Sizing Curve, Absorption Coefficient, Surface Chemistry, and Aliphatic Chain Structure of PbTe Nanocrystals

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Supporting Information

ABSTRACT: For colloidal semiconductor nanocrystals (NCs), the knowledge of the chemical structure and the size-dependent optical properties is of crucial importance, both from a practical and fundamental perspective. Here, we report the basic properties of PbTe NCs in order to complement the already existing knowledge on PbS and PbSe NCs. The band gap versus NC diameter (sizing) curve was determined by combining transmission electron microscopy with absorption spectroscopy; the energy of the primary optical absorption follows 1/d dependence with the diameter. The lead content of the NCs was determined by combining inductive coupled plasma optical emission spectrometry and the relative tellurium content with energy-dispersive X-ray spectroscopy. Combining these results yields a relation for the intrinsic absorption coefficient, which is independent of the NC size at 3.1 eV. The PbTe NCs are stabilized by Pb(oleate)₂, but different from PbS NCs, oleate is predominantly bound in a chelating bidentate coordination. Besides that, we analyzed the structure of the aliphatic chains on all lead chalcogenide NCs and showed that the aliphatic chains are partly crystalline near the core and more liquid-like at the solvent side.

Colloidal semiconductor nanocrystals (NCs) exhibit size-dependent optoelectronic properties, of interest, for a whole range of applications such as light-emitting devices,1−4 field-effect transistors,5−7 biomedical imaging,8−9 and photodetectors.10 PbX (X = S, Se, Te) NCs are of special interest due to their tunable near-IR emission and large exciton Bohr radii.10,11 Besides this, PbX NCs have been used as building blocks for several superstructures made by NC assembly, followed by oriented attachment.11,12−14 PbX NCs have a rock salt crystal structure; attachment occurs exclusively via (100) facets on which the oleate capping is less strongly bound.15 Two-dimensional superstructures with several periodic motifs such as the square and honeycomb have been obtained; interestingly, they can all be considered as 2D plane cutouts from a simple cubic lattice.14,16

Because of the low effective mass of the electrons in PbTe, the quantum coupling between attached NCs is even stronger than for the cases of PbS and PbSe.17 For superstructures of PbTe, novel electronic band structures can be expected, especially for the honeycomb geometry. Furthermore, because of the large mass of Pb and Te, the spin−orbit coupling is strong; PbTe superstructures thus hold promise for future spintronics.18 In addition, once a PbTe superstructure is fabricated, the Pb²⁺ ion can be exchanged for Cd²⁺ and possibly Hg²⁺.19 This can result in two-dimensional zinc blende geometric materials with exciting optoelectronics. For example, honeycomb superstructures composed of HgTe are predicted to show the quantum spin Hall effect almost up to room temperature.19 PbTe is also particularly promising for energy conversion in high-ZT thermoelectric devices.20−23

Control of the nanogeometry is of crucial importance for these thermoelectric devices because the efficiency can be improved by promoting phonon scattering at crystal interfaces or nanoinclusions.24,25 Hence, superstructures of PbTe NCs, fabricated in a bottom-up approach, can possibly result in cheap and well-defined materials for thermoelectrics.

Despite these prospects, colloidal PbTe NCs have been far less studied than the PbS and PbSe NC systems. This is due to the problematic chemistry, such as the low synthetic yield and extreme vulnerability to oxygen. Proper chemical synthesis and surface chemistry remains challenging even under the quasi-inert conditions in a glovebox.26 Other difficulties are the discrepancy in the relation between the absorption peak and the NC size,1−5 and the absence of a way to determine the NC concentration. Furthermore, it has never been examined how (oleate) ligands bind to the PbTe facets, and how the ligand layer is structured; these topics are important to understand issues such as chemical (in)stability, shell-epitaxy, and PbTe NC self-assembly.

