Supporting Information: A one-pot organic/CdSe nanoparticle hybrid material synthesis with in-situ π-conjugated ligand functionalization

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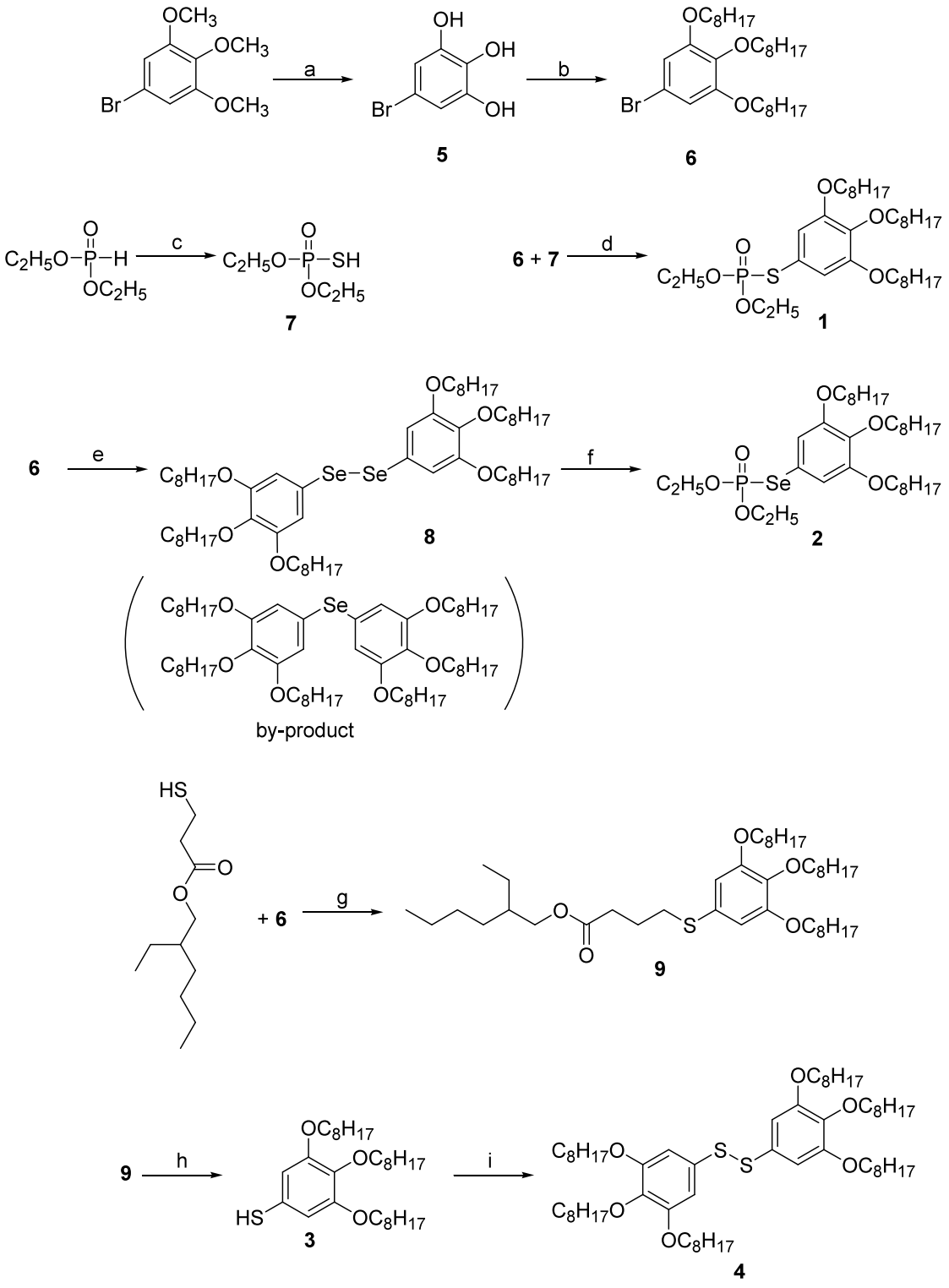
Experimental:

Ligand Synthesis.

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-300 or AV-500 spectrometers, respectively, using TMS (for ligand synthesis) or chloroform (for CdSe synthesis) as an internal standard. ^{31}P NMR spectra were recorded on the same instrument with 85% H_3PO_4 as an external standard. MALDI-TOF MS spectra were recorded on Bruker Autoflex II spectrometer using terthiophene as the sample matrix. Samples were prepared by dissolving 0.5 mg in 100 μL of matrix solution chloroform and approximately 2.0 μL of this solution was deposited on the plate. The MALDI-TOF MS experiments were performed in the reflection mode.

