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Electronic Supporting Information

for the manuscript entitled

The Effect of Molecular Isomerism on the Induced Circular Dichroism of Cadmium Sulfide Quantum Dots

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Materials

L- and D-carboxylic acids and tetramethylammonium hydroxide (TMAH) were purchased from Sigma-Aldrich or P212121, LLC. OA-CdS QDs were purchased from NNCrystal US Corporation. All commercial chemicals were used as received. D.I. water was obtained from a Milli-Q system with a resistivity of 18.2 $M\Omega$ •cm. The diameter of the QDs was determined using Peng's equation from the absorption spectra.¹

Methods and Instrumentation

<u>Circular Dichroism (CD).</u> CD spectra were collected at 22 °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 1.0 nm. A quartz cuvette with a 1.0 cm path length was used for all CD experiments. Each CD spectrum was an average of six scans.

<u>UV-vis absorption spectroscopy.</u> UV-vis spectra were collected at 22 °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 1.0 cm path length was used for all UV-vis experiments.

<u>Fluorescence spectroscopy</u>. Photoluminescence measurements were performed at 22 °C using a Jasco FP-8300 fluorescence spectrophotometer equipped with a single position Peltier temperature control system. Conditions were as follows: scan rate of 600 nm/min, low sensitivity and 10/10 nm excitation and emission slits. A quartz cuvette with a 1.0 cm path length was used.

<u>ATR-FTIR</u>. IR spectra were acquired at a Thermo Nicolet iS10 spectrometer using the OMNIC 8 software equipped with a Smart iTX ATR accessory. Laser: HeNe; Source: Mid-infrared Ever-Glo and Tungsten/halogen; beamsplitter: KBr/Ge mid-infrared optimized (7800 to 350 cm⁻¹), detector: DTGS; accumulations: 16.

<u>Transmission electron microscopy (TEM)</u>: Imaging was performed on a FEI Tecnai G2 F20 scanning transmission electron microscope (STEM) operating at 200 kV. Samples for TEM were prepared by ultrasonic dispersion of the crude solution of chiral carboxylic acid functionalized CdS QDs in methanol. The suspensions were then drop-cast onto carbon-coated copper grids and dried in air.

<u>Solution phase and solid state nuclear magnetic resonance (NMR)</u>: Magic Angle Spinning Solid State NMR (MAS ssNMR) experiments were carried out on Bruker Avance NEO 700 MHz NMR spectrometer equipped with a 4 mm E^{free} triple resonance HCN probe. Samples were packed into 4 mm Bruker MAS rotors. One dimensional (1D) ¹³C ssNMR spectra were acquired using ¹H-¹³C cross-polarization (CP) and ¹H decoupling during acquisition. ¹H-¹³C CP was achieved with a 50-100% ramped 56 kHz ¹H and 45 kHz

¹³C pulses for 1.0 ms. Spectra were acquired for 25 ms with 67 kHz of two-pulse phase modulated (TPPM) ¹H decoupling and with 4 s recycle delay. Experiments were performed at 258 K (variable temperature set point) and 10.0 kHz MAS frequency. All spectra were externally referenced to DSS using the adamantane downfield ¹³C peak at 40.48 ppm.² Data were processed with TopSpin using cosine squared window function.

Solution NMR spectra were collected on a Bruker Avance NEO 700 MHz NMR spectrometer equipped with a solution 5-mm triple resonance inverse TCI CryoProbe and using a standard Bruker pulse sequence with a 30° flip angle ¹H pulse. The recycle delay was 1.0 s.

