Supporting information

Low-Temperature Noninjection Approach to Homogeneously-Alloyed $PbSe_xS_{1-x}$ Colloidal Nanocrystals for Photovoltaic Applications

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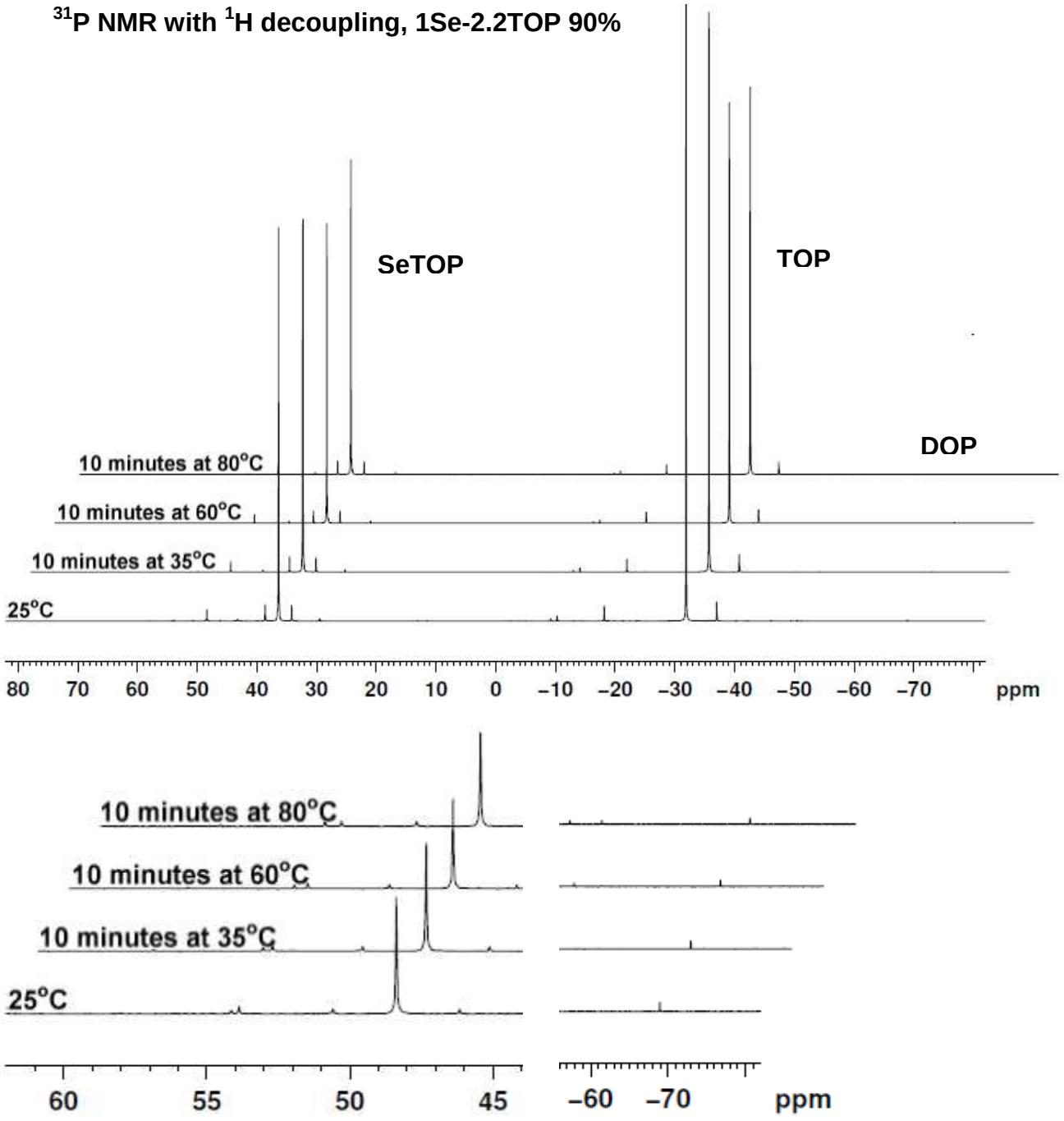
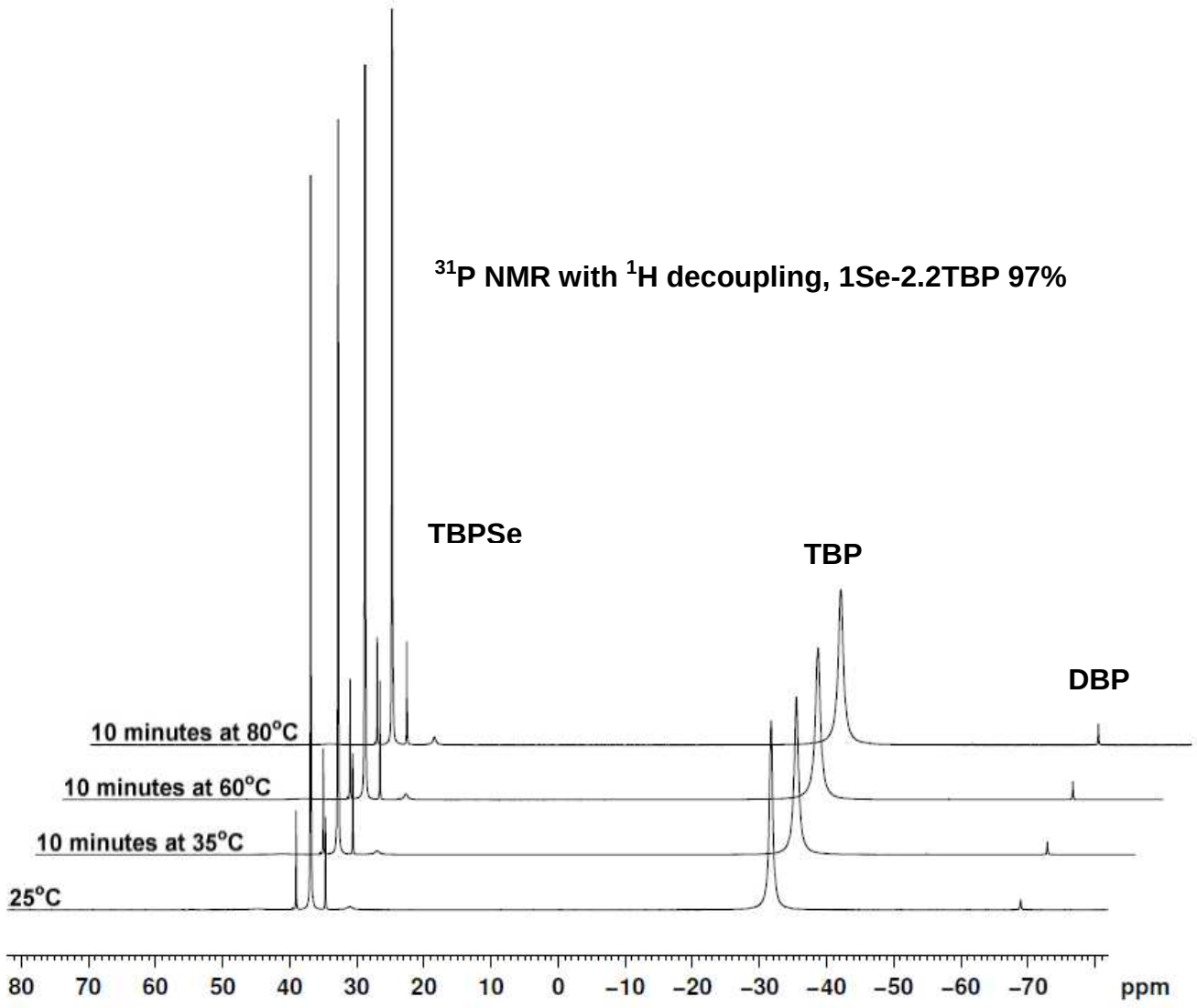
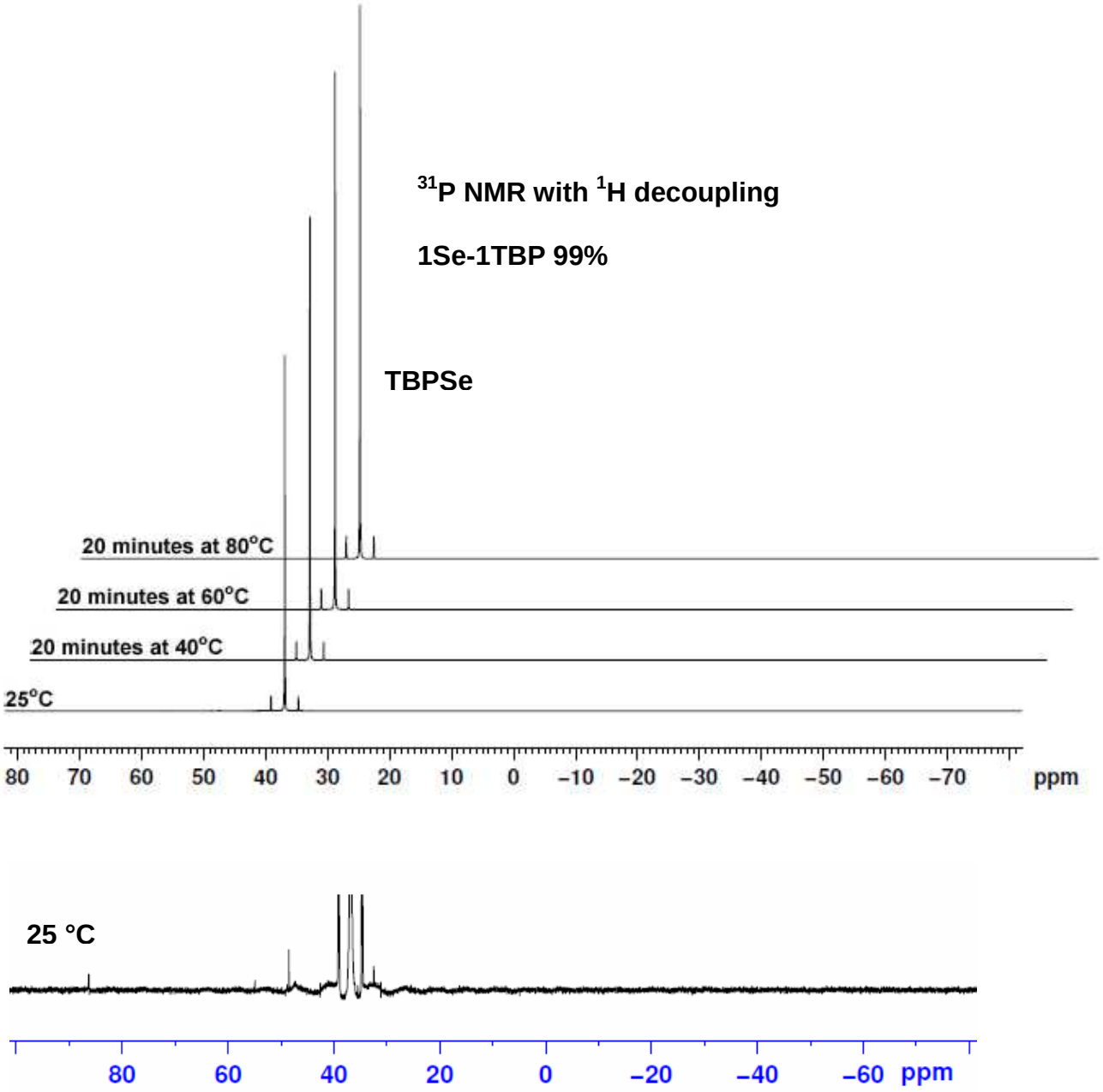