Here, we present experiments that resulted in the relation between the energy of the primary absorption peak and the PbTe NC size. An empirical fit establishes a sizing curve, which follows 1/d dependence. With the use of the Lambert−Beer law, we were able to determine the molar absorption coefficient at the band gap and at 3.1 eV. The intrinsic
absorption coefficient at 3.1 eV is size independent; the optical matrix element is entirely determined by the PbTe unit cells and crystal structure. We also investigated the surface chemistry with proton nuclear magnetic resonance (1H NMR) and Fourier transform infrared spectroscopy (FT-IR), and compared this with the other PbX NCs. This shows that all PbX are bound by z-type Pb(oleate)₂ ligands. Because of the larger unit cell, the oleate is predominantly bound in a chelating bidentate coordination in PbTe NCs instead of a bridging bidentate coordination for PbS. We also measured the structure of the oleate ligands on suspended PbX NCs and showed that the aliphatic chains are partly crystalline near the NC core, while the liquid-like part sticks into the solvent.

**THE PbTe SIZING CURVE**

The hot-injection method for the synthesis of PbTe NCs is developed by Murphy et al.²⁷ and Urban et al.² and used here to synthesize PbTe NCs in a diameter range between 3.5 and 7 nm. Control over the NC size was most easily achieved by varying the oleic acid/Pb ratio in the Pb precursor or by changing the growth time after injection. Both a higher oleic acid/Pb ratio and a longer growth time resulted in larger NCs. The high-resolution transmission electron microscopy (HR-TEM) images in Figure 1 show that the quasispherical PbTe NCs are single-crystalline, without an amorphous layer on the NC surface. To determine the average size of the PbTe NCs in a given batch, approximately 300 particles per batch were analyzed in the same manner for each batch. Although the size analyzed in the same manner for each batch.

Four examples of absorption spectra of the NCs are plotted in Figure 2a, normalized at 400 nm. Although the size dispersion is <10%, the band-edge peak overlaps with other transitions due to its complex band structure. This gives rise to a number of allowed transitions immediately after the first exciton peak.²⁷ Combining the peak position of the band edge with the NC size determined by transmission electron microscopy (TEM), we could establish a sizing curve as shown in Figure 2b. The red dots are PbTe NCs from this work, while the green dots are from Urban et al.² and the blue dots are of Murphy et al.²⁷ This shows that the data of Urban et al. deviate significantly from the other experimental data. We therefore excluded those data points in the fit for the sizing curve (black line).

The fitted sizing curve for PbTe is

\[ E_0 = 0.376 + \frac{1}{0.42d} \]  

Here, \( E_0 \) is the band gap in eV, and \( d \) is the NC diameter in nm. The sizing curve allows us to determine the size of the PbTe NCs immediately from an absorption spectrum, instead of a tedious TEM study. An important factor in this equation is the constant 0.376, which is close to the bulk band gap value of PbTe.²⁵,²⁸ Most sizing curves also have a \( 1/d^2 \) term, but its coefficient was too small to contribute in our equation. The predominance of the \( 1/d \) term was also found experimentally and by calculation for PbSe and Pb NCs.²⁶,⁵⁰ The \( 1/d \) dependence can be due to a combination of different effects, for example, exciton wave function spill-over, electron–hole many-body effects, and/or deviation from perfect parabolic bands.³¹ The same line of thought can be applied to PbTe, which has a more anisotropic band structure but does have a derivation from parabolicity near the band structure near the band edge.³² The contribution of the \( 1/d^2 \) term might become relevant if a larger NC size range is included. The current synthesis is however not suitable for very small or large NCs. Small NCs are often polydispersive which hinders the size determination, while for larger NCs, a shape change from spherical to quasicubical occurs, which broadens the absorption peak.

