

## Chirality Induction to CdSe Nanocrystals Self-Organized on Silica Nanohelices: Tuning Chiroptical Properties

Peizhao Liu, Yann Battie, Marion Decossas, Sisareuth Tan, Emilie Pouget,

Yutaka Okazaki, Takashi Sagawa, Reiko Oda

### ▶ To cite this version:

Peizhao Liu, Yann Battie, Marion Decossas, Sisareuth Tan, Emilie Pouget, et al.. Chirality Induction to CdSe Nanocrystals Self-Organized on Silica Nanohelices: Tuning Chiroptical Properties. ACS Nano, 2021, 15 (10), pp.16411-16421. 10.1021/acsnano.1c05819 . hal-03859924

## HAL Id: hal-03859924 https://hal.science/hal-03859924

Submitted on 18 Nov 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Chirality Induction to CdSe Nanocrystals Self-Organized on Silica Nanohelices: Tuning Chiroptical Properties

Peizhao Liu, Yann Battie, Marion Decossas, Sisareuth Tan, Emilie Pouget, Yutaka Okazaki, Takashi Sagawa,\* and Reiko Oda\*

**ABSTRACT:** CdSe nanocrystals (NCs) were grafted on chiral silica nanoribbons, and the mechanism of resulting chirality induction was investigated. Because of their chiral organization, these NCs show optically active properties that depend strongly on their grafting densities and sizes of the NCs. The effect of the morphology of the chiral silica templates between helical (cylindrical curvature) vs twisted (saddle like curvature) ribbons was investigated. The g-factor of NCs-silica helical ribbons is larger than that of the NCs-silica twisted ribbons. Finally, rod-like NCs (QR) with different lengths were grafted on the twisted silica ribbons. Interestingly, their grafting direction with respect to the helix surface changed from side-grafting for short QR to tip-grafting for long rods and the corresponding CD spectra switched signs.



KEYWORDS: optically active nanostructures, chiral silica ribbons, CdSe quantum dots, CdSe/CdS quantum rods, chiral organization

emiconductor nanocrystals (SNCs) exhibit excellent photoelectric properties which have been widely studied in solar cells, light-emitting diodes (LED) and displays.<sup>1,2</sup> Recently, chirality induction to SNCs has attracted a lot of attention due to their chiral-induced spin selectivity (CISS) effect which has shown promising prospective in biological electron transfer, enantioselective separation, and asymmetric catalysis as well as spintronics.<sup>3-6</sup> Optical activity of SNCs induced by chiral ligands are most widely studied since 2007,<sup>7</sup> when the optically active CdS quantum dots (QDs) capped with D- or L-penicillamine were reported. In 2009, Nakashima et al.<sup>8</sup> reported the chirality memory effects on CdTe QDs where the chiral nature of the QDs was maintained after the chiral ligands were exchanged with achiral ones. The magnetic, electrical, and optical properties of SNCs depend on their size, shape, and crystal structure. In 2011, Tang et al.9 and Markovich et al.10 simultaneously reported that the CdSe QDs combined with chiral ligands show optical activity which depends on the QDs' size (dissymmetry factor or g-factor decreased with increasing the QDs size) likely due to the decreasing surface-to-volume ratio. Meanwhile, more factors play roles in determining the g-factor, such as the types of chiral ligand, chiral ligand density, chiral ligands' binding mode, and the dipole moment of QDs.<sup>11</sup> In 2013, Balaz et al.<sup>1</sup> showed that the CdSe QDs combined with L/D cysteine show that the g-factor increased with the increasing QD size. In 2019, Gun'ko et al.<sup>11</sup> reported that the chiral ligand concentration and binding mode have an important effect on the g-factor. In 2018, Tang et al.<sup>13</sup> reported that the CdSe nanoplatelets (NPLs) with wurtzite (hexagonal) and zincblende (cubic) crystal structure combined with L/D cysteine show different chirality induction. CdSe NPLs with hexagonal crystal structure showed 10 times larger CD signal compared to those having cubic crystal structure. This was explained as the results of their different dipole moment and polarization. In 2017, Tang et al.<sup>14</sup> reported that the CdSe rods with different aspect ratios having L/D cysteine ligands show different gfactor. The g-factor increases with the increasing aspect ratio (sphere to rod) and reaches a plateau when the aspect ratio is about 4. In general, the CdSe QDs combined with chiral ligands suffer lower photoluminescence quantum yield (PLQY) and seldom circularly polarized luminescence (CPL) was reported. Core-shell structured QDs would boost the PLQY; however, it hampers the chirality induction.<sup>15</sup>



Figure 1. (a-c) TEM images of R-silica helices@NCs with different ratio samples (I, II, IV). (d) Cryo-EM in toluene of NCs-R-silica helical nanoribbons (IV). (e) CD and absorption spectra of NCs-R-silica helical nanoribbons film with different ratios. The diameter of the NCs is  $\sim$ 3.3 nm. (f) Experimental calculated electronic g-factor at first exciton absorption peak and simulated CD/Ext at first exciton absorption peak of the model helix with 18, 39, and 68 particles/pitch. Scale bars: 20 nm.

Recently, core–shell structured CdSe/CdS with various morphologies such as quantum rods<sup>16</sup> and tadpoles<sup>17</sup> also have been reported which could enhance the chirality induction compared to spherical QDs.

Chirality induction by the assemblies of nonchiral building blocks on the chiral templates has been widely studied in recent decades especially for various organic self-assemblies,<sup>18,19</sup> organic and inorganic hybrid self-organization such as plasmonic gold nanoparticles and QDs.<sup>20-24</sup> While the selforganization with organic molecules suffers limited organization stability with external parameters such as temperature, solvent, salinity, or pH,<sup>25,26</sup> the alternative inorganic chiral nanosystem is still at an emerging point to get stable dense and well-packed self-organization system. Recently, we reported that gold nanoparticles electrostatically or covalently bonded on the surface of nanometric inorganic silica helical ribbons show plasmonic induced CD mirror images in suspension,<sup>27,28</sup> the sign of which can simply be controlled by the handedness of the silica helices. More recently, we reported that semiconductor nanocrystals CsPbBr3 can also be chirally grafted on inorganic silica helical nanoribbons templates.<sup>29</sup> For this system, they do not show any optically active properties in suspension, but when they are drop-casted on a substrate and dried, they show large g-factor ( $6 \times 10^{-3}$ ) of CD and CPL. In the present study, we have investigated the effect of sizes and crystal structures of the NCs on their induced chroptical properties using CdSe NCs. We then grafted elongated CdSe/ CdS quantum rods (QRs) with different lengths around the silica nanoribbons and studied how their grafting orientation affects the induced CD signals. Finally, we investigated the effect of the morphological difference of the chiral templates

between helical (cylindrical curvature) and twisted (saddle-like curvature) ribbons. All these results were compared with the simulation performed using coupled dipole method (CDM) as described in Supporting Information.

