

Supplementary information for

Size Control by Rate Control in PbSe-QD Synthesis

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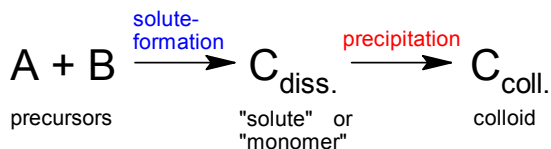
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Table of Contents

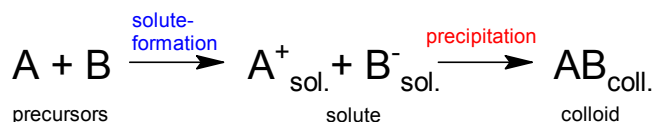
1. Discussion of terminology: solute or monomer	3
2. NMR-Spectrum of pure TOPSe	3
3. Yield Development according 31P-NMR and UV-Vis Spectroscopy	4
4. Concentration TOP and TOPSe in 0.4 M TOPSe	5
5. Interaction Pb(OA) ₂ /TOP	6
6. Selenium exchange between H(DPP) and TOP	7
7. Rate Dependence on the free acid concentration	9
8. Lead-DDP complex	10
9. Reaction kinetics Pb(OA) ₂	11
10. Mixtures of DPPSe and PbSe-CQDs in toluene	12
11. Mixtures of DPPSe, TOPSe and PbSe-CQDs in toluene	12
12. Spectral development for different DPP-concentrations	12
13. Size development and number of QDs dependent on the TOPSe amount	14
14. Spectral developments when up scaling	15
15. Summary: final samples for different reaction conditions	16
Literature	17

1. Discussion of terminology: solute or monomer.^{23, 24}

According to recent reported results it is known that the precursors do not correspond to the solute (dissolved material; also called monomer). Steckel et al. demonstrated that the solute (or monomer) formation precedes the precipitation reaction:¹⁰



Based on this picture and due the simplicity of describing the solute as “monomer-units” in modeling, the term “monomer” became strongly used in the recent years. However, in the synthesis of e.g. binary nanoparticles (like PbSe) salts are precipitated. Here the picture changes to:



This picture is more suitable for the discussion of the chemistry of a real colloidal synthesis, since it shows that the solubility has to be taken into account as solubility product. Since the following work doesn't discuss modeling in detail but focuses on real chemical reactions, we will use the term “solute” in this paper.

2. NMR-Spectrum of pure TOPSe

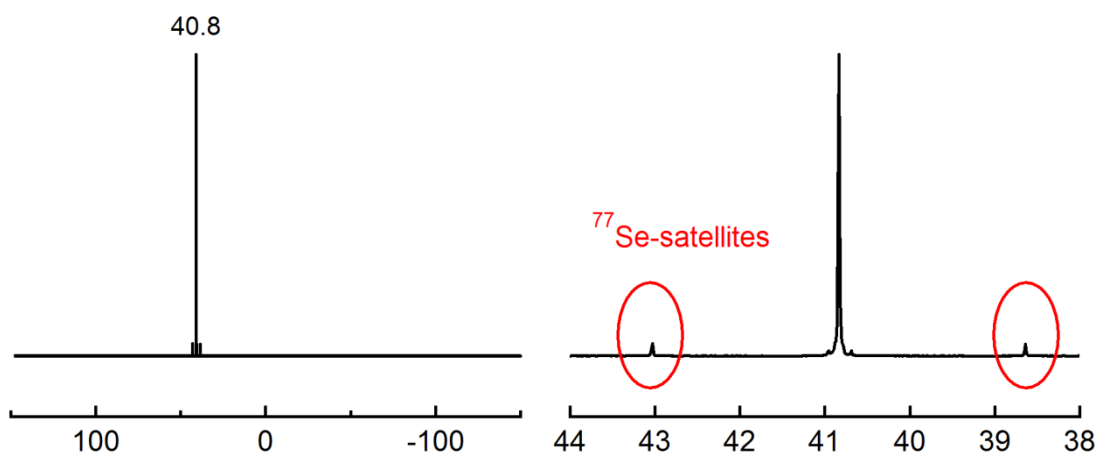


Figure S1: NMR-spectra of pure TOPSe. The NMR peak for TOPSe appears at 40.8 ppm. In the figure on the right, the area around the peak is magnified and we see satellites for the $J_{31P-^{77}\text{Se}}$ coupling. The ratio between the integral of the central peak to the satellite peaks is 92.37 (for the central peak) to 7.26 (sum of the integrals of both satellites). 92.37% corresponds to the percentage of the sum of the natural abundance of all Se-isotopes besides the NMR-active ⁷⁷Se, while the natural abundance of ⁷⁷Se is 7.63 %.

