Mechanistic Study of Precursor Evolution in Colloidal II-VI Semiconductor Nanocrystal Synthesis

Supporting Information

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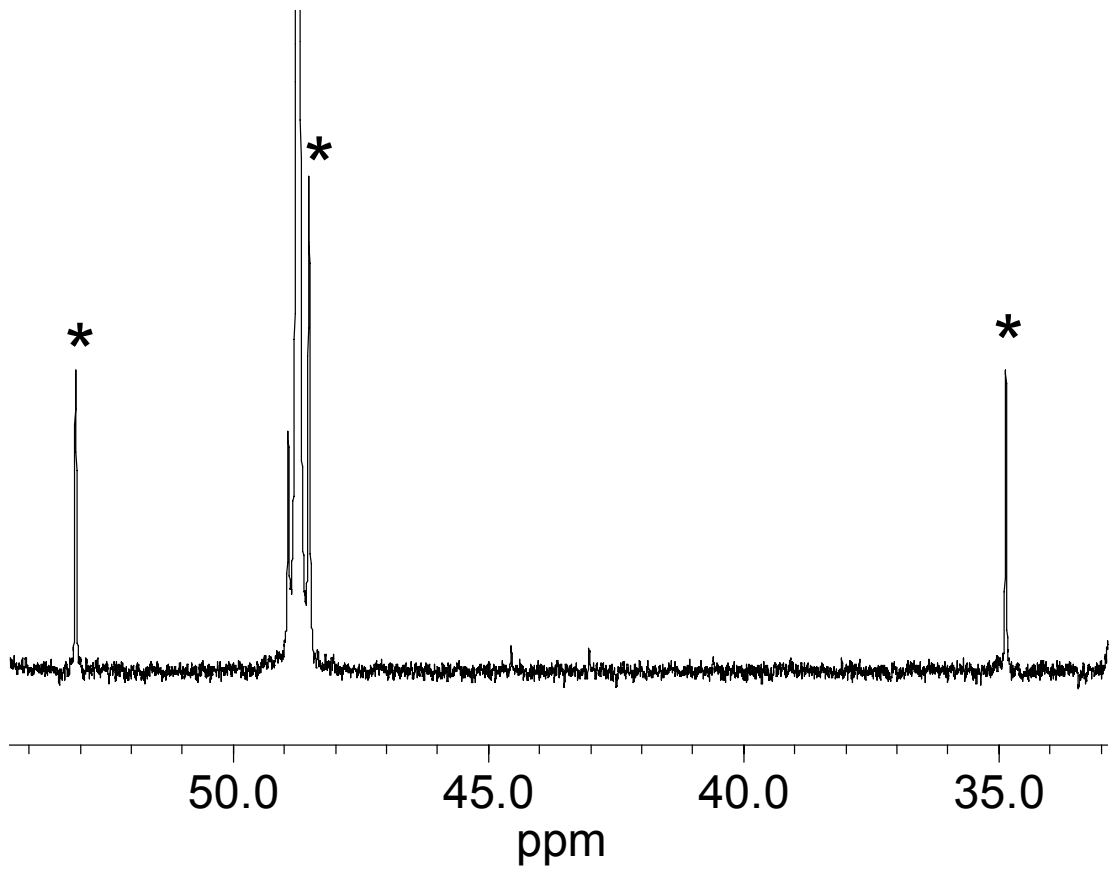
TOPO Purity. The purity of TOPO was analyzed with ^{31}P NMR spectroscopy. At least three impurities were found in 99% TOPO purchased from Aldrich (Figure S2) which are very similar to those in 90% TOPO from Aldrich.

Figure S1. ^{31}P NMR spectrum of 99% TOPO (Aldrich, lot # 24801MB) used in this study. The spectrum is enlarged to show the impurity peaks (*). One of the impurity peaks (δ = 48.5 ppm) overlaps with a ^{13}C satellite of TOPO. The purity of TOPO in this sample was estimated to be 93% (mol/mol).



Stability of TOPSe/TBPSe/TBPS in air. TOPSe, TBPSe, and TBPS were found to be stable to air. No change was observed in the ^{31}P NMR spectrum for a $CDCl_3$ solution of TOPSe that was left in air for 20 days (Figure S1). When Cd-ODPA was added to a $CDCl_3$ solution of TOPSe, < 2% of TOPSe was converted to TOPO after 20 days. Similar results were obtained for $CDCl_3$ solutions of TBPSe and TBPS after they were exposed to air for 5 days (data not shown).

Figure S2. ^{31}P NMR spectrum of a $CDCl_3$ solution of TOPSe after it was stored in air for 20 days.

