Optically Active Luminescent Nanocrystals Complexed with Chiral Silica Nanoribbons

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Chirality is the geometric property which cannot be superimposed on its mirror image by any combination of rotation and translations. Chiral materials show special optical activity which can have different interaction with different handedness of circularly polarized light. Optical activity (OA) observed from chiral materials could be classified into three contributions. a) Absorption and emission based OA[1-3]; b) Refraction based OA[4]; c) Elastic scattering or Non-Elastic Raman scattering based OA.[5-11] Absorption and emission based OA is the difference of absorption or emission of left-handed (LH) and right-handed (RH) circular polarized (CP) light. Absorption based OA (circular dichroism: CD) has been widely studied, such as gold and silver metal plasmonic absorption OA[12, 13], electronic transition OA[14, 15] and vibrational OA[16]. Emission based OA corresponds to circularly polarized luminescence (CPL)[17, 18]. Refraction based OA (circular birefringence) comes from the difference of the velocities of LH-CP light and RH-CP light which pass through the OA medium, which is determined by the different refractive indices of the material for the RH- and LH-CP light.

Semiconductor nanocrystals (SNCs) exhibit excellent photoelectric properties, such as high photoluminescence quantum yield, size-tunable and narrow emission spectra, wide absorption range which have been widely used in solar cells, light-emitting diodes (LED), and display.[19-21] Recently, chirality induction to SNCs has attracted lots of attention due to their chiral-induced spin selectivity (CISS) effect which has shown prospective applications in biological electron transfer, enantioselective separation, and asymmetric catalysis as well as spintronics.[22-24] In general, chirality generation in nanocrystals (NCs) can be roughly classified into four approaches, such as a) coordination of chiral ligands;[14, 25] b) chiral lattice;[26, 27] c) chiral shape;[27-30] and d) chiral self-organization.[31-34] Optical activity of SNCs induced by chiral ligands are most widely studied since 2007[35], the first reported optical activity of CdS quantum dots (QDs) capped with D- or L-penicillamine. In 2009, Nakashima[15] reported the chirality memory effects on CdTe QDs where the chiral nature of the QDs was maintained after the ligands were exchanged with achiral ones. The magnetic, electrical, and optical properties of SNCs depend on their size, shape, and crystals structure. In 2011, Tang[36] and Markovich[37] simultaneously reported that the CdSe QDs combined with chiral ligands show the optical activity which depends on the QDs' size (dissymmetry 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 the QDs.[14, 38, 39] In 2013, Balaz[1] 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[39] reported that the chiral ligand concentration and binding mode have an important effect on the g-factor with a 10 times difference. In 2018, Tang[25] reported that the CdSe nanoplatelets with wurtzite (hexagonal) and zincblende (cubic) crystal structure combined with L/D cysteine shown 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[38] reported that the CdSe rods with different aspect ratio having L/D cysteine ligands show different g-factor. 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 hampered the chirality induction.[40] Recently, core-shell structured CdSe/CdS with various morphologies such as quantum rods[41], tadpoles[42] also have been reported which could enhance the chirality induction compared to core-shell QDs. Chirality induction by chiral building block system also has been widely studied in recent decades, especially for all organic self-assembly,[43, 44] organic and inorganic hybrid self-organization such as plasmonic gold nanoparticles and nanorods.[45, 46] While the self-organization with organic molecules suffers limited organization stability with external parameters such as temperature, solvent, salinity or pH,[33, 34] the alternative inorganic chiral self-organization system is still at an emerging point to get stable self-organization system. Chirality induction by chiral shape and chiral lattice mainly focused on the HgS NCs or gold nanoparticles.[26, 47] The chiral lattice or chiral shape of NCs were mainly obtained with the help of chiral ligands and result in large CD signals with dissymmetric g-factor up to 10^{-2}, however, no CPL was reported so far. It would be promising to obtain the chiral shaped NCs with both CD and CPL signals.

In this thesis, the aims of project are to endow chirality to SNCs with both CD and CPL signals by the SNCs' self-organization on the surface of inorganic chiral silica ribbons or their chiral shape growth inside hollow silica ribbons. In this project, the chiral hollow silica ribbons are the chiral source to endow chirality to NCs. The scattering chiral properties of silica ribbons had been discussed in detail, and the magnitude of scattering dissymmetric g-factor is higher than 10^{-2}. Then chirality had been endowed to NCs by their self-organization on the surface of silica ribbons, and the magnitude of absorbance and emission dissymmetric g-factor is higher than 10^{-3}. Tunable optically active NCs have been achieved by tuning the NCs size, shape, silica templates, and drying conditions. Besides, chiral shaped NCs have been achieved by in-situ growth inside hollow silica ribbons with high g-factor up to 10^{-2}.

