

Supporting information

Solvent-less Solid State Synthesis of Dispersible Metal and Semiconducting Metal Sulfide Nanocrystals

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Experimental section

Chemicals required:

Octanethiol ($C_8H_{17}SH$), decanethiol ($C_{10}H_{21}SH$), dodecanethiol ($C_{12}H_{25}SH$), hexadecanethiol ($C_{16}H_{33}SH$), octadecanethiol ($C_{18}H_{37}SH$) and octyl amine (C_8NH_{19}) were purchased from Sigma Aldrich and were used as received. Silver nitrate, Gold(I) iodide, Cuprous(I) iodide, Cadmium acetate, Manganese acetate, Zinc acetate and Lead acetate were purchased from Sigma Aldrich. Solvents such as ethanol and toluene etc were also purchased from Merck Chemicals and were used as received.

Synthesis of Metal thiolates precursors

a) Synthesis of gold (I) thiolates:

Gold (I) thiolates were synthesized in an easy manner to furnish gram quantities of materials. Approximately 250 mg of gold (I) iodide was taken in an eppendorf tube. To this 500 μ L of n-alkanethiol in ethanol cold solution was added and the reaction mixture was shaken vigorously. After sometime the colour of this mixture changed to white. The resulting product was washed thoroughly several times (1-2 times) with ethanol. The obtained powder was dried at ambient conditions and was analyzed using several characterization techniques like powder XRD and SEM.

Caution! Addition of thiol solution to the solid Au(I)I was found to be highly exothermic and thiol has ability to reduce the gold, results bulk gold metal formed as a impurity in the gold-thiolates. Therefore instead of direct thiol, cold ethanolic solutions of thiol need to be used for gold thiolates preparation.

b) Synthesis of silver (I) thiolates:

To 500 mg of silver nitrate 1000 μ L of n-alkane thiol was added and the reaction mixture was shaken vigorously. The reaction mixture turned white. The mixture was then washed thoroughly with ethanol (1-2 times). The obtained powder was dried at ambient conditions and was analyzed using several characterization techniques like powder XRD and SEM.

c) Synthesis of lead (II)thiolates:

500 mg of lead acetate (II) trihydrate was taken in 15 mL glass vial and 1 mL of octanethiol was added into the solid directly, and the tube was shaken vigorously. The reaction mixture turned yellow in colour instantaneously. The mixture was washed thoroughly with ethanol, and the yellow product was dried inside vaccum oven at room temperature. The obtained yellow powder was characterized using PXRD, SEM and TEM.

d) Synthesis of cadmium (II) thiolates:

500 mg of cadmium acetate was taken in 15 mL glass vial and 1 mL of octanethiol was added into the solid directly, and the tube was shaken vigorously. The reaction mixture turned milky white in colour instantaneously. The mixture was washed thoroughly with ethanol, and the white product was dried inside vaccum oven at room temperature. The obtained yellow powder was characterized using PXRD and SEM.

e) Synthesis of Manganese (II) thiolates:

500 mg of manganes acetate was taken in 15 mL glass vial and 1 mL of octanethiol was added into the solid directly, and the tube was shaken vigorously. The reaction mixture turned white in colour instantaneously. The mixture was washed thoroughly with ethanol, and the white product was dried inside vaccum oven at room temperature. The obtained yellow powder was characterized using PXRD and SEM.

f) Synthesis of Zinc (II) thiolates:

500 mg of zinc acetate was taken in 15 mL glass vial and 1 mL of octanethiol was added into the solid directly, and the tube was shaken vigorously. The reaction mixture turned milky white in colour instantaneously. The mixture was washed thoroughly with ethanol, and the white product was dried inside vaccum oven at room temperature. The obtained yellow powder was characterized using PXRD and SEM.

g) Synthesis of octyl dithiocarbamic acid (C₈DTCA):

About 10 mL dry dichloromethane (DCM) was taken in 100 mL Rb flask and cooled. To this 50 mmol of CS₂ (large excess) was added and stirred for some time in argon atmosphere. After 15 min 10 mmol of octyl amine was added drop-wise into the CS₂ solution and stirred for 30 min. A white coloured precipitate formed immediately. This was dried under vacuum. The powder was recrystallised from toluene. The dried shiny organic tiny crystals were analyzed by NMR (Please see below in Figure S14).

Caution! Reaction is exothermic; solution became warm upon addition of amine, so reaction should be performed in ice cold condition and addition of amine should be drop wise. Otherwise some part of desired compound can convert to thiourea.

2) Synthesis of metal nanocrystals

(I) Ag NCs from Ag-thiolates

125 mg (0.5 mmol) of Ag (I) octanethiolate, the precursor for the silver nanoparticles synthesis, was weighed out and ground with 150 mg (3 mmol) of sodiumborohydride (excess amount). Here Ag-thiolates and NaBH₄ both are white in colour and insoluble in toluene. After sometime the colour of the mixture changed to brown indicating metal nanoparticle formation. When little amount of toluene was added to it, whatever Ag (I) octanethiolate was converted to Ag NCs got dispersed in toluene. This pure Ag NCs dispersion could be separated by decanting. The remaining solid was unreacted thiolates and NaBH₄. The remaining residue was again ground and Ag NCs was collected by adding toluene. This process could be continued for 3-5 times and upto 90% of Ag-thiolates was converted to Ag NCs. This same procedure was employed for preparing the silver nanoparticles from the other silver thiolates like silver (I) decanethiolate etc.

(II) Au NCs from Au thiolates

Au (I) octanethiolate was used as the precursor for the gold nanoparticles synthesis. 25 mg (~0.01 mmol) of the as prepared gold (I) octanethiolate and 50 mg (1 mmol) of sodium borohydride was taken in mortar-pestle and ground as was done above for the Ag NCs preparation. After sometime the colour of the mixture changed to reddish and bluish mixtures. When toluene was added to this mixture, Au NCs got dispersed in toluene. This same procedure was employed for preparing the gold nanoparticles from the other gold thiolates like gold (I) decanethiolate etc. In case of Au two different sized (<3nm and ~10~25nm) NCs formed. These were separated by centrifuging where the bigger particles settled down at the bottom and ultra small particles were in supernatant.

(III) Synthesis of PbS NCs by solid state

500 mg (1 mmol) of lead thiolate $\text{Pb}(\text{C}_8\text{H}_{17}\text{S})_2$ was taken and ground well till it spreads uniformly inside the mortar. To this, 10-100 mg (0.05 mmol-0.5 mmol) of octyldi-thiocarbamic acid (was added and ground for 10 minutes. The colour of the mixture changed to brownish black. To this mixture toluene was added and the dispersion was collected in Eppendorf tubes. After some time some precipitate appeared at the bottom of the Eppendorf, which was discarded. The remaining supernatant was precipitated and washed with methanol to obtain pure PbS NCs. These again could be re-dispersed in most of the non-polar organic solvents like toluene. This product was characterized by PXRD and UV-Vis absorption and fluorescence spectra.

Caution: Appropriate precautions (like wearing gloves, masks and carrying out the reactions in fume cupboard) should take while dealing with Pb salts and alkanethiols.

(IV) Synthesis of Ag_2S NCs by solid state

About 250 mg (1 mmol) of Silver thiolate $\text{Ag}(\text{C}_8\text{H}_{17}\text{S})$ was taken and ground well till it spreads uniformly inside the mortar. To this, 150 mg (~ 0.75 mmol) of octyldi-thiocarbamic acid was added and ground for 10 minutes. The colour of the mixture changed to brownish black. To this mixture toluene was added and the dispersion was collected in Eppendorf tubes. After some time some precipitate appeared at the bottom of the Eppendorf, which was discarded. The remaining supernatant was precipitated and washed with methanol to obtain pure Ag_2S NCs. This product was characterized by PXRD and UV-Vis absorption and fluorescence spectra.

(V) Synthesis of CdS NCs by solid state

500 mg (~ 1.25 mmol) of cadmium thiolate $\text{Cd}(\text{C}_8\text{H}_{17}\text{S})_2$ was taken and ground well till it spreads uniformly inside the mortar. To this, $\text{C}_8\text{DTCA-OIAm}$ (150 mg (~ 0.75 mmol) of octyldi-thiocarbamic acid dissolved in 200 μL OIAm) was added and ground for 10 minutes. The colour of the mixture changed to pale yellow. To the mixture toluene was added and collected in Eppendorf tubes, sonicated it for 5-10 min for proper mixing. Then it was centrifuged to obtain the supernatant. This supernatant was precipitated and washed with methanol to obtain pure CdS NCs. This product was characterized by PXRD and UV-Vis absorption and fluorescence spectra.

(VI) Synthesis of ZnS NCs by solid state

500 mg (~ 1.5 mmol) of Zinc thiolate $\text{Zn}(\text{C}_8\text{H}_{17}\text{S})_2$ was taken and ground well till it spreads uniformly inside the mortar. To this, $\text{C}_8\text{DTCA-OIAm}$ (150 mg (~ 0.75 mmol) of octyldi-thiocarbamic acid dissolved in 200 μL OIAm) was added and grinded for 10 minutes. The colour of the mixture changed to pale yellow. To this mixture toluene was added and the dispersion was collected in Eppendorf tubes. After some time some precipitate appeared at the bottom of the Eppendorf, which was discarded. The remaining supernatant was precipitated and washed with

methanol to obtain pure ZnS NCs. This product was characterized by PXRD and UV-Vis absorption and fluorescence spectra.

(VII) Synthesis of MnS NCs by solid state

500 mg (~1.5 mmol) of manganese thiolate $\text{Mn}(\text{C}_8\text{H}_{17}\text{S})_2$ was taken and ground well till it spreads uniformly inside the mortar. To this, $\text{C}_8\text{DTCA-OIAm}$ (150 mg (~0.75 mmol) of octyldi-thiocarbamic acid dissolved in 200 μL OIAm) was added and grinded for 10 minutes. The colour of the mixture changed to pale yellow. To this mixture toluene was added and the dispersion was collected in Eppendorf tubes. After some time some precipitate appeared at the bottom of the Eppendorf, which was discarded. The remaining supernatant was precipitated and washed with methanol to obtain pure MnS NCs. This product was characterized by PXRD and UV-Vis absorption and fluorescence spectra.

