Ligand Shell Structure in Lead Sulphide–Oleic Acid Colloidal Quantum Dots Revealed by Small-Angle Scattering

Michael P. Weir,* Daniel T. W. Toolan,‡,∥ Simon Dowland,‡,∥ Stephen M. King,‡ James Xiao,⊥ Zhilong Zhang,‡ Victor Gray,⊥ Simon Dowland,‡ Jurjen Winkel,⊥ Neil C. Greenham,⊥ Richard H. Friend,⊥ Akshay Rao,⊥ Anthony J. Ryan,*,† and Richard A. L. Jones‡

1Department of Physics and Astronomy, The University of Sheffield, Sheffield S3 7RH, United Kingdom
2Department of Chemistry, The University of Sheffield, Sheffield S3 7HF, United Kingdom
3ISIS Pulsed Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Didcot OX11 0QX, United Kingdom
4Cavendish Laboratory, Cambridge University, Cambridge CB3 0HE, United Kingdom

Supporting Information

ABSTRACT: Nanocrystal quantum dots are generally coated with an organic ligand layer. These layers are a necessary consequence of their chemical synthesis, and in addition they play a key role in controlling the optical and electronic properties of the system. Here we describe a method for quantitative measurement of the ligand layer in 3 nm diameter lead sulphide–oleic acid quantum dots. Complementary small-angle X-ray and neutron scattering (SAXS and SANS) studies give a complete and quantitative picture of the nanoparticle structure. We find greater-than-monolayer coverage of oleic acid and a significant proportion of ligand remaining in solution, and we demonstrate reversible thermal cycling of the oleic acid coverage. We outline the effectiveness of simple purification procedures with applications in preparing dots for efficient ligand exchange. Our method is transferrable to a wide range of colloidal nanocrystals and ligand chemistries, providing the quantitative means to enable the rational design of ligand-exchange procedures.

Colloidal quantum dots (QDs) show great promise across a wide range of applications for their stability and size-tunable light absorption and photoluminescence. In widely used wet chemical synthesis methods,1 colloidal QDs are formed with a residual coating of stabilizing organic surfactant ligands. This layer of ligands coating the outer surface of the QD core provides an immediate dielectric contrast with the semiconductor nanocrystal core and also acts to solubilize the dots in a range of organic solvents depending upon the exact ligand chemistry. Tuning the dot surface chemistry and interfacial properties is therefore readily achievable by exchanging the ligand layer in whole or in part for a molecule of choice. The ligand surface chemistry controls the QD solubility as well as the interactions between QDs, for example, driving their aggregation or assembly into ordered lattices. Furthermore, there are several applications where it is sensitive to the semiconductor nanocrystal QD core, and controlling their aggregation or assembly into ordered lattices.

The ligand present in solution. The distribution and conformation of the bound ligand layer is also of importance both for understanding the QD properties before and after exchange and for influencing the interaction between the native bound ligand and the incoming ligand species intended for exchange.

Here we demonstrate a rigorous structural approach, utilizing complementary techniques, that is applicable to a wide range of QD and ligand chemistries to resolve, in detail, the coverage of ligands, the ligand density distribution away from the QD surface, and the residual ligand concentration in solution. The application of this approach is demonstrated for a typical QD–ligand system, namely, oleic acid stabilized PbS nanoparticles with diameters around 3 nm, synthesized by the method of Hines and Scholes,1 in the purification form in which they are prepared for optoelectronic applications (see Experimental Methods). Importantly, the measurements in this Letter are performed on real-world materials rather than on a set of idealized standard samples. The combination of small-angle X-ray scattering (SAXS), which is extremely sensitive to the semiconductor nanocrystal QD core, and

Received: April 9, 2019
Accepted: July 30, 2019
Published: July 30, 2019
small-angle neutron scattering (SANS), which is highly penetrating and exploits natural (or isotopically labeled) nuclear contrast, demonstrates unique power in determining QD–ligand structure when used together in complement with rigorous physical–chemical analyses (e.g., concentration and mass measurements) and provides further information to complement measurements such as NMR.\(^7\) The excellent size control of PbS–OA, originally motivated by optimization of the QD absorption and emission, makes the interpretation of SANS and SANS data relatively straightforward. It reduces the loss of information normally associated with size polydispersity, thereby allowing the rigorous fitting of the scattering data using analytical models in order to extract the maximum information about QD core radius (our preferred measure of QD size, used rather than diameter for the remainder of this Letter, in order to fit with scattering convention) and ligand shell thickness and density. This analysis focuses on PbS–OA but is in principle transferrable to any QD–ligand system; therefore, it lays the foundation for a breadth of future scattering studies and has particular potential in determining the initial and final states of ligand-exchange procedures.

