

Supporting information for

Inorganically Functionalized PbS/CdS Colloidal Nanocrystals: Integration into Amorphous Chalcogenide Glass and Luminescent Properties

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Materials and methods.

I. Chemicals.

Didodecyldimethylammonium bromide (DDAB, 98%, Fluka), Lead acetate trihydrate ($\text{PbAc}_3 \times 3\text{H}_2\text{O}$, Aldrich), bis(trimethylsilyl) sulfide (TMS_2S , Aldrich), Cadmium oxide (99.995%, Aldrich), oleic acid (OA, 90%, Aldrich), propylamine ($\geq 99\%$), 1-octadecene (ODE, 90%, Aldrich), ammonium sulfide (40-48% solution in water, Aldrich), arsenic(III) sulfide (As_2S_3 , 99.999%, Alfa Aesar), dimethylsulfoxide (DMSO), formamide (FA, 99%, Aldrich), deuterated dimethylsulfoxide (DMSO-d_6 , 99.9 atom % D, Aldrich) and various solvents were used as received. Octadecene was dried at 140 °C for 2 hours under vacuum and stored in a nitrogen glovebox.

II. Synthesis of colloidal nanocrystals.

PbS/CdS NCs, Sample I (4.2 nm core-0.3 nm shell) and Sample II (3.5 nm core-0.7 nm shell) NCs. In a three-neck reaction flask, $\text{PbAc}_2 \times 3\text{H}_2\text{O}$ (2 mmol, 0.758g), ODE (12 mL) and OA (8 mL) were dried at 100 °C under vacuum for 2 hours to dissolve lead salt and to dry the solution. The temperature was raised to 145 °C. In a glovebox, sulfur precursor solution was prepared by mixing TMS_2S (0.21 mL, 1 mmol) with ODE (10 mL). Sulfur solution was quickly injected into the reaction flask at 145 °C followed by the removal of heating mantle and allowing solution slowly cool to room temperature. The washing procedure was carried out in air using anhydrous solvents. Hexane (20 mL) and ethanol (30 mL) were added to the crude solution followed by centrifugation to separate NCs. Obtained PbS NCs were redispersed in hexane (20 mL), again precipitated with ethanol (40 mL) and redispersed in toluene (15 mL). 12 mL of this solution containing ≤ 0.8 mmol PbS assuming complete conversion of sulfur precursor were used for the growth of PbS/CdS (Sample I) NCs. In a second flask, CdO (1g, ~ 7.8 mmol), OA (6 mL, ~ 18.9 mmol) and 20 mL ODE were heated to 200-250 °C until solution turned colorless. The solution was cooled to 100 °C and dried under vacuum for 30 min. The temperature was further decreased to 70 °C and 12 mL of PbS NCs were added via syringe. The solution was maintained at ~ 70 -75 °C for 30 min and cooled to room-temperature. To wash PbS/CdS NCs (Sample I), ethanol was added to precipitate NCs. The precipitate was redispersed in toluene and again

precipitated with ethanol. Redispersion/precipitation procedure was repeated additionally once or twice.

To vary the size of original PbS NCs and, correspondingly, to tune the emission of PbS/CdS NCs over the entire near-infrared spectral region, we varied the amount of oleic acid in the reaction mixture, in analogy to the procedure of Hines et al.¹

To grow thicker CdS shell of 0.7 nm (Sample **II**), higher temperature (100 °C) and longer time (45 min) were used for Pb-to-Cd cation exchange. See Figures S1 and S2 for optical properties of samples **I** and **II**, respectively.

The initial and final PbS NC core sizes of PbS were determined from the energy of the first absorption peak,^{2,3} and were in good agreement with TEM images (for initial PbS) and with ICP-OES analysis (for core-shell dots).

III. Surface ligand exchange and integration of PbS/CdS NCs into amorphous As-S glass films.

(NH₄)₃AsS₃⁴ was prepared by dissolving 0.492 g As₂S₃ in a solution containing (NH₄)₂S (0.86 mL, 40-48% in water) and 10 mL H₂O at room temperature forming a colorless solution. Solid (NH₄)₃AsS₃ can be isolated by adding acetone, centrifugation and additional washing with acetone. Unlike to colorless Na₃AsS₃, isolated ammonium salt appears yellow colored, which can be attributed to the presence of larger As_nS_m^{x-} species formed upon partial removal of NH₃ and H₂S (noticed by characteristic odor). Yellowish DMSO solution of this solid was used in further ligand exchange reactions.

As₂S₃/propylamine precursor solution was prepared in a glovebox by dissolving bulk As₂S₃ pieces (2g) in 10 mL propylamine at room temperature over 2 days. The resulting yellow solution was filtered through 0.45-μm filter to remove insoluble impurities. Note that As₂S₃/propylamine solution is moisture sensitive and becomes cloudy if small traces of water are present.