(VIII) Synthesis of CuS NCs by solid state

200 mg (~1 mmol) of Copper thiolate $\text{Cu}(\text{C}_8\text{H}_{17}\text{S})$ was taken and ground well till it spreads uniformly inside the mortar. To this, $\text{C}_8\text{DTCA-OIAm}$ (200 mg (~1 mmol) of octyldi-thiocarbamic acid dissolved in 200 μL OIAm) was added and grinded for 10 minutes. The colour of the mixture changed to greenish black. To this mixture toluene was added and the dispersion was collected in Eppendorf tubes. After some time, some precipitate appeared at the bottom of the Eppendorf, which was discarded. The remaining supernatant was precipitated and washed with methanol to obtain pure CuS NCs. This product was characterized by PXRD and UV-Vis absorption and fluorescence spectra.

3) Ligand Exchange with oleic acid:

The thiol/oleylamine ligands were replaced by adding oleic acid to semiconducting NCs dispersed in a 1:1 toluene + 1-octadecene (ODE) solution (40 mg/mL) in a ratio of 1:10 oleic acid: solvent (toluene + ODE) under inert atmosphere at 50-60 °C. After precipitation with ethanol and centrifugation, the semiconducting NCs were redispersed in toluene. This dispersion was characterized by PXRD and UV-Vis absorption, fluorescence spectra and FTIR spectra.

4) Metal halide (CdCl_2 treatment) post-treatment: Metal halide (CdCl_2) treatment was done according to a previously published report.¹ A stock CdCl_2 precursor solution was prepared by dissolving 600 mg of CdCl_2 (3.2 mmol) and 66 mg (0.24 mmol) of tetradecylphosphonic acid (TDPA) in 10 mL of oleylamine, then heated to 100 °C for 1 h under nitrogen. The PbS NCs toluene solution was heated to 60 °C under vacuum for 30 min; then 1.0 mL of metal halide precursor was introduced into the reaction flask. A 6:1 Pb:Cd molar ratio was maintained during

the treatment. The temperature was kept at 60 °C for 30 min and then cooled to room temperature. The nanocrystals were isolated by the addition of acetone followed by centrifugation. The nanocrystals were then purified by dispersion in toluene and reprecipitation with ethanol. Finally, they were re-dissolved in anhydrous toluene or octane.

5) Materials Characterization

Optical absorption measurements were carried out on a Shimadzu UV-vis-IR-3600 Plus spectrophotometer. NIR-Fluorescence spectra were recorded using Qunata Master 400, PTI spectrofluorometer. XRD profiles were recorded on an X'pert Pro model PANalytical diffractometer from Philips PANalytical instruments operated at a voltage of 40 kV and a current of 30 mA with Cu K α (1.5418 Å) radiation. The samples were scanned in a 2 θ range from 5° to 80° with a scan rate of 0.4° per minute. Scanning electron Microscopy (SEM) was carried out on Quanta 300 instrument. Transmission Electron Microscopy (TEM) was carried out on a TECHNAI G2-20 S-TWIN (T-20) instrument, operating at 200 keV and LaB₆ filament as the source of electrons. The metal sulfide NCs were dispersed in toluene through vigorous sonication and place on carbon coated Cu grid for TEM measurement. The particle size distributions were determined by measuring the size of a minimum of 200 particles manually from multiple images. XPS spectra were recorded using M/s Thermo Fisher Scientific Instruments and Al K α source was used with 6 mA beam current and 12KV. Binding energies were calibrated to C 1s at 284.8 eV BE (binding energy).

6) Calculation of the fluorescence quantum yield

Fluorescence quantum yield (ϕ) is defined as the number of the emitted photons to the number of the absorbed photons.

Here, the relative quantum yield of NCs was determined by using a reference dye (Rhodamine 800) with known quantum yield (0.277) and comparing the same with our NCs.

First diluted solutions of PbS QDs ($A < 0.1$) were prepared and the absorption and the emission spectra were recorded. The fluorescence quantum yields of PbS QDs were measured using a relative optical method. Rhodamine 800 (in methanol) was used as reference and the excitation wavelength for the samples was 500 nm.

The quantum yields of the PbS quantum dots has been calculated from the following equation:

$$\Phi = \Phi_{\text{ref}} \frac{I_s}{I_{\text{ref}}} * \frac{1 - 10^{-A_{\text{ref}}}}{1 - 10^{-A_s}} * \frac{n_s^2}{n_{\text{ref}}^2}$$

Where, ϕ is quantum yield of sample, $\Phi_{\text{ref}}=0.277$ quantum yield of Rhodamine 800, I_s is area under the sample emission curve, I_{ref} is area under the reference dye emission curve, A =absorbance of excitation wavelength and n is the refractive index of solvent.

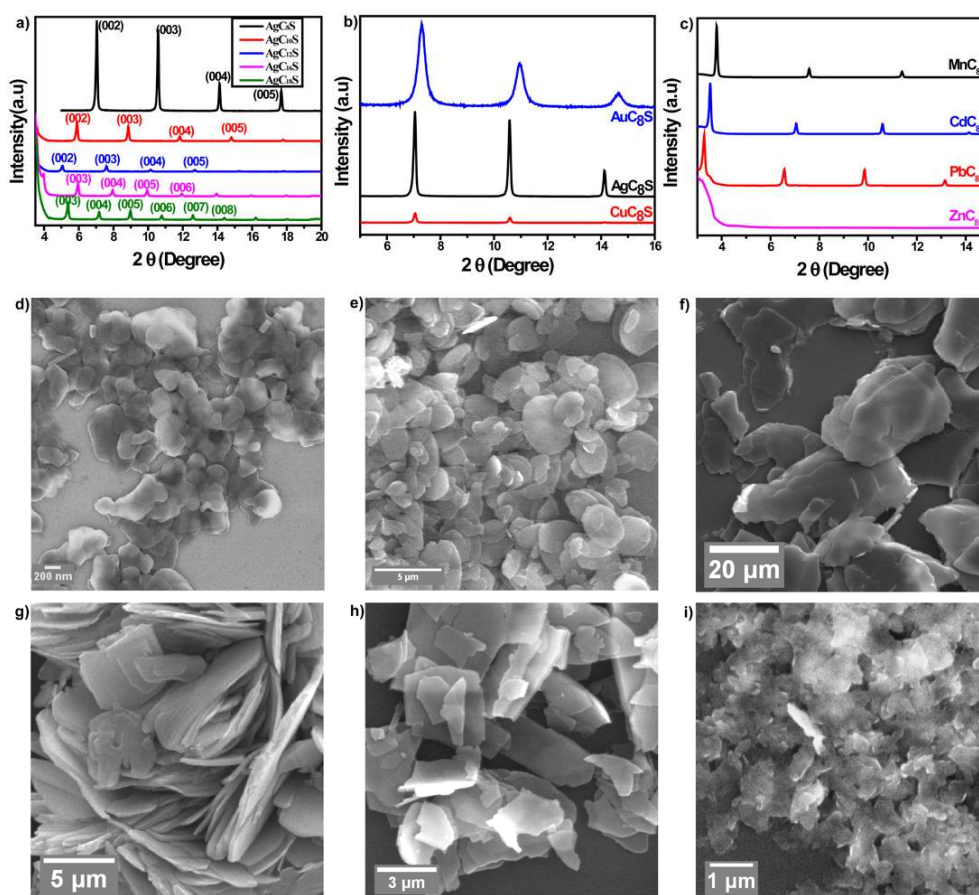
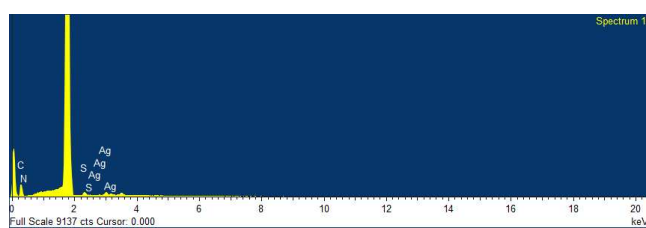
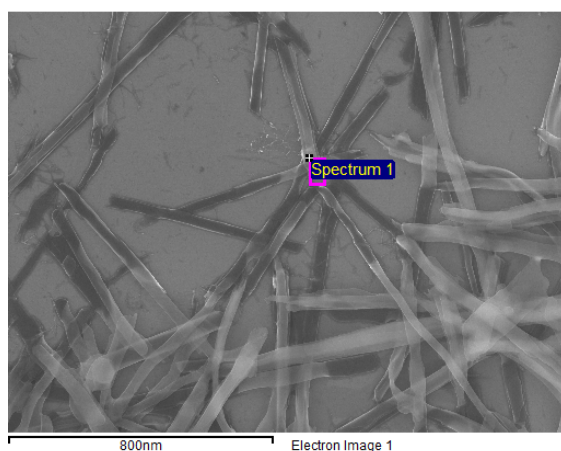


Figure S1: PXRD of metal thiolates: a) Silver thiolates of different chain length alkyl thiolates; silver octanethiolate denoted as AgC₈S and silver octadecanethiolate as AgC₁₈S, b) PXRD of gold octanethiolate(AuC₈S, blue coloured), AgC₈S (black), copper octanethiolate (CuC₈S, red coloured); c) PXRD of manganese octanethiolate(MnC₈S, black coloured), cadmium octanethiolate (CdC₈S, blue), lead octanethiolate (PbC₈S, red), zinc octanethiolate (ZnC₈S, pink coloured). SEM images of metal thiolates; d) AuC₈S, e) CuC₈S, f) MnC₈S, g) CdC₈S, h) PbC₈S and i) ZnC₈S.



