Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Exchange Equilibria of Carboxylate-Terminated Ligands at PbS Nanocrystal Surfaces

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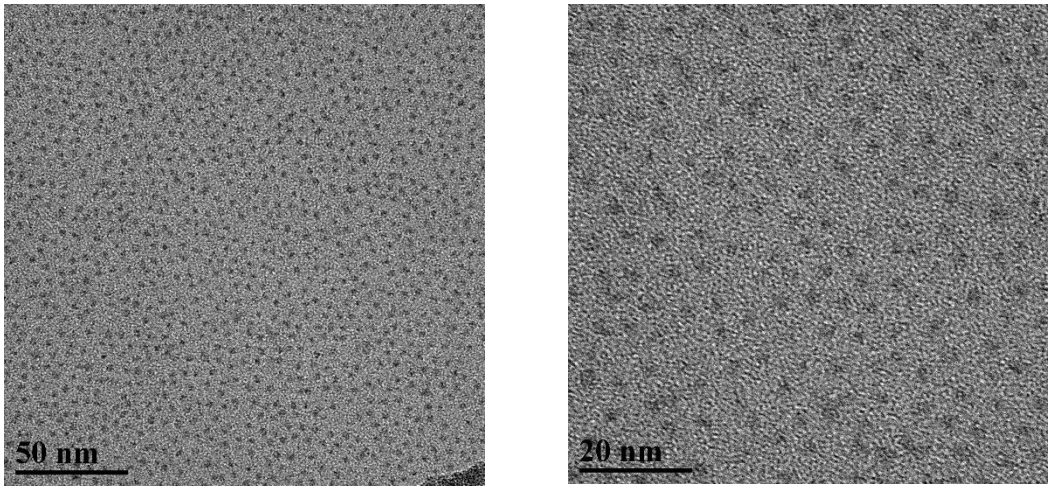
SI-1 Characterization of PbS nanocrystals

A.



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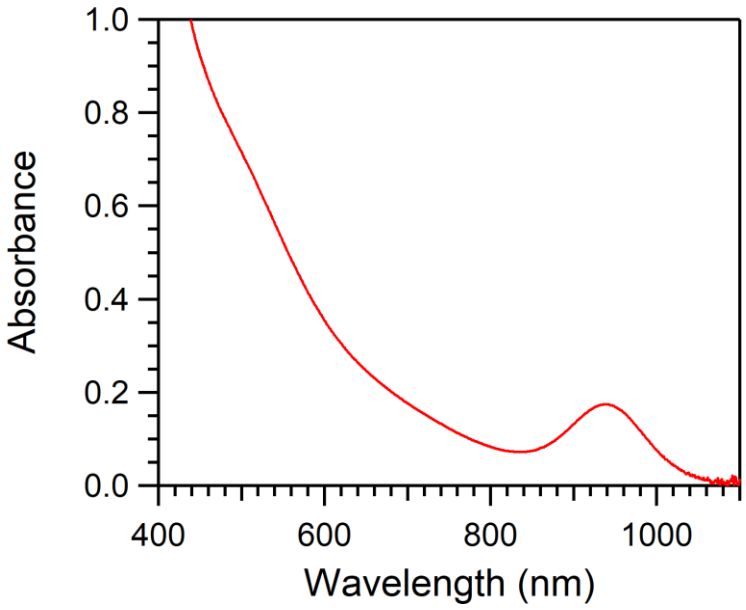
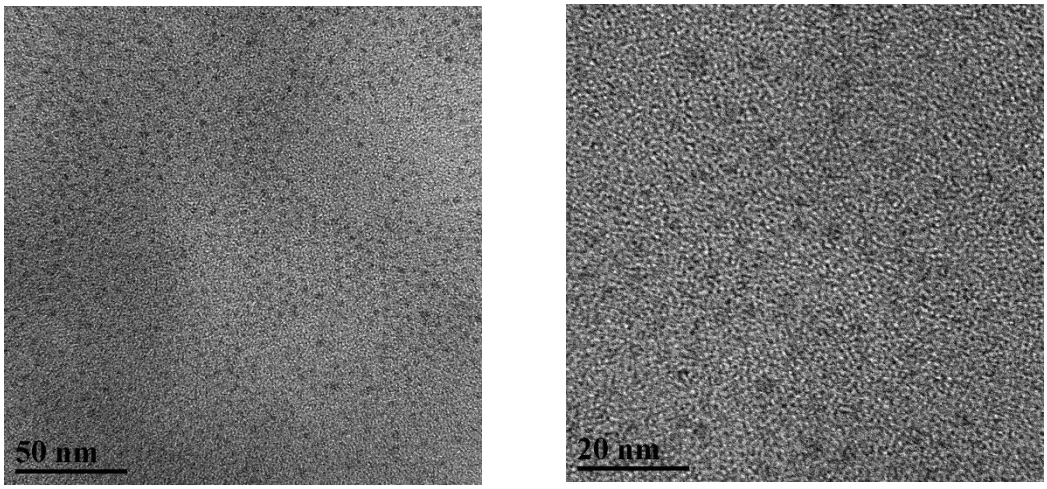


Figure S1. A) Representative TEM images of O-PbS QDs. B) UV-vis absorbance spectra of O-PbS (2.33 μM) in benzene.

A.



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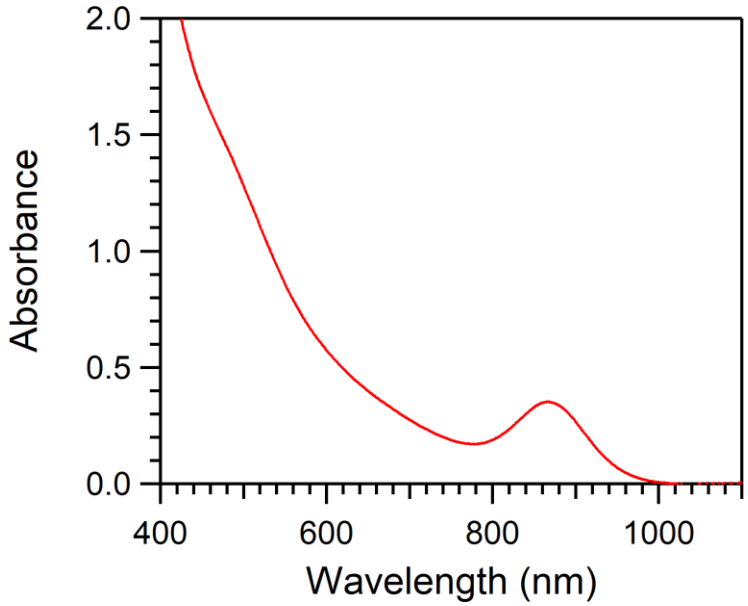

Figure S2. A) Representative TEM images of HS-PbS QDs. B) UV-vis absorbance spectra of HS-PbS (25 μM) in benzene.