**QUANTIFYING LIGHT ABSORPTION**

We used inductive coupled plasma optical emission spectrometry (ICP–OES) to determine the Pb content in the PbTe NC suspensions investigated. The Pb²⁺ concentrations and their relative standard deviations (RSDs) are shown in Table S1. The sample purity was checked with 1H NMR (see below). We were unable to reliably measure the Te²⁻ concentration with ICP–OES due to the formation of volatile hydrides. Therefore, we measured the atomic Pb/Te ratios by energy-dispersive X-ray spectroscopy (EDX) shown in Table 1. The total amount of atoms per NC is calculated using eq 2, assuming a spherical shape.

\[ N = \frac{4\pi}{3}(d/a)^3 \]  

Table 1. Atomic Ratio and Total Number of Atoms per NC for Some PbTe NCs²

| NC size (nm) | Pb atomic (%) | Te atomic (%) | Pb/Te ratio | N (atoms/NC) |
|--------------|---------------|---------------|-------------|--------------|
| 4.87         | 53.87 (0.15)  | 46.13 (0.10)  | 1.16        | 1827         |
| 5.74         | 55.24 (0.42)  | 44.75 (0.31)  | 1.24        | 2992         |
| 5.98         | 54.09 (0.49)  | 45.90 (0.30)  | 1.18        | 3383         |
| 6.85         | 53.59 (1.65)  | 46.40 (0.95)  | 1.15        | 5085         |

²The number between brackets is the RSDs directly from EDX.
where $a$ is the lattice parameter, and $d$ is the particle diameter, both in nm. The amount of atoms is corrected for the uneven Pb/Te ratio, $R$ in eq 3. The number of NCs then follows from the total amount of PbTe unit cells measured in the sample divided by the number of unit cells per NC. Or in other words, the NC concentration $C_{NC}$ is given by

$$C_{NC} = \frac{1}{N} \left( \frac{R}{R_{C}} \right) C_{m}$$

(3)

Here, $C_m$ is the lead concentration in the sample. We measured an absorption spectrum and combined it with the PbTe NC concentrations to calculate the molar absorption coefficient (also known as molar extinction coefficient) at the band gap, and at 3.1 eV.

**Absorption Coefficient at Band Gap**

The band-edge absorption peak is fitted with Gaussian and integrated to get a measure of the NC absorbance of a given sample. From this, the energy-integrated molar absorption coefficient at the band gap $\varepsilon_{gap}$ is derived using the Lambert–Beer law

$$\log \frac{I}{I_0} = -\varepsilon c l = -A$$

(4)

where $A$ is the absorbance or absorptivity of our suspension for an optical path length $l$. $A$ = dimensionless, $\varepsilon$ = the molar absorption coefficient (mol$^{-1}$ cm$^{-1}$), and $c$ = the molar concentration of PbTe NCs. Figure 3a presents an overview of the experimental data relating energy-integrated $\varepsilon_{gap}$ (meV mol$^{-1}$ cm$^{-1}$) to NC size. Similar as for PbSe and PbS, a power log is used to fit the data. This resulted in the following relation

$$\varepsilon_{gap} = 2.2d^{1.1}$$

(5)

The relation obtained from the data is similar compared to the energy-integrated molar absorption coefficients of PbS and PbSe$^{29,30}$ PbTe NCs, however, absorb less light at the band gap compared to other lead chalcogenides. An additional means of comparison is the energy-integrated absorption coefficient $\varepsilon_{gap/U}$ per unit cell (U), which is calculated with the following formula,$^{19}$ and shown in Figure 3b

$$\varepsilon_{gap/U} = \frac{6 \ln(10) \varepsilon_{gap}}{\pi d^3 N_A} = 15.6 d^{-1.9}$$

(6)

This shows that $\varepsilon_{gap/U}$ is size dependent and increases with decreasing size.

**Absorption Coefficient at 3.1 eV**

We also applied the Lambert–Beer law using the absorption at 3.1 eV. For other NCs, it was found that at this energy, far above the first optical transition, the effects of quantum confinement on the absorption coefficient per unit cell can be neglected. $^{29,30,33,34}$ This would mean that the absorbance per NC should be simply proportional to the number of PbTe unit cells, thus to the NC volume. The experimental results are presented in Figure 4a, which can be fitted with

$$\varepsilon_{3.1eV} = (0.05846 \pm 0.002) d^3$$

(7)

Figure 4. Absorption coefficient of PbTe NCs at 3.1 eV. (a) Molar absorption coefficient at 3.1 eV for different sizes of PbTe NCs. The data points follow $d^3$ dependence. (b) Intrinsic absorption coefficient $\varepsilon_{3.1eV/U}$ is size independent, as seen from the red dots. The blue line is the calculated $\varepsilon_{3.1eV/U}$ using the bulk PbTe dielectric function.
function of PbTe. The calculated value is added in Figure 4b as a blue line. It shows that the calculated and measured intrinsic absorption coefficients are in good agreement.