Processing option : All elements analyzed (Normalised)

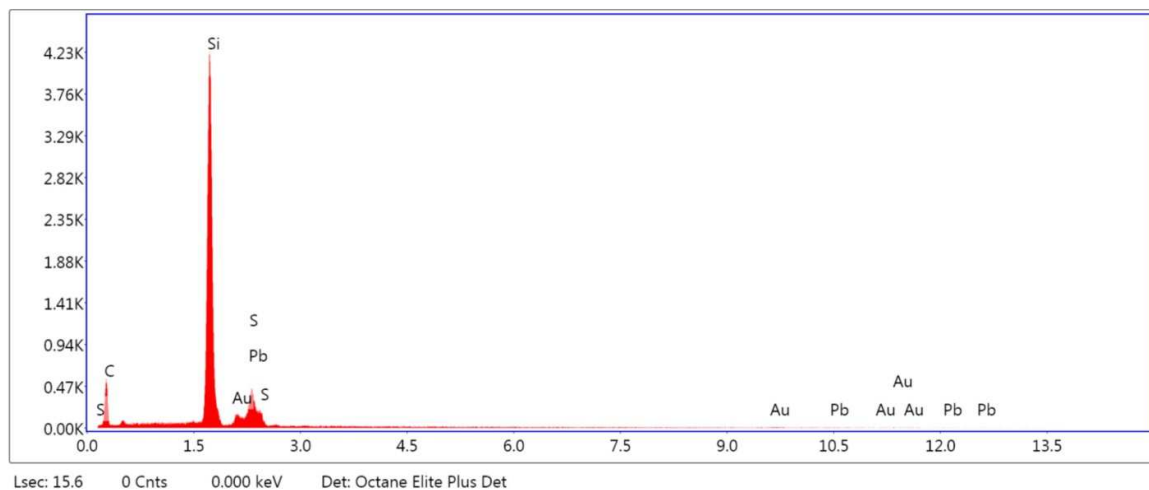
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Element	Weight%	Atomic%
C K	53.45	64.52
N K	31.18	32.27
S K	3.58	1.62
Ag L	11.79	1.58
Totals	100.00	

Figure S2: Energy dispersive X-ray analysis of Ag-SC₈H₁₇. Atomic percentage shows Ag:S ratio ~1:1.

kV: 15 Mag: 2005 Takeoff: 34.9 Live Time(s): 15.6 Amp Time(μs):

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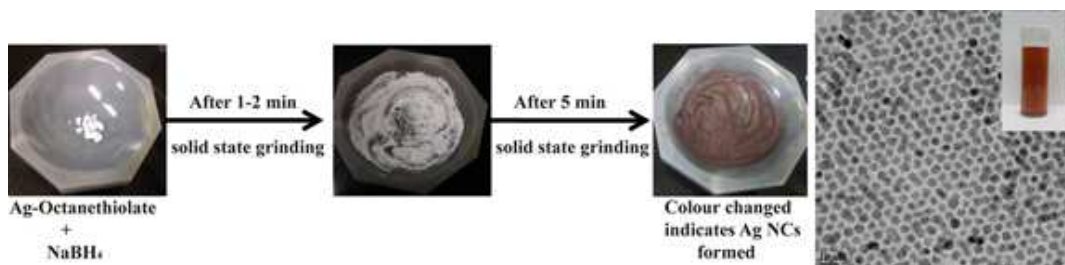


eZAF Smart Quant Results

Element Weight % Atomic % Error %

C K	33.85	60.69	11.94
SiK	45.71	35.05	2.54
AuM	4.66	0.51	10.37
S K	3.73	2.50	10.57
PbM	12.05	1.25	6.78

Figure S3: Energy dispersive X-ray analysis of $\text{Pb}-(\text{SC}_8\text{H}_{17})_2$. Atomic percentage shows Pb:S ratio ~1:2.



Scheme S1: Schematic of the Ag NCs preparation by solid state grinding.

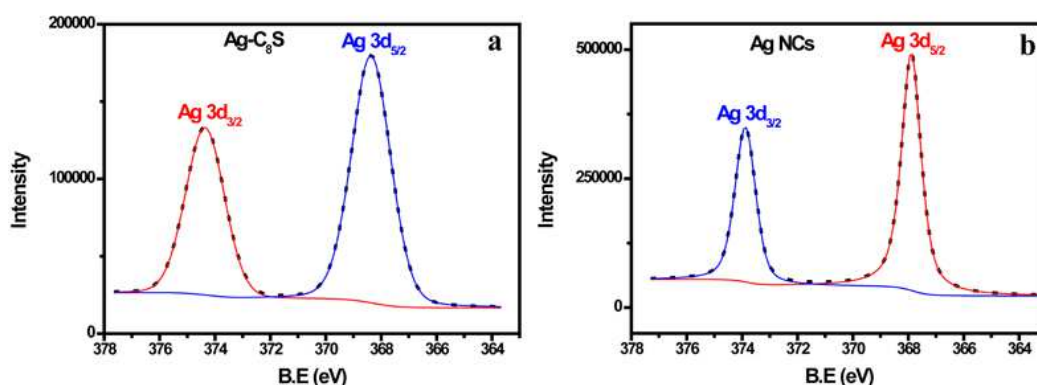
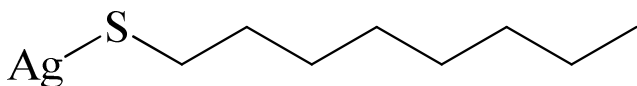


Figure S4: XPS spectra of Ag3d region; a) for Ag-C₈S, and b) for Ag NCs.

Synthesis of Ag NCs by solid state using Ag-C₈S as Ag-source and calculation of yield:

The empirical formula of Ag-thiolate (Ag-C₈S) is Ag-(SC₈H₁₇). The energy dispersive X-ray analysis of Ag-(SC₈H₁₇) also shows the atomic percentage of Ag:S ratio ~1:1.



Empirical molecular weight of Ag-(SC₈H₁₇) is ~252.86

0.5 mmol of Ag-C₈S (~125 mg of Ag-C₈S) and 3 mmol of NaBH₄ (~120 mg) were taken in mortar pestle and ground properly. After 3 min of proper grinding, solvent (toluene) was added to collect the Ag NCs. After centrifugation, supernatant was collected and solid material (unreacted NaBH₄ and Ag-C₈S) was discarded. Then the supernatant was precipitated with acetone and cleaned 2-3 times and finally dried sample was redispersed in 5 mL of toluene.

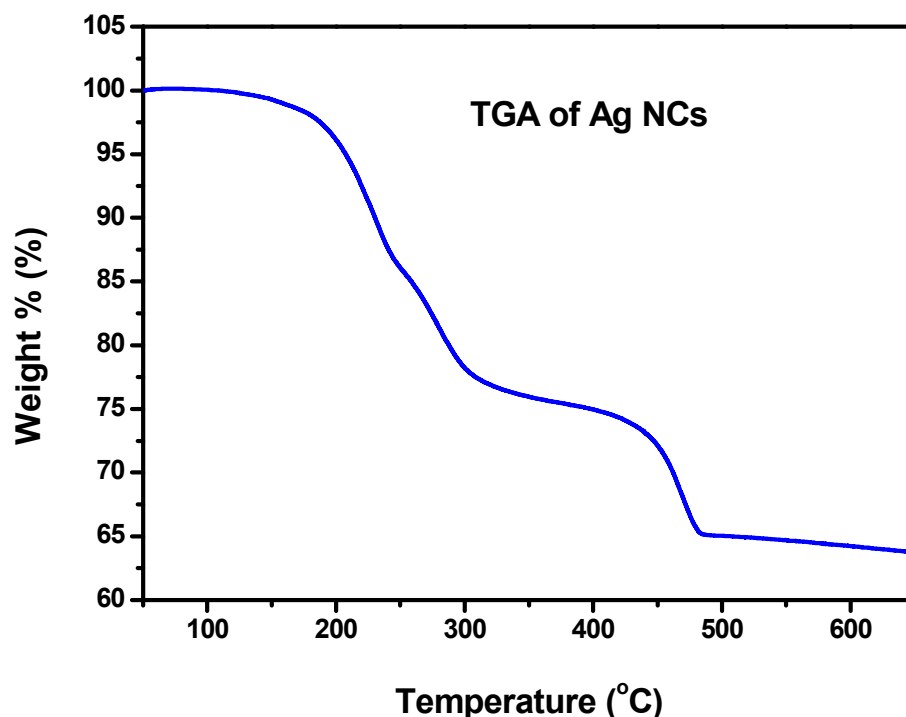


Figure S5: Thermogravimetric analysis (TGA) of thiol capped Ag NCs.

The thermogravimetric analysis (TGA) of thiol capped metallic Ag NCs displays three distinct mass loss events at temperatures near 140, 240, and 420 °C. We attribute the first mass loss in the TGA curve to loss of unbound surface ligands and second mass loss event beginning near 240 °C to desorption of surface-bound ligands. The high-temperature TGA feature (near 420 °C) suggesting it is a mass loss related to an unknown chemical transformation of the inorganic core formed (most probably Ag_2S formed after heating and its decomposition to Ag). Similar to PbS NCs, we estimated the actual Ag content and ligand content from TGA mass loss.

For these thiol capped Ag NCs, actual Ag NCs contain ~35 % of ligand and 65 % of Ag.

Here 12.18 mg of dry Ag NCs was taken for TGA analysis.

Based on the weight loss ~4.26 mg in 12.18 mg of Ag NCs corresponds to the ligands. Therefore the actual Ag content is ~7.917 mg. To determine the yield, aliquots (Ag NCs dispersion after purification) were weighed by drying a known volume of NC dispersion based on which it was determined that ~13 mg of Ag NCs were present in 1 mL. So, a 5 mL dispersion contains ~65 mg of Ag NCs in which the actual Ag content would be ~42.25 mg.

The yield of Ag NCs after purification with respect to starting material ($\text{Ag-C}_8\text{S}$) is thus ~78%.

