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

Rong Zhou, Ke-Yi Wei, Jin-Song Zhao and Yun-Bao Jiang*

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Developing of alternative chiral thiol stabilizers from the assembly of achiral thiol (e.g. thioglycolic acid) and chiral ligand (e.g. arginine) via both hydrogen bonding and electrostatic interactions was proposed and successfully applied to an efficient preparation of chiral CdS quantum dots (QDs). Chiral CdS QDs capped mainly with achiral thioglycolic acid were also obtained that may allow the chiral QDs to be modified for extended applications.

Chirality is one of the most important factors of chiral recognition in both chemical and biological systems. In this regard, development of chiral luminescent nanosized probes would therefore provide useful tools for understanding the chiral recognition.1–6 Compared to other chiral inorganic nanostructures such as optically active carbon nanotubes,7–9 chiral gold10–12 and silver nanoparticles,13–15 II–VI group chiral semiconductor photoluminescent nanocrystals (quantum dots, QDs) are much less investigated. The typical method for preparation of chiral QDs with circular dichroism (CD) activity is a given reaction in the presence of a chiral thiol as the chiral stabilizer16–20 or within a chiral biomacromolecular nanoaggregate.21–23 Commercially available chiral thiols (such as glutathione,12 penicillamine,16,19,20 and cysteine18) are limited, whereas the synthesis of chiral thiols is not feasible. Exploring alternative “chiral thiol stabilizer” utilizing the assembly of an achiral thiol and a chiral ligand that relies on the formation of the guanidinium-carboxylate salt bridge. We report here the rational design and synthesis of chiral CdS QDs in the presence of a chiral ligand Arg and an achiral thiol stabilizer thioglycolic acid (TGA). Arg and TGA are expected to form a “chiral thiol stabilizer” through hydrogen bonding and electrostatic interaction (Scheme 1) that may serve as an alternative chiral thiol stabilizer to allow for the synthesis of chiral CdS QDs.

Chiral CdS QDs (∩/-Arg-TGA-CdS QDs) were indeed successfully obtained via the aqueous phase synthetic method,28 in the presence of TGA and ∩- or 1-Arg. Since the acidity of the solution affects the existing forms of both Arg and TGA, solution pH was optimized in terms of the optical properties of the obtained CdS QDs (Fig. S1, ESI†). It was found that at pH 9–10 smooth CD spectra and strong CD signals were obtained. Referring to the pKₐ of Arg (pKₐ, COOH 2.17, pKₐ, NH₃+ 9.04, pKₐ, sidechain 12.84)29 and TGA (pKₐ, COOH 3.67, pKₐ, NH₃+ 10.31),30 it is evident that at pH 9–10 the carboxyl group of TGA is fully deprotonated and exists in the anionic form, while the guanidinium moiety of Arg exists in the cationic form. Therefore, electrostatic interaction between the carboxylate anion and guanidinium cation occurs, in addition to their hydrogen bonding interaction, as evidenced by the red-shifts in the –COO⁻ stretching bands of Arg-TGA-CdS QDs compared to those of TGA-CdS QDs (Fig. S2, ESI†). The observed strong CD signal of the successfully prepared CdS QD at solution pH of 9–10 is hence understandable and may serve as an indication of the necessity of the Arg–TGA interactions for the preparation of the chiral CdS QDs. Indeed, it was found that later addition of chiral

Scheme 1 Synthesis of chiral CdS QDs capped immediately by achiral thiol that links to the chiral ligand via guanidinium-carboxylate salt bridge.
Arg into the solution of prepared achiral TGA-CdS QDs did not lead to any CD signals from the CdS QDs. rac-(d- or l)-Arg-TGA-CdS QDs that were respectively obtained in the presence of racemic, d- or l-Arg exhibit similar and well-resolved absorption bands with maxima at around 316–320 nm of the first excitonic transition, irrespective of the chirality of Arg (Fig. 1a). The photoluminescence (PL) spectra (Fig. 1a) of the CdS QDs show a broad band between 382 and 665 nm with a large Stokes shift, suggesting that the emission is due to the defects or trapped states on the surface of the QDs. The emission maximum of the QDs was found to be independent of the excitation wavelength, implying a uniform size distribution, as also observed from high-resolution transmission electron microscopy (HRTEM) images (Fig. S3, ESI†). X-Ray diffraction (XRD) patterns of the as-prepared CdS QDs are indicative of cubic zinc blende structure of the CdS phase (Fig. S4, ESI†), in agreement with a lattice plane distance of 2.9 Å obtained from the HRTEM (Fig. S3a, ESI†). The chiral properties of CdS QDs stabilized by TGA and Arg were characterized by their CD spectra (Fig. 1b). CdS QDs obtained in the presence of d- or l-Arg exhibit splitting CD signals of mirror image, whereas no noticeable CD signal was observed when CdS QDs were prepared in the presence of rac-Arg. The CD spectra of CdS QDs are different from that of the Arg–Cd$^{2+}$ complex (Fig. S5a, ESI†). In the absence of TGA, addition of Na$_2$S into the solution of the Arg–Cd$^{2+}$ complex produced no products that exhibit CD signals similar to that of the chiral CdS QDs (Fig. S5b, ESI†). Compared to these two control experiments in which products show prominent CD signals at short-wavelength of 205 nm, Arg-TGA-CdS QDs show broad CD features at much longer wavelength between 250 and 370 nm. These observations indicate that the observed CD signals of the d-/l-Arg-TGA-CdS QDs originate from the chirality induced into the QDs rather than that due to surface adsorption of the chiral ligand.¹¹

