Electronic Supplementary Information

Facile synthesis of ultra-small PbSe nanorods for photovoltaic application

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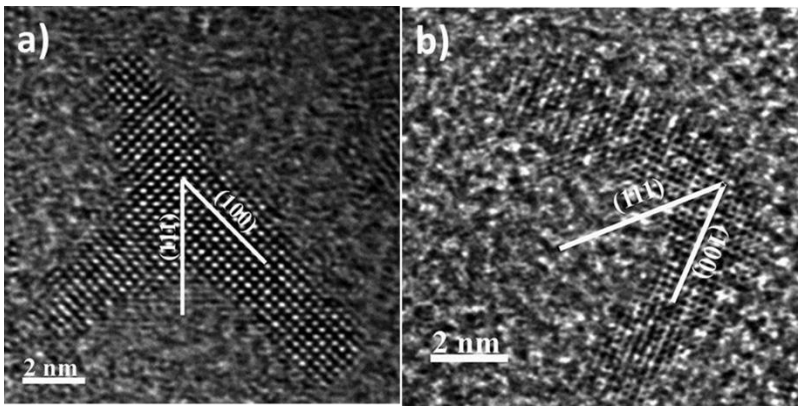

Fig. S1 (a) HRTEM image of T-shaped PbSe NCs. (d) HRTEM image of L-shaped PbSe NCs.

The effect of t-2-OA on the morphology of PbSe NCs at high temperature

A solution of 1 mmol PbO (0.22 g), 3 mmol carboxylic acid ligands (the optimized molar ratio: t-2-OA : OA=4:1) dissolved in 5 ml dried ODE was heated at 130 ^{o}C in a 25 mL three-neck flask under nitrogen for 1h. The solution was then degassed for additional 1 h at 100 ^{o}C under vacuum before setting the solution at 170 ^{o}C under nitrogen. Then 3 ml 1M TDPSe was injected under vigorous stirring. The reaction was allowed to continue for different growth times. However, the products became insoluble when the growth time was more than 4 min. The soluble products were purified by precipitation twice in hexane/isopropyl alcohol.

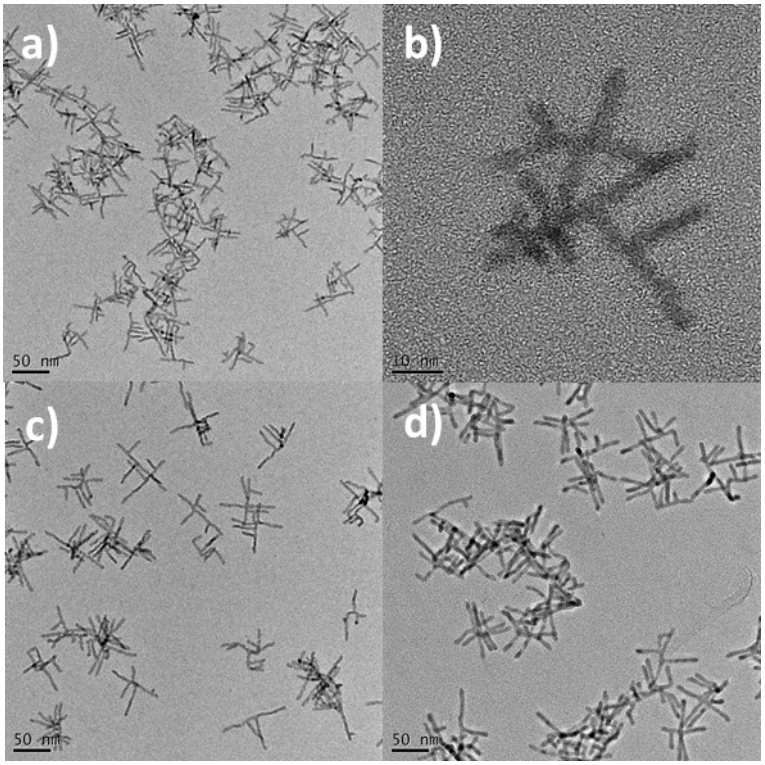

Fig. S2 TEM images of PbSe NCs synthesized using t-2-OA at 170 ^{o}C with different growth time: (a) 30 s (b) an individual PbSe NCs with the branched nanostructures at 30 s (c) 1 min (d) 2 min.

