Supporting Information

for the manuscript entitled

Achiral CdSe quantum dots exhibit optical activity in the visible region upon post-synthetic ligand exchange with D- or L-cysteine

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Instrumentation.

Circular Dichroism (CD). CD spectra were collected at 20 °C using a Jasco J-815 spectropolarimeter equipped with a single position Peltier temperature control system. Conditions were as follows: scanning speed 100 nm/min, data pitch 0.5 nm, DIT 1 s, and bandwidth 1 nm. A quartz cuvette with a 1 cm path length was used for all CD experiments. Each CD spectrum was an average of at least fifteen scans. UV-vis absorption spectroscopy. UV-vis spectra were collected at 20 °C using a Jasco V-600 UV-vis double beam spectrophotometer equipped with a single position Peltier temperature control system. A quartz cuvette with a 1 cm path length was used for all UV-vis experiments. Fluorescence spectroscopy. Photoluminescence measurements were done at 20 °C using a Varian fluorescence spectrophotometer using a scan rate of 600 nm/min, excitation wavelength 450 nm, with 5.0 nm excitation and emission slits. A quartz cuvette with a 1 cm path length was used. Fourier Transform Infrared spectroscopy (FTIR). FTIR spectra were acquired at 20 °C with a Bruker Platinum ATR single reflection diamond ATR module equipped with a one-finger clamp mechanism. X-Ray. Powder X-Ray diffraction data were collected on a Bruker – Axs Smart Apex II CCD Diffractometer. Dynamic Light scattering. DLS data were collected on Brookhaven ZetaPals Particle Size Analyzer. Transition Electron Microscopy. TEM data were recorded on FEI Tecnai F20 200kV Field emission transmission electron microscope. Solution NMR. Solution NMR spectra were acquired on Avance III 400 Bruker spectrometer equipped with a multi-nuclear probe. Solid state NMR (ssNMR). 1D $^{13}$C cross-polarization (CP) solid-state NMR magic angle spinning (MAS) spectrum was collected on a 600 MHz Avance III Bruker spectrometer equipped with a 3.2 mm E$^{\text{free}}$ triple resonance HCN probe. The solid state NMR sample was prepared by lyophilizing overnight the L-Cys-CdSe QDs in water. The powder sample was packed into 4 mm Bruker MAS rotor. The MAS spinning rate was maintained at 8.0 kHz, and the variable temperature set point was 0 °C. The width of the high power $\pi/2$ radio frequency (RF) $^1$H pulse was 3.2 µs, the $^1$H-$^{13}$C CP period was 1.2 ms, and the spectrum was acquired for 30 ms with 78 kHz TPPM $^1$H decoupling. Data was processed by MestReNova 6.0.3 with 30 Hz exponential line broadening.

Synthesis of TOPO/OA-CdSe QDs

TOPO/OA-CdSe QDs were synthesized using a modified literature procedure (Fig. S1). Trioctylphosphine selenide (TOPSe) was prepared by dissolving selenium (0.09 g) in trioctylphosphine (TOP, 2.1 mL) and ODE (10.2 mL) under nitrogen and sonication (light yellow solution). A stirred mixture of cadmium oxide (CdO, 0.075 g), trioctylphosphine oxide (TOPO, 4.7 g), oleic acid (OA, 1.9 mL) and octadecene (ODE, 17.0 mL) was heated to 300 °C under nitrogen. TOPSe solution (10 mL) was swiftly injected into the hot CdO solution. The reaction was stopped by placing the reaction mixture in a chilled toluene. The CdSe QDs were purified by three cycles of precipitating with 4:1 absolute
ethanol/toluene followed by centrifugation at 9,000 rpm for 10 min. The concentrations of all CdSe QD samples were determined by using size dependent extinction coefficients.²

**Fig. S1:** Synthetic scheme for synthesis TOPO/OA-CdSe QDs.¹

Synthesis of cysteine capped CdSe QDs by ligand exchange (Scheme S1): D- or L-cysteine (0.04 g) was dissolved in DI water (4.0 mL). The pH of the solution was adjusted to 12 with tetramethylammonium hydroxide (TMAH) followed by purging with nitrogen for 5 min. A solution of TOPO/OA-CdSe QDs in toluene (3.0 mL, 0.05 mM) was added. The mixture was stirred at room temperature under nitrogen in the absence of light. The cysteine capped CdSe QDs transferred to the aqueous layer. The cysteine-CdSe nanoparticles were precipitated with isopropanol/DI water (4:1) and centrifuged at 13,000 rpm for 5 min. The process was repeated three times and the resulting cysteine-CdSe were redissolved in DI water.

**Scheme S1:** Schematic ligand exchange on TOPO/OA-CdSe QDs with chiral cysteines (D- and L-cysteines).
Size determination of synthesized Cys-CdSe QDs

The sizes were determined by using empirical fitting functions developed by Peng et al. as shown below based on the first excitonic absorption wavelength.\textsuperscript{2}

**PENG EQUATION (UV-vis)**

\[
\text{CdSe: } D = (1.6122 \times 10^{-9}) \lambda^4 - (2.6575 \times 10^{-6}) \lambda^3 + (1.6242 \times 10^{-3}) \lambda^2 - (0.4277) \lambda + (41.57)
\]

D (nm) is the size of CdSe QDs, \(\lambda\) (nm) is the wavelength of the first excitonic peak.