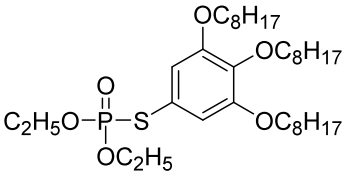


Synthesis of ArSP (1), ArSeP (2), ArSH (3), and ArSSAr (4)

Reagents and Conditions: (a) BBr_3, CH_2Cl_2; (b) 1-bromooctane, K_2CO_3, DMF; (c) $HPO(OEt)_2$,

S_8, K_2CO_3, THF, reflux; (d) $Pd_2(dba)_3$, Xantphos, Cs_2CO_3, THF, reflux; (e) 2.5 M *n*BuLi, THF, -78°C, then Se powder; (f) $HPO(OEt)_2$, AIBN, toluene, 60°C; (g) $Pd_2(dba)_3$, Xantphos, DIPEA, THF, reflux; (h) NaO*t*-Bu, EtOH, (i) 30w/v% H_2O_2, EtOAc.

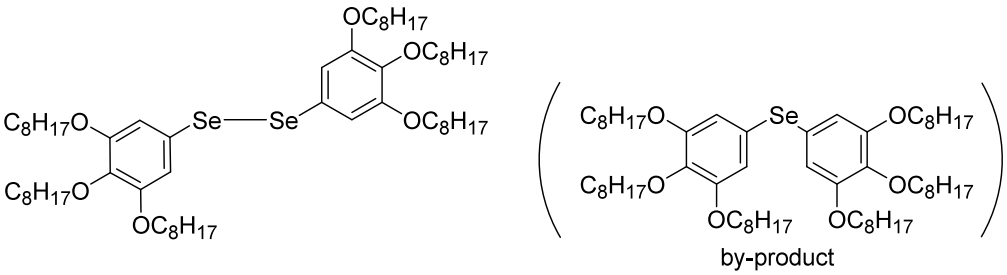
Compound **5** (5-Bromo-1,2,3-benzenetriol),[1] **6** (5-bromo-1,2,3-tris(octyloxy)benzene),[1,2] and Compound **7** (Thiophosphoric acid *O*,*O'*-diethyl ester)[3] were prepared according to established procedures.



ArSP (*O*,*O'*-Diethyl S-[3,4,5-tris(octyloxy)phenyl]phosphorothioate).

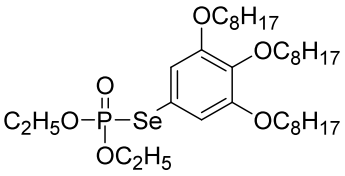
Synthesis of ArSP was based on a modification of Itoh's C-S coupling.[4] To a solution of **6** (1.74 mmol, 0.944 g) in dry THF 10ml, Cs_2CO_3 (3.48 mmol, 1.131g), catalyst $Pd_2(dba)_3$ (2.5 mol%, 0.025 g), Xantphos (5.0 mol%, 0.050 g) and the thiol **7** were added. The mixture was heated to reflux for 18 h. After cooling the reaction mixture to room temperature, the reaction mixture was poured into saturated NH_4Cl aqueous solution, and then concentrated. The aqueous layer was extracted with several portions of dichloromethane. The combined extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, and purified by silica gel chromatography using hexane:ethylacetate (2:1) as an eluent to afford 0.862 g (78%) of **ArSP** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 6.75 (2H, d, $J_{H\text{-}P}$ = 2.6 Hz), 4.18 (4H, q, J = 7.5 Hz), 3.94 (6H, t, J = 5.7 Hz), 1.85-1.64 (7H, m), 1.54-1.20 (40H, m), 0.88 (6H, t, J = 7.5 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.4, 139.3, 120.2 (d, $J_{C\text{-}P}$ = 6.9 Hz), 113.4 (d, $J_{C\text{-}P}$ = 5.3 Hz), 73.9, 69.6, 64.5 (d, $J_{C\text{-}P}$ = 6.0 Hz), 32.3, 32.2, 30.7, 29.9, 29.76, 29.69, 29.5, 26.5,

23.1, 16.5 (d, $J_{C\text{-}P}$ = 7.6 Hz), 14.5 ppm; ^{31}P NMR (202 MHz in $CDCl_3$): δ = 23.22; MALDI-TOF MS Calcd for $C_{34}H_{63}O_6PS$ 630.9; found *m/z* = 630.3.