#### **RESULTS AND DISCUSSION**

These silica helices were obtained by sol–gel transcription of self-assembled Gemini surfactants as previously reported,<sup>30-32</sup> the handedness of which can be controlled by the counterions of Gemini; L-tartrate forms right-handed (R-) helices, and D-tartrate forms left-handed (L-) helices. The NCs' size and molar concentration can be calculated by Peng et al.'s method<sup>33</sup> as shown in Figure S1 and Table S1. The synthesis of both helices and CdSe NCs are detailed in the Supporting Information.

**Grafting Density.** The grafting method of the CdSe NCs is the same as our previous report with ligand exchange methods: the ligand exchange (see details in Supporting Information).<sup>29</sup> We have chosen to use the NCs with 3.3 nm in diameter. Different numbers of NCs, (I)  $8.7 \times 10^{14}$ , (II)  $8.7 \times 10^{15}$ , (III)  $1.7 \times 10^{16}$ , (IV)  $8.7 \times 10^{16}$ , and (V)  $1.7 \times 10^{17}$ , were mixed with 0.5 mg of silica helical nanoribbons. The approximate surface area of silica helical and twisted nanoribbons is calculated as shown in Figure S2 and Table S2 obtained from TEM images. For the helical ribbons and twisted ribbons, their surface areas are around 8400 nm<sup>2</sup> and 6040 nm<sup>2</sup>/0.5 mg silica, respectively, for 1 pitch of helix. For helical ribbons, only the outer surface is accessible for NC grafting and for twisted ribbons, and both sides are equally accessible ( $7.6 \times 10^{16}$  or  $7.9 \times 10^{16}$  nm<sup>2</sup> for 0.5 mg of silica

helical or twisted nanoribbons, respectively). After the grafting, the ungrafted NCs were removed by washing with toluene and the silica helices @CdSe NCs were dispersed into 0.5 mL of toluene. Then 50  $\mu$ L of this suspension was drop-casted on the surface of quartz (around 1 cm  $\times$  1 cm) and dried at 4 °C. Figure 1a-c shows the TEM images of the drop-casted silica helix @CdSe NCs with different grafting densities as shown above, (I, II, and IV), and Figure 1d shows the solvated cryoelectron microscopy (cryo-EM) image of the sample (IV). On the basis of both types of TEM images, grafted NC numbers per pitch are obtained approximately as (I) 18, (II) 39, (III) 59, (IV) 65, and (V) 60. This indicates that the grafting density reaches a plateau at around 60-65 NCs/pitch. Higher grafting density cannot be achieved even if the initial NCs concentration is increased. As the amine surface density (~1  $amine/nm^2$ <sup>27</sup> is much higher than the NCs numbers/nm<sup>2</sup> (1/ 66), this is likely due to the sterical hindrance due to the ligands around the NCs. The CD spectra of both suspensions and dried films were recorded. In agreement with our previous report on perovskite nanocrystals on silica helices,<sup>29</sup> the silica helix @CdSe NCs in suspension does not show CD signals as shown in Figure S6. However, once deposited on the substrates and formed dried films, they show large CD signals as shown in Figure 1e and Figure S11. R-silica helix@CdSe NCs show positive CD signals, and L-silica helix@CdSe NCs show negative CD signals in the wavelength range of 300-600 nm. It is important to note that these observed CD signals are in fact composed of two factors, scattering from our hybrid nanoobjects and absorption from NCs. As it is difficult to separate these two factors experimentally, we used two methods to calculate the g-factor  $g_{abs} = \Delta \varepsilon / \varepsilon = \theta (mdeg) / \theta$ (32980A). One is by using the raw data (which includes the scattering) as shown in Supporting Information, and the second is by only taking into account the first exciton absorption peak at around 546 nm. In the latter case, we focus on the absorption peak of NCs at around 546 nm which originates from the first exciton absorption peak due to the transition between the valence band and conduction band of NCs as shown in Figure S7a. Indeed, the CD peak at around 546 nm is attributed to the exciton absorption peak which means the  $\Delta$ CD is attributed to the  $\Delta$ Abs as shown in Figure S7b and Table S3. In this case, the g-factor of electronic circular dichroism could be calculated as  $g_{\text{electronic-abs}} =$  $\Delta\theta(\mathrm{mdeg})/(32980{\cdot}\Delta\mathrm{A})$  approximately. As shown in Figure 1f, the  $g_{\text{electronic-abs}}$ -factors increased strongly with the NCs grafting density. Below 20 NCs/pitch, no detectable CD signal was observed; however beyond 40 NCs/pitch, they increase until about  $2.75 \times 10^{-3}$  for the grafting density of  $\sim 70$ /pitch.

The impact of the NCs grafting density is then investigated through the simulations based on CDM as described in the Supporting Information. Each NC is represented as a point dipole. Their diameter was set to 3.3 nm. The NCs were organized into a square lattice on a ribbon with a 30 nm width. The gap distance between two adjacent NCs was adjusted to control their density. Then, the ribbon was wound around into a helix. The pitch and the diameter of the helix as determined by TEM were 65 and 35 nm, respectively. The length of the helix was ~500 nm. As illustrated in Figure S8, the simulation globally reproduced well the measurements (Figure 1e). Indeed, extinction and CD spectra are dominated by an excitonic band located at ~550 nm. Some bands associated with critical point in the joint density of the state of NCs are also observed at 460, 480, and 530 nm. The CD results of

right-handed and left-handed NCs helices are opposite in sign (Figure 3 and Figure S11). Contrary to the measurements, the extinction cross-section of NCs helix is equal to 0 above the band gap ( $\sim$ 570 nm). This is because our simulations do not take into account the scattering losses induced by the silica helices. Therefore, when analyzing the experimental results of CD and absorbance, we will only consider the intensities at the band gap to calculate the g-factor (the residual intensity is due to the scattering).

The extinction cross-section, the CD, and the g-factor at 550 nm bands (Figure 1f) obtained experimentally increase with the density of NCs in the helices as the interaction between NCs are enhanced when the gap between NCs decreases. Inversely, below a certain grafting density, ~20 NCs/pitch, the CD signal is negligible if we only take into account the signal based on the band gap at ~550 nm. These results from experiments and simulation are in very good agreement and confirm that the CD signal comes from two contributions: (i) the dipolar interaction between NCs organized into chiral structure, which require their grafting density to be beyond 20 NCs/pitch, and (ii) the scattering from silica helices@NCs. Nevertheless, this comparison remains qualitative since the models used for the simulation show some important differences from the real system: First, the simulated systems are based on periodic and homogeneous grafting of NCs aligned perfectly helically, whereas the real system shows more heterogeneous grafting and therefore heterogeneous interparticle distances. In particular for the low grafting densities, simulated systems show homogeneous and larger interparticle distance whereas the TEM images show coexistence of domains with high density grafting and low density grafting. As the CD signals do not show linear dependence but rather sigmoidal dependence with the interparticle distances, this will lead to the discrepancies with the simulated systems and real/ measured systems. This is particularly visible for the data on the data points with 40 QDs per pitch. Simulated data show much lower g-factor than the experimental one.