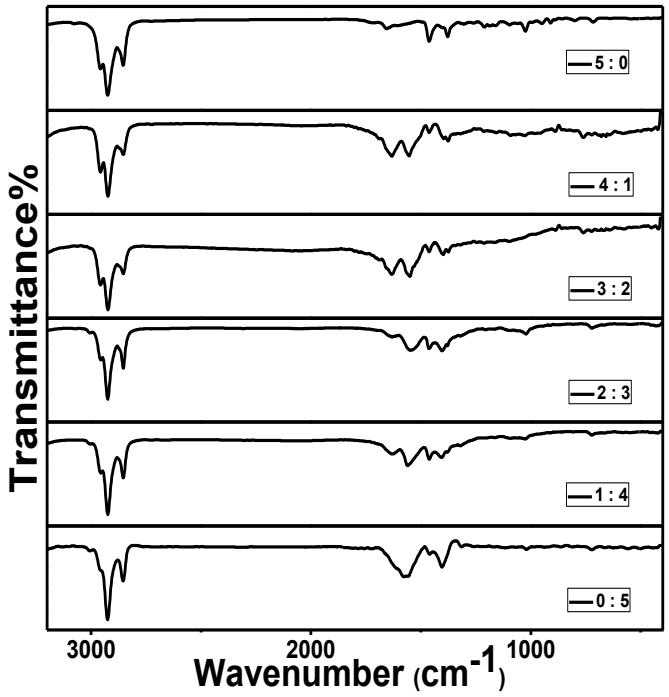

Fig. S3 FTIR spectra of PbSe NRs with the *t*-2-OA:OA molar ratio from 5:0 to 0:5.

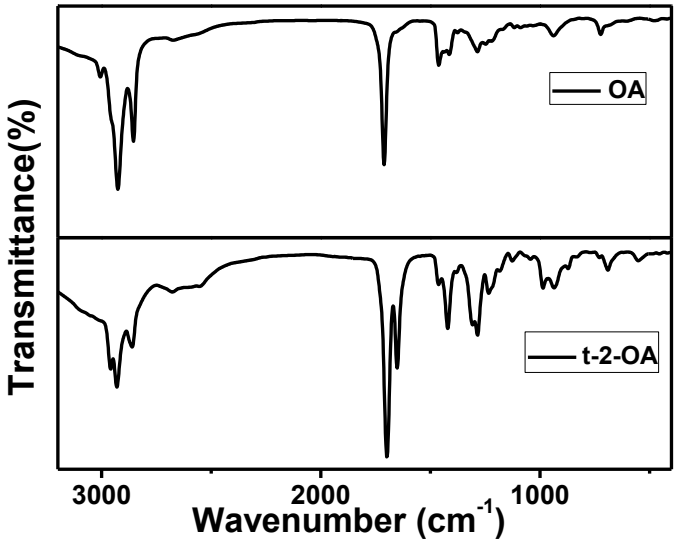

Fig. S4 FTIR spectra of free oleic acid (OA) and *trans*-2-octenoic acid (*t*-2-OA).

