

Supplementary information for

Identifying reactive organo-selenium precursors in the synthesis of CdSe nanoplatelets

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Materials

Cadmium propionate (#0520951210, anhydrous) was purchased from MP Biomedicals. Selenium (Se) (#209651, ≥ 99.5%), sulfur (#414980, 99.98%), tellurium (#264865, 99.997%), lithium aluminum hydride (LiAlH₄) (#199877, 95%), benzoyl chloride (#259950, 99%), 4-chlorobenzoyl chloride (#111902, 99%), sodium sulfate (#746363, ≥ 99%), toluene (#244511, 99.8%), myristic acid (#70082, ≥ 98%), acetonitrile (#34998, ≥ 99.9%), trifluoroacetic acid (#302031, ≥ 99%), diethyl ether (#676845, ≥ 98%), trifluoroacetic anhydride (#106232, ≥ 99%), deuterated chloroform (CDCl₃) (#236918, 99.6 atom % deuterium), 1-octadecene (ODE) (#O806, 90%), oleic acid (#364525, 90%), acetic anhydride (#320102, ≥ 99%), acetic acid (#33209, ≥ 99.8%), and cadmium acetate dihydrate (#289159, 98%) were purchased from Sigma Aldrich. Triethylamine (#157910010, 99%) and tetrahydrofuran (THF) (#348450010, 99.5%) were purchased from Acros Organics. Cadmium oxide (#48-0800, 99.999%) was purchased from Strem Chemicals. Stearoyl chloride (#S0404, > 97%) was purchased from TCI chemicals. Sodium chloride (NaCl) (#85139.360) was purchased from VWR Chemicals. Hexane, acetone, isopropanol, and methanol were purchased from Thommen-Furler AG. Absolute ethanol was purchased from Alcosuisse AG. All chemicals were used as received.

Characterization

Powder X-ray diffraction (XRD)

Samples were dispersed in hexane and drop-casted on zero background Si sample holders, allowing the solvent to evaporate. XRD patterns were recorded on a Bruker D8 Advance instrument (40 kV, 40 mA, $\lambda_{\text{CuK}\alpha} = 0.15418 \text{ nm}$).

Thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) coupled with mass spectrometry (MS)

Cd(propionate)₂ alone or with one molar equivalent of Te, Se, or S was weighed in Al₂O₃ crucibles (~10 mg in total) and loaded in a Netzsch STA 449 thermal analyzer. After keeping the samples under an argon flux for 30 min to remove residual air, the temperature was ramped up from 45 to 300 °C at a rate of 10 K/min under argon flow (50 mL/min). TGA and DSC profiles were recorded in synchronization with electron ionization MS of volatile decomposition products.

Nuclear magnetic resonance spectroscopy (NMR)

All spectra were collected on a Bruker Ascend Aeon 400 MHz spectrometer. ¹H-NMR, ¹³C-NMR, and ⁷⁷Se-NMR spectra were recorded with predefined pulse programs. The samples for NMR were prepared by dissolving the product in CDCl₃.

Absorption spectroscopy

Absorption spectra were recorded on a Varian Cary Scan 50 ultraviolet-visible spectrophotometer. Samples were diluted in 2 mL hexane and 100 µL oleic acid and measured in a 1 cm path-length quartz cuvette.

Photoluminescence spectroscopy

Photoluminescence (PL) spectra of samples were recorded on an AvaSpec-ULS2048L Starline spectrometer in right-angle geometry using a 380 nm light-emitting diode (LED) as an excitation source. The samples were diluted in 2 mL hexane and 100 µL oleic acid in a 1 cm path-length quartz cuvette (dilution factor = 22).

Transmission electron microscopy (TEM)

Samples were prepared on carbon-coated copper grids by drop-casting dilute dispersions (hexane) followed by slow evaporation of the solvent. TEM micrographs were recorded on a Philips CM12 (operated at 100 kV).

