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Magneto-optical Properties of Trions in Non-Blinking Charged Nanocrystals Reveal an Acoustic Phonon Bottleneck.

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Abstract

Charged quantum dots provide an important platform for a range of emerging quantum technologies. Colloidal quantum dots in particular offer unique advantages for such applications (facile synthesis, manipulation and compatibility with a wide range of environments), especially if stable charged states can be harnessed in these materials. Here we engineer the CdSe nanocrystal core and shell structure to efficiently ionize at cryogenic temperatures, resulting in trion emission with a single sharp zero-phonon line and a mono exponential decay. Magneto-optical spectroscopy enables direct determination of electron and hole g-factors. Spin relaxation is observed in high fields, enabling unambiguous identification of the trion charge.

Importantly, we show that spin flips are completely inhibited for Zeeman splittings below the low energy bound for confined acoustic phonons. This reveals a characteristic unique to colloidal quantum dots that will promote the use of these versatile materials in challenging quantum technological applications.

Introduction

The excited (or trion) state of singly charged semiconductor quantum dots is one of the most useful states in nano-scale materials[1-4]. This state can provide many prototypical quantum optical systems, such as two level systems, which are useful for single photon sources[1,2] and three level systems useful for coherent control applications.[3] It also offers complete optical control and readout of the spin of a single charge,[4] useful for quantum information. The use of colloidal nanocrystals in such applications is still nascent, despite their rapidly maturing technology and wide compatibility with different photonic technologies and environments.[5]Charged nanocrystals (NCs) serve as the ideal system for investigatingcharge carrier spin properties. Such properties are crucial for applications, butso far, have only been indirectly investigated in CdSe NC ensembles[6, 7] yieldingresults that could not be reconciled with theoretical estimates.[8] In a charged NC,both the ground state and the band-edge excited state have an angularmomentum determined by a single charge carrier. Therefore, it is possible todirectly measure both the electron and hole g-factors using magneto-opticalspectroscopy, gaining access to information on spin relaxation. This latterproperty has special relevance for colloidal NCs, where

their finite size (usuallyless than 10 nm) results in discrete phonon modes[9,10]with a well-definedminimum energy (i.e. the maximum phonon wavelength must be smaller thanthe NC size).[11]At low temperatures, as long-wave acoustic phonons modescannot develop, relaxation between states with energy separations smaller thanthe lowest phonon energy should be inhibited, giving rise to an "acousticphonon bottleneck".[12] In contrast, widely studied self-assembled quantum dots (SAQDs) have aquasi-continuous acoustic phonon spectrum that contributes to phononmediatedspin relaxation.[13,14] The potential benefit of an acoustic phonon bottleneck would be the ability to operate quantum spin technologies with high external fields suitable for aligning and freezing random environmental spins (e.g. nuclear spins or magnetic defects) that otherwise cause spin decoherence.[15]Thus, ultimately confined acoustic phonon modes in NCs could provide a decoherence-free subspace for spin states, if this property can be harnessed.

Spin relaxation in colloidal NCs has been a subject of recent interest that has so far been focused solely on neutral NCs with spin relaxation inferred from detailed knowledge of the band-edge exciton fine structure. A series of ensemble measurements using polarization resolved heterodyned transient grating spectroscopy has uncovered a range of different spin relaxation process at room temperature, indicating spin relaxation occurs on sub-picosecond time scales.[16,17]Single nanocrystal spectroscopy at cryogenic temperatures revealed spin relaxation times between the lowest bright and dark states extended into the ns time scale[18-20]. However, in these cases, the energy difference between the exciton fine structure states is of the order of acoustic phonon energies in the system. In addition, spin relaxation between these states involves two spins

(electron and hole) which complicates the interaction. In comparison, spin flips between trion states involve only a single charge, which considerably simplifies the system.

While prospective trion properties in NCs bode well for quantumapplications, reports of emission from charged CdSe NCs[19,21-25] indicate that it iseither inefficient at room temperature or unstable (because the NCs randomlyswitch between the neutral and charged state). Stable trion emission has beenreported at low temperatures, however, NCs exhibiting this emission were rare.[24]In addition, spectroscopic identification of the trion charge was tentative,[19,24]relying on conflicting numerical simulations.[26,27] In all cases the reported trionemission was incidental. Measurements of NCs designed to reliably remaincharged and exhibit stable bright trion emission have not yet been reported.