**SURFACE CHEMISTRY OF PBTE NCs**

In the case of PbSe and PbS NCs, the ligands have been investigated with FT-IR and \(^1\)H NMR.\(^{30,39,40}\) In Figure 5a, we show a typical \(^1\)H NMR spectrum for PbTe NCs dissolved in chloroform-\(d\). There are no sharp peaks visible, besides the peaks originating from the solvent molecules, chloroform-\(d\), and ferrocene (internal standard). This shows that all other moieties are bound to the NC surface and there are no unreacted precursors in the suspension. The \(^1\)H NMR peak positions and integrals correspond to oleate on the NC surface, which is also confirmed by the absence of an acid peak (left inset Figure 5a).

A typical FT-IR spectrum of PbTe NCs is shown in Figure 5b and also confirms the presence of oleates as major species on the PbTe NC surface. The two saturated peaks around 800 and 900 cm\(^{-1}\) originate from the tetrachloroethylene solvent. The inset of Figure 5b shows the CH stretch region, which matches with oleate ligands.\(^{39}\) There are no other broad or sharp peaks, which show the absence of hydroxide or water as a major component on the PbTe NC surfaces, similar as found for PbSe.\(^{38}\) Figure 5d shows a higher magnification on the carboxylic region, where there is no acid peak visible around 1710 cm\(^{-1}\). This confirms that it is oleate that is bound to the NC surface, not oleic acid.

PbTe NCs are dissolved in an apolar solvent, so this would suggest that the negatively charged oleate needs to be charge compensated by positively charged lead atoms. This is confirmed by our EDX analysis in Table 1 showing an excess of Pb\(^{2+}\) ions compared to Se\(^{\text{2-}}\); the excess of Pb\(^{2+}\) ions on PbTe NCs is similar to that reported for PbS and PbSe NCs.\(^{39,40}\) This strongly suggests that the PbTe NCs are capped by Pb\((\text{oleate})_2\) as z-type ligands, with oleate charge compensated by excess lead.

The ligand density of several samples was determined with either \(^1\)H NMR by the use of an internal standard or FT-IR by the use of a calibration curve.\(^{39,41,42}\) This resulted in similar values as found for other semiconductor NCs,\(^{39,40}\) ranging from 2.2 to 4.6 oleate/nm\(^2\).

**OLEATE COORDINATION**

The carboxylic vibrations for all three PbX NCs are shown in Figure 5d, normalized on the CH\(_2\) stretching vibration at 2925 cm\(^{-1}\). This shows remarkable differences in the intensities and positions of the symmetric (\(\nu_{\text{sym}}\)) and asymmetric (\(\nu_{\text{asym}}\)) stretch vibrations for the three types of Pb-chalcogenide NCs.

The energy difference between the symmetric and asymmetric carboxylate stretch is often used to assign the carboxylic coordination, but the effects seen here are stronger.\(^{39}\) Also, the NC size and solvent does not influence the coordination significantly (Figures S1 and S2). This means that the results should be related to differences between PbS, PbSe, and PbTe cores.