Silica helical/twisted ribbons have a chiral shaped structure, which might have different interaction with different handedness of circularly polarized light. While silica shows big band gap which have no absorbance and emission in UV-vis range. However, it has absorbance in IR range and scattering in UV range. The vibrational circular dichroism (VCD) of silica ribbons has been studied before, while the scattering CD is still lack. Indeed, the right-handed silica ribbons show positive scattering CD signals, while left-handed silica ribbons show negative scattering CD signals when the incident circularly polarized light perpendicular with the silica ribbons. Silica helical ribbons show larger scattering CD (scattering g-factor up to 10^{-2}) than the silica twisted ribbons. It should be noted that, the film composed of the silica ribbons and the NCs mixture (without grafting) does not show any CD signals in the NCs absorption range, while the scattering CD signals decreased due to the impregnation of the NCs which weaken the chiral structure of the silica ribbons. If the silica ribbons and NCs are separated, it does not show any changes in the scattering CD signals. That valuable information would be useful for the related functionalized materials design.

The perovskite nanocrystals (PNCs) $CsPbBr_3$ were grafted on the surface of silica helical ribbons by a ligand exchange method. In suspension, three different results were observed as follows: 1) When isolated PNCs were grafted randomly on the surface of left- and right-handed silica helical ribbons, no CD was observed in suspension; 2) When PNCs were grafted with oriented attachment, PNCs grew along with the silica helical ribbons, and mirror-image CD signals were observed from PNCs-R/L-silica helical ribbons in suspension. 3) When further growth of PNCs for full coverage on the silica surface was performed, partial alignment of PNCs-R/L-silica helical ribbons was confirmed, and strong apparent CD signals were observed due to the LD and vortex flow. Even though PNCs grafted silica helical ribbons do not show any observable optical activity in suspension. After drying on the substrates to form films, strong CD and CPL signals are observed with the dissymmetric factor of $> 6*10^{-3}$. Both of solvated and dried TEM images show densely attached PNCs on the surface of the helical ribbons. However, for the solvated helical ribbons, the PNCs show a thicker and swollen layer around the silica helical ribbons without detectable helical organization probably with strongly solvated ligands. On the other hand, for the dried helical ribbons, the PNCs are closely attached on the surface, suggesting ligands collapse and a higher interaction between the adjacent NCs, which may induce higher self-organization with a 3-dimensional spiral arrangement of the PNCs along with the inorganic chiral silica helical ribbons. Grazing-incidence small angle X-ray scattering (GISAXS) confirms a correlation between PNCs for the dried samples, which does not exist for solvated samples. Coupled dipole method (CDM) simulation confirms that for the dielectric nanoparticles such as PNCs, the correlation between the particles to "feel" the chirality, the inter-particle distances need to be very close to each other with good alignment, which is likely why solvated samples with larger particle distances with much less ordered organization do not show any detectable CD. The samples dried at 4 °C (with slower drying) show stronger CD signals than those dried at 20 °C (faster drying), which is probably due to the closer packing originating from the slower film drying. The films show excellent photostability in their absorbance and CD properties, however, lose significantly their emissivity upon heating up to 80 °C. Consequently, this Chapter confirms that the self-organization of NCs on the surface of silica helical ribbons is the key for the chirality induction.