L-AAs	AAs abbreviation	AAs (mg)	TMAH (eq)
Alanine	L-Ala	24	0.82
aspartic acid	L-Asp	38	1.93
cysteine	L-Cys.HCl.H ₂ O	72.5	3.01
glutamic acid	L-Glu	41	3.96
histidine	L-His	43	2.99
isoleucine	L-Ile	37	2.93
allo-isoleucine	L-allo-Ile	37	2.93
valine	L-Val	37	2.93
lactic acid	L-LA	24	0.00
malic acid	L-MA	37	4.00
methylsuccinic acid	R-MSA (L-MSA)	37	1.77
serine	L-Ser	34	1.71
isoserine	L-Isoser	34	1.71
proline	L-Pro	32	0.79
tartaric acid	L-TA	41	4.04
threonine	L-Thr	34	1.93
allo-threonine	L-allo-Thr	34	1.93

Table S1: Phase transfer ligand exchange condition for the synthesis of chiral carboxylic acids functionalized CdS from OA-CdS ($\emptyset_{CdS} \approx 4.1 \text{ nm}$).

Diastereomers



Positional (structural) isomers



Chart S1. Structures of chiral carboxylic acids used for functionalization of CdS QDs.



Figure S1. UV-vis absorption and emission spectra of OA-CdS QDs ($\emptyset_{CdS} = 4.1 \text{ nm}$). $\lambda_{ex} = 350 \text{ nm}$; low sensitivity, excitation/emission slits: 2.5 nm/2.5 nm.



Figure S2. Left: Histogram of hydrodynamic diameter from dynamic light scattering of the OA-CdS QDs in cyclohexane with average diameter of 6.5 nm ($Ø_{CdS} = 4.1$ nm determined from the absorption spectrum using the Peng's equation).



Figure S3. Alkene (left) and H α /H β (right) regions of ¹H NMR spectra of MSA-CdS QDs (blue lines) and OA-CdS QDs (green lines).



Figure S4. Alkene (left) and H α (right) regions of ¹H NMR spectra of Thr-CdS QDs (red lines) and OA-CdS QDs (green lines).



Figure S5. ¹H NMR spectra of TMAH in deuterated MeOH to determine the amount of dissolved cyclohexane in MeOH.



Figure S6. ¹³C MAS ssNMR spectra of L-Thr/TMAH/CdS solid samples prepared by evaporation or precipitation. Black dashed rectangles indicate new signals in L-Thr-CdS QDs. Spectra were referenced to DSS (sodium salt of 2,2-dimethyl-2-silapentane-5-sulphonic acid).



Figure S7. Left: Left: ATR-IR spectra of L-Thr, dropcasted MeOH solution of L-Thr + TMAH, and dropcasted MeOH solution of L-Thr-CdS + TMAH. Right: ATR-IR spectra of L-allo-Thr, dropcasted MeOH solution of L-allo-Thr + TMAH, and dropcasted MeOH solution of L-allo-Thr-CdS + TMAH. ($\emptyset_{CdS} = 4.1 \text{ nm}$).



Figure S8. Left: ATR-IR spectra of L-MA, dropcasted MeOH solution of L-MA + TMAH, and dropcasted MeOH solution of L-MA-CdS + TMAH. Right: ATR-IR spectra of L-MSA, dropcasted MeOH solution of L-MSA + TMAH, and dropcasted MeOH solution of L-MSA-CdS + TMAH. ($\emptyset_{CdS} = 4.1$ nm).



Figure S9. Left: ATR-IR spectra of L-Ile, dropcasted MeOH solution of L-Ile + TMAH, and dropcasted MeOH solution of L-Ile-CdS + TMAH. Right: ATR-IR spectra of L-allo-Ile, dropcasted MeOH solution of L-allo-Ile + TMAH, and dropcasted MeOH solution of L-allo-Ile-CdS + TMAH. ($\emptyset_{CdS} = 4.1 \text{ nm}$).



Figure S10. Left: ATR-IR spectra of L-Ser, dropcasted MeOH solution of L-Ser + TMAH, and dropcasted MeOH solution of L-Ser-CdS + TMAH. Right: ATR-IR spectra of L-Pro, dropcasted MeOH solution of L-Pro + TMAH, and dropcasted MeOH solution of L-Pro-CdS + TMAH.



Figure S11. Left: ATR-IR spectra of L-Asp, dropcasted MeOH solution of L-Asp + TMAH, and dropcasted MeOH solution of L-Asp-CdS + TMAH. Right: ATR-IR spectra of L-Glu, dropcasted MeOH solution of L-Glu + TMAH, and dropcasted MeOH solution of L-Glu-CdS + TMAH. ($\emptyset_{CdS} = 4.1$ nm).



