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Reversible ON/OFF switching of photoluminescence from CsPbX₃ quantum dots coated with silica using photochromic diarylethene

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Highly luminescent silica-coated CsPbX₃ quantum dots (QDs) with a good photostability were synthesized and coupled with photochromic diarylethene to modulate QDs' photoluminescence (PL). Upon successive UV and visible light irradiation, the PL emission from silica-coated CsPbX₃ QDs was repeatedly quenched and restored, demonstrating the promising feasibility of the QD/diarylethene-based photoswitches.

Lead halide perovskite, with novel electrical and optical properties,^{1–6} have drawn considerable attention as emerging photonic materials in recent years. They are applied in various fields such as light-emitting diodes (LEDs),^{5–9} displays,^{10,11} and solar cells.¹² Particularly, all inorganic CsPbX₃ (X = Cl, Br, I) perovskite quantum dots (QDs) possess many advantages including tunable photoluminescence (PL) emission color, sharp emission peak with a small FWHM (full width at half-maximum) and high PL quantum yields. In addition, CsPbX₃ QDs are easily synthesized by simple liquid phase routes, which produce cube-shaped nanocrystals (nanocubes).¹³ These characteristics make the QDs optimal candidates for several optoelectronic applications.

The reversible PL modulation of semiconductor QDs is attractive because of the expectation that their emission control would lead to many applications including imaging probes,¹⁶ chemo and biosensing,¹⁷ smart windows,¹⁸ information processing¹⁹ and optical memories.²⁰ The functionalization of QDs with organic materials has been extensively studied to create novel functional materials by synergetic combination of inorganic and organic components.^{21–23} In particular, photochromic molecules would be promising counterparts to control the PL emission from QDs because of their remote accessibility, robust reversibility, and no waste during switching processes.^{24–30} Among many kinds of photochromic molecules, diarylethene and its derivatives are ideal photoswitches due to their high fatigue resistance and excellent thermal stability.^{28,30}

Here, we demonstrate a strategy that can be used to reversibly modulate PL from colloidal CsPbBr₃ QDs using photochromic diarylethene. There have been pioneering reports in modulating PL of semiconductor QDs such as CdSe/CdS/ZnS using diarylethene derivatives.^{31–34} However, the PL quenching efficiency remains low, e.g. 40% and thus the substantial improvement is desired. **Fig. 1** shows the molecular structure of diarylethene, 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene **1**, which was used in this study, together with its UV-vis absorption spectra under UV and visible light irradiation. The molecular structure can be switched from open- to closed-ring forms via cyclization upon UV light irradiation and returned from closed- to open-ring forms via cycloreversion upon visible light irradiation. Accordingly, the absorbance and the color of the molecule reversibly change. **Scheme 1** shows the PL switching mechanism in the CsPbBr₃ QD/diarylethene system. Irradiating diarylethene with UV light produces a closed-ring isomer having absorption in the visible region, thus quenching

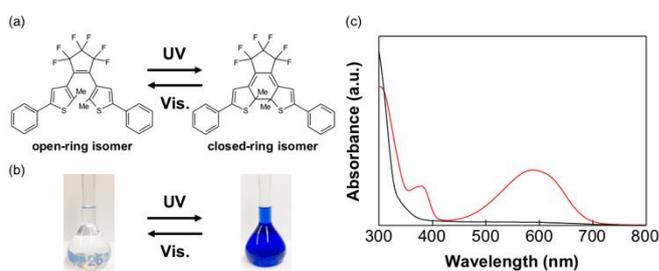


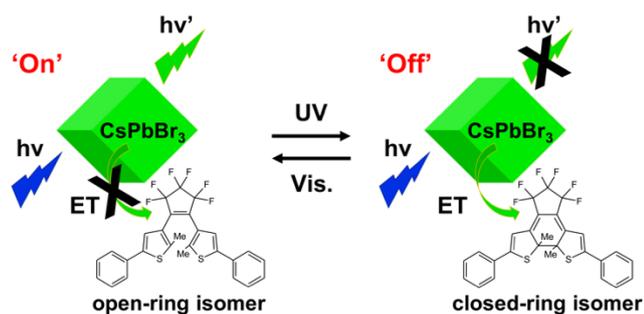
Fig. 1 (a) Molecular structures of open-ring and closed-ring isomers of diarylethene **1**. (b) Photographs of a solution containing diarylethene before and after UV (365 nm) and visible light irradiation ($\lambda > 530$ nm). (c) Absorption spectra of open-ring (black line) and closed-ring forms (red line) of diarylethene in a toluene solution.