The **ligand exchange with (NH₄)₃AsS₃** was conducted as a heterogeneous reaction in the mixture of two largely or completely immiscible solvents of nonpolar and polar character, e.g. toluene-formamide or hexane-DMSO, leading to the complete phase transfer of NCs from the non-polar to the polar phase and formation of colloiddally stable solutions. The (NH₄)₃AsS₃ to NC

molar ratio was in the range of 0.5-2, with lower $(\text{NH}_4)_3\text{AsS}_3$ amounts used for larger NCs. All experiments were carried out in air.

As an example of the preparation of AsS_3^{3-} -capped PbS/CdS NCs (**Sample II**), a hexane solution of PbS/CdS NCs (1 mL, ~17 mg/mL) was mixed with DMSO (2 mL), $(\text{NH}_4)_3\text{AsS}_3$ in DMSO (0.3 mL, 40 mg/mL) and 5 mL hexane. Solution was stirred for 0.5-2 hours until the organic phase turned colorless and DMSO phase became dark brown. The upper organic phase was carefully removed. The DMSO phase was further purified by triple washing with hexane and filtered through a 0.45 μm PTFE filter. The solution of AsS_3^{3-} -capped PbS NCs can be purified from excess MCC by adding equal or larger volume of acetonitrile, centrifuging and redispersing in pure DMSO or DMSO- d_6 (for optical measurements).

To exchange NH_4^+ surface counterions with DDA^+ , the solution of AsS_3^{3-} -capped PbS/CdS NCs (0.5 mL) obtained as described above was mixed with DDAB in toluene (5 mg/mL, 1 mL), stirred until the completion of the phase transfer of NCs from FA into toluene phase and formation of a stable colloidal solution. The following washing with water was applied to remove excess DDAB. Upon phase separation, the toluene phase was mixed with large amount of water (50 mL), vigorously shaken and centrifuged. The aqueous phase was discarded and the washing was repeated 1-2 times until both aqueous and toluene phases appeared completely clear.

To prepare PbS/CdS NCs in As_2S_3 -propylamine solutions, $(\text{NH}_4)_3\text{AsS}_3$ -stabilized PbS/CdS NCs in DMSO (without additional precipitation applied) were transferred into glovebox. NCs were precipitated by adding acetonitrile and collected by centrifugation. NCs are readily soluble in As_2S_3 /PA solution at NC concentrations of 10-60 mg/mL. This solution was additionally centrifuged to remove any insoluble impurities and was used for spin-coating onto SiO_2 , glass or Si substrates hydrophilized by O_2 -plasma or piranha treatments immediately before use.

IV. Structural and optical characterization of materials.

Dynamic light scattering and electrophoretic mobility data were collected using Zetasizer Nano-ZS (Malvern Instruments, UK). Colloidal solutions were filled in a quartz cuvette and the dip cell electrode assembly with Pd electrodes used to apply an electric field to solution. A

typical ζ -potential measurement included several scans of 100 runs each in the high-resolution mode. The concentration was optimized for each sample to achieve >100 kcps count rate and the best signal-to-noise ratio.

Transmission electron microscopy (TEM) of the samples was performed using FEI Tecnai F30 microscope operated at 300 kV.

Thermogravimetric analysis (TGA) was conducted using Shimadzu TGA-50 thermal analyzer with a heating rate of 5 °C/min under nitrogen.

The absorption spectra of NC solutions were collected using a Cary 5000 UV-Vis-NIR spectrometer. Thin film absorption spectra were obtained by recording transmittance and total reflectance using a DRA 2500 diffuse reflectance accessory (integrating sphere).

Fourier-transform infrared (FTIR) spectra were acquired in the transmission mode using a Nicolet Nexus-670 FTIR spectrometer with a resolution of 4 cm⁻¹, and averaging over 64 scans. For the measurements, thick films were deposited on KBr or CaF₂ crystal substrates (International Crystal Labs).

Elemental analysis by the inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed at the Analytical Chemistry Laboratory (ACL) at Argonne National Laboratory. Samples for ICP-OES analysis were prepared by digesting samples in half-concentrated aqua regia followed by extracting organic component with chloroform.