The energy difference between the symmetric and asymmetric carboxylate stretch is often used to assign the carboxylic bonding coordination.\(^{43-45}\) There is however quite some discussion regarding the generality of this method.\(^{46}\) Recently, it has been shown by a combination of FT-IR and structural information that similar band positions, as displayed, in Figure 5d, can be attributed to bidentate bridging and chelating coordinations,\(^{47,48}\) because a monodentate coordination has a higher \(\Delta \nu\).\(^{46}\) The broadening and non-Lorentzian shape of the bands shown here indicate that both types of carboxylic coordination are present on all PbX surfaces. In Figure S3 and Table S2, we deconvoluted \(\nu_{\text{sym}}\) and \(\nu_{\text{asym}}\) by fitting two Lorentzians under each \(\nu_{\text{sym}}\) and \(\nu_{\text{asym}}\) to separate the different components. Cass et al. found that the low wavelength peak of the \(\nu_{\text{sym}}\) vibration and the high wavelength peak of \(\nu_{\text{asym}}\) belong to the bridging bidentate carboxylic coordination,\(^{43}\) while the high wavelength peak of \(\nu_{\text{sym}}\) and the low wavelength peak of \(\nu_{\text{asym}}\) belong to the chelating coordination (see Figure 5d). The assignment was, among other things, based on the observation that the intensity of the coupled peaks vary simultaneously. This seems also to be true for our PbX NCs; the chelating combination has a higher intensity for PbTe (and PbSe NCs), while the bridging peaks are more intense for PbS. The energy difference also matches...
the assignment of the coordination because a chelating bidentate coordination generally has a lower $\Delta$ than a bridging bidentate coordination. The energy difference for the chelating bidentate coordination of all three PbX ranges from 90 to 97 cm$^{-1}$, while it ranges from 131 to 151 cm$^{-1}$ for the bridging bidentate coordination. The intensities of the bands for PbX NCs suggest that the amount of bridging coordinations decreases going from S and Se to Te. It should be noted that it is expected that there are some variations in the peak position and intensity of $\nu_{\text{sym}}$ and $\nu_{\text{asym}}$ for different PbX NCs due to differences in the lead carboxylate bonding angle and variation in the Pb--O bond distance.44,47,49

The dominant chelating bidentate coordination for PbTe NCs can be reasoned by the larger unit cell size. The Pb density on the (111) facet of the rock salt PbX crystal, which binds most of the oleate ligands,39 is 6.5S, 6.1S, and 5.53 nm$^{-2}$ for PbS, PbSe, and PbTe, respectively. The lead atoms on the (111) facets are partly integrated into the crystal lattice,39 which means that one exposed lead atom on the (111) facet should be charge compensated by one oleate. The density of aliphatic chains is however sterically limited to approximately 4--4.6 chains nm$^{-2}$ on planar surfaces.50,51 This means that in the case of PbS, there are much more lead atoms compared to carboxylate groups, meaning that some lead atoms might "share" one carboxylate, resulting in a bridging coordination. Similarly, it was recently found that the Pb--Pb distance in crystalline metal soaps is 4.45 Å. This crystal contained a combination of bridging and chelating bidentate coordinations.47 The Pb--Pb distance on the (111) facets in PbS, PbSe, and PbTe is, respectively, 4.20, 4.33 and 4.57 Å, which shows that the likelihood for bridging coordinations is the highest for PbS.

**ALIPHATIC CHAIN STRUCTURE IN SOLUTION**

FT-IR also provides structural information about the aliphatic part of the oleate ligands on the NC surface. The most important feature is the progression of bands between 1150 and 1400 cm$^{-1}$, which shows a series of well-defined peaks for all-trans crystalline chains and can be assigned to the twisting--rocking and wagging CH$_3$ vibration.52,53 The CH$_2$ groups in a liquid-like state can move freely, resulting in a large number of rotational isomers which smears the peaks out, and eventually even disappear for liquid chains.52,53 This is clearly visible when you compare dissolved Pb(oleate)$_2$ and solid Pb(oleate)$_2$ in Figure 5c. The only peak which is still recognizable in the dissolved Pb(oleate)$_2$ spectrum is the umbrella mode of CH$_3$ (indicated with a U), which does not depend on chain packing.

