

Electronic Supplementary Information

Photoswitchable Quantum Dots by Controlling the Photoinduced Electron Transfers

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Materials

Oleic acid, tech. (90%), tri *n*-octylphosphine, tech. (90%, TOP), tri *n*-octylphosphine oxide, tech. (TOPO, 90 %), 1-octadecene, tech. (90%, ODE), Oleylamine, tech. (70%), zinc acetate (99.99%), sulfur powder (99.98%), (±)- α -lipoic acid, tellurium shot (99.999 %), sodium borohydride (99%, NaBH₄), dimedone (95%), 4-nitrobenzaldehyde (98%), ammonium acetate (98%), dicyclohexylcarbodiimide (99%, DCC) were purchased from Aldrich. Calcium chloride anhydrous (CaCl₂) was purchased from Daejung Chemicals. Zinc powder was purchased from Shinyo Pure Chemicals. Cadmium acetate dihydrates (99.999%), and selenium shots (99.99%) were purchased from Alfa Aesar and Strem, respectively.

Synthesis of Quantum dots(QDs)

a) Synthesis of CdSe QDs

The CdSe core QDs were synthesized using standard methods^{S1} with slightly modification. 1 mmol of cadmium acetate dihydrate was dissolved in 3 mmol of oleic acid at 100 °C under vacuum for 1 hr. When the solution has cooled to room temperature, the cadmium precursor was mixed with selenium precursor. The selenium precursor was previously prepared by dissolving 2.5 mmol of selenium in 5 ml TOP in glove box. 20 ml of ODE and 4 mL of oleylamine were placed in a three-neck flask and heated to 300 °C under nitrogen gas flow. At this temperature, the mixture of cadmium and selenium precursors was quickly injected into the reaction flask and the temperature was maintained at 280 °C. The reaction mixture was kept stirred until CdSe QDs

of the desired size were obtained. The reaction mixture was cooled to room temperature, and diluted by hexanes. To remove excess organic materials, the QDs were precipitated by excess methanol, collected by centrifugation, and re-dispersed by small amount of hexanes.

b) Synthesis of CdSe/CdS/ZnS (Core/Shell/Shell) QDs

The synthesis of CdSe/CdS/ZnS (core/shell/shell) QDs followed the successive ionic layer adsorption and reaction (SILAR) approach^{S2} with modifications. 5 ml of ODE, 2 ml of oleylamine, and 200 nmol of CdSe QDs were loaded in a three-neck flask and heated to 250 °C under nitrogen gas flow. 0.1 M elemental sulfur dissolved in ODE, 0.1 M Cd-oleate in ODE and 0.1 M Zn-oleate were used as precursors for shell growth. The quantity of precursor used for each addition of shell monolayer (4 monolayers for CdS shell and 1 monolayer for ZnS shell) was calculated to account for the successive increases in particle volume as a function of increasing shell thickness. The reaction temperature was 250 °C and growth time was 10 min between each addition. The reaction mixture was cooled to room temperature, and diluted by hexanes. The product CdSe/CdS/ZnS (Core/Shell/Shell) QDs were purified by precipitation with excess methanol.

