Nanocrystal ligand exchange with 1,2,3,4-thiatriazole-5-thiolate and its facile *in-situ* conversion to thiocyanate: Supplementary information

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Experimental

Reagents. NaN_3 (EMD, "Practical" grade), CS_2 (Fisher, 99.9% "Certified ACS" grade), oleic acid (Alfa Aesar, 90%), and 1-octylamine (Alfa Aesar, 99%) were used as received. $(NH_4)_2SiF_6$ (Alfa, 98%) was recrystallized before use, as described below. Solvents were 99% purity (propylene carbonate, sulfolane) or better (e.g. dimethylformamide (DMF), ≥ 99.8%), and were used as received.

Note on hazards. NaN_3 has substantial acute toxicity, and is incompatible with acids, heavy metal salts, and alkyl halides. CS_2 is very volatile, displays serious chronic toxicity, and is extremely inflammable with a very low ignition temperature. TTT^- salts are generally explosive when dry and must only be handled in solution. Heavy metal TTT^- salts are likely insoluble and explosive and must not be prepared; likewise, TTT–alkyl compounds may also be hazardous, so alkyl halides (including CH_2Cl_2) should be strictly avoided. TTT^- salts are incompatible with oxidants, forming an explosive neutral disulfide dimer of low solubility (M.-J. Crawford, T. Klapötke, P. Klüfers, P. Mayer, P. S. White, *J. Am. Chem. Soc.*, 2000, **122**, 9052; A. W. Browne, A. B. Hoel, G. B. L. Smith, F. H. Swezey, *J. Am. Chem. Soc.*, 1923, **45**, 2541); therefore, it is not advisable to neutralize TTT^- waste with H_2O_2 or NaOCl. Instead, TTT^- waste was poured into a large excess of concentrated aqueous KOH and stored in a vented container for several weeks to ensure decomposition before disposal.

CdSe(TTT) nanocrystal films are likely safe, regardless of area, due to the unfavorable morphology for heat build-up or detonation propagation. However, extreme care and appropriate safety testing would be essential before preparing dry CdSe(TTT) solid on a large scale on account of the unexplored behavior of the material in bulk, or when ligating TTT^- on very small nanocrystals on account of the greater surface area and higher TTT^- content.

Recrystallization of $(NH_4)_2SiF_6$. It was found that as-purchased $(NH_4)_2SiF_6$ gave a cloudy aqueous solution, necessitating recrystallization. $(NH_4)_2SiF_6$ (60 g) was added to 150 mL distilled water by stirring and heating in a 94–100 °C water bath. The hot solution was filtered through a glass frit, allowed to cool slowly to room temperature, then kept at ~8 °C overnight. The resulting crystals were recovered by filtration through a coarse glass frit, washed with H_2O (2 × 5 mL) and MeOH (20 mL), then air-dried for ≥2 days. TGA data were consistent with expectations for pure dry $(NH_4)_2SiF_6$ (Figure S2a).

Preparation of NaTTT solution. NaN_3 (500 mg) was dissolved in distilled water (2 mL), and ^{n}PrOH (2 mL) was added to form a homogenous solution. Addition of CS_2 (0.50 mL) split the solution into two phases. The mixture was vigorously stirred in the dark for 40 min to produce a homogenous single phase of pale yellow color. Distilled H_2O (5 mL) and ^{n}PrOH (20 mL) were added, the mixture was filtered (450 nm), and stored cold (7–8 °C) in the dark.

Preparation of NaTTT in D_2O for NMR analysis. CS_2 (0.25 mL) was stirred in the dark with a solution of NaN_3 (250 mg) in D_2O (1.0 mL) and ^{n}PrOH (1 mL). Nitrogen gas was bubbled through the solution (3 min) to remove excess CS_2. An aliquot of the solution (0.25 mL) was diluted with D_2O (0.75 mL) to prepare the NMR sample.

Preparation of NH_4TTT solution. ^{n}PrOH (2 mL) and CS_2 (0.50 mL) were added to NaN_3 (500 mg) dissolved in distilled water (2 mL). The mixture was vigorously stirred in the dark for 40 min to produce a homogenous single phase of pale yellow color. A solution of $(NH_4)_2SiF_6$ (695 mg) in distilled H_2O (5.0 mL) was added dropwise to the NaTTT solution with vigorous stirring over ~8 min. ^{n}PrOH (20 mL) was added, followed by centrifugation (6000 rpm, 1 min), and filtration (450 nm) to give the final NH_4TTT solution. The solution was stored cold (7–8 °C) in the dark, and the solution was stable for >2 weeks under these conditions.

Synthesis of CdSe nanocrystals. CdSe(NL) nanocrystals were synthesised on a large scale using the procedure previously reported in detail (D. H. Webber, R. L. Brutchey, *J. Am. Chem. Soc.*, 2012, **134**, 1085). The product consisted of stearate-capped CdSe(NL) nanocrystals dispersed in toluene at a concentration of 38.9 mg mL^{-1} (gravimetrically determined, and corrected to pure CdSe content based on the 600 °C TGA mass).

