Alternative chiral thiols for preparation of chiral CdS quantum dots covered immediately by achiral thiols

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Electronic Supplementary Information (ESI)

Instruments

UV-visible absorption spectra were recorded on Varian Carry 300 absorption spectrophotometer using a 1-cm quartz cell. Photoluminescence spectra were taken on Hitachi F-4500 fluorescence spectrophotometer using excitation and emission slits of 5 nm and 10 nm, respectively. Circular dichroism (CD) spectra were measured on JASCO-810 CD spectrophotometer. High resolution transmission electron microscopy (HRTEM) experiments were carried out on Tecnai F30 300 KV. X-Ray diffractions (XRD) were recorded at room temperature on Panalytical X pert PRO diffractometer equipped with Cu $K\alpha$ radiation (λ = 1.5418 Å).

Materials

D-arginine (D-Arg, 99%), L-arginine (L-Arg, 99%), D-histidine (D-His, 99%) and L-histidine (L-His, 99%) were purchased from J & K Chemical LTD. 732-cation exchange resin was purchased from Xilong Chemical Factory Company Limited

(Shantou, China). All other reagents (AR) obtained from Guoyao (Shanghai, China) were used as received. Water used in the experiments was deionized (Millipore, Milli-Q RG, resistivity 18MΩ cm).

Preparation of chiral CdS quantum dots (QDs)

Preparation of CdS QDs capped with thioglycolic acid (TGA) and Arg (Arg-TGA-CdS QDs)

Arg was dissolved in Milli-Q water. 1 mL aqueous solution of TGA (pH = 7) was added to 1 mL Arg solution and the pH was adjusted to 9 by dropwise addition of 1M NaOH. The resulting solution was stirred for 20 min, to which Cd^{2+} in the form of $CdCl_2$ (1mL) was titrated under vigorous stirring to obtain a solution with a Cd^{2+} : Arg : TGA molar ratio of 1.0 : 2.5 : 2.5. The mixture of $CdCl_2$ and ligand solution was subsequently titrated by 0.5 eq. of sulfide using a standard solution of Na_2S. After continuously stirring at room temperature for another 20 h, the resulting colloids were examined using UV-Vis, PL and CD spectroscopy. Next, the QDs were purified by precipitation of the particles using ethanol and centrifugation. The sample was then re-dispersed into Milli-Q water and precipitated with ethanol. The precipitates were washed several times with ethanol and dried in a vaccum desiccator at room temperature.

Preparation of Arg-MPA-CdS QDs and His-TGA-CdS QDs

The Arg-MPA-CdS QDs and His-TGA-CdS QDs were prepared similarly.

Ligand exchange

Ligand-exchange from Arg-TGA to 1-dodecanethiol (DT) was carried out by the simultaneous phase transfer procedure.[S1] 1 mL of aqueous solution of Arg-TGA-CdS QDs was put in a vessel, to which 1 ml DT and then 1 ml acetone were respectively added on the top. The vessel was quickly placed in a water-bath set at 56 ºC and

vigorously stirred for 20 min. After phase transferring, CdS QDs in the organic phase was added methanol to precipitate the CdS QDs, which was collected by centrifugation and washed with methanol. A drop of chloroform was added to the washed CdS QDs to re-disperse them before next precipitation by methanol. This procedure was repeated for several times. Eventually, the particles were dispersed in chloroform for measurements of the optical properties.

Cation exchange

732-cation exchange resin was activated before use. For removal of Arg from the Arg-TGA-CdS QDs, the precipitated sample (Arg-TGA-CdS QDs, 250 mg) was dissolved in 3 mL Milli-Q water. 3 mL solution of Arg-TGA-CdS QDs was applied to cation-exchange column chromatography equipped with a 732-cation-exchange resin. After 40 min, Arg-TGA-CdS QDs were released from the column and collected. Arg was removed by five or more times of the cation-exchange column chromatography. Ethanol was added into the last solution received from the column to precipitate the particles. The particles were then collected by centrifugation, washed several times by ethanol, and dried in a vaccum desiccator.

Reference

S1. N. Gaponik, D. V. Talapin, A. L. Rogach, A. Eychmuller and H. Weller, *Nano Lett.*, 2002, **2**, 803-806.

