Tuning optical properties of perovskite nanocrystals by supermolecular mercapto-β-cyclodextrin†

Qi-Le Li,a Wen-Xiu Lu,a Neng Wanb and Shou-Nian Ding*a

This study reports a host–guest interaction strategy for systematically manipulating the optical properties of cesium lead halide perovskite nanocrystals (CsPbBr3 NCs) by protectant-mediated mercapto-β-cyclodextrin (SH-β-CD). The fluorescence of CsPbBr3 NCs can be adjusted over 405-510 nm with the quantum yields (QY) maintained at 50–90%.

Metal halide perovskites have come under intense investigation in the last six years, owing to their super conversion efficiencies of about 15%–22% in solar cell applications.1,2 The majority of research has been devoted to organic–inorganic3 compounds, thin films,4 microcrystals and bulk single crystals. The study of their fully inorganic analogues, like cesium lead halide (CsPbX3, X = Cl, Br, I) NCs, has also received great attention since early 20155 initiated by Kovalenko and his coworkers.6,7 These CsPbX3 NCs exhibit bright fluorescence (FL) with narrow emission full width at half maxima (FWHM) of 12 to 40 nm and high quantum yields (QY) up to 90%. Zero-dimensional spherical quantum dots (QDs), one-dimensional CsPbX3 QDs8,9 and two dimensional nanowires or nanoplatelets10–12 were also synthesized. The combination of unique optical and electrical properties have made all-inorganic perovskites such as these attractive candidates for light-emitting devices (LEDs),13,14 low threshold lasers15,16 and fluorescent materials.17

The ability to systematically manipulate the optic, electronic, catalytic, magnetic and plasmonic properties of inorganic nanocrystals remains a significant goal of modern nanotechnology. Previous studies on colloidal nanocrystals have revealed that adjustment of their optical-physics have been so far realized mainly during the synthesis step by controlling the size, shape, and surface capping ligands. For instance, in order to get blue-green emission, the size of common metal chalcogenide quantum dots such as CdTe QDs or CdSe QDs needs to be extremely small (≤5 nm). Very recently, continuous and accurate tuning of the CsPbX3 NCs bandgap energies over the whole visible spectral region (FL peaks from 410 nm to 700 nm) was made achievable through post-synthetic ion-exchange (mixed halide Cl/Br and Br/I systems). However, all of the tuning methods so far reported have relied on ion-exchange to adjust optoelectronic properties, which drastically reduce the PL quantum yield (QY) from 90% to 10% for violet emission QDs.18–20 The increasing interest in perovskite nanocrystals stimulated us to develop alternative processes for tuning the optical properties of CsPbX3 NCs.

Cyclodextrins (CDs) are cyclic oligosaccharides with hydrophobic inner cavities and hydrophilic rims. They are usually used for phase transfer of nanomaterials between solvents with considerably different polarities via hydrophilic–hydrophobic or host–guest interactions.21,22 For our purpose, we added a certain amount of SH-β-CD into the colloidal CsPbBr3 NCs. Unfortunately, the intended phase transfer was not achieved, but the FL of CsPbBr3 NCs was evidently blue shifted. This result presented the possibility that SH-β-CD could be used as an alternative to chloride ions for tuning the optical properties of perovskite nanocrystals. To date, we have found no previous research regarding supramolecular modification of perovskite nanocrystals.

Herein, we report for the first time, a host–guest interaction strategy to manipulate the optical properties of all-inorganic perovskite CsPbBr3 NCs by wrapping SH-β-CD via the host–guest interaction between the cavity of cyclodextrin and the aliphatic chain of oleic acid (OA) or oleylamine (OLA) on the surface of the NCs. In comparison with ion-exchange method, the packaged CsPbBr3 NCs maintain extremely high FLQY of 50%–90% after wrapping with SH-β-CD. The distinguished violet emission CsPbBr3@SH-β-CD NCs are a favorable candidate for use in the photoelectric materials field.

The SH-β-CD encapsulated CsPbBr3 NCs were efficiently synthesized by trapping the aliphatic chains into the cavities.