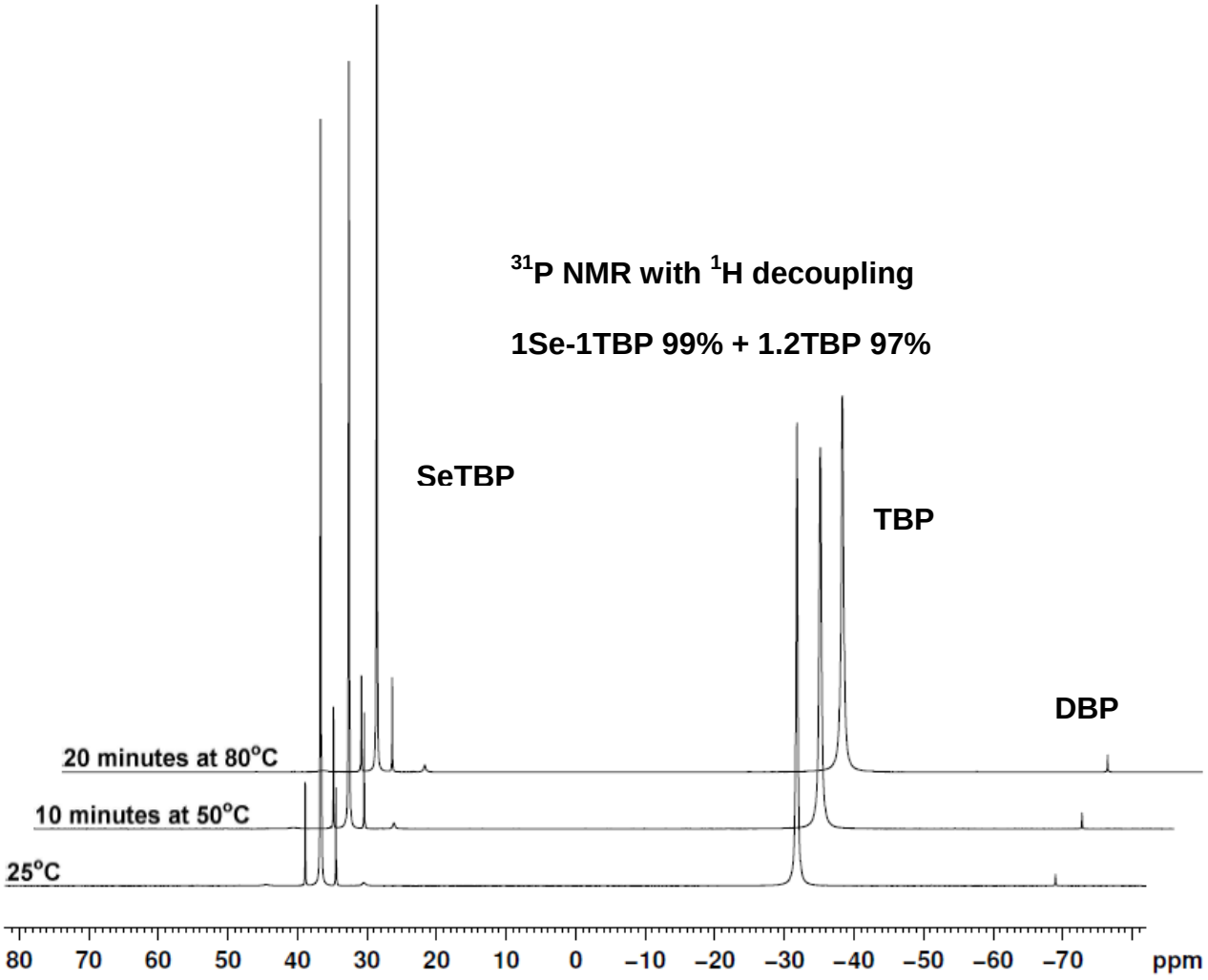
Scheme S1A. ^{31}P NMR spectra at different temperature of Figure 1 Batch (1) TOPSe stock solution made with a feed molar ratio of 1Se-2.2TOP 90%. 85% H_3PO_4 was used as an external standard. No DOPSe (δ 4.7 ppm[24]) was detected in the stock solution, but some DOP (δ -68.9 ppm[24]) (bottom right). It is worthy of notice that another Se-containing species (δ 48.4 ppm) was detected in the SeTOP solution (bottom-left).