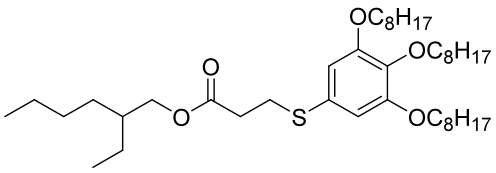
Compound 8 (bis[3,4,5-tris(octyloxy)phenyl]diselenide).

A modified literature procedure was used.[5] To a solution of **6** (8.125 g, 15 mmol) in THF (150 mL) at -78 °C under a N_2 atmosphere was added *n*-BuLi (2.5 M in hexanes; 6mL, 15 mmol) dropwise. After 15 min at 0 °C, the solution is cooled down to -78 °C then slowly Se power (15 mmol, 1 eq) was added. The resulting mixture was warmed to room temperature over 2 h then poured onto a mixture of ice water and ether followed by bubbling air through it for 1 h. During this workup, large amounts of red selenium formed. Layers were separated, and the aqueous layer was extracted with several portions of ether. The combined ethereal phases were washed with water, 1M HCl solution. The combined extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, and purified by silica gel chromatography using hexane:dichloromethane (1:1) as an eluent to afford 6.50 g of **7** as a yellow oil. MALDI-TOF MS Calcd for diselenide(**8**) $C_{60}H_{106}O_6Se_2$ 1081.4; found m/z 1081.3, monoselenide (byproduct) $C_{60}H_{106}O_6Se$ 1002.5; found *m/z* = 1003.3.



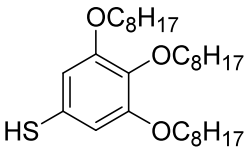
ArSeP (*O,O'*-Diethyl Se-[3,4,5-tris(octyloxy)phenyl]phosphoroselenoate).

Synthesis of ArSeP was based on a modification of Huang's procedure.[6] A solution of **8** (diselenide and monoselenide mixture) (8.231 g, ca. 7.6 mmol), diethyl phosphite (18 mmol, 2.35 mL), and AIBN (0.624 g, 50 mol%) in anhydrous toluene (10 mL) was stirred at 65 °C for 12 h under a N_2 atmosphere. After cooling the resulting mixture to room temperature the mixture was poured into water and ethyl acetate and the organic phase were separated. The aqueous layer was extracted with several portions of ethyl acetate. The combined extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, and purified by silica gel chromatography using hexane:ethylacetate (3:1) as an eluent to afford 1.545 g of **ArSeP** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 6.82 (2H, d, $J_{H\text{-}P}$ = 1.62 Hz), 4.07 (4H, q, J = 6.6 Hz), 3.93 (6H, t, J = 6.3 Hz), 1.88-1.68 (7H, m), 1.54-1.23 (40H, m), 0.91 (6H, t, J = 6.6 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.5, 139.1, 116.7 (d, $J_{C\text{-}P}$ = 8.5 Hz), 114.2 (d, $J_{C\text{-}P}$ = 4.2 Hz), 73.5, 69.3, 64.0 (d, $J_{C\text{-}P}$ = 5.9 Hz), 32.0, 31.9, 30.4, 29.6, 29.41, 29.37, 29.35, 26.1, 23.5, 22.7, 16.1 (d, $J_{C\text{-}P}$ = 7.6 Hz), 14.2 ppm; ^{31}P NMR (202 MHz in $CDCl_3$): δ = 17.50 ppm [s (isotope 76, 78, 80, 82) and d (isotope 77), $^1J_{P\text{-}Se}$ = 488.3 Hz]; MALDI-TOF MS Calcd for $C_{34}H_{63}O_6PSe$ 677.8; found *m/z* = 678.2.



Compound 9 (4-(3,4,5-Trisoctyloxyphenylsulfanyl)butyric acid 2-ethyl-hexyl ester).