To emphasize the importance of the NCs' self-organization and their close contact on the surface of silica helical nanoribbons during the drying process, we investigated how the presence of polymer in the suspension can affect/hinder the NCs' self-assembly. Poly(methyl methacrylate) (PMMA) is chosen due to their excellent optical properties (transparency) and good dispersity in toluene. Interestingly, in the presence of PMMA with higher concentration than 10 mg/mL, the CD signal disappeared as shown in Figure S9. The TEM images of silica helix @CdSe NCs with PMMA show clear swelling of the NCs around the helices from ~35 nm without PMMA to  $\sim$ 40 nm with PMMA. Along with the disappearance of the CD signal, this indicates that the presence of PMMA disturbs the close contact and self-organization of the NCs, even for the dried samples. This confirms the importance of the close contact organization of the NCs around the surface of silica helices for the inorganic template-assisted chirality induction. Either solvated silica helix @CdSe NCs or codried silica helix @CdSe NCs with PMMA prohibit the close packed helical self-organization of NCs, leading to the extinction of CD signals.

In parallel, we have simulated how the CD signals vary as a function of the distance between the NCs (diameter 3.3 nm) (Figure S9). It was clearly observed that in the range of inter-QD distance observed experimentally ( $\gtrsim 3.3 + 1 = 4.3$  nm), the CD signal decreases quickly as the inter-QD distance increases,



Figure 2. TEM images of R-silica helices@CdSe NCs with NCs having cubic and hexagonal crystal structures (C1-4 and H1-4). Scale bars: 50 nm.

by a factor of 10 when the distance increases only by 1 nm, which clearly confirms why the swelling and the resulting increase of the interparticle distance lead to the disappearance of the observable CD signals.

**Size and Crystal Structure Effect.** We then investigated the effect of the sizes of NCs having different crystal structures. The cubic and hexagonal crystal structured NCs with different sizes are labeled as C1–4 and H1–4, respectively. The NCs show size-tunable absorption and emission spectra as shown in Figure S1.

The NCs sizes are calculated based on the first exciton absorption peak as shown in Figure S1 and Table S1. The diameters of the NCs C1–4 were 2.2, 2.7, 2.9, and 3.3 nm, while those of NCs H1–4 were 3.0, 3.4, 3.5, and 3.9 nm. Obviously, the NCs alone in suspension do not show any CD and CPL signals as shown in Figure S3. They were then grafted on silica helical nanoribbons (Figures 2 and S10), and ungrafted NCs were washed away. The NCs before and after grafting on silica do not change their crystal structures as shown in Figure S5. These silica helices@NCs are drop-casted and dried on the quartz substrate at 4 °C, and the CD signals were measured.

Figure 3 shows the experimental and simulated CD spectra of C1–4 and H1–4 R-silica helices@NCs. All the NCs with right-handed silica helical nanoribbons show positive CD signals while all the NCs with left-handed silica helical nanoribbons show negative CD signals as shown in Figure S11. The absorption spectra, CD spectra as well as g-factors taking into account the scattering effect are shown in Figure S11.

We then performed simulations with the CDM to elucidate the impact of the NCs size and crystal on the CD. The NCs' sizes used for the simulation are equal to those measured by the TEM. The same procedure as presented in the previous section is used to organize NCs into helical structure. The distance between adjacent NCs is equal to 6.5 nm. The pitch and the diameter of the helix as determined by TEM were 65 and 35 nm, respectively. The length of the helix is equal to 500 nm.

The spectral variations observed in the measured spectra are globally well reproduced by the simulations. Indeed, the

excitonic band observed in the extinction cross-section and CD spectra is blue-shifted as the NCs size decreased. This behavior is attributed to the confinement effect. The amplitude of the CD and extinction cross-section increases with the quantum dot size. Indeed, the extinction cross-section and the magnitude of the scattered field of a dipole are proportional to its volume. The g-factors of each NCs helix (Figure S11d) are determined. No discontinuity between the data obtained for cubic and hexagonal crystal structured NCs is observed. In particular, the g-factors of C3 (2.88 nm diameter) and H1 (2.99 nm diameter) both grafted on the helices as well as C4 (3.31 nm diameter) and H2 (3.37 nm diameter) on the helices, both showing similar diameters, show very close gfactors in spite of the different crystal structures. Thus, we conclude that the magnitude and position of the excitonic band are mainly governed by the NCs' size and the crystal structure plays a minor role in the optical properties of NCs helices. A closer look at the data does show that the matching between the simulated and experimental data is qualitative due to the factors as described above on the homogeneous (simulation) vs heterogeneous (real system) grafting of the NCs. Furthermore, in the simulation, the NCs are all the same size whereas in the experiments, we observe some polydispersities of the NCs which should have an important effect on both the absorbance and CD signals. Another difference is that in the simulation, only inter-NCs interaction helically arranged is taken into account without the interaction between NCs and silica. Finally, the simulation is done on one helix without taking into consideration the interaction between neighboring helices. Nevertheless, the global agreement on the positions and their shift of the peaks of the different NCs are surprisingly good as observed in Figure 3.

**Effect of Chiral Morphologies: Helical vs Twisted Ribbons.** We then compared the effect of the chiral morphologies of the silica helices, having twisted shape vs helical shape. As we have previously reported, depending on the aging time of the Gemini surfactant self-assembly, twisted or helical Gemini tartrate bilayers can be obtained, which can be transcribed to silica to obtain twisted or helical silica nanoribbons. The helical ribbons and twisted ribbons show different chiral curvatures and different widths and pitches.



Figure 3. Experimental (red curves) and simulated (black curves) CD spectra of (a) C1, (b) C2, (c) C3, (d) C4, (e) H1, (f) H2, (g) H3, and (h) H4 NCs-R-silica helical nanoribbons.

Helical ribbons have cylindrical curvature and are 30 nm wide with 65 nm pitch, whereas twisted ribbons have Gaussian curvature and are 22.6 nm wide with 100 nm pitch (Figure S2).<sup>34</sup>

As shown in Figures 4 and S12, NCs are also grafted on the surface of these twisted silica ribbons. When drop-casted on the surface of the quartz, CD signals were observed as indicated in Figure 5. Here also, the right-handed (R-) samples and the left-handed (L-) samples show mirror image positive and negative CD signals, respectively. The CD signals obtained from twist ribbons are weaker than the ones obtained from helical samples.