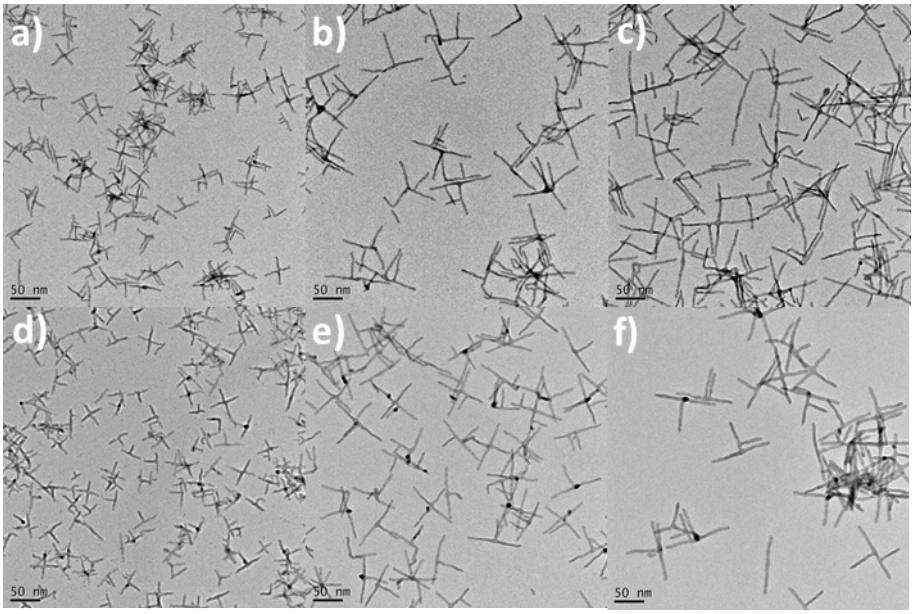

Fig. S5 TEM images of PbSe NRs synthesized without DPP at (a) 140 ^{o}C for 2 min (b) 140 ^{o}C for 5 min (c) 140 ^{o}C for 8 min (d) 160 ^{o}C for 30 s (e) 160 ^{o}C for 1 min (f) 160 ^{o}C for 2 min.

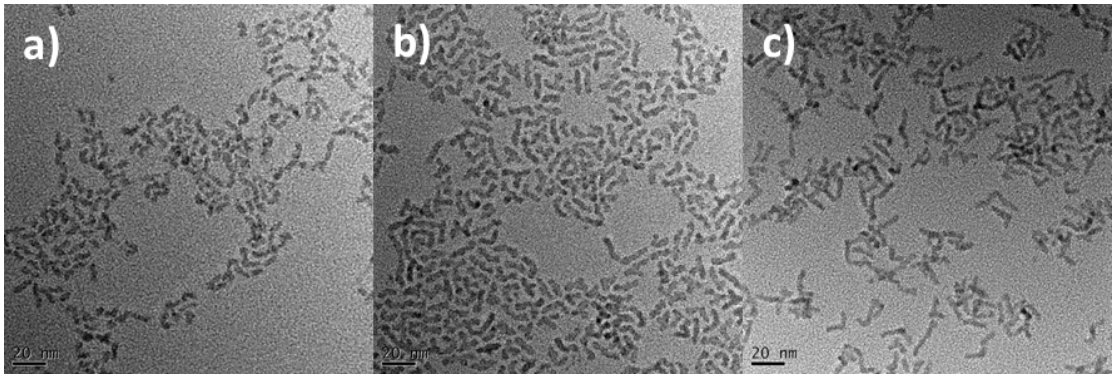

Fig. S6 TEM images of PbSe NRs synthesized at 120 ^{o}C with 10 ul DPP for (a) 1 min (b) 6 min (c) 12 min respectively.