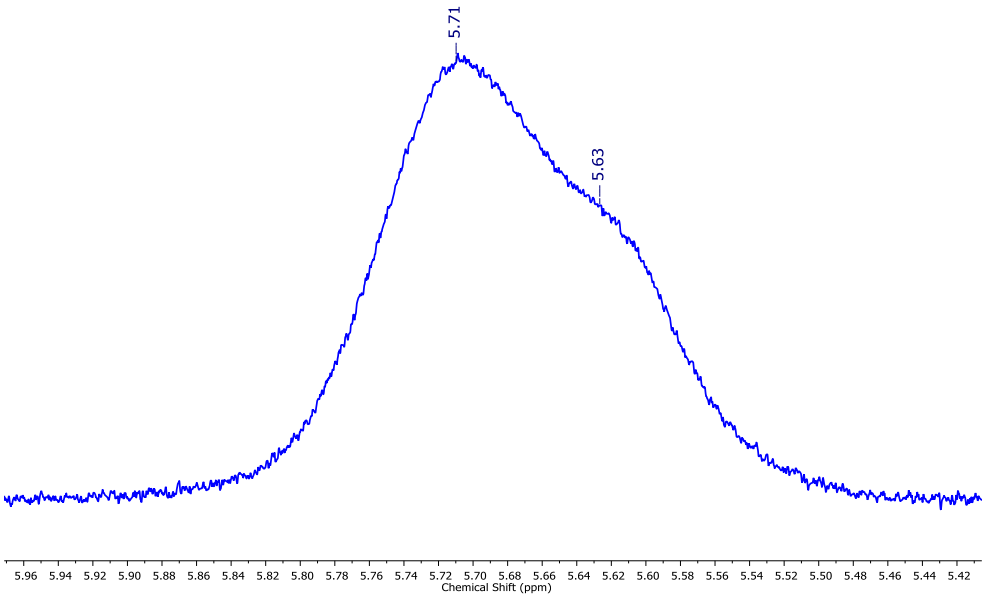

Figure S3. 600 MHz ^{1}H NMR spectrum of 50 μM HS-PbS in benzene-d_6, centered on the alkenyl resonances (H_{a1},H_{a2}) of the native oleate ligands.

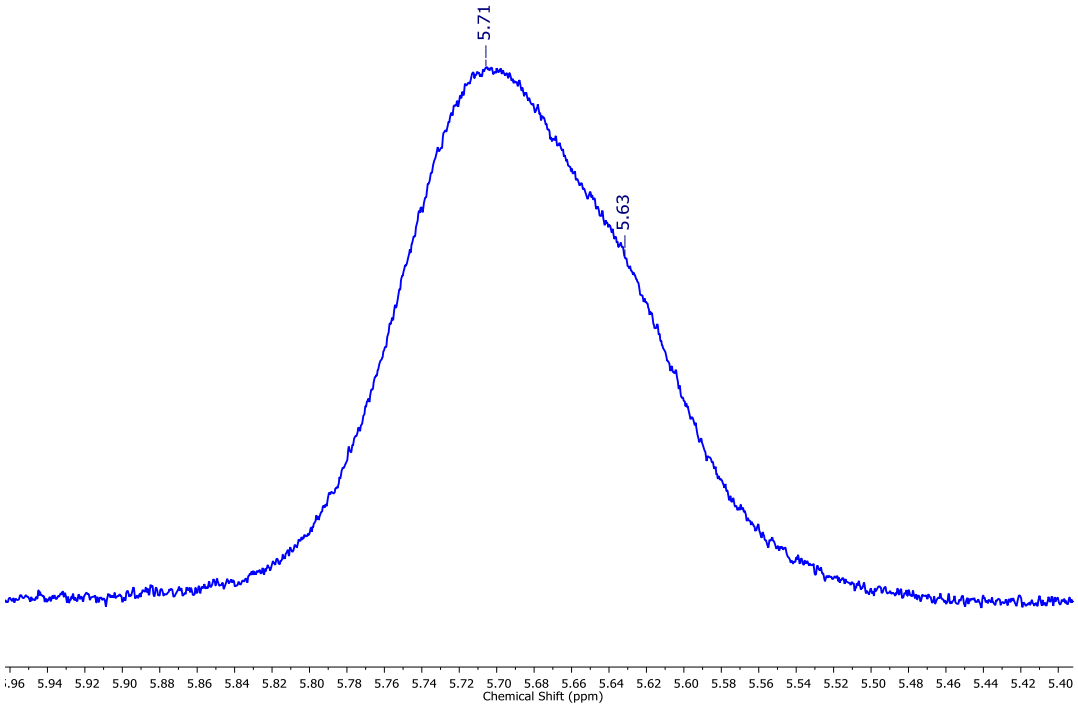

Figure S4. 600 MHz ^{1}H NMR spectrum of 50 μM O-PbS in benzene-d_6, centered on the alkenyl resonances (H_{a1},H_{a2}) of the native oleate ligands.

Table S1. Oleate ligand coverage for independently prepared 50 μM samples of O-PbS and HS-PbS QDs (each trial contained 10 μL of ferrocene standard).

QD Sample	Trial	Oleates/nm^2
O-PbS	**1**	**3.21**
	2	**2.91**
	3	**3.06**
	4	**2.67**
	5	**2.75**
	6	**2.64**
	Average ± SD	**2.87 ± 0.23**
HS-PbS	**1**	**3.45**
	2	**2.95**
	3	**3.04**
	4	**3.04**
	5	**2.58**
	6	**2.77**
	7	**2.34**
	8	**3.03**
	9	**3.10**
	Average ± SD	**2.92 ± 0.32**

Table S2. Literature comparison of native oleate density on PbS QDs.