The high electron density of the PbS quantum dot (QD) cores (X-ray scattering length density, xSLD, of PbS for a Ga source = 50.7 \(\times 10^{-6}\) Å\(^{-2}\)) translates into an excellent X-ray contrast with most organic materials and solvents (e.g., xSLD toluene = 8.03 \(\times 10^{-6}\) Å\(^{-2}\)). SANS is therefore well-suited\(^10\) to giving a preliminary measurement of the statistical averaged radius of the colloidal quantum dots with minimal influence from the attached ligand. Using an initial master batch (see Experimental Methods for materials and synthesis details) and performing dilutions, a concentration series was measured to establish the scaling of X-ray scattering with PbS–OA QDs dispersed in toluene at concentrations ranging from 1 to 51 mg/mL, with the concentrations double-checked prior to measurement by weighing the solid residues from known volumes of solution following overnight evaporation. Although only slight scattering contrast exists in these conditions (xSLD oleic acid = 8.51 \(\times 10^{-6}\) Å\(^{-2}\) at 0.895 g/cm\(^3\), i.e. even less visible when solvated), for completeness an oleic background was measured and subtracted from each of the concentrations (see the Supporting Information). The SANS data for the PbS–OA concentration series are shown in Figure 1 along with associated fits obtained from a sphere model with a hard-sphere structure factor and a log-normal distribution to describe the polydispersity in core radius, using the SasView software package. Analysis of both the scaling of the hard sphere volume fraction (Figure 1b) and the X-ray scattering indicated that multiple scattering becomes an issue at concentrations greater than approximately 30 mg/mL. The four lowest-concentration data sets (i.e., those without significant multiple scattering) were then co-refined with their radii constrained and gave a value of \(r = 16.3\) Å and a polydispersity of 0.1 (expressed using the SasView convention as the standard deviation divided by the median). We notice a flat background that was required to fit the data, which manifests itself mostly at high \(q\). Although we suspect this has a contribution from the difficulty in accurate subtraction of the toluene background in the region of its wide-angle solvent peak, we cannot rule out the presence of other scattering species present in these samples at relatively low concentrations. Transmission electron microscopy (see the Supporting Information) performed on dried PbS–OA films on a TEM grid showed that the particles are able to form highly ordered close-packed hexagonal arrays, thus confirming the highly monodisperse nature of the particles studied.

QDs were required for experiments on two small-angle diffractometers, LOQ and SANS2D, both situated at the STFC ISIS Pulsed Neutron and Muon Source (for a proper description, see Experimental Methods). The aforementioned set of PbS–OA QDs was used for the experiments carried out on SANS2D for proof of principle and also for the SANS concentration series data presented in Figure 1. A second batch was prepared for experiments carried out on LOQ and was measured using SANS at 10 mg/mL (with an appropriate OA background subtraction) to have \(r = 16.6\) Å and polydispersity = 0.1, which was considered as a good size match to the original batch.