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The FL emission spectra of colloidal CsPbBr\(_3\) NCs (Fig. 1A) can be tuned over half of the visible spectral region by adjusting the concentration of SH-β-CD that encapsulates the NCs. To confirm the surface coating effect of SH-β-CD on the optical properties of CsPbBr\(_3\) NCs, we performed a ligand-exchange experiment using glucose, glutathione (GSH), \(\text{S}_2\text{O}_3\) and β-CDs (Fig. 1B). With the addition of glucose or GSH, the optical emission of CsPbBr\(_3\) NCs was not shifted.

Moreover, the addition of β-CDs with a similar structure of the hydrophobic inner cavity to that of SH-β-CD could not change the FL emission. These results verified that neither the hydrosulfuryl group nor the cavity induces an emission shift individually. Furthermore, the addition of \(\text{S}_2\text{O}_3\) could quench the FL of CsPbBr\(_3\) NCs. The reason might be that unmatched anion exchange leads to a disincentive effect through the generation of high-density defects. In addition, the FL of the CsPbBr\(_3\) NCs was only slightly changed after the SH-β-CD cavities were filled with a variety of guest molecules (e.g. adamantane, phenyl, etc.), further demonstrating that the cavities play a vital role in the binding of SH-β-CD and CsPbBr\(_3\) NCs.

SH-β-CD is easily linked with CsPbBr\(_3\) NCs through the aliphatic chains of OA or OLA entrapped into the hydrophobic cavity. Fig. S1 (ESI†) depicts the typical Fourier transform infrared radiation (FT-IR) spectra of original CsPbBr\(_3\) NCs, SH-β-CDs and SH-β-CD capped CsPbBr\(_3\) NCs. The bands at 1128 and 1049 cm\(^{-1}\) can be assigned to a coupled stretch vibration, \(\nu(C–O/C–C)\), the strong band at 1189 cm\(^{-1}\) can be ascribed to an asymmetric glycoside vibration, \(\nu(C–O–C)\), and the broad band at 3438 cm\(^{-1}\) corresponds to O–H vibrations. In addition, the FT-IR spectrum of unconstrained SH-β-CD shows a peak for the S–H stretching mode (~2549 cm\(^{-1}\)), which is followed by its disappearance in SH-β-CD functionalized CsPbBr\(_3\) NCs, further confirming the successful attachment. From the above discussion, both spectral features and peak positions for several vibrational modes are strongly in support of the successful attachment of SH-β-CDs onto CsPbBr\(_3\) NCs.

The morphologies of the initial CsPbBr\(_3\) NCs and SH-β-CD encapsulated CsPbBr\(_3\) NCs were characterized using transmission electron microscopy (TEM). Supramolecular encapsulation preserved the cubic shape of the parent CsPbBr\(_3\) NCs, although...
their size decreased from 13 ± 1.5 nm to 8 ± 1.0 nm (Fig. 2A–C). The high-resolution TEM (HRTEM) images of the pristine CsPbBr₃ NCs, and the partially and fully SH-β-CD encapsulated NCs in Fig. 2D, E and F, respectively, clearly indicate their highly crystalline nature. Lattice fringe spacings of (001) and (110) were 0.58 nm and 0.41 nm, respectively, in all cases. The size decreased with increased concentration of SH-β-CD. We also observed a change in the 2θ locations of the X-ray diffraction (XRD) peaks. As revealed by XRD in Fig. S2 (ESI†), the 2θ of the (200) reflection is located at 30.6°, 30.8° and 31.0° for pristine CsPbBr₃ NCs, and partially and fully SH-β-CD encapsulated CsPbBr₃ NCs, respectively.

