

Electronic Supplementary Information for

**Solvent-like Ligand-Coated Ultrasmall Cadmium Selenide
Nanocrystals: Strong Electronic Coupling in a Self-Organized
Assembly**

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Synthesis and Purification of PEG_n-Thiolate-Coated CdSe SNCs. Briefly, stock solutions of CdSO₄•8/3 H₂O (1M) and Na₂SeSO₃ (0.25 M) were prepared in water. In a 100 mL two-neck round bottom flask 30 mL of nitrogen-purged water was mixed with 0.120 mL CdSO₄•8/3 H₂O and the required amount of PEG_n-SH. The reaction mixture was stirred at room temperature under nitrogen for 30 min. Next, 1.0 M NaOH was added dropwise to the reaction mixture under gentle stirring until a stable pH of 11.5 was achieved. The solution was then heated to 30 °C for 5 min with stirring. 0.36 mL of Na₂SeSO₃ was quickly injected and the formation of CdSe SNCs was followed by UV-vis spectroscopy. For PEG₆-thiolate-protected CdSe SNCs final concentrations of the reactants were calculated to be 4 mM CdSO₄, 32 mM PEG₆-thiols, and 3 mM Na₂SeSO₃. To prepare different PEG_n-thiolate-coated CdSe SNCs, concentration of Cd and Se precursors was kept identical but amount of PEG_n-thiols were varied: for n = 4, 18, 60, and 150 the amount of PEG_n-thiols used was 32, 32, 48, and 60 mM, respectively.

The PEG_n-thiolate-protected CdSe SNCs were purified by solvent extraction and precipitation techniques.⁽⁵¹⁾ An aqueous solution of prepared CdSe SNCs was transferred to a 500 mL separatory funnel followed by addition of a mixture of CH₂Cl₂ and isopropanol (1.0:0.5 of CH₂Cl₂ : isopropanol). The SNCs solution was shaken vigorously and then allowed to stand in the dark until two distinct layers appeared, where the top layer was clear and the bottom layer was yellow. The yellow solution was collected and brought to dryness using a rotary evaporator. The resulting yellow material was then redissolved in a minimum volume of CH₂Cl₂ and precipitated with hexane. The hexane precipitation was performed a minimum of two times. The yellow solid was then collected by centrifugation, dried under high vacuum, and stored under nitrogen in dark.

Synthesis and Purification of OLA-Coated CdSe SNCs. For 1.6 nm diameter CdSe SNCs synthesis 0.14 g of CdCl₂ was added to a 100 mL two-neck round-bottom flask and dissolved in 5 mL of OLA under nitrogen with stirring at 70 °C. Se-precursor stock solution was prepared by reacting 0.12 g of freshly ground selenium in a 25 mL two-neck round-bottom flask containing 1.57 mL OLA and 430 µL of 1-hexanethiol under nitrogen atmosphere until all selenium dissolved. The Cd-precursor was diluted with 10 mL toluene before addition of Se-precursor. After addition of Se-precursor, the reaction was allowed to stir at 70 °C for 4 h. The SNC growth was quenched by diluting with 20 mL of toluene. The SNCs were immediately precipitated by dropwise addition of CH₃CN until the solution become turbid. The SNCs were collected through centrifugation at 7000 rpm for 5 min. This precipitation step was repeated once more and then the resultant bright yellow solid was dissolved in chloroform and centrifuged for a final time to remove insoluble materials, decanted, and the yellow solution containing the OLA-coated CdSe SNCs was evaporated under reduced pressure. To synthesize larger CdSe SNCs (1.7-2.3 nm diameter) the Se-precursor was injected to Cd-OLA precursor at 100 °C and the aliquots were removed at specific time point and immediately diluted with toluene to obtain desirable sizes. We followed the same purification method as described for OLA-coated 1.6 nm CdSe SNCs.