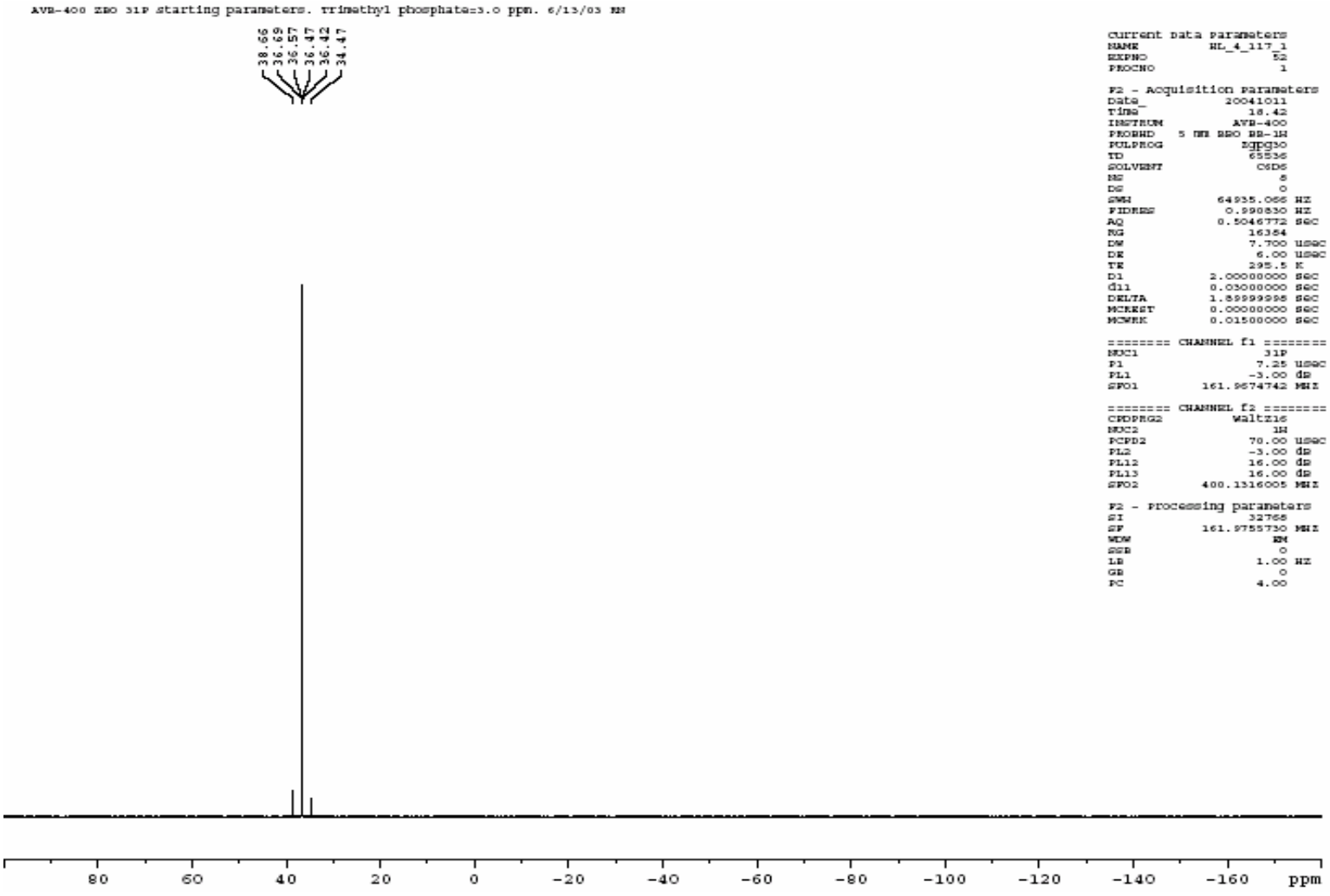
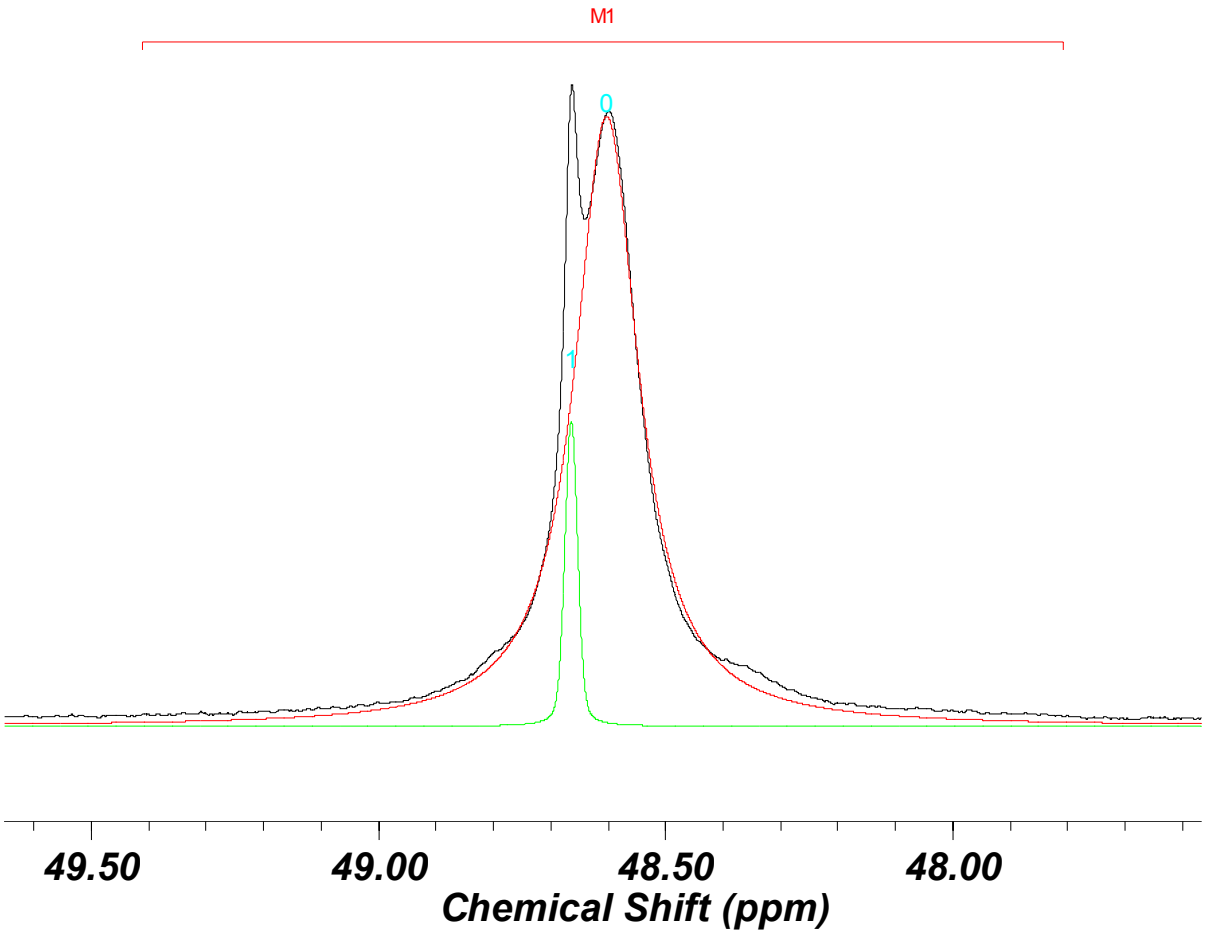


Figure S3. Deconvolution of the TOPO and TOPS resonances using MestRec.[a]



[a] Typical ^{31}P NMR spectrum of the crude reaction mixture of the synthesis of CdS in TOPO using 'double degassed' protocol. The red (TOPO) and green (TOPS) peaks are fitting result obtained using MestRec.

