Supporting Information

Quantifying Ligand Exchange on InP Using an Atomically-Precise Cluster Platform

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Chemicals

Indium acetate (99.99%), oleic acid (90%), magnesium turnings, 11-Bromo-1-Undecene (95%), potassium thioacetate (98%), lithium aluminum hydride (95%, powder), and mesitylene (98%) were purchased from Sigma-Aldrich and used without further purification. Triethyl phosphate (98%) was purchased from Sigma Aldrich and distilled under vacuum (50 mTorr) prior to use. NMR solvents were purchased from Cambridge Isotope Laboratories, dried over calcium hydride, vacuum-transferred, and stored over dried 4 Å molecular sieves under nitrogen in a glovebox. Nonvolatile hydrocarbon solvents were dried with calcium hydride and distilled whereas volatile hydrocarbon solvents were dried via a solvent system utilizing alumina and Q5 columns, and all were stored in the glovebox over 4 Å molecular sieves prior to use. Acetonitrile (99.8%, anhydrous) was purchased from Sigma-Aldrich and used without further purification. Biobeads (200 Mesh) for purification were purchased from Bio-Rad. Tris(trimethylsilyl)phosphine (P(SiMe₃)₃) was synthesized via literature procedure¹.

General Practices

Unless stated otherwise, all chemical reactions were performed under N₂ using standard Schlenk line air-free techniques and glassware. Chemicals were stored in a N₂ glovebox dried unless stated otherwise. Standard solutions were prepared immediately prior to use.

Experimental Procedures, Synthetic:

Synthesis of dodec-11-enoic acid (DDA):
DDA was synthesized via a Grignard reaction. A 100 mL Schlenk flask under nitrogen was charged with 30mL dry THF, 333 mg of Mg (3 eq), and one flake of I₂. Once the yellow color had dissipated, 4.0 g (17.1 mmol, 1.0 eq) of 11-bromo-1-undecene was added. The vessel was brought to 40 °C under N₂ with stirring for 2 hr, and a deep gold developed. A cannula was then used to sparge the solution with CO₂ for 1 hr. The solution was decanted and worked up with excess 1.0 M HCl and ammonium chloride. Following this it was extracted three times with saturated brine solution. The organic layer was concentrated by rotovap and purification was performed by column chromatography with a 1:8 ether:hexanes eluent followed by repeated washes with cold pentane. The product was a white powder with a tendency to melt from handling.

Synthesis of 10-undecene-1-thiol (UDTh):
UDTh was synthesized using a modified literature procedure via the synthesis and subsequent reduction of thioester². A 50 mL round bottom flask was loaded with 15 mL dry ethanol and 1.96 g potassium thioacetate (17.1 mmol, 1.0 eq) and sonicated until a homogenous but opaque pink color. A separate solution of 15 mL dry ethanol and 4.0 g 11-bromo-1-undecene (17.1 mmol, 1.0 eq) was prepared and both solutions were sparged with nitrogen for 30 m. The solutions were then combined in the round bottomed flask, equipped with a condensing column, and refluxed for 18 hr under nitrogen. The resulting product was a dark orange with white precipitate and was extracted three times with 50 mL pentane. This solution was concentrated by rotovap down to an oil and purified by silica column using a 1:10 ether:hexanes eluent. The product was concentrated and confirmed by ¹H NMR to be S-(undec-10-en-1-yl) ethanethioate (2.54 g, 65% yield). A 100 mL Schlenk flask was loaded with 740 mg LiAlH₄ (1.75 eq) and under nitrogen and cooled to 0 °C in an ice bath. The thioester was resuspended in 5 mL dry ether and added dropwise with stirring. The solution was then removed from the ice bath and allowed to stir for 1 hr. The mixture was quenched with 15 mL of 1.0 M HCl and filtered over Celite on a glass frit. The organic layer was dried over MgSO₄ and concentrated via rotovap to a clear oil yielding 10-undecene-1-thiol which was degassed and stored immediately in a glovebox freezer and used without further purification.
**Synthesis of 10-ene-undecyl-phosphonic acid (UDPA):**
UDPA was synthesized from 11-bromo-1-undecene via the Michaelis-Arbuzov reaction. In a Schlenk flask 3.0 g (12.9 mmol, 1.0 eq) of 11-bromo-1-undecene was combined with 6.2 mL distilled triethyl phosphite (38.6 mmol, 3.0 eq) and refluxed under nitrogen at 150 °C for 16 hr. Excess triethyl phosphite was removed by vacuum assisted distillation leaving a yellow oil and complete conversion was verified by $^{31}$P NMR spectroscopy. The flask was refilled with nitrogen and placed in an ice bath where a solution of 3.6 mL tris(trimethylsilyl)bromide in 10 mL dry toluene (27.1 mmol, 2.1 eq) was slowly injected. The flask was gently raised to 50 °C and allowed to stir for 2 hr where complete conversion was seen by $^{31}$P NMR spectroscopy. Toluene and volatiles were removed via distillation and the reaction was worked up with a dilute solution of HCl. The product was purified by four repeated recrystallizations from hot hexanes yielding white crystalline flakes.

