

Review

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Ligand-induced chirality and optical activity in semiconductor nanocrystals: theory and applications

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Abstract: Chirality is one of the most fascinating occurrences in the natural world and plays a crucial role in chemistry, biochemistry, pharmacology, and medicine. Chirality has also been envisaged to play an important role in nanotechnology and particularly in nanophotonics, therefore, chiral and chiroptical active nanoparticles (NPs) have attracted a lot of interest over recent years. Optical activity can be induced in NPs in several different ways, including via the direct interaction of achiral NPs with a chiral molecule. This results in circular dichroism (CD) in the region of the intrinsic absorption of the NPs. This interaction in turn affects the optical properties of the chiral molecule. Recently, studies of induced chirality in quantum dots (QDs) has deserved special attention and this phenomenon has been explored in detail in a number of important papers. In this article, we review these important recent advances in the preparation and formation of chiral molecule–QD systems and analyze the mechanisms of induced chirality, the factors influencing CD spectra shape and the intensity of the CD, as well as the effect of QDs on chiral molecules. We also consider potential applications of these types of chiroptical QDs including sensing, bioimaging, enantioselective synthesis, circularly polarized light emitters, and spintronic devices. Finally, we highlight the problems

and possibilities that can arise in research areas concerning the interaction of QDs with chiral molecules and that a mutual influence approach must be taken into account particularly in areas, such as photonics, cell imaging, pharmacology, nanomedicine and nanotoxicology.

Keywords: chirality; colloidal nanocrystals; induced chirality; nanoplatelets; optical activity; quantum dots; quantum rods.

1 Introduction

A chiral molecule has two mirror-image forms, known as enantiomers, which are nonsuperimposable in three-dimensional space [1]. Enantiomers have identical physical properties aside from the differing direction in which they rotate the plane of polarization of linear polarized light. The phenomenon of rotating the plane of polarized light is specifically known as optical activity and can be directly studied using circular dichroism (CD) spectroscopy [1], which is a technique of measurement of the difference in the absorption of left and right circularly polarized light (CPL) in optically active compounds.

Another crucial difference between enantiomers is the manner in which they interact with other chiral compounds. Most organic molecules in living organisms are chiral, including amino acids, carbohydrates, proteins and DNA [1]. Chirality plays an important role in many biological processes: the biological activity of chiral materials, such as intracellular uptake, enzymatic activity and toxicity strongly depend on the enantiomeric form. Therefore, the ability to analyze, interpret and apply the properties of chiral materials is highly important in the fields of chemistry, pharmacology, biology and medicine.

Many new synthetically produced chiral materials have been introduced recently including: metal nanoparticles (NPs) and surfaces, colloidal semiconductor nanocrystals (NCs) and nanoceramics [2–17]. The area of chiral nanomaterials research is rapidly expanding, due to

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the numerous potential applications, including asymmetric catalysis [18–20], enantiomeric separation [21, 22], chiral sensing [3, 23–25], cytotoxicity mediation [26], circular polarized light emitting devices [27–29] and spintronics [30, 31]. In the present review, we focus on semiconductor colloidal quantum dots (QDs) with chiral properties, a particularly exciting class of chiral nanomaterials. QDs are luminescent semiconductor NPs with outstanding tunability of the optical and physical properties as a result of their variable size dependent band electronic structure due to quantum confinement effect. QDs possess high photoluminescent (PL) quantum yield (up to 100%); large extinction coefficients continuous across a wide spectral range, in addition to excellent photo- and chemical stability [32, 33]. Due to these properties, QDs can be successfully used in a variety of potential applications, such as biological imaging, sensing, solar cells, photocatalysis, LEDs and others [32–36].

Chiroptical activity may be induced in nanomaterials including QDs by a variety of methods, such as:

- (i) Chiral crystal structure: NPs can have a chiral lattice structure and demonstrate optical activity without any external influences of chiral ligands or scaffolding. For example, it was shown that quartz, β -AgSe, α -HgS, selenium and tellurium crystals have chiral crystal structure and corresponding NCs have two enantiomers [37–39].
- (ii) Chiral NP shape: NCs of intrinsically achiral materials may be grown in a chiral shape, e.g., twisted CdTe nanoribbons [40–42], nanosprings [43], nanoscrolls [44–46], plasmonic and semiconductor gammadions [47, 48] and other chiral shapes [49, 50].
- (iii) Chiral assembly: achiral NPs may be assembled in chiral superstructures, e.g., DNA has been used to assemble NPs in helices [51, 52] and chiral “molecules” can be fabricated from coupled achiral semiconductor NCs [53, 54].
- (iv) Chiral defects: chiral surface and structural defects can be produced during the synthesis of NPs in the presence of chiral ligands, such as it has been done for aqueous penicillamine capped CdS QDs [55].
- (v) Spontaneous chiral defects: NPs can be synthesized with spontaneous chiral surface and structural defects (e.g., screw dislocations [56, 57] and dopant ions [58]) even without the presence of chiral ligands and can then be extracted from an achiral mixture by enantioselective phase transfer [40, 59, 60].
- (vi) Ligand-induced chirality (LIC): optical activity may be induced in colloidal NPs through interaction of NPs with chiral ligands, such as cysteine or penicillamine [27, 61–63].
- (vii) Optical activity can be induced in achiral NPs in vicinity of chiral metasurfaces [64] (Diagram 1).

A number of reviews on chiral NPs have been published [2–12, 14–17]. These reviews have covered a wide range of chiral NPs of various nature with particular attention paid to chiral plasmonics. In the present review, we decided to focus exclusively on LIC in colloidal semiconductor NCs (point VI; see paragraph above). Since the defects in NCs (points IV and V) often affect induced chirality, they will also be discussed in this review.

Over the last five years, many interesting studies have been focused on the field of induced optical activity, which has led to significant progress in understanding of the mechanisms of this phenomenon, with the influence of various factors on QD induced CD and CPL spectra having been investigated. The majority of these investigations are devoted to spherical QDs, but there is also an increased interest in chiral anisotropic NCs. Many possible options have been found to use LIC-QDs for different applications, including chiral sensing, asymmetric catalysis, circular polarized light emitters and spintronics. In addition, the study of LIC in QDs is important not only from a practical but also from a theoretical point of view, since the analysis of CD spectra enable the understanding of the fine energy structure of QDs and the principles governing the interaction of QDs with surrounding molecules. Moreover, since QDs have potential applications in biology and medicine, it is essential to consider the phenomena that can occur in

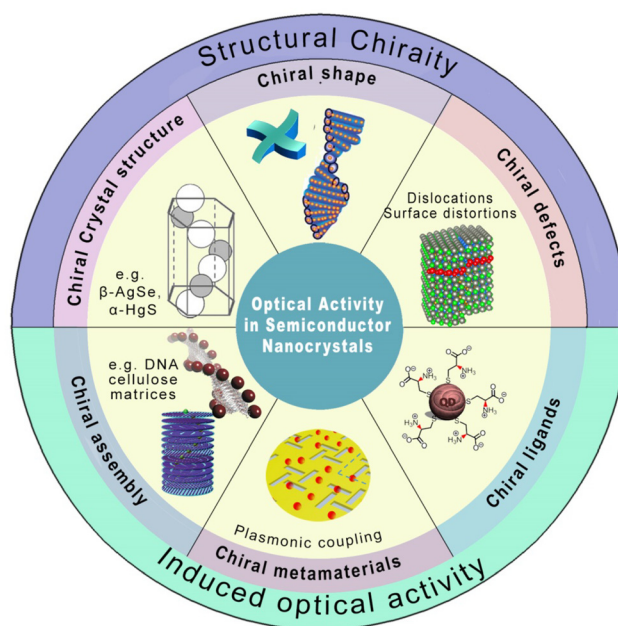


Diagram 1: Chiroptical activity induction in semiconductor nanocrystals.

biological media containing a multitude of various chiral molecules and interaction with drugs.

2 Ligand-induced optical activity in QDs

2.1 Preparation of QDs with ligand induced optical activity

The QDs with LIC can be obtained either by direct aqueous synthesis in the presence of chiral molecules, or by post-synthetic replacement of the initial nonchiral ligands with chiral alternatives. The first time optically active CdS QDs were reported, it was produced *via* an aqueous microwave synthesis in the presence of D- or L-penicillamine by Moloney et al. [55] in 2007. Gallagher et al. used a similar microwave synthesis techniques to obtain chiral CdSe QDs stabilized with D- and L-penicillamine [65]. Chiral CdTe QDs [66] and CdS tetrapods [67] have also been produced using reflux heating methods in the presence of chiral molecules. These works began the study of induced chirality in QDs. Nevertheless, QDs obtained by the aqueous method usually have a low quantum yield, defect luminescence with a very broad PL band and a large size distribution. In addition, the specifically applied ligands strongly affect the synthetic mechanism, which in turn affect the optical properties, size and shape of QDs. This makes the properties of the same semiconductor based QDs with differing ligands not easily comparable. Aside from this, the advantages of this kind of QD include high CD anisotropy, ease of synthesis, the absence of toxic long chain organic molecules and excellent aqueous stability, which makes them more suitable for biological applications.

In contrast, the second method involving post-synthetic ligand replacement allows the production of high-quality QDs by hot injection synthesis at high temperatures, that is essential to obtain QDs with a narrow size distribution, high quantum yield, narrow luminescence, well defined exciton absorption bands and a low number of crystal defects. After synthesis, the QDs can be relatively easily functionalized with various chiral ligands *via* the ligand exchange processes, which allows the comparison of ligand effect on the QD-induced chirality to be easily studied. Balaz et al. firstly obtained QDs with induced chirality by postsynthetic ligand exchange [27, 61], replacing initial hydrophobic ligands with L- and D-cysteine on CdSe QDs. As a result, the CdSe QDs displayed a CD signal in the excitonic absorption region of the QDs. Typically, thiol compounds such as cysteine,

penicillamine and glutathione are the most commonly used chiral ligands, while recently, non-thiol containing chiral compounds with several carboxylic groups, such as maleic and tartaric acid derivatives have demonstrated the ability to effectively induce optical activity in QDs also.

2.2 The mechanisms of ligand-induced chirality in QDs

Several distinct models have been developed to explain the mechanism of optical activity in QDs induced by chiral ligands.

Balaz et al. [27] have shown using time-dependent density functional theory (TD DFT) calculations that the QD CD signal is formed due to the interaction of the energy levels of the QD and chiral molecule resulting in the hybridization between the QD valence band and the highest occupied molecular orbitals (HOMOs) of the molecule. Ben-Moshe et al. [62] suggested that due to the hybridization the QD hole level splits into two sublevels which adsorb left and right circular polarized light differently. This leads to the appearance of a CD signal with derivative shape corresponding to each exciton transition, which cross zero at the wavelength of absorption band maximum, the so-called Cotton effect (Figure 1). Based on this assumption, Ben-Moshe et al. [62] also explained the complex shape of QD CD spectra in their study. QD absorption spectra can be fitted with a sum of Gaussians that correspond to each different exciton transition. Therefore, CD spectra can be reconstructed as a liner sum of the derivatives of each Gaussian. This was supported by an excellent match of experimentally obtained and reconstructed CD spectra of QDs. Similar results were also obtained by Martynenko et al. [68]. This model is often used to explain a wide range of observed phenomena including influence of QD size [62], shell thickness [62, 69], nature and binding mode of ligands [70–74] on the position, shape and intensity of CD peaks, as well as the influence of QDs on the properties of chiral molecules [75], which will be discussed in the present review. In addition, this method allows the investigation of the QD energy structure using CD spectra [68].

Tang et al. [76, 77] analyzed the CD spectra of CdSe quantum rods (QRs) and nanoplatelets (NPLs) capped with cysteine using the nondegenerate coupled-oscillator (NDCO) model. According to this model, the CD signal is produced by coupling of the electric dipole transition moments of different chromophores. The magnitude and direction of the CD signal are defined by the properties and mutual arrangement of the dipoles (Figure 2A). The authors suggested that NPs with bound

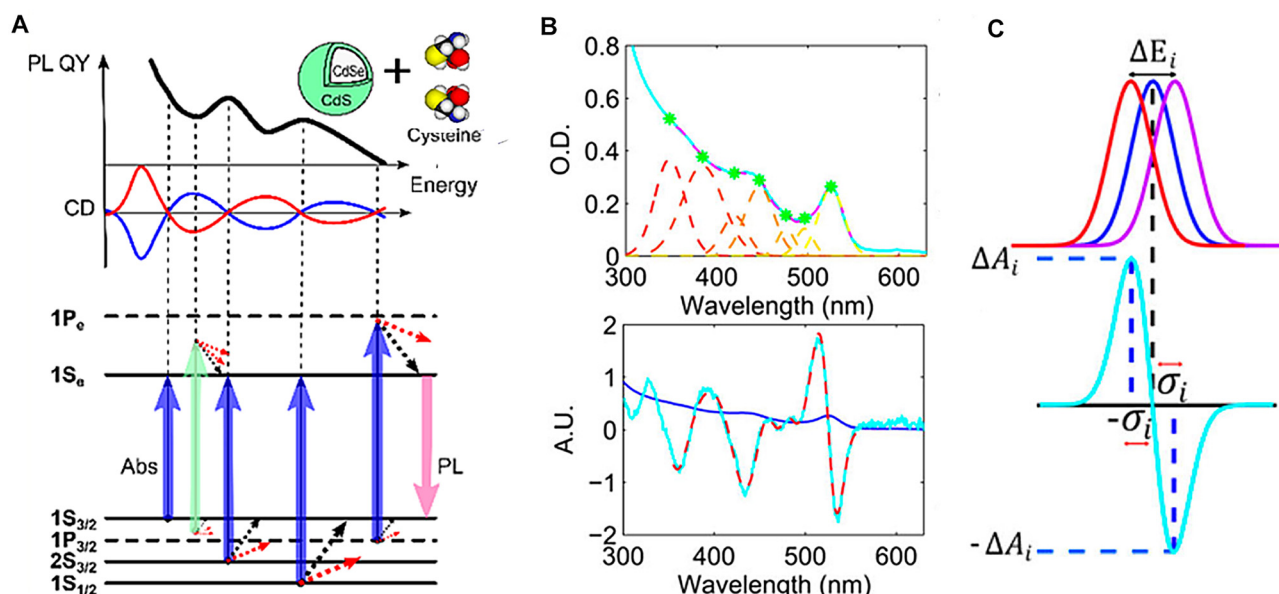


Figure 1: (A) Lowest energy transitions of CdSe/CdS core/shell quantum dots (QDs), the positions of which correspond to zero-crossing points of the CD signals (blue and red lines) and to the photoluminescent (PL) QY maxima. Adapted with permission from a study by Martynenko et al. [68]. Copyright 2018 American Chemical Society. (B) Analysis of absorption and CD spectra. Top: absorption spectra of CdSe QDs. The measured spectra appear in cyan. The Gaussians that reconstruct the spectra in dashed colored lines, where the green dots mark their maxima. These peaks can be assigned to the different excitonic transitions. The dashed pink lines mark the reconstructed absorption spectra. Bottom: reconstructed CD spectra for the same sample as in the top images, using the derivatives of the Gaussians at the same center wavelengths. The blue line marks again the measured absorption spectrum. The cyan lines mark the measured CD and the dashed pink lines the CD spectrum that was reconstructed using the sum of derivatives. (C) A scheme to determine energy splitting (ΔE_i) from the CD and absorption measurements. Reprinted with permission from a study by Ben-Moshe et al. [62]. Copyright 2016 American Chemical Society.

chiral ligands can be considered as one huge molecule, where the NP and chemical bonds are considered as the chromophores. In the case of CdSe NPs capped with cysteine, the chromophores are C=O groups of cysteine, Cd-O and Cd-S bonds and the CdSe NPs. The configuration and conformation of cysteine on the NP surface determines the mutual position of the chromophore

dipoles (Figure 2B). The dipoles of each bonds interact with each other and with the exciton transitions of the NP, showing the variety of CD bands, including the CD peaks of the bound cysteine which is different from the CD of the free molecules (Figure 2C and D).

Elliott et al. [78] have performed theoretical modeling of CdS QDs synthesized in aqueous medium in the presence

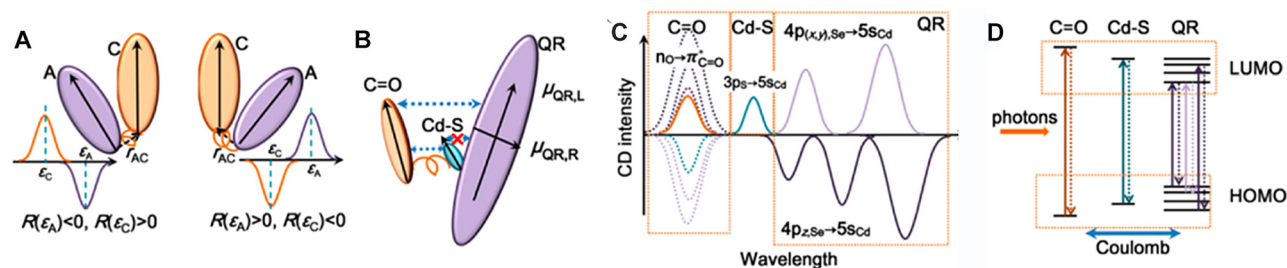


Figure 2: Schematic diagrams of the nondegenerate coupled-oscillator (NDCO) model, and qualitative analysis on the optical activity of L-cysteine-stabilized CdSe quantum rods (QRs).

(A) Scheme of coupling between two electric dipole transition moments in a chiral system, where coupling of two dipoles in different chromophores results in two opposite circular dichroism (CD) signs. (B) Simplified view of L-cysteine-stabilized CdSe QRs, where blue dotted arrows present coupling between two electric dipoles. (C) Charting CD spectrum of L-cysteine-stabilized QRs. CD signals of the Cd-S bond and CdSe QRs come from their coupling with C=O double bonds in cysteine, and the CD sign of C=O results from superposition of each coupling (dotted curves). (D) Quantum transition in the system. Solid vertical (horizontal) arrows represent light (coulomb)-induced transitions. Dotted vertical arrows stand for relaxation processes. Reprinted with permission from a study by Gao et al. [76]. Copyright 2017 American Chemical Society.

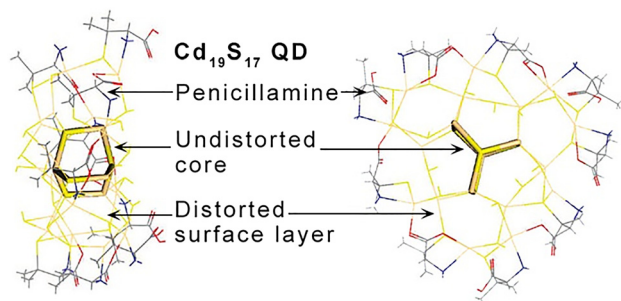


Figure 3: Top and side views of optimized cluster model of CdS quantum dots (QDs) covered with penicillamine. The ligands chirally distorted upper layer of CdS cluster (thin yellow lines) and almost does not influence the deeper CdS layer (solid yellow lines), thus the core reminds achiral. Adapted with permission from a study by Elliott et al. [78]. Copyright 2008 American Chemical Society.

of chiral molecules. These QDs possessed defective luminescence and high CD intensity. DFT calculations were used to construct the model of the QD as a CdS cluster, containing 19 Cd atoms, covered by the nine molecules of penicillamine (Figure 3). Calculations revealed that the presence of penicillamine leads to chiral distortion of the upper QD layer (chiral shell), while the deeper layers were practically nondistorted (achiral core). Based on the DFT data, it was proposed that QD surface defects located in the chiral distorted layer were responsible for the long wavelength CD response. However, it is not excluded that during the synthesis of the QDs in a chiral medium, that each deposited layer could be chirally distorted by ligands. This can lead to the appearance of not only surface, but also structural chiral defects, which can contribute to the formation of chiral memory as discussed below. It should be noted that Balaz et al. [27] used the $(\text{CdSe})_{13}$ cluster, in which all of the Cd and Se atoms were held fixed for TD DFT calculation of the hybridization of energy levels of QDs and chiral molecule. Possible chiral distortions of the nanocrystal lattice were not taken into account. Elliott et al. [78] did not consider the hybridization, but most likely it could contribute to the formation of QD optical activity. Also importantly, the intensity of QD CD signal in the paper [78] was much higher than one usually obtained as the result of the hybridization for spherical QDs. Therefore, probably both hybridization and distortion influence the appearance of the QD CD signal.