To understand and compare how the twist vs helical platforms for NC grafting affect the CD signal, we made simplified models for which 4 nm diameter NCs are organized on helical vs twisted platforms (based on the observed dimensions) keeping the adjacent NC distance (diameter 4 nm, center to center distance is 5 nm and the interparticle distance is 1 nm) organized parallel to the long axis of the ribbon (not helix) (Figure 6). When considering this model, it is obvious that for the NC grafted around helical silica ribbons, all the NCs are positioned at the same distance (distance between the center of the helical ribbon to the center of the NCs, 37/2 + 4/2 = 20.5 nm, Figure 6a) from the center of the helices, while for the NCs grafted around twisted silica ribbons, NCs have different distances from the center of the helices (Figure 6b); *i.e.*, the pink NCs are the farthest (12 nm), then the blue NCs (9 nm). The gray NCs are the closest (7 nm). Not only these three types of NCs have different helical routes to make one pitch, as the inter-NC distances are fixed, there are different numbers of NCs per pitch. The details of the models are described in Figure S13.

The CDM simulation on the model shows indeed that the NCs organized around twisted ribbon show lower *g*-factor (normalized by the number of NCs) than that for helical ribbon. Looking more in detail into the results of a simplified simulation for which we look at a helically arranged NCs with a fixed interparticle distance (1 nm), we observed that *g*-factors depend strongly on both the radius and the pitch of the helical arrangement of the NCs (Figures 6d and S13). For a given pitch, the *g*-factor is enhanced for a helix radius  $r_{\rm H}$  which minimized the angle between three adjacent NCs:

$$r_{\rm H} = \frac{p}{2\pi}$$

with p the pitch of helictical arrangement. This result suggests that the chiroptical properties of NCs helices can be optimized by controlling their geometrical parameters. For this optimal configuration, the curvature of the helical arrangement and the misalignment between three adjacent NCs are maximized.

Interestingly, the g-factor of the NCs on the helical ribbons (pitch 67 nm and radius 20.5 nm) is close to the maximum of the curve ( $\sim 0.0013$ ), whereas for those on the twisted ribbons (pitch 100 nm, radius 7 (gray), 9 (blue), and 12 (pink) nm NCs) they are globally much lower (0.00057, 0.0008, and 0.0011, respectively). This explains why helical ribbons show higher g-factors. In the Supporting Information (Figure S14), we show the simulated results on the variation of g-factors as well as the angles formed by three adjacent NCs in the direction tangent to the helix as a function of the helix radius for various pitches. Very good agreement between the g-factors and the angle variations was observed. The ensemble of the results shows that the g-factor is closely related to the arrangement of the NCs: (1) g-factor is higher when the higher curvature is formed by the consecutive NCs (lower angles), (2) for longer pitches, the maximum of g-factors are observed for the larger helix radius, and (3) the maximum of the *g*-factor decreases with the pitches. This result gives us clues for how to design the chiral assembling systems having high chiroptical systems by combining the factors such as angles formed by the NCs, helix radius, and pitches.

We also investigated the effect of the shape of NCs on their chiral arrangement and the resulting chiroptical properties. Here, we use CdSe/CdS core-shell structured quantum rods (QRs) combined with silica twisted nanoribbons. As shown in Figures 7 and S15, we synthesized QRs with different lengths labeled as R1-6, the lengths of which are 9.5 nm, 13 nm, 18 nm, 23 nm, 27 nm, and 32 nm with size distribution (Figure S16).

R1–6 CdSe/CdS QRs were then grafted on the surface of silica twisted nanoribbons.



Figure 4. TEM images of different sizes of cubic and hexagonal crystal structured NCs (C1-4 and H1-4) CdSe-R-silica twisted ribbons. Scale bars: 50 nm.



Figure 5. CD spectra of (a) R- and L-helical silica@C1-4 NCs and R- and L-twisted silica@C1-4 NCs, (b) R- and L-helical silica@H1-4 NCs and R- and L-twisted silica@H1-4 NCs.

In Figure 7, cryo-EM images of R1, 3, 5 QRs grafted on the silica nanoribbons in suspension in toluene are compared with the dried TEM images of R1–6 QRs grafted on silica ribbons. We observe that for the dried samples, the QRs R1 and R2 are mainly attached to silica ribbons by their side whereas R5 and R6 are mainly attached by their tips. For the R3 and R4, both orientations are observed.

When compared with the cryo-EM images of the same samples, not only do they show more swollen organization as we observe with NCs, they all are attached with helices with their tips regardless of their length. This grafting model is consistent with the ligand exchange grafting methods as shown in the experimental section. The ligands on the tips of QRs have higher activity than the side part<sup>35</sup> which is easier to be combined with the surface amine of silica twisted ribbons.

Once again, these silica helices@QRs in suspension do not show any CD signals as shown in Figure S17. When dried on the substrates, clear CD signals are observed as shown in Figure 8a. The R1 and R2 QRs with left-handed (L-) silica helices show negative signals in the wavelength range of 300– 500 nm, while with right-handed helices, they show positive CD signals (Figure S18). For the sample with R3–6 QRs, the CD signals switch their signs and L-silica helices@R3–6 QR show positive CD signals.

To investigate how this switching of the CD signals occurs, we have performed the simulation of QRs grafted on twisted ribbons with different orientations. In Figure 8b, four different types of grafting are shown: (1) QRs are oriented parallel to the axis of the helix; (2) they are oriented perpendicular to the axis and the surface of the helix (tip grafting); (3) they are tangent to the helix; (4) they are perpendicular to the tangent of the helix. The respective simulated CD signals for each



Figure 6. Models of NCs grafted on helical (a) or twisted ribbon (b) based on the relative dimensions of NC and silica helices (shown in red). (c) Simulated g-factors for NCs grafted around the twisted ribbon (black) and helical ribbon (red). (d) Simulated g-factors and the angles between the three consecutive particles (defined at the bottom of the figure) as a function of helix radius (defined at the bottom of the figure) for different helix pitches.

orientation are shown in Figure 8b. These simulations are performed by considering CdSe nanorods with 25 nm length and 5 nm width. The CdSe nanorods are organized into helical structures. The helix pitch, radius, and length are 70, 35, and 500 nm. The distance between two adjacent rods is 25.2 nm. The incident wave vector of light is perpendicular to the helix axis.

It is clearly observed that while the orientation of nanorods has a negligible impact on the extinction cross-section, the sign



Figure 7. (a-f) TEM images of dried silica helices@R1-6 QRs and (g-i) cryo-EM images in toluene of silica helices@R1,3,5 QRs. When dried, R1 and R2 are organized parallel to the silica surface, and R5 and R6 QRs are tip grafted. R3 and R4 show intermediate orientation. When solvated, all of them show tip grafting orientation. Scale bars: 20 nm.

of the CD spectra depends strongly on their orientation. Indeed, the CD is positive for configurations 1 and 2 while it becomes negative for configurations 3 and 4.