TTT^- Ligand exchange on CdSe nanocrystals. The ligand exchange was conducted in subdued light, keeping the sample covered as much as possible. An NH_4TTT solution (2.5 mL) was diluted with ^{n}PrOH (10 mL) in a 45-mL centrifuge tube, and CdSe (2.5 mL in toluene; 97 mg CdSe content) was rapidly injected. The mixture was shaken, centrifuged (6000 rpm, 30 s), and the almost colorless supernatant was discarded without allowing the nanocrystals to dry. Propylene carbonate (5 mL) was added to the solid precipitate, which easily dispersed upon agitation to give a transparent colloid. A solution of NH_4TTT (2.5 mL) was added, and the colloid was allowed to stand in the dark for 30 min. Dimethoxymethane was added (30 mL), followed by centrifugation (6000 rpm, 30 s), and disposal of the almost colorless supernatant. Addition of propylene carbonate (5 mL) to the nanocrystal solid resulted in easy redispersion. The colloid was filtered (450-nm filter) to remove residual fluorosilicate precipitates. Dimethoxymethane (30 mL) was added, followed by centrifugation (6000 rpm, 30 s), disposal of the supernatant, and redispersion in propylene carbonate (5 mL). Dimethoxymethane (80 mL) and pentane (20 mL) were added to flocculate the nanocrystals. The mixture was centrifuged (6000 rpm, 5 min) and the supernatant was discarded. The nanocrystal solid was redispersed in *N*,*N*-dimethylformamide (DMF; 1 mL), nitrogen gas was bubbled through the colloid to evaporate residual dimethoxymethane, and then the colloid was centrifuged (6000 rpm, 30 s) and decanted from the very small precipitate of agglomerates. The resulting colloidal suspension was stored in the dark at 7–8 °C. A CdSe concentration of 81 mg mL^{-1} was estimated by UV-vis spectrophotometry at 420 nm, based on an extinction coefficient of 6.058 mL mg^{-1} cm^{-1} experimentally determined for the corresponding CdSe(NL) nanocrystals at the same wavelength.

Preparation of dry CdSe(TTT). Due to the sensitive nature of the TTT ligand, preparation of dried CdSe(TTT) samples was done under low-intensity lighting, and as rapidly as possible. Typically, 0.2–0.5 mL CdSe(TTT) dispersion (~15–40 mg CdSe) was rapidly injected into 30 mL dimethoxymethane, followed by centrifugation (6000 rpm, 30 s) and disposal of the supernatant. The solid was broken up by adding dimethoxymethane (30 mL) and subsequently shaking and vortexing the mixture. After centrifugation (6000 rpm, 30 s) the supernatant was discarded, and the solid was transferred to a glass sample-bottle using cyclohexane (~2 mL). The sample was dried in the dark under a nitrogen stream (30 min) at room temperature.

Other ligand exchanges on CdSe. **(a)** CdSe(NL) was exchanged with tetradecylphosphonic acid (TDPA) as previously reported (D. H. Webber, R. L. Brutchey, *J. Am. Chem. Soc.*, 2012, **134**, 1085). (**b**) CdSe(NL) (5 mL; 195 mg CdSe content) was ligand exchanged by mixing with oleic acid (OA; 5.0 mL, 15.8 mmol) and 1-octylamine (OcAm; 3.5 mL, 21.2 mmol) with bath sonication for 1 h. The nanocrystals were recovered by addition of EtOH (20 mL), centrifugatoin (6000 rpm, 30 s), and disposal of the supernatant. Washing was conducted by agitating the solid with toluene (10 mL) to effect redispersion, flocculating with EtOH (20 ml), then centrifuging (6000 rpm, 30 s) and discarding the supernatant. Washing was repeated 7 more times before final redispersion in toluene (5 mL). CdSe recovery was quantitative. (**c**) CdSe(TDPA) and CdSe(OA/OcAm) were ligand exchanged with NH_4TTT using procedures similar that already given for CdSe(NL).

