Electronic Supplementary Information

Non-Injection Synthesis of Cu₂ZnSnS₄ Nanocrystals Using a Binary Precursors and Ligand Approach

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CZTS Nanoparticle Synthesis

During a standard synthesis Cul (2.66 g, 14 mmol), SnCl₄·5H₂O (2.80 g, 8 mmol) and Zn(EtXn)₂ (3.06 g, 10 mmol) were suspended in a 3:1 oleylamine:dodecanethiol (OA:DDT) solution (64 ml) and degassed for two hours. The yellow slurry was slowly heated under vacuum to 70 °C, at which point the reactants had dissolved to give a deep red solution, which was degassed for an additional 30 minutes. The reaction solution was then heated to 250 °C over a 15 minute period, at which point the temperature was maintained for 30 minutes, followed by cooling to 60 °C. A 4:1 acetone:methanol solution (60 ml) was added to the reaction solution, which was then centrifuged at 4400 rpm for four minutes, resulting in the precipitation of the CZTS NCs from solution. The supernatant was discarded and the CZTS NCs were redissolved in a minimal amount of chloroform. This solution. After centrifugation the unwanted solid was discarded and a 4:1 ethanol:methanol solution (40 ml) was added to the supernatant, which was again centrifuged at 4400 rpm for four minutes, resulting in the precipitation of pure CZTS NCs. The supernatant was discarded and the CZTS NCs were and solution was discarded and a 4:1 ethanol:methanol solution (40 ml) was added to the supernatant, which was again centrifuged at 4400 rpm for four minutes, resulting in the precipitation of pure CZTS NCs. The supernatant was discarded and the CZTS NCs were air dried.

For reactions that used differing amounts of reactants the volume of the 3:1 OA:DDT solvent solution was adjusted to maintain a constant concentration of 500 mM of reactants in the reaction solution (Table S1).

Cul	SnCl₄·5H2O	Zn(EtXn) ₂	3:1 OA:DDT
3.80 g, 20 mmol	3.50 g, 10 mmol	3.06 g, 10 mmol	80 ml
2.28 g, 12 mmol	2.80 g, 8 mmol	3.06 g, 10 mmol	60 ml
2.66 g, 14 mmol	2.80 g, 8 mmol	3.06 g, 10 mmol	64 ml
3.04 g, 16 mmol	2.80 g, 8 mmol	3.06 g, 10 mmol	68 ml
2.28 g, 12 mmol	3.50 g, 10 mmol	3.06 g, 10 mmol	64 ml
2.66 g, 14 mmol	3.50 g, 10 mmol	3.06 g, 10 mmol	68 ml
3.04 g, 16 mmol	3.50 g, 10 mmol	3.06 g, 10 mmol	72 ml
	Cul 3.80 g, 20 mmol 2.28 g, 12 mmol 2.66 g, 14 mmol 3.04 g, 16 mmol 2.28 g, 12 mmol 2.66 g, 14 mmol 3.04 g, 16 mmol	CulSnCl₄·5H2O3.80 g, 20 mmol3.50 g, 10 mmol2.28 g, 12 mmol2.80 g, 8 mmol2.66 g, 14 mmol2.80 g, 8 mmol3.04 g, 16 mmol2.80 g, 8 mmol2.28 g, 12 mmol3.50 g, 10 mmol2.66 g, 14 mmol3.50 g, 10 mmol3.04 g, 16 mmol3.50 g, 10 mmol3.04 g, 16 mmol3.50 g, 10 mmol	CulSnCl ₄ ·5H2OZn(EtXn)23.80 g, 20 mmol3.50 g, 10 mmol3.06 g, 10 mmol2.28 g, 12 mmol2.80 g, 8 mmol3.06 g, 10 mmol2.66 g, 14 mmol2.80 g, 8 mmol3.06 g, 10 mmol3.04 g, 16 mmol2.80 g, 8 mmol3.06 g, 10 mmol2.28 g, 12 mmol3.50 g, 10 mmol3.06 g, 10 mmol2.66 g, 14 mmol3.50 g, 10 mmol3.06 g, 10 mmol3.04 g, 16 mmol3.50 g, 10 mmol3.06 g, 10 mmol3.04 g, 16 mmol3.50 g, 10 mmol3.06 g, 10 mmol

Table S1. Mass of reactants and volume of solvents used in the synthesis of samples 1 - 7.