Accuracy of the ^{31}P NMR method used in the kinetics studies. Reactions in TOPO: Solutions of TOPO/TOPSe mixture were prepared with known molar ratio (R_M) based on the mass and assuming 100% purity. The corresponding ^{31}P spectra were collected and the molar ratio (R_N) was calculated from the integration. A highly linear correlation (R^2>0.999) was observed between R_M and R_N. The R_N/R_M value depends on the pulse program used, being 0.92 without proton decoupling and 1.07 with inverse gated proton decoupling (acquisition time =10 sec.). If the signals of TOPSe and TOPS are assumed to have 20% error, fits of the [TOPE] decay *versus* time showed < 5% change in the fitted decay constant, which is within the error of the fitting. *In-situ* reactions: The ^{31}P NMR spectra of these reactions were collected using inverse gated proton decoupling with shorter acquisition time (3 – 4 sec.) compared to the above case. The concentration of TBPSe/TBPO obtained by NMR in this case was found to be accurate within ± 2% by comparing to an internal standard (ethyl phosphonic acid diethyl ester).

Synthesis of TBPS: A mixture of TBP (2.02 g, 0.010 mol) and sulfur (0.435 g, 0.014 mol) was stirred at r.t. in glove box overnight. The supernatant was used in the experiments without further purification. ^{1}H ($CDCl_3$, δ ppm): 1.63-1.70 (m, 6H), 1.37-1.47 (m, 6H), 1.23-1.32 (m, 6H), 0.79 (t, 9H, *J*=7.3 Hz). ^{13}C ($CDCl_3$, δ ppm, more than 4 peaks appeared due to the coupling between ^{13}C and ^{31}P): 30.49, 29.99, 24.11, 24.07, 23.69, 23.54, 13.31. ^{31}P ($CDCl_3$, δ ppm): 48.7. Anal. (calcd, found): C (61.49, 61.11), H (11.61, 11.84). TBPSe, TBPTe, TOPSe, and TOPS were prepared similarly with longer reaction times.

TBPSe: ^{1}H ($CDCl_3$, δ ppm): 1.73-1.79 (m, 6H), 1.36-1.46 (m, 6H), 1.23-1.33 (m, 6H), 0.79 (t, 9H, *J*=7.3 Hz). ^{31}P ($CDCl_3$, δ ppm): 36.8, $J_{P\text{-}Se}$=680 Hz. Anal. (calcd, found): C (51.24, 51.37), H (9.68, 9.78).

TBPTe: The mixture solidified into a yellow crystalline solid after it was stored in glove box at r.t. for 30 days. ^{1}H ($CDCl_3$, δ ppm): 1.96-2.03 (m, 6H), 1.38-1.56 (m, 12 H), 0.93 (t, 9H, *J*=7.2Hz). ^{13}C ($CDCl_3$, δ ppm): 30.45, 30.09, 26.56, 26.52, 23.55, 23.40, 13.61. ^{31}P ($CDCl_3$, δ ppm): -13.2. $J_{P\text{-}Te}$(^{125}Te)=1655 Hz, $J_{P\text{-}Te}$(^{123}Te)=1370 Hz.

TOPSe: ^{1}H ($CDCl_3$, δ ppm): 1.83-1.90 (m, 6H), 1.49-1.59 (m, 6H), 1.32-1.39 (m, 6H), 1.22-1.29 (m 24H), 0.84 (t, 9H, *J*=6.8 Hz). ^{31}P ($CDCl_3$, δ ppm): 36.4. $J_{P\text{-}Se}$=678 Hz. ^{77}Se ($CDCl_3$, δ ppm): -377, -386. Anal. (calcd, found): C (64.11, 64.46), H(11.3, 11.65).

TOPS: ^{1}H ($CDCl_3$, δ ppm). 1.72-1.79 (m, 6H), 1.49-1.59 (m, 6H), 1.32-1.37 (m, 6H), 1.21-1.32 (m, 24H), 0.85 (t, 9H, *J*=6.6 Hz). ^{31}P ($CDCl_3$, δ ppm): 48.6. Anal. (calcd, found): C (71.58, 72.05), H(12.77, 13.06).