The progression bands of solid Pb(oleate)$_2$ show much resemblance with progression bands recently resolved for the crystalline aliphatic chain of Zn(oleate)$_2$.54 These authors showed that in comparison with Zn(stearate)$_2$, the hydrocarbon chain before and after the double bond melts independently and therefore has a rather complicated peak pattern.54 Recently, Martinez-Casado et al. identified all phase transitions of several saturated lead(II) soaps.57 The hydrocarbon chain packing changes from a completely crystalline phase to a rotator phase in which the alkyl chains have rotational freedom. The phase can change further to a liquid crystal before it completely melts to a stable isotropic liquid.47 Research on gold and silver NCs showed that the saturated aliphatic chains are partly crystalline; the chains pack in an all-trans conformation near the NC core, while the chains are more liquid-like at the end of the chain.55-60 Another indication of a partially crystalline phase is the exact peak position of the CH$_3$ stretch vibration. The exact peak positions of the symmetric and asymmetric CH$_3$ stretch vibration for the crystalline chain are 2850 and 2920 cm$^{-1}$, respectively. Because of the presence of gauche disorder in the alkyl chain, these peaks shift to higher frequencies for the rotator phase, namely, 2856 and 2928 cm$^{-1}$.47 We found a frequency in the range of 2852--2854 and 2924--2926 cm$^{-1}$ for PbX NCs larger than approximately 4 nm. More freedom of movement at the end of the chain can be seen from the absence of peak splitting of the methyl (CH$_3$) group at 2957 cm$^{-1}$ ($\gamma$, inset Figure 5b). This points to aliphatic chains that are neither fully crystalline nor fully liquid-like. Because of the different melting behaviors of the aliphatic chain before and after the double bond of oleate,54 it is tempting to suggest a predominantly liquid-like phase outward from the double bond to the methyl group and a more crystalline phase inward from the double bond to the NC core.

**ALIPHATIC CHAIN STRUCTURE IN DIFFERENT SOLVENTS**

NCs which are dissolved in benzene show an even more pronounced sequence of peaks, indicating a more solid-like ligand shell (see Figure 5c). The energy difference between the six peaks is approximately equal, suggesting that the complete chain from the core to the double bond is in a solid-like state. Recently, it was found that a broader peak in $^{1}H$ NMR indicates less solvated ligands.51 The peak width of 5.1 nm PbSe NCs dissolved in different solvents confirms this trend. The $^{1}H$ NMR spectra are shown in Figure S4, and a comparison of the vinyl peak width is shown in Table 2.

| solvent            | vinyl peak width [Hz] |
|--------------------|-----------------------|
| chloroform-d       | 23                    |
| hexane-d$_4$       | 30                    |
| benzene-d$_4$      | 54                    |
| toluene-d$_6$      | 56                    |
| chlorobenzene-d$_6$ | 47                    |

There is more broadening of the peaks when NCs are dissolved in an aromatic solvent, compared to the smaller tetrachloroethylene and hexane. This indicates that the aromatic solvent molecules are too large to penetrate deeply into the ligand chain, which results in a more solid-like ligand shell. Similar as found before, also halocarbons seem to penetrate deeper into the ligand corona compared to hydrocarbons.52

These findings not only contribute to a better understanding of ligand--ligand interaction in a capping layer but also of the interaction between NCs during self-assembly. Recently, it was shown that these interactions have a large influence on the NC nucleation and growth,63 solubility,14,65 and self-assembly.62,66--68

**CONCLUSIONS**

Unlike for PbS and PbSe NCs, a number of basic properties of PbTe NCs were not investigated so far. Above, we reported some crucial optical, chemical, and structural characteristics of state-of-the-art PbTe NCs. First, we established the size dependency of the band gap, demonstrating strong quantum
PbTe surface cannot be excluded,
we could not possible under inert conditions. Although a slight oxidation of the 
wash was then separated from the supernatant and redispersed in hexane.
was su
al.2 The Pb precursor was synthesized in a fumehood by the addition 
and PbS has the most bridging con
coordination. Because of limited space on the NCs surface,
is a combination of bridging and chelating bidentate 
chemistry.