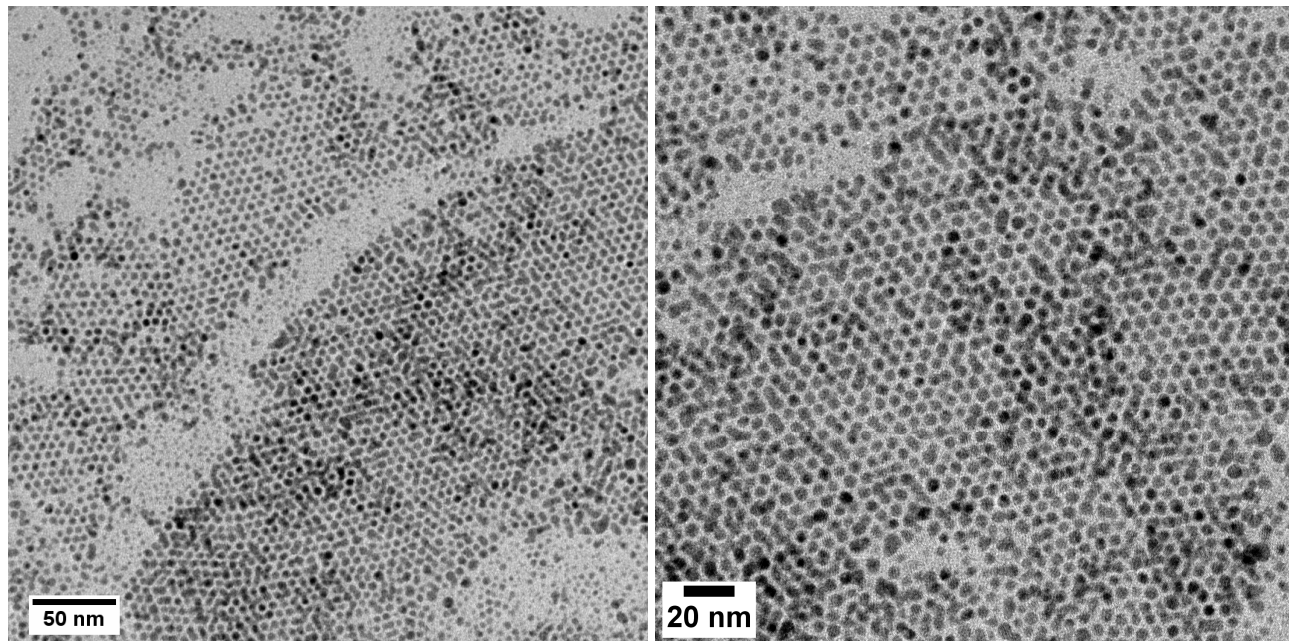


Figure S6: TEM images of Ag NCs prepared from Ag-C₈S.

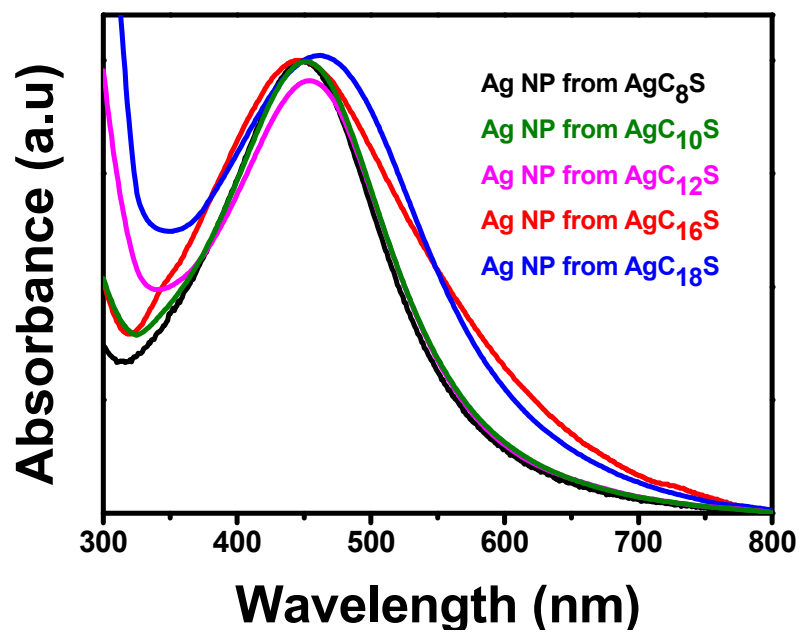


Figure S7: UV-Vis Absorption spectra of Ag NCs obtained from different chain length silver thiolates.

Table S1. FWHM of Ag NCs prepared from different Ag-thiolate

Serial No	Thiolates used for Ag NCs	FWHM
1	Ag-C ₈ S	170.2
2	Ag-C ₁₀ S	178.5
3	Ag-C ₁₂ S	184.1
4	Ag-C ₁₆ S	229.8

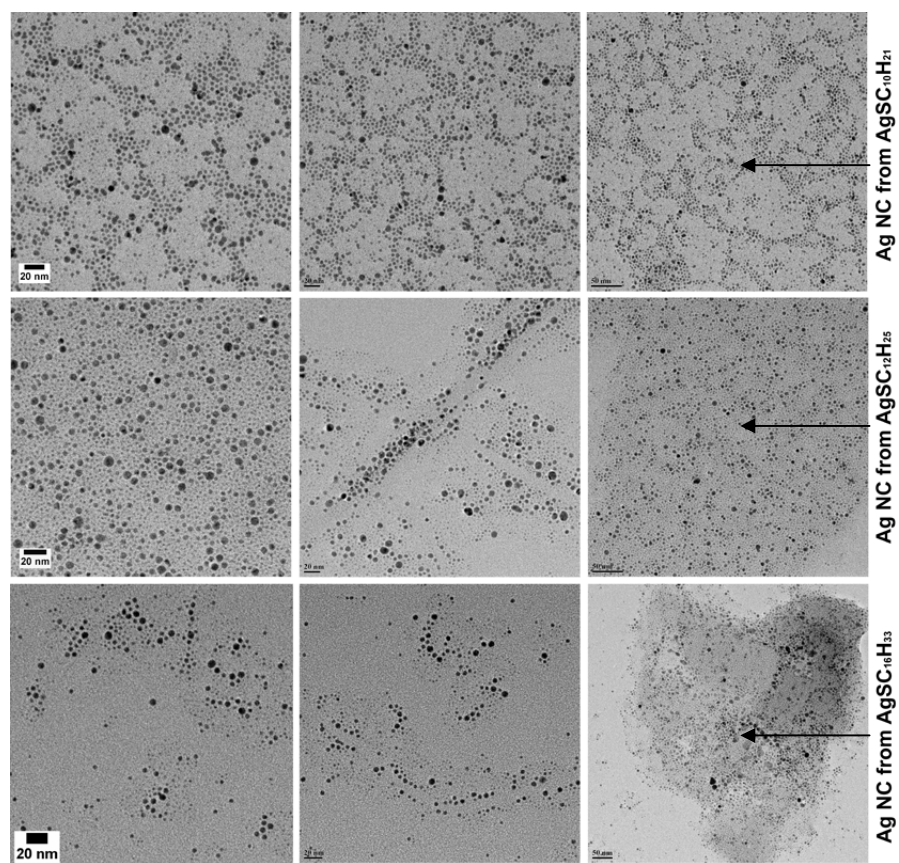


Figure S8: TEM images of Ag NCs obtained from different chain length silver thiolates.

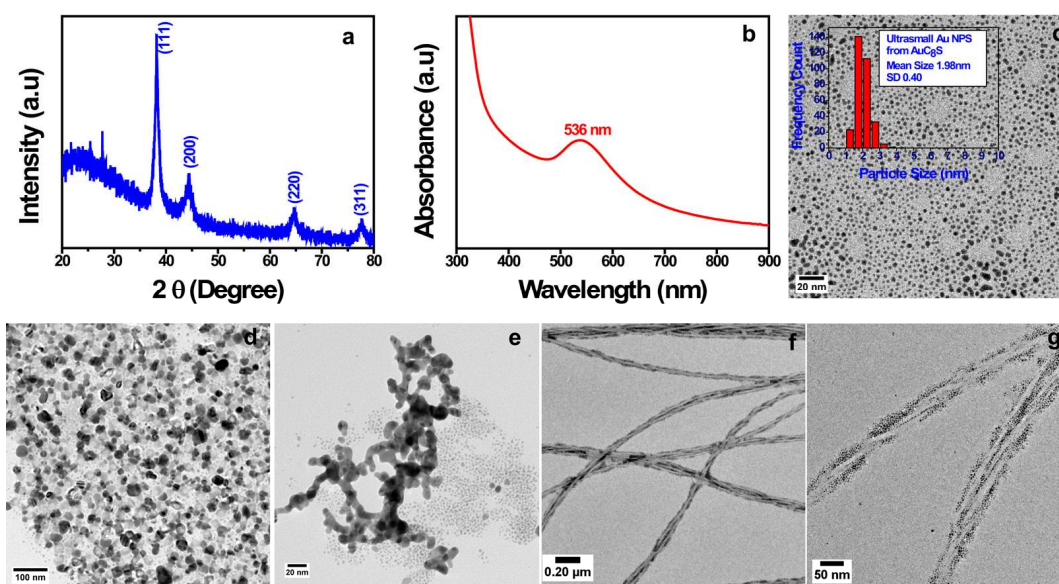


Figure S9: a) PXRD of Au NCs. b) UV-Vis spectra of Au NCs from gold octanethiolates (AuC₈S)[black is for bigger sized particles and red is for small sized particles]. TEM images of Au NCs; c) smaller sized particles from Au-octanethiolate (AuC₈S). The inset shows the size distribution plot. d) Bigger sized particles from Au-octanethiolate (AuC₈S), e) mixed sized particles from Au-octanethiolate (AuC₈S)[no separation], f) self assembled chain of smaller sized Au NCs, g) enlarged TEM image of self assembled chain of smaller sized Au NCs.