3. Yield Development according ^{31}P -NMR and UV-Vis Spectroscopy

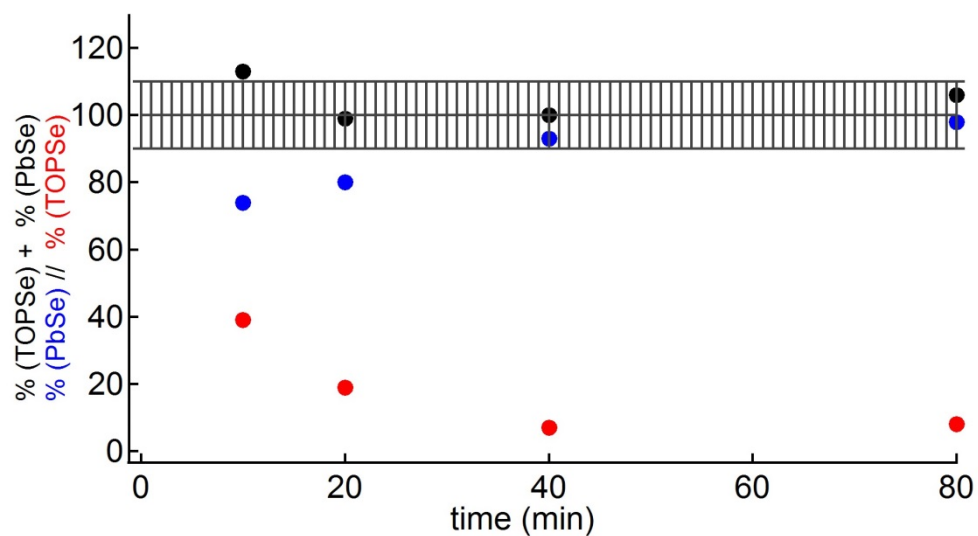


Figure S2. Development of the reaction yield of colloidal PbSe (blue) and the percentage of residual TOPSe (red). Sum of the reaction yield of PbSe (%) and the percentage of residual TOPSe (black). Reaction mixture: 0.4 mmol PbO, 1.2 mmol OA and HDC (total mass 8 g). Injection mixture: 2 mL 0.2 M TOPSe in HDC (total volume 4 mL). Inj. T. 140 °C, Gr. T. 125 °C. Percentage of residual TOPSe determined by ^{31}P -NMR as the ratio of the integrals of: $\text{TOPSe}/(\text{TOPSe} + \text{TOP} + \text{TOPO})$.

4. Concentration TOP and TOPSe in 0.4 M TOPSe, and TOP-concentration at 50 % reaction yield for a reaction using 0.4 M TOPSe (cf. Fig 1)

Trioctylphosphine has a density of 0.831 g/mol and a molar mass of 370.64 g/mol at 25 °C. The concentration of pure TOP is 2.24 mol/L.

Material	Density (measured at 24 °C// <i>lit. at 25 °C</i>)	Molar concentration
TOP	$0.84 \pm 0.01 \text{ g/ mL} // 0.83 \text{ g/ mL}$	$2.27 \pm 0.03 \text{ mol / L} //$ 2.24 mol/L
TOPSe	$1.02 \pm 0.01 \text{ g/ mL}$	$2.27 \pm 0.03 \text{ mol/L}$

As seen in the table, the concentration (i.e. the molar volume) of TOPSe is almost identical with that of TOP, so we roughly estimate that the sum of the concentrations of TOPSe and TOP is constant, about 2.24 mol/L.

1 mL of 0.4 M TOPSe consists of 0.4 mmol TOPSe and about 1.84 mmol TOP.

According eq. (2), we expect the amount of in situ formed TOP to be maximal 0.2 mmol for reaction yields of 50 % on lead. Further, TOPSe, TOP and mixtures of TOPSe and TOP have roughly the same molar volume ($\sim 2.24 \text{ mmol/ml}$ at room temperature). Thus, the ratio of the TOP concentration (at 50 % reaction yield, assuming a reaction according eq. 2) can be estimated to be

$$R = \frac{TOP_{initial(0.04 \text{ M TOPSe})} + TOP_{in situ (0.04 \text{ M TOPSe})}}{TOP_{in situ (TOPSe pure)}}$$