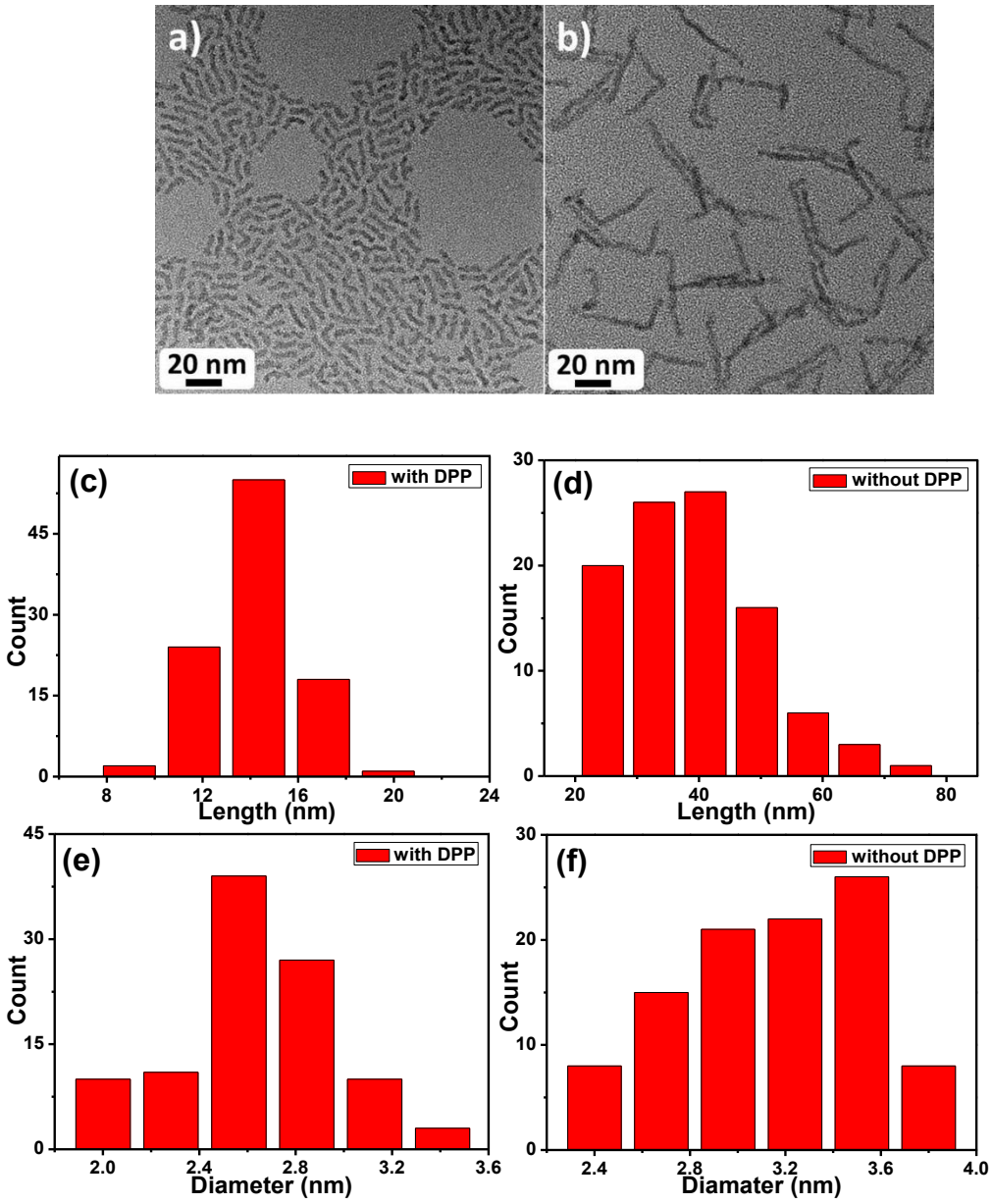

Fig. S7 TEM images of PbSe NRs synthesized at 120 ^{o}C: (a) with 10 ul DPP (growth for 2 min) and (b) without DDP (growth for 12 min); length distribution of PbSe NRs with 10 ul DPP (c) and without DPP (d); diameter distribution of PbSe NRs with 10 ul DPP (e) and without DPP (f).