Synthesis

Synthesis of LiAlHSeH

Bis(acyl) selenides were synthesized by modifying a previously reported method based on LiAlHSeH as a selenating reagent.⁸¹ Briefly, LiAlH₄ (0.76 g, 20 mmol) was added to a suspension of elemental Se (1.92 g, 24 mmol) in 200 mL of dry THF in a 500 mL four-neck flask at -10 °C under nitrogen atmosphere. The mixture was stirred for 30 min. The lithium

aluminium hydride hydrogen selenide (LiAlHSeH) was formed *in situ* as a greyish dispersion and could be further reacted with carboxylic acid chlorides without purification.

Synthesis of bis(acyl) selenides (**1**, **2**, and **3**) with LiAlHSeH

Bis(stearoyl) selenide (1)

80 mmol (27.2 mL) of stearoyl chloride was slowly added to the dispersion of 20 mmol LiAlHSeH , prepared as described above. The mixture was stirred at -10 °C under nitrogen atmosphere. After 2 h, 5 mL of deionized water was added to quench unreacted reagents. The organic reaction mixture was diluted with 250 mL of diethyl ether and washed four times with 100 mL brine. The organic layer was dried over sodium sulfate for 2 h, filtered, and the volume was reduced to ~150 mL by rotary evaporation under reduced pressure. Bis(stearoyl) selenide was crystallized at room temperature (12 h), filtered, and dried under high vacuum for 12 h. The volume of the filtrate was reduced to ~100 mL by rotary evaporation under reduced pressure and the remaining solution was kept at -20 °C for ~10 h to crystallize residual bis(stearoyl) selenide. The crystals were separated by filtration, dried under vacuum for 12 h, and stored under N_2 . The isolated yield was 53.3%.
 ^1H NMR (CDCl_3 , 400 MHz): δ 0.88 (t, 6H, J = 6.8 Hz), 1.25 (s, 56H), 1.65 (quint, 4H, J = 7.5 Hz), 2.81 (t, 4H, J = 7.4 Hz). ^{13}C NMR (CDCl_3 , 400 MHz): δ 14.3, 22.9, 25.0, 28.9, 29.4, 29.5, 29.7, 32.1, 49.7, 198.4. ^{77}Se NMR (CDCl_3 , 400 MHz): δ 810.3. See also Fig. S4.

Bis(benzoyl) selenide (2)

80 mmol (9.2 mL) of benzoyl chloride was added slowly to the dispersion of 20 mmol LiAlHSeH , prepared as described above. The mixture was stirred at -10 °C under nitrogen atmosphere. After 2 h, 5 mL of deionized water was added to quench unreacted reagents. The organic reaction mixture was diluted with 250 mL of diethyl ether and washed four times with 100 mL brine. The organic layer was dried over sodium sulfate for 2 h, filtered, and concentrated to ~15 mL by rotary evaporation under reduced pressure. Then 10 mL of a 1:1 (volume %) hexane/diethyl ether mixture was added. Bis(benzoyl) selenide was crystallized from this mixture at -20 °C. The crystals were separated by filtration, dried under high vacuum for 12 h at 20 °C, and stored under N_2 . The isolated yield was 60.7%.
 ^1H NMR (CDCl_3 , 400 MHz): δ 7.50 (t, 4H, J = 7.8 Hz), 7.64 (t, 2H, J = 7.4 Hz), 7.96 (dd, 4H, J = 8.1 Hz). ^{13}C NMR (CDCl_3 , 400 MHz): δ 128.7, 129.2, 134.6, 138.8, 188.7. ^{77}Se NMR (CDCl_3 , 400 MHz): δ 746.8. See also Fig. S4.

Bis(4-chlorobenzoyl) selenide (3)

Bis(4-chlorobenzoyl) selenide was prepared following the same procedure as bis(benzoyl) selenide except using 80 mmol (10.3 mL) of bis(4-chlorobenzoyl) chloride. The isolated yield was 32.2%. ^1H NMR (CDCl_3 , 400 MHz): δ 7.48 (d, 4H, $J = 8.7$ Hz), 7.89 (d, 1H, $J = 8.7$ Hz). ^{13}C NMR (CDCl_3 , 400 MHz): δ 129.6, 130.0, 136.9, 141.4, 187.1. ^{77}Se NMR (CDCl_3 , 400 MHz): δ 749.5. See also Fig. S4.