In this article, we use an engineered synthesis of CdSe NCs with core and shell properties designed to promote efficient photo-chargingandstable trion emission at cryogenic temperatures. Dispersion of the NCs aspect ratio leads to trion emission covering a wide range of heavy hole and light hole mixing. We use magneto-optical spectroscopy to directly measure the electron and hole g-factors, for the first time. Relaxation of the trion spin identifies the trion charge. Spin relaxation is found to sensitively dependent on the magnitude of the Zeeman splitting, the onset of which displays a well defined threshold;the signature of an acoustic phonon bottleneck.

Results:

Engineering trion emission

We synthesize CdSe/CdS_4/ZnS_1core/shell/shell NCs to promotestable and efficient trion emission at cryogenic temperatures. A large NC core isused to minimize Auger effects,[28] a CdS shell promotes electron access to the NCsurface[23,29,30](figure 1a) and a thin ZnS shell improves chemical stability. A CdSezinc-blende crystal structure was chosen in order to allow investigations of NCs with varyingheavy-hole and light-hole influence (figure 1b-c). The exciton finestructure is calculated for a 5.4 nm width core(matching that determined from the synthesis sizing calibration), across an aspect ratio range determined by TEM analysis. The predicted energies closely match those found with these NCs, indicating that the core size predominantly defines the fine structure splitting in these nanoheterostructures. The synthesized NCs are easilyphoto-charged, (ie. they readily eject a charge carrier when excited above the band-edge using a 532 nm laser) resulting in efficient trion emission at cryogenic temperatures.An example of single NC photo-charging (transitioning from neutral to trionemission) is shown in Fig. 1d. We categorize two trions with different bindingenergies: ~20 meV for 90% of the NCs and ~2 meV for the remaining. Thequality of single NC trion emission is demonstrated in long periods of blink-freeshot noise limited emission (Fig 1e) that can continue for hours. Trion QYs closeto unity are indicated by an unvarying count rate for both neutral and trionemission in the weak pump regime as shown in figure 1d. Photon-correlationmeasurements under pulsed excitation (figure 1f) show that the chargedbiexciton is highly efficient (~80%) indicating that the emission from

both trioncharge species is efficient.[31] This suggests that the main NC ionization pathway is not Auger-assisted,[28] but most likely a tunneling process and hence dependenton the shell and surface properties.

Heavy hole and light hole spectra

Magneto-optical spectroscopy conclusively identifies the trion emission,as the absence of the electron-hole exchange interaction leads to the symmetricZeeman splitting of a single spectral line into either two, three or four spectrallines.[32] In figure 2a-d we show spectra of four different trions obtained under a 7T magnetic field, which reveal an evolution from four peaks towards three peaks.Prior to photo-charging, we could characterize the neutral emission[18-20]ofthree of these NCs (figures 2e-g) where the hole band-edge state (heavy-hole,light-hole) was identified by the angular momentum of the lowest energyexcitonic state.[33] The three-peak trion of figure 2a is associated with a light holewhere the lowest energy exciton state, 0^L, is dark and only appears with theapplication of a magnetic field.[33] The four-peak spectra of trions in figure 2b,ccorrespond to a "cross-over" regime of strong heavy hole/light hole mixing.[33]The last four-peak trion of figure 2d with depressed central peaks is consistentwith a heavy hole regime.[34] Electron and hole g-factors are determined bymeasuring the peak positions of the split trions (figure 2h). The data comprise g-factorsdetermined from 4-peak, 3-peak and 2-peak spectra. The electron g-factoris expected to be nearly isotropic,[34] which we associate to the minimalspread of the g_2 values indicating a single electron g-factor between 1.4 and 1.5.The hole g-factor (given by $g_1$values), on the other hand, is spread

between 0 and1.9.

