

Spectroscopic studies of chiral perovskite nanocrystals

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As an emerging type of optically active material, semiconductor nanocrystals (NCs) stabilized by chiral molecules have attracted much attention. Owing to the wide range of potential applications of chiral perovskite NCs, the development of these materials is of great importance, but there has been a lack of relevant studies. Here, we describe an investigation of the properties of chiral perovskite NCs obtained using post-synthetic ligand exchange (achiral ligand/chiral ligand). These are found to exhibit mirror-image circular dichroism spectra. It is the chirality of the ligand (enantiomeric 1,2-diaminocyclohexane, DACH) that is most likely responsible for the induction of chiroptical activity in these NCs. Furthermore, their chiroptical properties and the corresponding mechanisms are found to depend strongly on the amount of capping ligand. When excess DACH is used to cap the surface of the NCs, their chiroptical properties are induced mainly by aggregation of DACH on the surface in a chiral pattern. In contrast, when small amounts of DACH are used for the capping, it is mainly surface distortion (or defects) and electronic interaction mechanisms that contribute to the chiroptical behavior of the NCs. In both cases, the anisotropy factors of the NCs are of the order of 10^{-3} , which is comparable to or larger than the values reported for other chiral semiconductor and metal NCs. This work opens the door toward further understanding of chiroptical perovskite NCs and their potential applications. *Published by AIP Publishing.*

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Chirality in various materials is a very active research topic with a broad range of promising applications, and the preparation of chiral materials with tunable chiroptical properties is of great practical importance.¹ Compared with simple organic molecules, chiral semiconductor nanocrystals (NCs) have been investigated only relatively recently, and to only a limited extent.^{2–4} To date, several chiral optically active NCs, for example, CdSe and CdS, have been synthesized, and some of these show potential for technological application.¹ For instance, CdSe and CdS NCs prepared in the presence of chiral ligands exhibit a chiral shell and an achiral core.^{5–7} More significantly, circularly polarized luminescence (CPL) has been observed in chiral NCs.^{3,8} From the viewpoint of applications, the development of diverse chiral inorganic nanostructures is extremely important. Several chiral semiconductor NCs have been developed, but there is still a great need for the development of promising chiral semiconductor NCs with chiroptical properties suitable for various practical uses.

Recently, perovskite NCs have attracted considerable attention because of their wide range of applications in nonlinear optics, lasers, light-emitting diodes, photovoltaics, and photon detection.^{9–13} Therefore, a great deal of effort has been devoted to synthesizing perovskite NCs and investigating their photophysical properties as well as their potential applications in optoelectronic devices. Although a paper has very recently been published on the chiroptical properties of

organic-inorganic hybrid perovskite films,¹⁴ there are no reports in the literature concerning the chiroptical properties of perovskite NCs. The development of chiral perovskite NCs would be of great importance in view of the number of potential applications of these materials.

Meanwhile, given the limited number of commercially available chiral thiols (e.g., glutathione, penicillamine, and cysteine) that have previously been used to obtain chiral semiconductor NCs,¹ there is a critical need to widen the range of chiral stabilizers. Owing to the strong chiral properties of 1,2-diaminocyclohexane (DACH), we utilize this molecule as an alternative chiral stabilizer to obtain chiral perovskite NCs. On the basis of previous work, it is known that the interactions between chiral stabilizers and NCs have a great influence on the chirality of the latter.¹⁵ In this work, we report on perovskite NCs capped with enantiomeric DACH, which is expected to act as a chiral stabilizer through a coordination interaction with the NC surface. This strong interaction between the DACH and the perovskite NCs allows transmission of chirality from the former to the latter.

Perovskite [CsPb(I/Br)₃] NCs capped with oleylamine (OA) were fabricated following procedures described in the literature.¹⁶ The perovskite NCs appear to be nanocubes with an average size of ~ 17 nm, as determined by transmission electron microscopy (TEM) analysis [Fig. 1(a)]. The clear lattice structure observed by high-resolution TEM (HR-TEM) reveals the high quality of the prepared perovskite NCs [Fig. 1(b)]. Room-temperature photoluminescence (PL) emission of NCs peaked at 580 nm with a quantum yield of 30% [Fig. 1(c)].

