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Exciton–Ligand Interactions in PbS Quantum Dots Capped with Metal Chalcogenides

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ABSTRACT: Colloidal quantum dots (CQDs) are typically decorated with organic molecules that provide surface passivation and colloidal solubility. An alternate but less studied surface functionalization approach *via* inorganic complexes can produce stable CQDs with attractive transport and optical properties. Further development of such all-inorganic CQD solids is dependent on the deeper understanding of the energetic and dynamic interactions of the new ligands with the CQD excitons. Herein, a series of four metal chalcogenide (MCC) ligands of the K_2XS_4 type were attached to PbS CQDs. Out of the four MCC complexes studied, we find that only K_4GeS_4 ligands yield robust PbS CQD films with bright photoluminescence (PL) in the solid state. A systematic spectroscopic investigation of the K_4GeS_4 -capped CQD films provides evidence of the temperature-dependent ligand-mediated exciton delocalization and trapping processes. At low temperatures, efficient trapping at ligand-induced states is found to occur within ~ 6 ns after photoexcitation, followed by a considerably slower exciton back transfer to the CQD core. At elevated temperatures, the CQD films become photoconductive, providing evidence of exciton dissociation *via* carrier transfer within adjacent dots. The addition of a thin CdS shell suppresses the delocalization and trapping of excitons, resulting in brighter emission and significantly slower transient absorption and PL dynamics.

INTRODUCTION

Colloidal quantum dots (CQDs) are solution-processed semiconductors with versatile optoelectronic properties that can be tailored by their nanoscale size, shape, and composition.^{1,2} In parallel to developments in their synthesis that allow precise control of their structural characteristics producing high quality, monodisperse particles, a surge in surface chemistry research³ has enabled efficient sensitization of the CQD surface by conductive surfactant molecules, producing electronically active CQD solids.^{2,4–6} A promising surface functionalization approach was demonstrated in 2009, employing a liquid-phase ligand exchange process to yield stable colloids in polar solvents with small metal chalcogenide (MCC) complexes replacing the organic surface ligands.⁷ The technique had soon evolved into a surface-functionalization route for CQDs by a variety of inorganic and hybrid complexes that include MCCs, halides, oxo-anions, and oxo- or halo-metallates.^{8–35} Some of the most notable successes have been demonstrated in structures employing MCC-capped CQDs

including high-mobility transport,^{9,21,25–28} photoconductive devices,^{22,29,33} and highly luminescent CQD–chalcogenide matrixes.^{23,34,36} Furthermore, more recent work demonstrated that utilization of a host–guest chemical approach can successfully extend the solubility of such inorganic-capped CQDs to solvents of any polarity, improving their solid-state handling and paving the way toward long-range ordered MCC-capped CQD superlattices.³⁷ Such impressive attributes combined with the high MCC molecular linking ability⁹ and their overall versatile chemistry allowing the development of various materials and phases,³⁸ nominate chalcogenidometal-

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lates as an attractive capping ligand of choice for metal and semiconducting CQDs.

Further development of such chalcogenidometalate-capped CQDs relies on a deeper understanding of the energetic and dynamic interactions of excitons and MCC ligands. Various studies have reported on the significance of electronic and/or vibrational coupling of the core and ligand states on the CQD exciton energetics and dynamics.^{39,40} The great majority of the work focused on the impact of organic or organometallic ligand complexes on the optoelectronic properties of CQDs as reported in the seminal review by the Weiss group,⁴⁰ while the influence of CQD excitons on the ligand vibrational properties has also been recently explored.^{41,42} Less is known about the impact of inorganic ligands, especially in the solid state, with reports on MCC–CQD interactions that result in ligand-induced exciton delocalization,^{7,15,25,43,44} photoluminescence (PL) quenching,^{7,16,43} dielectric screening,²³ and electron^{16,29} and hole^{23,45} trapping.