**Synthesis of the In$_{37}$P$_{20}$ Cluster [In$_{37}$P$_{20}$(O$_2$C$_{18}$H$_{33}$)$_{51}$]**
Oleate ligated cluster was synthesized via the established literature procedure using in-situ formed In(Ol)$_3$. After synthesis the clusters were taken into a glovebox where they were flocculated out of solution with acetonitrile. The crude material was purified by two elutions through a size-exclusion column using a BioBead stationary phase, followed by further resuspensions in toluene and acetonitrile flocculation until no free acid was visible by NMR spectroscopic analysis. The clusters were dried under vacuum and stored as a solid with a wax consistency.

**Synthesis of InP QDs**
The InP QDs used were synthesized by heatup of oleate-capped cluster. A solution of 200 mg as prepared cluster was dissolved in 10 ml octadecene and transferred to a 3-neck flask on the Schlenk line. The solution was raised to 280 °C at a rate of 10 °C/min. The solution was held at temperature for 1 hr, then allowed to cool. After vacuum assisted distillation at 120 °C the QD’s were purified in the same manner as the cluster.

**Titrations**
Samples of 20.0 mg of cluster (1.04 μmol) were weighed and suspended in 400 μL C6D6, or in the case of variable temperature experiments toluene-d8. Prior to use, deuterated solvents were prepared with mesitylene as an internal standard at a concentration of 0.050 M. Sufficient delay time was determined via the inversion recovery experiment of mesitylene (SI 10). Titrating solutions were prepared using this internally standardized solvent for each sample at a concentration of 1 equivalent ligand/ 10 μL of solvent. Between trials the J Young tube was brought into the glovebox where the appropriate amount of titrant was added via microliter syringe. Amounts beyond 50 eq (~10 mg) were weighed and added neat. The sample was allowed 30 min to equilibrate with agitation between additions.

**Experimental Procedures, Analytical**

**UV-Vis Spectrometry**
Ex situ UV-Vis spectra were measured using a Varian Cary model 5000 dual beam spectrometer. The spectrometer was equipped with a Mercury light source and measurements were made with 1 nm resolution between 300 and 800 nm. Samples were loaded into polished quartz cuvettes for analysis.

**NMR $^1$H and $^{31}$P($^1$H) Spectrometry:**
$^1$H and $^{31}$P($^1$H) spectra were acquired on a Bruker base 700 MHz frequency instrument using a BBO $^1$H{X} probe unless otherwise stated. Deuterated solvents were acquired from Cambridge
Isotope Labs and dried over calcium hydride, vacuum-transferred, and stored over 4 Å sieves in a nitrogen glovebox. For $^1$H NMR spectra mesitylene was used as an internal standard and reference, while for $^{31}$P NMR spectra 85% phosphoric acid was used as an external reference. A 30° tilt pulse sequence was used to reduce quantitative delay times. Pulse and shim recalibrations were performed between all temperature changes during variable temperature experiments.

**NMR DOSY Spectrometry:**

DOSY spectra were acquired on a Bruker 500 MHz instrument using a TXO{$^1$H} probe. A basic STE DOSY pulse sequence with a single gradient was used. The gradient dimension was acquired over 32 evenly spaced datapoints from 5% to 90% gradient strength at 8 scans each. Scans were run using a $T_1$ delay of 30 s and a DOSY gradient pulse $\Delta$ delay of 400 ms.
**SI 1.** Deriving a multi-site, multi-species-competitive Langmuir isotherm in terms of measurable variables:

A site balance on site-type \( n \) for multiple adsorbate species \( i \) is described by:

\[
[S_n] = [S_{n0}] - \sum_i [i_{n,ad}]
\]  
(1)

Where individual equilibria are described by kinetics in the Langmuir model as:

\[
[i_{n,ad}] = K_{eq,n}^i [S_n] [i_f]
\]  
(2)

Combining (1) and (2) one can then define the fractional occupation of site-type \( n \) by species \( j \):

\[
\theta_{n,j} = \frac{K_{eq,n}^j [j_f]}{1 + \sum_i K_{eq,n}^i [i_f]}
\]  
(3)

Summing over all site-types, the total fractional occupancy by species \( j \) becomes:

\[
\theta_j = \sum_n \chi_n \frac{K_{eq,n}^j [j_f]}{1 + \sum_i K_{eq,n}^i [i_f]}
\]  
(4)

Using (5) one can rewrite (4) in the context of nanoparticles of concentration \([NP]\) with \( z_n \) number of sites of type \( n \) per-particle:

\[
\theta_j = \frac{[J_{ad}]}{\sum_n z_n [NP]}
\]  
(5)

\[
[J_{ad}] = [NP] \sum_n z_n \frac{K_{eq,n}^j [j_f]}{1 + \sum_i K_{eq,n}^i [i_f]}
\]  
(6)

(6) is general for \( n \geq 1 \) and \( i \geq 1 \), reducing to the competitive Langmuir isotherm for \( n = 1 \) and the multisite Langmuir isotherm for \( i = 1 \).