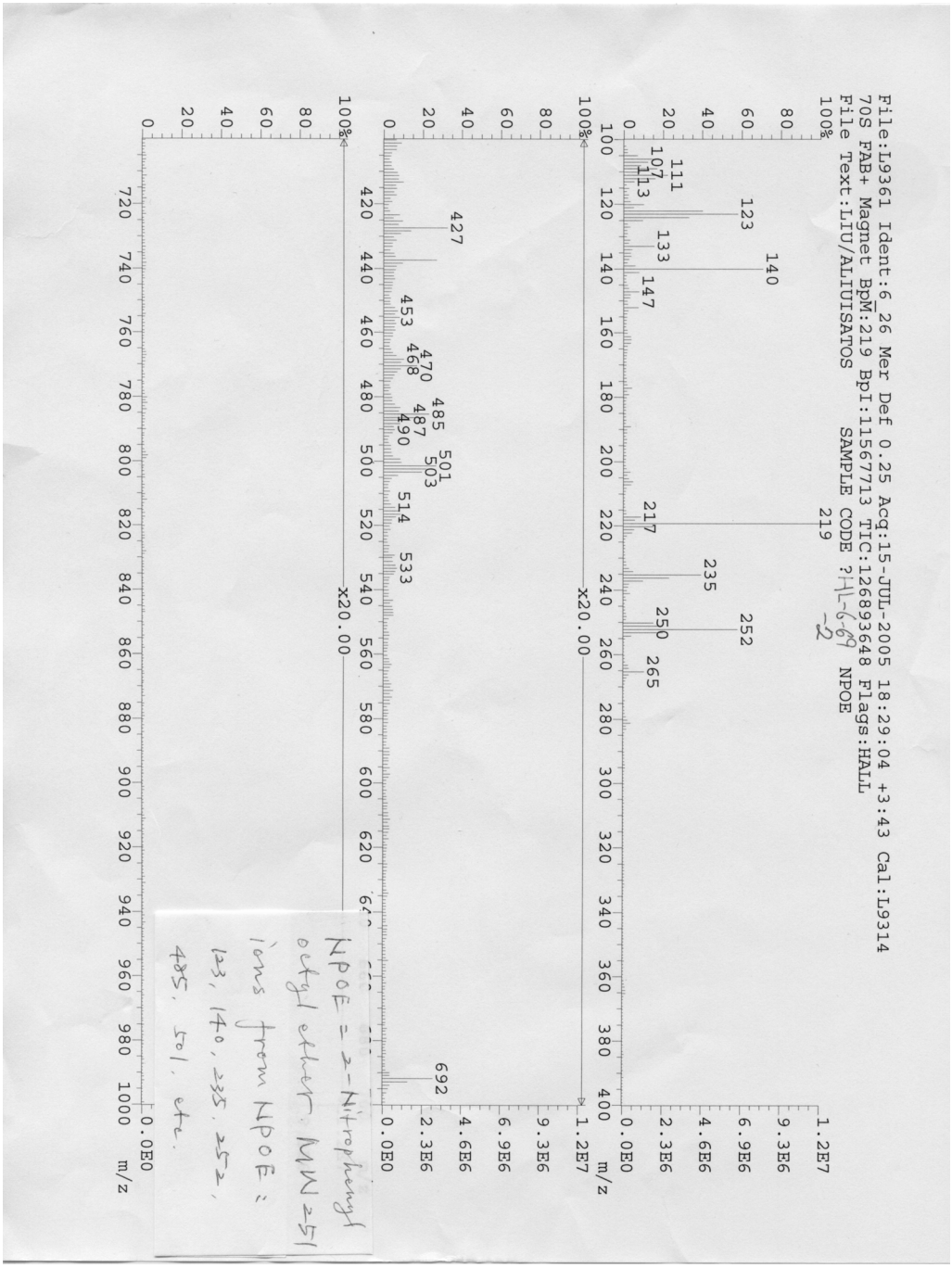
***i*-TPPSe:** To a vial in a glove box was added tri-*iso*-propylphosphine (0.80 g, 5.0 mmol) and Se powder (0.40 g, 5.0 mmol). The mixture was stirred for 24 hours to give a white precipitate. Toluene (1 mL) was added to dissolve the precipitated material. The mixture was stirred for another two days before it was taken out of glovebox. Toluene (1 mL) was added to the mixture and unreacted Se was removed by filtration. The toluene solution was evaporated under N_2 flow to crystallize the product. The solid product was collected by filtration and washed with cold toluene. Yield: 0.62 g, 52%. ^{1}H ($CDCl_3$, δ ppm): 2.22-2.34 (m, 3H), 1.25-1.31 (dd, 18H, J_1=7.2 Hz, J_2=16.2 Hz). ^{13}C ($CDCl_3$, δ ppm): 26.99, 26.60, 18.11, 18.09. ^{31}P ($CDCl_3$, δ ppm): 69.6, $J_{P\text{-}Se}$=688 Hz.

Karl-Fischer titration. The moisture content of reactions and reagents in this study was determined by volumetric Karl-Fischer titration using HYDRANAL reagents (Aldrich). Briefly, 1.0 g of the sample to be titrated was mixed with 5.0 g of HYDRANAL-Solvent 2E and titrated by dropwise addition of HYDRANAL-Titrant 2E via a syringe in a glove box. The titration was stopped when the solution turns into yellow-brown color, which indicates the presence of unreacted titrant. A control experiment was done to determine the moisture content in the HYDRANAL-Solvent 2E which was deducted as a background from all the titration results.

Titration of the water produced during the dissolution of CdO in H_2-ODPA/TOPO. To a 30 mL vial in a glove box was added TOPO (1.0 g), H_2-ODPA (1.07 g, 3.2 mmol), and CdO (0.212 g, 1.6 mmol). The vial was tightly capped and brought out of the glove box before it was heated to dissolve CdO. The vial was then brought into the glove box and the mixture was titrated using the method described above.

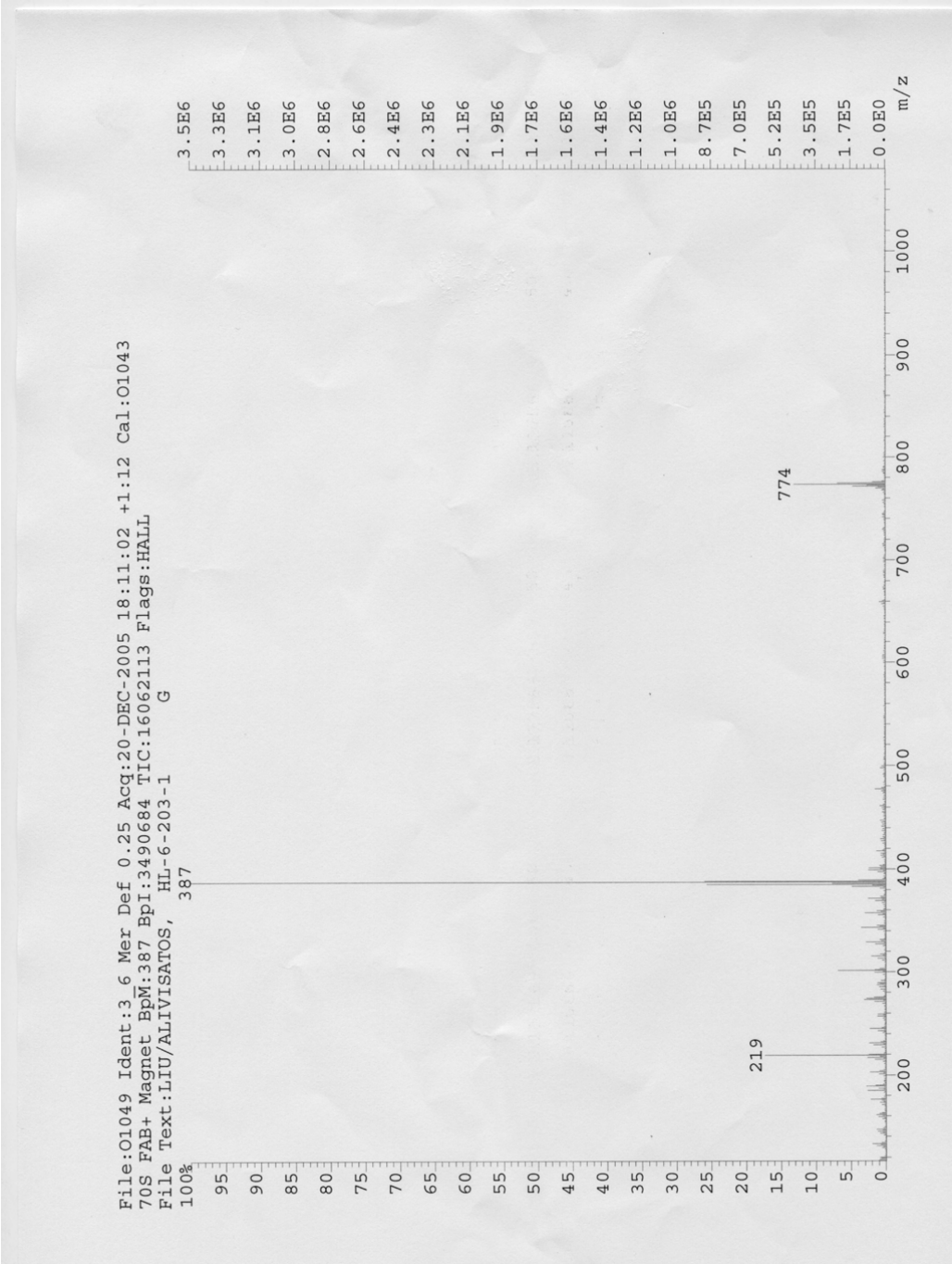
Determine the amount of water in the 'double degassed' reaction mixture. A mixture of TOPO/Cd-ODPA was prepared following the 'double degassed' protocol described in the main text using TOPO (2.73 g), H_2-ODPA (1.07 g), and CdO (0.205 g). The second degassing was carried out at 150 °C, 300 mtorr for 5 min. HYDRANAL-Solvent 2E (10 mL) was added to the flask via a syringe at 100 °C. The mixture was cooled to 30 °C and titrated as described above. The reaction mixture was vigorously shaken to ensure that water adsorbed on the reaction vessel and lower part of the condenser was also titrated.