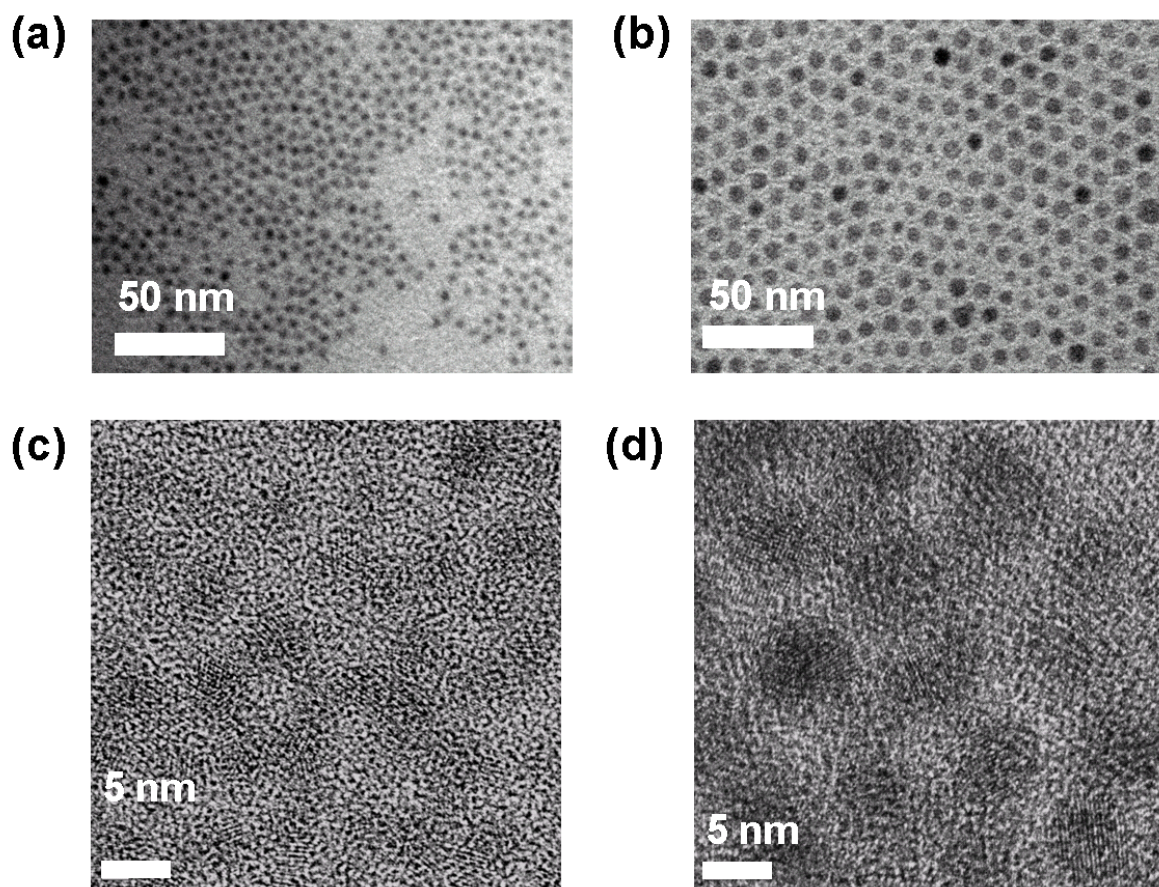


Figure S1. TEM image of (a) the b-QDs, and (b) the o-QDs. High-resolution TEM (HRTEM) images of (c) b-QDs, and (d) o-QDs.

c) Synthesis of CdTe/CdSe (Core/Shell) QDs^{S3}

For CdTe bare QD, 0.5 mmol of cadmium acetate dihydrate was dissolved in 1.5 mmol of oleic acid at 100 °C under vacuum for 1 hr. When the solution has cooled to room temperature, the cadmium precursor was mixed with tellurium precursor. The tellurium precursor was previously prepared by dissolving 2 mmol of tellurium in 4 ml TOP in glove box. 7 g of TOPO and 4 ml of oleylamine were used for both solvent and surfactant. They were loaded into a 50 ml 3-neck flask, and heated to 290 °C under nitrogen gas flow. At this temperature, the mixture of cadmium and tellurium precursors was quickly injected into the reaction flask and was kept stirred until CdTe QDs of desired size were obtained. The reaction mixture was cooled to room temperature, and diluted by hexanes. To remove excess organic materials, the QDs were

precipitated by excess methanol, collected by centrifugation, and re-dispersed by small amount of hexanes.