The crucial role of chiral defects in the formation of optical activity in QDs was also confirmed in other reports [60, 79]. CdS nanotetrapods [60, 67] and CdTe QDs [79] were synthesized by the microwave-assisted heating in the presence of L- and D-enantiomers of penicillamine and cysteinemethylester (MeCys), respectively. The original chiral ligands were exchanged for non-chiral

dodecanethiol and transferred to chloroform. In the paper of Nakashima et al. [79], elemental analyses suggested that more than 92% of chiral molecules were exchanged, whereas in other reports [59, 60] have shown using Fourier transform infrared spectroscopy analysis that no trace of chiral ligands were present after phase transfer. Nevertheless, NPs retained their optical activity (Figure 4) which has been called the chiral memory effect. While in the paper by Nakashima et al. [79], the effect can be explained by the remaining 8% of chiral ligands on the surface of NPs, but in other papers by Mukhina et al. [59, 60] chiral aminoacid molecules were removed completely. These experiments confirmed that the optical activity of QDs can originate from chiral defects of NPs, which can be retained without any chiral ligands present. Nakashima et al. [79] additionally proved the origin of the QD optical activity from the surface chiral defects by the following statements: the lattice distortions were more significant for the surface than for the core of CdTe QDs; CD profiles of CdS, CdSe and CdTe QDs almost coincided and did not correspond to the

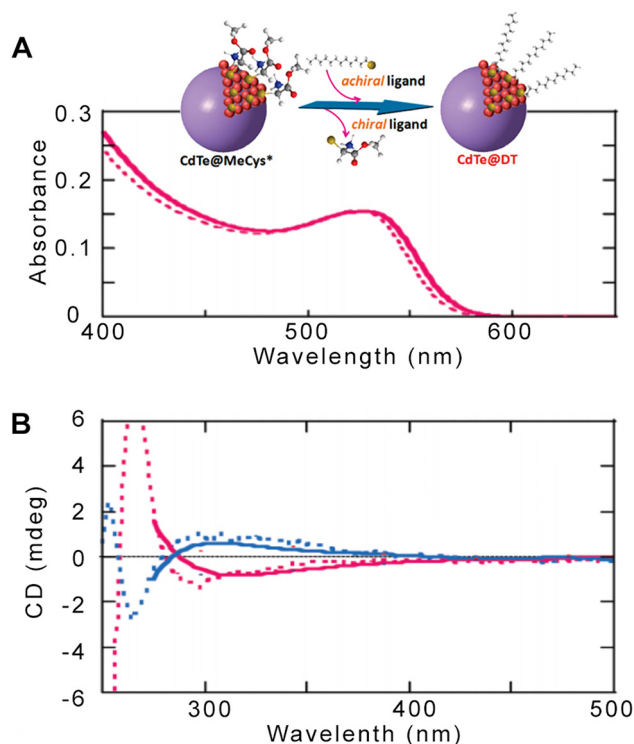


Figure 4: Schematic illustration of ligand-exchange reaction. (A) UV-vis absorption spectra of d-MeCys-capped CdTe nanocrystals (NCs) (dotted line) and DT-capped CdTe NCs (solid line) after ligand-exchanged from d-MeCys. (B) Circular dichroism (CD) spectra of d-MeCys (red) and L-MeCys (blue)-capped CdTe NCs (dotted lines) in water and DT-capped CdTe NCs (solid lines) in chloroform ligand-exchanged from d-MeCys (red) and L-MeCys (blue)-capped CdTe NCs. Adopted from a study by Nakashima et al. [79].

QD exciton absorption regions; QDs did not possess CPL signal from the core.

The influence of QD defects on the formation of a CD signal is also demonstrated in a recently published study [69], where CdSe/CdS QDs were obtained by a hot injection method. After synthesis, the QDs were annealed at different times from 0 to 240 min to reduce the number of crystalline defects and were then transferred to water using L- and D-cysteine. It was shown that longer annealing time, and therefore the smaller number of surface defects, led to a lower CD signal intensity.

It is also important to mention that even during synthesis in a non-chiral medium, QDs can acquire spontaneous chiral defects, for example, chiral dislocations [59]. In this case, L- and D-forms of QDs are formed with equal probability, therefore, they compensate each other, and as a result the CD signal does not appear. However, it was found that such QD enantiomers have different affinities for the L and D-form of chiral ligands [59]. It is well known that biomolecules discriminate between left-handed (l) and right-handed (d) enantiomers of target molecules via structural and energetical differences in the interaction. Mukhina et al. [21] have demonstrated that similarly to biomolecules, it is energetically more favorable for chirally distorted CdSe QDs, due to steric factors, to form L-D heterocomplexes with cysteine molecules. Experimental findings were supported by DFT calculations predicting that the difference between binding energies of the L-cys and D-distorted $\text{Cd}_{13}\text{Se}_{13}$ complex and the L-cys-L- $\text{Cd}_{13}\text{Se}_{13}$ is equal to 198 meV. Due to this, when special thermodynamically favorable conditions are created, one of the enantiomers of the QDs can be isolated from the organic solution by a ligand exchange method using the opposite enantiomer of the chiral ligand [59] or protein [40]. Mukhina et al. [59] emphasized that in order to increase the enantioselectivity of the interaction, it is necessary to provide a low temperature and low concentration of the ligands, and only a part of the QDs should be transferred to the aqueous phase. While the QDs which remained in the organic phase would have an opposite chirality. Enantioselective transfer was compared with a complete phase transfer using chiral ligands, which was carried out at room temperature and with an excess of chiral ligand. Interestingly, the CD signal after a reversed phase transfer with dodecanethiol was observed only for the QDs obtained by the enantioselective separation. It should be noted that authors of the paper [71] claimed that they did not succeed to separate the QD enantiomers using chiral ligands. In addition they did not specify in the paper if they used low temperature and ligand

concentration, and if the transfer was full or partial. The concept of intrinsic chiral defects was applied as an explanation of optical activity induced in ensemble of initially nonchiral quantum nanostructures under CPL irradiation [80, 81]. Hydrophobic CdSe/ZnS QDs [80], CdSe/ZnS rods and CdSe/CdS dot in rods [81] were irradiated by left (right) circular polarized light with wavelength close to the exciton transition. Circular polarized light was absorbed predominantly by one enantiomer of NCs. As a result, these NCs aggregated and precipitated and become less present in solution, therefore the opposite enantiomers gave rise to the detected CD signal.

2.3 Factors which influence ligand-induced CD

2.3.1 QD size

QD size affects the shape and intensity of the CD signal. The CD peaks shift to the red region with the increase of QD size according to the shift of the absorption exciton band [27, 61, 62]. The intensity of CD signal varies with size ambiguously. Dissymmetry factor, or g-factor, is usually used instead of CD signal intensity to avoid the concentration dependence. g-factor is calculated by formula $g = (A_L - A_R)/A$, where A_L and A_R are the absorbance of circularly polarized left-handed and right-handed light, respectively, and A is the absorbance of unpolarized light. Balaz et al. [27] noted a general tendency that the g-factor grew with QD size. CdSe QDs were synthesized by hot injection and then transferred to aqueous phase using cysteine. Ben Moshe et al. [82] have reported, that the dissymmetry factor, on the contrary, strongly decreased with an increase in the size of CdS QDs, obtained by aqueous synthesis with penicillamine. Interestingly, the size dependence was nonlinear, and in fact close to exponential.

2.3.2 Shell thickness

The physical and chemical properties of semiconductor QDs can be modified via the growth of a shell of another semiconductor material [83]. For example, if the shell of the QDs is made of a material with a larger band gap energy than the core, and the band offset is correctly positioned, a type I band alignment results, in which the exciton is confined to the core and the probability of electron transfers and other nonradiative processes become much lower (Figure 5B). As a result, the PL quantum yield of QDs increases. QDs of reverse type I have instead a core material

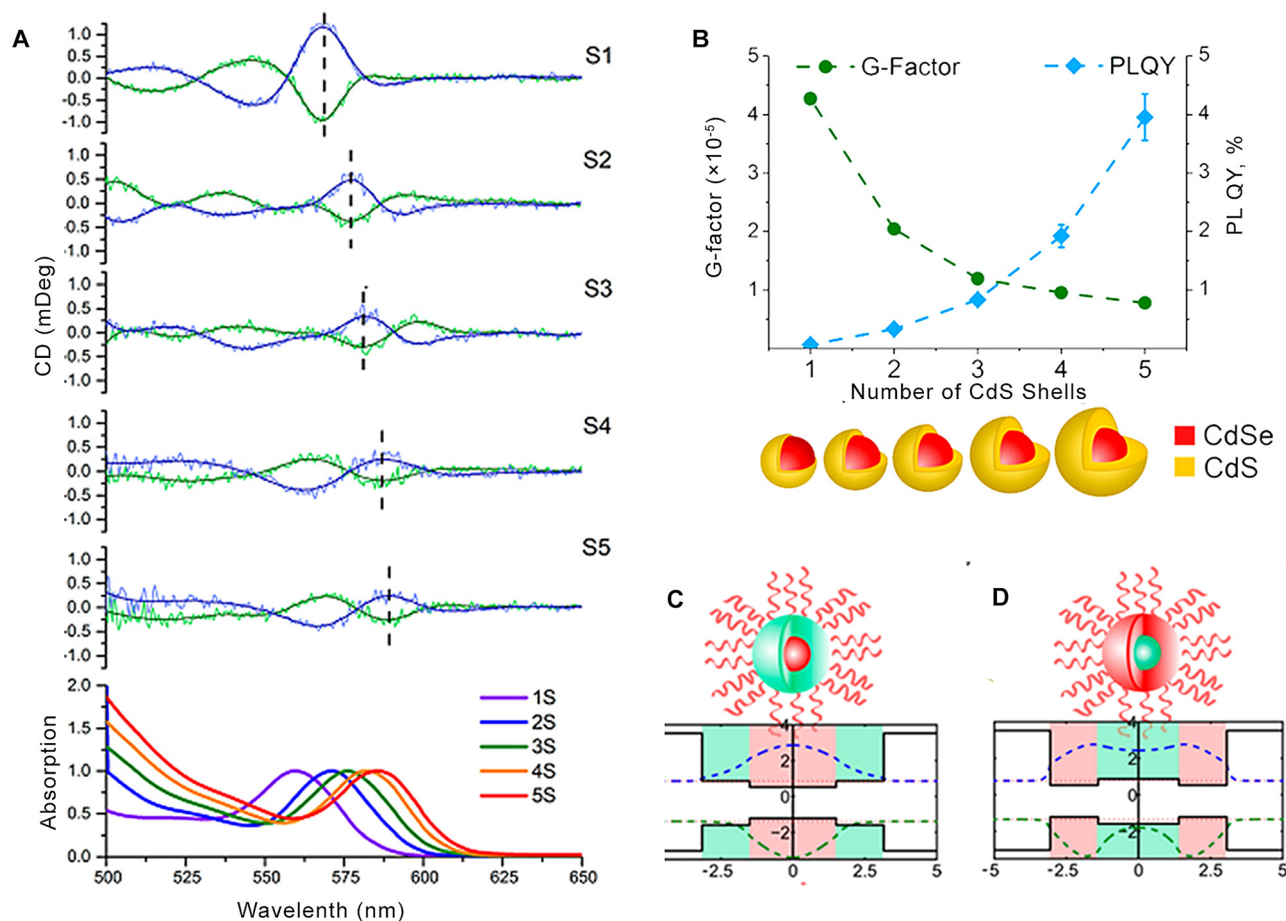


Figure 5: (A) *g*-factor graphs of D-cysteine (blue) and L-cysteine (green) functionalized CdSe/CdS quantum dots (QDs) with varying thickness of CdS shell, marked S1–S5. (B) Dependence of *g*-factor (green) and photoluminescent (PL) QY (blue) of CdSe/CdS QDs on the amount of CdS shell layers. On the bottom: schematic representation of CdSe/CdS QDs with 1–5 layers of CdS shell. Reprinted with permission from a study by Purcell-Milton et al. [69]. Copyright 2017 American Chemical Society. (C, D) Diagrams showing effective mass calculations of the electron and hole wave functions for the final samples of each series with the thickest shell. In the diagram of CdSe/CdS (C), the hole is completely localized in the core. For the diagram of CdS/CdSe (D), it is localized in the shell. Reprinted with permission from a study by Ben-Moshe et al. [62]. Copyright 2016 American Chemical Society.

with a larger band gap energy covered with the shell made of a material with a smaller band gap energy, with an appropriate band alignment and results in partial exciton delocalization in the shell. In addition, as the exciton is transferred to the lower energy level of the shell, the absorption red shifts with the shell growth.

Several studies were devoted to the effect of shell thickness on the induced optical activity in CdSe/CdS [62, 68, 69] and CdS/CdSe QDs [62]. In all cases, QDs were synthesized by a hot injection method and then transferred to aqueous phase using chiral cysteine ligands. From this, it was found that the CD signal intensity of CdSe/CdS QDs decreased with shell thickness [62, 69]. In the report by Purcell-Milton et al. [69], an exponential decrease of CD intensity was unambiguous (Figure 5B), while in the study by Ben-Moshe et al. [62], the dependence was more

complicated. The observed behavior is easy to explain by the hybridization theory [62], where chirality originates from the hybridization of the energy level of the QD hole and HOMO level of the chiral molecules. In CdSe/CdS, the hole is localized in the CdSe core and the shell works like a spacer between holes and chiral ligands (Figure 5C). An increase of the shell thickness reduces the interactions between holes and ligands exponentially. The deviations from the exponential trend can be explained by the influence of other factors, e.g., dependence of CD signal on ligand concentration [84], discussed in Section 2.3.4. The addition of shell layers can also reduce the confinement energy of the hole and pushes it close to the molecule level, increasing interaction between them [62]. In the case of CdS/CdSe QDs, no such sharp drop in CD intensity with shell growth was found as for CdSe/CdS. This trend was observed due to the hole

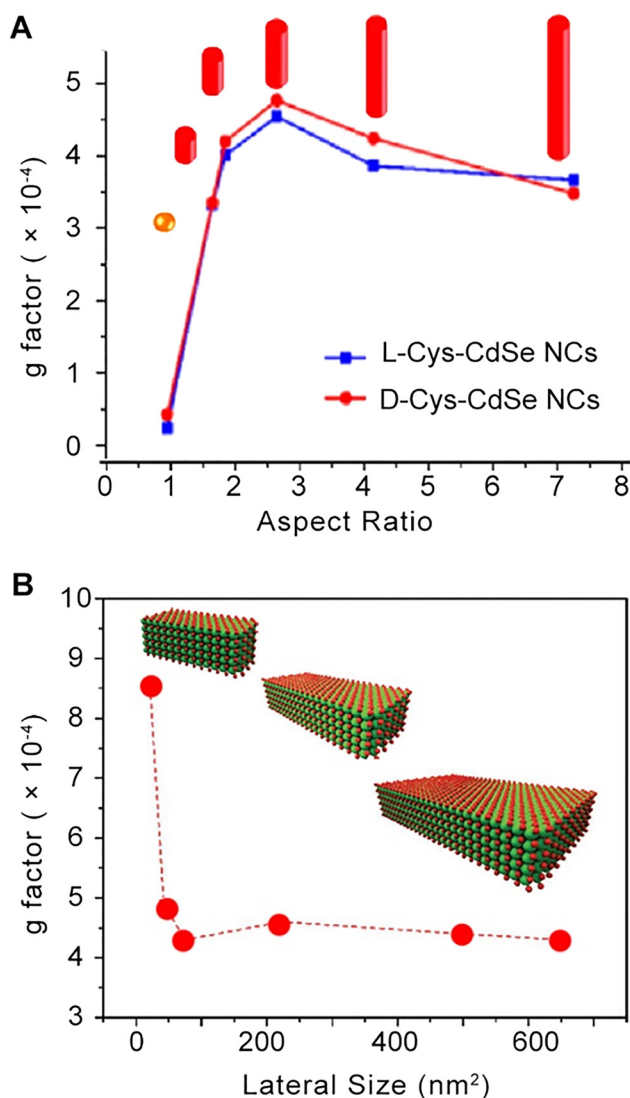


Figure 6: The dependences of g-factor in the excitonic region (A) of L- and D-cysteine stabilized (blue and red curves, respectively) CdSe quantum dots (QRs) on aspect ratio; (B) of L-cysteine-stabilized CdSe nanotetrapods and nanoplatelets (NPLs) on the lateral sizes. The QRs and NPLs are schematically depicted on the (A) and (B) figures, respectively. (A) is adapted with permission from a study by Gao et al. [76]. Copyright 2017 American Chemical Society. (B) is adapted with permission from a study by Yang et al. [74]. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

localized in the CdS shell, as demonstrated in Figure 5D, and therefore contact with molecules on the surface is maintained regardless of the shell thickness [62].

2.3.3 Shape of quantum nanocrystals

Spherical QDs are the most typical representative of the quantum confined colloidal nanocrystal family; however, by adjusting the reaction conditions a variety of different

anisotropic nanostructures may be formed, including QRs, nanotetrapods and NPLs [67, 85–87]. Anisotropic NPs can also be heterogeneous, for example, dot in rods, which consist of a spherical CdSe core and rod shape CdS shell.

The first work on the preparation of LIC anisotropic NCs was reported in 2010 [67]. CdS tetrapods were obtained by aqueous synthesis in the presence of L- and D-penicillamine. Since then, there have been several reports on the study of semiconductor anisotropic nanostructures with LIC, including detailed investigations of the effect of various anisotropy factors on the shape and intensity of CD spectra [28, 74, 76, 77]. All these studies involved NPs obtained by hot injection synthesis, with the subsequent replacement of ligands with chiral alternatives, with most cases utilizing cysteine or penicillamine as the chiral ligand. It has been shown that structural anisotropy significantly affects the optical and chiroptical properties of semiconductor NPs.

It is worth noting several general patterns have been reported in literature:

- I. G-factor increases with the transition from spherical QDs to QRs [76], and then from QRs to NPLs [77] by about an order of magnitude. For spherical QDs, the g-factor is usually in the order of 10^{-5} – 10^{-4} , for QRs 10^{-4} , and for NPLs – up to 10^{-3} .
- II. After the exchange of original ligands for chiral alternatives, the absorption peaks and associated CD bands of anisotropic particles have much larger red shifts than spherical QDs. The rods and NPLs have a red shift of approximately 10–15 nm, sometime even up to about 30 nm for NPLs [77], while the shift of spherical QDs is approximately 1 nm [74].
- III. The red shift and the increase in g-factor, change dramatically at low aspect ratio (length/width/height), and then alter more slowly or remain at the same level with the increase of aspect ratio (Figure 6).
- IV. The exciton absorption bands correspond to the derivative shape peaks (Cotton effect) in the CD spectrum of spherical QDs and rods, and to the single non-derivative peak in the case of NPLs. The origin of the Cotton effect is explained in Section 2.2, and the appearance of an undifferentiated CD peak in NPLs will be discussed below in this section.
- V. Usually, increase of the rod length or NPL lateral size and thickness results in the red shift of the exciton absorption bands and consequently CD peaks. Moreover, the bathochromic shift occurs after the shell growth, both in the case of dot in rod and core/shell NPLs.