Synthesis of cadmium myristate

The synthesis of cadmium myristate was based on the synthesis of lead oleate carried out by Hendricks *et al.*^{S2} Briefly, 44.8 mmol (5.75 g) of cadmium (II) oxide was added to 20 mL of acetonitrile in a 100 mL three-neck flask. The suspension was stirred while being cooled in an ice bath for 10 min before 8.96 mmol (0.7 mL, 0.2 eq) of trifluoroacetic acid and 44.8 mmol (6.2 mL, 1 eq) trifluoroacetic anhydride were added. After 15 min, the ice bath was removed. The brown reaction mixture was stirred for 1 h at room temperature and slowly turned white. Then, the mixture was heated to 60 °C for 15 min, resulting in a significant reduction of turbidity. In a 500 mL Erlenmeyer flask, 90.05 mmol of myristic acid (20.56 g, 2.01 eq) and 101.25 mmol of triethylamine (10.246 g, 2.26 eq) were added to 180 mL of isopropanol. The solution of cadmium trifluoroacetate was added dropwise to the myristic acid solution under stirring, resulting in the formation of a white precipitate of cadmium myristate, which was isolated by suction filtration using a glass-fritted funnel, washed with methanol (3 times 300 mL), and then dried under vacuum for 12 h.

Synthesis of quantum dots with compound 1, 2, or 3

In a 50 mL three-neck flask, 0.3 mmol (80 mg) of cadmium acetate dihydrate, and 0.7 mmol (197.7 mg, 222 μL) of oleic acid were added to 15 mL of 1-octadecene (ODE). The mixture was degassed under vacuum and magnetic stirring at 110 °C for 90 min. After degassing, the flask was switched to nitrogen and the temperature was set to 180 °C. Once the system reached 180 °C, 0.15 mmol of either **1**, **2**, or **3** dissolved in 2 mL of toluene was swiftly injected. Aliquots were taken during the reaction, and after 15 min the mixture was quickly cooled down to room temperature with a water bath. 2 mL of ethanol was added, and the mixture was centrifuged for 10 min at 5000 r.p.m. The supernatant was discarded and the precipitated quantum dots were re-dispersed in ~10 mL hexane. The washing cycle was repeated two more times and the final product was re-dispersed and stored in 10 mL of hexane.

Synthesis of nanoplatelets with compound **1**, **2**, or **3**

In a 50 mL three-neck flask, 0.225 mmol (127.5 mg) of cadmium myristate was added to 15 mL of ODE. The mixture was degassed under vacuum and magnetic stirring at room temperature for 30 min. After degassing, the flask was switched to nitrogen and the temperature was set to 240 °C. When the temperature reached 240 °C, 0.227 mmol (23.2 mg, 21.5 µL) of acetic anhydride was injected. After 1 min, 0.075 mmol of either **1**, **2**, or **3** dissolved in 1 mL of toluene at room temperature was swiftly injected into the reaction mixture. Aliquots were taken after 2 min, 4 min, and 9 min. Then, the flask was quickly cooled down to room temperature with a water bath, and 2 mL oleic acid was injected. The nanoplatelets were precipitated by centrifugation at 6000 r.p.m. for 10 min. The supernatant was discarded and the precipitate was re-dispersed in 8 mL hexane. Acetone (1 mL) was added and the sample was centrifuged again. The supernatant was discarded and the precipitate was re-dispersed in hexane. This cleaning cycle was repeated one more time and the final product was re-dispersed and stored in 10 mL hexane. XRD patterns for the products are shown in Fig. S5.