Infrared measurements of quantum yields from colloidal solutions. QuantaMaster spectrofluorimeter (Photon Technologies International) equipped with InGaAs detector was used for initial characterization of PbS and PbS/CdS NCs in solution and for quantum yield estimations. Typical excitation wavelengths were 700-900 nm with bandwidths of 10 nm, provided by a 450W Xenon lamp dispersed with a monochromator. For quantum yield measurements, all samples were excited at 960 nm. Measured intensities were corrected with the spectral response of the setup. Oleic-acid capped NCs were dispersed in TCE, whereas inorganically functionalized NCs were dispersed in dimethylsulfoxide-d₆ (DMSO-d₆, 99.9 atom% D). Infrared dye IR-26 (Exciton Inc.) dissolved in 1,2-dichloroethane was used as fluorescence reference with recently corrected absolute quantum yields by Beard et al.⁵ To obtain absolute quantum yields for PbS and PbS/CdS NCs in colloidal solutions, we compared their integrated luminescence intensities with that of IR-26 dye taking into account optical densities at the excitation wavelengths. To avoid the reabsorption of emitted light, optical density of PbS

colloids at the excitation wavelength was kept below 0.1. We also corrected for a strong concentration dependence of quantum yield of IR-26, ranging from $0.048 \pm 0.002\%$ for infinitely dilute solutions to 0.02% for highly concentrated IR-26 solutions due to reabsorption effects (Figure S13).

Time-resolved and steady state PL measurements from films and solutions. Two setups in two different laboratories were used.

Setup 1. Static and time-resolved PL measurements were performed using a 705-nm pulsed diode laser operating at either 40MHz for static spectra or 300kHz for life time measurements. The excitation wavelength was chosen in order to prevent excitation of the medium surrounding the NC samples. PL photons were collected and directed to a 0.3m spectrograph. An InGaAsP photomultiplier tube detector with time-to-amplitude conversion photon counting electronics was utilized in order to produce decay dynamics and an cooled InSb detector was utilized in order to produce time-integrated spectral profiles. Presented decays represent between 3 and 5 minutes integration.

Setup 2. For steady state and time resolved PL measurements the samples were excited at ~ 760 nm by a Ti:sapphire laser delivering 150 fs pulses. To vary the repetition frequency of the exciting pulse an optical pulse selector was used. The time resolved PL signal was recorded with a Hamamatsu streak camera, with photocathode sensitive in the near-infrared spectral range. Depending on the PL lifetime, the streak cameras were used in synchroscan or in single sweep mode. The steady state PL spectra were detected with a InGaAs detector from Andor. The PL spectra were corrected for the spectral response of the set up. The traces of the PL decay time were integrated in spectral region of about 20 nm in the excitonic peak of the NCs. All samples showed no wavelengths dependence.

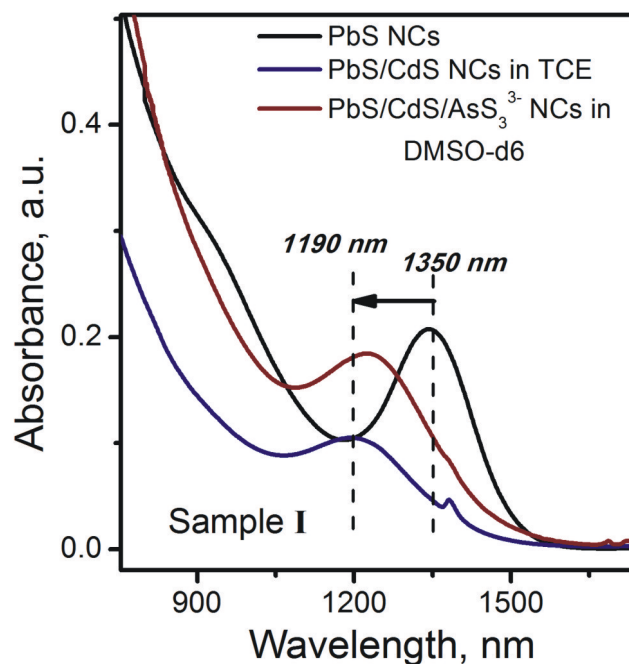


Figure S1. Absorption spectra for original ~ 4.8 nm oleate-capped PbS NCs (black curve) and for cation-exchanged samples of PbS/CdS NCs (**Sample I**, ~ 4.2 PbS core, ~ 0.3 nm CdS shell), stabilized with oleic acid in TCE (blue curve) and with $(\text{NH}_4)_3\text{AsS}_3$ in DMSO- d_6 (red curve).