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Scheme 1 Schematic illustration of the PL switching mechanism. The energy transfer from CsPbBr₃ QD to diarylethene occurs after UV light irradiation (Off state), but it does not occur after visible light irradiation (On state).

PL from QDs by Förster Resonance Energy Transfer (FRET). The QD and diarylethene with the closed-ring form act as a fluorescence donor and acceptor, respectively. When irradiated with visible light, the closed-ring isomer is converted to the open-ring one having no absorbance in the visible region, resulting in the restoration of PL. This quenching and restoration process can be repeated because of the excellent photochromic properties of diarylethene.

The synthesis route of diarylethene **1** and its detailed procedure are depicted in Electronic Supplementary Information (ESI†). CsPbBr₃ QDs were synthesized from CsBr and PbBr₂ in toluene by a supersaturated-recrystallization method according to the literature.⁵ However, the chemical stability of CsPbX₃ QDs is poor; they immediately decompose when in contact with water and polar solvents.^{14,15} Their stability improvement is one major challenge for practical applications. In this study, we coated the QDs with silica shells to improve the stability and ensure reversible PL modulation. Coating QDs with silica shells was carried out just by adding (3-aminopropyl)trimethoxysilane (APTMS) in a precursor solution and crystallizing QDs that were coated with amorphous silica. The detailed procedure is described in ESI†. **Fig. 2a** shows a representative transmittance electron microscopy (TEM) image of native CsPbBr₃ QDs. A lower magnification image is also shown in **Fig. S1** (ESI†). The image clearly shows the formation of cube-shaped nanocrystals (NCs) of 12 nm in size. The crystal structure of the QDs was identified to be cubic by XRD analysis, as shown in **Fig. S2** (ESI†). The highly oriented XRD peaks in (100) direction also supports the formation of well-defined cube-shaped NCs with {100} plane. **Fig. 2b** shows UV-vis absorption and PL emission spectrum of the CsPbBr₃ QDs in toluene. There is a clear excitonic peak at 501 nm in the absorption spectrum. The QDs exhibited a sharp emission peak centered at 515 nm with a FWHM of 19 nm. The results suggest the good crystal quality of the QDs, which are comparable with high quality II–VI semiconductor QDs such as CdSe.³⁵ TEM images of silica-coated CsPbBr₃ QDs are displayed in **Fig. 2c** and **Fig. S3** (ESI†). The images show that the aggregation of NCs occurred by introduction of aminosilane to produce nanoparticles of ca. 30–40 nm in size. It is probable that the surface of QDs were capped with APTMS in the course of synthesis. By the

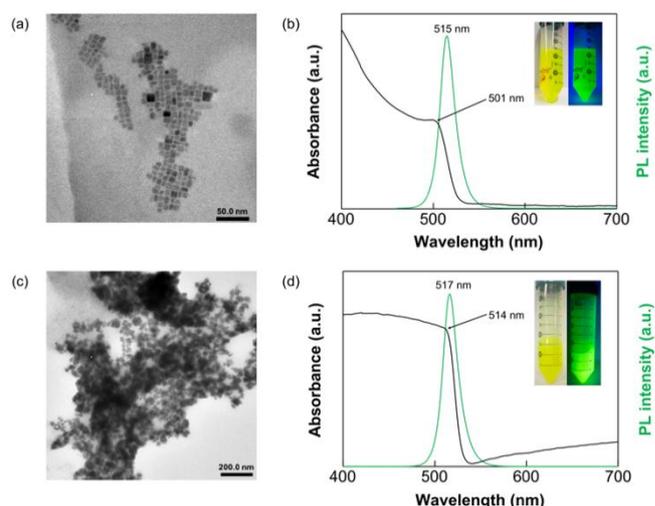


Fig. 2 TEM image of (a) native CsPbBr₃ and (c) silica-coated CsPbBr₃ QDs. UV-vis absorption and PL emission spectra of (b) native CsPbBr₃ and (d) silica-coated CsPbBr₃ QDs. The excitation wavelength is 390 nm for both QDs.