$$= \frac{3,68 \text{ mmol} + 0.2 \text{ mmol}}{0.2 \text{ mmol}} = 19.4$$

5. Interaction Pb(OA)₂/TOP

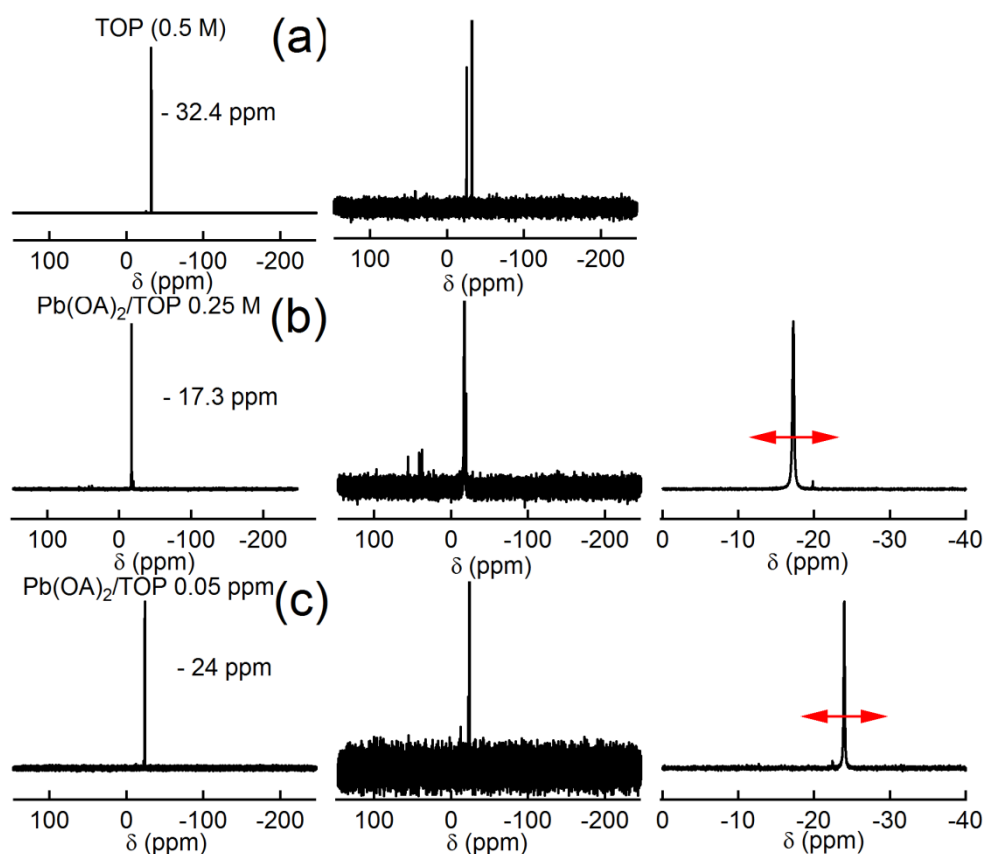


Figure S3. NMR-spectra of (a) TOP in toluene, (b) of a mixture of Pb(OA)₂ and TOP, both 0.25 M and (c) of a mixture of Pb(OA)₂ and TOP, both 0.05 M. Red arrows indicates a coupling constant of 2000 Hz.

In figure S2, NMR spectra of TOP are compared to NMR spectra of mixtures of lead oleate and TOP. It appears that the position of the TOP-resonance is strongly shifted to higher ppm-values if Pb(OA)₂ is added. However, there are no indications for any interactions between Pb²⁺ and TOP in the spectra: we see no satellites which indicate a J_{P31-Pb207}-coupling. Although it can appear that scalar coupling can't be observed for intermediate exchange rates, the scalar coupling of magnetic spins always persists, even though for species in exchange. Therefore the scalar coupling will be resolved in a NMR-spectrum, as long the width of the individual NMR-peaks does not exceed significantly the coupling constant of the scalar coupling.³ We observe here a FWHM of the NMR-peaks around 40 Hz while the J_{31P-207Pb}-coupling should be around

2000 Hz.⁴ Thus, $J_{31\text{P}-207\text{Pb}}$ -couplings, if appearing, would be well resolved, even if we would have an exchange between free TOP and TOP, which would be bound to $\text{Pb}(\text{OA})_2$.

In summary, since we see no indication for any satellites indicating $J_{31\text{P}-207\text{Pb}}$ -coupling, we can rule out a significant concentration of a Pb-TOP complex, and assign the shifts of the TOP-NMR peak to a solvent effect: in 0.25 M $\text{Pb}(\text{OA})_2 \cdot \text{OA}$, the lead oleate represents 50% of the solvent volume. Since the solvent also influences the magnetic field inside the sample, a change of the solvent will also change the chemical shifts. Further acid-base interactions between TOP (base) and oleic acid might play a role.

6. Selenium exchange between H(DPP) and TOP

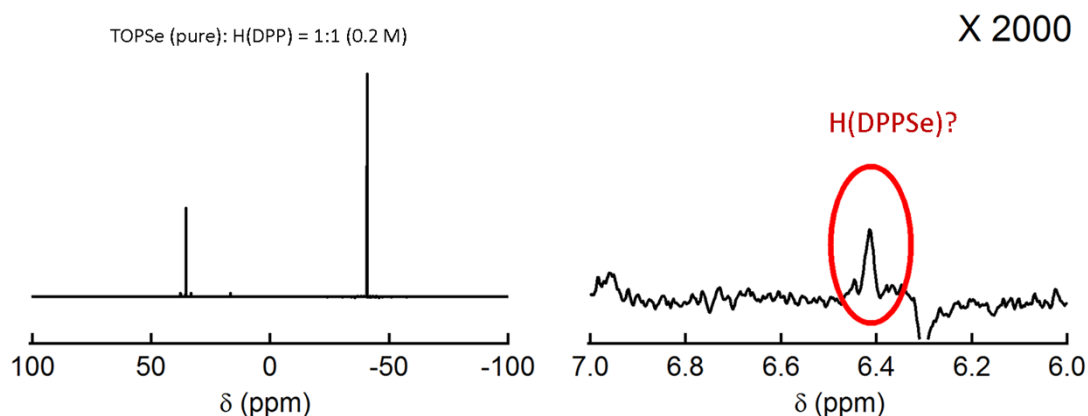


Figure S4: ^{31}P -NMR Spectra of a mixture of H(DPP) and pure TOPSe in toluene.

As seen in the figure, a signal around 6.4 ppm indicates the presence of H(DPPSe). However, the intensity is very low, close to the detection limit.