For CdSe shell deposition, 0.2 mmol of cadmium acetate dehydrate was dissolved in 0.6 of oleic acid at 100 °C under vacuum for 1 hr. When the solution has cooled to room temperature, the cadmium precursor was mixed with selenium precursor. The selenium precursor was previously prepared by dissolving 0.2 mmol of selenium in 2 ml of TOP in glove box. 9 g of TOPO was loaded to the 50 ml 4-neck flask. Under nitrogen gas flow, CdTe bare QDs were added to the reaction flask. When the temperature of the reaction flask reached 210 °C, the shell precursor mixture was added dropwise for 3 hr and the temperature was kept at 210~220 °C during the CdSe shell growth. The reaction mixture was cooled to room temperature, and diluted by hexanes. The product CdSe/CdTe (Core/Shell) QDs were purified by precipitation with excess methanol.

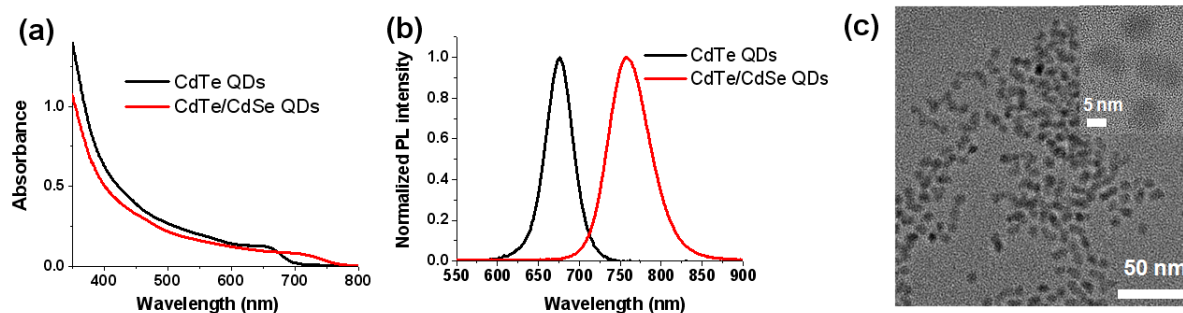


Figure S2. (a) UV-vis spectra and (b) normalized PL spectra of bare CdTe QDs (black) and CdTe/CdSe (Core/Shell) QDs (red). (c) TEM image of the CdTe/CdSe (Core/Shell) QDs. Image obtained at a higher magnification is shown in the inset.

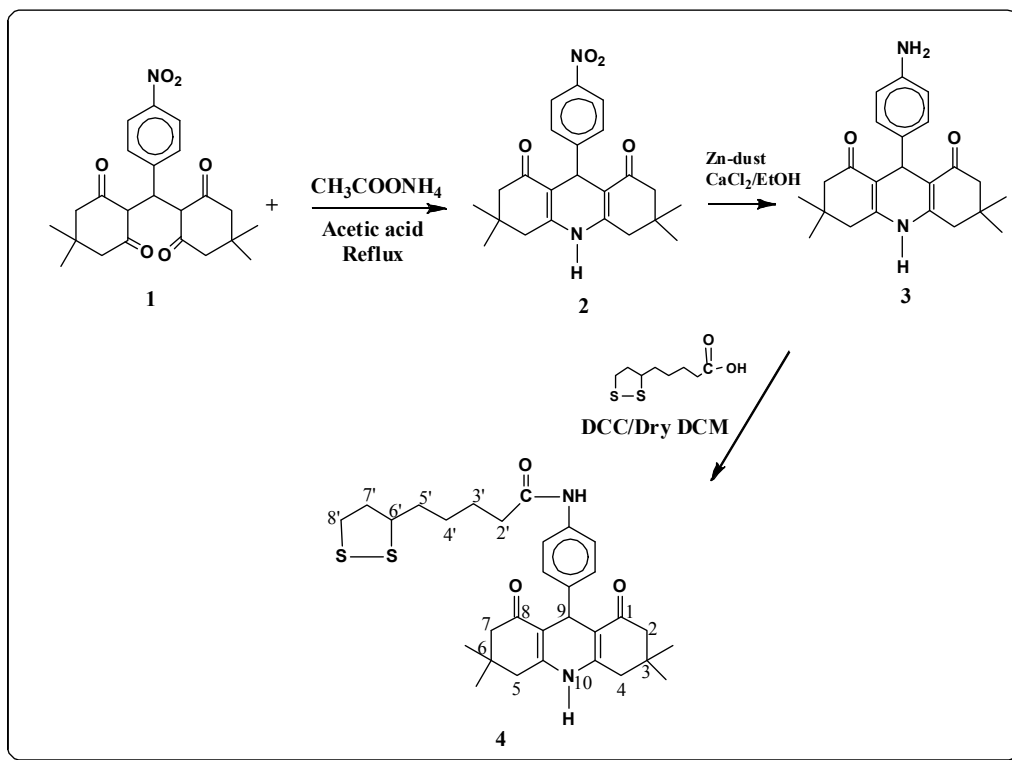
Synthesis of Acridinedione disulfide (N-[4-{3,3,6,6-tetramethyl 3,4,6,7,9,10-hexahydro-1,8 (2H,5H)-acridinedion-9-yl}-phenyl] lipoic acid amide)^{S4}