hydrolysis of methoxy groups in APTMS, followed by a condensation reaction that produced -Si-O-Si- networks, amorphous silica layers should form on the QD's surface. The progressive extension of -Si-O-Si- networks involving neighbouring NCs finally produced rather aggregated nanoparticles. The XRD results (**Fig. S2**, ESI†) confirmed that the silica coating also changed the shape of individual QDs, producing particles without oriented growth direction. The crystal structure changed to orthorhombic. TEM and high angle annular dark-field scanning transmission electron microscopy (HAADF) images (**Fig. S4**, ESI†) show that the particles were covered by shells with a less contrast. The presence of SiO₂ shells was confirmed by energy dispersive X-ray spectroscopy (EDS) point analysis. A high-resolution TEM (HR-TEM) image (**Fig. S4**) clearly indicates that the core of CsPbBr₃ nanocrystals remained intact even after amorphous SiO₂ coating. **Fig. 2d** shows UV-vis absorption and PL emission spectrum of the CsPbBr₃ QDs coated with silica. The emission peak and the excitonic peak were red-shifted after silica coating, which is probably due to the delocalization of the electron wave function from CsPbBr₃ core into silica shell. This would lower the electron confinement energy, as often seen for CdSe/CdS core/shell nanocrystals.³⁶ The results suggest that the silica coating did not significantly change the optical properties of CsPbBr₃.

First, the native CsPbBr₃ QDs was mixed with diarylethene **1** and changes in optical properties of the system were monitored. **Fig. 3a** and **3b** show the emission spectra changes and photographs of a toluene solution containing the native CsPbBr₃ QDs coupled with diarylethene **1** upon photoirradiation, respectively. After irradiation with 365 nm UV light (0.5 mW), the color of the solution changed to blue. As a result, the intensity of PL emission from the QDs significantly decreased ("OFF" state). Very weak PL emission was observed even under UV excitation. Upon irradiation with visible light ($\lambda > 530$ nm, 150

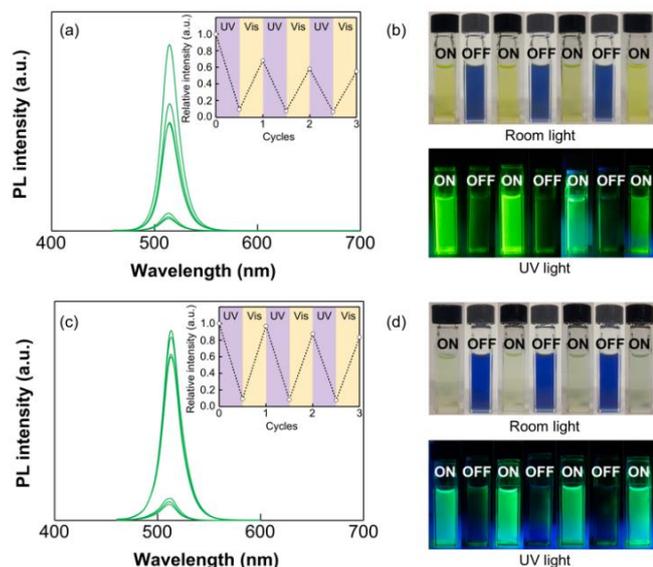


Fig. 3 PL emission spectra of (a) native CsPbBr₃ QDs and (c) silica-coated CsPbBr₃ QDs in toluene containing diarylethene upon alternate irradiation with UV (365 nm) and visible light ($\lambda > 530$ nm). Photographs depicting the PL modulation cycles of (b) native CsPbBr₃ QDs and (d) silica-coated CsPbBr₃ QDs in toluene containing diarylethene under room light and UV light.