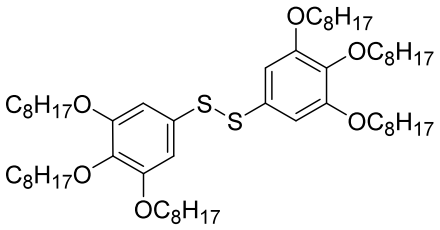
Synthesis of compound 9 was based on a modification of Itoh's C-S coupling procedure.[4] To a solution of **6** (3.00 mmol, 1.625 g) in dry THF (15 mL), *i*-Pr_2NEt (6.00 mmol, 1.05 mL), the catalyst $Pd_2(dba)_3$ (2.5 mol%, 0.025 g), Xantphos (5.0 mol%, 0.050 g) and the thiol were added. The mixture was heated to reflux for 18 h. After cooling the reaction mixture to room temperature, the reaction mixture was poured into saturated NH_4Cl aqueous solution, and then concentrated. The aqueous layer was extracted with several portions of ether. The combined extracts were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, and purified by silica gel chromatography using hexane:dichloromethane (2:1) as an eluent to afford 1.220 g (60%) of **9** as a light yellow oil. The obtained oil was carried forward to the next step without further purification. ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ = 6.59 (2H, s), 4.10 (1H, m), 3.99 (2H, t, *J* = 5.7 Hz), 3.93 (6H, t, *J* = 6.3 Hz), 3.08 (2H, t, *J* = 7.2 Hz), 2.59 (2H, t, *J* = 7.2 Hz), 1.85-1.60 (6H, m), 1.62-1.20 (38H, m), 0.89-0.78 (15H, m) ppm; MALDI-TOF MS Calcd for $C_{41}H_{74}O_5S$ 679.1; found *m/z* = 678.5.



ArSH (3,4,5-trisoctyloxybenzenethiol).

Synthesis of ArSH was based on a modification of Itoh's deprotection procedure.[7] To a solution of **9** (1.50 mmol, 1.019 g) in EtOH (20 mL), NaO*t*-Bu (3.0 mmol, 0.204 g) was added and then the mixture was stirred at ambient temperature for 10 h. After verifying the completion of the

reaction by TLC, the mixture was poured into ethyl acetate and water. The separated organic layer was dried over Na_2SO_4 and concentrated under reduced pressure, and purified by silica gel chromatography using hexane:ethylacetate (9:1) as an eluent to afford in 65% of **ArSH** as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 6.490 (2H, s), 3.94 (6H, m), 3.42 (1H, s), 1.81-1.65 (6H, m), 1.51-1.20 (40H, m), 0.88 (6H, m) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.5, 136.9, 123.9, 109.1, 69.3, 32.04, 31.97, 31.72, 30.4, 29.68, 29.47, 29.42, 26.24, 26.19, 22.8, 14.2 ppm; MALDI-TOF MS Calcd for $C_{30}H_{54}O_3S$ 494.3; found *m/z* = 495.0, 517.3 [M+Na^+].



ArSSAr (bis[3,4,5-tris(octyloxy)phenyl]disulfide).

Following the synthesis procedure of **ArSH**, the reaction mixture was poured into 30w% H_2O_2 aqueous solution. The mixed solution was stirred at room temperature for 3 h, and the mixture poured into ethyl acetate and water. The separated organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure, and purified by silica gel chromatography using hexane:ethylacetate (9:1) as an eluent to afford **ArSSAr** as an yellow waxy substance in 85% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ = 6.70 (4H, s), 3.90 (6H, t, *J* = 7.5 Hz), 1.81-1.65 (10H, m), 1.51-1.20 (80H, m), 0.88 (6H, t, *J* = 7.5 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.4, 138.2, 131.6, 107.8, 73.6, 69.2, 32.05, 31.97, 30.45, 29.69, 29.52, 29.45, 26.2, 22.8, 14.2 ppm; MALDI-TOF MS Calcd for $C_{60}H_{106}O_6S_2$ 987.6; found *m/z* = 986.8.

Synthesis of CdSe Nanocrystals.

For all reactions, 1-octadecene (ODE, 90%), CdO, Oleic Acid (90%), Octadecylamine (95%), and tri-*n*-octylphosphine oxide (90%, technical grade), and 1-octadecene (ODE, 95%, GC) were purchased from Sigma-Aldrich. Se (99.9%) was purchased from Fluka, and tri-*n*-butylphosphine (TBP) was purchased from Strem. All chemicals and reagents were used as received.