The highest amplitudes of CD signal are observed for configurations 3 and 4. Although it is not easy to clearly define the orientation of the QRs with respect to the surface of the silica helix from the TEM images, it seems obvious that the tip grafted QRs as seen in  $R_3-6$  (Figure 7) are in agreement with case 2, which shows positive signals in the wavelength range 300–500 nm. For the sample L helices@R1,2 QRs, they show negative CD signals, which is in agreement with either 3 or 4 orientation in Figure 8b.

To summarize these results on QR, we have performed in parallel the detailed TEM studied and the simulation studies on the effect of the grafting orientation of QRs with different lengths, with respect to the surface of a twisted ribbon. TEM studies showed that when they are dried on the substrates, short QRs lie parallel to the silica surface (side grafting) while the long QR remains tip grafted. CD signals of these samples showed that the side grafted QRs on the L-twist ribbons show negative CD signals and the tip grafted QRs show positive CD signals. This change in the grafting orientation is likely due to the gain in van der Waals interaction between QRs vs between QR and silica surfaces which depend on the length of the QRs: *i.e.*, for longer QRs, they gain in energy by remaining parallel to each other (tip grafting), whereas for shorter QRs it is more favorable that they lie parallel to the silica surface (side grafting). The simulation independently confirmed that when QRs are side grafted along with the L-twist ribbons, they show negative CD signals while when they are tip grafted, they show positive CD signals.



Figure 8. (a) CD and absorption spectra of L-silica helices@R1-6 QRs. (b) Simulated CD and absorption spectra of L-silica helix@ QRs with four different orientations with respect to the helix.

#### **CONCLUSIONS**

In this paper, we report how chirality is induced to achiral CdSe NCs or QRs which are organized around chiral inorganic platforms by looking into the effect of various parameters and comparing the experimental observations and the simulation. The helices@NCs in suspension do not show CD signals, whereas when they are dried on a substrate, clear CD signals were observed. The g-factor of the induced CD increased strongly with the grafting density. The NCs with different sizes and different crystal structures have been grafted on the silica helical/twisted nanoribbons for which the CD signals were mainly controlled by the size of the NCs. The induced chiroptical signals from NCs grafted on helical ribbons and twisted ribbons were compared. The NC grafted on the helical ribbons showed stronger CD signals, and by analyzing the system by simulation, we demonstrated that chiroptical signals of the helically arranged NCs are strongly dependent on both the helical pitch and the radius which in turn depends on the angles formed by the three consecutive NCs in the helical arrangement. Finally, elongated QRs grafted around the twisted ribbons showed grafting orientation-dependent sign inversion of the optical activity. The QRs with lower aspect ratio showed the orientation tangent to the helix and negative CD signals for the left-hand helix, whereas those with higher

aspect ratio show tip-grafting (perpendicular to the helix axis) and show positive CD signals. The ensemble of this study shows the versatility of the system to tune and control the chiroptical properties, giving us powerful hints for designing efficient chiroptical nanosystems based on inorganic silica-NC components.

#### METHODS AND EXPERIMENTAL DETAILS

**Chemical and Reagents.** Se powder (100 mesh, 99.99%), CdO (99.99%), S powder (100 mesh, 99.998%), 1-octadecene (90%), tri-*n*-octylphosphine (97%), trioctylphosphine oxide (99%), tetradecylphosphonic acid (97%), oleylamine (70%), oleyl acid (90%), and toluene were purchased from Sigma Company.

Characterizations. Transmission electron microscopy (TEM) was performed with CM 120 (Philips) at 120 kV. Cryogenic electron microscopy (cryo-EM) was performed with Tecnai F20 (FEI). For TEM experiments, samples were applied to carbon-coated copper 300 mesh grids. Observations were performed using a Philips EM 120 electron microscope operating at 120 kV, and the images were collected by 2K × 2K Gatan ss CCD camera. For cryo-EM experiments (samples in toluene), lacey carbon formvar 300 mesh copper grids were used. Plunge freezing was realized using the EM-GP apparatus (Leica) directly in liquid nitrogen. Specimens were observed at -175 °C using a cryo holder (626, Gatan), with a ThermoFisher FEI Tecnai F20 electron microscope operating at 200 kV under low-dose conditions. Images were acquired with an Eagle  $4K \times 4K$  camera (ThermoFisher FEI). The X-ray diffraction (XRD) spectra of NCs and NCs-silica ribbons were measured with Bruker D8 Advance X-ray diffractometer.

Circular dichroism (CD), linear dichroism (LD), and absorption spectra were measured by J-815 (JASCO). The UV–visible spectra of NCs solution were measured by JASCO V-550 UV–vis spectrophotometer.

**Cubic Crystal Structured CdSe NCs Synthesis and Purification.** The different sizes of cubic crystal structured CdSe were synthesized according to Peng's method.<sup>36</sup> The size of NCs was controlled by the growth temperature and concentration. The typical synthesis protocol is as below:

Se-ODE precursor: 0.1 mmol Se powder (100 mesh) mixed with 2 mL of 1-octadcence (ODE) and sonication for 5 min before injection.

0.0256 g (0.2 mmol) of CdO, 0.2 mL of oleic acid (OA), and 8 mL of ODE were loaded into a 50 mL three-neck flask, bubbling with nitrogen for 30 min at 100 °C. Then increasing the temperature at 250 °C, 2 mL of Se-ODE suspension solution was injected quickly and the temperature was set at 220 °C, growth for 5 min. Then the sample is cooled down to room temperature.

**CdSe Quantum Dots Purification.** 10 mL of hexane and 10 mL of ethanol were added into the crude CdSe solution, stirring and sonicating for 10 min until the solution stratification, and the bottom white part solution was discarded. This step was repeated twice. 10 mL of ethanol was added, and samples were centrifuged at 9000g. All the supernatant was removed, and 2 mL of toluene was added to disperse the precipitate. Samples were centrifuged again at 9000g, and the supernatant was collected and kept at 4 °C.

Hexagonal Crystal Structured CdSe NCs Synthesis and Purification. The different sizes of hexagonal crystal structured CdSe were synthesized according to the previous report.<sup>37</sup> The size was controlled by the growth time and the typical synthesis protocol is as below:

Se-TOP precursor: 0.789 g of Se powder dissolved into 10 mL of tri-*n*-octylphosphine (TOP) with stirring.

54 mg of CdO, 224 mg of tetradecylphosphonic acid (TDPA), 3 g of trioctylphosphine oxide (TOPO) were placed in a 100 mL threenecked flask and degassed for 60 min at 150 °C. The temperature was increased to 330 °C, the flask was shaken manually to let the CdO dissolve quickly. After the CdO was dissolved, the temperature was increased to 350 °C, and 1.5 mL of TOP was injected. Then the temperature was increased to 370 °C, and 0.63 mL of Se-TOP was injected quickly. 10 s later, the CdSe crude solution was cooled down to room temperature.