In the present work, we study PbS CQDs that are decorated by a series of MCC complexes of the K_2XS_4 type, with K^+ as a cation, and X being Ge, Sn, As, or Sb. Four complexes, namely, K_4GeS_4 , K_4SnS_4 , K_3AsS_4 , and K_3SbS_4 , appear to yield stable PbS CQDs in polar solvents. In the solid state, however, we find that only K_4GeS_4 ligands produce robust films that retain bright luminescence. Furthermore, K_4GeS_4 -capped CQDs appear well suited to study the inorganic core–inorganic surface interactions, as exciton recombination channels are found to occur relatively slowly within the nanosecond regime and can be clearly resolved by transient luminescence. Optical spectroscopy provides evidence of two, low-temperature, ligand-mediated exciton recombination processes, namely, exciton trapping occurring within few ns after photoexcitation and exciton back transfer to the CQD core that takes place at significantly longer timescales. The two processes compete with intrinsic core exciton recombination, with the efficiency and dynamics of the competition influenced by temperature. At room temperature (RT), a third process of exciton breaking via interdot charge transfer is witnessed by photo-current measurements, confirming the electronic linking of the CQDs via the MCC ligands. When PbS QDs are coated with a thin CdS shell, trapping and delocalization of excitons mediated by the K_4GeS_4 ligands is suppressed, resulting in significantly brighter emission and longer transient absorption and PL dynamics.

METHODS

Synthesis of PbS CQDs. *Materials.* CdO (Aldrich, 99.99%), $PbAc_2 \cdot 3H_2O$ (Aldrich, 99.99%), hexamethyldisilathiane (TMS_2S , Aldrich), oleic acid (OA, 90%, Aldrich), 1-octadecene (ODE, 90%, Aldrich), methanol (Aldrich, 98%), hexane (>95% Sigma-Aldrich), ethanol (99.8%, Fluka), toluene (99%, Fischer), acetonitrile (MeCN, 99.9%, Sigma-Aldrich), *N*-methyl formamide (MFA, 99%, Aldrich), dimethylformamide (DMF, 99.8%, Sigma-Aldrich), potassium sulfide (K_2S , 99.5%, Strem), germanium(II) sulfide (GeS , 99.99%, Aldrich), sulfur (99.998%, Sigma-Aldrich), C_6D_6 (99.9%, CIL), and DMSO- d_6 (99.9%, CIL) were used as received.

Synthesis. PbS and PbS/CdS core/shell CQDs were synthesized using the hot injection method according to the literature.²³ In a three-neck reaction flask, $PbAc_2 \cdot 3H_2O$ (2 mmol, 0.758 g), ODE (20 mL), and OA (2.25 mL) were dried at 100 °C under vacuum for 2 h to dissolve lead salt and to dry the solution. The temperature was raised to 140 °C. In a

glovebox, a sulfur precursor solution was prepared by mixing TMS_2S (0.21 mL, 1 mmol) with ODE (10 mL). The sulfur solution was quickly injected into the reaction flask at 145 °C, followed by the removal of the heating mantle for 3 min and cooling to RT in a water bath. The washing procedure was carried out in air. Hexane (20 mL) and ethanol (40 mL) were added to the crude solution, followed by centrifugation to separate the CQDs. The obtained PbS CQDs were redispersed in hexane (20 mL) and again precipitated with ethanol (15 mL). After one more washing step with ethanol/hexane, the particles were redispersed in toluene (6 mL).

In a second flask, CdO (1 g, ~7.8 mmol), OA (6 mL, ~18.9 mmol), and 20 mL ODE were heated to 200–250 °C until the solution turned colorless. The solution was cooled to 100 °C and dried under vacuum for 30 min. The temperature was further decreased to 100 °C, and 12 mL of PbS NCs were added via a syringe. The solution was maintained at 100 °C for 45 min and then cooled to RT. To wash PbS/CdS CQDs, ethanol was added to precipitate the CQDs. The precipitate was redispersed in toluene and again precipitated with ethanol. The redispersion/precipitation procedure was repeated three times. High-resolution transmission electron microscopy (HRTEM) images from the two CQD materials are displayed in Supporting Information Figure S1. The presence and crystalline phase of the CdS shell was confirmed via X-ray diffraction experiments presented in Supporting Information Figure 2.