Here, we are going to discuss more particular patterns noted in the recent innovative papers not covered by

previous reviews [2–6, 8, 15]. We consider the influence of various anisotropy factors, such as the aspect ratio, the presence and thickness of the shell, the type of the crystal lattice of the NPs and the configuration of the ligands on the position, shape of the peaks, and the magnitude of the CD signal and describe the physical mechanisms underlying these phenomena.

2.3.3.1 Homogeneous anisotropic nanocrystals

It was demonstrated that the ratio of the length, width, and height of anisotropic NCs has a great influence on the chiroptical properties. Tang et al. [76] investigated CdSe rods with different aspect ratios. It was shown that the g-factor increased strongly in the range of aspect ratio from 1 to 1.7, and further changed just slightly (Figure 6A). The shape of the CD spectra in the exciton region remained approximately the same. Yang et al. [74] studied in detail the zinc-blende CdSe NPLs with different lateral size and thickness. As the g-factor of the NPLs decreased (Figure 6B), the red shift of CD bands increased with the lateral size. Both effects were more pronounced for small particles. The shape of CD peaks almost did not change, but the dip in the CD spectrum corresponding to the first excitonic peak was broadened. Then authors compared the

CD spectra of CdSe NPLs with thickness of three, four and five monolayers. A regular red shift was observed for absorption and CD, with the increase in NPL thickness, while the CD intensities were approximately at the same level. In addition, the thinnest NPLs have shown a significant broadening of the exciton.

2.3.3.2 Heterogeneous anisotropic nanocrystals

In heterogeneous anisotropic CdSe/CdS NCs, the exciton is localized in the core, and the shell separates the core from direct contact with chiral molecules, which affects chiroptical properties, both for spherical particles (this was discussed in section 2.3.2) and for anisotropic structures.

He et al. [28] studied CdSe/CdS dot in rods and the influence of the absorption ratio of shell to core (ARSC), $A_{\text{shell}}/A_{\text{core}}$ on chiroptical properties. The ARSC is not directly related to the length and thickness of the dot in rods, but it affects the ratio of optical densities at the CdS shell and at the CdSe core exciton absorption wavelengths. However, in spite of this the CD signal did not have an unambiguous correlation with geometric parameters, with an increase in ARSC, the CD intensity in the core absorption area decreased. It was suggested that dot in rods with smaller ARSC values should have larger absorption cross

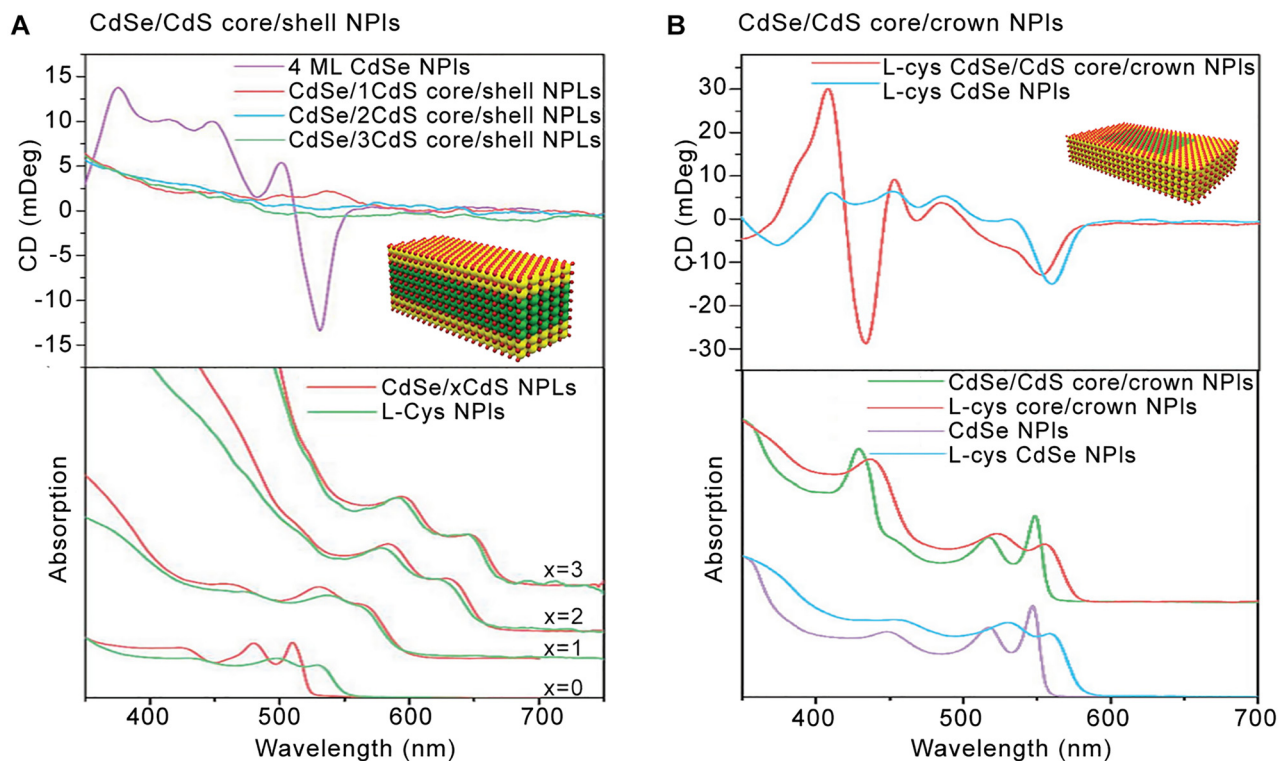


Figure 7: (Top) CD spectra and schematic representation and (bottom) absorption spectra of (A) CdSe-CdS core-shell NPLs with 0–3 layers of shell; and (B) CdSe core NPLs and CdSe-CdS core-crown NPLs. Reprinted with permission from a study by Yang et al. [74]. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

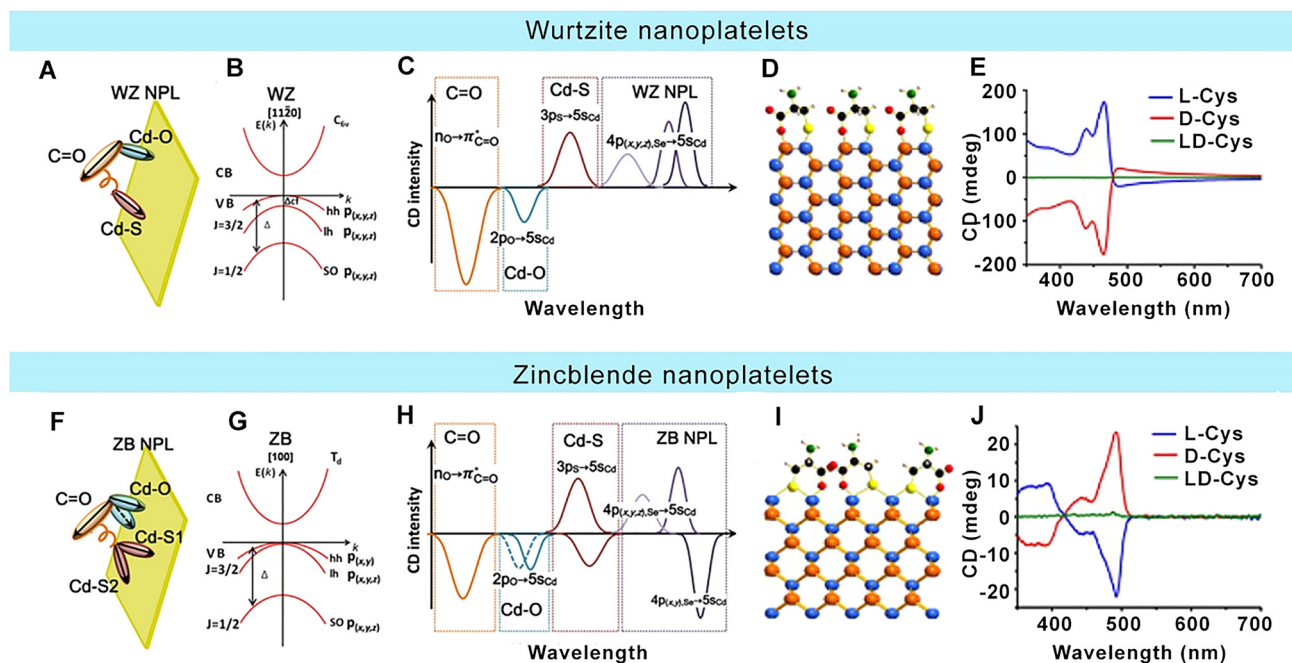


Figure 8: Simplified view of L-Cys-wurtzite (WZ) (A) and L-Cys zinc-blende (ZB) (F) CdSe nanotetrapods and nanoplatelets (NPL). Electronic energy band structure of WZ CdSe along the [1120] direction (B) and of ZB CdSe along the [100] direction (G). Charted CD spectrum of L-Cys-WZ (C) and L-Cys-ZB (H) CdSe CdSe NPLs. Model of possible configuration of L-cysteine on surface of WZ CdSe NPLs (D) and ZB CdSe NPLs (I). CD spectra of cysteine stabilized WZ (E) and ZB (J) CdSe NPLs. Adapted with permission from a study by Gao et al. [77]. Copyright 2018 American Chemical Society.

sections of the core, leading to stronger orbital and Coulomb couplings between the excited chiral ligands and the excited dot in rods, which results in strong CD activity. The CdSe core, prior to the extension of the rod shell, had a CD signal of lower intensity than with the shell.

Oron et al. [74] investigated heterogeneous CdSe/CdS NPLs with two types of CdS shell: sandwich-like core-shell and core-crown structures. These two types of structures behaved fundamentally differently. In the sandwich NPLs, the CD signal of the cores in the exciton region dropped sharply with an increase in the shell thickness (Figure 7A), while in the core-crown NPLs it practically did not change; the CD signal of the entire structure was a superposition of core and shells CD independent of each other (Figure 7B). It was suggested that induced CD was associated primarily with in-plane dipoles coupled with the surface layer of ligands. Then, in the case of a sandwich structures, the shell layers separated the core from the ligands and therefore reduced overlap of the carrier wave function with the ligand molecules; hence, the CD signal dropped, as in the case of spherical QDs [69], but more significantly. In contrast, in the case of the core-crown NPLs, the interaction of the core with the ligands remained unchanged relative to the growth of the shell.

2.3.3.3 Crystal lattice of the NPLs and ligand coordination

Tang et al. [77] had demonstrated that cysteine functionalized CdSe NPLs of the same thickness, but different crystal structure – wurtzite (WZ) and zinc blende (ZB) – differed in the intensity of the CD signal and the shape of the CD spectrum. The CD signal intensity of wurtzite was 7.5 times stronger than zinc-blend NPLs. Each exciton energy transition of the NPLs corresponded to a single nonderivative CD peak for both structures, but direction and ratio of peaks were different.

These patterns were explained using the NDCO model, described in section 2.2 of the present review. Cysteine attached to the surface of wurtzite and zinc-blende CdSe NPLs in different ways. Cysteine bound to wurtzite with one Cd–O and one Cd–S bonds (Figure 8A and D), together with the C=O double bond, they formed three CD bands: the C=O and Cd–O were directed downward, and the Cd–S was directed upward because the dipole of this bond was directed opposite to the others (Figure 8C). The CD spectrum of the zinc blende NPLs was more complicated: the Cd–O bond had two alternative positions with different energies, but unidirectional dipoles (Figure 8F), therefore, the Cd–O formed two unidirectional CD peaks (Figure 8H). The Cd–S was a bridging bond between two cadmium ions

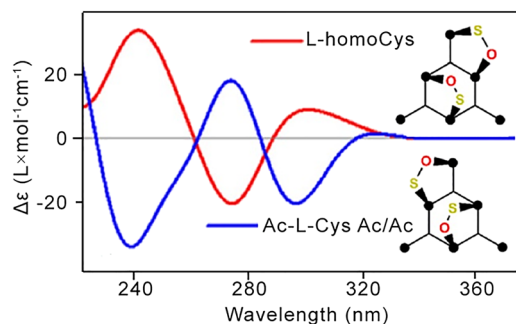


Figure 9: Simulated circular dichroism (CD) spectra for model CdSe complexes with two L-HomoCys and *N*-Ac-L-Cys ligands. CD spectra of the L-HomoCys-CdSe complex bound through carboxylate compared to the CD spectra of the *N*-Ac-L-Cys complex bound through acetyl group. Schematic representation of the possible binding arrangements for two bidentate ligands, with S (thiol) and O (carboxyl or acetyl) binding sites, on the model QD fragment. Adapted with permission from a study by Choi et al. [70]. Copyright 2016 American Chemical Society.

with two dipoles of opposite orientation, therefore, this bond corresponded to two CD peaks with opposite sign.

The CD spectra in the NPL excitonic absorption region can be explained by the interaction of exciton transition dipoles with the dipoles of cysteine bounds. NPLs possess three exciton transitions: first heavy hole–first electron (1hh–1e), the first light hole–first electron (1lh–1e), and the first spin orbital coupling–first electron (1SO–1e) transitions, respectively. Wurtzite CdSe NPLs have a quantum confinement direction along the low symmetry $[11\bar{2}0]$ direction. The dipoles of all exciton transitions in the wurtzite NPLs have the same orientation, and in the CD spectrum they corresponded to three peaks with a positive CD value (Figure 8C). In contrast, for zinc-blende NPLs, the quantum confinement direction is along the $[100]$. In this case, 1hh–1e exciton transition has different polarization with 1lh–1e and 1SO–1e transitions, therefore their CD peaks correspond to a negative and positive signal, respectively (Figure 8H). The authors also analyzed the CD spectrum of CdSe rods in a similar way in a different paper [76].

2.3.4 Ligands: chemical composition, binding mode

Choice of chiral ligands is crucial for adjusting the optical activity of NCs. The chemical nature of the ligands, together with their binding mode to the QD surface, influences the shape and intensity of the induced CD signal. Thiol-containing amino acids such as cysteine, penicillamine and glutathione were traditionally used as chiral ligands for the induction of optical activity in QDs. However,

recently, there have been several reports in which thiol-free chiral compounds containing several carboxyl groups were used successfully to induce CD signals, using such ligands as maleic and tartaric acid.

For now, there is no unified theory which connects the ligand structure and composition to the induced CD spectra, with reports sometimes giving contradicting results on trends regarding induced CD signals. For example, Puri and Ferry [72] showed that carboxylate compounds bound to CdSe QDs in DMF yield more intense and sharp signals than their thiolate counterparts. In contrary, Balaz et al. [71] found that *g*-factor of cysteine functionalized CdSe QDs in water was 2–3 times higher than in maleic acid capped QDs. It should be noted, that the authors used different exchange methods: Puri and Ferry et al. [72] added an excess of the solid ligand to the QD toluene solution, while Balaz et al. [71] carried out the phase transfer using an aqueous solution of chiral carboxylic acid. However, it is difficult to compare different ligands since even close derivatives of soft carboxylic acid can induce up to 30-fold increase in *g*-factors depending on the exact chemical structure [72].

The peak positions of the CD spectra of QDs with different ligands often do not match, although the position of the absorption peaks is almost the same [72]. It has been suggested that chiral ligands, depending on the chemical structure and conditions, split the excitonic levels of QDs with different efficiency. Therefore, due to this, the sum of the CD derivative peaks corresponding to exciton transitions of QDs forms a CD spectrum with different peak positions and intensities [72].

CD spectra of QDs can vary not only due to the different functional groups of chiral ligands binding but also due to minor derivatives of the same compound. In addition, even the same ligand can induce a different CD spectrum depending on conditions. In many cases, this can be explained by the different ligand binding mode and geometrical configuration on the QD's surface. For example, *N*-acetyl-L-cysteine and L-homocysteine lead to formation of mirror image CD spectra in CdSe QDs [70] (Figure 10). According to DFT calculations, L-homocysteine bound to cadmium ions on the QD surface through the thiol and carboxyl groups, while *N*-acetyl-L-cysteine attached through a thiol and acetyl groups. These configurations of the ligands were shown to be diastereoisomers in relation to the ligand surface (Figure 9).

Importance of ligand binding mode was confirmed further in a number of other papers [71, 73, 84]. For example, CdSe QDs functionalized with thiol-free chiral carboxylic acids containing two carboxyl groups with a similar structure but with different substituents were studied [71]. In this study, not all considered acids produced a CD signal in the QDs, in fact only molecules with an

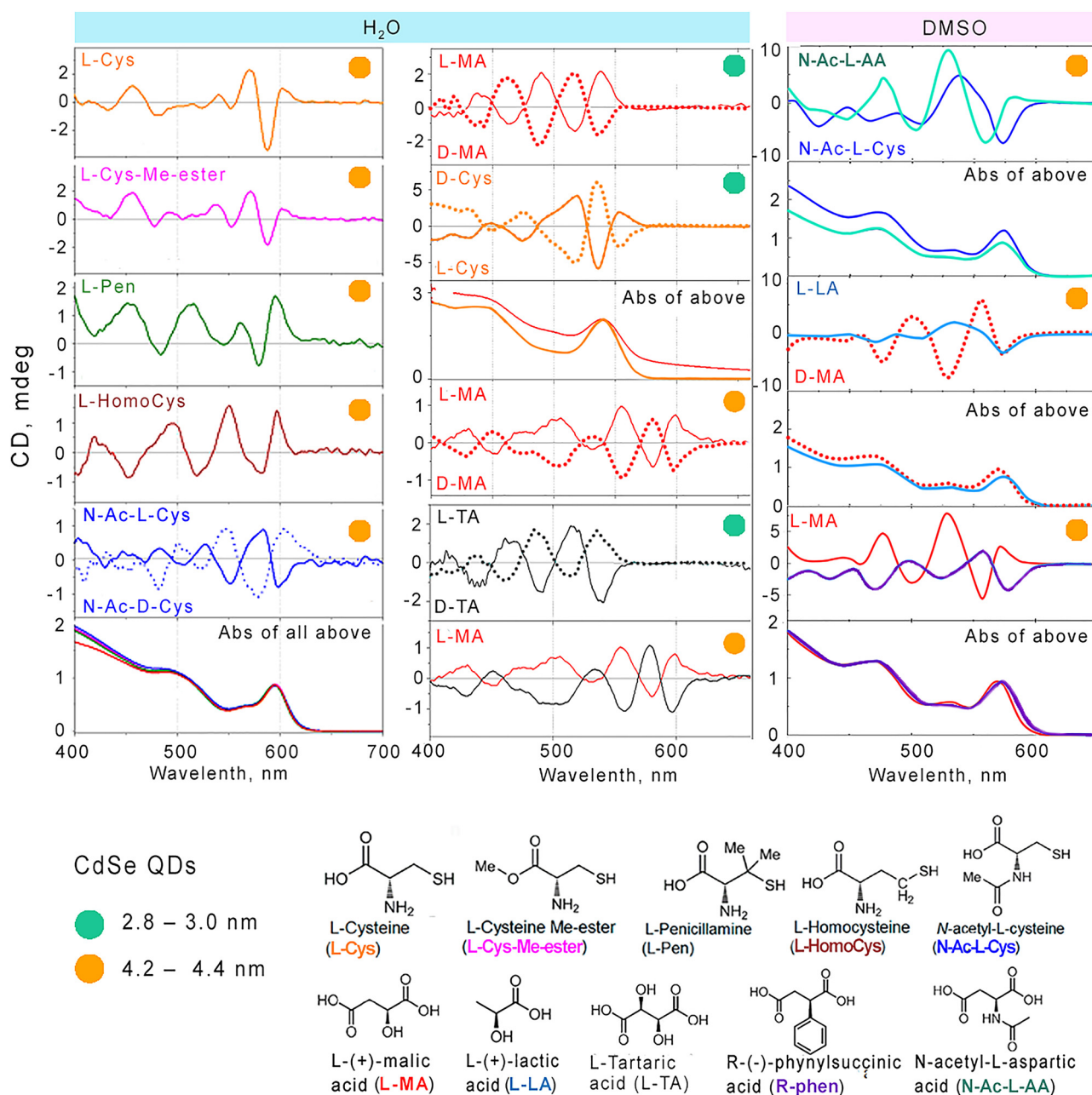


Figure 10: Circular dichroism (CD) and absorption spectra of CdSe quantum dots (QDs) with different sizes, chiral ligands and solvents. Adapted with permission from a study by Choi et al. [70] and Varga et al. [71] and Puri and Ferry [72]. Copyright 2016 American Chemical Society. Adapted with permission from a study by Choi et al. [70] and Varga et al. [71] and Puri and Ferry [72]. Copyright 2017 American Chemical Society. Adapted with permission from a study by Choi et al. [70] and Varga et al. [71] and Puri and Ferry [72]. Copyright 2017 American Chemical Society.

additional oxygen donor atom, for example, a hydroxyl group, were effective. DFT calculations revealed that these ligands can be bound to Cd atoms on the QD surface in two different ways and therefore could give the opposite CD spectra depending on the binding mode, similar to other reports [70]. Ligands containing three oxygen atoms of carboxyl or hydroxyl groups have a greater energy

difference between the stereo enantiomeric forms than the others due to anchoring. The authors suggested that ligands without a third oxygen do not induce a CD signal because the two forms continually convert into each other and therefore the CD signal is compensated. However, it was found that lactic acid containing two oxygen atoms can induce a weak CD signal in CdSe QDs [72].