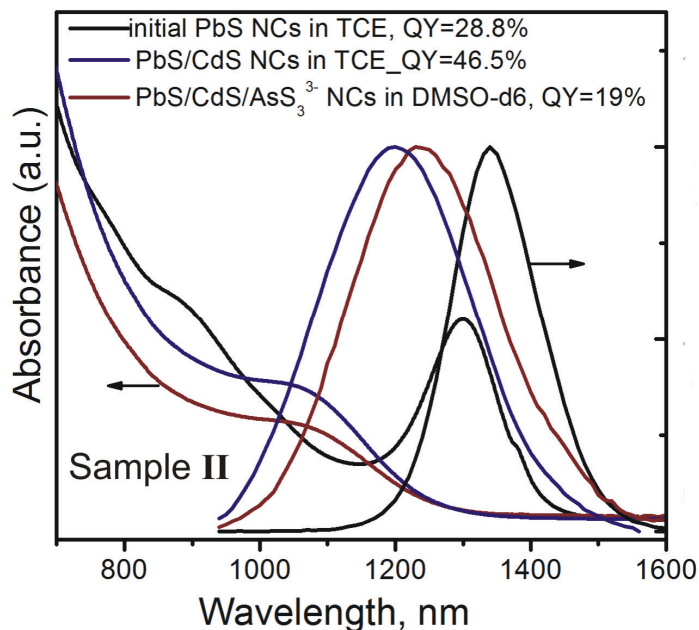


Figure S2. Absorption spectra and for original ~ 4.8 nm oleate-capped PbS NCs (black curve) and for cation-exchanged samples of PbS/CdS NCs (**Sample II**, ~ 3.4 PbS core, ~ 0.7 nm CdS shell), stabilized with oleic acid in TCE (blue curve) and with $(\text{NH}_4)_3\text{AsS}_3$ in DMSO- d_6 (red curve).

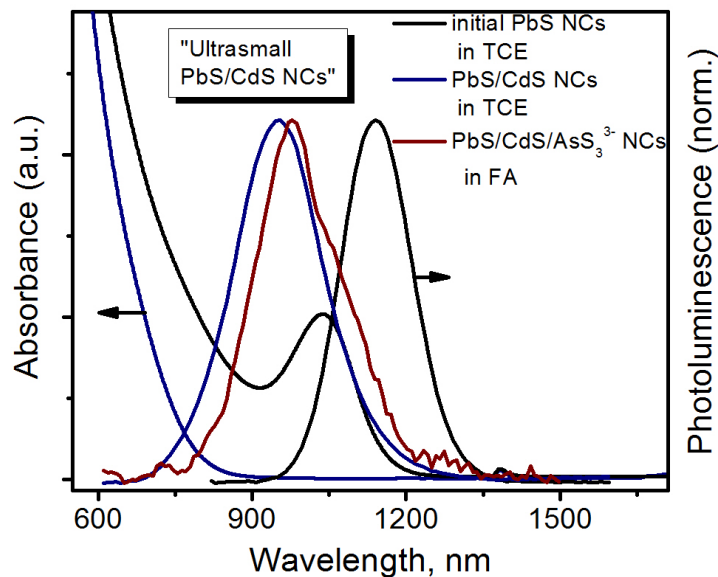


Figure S3. Absorption and emission spectra for original 3.5 nm oleate-capped PbS NCs (black curve) and for cation-exchanged samples of PbS/CdS NCs with sub-2nm PbS cores overcoated with ~ 0.7 nm CdS shell and stabilized with oleic-acid (blue) or with $(\text{NH}_4)_3\text{AsS}_3$ in FA. Emission spectra were measured under excitation at 550 nm for PbS/CdS NCs and at 800 nm for PbS NCs.

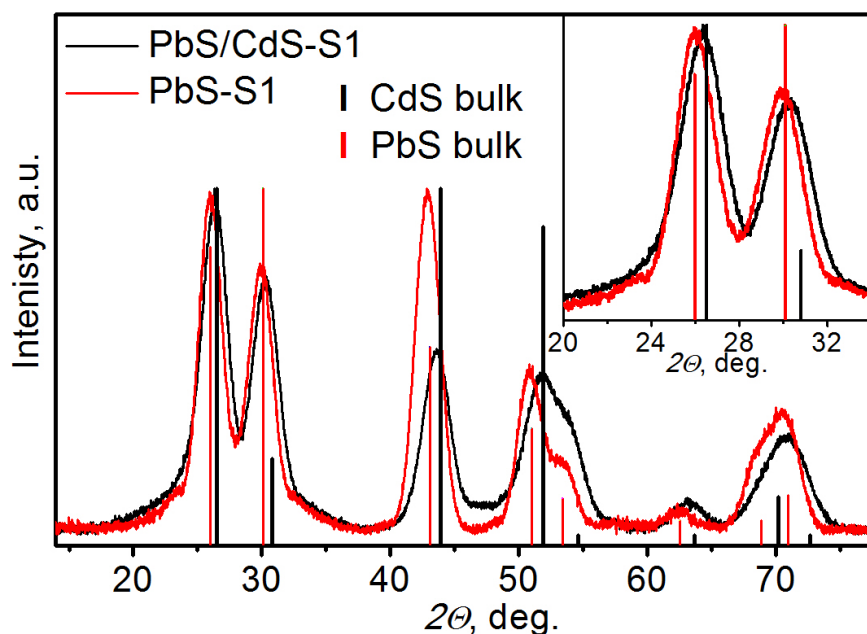


Figure S4. Powder X-ray diffractions spectra for original PbS NCs and for cation-exchanged PbS/CdS NCs (**Sample I**). Vertical lines indicate reflections for bulk PbS (rock-salt structure) and bulk CdS (zinc-blende structure).