Ligand Preparation and Ligand Exchange. $(NH_4)_3AsS_3$ was synthesized according to ref 16. K_4GeS_4 was prepared by dissolving 0.104 g GeS in a solution containing K_2S (0.27 g), 0.064 g of S, and 10 mL H_2O at 50 °C. SnS_2 was prepared according to ref 7. K_4SnS_4 was obtained by combining K_2S (0.22 g, 2 mmol) and SnS_2 (0.183 g, 1 mmol) in 4 mL of water (stirring for 4 h at RT). K_3AsS_4 was prepared by combining As_2S_5 (0.310 g, 1 mmol), K_2S (0.33 g, 3 mmol), and 10 mL of H_2O at RT. K_3SbS_4 was prepared by dissolving Sb_2S_3 (0.339 g, 1 mmol) in a solution containing K_2S (0.33 g, 3 mmol) and S (0.064 g, 2 mmol) in 10 mL of H_2O at RT. For all these compositions, the pure compound was isolated by adding acetone (40 mL), followed by three rinses with acetone and vacuum-drying.

In a typical organic-to-inorganic ligand exchange, 0.14 mmol of K_4GeS_4 (or K_4SnS_4 , K_3AsS_4 , or K_3SbS_4) was dissolved in 10 mL of MFA, and 1 mL of PbS/oleate or core–shell PbS/CdS/oleate (40–55 mg) was carefully dispersed in 10 mL of hexane. The mixture was stirred for 1 h until the hexane is completely clear (Supporting Information Figure S3), and the solution was rinsed three times with hexane. PbS/ K_4GeS_4 (or K_4SnS_4 , K_3AsS_4 , or K_3SbS_4) were filtered and precipitated with an acetonitrile/toluene (2:1) mixture. For $(NH_4)_3AsS_3$, the procedure followed is described in ref 16.

Film Deposition. To deposit the films under study, material solutions with concentration of 30 g/L were prepared. The films were deposited under ambient conditions on ~1 cm² square quartz substrates using spin-coating at 1500 rpm for 1 min or doctor bladed at 90 °C and a speed of ~2 mm/s.

Structural Characterization. *Transmission Electron Microscopy.* TEM images were recorded using a JEOL JEM-2200FS operated at 200 kV and with a double aberration-corrected FEI Themis Z, operated at 300 kV. High-angle annular dark-field STEM images were recorded with a probe current between 50 and 200 pA.

Figure 1. 3D AFM topography images of (a) oleate-capped PbS QD and (b) GeS_4^{4-} -capped PbS QD films. A similar surface roughness of ~ 3 nm is estimated from the images. Optical properties of oleic acid (OA)-, GeS_4^{4-} -, and As_2S_3 -capped PbS CQD films: (c) absorbance, in the exciton spectral range; for the As_2S_3 -capped CQDs, a pronounced Urbach tail is observed, implying a wider trap distribution in such systems. Comparative PL under (d) UV (375 nm) and (e) near-IR (785 nm) excitation. In all cases, GeS_4^{4-} -capped CQDs exhibit brighter emission compared to the reference As_2S_3 -capped material. (f) Time-resolved PL decays obtained at the PL peak for the three samples. (g) Transient pump-probe transmission monitoring the exciton bleaching region; state filling is observed only for the reference and GeS_4 -capped samples.

Atomic Force Microscopy. Atomic force microscopy (AFM) was carried out using a Nanosurf Easyscan2 AFM system in the tapping mode with TapA1190-G cantilevers (BudgetSensors). All measurements were taken at RT and under ambient conditions, and the images were processed using Gwyddion open source data analysis software.