Similar results were reported in another paper by Kuznetsova et al. [84], showing that cysteine has different binding modes to the surface of CdSe/CdS QDs, dependent on ligand concentration. At low concentrations, cysteine bound to the QD through three functional groups, thiol-, amino-, and carboxyl, but with increasing ligand concentration, more cysteine molecules attached via the thiol- and amino groups, while the carboxyl group remained free. In this case, the CD signal of the QD firstly increased with the cysteine concentration, and then decreased at higher concentrations. The authors suggested that the cysteine molecules were bound to the CdSe/CdS QDs differently, and therefore had the opposite stereo conformations, which produced an inversion of the CD signal. Therefore, superimposed CD signals quenched each other, and this led to an overall decrease in the CD signal. In addition, these results were supported by DFT calculations.

L- and D-Cys was added to the solutions of L-/D-Cys functionalized CdTe QDs to create hetero- or homochiral complexes [73]. Formation of heterocomplexes resulted in the large decrease of CD intensity and PL enhancement, unlike the formation of homocomplexes which resulted in values remaining almost at the same level. Authors suggested that it can be explained by the transformation of binding configuration of chiral cysteine molecules.

Another paper reported [72] studies of CdSe QDs with chiral carboxylic acids as ligands. Measurements revealed that g -factors for CdSe QDs bound by D-(+)-malic with two carboxylic groups were three times larger than QDs with L-(+)-lactic acid, an acid which contains only one carboxylic group. Increasing the number of stereocenters of the chiral ligand also produced an increase in the QD induced g -factor, therefore the tartaric acid appeared to be twice as effective relative to maleic acid. Although in another paper by Varga et al. [71], it was found that the difference in the g -factor of CdSe QDs induced by these two acids was much lower, it is worth noting that in the paper [71], the authors used the classical ligand exchange method, while in another work [72] ligands were added to a solution of QDs in toluene in a very large excess in dry form. This second approach produced QDs with a g -factors of one order of magnitude larger than in report [71] for the same carboxylic acids. Overall, the authors of the study [72] achieved a 30-fold range in QD g -factors by varying the exact chemical structure of the chiral carboxylic acids.

Another interesting study covered the effects of ligand conformation on the chiroptical properties of CdSe NPs capped by cysteine [77]. Briefly, the CD spectrum was considered as a result of the interactions of the ligand's electronic transitions dipoles with the dipoles of the NPs. When cysteine bound to the surface of the CdSe NPs with either a wurtzite [11 $\bar{2}$ 0] or a zinc-blende [100] structure, the

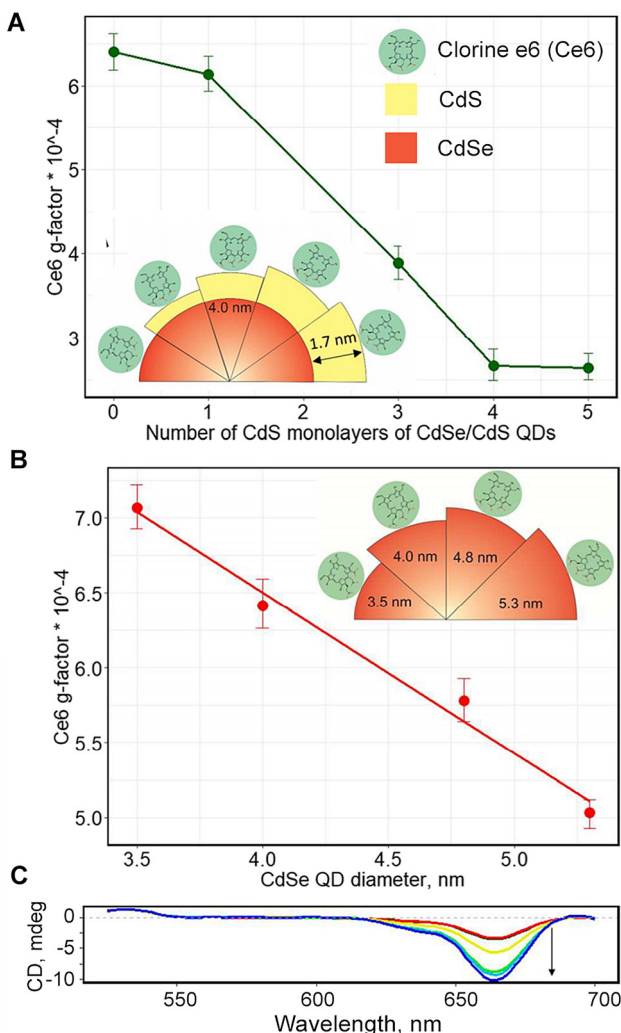


Figure 11: G -factors at the lowest electronic transition of chlorin e6 in complexes with (A) CdSe/CdS quantum dots (QDs) with 1–5 monolayers of CdS shell and (B) CdSe QDs of different size. (C) Circular dichroism (CD) spectra of chlorin e6 in a free form (red) and bound to the QDs. Adapted from a study by Visseratina et al. [75] with permission from The Royal Society of Chemistry.

dipoles of cysteine and the NPs were shown to have different mutual directions. As a result, the signs and positions of the CD peaks were distinctly different between the crystal phases, with authors analyzing in detail the mechanism of formation of each peak.

Examples of the CDs of CdSe QDs with different ligands are summarized in Figure 10.

2.4 Influence of QDs on optical activity of chiral molecule

A lot of effort has been made to investigate LIC in QDs. At the same time, only a few studies are devoted to the

opposite effects: the influence of semiconductor NCs on optical activity of surface molecules, nevertheless such studies are crucial since chiroptical properties of molecules can be significantly changed near NCs. In some reports it was observed that the CD signal of chiral molecules altered after binding with the QDs compared to that of free molecules [25, 55]. In many publications, it was shown that the conformation of chiral ligands is altered on the surface of the QDs [70–72, 84], which can possibly affect the molecule optical activity. Moreover, it has been theoretically predicted by Govorov et al. [88–90] that a nonchiral planar molecule can become optically active when it forms a complex and couples *via* dipole and multipole Coulomb interactions with achiral NCs.

In another important piece, it has also been demonstrated that CD signal intensity of the chiral molecule chlorine e6 can be significantly increased due to interaction with QDs [75, 91]. Visheratina et al. [75] has shown that the effect of QDs on the chlorin e6 weakens with increase in size of CdSe QDs and with an increase in CdS shell thickness of CdSe/CdS QDs. This was explained by a decrease in the efficiency of hybridization of the electronic levels of the QD and the chiral molecule [62].

Tang et al. [76, 77] studied the manner in which the cysteine ligands bonded with various anisotropic CdSe NPs. Depending on the shape and crystal structure of the NPs, the number of CD bands of the cysteine, their position, sign and intensity varied significantly. The CD spectra and detailed description of the mechanism in the term of NDCO model are given in sections 2.2 and 2.3.3.

Potentially, the change in optical activity and spatial configuration of a molecule can be accompanied by a transformation of its functional properties, such as biochemical activity in sensing or drug delivery, and catalytical activity in asymmetric synthesis. Furthermore, cells contain a large number of chiral molecules, which can attach to the NP surface and alter the enantioselective biochemical processes. Therefore, this interaction can be one of the causes of NP cytotoxicity, which has not yet been sufficiently investigated. Therefore, studying NP influence on the chiral properties of organic molecules is of great interest from a fundamental and applied point of view (Figure 11).

3 Applications

The unique properties of chiral semiconductor NCs open up a range of applications in different areas. In this section, we will discuss potential and existing applications of these NCs including sensing, catalysis, generation of circular polarized light and spintronics. A number of previously

published reviews on the applications of chiral nanocrystal exist [3, 92]. In this section, we have focused on the most significant practical results and review the latest achievements.

3.1 Sensing

A multitude of studies consider semiconductor NCs as promising components of optical sensors [93–95]. Chiral ligands further extend the sensing capabilities of NCs *via* chiral recognition, enabling enantiomer recognition and separation [21, 22].

Generally, chiral recognition is based on the stereospecific binding of target molecules with nanocrystal ligands or surfaces. The complex formation leads to change in PL intensity due to electron transfer or fluorescence resonance energy transfer (FRET), while another type of sensor is based on CD signal change in the presence of specific targets (e.g., metal ions).

We summarized the reported chiral sensors in Table 1. The range of analyte concentrations within linear sensor response and limit of detection (LOD) are given where available.

3.2 Circularly polarized light emitters

Another emerging photonics application of chiral luminescent nanomaterials are their use in CPL emissive devices, e.g., components of CD spectrometers. The availability of a direct source of CPL shows huge potential, enabling device miniaturization, reduced energy consumption and production cost. CPL sources can also be used in 3D displays [112–114], chiral asymmetric photosynthesis [115, 116] and spintronics [30].

To estimate the degree of PL circular polarization, one usually uses the luminescence dissymmetry ratio $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the intensities of left and right CPL, respectively. Most chiral samples, like organic molecules, polymers, or biochemical systems, exhibit g_{lum} of about 10^{-2} to 10^{-3} [117] which is too low for practical applications. Therefore, recent trends in the engineering of new materials for CPL generation focus on maximizing g_{lum} .

The earliest reported chiral QDs prepared in the presence of chiral thiol ligands showed a CD signal but did not display CPL [55]; however, the PL of those QDs was attributed to surface defects states. Only a few works demonstrate CPL emission by colloidal NCs after chiral

Table 1: Summary of chiral sensors based on quantum nanostructures.

Probe	Analyte	Working concentration/LOD	Operation principle	Reference
<i>Detection of ions based on CD signal changes</i>				
L-pen, cysteamine CdS QDs	Cd ²⁺	65–200 µM/59.7 µM	Target ions enhance CD signal of probe	[96]
	S ²⁻	7–125 µM/1.6 µM		
L-cys CdS QDs	Ni ²⁺	10–60 µM/7.33 µM	Target ions enhance CD signal and change spectra shape probably due to complex formation with ligands.	[97]
	Co ²⁺	4–80 µM/1.13 µM		
L or D-cys CdSe nanoplatelets (NPLs)	Pb ²⁺	–/4.9 nM.	Pb ²⁺ detaches cysteine from NPLs surface due to high affinity to sulfur group of cysteine. As a result, CD signal is reduced.	[98]
D-pen, cysteamine CdSe QDs	Cu ²⁺	–/0.34 µM	Cu ²⁺ oxidizes ligands and removes it from the QD surface. As a result, CD signal is decreased	[99]
<i>Cyclodextrin based sensors working on stereospecific PL changes</i>				
Mono-6-SH-β-cyclodextrin Mn-doped ZnS QDs	D/L tryptophan	0–6.0 µM/5.4 nM	In all cases, enantiomer recognition is associated with stereospecific interaction of amino acids with cyclodextrins. One enantiomer leads to QD PL enhancement or quenching, while the opposite has a minor influence on PL or in some cases demonstrate the opposite effect.	[100]
β-cyclodextrin CdSe/ZnS QDs	D/L penicillamine	0.1–5.0 mg L ⁻¹ /0.06 mg L ⁻¹ 0.8–5.0 mg L ⁻¹ /0.2 mg L ⁻¹ –/–		[101]
α- or β- cyclodextrin CdSe/ZnS QDs	D/L tyrosine D/L methionine			[24]
CdTe QDs with silica shell modified by cyclodextrine	D/L histidine	0–60 µM/– 0–20 µM/–		[102]
<i>Stereospecific PL quenching of sensors based on cysteine derivatives</i>				
N-acetyl-L-cysteine CdTe QDs	R/S Phenylglycinol (in presence of AgNO ₃)	10 ⁻⁵ –10 ⁻⁷ mol L ⁻¹ /–	The analytes quench the QD emission in a concentration-dependent mode. In all cases, one enantiomer leads to more significant quenching than the other. Authors supposed that one enantiomer attaches stereoselectivity to QD surface or forms a complex with chiral ligands. The PL quenching is attributed generally to charge transfer between QDs and analytes.	[103]
N-acetyl-L-cysteine CdSe/ZnS	D/L tyrosine	/–		[104]
N-acetyl-L-cysteine methyl ester CdSe/ZnS QDs	R/S ketoprofen R/S flurbiprofen R/S naproxen	/–		[105]
L- or D-cys CdSe QDs	D/L tryptophan	/–		[106]
L-cys/D-cys CdSe/ZnS QDs	D/L carnitine	/0.05 mM		[107]
<i>Multicomponent sensors</i>				
Chiral self-assembly of CdTe QDs and zinc-based porphine (ZnTPVP)	D-proline, D-lysine, L-Serine	–/4.46 × 10 ⁻¹⁰ mol L ⁻¹ –/7.13 × 10 ⁻¹¹ mol L ⁻¹ –/3.35 × 10 ⁻¹¹ mol L ⁻¹	Initially, ZnTPVP quenches QD PL. Analytes stereospecifically interact with chiral assemblies. In new complexes, quenching condition is released, and PL is enhanced	[108]
L-cys or D-cys modified CdTe QDs and gold nanorods	D/L cysteine	/–	Cysteine triggers the assembly of QDs around gold nanorods. Homo and hetero chiral cysteine pairs induce aggregates with different shapes and different conditions for energy transfer from the QDs to the nanorods. As a result, different PL quenching is observed in the presence of L- or D-cys.	[109]
Mixture of MoS ₂ QDs capped by L(+)-ascorbic acid and magnetic nanoparticles both functionalized by antiothermaglobulin antibody	Avian influenza virus (H4N6)	PL detection: 128–0.0012 HAU/50 µL/0.00403 HAU/50 µL CD detection 128–0.0128 HAU/50 µL/0.0381 HAU/50 µL 50–250 µM/31 µM	Antibodies on the surface of QDs and MNPs bind to virus with formation of magneto luminescent aggregates. After magnetic separation, the intensity of PL and CD is decreased due to concentration loss.	[110]
D-pen and cysteamine CdS QDs	Glucose		Enzymatic reaction of glucose oxidase and glucose generates H ₂ O ₂ , which etches the QDs. CD signal is decreased as a linear function of the glucose concentration.	[111]

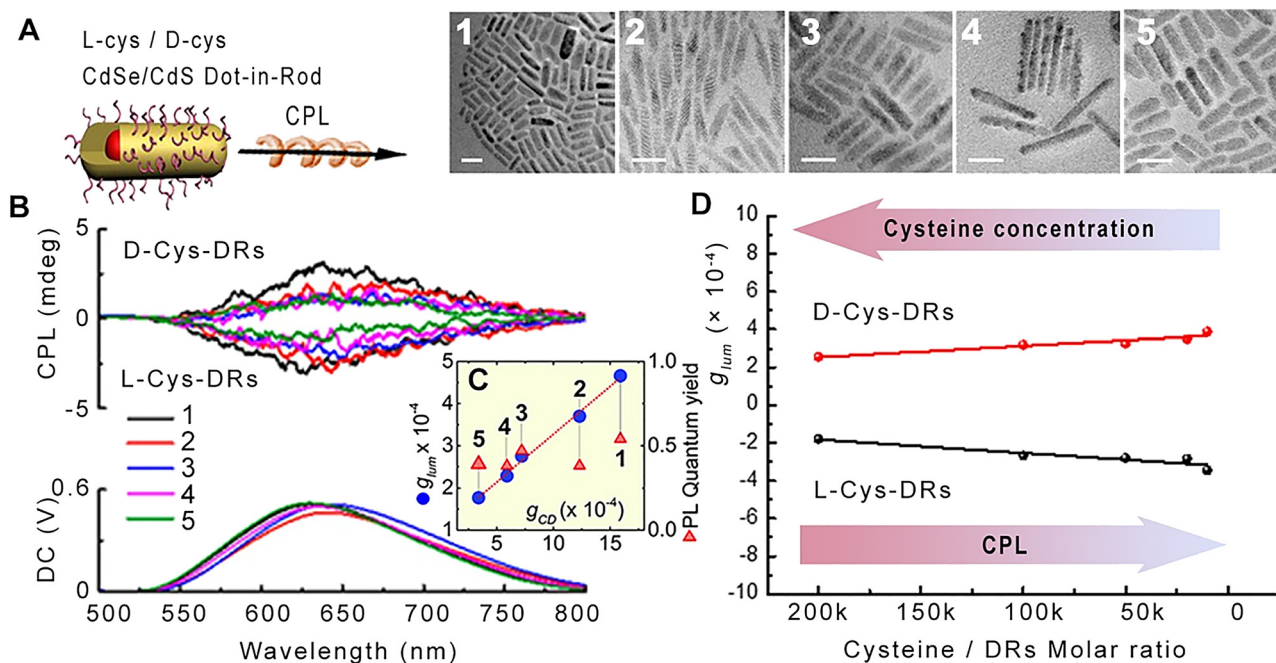


Figure 12: (A) Sketch and Transmission Electron Microscopy (TEM) images of L-cys/D-cys CdSe/CdS DiR samples. Scale bars represent 20 nm. (B) CPL and PL spectra of the L- and D-Cys-CdSe/CdS dot in rods (DRs). Numbers of spectra coincide with TEM image number. (C) Correlation between photoluminescent (PL) and circular dichroism (CD) g -factors (blue circles). PL quantum yield (red triangles). The point numbers match with no of TEM images. (D) Plot of the g_{lum} at PL maximum of the L- and D-Cys-CdSe/CdS DiRs (TEM No. 1) against the cysteine/DiR molar ratio and their linear fittings. The black dots and line represent the L-Cys-CdSe/CdS DRs, whereas the reds dots and line represent the D-Cys-CdSe/CdS DRs. In all cases, sample concentration is 1×10^{-6} M. PL excitation wavelength is 400 nm. Adapted with permission from a study by Cheng et al. [28]. Copyright 2018 American Chemical Society.