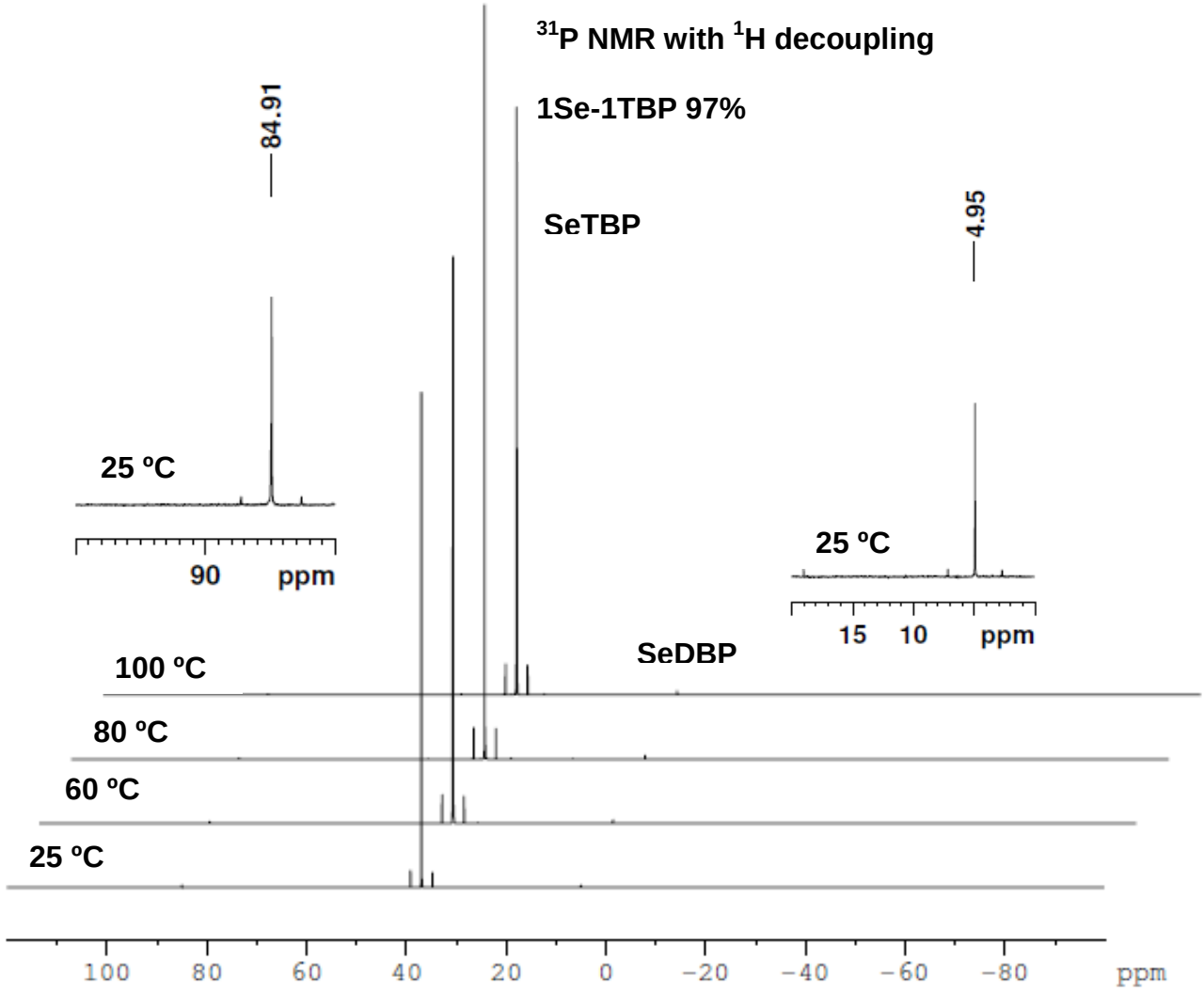
Scheme S1B. ^{31}P NMR spectra at different temperature of Figure 1 TBPSe stock solution made with a feed molar ratio of 1Se-2.2TBP 97%. 85% H_3PO_4 was used as an external standard. No DBPSe (δ 4.95 ppm[24]) was detected in the stock solution, but DBP (δ -69.1 ppm) was.



Scheme S2A. ^{31}P NMR spectra (top) at different temperature of Figure 2 Batch (1) TBPSe stock solution made with a feed molar ratio of 1Se-1TBP 99%. 85% H_3PO_4 was used as an external standard. A larger view (bottom) shows clearly that no DBPSe, no TBP, nor DBP was detected.



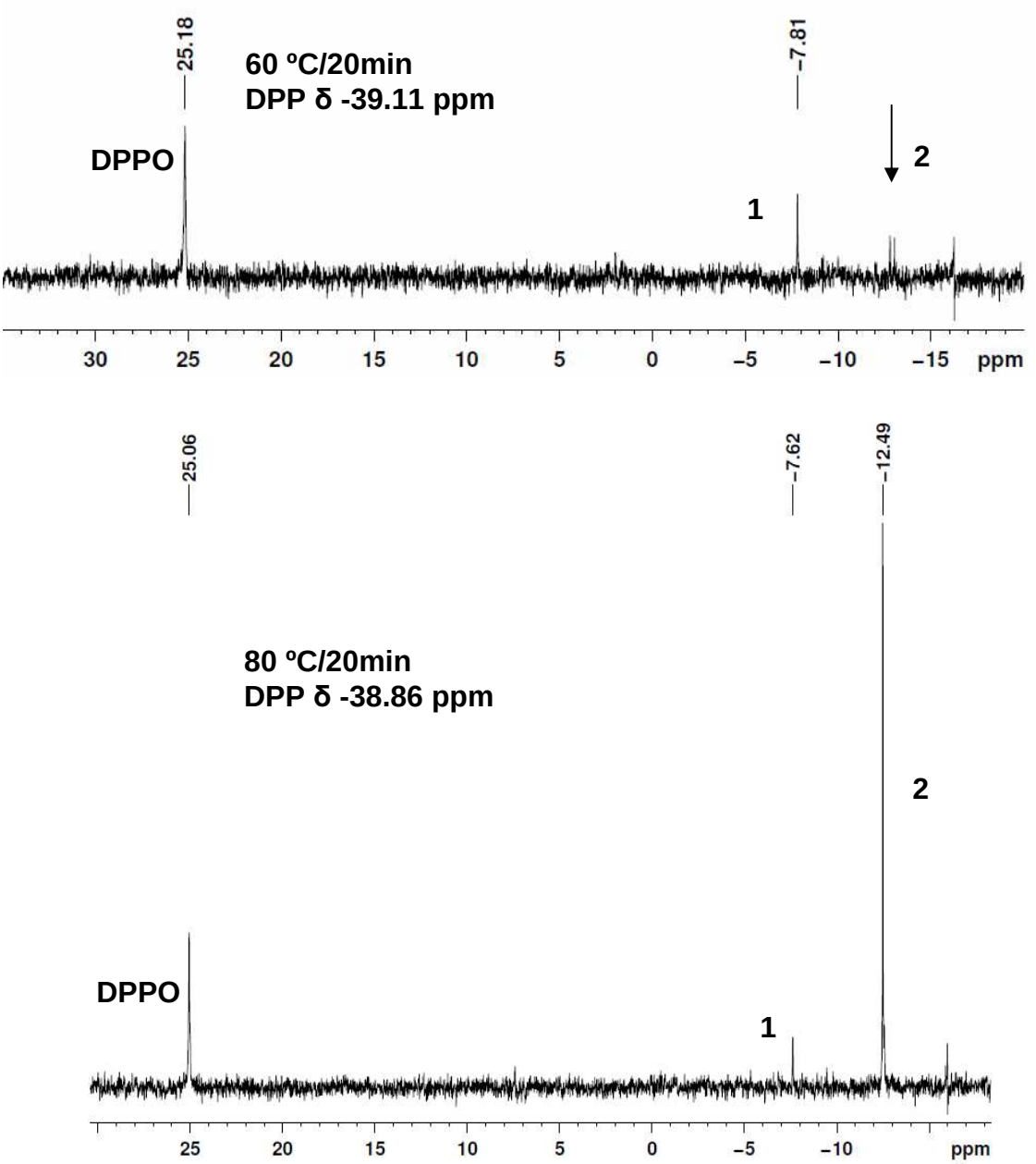
Scheme S2B. ^{31}P NMR spectra at different temperature of Figure 2 Batch (2) TBPSe solution made with a feed molar ratio of 1Se-1TBP 99% together with 1.2TBP 97%added. 85% H_3PO_4 was used as an external standard. No DBPSe was detected.