To a mixture of dimedone (5.0g, 36 mmol) in 15 mL of methanol-water (1:1, v/v) was added 4-nitrobenzaldehyde (2.7g, 18 mmol) and the mixture was warmed until the solution became cloudy. The (4-nitrobenzylidene) bis dimedone started to separate out. The reaction mixture was diluted with water (250 mL) and allowed to stand overnight; the 2,2'-(4-nitrobenzylidene) bis (5,5-dimethylcyclohexane-1,3-dione) **1** was collected by filtration, dried and recrystallised from methanol.^{S5} Yield : 6.9 g (94%).

A mixture of 2,2'-(4-nitrobenzylidene) bis (5,5-dimethylcyclohexane-1,3-dione) **1** (2.0 g, 4.8 mmol) and ammonium acetate (1.8 g, 24 mmol, excess) in acetic acid (20 mL) was refluxed for 40 hours. The reaction mixture was cooled and poured into crushed ice. The solid obtained was filtered and dried. The 9-(4-nitrophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2H,5H) acridinedione **2** was purified by recrystallisation from a mixture of methanol and chloroform (1:4).

The 9-(4-nitrophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2H,5H)acridinedione **2** (1.0 g, 2.5 mmol) was dissolved in 95% ethanol (25 mL) and added a solution of a catalytic amount of CaCl₂ in water followed by zinc (10 g). The mixture was thoroughly mixed and refluxed for 2 hours. After completion of the reaction as indicated by TLC, the excess of zinc and zinc oxide formed were filtered off from the hot solution. The filtrate was then diluted with ice-cold water and the separated solid was filtered and dried. The product **3** (aminoacridinedione) was purified by column chromatography over silica gel and eluting with 4% methanol in chloroform. Yield: 0.64 g (70%), Pale yellow solid. An equimolar mixture of **3** (1.0 g, 2.7 mmol) and lipoic acid (0.56 g, 2.7 mmol) in 15 ml dry dichloromethane in the presence of dicyclohexylcarbodiimide (0.84 g, 4.1 mmol, DCC) on refluxing, afforded the acridinedione disulfide **4**. Yield: 1.1 g (73%). ¹H-NMR (600 MHz, DMSO-d₆): δ 9.68 (s, 1H, N-H amide), δ 9.24 (s, 1H, N-H), 7.35 and 7.0 (ABq, J= 8.4 Hz, 4H, Ar-H), 4.76 (s, 1H, C9-H), 3.62 (m, 1H, C6'), 3.17- 3.1 (m, 2H, C8'), 2.46 and 2.40 (ABq, J= 17.4 Hz, 4 H, C4 & C5-CH₂), 2.43 (m, 1H, C7'), 2.25 (t, J = 7.2 Hz, 2 H, C2'), 2.18 & 1.97 (ABq, J = 16.2 Hz, 4 H, C2 & C7-CH₂), 1.87 (m, 1H, C7'), 1.68 – 1.58 (m, 4H two CH₂, C5', C4'), 1.39 (m, 2H C3'), 1.0 & 0.87 (2 s, 12H); ¹³C - NMR (600 MHz, DMSO-d₆): δ 194.8 (ring-CO), 171.21 (NH-CO), 149.5(4a),