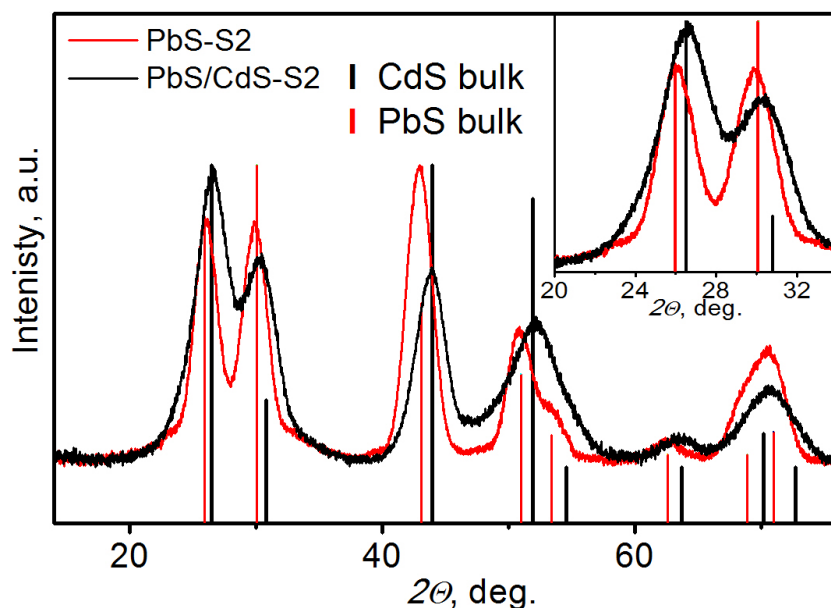


Figure S5. Powder X-ray diffractions spectra for original PbS NCs and for cation-exchanged PbS/CdS NCs (**Sample II**). Vertical lines indicate reflections for bulk PbS (rock-salt structure) and bulk CdS (zinc-blende structure). Because of the slightly smaller CdS lattice constant, the diffraction peaks appear to shift towards larger 2θ angles. Since the average size of both samples is approximately same, the broadening is likely a result of PbS and CdS reflections overlap, similar to PbSe/CdSe NCs reported by Pietryga et al.⁶

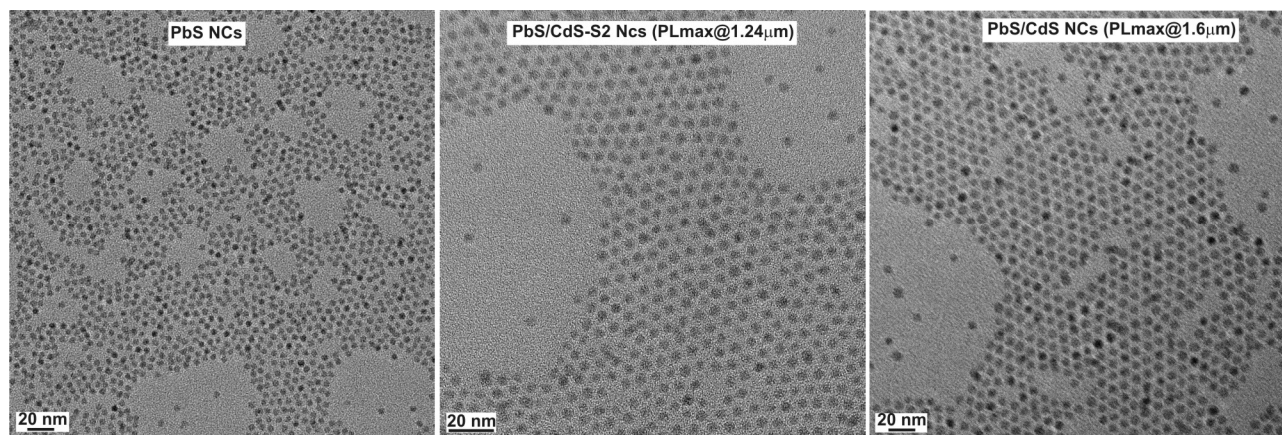


Figure S6. TEM images of PbS NCs (left, ~ 4.8 nm) used in the preparation of PbS/CdS NCs (**Sample II**, middle, 3.5 nm PbS core, 0.7 nm CdS shell; larger PbS/CdS NCs (**Sample III**, right, 5.9 nm PbS core, 0.3 nm CdS shell).