The synthetic approach was also applied to other achiral thiol stabilizer and amino acid combinations that may have interactions similar to those between TGA and Arg. Easily available thiol 3-mercaptopropionic acid (MPA) that is structurally similar to TGA was examined. Chiral Arg-MPA-CdS QDs were obtained, the optical activity or anisotropy factor was however only ca. 40% of that of the Arg-TGA-CdS QDs (Fig. S6, ESI†). This means that an increase in the chain length of the achiral thiol stabilizer reduces the efficiency of chirality transmission from the chiral ligand Arg, which is not unexpected. We next took another chiral ligand while employing TGA. Amidinium–carboxylate salt bridge has a well-defined geometry with high affinity even in polar solvents. We obtained chiral His-TGA-CdS QDs by using histidine (His) that contains an imidazolyl moiety (Fig. 2 and S7, ESI†). On the basis of these observations, we conclude that the chirality of Arg or His can be transmitted to the CdS QDs, relying on the noncovalent interactions between guanidinium or imidazolium and carboxylate, thereby leading to chiral CdS QDs with induced CD signals. This is of significance in terms of the long distance of the chiral centre in the amino acid away from the surface of the CdS QDs, for example by 11 atoms in the case of Arg (Scheme 1). It means that the thiol or amino acid assembling species must have packed tightly on the surface of the CdS QDs. Indeed, we found that the molar ratio of the achiral thiol stabilizer and/or the chiral amino acid was critical for obtaining chiral CdS QDs. It was shown that for the chiral CdS QDs to be successfully prepared, the molar ratio of TGA or Arg to Cd$^{2+}$ should be not lower than 2:1, while the ratio of Arg to TGA is required to be not less than 0.8:1 (Fig. S8 and S9, ESI†).

Postsynthetic ligand-exchange often provides insights into the origin of the optical activity of chiral nanoparticles. It was observed that when Arg and TGA on the surface of the chiral CdS QDs were largely exchanged by achiral 1-dodecanethiol (DT) (Table S1, ESI†), no significant change in the CD and absorption spectra was observed, except a slight red-shift in the spectra (Fig. S10, ESI†), indicating that the chirality has been memorized in the CdS QDs.¹⁷

Cation-exchange column chromatography was next applied to remove the chiral ligand Arg on the surface of chiral Arg-TGA-CdS QDs. Chiral TGA-CdS QDs were indeed obtained, that are expected to be readily subject to further covalent coupling to various biomolecules by, for example, cross-linking to reactive amine groups.³⁷ Elemental analyses

![Fig. 1](image1.png)  (a) Absorption (left) and PL (right) and (b) CD spectra of CdS QDs capped with TGA and d-Arg (red), l-Arg (blue) or rac-Arg (green). Excitation wavelength for all emission spectra is 364 nm.

![Fig. 2](image2.png)  (a) Absorption (left) and PL (right) and (b) CD spectra of CdS QDs capped with TGA and d-His (red) or l-His (black). Excitation wavelength for the emission spectra is 362 nm.
showed that most of the Arg molecules were removed (Table S2, ESI†), to our surprise however, no significant change in the absorption and PL spectra was observed while the CD signal was increased by 25% (Fig. 3). We therefore obtained chiral CdS QDs capped mainly with achiral thiol TGA. The fact that the TGA capped chiral CdS QDs can survive from the harsh cation-exchange chromatography suggests that the CdS QDs should allow for further functionalizations. We also synthesized CdS QDs in the presence of TGA and Arg of molar ratio (Cd²⁺:L-Arg : TGA molar ratio of 1.0 : 0.5 : 2.5) close to that found in the cation-exchanged chiral CdS QDs (ca. 0.2, Table S2, ESI†). However, no chiral CdS QDs were obtained (Fig. S9a, red curve), which means that the optical activity of the cation-exchanged CdS QDs (Fig. 3) does not result from the remaining Arg on the surface but from the chirality memory. 17

In conclusion, a new strategy has been presented for preparing chiral CdS QDs in aqueous solution that relies on the development of an alternative chiral thiol stabilizer by noncovalently linking an achiral thiol stabilizer to a chiral ligand that leads to an assembled “chiral thiol stabilizer”. It was shown that at such concentrations of the assembled thiol that allows it to pack tightly on the surface of the produced QDs, chiral QDs can be feasibly obtained. Chiral CdS QDs capped mainly with the achiral thiols can also be obtained by removing most of the chiral ligand, with the optical activity of the resultant CdS QDs remaining unchanged. As many other achiral thiols and chiral ligands can in principle be chosen to form these alternative chiral thiol stabilizers, the new strategy broadens the scope of the chiral “thiol stabilizer” and thus the diversity of the chiral inorganic nanomaterials of varying functionalities. The synthetic protocol that affords chiral QDs capped with reactive achiral stabilizers will provide more opportunities for potential applications of chiral QDs, for example, in chemical and biochemical chiral sensing and chiral recognition nanodevices.

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Notes and references
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