The SANS data enable an accurate measurement of the volume fraction of PbS in the system, which allows a calculation of the relative mass fractions of PbS and OA in a QD solution. Using the data from the highest reliable concentration of 32 mg/mL (i.e., using as many QDs as possible but staying below the threshold for multiple scattering), a scale factor (PbS volume fraction) of 1.71 \(\times 10^{-3}\) indicates a true “PbS” core concentration of 13.0 mg/mL, which is notably less than the concentration of the solution. This important discrepancy exists because not all of the material in solution is PbS. A fair assumption is that the

![Figure 1](https://example.com/figure1.png)

**Figure 1.** (a) Small-angle X-ray scattering (SAXS) data from a concentration series of PbS–OA quantum dots at 1, 6, 12, 32, and 51 mg/mL at 25 °C, with oleic acid backgrounds subtracted at 0.25 times the solution concentration, with the associated model fits to a sphere model modified by a hard sphere structure factor. (b) The volume fraction of PbS cores (left axis), and the effective concentration of PbS cores (right axis) as calculated from the SAXS fits, as a function of the PbS–OA solution concentration.
remaining material is oleic acid, either attached to, or not attached to, PbS cores. While SAXS provides excellent contrast for quantifying the size, dispersity, and volume fraction of the PbS cores, there is insufficient scattering contrast between solvent and ligand to quantify the ligand envelope of the PbS−OA QDs. As the ligand plays a crucial role in determining QD optical properties and dispersion properties (as well as any consequent self-assembly\textsuperscript{11,12}) more quantitative measurements of the ligand shell composition, which we demonstrate using SANS, are therefore vital.

Unlike SAXS measurements, where elemental contrast increases with electron density, contrast for SANS measurements does not follow the same linear trend as neutron scattering length density (nSLD) is decoupled from atomic number. As such the nSLD values for PbS, oleic acid (in its bulk crystalline form, tails only), h-toluene, and d-toluene are 2.34 × 10\textsuperscript{-6}, −0.24 × 10\textsuperscript{-6}, 0.95 × 10\textsuperscript{-6}, and 5.68 × 10\textsuperscript{-6} Å\textsuperscript{-2} respectively. SANS-based measurements, exploiting the ability to change the contrast with the solvent through the use of deuteration, offer scope to understand how the OA is distributed within a PbS−OA QD dispersion.

SANS experiments were carried out to study the conformation of oleic acid on the PbS−OA QDs and to establish the behavior of the ligand envelope as a function of some simple thermal cycles. The penetrating power of SANS between organic material and the QD core allows (and to an extent, necessitates) larger concentrations to be used in the SANS experiments relative to SAXS. PbS−OA QD solutions were prepared at approximately 82 mg/mL in deuterated toluene (d-toluene) and a blend of hydrogenous and deuterated toluene (h/d-toluene), in order to produce two “contrasts” to be simultaneously fitted to a pair of constrained models (“co-refined”) in order to increase the reliability of the result. The reduced contrast and radiation flux in SANS with respect to SAXS means that higher concentrations are required to achieve good counting statistics, but the penetrating power of neutrons ensures that such concentrations (i.e., in excess of 30 mg/mL) do not present issues of low transmission or multiple scattering that would otherwise render model fitting inapplicable. Figure 2 shows the SANS data, associated fits, and extracted parameters. Figure 2a describes the relationship between the PbS−OA SANS data in d-toluene and the oleic acid background (pictured at 20 mg/mL, i.e. about 0.25 times the solution concentration, based on initial SAXS estimates of PbS core volumes), which is essential to take into account as it affects the data in the important region of the first intensity fringe. Figure 2b shows the oleic acid background-subtracted data from both contrasts at the extremes of temperature (25 and 75 °C) and shows the systematic changes in the SANS profiles. Using the PbS core radius and polydispersity obtained from SAXS as constraints for fitting the SANS data, the
simplest possible model providing an adequate fit to the data was a spherical core with a single shell ("core–shell sphere") with a hard-sphere structure factor whose effective radius is constrained to be the sum of the core radius and the shell thickness.\textsuperscript{13} The volume fraction of PbS–OA is fixed from the initial 25 °C data in subsequent data fits, using the core–shell sphere\textsuperscript{*}hard sphere volume fraction. Visually, the overall level of the scattering curve is reduced when additional solvent (relatively high SLD) enters the corona of OA and ∼20% solvent (relatively low SLD), effectively reducing the contrast between the core and the shell of the particles, and also between the overall particles and the surrounding solvent. This also marginally reduces the intensity of the first fringe centered around 0.18 Å\textsuperscript{−1} as measured relative to the first minimum in $I$ versus $q$. The fixing of the volume fraction is further vindicated by the lack of variation in the shell thickness with temperature, indicating that the particles do not undergo large swelling or deswelling as a function of temperature. The data from the two contrasts were co-refined using SasView by constraining the shell thicknesses and polydispersities. Figure 2c shows an example pairing of nSLD profiles for the two contrast situations. The neutron scattering length density profiles from the two contrasts were used to calculate (see the Supporting Information) the volume fractions of oleic acid and solvent as a function of radius as measured from the PbS quantum dot core, which are expressed in terms of the solvent penetration into the OA layer, defined at 0% within the PbS core and 100% outside the ligand envelope. The solvent/OA volume fraction profiles were consistent when calculated from either contrast, indicating that the co-refinement was successful (see the Supporting Information). Therefore, the values of thickness and solvent penetration that are quoted subsequently are the mean of those obtained from the two contrasts. It is obvious that ∼3 nm particles of crystalline PbS are not in fact spheres, but faceted nanoparticles; however, spherical averaging on both the rotational diffusion of the particles and sampling of all orientations means that the faceted nature of the PbS cores does not appear to preclude the use of sphere (or other spherically symmetric models, e.g., core–shell sphere) models,\textsuperscript{10} at least for QDs of this size. Elegant and rigorous analysis has been done of the representation of faceted PbS nanoparticle shapes as radially varying scattering length density profiles.\textsuperscript{14,15} When coupled with Bayesian parameter estimation methods for quantification of the ligand envelope, this approach provides intriguing results that are very interesting to compare with our current work, demonstrating the contrast between our simple approach and a highly mathematical one.\textsuperscript{14}