Optical Spectroscopy. Film steady-state absorbance was carried out using a PerkinElmer Lambda1050 UV/vis/NIR spectrophotometer. Steady-state PL was performed in a Fluorolog iHR320 HORIBA Jobin Yvon spectrometer equipped with an infrared photomultiplier tube. All the PL spectra were acquired using 25 mW/cm^2 excitation by a 785 nm laser diode apart from the PL data presented in Figure 1b where a 375 nm, 5 mW/cm^2 laser diode was used, instead. An unfocused laser spot with a diameter of ~ 3 mm was employed in all the measurements to spatially average the PL intensity across the film's surface and provide sufficiently low power to avoid photocharging or multiexciton effects. All PL spectra were corrected to account for the spectral response of the

spectrometer system. To account for thickness variations within the CQD films, the PL spectra were normalized to the absorbance of each film at the excitation wavelength.

Time-resolved PL (TR-PL) was measured on the same Fluorolog spectrometer using a monochromator-based time-correlated single photon counting method. The PL was excited by a picosecond laser diode at 785 nm (DeltaDiode-785L) with a pulse width of ~ 80 ps, operating at 100 KHz, using a defocused laser beam (spot diameter ~ 2 mm). The PL decays were obtained while monitoring the CQD emission peaks with a spectral bandwidth of ~ 20 meV.

All steady-state and time-resolved PL experiments were performed under vacuum conditions (10^{-5} mbar). For temperature-dependent PL measurements, the samples were loaded into a Janis liquid nitrogen optical cryostat (77–500 K).

Ultrafast time-resolved pump-probe absorption measurements were carried out using a mode-locked Ti:sapphire ultrafast amplifier generating 100 fs pulses at 800 nm running

Figure 2. PL spectra and Gaussian lineshape analysis via a three-peak model from a K_4GeS_4 –PbS CQD film at temperatures of (a) 78 K and (b) 280 K. The schematic illustrates three exciton recombination channels.

at a repetition rate of 1 kHz. A nonlinear β -barium borate crystal was used to frequency-double the amplifier output at 400 nm with the energy of 1.3 mJ per pulse. The beam served as the pump excitation pulse. A fraction of the fundamental beam was used to generate a super continuum light for probing at different QD energy states in the 500–1100 nm range. Measurements were carried out using a typical pump–probe optical setup in a noncollinear configuration, where differential transmission was measured as a function of optical delay between the pump and probe pulses. The probing wavelengths were selected using 10 nm narrow bandpass filters. Measurements were performed in an inert nitrogen atmosphere.

Photoconductivity Measurements. Interdigitated ITO substrates (Ossila) with ITO 100 nm thick stripes separated by channels of 50 μm were sonicated in Helmanex (Ossila):deionized water solution 1:10 v/v for 10 min, thoroughly washed with deionized water and dried with compressed air. 70 μL of the CQD solution at 30 g/L was drop casted on the substrates and vacuum dried to ensure thickness uniformity, covering the 100 nm deep channels. The devices were illuminated with monochromatic light at 410 nm and constant excitation power density of 80 mW cm^{-2} under ambient conditions. The excitation spot size was set to $\sim 400 \mu\text{m}$ to excite only the probed area of the device. The photocurrent was recorded by a Keithley S2461 sourcemeter in the range of -10 to 10 V.

RESULTS AND DISCUSSION

PbS CQDs were chosen for their high binding affinity to MCC complexes and good air-stability upon MCC capping.^{7,8} $(\text{NH}_4)_3\text{AsS}_3$ is a promising MCC complex for CQDs with specific affinity to the PbS system and niche optoelectronic applications.^{8,10,12,16,22,23,29,34} The compelling properties of such sulfido-arsenites arise from their facile transformation to As_2S_3 in the dry phase, yielding stable CQD solids. The material integrity and well-studied properties in the solid state^{16,29} appoint PbS– As_2S_3 CQDs as the reference MCC-capped CQD material for the present studies. The chalcogenidometalates of interest are a series of four complexes, namely, K_4GeS_4 , K_4SnS_4 , K_3AsS_4 , and K_3SbS_4 . The motivation for the use of such ligands is two-fold. First, a comprehensive study investigated the binding motifs of such MCCs on Cd chalcogenide CQDs and revealed a good binding affinity to the CQD surfaces.³⁰ According to our studies, such ligands appear to also yield stable PbS CQD colloids in polar