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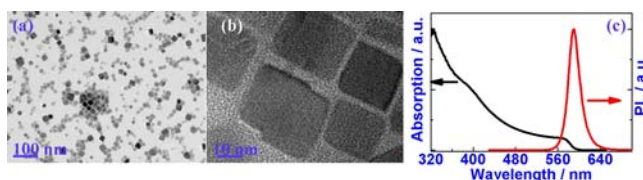


FIG. 1. Typical TEM (a) and HR-TEM (b) images of OA-stabilized perovskite NCs. (c) Absorption and PL spectra ($\lambda_{\text{ex}} = 365$ nm) of perovskite NCs.

Chiroptical perovskite NCs capped with *R*- and *S*-DACH were prepared. In order to confirm the influence of the amount of ligand on the chiroptical properties of the NCs, we added different equivalents of chiral stabilizer to NC solutions. Different masses of (1*R*, 2*R*)- or (1*S*, 2*S*)-DACH were first dissolved in 2.5 ml *n*-hexane and then added to 500 μ l of a solution of perovskite NCs (5 mg/ml). Different mass ratios of DACH to NCs (6.8 or 0.08) were used. The mixture was exposed to microwave radiation and stirred at 100 °C for 30 min (Fig. 2). With the aid of this microwave irradiation, smooth progress of the ligand exchange can be ensured in a very short time. The mixed solution was then cooled to room temperature, and a suspension was obtained. The crude DACH-capped NCs were purified by precipitation. The ligand exchange was confirmed by Fourier-transform infrared spectroscopy (FTIS).

The circular dichroism (CD) spectrum can reveal the chiral properties of NCs in the ground state. For a high equivalent of chiral stabilizer, the *R*- and *S*-DACH-capped NCs (henceforth abbreviated as *R*- and *S*-DACH-NCs) exhibited mirror-image CD signals. Negative and positive signals were observed at short wavelength (247 nm) for the *R*- and *S*-DACH-NCs, respectively (Fig. 3). By contrast, the pure *R*- and *S*-DACH solutions showed reversed CD signals at a shorter wavelength of 223 nm, confirming that the peaks exhibited by the DACH-capped NCs solutions do not arise from the chirality of the free ligands.

In order to reveal the chiral interactions more clearly, the anisotropy factor g_{abs} of the NCs was estimated. This factor is defined as

$$g_{\text{abs}} = \frac{\Delta A}{A} = \frac{CD(\text{mdeg})}{32980A},$$

where ΔA is the difference in the sample's absorbance between left and right circularly polarized light and A is its absorbance of unpolarized light.¹⁷ The maximum value of $|g_{\text{abs}}|$ was found to be about 1.5×10^{-3} at 247 nm, which is

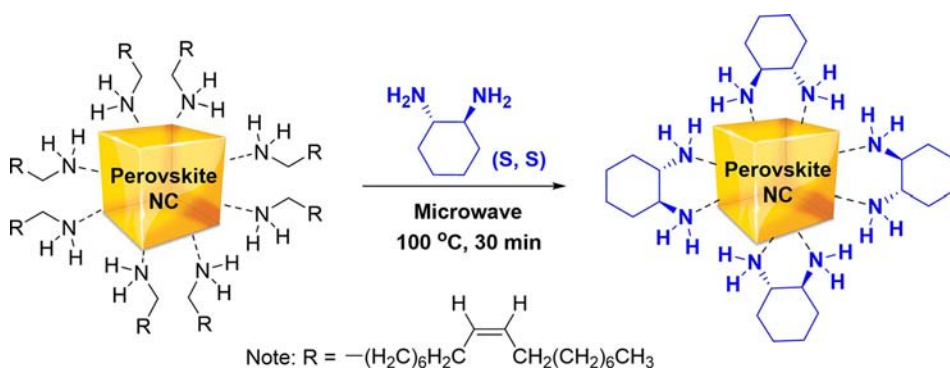


FIG. 2. Ligand exchange on an OA-capped perovskite NC using pure enantiomers of DACH: OA-capped perovskite NC in *n*-hexane (left) and *S*-DACH-capped perovskite NC in *n*-hexane obtained by ligand exchange (right).

