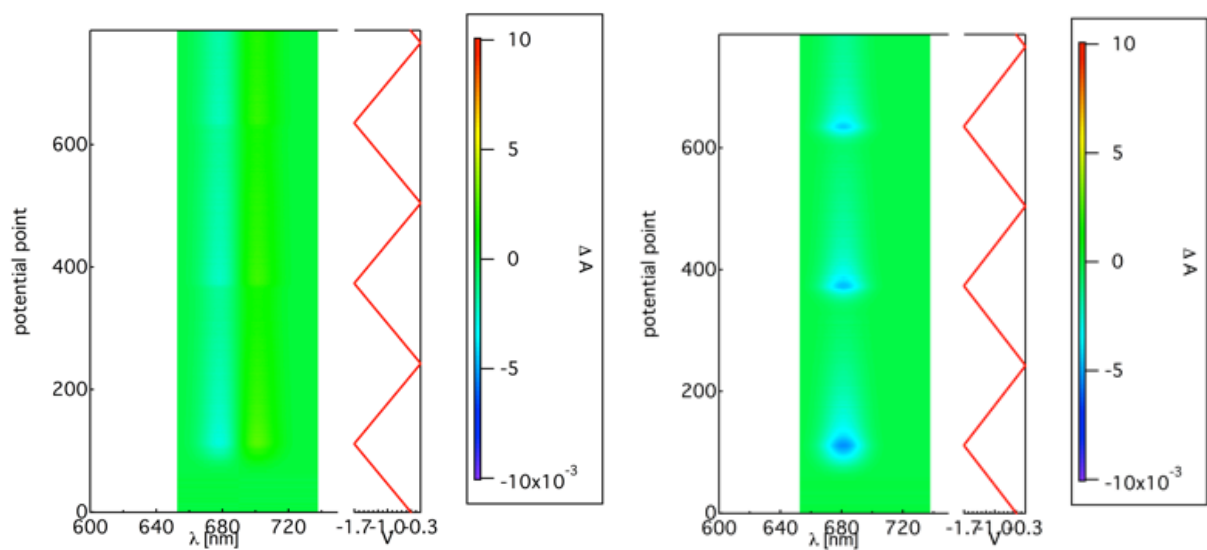

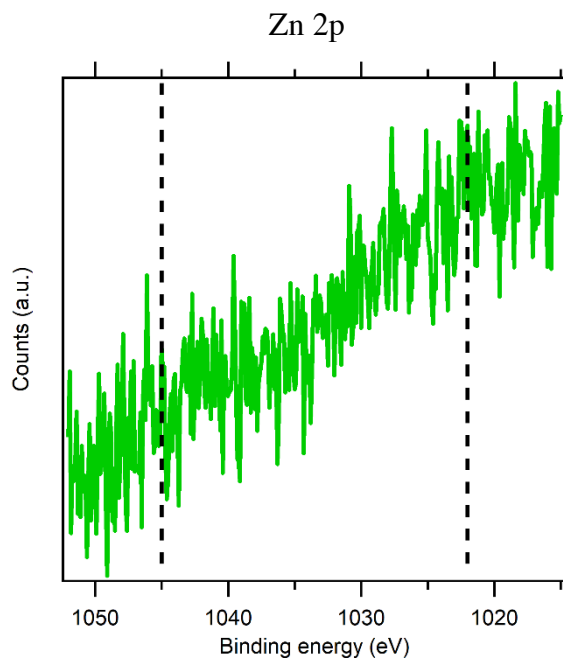**Figure S12.** (a) Stark shift correction for CdCl₂ treated CdTe NC films. (b) Effective bleach after correction.

Figure S13. XPS characterization of the ZnCl$_2$-passivated film. The dotted lines indicate the expected positions of the Zn 2p peaks.
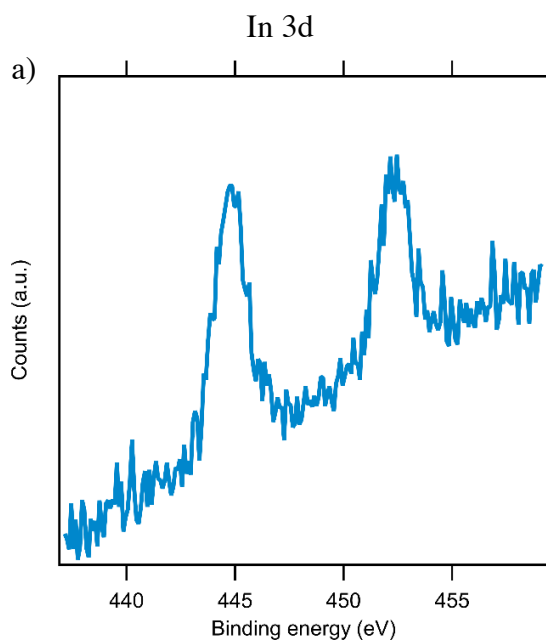

Figure S14. XPS characterization of the InCl$_3$-treated film. The In 3d peaks are clearly visible.

Supporting Discussion 1

Since the passivation of undercoordinated Te anions on neutral CdTe NCs with neutral Z-type metal chloride species will automatically retain charge balance, a balanced equation for this reaction can be easily constructed:

$$(CdTe)_{QD} + CdCl_2 \rightarrow (CdTe)_{QD}CdCl_2$$
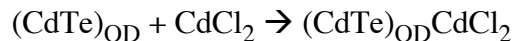
However, since we do not exactly know what causes the Cd-related trap state, we cannot provide an unambiguous equation for the reaction with chloride anions which ensures charge balance. We can construct equations taking one of the following assumptions into account: (1) The NCs are doped after the passivation with chloride ions, due to electron removal to ensure charge balance. (2) An ion pair is formed at the surface, possibly with protons or other cations. (3) Charge balance is not an absolute requirement at room temperature, and the NC can sustain a few charges. At this point, we cannot distinguish between these possibilities.