Figure S12. Left: ATR-IR spectra of L-Cys, dropcasted MeOH solution of L-Cys + TMAH, and dropcasted MeOH solution of L-Cys-CdS + TMAH. Right: ATR-IR spectra of L-His, dropcasted MeOH solution of L-His + TMAH, and dropcasted MeOH solution of L-His-CdS + TMAH. ($\emptyset_{CdS} = 4.1$ nm).



Figure S13. Left: ATR-IR spectra of L-IsoSer, dropcasted MeOH solution of L-IsoSer + TMAH, and dropcasted MeOH solution of L-IsoSer-CdS + TMAH. Right: ATR-IR spectra of L-TA, dropcasted MeOH solution of L-TA + TMAH, and dropcasted MeOH solution of L-TA-CdS + TMAH. ($\emptyset_{CdS} = 4.1$ nm).



Figure S14. Left: ATR-IR spectra of L-Ala, dropcasted MeOH solution of L-Ala + TMAH, and dropcasted MeOH solution of L-Ala-CdS + TMAH. Right: ATR-IR spectra of L-LA (neat liquid), dropcasted MeOH solution of L-LA, and dropcasted MeOH solution of L-LA-CdS. ($\emptyset_{CdS} = 4.1$ nm).



Figure S15. UV-vis absorption and emission ($\lambda_{ex} = 355$ nm; low sensitivity, excitation/emission slits: 10 nm/10 nm) spectra of Ala-CdS QDs ($\emptyset_{CdS} = 4.1$ nm).



Figure S16. UV-vis absorption and emission ($\lambda_{ex} = 355$ nm; low sensitivity, excitation/emission slits: 10 nm/10 nm) spectra of allo-Ile-CdS QDs ($\emptyset_{CdS} = 4.1$ nm).



Figure S17. UV-vis absorption and emission ($\lambda_{ex} = 355$ nm; low sensitivity, excitation/emission slits: 10 nm/10 nm) spectra of Ile-CdS QDs ($\emptyset_{CdS} = 4.1$ nm).



Figure S18. UV-vis absorption and emission ($\lambda_{ex} = 355$ nm; low sensitivity, excitation/emission slits: 10 nm/10 nm) spectra of allo-Thr-CdS QDs ($\emptyset_{CdS} = 4.1$ nm).



Figure S19. UV-vis absorption and emission ($\lambda_{ex} = 355$ nm; low sensitivity, excitation/emission slits: 10 nm/10 nm) spectra of Thr-CdS QDs ($\emptyset_{CdS} = 4.1$ nm).



Figure S20. UV-vis absorption and emission ($\lambda_{ex} = 355$ nm; low sensitivity, excitation/emission slits: 10 nm/10 nm) spectra of Cys-CdS QDs ($\emptyset_{CdS} = 4.1$ nm).



Figure S21. UV-vis absorption and emission ($\lambda_{ex} = 355$ nm; low sensitivity, excitation/emission slits: 10 nm/10 nm) spectra of Asp-CdS QDs ($\emptyset_{CdS} = 4.1$ nm).



Figure S22. UV-vis absorption and emission ($\lambda_{ex} = 355$ nm; low sensitivity, excitation/emission slits: 10 nm/10 nm) spectra of Glu-CdS QDs ($\emptyset_{CdS} = 4.1$ nm).



Figure S23. UV-vis absorption and emission ($\lambda_{ex} = 355$ nm; low sensitivity, excitation/emission slits: 10 nm/10 nm) spectra of His-CdS QDs ($\emptyset_{CdS} = 4.1$ nm).



Figure S24. UV-vis absorption and emission ($\lambda_{ex} = 355$ nm; low sensitivity, excitation/emission slits: 10 nm/10 nm) spectra of Ser-CdS QDs ($\emptyset_{CdS} = 4.1$ nm).