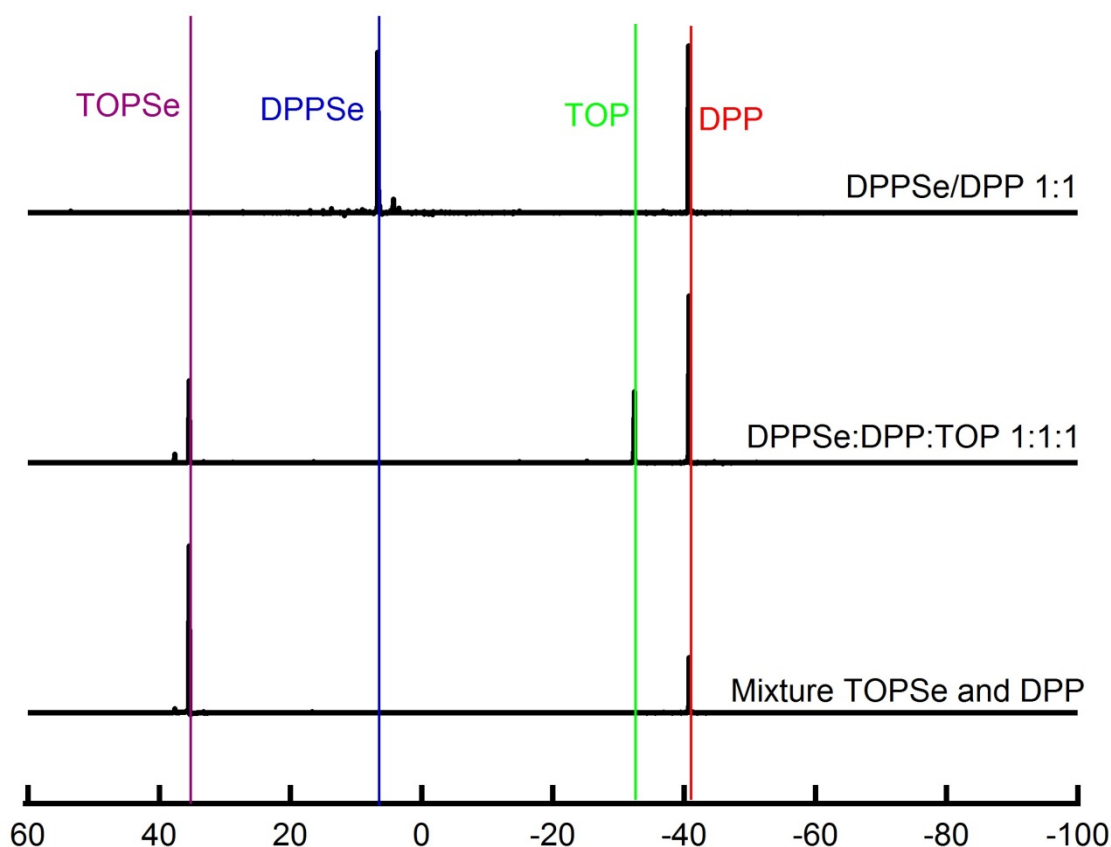


Figure S5: ^{31}P -NMR spectra of different mixtures of TOPSe, H(DPPSe), TOP and H(DPP) in D8-Toluene.

When H(DPPSe) is mixed with an excess of TOP, almost all selenium is transferred from the DPPSe to TOP, so that the DPPSe concentration falls below the detection limit (fig. S4). A selenium exchange between DPP and TOP according eq. (4) is possible, and this equilibrium is almost completely on the side of TOPSe and DPP.

7. Rate Dependence on the free acid concentration

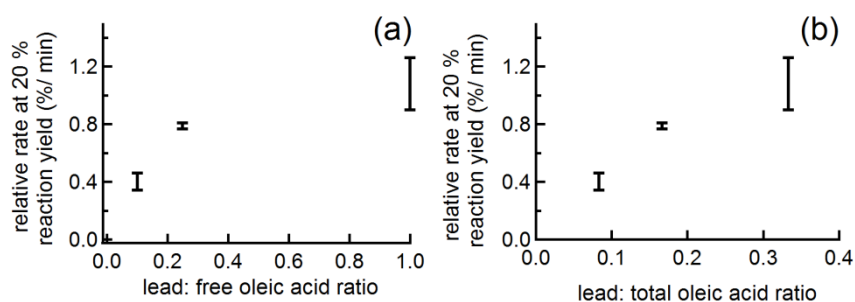


Figure S6. Relative reaction rate at 20 % reaction yield in dependence of the lead to total oleic acid (A) and the lead to free oleic acid to lead ratio (cf. Fig. 5). Error bars give the error of the fit-functions.

Free OA: Pb ratio	CFR _{20%}	CFR _{20%} (normalized relative to Pb:OA _{free} = 1)
1	108 %/ min	1
0.25	78,6 %/ min	0.73
0.1	40 %/ min	0.37

Table S1.

As seen in the figure, the reaction rate increases with an increasing lead to free oleic acid ratio and lead to total oleic acid ratio. However, since development of the relative reaction rate is neither linear relative to the lead to free acid ratio, nor to the lead to total oleic acid ratio, the rate is not in inverse proportion to the acid concentration (cf. table S1).