The encapsulation reaction of CsPbBr₃ to form CsPbBr₃@SH-β-CD NCs with different concentrations of SH-β-CD was monitored using UV-vis and FL spectroscopy. Blue shifts in both the UV-vis absorption and FL emission spectra were observed after SH-β-CD coating (Fig. 3). The FL emission spectra of colloidal CsPbBr₃ NCs can be tuned over half of the visible spectral region (405–510 nm) by adjusting the concentration of SH-β-CD. Previous reports have already demonstrated that CsPbX₃ NCs are highly ionic, both experimentally and theoretically. 23 Like most ionic crystals, considerable stoichiometric deviation at the CsPbX₃ NC surface leads to generation of a large amount of donor–acceptor states, which serve as point defects for absorption of foreign atoms. In this experiment, the hydrosulfuryl group easily coordinates the vacancies or interstitials of CsPbBr₃ NCs after NH-β-CD to the surface. In addition, the QY of the protectant-modified CsPbBr₃ NCs was about 50% (Fig. S3 ESI†) after SH-β-CD coating (Fig. 3). The FL emission spectra of colloidal CsPbBr₃ NCs with different concentrations of SH-β-CD was monitored experimentally and theoretically. 23 Like most ionic crystals, considerable stoichiometric deviation at the CsPbX₃ NC surface leads to generation of a large amount of donor–acceptor states, which serve as point defects for absorption of foreign atoms. In this experiment, the hydrosulfuryl group easily coordinates the vacancies or interstitials of CsPbBr₃ NCs after NH-β-CD to the surface. In addition, the QY of the protectant-modified CsPbBr₃ NCs was about 50% (Fig. S3 ESI†) at emission 405 nm; this is substantially higher than the ~10% QY at 410 nm that was measured for CsPbCl₃ synthesized directly or obtained by chloride ion exchange. 18,20 The nanocrystal powders encapsulated with different concentrations of SH-β-CD were confirmed by TGA measurements in Fig. S4A–C (ESI†). Two major weight losses were observed for all of the samples at about 300 °C and 550 °C attributed to the organic wrapping agent and loss of all inorganic NCs, respectively. The first weight loss for pristine CsPbBr₃ NCs, and partially and fully SH-β-CD of encapsulated CsPbBr₃ NCs was about 5.5%, 9.7% and 18.1%, respectively, which demonstrated the changes in the total amount of surfactant. The different concentrations of SH-β-CD in the coated samples retained their different colors of shiny fluorescence, as shown in Fig. S4D–F (ESI†).

The FL decay curves were well fitted by a three-exponential fitting, which suggests that the FL decay time was adjustable by the concentration of SH-β-CD. The slower components, τ₁ and τ₂, likely correspond to bulk recombination, while the faster component corresponds to surface site recombination. 24 With the increasing concentration of SH-β-CD, the variations of the long-lived FL lifetime τ₁ and τ₂ were small, with gradient less than 20%, but the short-lived FL lifetime (τ₃) was decreased tremendously with a gradient of more than 70%, which was contrary to the result of the ion exchange experiment. These results further proved that the FL blue shift was caused by surface replacement of SH-β-CD. However, the average FL lifetime (τave) of high-concentration SH-β-CD colloidal CsPbBr₃ NCs was shorter than that of the low-concentration NCs (Fig. 4), which was similar to previously reported phenomena in which CsPbX₃ obtained either by direct synthesis or halogen ion-exchange systematically exhibited faster emission decay for higher emission energy NCs (Table 1).

Another striking finding of our research is the reversibility and homogenization of the SH-β-CD coating reaction. The violet emission of CsPbBr₃@SH-β-CD can be reversed to partially encapsulated blue emission NCs by reaction with pristine CsPbBr₃ NCs. Time-dependent FL spectra in Fig. S5 (ESI†) show a fast cross-exchange and homogenization of CsPbBr₃ NCs and CsPbBr₃@SH-β-CD NCs, in which two distinct NC species coexist with altered compositions. The time taken to reach full homogeneity in this case is 1–2 min. In a similar way, the entirely encapsulated CsPbBr₃@SH-β-CD NCs can be reversed back to CsPbBr₃ using ZnBr₂.

In summary, we successfully developed a supramolecular SH-β-CD functionalization strategy for systematically manipulating the optical properties of cesium lead halide perovskite nanocrystals.

![Fig. 3](image_url) UV-vis absorption and FL spectra of encapsulated CsPbBr₃ NCs with different concentration of SH-β-CD.

![Fig. 4](image_url) Time-resolved FL decays of pristine CsPbBr₃ NCs, and partially and fully SH-β-CD encapsulated CsPbBr₃ NCs.

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In addition, the blue shift or hypsochromic effects disappear in the presence of guest molecules (e.g. adamantane, phenyl, etc.), due to severing of the bond between the surface ligand of the NCs and SH-β-CD. Hence, we have demonstrated the cavities and the hydrosulfuryl group work in synergy to cause the blue shift. We envision that the supramolecular functionalized perovskite nanocrystals will find popular research interests, such as in LEDs, lasering, photovoltaic, and fluorescent materials.

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Notes and references

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