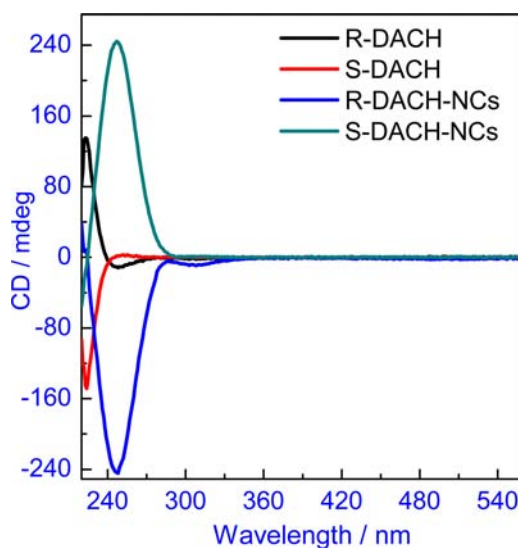


FIG. 3. CD spectra of high concentrations of DACH and of perovskite NCs stabilized with an excess amount of DACH. The mass ratio of DACH to NCs was 6.8.

comparable to or larger than the values reported for other chiral semiconductor and metal NCs.^{18,19}

Explanations for the origin of chirality in NCs can be broadly divided into three classes:^{1,20} (i) the whole NC is encouraged to crystallize with a chiral space group (the chiral core model); (ii) NCs have an achiral core and a chiral surface due to chiral distortion or ligand aggregation in a chiral pattern; and (iii) chiroptical effects are induced in achiral NCs by electronic interactions between chiral ligands and the NCs, i.e., through orbital hybridization or short-range dipolar Coulomb interaction. Most recent publications have rejected (i) as an explanation of the chirality of NCs, although the recent discovery of chirality in CdSe/ZnS NCs due to defects in the chiral core may lead to reconsideration of this.²¹ Since our NCs were synthesized in the presence of achiral ligands, (i) can be also excluded.

Heating of the chiral NCs solution from 0 °C to 80 °C resulted in a decrease in the CD signal intensity by 36% (Fig. S1 in the supplementary material), suggesting that the CD behavior of NCs in the presence of excess equivalent of chiral stabilizer should be attributed to aggregation of ligand in a chiral pattern onto the NC surface, and this was further confirmed by the TEM images. From these images [Figs. 4(a) and 4(c)], it can be clearly seen that the average size of DACH-capped NCs (~ 100 nm) is much greater than that of

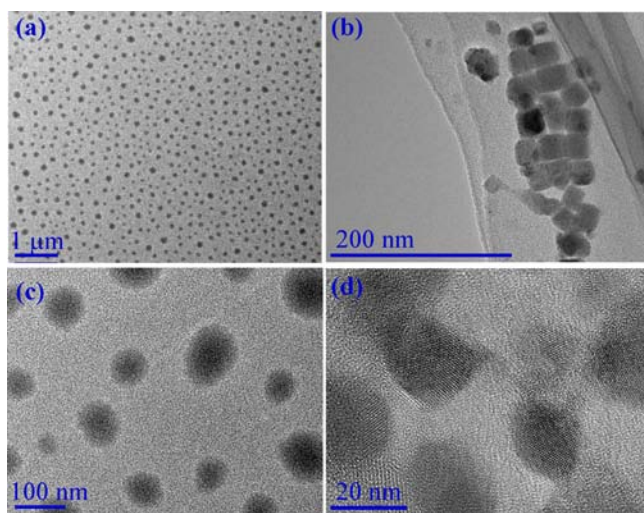


FIG. 4. Typical TEM and HR-TEM images of perovskite NCs stabilized by different amounts of DACH: in (a) and (c) the mass ratio of DACH to NCs is 6.8, while in (b) and (d) it is 0.08.

OA-capped NCs (~ 17 nm), when an excess equivalent of chiral stabilizer was used. Meanwhile, it should be noted that other effects will also be present in this case, such as chiral distortion and exciton coupling, although they will not play a dominant role. This will be further confirmed by the following experimental results.