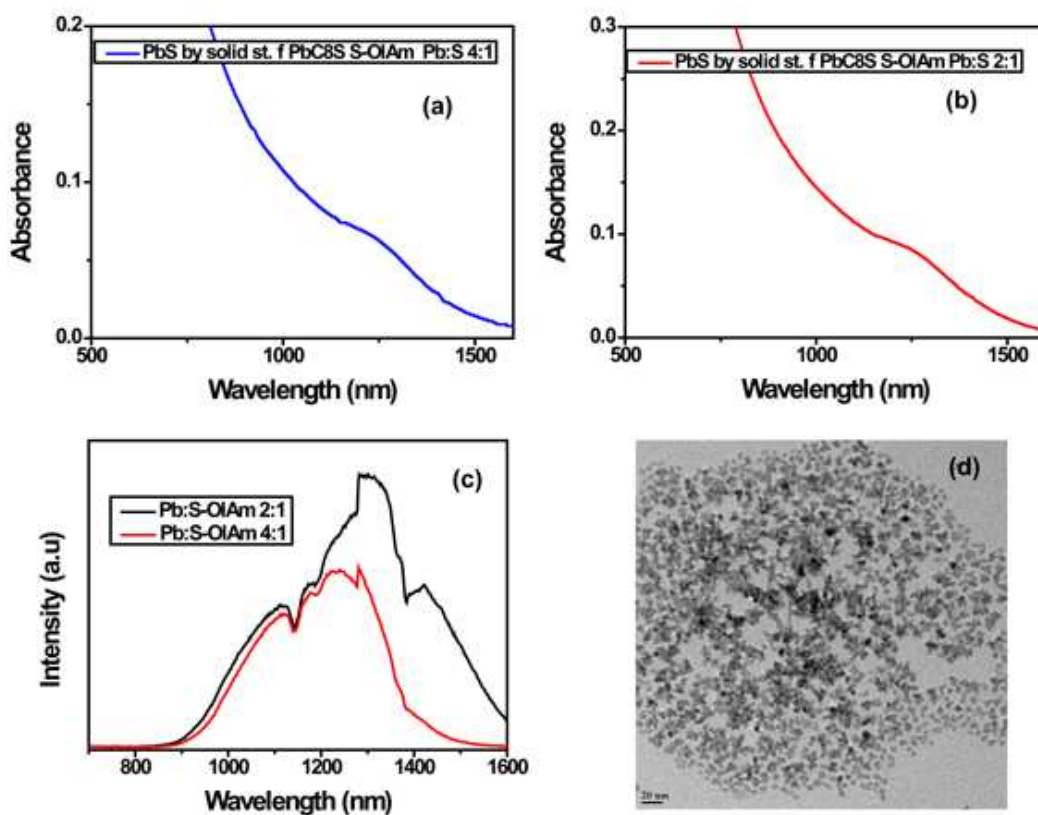


Figure S10: PbS NCs synthesized by solid state using S-OIAM as a sulfur source; NIR absorption spectra of PbS; a) Pb:S-OIAM 4:1, b) Pb:S-OIAM 2:1. c) NIR-emission spectra of PbS NCs, black solid line is for Pb:S-OIAM 2:1 and red solid line for Pb:S-OIAM 4:1. d) TEM image of PbS NCs synthesized by solid state using S-OIAM as a sulfur source.

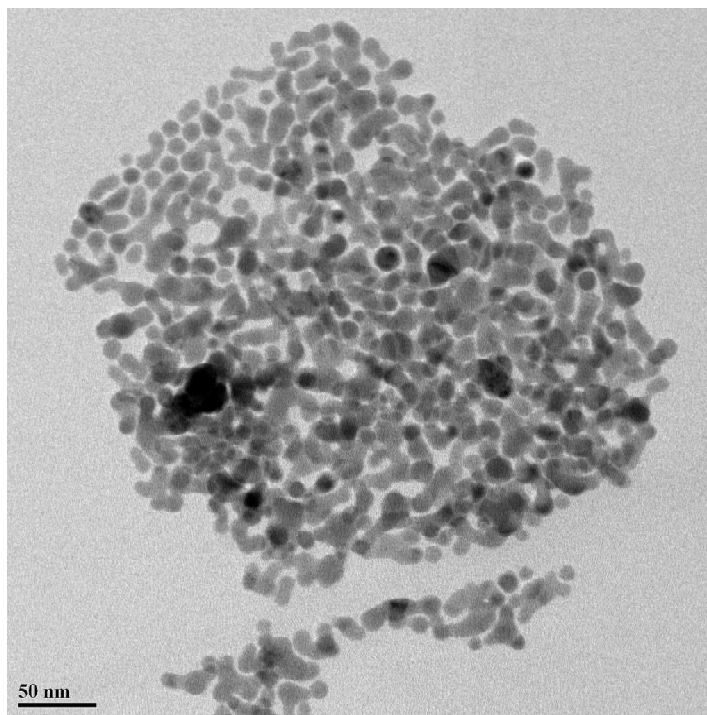


Figure S11: TEM image of Ag_2S NCs synthesized by solid state grinding method using S-OlAm as a sulfur source.

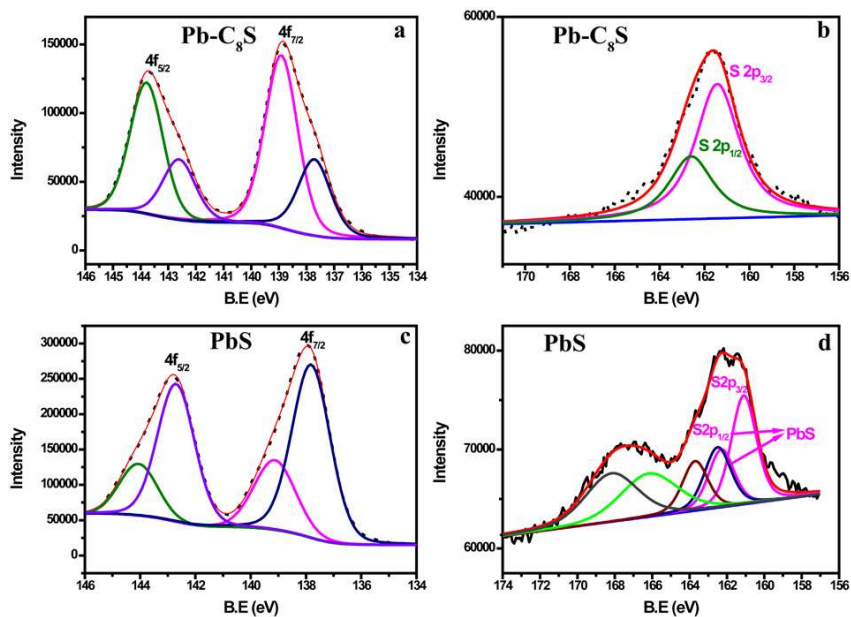
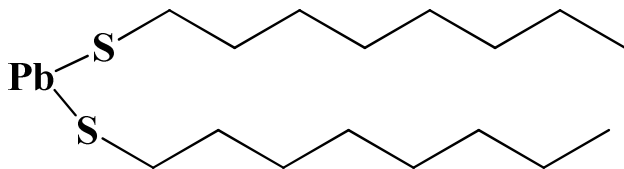


Figure S12: XPS spectra of a) Pb 4f of Pb-C8S; b) S 2p of Pb-C8S; c) Pb 4f of PbS NCs and d) S 2p of PbS NCs.

Synthesis of PbS NCs by solid state using Pb-C₈S as Pb-source and calculation of yield

The empirical formula of Pb-thiolate is Pb-(SC₈H₁₇)₂. The energy dispersive X-ray analysis of Pb-thiolate also reveals the atomic percentage of Pb:S ratio to be ~1:2.



Thus the empirical molecular weight of PbC₈S : ~498.3

0.5 mmol of PbC₈S (~250 mg of PbC₈S) and 0.25 mmol of C₈DTCA (~50 mg) were taken in mortar pestle and ground properly. After 2 min of proper grinding, solvent (toluene) was added to collect the PbS NCs. After centrifugation, supernatant was collected and solid material (unreacted PbC₈S and some of the bigger sized PbS) was discarded. Then the supernatant was precipitated with acetone and cleaned 2-3 times and finally dried sample was redispersed in 3 mL of toluene.

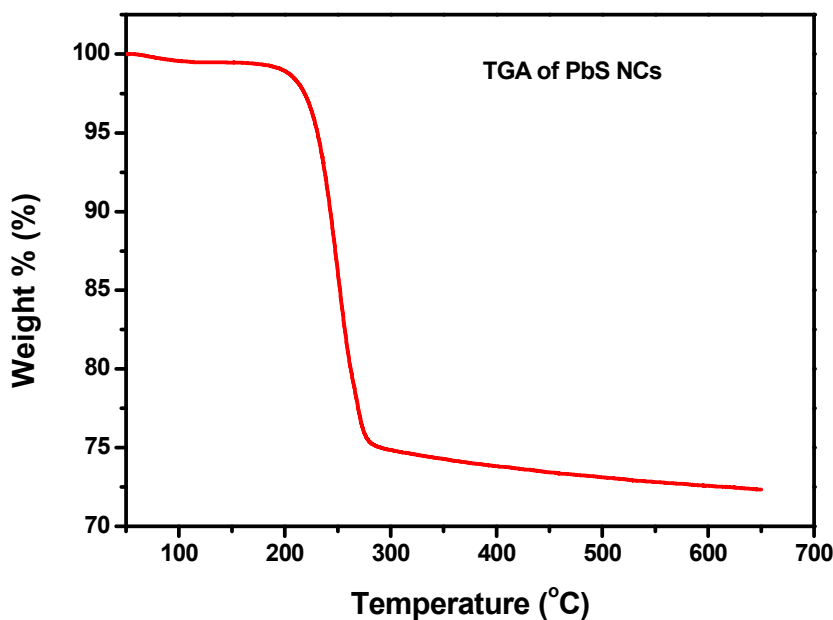


Figure S13: Thermogravimetric analysis (TGA) of thiol PbS NCs.

The thermogravimetric analysis (TGA) of thiol capped PbS NCs shows one major weight loss in the temperature region 170 - 300 °C. We attribute this major mass loss (~24.7 %) event to the desorption of surface-bound ligands. Using a simple mathematical model where the inorganic

cores are assumed to be perfect spheres with the mass density of bulk PbS uniformly covered by organic ligands with known molecular weight, we can estimate the ligand coverage and actual PbS content. For these thiol capped PbS NCs, we estimated from TGA that actual PbS NCs contain ~25 % of ligand and 75 % of PbS.

Here 14.076 mg of dry PbS NCs were taken for TGA analysis. Based on the above arguments the ligand content would be ~3.47 mg in 14.076 mg of PbS NCs. The rest (~10.6 mg) is PbS.