Scheme S2C. ^{31}P NMR spectra of Figure 2 Batch (3) TBPSe stock solution made with a feed molar ratio of 1Se-1TBPSe 97% at 25 ºC. 85% H_3PO_4 was used as an external standard. A noticeable amount of DBPSe (δ 4.95 ppm) was detected in this stock solution, while no TBP nor DBP was detected.

The presence of DBPSe in Figure 2 Batch (3) and not in Figure 1 Batch (2) (as shown in Scheme S1B) is worthy of notice.

Also, it is noteworthy that another Se-containing species (δ 84.91 ppm) was detected in the Figure 2 SeTBP solutions.



Scheme S3. ^{31}P NMR spectra collected from a mixture of the Pb(oleate)$_2$ stock solution (used for Figures 1 and 2) and DPP with a 1Pb-to-1DPP feed molar ratio at 60 °C/20 min (top) and 80 °C/20 min (bottom). 85% H_3PO_4 was used as an external standard. Note DPP δ was -39.11 ppm (top) and -38.86 ppm (bottom). Diphenylphosphine oxide (DPPO, δ ~25.2 ppm (top) and ~25.1 ppm (bottom)) was detected, together with two peaks labeled as 1 at ~-7.8 ppm (top) and ~-7.6 ppm (bottom) while 2 at ~-12.5 ppm (top and bottom). The increase of Peak 2 at 80 °C is worthy of notice. The ~-12.5 ppm peak was close to that of Compound 12 (Ph_2PPPh_2, δ -14.5 ppm) in Ref 24 (with DPP δ -40.2 ppm).

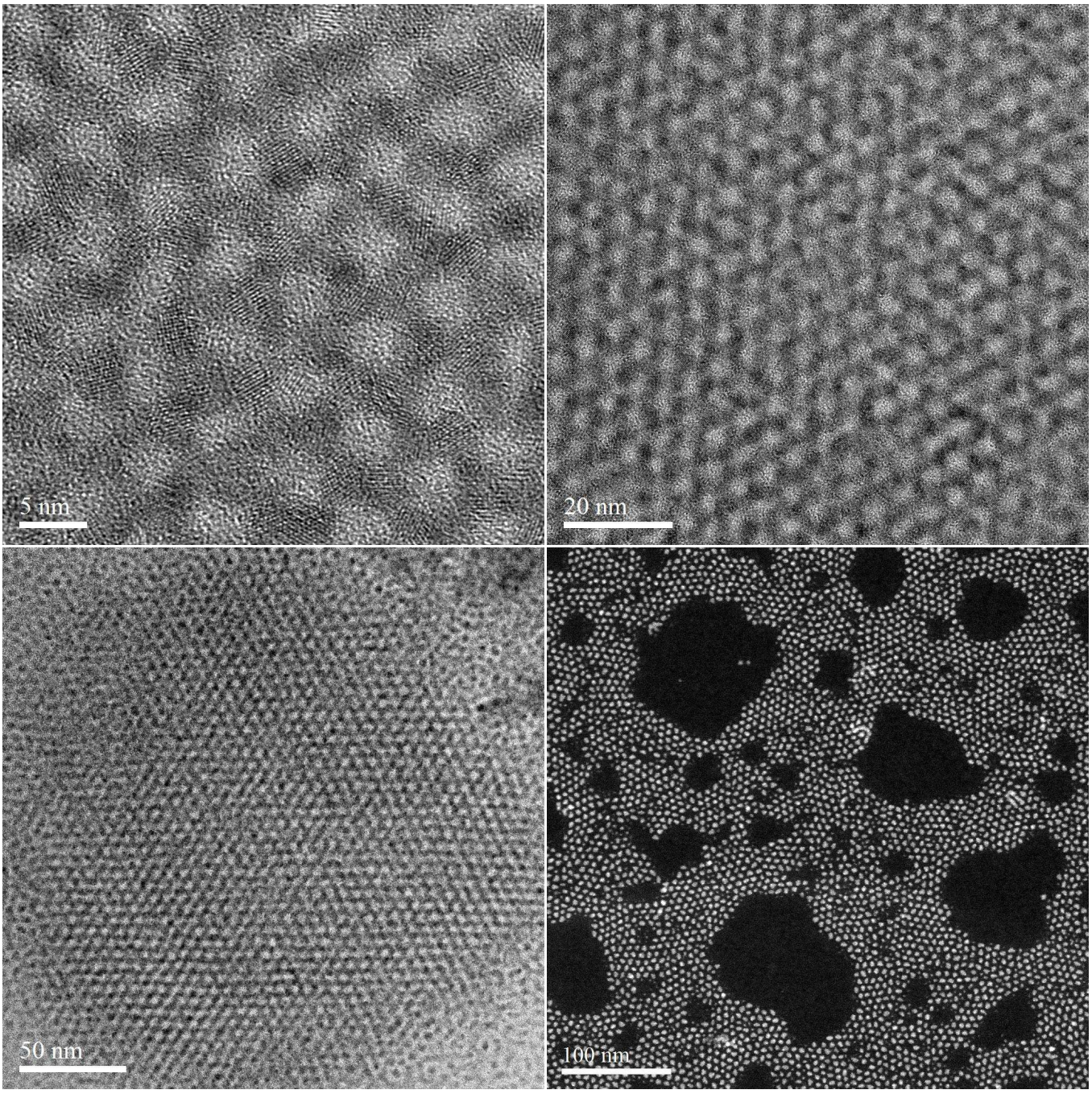


Figure S1A. TEM images of the PbSeS NCs shown in Figure 6 Batch d. The size is estimated to be ~4 nm. See Figure S1B for TEM size calculation together with absorption. See Figure S1C for EDX, and Figure S1D for XPS.