In order to further clarify the potential interaction mechanisms between the chiral stabilizer and the NCs, we have investigated the chiroptical properties of NCs capped with a small amount of DACH. In this case, the mass ratio of DACH to NCs is 0.08. Clear differences could be observed between NCs capped with an excess of DACH and those capped with a small amount. Again, the NCs capped with a small amount of enantiomeric DACH exhibited mirror-image CD spectra, which are expected from the *R*- and *S*-relationship. Meanwhile, the spectra clearly show the appearance of other CD bands and a more intense CD signal at longer wavelengths. It can also be seen that the CD spectra of *R*- and *S*-DACH (signals above 240 nm) shown in Figs. 3 and 5 are not exactly the same, which can be attributed to the effect of excess DACH on aggregation in Fig. 3. The CD spectra of NCs differ from those of the free ligand, and there is no CD signal in the region of the first excitonic transition band, indicating that the observed CD signals cannot be attributed to the free ligand or to the first excitonic transition in the NC core. *R*-DACH-NCs display a strong trisignate CD feature with negative CD signals at 290 and 400 nm and a positive CD signal at 333 nm (Fig. 5). Obviously, the amount of capping ligand could greatly influence the CD spectra of chiral perovskite NCs. It is postulated that the different CD spectra in Figs. 3 and 5 originate from different mechanisms of interaction between the chiral stabilizer and the NCs. This phenomenon provides the possibility to further modulate the chiroptical properties of NCs by changing the amount of capping ligand. Meanwhile, the maximum value of $|g_{\text{abs}}|$ was found to be about 1.1×10^{-3} for *R*- and *S*-DACH-capped perovskite NCs. The values are also comparable to or larger than those for previously observed chiral-ligand-induced CD in semiconductor NCs.¹⁸

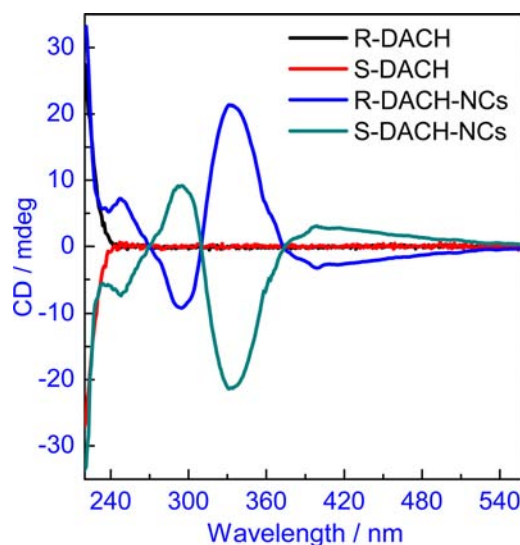


FIG. 5. CD spectra of low concentrations of DACH and of perovskite NCs stabilized with small amounts of DACH. The mass ratio of DACH to NCs was 0.08.

To confirm whether the CD signals were induced by aggregation in the case of small amounts of chiral stabilizer, we also obtained temperature-dependent CD spectra on *R*-DACH-NCs. The results indicated that the CD signal intensity of the NCs dropped by 10% when the temperature increased from 0 °C to 80 °C (Fig. S2 in the [supplementary material](#)). From the TEM images [Figs. 4(b) and 4(d)], it can be seen that the average size of *R*-DACH-NCs is almost the same as that of OA-capped NCs, and the core crystal structure remains intact. Furthermore, for perovskite NCs capped with small amounts of DACH, it was found that the CD signal intensity was proportional to the absorption intensity when the solution was diluted from 20% to 150%. Based on these results, we ruled out the aggregation of DACH in a chiral pattern as a significant contributor to the CD activity.²²