8. Lead-DDP complex

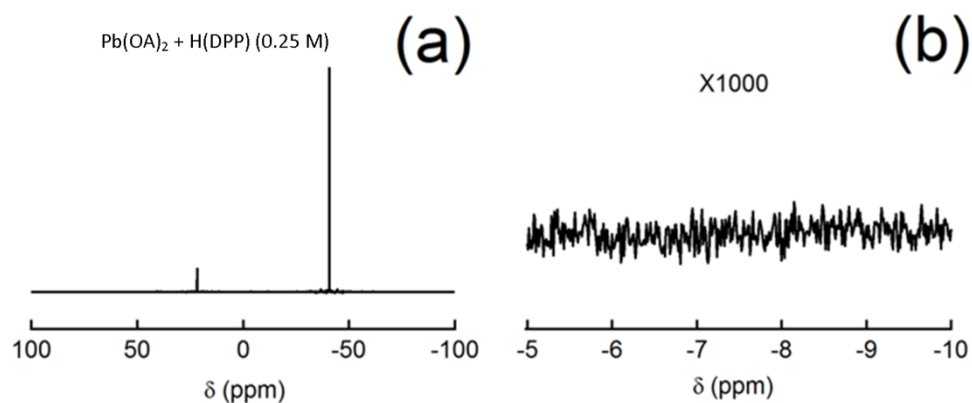


Figure S7. ^{31}P -NMR spectra of a mixture of $\text{Pb}(\text{OA})_2$ and $\text{H}(\text{DPP})$ (each 0.25 M) in toluene.

In figure S 4, we see NMR-spectra of a mixture of lead oleate and $\text{H}(\text{DPP})$. The main peak at -40.7 ppm corresponds to $\text{H}(\text{DPP})$, while the peak at about 21.7 ppm might be attributed to DPPO .

We see no indication for a Pb - DPP complex, which would show 2 satellites for the ^{31}P - ^{207}Pb -coupling (compare section 4, SI), and also no signal appears at -7.8 ppm, as observed by Yu et al.

9. Reaction kinetics $\text{Pb}(\text{OA})_2$

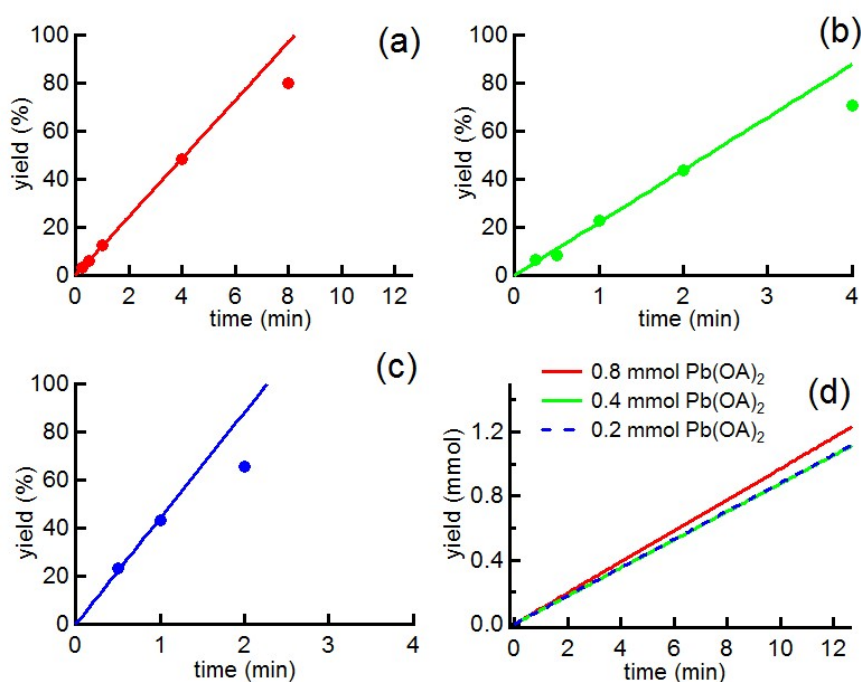


Figure S8. Yield developments for different $\text{Pb}(\text{OA})_2$ concentrations. Red: 0.8 mmol $\text{Pb}(\text{OA})_2 \cdot \text{OA}$, green: 0.4 mmol $\text{Pb}(\text{OA})_2 \cdot \text{OA}$, blue: 0.2 mmol $\text{Pb}(\text{OA})_2 \cdot \text{OA}$. For detailed reaction conditions, see Figure 4 in the manuscript.

In figure S7, the yield development is shown for different $\text{Pb}(\text{OA})_2$ concentrations. We see a linear yield development for all reactions for yields until about 50 % (straight lines, Fig S7 (a)-(c)). Further, it appears that the linear fits until 50% coincide almost perfectly.