The anisotropy in the hole g-factors can be understood in terms of the underlying valence band states, which are constructed from Bloch functions associated with p-like bonding orbitals and hence are 3-fold degenerate. The degeneracy is lifted by the NC shape anisotropy in the case of zinc-blende NCs, hence we expect the anisotropy of the hole g-factors to be associated with the shape of the NC and hence the magnitude of the g-factors can have an orientation dependence. The wide variation of hole g-factors plotted in Fig 2h is consistent with anisotropic hole wavefunctions.[35]Using the spectroscopic assignments of the neutral state[33] (as shown in Fig 2e-g), we can assign the various spectra to different aspect ratio regions. The red circles in Fig 2h are consistent with oblate NCs, which are dominated by heavy holes. In this case, a g-factor of zero is predicted when a crystallographic axis is perpendicular to the magnetic field.[8]The blue squares correspond to NCs, which split into 4 peaks and reveal hole g-factors tightly clustered around a value of 0.75. These g-factors are associated with predominately spherical zinc-blende NCs, which places them in the regime of maximal heavy hole/light hole mixing where the hole wavefunction becomes approximately isotropic. Finally, the data from 3-peaked trions originate from prolate NCs, which are increasingly dominated by light hole properties and thus should be more dispersed.[8] Overall, our measurements provide a direct route to determining single charge g-factors, which now enables unambiguous assignment of g-factors extracted from indirect ensemble measurements.[6,7]

Trion charge assignment

Asymmetry in the peak heights of the trion Zeeman spectra arises fromspin relaxation in the excited state. Observation of symmetric Zeeman spectra is indication of spin relaxation much slower than the trion lifetime (see discussion). Otherwise the asymmetry of the two innerpeaks resulting from significant spin relaxation will depend on the trion charge and relative g-factor magnitudes. For 4-peak spectra, $g_e > g_h$(squares in figure 2h), the asymmetry of the inner peaks canidentify the trion charge (see Fig. 3a,b). In Figs 3 c-d we show two examples of 4- peak trion lines at 7 T. Amongst the ~100 NCs we have analyzed, 3 NCs had an asymmetry associated with positive trions (fig 3c) and7 NCs displayed the asymmetry associated with negative trions (fig 3d). All spectra that exhibited a small binding energy displayed the asymmetry of a negative trion and conversely all the spectra that exhibited a large binding energy displayed the asymmetry of a positive trion. We note that most of the trions with large binding energy (positive trions) show no visible peak height asymmetry, indicating that the electron spin relaxation is likely to be slow in these systems. On the contrary, all negative trions exhibit clear peak height asymmetries, indicating that hole spin relaxation is more efficient. As 90% of the NCs display large trion binding energies, charge identification indicates that electron ejection is the dominant ionization path in these NCs, validating our design criterion. Indeed, it has been shown that holes are predominantly trapped in interfacial defects,[36] which should be rare in NCs with good crystal quality. For our core/shell/shell NCs, CdS provides only a ~4% lattice mismatch with CdSe, which facilitates good epitaxial continuation of the crystal structure.[37,38]While boundary strain may cause slight energy shifts,[38] the high quantum yield of these NCs is indicative of a continuous

crystal structure,[37] precluding the presence of dangling bonds that can trap a charge carrier. As the hole is predominantly confined within the CdSe core, a lack hole traps at the core/shell interface can explain the low occurrence of negative trions in our NCs.

An acoustic phonon bottleneck

Acoustic phonon-mediated spin relaxation should be strongly influencedby the discrete phonon-mode spectrum, which has a low energy bound imposedby the size of the NCs (total diameter ~10 nm). In the trion spectrum of figure 4a, the first acoustic phonon line is clearly resolved at an energy 650μeV below the trion zero phonon line. Using an average longitudinal sound velocity for the core/shell composite material, we estimate the lowest l=2 acoustic phonon energy as 600 μeV for a 10 nm NC, which is close to the observed phonon line. In addition, we resolve two more acoustic phonon peaks including a dominant peak, which is generally attributed to the l=0 breathing mode.[9,10] The relative position of the phonon peaks confirm the previous assignment (see methods), avoiding size dependent material properties.[39]