Figure S4. FAB-MS spectrum of the reaction between Cd-OA and TBPSe.[a]



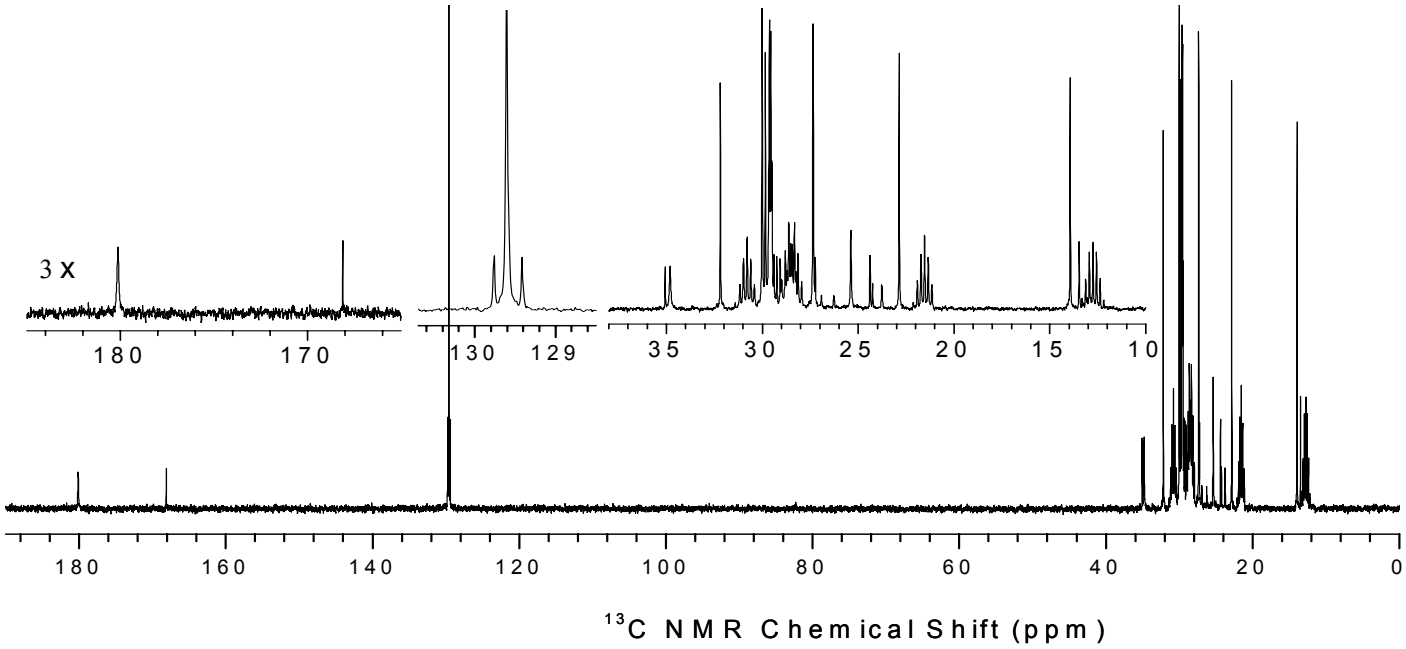
[a] $[TBPO+H]^+$ (m/z= 219),

Figure S5. FAB-MS of the reaction between Cd-ODPA and TBPSe in TOPO.[a]



[a] $[TBPO+H]^+$ (*m/z*= 219), $[TOPO+H]^+$ (*m/z*=387), and $[2TOPO+H]^+$ (*m/z*=774)

Figure S6. Full ^{13}C NMR spectrum of the reaction between Cd-OA and TBPSe in *n*-nonane-d_{20}.



Synthesis of ME (M=Cd, Zn; E=S, Se, Te) in non-coordinating solvent in sealed NMR tube.

CdS: In a 5 mm NMR tube was added Cd-OA stock solution (0.14 g, 0.060 mmol Cd), TBPS (16 mg, 0.068 mmol), and *n*-decane-d_{22} (0.30 g). The mixture was degassed by three cycles of freeze-pump-thaw before it was flame sealed under reduced pressure (300 mtorr). The mixture was heated to 150 °C for 2.5 h. ^{31}P NMR ($C_9D_{20}/C_{10}D_{22}$, δ ppm): 57.0 (TBPO, identified by addition of TBPO), 50.7 (TBPS). Selected $(OA)_2O$ peaks in the ^{13}C NMR spectrum ($C_9D_{20}/C_{10}D_{22}$, δ ppm): 168.5, 130.1, 129.7, and 35.4.