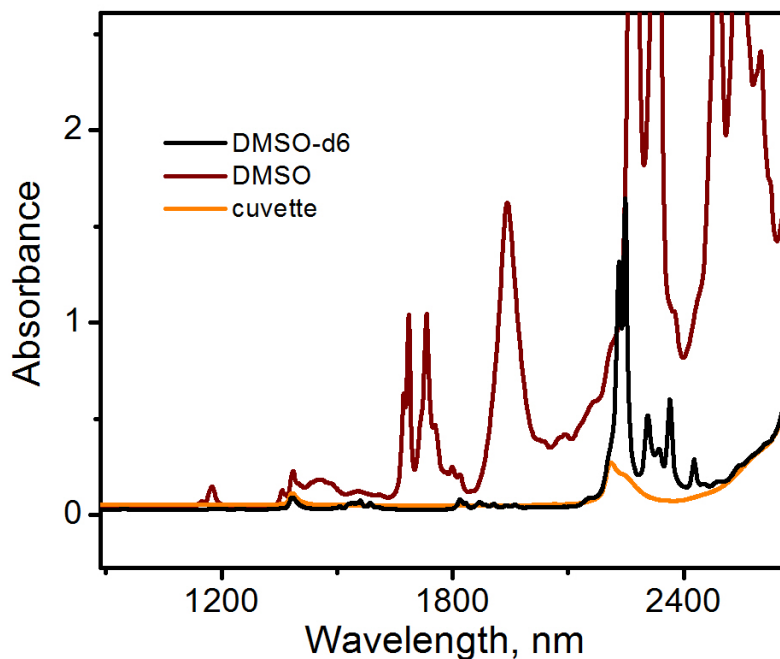


Figure S7. Optical absorption spectra of conventional and deuterated dimethylsulfoxide (DMSO-d6). Cuvette spectrum is shown for comparison.

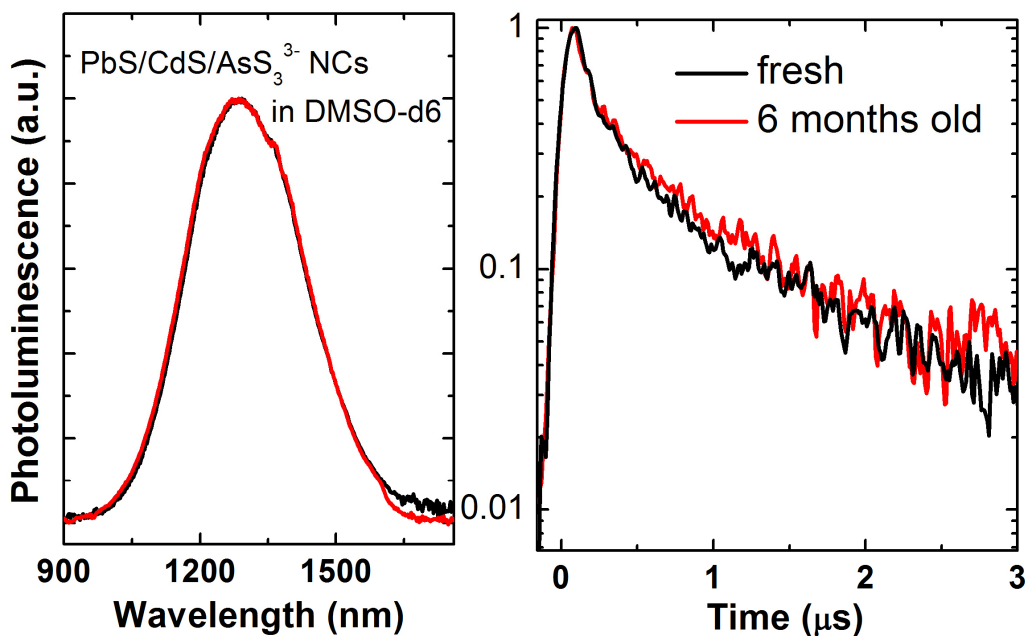


Figure S8. Photoluminescence spectra and decay traces for (NH₄)₃AsS₃-stabilized PbS/CdS NCs (**Sample II**) in DMSO-d6 freshly prepared colloids (black curve) and for 6-months aged samples (red curve, same sample).