this in the TEM images and in our large data set on the surface 
can be formed through varying reaction times, injection temperature, 
are concentration gradients in the mixture. After 4 min, the growth 
injected under vigorous stirring. Upon injection, the solution 
inside the glovebox. 90 mL of 
was allowed to warm to room temperature. Oleic acid (25.437 g, 90.05 mmol, 2.01 equiv), isopropanol (∼180 mL), and triethylamine (10.246 g, 101.25 mmol, 2.26 equiv) were added in a 500 mL Erlenmeyer flask. The lead trifluoroacetate solution was slowly added to the oleic acid solution while stirring, resulting in the formation of a white precipitate. The mixture was heated to reflux and dissolve the precipitate, after which a clear and colorless solution was obtained. The heat was turned off, and the flask was allowed to cool to room temperature, followed by further cooling in a −20 °C freezer for >2 h. The resulting white powder was isolated by suction filtration using a glass-fitted funnel, and the filtrate is thoroughly washed with methanol (3 × 300 mL). Large pieces were crushed to get a white powder. This was subsequently dried under vacuum for > 6 h to get a fluffy white powder.

PbSe NCs used for the comparison were made using a procedure described by Campos et al.7 The solid Pb-oleate was used as a Pb precursor, while the selenium precursor (N-cyclohexylpyrrolidine-1-carboselenoamide) was prepared by mixing selenium (9.0 mmol), pyrrole (9.0 mmol), cyclohexyl isocyanide (9.0 mmol), and 10 mL toluene. This mixture was heated to ∼100 °C until a clear solution was obtained. If black solid selenium was still present, additional pyrrole and/or cyclohexyl isocyanide was added to make sure that all selenium reacted. The mixture was allowed to cool to room temperature at which the selenourea precipitated. The liquid was decanted, and the obtained white solid was placed under vacuum for 24 h. Subsequently, the solid was redissolved in 10 mL toluene at 100 °C and allowed to cool down. The precipitate was filtered, and the solid was placed under vacuum for another 24 h.

The synthesis of PbSe was performed in a Schlenk line where 1.6 g (2.08 mmol, 1.2 equiv) Pb(oleate)2 was dissolved in 140 mL hexadecane in a 250 mL three-neck flask. 0.45 g (1.7 mmol, 1 equiv) N-cyclohexylpyrrolidine-1-carboselenoamide was dissolved in 8 mL diphenyl ether. Both precursors were heated to 100 °C to yield a clear colorless solution. The selenourea was quickly injected into the Pb(oleate)2 solution which turned brown in approximately 8 s. After 110 min, the reaction was cooled down with an ice bath and inserted inside the glovebox. 90 mL of n-butanol and 60 mL of methanol was added to precipitate the NCs. The mixture was centrifuged, and the black residue was dissolved in 10 mL toluene. This solution was washed three more times with methanol.

Characterization. UV–Vis. A PerkinElmer LAMBDA 950 UV/vis spectrometer was used to conduct absorption measurements in the wavelength range from 300 to 2300 nm. The samples were prepared in the glovebox by drying 5–30 μL of PbTe solution under vacuum. The residue was then redispersed in 3 mL TCE because of the absence of absorption features in the near-infrared.

The information captured in the absorption spectrum was acquired in two different ways. First, in the 300–400 nm wavelength region, the volume-corrected absorption was used for further calculations. The second region is the first exciton peak and is different per sample in terms of the peak position and width.

Fourier Transform Infrared Spectroscopy. FT-IR measurements were performed in Bruker vertex 70. A special air-tight liquid cell was used (International Crystal Laboratories) with a path length of 0.5 mm and two KBr crystals at back and front sides to make it transparent for IR light. Spectra were recorded from 400 to 7500 cm−1, with a KBr beam splitter, a DTGS D301 detector, and a mid-IR source. Different solvents were used as indicated in the main text.

TEM and EDX. A Tecnai 20 or a Talsos F20XX (both 200 keV) electron microscope was used. The latter TEM also has the functionality of EDX.

Inductively Coupled Plasma Optical Emission Spectrometry. The exact concentration of lead in PbTe NCs could be obtained with the
ICP–OES, inductive coupled plasma optical emission spectrometry

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