After that, a full view of the chirality induction by quantum dots (QDs) or quantum rods (QRs) chiral arrangement on the inorganic silica ribbons was discussed. The QDs-silica helical ribbons film was optimized in terms of the QDs grafting density. The g-factor is increased with the QDs grafting density. The QDs-silica helical ribbons drying temperature effect and solvent effect on the optical activity of the obtained materials have been studied. Lower temperature and lower vapor pressure solvent result in remarkable optical activities with dissymmetric g-factor $1.2*10^{-3}$ (Octane as solvent and evaporated at 4 °C) and $0.65*10^{-3}$ (Octane as solvent and evaporated at 20 °C). It was also found that the QDs self-organization would be hindered by applied PMMA or enhanced by annealing. The QDs with different sizes and different crystal structures have also been grafted on the silica helical/twisted ribbons. QDs with helical arrays show stronger optical activities than the twisted array. Also high fluorescence core-shell QDs and QRs have been grafted on the silica helical ribbons. The core-shell structured QDs and QRs also show optically active properties though they have smaller g-factor as compared with those of bare CdSe QDs. The QRs trend to tip grafting on the surface of silica twisted ribbons in suspension. While after drying in a film state, the QRs grafting models are modified depending on the length of QRs due to the drying effect. QRs with tip grafting or side grafting show reversed CD spectra. While with QRs length increasing, the QRs-silica twisted ribbons show strong LD which affects the CPL measurement. The chirality induction by chiral self-organization with solvent evaporation technology would be very promising in the future commercial photoelectric application to address some energy issues, such as chiral catalysis and spintronics.

The chiral shape of PNCs assisted by the hollow silica ribbons *via* supersaturated recrystallization methods has been successfully prepared by two ways. Both of the one-step method and two-step method show remarkable optically active properties. The one-step method is to drop-cast the mixture of ions and silica ribbons precursor and drying, while the two-step method is to drop-cast the silica ribbons and drying first, then drop-cast the ions precursor and drying. While the two-step method shows a larger g-factor and easier controlling of the ratio of the silica and the precursor ions as compared with those of the one-step method. The left- and right-handed chiral PNCs prepared by two-step method show strong CD and CPL mirror images and the dissymmetric g-factor is up to $2*10^{-2}$. Both of the ratios of the silica and the precursor ions and the temperature for the solvent evaporation affect crucially for the PNCs growth inside and outside the hollow silica ribbons. The g-factor decreased a lot when the hollow silica ribbons was calcined at 900 °C due to the modification of the silica surface state which might hinder the penetration of the precursor ions into the hollow silica ribbons. For the mixed halide precursor ions, yellow nonperovskite nanocrystal growth inside the hollow silica helical ribbons was confirmed and those materials show strong CD while no emission was observed. The relative larger g-factor of chiral shaped PNCs prepared inside the hollow silica ribbons would enrich the chiral group of PNCs which can be beneficial to their applications.

In conclusion, chirality has been succeeded induced to NCs by self-organization or chiral shape of NCs. For the NCs self-organization on the surface of silica ribbons, the key point is the drying of NCs-silica ribbons suspension which result in NCs densification and self-organized. The whole process can be described as below, NCs preparation, silica ribbons preparation, NCs combined with silica ribbons, NCs-silica ribbons in suspension (no chirality induction), solvent evaporation (NCs self-organization on the surface of silica ribbons), and NCs-silica ribbons film (strong chirality induction). To systematically understand the chirality induction process, the NCs, silica ribbons, combination, and drying process can be modified and tunable chiroptical properties were obtained. For the chiral shape of NCs preparation, the main steps are ions and silica precursor preparation, and solvent evaporation. The two-step method prepared chiral PNCs to show better g-factor and easier to control the ratio of silica and ions precursors compared with the one-step method. The silica ribbons concentration, silica ribbons surface modification, ions halide composition, and drying temperatures were discussed in detail.