The solvent penetration into the ligand shell (Figure 2d) increases with increasing temperature from 25 to 75 °C. To gain further insights into the reversibility of solvent ingress, SANS measurements were carried out across three temperature cycles: cycle 1 (25–50–75–50–25 °C), cycle 2 (25–75–25 °C), and cycle 3 (25–75 °C (ex-situ) followed by a
rapid quench in ice to 25 °C). The synopsis of the fit data across the cycles is displayed in Figure 3. The overall ligand shell thickness (Figure 3a) does not vary significantly across the temperature cycles; however, the degree of solvent penetration varies significantly, where the error bars are set to the extremes from the two contrast scenarios (Figure 3b; see also the Supporting Information). This naturally suggests that material is expelled from the OA shell upon heating, which is consistent with an equilibrium between OA that is attached to the QD surface and OA in solution. This is borne out by the data in Figure 3c which shows the number of OA molecules within the ligand shell of the typical dot in the statistical ensemble. Briefly, this is obtained by calculating the shell volume \( V_{\text{shell}} = \frac{4}{3} \pi [(R + r)^3 - r^3] \), where \( R \) is the shell thickness and \( r \) is the dot core radius, and further considering the relative volume fractions of solvent (\( \rho_{\text{solv}} \)) and oleic acid (\( \rho_{\text{OA}} \)) as determined from the shell SLD (see the Supporting Information). Then by simple dimensional arguments, the mass of oleic acid per QD, \( M_{\text{OA}} = \rho_{\text{OA}} \text{OA} \rho_{\text{OA}} V_{\text{shell}} \) (e.g., in units of grams), and hence the number of ligands present in the shell per QD, \( N_{\text{OA}} = \frac{M_{\text{OA}}}{m_{\text{OA}}} \), may be determined (where \( m_{\text{OA}} = 282.468 \text{ g mol}^{-1} \) and \( N_A \) is the Avogadro constant \( 6.022 \times 10^{23} \text{ mol}^{-1} \)). The overall number of OA molecules decreases upon heating and recover upon cooling in all three phases of the cycle. One important consideration is that the SAXS and SANS data show that the OA coverage is greater than a single monolayer of OA when compared to the size of the PbS core within the ligand envelope. A given PbS core size offers a surface area which is at least the same as that for a sphere of equivalent volume. A cube of equivalent volume has 1.2 times that surface area (see the Supporting Information), which gives an estimate of the degree of uncertainty in the estimate. Using a spherical surface for simplicity, the density of OA molecules in a packed Langmuir monolayer yields a monolayer coverage of approximately 120 OA molecules per QD, or rather 3.51 ligands/nm² (for the QD used in this study with mean radii between 16.3 and 16.6 Å). In mass terms, it is apparent that this is a great deal less OA than is present both in solution or indeed in close proximity to the dot as measured by SAXS. This is illustrated in Figure 3d where the mass balance obtained from the SANS at 25 °C (bottom, see also Figure 1) is further annotated with the proportion theoretically attributed to an OA monolayer covering each QD, showing a greater-than-monolayer coverage that fluctuates with temperature.