CdSe nanocrystals were synthesized by a modified version of the CdO/amine route synthesis of Yu and Peng.[8] In a typical reaction, 0.0385 g CdO was heated with 0.34 g Oleic Acid in 1g ODE in a N_2 purged three neck flask to 220 °C until the solution turned clear, indicating the reaction of CdO with Oleic Acid to form Cd-Oleate. The solution would then be allowed to cool to room temperature, at which point the ligands could be added, followed by a N_2 purge. For the growth of CdSe nanoparticles with in-situ aryl functionalization, 0.75 g ODA, and 0.406 g **ArSP** or 0.436 g **ArSeP** would be added to the reaction mixture. For standard CdSe nanoparticles for ligand exchange processes, 0.75 g ODA and 0.25 g TOPO would be added to the reaction mixture at this step. The solutions were then put under vacuum for ~20 minutes at 110 °C until the solution was clear and no longer bubbling. The temperature would then be increased to 260-270 °C, and 1.5 g Se-TBP (from a stock solution of 1.4 g Se, 3.84 g TBP, and 12.33 g ODE that was previously prepared in a glovebox) would be swiftly injected to the reaction mixture and the dots would then be allowed to grow at 260 °C for 8 (for pyridine capped dots) or 18 minutes (all other dots), at which point the solution would then be removed from heat and allowed to air cool. All reactions were performed under N_2 on a schlenk line. After cooling to less than 60 °C, the nanoparticles were extracted several times in methanol and hexanes. The final hexanes solution

containing the desired nanoparticles was dried by rotary evaporation, with samples stored in the dark in air.

For the pyridine ligand exchange process, CdSe nanoparticles were redispersed in 3 mL of pyridine and sonicated for 1 hour in air. The dots were then precipitated and centrifuged in hexanes three times. A modified ligand exchange process with increased temperature was employed for ligand exchange processes[9] with either **ArSH** or **ArSSAr,** standard nanoparticles were redispersed in chloroform and about 0.4 g of the desired capping ligand were added to the mixture. This mixture was then stirred at 60 °C for 3 days under N_2 atmosphere, with an additional 10 mL of chloroform added each day to compensate for solvent lost over night.

CdSe Nanocrystal Characterization

XPS

All XPS experiments were performed in a commercially available multi-chamber ultrahigh vacuum (UHV) system manufactured by SPECS Surface Nano Analysis GmbH (Berlin, Germany), at a base pressure of approximately 2 x 10^{-10} mbar. A homebuilt electrospray injection system is attached to one of the preparation chambers that allows the direct injection of macromolecular material from suspension into vacuum. For more detail on the system see Dam et al.[10]

For sample preparation, highly oriented pyrolytic graphite (HOPG) crystal substrates (Mikromasch, USA, "ZYA" quality) were cleaved to obtain a pristine surface. These crystals were attached to the substrate holder with conductive silver epoxy and a thin metal sheet was

attached to the top of the HOPG crystal that was removed after loading the sample, creating a clean graphite surface. The materials to be analyzed were each dispersed in toluene at a concentration of 1 mg/mL and sprayed onto the intake orifice of the electrospray deposition system. After passing through the system, the molecular beam was captured on the substrate forming a thin film. The syringe tip had a 100 μm inner diameter and the spray rate was 4 mL/h. The syringe needle was kept at a potential of -2 kV relative to ground during depositions, and the tip-to-orifice distance was 3 mm. To reduce ambient contamination to negligible levels, during deposition the needle tip was kept in an enclosure that was filled with a slight overpressure of nitrogen gas relative to atmosphere during deposition.

Surface characterization of the substrates and prepared thin films was carried out using standard XPS (Mg *K*α, 1253.6 eV, 20 mA emission current). Analysis of the photoelectrons was performed with a SPECS PHOIBOS 100 hemispherical analyzer. The spectrometer was calibrated to yield the standard Cu $2p_{3/2}$ line at 932.66 eV and the Cu $3p_{3/2}$ line at 75.13 eV. Data evaluation of all photoemission spectra was carried out using Igor Pro software (WaveMetrics, Inc.). For the determination of the maximum core-level peak position a mixed Gaussian-Lorenzian line shape was used.

PL

PL spectra for the data presented were measured on a homebuilt optical fiber photoluminescence measurement system with a Stellarnet BLUE Wave portable spectrometer, and Stellarnet LED illumination source, and a Stellarnet Y type ‘7-around-1’ 600 micron fiber optic cable fluorescence probe tip. An excitation wavelength of 390 nm was used with an average of 3 scans

and a 10 s detector integration time.