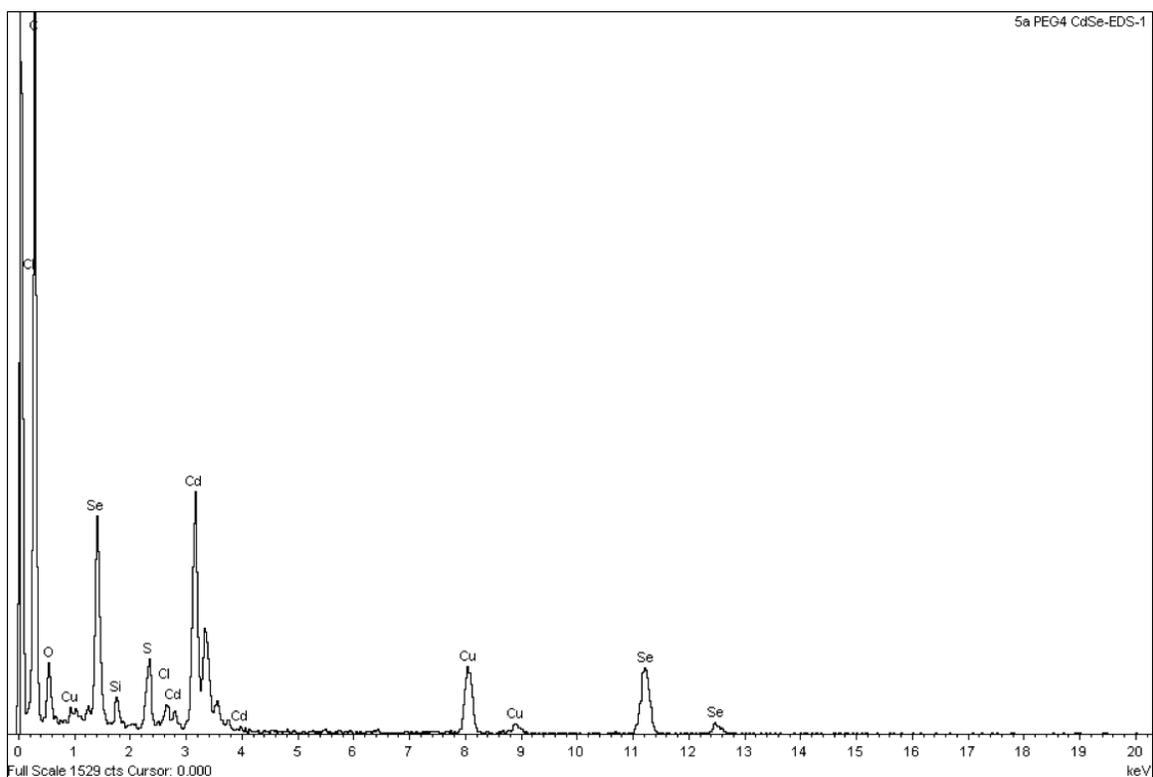


Figure S1: EDS spectrum of PEG₄-thiolate-coated 1.6 nm CdSe SNCs. The spectrum was collected in the TEM instrument with the same sample as shown in Figure 2A. The atomic percentage of Cd:Se was 3.79:2.85. Considering the CdSe SNC contains a stoichiometric core, therefore 0.94 atomic percent of Cd²⁺ was present on the surface in the form of Z-type of ligand. Therefore, theoretically 1.88 atomic percent of sulfur from PEG₄-thiolate should be present in the purified sample. The EDS analysis showed the atomic percentage of sulfur present in the sample was 1.97. Presence of slightly higher percentage of sulfur could be due to presence of free PEG₄-thiols in the sample.