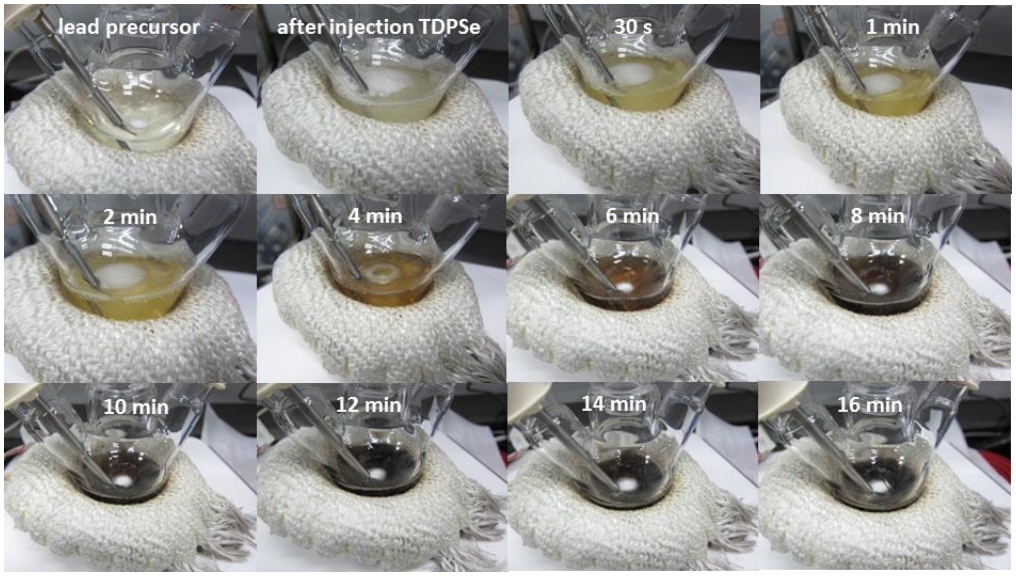

Fig. S8 The color change of reaction solution with time under 120 ^{o}C in the absence of DPP.

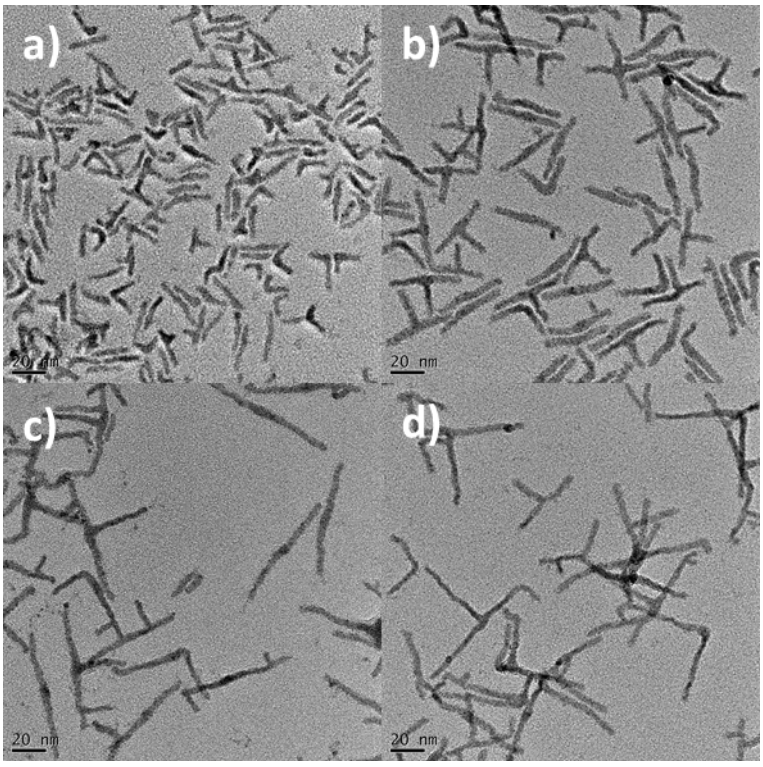

Fig. S9 TEM images of PbSe NRs synthesized under 120 ^{o}C without DPP at different growth times: (a)8 min (b)10 min (c)14 min (d)16 min.

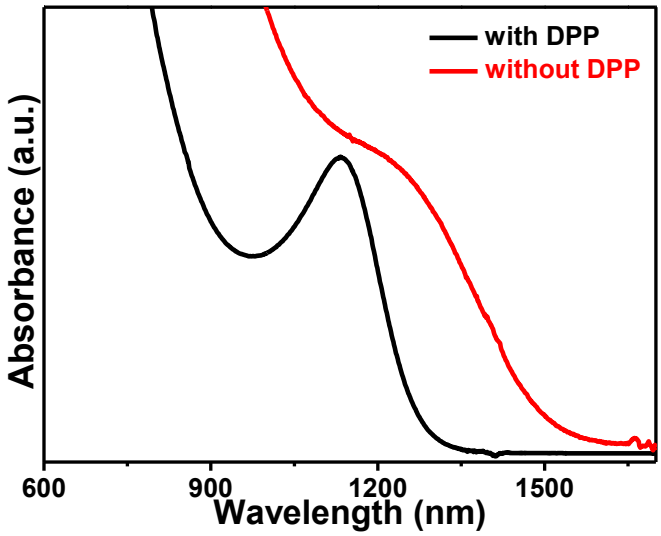

Fig. S10 Absorption spectra of PbSe NRs synthesized with 10 ul DPP in TDPSe (black line) and without DPP (red line).