To determine the yield, aliquots (PbS NCs dispersion after clean) were weighed by drying a known volume of NCs dispersion. From this it was determined that ~23 mg of PbS NCs were present in 1 mL dispersion. So, a 3 mL dispersion contains ~70 mg of PbS NCs. This corresponds to ~52.7 mg of PbS in 70 mg of PbS NCs.

From the above calculations, the actual yield (purified end product) of PbS NCs with respect to Pb-C₈S was determined to be 44%. it may be noted that in case of PbS there was always some unreacted Pb-C₈S and some large particles of PbS were also formed (which did not get dispersed). Similarly, the yield of PbS NCs which were prepared in 10 mmol batch was determined to be ~35 %.

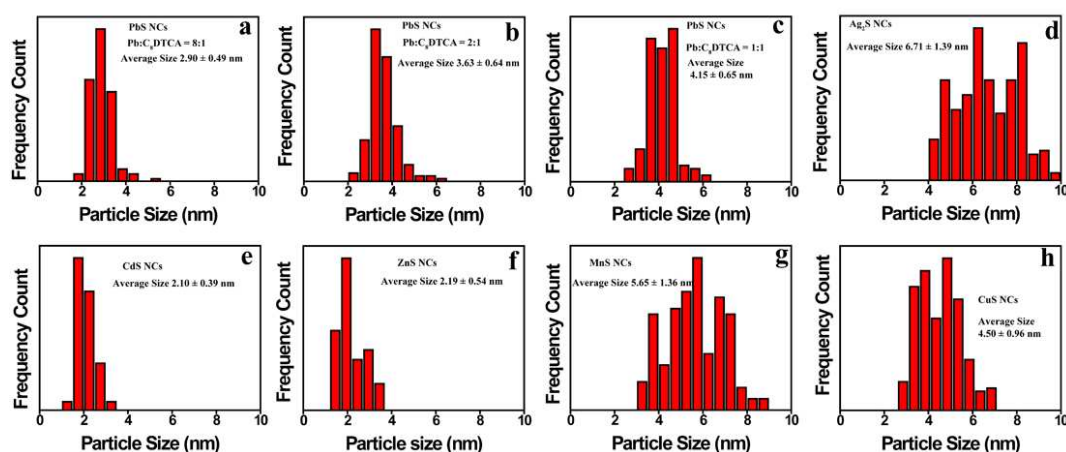


Figure S14: Size distribution plot of different metal sulfide NCs synthesized by solid state method. PbS NCs synthesized at different Pb: C₈DTCA ratio; a) PbS NCs at 8:1, b) PbS NCs at 2:1, c) PbS NCs at 1:1. d) Ag₂S NCs, e) CdS NCs, f) ZnS NCs, g) MnS NCs, h) CuS NCs.

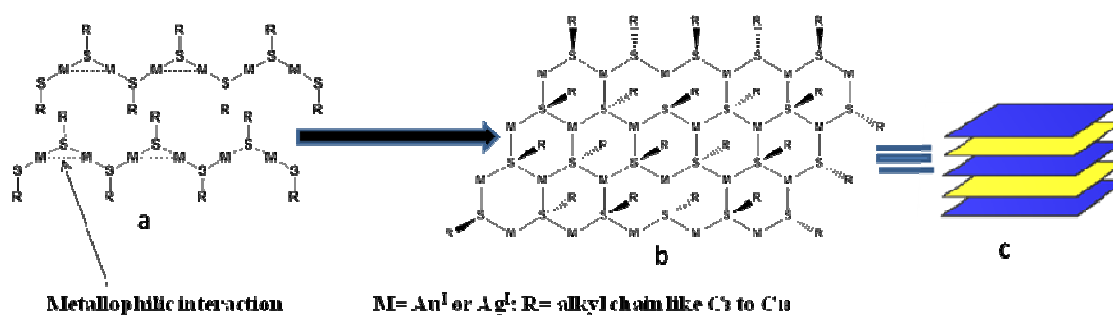


Figure S15: Primary structure of a metal(I) thiolate (a) bilayer structure of metal thiolates, showing that the metal atoms are placed very close to each other, stabilized by metallophilic interactions; (b) Top view showing the two-dimensional arrangement; (c) Sheets like morphology formed .

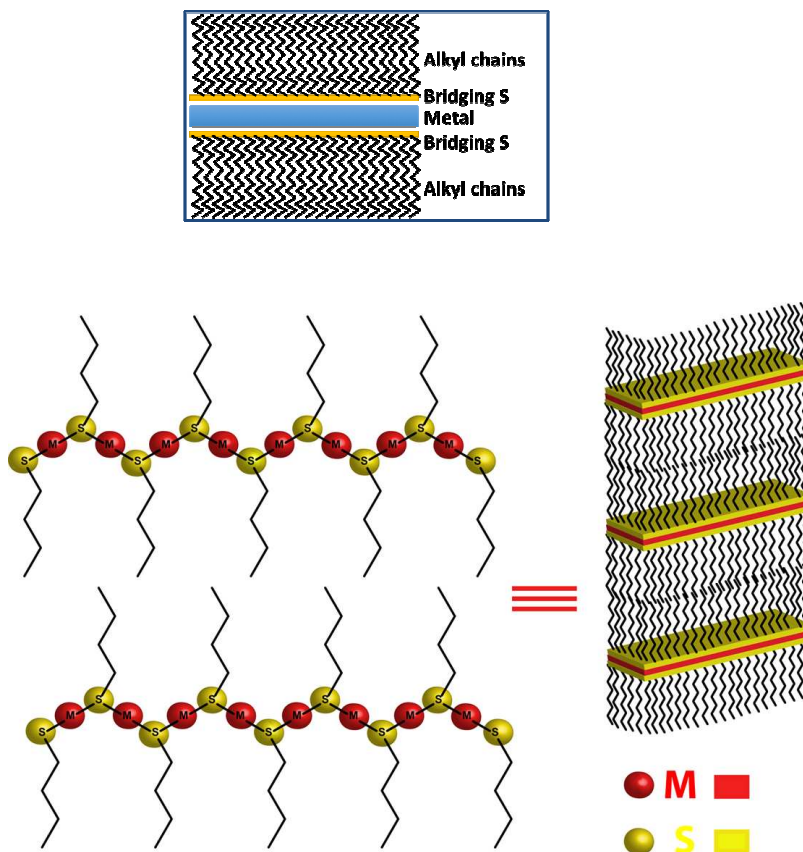


Figure S16: Cross sectional view of the layered structure of metal-thiolates.

^1H NMR spectrum of octyl dithiocarbamic acid. ^1H NMR (200 MHz, Chloroform- d) δ 5.44 (s, 2H, N-H, S-H), 3.60 - 3.48 (m, 1H), 3.02 (t, $J = 7.3$ Hz, 1H), 1.70 - 1.59 (m, 2H), 1.27 (m, 10H), 0.88 (t, $J = 6.1$ Hz, 3H).

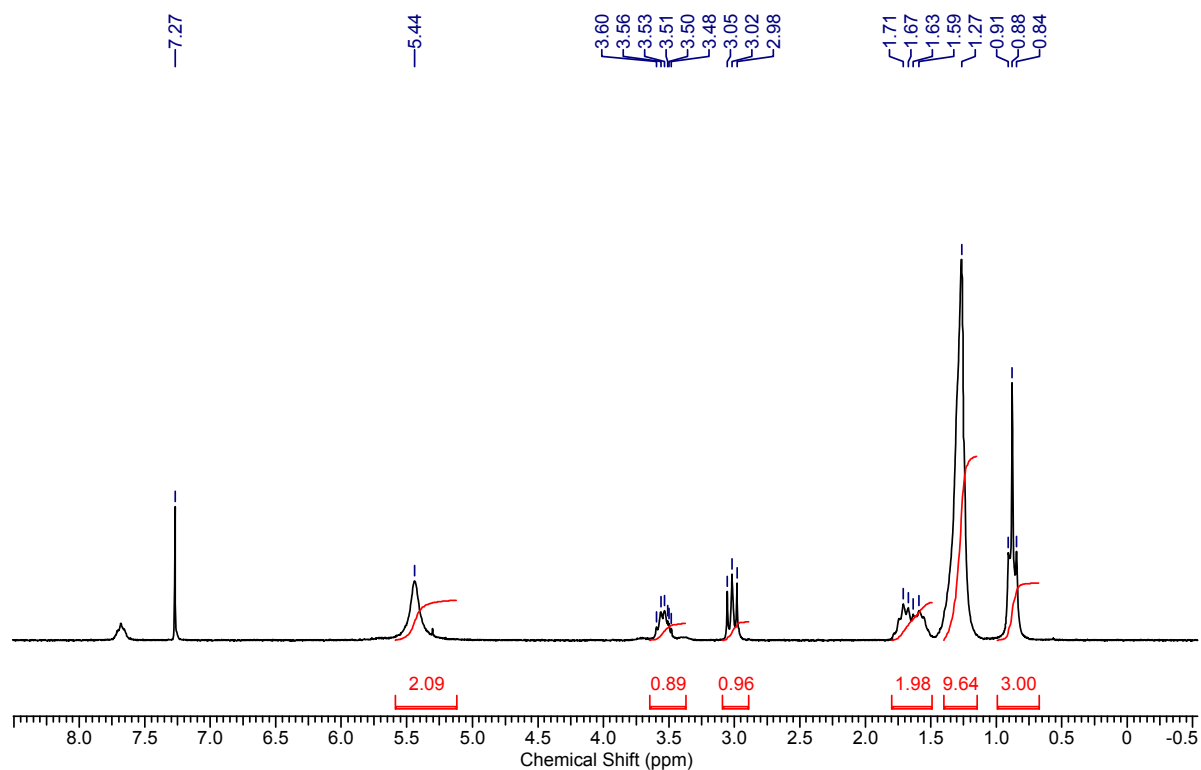


Figure S17: ^1H NMR spectrum of octyl dithiocarbamic acid.

Octyl dithiocarbamic acid was taken in mortar-pestle and was ground for 15-20 min in open air atmosphere at 25 °C. The NMR spectra shown below indicates that it does not undergo any change under these grinding conditions.