CdTe: This is similar to the synthesis of CdSe in non-coordinating solvent using TBPTe. The mixture was heated to 120 °C in an oil bath for 20 min. ^{31}P NMR ($C_9D_{20}/C_{10}D_{22}$, δ ppm): 52.9 ppm (TBPO).

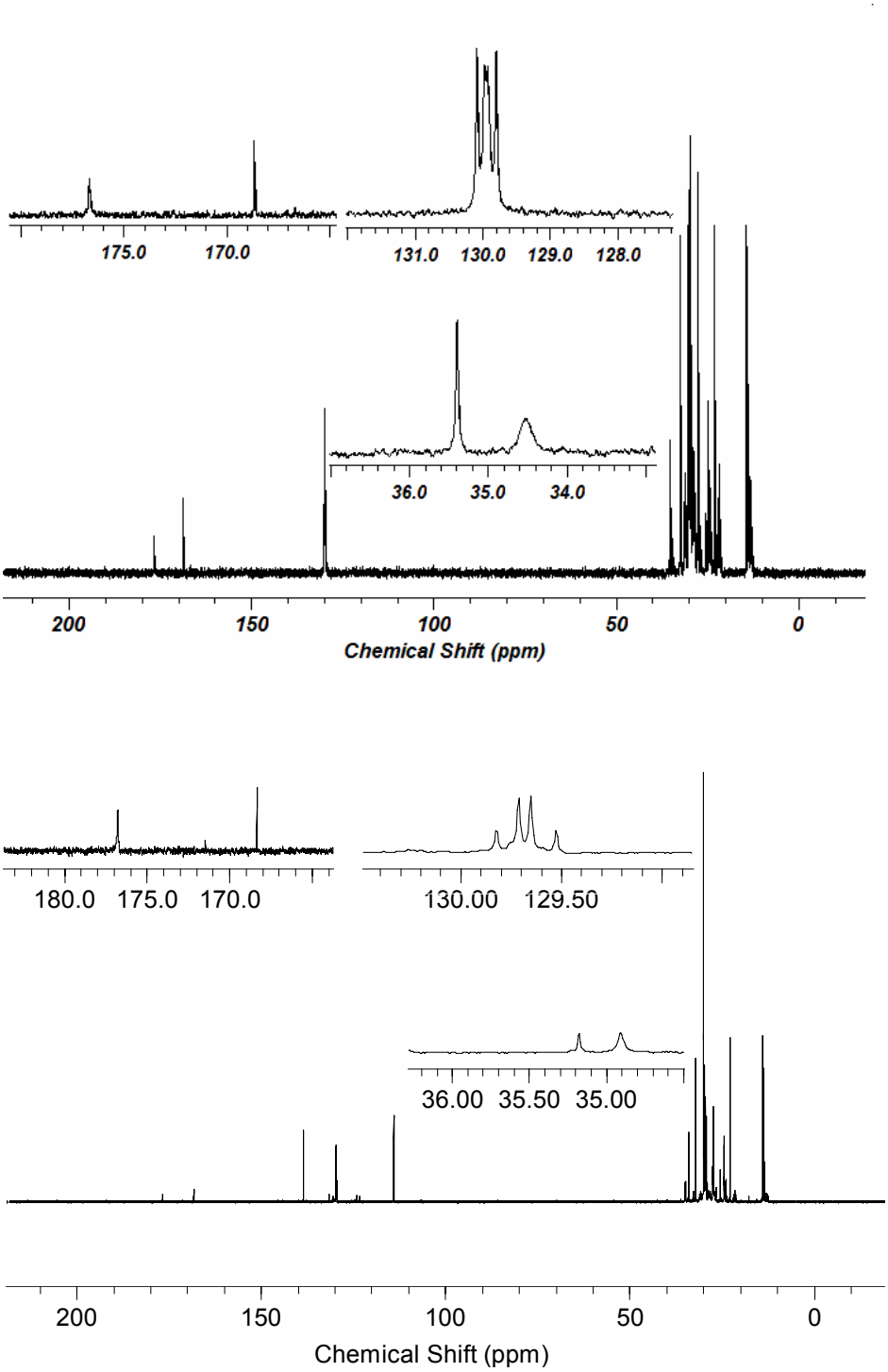
Selected $(OA)_2O$ peaks in the ^{13}C NMR spectrum ($C_9D_{20}/C_{10}D_{22}$, δ ppm): 168.7, 130.1, 129.8, 35.4. Figure S7 top.

ZnS: This is similar to the synthesis of CdSe in non-coordinating solvent using TBPS (62 mg, 0.26 mmol) and Zn-OA stock solution (0.64 g, 0.25 mmol Zn) in ODE solvent. The mixture was heated to 265 °C in an oil bath for 42 min. ^{31}P NMR (crude reaction mixture, without ^{2}H lock, δ ppm): 56.6 (TBPO), 46.3 (TBPS). Selected $(OA)_2O$ peaks in the ^{13}C NMR spectrum (crude reaction mixture, without ^{2}H lock, δ ppm): 167.9, 129.3, 129.0, 34.6.

ZnSe: This is similar to the synthesis of CdSe in non-coordinating solvent using TBPSe (77 mg, 0.27 mmol) and Zn-OA stock solution (0.64 g, 0.25 mmol Zn) in ODE solvent. The mixture was heated to 265 °C in an oil bath for 42 min. ^{31}P NMR (without ^{2}H lock, δ ppm): 53.6 ppm (TBPO), 35.0 (TBPSe). Selected $(OA)_2O$ peaks in the ^{13}C NMR spectrum (without ^{2}H lock, δ ppm): 167.9, 129.3, 129.0, 34.6.

ZnTe: This is similar to the synthesis of CdSe in non-coordinating solvent using TBPTe (0.12 g, 0.36 mmol), TBP (0.12 g, 0.59 mmol), Zn-OA stock solution (0.82 g, 0.32 mmol Zn), and *n*-decane-d_{22} (0.39 g). The mixture was heated to 230 °C in an oil bath for 150 min. ^{31}P NMR (δ ppm): 53.5 ppm (TBPO), -25.0 (TBPTe and TBP, due to fast exchange of Te between TBPTe and TBP). ^{13}C NMR: Figure S7 bottom.

Figure S7. ^{13}C NMR spectrum of the reaction between (Top) Cd-OA and TBPTe (Bottom) Zn-OA and TBPTe.[a]



[a] The inserts show the peaks used to identify $(OA)_2O$.