Supplementary figures

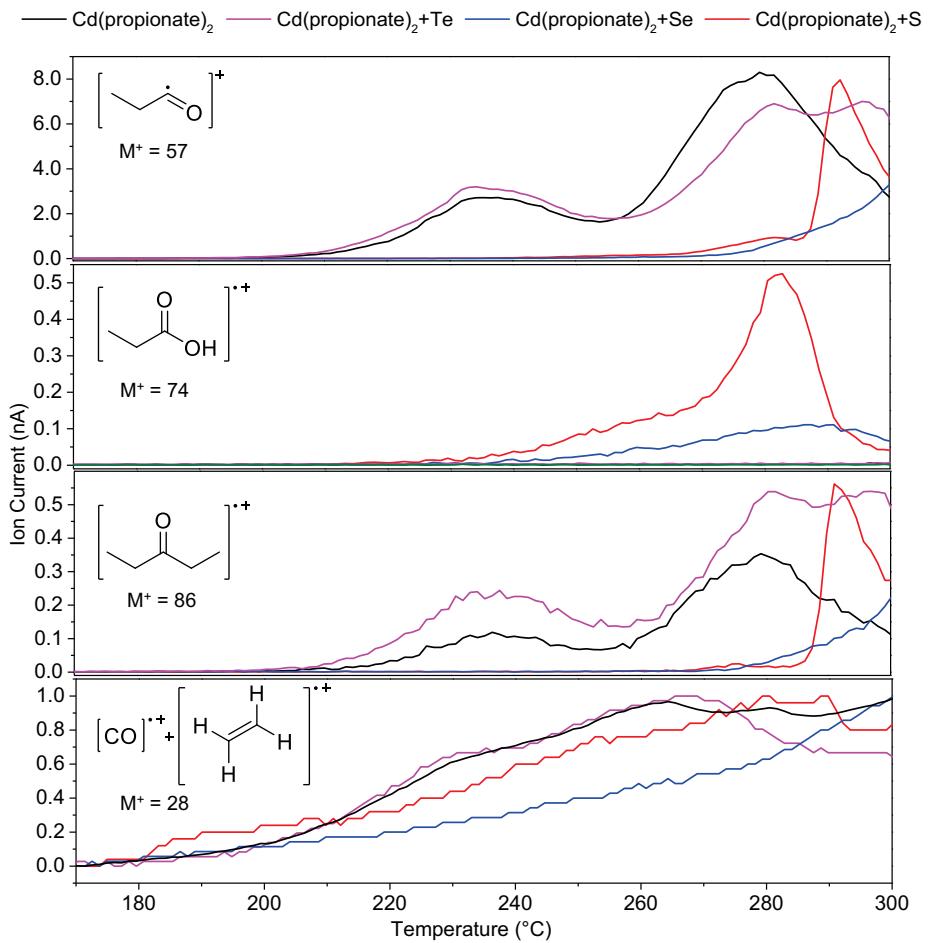


Fig. S1. Additional mass traces for Cd(propionate)₂ alone or with Te, Se, or S. Below 260 °C, the typical propionate decomposition products of Cd(propionate)₂ (propionyl radical and 3-pentanone) were observed only in samples that did not contain Se or S. This finding led to the proposed mechanism depicted in Fig. 2e in the main text in which elemental Se (S) reacts with the propionyl radicals to bis(propionyl) selenide (sulfide). This then reacts with remaining Cd(propionate)₂ to CdSe (CdS) with the release of propionyl cations [from bis(propionyl) selenide] and propionate ions [from Cd(propionate)₂]. While propionate ions can bind to the surface of the formed CdSe NPLs, propionyl cations are unstable and decompose to ethene, carbon monoxide, and protons. Indeed, with increasing temperature, mass signal at $m/z=28$ (which corresponds to both CO and ethene) increases for all samples (starting already at 180–200 °C), while the signal for $m/z=74$ (corresponding to propionic acid) was only observed for samples containing Se or S. This indicates that, with increasing CdSe (CdS) formation, increasing amounts of propionate ions combine with protons of decaying propionyl cations, leading to the formation of propionic acid.