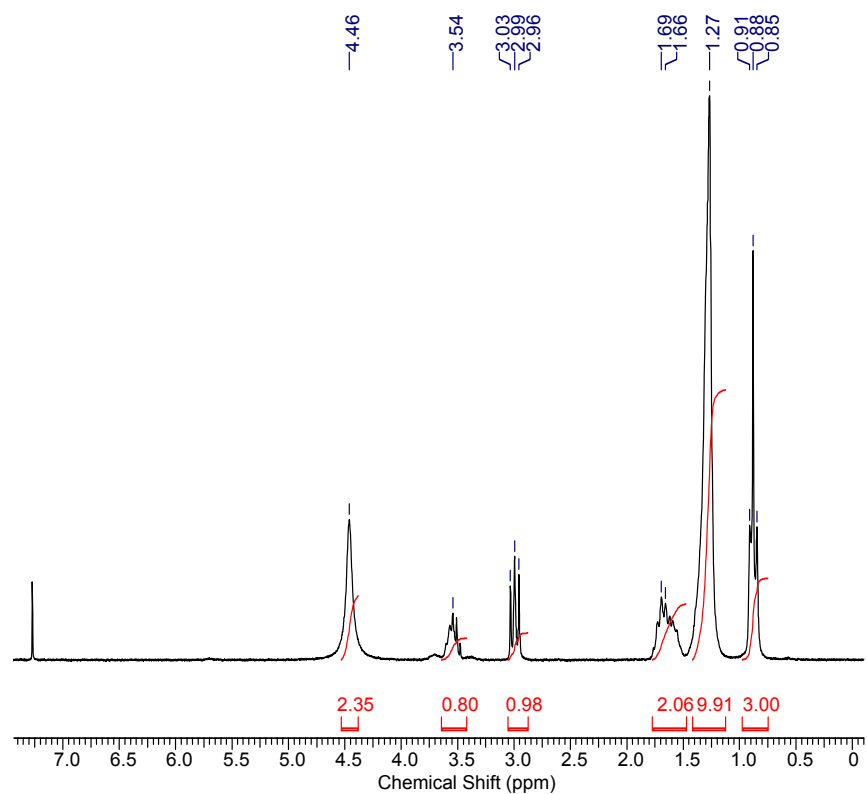


Figure S18: ^1H NMR spectrum of octyl dithiocarbamic acid, after it was ground for 15 min at room temperature (25 °C).

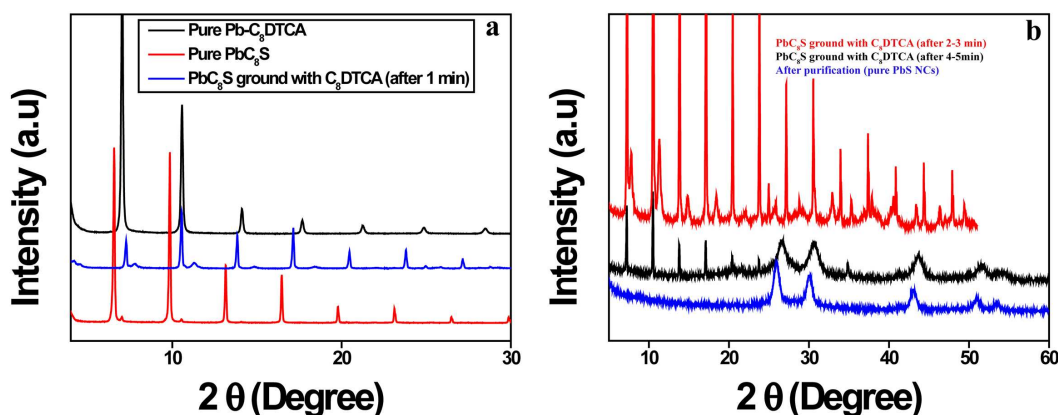


Figure S19: PXRD data of (a) Pure Pb-C₈DTCA complex prepared at room temp. (black), pure Pb-octanethiolate (red) and solid state mixing of Pb-octanethiolate and C₈DTCA (after 1 min, solid blue line). (b) Pb-octanethiolate mixed with C₈DTCA by solid state, two different set of lamellar peaks appeared after 1-3 min (red), black solid line represent after 4-5 min of solid state grinding (before separation) and blue solid line represent after separation (pure PbS NCs).

Both, the pure Pb-complex (Pb-C₈S or Pb-C₈DTCA), showed lamellar peaks in PXRD pattern and when Pb-C₈S was ground with highly reactive bidentate ligand (C₈DTCA), first Pb-C₈DTCA complex formed. This is confirmed by the appearance of two set of lamellar peaks in the PXRD pattern as showed in Figure S19a (blue) and Figure S19b. As we continued grinding, the new set of lamellar peaks shifted towards the pure Pb-C₈DTCA peaks indicating more of Pb-C₈DTCA complex forming with concomitant release of alkane thiolate (⁻SC₈H₁₇) and slow formation of PbS.

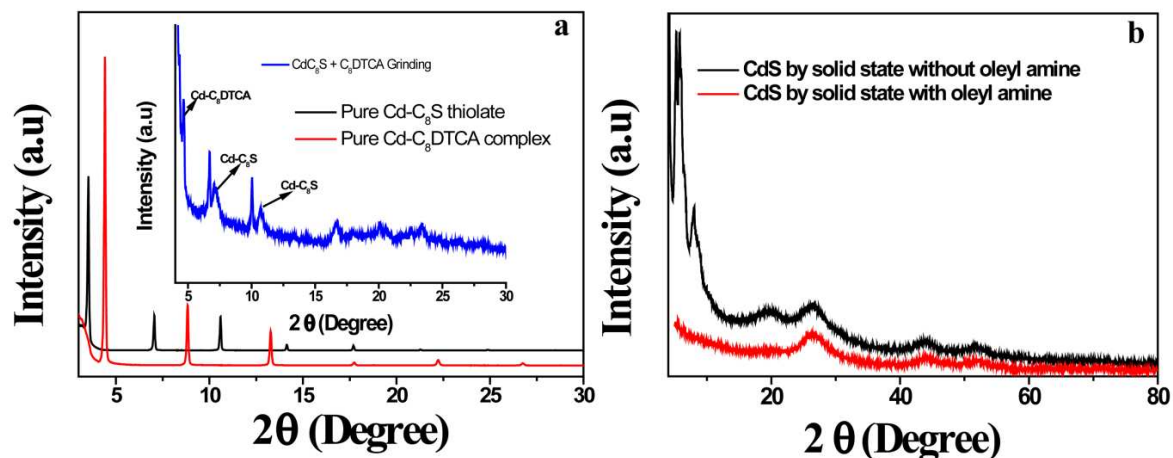


Figure S20: PXRD of a) pure Cd-C₈S thiolate (black solid line); pure Cd-C₈DTCA complex (red solid line) and Cd-C₈S thiolate ground with C₈DTCA (blue solid line). It can be noticed that in the blue curve both of the Cd-C₈S and Cd-C₈DTCA peaks are present indicating after grinding with C₈DTCA, Cd-C₈S converts to Cd-C₈DTCA complex. b) CdS prepared by solid state using only C₈DTCA as sulfur source. Black solid line; Cd-octanethiolate ground with C₈DTCA where CdS formed as well as highly stable Cd-C₈DTCA complex also formed which is very difficult to separate from CdS. Here catalytic amount of oleyl amine helps to decompose the Cd-C₈DTCA complex fully. Red line represents PXRD of CdS synthesized by using C₈DTCA-OIAm as a sulfur source.

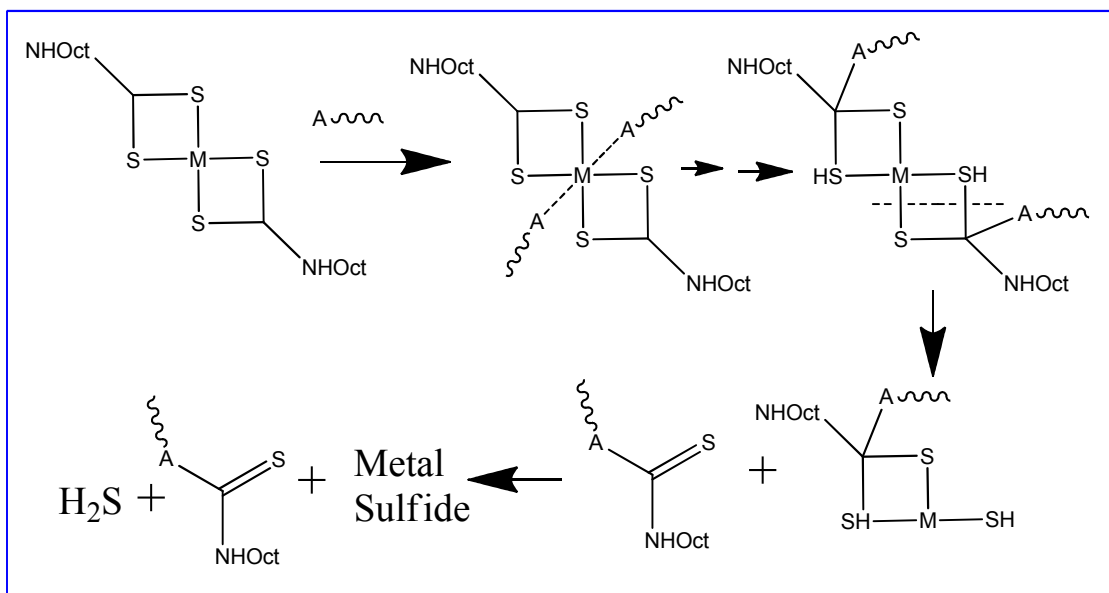
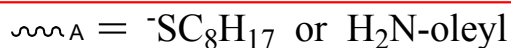
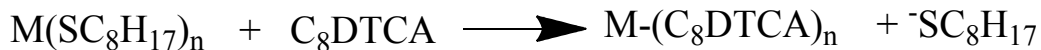


Figure S21: Probable reaction mechanism of metal sulfide formation by solid state grinding method using only C_8DTCA or $C_8DTCA\text{-OIAm}$ as a sulfur source.