Author	QD diameter (nm)	Ligand density (oleates/nm^2)	Synthetic Method	Reference
Weiss	3.2	6.7	Hines-Scholes[1]	[2]
Owen	3.4	5.7	Owen[3]	[4]
Owen	6.5	2.9	Owen[3]	[4]
Beard	3.5	3.2	Owen[3]	[5]
Beard	3.2	3.1	Owen[3]	[6]
Hens	5.2	2.6	Cademartiri*[7]	[8]
Hens	5.5	3.0	Cademartiri[7]	[8]
Hens	7.1	3.5	Cademartiri[7]	[8]

*The synthetic procedure reported by Cademartiri and coworkers utilizes a mixture of oleylamine and $PbCl_2$ as the lead precursor, to which a stock solution of sulfur dissolved in oleylamine is injected at the desired temperature.[7] Moreels et al. reported that the PbS QDs prepared by the Cademartiri synthetic procedure lost solubility during purification after one precipitation cycle. Additional oleic acid was added to the solution of QDs in toluene to facilitate ligand exchange.[8] Excess oleic acid was removed via precipitation and centrifugation, then ligand exchange was performed once more to complete the

ligand exchange. Several precipitation steps and subsequent NMR characterization confirmed that the PbS QDs were capped with oleate ligands.

Table S3. Ligand coverage* (oleates/nm^2) of PbS QD samples at different QD concentrations.

Sample	100 μM	75 μM	50 μM	33 μM
O-PbS	2.31 ± 0.01	2.28 ± 0.16	2.29 ± 0.03	2.30 ± 0.11
HS-PbS	2.71 ± 0.13	2.65 ± 0.34	2.65 ± 0.22	-

*Each set of data was normalized to conserve the total integrated area of the alkene resonance for bound and free oleic acid.

For independently prepared 50 μM samples of PbS QDs, the surface oleate ligand density was determined to be 2.87 ± 0.23 oleates/nm^2 for O-PbS QDs and 2.92 ± 0.32 oleates/nm^2 for HS-PbS QDs. There is a clear discrepancy between the data reported in Table S1 and the values in Table S3 for the dilution study, with higher ligand densities observed in our independently prepared 50 μM values. Given that the ligand coverage is consistent throughout the dilution experiment, we attribute discrepancies to a systematic error with the micropipettes utilized in dilution studies. The most likely source of error stems from the larger volume of PbS QD stock solution that must be pipetted into solvent for the dilution study. Employing a larger volume increases the likelihood that some QDs are not transferred to the NMR tube, leading to a consistently lower integration for the QD-bound OA signal relative to the ferrocene standard. The discrepancies in initial oleate coverage will not have a major impact on the derived K_{eq} values as the data from several independent 50 μM samples were used to calculate equilibrium constants. This ensures that inconsistencies will be averaged out and accounted for in the standard deviation.

SI-2 Probing the mechanism of ligand exchange

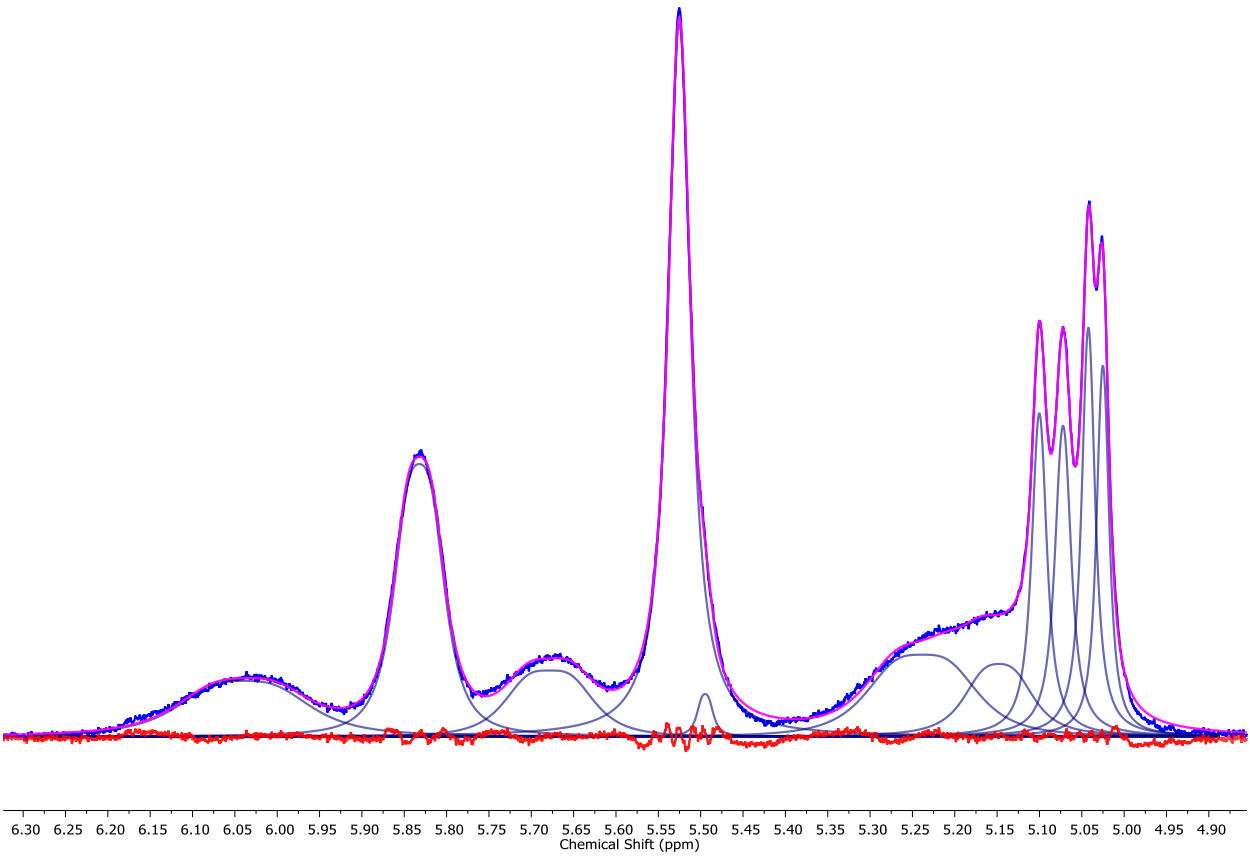

Figure S5. Fitting of bound and free OA and UDA peaks in a 600 MHz ^{1}H NMR spectrum after addition of 150 equiv. UDA in benzene-d_6. The blue trace is the sample spectrum, the magenta trace is the sum of the fits, and the red trace is the fit residual.