Spin relaxation should depend on the magnitude of the applied magnetic field since the lowest energy l=2 phonon mode energy is comparable to the Zeeman splitting found at 7 T. For small Zeeman splittings relaxation between the two spin states via the emission of a single acoustic phonon would violate energy conservation (see diagram Fig 4b), which represents the acoustic phonon bottleneck. In Fig. 4c we show an example of a trionspectra splitting with increasing magnetic field. The peak positions found fromfitting the spectra are plotted in Fig. 4d, revealing four trion transitions.Noticeably, at fields below 6 T,

the spectra appear symmetric, with a peak heightasymmetry marking the onset of spin relaxation. In Fig 4e we plot the ratio of thehigher energy to lower energy side-peak heights, *r*, as a function of the splittingenergy. As these two side transitions have the same emission rates and the samepolarization, *r* is simply the ratio of the two excited state spin populations. Up toa splitting of 300 μeV the two populations are approximately equal, indicating aspin relaxation time longer than the trion lifetime. An upper bound for the spin decay rate determined by the precision for estimating *r* (~5%) is ~0.005 ns^{-1}. Above 300 μeV spin relaxation increases quickly to a rate comparable to the trion recombination rate (~0.25 ns^{-1}).

We fit the data with a thermal mixing model[18,19]that includes a spontaneous decay rate that depends on a phonon density of states, $\rho(E)$(as given by Fermi's golden rule),

$$r = \frac{n\rho(E)\gamma_0 + 0.5\Gamma}{(n+1)\rho(E)\gamma_0 + 0.5\Gamma}, \qquad (1)$$

where the product, $\rho(E)\gamma_0$ is the spontaneous spin-flip rate, Γ is the trion recombination rate and*n* is the Bose-Einstein occupation number for phonons with energy *E* equal to thesplitting energy. In the fit to the data we use a density of states (shown as a reddotted curve in the figure 4e) centered on the low energy acoustic phonon line ofthe inset of figure 4a. For comparison, the black dashed curve shows *r* calculatedusing a constant spontaneous decay rate. While a constant spontaneous decay rate explains the behavior observed in CdSe SAQDs,[13] it clearly does not fit our data.

Discussion

The demonstration of stable trion emission via a photo-charging route highlights the role of NC heterostructure engineering in modifying photophysical properties of these materials. This is particularly relevant to NC dynamics, as transitions to the trion state have been held responsible for photoluminescence blinking.[40] This random charge ejection/recombination cycle has even been observed in a recently reported "lifetime blinking" in non-blinking giant NCs.[25] Here we are able to promote the NC to emit solely from its trion state, resulting in "true" non-blinking behavior; that is continuous emission from a *single* state of the system.Furthermore, we have shown that both trion charge states and concomitantly their charged biexcitons have high luminescence quantum yields, contrary to observations at room temperature,[25] indicating that Auger recombination is inefficient in these materials. Thus the photo-charging mechanism of our NCs can be attributed to a tunneling process, which has significant implications for alternative photoluminescence blinking mechanisms.[41,42]

Another interesting consequence of NC engineering is revealed in the g-factor measurements. The useof a symmetric zinc-blende crystal lattice enabled us to test the different influences of heavy holes and light holes arising from natural variations in the NC shape. NCs exhibiting 4-peaked trion spectra in a magnetic field were identified as corresponding to those with aspect ratios close to unity (spherical), which corresponds to a region of maximal heavy hole/light hole mixing. These NCs displayed a remarkable property;approximately

isotropic electron and hole g-factors. Thus we find that spherical zinc-blende NCs effectively overcome the orientation sensitivity of colloidal nanoparticles for which the control of orientation is extremely challenging.

We have also demonstrated an exciting property of colloidal NCs that sets them apart from other quantum dots: An acoustic phonon bottleneck that inhibits spin relaxation. This property arises purely due to their finite nanometer size, which results in a low energy cutoff for acoustic phonon modes. This is the acoustic equivalent to the inhibition of spontaneous emission in cavity quantum electrodynamics, and like its optical equivalent, should promote new research directions with these materials. In particular, the potential to operate at higher magnetic fields without incurring acoustic phonon-induced spin relaxation should be beneficial in stabilizing the spin state against perturbations from environmental nuclei, resulting in longer spin coherence times.[15] Thus colloidal NCs offer the possibility to considerably extend the operating parameter space for spin-based technologies. The next step will be the study of the ground state of charged NCs. Overall, this realization of a long heralded beneficial finite size effect in *single* NCs will promote further investigation and open these materials to new applications inquantum information.