TEM

All transmission electron microscopy (TEM) images were taken on an FEI Tecnai G2 F-20 TEM operating in bright field mode. TEM samples were prepared by dispersing a small amount of dry CdSe nanoparticles in hexanes, and dropping onto ultrathin carbon film substrates with holey carbon support films on 400 mesh copper grids (Ted Pella, Inc.).

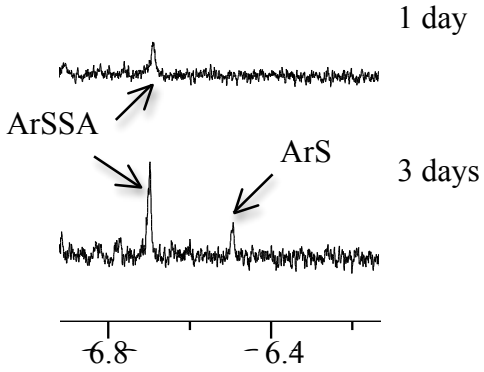


Figure S1: ^{1}H NMR spectra in the aryl region for ArSH ligand exchange after 1 and 3 days.

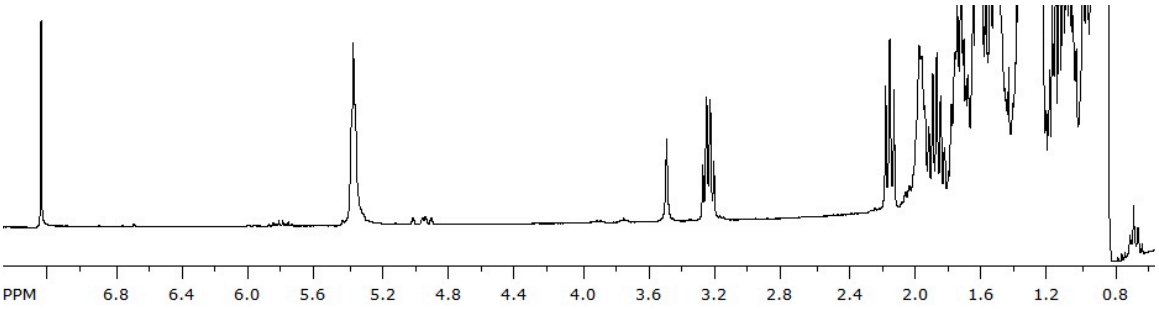


Figure S2: ^{1}H NMR spectrum of CdSe nanoparticles grown for 18 min. at 260 C under standard conditions, but with ArSH injected immediately prior to SeTBP. This ^{1}H NMR spectrum shows that there is not a ligand exchange at under standard growth conditions, as there is no signal from the ArSH ligand.