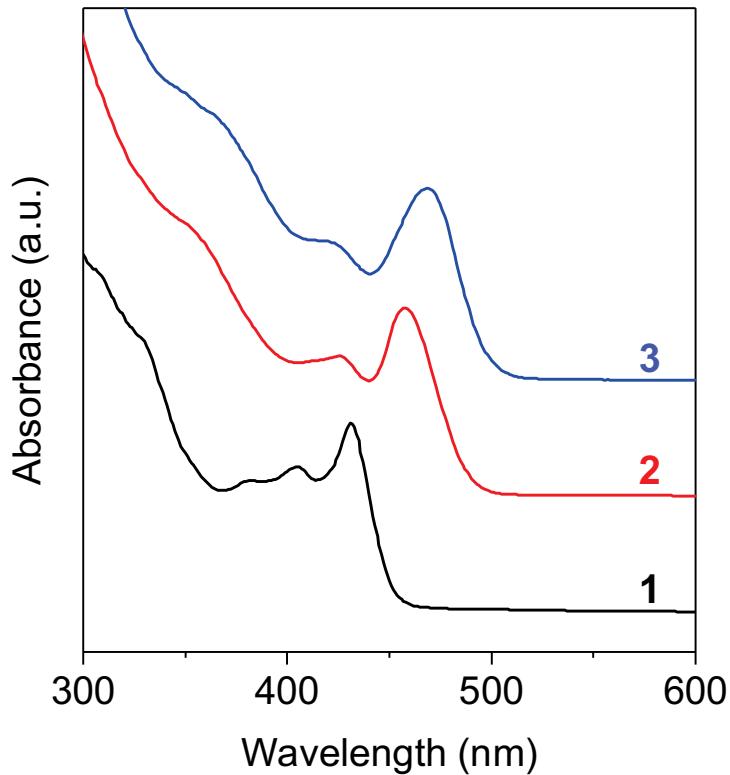


Fig. S2. Absorption spectra of CdSe quantum dots (QDs) at reaction completion. The nanocrystals are synthesized by combining **1**, **2**, or **3** with Cd(oleate)₂ in ODE at 180 °C. With decreasing Lewis basicity of the bis(acyl) selenides (**1** > **2** > **3**), the wavelength of the lowest energy exciton feature (and thus the QD size) increases, consistent with a decrease in reactivity from **1** to **2** to **3**. See the Synthesis section above for more details.