Methods:

The $CdSe/CdS_4/ZnS_1$NCs were synthesized in two steps:

Zinc blende CdSe cores:[43]

A cadmium oleate (Cd-OA) stock solution was prepared by first

degassing9.3mmol (1.2g) of CdO and 106mmol (30g) of oleic acid in 120g of 1-octadecene(ODE) at 100°C for 30 minutes. This solution was heated to 300°C under nitrogenuntil it became transparent and homogeneous. The Cd-OA solution was thencooled to 100°C and degassed for a further 30 minutes to remove any residualwater formed during the reaction. The selenium precursor (TOP-Se) wasprepared by dissolving 0.47mmol (0.037g) of selenium in 3.1mmol (1.16g) oftrioctylphosphine by sonicating and mixing using a vortex mixer before adding5.25g of ODE.

The CdSe cores were prepared by rapidly injecting a TOP-Se solution into 7.5g ofthe Cd-OA stock solution at 300°C under nitrogen, after which the temperaturewas allowed to drop to 230°C for the growth of crystallite. The growing processwas monitored using absorption spectroscopy and the reaction was quenched,by removing it from heat, once the first exciton peak reached 614nm for adesired QD diameter of 5.25nm.The QDs were purified using a liquid-liquid extraction process using acombination of methanol, chloroform and acetone to remove excess surfactants.The purified QDs remained in the ODE layer for shelling.

CdSe/CdS/ZnS core/shells:

The graded-seal shelling process was adapted from the successive ion layeradsorption and reaction (SILAR) method.[44] The required amount of washed coreparticles in ODE was added to a three-necked round bottom flask along with amixture of ODE/octadecylamine (ODA) in a 2.5:1 ratio by weight in order toproduce a 40μM dispersion of NCs. The mixture was degassed at 80°C for 20minutes, pump/purged three times and then heated to 230°C for shell

growth.The calculated amounts of the injection solutions were then added in sequentialorder beginning with cadmium. Each metal and sulfur injection was allowed toreact for 20 and 15 minutes respectively. The growth temperature was graduallyincreased by 5°C for every metal layer added. Once the final zinc layer wasinjected, the reaction solution was then annealed at 200°C for one hour. The finalQD core/shells have 4.5 monolayers of CdS and 1 monolayer of ZnS and are 8.7nmin diameter. They were again purified using the liquid-liquid extractiontechnique, and then finally separated from ODE using excess acetone andcentrifugation. The resulting pellet was redispersed in toluene for spectroscopymeasurements.

Cryogenic characterization:

For cryogenic study, samples were prepared by spin coating clean glasscoverslips with approximately nano-molar solutions of NCs into a polymethylmethacrylate matrix. A scanning confocal microscope was used to image singleNCs excited with the 532 nm line of a cw frequency doubled Nd:YAG laser. It isbased on a 0.95 numerical aperture objective housed in a magnetic cryostatcapable of operation up to 7 Tesla. The sample was mounted on top of apiezoscanner used for raster scanning and for precise NC positioning on theoptical axis. The objective axis was perpendicular to the magnetic field, allowingmagneto-optical studies in the Voigt configuration. The emitted photons werefiltered from the scattered excitation light by a band-pass filter (60 nm FWHM)and sent to 30/70 beam splitter that sends the emission to a single photoncounting avalanche photodiode (APD) and a spectrometer (1800

lines/mmgrating, focal length 500 mm with a measured spectral resolution of 120 μeV)respectively. Unless otherwise stated, spectra were obtained at 2 K with a pumpirradiance of 25 W/cm2 and a 20 s integration time. Single NCs were selected fortheir spectral and photophysical stability.