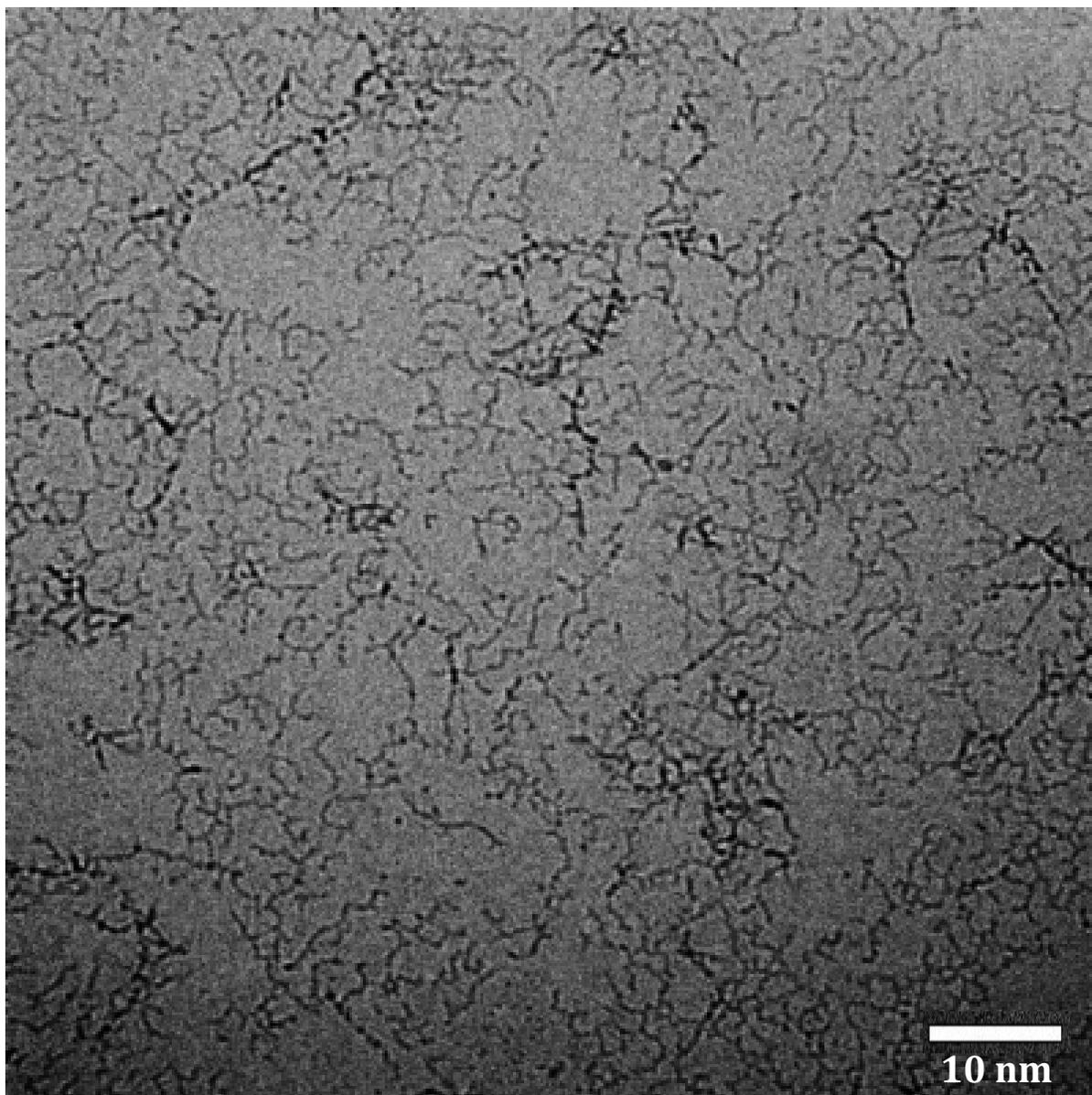


Figure S2: Cryo-TEM images of PEG₄-thiolate-coated CdSe SNCs.

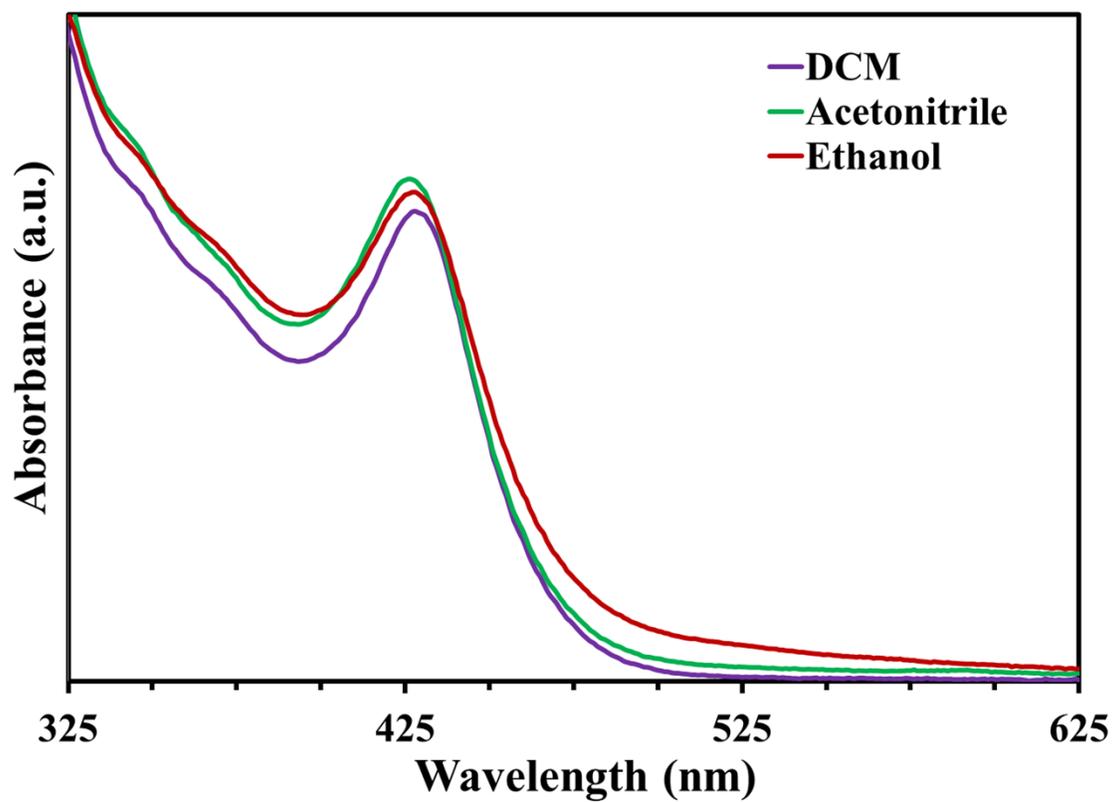


Figure S3: Room temperature UV-visible absorption spectra of PEG₆-thiolate-coated CdSe SNCs in different solvent.