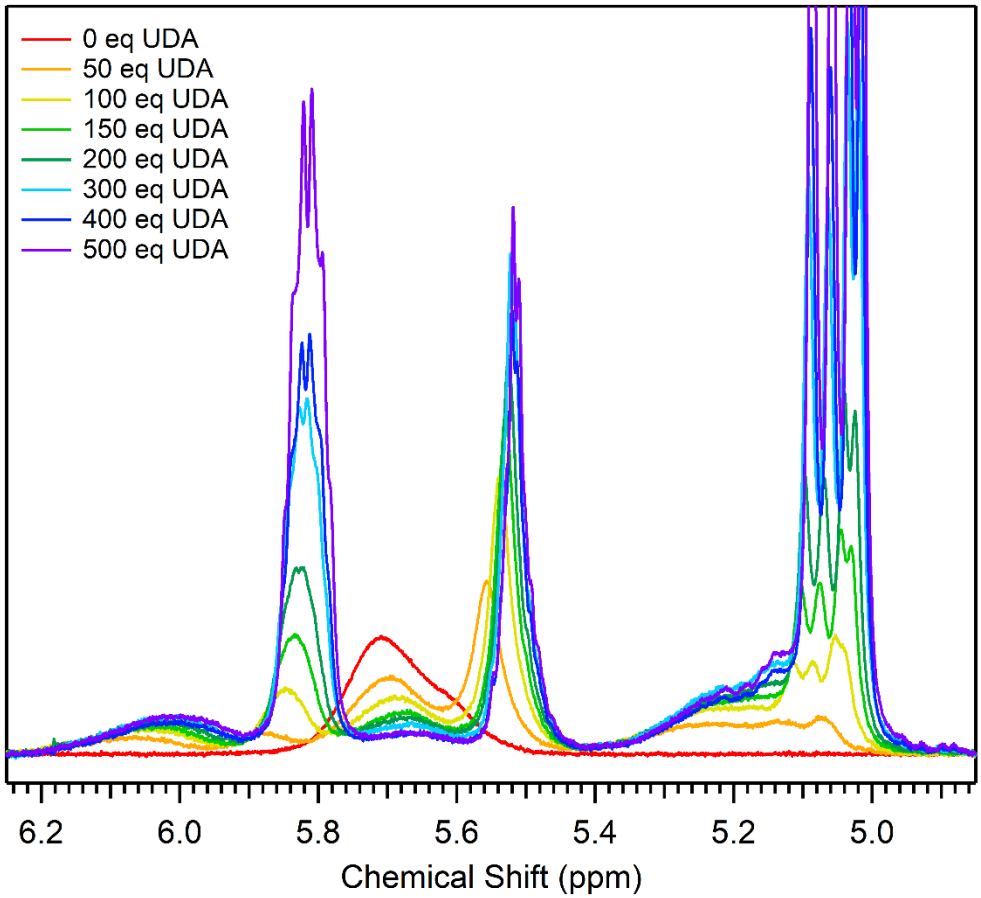

Figure S6. 600 MHz ^{1}H NMR spectra of 50 μM HS-PbS QDs (2.78 nm) upon titration of 500 equivalents undec-10-enoic acid (UDA) in benzene-d_6.

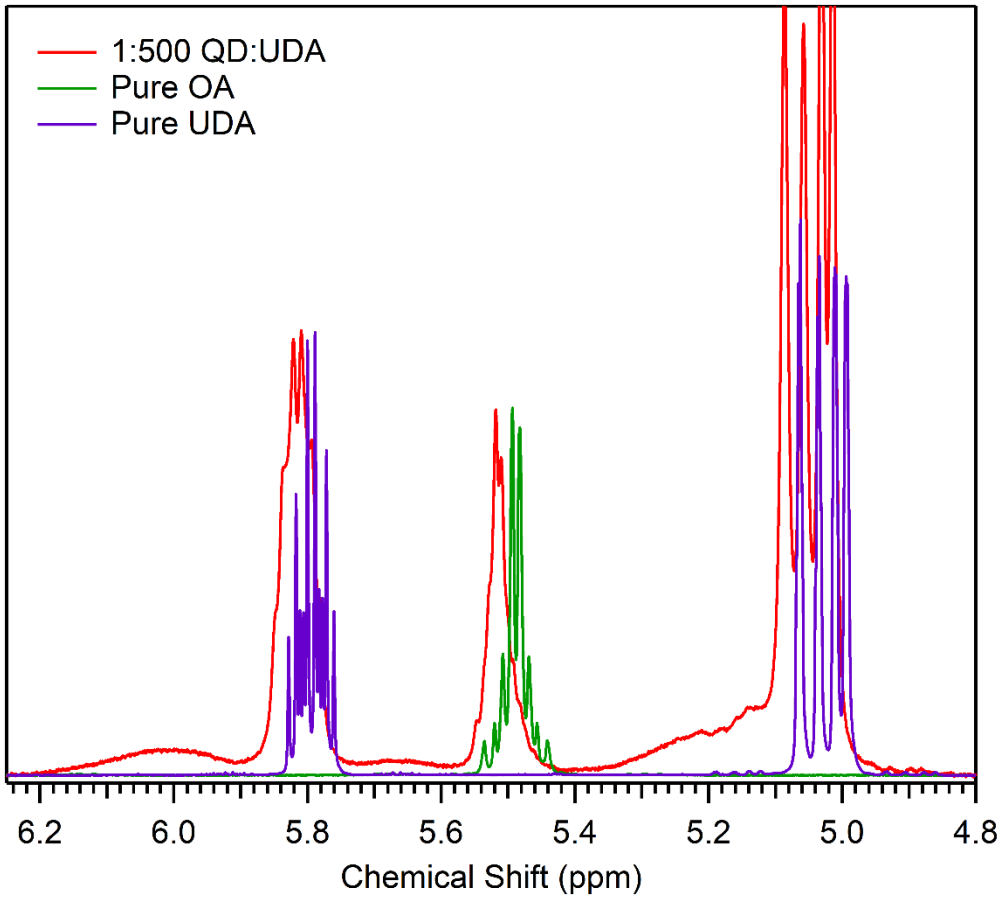

Figure S7. 600 MHz ^{1}H NMR spectra of pure OA (green), pure UDA (purple), and 1:500 QD:UDA for HS-PbS QDs (red). The chemical shift, splitting, and resolution of peaks for the freely diffusing OA and UDA in the 1:500 QD:UDA spectrum become increasingly similar to that of pure OA and pure UDA, respectively, at higher UDA equivalents because the mole fraction of each species freely diffusing in solution represents a greater proportion than the mole fraction entangled within the ligand shell.