Figure S8 Transmission electron micrograph of (A) CdSe nanocrystals prepared using Cd-ODPA and TOPSe in TOPO at 260 °C (B) CdS nanocrystals prepared using Cd-OPDA and TOPS in TOPO at 290 °C. Scale bars represent 20 nm and 100 nm for CdSe and CdS, respectively.

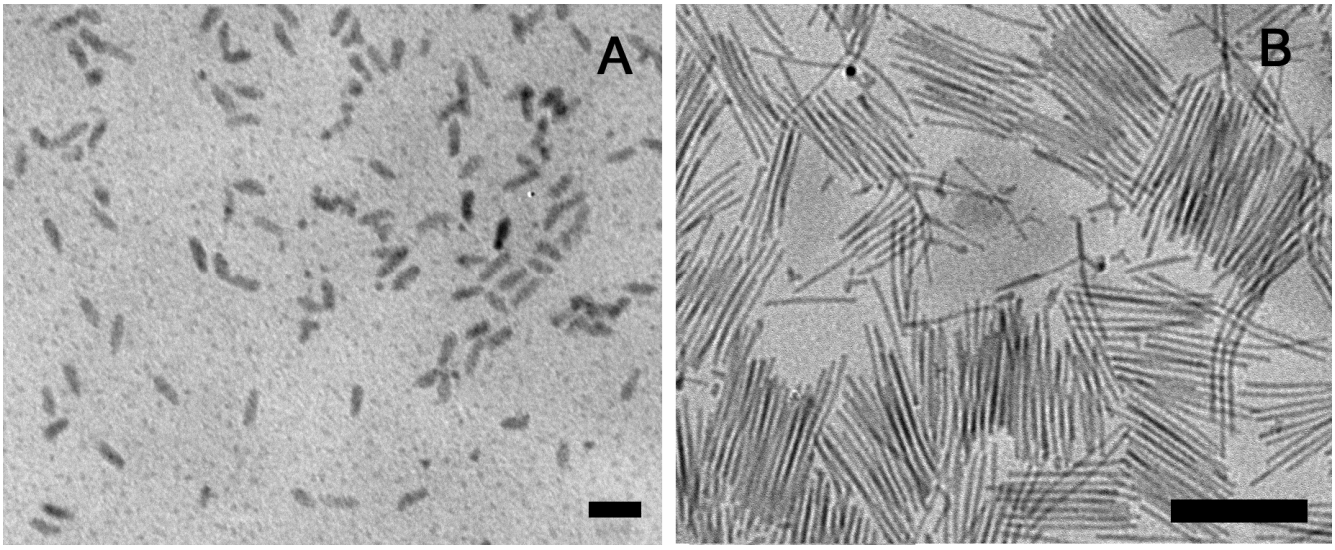
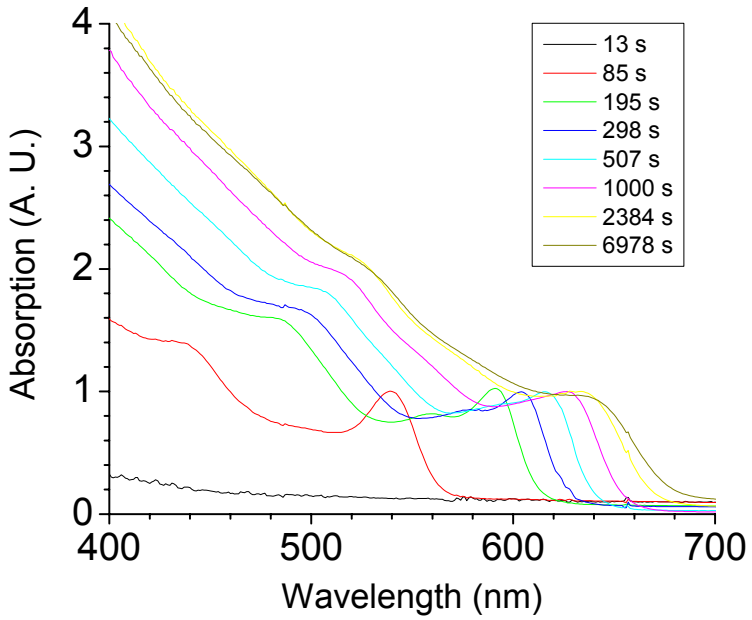
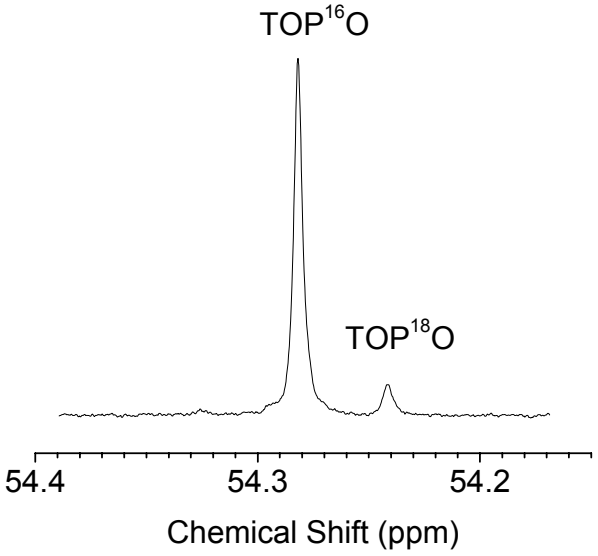


Figure S9 UV-Vis spectrum of CdSe nanocrystals prepared using Cd-ODPA and TOPSe in TOPO at 260 °C using double degassed protocol.