Isolation and analysis of co-products generated during CZTS NC synthesis

Isolation of the co-products was achieved in two key stages: (1) volatile co-products were condensed in a cold trap that was cooled with liquid nitrogen (LN_2) when the reaction solution was under vacuum as it was heated up to 70 °C; (2) for the remainder of the reaction a dynamic nitrogen flow directed the co-products evolved at higher temperatures into a flask and a cold trap (cooled by dry ice/ethanol), which were attached to the reaction vessel (Fig. S1).



Fig. S1. The experimental setup used during the batch synthesis of CZTS NCs. An additional LN_2 cold trap, which was used to isolate volatile species while the reaction was under vacuum during degassing and initial heating, is not shown in the image.

The first co-product to be distilled from the reaction solution was ethanol, which was detected in the condensate in the LN₂ cooled cold trap (Fig. S2), and the dry ice/ethanol cooled cold trap (Fig. S3). Ethanol is known to be a common co-product of xanthate decomposition,¹ confirming the ethyl xanthate ligand decomposed below 70 °C. When the cold traps were removed from the LN₂ and dry ice/ethanol baths there was a colorless solid within the traps that melted and then evaporated upon warming to room temperature. The gas had a highly pungent sulfurous odor, suggesting it may have contained volatile COS, which is also known to be a co-product of xanthate decomposition.¹⁻³ Hydrogen sulfide was detected by HS GC –MS only in the dry ice/ethanol cold trap (Fig. S3), which was used in the isolation of co-products that were generated above 70 °C, and not in the LN₂ cold trap which was used in the in the isolation of co-products that were generated during degassing at

temperatures below 70 °C. This suggests that its generation is most likely due to the high temperature decomposition of DDT and not the lower temperature decomposition of ethyl xanthate (see below).

Dodecane was identified as a key component of the liquid which condensed in the attached flask at higher temperatures (Fig. S4). The role of DDT in the formation of metal sulfide NCs has been well established,^{4, 5} and dodecane has previously been observed as a co-product when DDT is used as a sulfur precursor in NC synthesis.⁴ Also detected in the distillate was DDT and didodecyl disulfide. The dodecane could not be attributed to an impurity in either of the solvents used in the reaction (Figs. S5 and S6). Although DDT has a boiling point in the range 266–283 °C,⁶ it is likely there would be some present in the gas phase when the reaction solution was heated to 250 °C, and it would have been carried over into the attached flask by the nitrogen flow. While didodecyl disulfide is a known co-product of metal sulfide synthesis using metal thiolates,⁷ it has a boiling point of approximately 480 °C and is unlikely to have been evolved from the reaction solution as the maximum reaction temperature was 250 °C. Therefore, it is most likely to have formed by the oxidative coupling of DDT in the condensate upon cooling.

Another known co-product of DDT decomposition during the formation of NCs is didodecyl sulfide.⁸ However, as its boiling point of approximately 465 °C precludes its isolation from the reaction solution by distillation, the detection of didodecyl sulfide required a different approach. The supernatant from the first step of the isolation and purification of CZTS NCs (see above) was analyzed by mass spectrometry in order to determine whether didodecyl sulfide was present in the reaction solution. Due to the presence of unreacted precursors, reaction co-products, DDT, OA and other long chain amines that are present in 70 % technical grade OA (Fig. S6b), the mass spectrum of the sample was convoluted, and the presence of didodecyl sulfide could not be ascertained with absolute certainty. However, an ion with an m/z value of 370 was detected, and since this corresponds to the mass ion of didodecyl sulfide and it could not be readily assigned to a mass ion or fragment of another known species in solution, this would strongly suggest that didodecyl sulfide was present.

The isolation and identification of co-products generated at different stages of the CZTS NC synthesis allows us to determine at what temperatures particular sulfur precursors are decomposing. Ethanol was generated below 70 °C, and it is a co-product of ethyl xanthate decomposition during the CZTS NC nucleation phase of the reaction. Dodecane, didodecyl sulfide and hydrogen sulfide were generated above 70 °C, and their presence can be attributed to DDT decomposition during the CZTS NC growth phase.^{4, 5}



Fig. S2. HS GC-MS spectrum of the solution in the LN_2 cooled cold trap.



Fig. S3. HS GC-MS spectrum of the solution in the dry ice/ethanol cooled cold trap.



Fig. S4. GC-MS spectrum of condensate present in the flask attached to the reaction vessel.



Fig. S5. GC-MS spectrum of the 1-dodecanethiol used in the synthesis of CZTS NCs, showing no detectable impurities were present.