References

1. 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), 11094-110102.
2. Tanaka, H.; Inoue, Y.; Mori, T., Circularly Polarized Luminescence and Circular Dichroisms in Small Organic Molecules: Correlation between Excitation and Emission Dissymmetry Factors. *ChemPhotoChem* **2018,** *2* (5), 386-402.
3. Gao, X.; Han, B.; Yang, X.; Tang, Z., Perspective of Chiral Colloidal Semiconductor Nanocrystals: Opportunity and Challenge. *J. Am. Chem. Soc.* **2019,** *141* (35), 13700-13707.
4. Moxon, J. R. L.; Renshaw, A. R.; Tebbutt, I. J., The simultaneous measurement of optical activity and circular dichroism in birefringent linearly dichroic crystal sections. II. Description of apparatus and results for quartz, nickel sulphate hexahydrate and benzil. *J. Phys. D: Appl. Phys.* **1991,** *24* (7), 1187-1192.
5. Robbie, K.; Broer, D. J.; Brett, M. J., Chiral nematic order in liquid crystals imposed by an engineered inorganic nanostructure. *Nature* **1999,** *399* (6738), 764-766.
6. Schellman, J. A., Circular dichroism and optical rotation. *Chem. Rev.* **1975,** *75* (3), 323-331.
7. Tinoco, I.; Maestre, M. F.; Bustamante, C., Circular dichroism in samples which scatter light. *Trends Biochem. Sci* **1983,** *8* (2), 41-44.
8. Bustamante, C.; Tinoco, I., Jr.; Maestre, M. F., Circular differential scattering can be an important part of the circular dichroism of macromolecules. *Proc Natl Acad Sci U S A* **1983,** *80* (12), 3568-3572.
9. Shopsowitz, K. E.; Qi, H.; Hamad, W. Y.; Maclachlan, M. J., Free-standing mesoporous silica films with tunable chiral nematic structures. *Nature* **2010,** *468* (7322), 422-425.
10. Ottaway, C. A.; Wetlaufer, D. B., Light-scattering contributions to the circular dichroism of particulate systems. *Arch. Biochem. Biophys.* **1970,** *139* (2), 257-264.
11. van Popta, A. C.; Sit, J. C.; Brett, M. J., Optical properties of porous helical thin films. *Appl. Opt.* **2004,** *43* (18), 3632-3639.
12. Gautier, C.; Burgi, T., Chiral inversion of gold nanoparticles. *J. Am. Chem. Soc.* **2008,** *130* (22), 7077-7084.

13. Li, T.; Park, H. G.; Lee, H.-S.; Choi, S.-H., Circular dichroism study of chiral biomolecules conjugated with silver nanoparticles. *Nanotechnology* **2004,** *15* (10), S660-S663.
14. Choi, J. K.; Haynie, B. E.; Tohgha, U.; Pap, L.; Elliott, K. W.; Leonard, B. M.; Dzyuba, S. V.; Varga, K.; Kubelka, J.; Balaz, M., Chirality Inversion of CdSe and CdS Quantum Dots without Changing the Stereochemistry of the Capping Ligand. *ACS Nano* **2016,** *10* (3), 3809-3815.
15. 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.
16. 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.
17. Kumar, J.; Nakashima, T.; Tsumatori, H.; Kawai, T., Circularly Polarized Luminescence in Chiral Aggregates: Dependence of Morphology on Luminescence Dissymmetry. *J Phys Chem Lett* **2014,** *5* (2), 316-321.
18. Chen, W.; Zhang, S.; Zhou, M.; Zhao, T.; Qin, X.; Liu, X.; Liu, M.; Duan, P., Two-Photon Absorption-Based Upconverted Circularly Polarized Luminescence Generated in Chiral Perovskite Nanocrystals. *J Phys Chem Lett* **2019,** *10* (12), 3290-3295.
19. De Yoreo, J. J.; Gilbert, P. U.; Sommerdijk, N. A.; Penn, R. L.; Whitelam, S.; Joester, D.; Zhang, H.; Rimer, J. D.; Navrotsky, A.; Banfield, J. F.; Wallace, A. F.; Michel, F. M.; Meldrum, F. C.; Colfen, H.; Dove, P. M., CRYSTAL GROWTH. Crystallization by particle attachment in synthetic, biogenic, and geologic environments. *Science* **2015,** *349* (6247), aaa6760.
20. Dong, Q.; Fang, Y.; Shao, Y.; Mulligan, P.; Qiu, J.; Cao, L.; Huang, J., Solar cells. Electron-hole diffusion lengths > 175 mum in solution-grown CH3NH3PbI3 single crystals. *Science* **2015,** *347* (6225), 967-970.
21. Shi, D.; Adinolfi, V.; Comin, R.; Yuan, M.; Alarousu, E.; Buin, A.; Chen, Y.; Hoogland, S.; Rothenberger, A.; Katsiev, K.; Losovyj, Y.; Zhang, X.; Dowben, P. A.; Mohammed, O. F.; Sargent, E. H.; Bakr, O. M., Solar cells. Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals. *Science* **2015,** *347* (6221), 519-522.
22. Bloom, B. P.; Liu, R.; Zhang, P.; Ghosh, S.; Naaman, R.; Beratan, D. N.; Waldeck, D. H., Directing Charge Transfer in Quantum Dot Assemblies. *Acc. Chem. Res.* **2018,** *51* (10), 2565-2573.
23. 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.
24. Naaman, R.; Paltiel, Y.; Waldeck, D. H., Chiral molecules and the electron spin. *Nature Reviews Chemistry* **2019**, *3* (4), 250-260.
25. 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.