$H_2{}^{18}O$-TOP^{16}O isotope exchange. To a 25 mL three-neck flask was added TOPO (2.73 g, 7.06 mmol), H_2-ODPA (1.07 g, 3.2 mmol), and CdO (0.207 g, 1.6 mmol). The mixture was degassed at 120 °C, 300 mtorr for 20 min. The flask was then filled with Ar and heated to 320 °C to dissolve CdO giving a pale yellow solution. The reaction was cooled to 160 °C and the pressure was reduced to ~500 mtorr for 33 min. The mixture was heated to 290 °C under Ar and $H_2{}^{18}O$ (Isotech, 95% min ^{18}O, 56 mg, 3.1 mmol $H_2{}^{18}O$) was injected at this temperature via a syringe. Aliquots of the mixture were taken via a syringe and dissolved in methanol. ^{31}P NMR spectrum of the methanol solution showed presence of TOP^{18}O (Figure S10).[1] A S_N2 mechanism has been suggested for this isotope exchange reaction.{Denney, 1964 #312}

Figure S10. ^{31}P NMR ($CH_3OH/CDCl_3$) of TOPO after injecting $H_2{}^{18}O$ to a mixture of TOPO and Cd -ODPA at 290 °C.[a]

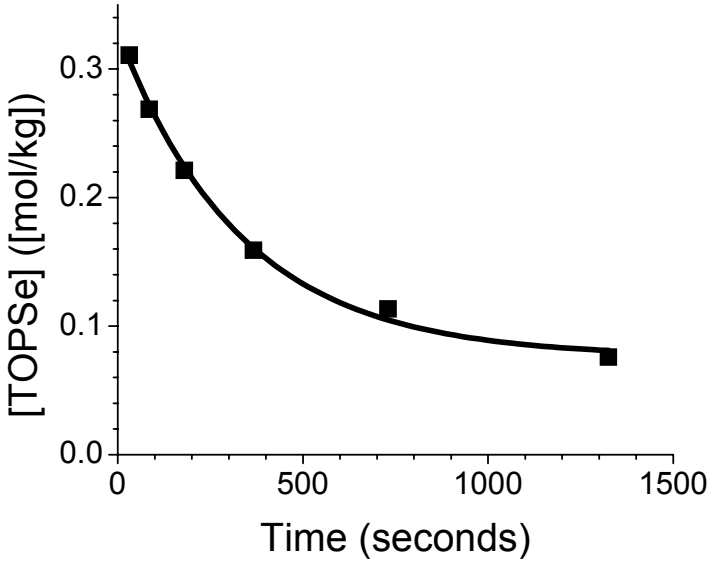


[a] This sample was taken 24 min after the injection of $H_2{}^{18}O$.

Activation parameters of the CdSe synthesis using Cd-OA and TBPSe. A stock solution was prepared by mixing Cd-OA complex (The crude reaction mixture of the Cd-OA synthesis instead of the stock solution was used in this case. 0.8014 g, Cd: 0.65 mmol, OA: 2.6 mmol), TBPSe (0.1823 g, 0.64 mmol), ethylphosphonic acid diethyl ester (internal standard, 0.0163 g, 0.64 mmol), and *n*-decane-d_{22} (0.8129 g). The stock solution was dispersed into four 5 mm NMR tubes. The samples were degassed by 4 cycles of freeze-pump-thraw before the NMR tubes were flame sealed under vacuum. The reaction kinetics were measured at 357.9 K, 379.9 K, 389.6 K, and 399.8 K following the method described in the main text. $\Delta H^{\neq}$=(62.0±2.8) kJ·mol^{-1}, $\Delta S^{\neq}$=-(145±8) J·mol^{-1}·K^{-1}. To rule out the possible interference of ethylphosphonic acid diethyl ester to the reaction, another set of 3 experiments were carried out at 379.5 K, 389.6 K, and 399.8 K without adding any internal standard and gave $\Delta H^{\neq}$=(55.7±1.7) kJ·mol^{-1} and $\Delta S^{\neq}$=-(157±5) J·mol^{-1}·K^{-1}.

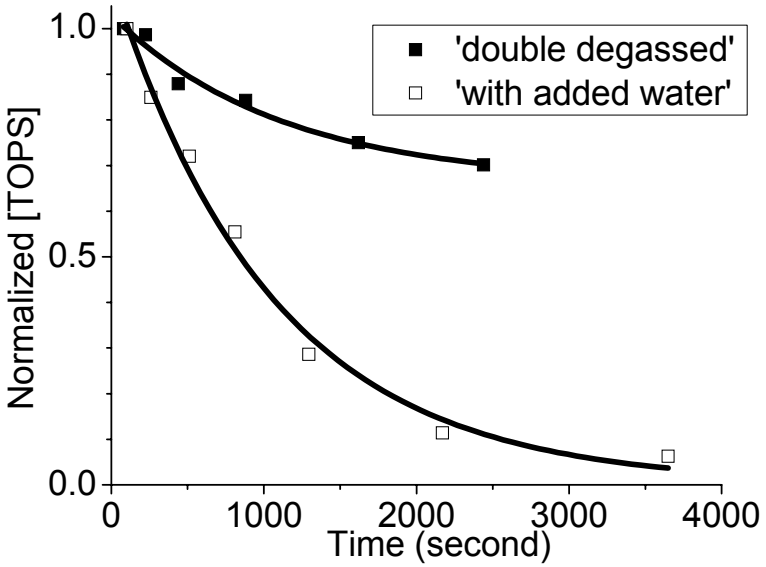
Reaction kinetics of CdSe synthesis using $CdMe_2$ in TOPO. TOPO (2.73 g) and H_2-ODPA (1.07 g) was degassed at 120 °C, 200 mtorr for 47 min. The flask was then filled with Ar and $CdMe_2$ (0.225 g, 1.6 mmol) was added dropwise via a syringe. The mixture was then heated to 267 °C and TOPSe (0.638 g, 1.4 mmol) was injected. The temperature was set to 260 °C after the injection and aliquots were taken and analyzed according to the procedure described in the main text (Figure S11).

Figure S11. Reaction kinetics of CdSe synthesis using $CdMe_2$ as Cd precursor at 260 °C. k_{obs} = $(3.0\pm0.4)10^{-3}$ s^{-1}.



Decomposition of TOPSe in TOPO/H_2-ODPA in the absence of Cd^{2+}. TOPO (1.0 g) and H_2-ODPA (0.50 g) were heated to 290 °C under Ar before TOPSe (0.537 g) was injected at this temperature. Water (0.1 mL) was added to the reaction mixture via a syringe 83 min after the injection of TOPSe. ^{31}P NMR showed that 7% and 15% of TOPSe was consumed at 79 min and 265 min after the injection of TOPSe, respectively.

Figure S12. Reaction kinetics of CdS synthesis using CdO as Cd precursor at 290 °C. k_{obs} = (9.5±1.5)10^{-4} s^{-1} (with added water) and (9.0±5.4)10^{-4} s^{-1} (double degassed)



Reference