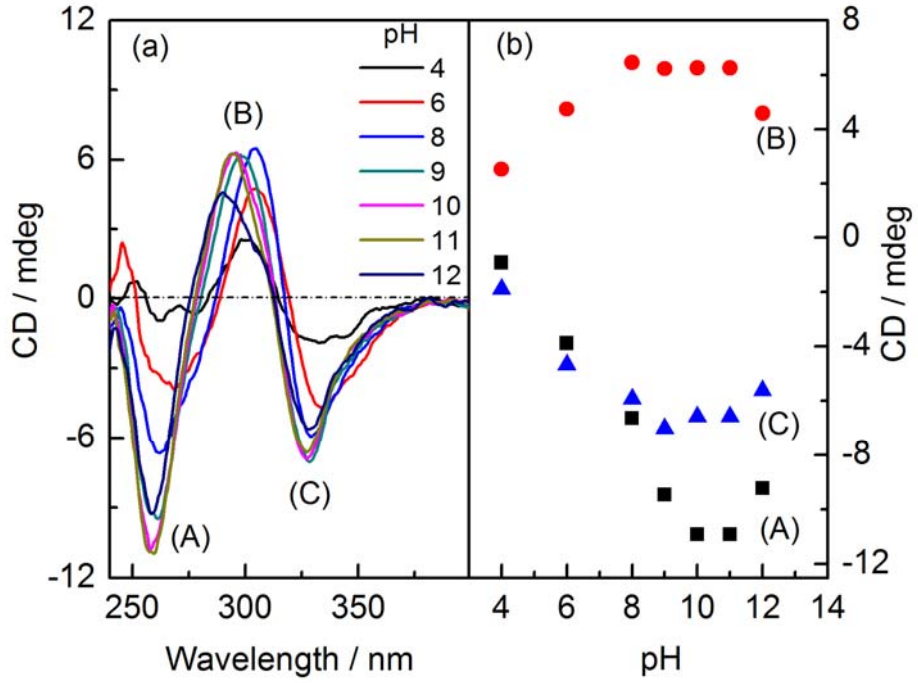

Figure S1. (a) CD spectra of CdS QDs prepared in the presence of L-Arg and TGA under different pH and (b) plots of CD signals as a function of pH. A, B and C represent CD bands of increasing wavelength, respectively.

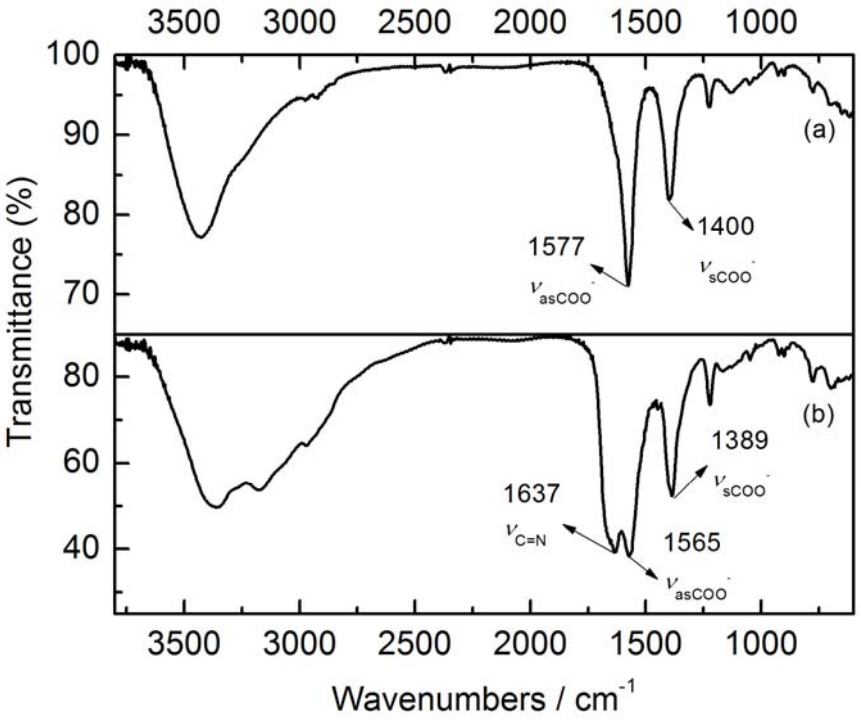

Figure S2. IR spectra of (a) TGA-CdS QDs and (b) L-Arg-TGA-CdS QDs.