Purification: 6 mL chloroform was added to the crude solution and centrifuged for 3 min at 9000g. The supernatant was collected, and 12 mL of ethanol was added, centrifuged for 3 min at 9000g. The supernatant was removed, and 12 mL of toluene was added to disperse the precipitate, and then 12 mL of ethanol was added, centrifuged for 3 min at 9000g again. The supernatant was removed, and around 2 mL of toluene was added to disperse the precipitate. The solution was kept at 4 °C.

**CdSe/CdS Quantum Rods (QRs) Synthesis and Purification.** CdSe core seeds: the CdSe seeds were prepared with the same step of hexagonal crystal structured CdSe NCs. The purified CdSe was dispersed into 4 mL of TOP instead of a toluene solution, and the CdSe TOP solution was used to prepare the CdSe/CdS QRs. Then the molar concentration was calculated by Peng et al.'s methods.<sup>33</sup>

S-TOP precursor: 1.202 g of S powder dissolved into 15 mL of TOP solution by heating to 100  $^\circ C$  with stirring,

CdSe/CdS QRs synthesis according to the previous report: 40 mg of CdO, 52 mg of hexylphosphonic acid (HPA), 200 mg of TDPA, and 2 g of TOPO were placed in a three-necked flask, degassed for 60 min at 150 °C, and then the temperature was increased to 300 °C to dissolve the CdO. After the CdO was completely dissolved, 1 mL of TOP was injected. The temperature was increased to 320 °C, the mixture of 53.3 nmol of CdSe TOP NCs and 1 mL of S-TOP was injected, keeping its growth at 320 °C for 8 min, and then the samples were cooled down to room temperature.

The length of CdSe/CdS rods was controlled by the mass of CdO and the number of CdSe-TOP seeds.

**Quantum Dots Size and Molar Concentration Calculation.** The CdSe NCs molar concentration calculation is based on Peng et al.'s method.<sup>33</sup> The purified NCs toluene solution was diluted 40 times and measured by a UV–vis spectrophotometer. The first absorption peak position ( $\lambda$ ) and absorbance (A) were recorded. On the basis of the Beer–Lambert law, the size and molar concentration could be calculated.

 $A = \varepsilon cl$ 

$$D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + 41.57$$

 $\varepsilon = 5857(D)^{2.65}$ 

where *A*,  $\varepsilon$ , *c*, *l*,  $\lambda$ , and *D* are absorbance, molar absorptivity (L/(molcm)), CdSe NCs concentration (mol/L), cuvette path length (cm), first absorption peak wavelength, and diameter of NCs, respectively.

Silica Helical and Twisted Ribbons Preparation and Surface Modification. The preparation of silica helices was done as in our previous report.<sup>38</sup> 3.6 mg 16–2–16 L-(or D-)tartrate was dissolved into 5 mL of Milli-Q water and heated to 60 °C and kept for 20 min. Then, the clear solution was kept at 20 °C incubator to let selfassembly age for 2 h (twisted ribbons) or 3 days (helical ribbons). After that, 5 mL of prehydrolyzed tetraethyl orthosilicate (TEOS) aqueous solution (0.5 mL of TEOS mixed with 10 mL of 0.1 mM aqueous solution of L/D-tartaric acid for 7 h on the roller-mixer) was added to the self-assembly aging solution, and the mixture was kept at 20 °C incubator overnight. The unreacted TEOS and 16–2–16 L/D tartrate template were removed by washing with methanol (twice) and absolute ethanol (three times) by centrifugation at 3893g for 6 min alternately. Finally, the obtained silica helices were dispersed into a 5 mL of absolute ethanol solution.

Into the purified 5 mL of silica helices ethanol solution, 10  $\mu$ L of APTES was added and sonicated for 10 min, and then the mixture was kept in an oil bath at 80 °C overnight. The sample was then washed with absolute ethanol (twice) alternatively by centrifugation at 10000g for 10 min. The surface modification step is repeated once and samples were washed with toluene twice by centrifugation at 10000g for 10 min. The silica helical/twisted ribbons were dispersed

into 5 mL of toluene. The mass concentration was calculated based on the average mass of the dried 100  $\mu$ L sample three times.

Method for NCs grafted on the surface of silica ribbon. Different types and numbers of purified NCs were mixed 0.5 mg amine modified silica ribbons in 0.5 mL toluene solution, then sonication for 10 min. The mixture was shaken on a roller-mixer for 3 days at 4  $^{\circ}$ C. After that, 0.5 mL toluene was added into the mixture and centrifuged at 9800g for 10 min to separate the NCs-silica ribbons and free NCs. The supernatant was discarded and 1 mL toluene was added to disperse the precipitate. Centration again and the precipitate of NCs-silica ribbons were re-dispersed into 0.5 mL toluene.

**NCs-silica ribbons film preparation.** The quartz was cut into 1 cm  $\times$  1 cm plates, then the prepared NCs-silica ribbons solution 50 uL was drop-casted on the quartz plate and dried at 4 °C. After drying, the CD was measured at 0° and 90° to eliminate the LD effects.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.1c05819.

Detailed experimental conditions and characterization; additional figures describing the QDs and helices characterization, CD *vs* LD evaluation, *g*-factor evaluation, and simulation methods (PDF)

#### **AUTHOR INFORMATION**

#### **Corresponding Authors**

- Takashi Sagawa Graduate School of Energy Science, Kyoto University, 606-8501 Kyoto, Japan; o orcid.org/0000-0002-0908-0487; Email: sagawa.takashi.6n@kyoto-u.ac.jp
- Reiko Oda Univ. Bordeaux, CNRS, Bordeaux INP, CBMN, UMR 5248, F-33600 Pessac, France; orcid.org/0000-0003-3273-8635; Email: r.oda@cbmn.u-bordeaux.fr

#### Authors

- Peizhao Liu Univ. Bordeaux, CNRS, Bordeaux INP, CBMN, UMR 5248, F-33600 Pessac, France; Graduate School of Energy Science, Kyoto University, 606-8501 Kyoto, Japan; ⊚ orcid.org/0000-0002-6367-6847
- Yann Battie Laboratoire de Chimie et Physique, Approche Multi-échelles des Milieux Complexes (LCP-A2MC), Université de Lorraine, 57078 Metz, France; orcid.org/ 0000-0003-2421-2684
- Marion Decossas Univ. Bordeaux, CNRS, Bordeaux INP, CBMN, UMR 5248, F-33600 Pessac, France
- Sisareuth Tan Univ. Bordeaux, CNRS, Bordeaux INP, CBMN, UMR 5248, F-33600 Pessac, France
- Emilie Pouget Univ. Bordeaux, CNRS, Bordeaux INP, CBMN, UMR 5248, F-33600 Pessac, France; Orcid.org/ 0000-0002-3175-6201
- Yutaka Okazaki Graduate School of Energy Science, Kyoto University, 606-8501 Kyoto, Japan