142.5 (Ar-C₄), 137.2 (Ar-C1), 128.2 (Ar-CH), 119.0 (Ar-CH), 112.0 (9a), 56.5 (S-CH₂, C-6'), 50.7 (CH₂, C2), 40.4 (CH₂, C7'), 39.6 (CH₂, C4), 38.5 (CH₂, C8'), 36.6 (CH₂, C2'), 34.6 (CH₂, C5'), 32.7 (C3), 30.6 (C9), 29.6 (CH₃), 28.7 & 25.4 (C3' & C4' two CH₂), 26.94 (CH₃).



Scheme S1. Synthesis of acridinedione disulfide

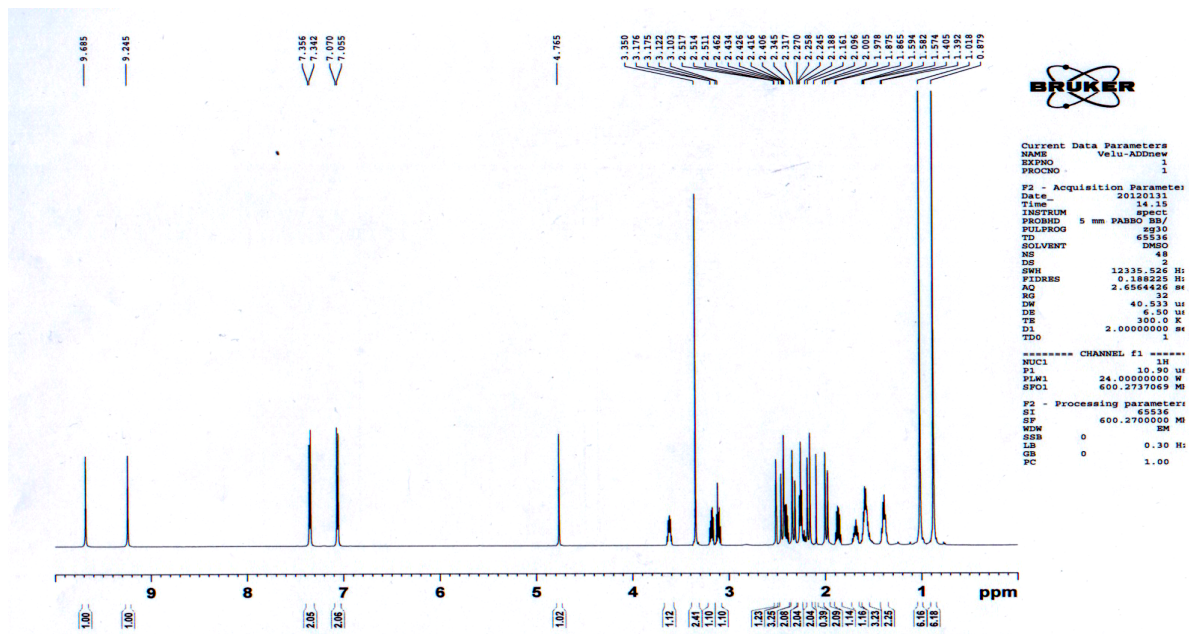


Figure S3. ^1H NMR data of acridinedione disulfide.