The combination of SAXS and SANS measurements has enabled us to quantify ligand density for PbS–OA QDs, showing the potential for ligands to be in three different environments: (i) bound to the PbS surface, (ii) physisorbed to the QD but not bound directly to the PbS core, and (iii) as free ligand in solution. However, SANS cannot distinguish case i from case ii and resolves only as a single mass of ligand in a shell with a given penetration of solvent on average. We can only hypothesize that material must be physisorbed to the QD when greater-than-monolayer coverage exists, because there is no more room on the PbS surface for it to be chemically bound. We are careful not to stretch our hypothesis too far.

These observations of ligand structure may explain why the PbS–OA QD system is highly robust, with QDs having stable optical properties and maintaining performance at elevated temperatures. However, the excess ligand present is a significant barrier for ligand exchange, where the native OA ligand is replaced with a functional ligand. As such, in the case of PbS–OA QDs, free OA in solution will compete with any different ligand added to the QD dispersion and the dense OA shell will act as a physical barrier to ligand diffusion from solution to the PbS surface. SAXS and SANS therefore present an attractive method to gain a greater understanding of ligand exchange. The principal SAXS contrast arises from the high electron density of the semiconductor nanocrystal core relative to organic solvents and ligands. The SANS contrast can be manipulated by the use of isotopic substitution, i.e., by using deuterated solvents or ligands to uniquely label chosen components of the system. These contrast conditions for both SAXS and SANS transfer favorably to a very wide range of QD core materials and ligand chemistries.

In order to obtain PbS–OA dispersions that may be more effectively exchanged with functional ligands, an approach of successive precipitation was employed in order to achieve PbS–OA QDs with PbS:OA mass fractions approaching those of monolayer ligand coverage. It is important to note that these QD have already undergone standard purification procedures (as described in the Experimental Methods) prior to the following purification. Precipitation was induced in PbS–OA QD dispersions in toluene, by adding methanol:isopropanol, resulting in a solvent composition of toluene:methanol:IPA of 2:1:1, followed by centrifugation and redispersion in toluene. Utilizing the aforementioned methodology for measuring the PbS:OA mass balance utilizing SAXS, data show (Figure 4) that successive purifications via precipitation shift the mass balance of PbS:OA toward expected values for monolayer, or even submonolayer, ligand coverage. We therefore conclude that this part of the work will be of particular value to those seeking to perform custom functionalizations of QDs in the future.

In conclusion, the combination of SAXS and SANS allows a rigorous study of the native oleic acid ligand layer on PbS–OA colloidal QD. The excellent SAXS contrast for PbS QDs allows their average core dimensions to be measured with very small
relative errors. Despite their true nature as highly faceted cubes, spherical models are adequate to describe their scattering data allowing full fitting of the data. The use of two co-refined contrasts in SANS reveals that the PbS–OA structure is adequately described by a simple core–shell sphere model (with a hard sphere structure factor). In particular, the OA coverage is greater than a single monolayer coverage and further OA is present in solution, which contributes in particular to SANS in fully deuterated solvent. Some of the OA is attached to the actual PbS, but only up to a monolayer coverage, meaning that some is hypothesized to be simply adsorbed to the ligand envelope, i.e. without its headgroup in direct contact with the QD surface. This latter category is referred to as physisorbed. Material can be removed from the OA envelope by heating, and the process is reversible. The ‘excess’ above a single monolayer coverage can be removed by precipitation, centrifugation, and redisruption. The effective control of ligand exchange on quantum dots, which is expected to have wide-ranging applications in optics, electronics, energy harvesting, and photocatalysis, relies on a detailed knowledge of the conformation of the native ligand shell to achieve functionally optimum outcomes. The techniques demonstrated in this Letter are highly transferrable to other QD and ligand chemistries and have particular potential in the benchmarking of QD ligand-exchange procedures by making accurate structural measurements of the initial and final states.