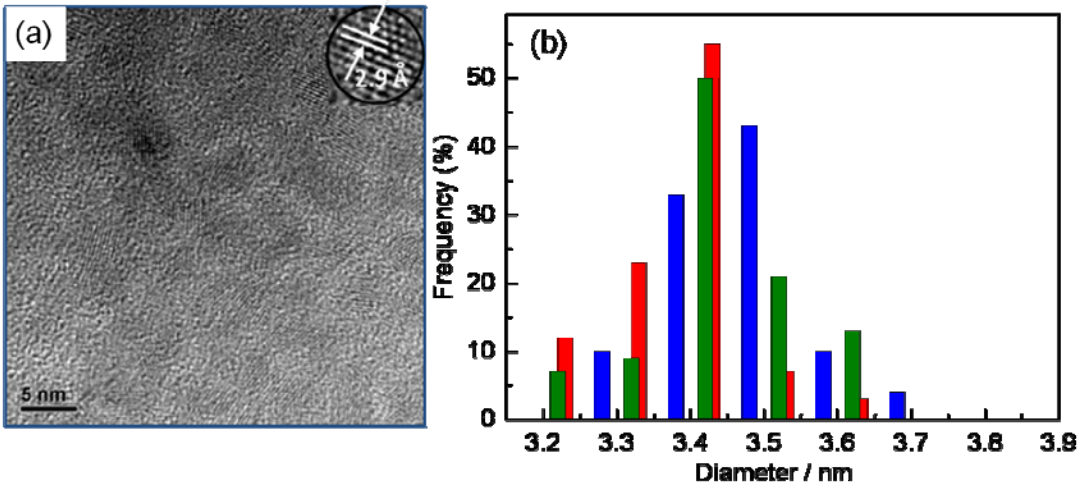

Figure S3. (a) TEM image of D-Arg-TGA-CdS QDs and (b) size distributions of the D-Arg-TGA-CdS (red), L-Arg-TGA-CdS (blue) and Rac-Arg-TGA-CdS (green) QDs. Particle sizes were estimated to be 3.42±0.28 nm, 3.45±0.29 nm and 3.41±0.25 nm for D-, L- and Rac- Arg-TGA-CdS QDs, respectively.

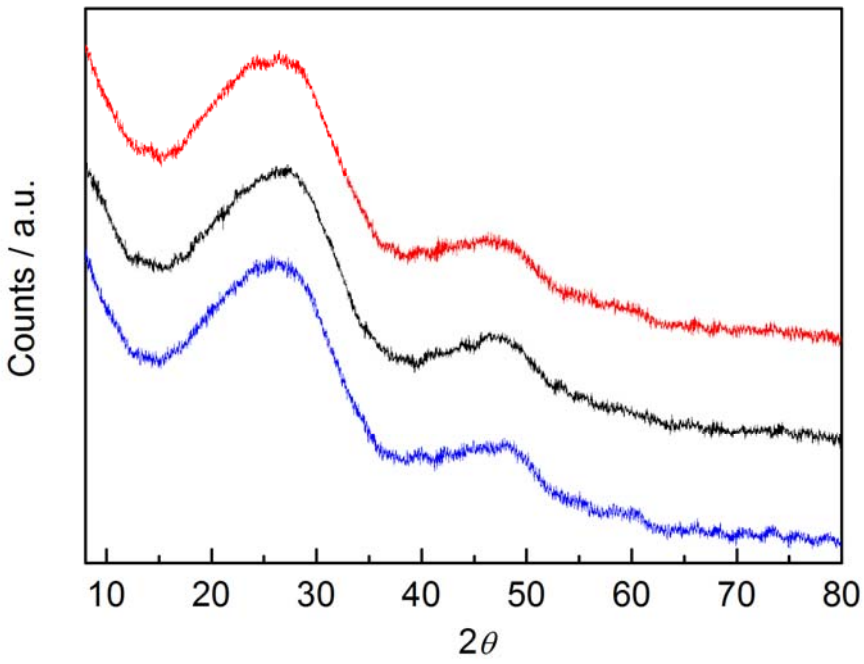

Figure S4. X-ray diffraction patterns of D-Arg-TGA-CdS (red), L-Arg-TGA-CdS (black) and Rac-Arg-TGA-CdS (blue) QDs.