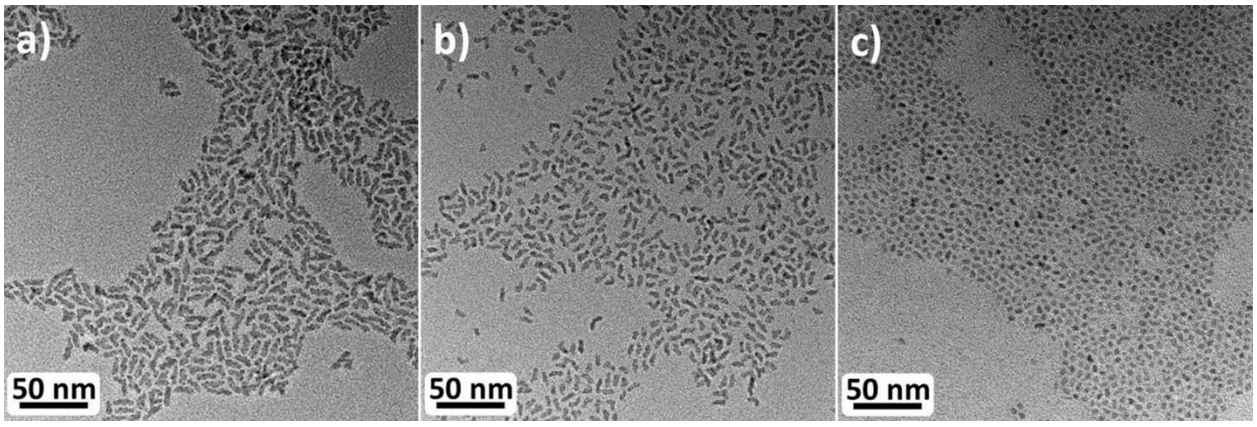

Fig. S11 TEM images of PbSe NRs synthesized at 120 ^{o}C with varied *t*-2-DA:OA molar ratio: (a) 5:0 (b) 4:1 (c) 3:2.