### EXPERIMENTAL METHODS

**Synthesis of Oleic Acid-Capped Lead Sulfide Colloidal Quantum Dots (PbS–OA).** A master batch of oleic acid-capped PbS nanocrystals was synthesized by the method of Hines and Scholes.1 Lead oxide (PbO, 99.999%) was purchased from Alfa Aesar. Ethanol and 1-butanol (Hi-Dry anhydrous) were purchased from Romil. All other chemicals were purchased from Sigma-Aldrich. All materials were used as received without further purification. Lead oxide (1.25 g, 5.6 mmol), oleic acid (OA, 90%, 4 mL, 12.6 mmol), and 1-octadecene (ODE, 90%, 25 mL, 78 mmol) were placed in a three-necked round-bottomed flask and degassed under vacuum (<10−2 mbar) at 110 °C for 2 h with stirring, forming a colorless solution. In a nitrogen glovebox, a syringe was prepared (ODE, 90%, 25 mL, 78 mmol) were placed in a three-necked round-bottomed flask and degassed under vacuum (<10−2 mbar) at 110 °C for 2 h with stirring, forming a colorless solution. In a nitrogen glovebox, a syringe was prepared with ethanol/butanol and centrifuged at 12 000 × g. The as-formed nanocrystals were then suspended with hexane and precipitated again with ethanol. The purified nanocrystals were suspended in toluene for storage.

**Small-Angle Neutron Scattering.** SANS was carried out on the LOQ16 and SANS2D17 small-angle diffractometers at the ISIS Pulsed Neutron Source (STFC Rutherford Appleton Laboratory, Didcot, U.K.).18 Samples were prepared in deuterated solvents or blends of hydrogens and deuterated solvents, providing the necessary contrast, and were contained in 1 or 2 mm path length quartz cells (Hellma GmbH), with the longer path length reserved for fully deuterated solvents and the shorter path length required to reduce the absorbance and incoherent background in h/d solvent blends. Sample solutions of a desired concentration were prepared through drying aliquots of stock solutions of PbS–OA, followed by the addition of the relevant solvent (d-toluene, h/d-toluene blend, d-dodecane). In the following, the magnitude of the scattering vector is defined as $q = \frac{4\pi \sin \theta}{\lambda}$ where $\theta$ is the angle between the incident and scattered X-ray or neutron of wavelength $\lambda$.

**LOQ.** This is a fixed-geometry time-of-flight instrument which utilizes neutrons with wavelengths between 2.2 and 10 Å. Data are simultaneously recorded on two, two-dimensional, position-sensitive, neutron detectors, to provide a simultaneous $q$-range of 0.007–1.0 Å⁻¹.

SANS2D. A simultaneous $q$-range of 0.006–1.2 Å⁻¹ was achieved utilizing an incident wavelength range of 1.65–16.5 Å and employing an instrument set up of L1 = L2 = 4 m, where L1 and L2 are the pre and post sample flight paths respectively, with the rear detector offset vertically 75 mm and horizontally 100 mm.

For both instruments, the beam diameter was collimated to 12 mm at the sample. For all collected data, each raw scattering data set was corrected for the detector efficiencies, sample transmission, and background scattering and converted to scattering cross-sectional data ($\partial \Sigma / \partial \Omega$ vs $q$) using the instrument-specific software.19 These data were placed on an absolute scale (cm⁻¹) using the scattering from a standard sample (a solid blend of hydrogenous and perdeuterated polystyrene) in accordance with established procedures.20 Fitting was performed using the SasView software package.13