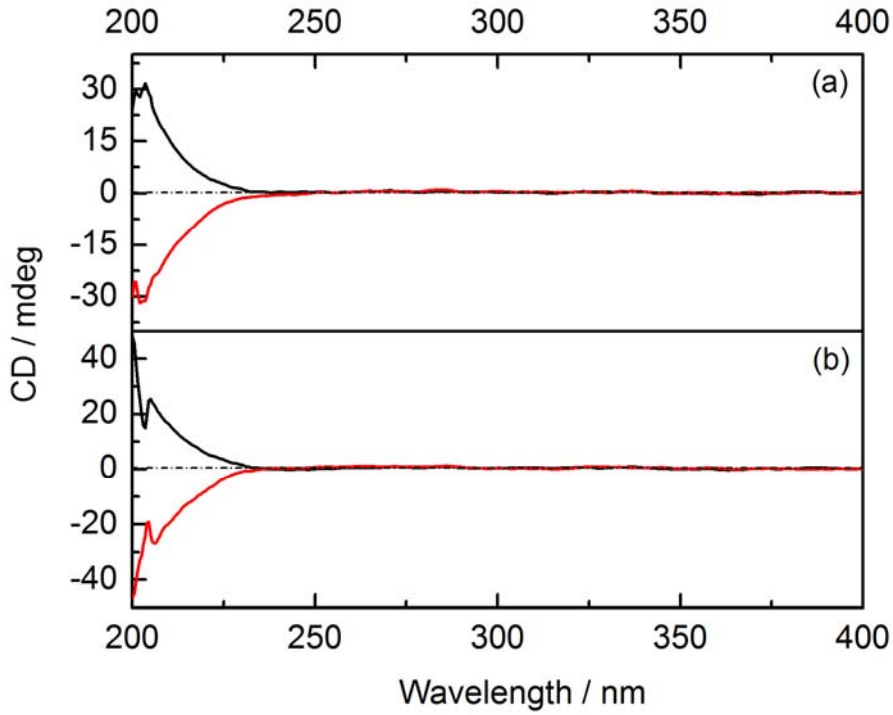

Figure S5. CD spectra of Arg-Cd^{2+} complex (a) and mixture of Arg-Cd^{2+} complex and Na_2S (b). Red and black curves represent the cases with D-Arg and L-Arg, respectively.

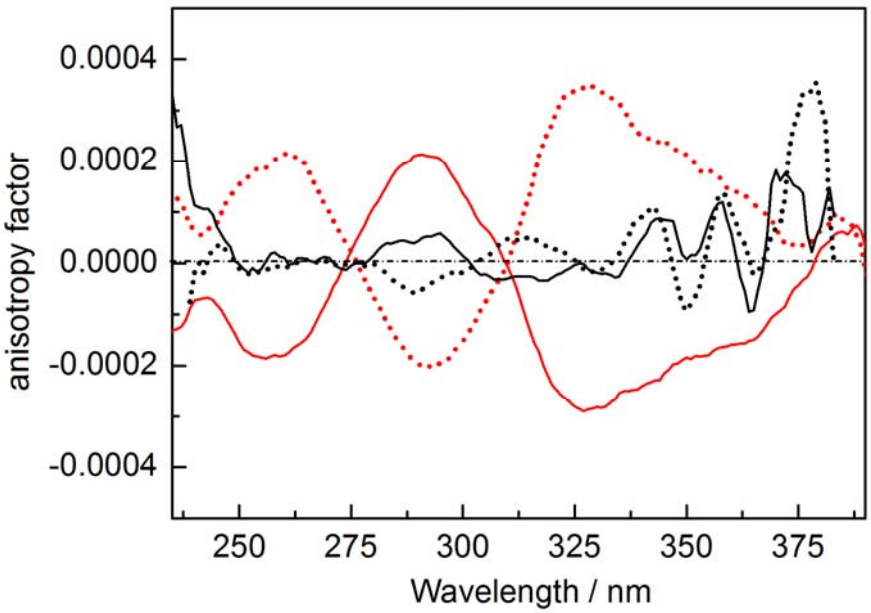

Figure S6. Anisotropy factor (*g*-factor) for Arg-TGA-CdS QDs (red) and Arg-MPA-CdS QDs (black). Short dot and solid lines represent cases with D-Arg and L-Arg, respectively.