Fig. S6. (a) GC-MS spectrum of 70 % technical grade oleylamine; (b) expansion of 8.5 – 11.5 min retention time region, showing that the impurities present are long chain aliphatic amines.

Dataset	Temperature (°C) †	Time (mins)	NC size (nm) ± esd
1	25	0	ND
2	71	3.2	ND
3	111	6.3	ND
4	153	9.4	2.7 ± 1.2
5	196	12.5	2.6 ± 1.0
6	239	15.6	3.2 ± 0.5
7	250	18.8	3.9 ± 0.2
8	250	22.0	4.0 ± 0.2
9	250	25.1	4.4 ± 0.2
10	250	28.2	4.0 ± 0.2
11	250	31.5	4.4 ± 0.2
12	250	34.6	4.3 ± 0.2
13	250	37.7	4.4 ± 0.2
14	250	41.0	4.1 ± 0.2
15	250	44.1	4.3 ± 0.2
16	250	47.3	4.3 ± 0.2
17	250	50.4	4.3 ± 0.2
18	250	53.6	4.4 ± 0.2
19	250	56.7	4.3 ± 0.2
20	250	59.9	4.3 ± 0.2
21	250	63.0	4.5 ± 0.2
22	250	66.1	4.2 ± 0.2
23	250	69.4	4.5 ± 0.4
24	250	72.5	4.8 ± 0.4

Table S2. In situ XRD measurements of reaction solution, monitoring CZTS NC formation.

⁺ Temperature as measured at the start of the dataset collection. ND = not detected

Xanthate Free Reaction

SnCl₄·5H₂O (875 mg, 2.50 mmol), Cul (831 mg, 4.36 mmol) and ZnCl₂ (423 mg, 3.11 mmol) were suspended in a 3:1 OA:DDT (20 ml) solution to give a white slurry. The reaction solution was degassed for two hours at room temperature and then heated slowly under vacuum to 70 °C. At this temperature the reaction solution still appeared to be a white slurry. The reaction solution was then heated to 250 °C under nitrogen. At 140 °C the reaction solution began to turn orange, and at 145 °C it appeared all the reactants had dissolved. However, when a sample of the solution was removed for UV-vis spectroscopy measurements, the solution turned a light yellow colour and a white precipitate immediately formed in solution upon cooling. This precluded taking UV-vis spectroscopic measurements of the reaction solution until the temperature reached 205 °C, at which point the no precipitate formed when the sample was cooled to room temperature. Once the temperature reached 250 °C the reaction was ceased as extensive aggregation had occurred, and separation of the desired soluble product from the aggregate was deemed to be impractical.



Fig. S7. Normalized UV-vis absorbance spectra taken during the course of the xanthate free CZTS synthesis.

DDT Free Reaction

SnCl₄·5H₂O (250 mg, 713 μ mol), CuI (380 mg, 2.00 mmol) and Zn(EtXn)₂ (306 mg, 1.00 mmol) were suspended in OA (8ml) to give a deep red solution. The reaction solution was degassed at room temperature for two hours and then heated slowly under vacuum to 50 °C. At this temperature the reactants had dissolved to give a deep red solution. The reaction solution was then heated to 250 °C over a 15 minute period, at which point the temperature was maintained for 30 minutes, followed by cooling to 60 °C. The product was isolated using the methodology used in the isolation of CZTS NCs at the beginning of the Supplementary Information.



Fig. S8. Normalized UV-vis absorbance spectra taken during the course of the DDT Free reaction.

Oleylamine Free Reaction

SnCl₄·5H₂O (875 mg, 2.50 mmol), CuI (831 mg, 4.36 mmol) and Zn(EtXn)₂ (956 mg, 3.11 mmol) were suspended in DDT (20 ml) to give a brown slurry. The reaction solution was degassed at room temperature for five hours and then heated slowly under vacuum to 70 °C. At this temperature the reactants had dissolved to give a deep red solution. The reaction solution was heated to 250 °C under nitrogen. As the temperature reached 150 °C the reaction solution started to become opaque as aggregation of the NCs started to occur. This is due to the absence of the OA ligand, which is required to stabilise the NCs during the growth phase. Once the temperature reached 250 °C the reaction was ceased as extensive aggregation had occurred, and separation of the desired soluble product from the aggregate was deemed to be impractical.



Fig. S9. Normalized UV-vis absorbance spectra taken during the course of the OA free reaction.