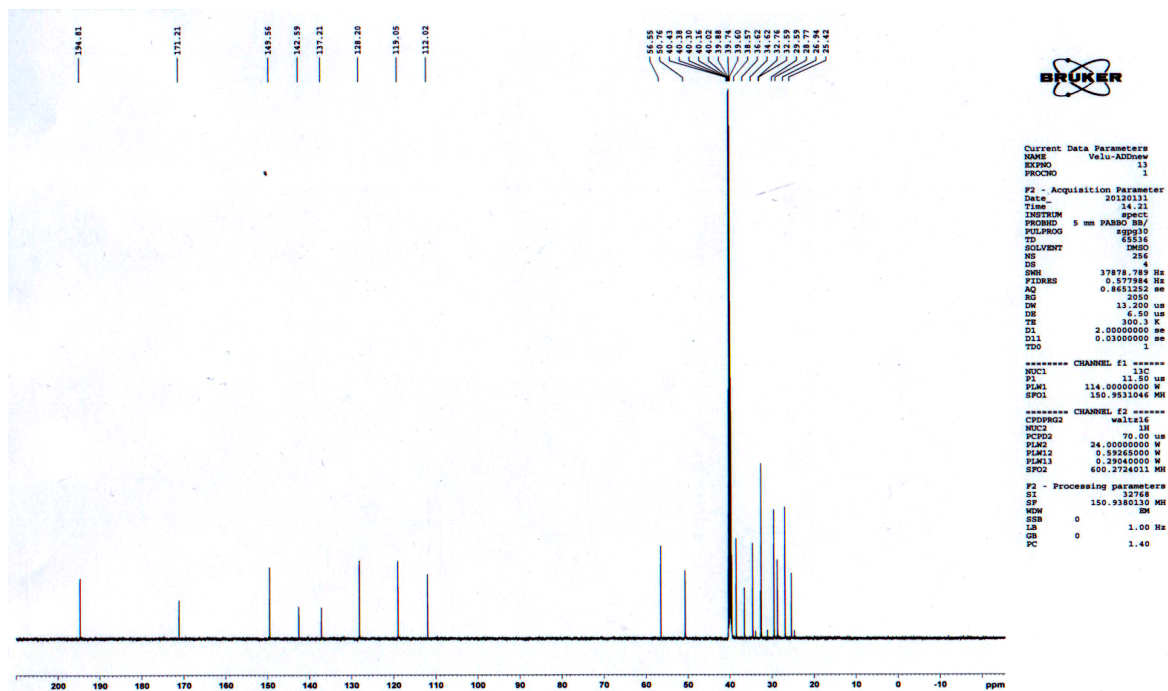


Figure S4. ^{13}C NMR data of acridinedione disulfide.