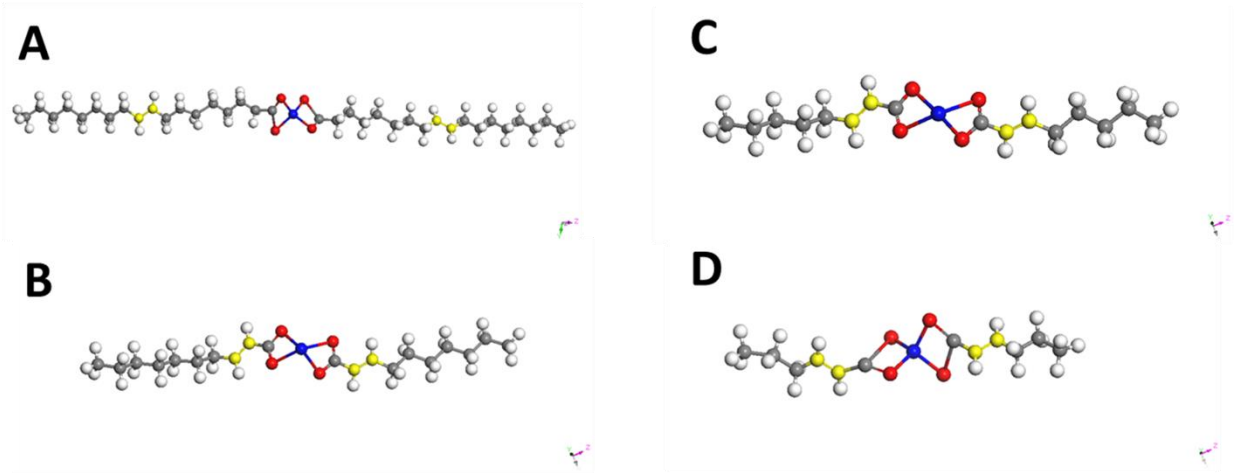

Fig. S12 Ball-and-stick view of the four lead carboxylates of $Pb(OA)_2$ (A); $Pb(t\text{-}2\text{-}DA)_2$ (B); $Pb(t\text{-}2\text{-}OA)_2$ (C); $Pb(t\text{-}2\text{-}HA)_2$ (D). (Ball: red-oxygen atom, blue-lead atom, grey-carbon atom, white-hydrogen atom, yellow-C=C double bond).

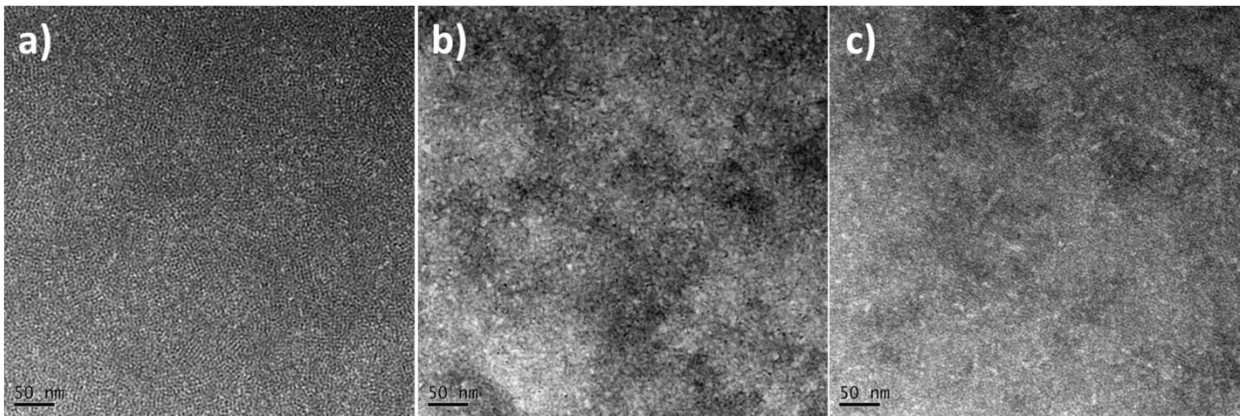

Fig. S13 TEM images of device films with (a) QD layers; (b) NR layers; (c) QD/NR layers.