solvents. However, we consistently found in our studies that only K_4GeS_4 -capped CQDs can be processed into films with sufficiently strong emission, suitable for the present spectroscopic studies, as summarized in the comparative PL study of Supporting Information Figure S4. The second reason lies on the nature of exciton–ligand interaction on the better-studied PbS– As_2S_3 CQD system. Spectroscopic¹⁶ and photocurrent²⁹ studies reveal that in the solid state, recombination is dominated by fast electron trapping at ps timescales. Such fast trapping appears beneficial for the development of highly efficient photoconductors²⁹ but is rather detrimental for the implementation of the material in other devices. This motivated the quest for other MCCs that can support better surface passivation against trap recombination, a parameter that can make such materials beneficial for light emitting diodes and photovoltaic cell applications.

Oleate and MCC-capped CQDs can be casted into uniform films suitable for spectroscopic studies. As an example, 3D topographic AFM images of spin-coated films of oleate and GeS_4^{4-} -capped PbS CQDs are presented in Figure 1a,b, respectively, while respective 2D AFM images are included in Supporting Information Figure S5. The microscopy indicates that both CQD film types exhibit smooth surface topography with small average surface roughness of the order of ~ 3 nm. Absorption spectra of oleic-acid and MCC (As_2S_3 and GeS_4^{4-})-capped CQDs are shown in Figure 1c. The MCC-capped CQD films exhibit quenched, broadened, and red-shifted exciton peaks that may be an effect of the increased interdot interactions enabled by the shorter ligands,^{7,8} dielectric-induced shifts,⁴⁵ and/or orbital interactions of core-ligand states.⁴²

Comparative PL spectra are displayed in Figure 1d,e for UV and near-IR photoexcitation, respectively; the figure trends can be reasonably reproduced within different film series. GeS_4^{4-} –PbS CQDs retain a significant fraction of the organic-capped QD emission with consistently higher PL intensity compared to As_2S_3 -capped CQD films, especially for high-energy UV excitation. The quenched emission of the latter under UV excitation is attributed to trapping sites in the yellow As_2S_3 ligand phase, as demonstrated in previous studies.¹⁶ Steady-state PL results are consistent with transient PL and transient absorption spectra displayed in Figure 1f,g, respectively. Organic-capped CQD films show long-lived exciton bleaching ($\Delta T/T > 0$) and slow PL decay at the μs -scale. After ligand exchange to As_2S_3 , no ground state filling is observed while the

Figure 3. (a) Temperature-dependent PL spectra in the range of 78–380 K from a GeS_4^{4-} –PbS CQD film. Variation of (b) peak position and (c) integrated intensity of the three emissive species in the film as a function of temperature.

PL lifetime appears severely quenched, consistent with the presence of efficient trapping of the photoexcited electrons.¹⁶ On the contrary, the weak but long-lived absorption bleaching and the much slower PL transients in combination with the brighter emission present in the GeS_4^{4-} -capped CQDs indicate that excitons are not subjected to such fast ligand-induced recombination in the aforementioned films.

To further clarify the spectroscopic differences between the two MCC-capped CQDs, an optical study of spin- and drop-casted free MCC ligand films was performed, the results of which are summarized in Supporting Information Figure S6, along with the relevant discussion. The data reveal that the free ligand films are dominated by the semiconducting As_2S_3 and the insulating K_4GeS_4 material phase, respectively. However, lower gap phases with weak low-temperature emission in the near-IR are also present.

Temperature-dependent PL experiments give insight into the mechanism of the exciton–ligand interaction in K_4GeS_4 –PbS CQDs. The luminescence can be consistently reproduced using a triple Gaussian model, as displayed in Figure 2 for temperatures of 78 and 280 K. The dominant, high-energy peak labeled CX exhibits a relatively narrow linewidth of 100–150 meV, lying slightly below the respective 1S CQD absorption transition. Fitting of the main emission feature also requires the addition of a weaker and slightly red shifted DX peak that exhibits a considerably larger linewidth of ~300–450 meV. A low-energy PL satellite that appears more intense at cryogenic temperatures is modeled by a third Gaussian (TX), peaked at 0.25–0.35 eV below the main PL feature.