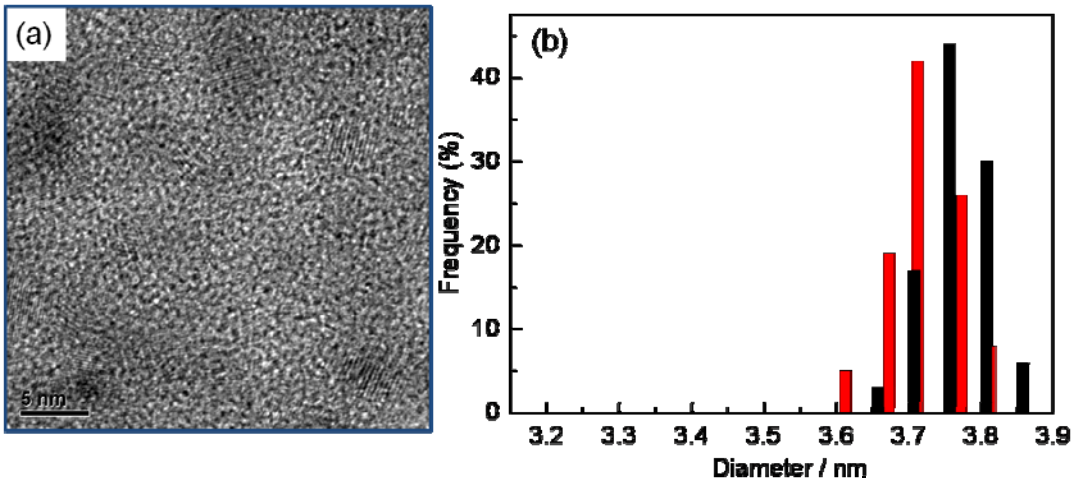

Figure S7. (a) TEM image of D-His-TGA-CdS QDs and (b) size distributions of D-His-TGA-CdS (red) and L-His-TGA-CdS (black) QDs. Particle sizes were measured as 3.72±0.20 nm and 3.75±0.22 nm for D- and L-His-TGA-CdS QDs, respectively.