TEM size measurements and PXRD analysis of isolated CZTS NCs

Sample	size (nm) (σ)	
2	6.5 (1.4)	
3	5.5 (1.2)	
4	7.8 (1.7)	
5	5.8 (1.2)	
6	6.0 (1.0)	
7	5.9 (1.4)	

Table S3. Size distribution of CZTS nanocrystals.

 σ = standard deviation



Fig. S10. PXRD of samples 2 - 7, and the calculated pattern for kesterite Cu₂ZnSnS₄ (JCPDS 26-0575) (top to bottom).

Analysis of NC composition by Raman spectroscopy



Fig. S11. Normalized Raman spectra of samples 2 - 7 (top to bottom), as deposited without annealing. Sharp, weak peaks in the spectra of samples 6 and 7 are due to uncorrected cosmic events.



Fig. S12. Normalized Raman spectra of thin-film of sample **3** as deposited, and annealed at various temperatures (300 - 400 °C).

All samples showed a major peak at 337 cm⁻¹ and a minor peak at 374 cm⁻¹, both characteristic of CZTS (Fig. S11).⁹ Peaks at 318 cm⁻¹, 355 cm⁻¹ and 475 cm⁻¹, which would be present due to Cu₂SnS₃, ZnS and Cu_{2-x}S contamination, respectively, were not observed.^{10, 11} A weak peak at 302 cm⁻¹, which could not be attributed to CZTS, was however present. This could arise from the contribution of a Sn₂S₃ impurity phase;¹² however, the absence of peaks attributable to crystalline Sn₂S₃ (JCPDS card No. 14-0619) in the PXRD analysis suggests this is unlikely. Instead, we believe that its origin stems from the cross-linking EDT or residual DDT ligands,¹³ which have a Raman peak in this region due to a trans-CCS deformation.¹⁴ This assumption is supported by the fact that when such thin films were annealed at temperatures above 300°C, the ligands were thermalized and this peak was no longer observed (Fig. S12). After the removal of the ligands, another weak, broad peak characteristic of CZTS at 285 cm⁻¹ was observed.⁹



Fig. S13. Optical band gap estimation from the (α hv) vs. photon energy (hv) plots of samples **2** – **7**.

Analysis of NC surface by infrared (IR) and ¹H NMR spectroscopy

IR and NMR spectroscopy were employed in our investigation into whether OA or DDT remained coordinated to CZTS NCs after isolation and purification, as typically they offer the best means of analyzing the surface chemistry of NCs.

IR spectroscopy offered limited insight into the problem due the dominant contributions of the aliphatic groups common to both OA and DDT (Fig. S14). Nonetheless, the IR spectrum of CZTS NCs did exhibit a weak, broad peak at 1590 cm⁻¹, which can be attributed to the NH₂ scissoring mode of OA.¹⁵ The presence of a C–S stretch in the CZTS NCs' IR spectra would confirm the presence of DDT, but this band is very weak in the IR and cannot be clearly observed.¹⁶ Therefore, IR spectroscopy could neither confirm nor deny the presence of DDT in this system.



Figure S14. IR spectra of OA, DDT and CZTS NCs (Sample 7).

To better appreciate the surface chemistry we employed ¹H NMR spectroscopy (Fig. S15). A series of peaks in the vicinity of 5.32 ppm, which is unique to the alkene group of OA, were observed in the spectrum of the CZTS NCs. In comparison to the spectra of the neat solvents this signal is significantly broader, a phenomenon which arises due to the reduced degree of rotational freedom leading to an increased dephasing time for the ligands, proving the ligands are coordinated to the NC surface.¹⁷

Determining the presence of DDT by NMR spectroscopy proved to be more difficult. The NMR spectra of the CZTS NCs contained a signal at 1.65 ppm, which could probably be attributed to hydrogen atoms which can be found in the spectrum of neat DDT at around 1.58 ppm. However, we are unable to eliminate the possibility that it may also be due to the hydrogen atoms present in the spectrum of OA at 1.40 ppm, which have shifted upon coordination of the ligand. While the spectrum of neat DDT shows a quartet of peaks at 2.50 ppm, which originate from the CH₂ group adjacent to the S–H moiety, this signal is not present in the spectrum of CZTS NCs. While this conspicuous absence may initially suggest that DDT is not present on the CZTS NCs' surface, there are reports that state that this signal may not be present if the DDT ligand coordinates to a metal centre as a thiolate.¹⁸

Another method of determining by NMR spectroscopy if DDT is present on the surface of CZTS NCs is by examining the integration of the alkyl hydrogen atoms in the spectra. Neat technical grade OA spectrum gives 48 alkyl and amine hydrogen atoms per two alkene hydrogen atoms,¹⁹ while a comparable measurement for CZTS NCs shows 68 hydrogen atoms in this region. As DDT contains no alkene groups, its coordination would increase the number of alkyl hydrogen atoms relative the number of alkene hydrogen atoms detected in the NMR spectrum of the CZTS NCs, indicating that DDT is indeed present on the isolated surface of the CZTS NCs.