10. Mixtures of DPPSe and PbSe-CQDs in toluene

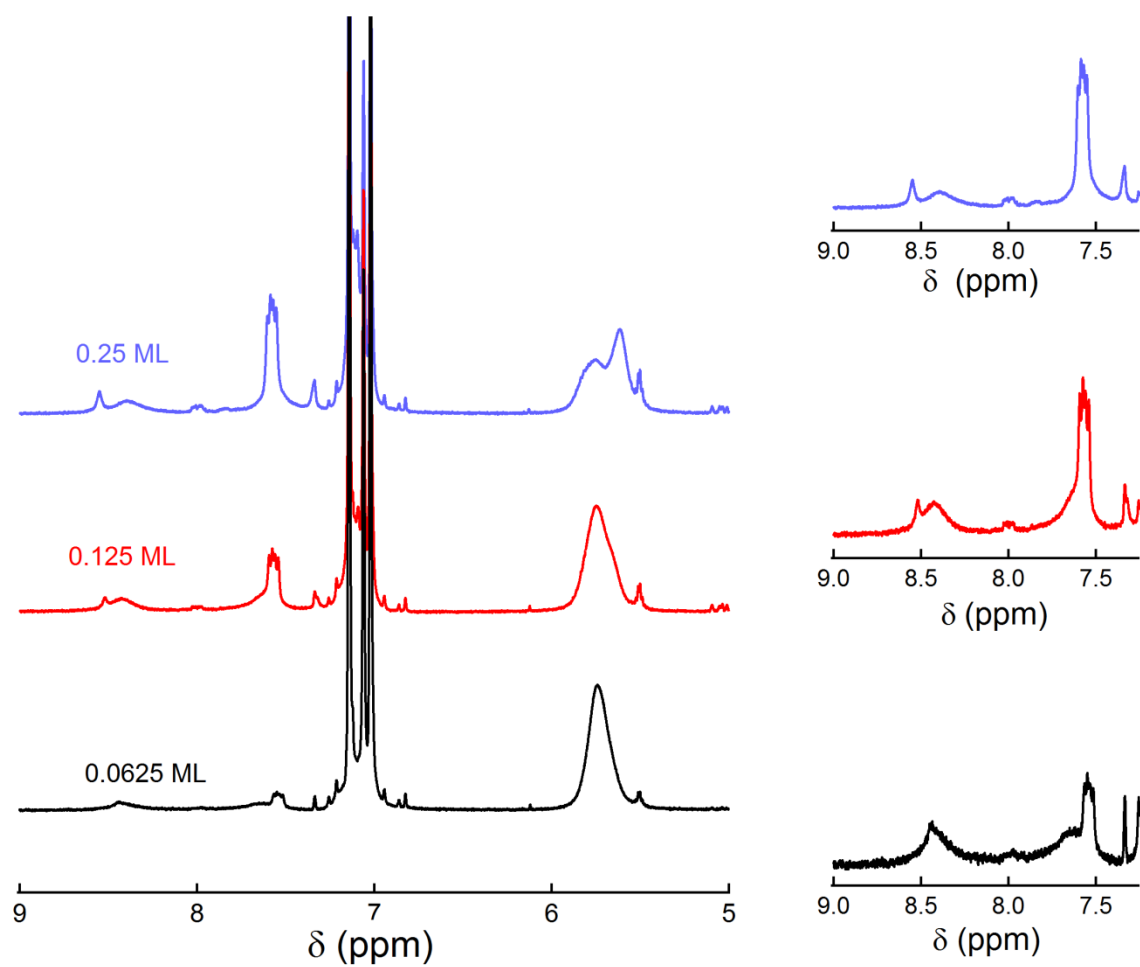


Figure S9. ^{31}P NMR-spectra of PbSe CQDs in toluene- D_8 after addition of H(DPPSe) for 0.0625, 0.125 and 0.25 monolayers of selenium.

11. Mixtures of DPP, TOPSe and PbSe-CQDs in Toluene

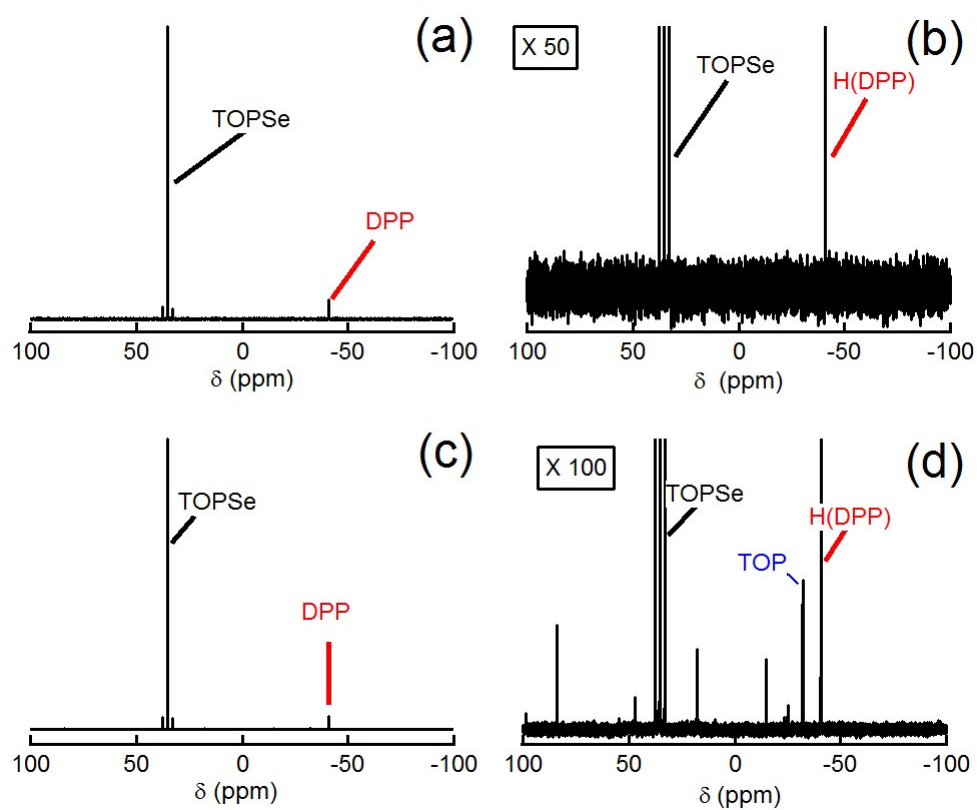


Figure S10. ^{31}P NMR-spectra of PbSe CQDs in toluene- D_8 after addition of H(DPP) and TOPSe for 0.25 monolayers of selenium (H(DPP):TOPSe = 1:8). (a) and (b) directly after addition, (c) and (d) after 3 days.