Figure S25. UV-vis absorption and emission ($\lambda_{ex} = 355$ nm; low sensitivity, excitation/emission slits: 10 nm/10 nm) spectra of IsoSer-CdS QDs ($\emptyset_{CdS} = 4.1$ nm).



Figure S26. UV-vis absorption and emission spectra ($\lambda_{ex} = 355$ nm; low sensitivity, excitation/emission slits: 5 nm/5 nm) spectra of MA-CdS QDs ($\emptyset_{CdS} = 4.1$ nm).



Figure S27. UV-vis absorption and emission ($\lambda_{ex} = 355$ nm; low sensitivity, excitation/emission slits: 10 nm/10 nm) spectra of MSA-CdS QDs ($\emptyset_{CdS} = 4.1$ nm).



Figure S28. UV-vis absorption and emission ($\lambda_{ex} = 355$ nm; low sensitivity, excitation/emission slits: 10 nm/10 nm) spectra of TA-CdS QDs ($\emptyset_{CdS} = 4.1$ nm).



Figure S29. UV-vis absorption and emission ($\lambda_{ex} = 355$ nm; low sensitivity, excitation/emission slits: 10 nm/10 nm) spectra of LA-CdS QDs ($\emptyset_{CdS} = 4.1$ nm).



Figure S30. UV-vis absorption and emission ($\lambda_{ex} = 355$ nm; low sensitivity, excitation/emission slits: 10 nm/10 nm) spectra of Pro-CdS QDs ($\emptyset_{CdS} = 4.1$ nm).



Figure S31. Emission spectra of CdS QDs ($Ø_{CdS} = 4.1 \text{ nm}$) capped with chiral carboxylic acids ($\lambda_{ex} = 355 \text{ nm}$, low sensitivity). Left: excitation/emission slits: 10 nm/10 nm. Right: excitation/emission slits: 5 nm/5 nm. The numbers in parathesis indicate the areas underneath the curves.



Figure S32. CD and UV-vis absorption spectra of (a) L-Cys- and D-Cys-CdS, (b) L-Thr- and D-Thr-CdS.



Figure S33. Reconstruction of UV-vis absorption and CD spectra of L-Thr-CdS QDs.³ (a) Absorption spectra: Individual Gaussians and the reconstructed (black line) and measured (red line) spectra. (b) Derivatives of the Gaussians shown in (a). (c) CD spectra of L-Thr-CdS QDs. Reconstructed CD spectrum from the derivatives of Gaussians (black) and measured CD spectrum (red).



Figure S34. Reconstruction of UV-vis absorption and CD spectra of L-allo-Thr-CdS QDs.³ (a) Absorption spectra: Individual Gaussians and the reconstructed (black line) and measured (red line) spectra. (b) Derivatives of the Gaussians shown in (a). (c) CD spectra of L-allo-Thr-CdS QDs. Reconstructed CD spectrum from the derivatives of Gaussians (black) and measured CD spectrum (red).



Figure S35. Reconstruction of UV-vis absorption and CD spectra of L-Ser-CdS QDs.³ (a) Absorption spectra: Individual Gaussians and the reconstructed (black line) and measured (red line) spectra. (b) Derivatives of the Gaussians shown in (a). (c) CD spectra of L-Ser-CdS QDs. Reconstructed CD spectrum from the derivatives of Gaussians (black) and measured CD spectrum (red).



Figure S36. CD spectra of L-MA-CdS and L-TA-CdS prepared by (a) precipitated from toluene, then redissolved in MeOH, and (b) toluene \rightarrow water ligand exchange.

References

- 1. Yu, W. W.; Qu, L.; Guo, W.; Peng, X., Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals. *Chem. Mater.* **2003**, *15* (14), 2854-2860.
- Morcombe, C. R.; Zilm, K. W., Chemical shift referencing in MAS solid state NMR. J. Magn. Reson. 2003, 162 (2), 479-486.
- 3. Ben-Moshe, A.; Teitelboim, A.; Oron, D.; Markovich, G., Probing the Interaction of Quantum Dots with Chiral Capping Molecules Using Circular Dichroism Spectroscopy. *Nano Lett.* **2016**, *16* (12), 7467-7473.