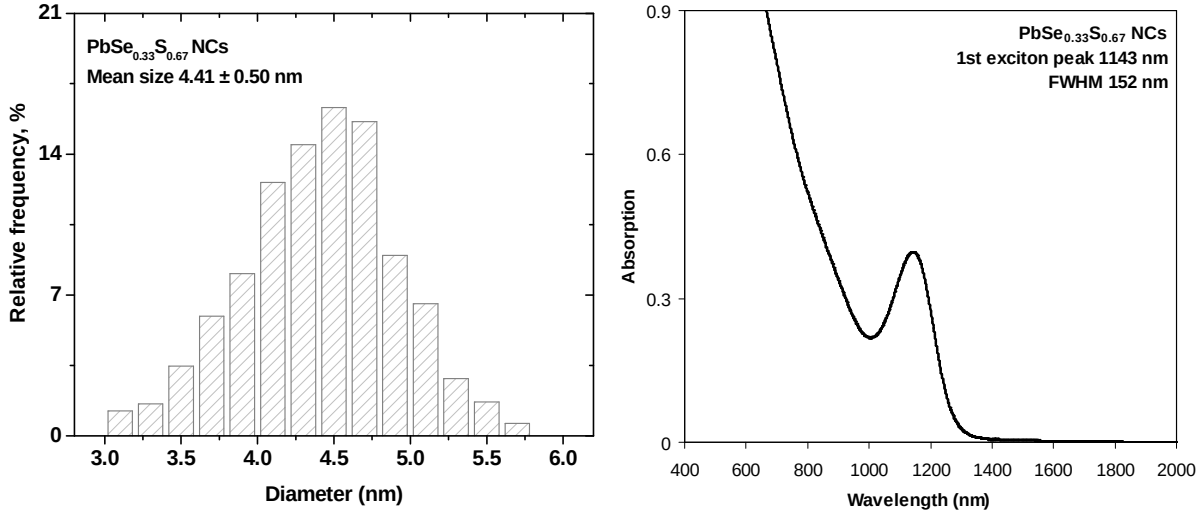


Figure S1B. (Left) The size histogram of a typical ensemble of $PbSe_{0.33}S_{0.67}$ NCs (see Figure S1A for TEM images). The mean size is 4.41 ± 0.50 nm, with a standard deviation of ~11%.

Also, we estimated the mean size with our XRD measurement shown in **Figure 6b** Curve (d), using Scherrer equation, $D \approx 0.9\ \lambda / \beta \cos(\theta)$, where λ = 0.15406 nm (Cu kα1 wavelength), β = full width at the half maximum of the diffraction peak in radians, and θ = Bragg angle.

The mean size is, then, 3.32 nm by (220) plane, 3.95 nm by (111) plane, and 3.92 nm by (200) plane.

(Right) The corresponding absorption spectrum of this $PbSe_{0.33}S_{0.67}$ NC ensemble dispersed in toluene, with its first exciton peaking at 1143 nm and fwhm of 152 nm (Gaussian fitting).

Processing option : All elements analysed (Normalised)

Spectrum	In stats.	S	Se	Pb
Spectrum 1	Yes	31.35	13.54	55.11
Spectrum 2	Yes	30.48	16.98	52.54
Spectrum 3	Yes	30.55	16.18	53.27
Spectrum 4	Yes	29.15	13.64	57.21
Mean		30.38	15.08	54.53
Std. deviation		0.91	1.76	2.09
Max.		31.35	16.98	57.21
Min.		29.15	13.54	52.54

All results in atomic%

Figure S1C. The EDX analysis table for the typical ensemble of $PbSe_{0.33}S_{0.67}$ NCs (also shown in Figures S1A and S1B). The composition is $Pb_{1.2}Se_{0.33}S_{0.67}$ by EDX. The standard deviations for S, Se, and Pb are 3.0%, 11.7%, and 3.8%, respectively.

Angle	Name	Block Name	Position	FWHM	Line Shape	R.S.F.	Area	% Conc.		Average				
4	O 1s	O 1s/8	530.8656	0.9716	GL(30)	2.93	722.075	2.31	Pb/(Se+S)	**2.11**				
	O 1s	O 1s/8	532.2205	1.2592	GL(30)	2.93	4018.62	12.88	Se+S	**1.75**				
	C 1s C-C, C-H	C 1s/9	285	0.9653	GL(30)	1	6225.26	58.46	Se/(Se+S)	**0.30**				
	C 1s	C 1s/9	285.7641	0.965	GL(30)	1	618.829	5.81	S/(Se+S)	**0.70**				
	C 1s	C 1s/9	286.879	1.1186	GL(30)	1	171.675	1.61						
	C 1s	C 1s/9	288.211	1.0164	GL(30)	1	254.856	2.39						
	C 1s	C 1s/9	289.498	1.0163	GL(30)	1	63.526	0.6						
	S 2s	S 2s/10	225.2593	2.2051	GL(30)	1.43	200.629	1.32	**S**	**S**	**S**	**Mean**	**Std. deviation**	
	Si 2p	Si 2p/12	102.5914	1.2481	GL(30)	0.817	901.354	10.36	**1.32**	**1.15**	**1.23**	**1.23**	**0.09**	
	Pb 4f	Pb 4f/13	137.9549	1.0662	A(0.1,0.9,0)GL(30)	22.7	5072.889	2.1	**Pb**	**Pb**	**Pb**			
	Pb 4f	Pb 4f/13	142.8149	1.0662	A(0.1,0.9,0)GL(30)	22.7	3916.759	1.62	**3.72**	**3.49**	**3.9**	**3.70**	**0.21**	
	Se 3d PbSe	Se 3d/14	53.6689	0.8764	GL(30)	2.29	78.623	0.32	**Se**	**Se**	**Se**			
	Se 3d PbSe	Se 3d/14	54.5289	0.8764	GL(30)	2.29	52.638	0.22	**0.54**	**0.5**	**0.52**	**0.52**	**0.02**	
5	O 1s	O 1s/16	530.9237	0.9951	GL(30)	2.93	695.85	2.25						
	O 1s	O 1s/16	532.2678	1.2447	GL(30)	2.93	3989.888	12.92						
	C 1s C-C, C-H	C 1s/17	285.0001	0.9653	GL(30)	1	5835.098	55.36						
	C 1s	C 1s/17	285.6627	0.965	GL(30)	1	911.309	8.65						
	C 1s	C 1s/17	286.6872	1.1186	GL(30)	1	152.963	1.45						
	C 1s	C 1s/17	288.1618	1.2085	GL(30)	1	303.115	2.88						
	C 1s	C 1s/17	289.6557	0.7769	GL(30)	1	70.606	0.67	**S**					
	S 2s	S 2s/18	225.2595	2.0415	GL(30)	1.43	173.86	1.15	**1.15**					
	Si 2p	Si 2p/20	102.6233	1.2483	GL(30)	0.817	918.489	10.67						
	Pb 4f	Pb 4f/21	137.9876	1.065	A(0.1,0.9,0)GL(30)	22.7	4723.682	1.97	**Pb**					
	Pb 4f	Pb 4f/21	142.8476	1.065	A(0.1,0.9,0)GL(30)	22.7	3647.43	1.52	**3.49**					
	Se 3d	Se 3d/22	53.7108	0.8648	GL(30)	2.29	71.959	0.3	**Se**					
	Se 3d	Se 3d/22	54.5708	0.8648	GL(30)	2.29	48.177	0.2	**0.5**					
6	O 1s	O 1s/24	530.8753	0.9847	GL(30)	2.93	789.835	2.36						
	O 1s	O 1s/24	532.2519	1.2912	GL(30)	2.93	4274.206	12.79						
	C 1s C-C, C-H	C 1s/25	284.9998	0.9653	GL(30)	1	6454.475	56.6						
	C 1s	C 1s/25	285.6842	0.965	GL(30)	1	874.744	7.67						
	C 1s	C 1s/25	286.6961	1.1186	GL(30)	1	208.521	1.83						
	C 1s	C 1s/25	288.1617	1.2141	GL(30)	1	340.005	2.98						
	C 1s	C 1s/25	289.4651	0.7856	GL(30)	1	40.551	0.36	**S**					
	S 2s	S 2s/26	225.2589	1.906	GL(30)	1.43	200.496	1.23	**1.23**					
	Si 2p	Si 2p/28	102.6003	1.2618	GL(30)	0.817	908.528	9.75						
	Pb 4f	Pb 4f/29	137.935	1.0687	A(0.1,0.9,0)GL(30)	22.7	5700.519	2.2	**Pb**					
	Pb 4f	Pb 4f/29	142.795	1.0687	A(0.1,0.9,0)GL(30)	22.7	4401.35	1.7	**3.9**					
	Se 3d	Se 3d/30	53.667	0.8531	GL(30)	2.29	81.131	0.31	**Se**					
	Se 3d	Se 3d/30	54.527	0.8531	GL(30)	2.29	54.317	0.21	**0.52**					

Figure S1D. The corresponding XPS analysis of Sample Figure S1C. The composition is $Pb_{2.1}Se_{0.30}S_{0.70}$ by XPS. The standard deviations for S, Se, and Pb are 7.3%, 5.7%, and 3.8%, respectively.