For example, the concentration of adsorbed oleate (Ol) competing with dodec-11-enoic acid (DDA) for L and X type sites becomes:

\[
[Ol_{Ad}] = [NP] \left( z_L \frac{K_{eq,L}^{Ol} [Ol_f]}{1 + K_{eq,L}^{Ol} [Ol_f] + K_{eq,L}^{DDA} [DDA_f]} + z_X \frac{K_{eq,X}^{Ol} [Ol_f]}{1 + K_{eq,X}^{Ol} [Ol_f] + K_{eq,X}^{DDA} [DDA_f]} \right)
\]  
(7)

And

\[
[DDA_{Ad}] = [NP] \left( z_L \frac{K_{eq,L}^{DDA} [DDA_f]}{1 + K_{eq,L}^{DDA} [DDA_f] + K_{eq,L}^{Ol} [Ol_f]} + z_X \frac{K_{eq,X}^{DDA} [DDA_f]}{1 + K_{eq,X}^{DDA} [DDA_f] + K_{eq,X}^{Ol} [Ol_f]} \right)
\]  
(8)
Definitions:

\[
\begin{align*}
[S_n] & \quad \text{Total concentration of sorption sites of type } n \\
[S_{n0}] & \quad \text{Concentration of open sites of type } n \\
[i_{n,ad}] & \quad \text{Concentration of species } i \text{ bound on } n\text{-sites} \\
[i] & \quad \text{Concentration of species } i \text{ free in solution} \\
K_{eq,n}^i & \quad \text{Equilibrium constant of species } i \text{ towards } n\text{-site type binding} \\
\Theta_{n,i} & \quad \text{Fractional occupancy of species } i \text{ over } n\text{-type sites (i.e. } [i_{n,ad}] / [S_{n0}] \text{)} \\
\chi_n & \quad \text{Fraction of total sites that are type } n \text{ (i.e. } [S_{n0}] / \sum_n [S_{n0}] \text{)} \\
\Theta_i & \quad \text{Fractional occupancy of species } i \text{ over all sites (i.e. } [i_{ad}] / \sum_n [S_{n0}] \text{)} \\
[NP] & \quad \text{Concentration of nanoparticles} \\
z_n & \quad \text{Number of sites of type } n \text{ per nanoparticle (i.e. } [S_{n0}] = z_n[NP] \text{)}
\end{align*}
\]

A note on X-type binding in this model:
Modeling X-Type binding using the Langmuir model physically implies a sorption reaction of:

\[
X^- + NP^+ \rightleftharpoons XNP
\]

Which is a physically unreasonable reaction in non-polar solvent. However, the net combination of two such reactions:

\[
\begin{align*}
XA^- + NP^+ & \rightleftharpoons XANP \\
XB^- + NP^+ & \rightleftharpoons XBNP \\
(XBNP & \leftarrow K_{XB}^{-1} XB^- + NP^+) \\
\end{align*}
\]

Reduces at equilibrium to the X-Type exchange reaction for reversible reactions A and B:

\[
XA^- + XBNP \rightleftharpoons \frac{K_{XA}^{-1} K_{XB}}{K_{XB}^{-1} K_{XB}} XANP + XB^-
\]

Thus if the reactions are at equilibrium and the exchange is one-to-one the net X-type equilibrium constant can be directly obtained from the isotherm variables:

\[
K_{eq,X} = \frac{K_{eq,A}}{K_{eq,B}}
\]
**SI 2.** Variable temperature $^1$H NMR spectra. The spectra were acquired from 268 K (red trace) to 328 K (magenta trace) in 10 K increments. To reduce systematic error spectra were acquired in staggered order (K): 298, 278, 268, 288, 308, 318, 328, 298(2).

+ 44 eq DDA (High regime), toluene-d8, 700 MHz

Start vs return spectra at 298 K:

Red trace initial scan, blue trace final scan. These scans were taken approximately 3 hours apart with the first being taken 20 minutes after mixing. This demonstrates that the surface equilibrates rapidly as has been observed in similar systems.
+ 7 eq DDA (Low regime), toluene-d8, 700 MHz

The spectra were acquired from 268 K (red trace) to 318 K (magenta trace) in 10 K increments. To reduce systematic error spectra were acquired in staggered order (K): 298, 278, 268, 288, 308, 318, 298(2).