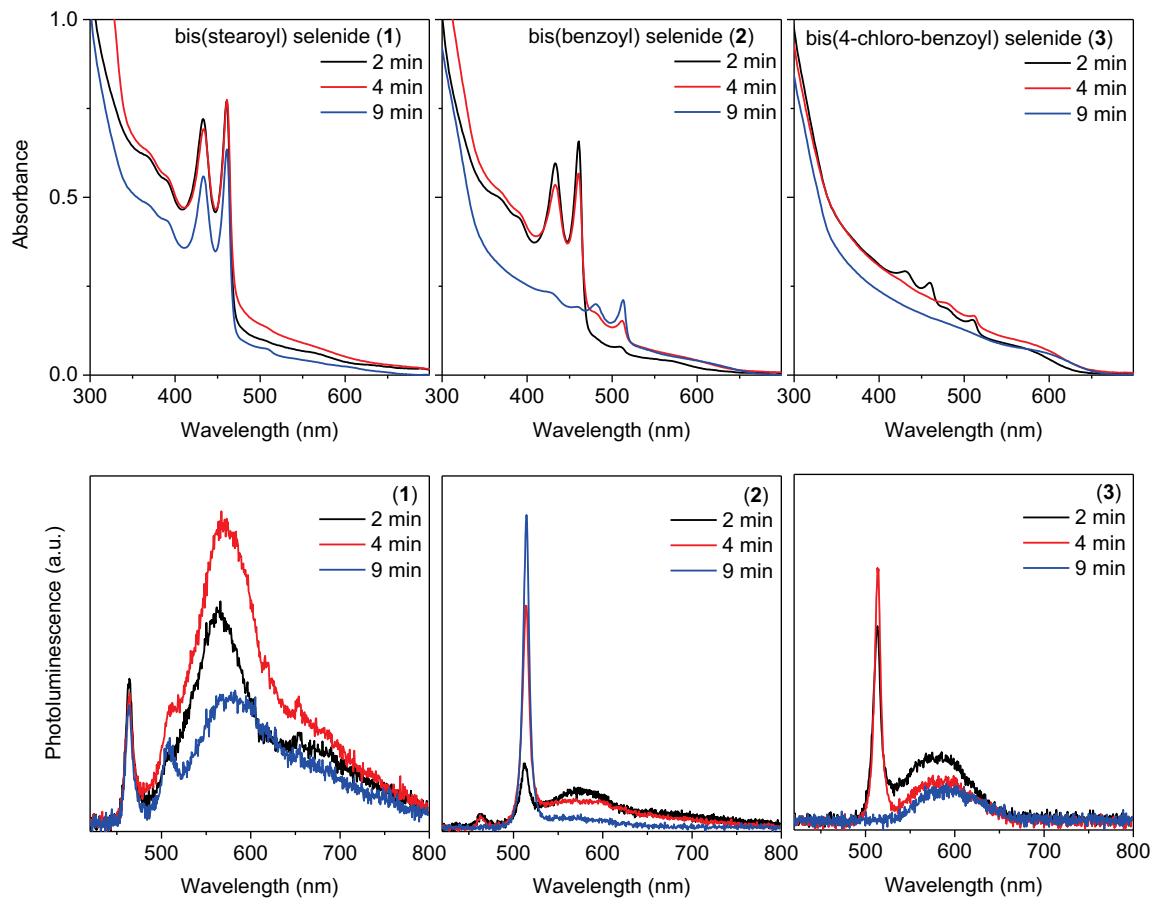


Fig. S3. Absorption and photoluminescence spectra of aliquots (without purification and size selection) taken during the syntheses of CdSe NPLs with bis(acyl) selenides **1**, **2**, or **3**. After 9 min, the reaction with **1** yielded predominantly 3 monolayer (ML) thick nanoplatelets (NPLs), **2** yielded 4ML thick NPLs, and **3** predominantly quantum dots (QDs).