The temperature evolution of the PL spectrum from the GeS_4^{4-} –PbS CQD film, in the 78 to 380 K range, is displayed in Figure 3a. The higher energy CX and DX peaks exhibit an almost identical behavior with temperature, yielding a similar blue shift and emission quenching as sample temperature increases. The anomalous temperature-dependent blue shift of the gap is characteristic of PbS and is also evidenced in the PL data of the reference oleate-capped CQD sample (Supporting Information Figure 7). Based on the narrow linewidth, the energetic proximity to the exciton absorption peak, and the temperature-dependent luminescence characteristics, CX is assigned to the radiative recombination of the CQD core exciton. The DX species exhibit an almost identical PL temperature dependence with the CX peak, as observed in

Figure 3b,c, which indicates that the nature of the channel is also excitonic. However, the DX emission lineshape is significantly broader, and the respective peak is consistently red-shifted compared to the core exciton emission. Such characteristics, combined with the absence of such peaks in the PL lineshape of the oleic-acid capped CQDs, as seen in Supporting Information Figure S8, are consistent with a delocalized exciton species. Such ligand-induced delocalization of carriers or excitons have been observed in QD solids with short conducting organic ligands,^{39,40} in this work, delocalization of exciton is mediated by the short GeS_4^{4-} ligands, enabling surficial electronic coupling of adjacent dots. Evidence of such electronic linking in the solid state of adjacent GeS_4^{4-} –PbS CQDs is provided later on in the article by photoconductivity experiments.

The third lower energy peak, coded TX, exhibits a red shift as temperature rises, which indicates that it is not related to the PbS electronic states. An emission feature, peaked at similar energies to TX, is observed at the low-temperature PL data of free K_4GeS_4 films, assigned to emission from lower gap GeS_4^{4-} phases as shown in Supporting Information Figure S6 and discussed in more detail within the relevant Supporting Information text. It is plausible then that the TX peak is either (i) due to emission from such a ligand phase, that is the CQDs exhibit luminescence from both the PbS core and the MCC ligand states, or (ii) due to emission from excitons trapped within MCC-induced surface states. Further experimental evidence discussed below provides support for the latter hypothesis.

The PL dynamics of the CX and DX peak species are analyzed in the upper three graphs of Figure 4a–c for low (78 K), intermediate (180 K) and high (300 K) temperature, respectively. The decays can be reproduced at all cases *via* a fast decay of few ns and a slow decay in the μs timescale. At low and intermediate temperatures, a significant growth component of hundreds of ns is also needed to provide adequate fitting of the dynamics. The fast decay has a lifetime of ~6 ns at 78 K, decreasing slightly to ~5 ns at 300 K; however, its relative weight increases substantially as temperature rises. Plausible origins of the channel, based on its timescale and temperature behavior, are (i) exciton trapping, (ii) exciton transfer within CQDs, (iii) exciton dissociation via charge (*i.e.* electron or hole) transfer, and (iv) multiexciton quenching via Auger.

Figure 4. Time-resolved PL data monitoring the main CQD emission peak (black solid line) at (a) 78 K, (b) 180 K, and (c) 300 K. The inset displays early times of the decays probed. At low/intermediate temperatures, the dynamics can be decomposed into a decay and a growth (green) term. Exponential fits of the growth component (blue) and the overall dynamics (red) are presented. (d) Rise signal PL dynamics of the core (CX) and trapped (TX) exciton. (e) Temperature variation of the relative amplitude of the intrinsic, trapping, and de-trapping processes in the CQDs. (f) Photocurrent measurements from lateral ITO–CQD–ITO devices for the oleate-capped PbS QDs (grey) and GeS_4^{4-} -capped PbS QDs (blue). The illustration shows the device structure. ITO contact spacing was $\sim 50 \mu\text{m}$. The device based on the organic-capped CQDs exhibits negligible photocurrent, 5×10^5 times smaller than that employing the GeS_4^{4-} -capped CQDs. Schematics illustrating the dominant exciton recombination channels at (g) low temperature and (h) high temperature.