Figure S15. ¹H NMR spectra of OA, DDT and CZTS NCs (Sample 3) (top to bottom).

Experimental

Reagents

Cul (99 %), dodecanethiol (98 %), technical grade oleylamine (70 %), and $SnCl_4 \cdot 5H_2O$ (98 %) were purchased from Aldrich. Acetone (99.8 %), chloroform (99.8 %), ethanol (99.5 %) and methanol (99.8 %) were purchased from Merck. Eu(NO₃)₃·6H₂O (99.9 %) was purchased from Strem. All reagents and solvents were used as received without further purification. Zn(EtXn)₂ was synthesised according to a literature procedure.²⁰

CZTS NC Thin-Film Immobilisation for Raman Spectroscopy Measurements.

A standard CZTS nanoparticle solution was prepared by dissolving CZTS nanocrystals in heptane to give a solution with an absorbance of 0.3 at 600 nm in a quartz cuvette with an optical path length of 1 cm, as measured by UV-vis spectroscopy. A 40 μ L aliquot of the CZTS nanocrystal solution was deposited onto a 9 mm × 25 mm ITO glass substrate by spin coating at 1000 rpm for 15 seconds. The substrate was then dipped into a solution of ethanedithiol (0.1 M) in ethanol, then dipped into ethanol and dried with a N₂ flow. This process was repeated an additional nine times.

Instrumentation

Gas Chromatography Mass Spectrometry (GC-MS)

Spectra were obtained with a ThermoQuest TRACE DSQ GC mass spectrometer, with gas chromatography performed with a SGE BPX5 column (15 m \times 0.1 mm ID, 0.1 μ m film thickness)

¹H Nuclear Magnetic Resonance Spectroscopy (NMR)

¹H NMR spectroscopy was performed on a Bruker BioSpin Av400H equipped with a with 9.4 T magnet and a 5 mm inverse ¹H-X BBI auto-tuning broadband probe. The samples were dissolved in CDCl₃.

Headspace Gas Chromatography Mass Spectrometry (HS GC-MS)

HS-GC MS spectra were obtained with an Agilent 6890 GC and a 5971 mass selective detector (MSD) in full scan mode and a HP PLOT Q column (39 m × 0.32 mm ID, 20 μ m film thickness).

Infrared (IR) Spectroscopy

Infrared data were collected on a Thermo Scientific Nicolet 6700 FT-IR spectrometer on a laminated diamond mounted in a stainless steel plate in the 4000–600 cm⁻¹ range with a resolution of 4 cm⁻¹.

Oleylamine and dodecanethiol were measured as liquids while CZTS NCs were drop cast from chloroform to form a thin-film upon evaporation of the solvent.

In situ X-ray Diffraction (is-XRD)

To simulate the reaction solution used to synthesize sample **6**, Cul (0.380 g, 2.00 mmol), $SnCl_4 \cdot 5H_2O$ (0.350 g, 1.00 mmol) and $Zn(EtXn)_2$ (0.306 g, 1.00 mmol) were suspended in a 3:1 oleylamine:dodecanethiol solution (8 ml). The reaction solution was degassed with stirring at room temperature for one hour, and then heated at 70 °C for four hours under vacuum to remove all of the ethanol and other volatile co-products that are formed during the decomposition of the ethyl xanthate precursor. While this initiates nucleation it is necessary to ensure the capillary containing the reaction solution does not shatter upon heating to 250 °C.

A small portion of the reaction solution was then transferred to a 1 mm outer diameter quartz-glass capillary (Charles Supper Company) using a syringe. The open end of the capillary was fitted with a graphite ferrule (Supelco, Supeltex M-2A) for attachment to a stainless steel fitting similar to the one described by Norby²¹ and implemented by Webster *et al.*²² This capillary reaction vessel was positioned in a goniometer head and attached to an Inel diffractometer, which incorporates a CPS120 position-sensitive detector allowing for simultaneous collection of 120° in 20 of diffraction data. Static pressure of 60 psi was applied to the vessel via Teflon tube connected to a N₂ gas cylinder, in order to prevent movement of the sample along the length of the capillary after application of heat to the capillary/sample.