Analytical Procedures

Characterization. UV-vis spectra were acquired on a Shimadzu UV-1800 spectrophotometer, using a quartz cuvette for liquid samples (1-cm path length), or borosilicate glass microscope slide substrate for films. NMR spectra were obtained on a sample in D_2O (prepared as described in the experimental above) using a Varian VNMRS-500 instrument (^{13}C frequency = 125.68 MHz). Samples for powder X-ray diffraction (XRD) were prepared by drop-casting dispersions onto a zero-diffraction silicon plate and analyzed on a Rigaku Ultima IV diffractometer in parallel beam geometry (10-mm beam width) using Cu K_α radiation. Energy-dispersive X-ray spectroscopy (EDX) data were acquired on drop-cast samples (Si or Cu substrate) using an EDAX Apollo silicon-drift detector (model JSM 6490) mounted on a JEOL JSM-6610 scanning electron microscope (SEM) with an accelerating voltage of 10 kV. For transmission electron microscopy (TEM) analysis, samples were cast onto an ultra-thin carbon film supported on holey carbon (Ted Pella, Inc.). TEM images were acquired on a JEOL JEM-2100 fitted with a Gatan Orius CCD digital camera with a 200 kV accelerating voltage. Thermogravimetric analysis (TGA) was conducted on a TA Instruments TGA Q50 instrument, using sample sizes of ~10-20 mg in an alumina crucible. The program for CdSe(NL) utilized a 10 min nitrogen gas purge (200 mL min^{-1}) at room temperature, followed by 10 min drying at 100 °C, then a reduction in flow to 120 mL min^{-1} and a 10 °C min^{-1} ramp to 610 °C. For CdSe(TTT), the program was 10 min nitrogen gas purge (200 mL min^{-1}) at room temperature, reduction in flow to 120 mL min^{-1}, 5 °C min^{-1} ramp to 100 °C, then 10 °C ramp 100–610 °C. Samples (~10 mg) for differential scanning calorimetry (DSC) were placed in an alumina pan in a Perkin Elmer DSC 8000 instrument; 20 mL min^{-1} N_2 flow, 5 °C min^{-1} ramp to 100 °C, then 10 °C min^{-1} ramp 100−250 °C. For FT-IR spectropscopic analysis, CdSe(NL) was dried at 100 °C under flowing nitrogen gas; CdSe(TTT) was prepared as a dry powder as described in the experimental. The samples were dispersed by manual grinding, using *ca.* 6 mg CdSe per ~200 mg KBr. One half of the KBr/CdSe(TTT) was heat treated under nitrogen gas (100 °C, 30 min). Pressed pellets were analyzed using a Bruker Vertex 80v FT-IR spectrophotometer under vacuum atmosphere.

Spin coating of films and heat treatment. Spin coating was carried out on borosilicate glass substrates (75×25×1 mm^3) using a Laurell Technologies Corporation WS400Ez-6NPP-LITE Single Wafer Spin Processor, fitted with a continuous nitrogen purge, and set to an acceleration of 1650 rpm s^{-1}. Conditions were as follows: CdSe(NL), 20 mg mL^{-1} in toluene, 1500 rpm, 30 s; CdSe(TTT), 81 mg mL^{-1} in DMF, 2000 rpm, 30 s. Heat treatment was done by placing the films on a covered pre-heated aluminium block (200 °C) for 6 min, in air.

TGA investigation of fluorosilicate precipitate from NH_4TTT synthesis

A batch of NH_4TTT was synthesised using NaN_3 (499.7 mg, 7.687 mmol), 0.50 mL CS_2 (0.63 g, 8.3 mmol), $(NH_4)_2SiF_6$ (694.5 mg, 3.898 mmol), and quantities of H_2O and ^{n}PrOH as given in the experimental procedure above. Following centrifugation and decantation of the NH_4TTT solution, the precipitate was thoroughly vortexed with 10 mL MeCN, centrifuged (6000 rpm, 1 min), and the supernatant was discarded. Using the same procedure, a second washing was done with 10 mL ethyl acetate. The solid was dried at ~40 °C for 4 days before careful weighing. The mass of precipitate obtained was 717.9 mg, and TGA showed the precipitate to be completely free of solvent (Fig. S2a–b). The TGA mass loss to 320 °C (0.63%) was assumed to be due to complete loss of $(NH_4)_2SiF_6$ as gases, *i.e.* $(NH_4)_2SiF_6 \rightarrow 2\ NH_3 + 2\ HF + SiF_4$, whereas all mass loss 320–750 °C was assigned to $Na_2SiF_6 \rightarrow 2\ NaF_{(s)} + SiF_{4(g)}$. The 750 °C mass (44.35%) was taken as being the mass of NaF residue. Based on these data, the precipitate was calculated to contain 713.6 mg Na_2SiF_6 and 4.3 mg $(NH_4)_2SiF_6$. Therefore, the NH_4TTT solution contained 7.69 mmol TTT^- (assumed ~100 % conversion of N_3^-), 7.75 mmol NH_4^+, 0.097 mmol Na^+, and 0.080 mmol SiF_6^{2-}, *i.e.* 98.8% of the cations were NH_4^+ and 99.0% of the anions were TTT^-. Thus, the fluorosilicate-based metathesis was highly effective, not least due to the 32 times molar solubility difference between Na_2SiF_6 and $(NH_4)SiF_6$.