Excitation-dependent TR-PL confirms the presence of the (iv) process, that is bi-exciton recombination in the CQDs both before and after the ligand exchange process, as witnessed by the quenching of the average PL lifetime observed in Supporting Information Figure S9. However, for the MCC-capped CQDs, the relative amplitude and the temporal characteristics of the fast decay term appear unaffected by excitation fluence, which excludes multiexciton recombination as its origin. Information on the nature of the channel is provided by comparing the rise signal dynamics of the CX species, that is the main PL peak, with those of the low-energy TX channel, that is the satellite low-energy PL peak, as

illustrated in Figure 4d. The rise of the TX emission signal is retarded by ~ 6 ns compared to the rise of the CX emission, a delay that perfectly matches the fast decay time of the PbS CQD exciton species. The above is consistent with a nonradiative energy transfer process that quenches the CQD exciton and funnels some of this energy to activate the lower energy TX emission. Based on such evidence, we tentatively assign the ~ 6 ns channel to CQD exciton trapping at MCC-induced states and the TX peak is concomitantly interpreted as the emission from such trapped exciton species. The assignment to a trapped exciton rather than emission from lower gap GeS_4^{4-} ligand phases peaked at similar energies (see

Figure 5. Normalized (a) steady-state PL spectra, (b) time-resolved PL decays, and (c) transient absorption dynamics of core only (black) and PbS/CdS core/shell (red) CQDs capped with GeS₄⁴⁻ ligands. (d) An illustration of the suppression of exciton trapping at the core–shell PbS CQDs.

Supporting Information Figure S6) is further supported by variable temperature-transient PL spectra monitoring the TX emission and the free ligand emission, as displayed in Supporting Information Figure S10. The TX luminescence appears to be highly temperature sensitive with an average lifetime of ~120 and ~40 ns at 77 and 180 K, respectively; on the other hand, the free ligand PL decay appears temperature insensitive and occurs at significantly slower timescales of ~400 ns.

The CQD exciton species also exhibit a longer PL decay channel and a slow emission growth component. The first is assigned to a convolution of the recombination dynamics of the CQD core and delocalized exciton species. The assignment is consistent with the excitation-dependent character of the channel due to Auger recombination of multiexcitons, which have been discussed previously within the text. The growth signal on the other hand, exhibits a timescale of ~350 ns and relative amplitude that reduces as temperature is increased; that is, it is 17 and 13% at 77 and 180 K, respectively. A decay channel of similar timescales to the ~350 ns growth signal is present in the trapped exciton (TX) emission decays presented in Supporting Information Figure S10; this is consistent with a process of exciton back transfer from the ligand to the PbS states, that is an exciton detrapping process. It then appears that at low to intermediate temperatures, energy outflows from the PbS states to the MCC states at relatively fast timescales of ~6 ns, and then part of this energy is funneled back to the CQD core states at a significantly slower rate of hundreds of

ns. As the temperature increases, the growth component of the PL signal disappears, which indicates that excitons are not back transferred to the CQD states.

Relative amplitudes of the three processes for different temperatures are displayed in Figure 4e. Laser excitation photogenerates core (CX) and delocalized (DX) excitons. At 78 K, approximately 60% of the excitons recombine within the CQDs core and the remaining 40% trap within 6 ns at surface traps; almost half of those trapped excitons are funneled slowly back to the CQDs. The efficiency of the exciton trapping increases with temperature up to 300 K, but still an appreciable fraction of the excitons (*i.e.*, ~45%) recombine within the PbS CQDs, being responsible for the bright (RT) luminescence observed. The yield of the slow exciton back transfer decreases by ~25% as temperature rises from 78 to 180 K, approaching zero at 300 K as trapped excitons quench before the slow back transfer occurs. The absence of the back-transfer growth signal in combination with the complete quenching of the TX emission at elevated temperatures indicates that as thermal energy increases, trapped excitons quench fast at the ligand states before detrapping or that CQD excitons are dissociated *via* other processes such as electron and/or hole transfer to adjacent dots.