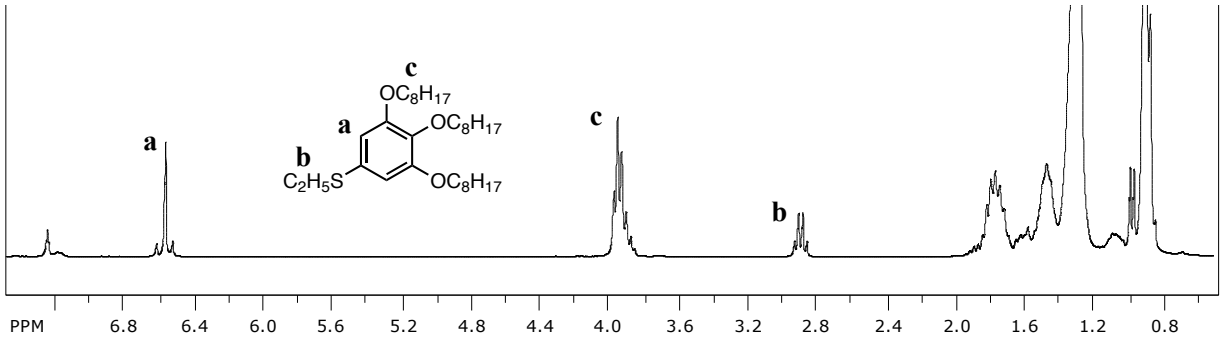


Figure S3: $ArSC_2H_5$ ^1H NMR Spectrum

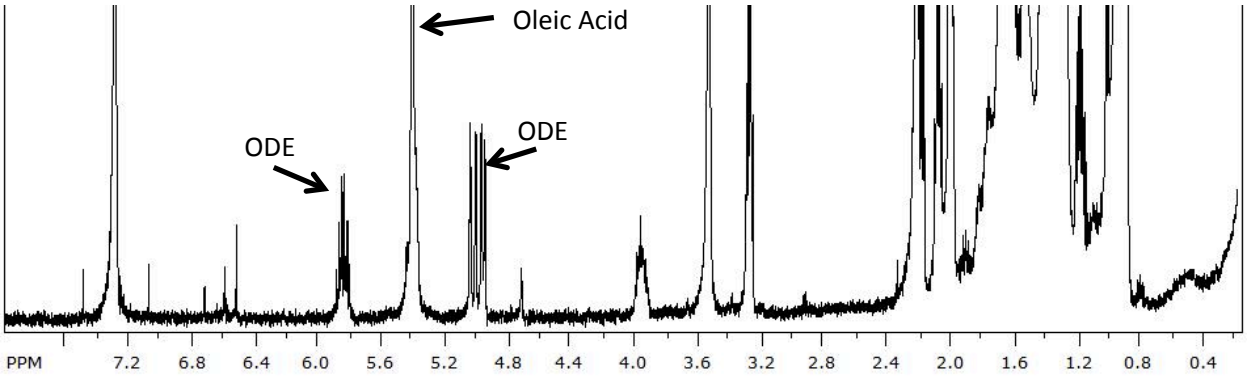


Figure S4: Full ^1H NMR spectrum of ArS-CdSe QDs showing the presence of oleic acid at 5.34 ppm and the presence of residual ODE at 5.81 and 4.86 ppm after washing with MeOH and hexanes. Evidence of other remaining ligands is obscured by the presence of oleic acid, ODE, and ArS- in the alkyl region.

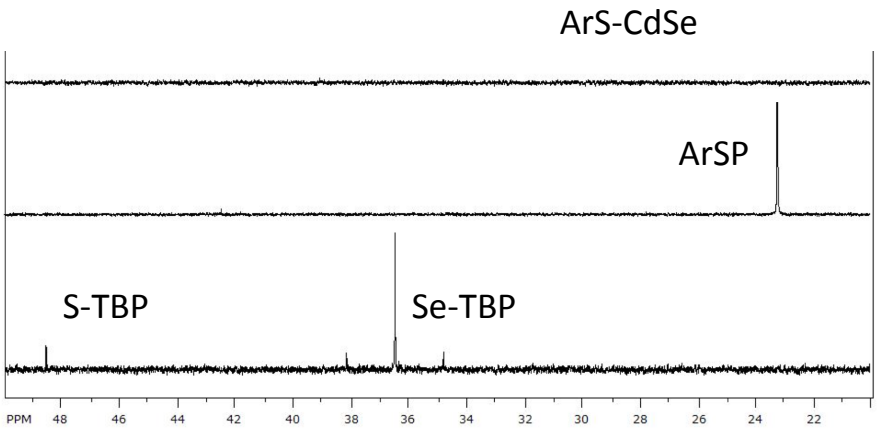


Figure S5: ^{31}P NMR Spectra of ArS-CdSe hexanes wash (top, desired product), neat ArSP (middle), and ArS-CdSe methanol wash (bottom, reaction byproducts), with the peak at 36.8 ppm

corresponding to residual Se precursor (TBPSe), and the peak at 48.7 corresponding to TBPS, a reaction byproduct.[11]