Complete contact information is available at: https://pubs.acs.org/10.1021/acsnano.1c05819

#### **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This work was supported in the context of the France-Japan International Associated Laboratory, Chiral Nanostructures for Photonic Applications (LIA-CNPA) supported by the Centre National de la Recherche Scientifique and Université de Bordeaux, Kyoto University Strategic Partnership Program with the University of Bordeaux. The work was partially supported by Special Grants from Ministry of Education, Culture, Sports, Science and Technology (MEXT) 2018-2021 entitled Development of International Liaison Laboratory in International Advanced Energy Science Research and Education Center (IAESREC) at Graduate School of Energy Science, Kyoto University. Y.O. thanks Japan Society for Promotion of Science KAKENHI (Grant 19K15376) and the Supporting Program for InteR Action-Based Initiative Team Studies (SPIRITS) 2020 of Kyoto University. P.L. is grateful for financial support from the Chinese Scholarship Council (CSC).

#### REFERENCES

(1) Bera, D.; Qian, L.; Tseng, T.-K.; Holloway, P. H. Quantum Dots and Their Multimodal Applications: A Review. *Materials* **2010**, *3* (4), 2260–2345.

(2) Dai, X.; Deng, Y.; Peng, X.; Jin, Y. Quantum-Dot Light-Emitting Diodes for Large-Area Displays: Towards the Dawn of Commercialization. *Adv. Mater.* **2017**, *29* (14), 1607022.

(3) Chen, C.; Gao, L.; Gao, W.; Ge, C.; Du, X.; Li, Z.; Yang, Y.; Niu, G.; Tang, J. Circularly Polarized Light Detection Using Chiral Hybrid Perovskite. *Nat. Commun.* **2019**, *10* (1), 1927.

(4) Kim, Y. H.; Zhai, Y.; Lu, H.; Pan, X.; Xiao, C.; Gaulding, E. A.; Harvey, S. P.; Berry, J. J.; Vardeny, Z. V.; Luther, J. M.; Beard, M. C. Chiral-Induced Spin Selectivity Enables a Room-Temperature Spin Light-Emitting Diode. *Science* **2021**, *371* (6534), 1129–1133.

(5) Michaeli, K.; Kantor-Uriel, N.; Naaman, R.; Waldeck, D. H. The Electron's Spin and Molecular Chirality - How Are They Related and How Do They Affect Life Processes? *Chem. Soc. Rev.* **2016**, *45* (23), 6478–6487.

(6) Naaman, R.; Paltiel, Y.; Waldeck, D. H. Chiral Molecules and the Electron Spin. *Nature Reviews Chemistry* **2019**, 3 (4), 250–260.

(7) Moloney, M. P.; Gun'ko, Y. K.; Kelly, J. M. Chiral Highly Luminescent CdS Quantum Dots. *Chem. Commun. (Cambridge, U. K.)* **2007**, No. 38, 3900–3902.

(8) Nakashima, T.; Kobayashi, Y.; Kawai, T. Optical Activity and Chiral Memory of Thiol-Capped CdTe Nanocrystals. J. Am. Chem. Soc. 2009, 131 (30), 10342–10343.

(9) Li, Y.; Zhou, Y.; Wang, H. Y.; Perrett, S.; Zhao, Y.; Tang, Z.; Nie, G. Chirality of Glutathione Surface Coating Affects the Cytotoxicity of Quantum Dots. *Angew. Chem., Int. Ed.* **2011**, *50* (26), 5860–5864.

(10) Ben Moshe, A.; Szwarcman, D.; Markovich, G. Size Dependence of Chiroptical Activity in Colloidal Quantum Dots. ACS Nano 2011, 5 (11), 9034–9043.

(11) Kuznetsova, V. A.; Mates-Torres, E.; Prochukhan, N.; Marcastel, M.; Purcell-Milton, F.; O'Brien, J.; Visheratina, A. K.; Martinez-Carmona, M.; Gromova, Y.; Garcia-Melchor, M.; Gun'ko, Y. K. Effect of Chiral Ligand Concentration and Binding Mode on Chiroptical Activity of CdSe/CdS Quantum Dots. *ACS Nano* **2019**, *13* (11), 13560–13572.

(12) Tohgha, U.; Deol, K. K.; Porter, A. G.; Bartko, S. G.; Choi, J. K.; Leonard, B. M.; Varga, K.; Kubelka, J.; Muller, G.; Balaz, M. Ligand Induced Circular Dichroism and Circularly Polarized Luminescence in CdSe Quantum Dots. *ACS Nano* **2013**, *7* (12), 11094–11102.

(13) Gao, X.; Zhang, X.; Zhao, L.; Huang, P.; Han, B.; Lv, J.; Qiu, X.; Wei, S. H.; Tang, Z. Distinct Excitonic Circular Dichroism between Wurtzite and Zincblende CdSe Nanoplatelets. *Nano Lett.* **2018**, *18* (11), 6665–6671.

(14) Gao, X.; Zhang, X.; Deng, K.; Han, B.; Zhao, L.; Wu, M.; Shi, L.; Lv, J.; Tang, Z. Excitonic Circular Dichroism of Chiral Quantum Rods. J. Am. Chem. Soc. **201**7, 139 (25), 8734–8739.

(15) Purcell-Milton, F.; Visheratina, A. K.; Kuznetsova, V. A.; Ryan, A.; Orlova, A. O.; Gun'ko, Y. K. J. A. n. *ACS Nano* **2017**, *11* (9), 9207–9214.

(16) Cheng, J.; Hao, J.; Liu, H.; Li, J.; Li, J.; Zhu, X.; Lin, X.; Wang, K.; He, T. Optically Active CdSe-Dot/CdS-Rod Nanocrystals with Induced Chirality and Circularly Polarized Luminescence. *ACS Nano* **2018**, *12* (6), 5341–5350.

(17) Hao, J.; Li, Y.; Miao, J.; Liu, R.; Li, J.; Liu, H.; Wang, Q.; Liu, H.; Delville, M.-H.; He, T.; Wang, K.; Zhu, X.; Cheng, J. Ligand-Induced Chirality in Asymmetric CdSe/CdS Nanostructures: A Close Look at Chiral Tadpoles. *ACS Nano* **2020**, *14* (8), 10346–10358.

(18) Liu, M.; Zhang, L.; Wang, T. Supramolecular Chirality in Self-Assembled Systems. *Chem. Rev.* 2015, *115* (15), 7304–7397.

(19) Mateos-Timoneda, M. A.; Crego-Calama, M.; Reinhoudt, D. N. Supramolecular Chirality of Self-Assembled Systems in Solution. *Chem. Soc. Rev.* **2004**, *33* (6), 363–372.