12. Spectral development for different DPP concentrations

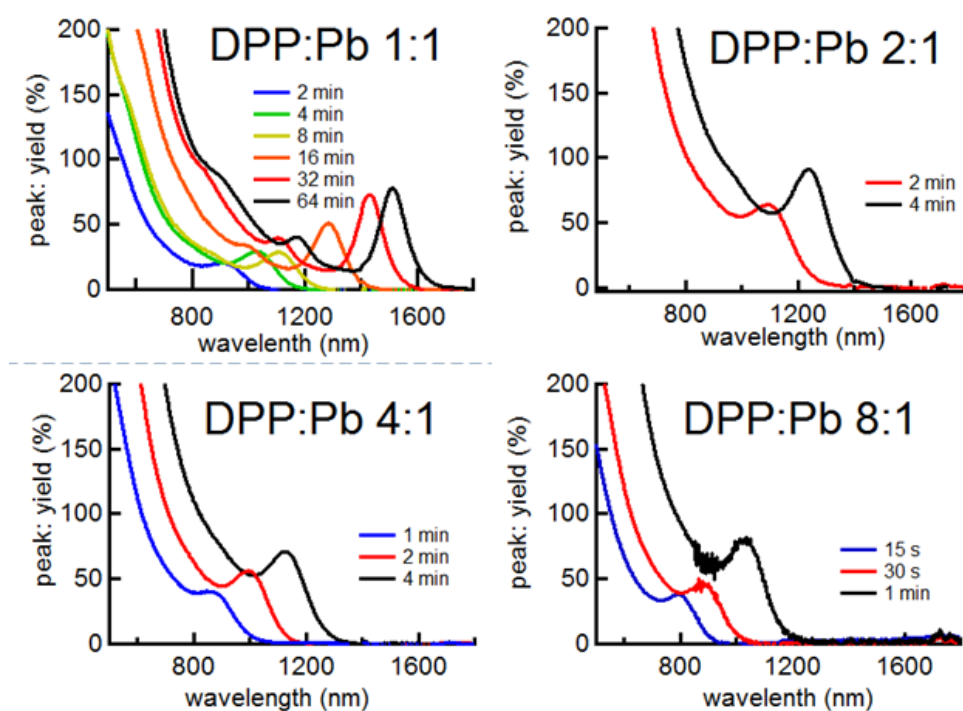


Figure S 11. Spectral development for different H(DPP) concentrations (cf. fig 5). Peak height of λ_{1s-1s} normalized to reaction yield.

13. Size development and number of QDs dependent on the TOPSe amount

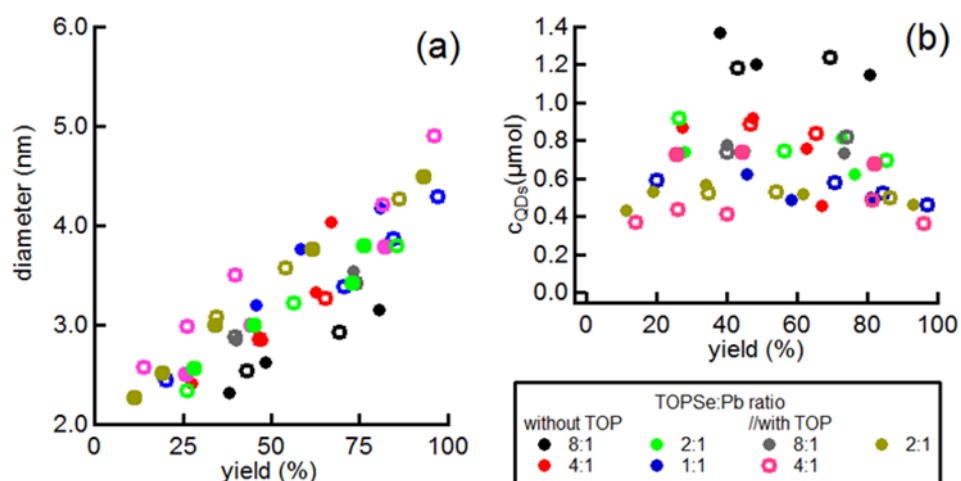


Figure S 12. (a) Diameter to yield development for different TOPSe-amounts in the injection mixture. TOP-amount 0 or 3.2 mmol. Reaction conditions, see manuscript (Figure 3). (b) Development of the number of QDs under the same conditions.