TGA mass loss from CdSe(TTT)

Approximate calculations were done to compare the measured mass of N_2 lost from CdSe(TTT) (2.47%) to what might be expected based on the total mass loss to 600 °C (12.98%). The CdSe(NL) starting material had a mass loss to 600 °C of 26.36% (after drying at 100 °C), which corresponds to 1.075 mmol stearate per 1 g pure CdSe (see D. H. Webber, R. L. Brutchey, *J. Am. Chem. Soc.*, 2012, **134**, 1085 for further discussion of native ligand identity and its relation to TGA mass loss). It is assumed that this stearate is charge balanced by a surface-excess of Cd^{2+}, as commonly found for CdSe nanocrystals. Thus, if none of the excess Cd^{2+} was leached during ligand exchange, 1.075 mmol TTT^{-} can bind to 1 g pure CdSe, and any extra TTT^{-} ligand must be charge balanced by NH_4^{+}. There is a further assumption that after 600 °C pyrolysis of CdSe(TTT), a residue of S^{2-} remains on the particles to give charge balance (which is qualitatively verified by EDX). Given these data and assumptions, the CdSe(TTT) can be calculated to contain 0.18 mmol NH_4TTT per 1 g pure CdSe, in addition to the 1.075 mmol TTT^{-} charge balanced by Cd^{2+}, leading to an expected TGA N_2 mass loss of 3.1%. Alternatively, if the excess Cd^{2+} were lost during the ligand exchange and the ligand shell of CdSe(TTT) were composed entirely of NH_4TTT, then a much simpler calculation shows that the total mass loss of 12.98% would correspond to an estimated N_2 loss of 2.7%. Thus, the TGA data appear consistent with the presence of some combination of TTT^{-} and NH_4TTT in the ligand shell of CdSe(TTT).

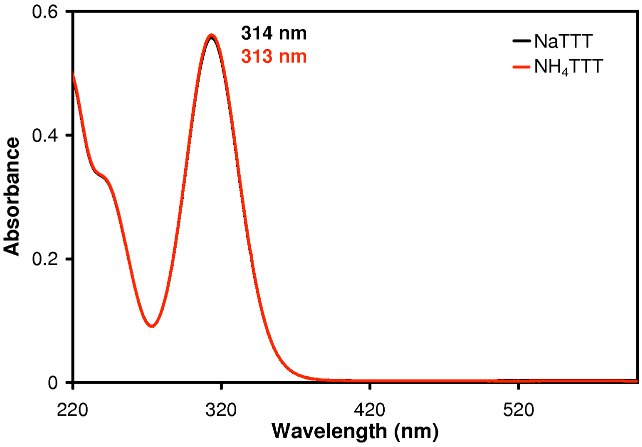

Fig. S1 UV-vis spectra of NaTTT and NH_4TTT solutions, diluted in water to concentration of ~7×10^{-5} M (2.6 μL of as-made NaTTT or NH_4TTT in 10 mL water). The curves are an almost perfect overlay, indicating no loss of TTT^{-} during the Na^{+}-to-NH_4^{+} anion exchange.

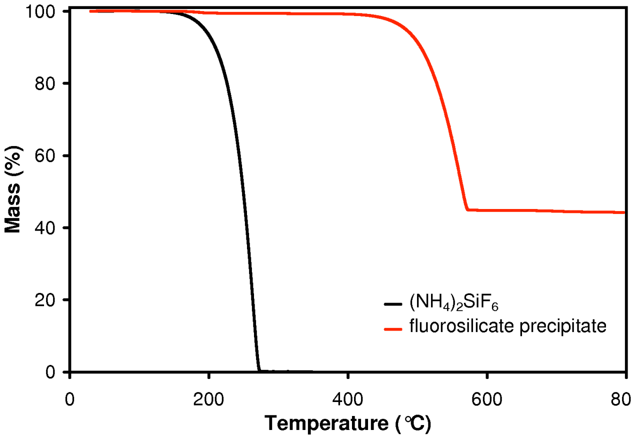

Fig. S2a TGA data for recrystallized $(NH_4)_2SiF_6$ and for the washed and dried fluorosilicate precipitate from the cation exchange. The main mass loss step for the precipitate closely matches theoretical for the reaction $Na_2SiF_6 \rightarrow 2\ NaF + SiF_6$.

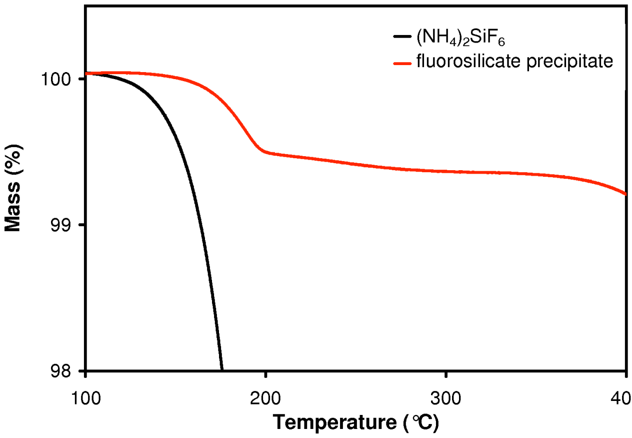

Fig. S2b Zoomed-in section of the same TGA data shown in Fig. S2a, showing a small loss of mass between *ca.* 150-200 °C for the fluorosilicate precipitate. The mass loss is attributed to a small quantity of $(NH_4)_2SiF_6$, calculated to be 6.3 mg g^{-1} of precipitate, with the balance being Na_2SiF_6.