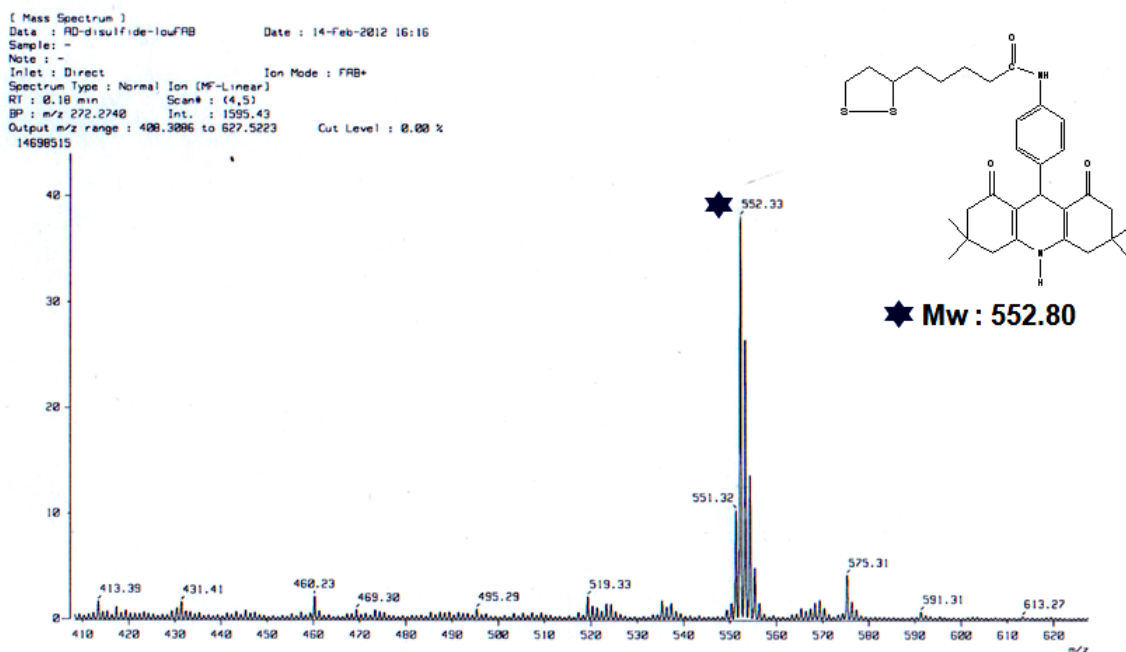


Figure S5. Mass spectra of acridinedione disulfide.

Preparation of QD-ADD complex

QD-ADD complex was prepared by adding 2-100 fold molar excess of ADDs to QDs in THF solution followed by introducing NaBH_4 in ethanol reaching $\sim 1 \mu\text{M}$ THF/ethanol (3:1 by volume) solution. The mixture solution was stirred at room temperature for 2 hrs under inert atmosphere.

Optical measurements

Quartz cuvettes of 1 cm path length with teflon cap were used for absorption and emission measurements. UV-Vis spectrophotometer (Agilent Technology 8453) and SPEX FluoroLog 3 (Jobin Yvon Horiba) Spectrofluorometer were used for absorption and emission measurements. The 532 nm *cw* DPSS laser (AIX-532-XXX), and monochromatic light of wavelength 365 nm produced by the 450 W Xe lamp (grating: 1200 grooves/mm, 330 nm blaze) was used for visible and UV light source, respectively. Time-resolved photoluminescence (TRPL) was measured using a time-correlated single photon counting (TCSPC) technique. The light source was a home-built cavity-dumped femtosecond Ti:sapphire oscillator that gives pulses at 750 nm with a pulse duration of ~20 fs. Pump pulses at 375 nm were generated by the second harmonic generation in a β -barium borate crystal. Fluorescence was collected by a parabolic mirror, dispersed by a monochromator (SP300i, Acton Research), and detected with an avalanche photodiode (Id100-50, Idquantique). Magic angle detection was used to avoid the effect of polarization. Full width at half-maximum of the instrumental response was 50 ps to provide ~10 ps of time resolution with deconvolution. The PL quantum yield (QY) of samples were estimated by comparing the integrated PL intensities to that of the rhodamine 101 standard (QY = 1).