14. Spectral developments when up scaling

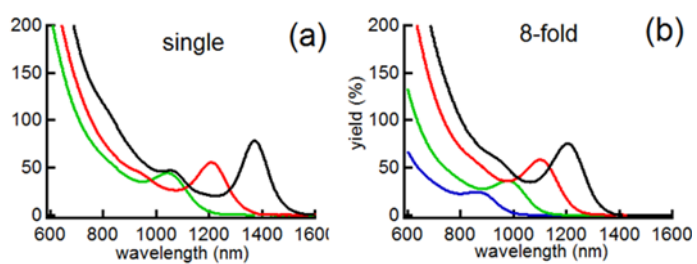


Figure S13. Spectral development for upscaling a reaction mixture by a factor of 8 (cf. fig 8). Peak height of λ_{1s-1s} normalized to reaction yield.

15. Summary: final samples for different reaction conditions

H(DPP)-dependence: Pb(OA) ₂ = 0.4 mmol; OA:Pb = 3:1; TOPSe:Pb = 8:1, Inj.T./Gr.T = 80/70 °C					
DPP:Pb ratio	time (min)	yield	λ	d	n (QDs)
8:1	1	74.9 ± 8 %	998 ± 45 nm	3.04 ± 0.16 nm	1.19 ± 0.06 μmol
4:1	4	66.1 ± 1.2 %	1087 ± 35 nm	3.65 ± 0.55 nm	0.646 ± 0.271 μmol
2:1	8	80.8 ± 6.3 %	1211 ± 1 nm	3.80 ± 0 nm	0.660 ± 0.052 μmol
1:1	32	73.6 ± 0.5 %	1334 ± 45 nm	4.23 ± 0.2 nm	0.480 ± 0.049 μmol
DPP-dependence: Pb(OA) ₂ = 0.4 mmol; OA:Pb = 3:1; TOPSe: Pb = 8:1, TOP:Pb = 8:1; Inj.T./Gr.T = 80/70 °C					
DPP:Pb ratio	time (min)	yield	λ	d	n (QDs)
8:1	4	73.6 ± 0.5 %	1125 ± 25 nm	3.49 ± 0.08 nm	0.779 ± 0.061 μmol
4:1	8	81.7 ± 0.4 %	1268 ± 83 nm	4.00 ± 0.30 nm	0.583 ± 0.131 μmol
2:1	16	89.7 ± 4.7 %	1376 ± 45 nm	4.38 ± 0.15 nm	0.479 ± 0.026 μmol
TOPSe-dependence: Pb(OA) ₂ = 0.4 mmol; OA:Pb = 3:1; DPP: Pb = 8:1, Inj.T./Gr.T = 80/70 °C					
TOPSe:Pb ratio	time (min)	yield	λ	d	n (QDs)
8:1	1	74.9 ± 8 %	998 ± 45 nm	3.04 ± 0.16 nm	1.19 ± 0.06 μmol
4:1	4	69.2 ± 2.6 %	1101 ± 40 nm	3.40 ± 0.14 nm	0.789 ± 0.068 μmol
2:1	8	95.5 ± 5.9 %	1267 ± 37 nm	4.00 ± 0.13 nm	0.672 ± 0.026 μmol
1:1	64	80.4 ± 2.9 %	1493 ± 32 nm	4.80 ± 0.11 nm	0.328 ± 0.035 μmol
TOPSe-dependence: Pb(OA) ₂ = 0.4 mmol; OA:Pb = 3:1; DPP: Pb = 8:1, TOP:Pb = 8:1; Inj.T./Gr.T = 80/70 °C					
TOPSe:Pb ratio	time (min)	yield	λ	d	n (QDs)
8:1	4	73.6 ± 0.5 %	1125 ± 23 nm	3.49 ± 0.08 nm	0.779 ± 0.061 μmol
4:1	8	55.5 ± 2.8 %	1170 ± 2.8 nm	3.65 ± 0.01 nm	0.512 ± 0.022 μmol
2:1	32	88.7 ± 2.9 %	1482 ± 30 nm	4.76 ± 0.11 nm	0.369 ± 0.013 μmol

Table S2. Final samples of different syntheses varying the anion precursor concentrations.

Pb(OA) ₂ -dependence: OA:Pb = 3:1; TOPSe = 3.2 mmol; DPP = 3.2 mmol; TOP = 3.2 mmol; Inj.T./Gr.T = 80/70 °C					
n(Pb(OA) ₂)	time (min)	yield	λ	d	n (QDs)
1.6 mmol	35	99.5 %	1571 nm	5.07 nm	1.35 μmol
0.8 mmol	8	63.8 %	1255 nm	3.95 nm	1.15 μmol
0.4 mmol	4	70.7 %	1120 nm	3.00 nm	0.757 μmol
TOPSe-dependence: Pb(OA) ₂ = 0.4 mmol; OA:Pb = 3:1; DPP: Pb = 2:1, TOP:Pb = 8:1; TOPSe:Pb = 2:1;					
Temperature Inj.T./Gr.T	time (min)	yield	λ	d	n (QDs)
80 °C/ 70 °C	128	80.5 %	1507	4.85 nm	0.317 μmol
110 °C/ 100 °C	16	75.4 %	1673 nm	5.44 nm	0.210 μmol
145 °C/ 130 °C	4	89.8 %	1812 nm	5.93 nm	0.193 μmol

Table S3. Final Samples of different syntheses varying the Pb(OA)₂ concentration and temperature.

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