Table S4. Equilibrium constants (K_{eq}), exchange ratios (1 free OA = X bound UDA), and percent change of ligand coverage relative to 0 equivalents UDA (Lig. %Δ) for O-PbS QDs.

	Trial 1			Trial 2			Trial 3			Trial 4			Trial 5		
Eq. UDA	K_{eq}	**X**	**Lig. %Δ**	K_{eq}	**X**	**Lig. %Δ**	K_{eq}	**X**	**Lig. %Δ**	K_{eq}	**X**	**Lig. %Δ**	K_{eq}	**X**	**Lig. %Δ**
0			**0**			**0**			**0**			**0**			**0**
50										**3.99**	**1.75**	**24.7**	**2.49**	**1.23**	**22.1**
60							**2.28**	**1.31**	**15.7**						
80	**2.01**	**1.04**	**10.8**	**2.40**	**1.04**	**10.7**	**1.50**	**1.27**	**18.3**						
100							**2.14**	**1.07**	**12.2**	**1.66**	**1.38**	**19.7**	**1.79**	**1.01**	**7.02**
120	**1.86**	**1.01**	**7.19**	**1.97**	**1.05**	**5.86**	**2.15**	**1.31**	**26.1**						
140							**2.28**	**1.21**	**14.3**						
150										**1.96**	**1.27**	**11.0**	**2.36**	**1.25**	**13.8**
160	**2.01**	**0.96**	**-0.13**	**2.22**	**1.10**	**6.39**	**2.20**	**1.18**	**9.12**						
200							**2.47**	**1.12**	**15.3**	**2.54**	**1.49**	**24.2**	**2.58**	**1.18**	**11.8**
240	**2.35**	**1.10**	**12.8**	**2.44**	**1.24**	**15.4**									
250													**3.28**	**1.12**	**8.18**
300										**2.86**	**1.39**	**16.4**	**1.64**	**1.19**	**9.08**
320	**2.74**	**1.00**	**6.46**	**1.90**	**1.16**	**7.17**									
400										**1.98**	**1.55**	**32.2**	**1.98**	**1.23**	**18.9**
500										**1.65**	**1.35**	**24.3**	**1.81**	**1.16**	**17.6**

The average K_{eq} value reported in the main text for O-PbS QDs (2.23 ± 0.50) is the mean of all individual K_{eq} values from each titration point in this table weighted equally with a sample standard deviation. The average exchange ratio for O-PbS QDs is 1:1.21 ± 0.17 freeOA:boundUDA.

Table S5. Equilibrium constants (K_{eq}), exchange ratios (1 free OA = X bound UDA), and percent change of ligand coverage relative to 0 equivalents UDA (Lig. %Δ) for HS-PbS QDs.

	Trial 1			Trial 2			Trial 3			Trial 4		
Eq. UDA	K_{eq}	**X**	**Lig. %Δ**	K_{eq}	**X**	**Lig. %Δ**	K_{eq}	**X**	**Lig. %Δ**	K_{eq}	**X**	**Lig. %Δ**
0			**0**			**0**			**0**			**0**
50							**1.63**	**0.85**	**2.65**	**1.70**	**1.12**	**16.9**
60	**1.44**	**1.22**	**24.1**	**2.15**	**1.54**	**21.9**						
100	**1.88**	**1.19**	**9.55**	**1.67**	**1.47**	**36.9**	**2.20**	**0.95**	**-3.99**	**2.56**	**1.12**	**8.55**
150							**2.16**	**0.89**	**-8.02**	**2.45**	**1.06**	**6.31**
160	**2.41**	**1.25**	**13.7**	**2.52**	**1.50**	**32.2**						
200							**2.43**	**0.93**	**-7.93**	**1.97**	**1.20**	**16.9**
240	**2.37**	**1.16**	**14.4**	**2.91**	**0.99**	**13.7**						
250							**2.71**	**1.06**	**3.25**	**1.52**	**1.21**	**26.8**
300							**2.23**	**0.99**	**-6.13**	**1.86**	**1.01**	**14.3**
400	**2.04**	**1.28**	**16.5**	**2.12**	**1.01**	**-1.43**	**2.82**	**1.04**	**10.3**	**1.50**	**1.23**	**30.3**
500							**2.69**	**1.01**	**12.7**	**1.70**	**0.89**	**-4.65**
600							**2.14**	**0.92**	**-9.04**	**2.14**	**0.92**	**-1.84**

	Trial 5			Trial 6			Trial 7		
Eq. UDA	K_{eq}	**X**	**Lig. %Δ**	K_{eq}	**X**	**Lig. %Δ**	K_{eq}	**X**	**Lig. %Δ**
0			**0**			**0**			**0**
50	**1.52**	**1.12**	**9.52**	**1.91**	**0.90**	**9.74**	**1.58**	**0.94**	**-6.34**
60									
100	**1.97**	**1.01**	**-6.72**	**2.10**	**1.08**	**10.6**	**2.48**	**1.07**	**-1.55**
150	**1.88**	**1.12**	**4.48**	**2.31**	**0.96**	**-2.24**	**2.22**	**0.99**	**-11.3**
160									
200	**2.39**	**1.09**	**-0.07**	**2.12**	**1.04**	**4.63**	**2.43**	**1.09**	**-6.20**
240									
250							**2.80**	**1.00**	**-11.4**
300	**2.57**	**1.11**	**-3.47**	**1.73**	**0.97**	**-3.59**	**3.06**	**1.02**	**-5.72**
400	**2.87**	**1.14**	**0.28**	**1.69**	**0.98**	**-3.71**	**1.65**	**1.14**	**-1.31**
500	**1.80**	**1.02**	**45.0**	**2.08**	**1.08**	**7.78**	**1.95**	**1.08**	**-6.34**

The average K_{eq} value reported in the main text for HS-PbS QDs (2.14 ± 0.42) is the mean of all individual K_{eq} values from each titration point in this table (Trials 1-7) weighted equally with a sample standard deviation. The average exchange ratio for HS-PbS QDs is 1:1.08 ± 0.15 freeOA:boundUDA.