To gain further insight into the origin of the observed CD activity, we performed an additional experiment on the *S*-DACH-capped NCs. If the chiroptical properties of NCs originate from the DACH, then its removal should result in loss of the NCs' surface chirality.²³ We used acetyl chloride to react with the *S*-DACH on the NCs. In order to determine whether all chiral ligands had been removed, FTIS measurements were performed. No obvious signals of DACH were detected, and therefore it can be concluded that the contribution of DACH to the CD signals of NCs treated by acetyl chloride can be neglected. More importantly, the NCs thus obtained gave a CD profile almost identical to that of the original enantiomeric DACH-capped NCs above 260 nm, even though there was no chiral ligand on the NC surface (Fig. S3 in the [supplementary material](#)). Therefore, it can be concluded that the chiral structure can be partially retained by the NCs themselves.²⁴ Meanwhile, we also noticed that the CD spectrum of these NCs was very different from that of the DACH-capped NCs, especially in the wavelength range 260–530 nm. Therefore, it can be concluded that there are at least two mechanisms contributing to the observed CD behavior: surface distortion (or defects) and electronic interactions. The presence of the former mechanism was

confirmed by measurements of PL spectra. It was found that the emission of NCs was almost fully quenched in the DACH-capped NC solution (Fig. S4 in the [supplementary material](#)). As is well known, changes in PL intensity can be due to surface states^{25–27} or to charge or energy transfer.^{28,29} However, a mechanism involving charge or energy transfer can be excluded in the present context owing to the lower bandgap of perovskite NCs and the unchanged lifetime of the chiral stabilizer in the presence of NCs (Fig. S5 in the [supplementary material](#)). Therefore, we argue that the strong quenching of NC PL at low equivalents of stabilizer can be attributed to the surface states introduced in a perovskite NC when the chiral DACH binds to the outermost Cs or Pb atoms of the NC. Meanwhile, the crystal symmetry of the NC surface is destroyed. This electronic interaction mechanism could be confirmed by time-dependent density functional theory calculations, which are now in progress.

Based on the above discussion, we propose that two factors contribute to the CD behavior of perovskite NCs capped with small amounts of DACH: (1) chiral surface distortion of the NCs induced by the capping DACH and (2) electronic interactions between the DACH and the perovskite NCs. It should be noted that perovskite NCs capped with excess amounts of DACH exhibit similar PL behavior, with quenching of NC PL and the PL lifetime both being independent of the amount of DACH, indicating that chiral distortion and electronic interactions also contribute to the observed CD behavior (Fig. 3). The reason why distortion is not the main mechanism for NCs capped with excess amounts of DACH is still unclear, but it is possible that the force between the inner DACH molecules and the NC surface and that between the inner and outer DACH molecules are canceled out to a large extent.

In conclusion, we have reported a simple way to obtain CsPb(I/Br)₃ NCs with good chiroptical activity. Both *R*- and *S*-DACH-capped perovskite NCs exhibited different mirror-image CD spectra between 220 and 530 nm in the cases of excess and small amounts of chiral stabilizer. More significantly, the CD behavior can be tuned by altering the amount of capping ligand, leading the way to the creation of intelligent materials with multiple chiroptical responses, as well as to other potential applications.

See [supplementary material](#) for CD spectra of *R*-DACH capped perovskite NCs at different temperature and of perovskite NCs with DACH removed, fluorescence spectra for perovskite NCs, *S*-DACH and *S*-DACH-NCs solutions, and fluorescence decay curves for DACH alone and *S*-DACH-NCs.