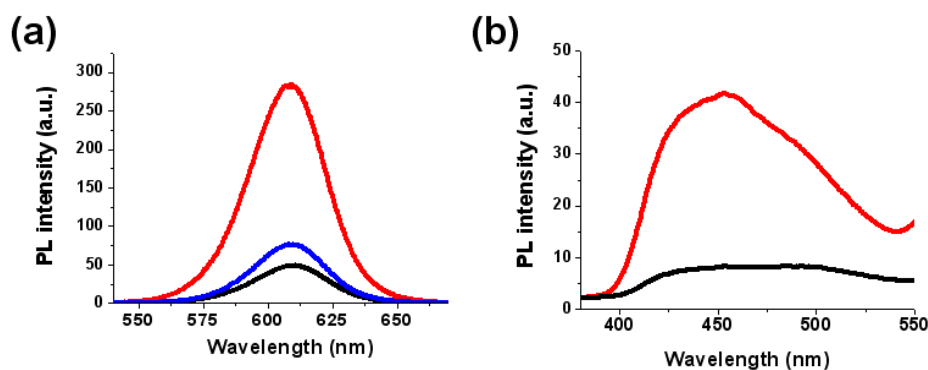


Figure S6. (a) PL spectra of o-QD samples before the ADD functionalization (red), after the o-QD-ADD complexation by 1:2 molar ratio under inert atmosphere (black), and o-QD-ADD complexation by 1:2 molar ratio after intentional exposure of the sample to air (blue). All the samples were excited at 365 nm. (b) PL spectra of a mixture of ADDs in their disulfide form and o-QD (red), and ADD-dithiol surface derivatized o-QDs (black) excited at 365 nm. The molar ratio of QD:AD chromophore is 1:100.

Table S1. Room-temperature quatro-exponential photoluminescence decay lifetimes of the CdSe QD and CdSe/CdS/ZnS (core/shell/shell) QD samples that are shown in manuscript Figure 2c and 2f.

Sample	A ₁ (%)	τ ₁ (ns)	A ₂ (%)	τ ₂ (ns)	A ₃ (%)	τ ₃ (ns)	A ₄ (%)	τ ₄ (ns)	τ _{ave} (ns)
CdSe QD-DHLA	50	0.043	26	0.54	20	2.71	4	16	1.4
CdSe QD-ADD	78	0.023	11	0.32	7	2.3	4	10	0.64
CdSe/CdS/ZnS QD-DHLA	48	0.70	17	1.0	21	6.7	14	28	5.5
CdSe/CdS/ZnS QD-ADD	48	0.49	18	0.74	26	4.3	8	21	3.0

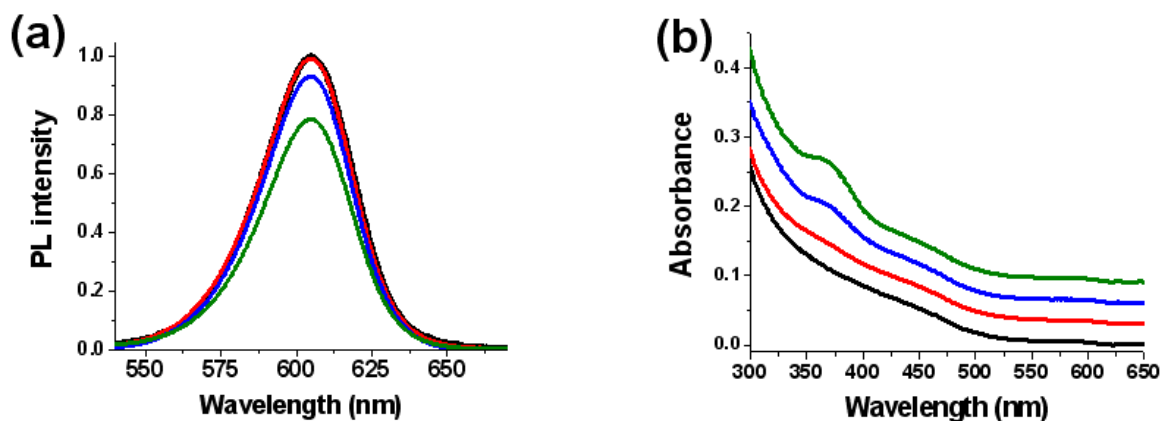


Figure S7. (a) PL spectra (exc. @ 365 nm) and (b) UV-vis spectra of mixtures of ADDs in their disulfide form with as-prepared o-QDs by different QD/ADD molar ratios of 1:2 (red), 1:20 (blue), and 1:100 (green). The QD sample before the ADD functionalization was measured for a control (black).

Supporting References:

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