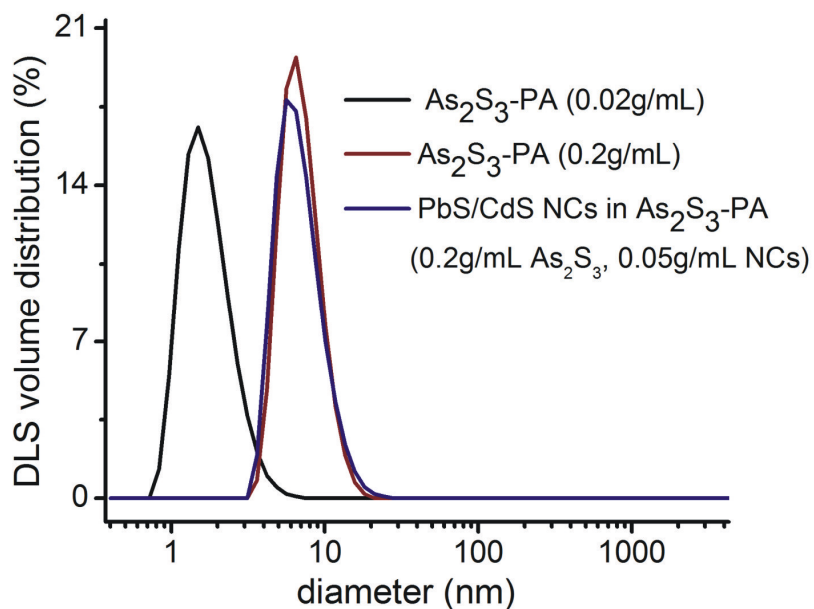


Figure S9.

Figure S9. DLS intensity distribution for highly concentrated As_2S_3 solutions in propylamine (0.2g/mL, close to saturation, red), for x10 dilute sample (black curve), and for dispersion of PbS/CdS NCs (**Sample III**, blue curve). Hydrodynamic diameters measured by DLS in concentrated solutions are strongly affected by a much higher solution viscosity, according to the Einstein–Stokes equation, providing overestimated values.

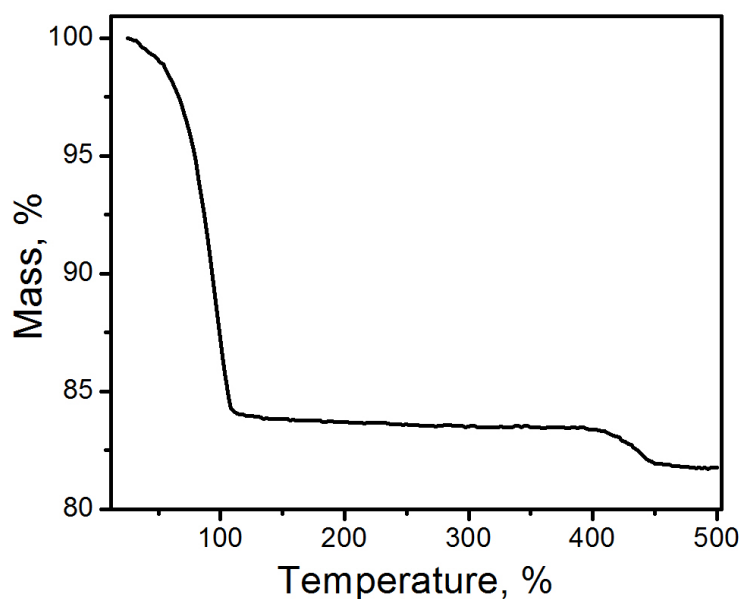


Figure S10. Thermogravimetric plot for $(\text{NH}_4)_3\text{AsS}_3$ recorded under nitrogen.