For the $g^{(2)}(\tau)$ measurement, the spectrometer was replaced by a secondAPD with the outputs from both APDs being sent to a time-correlated singlephoton counting card, providing both the start and stop pulses. A picosecondpulsed laser pumps a frequency doubled optical parametric oscillator to providea 76 MHz pulse train of ~ 2ps pulses at 570 nm. A pulse picker was used toreduce the pulse frequency to 7.6 MHz for the experiment. Residual coincidencesinvolving background photons were negligible in $g^{(2)}(\tau)$ histograms due to thehigh signal-to-background ratio.

Modeling details:

The radial wavefunctions plotted in figure 1a were obtained by solvingthe radial wave equation by mapping onto the 1-D wave equation via, $r\,\psi(r) \rightarrow \psi'(x)$. The solutions of the 1-D wave equation are trivial, however, theboundary conditions must include $\psi'(0) = 0$, as the wavefunction must be finiteat the origin. In addition due to the different charge carrier effective masses indifferent regions of the NC, the lowest energy eigenvalue is proportional to $u^2$and found as the lowest energy solution to the equation, $u\cot u = \sqrt{m_1/m_2}\sqrt{u_0^2 - u^2}$, where $m_1$and $m_2$are the effective masses of thecharge

carrier in the regions on either side of the heterojunction. The effectivemasses and potentials used in the solution were, CdSe: m_e=0.13, m_{hh}=0.9,m_{lh}=0.19, V_e=V_h=0. CdS: m_e=0.2, m_h=0.8, V_e=0.19, V_h=0.55. ZnS: m_e=0.28,m_h=0.57, V_e=0.9, V_h=0.9. Ligand shell: m_e=m_h=1, V_e=V_h=10.

The exciton fine structure for CdSe NCs with a zinc-blende crystalstructure was adapted from the theory of Efros et al.[35]by neglecting the crystalfield splitting term and substituting the band-edge effective mass parametersappropriate for the zinc-blende structure.[45] The eigenvalue solutions aremodified in order to express them in terms of the aspect ratio for ellipsoidalperturbations for a constant radius parameter, *a*.

In order to estimate the energy of the lowest *l*=2 acoustic phonon mode,in a composite core/shell NC, we use the estimates of the core size (5.3 nm) andtotal NC size (10 nm) to calculate the ratio of the core to shell material.Considering only the CdSe core and the CdS shell, the NC comprises ~85% shell,so the longitudinal sound velocity is estimated as a weighted average of v_L=3559 m/s and 4289 m/s for CdSe and CdS respectively. The *l*=2 mode frequencyis then calculated according to, $\omega_{02} \approx 1.09\, v_L / R$, where *R* is the radius.

Identification of the acoustic phonon peaks is also conducted in fashion that is independent of the NC size and absolute elastic properties, assuming only that the *ratio* of the longitudinal to transverse sound velocities remain constant. The material properties of CdSe and CdS are such that the ratio of the longitudinal to transverse sound velocities is nearly equivalent in the bulk

materials.[46] This means the solutions for the acoustic phonon energies will have a common scaling factor. Thus we can write the size dependent energy for the following three acoustic phonon modes as,

$\omega_{02} \approx 1.09\, v_L/R,\ \omega_{12} \approx 2.10\, v_L/R,\ \omega_{00} \approx 2.86\, v_L/R,$ representing the first two l=2 modes and the l=0 breathing mode respectively. Any ratio of these energy solutions will be independent of the NC size and material properties, providing a robust fingerprint of the mode structure, which is used to identify the acoustic phonons observed in Fig 4a.

The density-of-states function used in fitting the rate equation model (eq. 1) to the acoustic phonon bottleneck data was approximated by a Voigt functioncentered on the l=2 acoustic phonon energy (650μeV). A good fit was only possible with asmall Lorentzian width of 2 μeV and a 120 μeV Gaussian width.

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Author contributions

PT and BL conceived the experiments. MJF, YL,CS and PT conducted the experiments. MJF and PM designed the NCs. CP synthesized the NCs. TLN conducted TEM. MJF, CS analyzed the results. MJF and BL wrote the manuscript. BL supervised the project.

Competing financial interests

The authors declare no competing financial interests.