(20) Schreiber, R.; Luong, N.; Fan, Z.; Kuzyk, A.; Nickels, P. C.; Zhang, T.; Smith, D. M.; Yurke, B.; Kuang, W.; Govorov, A. O.; Liedl, T. Chiral Plasmonic DNA Nanostructures with Nwitchable Circular Dichroism. *Nat. Commun.* **2013**, *4*, 2948.

(21) Guerrero-Martinez, A.; Auguie, B.; Alonso-Gomez, J. L.; Dzolic, Z.; Gomez-Grana, S.; Zinic, M.; Cid, M. M.; Liz-Marzan, L. M. Intense Optical Activity from Three-Dimensional Chiral Ordering of Plasmonic Nanoantennas. *Angew. Chem., Int. Ed.* **2011**, *50* (24), 5499–5503.

(22) Szustakiewicz, P.; Kowalska, N.; Grzelak, D.; Narushima, T.; Gora, M.; Baginski, M.; Pociecha, D.; Okamoto, H.; Liz-Marzan, L. M.; Lewandowski, W. Supramolecular Chirality Synchronization in Thin Films of Plasmonic Nanocomposites. *ACS Nano* **2020**, *14* (10), 12918–12928.

(23) Hentschel, M.; Schaferling, M.; Duan, X.; Giessen, H.; Liu, N. Chiral Plasmonics. *Sci. Adv.* **201**7, *3* (5), e1602735.

(24) Wang, Y.; Wan, K.; Pan, F.; Zhu, X.; Jiang, Y.; Wang, H.; Chen, Y.; Shi, X.; Liu, M. Bamboo-Like Pi-Nanotubes with Tunable Helicity and Circularly Polarized Luminescence. *Angew. Chem., Int. Ed.* **2021**, *60* (30), 16615–16621.

(25) Huo, S.; Duan, P.; Jiao, T.; Peng, Q.; Liu, M. Self-Assembled Luminescent Quantum Dots To Generate Full-Color and White Circularly Polarized Light. *Angew. Chem., Int. Ed.* **2017**, *56* (40), 12174–12178.

(26) Shi, Y.; Duan, P.; Huo, S.; Li, Y.; Liu, M. Endowing Perovskite Nanocrystals with Circularly Polarized Luminescence. *Adv. Mater.* **2018**, *30* (12), 1705011.

(27) Cheng, J.; Le Saux, G.; Gao, J.; Buffeteau, T.; Battie, Y.; Barois, P.; Ponsinet, V.; Delville, M. H.; Ersen, O.; Pouget, E.; Oda, R. GoldHelix: Gold Nanoparticles Forming 3D Helical Superstructures with Controlled Morphology and Strong Chiroptical Property. *ACS Nano* **2017**, *11* (4), 3806–3818.

(28) Gao, J.; Wu, W.; Lemaire, V.; Carvalho, A.; Nlate, S.; Buffeteau, T.; Oda, R.; Battie, Y.; Pauly, M.; Pouget, E. Tuning the Chiroptical Properties of Elongated Nano-objects *via* Hierarchical Organization. *ACS Nano* **2020**, *14* (4), 4111–4121.

(29) Liu, P.; Chen, W.; Okazaki, Y.; Battie, Y.; Brocard, L.; Decossas, M.; Pouget, E.; Muller-Buschbaum, P.; Kauffmann, B.; Pathan, S.; Sagawa, T.; Oda, R. Optically Active Perovskite CsPbBr3 Nanocrystals Helically Arranged on Inorganic Silica Nanohelices. *Nano Lett.* **2020**, *20* (12), 8453–8460.

(30) Delclos, T.; Aime, C.; Pouget, E.; Brizard, A.; Huc, I.; Delville, M. H.; Oda, R. Individualized Silica Nanohelices and Nanotubes: Tuning Inorganic Nanostructures Using Lipidic Self-Assemblies. *Nano Lett.* **2008**, *8* (7), 1929–1935.

(31) Oda, R.; Huc, I.; Schmutz, M.; Candau, S.; MacKintosh, F. Tuning Bilayer Twist Using Chiral Counterions. *Nature* **1999**, 399 (6736), 566–569.

(32) Gao, J.; Okazaki, Y.; Pouget, E.; Nlate, S.; Kauffmann, B.; Artzner, F.; Buffeteau, T.; Oda, R. Slow Kinetic Evolution of Nanohelices Based on Gemini Surfactant Self-Assemblies with Various Enantiomeric Excess; Chiral Segregation towards a Racemic Mixture. *Materials Chemistry Frontiers* **2021**, *5* (7), 3021–3028.

(33) Yu, W. W.; Qu, L.; Guo, W.; Peng, X. Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals. *Chem. Mater.* **2003**, *15* (14), 2854–2860.

(34) Okazaki, Y.; Buffeteau, T.; Siurdyban, E.; Talaga, D.; Ryu, N.; Yagi, R.; Pouget, E.; Takafuji, M.; Ihara, H.; Oda, R. Direct Observation of Siloxane Chirality on Twisted and Helical Nanometric Amorphous Silica. *Nano Lett.* **2016**, *16* (10), 6411–6415.

(35) Talapin, D. V.; Nelson, J. H.; Shevchenko, E. V.; Aloni, S.; Sadtler, B.; Alivisatos, A. P. Seeded Growth of Highly Luminescent CdSe/CdS Nanoheterostructures with Rod and Tetrapod Morphologies. *Nano Lett.* **2007**, 7 (10), 2951–2959.

(36) Pu, C.; Zhou, J.; Lai, R.; Niu, Y.; Nan, W.; Peng, X. Highly Reactive, Flexible yet Green Se Precursor for Metal Selenide Nanocrystals: Se-Octadecene Suspension (Se-SUS). *Nano Res.* **2013**, 6 (9), 652–670.

(37) Carbone, L.; Nobile, C.; De Giorgi, M.; Sala, F. D.; Morello, G.; Pompa, P.; Hytch, M.; Snoeck, E.; Fiore, A.; Franchini, I. R.; Nadasan, M.; Silvestre, A. F.; Chiodo, L.; Kudera, S.; Cingolani, R.; Krahne, R.; Manna, L. Synthesis and Micrometer-Scale Assembly of Colloidal CdSe/CdS Nanorods Prepared by a Seeded Growth Approach. *Nano Lett.* **2007**, 7 (10), 2942–2950.

(38) Okazaki, Y.; Ryu, N.; Buffeteau, T.; Pathan, S.; Nagaoka, S.; Pouget, E.; Nlate, S.; Ihara, H.; Oda, R. Induced Circular Dichroism of Monoatomic Anions: Silica-Assisted transfer of Chiral Environment from Molecular Assembled Nanohelices to Halide Ions. *Chem. Commun.* (*Cambridge, U. K.*) **2018**, *54* (73), 10244–10247.