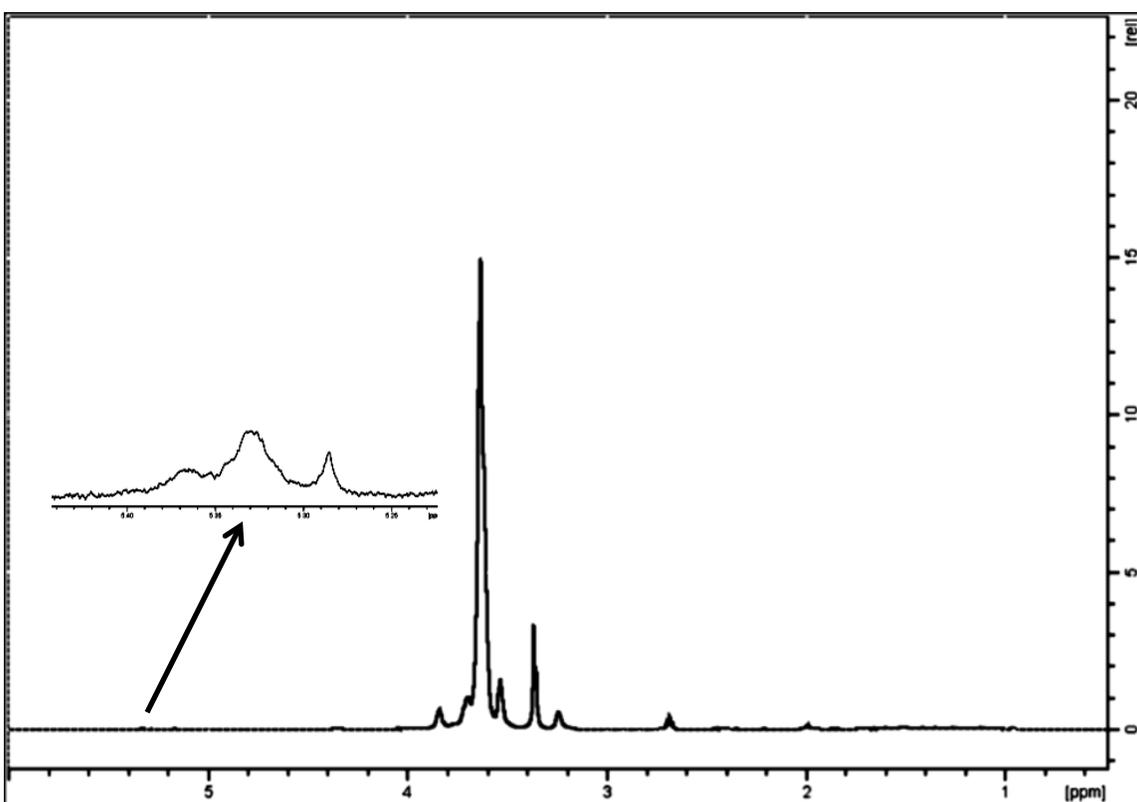


Figure S4: ^1H spectrum of PEG_6 -thiol-coated CdSe SNCs. The ligand exchange reaction on OLA-coated SNCs was conducted with PEG_6 -SH. The insert shows zoom OLA double bond region. The spectrum indicates that 95% of the original surface bound OLA ligand was replaced by PEG_6 -SH.