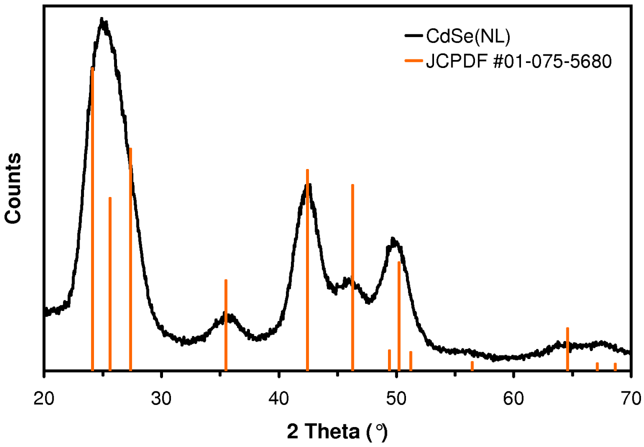

Fig. S3 Powder X-ray diffractogram of CdSe(NL) nanocrystals.

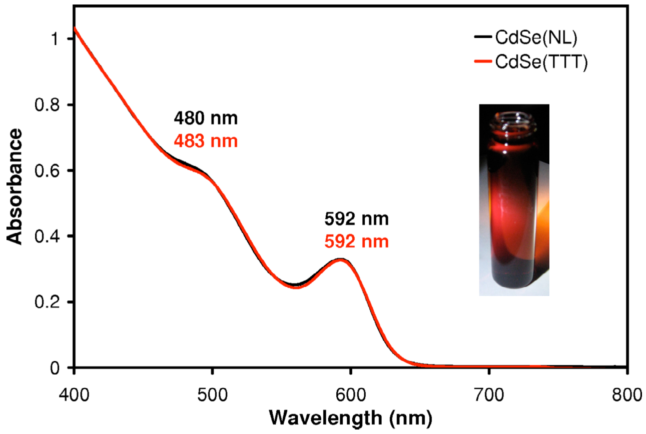

Fig. S4 UV-vis spectra of colloidal CdSe(NL) (150 µg mL^{-1} in $CHCl_3$) and CdSe(TTT) in propylene carbonate. The CdSe(TTT) curve has been normalized to show the close fit to the CdSe curve. The first exciton peaks of colloidal CdSe(NL) and CdSe(TTT) are identical at 592 nm, and the higher energy points of inflection are very similar, being 480 and 483 nm, respectively. A photograph of a colloidal suspension of CdSe(TTT) in propylene carbonate is shown as the inset.

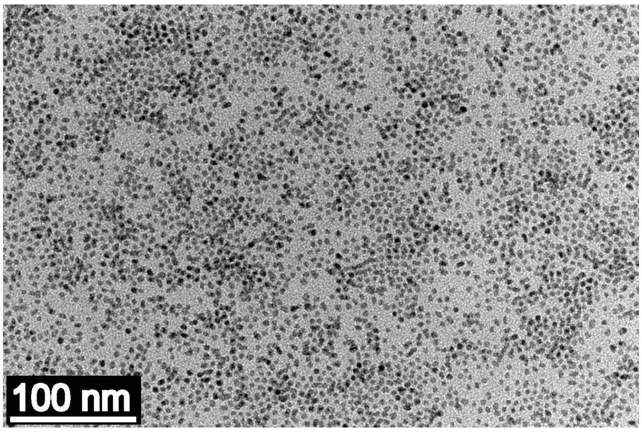

Fig. S5 A TEM micrograph showing a typical field of CdSe(NL) nanocrystals.

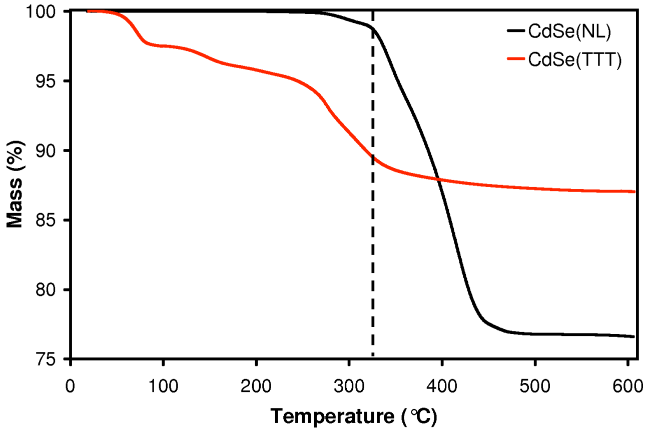

Fig. S6 TGA data for CdSe(NL) and CdSe(TTT) nanocrystals. The CdSe(NL) data is consistent with loss of a monolayer of stearate. The CdSe(TTT) shows a distinctive loss between ~50-90 °C, attributed to N_2 release during the decomposition of TTT$^-$, followed by a complex multistep SCN$^-$ decomposition at higher temperatures. The dashed line at ~325 °C has been included to aid seeing the lack of a stearate signature in the CdSe(TTT) data.