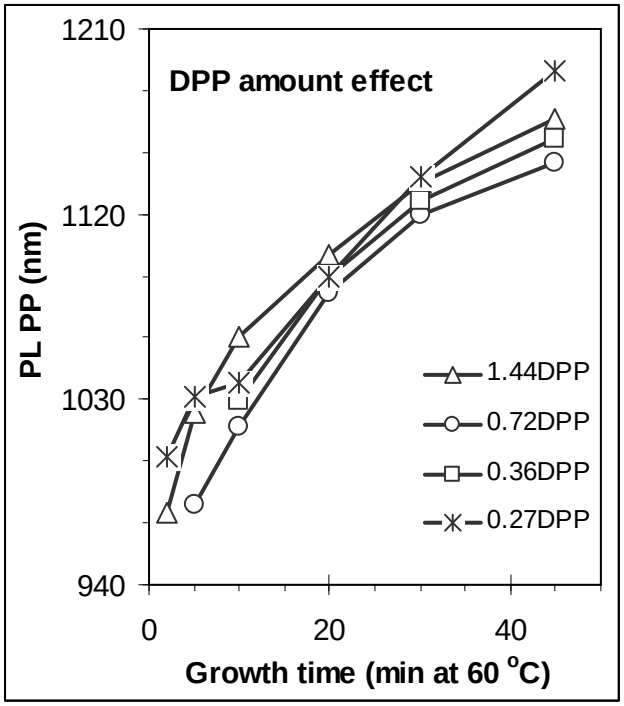


Figure S1E. Summary of the photoemission redshift of the $PbSe_xS_{1-x}$ NCs from the four batches shown in Figures 3 and 4. The absorption/emission peak positions of the 45-min $PbSe_xS_{1-x}$ NCs were 1081/1190 nm (0.27DPP), 1081/1157 nm (0.36DPP), 1074/1145 nm (0.72DPP), and 1099/1166 nm (1.44DPP).

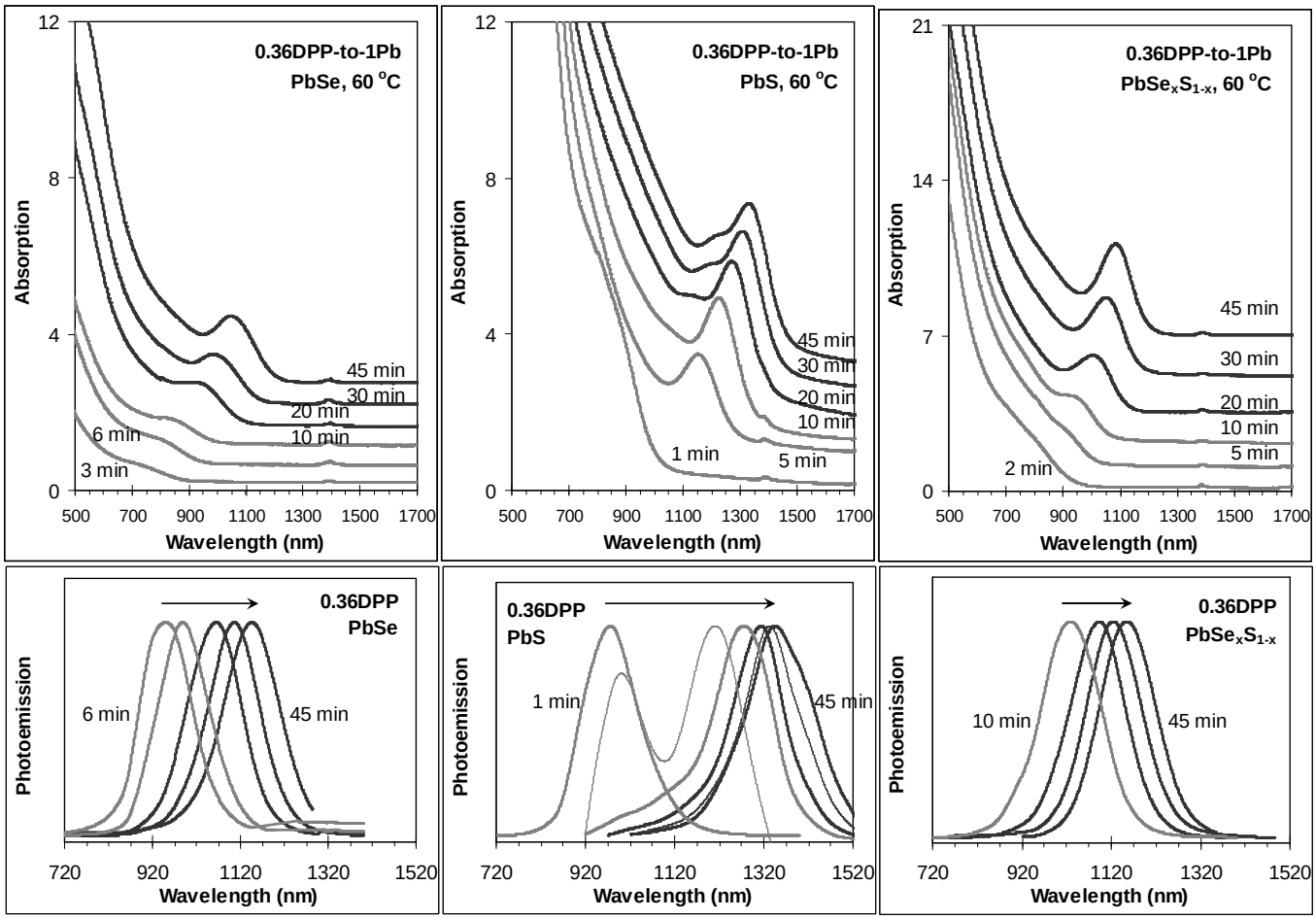


Figure S2A. Comparison of the noninjection low-temperature growth of PbSe (left), PbS (middle), and $PbSe_xS_{1-x}$ (right) NCs. The temporal evolution of absorption (offset, top) and emission (normalized, bottom) of the NCs from three batches, left, middle, and right, with the feed molar ratios of 4Pb-to-2TBPSe, 4Pb-to-2TAA, and 4Pb-to-1.5TBPSe-to-0.5TAA, and the feed [Se], [Se + S], and [S] of ~55 mmol/Kg, respectively. The absorption spectra were normalized to 1.0 gram of crude growth mixtures and dispersed in 1.0 mL TCE. The DPP amount used is indicated as the 0.36DPP-to-1Pb feed molar ratio, together with the growth periods. The growth temperature was 60 °C. It is clear that ternary $PbSe_xS_{1-x}$ NCs were synthesized from our Batch right, while binary PbSe and PbS NCs from Batch left and Batch middle.