The grinding of metal thiolate with C_8DTCA or $C_8DTCA\text{-OIAm}$, the stronger bidentate ligand (C_8DTCA) first react with metal-thiolate to form metal- C_8DTCA complex (clear change in PXRD pattern showed in Figure S19 and S20) with concomitant release of alkanethiolate (SC_8H_{17}). Here released alkane thiolate (SC_8H_{17}) or oleyl amine present in the medium (when $C_8DTCA\text{-OIAm}$ used as sulfur source) helps to decompose the metal- C_8DTCA complex to metal sulfide (probable reaction mechanism showed above in Figure S21). Adapted from ref. 2-3.

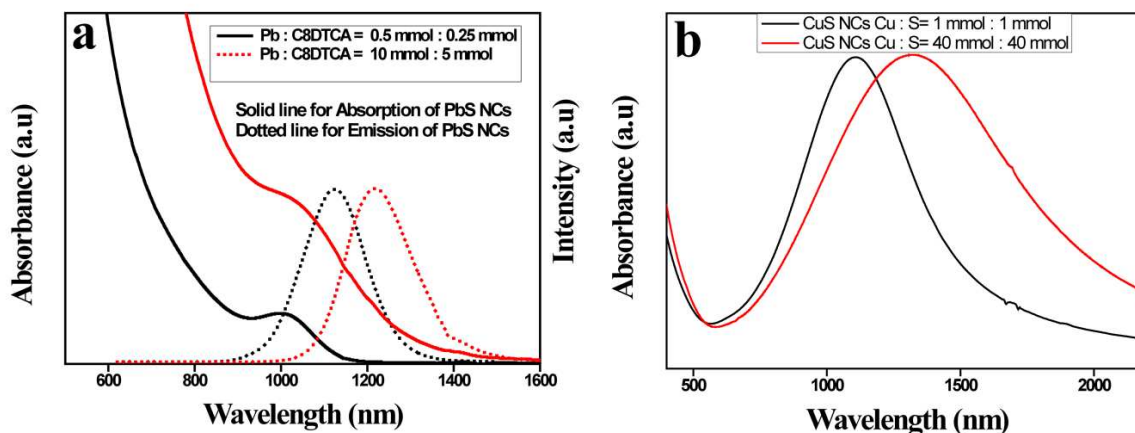


Figure S22: Scalability of metal sulfide NC synthesis by solid state grinding method. a) absorbance (solid line) and emission spectra (dotted line) of PbS NCs synthesized at different ~mmol scale. Black line represent 0.5 mmol of Pb-precursors and red line is the spectrum recorded from 10 mmol batch. b) absorbance spectra of CuS NCs synthesized at different ~mmol scale. Black solid line represents 1 mmol of Cu-precursors and red solid line is for 40 mmol batch.

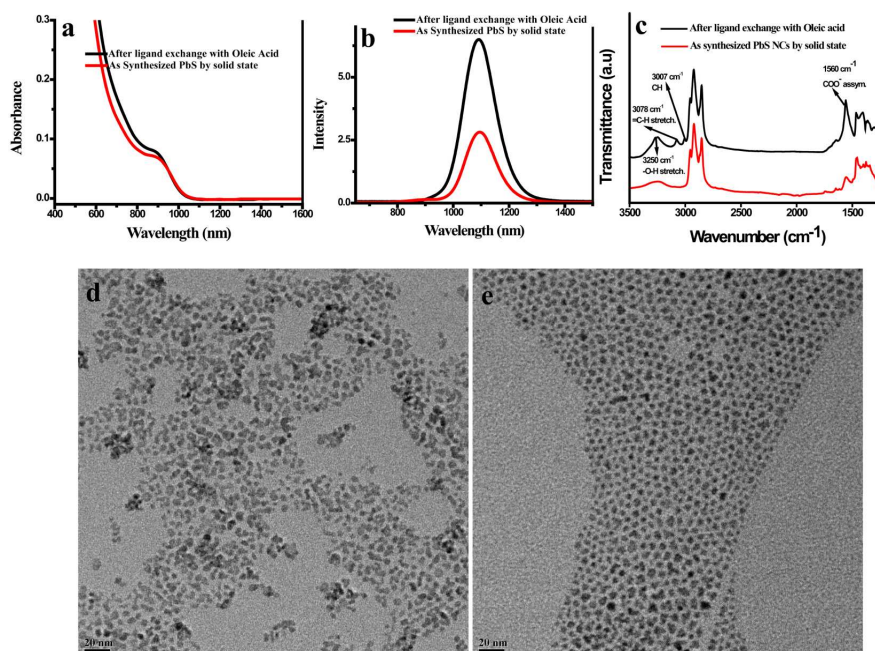


Figure S23: PbS synthesized by solid state. a) Absorption spectra of PbS, b) NIR-Emission spectra of PbS; before ligand exchange (as prepared red solid line) and after ligand exchange with oleic acid (black solid line). c) ATR FTIR spectra of PbS NCs; as synthesized (thiol capped) showed in red solid line and after ligand exchange with oleic acid showed in black solid line. TEM images of PbS synthesized by solid state, d) as prepared (before ligand exchange) and e) after ligand exchange with oleic acid.

As synthesized PbS NCs are basically octane thiol capped. The peaks at wave numbers 2955 cm^{-1} , 2920 and 2652 cm^{-1} are assigned as CH_3 stretch, asymmetric and symmetric CH_2 stretching frequencies respectively (solid red line) of these molecules. After ligand exchange with oleic acid all peaks related to CH_3 stretching and CH_2 stretching (symmetric and asymmetric) are present (showed in blue box) and new set of peaks appear at 1560 , 3007 and 3078 cm^{-1} which can be undoubtedly ascribed to the asymmetric stretching vibration of COO^- (from bounded oleic acid) and stretching vibration (for cis and trans) of CH ($-\text{C}=\text{C}-\text{H}$) respectively. FTIR analysis thus confirms that the as synthesized PbS NCs are thiol capped and ligand exchange with oleic acid is successful.

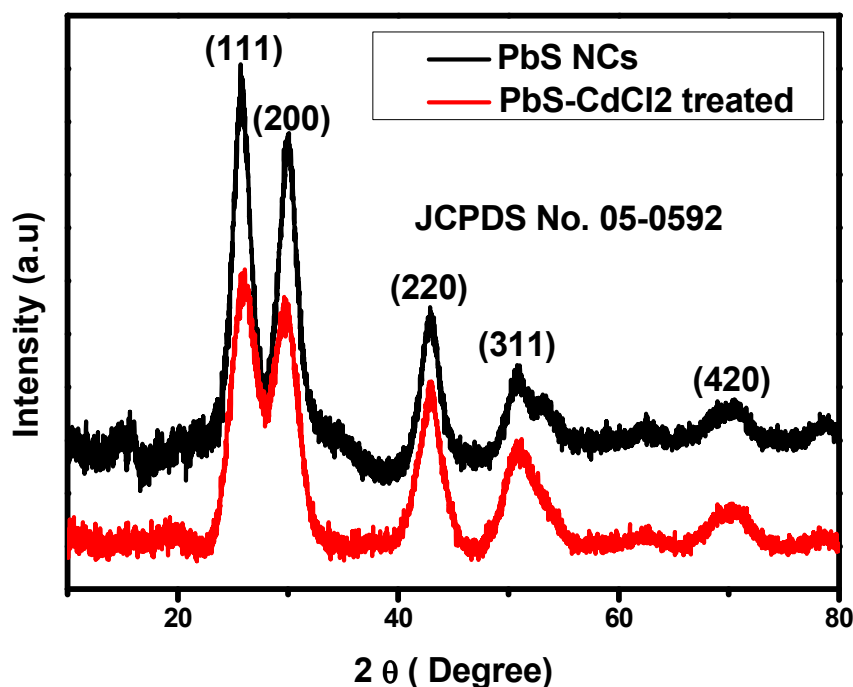


Figure S24: PXRD of PbS NCs synthesized by solid state using C_8DTCA as a sulfur source (black) and after CdCl_2 surface passivation (red).

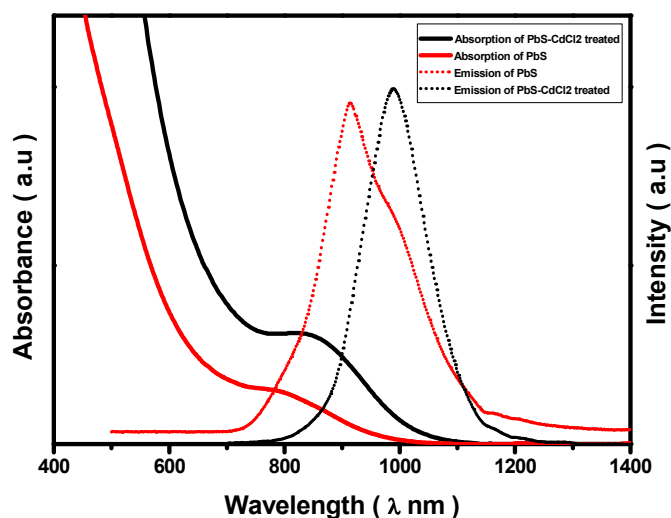


Figure S25: NIR UV-Vis spectra and PL spectra of PbS NCs synthesized by solid state (Pb:C₈DTCA 2:1). Solid line for NIR- absorption spectra of PbS; as prepared (red solid line) and after CdCl₂ passivation (black solid line). Dotted line for NIR-Emission spectra of PbS; as prepared (red dotted line) and after CdCl₂ passivation (black dotted line).

References

1. Yuan, M.; Kemp, K. W.; Thon, S. M.; Kim, J. Y.; Chou, K. W.; Amassian, A.; Sargent, E. H., High-performance quantum-dot solids via elemental sulfur synthesis. *Adv. Mater.* **2014**, 26, 3513-3519.
2. Jung, Y. K.; Kim, J. I.; Lee, J. K. Thermal decomposition mechanism of single-molecule precursors forming metal sulfide nanoparticles. *J. Am. Chem. Soc.* **2009**, 132, 178-184.
3. Bera, A.; Mandal, D.; Goswami, P. N.; Rath, A. K.; Prasad, B. L., A generic and scalable method for the preparation of monodispersed metal sulfide nanocrystals with tunable optical properties. *Langmuir* **2018**, 34, 5788-5797.