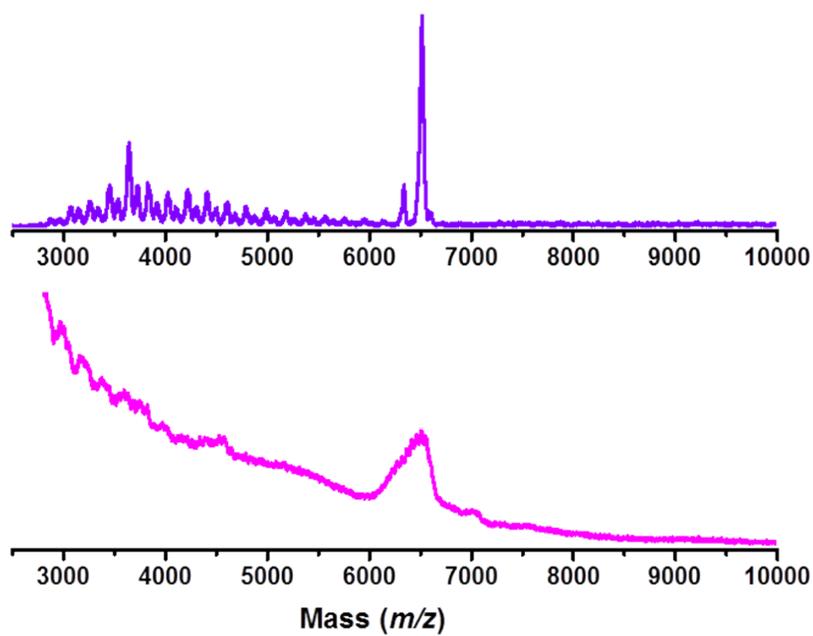


Figure S5: MALDI-TOF-MS spectra of OLA-(blue) and PEG₆-thiol (purple) -coated 1.6 nm CdSe SNCs. The highest intensity peak at m/z 6505 indicate (CdSe)₃₄ core composition.

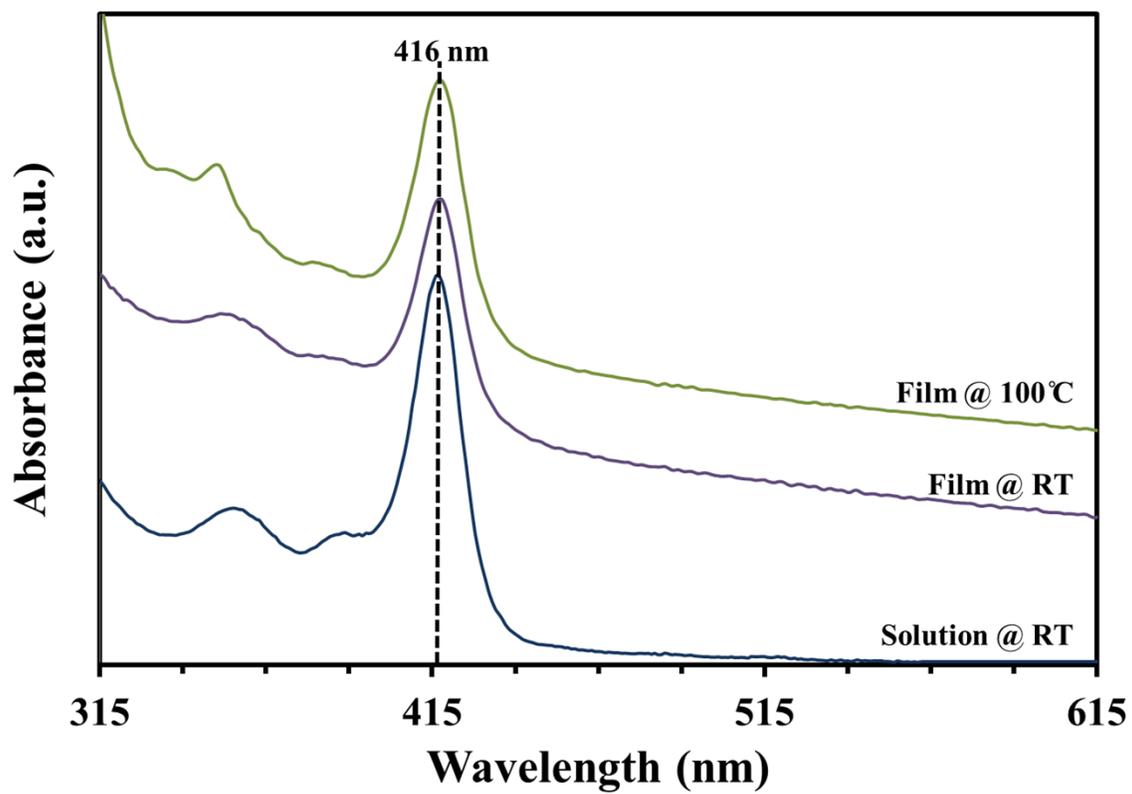


Figure S6: UV-visible absorption spectra of OLA-coated 1.6 nm CdSe SNC films on a glass substrate. CdSe SNCs did not display any electronic coupling when they were assembled onto solid surface as a dry film. The electronic coupling was not observed even after annealing at 100 °C.