Evidence of the latter process, is provided by photoconductivity experiments obtained from 50 μm channel lateral ITO–CQD–ITO devices. Figure 4f shows representative photocurrent data from such devices. For the reference oleate-capped PbS CQD sample, the recorded current density is more

than 5 orders (5×10^5) of magnitude lower than the photocurrent measured in devices employing GeS_4^{4-} -capped PbS QDs, demonstrating the absence (presence) of dot-to-dot electronic communication in the former (latter). Such observation implies that the increase in the relative amplitude of the fast PL quenching term at elevated temperatures, observed in Figure 4c, is associated with the thermal activation of QD exciton dissociation and subsequent carrier transfer within the GeS_4^{4-} -capped CQDs. The processes are illustrated in the schematic included in Figure 4g,h for low temperatures and high temperatures respectively.

The proposed model is further supported by studies performed on PbS CQDs passivated with a thin (~ 1 nm) CdS shell that spatially separates core and ligand states. The presence of the shell was confirmed by HRTEM images (Supporting Information Figure S1) and X-ray diffraction pattern spectra (Supporting Information Figure S2). Figure 5a contains comparative PL spectra of GeS_4^{4-} -capped PbS and GeS_4^{4-} -capped PbS/CdS core/shell CQDs. The latter exhibits luminescence intensity more than an order of magnitude larger than the unshelled dots. Furthermore, the PL spectrum in the core/shell CQDs can be sufficiently reproduced via a single Gaussian peak assigned to the CQD core exciton, implying that contributions from the delocalized exciton and the ligand-trapped exciton species are quenched as the CdS shell suppresses exciton–ligand interactions. This is further confirmed by the time-resolved PL study of Figure 5b, in which the RT fast PL transient assigned to a convolution of the exciton trapping and exciton dissociation via interdot charge transfer processes is completely absent in the shelled CQDs. Suppression of the ligand-induced exciton recombination is also supported by the transient absorption data of Figure 5c, providing evidence of a stronger and longer lived CQD state bleaching in the CdS-passivated PbS CQDs.

CONCLUSIONS

A detailed photophysical investigation of PbS CQDs decorated with MCC K_4GeS_4 complexes is reported. K_4GeS_4 is found to provide better surface passivation compared to the traditionally used As_2S_3 –PbS CQD system, as excitons trap at slower timescales of few ns in the former compared to the efficient ps-scale electron trapping present in the latter. As a result, GeS_4^{4-} -capped PbS CQDs in the solid state, retain a significant fraction of their luminescence and exhibit relatively long-lived exciton bleaching upon ligand exchange. In addition to the ns-scale exciton trapping, spectroscopy provides evidence of a significantly slower and temperature-sensitive, exciton detrapping channel that back transfers some of the energy to the core PbS CQD excitons. Furthermore, Gaussian lineshape analysis indicates the presence of a second, red-shifted exciton species that is tentatively assigned to a delocalized exciton enabled by the short GeS_4^{4-} ligands that allow electronic coupling of adjacent dots and current transport at RT, as evidenced by photoconductivity experiments. Trapping and delocalization of excitons is suppressed when CdS shells are employed; a concomitant order of magnitude emission enhancement is observed as a result of the better surface passivation. The present work highlights the impact of inorganic ligand–exciton interactions on the energetics and dynamics of PbS CQD excitons, providing a rational explanation of the role of MCCs as exciton trapping or transporter sites.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c09790>.

TEM images, X-ray diffraction spectra, CQD vessel images before/after ligand exchange, AFM images, comparative PL spectra of various MCC-capped CQDs, temperature-dependent PL, excitation-dependent PL, PL Gaussian lineshape analysis, and absorption and emission spectra of free ligands (PDF)

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Notes

The authors declare no competing financial interest.

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