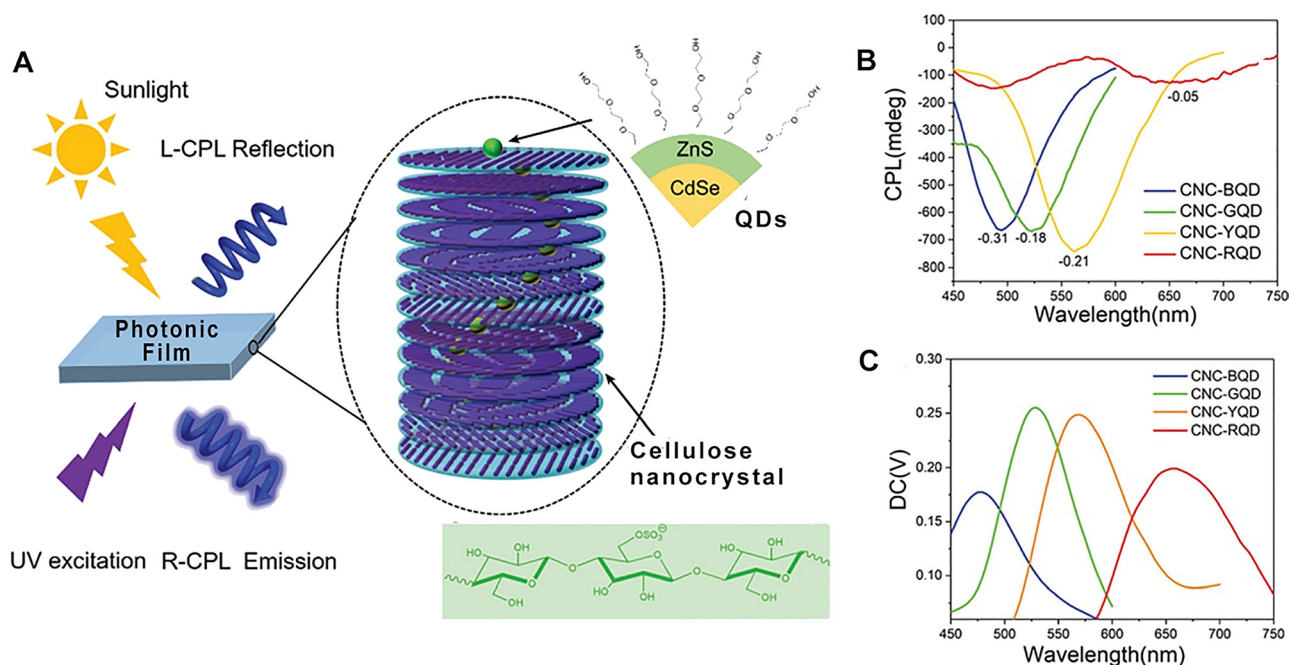


Figure 13: (A) Illustration of L-CPL reflection and R-CPL emission of circularly polarized light (CPL) photonic films through the coassembly of cellulose nanocrystals and semiconductor quantum dots (QDs). (B) CPL and (C) DC – direct current (proportional to PL) spectra of cellulose films doped with diaerent semiconductor QDs with PL of different colors. Adapted from a study by Xu et al. [120] with permission from The Royal Society of Chemistry.

ligand exchange, in all cases, the emission is assigned to excitonic emission [27, 28, 118]. Balaz et al. [27] reported a mirror image CPL signal for L-/D-cys CdSe QDs with a g_{lum} of $3-4 \times 10^{-3}$. He et al. [28] demonstrated CPL of L-/D-cys CdSe/CdS dot in rods with a g_{lum} of about 5×10^{-4} [28]. Mukhina et al. [118] also reported CPL studies of L-cysteine-capped CdSe/CdS dot in rods and ZnS QDs doped by Mn QDs without giving g_{lum} values.

The investigation of a set of different CdSe/CdS dot in rods (Figure 12A) [28] revealed that the value of g_{lum} linearly increases with g_{CD} growth (Figure 12B and C). PL quantum yield also influenced the value of g_{lum} since PL quenching leads to the decreasing of CPL intensity as well and excellent example being CdSe QDs which showed the lack of CPL because of PL quenching by thiol ligands [28]. Therefore, on one hand, the shell protects the PL from quenching which is essential for CPL detection. On the other hand, it was shown that g_{CD} drops with increasing shell thickness [69], consequently g_{CPL} will decrease in samples with a thin shell as well. The molar ratio of cysteine to the dot-in-rods also influences the CPL intensity. Similarly it was reported [84] that the excess of cysteine molecules in aqueous solutions decreases the intensity of both the CD and CPL signals (Figure 12D).

An attempt to increase g_{lum} value was also made in another report [119], in which the authors reported CPL

signals with g_{lum} up to 0.008 in CdS QDs synthesized in the presence of a chiral protein named horse spleen ferritin. It was proposed that due to the chiral configurations of the chelating amino acids in the ferritin, it might be transferred to the QD crystal lattices during an anisotropic crystal growth causing chiral distortions in the crystal structures.

To further enhance g_{lum} , NCs might be spatially arranged in a helix structure. For example, Duan et al. [29] encapsulated achiral CdSe/ZnS QDs into a chiral peptide dendron hydrogel through coagulation. These cogels displayed CPL with g_{lum} up to 0.03 with the helix arrangement of the QDs inducing chirality in the composite. Also, assembled peptide dendrons can endow chirality to the QDs through ligand exchange with mercaptoethylamine on the surface of the QDs.

Strong CPL signals have been observed in photonic films prepared from a mixture of achiral semiconductor NCs and lyotropic liquid crystals of cellulose using CdSe/ZnS QDs [120] and CdSe/CdS QRs [121]. In both cases the formation of a left-handed helical structure leads to the emission of right-handed circularly polarized luminescence with g_{lum} up to -0.3 for QDs and -0.45 for QRs. Schematic images of the helical structure based on QDs and cellulose NCs together with CPL and PL signals are shown in Figure 13.

Similar effect were observed for FeS₂ QDs capped by L/D-cysteine which can assemble within chiral hydrogels

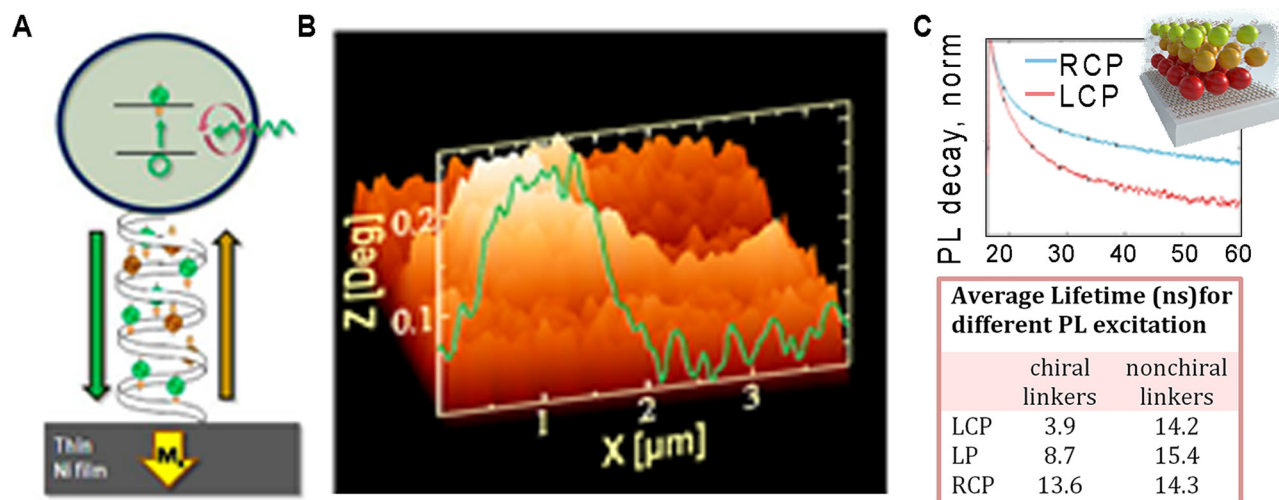


Figure 14: (A) Illustration of the spin torque transfer mechanism. When the NCs are excited, charges oscillate between the NCs and the surface, passing through the chiral molecules. Owing to the CISS effect, mostly electrons with spin of one type are injected into the Ni layer. The electrons with opposite spins are transferred back in the opposite direction. Both effects together generate spin torque transfer with no charge transport. Exciting light in the right direction of circular polarization can enhance the torque transfer. (B) Magnetic Force Microscope image of Ni substrate decorated by CdSe quantum dots (QDs) through chiral molecules layers after RCP illumination through a light mask. Magnetic phase image of the illuminated area displays a highly localized magnetic response. Reprinted with permission from a study by Ben Dor et al. [129]. Copyright 2014 American Chemical Society. (C) Schematic illustration of solid-state structure composed of CdSe QDs of three sizes interconnected by chiral linker (α -helix L-polyalanine) and PL lifetime decays under irradiation of RCL and LCL. PL decay lifetimes also given in table. Reprinted with permission from a study by Fridman et al. [133]. Copyright 2019 American Chemical Society.

[122]. The resulting superstructures have a shape of twisted nanofibers and demonstrate both CD and CPL signals. Nontwisted nanofibers have no optical activity and indicate the absence of LIC in these FeS₂ QDs.

The highest g_{lum} of 1.3 has been demonstrated by Nabiev et al. [123] for the fluorescence emission of achiral CdSe/ZnS QDs embedded in cholesteric liquid crystals. Degree of PL polarization may be optically or electrically controlled via conformational changes in the helical structure of the liquid crystal matrix.

In conclusion, we can summarize that the degree of PL polarization in NCs capped by chiral ligand is still quite low. Only 0.025–0.4% of emitted light is actually circular polarized. Chiral assembly of NCs might increase PL polarization degree up to 65%. Experimentally observed linear correlations between CD and CPL g -factors is quite predictable. According to Kasha's rule, PL originates from the lowest energy excited electronic state. For singlet states, the same dipole transition moments (either electric or magnetic) govern the phenomena of both CD and CPL. However, according to theoretical calculations for electric-dipole-allowed transitions given in a study by Berova et al. [124], g_{CPL} factor is inherently low. The highest g_{CPL} factor occurs when the transition is electric dipole forbidden and magnetic dipole allowed. This situation is observed, for example, in chiral lanthanide complexes which emit CPL with a polarization degree up to 50% [125]. Therefore, precise engineering of the QD electronic structure and searching for new more effective materials might be the answer to demands for nanomaterials emitting light with high degree of circular polarization.

3.3 Spintronics

Spintronics uses electron spins for information processing. Carrying information in both the charge and spin of an electron potentially offers devices with a greater diversity of functionality. For these devices to be functional, it is necessary to have materials in which electrons will maintain their spins during propagation. Chiral molecules could be used as filters for spin selective electron transport based on the chiral induced spin selectivity (CISS) effect.

The CISS effect [126, 127] postulates that chiral compounds have a preferred orientation of the electron spin after charge polarization. Charge can polarize when a chiral molecule approaches a substrate or another molecule. After charge polarization, the resulting spin density and spin direction are determined by the molecule geometry. Upon chemical adsorption, electron spin on the surface that is opposite to the spin on the electric pole of the chiral molecule has the more stable spatial

orbital, meaning that adsorbate interactions with antiparallel spins (one on the surface and one on the molecule) should be more stable. As a result, attaching chiral molecules to surfaces might induce spin orientation in the surface. This effect was previously used to magnetize superparamagnetic iron oxide NPs (with size down to ~ 10 nm) at room temperature by chiral surfactant absorption [128].

Chiral molecules also can transport selectively photogenerated electrons between QDs and substrate. For example, it has been shown [129, 130] that optical excitation of CdSe QDs promotes spin torque to a thin Ni substrate through an interconnecting layer of chiral molecules (6 helix L-polyalanine) without charge transfer. As a result, spins in Ni substrates align perpendicular to the surface and induce local magnetization (Figure 14A and B). Therefore CISS effect may induce a local magnetization without the traditional use of an external magnet and therefore could form the basis for highly localized nanometric spintronic 3D logic devices.

Magnetic surfaces can also have different impacts on QD PL, depending on interconnecting ligand chirality and substrate magnetization orientation. If spin orientation is preferable for electron transport through a chiral linker, QD PL is quenched [131], while reorientation of spins at a magnetic substrate diminishes QD PL quenching.

L-/D-cysteine can act as a spin selective filter for charge separation as well. For example, cysteine-capped QDs were deposited on highly oriented pyrolytic graphite [132] and a magnetic conductive probe of atomic force microscope was used to apply a voltage through the QD layer. Interestingly, the conductivity of this QD layer depended on chirality and magnetization of the conducting probe tip, while for achiral QDs, no spin filtering was found.

The CISS effect also allows for controlling the electron transfer between QDs in a multilayer structure (Figure 14C) [133]. In CdSe QD layers connected by chiral linkers, PL decay time under excitation by right circular polarized light is 3.5 times longer than under excitation by left circular polarized light. While in the structure with achiral linkers, PL decay time was independent of polarization of the excitation wavelength. This effect was explained by spin-dependent electron delocalization through chiral molecules.

Finally, an emerging potential application for chiral two-dimensional (2D) quantum nanomaterials is valleytronics, which involves the use of the electron wave quantum number in a crystalline material to encode data by controlling the photon angular momentum (circular polarization state) via circular polarized light. This area is rapidly developing and so far is mostly focused on the use of atomic layered transition metal dichalcogenides, such as MoS₂, while more recently

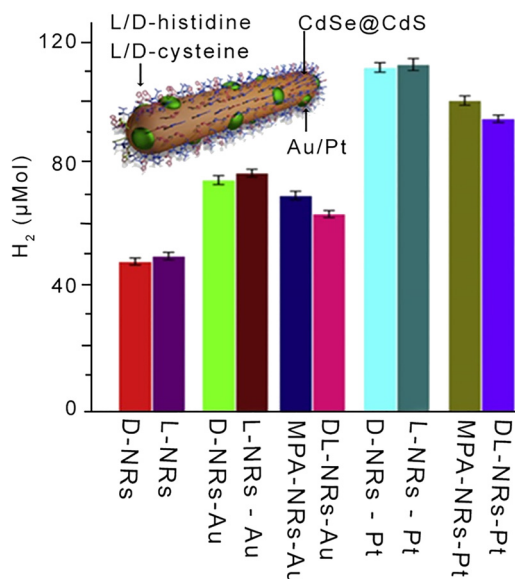


Figure 15: Schematic illustration of the chiral CdSe@CdS nanorod decorated by metal nanoparticles and chart of H₂ production by nanorods with different surface functionalization under illumination by linear polarized light. Adapted with permission from a study by Ma et al. [18]. Copyright 2019 Elsevier.

new 2D quantum nanostructures have emerged as also very promising materials for this field [31, 134–138].

3.4 Catalysis and asymmetric synthesis

The development of new asymmetric chemical reactions is crucial for the synthesis of enantiomers of chiral drugs, fragrances, food additives and various biomolecules. NCs with chiral ligands can be used as photocatalysts in these reactions. The basic mechanism of semiconductor photocatalysis involves three main steps [139]:

- (i) photoexcitation of surface redox centers (electron–hole pairs);
- (ii) electron transfer between catalyst and working compound (often coupled with proton transfer);
- (iii) conversion of primary redox intermediates into products.

A recent minireview [140] highlights the progress in stereoselective photochemical reactions on the surfaces of bulk semiconductors. Here, we will focus on recent progress of the use of chiral NPs in catalysis and asymmetric synthesis.

Naaman et al. [141, 142] showed that chiral coating of NPs may enhance the efficiency of water splitting in an electrochemical cell. Water splitting is an energy consuming process and the production of hydrogen peroxide as a by-product also decreases efficiency of this process. According

to recent work [141], spin alignment of the unpaired electrons in the intermediate radicals of OH^- might increase the efficiency of the reaction: $\text{OH}^- + \text{OH}^- \rightarrow \text{H}_2 + \text{O}_2$, since there is no spin restrictions in forming an oxygen molecule which is triplet in the ground state. Hydrogen peroxide is a singlet in the ground state and its production is suppressed in this situation. To achieve spin alignment in OH^- radicals, authors of a study by Mtangi et al. [141] used TiO_2 electrodes linked with CdSe QDs by chiral linkers. Due to CISS (an effect discussed in section 3.3), following photoexcitation, electrons with only a particular spin are favoured to transfer from the QD to the TiO_2 through the chiral ligands. As a result, holes with the same spin remain in the QDs. This spin alignment is maintained during the further electron transfer steps, which take place in the electrolyte. As a result, water splitting overpotential is reduced and the amount of hydrogen peroxide by-product is decreased.

Ma et al. [18] also demonstrate that chiral ligands increase H₂ production during photocatalytic water splitting, using CdSe@CdS nanorods decorated by Au or Pt NPs. The highest H₂ outcome was detected for nanorods capped by the mixture of cysteine and histidine enantiomers. Nanorods capped by the racemic mixture of these ligands or by achiral 3-mercaptopropionic acid demonstrated lower H₂ production (Figure 15).

NCs capped with certain chiral ligands also can be used for photodegradation of different organic compounds. L-arginine-capped CdS QDs effectively degrade methylene blue and Rhodamine B under visible light irradiation [143]. Photogenerated holes possess high oxidative potential which permits the oxidation of the dyes adsorbed on the QD surface. In water, QDs also may generate hydroxyl radicals which also can be responsible for the degradation of the dyes. Therefore, CdS QDs might be used as potential photocatalyst to effectively treat the organic pollutants under visible light irradiation. Taking into account enantioselectivity of adsorption of some chiral compounds on QD surfaces (mentioned in Table 1), it is potentially possible to use QDs for enantiomeric enrichment of racemic mixtures of drugs or other artificial biomolecules. This approach was investigated by Zhang et al. [144] for spherical MoS_2 and WS_2 QDs. These particles after coating by chiral ligands demonstrate enantioselective peroxidase-like activity in the presence of copper ions. It was found that L-tyrosine displays higher binding affinity to L-cys QDs while D-tyrosine preferably binds to D-cys QDs. As a result, during photoexcitation of a homochiral mixture, L-tyrosinol was produced twice as much as D-tyrosinol than was observed in heterochiral mixtures.