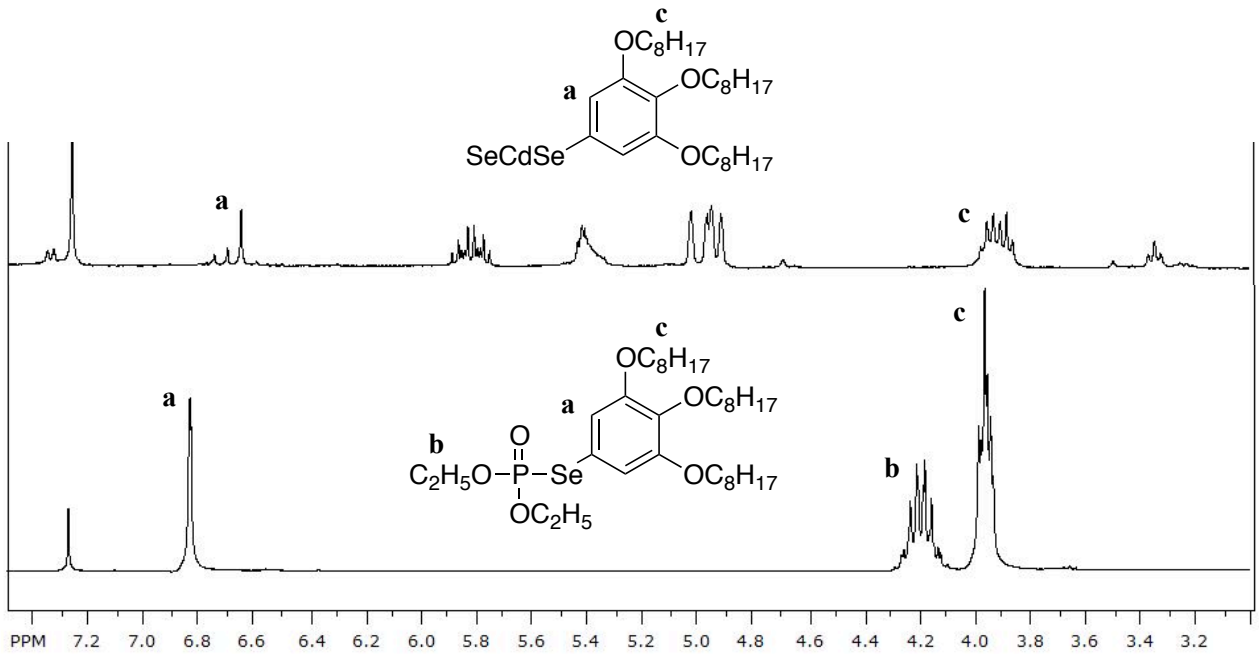


Figure S6: ^{1}H NMR Spectra of ArSe-CdSe (top) and neat ArSeP (bottom), highlighting the disappearance of the ethoxy protons of the phosphonate group at 4.2 ppm and the change in the aryl region response with functionalization, similar to that observed for the attachment of ArSP to CdSe.

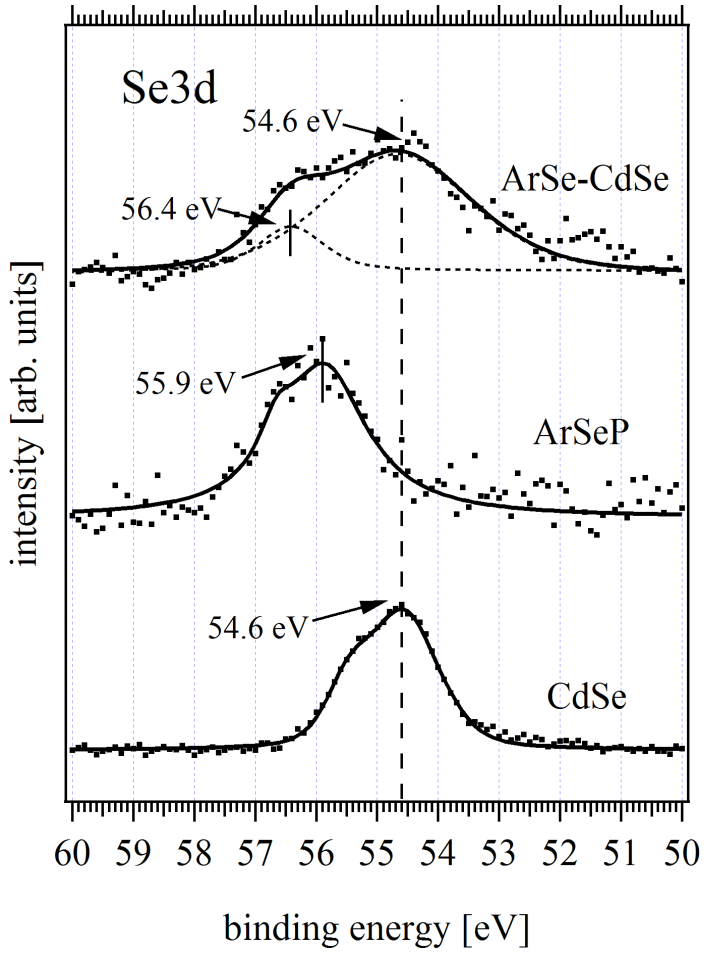


Figure S7: Se3d XPS for neat CdSe (bottom), neat ArSeP (middle), and ArSe-CdSe (top), highlighting the shift in Se binding energy of the ArSeP Se3d signal to higher binding energies with attachment to CdSe.

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