The goniometer head and capillary reaction vessel were oscillated about the capillary axis in order to ensure uniformity of heating and accurate observed relative peak intensities through improved particle statistics. The presence of the Teflon tube meant that the capillary was only oscillated through 270° to avoid tangling of the tube. The solution was heated at 15 °C min⁻¹ from 25 to 250 °C using a hot air blower, which was controlled using a K-type thermocouple positioned underneath the capillary and a Eurotherm model 2408 temperature controller. 3 min *in situ* XRD datasets were collected continuously during the temperature ramp, and a further 18, 3 min datasets were collected at 250 °C. The diffractometer was fitted with a Cu tube operated at 40 kV and 40 mA.

Crystallite size values were determined from the *in situ* XRD data by a whole-powder pattern refinement method implemented in the graphical user interface of TOPAS (Version 4.2; Bruker, 2009). Fig. S16 shows the fit to the final dataset collected at 250 °C; the broad peak centered at $\approx 19^{\circ}$

20 is attributed to scattering from the quartz-glass of the capillary and solution within the capillary (Fig. S17), and was fit using a single-peak in the refinement model; the peaks at 28.4, 47.6 and 56.5° 20, corresponding to the (112), (220) and (312) reflections in JCPDS No. 26-0575 for Cu₂ZnSnS₄, were fit using an hkl phase in space group $I\overline{4}2m$ (No. 121) and with starting lattice parameters a = 5.427 and c = 10.848 Å. The background was modeled using a five-parameter Chebychev polynomial. The instrumental contribution to peak width and shape was determined using data collected for a corundum sample (National Institute of Standards and Technology, Standard Reference Material 676) in a 1 mm capillary.



Fig. S16. Fit to the final *is*-XRD dataset collected at 250 °C for sample **6**. The experimental data are shown as a blue solid line, the calculated pattern as a red solid line, and the difference pattern as a solid line below.



Fig. S17. XRD data collected for the capillary and solution at 250 °C.

Mass spectrometry (MS)

Mass spectrometry of the supernatant from the first step of the isolation and purification of CZTS NCs was performed on a ThermoQuest MAT95XL mass spectrometer.

Powder X-ray Diffraction (PXRD)

X-ray powder diffraction experiments were performed on a Bruker D8 Focus diffractometer using the Diffrac Plus XRD Commander software. Scans were run at a rate of 0.5 $^{\circ}$ min⁻¹ using a scan step size of 0.1°. Thin-films were formed by drop casting CZTS nanoparticles dissolved in chloroform. An Y₂O₃ standard was used to determine that instrumental broadening had a negligible effect on crystallite size calculations.

Raman Spectroscopy

Raman measurements were performed on a Renishaw inVia confocal microscope with a 514 nm argon ion laser operating at 10 mW and 10 % power, in the range 172 – 850 nm with a resolution of 2 nm. Acquisition time was 5 seconds per scan with the final spectrum from the co-addition of 256 scans.

Transmission Electron Microscopy (TEM)

TEM measurements were performed on a Tecnai 12 G2 TEM (FEI, Eindhoven, The Netherlands) operating at 120 kV, and imaged using a Megaview III CCD camera and AnalySiS software (Olympus, Tokyo). High resolution transmission electron microscopy (HRTEM) measurements were performed on a CM30 TEM (FEI, Eindhoven, The Netherlands) operating at 200 kV, and imaged using a Gatan Orius CCD camera (Gatan, Pleasanton, CA, USA).

UV-Vis Spectroscopy

Absorption spectra were collected at room temperature using a Varian Cary 5 spectrophotometer in the range $350 - 1200 \text{ cm}^{-1}$. NCs were dissolved in chloroform for UV-vis spectroscopic measurements.

X-ray Fluorescence (XRF) Spectrometry

XRF measurements were performed on a Philips PW2404 Wavelength Dispersive X-ray Fluorescence Spectrometer. Samples and standards were formed into 12 mm pellets in a die of the same diameter at pressures of up to 3 tonne per square inch, with the analytical surface formed on a 6 um Mylar film. The pellet and Mylar film were presented to the instrument in a sample cup with a 6 mm diameter aperture. Calibration standards were prepared from pure oxides and sulphate salts of the elements required. The error of the XRF measurements is estimated to be within 5 % relative to the measured value.

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