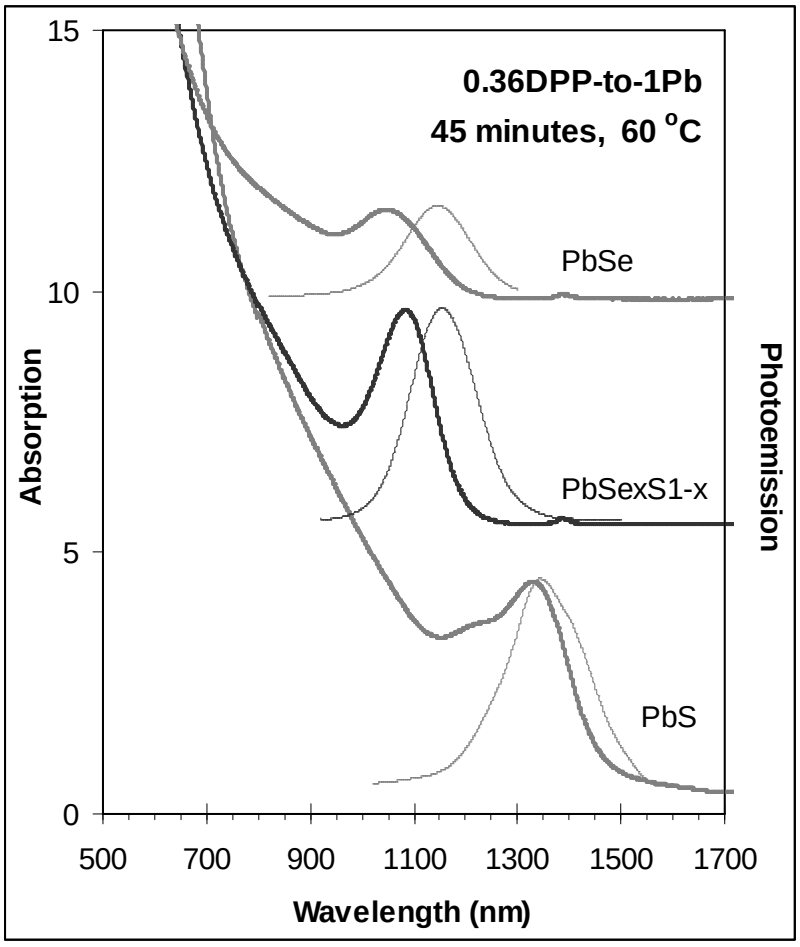


Figure S2B. Comparison of the optical properties of the 45-minute PbSe (top), $PbSe_xS_{1-x}$ (middle), and PbS (bottom) NCs from the three batches shown in the parts of left, right, and middle of Figure S2A. The absorption spectra (solid lines) were offset and normalized to 1.0 gram of crude growth mixtures and dispersed in 1.0 mL TCE, while the emission spectra (dashed lines) were normalized accordingly. It is clear that the experimental condition of Figure S2A Batch right, including the use of DPP and the growth temperature, is excellent for the formation of ternary $PbSe_xS_{1-x}$ NCs.

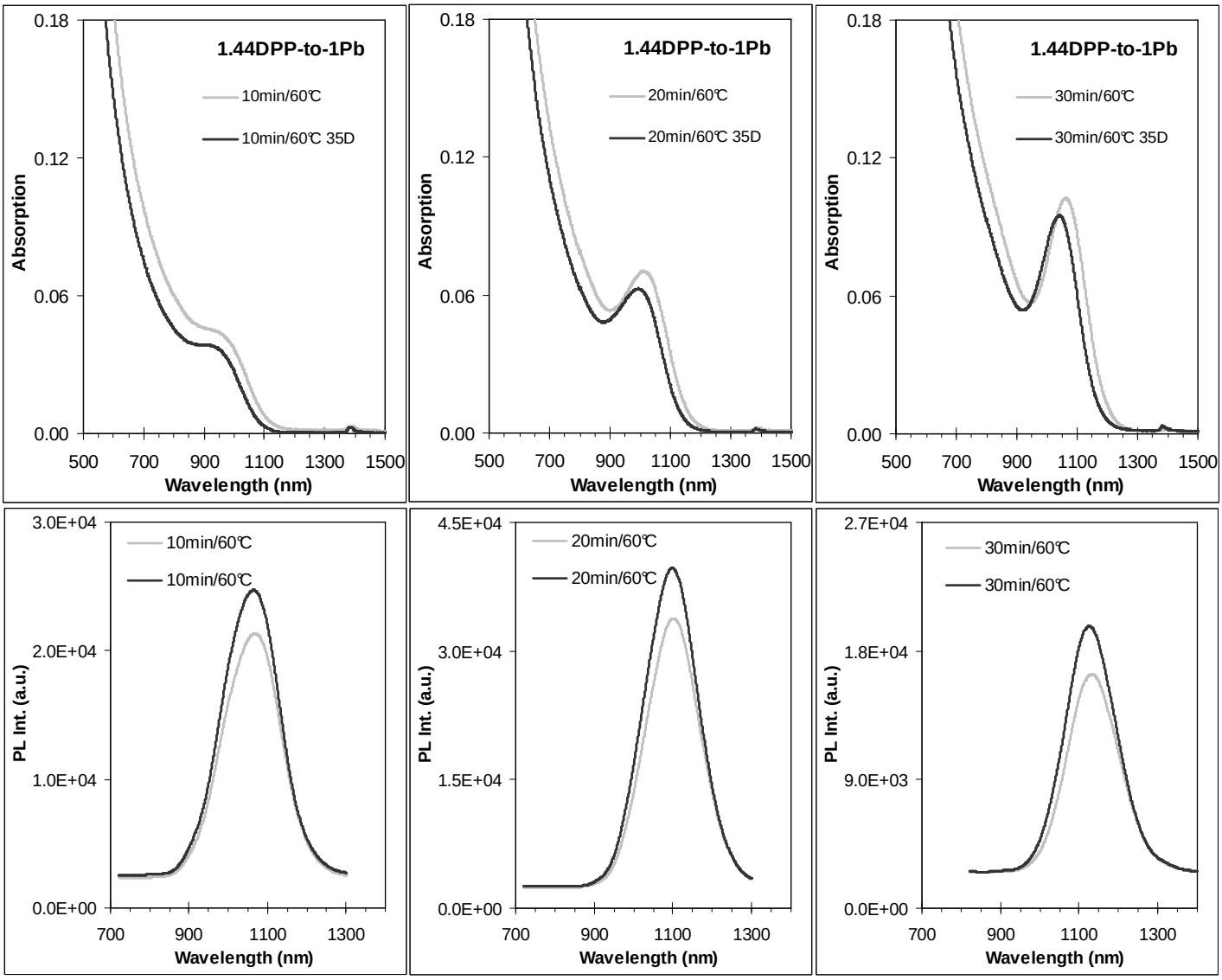


Figure S3A. Investigation on the change of the absorption (top) and emission (bottom), after dark storage at -20 °C with air contact up to 35 days. The $PbSe_xS_{1-x}$ NCs, also shown in Figure 4 Batch 1.44DPP, exhibited excellent storage stability. The solvent used to disperse the PbSe NCs was TCE. The excitation wavelength was 710 nm for the 10-min and 20-min samples and 810 nm for the 30-min sample.