mW), the solution color returned to the original and the green emission from the QDs became visible again under UV irradiation ("ON" state). The results prove the validity of our idea to control the emission from perovskite QDs using photochromic molecules, as shown in **Scheme 1**. **Inset of Fig. 3a** shows repeating cycles of the PL ON/OFF switching. The PL intensity reversibly changed upon alternating the irradiation with UV and visible light. The cycle was repeated three times. In each cycle, the "ON" and "OFF" states can be clearly distinguished. The response time of the photoswitching from the "ON" to "OFF" states was 5 min when irradiated with 365 nm UV light (0.5 mW). On the other hand, a change in PL intensity was saturated after 60 sec when using high intensity UV light (300 mW), as shown in **Fig.S5** (ESI[†]), suggesting that the response time was strongly dependent on the power of light sources. Thus, the control of light intensity and also the concentrations of QDs and diarylethene in solution is important to achieve a quick ON/OFF switching.

A noticeable finding is that the reversible PL modulation was realized just by mixing the fluorescence donor and the acceptor in solution without chemically binding the two together. The quenching efficiency was more than 90%, which is higher than that of the previous reports that chemically attached diarylethene onto QDs.^{31–34} The sharp PL at 515 nm did not efficiently drive pre-existing closed-form diarylethene back to its open form that has no quenching capability. In this experiment, QDs and diarylethene **1** were mixed in toluene at 2 : 1 in molar ratio, which corresponds to ca. 3400 molecules of diarylethene per one nanocube of CsPbBr₃. Taking into consideration the molecular cross section of diarylethene **1** (ca. 0.5 nm² at the maximum) and the surface area of a single 12 nm nanocube (864 nm²), the

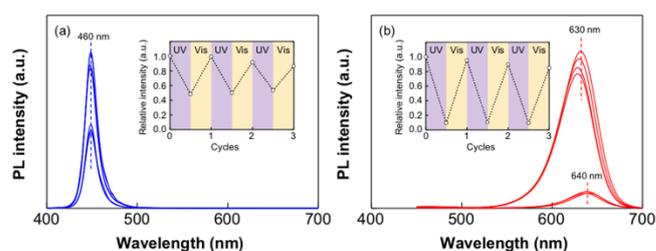


Fig. 4 PL emission spectra of (a) silica-coated CsPbBr₂Cl and (b) silica-coated CsPbBrI₂ QDs in toluene containing diarylethene (**1**) upon alternate irradiation with UV and visible light.

number of diarylethene relative to that of QDs is sufficient to completely cover the whole surface of all of QDs.

Despite the successful PL modulation at the first cycle, a 40% decrease in PL intensity at the "ON" state was observed after the 2nd cycle. This should be due to the degradation of CsPbBr₃ QDs. A significant decrease in PL intensity of CsPbBr₃ QDs by continuous light irradiation, oxygen and moisture exposure, and annealing has been reported.^{14,15} To avoid the PL loss due to the degradation of the QDs, we performed the reversible PL modulation using the silica-coated CsPbBr₃ QDs. **Fig. 3c** shows the emission spectra of the silica-coated CsPbBr₃ QDs in the presence of diarylethene **1** upon alternate irradiation with UV and visible light. The PL intensity reversibly decreased and recovered upon alternate irradiation with UV and visible light, respectively. It should be noted that the gradual decrease in PL intensity at the "ON" state was successfully suppressed, enabling the reversible PL modulation. In a separate experiment, we examined the photostability of the QDs. The silica-coated CsPbBr₃ QDs showed better stability than the uncoated QDs against alternate irradiation with UV and visible light in air, as shown in **Fig. S6** (ESI[†]). It is possible that some of photogenerated electrons and holes in native QDs can reach the surface and react with oxygen in solution to produce reactive radical species that attack the QDs themselves under UV irradiation. Direct hole attack to the QDs is also possible. Contrary to that, coating the surface with an insulating silica layer prevented such photocatalytic reactions, which resulted in the stable ON/OFF switching of PL. The long-term photostability of the QDs was also tested by irradiating them with strong UV (196 mW) and visible light (160 mW) for 120 h (**Fig. S7**). The silica-coated CsPbBr₃ QDs showed much better photostability than the native QDs although the PL intensity decreased to almost half of the original value after 120 h irradiation. In addition, we revealed that the silica-coated QDs were much more stable in ethanol and acetone than the native QDs, as shown in **Fig. S8** (ESI[†]).