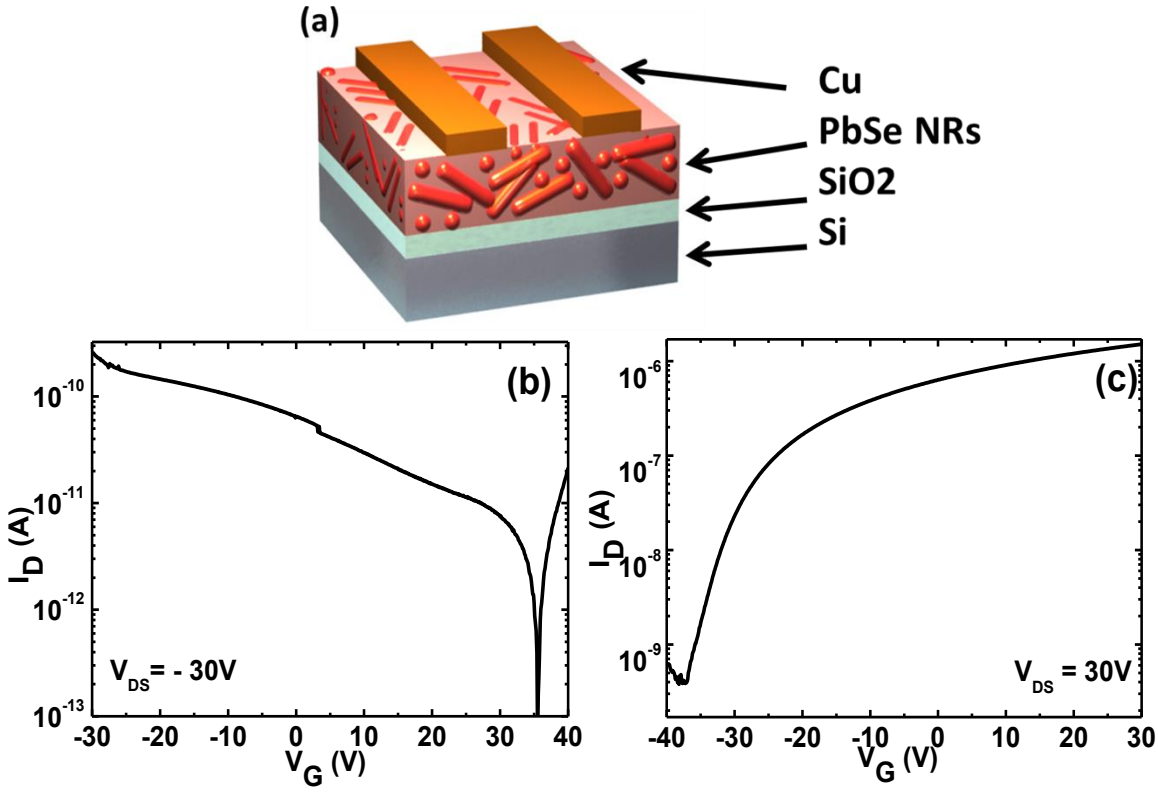

Fig. S14 (a) Schematic of a PbSe NRs thin-film FET; (b) I_D versus V_G plot at a constant V_{DS} = -30V for a PbSe QDs FET; (c) I_D versus V_G plot at a constant V_{DS} = 30V for a PbSe NRs FET.

Table S1 PbSe NRs dimension variation with different *t*-2-OA : OA molar ratios.

***t*-2-OA:OA**	**Aspect ratio**	**Diameter (nm)**	**Length (nm)**	**The yield of NCs (%)**	**The percent of branched nanostructures (%)**
5 : 0	9±4	2.6±0.4	21±10	51.5	62
4 : 1	6±2	2.6±0.4	14±4	47.3	21
3 : 2	3.4±1	2.7±0.2	9±2	40.2	16
2 : 3	2.6±0.6	2.4±0.3	6±1	32.3	9
1 : 4	1.8±0.7	2.3±0.3	4±1	27.6	----
0 : 5	1.3±0.3	2.2±0.2	3±0.5	20.8	----

Table S2 PbSe NRs dimension variation with different reaction temperatures.

Reaction temperature (T/^{o}C)	Growth time (min)	Aspect ratio	Diameter (nm)	Length (nm)
80	50	4.8±1.2	2.2±0.2	10±2
100	15	4.5±1.5	2.3±0.2	10±4
120	2	6±2	2.6±0.4	14±4
140	1	5±3	3.2±0.6	15±8
160	0.5	3.8±1	3.6±0.4	13±3

Table S3 PbSe NRs dimension variation is determined by adding trace DPP in TDPSe.

Addition in TDPSe	Growth time (min)	Aspect ratio	Diameter (nm)	Length (nm)
10 ul DPP	1	4±0.7	2.3±0.2	9±1
10 ul DPP	2	6±2	2.6±0.4	14±4
10 ul DPP	6	5±1.5	3.1±0.4	15±3
10 ul DPP	12	4.8±1	3.5±0.3	17±5
no DPP	12	14±3	3.3±0.7	32±12

Table S4 Calculated energy parameter ΔE for binding strength of different ligands.

Lead carboxylates	ΔE(eV)
Pb-OA	-25.223
Pb-(*t*-2-DA)	31.040
Pb-(*t*-2-OA)	38.592
Pb-(*t*-2-HA)	38.695