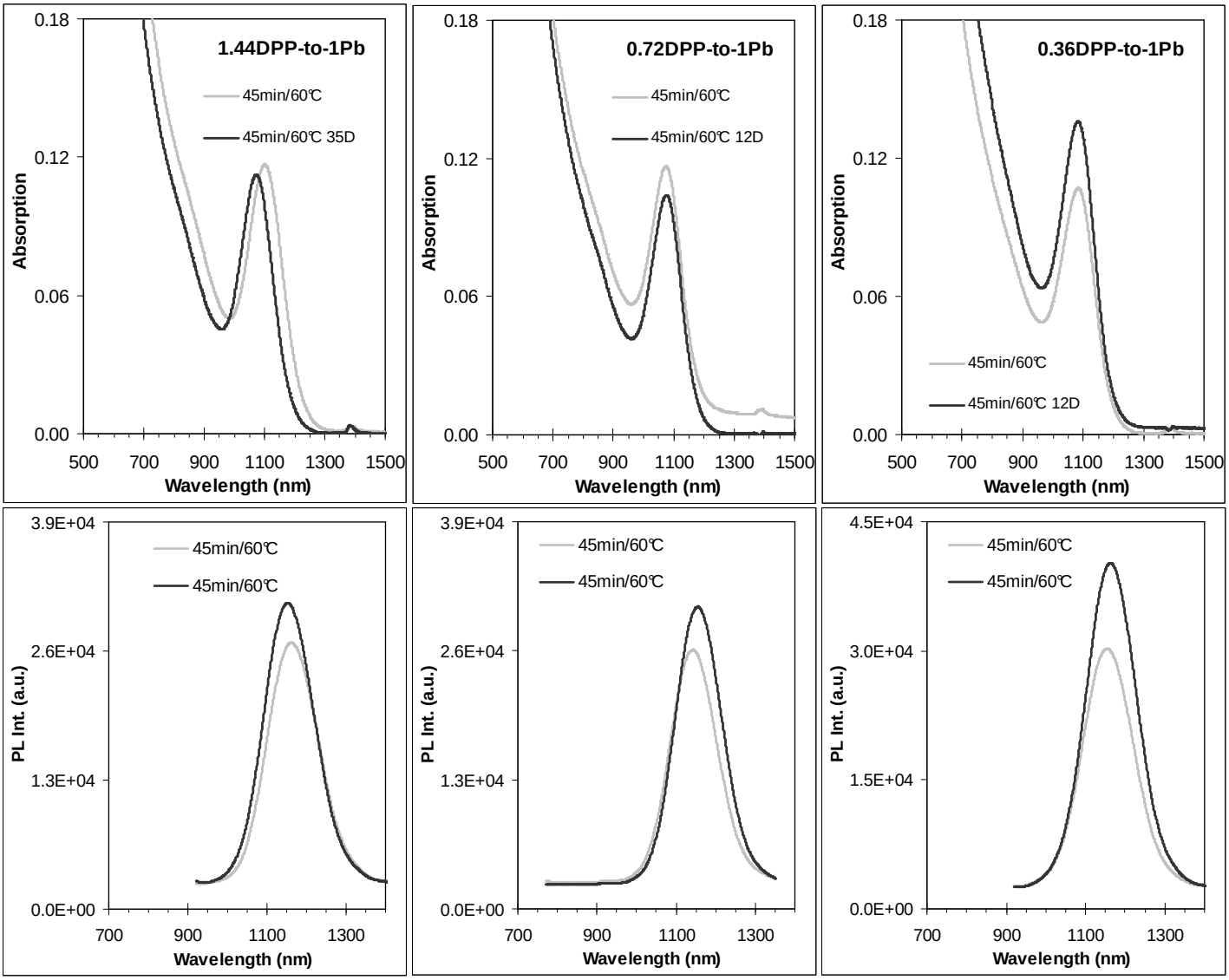


Figure S3B. Investigation on the change of the absorption (top) and emission (bottom), after dark storage at -20 °C with air contact up to 35 (left) and 12 (middle and right) days. The $PbSe_xS_{1-x}$ NCs, also shown in Figure 4 Batch 1.44DPP (left), Batch 0.72DPP (middle), and Batch 0.36DPP (right) exhibited excellent storage stability. The solvent used to disperse the PbSeS NCs was TCE. The excitation wavelength was 910 nm for the left and right samples, while 760 nm for the middle samples.

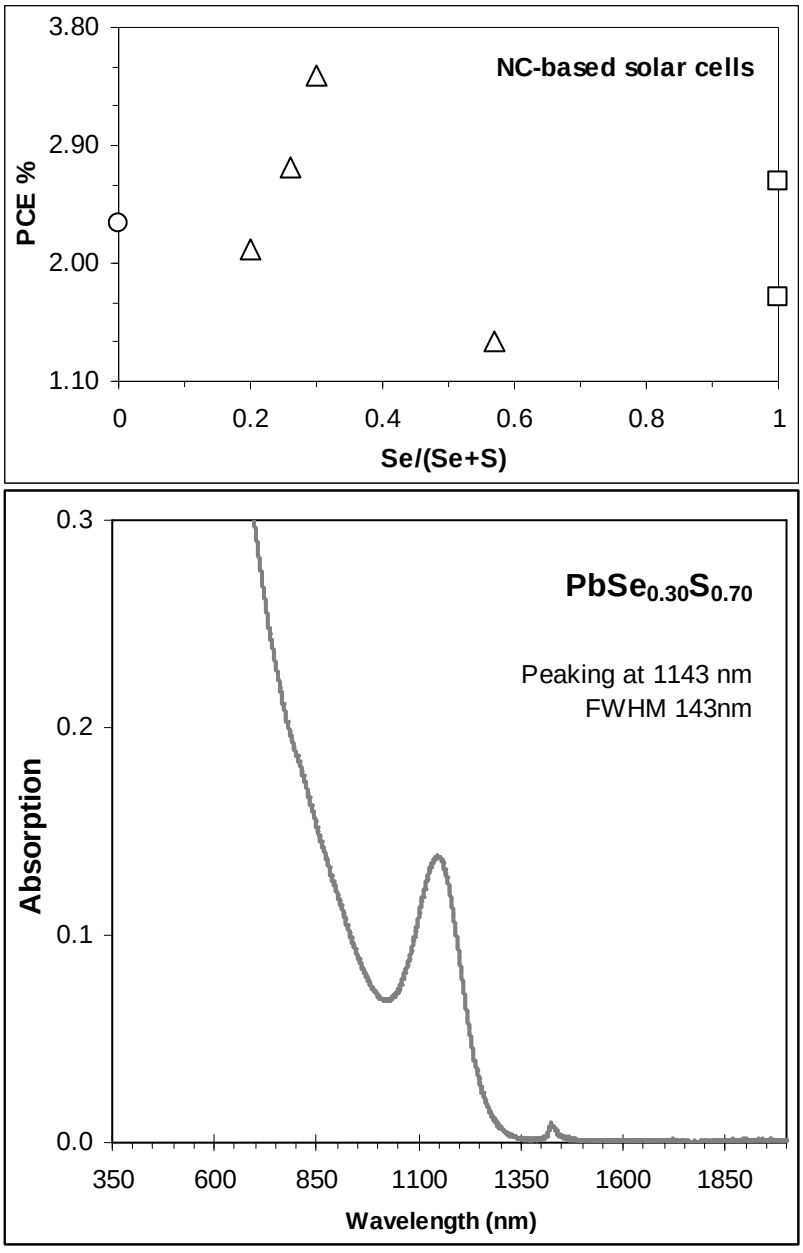


Figure S4. (Top) Investigation on the PCE from NC-based Schottky-type solar cells fabricated with various $PbSe_xS_{1-x}$ NCs. The NCs were prepared via our eq (2) approach. (Bottom) Absorption of the $PbSe_{0.30}S_{0.70}$ NC ensemble which produced ~3.44% PCE. The relevant device data are summarized in Table S1.

TABLE S1. Summary of power conversion efficiency (PCE%) from our NC-based Schottky-type solar cells fabricated, together with the bandgap and thickness of the NCs, open circuit voltage (V_{oc}), short circuit photocurrent (J_{sc}), and fill factor (FF). The device structure was ITO/Pb-based NCs/LiF(1nm)/Al(100nm). The active layers of the devices were cast with a layer-by-layer cross-linking technique using 1,3-benzenedithiol as the cross-linker.

NCs	1st absorption peak	NC Thickness	V_{oc} (V)	J_{sc} (mA)	FF	PCE%
PbS	1066 nm	120 nm	0.61	8.66	0.46	2.42
$PbSe_{0.20}S_{0.80}$	1083 nm	115 nm	0.41	10.32	0.50	2.11
$PbSe_{0.26}S_{0.74}$	1124 nm	115 nm	0.45	13.16	0.46	2.73
$PbSe_{0.30}S_{0.70}$	1143 nm	115 nm	0.49	13.09	0.54	3.44
$PbSe_{0.57}S_{0.43}$	1124 nm	115 nm	0.31	11.15	0.41	1.41
PbSe-1	1289 nm	120 nm	0.33	11.41	0.46	1.74
PbSe-2	1086 nm	100 nm	0.45	11.75	0.50	2.62