Photocatalytic decomposition of L- or D-tyrosine to dityrosine in pores of chiral microspheres was demonstrated

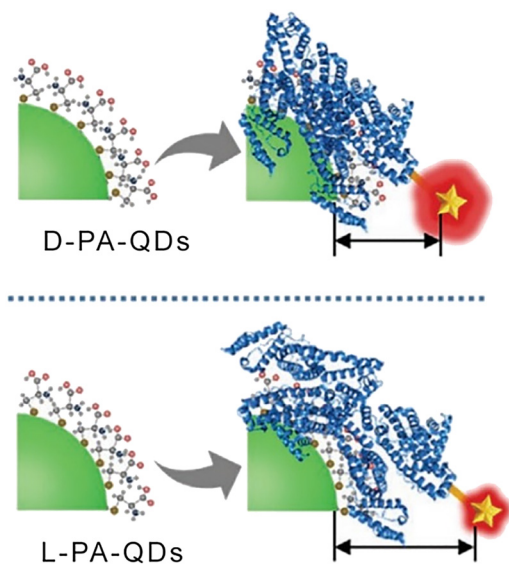


Figure 16: Adsorption orientation of HSA onto the surface of D- and L-penicillamine capped InP/ZnS QDs, determined using fluorescence resonance energy transfer (FRET) data. Adapted with permission from Qu et al. [147]. Copyright 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

by Kotov et al. [19]. ZnS NPs covered by L- or D-penicillamine and Au NPs covered by glutathione were self-assembled into 70–100 nm spheres. Enantioselective decomposition of tyrosine was determined by the chiral preferences of L- and D-tyrosine to interact with individual NPs and penetrate into the interstitial spaces between NPs in spheres. An addition of Au NPs enhanced photocatalytic conversion of the substrates. Au NPs improved electron–hole separation and increased light absorption by the ZnS via plasmonic effects.

There is also an example of the use of ZnS QDs with an induced chirality as a catalyst for asymmetric aldol condensation reactions [20]. L-proline-capped ZnS NPs were used as a catalyst for direct asymmetric aldol condensation reactions between aldehydes and acetone. Acetone was used as a solvent as well as a reactant. It was found that the selectivity of ZnS NPs enables the production of only (R)-b-hydroxy carbonyl compounds and restricted the reaction to the aldolization stage only. Importantly, the ZnS catalyst was recovered and reused several times without any considerable loss of activity.

3.5 Chiral biorecognition: interaction of chiral nanomaterials with biological objects

Chirality, in addition to affecting the polarization of light, plays an important role in the interaction with biological

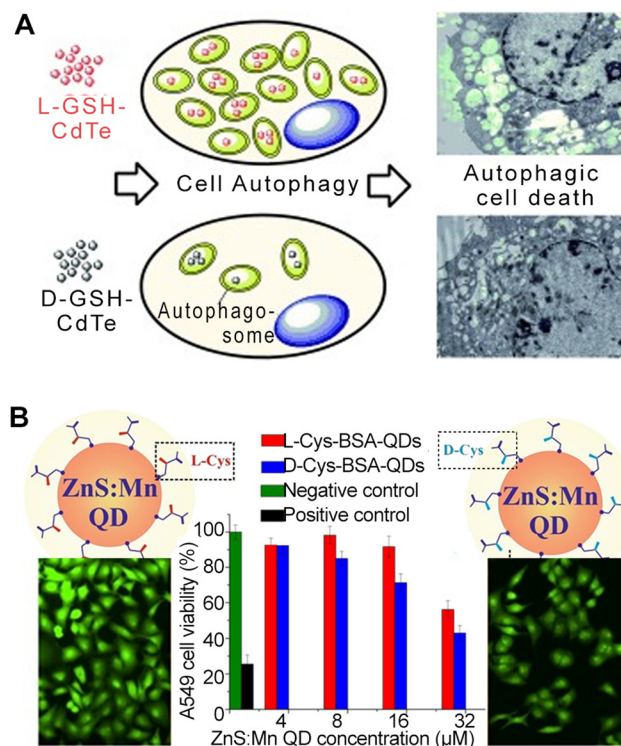


Figure 17: (A) Schematic representation of autophagy caused by chiral CdTe quantum dots (QDs) coated with L- or D-glutathione (GSH) Reprinted with permission from a study by Li et al. [25]. Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (B) Schematic representation of the ZnS:Mn QDs capped with L- and D-cysteine and difference between cell uptake and cytotoxicity on A549 cells. Adopted from a study by Kuznetsova et al. [26].

systems. This is because the response of cells to a certain molecule depends on the stereospecific chiral recognition. In the same way that the right hand fits only in the right glove, certain cellular receptors recognize only one enantiomeric form and not the opposite, or produce a different response depending on the enantiomer. As past experience has shown in the case of drug thalidomide [145], sometimes not controlling the stereoisomerism of drugs can have serious consequences. The racemic drug thalidomide was widely used in the 1960s to treat nausea during pregnancy in many countries. While the D-form of thalidomide was a safe sedative, the L-form was later discovered to be harmful, tragically causing severe birth defects [146]. Thus, the use of single-enantiomer drugs is absolutely vital for providing safe medical treatment.

The importance of controlling isomerism is not exclusive to small organic molecules but can be extrapolated to any chiral object that interact with biological systems including QDs. The use of chiral QDs for medical purposes is fairly recent and is likely the reason for minimal number

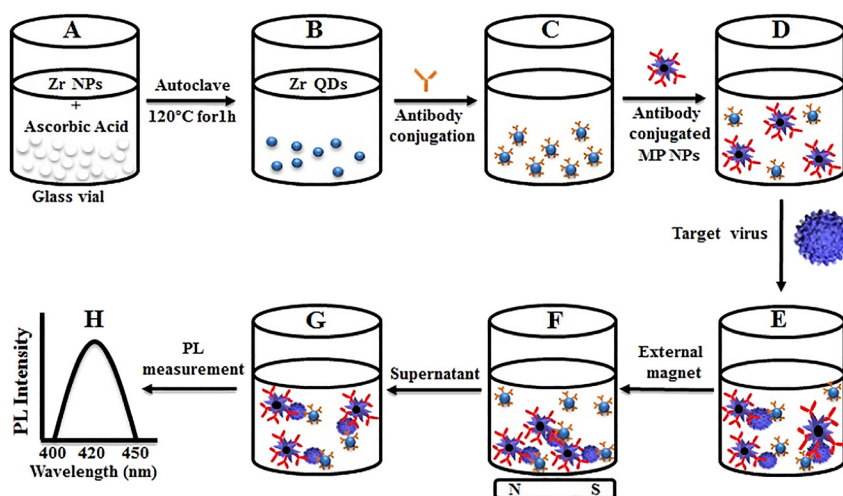


Figure 18: Scheme of sensor design: (A) Zr nanoparticles and reducing agent keep on vial; (B) Zr quantum dots (QDs) formation; (C) antibody conjugated QDs; (D) the addition of antibody-conjugated MP NPs; (E) formation of nanostructured magneto-plasmonic fluorescent with the addition of target, then separated (F); (G) the nanostructure was dispersed and measure the optical properties (H). Reprinted from a study by Ahmed et al. [151] under the Creative Commons CC-BY-NC-ND license.

of published articles in this field. Here we will review the main *in vitro* experiments as well as the first *in vivo* results obtained for chiral QDs.

As far as interactions with biological systems are concerned, chiral QDs can have effects at three different levels: (i) firstly *via* interactions with proteins or other free molecules present in the medium; (ii) secondly *via* cell recognition/internalization; (iii) thirdly due to the differences in the distribution inside the cell or in the interactions with intracellular components. It is important to note, that even greater complexity arises due to the extent of these interactions being closely dependent upon each other. Therefore, variations in the protein crown may lead to differences in cell recognition/internalization and to the subsequent effects depending on how these particles interact with intercellular components.

1st level – Interactions with proteins or other free molecules. Kotov et al. [40] reported that bovine serum albumin adsorbed one enantiomer of TGA-stabilized CdTe QDs with spontaneous chiral defects more effectively than the alternative, which allowed chiral separation of the CdTe QDs. Shang [147] has demonstrated that human serum albumin had different affinity and adsorption orientation onto the surface of D- and L-penicillamine capped InP/ZnS QDs, which was confirmed by CD and FRET data (Figure 16).

2nd level – Cell recognition/internalization. A study performed with CdSe/ZnS QDs functionalized with L- and D-cysteine in Ehrlich Ascite carcinoma cells showed that the internalization process was enantioselective, observing twice as much internalization for L-Cys QDs than for D-Cys QDs [23]. Li et al. [25] also studied the effects of chiral glutathione (GSH)-capped QDs on cytotoxicity and induction of autophagy in HepG2 cells. Regardless of size, L-GSH-QDs induced greater autophagy and cytotoxicity than the D-form, with greater effects observed for smaller

particles (Figure 17A). *N*-isobutyryl-D-cysteine-capped β -HgS QDs were found to be more biocompatible to CCK8 cells than that of the L-form [38]. In a report by Kuznetsova et al. [26], oppositely D-Cys-capped ZnS/Mn QDs were found to be more toxic than the L-form (Figure 17A). However, as evidenced by the investigations carried out by Govan et al. [67], chirality does not always entail differences in behavior. These authors reported CdS nanotetrapods functionalized with enantiomeric forms of penicillamine for which they did not observe significant differences in either cytotoxicity or internalization. It should be noted that the concentration of nanotetrapods was relatively low and cytotoxicity did not exceed 10%. At higher concentrations, the effect could appear.

3rd level – Differences in the distribution inside the cell or in the interactions with intracellular components due to chiral differences. In the search for an effective treatment against bacteria, which is harmless to mammals, Xin et al. designed Glutamic acid (Glu) functionalized graphene quantum dots (GQD) that selectively act on MurD ligase. MurD ligase is an enzyme present in the cytoplasm of bacteria responsible for the synthesis of peptidoglycan, one of the main components of the bacterial cell wall. They observed that D-Glu-GQD penetrated into the bacteria and bonded to MurD, inhibiting the synthesis of peptidoglycan and damaging the bacteria. In contrast, L-Glu-GQD showed negligible influence on bacteria [148].

Kuang et al. [149] reported the cleavage of BSA using Cu_{2-x}S QDs capped by D-/L-penicillamine, with this cleavage associated with generation of hydroxyl radicals as the reactive species. L-pen QDs displayed the highest catalytic performance under left- CPL irradiation, while D-pen QDs worked better under the right CPL irradiation. In this study, the authors proposed that light of a given chirality activates

a larger number of QDs with a matching chirality than the opposite, which leads to increased number of hot electrons and therefore hydroxyl radicals.

In addition to the previously described differences in the cellular interaction/response due to the chirality of the QDs, certain QD-based systems have shown a greater capacity to detect or elicit a specific response due to their chiral nature, regardless of the enantiomer used. Recently, it has been reported that chiral cysteine modified CdTe nanostructures can specifically recognize and cut, after CPL irradiation, a characteristic double DNA strand. In this case, both enantiomeric forms have the same cutting efficiency, both *in vitro* and *in vivo*, but only when irradiated with the appropriate polarized light [150].

In another report by Ahmed et al. [151], chiral zirconium QDs stabilized with L(+)-ascorbic acid have been used for the optical detection of coronavirus. QDs were conjugated with anti-infectious bronchitis virus (IBV) antibodies of coronavirus to form an immunolink at the presence of the target analyte and anti-IBV antibody-conjugated magnetoplasmonic NPs (Figure 18). The analyte bound to nanohybrid was separated using an external magnetic field and fluorescent analysis enabled the detection of coronavirus with a limit of 79.15 EID/50 μ L.

4 Conclusions and outlook

Great breakthroughs have been achieved in the investigation of the nature and properties of LIC colloidal semiconductor NCs in recent years. Theoretical calculations together with experimental observations have revealed how chiroptical activity of these QDs depends on the many properties of the ligands used including, ligand type, binding modes and concentration. These studies provide a deep understanding of chiroptical phenomena in QDs and an opportunity to control their properties. However, the following critical challenges still exist.

- (i) Most of the studies of induced chirality have been carried out on Cd-based QDs, containing toxic Cd ions. Nevertheless, at the present time, the main focus in the field of QD research is the investigation of nontoxic QDs, for example, Cu- and In-based binary, ternary and quaternary semiconductors, which are potentially more appropriate for biomedical applications, and less harmful to the environment. It is crucial to shift the studies to the interaction of chiral molecules with exclusively nontoxic QDs.
- (ii) The PL intensity of QDs significantly decreases after a ligand exchange procedure. Therefore, there is a clear need for a method of preparation of LIC QDs with high PL quantum yield.
- (iii) Colloidal QDs are very suitable for the incorporation in different matrices. However, there is almost no information on bulk nanocomposite materials based on colloidal chiral QDs. Using appropriate matrixes and the addition of extra components e.g. plasmonic or magnetic NPs, can extend the functionality of chiral NCs significantly.
- (iv) Despite the fact that a number of studies demonstrate the difference in biological activities of L- and D-enantiomeric forms of LIC QDs, the development of exact biochemical mechanisms that explain the cause of this phenomenon is still a significant challenge that must be addressed in the near future.
- (v) It has been shown that QDs affect chiral molecules bound to their surface, changing their spatial configuration. As a result, the chiral molecules can be transformed into the opposite stereoisomeric forms. Since the biochemical activity of a substances is strongly dependent on its stereoisomeric configuration, NPs can change the biochemical properties of the molecule. It is important to take this into account when using QDs for drug delivery, photodynamic therapy, enantioselective sensing and asymmetric catalysis. Moreover, it can be one of the sources of QD cytotoxicity: when ordinary chiral molecules inside cells bind to a NP, their configuration and properties can change and become unfavorable for the cell's vital functions. The investigation of the influence of QDs on chiral molecules and their biochemical activity are highly demanding.

In overall, chiroptically active NCs are promising candidates for different practical application. In particular, the demonstration of CPL emission by QDs with induced chirality can find a range of potential applications in various optical devices, components of chiroptical detectors, polarimeters, CD spectrometers and possibly in the long term even in 3D color displays. However, one of the main roadblocks for all these applications is a very low degree of PL polarization in NCs capped by chiral ligand, when only 0.025–0.4% of emitted light is circular polarized. Therefore, there is an urgent need in development of new efficient circular polarized light emitters based on chiral assemblies of QDs that might increase PL polarization degree by several orders of magnitude.

In addition, over the last years there have been significant achievements in the development of applications

of chiral QDs in sensing of various chiral organic molecules spintronics, valleytronics and photocatalysis. The reported QD based chiral sensors are very promising but still require further improvements of LODs and enantioselectivity particularly when several different chiral species can be present in an analyte mixture. The design of new QDs functionalised with specific chiral ligands providing high sensitivity and enantioselective recognition will be crucial for further development of chiral sensing.

The use of chiral QDs has opened up new horizons in spintronics enabling the use of the CISS effect to induce a local magnetization without the application of an external magnet and to control the electron transfer between QDs in multilayer structures. The development of new layered quantum nanostructures should also play a critical role for design of new 2D heterostructures which are necessary for further development of valleytronics.

The application of chiral quantum dots to photocatalytic water splitting, is another exciting new research direction, particularly in regard to dihydrogen production, photodecomposition and asymmetric synthesis. This is possible due to the CISS effect and enantioselective adsorption of chiral compounds on QD surfaces. However, this area is still in its infancy and further detailed studies and theoretical work are necessary to fully understand all phenomena and develop new chiral photocatalysts that will be crucial for advancing of various chemistry and biopharmaceutical sectors.

Since chirality plays a crucial role in chemical recognition and interactions between chemical and biological species, it is essential to investigate and understand the interactions of chiral quantum nanostructures with various biological objects such as cell cultures, bacteria and viruses. In particular, the current COVID-19 pandemic has revealed an alarming lack of access to cost-effective, rapid diagnostic testing. It was recently demonstrated that chiral metallic nanostructures can be used to sense structural difference in biomolecules and detect multiple proteins for each genus of virus, both strain-specific surface proteins and the highly conserved proteins internals of the virion [152–154]. The uses of ligand induced chiroptically active quantum nanostructures and their combinations with chiral plasmonic nanostructures could open new opportunities in rapid detection of influenza viruses at early stages and result in new breakthroughs in medical diagnostics. In overall, this important research is expected to have significant impacts on further development of nanobiotechnology area including nanotoxicology, nanomedicine and applications of NPs to medical diagnostics, drug delivery and potential treatment of many diseases.

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References

- [1] N. Berova, L. Di Bari, and G. Pescitelli, "Application of electronic circular dichroism in configurational and conformational analysis of organic compounds," *Chem. Soc. Rev.*, vol. 36, no. 6, pp. 914–931, The Royal Society of Chemistry, 2007.
- [2] A. Ben-Moshe, B. M. Maoz, A. O. Govorov, and G. Markovich, "Chirality and chiroptical effects in inorganic nanocrystal systems with plasmon and exciton resonances," *Chem. Soc. Rev.*, vol. 42, no. 16, pp. 7028–7041, The Royal Society of Chemistry, 2013.
- [3] F. P. Milton, J. Govan, M. V. Mukhina, and Y. K. Gun'ko, "The chiral nano-world: chiroptically active quantum nanostructures," *Nanoscale Horiz.*, vol. 1, no. 1, pp. 14–26, The Royal Society of Chemistry, 2016.
- [4] W. Paiva-Marques, F. Reyes Gómez, O. N. Oliveira, and J. R. Mejía-Salazar, "Chiral plasmonics and their potential for point-of-care biosensing applications," *Sensors*, vol. 20, p. 944, 2020.
- [5] H. Okamoto, "Local optical activity of nano- to microscale materials and plasmons," *J. Mater. Chem. C*, vol. 7, 2019, <https://doi.org/10.1039/C9TC05141D>.
- [6] S. Yoo and Q.-H. Park, "Metamaterials and chiral sensing: a review of fundamentals and applications," *Nanophotonics*, vol. 8, pp. 249–261, 2019.
- [7] J. Mejía-Salazar and O. Oliveira, "Focus review – plasmonic biosensing," *Chem. Rev.*, vol. 118, no. 20, pp. 10617–10625, 2018.
- [8] C. Zhou, X. Duan, and N. Liu, "DNA-Nanotechnology-Enabled chiral plasmonics: from static to dynamic," *Acc. Chem. Res.*, vol. 50, no. 12, pp. 2906–2914, 2017.
- [9] Y. Y. Lee, R. M. Kim, S. W. Im, M. Balamurugan, K. T. Nam, "Plasmonic metamaterials for chiral sensing applications," *Nanoscale*, vol. 12, no. 1, pp. 58–66, The Royal Society of Chemistry, 2020.