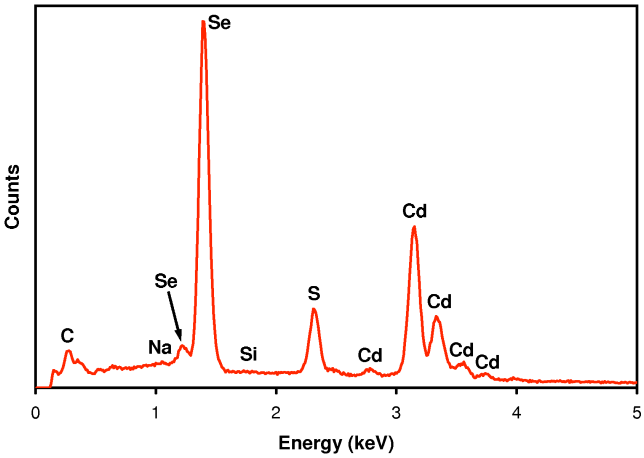

Fig. S7 EDX data for CdSe(TTT) showing the presence of sulfur and the absence of detectable residual sodium or silicon.

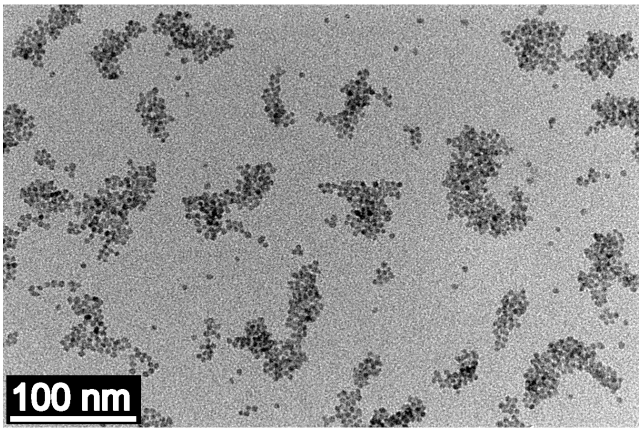

Fig. S8 A TEM micrograph showing a typical field of CdSe(TTT) nanocrystals.

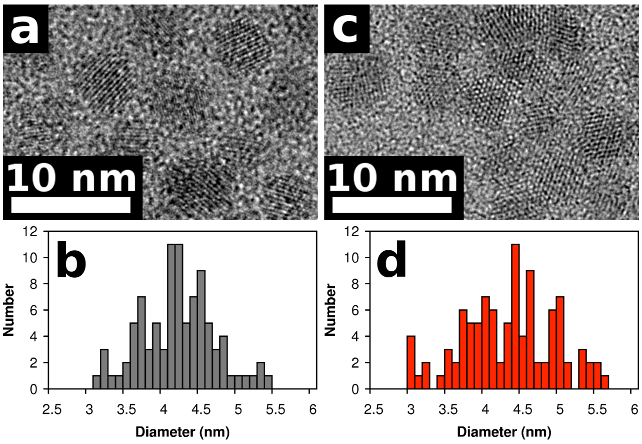

Fig. S9 (**a**) High resolution TEM (HRTEM) image of CdSe(NL) nanocrystals and (**b**) the corresponding size histogram; (**c**) HRTEM image of CdSe(TTT) nanocrystals and (**d**) the corresponding size histogram. CdSe(NL) and CdSe(TTT) nanocrystals are of the same diameter, within error. Interparticle spacing of adjacent nanoparticles is ~1.5 nm for CdSe(NL) but negligibly small for CdSe(TTT).

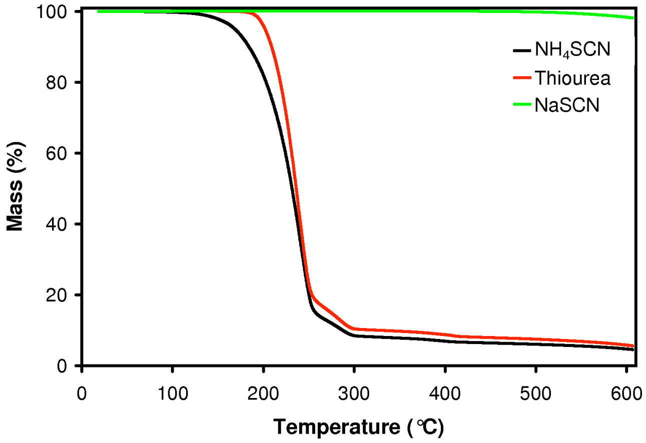

Fig. S10 TGA data for NH_4SCN, thiourea, and NaSCN.