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- ¹W. Ma, L. Xu, A. F. de Moura, X. Wu, H. Kuang, C. Xu, and N. A. Kotov, *Chem. Rev.* **117**, 8041 (2017).
- ²M. P. Moloney, J. Govan, A. Loudon, M. Mukhina, and Y. K. Gun'ko, *Nat. Protoc.* **10**, 558 (2015).
- ³J. K. Choi, B. E. Haynie, U. Tohgha, L. Pap, K. W. Elliott, B. M. Leonard, S. V. Dzyuba, K. Varga, J. Kubelka, and M. Balaz, *ACS Nano* **10**, 3809 (2016).
- ⁴A. Ben-Moshe, A. Teitelboim, D. Oron, and G. Markovich, *Nano Lett.* **16**, 7467 (2016).
- ⁵U. Tohgha, K. K. Deol, A. G. Porter, S. G. Bartko, J. K. Choi, B. M. Leonard, K. Varga, J. Kubelka, G. Muller, and M. Balaz, *ACS Nano* **7**, 11094 (2013).
- ⁶A. Ben Moshe, D. Szwarcman, and G. Markovich, *ACS Nano* **5**, 9034 (2011).
- ⁷Y. Zhou, Z. Zhu, W. Huang, W. Liu, S. Wu, X. Liu, Y. Gao, W. Zhang, and Z. Tang, *Angew. Chem., Int. Ed.* **50**, 11456 (2011).
- ⁸M. Naito, A. K. Iwahori, M. Yamane, and I. Yamashita, *Angew. Chem., Int. Ed.* **49**, 7006 (2010).
- ⁹Y. Wang, X. Li, J. Song, L. Xiao, H. Zeng, and H. Sun, *Adv. Mater.* **27**, 7101 (2015).
- ¹⁰D. Amgar, S. Aharon, and L. Etgar, *Adv. Funct. Mater.* **26**, 8576 (2016).
- ¹¹Y. Lee, J. Kwon, E. Hwang, C.-H. Ra, W. J. Yoo, J.-H. Ahn, J. H. Park, and J. H. Cho, *Adv. Mater.* **27**, 41 (2015).
- ¹²Y. Wang, X. Li, X. Zhao, L. Xiao, H. Zeng, and H. Sun, *Nano Lett.* **16**, 448 (2016).
- ¹³Y. Wang, X. Li, V. Nalla, H. Zeng, and H. Sun, *Adv. Funct. Mater.* **27**, 1605088 (2017).
- ¹⁴J. Ahn, E. Lee, J. Tan, W. Yang, B. Kim, and J. Moon, *Mater. Horiz.* **4**, 851 (2017).
- ¹⁵R. Zhou, K. Wei, J. Zhao, and Y. Jiang, *Chem. Commun.* **47**, 6362 (2011).
- ¹⁶L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh, and M. V. Kovalenko, *Nano Lett.* **15**, 3692 (2015).
- ¹⁷X. Jin, J. Jiang, and M. Liu, *ACS Nano* **10**, 11179 (2016).
- ¹⁸X. Gao, X. Zhang, K. Deng, B. Han, L. Zhao, M. Wu, L. Shi, J. Lv, and Z. Tang, *J. Am. Chem. Soc.* **139**, 8734 (2017).
- ¹⁹J. Kumar, T. Kawai, and T. Nakashima, *Chem. Commun.* **53**, 1269 (2017).
- ²⁰L. Jing, S. V. Kershaw, Y. Li, X. Huang, Y. Li, A. L. Rogach, and M. Gao, *Chem. Rev.* **116**, 10623 (2016).
- ²¹M. V. Mukhina, V. G. Maslov, A. V. Baranov, A. V. Fedorov, A. O. Orlova, F. Purcell-Milton, J. Govan, and Y. K. Gun'ko, *Nano Lett.* **15**, 2844 (2015).
- ²²A. O. Govorov, Y. K. Gun'ko, and J. M. Slocik, *J. Mater. Chem.* **21**, 16806 (2011).
- ²³U. Tohgha, K. Varga, and M. Balaz, *Chem. Commun.* **49**, 1844 (2013).
- ²⁴T. Nakashima, Y. Kobayashi, and T. Kawai, *J. Am. Chem. Soc.* **131**, 10342 (2009).
- ²⁵Y. Wang, K. S. Leck, V. D. Ta, R. Chen, V. Nalla, Y. Gao, T. He, H. V. Demir, and H. Sun, *Adv. Mater.* **27**, 169 (2015).
- ²⁶M. Jones, S. S. Lo, and G. D. Scholes, *Proc. Natl. Acad. Sci. U.S.A.* **106**, 3011 (2009).
- ²⁷T. C. He, R. Chen, W. W. Lin, F. Huang, and H. D. Sun, *Appl. Phys. Lett.* **99**, 081902 (2011).
- ²⁸Q. Zhang, T. Atay, J. R. Tischler, M. S. Bradley, V. Bulović, and A. V. Nurmikko, *Nat. Nanotechnol.* **2**, 555 (2007).
- ²⁹T. He, Y. Gao, Y. Gao, X. Lin, R. Chen, W. Hu, X. Zhao, Y. Wang, H. V. Demir, Q. Fan, A. C. Grimsdale, and H. Sun, *Macromol. Chem. Phys.* **217**, 24 (2016).