- [10] J. Kumar, K. G. Thomas, and L. M. Liz-Marzán, “Nanoscale chirality in metal and semiconductor nanoparticles,” *Chem. Commun.*, vol. 52, no. 85, pp. 12555–12569, The Royal Society of Chemistry, 2016.
- [11] W. Ma, L. Xu, A. F. de Moura, et al., “Chiral inorganic nanostructures,” *Chem. Rev.*, vol. 117, no. 12, pp. 8041–8093, American Chemical Society, 2017.
- [12] A. Ben Moshe, G. Markovich, and Z. Tang Tang, “Optically active and chiral semiconductor nanocrystals,” in *Chiral Nanomaterials: Preparation, Properties and Applications*, 2017, pp. 85–98, <https://doi.org/10.1002/9783527682782.ch4>.
- [13] S. Jiang, M. Chekini, Z.-B. Qu, et al., “Chiral ceramic nanoparticles and peptide catalysis,” *J. Am. Chem. Soc.*, vol. 139, no. 39, pp. 13701–13712, American Chemical Society, 2017.
- [14] X. Gao, B. Han, X. Yang, and Z. Tang, “Perspective of chiral colloidal semiconductor nanocrystals: opportunity and challenge,” *J. Am. Chem. Soc.*, vol. 141, no. 35, pp. 13700–13707, American Chemical Society, 2019.
- [15] V. Anastasia and N. A. Kotov, “Inorganic nanostructures with strong chiroptical activity,” *CCS Chem.*, vol. 2, no. 3, pp. 583–604, Chinese Chemical Society, 2020.
- [16] M. J. Urban, C. Shen, X.-T. Kong, et al., “Chiral plasmonic nanostructures enabled by bottom-up approaches,” *Annu. Rev. Phys. Chem.*, vol. 70, no. 1, pp. 275–299, Annual Reviews, 2019.
- [17] A. Govorov, Y. K. Gun’ko, J. M. Slocik, V. A. Gérard, Z. Fan, and R. R. Naik, “Chiral nanoparticle assemblies: circular dichroism, plasmonic interactions, and exciton effects,” *J. Mater. Chem.*, vol. 21, pp. 16806–16818, 2011.
- [18] W. Ma, J. Mao, C. Hao, L. Xu, C. Xu, and H. Kuang, “Chiral semiconductor nanorod heterostructures with high photocatalysis activity,” *Appl. Catal. B Environ.*, vol. 245, pp. 691–697, Elsevier B.V., 2019.
- [19] S. Li, J. Liu, N. S. Ramesar, et al., “Single- and multi-component chiral supraparticles as modular enantioselective catalysts,” *Nat. Commun.*, vol. 10, no. 1, pp. 1–10, Nature Publishing Group, 2019.
- [20] E. Shah and H. P. Soni, “Inducing chirality on ZnS nanoparticles for asymmetric aldol condensation reactions,” *RSC Adv.*, vol. 3, no. 38, pp. 17453–17461, The Royal Society of Chemistry, 2013.
- [21] M. V. Mukhina, I. V. Korsakov, V. G. Maslov, et al., “Molecular recognition of biomolecules by chiral CdSe quantum dots,” *Sci. Rep.*, vol. 6, p. 24177, The Author(s), 2016.
- [22] A. Gogoi, N. Mazumder, S. Konwer, H. Ranawat, N.-T. Chen, and G.-Y. Zhuo, “Enantiomeric recognition and separation by chiral nanoparticles,” *Molecules*, vol. 24, no. 6, p. 1007, MDPI AG, 2019.
- [23] I. V. Martynenko, V. A. Kuznetsova, I. K. Litvinov, et al., “Enantioselective cellular uptake of chiral semiconductor nanocrystals,” *Nanotechnology*, vol. 27, no. 7, p. 075102, 2016.
- [24] C. Han and H. Li, “Chiral recognition of amino acids based on cyclodextrin-capped quantum dots,” *Small*, vol. 4, no. 9, pp. 1344–1350, John Wiley & Sons, Ltd, 2008.
- [25] Y. Li, Y. Zhou, H.-Y. Wang, et al., “Chirality of glutathione surface coating affects the cytotoxicity of quantum dots,” *Angew. Chem. Int. Ed.*, vol. 50, no. 26, pp. 5860–5864, John Wiley & Sons, Ltd, 2011.
- [26] V. A. Kuznetsova, A. K. Visheratina, A. Ryan, et al., “Enantioselective cytotoxicity of ZnS:Mn quantum dots in A549 cells,” *Chirality*, vol. 29, no. 8, pp. 403–408, United States, 2017.
- [27] U. Tohgha, K. K. Deol, A. G. Porter, et al., “Ligand induced circular dichroism and circularly polarized luminescence in CdSe quantum dots,” *ACS Nano*, vol. 7, no. 12, pp. 11094–11102, American Chemical Society, 2013.
- [28] J. Cheng, J. Hao, H. Liu, et al., “Optically active CdSe-dot/CdS-rod nanocrystals with induced chirality and circularly polarized luminescence,” *ACS Nano*, vol. 12, no. 6, pp. 5341–5350, American Chemical Society, 2018.
- [29] C. Li, X. Jin, T. Zhao, J. Zhou, and P. Duan, “Optically active quantum dots with induced circularly polarized luminescence in amphiphilic peptide dendron hydrogel,” *Nanoscale Adv.*, vol. 1, no. 2, pp. 508–512, Royal Society of Chemistry, 2019.
- [30] I. Žutić, J. Fabian, and S. Das Sarma, “Spintronics: fundamentals and applications,” *Rev. Mod. Phys.*, vol. 76, no. 2, pp. 323–410, American Physical Society, 2004.
- [31] Y. Liu, S. Zhang, J. He, Z. M. Wang, and Z. Liu, “Recent progress in the fabrication, properties, and devices of heterostructures based on 2D materials,” *Nano-Micro Lett.*, vol. 11, no. 1, p. 3, SpringerOpen, 2019.
- [32] U. Resch-Genger, M. Grabolle, S. Cavaliere-Jaricot, R. Nitschke, and T. Nann, “Quantum dots versus organic dyes as fluorescent labels,” *Nat. Methods*, vol. 5, p. 763, Nature Publishing Group, 2008.
- [33] P. Linkov, V. Krivenkov, I. Nabiev, and P. Samokhvalov, “High quantum yield CdSe/ZnS/CdS/ZnS multishell quantum dots for biosensing and optoelectronic applications,” *Mater. Today Proc.*, vol. 3, no. 2, pp. 104–108, 2016.
- [34] Y. Volkov, “Quantum dots in nanomedicine: recent trends, advances and unresolved issues,” *Biochem. Biophys. Res. Commun.*, vol. 468, no. 3, pp. 419–427, 2015.
- [35] D. R. Baker and P. V. Kamat, “Tuning the emission of CdSe quantum dots by controlled trap enhancement,” *Langmuir*, vol. 26, no. 13, pp. 11272–11276, American Chemical Society, 2010.
- [36] I. L. Medintz, H. T. Uyeda, E. R. Goldman, and H. Mattoussi, “Quantum dot bioconjugates for imaging, labelling and sensing,” *Nat. Mater.*, vol. 4, no. 6, pp. 435–446, 2005.
- [37] A. Ben-Moshe, A. O. Govorov, and G. Markovich, “Enantioselective synthesis of intrinsically chiral mercury sulfide nanocrystals,” *Angew. Chem. Int. Ed.*, vol. 52, no. 4, pp. 1275–1279, John Wiley & Sons, Ltd, 2013.
- [38] F. Yang, G. Gao, J. Wang, et al., “Chiral β -HgS quantum dots: aqueous synthesis, optical properties and cytocompatibility,” *J. Colloid Interface Sci.*, vol. 537, pp. 422–430, 2019.
- [39] J. Kuno, K. Miyake, S. Katao, T. Kawai, and T. Nakashima, “Enhanced enantioselectivity in the synthesis of mercury sulfide nanoparticles through ostwald ripening,” *Chem. Mater.*, vol. 32, no. 19, pp. 8412–8419, American Chemical Society, 2020.
- [40] J. Yeom, B. Yeom, H. Chan, et al., “Chiral templating of self-assembling nanostructures by circularly polarized light,” *Nat. Mater.*, vol. 14, no. 1, p. 66, Nature Publishing Group, Department of Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, USA, 2014.
- [41] A. S. Baimuratov, T. P. Pereziabova, N. V. Tepliakov, et al., “Electric-field-enhanced circular dichroism of helical semiconductor nanoribbons,” *Opt. Lett.*, vol. 44, no. 3, pp. 499–502, OSA, 2019.
- [42] A. S. Baimuratov, T. P. Pereziabova, W. Zhu, et al., “Optical anisotropy of topologically distorted semiconductor

- nanocrystals,” *Nano Lett.*, vol. 17, no. 9, pp. 5514–5520, American Chemical Society, 2017.
- [43] A. S. Baimuratov, T. P. Pereziabova, M. Y. Leonov et al., “Optically active semiconductor nanosprings for tunable chiral nanophotonics,” *ACS Nano*, vol. 12, no. 6, pp. 6203–6209, American Chemical Society, 2018.
- [44] C. Bouet, B. Mahler, B. Nadal, et al., “Two-dimensional growth of CdSe nanocrystals, from nanoplatelets to nanosheets,” *Chem. Mater.*, vol. 25, no. 4, pp. 639–645, American Chemical Society, 2013.
- [45] A. S. Baimuratov, Y. K. Gun’ko, A. G. Shalkovskiy, A. V. Baranov, A. V. Fedorov, and I. D. Rukhlenko, “Optical activity of chiral nanoscrolls,” *Adv. Opt. Mater.*, vol. 5, no. 16, p. 1600982, John Wiley & Sons, Ltd, 2017.
- [46] N. V. Teplakov, A. S. Baimuratov, I. A. Vovk, et al., “Chiral optical properties of tapered semiconductor nanoscrolls,” *ACS Nano*, vol. 11, no. 7, pp. 7508–7515, American Chemical Society, 2017.
- [47] J. García-Guirado, M. Svedendahl, J. Puigdollers, R. Quidant, “Enantiomer-selective molecular sensing using racemic nanoplasmonic arrays,” *Nano Lett.*, vol. 18, no. 10, pp. 6279–6285, American Chemical Society, 2018.
- [48] N. V. Teplakov, I. A. Vovk, A. S. Baimuratov, et al., “Optical activity of semiconductor gammadions beyond planar chirality,” *J. Phys. Chem. Lett.*, vol. 9, no. 11, pp. 2941–2945, American Chemical Society, 2018.
- [49] N. Teplakov, A. S. Baimuratov, A. V. Baranov, A. V. Fedorov, and I. D. Rukhlenko, “Optical activity of chirally distorted nanocrystals,” *J. Appl. Phys.*, vol. 119, p. 194302, 2016.
- [50] I. D. Rukhlenko, A. S. Baimuratov, N. V. Teplakov, A. V. Baranov, and A. V. Fedorov, “Shape-induced optical activity of chiral nanocrystals,” *Opt. Lett.*, vol. 41, no. 11, pp. 2438–2441, OSA, 2016.
- [51] S. Mokashi-Punekar, Y. Zhou, S. C. Brooks, and N. L. Rosi, “Construction of chiral, helical nanoparticle superstructures: progress and prospects,” *Adv. Mater.*, vol. 32, no. 41, p. 1905975, John Wiley & Sons, Ltd., 2019.
- [52] A. S. Baimuratov, Y. K. Gun’ko, A. V. Baranov, A. V. Fedorov, and I. D. Rukhlenko, “Chiral quantum supercrystals with total dissymmetry of optical response,” *Sci. Rep.*, vol. 6, no. 1, p. 23321, 2016.
- [53] A. I. Shlykov, A. S. Baimuratov, A. V. Baranov, A. V. Fedorov, and I. D. Rukhlenko, “Optically active quantum-dot molecules,” *Opt. Express*, vol. 25, no. 4, pp. 3811–3825, OSA, 2017.
- [54] N. V. Teplakov, I. A. Vovk, A. I. Shlykov, et al., “Optical activity and circular dichroism of perovskite quantum-dot molecules,” *J. Phys. Chem. C*, vol. 123, no. 4, pp. 2658–2664, American Chemical Society, 2019.
- [55] M. P. Moloney, Y. K. Gun’ko, and J. M. Kelly, “Chiral highly luminescent CdS quantum dots,” *Chem. Commun.*, vol. 7345, no. 38, pp. 3900–3902, The Royal Society of Chemistry, 2007.
- [56] A. S. Baimuratov, I. D. Rukhlenko, Y. K. Gun’ko, A. V. Baranov, and A. V. Fedorov, “Dislocation-induced chirality of semiconductor nanocrystals,” *Nano Lett.*, vol. 15, no. 3, pp. 1710–1715, American Chemical Society, 2015.
- [57] A. S. Baimuratov, I. D. Rukhlenko, R. E. Noskov, et al., “Giant optical activity of quantum dots, rods and disks with screw dislocations,” *Sci. Rep.*, vol. 5, no. 1, p. 14712, 2015.
- [58] N. V. Teplakov, A. S. Baimuratov, Y. K. Gun’ko, A. V. Baranov, A. V. Fedorov, and I. D. Rukhlenko, “Engineering optical activity of semiconductor nanocrystals via ion doping,” *Nanophotonics*, vol. 5, no. 4, pp. 573–578, De Gruyter, Berlin, Boston, 2016.
- [59] M. V. Mukhina, V. G. Maslov, A. V. Baranov, et al., “Intrinsic chirality of CdSe/ZnS quantum dots and quantum rods,” *Nano Lett.*, vol. 15, no. 5, pp. 2844–2851, American Chemical Society, 2015.
- [60] M. P. Moloney, J. Govan, A. Loudon, M. Mukhina, and Y. K. Gun’ko, “Preparation of chiral quantum dots,” *Nat. Prot.*, vol. 10, p. 558, Nature Publishing Group, a division of Macmillan Publishers Limited. All Rights Reserved, 2015.
- [61] U. Tohgha, K. Varga, and M. Balaz, “Achiral CdSe quantum dots exhibit optical activity in the visible region upon post-synthetic ligand exchange with d- or l-cysteine,” *Chem. Commun.*, vol. 49, no. 18, pp. 1844–1846, The Royal Society of Chemistry, 2013.
- [62] A. Ben-Moshe, A. Teitelboim, D. Oron, and G. Markovich, “Probing the interaction of quantum dots with chiral capping molecules using circular dichroism spectroscopy,” *Nano Lett.*, vol. 16, no. 12, pp. 7467–7473, American Chemical Society, 2016.
- [63] A. S. Baimuratov, N. V. Teplakov, Y. K. Gun’ko, A. V. Baranov, A. V. Fedorov, and I. D. Rukhlenko, “Mixing of quantum states: a new route to creating optical activity,” *Sci. Rep.*, vol. 6, no. 1, p. 5, 2016.
- [64] Z. Wang, Y. Wang, G. Adamo, J. Teng, and H. Sun, “Induced optical chirality and circularly polarized emission from achiral CdSe/ZnS quantum dots via resonantly coupling with plasmonic chiral metasurfaces,” *Laser Photon. Rev.*, vol. 13, no. 3, p. 1800276, John Wiley & Sons, Ltd, 2019.
- [65] S. A. Gallagher, M. P. Moloney, M. Wojdyla, S. J. Quinn, J. M. Kelly, and Y. K. Gun’ko, “Synthesis and spectroscopic studies of chiral CdSe quantum dots,” *J. Mater. Chem.*, vol. 20, no. 38, pp. 8350–8355, The Royal Society of Chemistry, 2010.
- [66] M. Moloney, S. Gallagher, and Y. Gun’ko, “Chiral CdTe quantum dots,” in *MRS proceedings*, vol. 1241, 2009, <https://doi.org/10.1557/PROC-1241-XX02-10>.
- [67] J. E. Govan, E. Jan, A. Querejeta, N. A. Kotov, and Y. K. Gun’ko, “Chiral luminescent CdS nano-tetrapods,” *Chem. Commun.*, vol. 46, no. 33, pp. 6072–6074, The Royal Society of Chemistry, 2010.
- [68] I. V. Martynenko, A. S. Baimuratov, V. A. Osipova, et al., “Excitation energy dependence of the photoluminescence quantum yield of core/shell CdSe/CdS quantum dots and correlation with circular dichroism,” *Chem. Mater.*, vol. 30, no. 2, pp. 465–471, 2018.
- [69] F. Purcell-Milton, A. K. Visheratina, V. A. Kuznetsova, A. Ryan, A. O. Orlova, and Y. K. Gun’ko, “Impact of shell thickness on photoluminescence and optical activity in chiral CdSe/CdS core/shell quantum dots,” *ACS Nano*, vol. 11, no. 9, pp. 9207–9214, United States, 2017.
- [70] J. K. Choi, B. E. Haynie, U. Tohgha, et al., “Chirality inversion of CdSe and CdS quantum dots without changing the stereochemistry of the capping ligand,” *ACS Nano*, vol. 10, no. 3, pp. 3809–3815, American Chemical Society, 2016.
- [71] K. Varga, S. Tannir, B. E. Haynie, et al., “CdSe quantum dots functionalized with chiral, thiol-free carboxylic acids: unraveling structural requirements for ligand-induced chirality,” *ACS Nano*, vol. 11, no. 10, pp. 9846–9853, American Chemical Society, 2017.
- [72] M. Puri and V. E. Ferry, “Circular dichroism of CdSe nanocrystals bound by chiral carboxylic acids,” *ACS Nano*, vol. 11, no. 12, pp. 12240–12246, American Chemical Society, 2017.