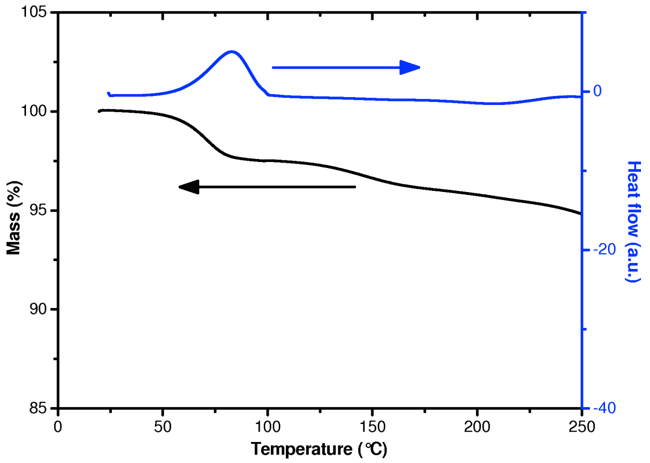

Fig. S11 DSC data (blue line) overlaid with TGA data (black) for CdSe(TTT). The exothermic nature of TTT^- decomposition is clearly seen.

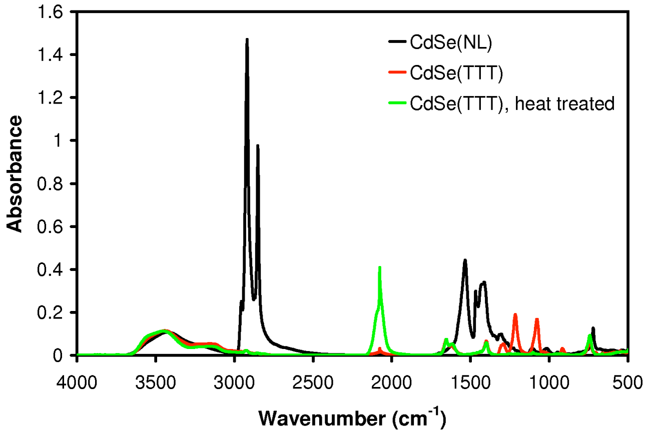

Fig. S12a FT-IR spectra of CdSe(NL) and CdSe(TTT) nanocrystals dispersed in KBr, and CdSe(TTT) after heat treatment at 100 °C. Details of peaks and assignments are given in Table S1.

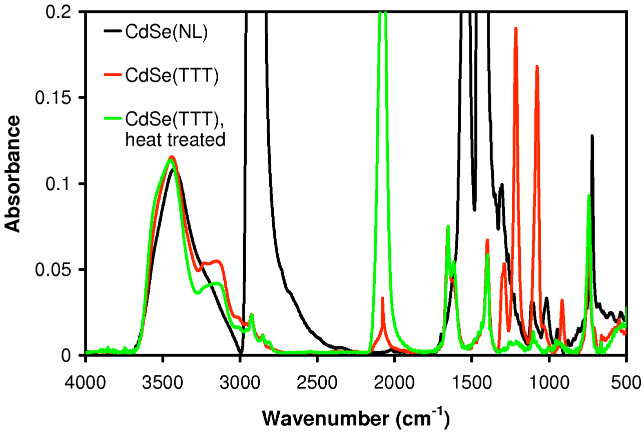

Fig. S12b FT-IR spectra of CdSe(NL), CdSe(TTT), and heat-treated CdSe(TTT), magnified to better display the NH_4^+ and TTT^- bands. Details of peaks and assignments are given in Table S1.

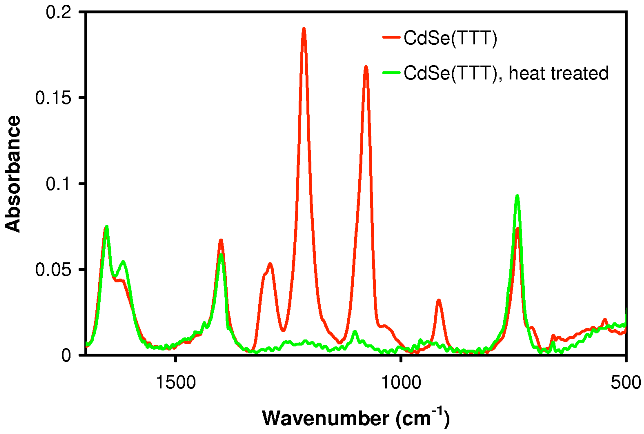

Fig. S12c FT-IR spectra of CdSe(TTT) and heat-treated CdSe(TTT), magnified to better display the TTT^- bands. Details of peaks and assignments are given in Table S1.

Table S1a. Observed FT-IR peaks, assignments, and corresponding literature values for CdSe(NL) dispersed in KBr.