Absorption wavelength = 528.0 nm (\(\lambda\) in equation above)
Estimated size = \((1.6122 \times 10^{-9}) \times (528)^4 - (2.6575 \times 10^{-6}) \times (528)^3 + (1.6242 \times 10^{-3}) \times (528)^2 - (0.4277) \times (528) + (41.57) = 2.60\text{ nm}\)

**SCHERRER EQUATION (XRD)**

Average size was calculated using the Scherrer equation:

\[
t = \frac{0.9 \lambda}{\beta \cos \theta}
\]

t: average size of the ordered (crystalline) domain
\(\beta\): line broadening at half the maximum intensity (FWHM) in radians
\(\theta\): Bragg angle
\(\lambda\): X-ray wavelength from Mo source = 0.709 Å

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<th>(111) Peak</th>
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<th>(113) Peak</th>
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<td>(\beta) (in radians) = 0.026</td>
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<tr>
<td>(t = 2.67\text{ nm})</td>
<td>(t = 2.46\text{ nm})</td>
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Average size of cysteine-CdSe QDs from XRD = 2.53 nm
**Fig. S2:** DLS results of *L*-cysteine-capped CdSe in water (Ø = 3.0 nm determined from absorption spectrum).

**Fig. S3:** Representative sets of TEM micrographs for the *L*-cysteine-capped CdSe (Ø = 3.0 nm determined from absorption spectrum).

**Fig. S4:** $^{13}$C solid state NMR spectra of *L*-cysteine-capped CdSe (Ø = 3.3 nm). Asterisk denotes the spinning side band of COO peak.
Fig. S5: Changes in UV-vis absorption (left) and raw circular dichroism (CD, without solvent subtraction, right) spectra with decrease in concentration of L-cysteine-CdSe QDs (DI water). Ø = 2.5 nm.

Fig. S6: Changes in intensity of UV-vis absorption and CD spectra as a function of decreasing concentration of L-cysteine-CdSe QDs in DI water. Ø = 2.5 nm.

Fig. S7: Left: CD spectra of L-cysteine-capped CdSe (Ø = 3.0 nm) in DI water at 20 °C and 80 °C. Right: Thermal cycle CD spectra of L-cysteine-capped CdSe (Ø = 3.0 nm). A solution of L-cysteine-CdSe was heated from 20 °C to 80 °C then cooled back to 20 °C. The heating-cooling cycle was repeated twice consecutively. Inset: The 550 nm CD signal recorded at 20 °C nm as a function of heating-cooling cycle.
**Fig. S8:** FTIR spectrum of L-cysteine-CdSe (left) and TOPO/OA-CdSe (right). Ø = 3.0 nm.

**Fig. S9:** $^1$H NMR spectra (400 MHz) of oleic acid-capped CdSe (Ø = 3.3 nm) in CDCl$_3$ (top) and solution of L-cysteine-capped CdSe (Ø = 3.3 nm) in D$_2$O prepared by ligand exchange (bottom).

**Ligand exchange on L-cysteine-CdSe QDs with 1-dodecanethiol (DDT-CdSe synthesis):** Dodecanethiol (DDT) capped CdSe QDs were synthesized by a phase transfer of cysteine-CdSe QDs from water to toluene by replacing the cysteine ligands with DDT ligands. A aqueous solution of L-cysteine-CdSe QDs (2.0 mL, 20 µM) was placed in a round bottom flask and DDT (1.0 ml) was added followed by addition of acetone (2.5 mL). The flask was vigorously stirred while heated to 55 °C. The phase transfer occurred within 10 min as indicated by the color change of both phases. Toluene (1.0 mL) was added to the flask and the organic layer containing the QDs was decanted and purified by mixing with water, shaking, then centrifuging at 13,000 rpm for 5 min. The process was repeated three times and the top toluene layer was collected by a syringe.
Fig. S10: Absorption spectra of DDT-CdSe (toluene, red curve) and L-cysteine-CdSe (DI water, black curve). Ø = 2.5 nm.

Fig. S11: Emission spectra of D-cysteine-CdSe (blue curve) and L-cysteine-CdSe (red curve) in DI water (left) and emission spectra of TOPO/OA-CdSe in toluene (right). Ø = 2.5 nm.

Fig. S12: Absorption (left) and emission (right) spectra of 3.0 nm D-cysteine-CdSe (blue curve) and L-cysteine-CdSe (red curve) in DI water.
Fig. S13: CD spectra of 3.0 nm D-cysteine-CdSe (blue curve) and L-cysteine-CdSe (red curve) in DI water.

Fig. S14: Absorption (left) and emission (right) spectra of 3.3 nm D-cysteine-CdSe (blue curve) and L-cysteine-CdSe (red curve) in DI water.

Fig. S15: CD spectra of 3.3 nm D-cysteine-CdSe (blue curve) and L-cysteine-CdSe (red curve) in DI water.

References