Furthermore, we tried to achieve multi-color ON/OFF switching using blue emitting silica-coated CsPbBr₂Cl QDs and red emitting silica-coated CsPbBrI₂ QDs. The optical properties of the above QDs are shown in **Fig. S9** (ESI[†]). As seen in **Fig. 4**, reversible ON/OFF switching of blue and red PL was attained using the two different QDs. The decrease in PL at the "ON" state was also suppressed by coating the QDs' surface with silica. The success of this reversible modulation of different colours

would allow for the modulation of white light upon alternate irradiation with UV and visible light. However, the complete quenching of PL was not achieved in all the cases. One probable reason is the mismatch of the absorption peak of the closed ring-isomer and the emission peaks of the QDs, i.e. a small FRET overlap integral particularly for the blue and green emitting QDs. Note that the emission from the red emitting QDs was more efficiently quenched although a red shift in emission wavelength was seen after ON/OFF switching. It is probable that the emission peak of the CsPbBr₂ QDs can be deconvoluted into two peaks peaking at 630 and 640 nm that occurred via different electron-hole recombination pathways. The results suggest that the peak at 630 nm was dominantly quenched because of the larger FRET overlap integral, leading to the apparent shift in emission wavelength from 630 to 640 nm, as shown in **Fig. 4b**. Currently, tuning the molecular structure of diarylethene **1** and the composition of the QDs are under way to perfectly quench the PL emission.

In conclusion, we demonstrate a simple, convenient, and efficient way to modulate photoluminescence using colloidal CsPbX₃ QDs coupled with diarylethene. The photogenerated closed-ring isomer of diarylethene **1** efficiently quenched the photoluminescence by energy transfer after UV irradiation. This has been achieved by just simply mixing the QDs and diarylethene in a solution. The photoluminescence was recovered after visible light irradiation. Silica coating was very effective in sustaining the reversible ON/OFF switching. The ON/OFF switching of the very sharp photoluminescence with a FWHM of 19 nm from perovskite QDs would open up new opportunities for several new optical applications.

Acknowledgement

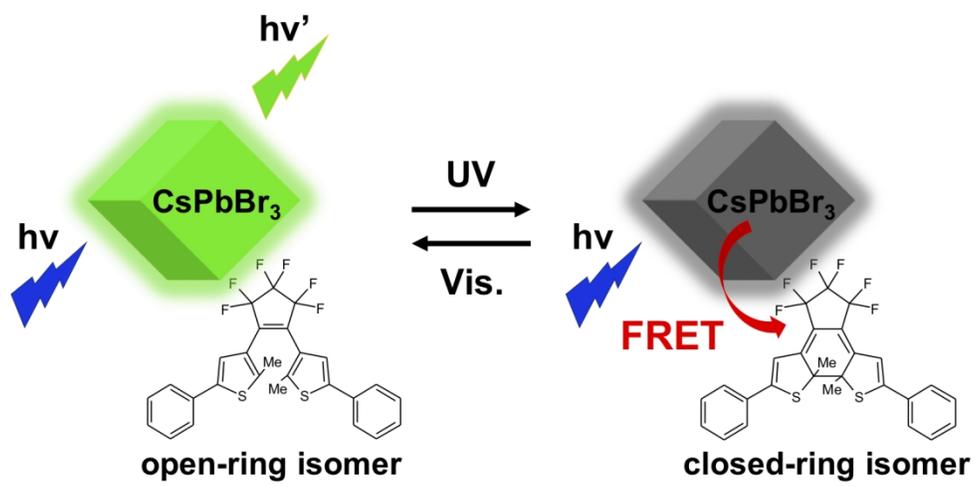
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Conflicts of interest

There are no conflicts to declare.

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