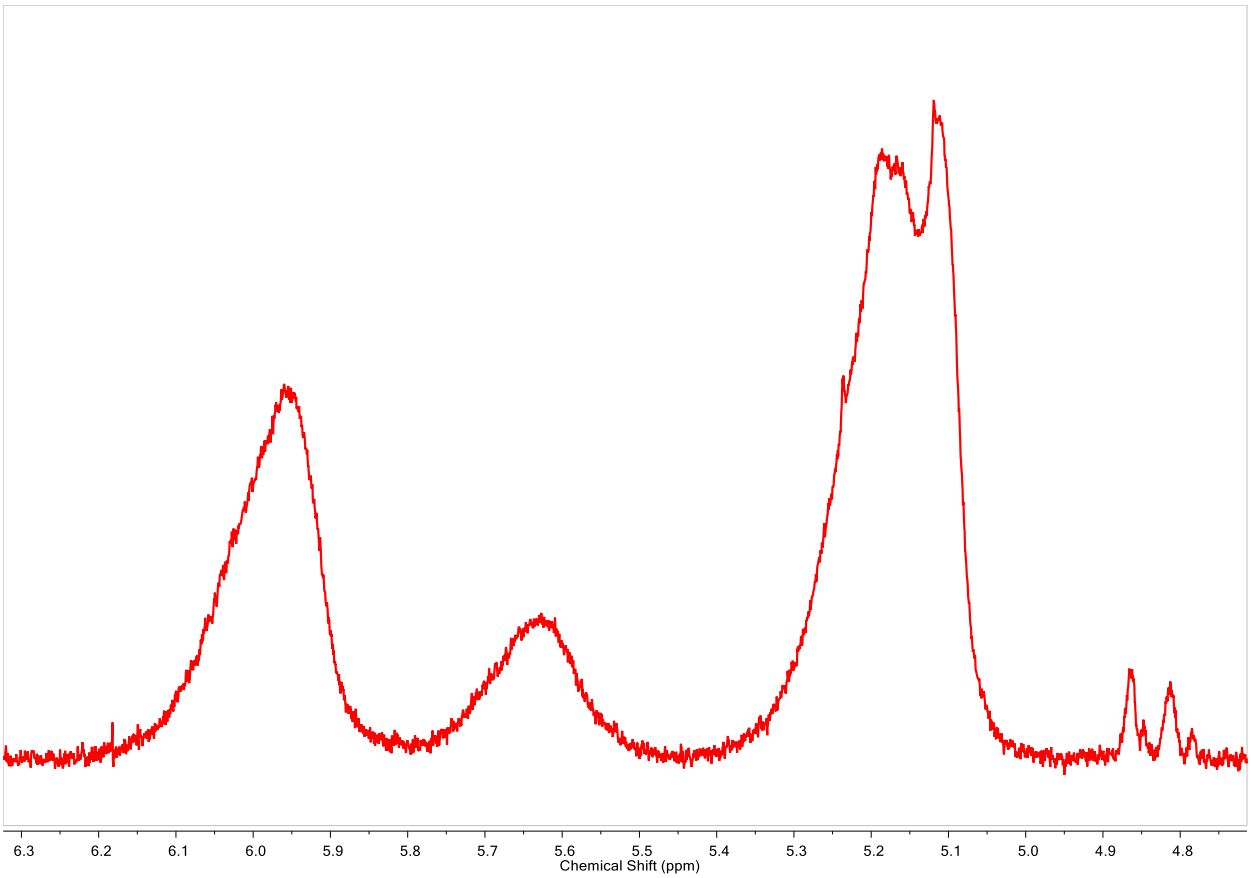

Figure S8. 600 MHz ^{1}H NMR spectrum of O-PbS QDs after QDs were stirred overnight with 1000 equivalents of UDA then precipitated by centrifugation. This spectrum confirms that all unbound ligands were removed (there is an absence of free OA and free UDA resonances) after the exchange reaction of O-PbS with UDA. Free ligands were separated from the PbS QDs prior to XPS studies to ensure that the Pb contribution to the Pb:S ratio is due solely to the Pb in the QD core and not due to any dissociated Z-type ligands.