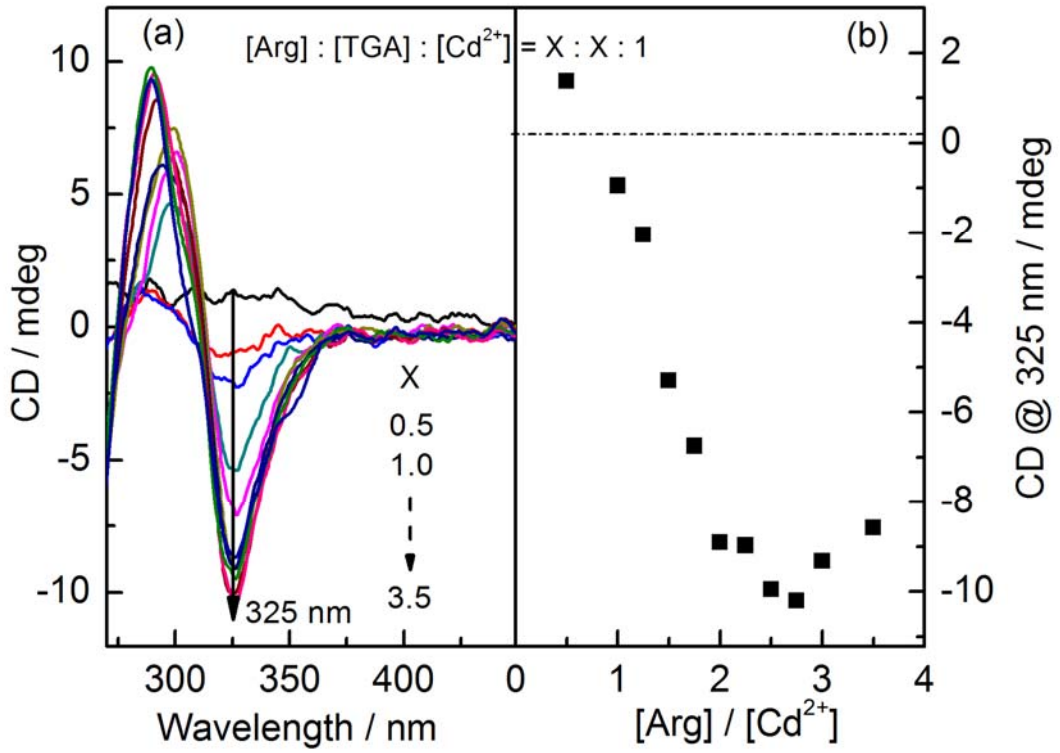

Figure S8. (a) CD spectra of CdS QDs prepared in the presence of mixture of TGA and L-Arg of different concentration ratio. The concentration of Cd^{2+} was kept constant. (b) CD signal at 325 nm as a function of ratio of L-Arg and Cd^{2+}.

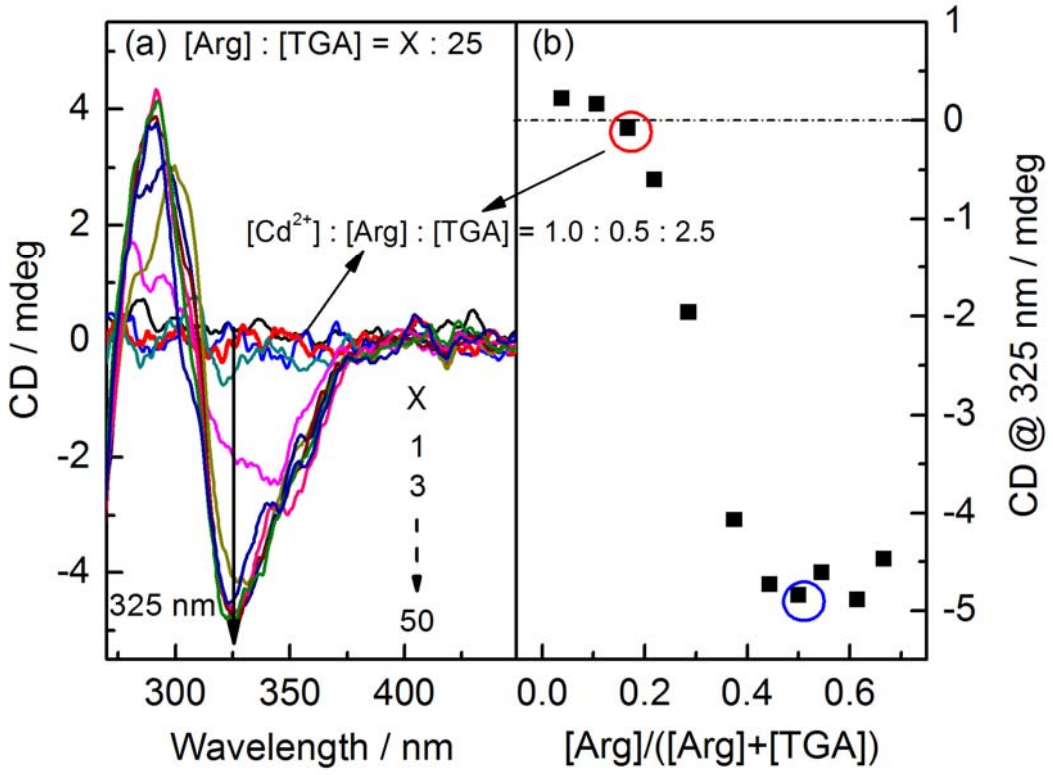

Figure S9. (a) CD spectra of CdS QDs prepared in the presence of mixture of TGA and L-Arg of different L-Arg molar fraction at fixed concentrations of TGA and Cd^{2+} and (b) CD signal at 325 nm as a function of L-Arg molar fraction. The data point in the blue circle in (b) represents CdS QDs synthesized at a Cd^{2+} : L-Arg : TGA molar ratio of 1.0 : 2.5 : 2.5. The red curve in (a) and the data point in the red circle in (b) represent CdS QDs synthesized at a Cd^{2+} : L-Arg : TGA molar ratio of 1.0 : 0.5 : 2.5, from which no CD signal was observed.