Observed absorption (cm^{-1})	Assignment
~3434 br	H_2O stretch
2918 vs	CH stretch
2850 vs	CH stretch
1535 s	CH bend
1468 s	CH bend
1413 s	CH bend
1304 m, shoulder	CH bend
1113 w	unknown
1017 w	unknown
721 m sh	unknown

Table S1b. Observed FT-IR peaks, assignments, and corresponding literature values for CdSe(TTT) dispersed in KBr. (TTT$^-$ salts; M.-J. Crawford, T. M. Klapötke, P. Mayer, M. Vogt, *Inorg. Chem.*, 2004, **43**, 1370: NH_4^+; L. F. H. Bovey, *Journal of the Optical Society of America*, 1951, **41**, 836.)

Observed absorption (cm^{-1})	Assignment
~3449 br	H_2O stretch
~3128 m br	NH_4^+ ν_3 stretch
2929 vw	residual CH stretch
2076 vw	NCS$^-$ C≡N stretch
1656 m	C=O stretch in residual DMF NH_4^+ ν_2 bend (uncertain assignment)
~1615 shoulder	H_2O bend
1401 m sh	NH_4^+ ν_4 bend
1290 w-m sh	TTT$^-$ (corresponding literature peak: NH_4TTT 1282 m)
1216 s sh	TTT$^-$ (corresponding literature peak: NH_4TTT 1210 s)
1077 s sh	TTT$^-$ (corresponding literature peak: NH_4TTT 1074 s)
910 w-m sh	TTT$^-$ (corresponding literature peak: NH_4TTT 911 m)
740 m sh	unknown

Table S1c. Observed FT-IR peaks, assignments, and corresponding literature values for CdSe(TTT) dispersed in KBr and heat-treated at 100 °C. (NH_4^+; L. F. H. Bovey, *Journal of the Optical Society of America*, 1951, **41**, 836.)

Observed absorption (cm^{-1})	Assignment
~3450 br	H_2O stretch
~3128 br m	NH_4^+ ν_3 stretch
2923 vw	residual CH stretch
2076 vs	NCS$^-$ C≡N stretch
1655 m	C=O stretch in residual DMF NH_4^+ ν_2 bend (uncertain assignment)
~1615 w-m	H_2O bend
1401 m sh	NH_4^+ ν_4 bend
1103 vw	unknown
741 m sh	unknown

General assignments: G. Socrates, *Infrared Characteristic Group Frequencies*, Wiley, Chichester, 2nd ed., 1994.

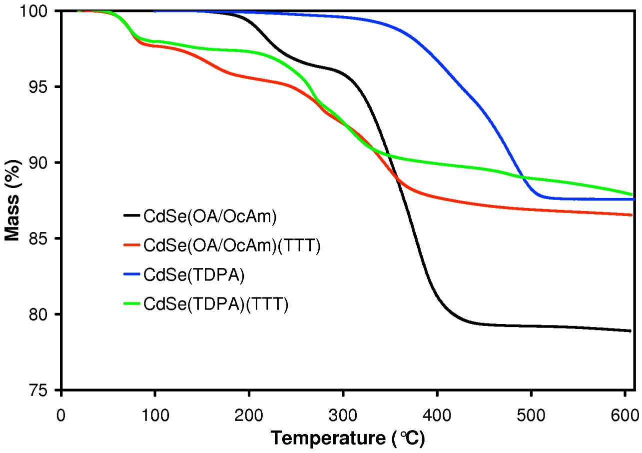

Fig. S13 TGA data for CdSe exchanged with oleic acid and 1-octylamine [CdSe(OA/OcAm)], CdSe exchanged with tetradecylphosphonic acid [CdSe(TDPA)], and both of the above subsequently exchanged with NH_4TTT (*i.e.* CdSe(OA/OcAm)(TTT) and CdSe(TDPA)(TTT), respectively).

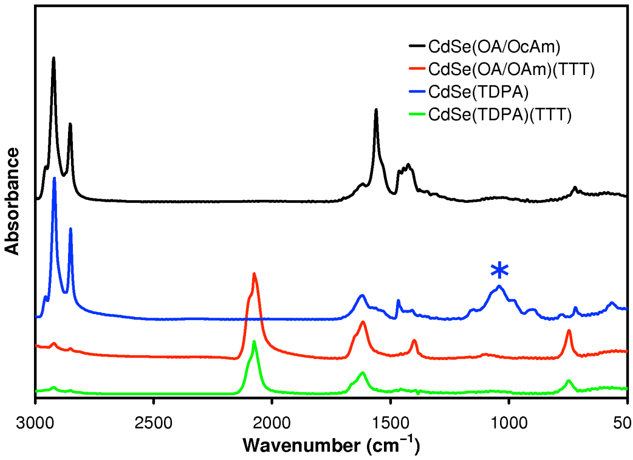

Fig. S14 FT-IR data for CdSe(OA/OcAm), CdSe(TDPA), CdSe(OA/OcAm)(TTT), and CdSe(TDPA)(TTT). All samples were dried under flowing N_2 at 100 °C and dispersed in KBr. It is evident that negligible ν(C–H) remains after TTT$^-$ exchange. The prominent feature marked on the CdSe(TDPA) spectrum is characteristic of ν(P–O) stretching in phosphonate; it too is lost after TTT$^-$ exchange.