26. Ben-Moshe, A.; Govorov, A. O.; Markovich, G., Enantioselective synthesis of intrinsically chiral mercury sulfide nanocrystals. *Angew. Chem. Int. Ed. Engl.* **2013,** *52* (4), 1275-1279.
27. Wang, P. P.; Yu, S. J.; Govorov, A. O.; Ouyang, M., Cooperative expression of atomic chirality in inorganic nanostructures. *Nat Commun* **2017,** *8*, 14312.
28. Wang, P. P.; Yu, S. J.; Ouyang, M., Assembled Suprastructures of Inorganic Chiral Nanocrystals and Hierarchical Chirality. *J. Am. Chem. Soc.* **2017,** *139* (17), 6070-6073.
29. Ben-Moshe, A.; Wolf, S. G.; Bar Sadan, M.; Houben, L.; Fan, Z.; Govorov, A. O.; Markovich, G., Enantioselective control of lattice and shape chirality in inorganic nanostructures using chiral biomolecules. *Nat Commun* **2014,** *5*, 4302.
30. Rukhlenko, I. D.; Baimuratov, A. S.; Tepliakov, N. V.; Baranov, A. V.; Fedorov, A. V., Shape-induced optical activity of chiral nanocrystals. *Opt. Lett.* **2016,** *41* (11), 2438-2441.
31. 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. Engl.* **2011,** *50* (24), 5499-5503.
32. Kuzyk, A.; Schreiber, R.; Fan, Z.; Pardatscher, G.; Roller, E. M.; Hogele, A.; Simmel, F. C.; Govorov, A. O.; Liedl, T., DNA-based self-assembly of chiral plasmonic nanostructures with tailored optical response. *Nature* **2012,** *483* (7389), 311-314.
33. Shi, Y.; Duan, P.; Huo, S.; Li, Y.; Liu, M., Endowing Perovskite Nanocrystals with Circularly Polarized Luminescence. *Adv. Mater.* **2018,** *30* (12), e1705011.
34. 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.
35. Moloney, M. P.; Gun'ko, Y. K.; Kelly, J. M., Chiral highly luminescent CdS uantum dots. *Chem Commun (Camb)* **2007,** (38), 3900-3902.
36. Zhou, Y.; Zhu, Z.; Huang, W.; Liu, W.; Wu, S.; Liu, X.; Gao, Y.; Zhang, W.; Tang, Z., Optical coupling between chiral biomolecules and semiconductor nanoparticles: size-dependent circular dichroism absorption. *Angew. Chem. Int. Ed. Engl.* **2011,** *50* (48), 11456-11459.
37. Moshe, A. B.; Szwarcman, D.; Markovich, G., Size dependence of chiroptical activity in colloidal quantum dots. *ACS Nano* **2011,** *5* (11), 9034-9043.
38. 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.* **2017,** *139* (25), 8734-8739.
39. Kuznetsova, V. A.; Mates-Torres, E.; Prochukhan, N.; Marcaste, 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.

40. Purcell-Milton, F.; Visheratina, A. K.; Kuznetsova, V. A.; Ryan, A.; Orlova, A. O.; Gun'ko, Y. K., Impact of Shell Thickness on Photoluminescence and Optical Activity in Chiral CdSe/CdS Core/Shell Quantum Dots. *ACS Nano* **2017,** *11* (9), 9207-9214.
41. 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.
42. 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.
43. Liu, M.; Zhang, L.; Wang, T., Supramolecular Chirality in Self-Assembled Systems. *Chem. Rev.* **2015,** *115* (15), 7304-7397.
44. 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.
45. 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 switchable circular dichroism. *Nat Commun* **2013,** *4*, 2948.
46. Hentschel, M.; Schaferling, M.; Duan, X.; Giessen, H.; Liu, N., Chiral plasmonics. *Sci Adv* **2017,** *3* (5), e1602735.
47. Lee, H. E.; Ahn, H. Y.; Mun, J.; Lee, Y. Y.; Kim, M.; Cho, N. H.; Chang, K.; Kim, W. S.; Rho, J.; Nam, K. T., Amino-acid- and peptide-directed synthesis of chiral plasmonic gold nanoparticles. *Nature* **2018,** *556* (7701), 360-365.