**Small-Angle X-ray Scattering.** Small-angle X-ray scattering measurements were carried out on a Xeuss 2.0 instrument equipped with an Excillum MetalJet liquid gallium X-ray source. Samples were measured in 2 mm external diameter borosilicate glass capillaries with a 0.01 mm wall thickness, with scattering data collected for 900 s using collimating slits of 0.5 × 0.6 mm (‘high flux’ mode). Scattering patterns were recorded on a vertically offset Pilatus 1 M detector with a sample-to-detector distance of 555 mm calibrated using a silver behenate standard to achieve a q-range of 0.03–1.0 Å⁻¹. Data were adjusted for transmission, backgrounds (solvent and glass capillary), sample thickness, and acquisition time before the data were placed on an absolute scale (cm⁻¹) using scattering from a standard sample of glassy carbon.21 Data reduction was performed using the instrument-specific Foxtrot software and the IRENA22 macros for Igor Pro, before fitting was performed using SasView. Additional measurements were taken on a laboratory SAXS instrument (NanoStar, Bruker) equipped with a microfocus Cu Ka X-ray source, collimating system with motorized scatterless slits (Xenocs, France), and HiStar 2D multiwire gas detector (Siemens/Bruker). Scattering patterns were collected with a sample-to-detector distance of 26 cm and a beam size of 1 × 1 mm, corrected for the detector’s dark current, spatial distortion, and flat field, normalized using sample thickness, exposure time, sample transmission, and the detector normalization coefficient.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.9b01008.

Transmission electron microscopy, further small-angle scattering information including SAXS background calculations, results from SAXS fitting, synopsis of all SANS data, details for scattering length density
calculations, quantum dot surface area considerations, and comparisons between SANS contrasts. (PDF)

Author Information

Corresponding Author
E-mail: weir.mp@gmail.com.

ORCID
Michael P. Weir: 0000-0001-8283-1040
Daniel T. W. Toolan: 0000-0003-3228-854X
Nicholas J. W. Penfold: 0000-0002-6505-3782
Zhilong Zhang: 0000-0001-9903-4945
Victor Gray: 0000-0001-6583-8654
Simon Dowland: 0000-0002-3613-5666
Neil C. Greenham: 0000-0002-2155-2432
Richard H. Friend: 0000-0001-6565-6308
Akshay Rao: 0000-0003-4261-0766

Author Contributions
M.P.W. and D.T.W.T. contributed equally to this work.

Notes
The authors declare no competing financial interest. The underlying data from this Letter are available at 10.15131/shef.data.9206123.

Acknowledgments
The authors acknowledge funding through the Engineering and Physical Sciences Research Council (UK) via grant numbers EP/P027814/1 and EP/P027741/1. The authors acknowledge beamtime awarded at the ISIS Pulsed Neutron and Muon Source through experiment numbers RB1810513 (DOI: 10.5286/ISIS.E.RB1810513), RB1820367 (DOI: 10.5286/ISIS.E.RB1820367), and RB1910086 (DOI: 10.5286/ISIS.E.RB1910086). The authors acknowledge Dr. O. Mykhaylyk and Dr. J. Jennings for their assistance with additional SAXS measurements performed on the NanoStar instrument.