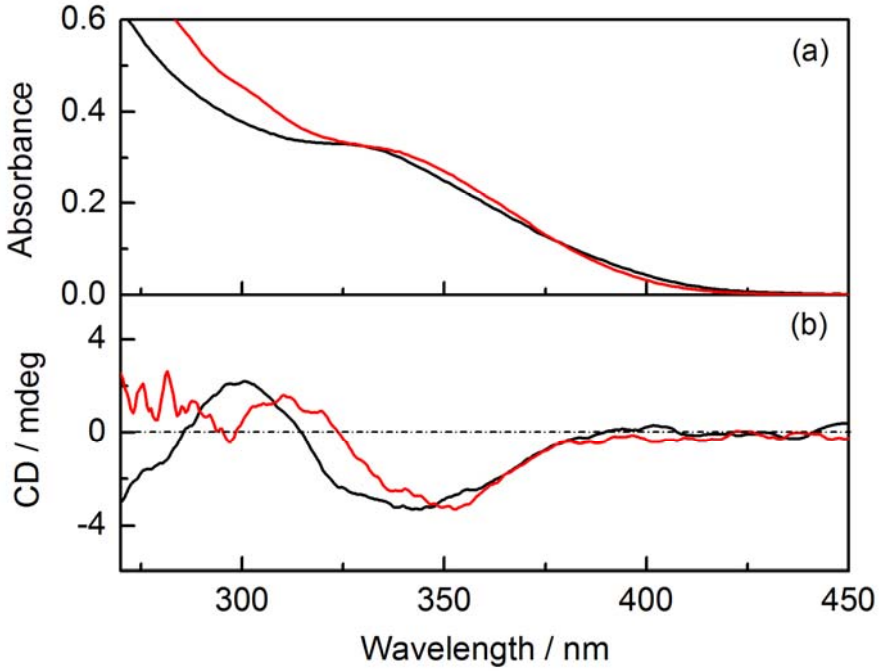

Figure S10. (a) Absorption and (b) CD spectra of L-Arg-TGA-CdS QDs in water (black) and DT-CdS QDs in chloroform obtained from ligand-exchange from L-Arg-TGA-CdS QDs (red).

Table S1. Elemental analyses of L-Arg-TGA-CdS QDs before and after ligand-exchange

	L-Arg-TGA-CdS QDs (before ligand-exchange)			DT-CdS QDs (after ligand-exchange)		
	C	H	N	C	H	N
Measured (wt%)	20.32	3.46	10.15	53.84	9.42	1.13
Calculated [a] (wt% in Arg)	13.06	2.56	10.15	1.45	0.28	1.13
Calculated [a] (wt% in [thiol-H])	7.26	0.91 [TGA-H]	—	52.39	9.16 [DT-H]	—
Arg : thiol (mol)	0.60 : 1 Arg : TGA			0.05 : 1 Arg : DT		
Arg : (Arg+thiol) (%)	37.50			5.21		

[a] The calculations were based on the assumption that the measured content of N is due to that from Arginine (Arg) molecules, from which the contents of C and H from Arg molecules can be calculated and consequently the C and H contents from thiol molecules were calculated by respectively subtracting these data from the measured total contents of C and H.

Table S2. Elemental analyses of L-Arg-TGA-CdS QDs before and after cation-exchange

	L-Arg-TGA-CdS QDs [a] (before cation-exchange)			L-Arg-TGA-CdS QDs [a] (after cation-exchange)			L-Arg-TGA-CdS QDs [b] (before cation-exchange)		
	C	H	N	C	H	N	C	H	N
Measured (wt%)	21.27	3.71	11.39	11.00	1.65	2.87	14.27	2.19	4.19
Calculated [c] (wt% in Arg)	14.65	2.87	11.39	3.69	0.72	2.87	5.39	1.06	4.19
Calculated [c] (wt% in TGA-H)	6.62	0.83	—	7.31	0.92	—	8.88	1.12	—
Arg : TGA (molar)	0.74 : 1			0.17 : 1			0.20 : 1		
Arg : (Arg+TGA) (%)	42.53			14.52			16.67		

[a] L-Arg-TGA-CdS QDs were synthesized with a Cd^{2+} : L-Arg : TGA molar ratio of 1.0 : 2.5 : 2.5 (data point in blue circle in Fig. S9b). [b] L-Arg-TGA-CdS QDs were synthesized with a Cd^{2+} : L-Arg : TGA molar ratio of 1.0 : 0.5 : 2.5 (data point in red circle in Fig. S9b), from which no CD signal was observed (red curve in. Fig. S9a). [c] The same as note (a) in Table S1.