Figure captions:

Figure 1: Designing CdSe nanocrystals (NCs) for efficient trion emission (a) Radial electron and hole wavefunctions (heavy hole hh and light hole lh) for a 5.25 nm spherical CdSe core with a two-part shell consisting of 4 monolayers of CdS and 1 monolayer of ZnS. The relative confinement potentials are also indicated (dashed). (b) The band-edge fine structure calculated for a CdSe NC with a 5.4 nm zinc blende core verses aspect ratio (for ellipsoidal perturbations). The angular momentum of the states is indicated in the figure. Dark states are indicated by dotted lines. (c) Transmission electron microscope image of the $CdSe/CdS_4/ZnS_1$ NCs with an approximately spherical shape with a mean diameter of 10 nm(a 20 nm scale bar is indicated). (d) Single NC spectra before (X) and after (T) photo-charging. The accumulated photocounts for each spectrum are equivalent indicating unity quantum yield of the trion (obtained at 2 K and 125 W/cm^2 pump irradiance). (e) Typical time trace of trion emission obtained from a single NC (50 ms time resolution) at 2 K showing blink-free shot noise limited emission over 5 min. The red dashed curve is the Poisson distribution calculated using the mean counts/time bin. (f) $g^{(2)}(\tau)$ measurement of a single NC trion emission under pulsed emission at 570 nm and 20 K. A pulse irradiance of 68 $\mu J/cm^2$ corresponds to a mean number of excitations per pulse of $\langle N \rangle \approx 0.1$. The fit is a sum of three two-sided exponentials corresponding to a trion lifetime of 4.8 ns.

Figure 2: Splitting of the trion line at 7 Tesla (a)-(d) Trion spectra from 4 individual NCs. (a),(b) and (c) have associated neutral spectra (e), (f) and (g) respectively. The neutral spectra are assigned according to the spectroscopic identifications previously

reported in reference 33. The four peaked spectra are consistent heavy hole (right) or mixed heavy hole/light hole trions (according to the neutral spectra). The three peaked splitting is matched to the light hole trion due to the neutral exhibiting a lowest energy 0^L dark state.[33](h): Splitting energies obtained from 27 nanocrystals and expressed as g-factors according to $g_i = \Delta_i / \mu_B B$, μ_B is the Bohr magneton and the applied magnetic field B=7T. The data are characterized by nanocrystals that split into two peaks (circles), three peaks (triangles) and four peaks (squares). The measurement protocol is depicted in the inset diagram.Note the error in each measurement is approximated by the size of the markers.

Figure 3: Identification of trion charge (a) Relaxation scheme for a positive trion with Landé factors $g_e > g_h$ and resultant anisotropic spectrum below. (b) Relaxation scheme for a negative trion with $g_e > g_h$.and resultant anisotropic spectrum below. (c) An anisotropic 4-peak spectrum from a positive trion. (d) An anisotropic 4-peak spectrum from a negative trion. Corresponding binding energies, E_b and spin-flip rates, γ are indicated.

Figure 4: An acoustic phonon bottleneck (a) Trion spectrum at 2 K and 0 T obtained with a 125 W/cm^2, revealing the lowest energy *l*=2 acoustic phonon replica (α), the second order *l*=2 mode (β) and the radial breathing mode (γ). (b) Illustration of the acoustic phonon bottleneck effect. Zeeman splittingas a function of magnetic field. Spin relaxation commences (red shaded region) for Zeeman splittings approaching the first acoustic phonon mode energy (blue shaded region). An acoustic phonon bottleneck inhibits spin relaxation in the unshaded region inside the graph.(c) Splitting of the trion line with increasing

magnetic field (fitting is used to determine the peak positions – dashed). (d) The peak positions determined by fitting the spectra in (c). Note the error in each measurement, ±20 μeV, is approximated by the size of the markers. (e) Relative population of the higher energy spin state, *r*, as a function of the splitting energy. A fit to the data (solid line) is provided using a thermal mixing model with a density of states, $\rho(E)$.The $\rho(E)$function,shown by the red dotted curve,is a Voigt profile centered at the position of the lowest energy acoustic phonon mode (650μeV) with a width of ~120μeV. The expected behaviour for a constant spin relaxation rate is also indicated (dashed line).