Start vs return spectra at 298 K:

Red trace initial scan, blue trace final scan.
**SI 3.** (Top) UV-Vis spectra of oleate capped cluster vs added dodec-11-enoic acid acid. Spectra were normalized at the peak maximum to 1 absorbance unit. (Bottom) Shift in the lowest energy peak maximum as a function of added carboxylic acid. The redshift and subsequent blueshift are reversible upon purification and attributed to changes in configurational differences of ligands at the surface.
SI 4. (Top) UV-Vis spectra of oleate capped cluster vs added 10-ene-undecyl-phosphonic acid. Spectra for 1-25 equivalents were normalized at the peak maximum to 1 absorbance unit. (Bottom) Shift in the lowest energy peak maximum as a function of added phosphonic acid. This blueshift is attributable to effects of the ligand identity on the excitonic wavefunction, whereas the decrease in intensity is due to particle decomposition.
SI 5. $^{31}$P NMR spectra of oleate capped clusters as a function of added phosphonic acid showing a zoom in of the phosphide region between -145 and -285 ppm. The sharp peak at $\delta = -243$ ppm corresponds to PH$_3$, integration $\sim$3% of the phosphide region in the 30 equivalent sample.
Full $^{31}\text{P}$ NMR spectra of oleate capped clusters as a function of added phosphonic acid. Increasing the amount of phosphonic acid added in excess of 100 eq resulted in a thick white emulsion in the NMR tube which could not be measured.

+10 Eq UDPA

+30 Eq UDPA
SI 6. Thiol titration data showing the number of ligand equivalents bound (oleate and thiolate) as a function of added UDTh. Total bound ligands = 50 ± 1 over the first eight additions.
SI 7. $^{31}$P NMR spectrum of cluster and added thiol. The sharp peak at $\delta = -241$ ppm corresponds to PH$_3$, integration <1% of the phosphide region.
SI 8. DOSY NMR experiments supporting thiol etching.

$^1$H 500 MHz, C$_6$D$_6$, a basic STE pulse sequence with one gradient was used.

Characteristic examples of monodisperse DOSY decays that reveal linear trends when plotted on a logarithmic axis.
Examples of polydisperse DOSY decay curves revealing nonlinear trends when plotted on a logarithmic axis.
The polydisperse-diffusing spectra can be fit to a bi-exponential function

\[ I = A_1 e^{-\frac{g^2}{\tau_1}} + A_2 e^{-\frac{g^2}{\tau_2}} \]

Where

\[ \tau = \frac{D(\Delta - \frac{\delta}{3})}{(2\pi\gamma\delta)^2} \]

Where \( \delta \) and \( \Delta \) are the pulse sequence parameters and \( \gamma \) is the proton gyromagnetic ratio.

Example of fitting as a bi exponential at 5.079 PPM:

In this representation the curves of the two species do not sum but are tangential to the ‘slow’ and ‘fast’ regimes of the measurement.
**S9. InP QD TEM**

TEM images acquired on an FEI Tecnai G2 F20 instrument at 200 keV.

3.0 nm ± 0.1
S10. T1 Recovery Determination of Mesitylene

700 MHz, C₆D₆, air free, aryl resonance 6.72 ppm.

\[ \text{Fit} = I_0 \left[ 1 - 2 \times \exp\left( -\frac{t}{29.62 \text{ s}} \right) \right] \]

\[ T1 = \frac{29.62 \text{ s}}{\ln(2)} = 42.7 \text{ s} \]

Mesitylene was chosen as a standard to ensure that the standard would be completely innocent towards the clusters and nanoparticles used, something that is not obviously true for other common standards in the literature such as ferrocene.

This relaxation is exceptionally slower than seen in the presence of air due to paramagnetic quenching by oxygen, a fact not often accounted for in the quantum dot literature and suggests 120-200 s delays between scans are necessary. It was determined that using a 30° pulse sequence with a 75 s delay gave integrations at 99% agreement with other resonances.
S11. $^1$H NMR Spectra Fitting Procedure

Deconvolution of overlapping resonances was aided by using a high field instrument but still required the fitting of two or more functions for accurate integrations. For this the MestReNova software fitting tools were used which employ Global Spectral Deconvolution (GSD) to fit the overlapping alkene resonances to generalized Lorentzians.

A typical example of fitting, the 20 eq DDA titration, DDA (left), oleate (right). Black: baselined spectrum, blue: fit Lorentzians, magenta: fit sum, red: residual. The sinusoidal residual is a reasonable indicator that all underlying species are accounted for. Splitting was not usually seen at higher concentrations and temperatures due to rapid exchange.

A typical example of fitting resolved alkene resonances of less rapidly exchanging species, thiol 12 eq.
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