- [73] G. Li, X. Fei, H. Liu, et al., “Fluorescence and optical activity of chiral CdTe quantum dots in their interaction with amino acids,” *ACS Nano*, vol. 14, no. 4, pp. 4196–4205, American Chemical Society, 2020.
- [74] G. Yang, M. Kazes, and D. Oron, “Chiral 2D colloidal semiconductor quantum wells,” *Adv. Funct. Mater.*, vol. 28, no. 28, p. 1802012, John Wiley & Sons, Ltd, 2018.
- [75] A. K. Vishneratina, A. O. Orlova, F. Purcell-Milton, et al., “Influence of CdSe and CdSe/CdS nanocrystals on the optical activity of chiral organic molecules,” *J. Mater. Chem. C*, vol. 6, no. 7, 2018, <https://doi.org/10.1039/c7tc03457a>.
- [76] X. Gao, X. Zhang, K. Deng, et al., “Excitonic circular dichroism of chiral quantum rods,” *J. Am. Chem. Soc.*, vol. 139, no. 25, pp. 8734–8739, American Chemical Society, 2017.
- [77] X. Gao, X. Zhang, L. Zhao, et al., “Distinct excitonic circular dichroism between wurtzite and zincblende CdSe nanoplatelets,” *Nano Lett.*, vol. 18, no. 11, pp. 6665–6671, American Chemical Society, 2018.
- [78] S. D. Elliott, M. P. Moloney, and Y. K. Gun’ko, “Chiral shells and achiral cores in CdS quantum dots,” *Nano Lett.*, vol. 8, no. 8, pp. 2452–2457, American Chemical Society, 2008.
- [79] T. Nakashima, Y. Kobayashi, and T. Kawai, “Optical activity and chiral memory of thiol-capped CdTe nanocrystals,” *J. Am. Chem. Soc.*, vol. 131, no. 30, pp. 10342–10343, American Chemical Society, 2009.
- [80] F. Safin, E. Kolesova, V. Maslov, Y. Gun’ko, A. Baranov, and A. Fedorov, “Photochemically induced circular dichroism of semiconductor quantum dots,” *J. Phys. Chem. C*, vol. 123, no. 32, pp. 19979–19983, American Chemical Society, 2019.
- [81] F. M. Safin, V. G. Maslov, A. Y. Dubavik, E. P. Kolesova, A. V. Baranov, and A. V. Fedorov, “Photochemically induced circular dichroism of semiconductor nanocrystals,” *Optic Spectrosc.*, vol. 128, no. 8, pp. 1230–1235, Ioffe Institute Russian Academy of Sciences, 2020.
- [82] A. Ben Moshe, D. Szwarcman, and G. Markovich, “Size dependence of chiroptical activity in colloidal quantum dots,” *ACS Nano*, vol. 5, no. 11, pp. 9034–9043, American Chemical Society, 2011.
- [83] P. Reiss, M. Protière, and L. Li, “Core/shell semiconductor nanocrystals,” *Small*, vol. 5, no. 2, pp. 154–168, John Wiley & Sons, Ltd, 2009.
- [84] V. A. Kuznetsova, E. Mates-Torres, N. Prochukhan, et al., “Effect of chiral ligand concentration and binding mode on chiroptical activity of CdSe/CdS quantum dots,” *ACS Nano*, vol. 13, no. 11, pp. 13560–13572, American Chemical Society, 2019.
- [85] D. V. Talapin, J. H. Nelson, E. V. Shevchenko, S. Aloni, B. Sadler, A. P. Alivisatos, “Seeded growth of highly luminescent CdSe/CdS nanoheterostructures with rod and tetrapod morphologies,” *Nano Lett.*, vol. 7, no. 10, pp. 2951–2959, American Chemical Society, 2007.
- [86] J. I. Wong, N. Mishra, G. Xing, et al., “Dual wavelength electroluminescence from CdSe/CdS tetrapods,” *ACS Nano*, vol. 8, no. 3, pp. 2873–2879, American Chemical Society, 2014.
- [87] T. K. Kormilina, S. A. Cherevko, A. V. Fedorov, and A. V. Baranov, “Cadmium chalcogenide nano-heteroplatelets: creating advanced nanostructured materials by shell growth, substitution, and attachment,” *Small*, vol. 13, no. 41, p. 1702300, John Wiley & Sons, Ltd, 2017.
- [88] A. O. Govorov, Z. Fan, P. Hernandez, J. M. Slocik, and R. R. Naik, “Theory of circular dichroism of nanomaterials comprising chiral molecules and nanocrystals: plasmon enhancement, dipole interactions, and dielectric effects,” *Nano Lett.*, vol. 10, no. 4, pp. 1374–1382, American Chemical Society, 2010.
- [89] A. O. Govorov, “Plasmon-induced circular dichroism of a chiral molecule in the vicinity of metal nanocrystals. Application to various geometries,” *J. Phys. Chem. C*, vol. 115, no. 16, pp. 7914–7923, American Chemical Society, 2011.
- [90] A. O. Govorov and Z. Fan, “Theory of chiral plasmonic nanostructures comprising metal nanocrystals and chiral molecular media,” *ChemPhysChem*, vol. 13, no. 10, pp. 2551–2560, John Wiley & Sons, Ltd, 2012.
- [91] E. V. Kundelev, A. O. Orlova, V. G. Maslov, A. V. Baranov, and A. V. Fedorov, “Circular dichroism spectroscopy of complexes of semiconductor quantum dots with chlorin e6,” in *Proc. SPIE*, 2016, p. 9884.
- [92] L. Xiao, T. An, L. Wang, X. Xu, and H. Sun, “Novel properties and applications of chiral inorganic nanostructures,” *Nano Today*, vol. 30, p. 100824, Elsevier B.V., 2020.
- [93] A. Lesiak, K. Drzozga, J. Cabaj, M. Bański, K. Malecha, and A. Podchorodecki, “Optical sensors based on II–VI quantum dots,” *Nanomaterials*, vol. 9, no. 2, p. 192, MDPI AG, 2019.
- [94] M. Chern, J. C. Kays, S. Bhuckory, and A. M. Dennis, “Sensing with photoluminescent semiconductor quantum dots,” *Methods Appl. Fluoresc.*, vol. 7, no. 1, p. 12005, IOP Publishing, 2019.
- [95] S. Silvi and A. Credi, “Luminescent sensors based on quantum dot-molecule conjugates,” *Chem. Soc. Rev.*, vol. 44, no. 13, pp. 4275–4289, Royal Society of Chemistry, 2015.
- [96] P. Sianglam, S. Kulchat, T. Tuntulani, W. Ngeontae, “A circular dichroism sensor for selective detection of Cd²⁺ and S²⁻ based on the in-situ generation of chiral CdS quantum dots,” *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, vol. 183, pp. 408–416, Elsevier B.V., 2017.
- [97] W. Tedsana, T. Tuntulani, and W. Ngeontae, “A circular dichroism sensor for Ni²⁺ and Co²⁺ based on L-cysteine capped cadmium sulfide quantum dots,” *Anal. Chim. Acta*, vol. 867, pp. 1–8, Elsevier, 2015.
- [98] X. Wang, J. Hao, J. Cheng, et al., “Chiral CdSe nanoplatelets as an ultrasensitive probe for lead ion sensing,” *Nanoscale*, vol. 11, no. 19, pp. 9327–9334, Royal Society of Chemistry, 2019.
- [99] K. Ngamdee, K. Chaiendoo, C. Saiyasombat, et al., “Highly selective circular dichroism sensor based on D-penicillamine/cysteamine-cadmium sulfide quantum dots for copper (II) ion detection,” *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, vol. 211, pp. 313–321, Elsevier B.V., 2019.
- [100] Y. Wei, H. Li, H. Hao, Y. Chen, C. Dong, and G. Wang, “β-Cyclodextrin functionalized Mn-doped ZnS quantum dots for the chiral sensing of tryptophan enantiomers,” *Polym. Chem.*, vol. 6, no. 4, pp. 591–598, Royal Society of Chemistry, 2015.
- [101] G. M. Durán, C. Abellán, A. M. Contento, and Á. Ríos, “Discrimination of penicillamine enantiomers using β-cyclodextrin modified CdSe/ZnS quantum dots,” *Microchim. Acta*, vol. 184, no. 3, pp. 815–824, Springer-Verlag Wien, 2017.
- [102] J. Zhou, Y. Liu, Z. Zhang, et al., “Cyclodextrin-clicked silica/CdTe fluorescent nanoparticles for enantioselective recognition of amino acids,” *Nanoscale*, vol. 8, no. 10, pp. 5621–5626, Royal Society of Chemistry, 2016.

- [103] Y. Guo, X. Zeng, H. Yuan, et al., "Chiral recognition of phenylglycinol enantiomers based on *N*-acetyl-L-cysteine capped CdTe quantum dots in the presence of Ag⁺," *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, vol. 183, pp. 23–29, Elsevier B.V., 2017.
- [104] F. Gao, S. Ma, X. Xiao, Y. Hu, D. Zhao, and Z. He, "Sensing tyrosine enantiomers by using chiral CdSe/CdS quantum dots capped with *N*-acetyl-L-cysteine," *Talanta*, vol. 163, pp. 102–110, Elsevier B.V., 2017.
- [105] T. Delgado-Pérez, L. M. Bouchet, M. de la Guardia, R. E. Galian, and J. Pérez-Prieto, "Sensing chiral drugs by using CdSe/ZnS nanoparticles capped with *N*-acetyl-L-cysteine methyl ester," *Chem. Eur. J.*, vol. 19, no. 33, pp. 11068–11076, John Wiley & Sons, Ltd, 2013.
- [106] S. Zare and J. Tashkhourian, "Ultrasound-assisted synthesis of chiral cysteine-capped CdSe quantum dots for fluorometric differentiation and quantitation of tryptophan enantiomers," *Microchim. Acta*, vol. 187, no. 1, pp. 1–10, Springer, 2020.
- [107] C. Carrillo-Carrión, S. Cardenas, B. M. Simonet, and M. Valcarcel, "Selective quantification of carnitine enantiomers using chiral cysteine-capped CdSe(ZnS) quantum dots," *Anal. Chem.*, vol. 81, no. 12, pp. 4730–4733, American Chemical Society, 2009.
- [108] H. Fu, O. Hu, Y. Fan, et al., "Rational design of an 'on-off-on' fluorescent assay for chiral amino acids based on quantum dots and nanoporphyrim," *Sens. Actuator B Chem.*, vol. 287, pp. 1–8, Elsevier B.V., 2019.
- [109] L. Song, S. Wang, N. A. Kotov, Y. Xia, "Nonexclusive fluorescent sensing for L/D enantiomers enabled by dynamic nanoparticle-nanorod assemblies," *Anal. Chem.*, vol. 84, no. 17, pp. 7330–7335, 2012.
- [110] S. R. Ahmed and S. Neethirajan, "Chiral MoS₂ quantum dots: dual-mode detection approaches for avian influenza viruses," *Glob. Challenges*, vol. 2, no. 4, p. 1700071, Wiley, 2018.
- [111] K. Ngamdee and W. Ngeontae, "Circular dichroism glucose biosensor based on chiral cadmium sulfide quantum dots," *Sens. Actuator B Chem.*, vol. 274, pp. 402–411, Elsevier B.V., 2018.
- [112] M. Khorasaninejad, A. Ambrosio, P. Kanhaiya, and F. Capasso, "Broadband and chiral binary dielectric meta-holograms," *Sci. Adv.*, vol. 2, no. 5, p. e1501258, American Association for the Advancement of Science, 2016.
- [113] P. Boher, T. Leroux, T. Bignon, and V. Collomb-Patton, "Multispectral polarization viewing angle analysis of circular polarized stereoscopic 3D displays," in *Stereoscopic Displays and Applications XXI*, A. J. Woods, N. S. Holliman, and N. A. Dodgson, Eds, SPIE, 2010, vol. 7524, p. 75240R.
- [114] T. Tanabe, T. Sato, K. Fukaishi, and Y. Kakubari, "66.4: invited Paper: circularly polarized (CPL) 3D monitors attract attention again for medical applications," *SID Symp. Dig. Tech. Pap.*, vol. 46, no. 1, pp. 987–990, Wiley-Blackwell, 2015.
- [115] T. Kawasaki, M. Sato, S. Ishiguro, et al., "Enantioselective synthesis of near enantiopure compound by asymmetric autocatalysis triggered by asymmetric photolysis with circularly polarized light," *J. Am. Chem. Soc.*, vol. 127, no. 10, pp. 3274–3275, American Chemical Society, 2005.
- [116] P. K. Hashim and N. Tamaoki, "Enantioselective photochromism under circularly polarized light," *ChemPhotoChem*, vol. 3, no. 6, pp. 347–355, Wiley, 2019.
- [117] G. Longhi, E. Castiglioni, J. Koshoubu, G. Mazzeo, and S. Abbate, "Circularly polarized luminescence: a review of experimental and theoretical aspects," *Chirality*, vol. 28, no. 10, pp. 696–707, John Wiley and Sons Inc, 2016.
- [118] M. V. Mukhina, V. G. Maslov, I. V. Korsakov, et al., "Optically active II–VI semiconductor nanocrystals via chiral phase transfer," *MRS Proc.*, vol. 1793, pp. 27–33, Cambridge University Press, 2015.
- [119] M. Naito, K. Iwahori, A. Miura, M. Yamane, and I. Yamashita, "Circularly polarized luminescent CdS quantum dots prepared in a protein nanocage," *Angew. Chem. Int. Ed.*, vol. 49, no. 39, pp. 7006–7009, John Wiley & Sons, Ltd, 2010.
- [120] M. Xu, C. Ma, J. Zhou, et al., "Assembling semiconductor quantum dots in hierarchical photonic cellulose nanocrystal films: circularly polarized luminescent nanomaterials as optical coding labels," *J. Mater. Chem. C*, vol. 7, no. 44, pp. 13794–13802, Royal Society of Chemistry, 2019.
- [121] Y. Shi, Z. Zhou, X. Miao, et al., "Circularly polarized luminescence from semiconductor quantum rods templated by self-assembled cellulose nanocrystals," *J. Mater. Chem. C*, vol. 8, no. 3, pp. 1048–1053, Royal Society of Chemistry, 2020.
- [122] C. Hao, Y. Gao, D. Wu, et al., "Tailoring chiroptical activity of iron disulfide quantum dot hydrogels with circularly polarized light," *Adv. Mater.*, vol. 31, no. 36, p. 1903200, Wiley-VCH Verlag, 2019.
- [123] A. Bobrovsky, K. Mochalov, V. Oleinikov, et al., "Optically and electrically controlled circularly polarized emission from cholesteric liquid crystal materials doped with semiconductor quantum dots," *Adv. Mater.*, vol. 24, no. 46, pp. 6216–6222, John Wiley & Sons, Ltd, 2012.
- [124] N. Berova, P. L. Polavarapu, K. Nakanishi, and R. W. Woody, "Comprehensive chiroptical spectroscopy," in *Comprehensive Chiroptical Spectroscopy*, N. Berova, et al., Eds., Hoboken, NJ, USA, John Wiley & Sons, Inc, 2011, vol. 1, <https://doi.org/10.1002/9781118120187>.
- [125] F. Zinna and L. Di Bari, "Lanthanide circularly polarized luminescence: bases and applications," *Chirality*, vol. 27, no. 1, pp. 1–13, John Wiley and Sons Inc, 2015.
- [126] R. Naaman and D. H. Waldeck, "Chiral-induced spin selectivity effect," *J. Phys. Chem. Lett.*, vol. 3, no. 16, pp. 2178–2187, American Chemical Society, 2012.
- [127] R. Naaman, Y. Paltiel, and D. H. Waldeck, "Chiral molecules and the electron spin," *Nature Reviews Chemistry*, vol. 3, no. 4, pp. 250–260, Nature Publishing Group, 2019.
- [128] G. Koplovitz, G. Leituss, S. Ghosh, et al., "Single domain 10 nm ferromagnetism imprinted on superparamagnetic nanoparticles using chiral molecules," *Small*, vol. 15, no. 1, p. 1804557, Wiley-VCH Verlag, 2019.
- [129] O. Ben Dor, N. Morali, S. Yochelis, L. T. Baczewski, and Y. Paltiel, "Local light-induced magnetization using nanodots and chiral molecules," *Nano Lett.*, vol. 14, no. 11, pp. 6042–6049, American Chemical Society, 2014.
- [130] O. Ben Dor, S. Yochelis, H. Ohldag, and Y. Paltiel, "Optical chiral induced spin selectivity XMCD study," *Chimia (Aarau)*, vol. 72, no. 6, pp. 379–383, Swiss Chemical Society, 2018.
- [131] P. C. Mondal, P. Roy, D. Kim, E. E. Fullerton, H. Cohen, and R. Naaman, "Photospintronics: magnetic field-controlled photoemission and light-controlled spin transport in hybrid chiral oligopeptide-nanoparticle structures," *Nano Lett.*, vol. 16, no. 4, pp. 2806–2811, American Chemical Society, 2016.

- [132] B. P. Bloom, V. Kiran, V. Varade, R. Naaman, and D. H. Waldeck, "Spin selective charge transport through cysteine capped CdSe quantum dots," *Nano Lett.*, vol. 16, no. 7, pp. 4583–4589, American Chemical Society, 2016.
- [133] H. T. Fridman, J. Dehnell, S. Yochelis, E. Lifshitz, and Y. Paltiel, "Spin-exciton delocalization enhancement in multilayer chiral linker/quantum dot structures," *J. Phys. Chem. Lett.*, vol. 10, no. 14, pp. 3858–3862, American Chemical Society, 2019.
- [134] T. Cao, G. Wang, W. Han, et al., "Valley-selective circular dichroism of monolayer molybdenum disulphide," *Nat. Commun.*, vol. 3, no. 1, pp. 1–5, Nature Publishing Group, 2012.
- [135] G. Kioseoglou, A. T. Hanbicki, M. Currie, A. L. Friedman, D. Gunlycke, and B. T. Jonker, "Valley polarization and intervalley scattering in monolayer MoS₂," *Appl. Phys. Lett.*, vol. 101, no. 22, p. 221907, American Institute of PhysicsAIP, 2012.
- [136] H. Zeng, J. Dai, W. Yao, D. Xiao, X. Cui, "Valley polarization in MoS₂ monolayers by optical pumping," *Nat. Nanotechnol.*, vol. 7, no. 8, pp. 490–493, Nature Publishing Group, 2012.
- [137] L. Zhang and Q. Niu, "Chiral phonons at high-symmetry points in monolayer hexagonal lattices," *Phys. Rev. Lett.*, vol. 115, no. 11, p. 115502, American Physical Society, 2015.
- [138] J. R. Schaibley, H. Yu, G. Clark, et al., "Valleytronics in 2D materials," *Nat. Rev. Mater.*, vol. 1, no. 11, pp. 1–15, Nature Publishing Group, 2016.
- [139] H. Kisch, "Semiconductor photocatalysis for chemoselective radical coupling reactions," *Acc. Chem. Res.*, vol. 50, no. 4, pp. 1002–1010, American Chemical Society, 2017.
- [140] S. Kohtani, A. Kawashima, and H. Miyabe, "Stereoselective organic reactions in heterogeneous semiconductor photocatalysis," *Front. Chem.*, vol. 7, p. 630, Frontiers Media S.A, 2019.
- [141] W. Mtangi, V. Kiran, C. Fontanesi, and R. Naaman, "Role of the electron spin polarization in water splitting," *J. Phys. Chem. Lett.*, vol. 6, no. 24, pp. 4916–4922, American Chemical Society, 2015.
- [142] W. Zhang, K. Banerjee-Ghosh, F. Tassinari, and R. Naaman, Enhanced electrochemical water splitting with chiral molecule-coated Fe₃O₄ nanoparticles. *ACS Energy Lett.*, vol. 3, no. 10, pp. 2308–2313, American Chemical Society, 2018.
- [143] Y. Guo, L. Wang, L. Yang, J. Zhang, L. Jiang, and X. Ma, "Optical and photocatalytic properties of arginine-stabilized cadmium sulfide quantum dots," *Mater. Lett.*, vol. 65, no. 3, pp. 486–489, Elsevier B.V, 2011.
- [144] H. Zhang, H. He, X. Jiang, Z. Xia, and W. Wei, "Preparation and characterization of chiral transition-metal dichalcogenide quantum dots and their enantioselective catalysis," *ACS Appl. Mater. Interfaces*, vol. 10, no. 36, pp. 30680–30688, American Chemical Society, 2018.
- [145] G. Blaschke, H. P. Kraft, K. Fickentscher, and F. Köhler, "Chromatographic separation of racemic thalidomide and teratogenic activity of its enantiomers (author's transl)," *Arzneimittelforschung*, vol. 29, no. 10, pp. 1640–1642, Germany, 1979.
- [146] H. Caner, E. Groner, L. Levy, I. Agranat, "Trends in the development of chiral drugs," *Drug Discov. Today*, vol. 9, no. 3, pp. 105–110, 2004.
- [147] S. Qu, F. Sun, Z. Qiao, J. Li, and L. Shang, "In situ investigation on the protein corona formation of quantum dots by using fluorescence resonance energy transfer," *Small*, vol. 16, no. 21, p. 1907633, John Wiley & Sons, Ltd, 2020.
- [148] Q. Xin, Q. Liu, L. Geng, Q. Fang, J. R. Gong, "Chiral nanoparticle as a new efficient antimicrobial nanoagent," *Adv. Healthc. Mater.*, vol. 6, no. 4, p. 1601011, 2017.
- [149] C. Hao, R. Gao, Y. Li, et al., "Chiral semiconductor nanoparticles for protein catalysis and profiling," *Angew. Chem. Int. Ed.*, vol. 58, no. 22, pp. 7371–7374, John Wiley & Sons, Ltd, 2019.
- [150] M. Sun, L. Xu, A. Qu, et al., "Site-selective photoinduced cleavage and profiling of DNA by chiral semiconductor nanoparticles," *Nat. Chem.*, vol. 10, no. 8, pp. 821–830, Springer US, 2018.
- [151] S. R. Ahmed, S. W. Kang, S. Oh, J. Lee, and S. Neethirajan, "Chiral zirconium quantum dots: a new class of nanocrystals for optical detection of coronavirus," *Heliyon*, vol. 4, no. 8, p. e00766, 2018.
- [152] M. Rodier, C. Keijzer, J. Milner, et al., "Biomacromolecular charge chirality detected using chiral plasmonic nanostructures," *Nanoscale Horiz.*, vol. 5, no. 2, pp. 336–344, The Royal Society of Chemistry, 2020.
- [153] M. Rodier, C. Keijzer, J. Milner, et al., "Probing specificity of protein–protein interactions with chiral plasmonic nanostructures," *J. Phys. Chem. Lett.*, vol. 10, no. 20, pp. 6105–6111, American Chemical Society, 2019.
- [154] C. Kelly, R. Tullius, A. J. Laphorn, et al., "Chiral plasmonic fields probe structural order of biointerfaces," *J. Am. Chem. Soc.*, vol. 140, no. 27, pp. 8509–8517, American Chemical Society, 2018.