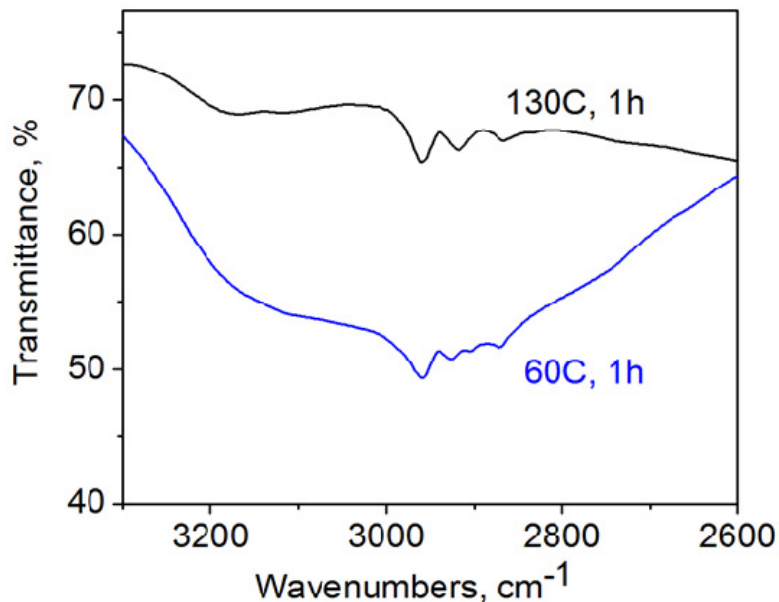


Figure S11. FTIR transmission spectra for a 1- μm thick film obtained by spin coating of As_2S_3 /propylamine solutions and vacuum baked at 60 $^{\circ}\text{C}$ (blue) and 130 $^{\circ}\text{C}$ (black) showing nearly complete removal of solvent residue.

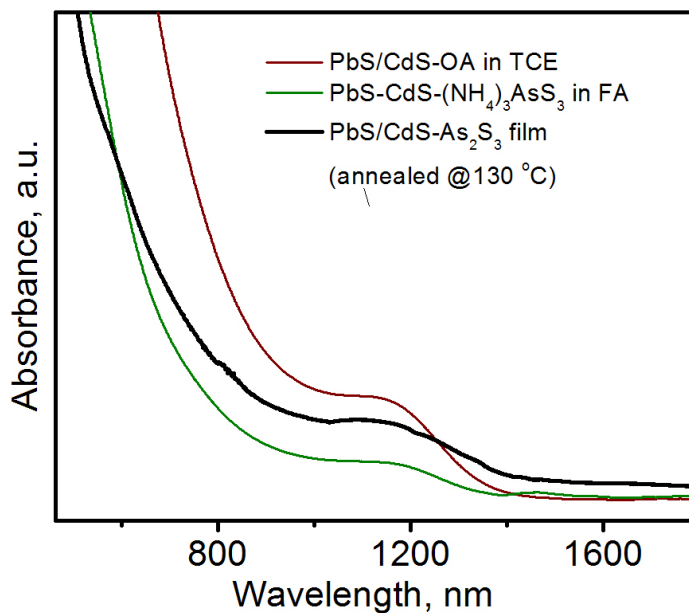


Figure S12. Optical absorption spectra of PbS/CdS in As_2S_3 matrix deposited as inhomogeneous films. Solution spectra of the same NCs before and after the ligand exchange are added for comparison. To obtain film spectrum, the transmission and total reflectance were recorded using an integrating sphere.

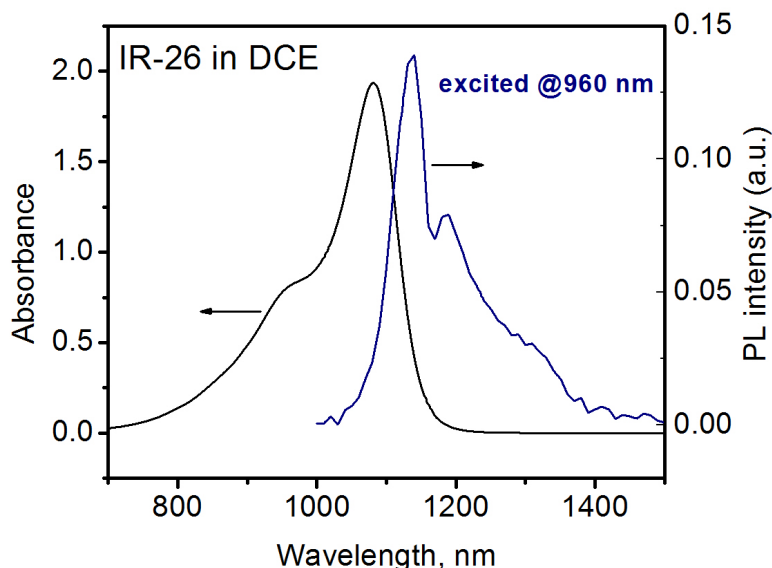


Figure S13. Absorption (black) and photoluminescence (blue) spectra of IR-26 dye dissolved in 1,2-dichloroethane (DCE). Considering re-absorption effect, the absolute quantum yield (Φ_{PL}) was related to the optical density at the absorption peak as:⁵

$$\Phi_{\text{PL}} = \Phi_{\text{PL}_0} \frac{1 - 10^{-O \cdot A_{\text{peak}}}}{O \cdot A_{\text{peak}} \cdot \ln 10}$$

where A_{peak} is the peak optical density, O is normalized weighted average of the overlap between the absorbance and the emission (0.45 for IR-26), and Φ_{PL_0} is absolute quantum yield of IR-26 in infinitely dilute solution, equal to $0.048 \pm 0.002\%$.

Supplementary references:

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