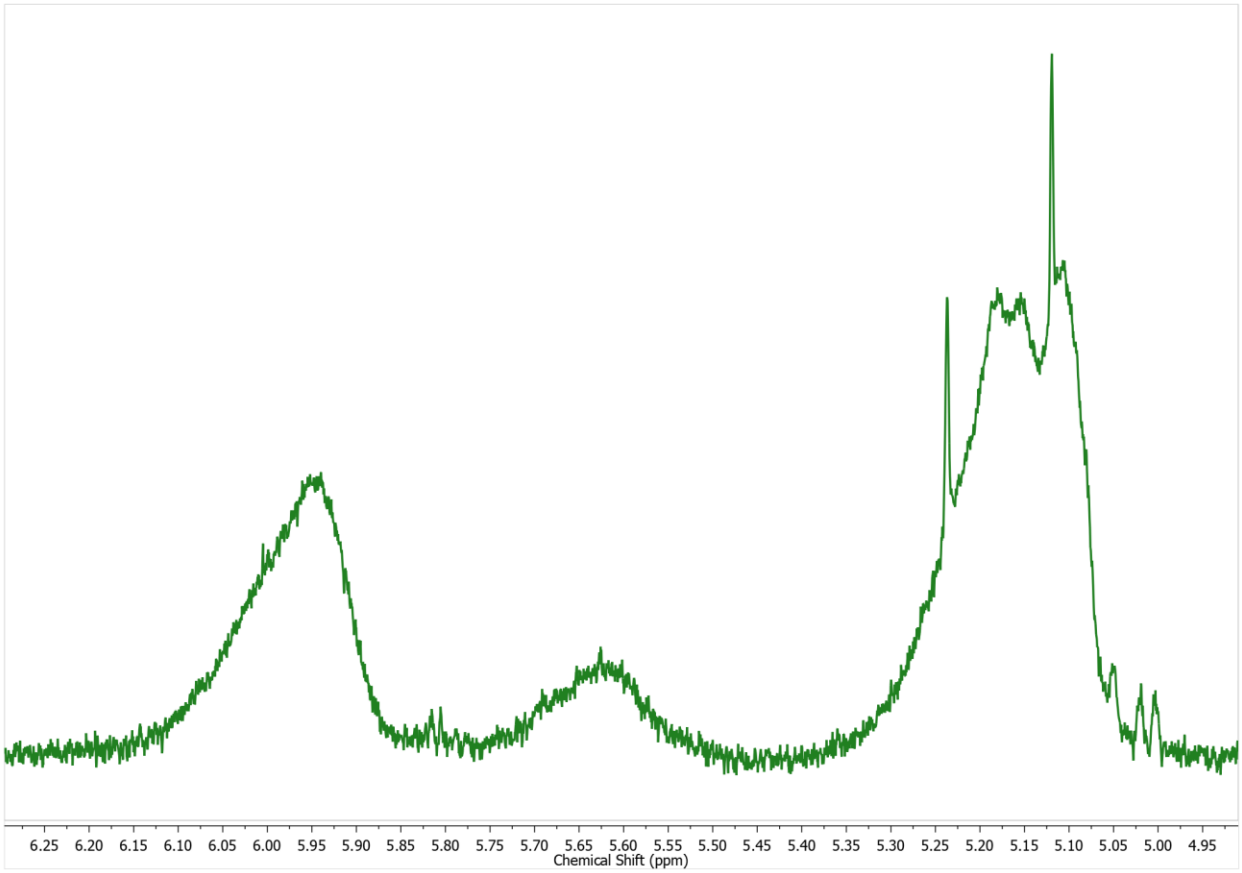

Figure S9. 600 MHz ^{1}H NMR spectrum of HS-PbS QDs after precipitation by centrifugation from stirring overnight with 1000 equivalents of UDA.

Theoretical calculations of Pb:S ratio

Pb:S stoichiometry calculations utilize an inorganic core with a 1:1 Pb:S ratio and surface Pb^{2+} ions that are estimated as half of the number of oleates quantified by ^{1}H NMR (2 oleates per Pb^{2+} ion for charge balance). For rock salt PbS, the molar volume is 19.12 PbS/nm^3.[9]

O-PbS: The volume of QDs can be calculated based on the diameter derived from UV-Vis analysis (d=3.05 nm). The number of PbS units can then be calculated from the volume of a sphere and the molar volume of rock salt PbS as follows:

$$\frac{4}{3}\pi\left(\frac{3.05\ nm}{2}\right)^3 (19.12\ PbS\ units\ nm^{-3}) = 284\ \text{PbS units}$$

Based on the surface oleate coverage of 83.8 oleates/QD – as determined from the surface area of the QD and the average oleate coverage given in Table S1 – and a 2:1 oleate:Pb ratio for charge balance, an estimated 42 Pb atoms are on the surface. To determine the Pb:S ratio, the nanocrystal stoichiometry includes an estimated 42 additional Pb ions, either as Z-type ligands or as part of a non-stoichiometric core. To

determine the Pb:S ratio, the additional Pb atoms are added to the 284 core Pb atoms and divided by the number of sulfur atoms to give

$$\frac{42\ surface\ Pb + 284\ core\ Pb}{284\ S} = 1.15\ Pb{:}S$$

From these calculations, O-PbS has a Pb:S ratio of 1.15 and HS-PbS has a Pb:S ratio of 1.16. The discrepancy between theoretical calculations and experimental values of Pb:S ratios may arise from approximating the surface area of (111) and (001) rock salt crystal facets as equal to the surface area of a sphere. In addition, it has been shown that X-type hydroxide ions can coordinate to the surface of oleate-capped PbS QDs due to the formation of water in the reaction of PbO and oleic acid during synthesis.[10,11] If hydroxide ions have coordinated to the PbS QDs, a 2:1 oleate:Pb^{2+} ratio will be an overestimation and additional Pb^{2+} ions are likely present that are not accounted for when calculating the number of additional Pb^{2+} ions based on the quantification of OA. Thus, the imposed charge balance restriction on the above calculation yields a lower limit for the Pb:S ratio.

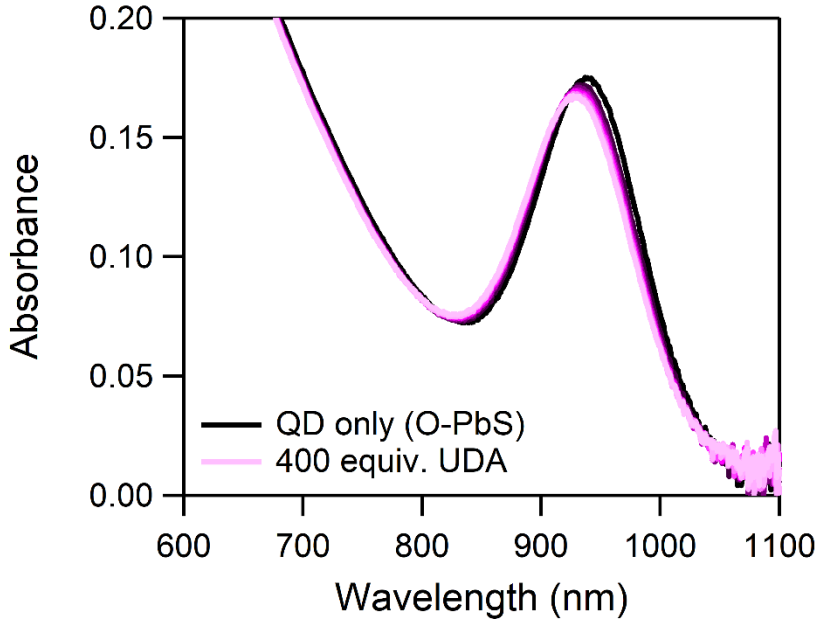

Figure S10. UV-Vis absorbance spectra of 2.33 μM O-PbS QDs titrated with up to 400 equivalents of UDA in benzene.

Table S6. Excitonic transition maxima and calculated change in diameter upon addition of 400 equivalents of UDA.

QD batch	λ_{max}, QD only (nm)	λ_{max}, 400 eq. UDA (nm)	Δd (nm)
O-PbS	937 (d = 3.04 nm)	927 (d = 3.01 nm)	$3.87 \cdot 10^{-2}$
HS-PbS	867 (d = 2.78 nm)	860 (d = 2.75 nm)	$2.62 \cdot 10^{-2}$

The λ_{max} of the first excitonic transition of each batch of PbS QDs was inserted into the empirical sizing curve derived by Moreels et al.[12] to calculate the diameter of the QDs in the absence of added UDA and QDs with 400 equivalents of UDA added. Next, the change in the diameter, Δd, was compared with the lattice constant of rock salt PbS, $5.936 \cdot 10^{-1}$ nm. The Δd values are <10% of the lattice constant, which supports the conclusion in the main text that the observed hypsochromic shifts in our UV-Vis titrations are not due to surface etching, but rather result from decreased solvent shielding upon passivation with the shorter UDA ligand.