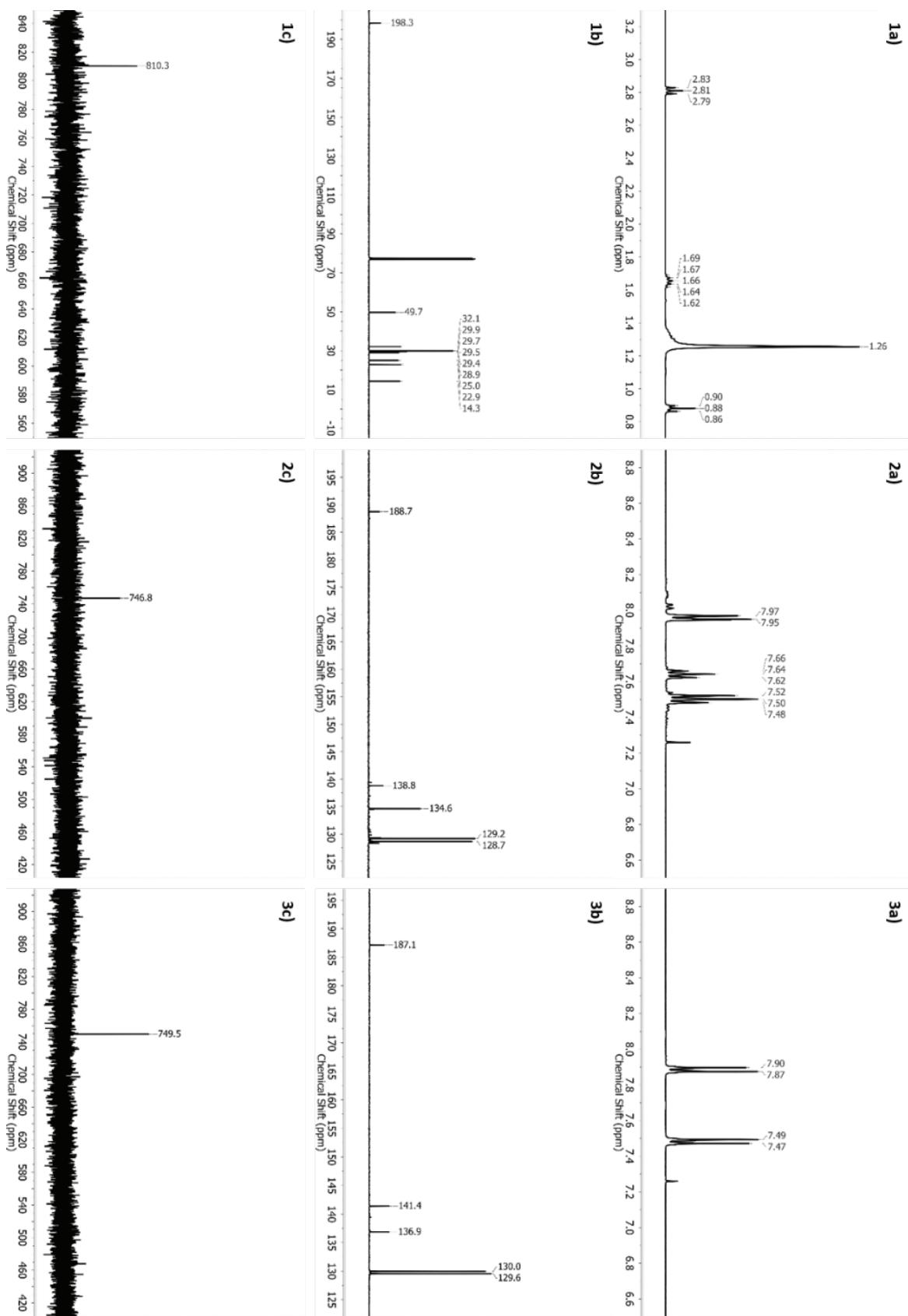


Fig. S4. Characterization of compounds **1** (1a-c), **2** (2a-c), and **3** (3a-c) by ^1H (a), ^{13}C (b), and ^{77}Se (c) nuclear magnetic resonance (NMR) spectroscopy. The chemical shifts and coupling constants for each compound are listed in the experimental section above.

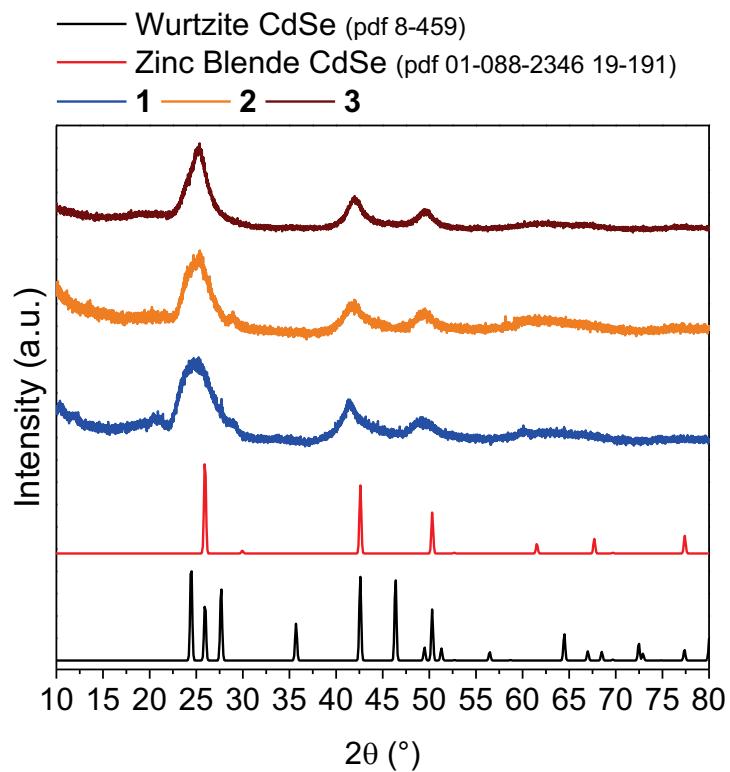


Fig. S5. XRD of products synthesized with compound **1**, **2**, and **3** as reported in Fig. 3 of the main text.
All products crystallized in the cubic zinc blende structure.

Supplementary references

- (S1) Koketsu, M.; Nada, F.; Hiramatsu, S.; Ishihara, H. *J. Chem. Soc., Perkin Trans. 1* **2002**, 737-740.
- (S2) Hendricks, M. P.; Campos, M. P.; Cleveland, G. T.; Jen-La Plante, I.; Owen, J. S. *Science* **2015**, 348, 1226-1230.