References

(1) Hines, M. A.; Scholes, G. D. Colloidal PbS Nanocrystals with Size-Tunable near-Infrared Emission: Observation of Post-Synthesis Self-Narrowing of the Particle Size Distribution. Adv. Mater. 2003, 15, 1844–1849.
(2) Harris, R. D.; Bettis Homan, S.; Kodaimati, M.; He, C.; Nepomnyashchii, A. B.; Swenson, N. K.; Lian, S.; Calzada, R.; Weiss, E. A. Electronic Processes within Quantum Dot-Molecule Complexes. Chem. Rev. 2016, 116, 12865–12919.
(3) Zhang, Z.; Edme, K.; Lian, S.; Weiss, E. A. Enhancing the Rate of Quantum-Dot-Photocatalyzed Carbon–Carbon Coupling by Tuning the Composition of the Dot’s Ligand Shell. J. Am. Chem. Soc. 2017, 139, 4246–4249.
(4) Huang, Z.; Li, X.; Mahboub, M.; Hanson, K. M.; Nichols, V. M.; Le, H.; Tang, M. L.; Bardeen, C. J. Hybrid Molecule–Nanocrystal Photon Upconversion across the Visible and near-Infrared. Nano Lett. 2015, 15, 5552–5557.
(5) Mongin, C.; Garakarayagh, S.; Razgoniaev, N.; Zamkov, M.; Castellano, F. N. Direct Observation of Triplet Energy Transfer from Semiconductor Nanocrystals. Science 2016, 351, 369–372.
(6) Davis, N. J.; Le, K.; Allardice, J. R.; Xiao, J.; Petty, A. J.; Greenham, N. C.; Anthony, J. E.; Rao, A. Singlet Fission and Triplet Transfer to PbS Quantum Dots in Triphenylamine Derivatives. J. Phys. Chem. Lett. 2018, 9, 1454–1460.
(7) Mongin, C.; Moroz, P.; Zamkov, M.; Castellano, F. N. Thermally Activated Delayed Photoluminescence from Pyrenyl-Functionalized CdSe Quantum Dots. Nat. Chem. 2018, 10, 225–230.
(8) Choi, J.-H.; et al. Exploiting the Colloidal Nanocrystal Library to Construct Electronic Devices. Science 2015, 351, 369–372.
(9) Moreels, L.; Justo, Y.; De Geyter, B.; Haustraete, K.; Martins, J. C.; Hens, Z. Size-Tunable, Bright, and Stable PbS Quantum Dots: A Surface Chemistry Study. ACS Nano 2011, 5, 2004–2012.
(10) Maes, J.; Castro, N.; De Nolf, K.; Walravens, W.; Abécassis, B.; Hens, Z. Size and Concentration Determination of Colloidal Nanocrystals by Small-Angle X-Ray Scattering. Chem. Mater. 2018, 30, 3952–3962.
(11) Baumgardner, W. J.; Whitham, K.; Hanrah, T. Confined-but-Connected Quantum Solids Via Controlled Ligand Displacement. Nano Lett. 2013, 13, 3225–3231.
(12) Whitham, K.; Smailgie, D.-M.; Hanrah, T. Entropic, Enthalpic, and Kinetic Aspects of Interfacial Nanocrystal Superlattice Assembly and Attachment. Chem. Mater. 2018, 30, 54–63.
(13) Sasview Home Page. http://www.sasview.org/ (accessed July 4, 2019).
(14) Winslow, S. W.; Scherbakov-Wu, W.; Liu, Y.; Tisdale, W. A.; Swan, J. W. Characterization of Colloidal Nanocrystal Surface Structure Using Small Angle Neutron Scattering and Efficient Bayesian Parameter Estimation. J. Chem. Phys. 2019, 150, 244702.
(15) Winslow, S. W.; Liu, Y.; Swan, J. W.; Tisdale, W. A. Quantification of a PbClx Shell on the Surface of PbS Nanocrystals. ACS Materials Letters 2019, 1, 209–216.
(16) Heenan, R. K.; Penfold, J.; King, S. M. SANS at Pulsed Neutron Sources: Present and Future Prospects. J. Appl. Crystallogr. 1997, 30, 1140–1147.
(17) Heenan, R. K.; Rogers, S. E.; Turner, D.; Terry, A. E.; Treadgold, J.; King, S. M. Small Angle Neutron Scattering Using Sans2d. Neutron News 2011, 22, 19–21.
(18) STFC ISIS Neutron and Muon Source Home Page. https://www.stfc.ac.uk/ (accessed July 4, 2019).
(19) Mantid Project Home Page. http://www.mantidproject.org/ (accessed July 4, 2019).
(20) Wignall, G. D.; Bates, F. S. Absolute Calibration of Small-Angle Neutron Scattering Data. J. Appl. Crystallogr. 1987, 20, 28–40.
(21) Fan, L.; Degen, M.; Bendle, S.; Grupido, N.; Ilavsky, J. The Absolute Calibration of a Small-Angle Scattering Instrument with a Laboratory X-Ray Source. Journal of Physics: Conference Series 2010, 247, 012005–012005.
(22) Ilavsky, J.; Jemian, P. R. Irena: Tool Suite for Modeling and Analysis of Small-Angle Scattering. J. Appl. Crystallogr. 2009, 42, 347–353.