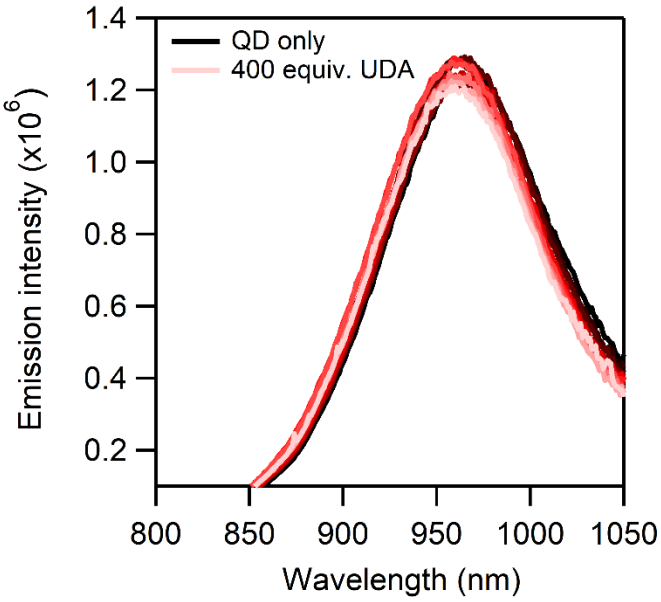

Figure S11. Emission spectra of 4.75 µM HS-PbS QDs titrated with up to 400 equivalents of UDA in benzene.

SI-3 Quantification of ligand exchange equilibria

Table S7. K_{eq} values determined upon the addition of OA at the end of the UDA titration on O-PbS QDs (determined from Eq. 2).

	Trial 1	**Trial 2**	**Trial 3**	**Trial 4**	**Trial 5**
Eq. OA added	K_{eq}				
20 eq	2.45	2.26			
50 eq			-	2.99	1.85
60 eq	2.44	2.59			
100 eq			-	1.76	1.81
200 eq			2.20	-	-
260 eq	2.62				

The average K_{eq} value reported in the main text for the addition of OA on O-PbS QDs (2.30 ± 0.40) is the mean of all individual K_{eq} values from each titration point in this table weighted equally with a sample standard deviation. Trial names are consistent with those in Table S4.

Table S8. K_{eq} values determined upon the addition of OA at the end of the UDA titration on HS-PbS QDs (determined from Eq. 2).

	Trial 1	**Trial 2**	**Trial 5**	**Trial 6**	**Trial 7**
Eq. OA added	K_{eq}				
50 eq			1.56	1.89	1.95
100 eq			2.94	2.06	1.36
200 eq	2.08	1.93			
400 eq	1.68	1.77			

The average K_{eq} value reported in the main text for the addition of OA on HS-PbS QDs (1.92 ± 0.42) is the mean of all individual K_{eq} values from each titration point in this table weighted equally with a sample standard deviation. Trial names are consistent with those in Table S5.

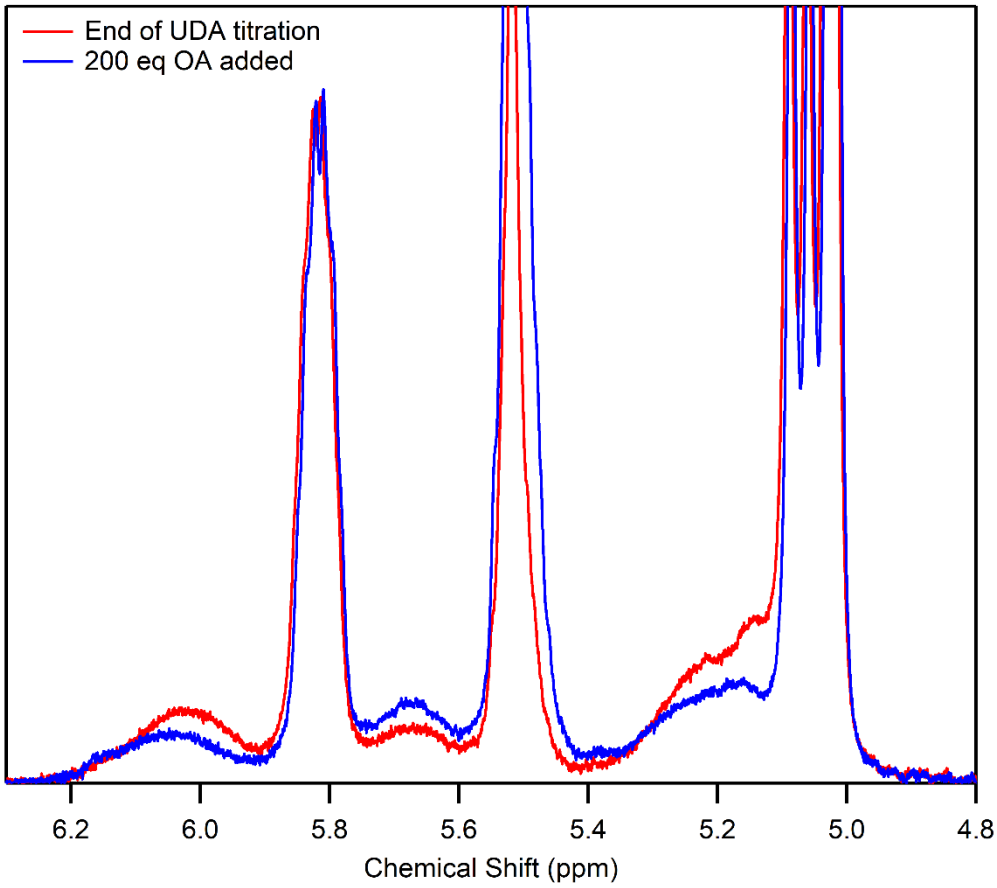

Figure S12. 600 MHz ^{1}H NMR spectrum of HS-PbS QDs in benzene-d_6 at the end of an UDA titration in which 400 equivalents of UDA were added to the solution (red). Addition of 200 equivalents of OA after the titration with UDA was completed (blue) demonstrates the reversibility of the carboxylate exchange.

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