Supporting Information

Strong Upconversion Emission in CsPbBr$_3$ Perovskite Quantum Dots through Efficient BaYF$_5$: Yb, Ln Sensitization

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Fig. S1 Size distribution histograms of (a) BaYF$_5$: Yb, Tm UCNPs and (b) CsPbBr$_3$ QDs.

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**Fig. S2** EDX spectrum of the BaYF₃: Yb, Tm/CsPbBr₃ composite with 1: 1 ratio. The results are summarized in the following Table.

**Table S1.** EDX elemental analysis of the BaYF₃: Yb, Tm/CsPbBr₃ composite with 1: 1 ratio, indicating the existence of Ba, Y, F, Yb, Tm, Cs, Pb and Br elements which are assigned to BaYF₃: Yb, Tm UCNPs and CsPbBr₃ QDs. The value of lanthanide does not represent the actual composition because of instrument limitations.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ba</th>
<th>Y</th>
<th>F</th>
<th>Yb</th>
<th>Tm</th>
<th>Cs</th>
<th>Pb</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>At %</td>
<td>8.02</td>
<td>6.4</td>
<td>35.45</td>
<td>0.95</td>
<td>0.42</td>
<td>8.26</td>
<td>9.88</td>
<td>30.63</td>
</tr>
</tbody>
</table>
FT-IR spectra evidence a strong resemblance of the transmission bands appearing at 2925 and 2854 cm$^{-1}$, which are assigned to the asymmetric and symmetric stretching vibrations of methylene groups (–CH$_{2}$), respectively.$^{1}$ The bands at 1454 cm$^{-1}$ in the spectrum of UCNPs (a) and 1548 cm$^{-1}$ in the three spectra are attributed to the symmetric and antisymmetric stretching of the carboxylate (COO$^{-}$), respectively. The result indicates that OA molecules were chemisorbed onto the UCNPs as a carboxylate.$^{2}$ In the spectra of CsPbBr$_{3}$ QDs (b) and BaYF$_{5}$: Yb, Tm/CsPbBr$_{3}$ composite (c), the characteristic peaks of OLA are observed at 1465, 1641, and 3295 cm$^{-1}$, which are associated with –C–H bending, C=O stretching and N–H stretching, respectively.$^{3-4}$ It is interesting to notice that the very broad shoulder at around 3400 cm$^{-1}$, related to the OH groups of OA in the spectrum of UCNPs (a), completely disappeared in the spectrum of the composite (c), indicating a thoroughly deprotonation of the carboxylic group in the presence of OLA, to form oleate.

**Fig. S3** FT-IR spectra of (a) BaYF$_{5}$: Yb, Tm UCNPs, (b) CsPbBr$_{3}$ QDs and (c) BaYF$_{5}$: Yb, Tm/CsPbBr$_{3}$ composite with 1: 0.25 ratio.
**Fig. S4** TEM images of (a) BaYF₃: Yb, Tm/CsPbBr₃ composite with 1:1 ratio synthesized through the *in-situ* growth method, (b) mixture of BaYF₃: Yb, Tm UCNPs and CsPbBr₃ QDs with 1:1 ratio assembled by physical mixing. The red arrows indicate small black dots with poor crystallinity of about 2 nm which are attributed to PbBr₂ nanoparticles (coexisting along the CsPbBr₃ QDs⁵), which can be easily distinguished from UCNPs by different sizes and crystallinity.

**Fig. S5** Emission spectrum of the pristine CsPbBr₃ QDs excited at 466 nm (blue line), UCL emission spectrum of the BaYF₃: Yb, Tm/CsPbBr₃ QDs composite (red line) excited at 975 nm.
Fig. S6 Absorption spectra of CsPbBr$_3$ QDs (black line) and normalized UCL emission spectra of (a) BaYF$_5$: Yb, Tm (blue line), (b) BaYF$_5$: Yb, Ho (pink line), and (c) BaYF$_5$: Yb, Er (green line), which are used to calculate the overlap integral ($J$). There is partial spectral overlap between the BaYF$_5$: Yb, Er FRET donor and the CsPbBr$_3$ acceptor.

Fig. S7 UCL emission spectra of BaYF$_5$: Yb, Tm UCNPs (black line), BaYF$_5$: Yb, Tm/CsPbBr$_3$ QDs composite with 1: 1 ratio (blue line), physical mixture of BaYF$_5$: Yb, Tm and CsPbBr$_3$ QDs with the same composite ratio (red line).
Förster-resonance-energy-transfer

The FRET efficiency can be experimentally estimated based on the corresponding decay lifetimes:

\[ \eta = 1 - \frac{\tau_{DA}}{\tau_D} \]  

(S1)

where \( \tau_D \) and \( \tau_{DA} \) are the luminescence lifetimes of the donor in the absence and presence of the acceptor, respectively.

Efficient FRET between UCNPs donors and CsPbBr\(_3\) QDs acceptors will only take place at short distances.\(^7\) The distance at which energy transfer efficiency is 50\%, defined as the Förster radius \((R_0)\), is given by:\(^8\)

\[ R_0 = \left[ \frac{9(\text{In}10)\kappa^2\Phi_D J}{128\pi^2 N_A n^2} \right]^{1/6} \]  

(S2)

where \( \kappa^2 \) is the orientation factor of the interacting dipoles, \( \Phi_D \) is the luminescence quantum yield of the donor in the absence of the acceptor, \( n \) is the average refractive index of the medium, \( N_A \) is the Avogadro constant, and \( J \) is a spectral overlap integral \((\text{M}^{-1} \text{cm}^{-1} \text{nm}^4)\). The integral \( J \) can be defined as:\(^8\)

\[ J(\lambda) = \int F_D(\lambda) \varepsilon_A(\lambda) d\lambda \]  

(S3)

where \( F_D(\lambda) \) is the UCL spectrum of the donor normalized to unit area \((\int F_D(\lambda) d\lambda = 1)\), and \( \varepsilon_A \) is the acceptor’s molar extinction coefficient \((\text{M}^{-1} \text{cm}^{-1})\) as a function of the wavelength \( \lambda \) (nm), as shown in Fig. S4. Herein, the value of 2/3 was used for \( \kappa^2 \) (assuming a random orientation of donor and acceptor dipoles), while \( \kappa^2 = 4 \) was also used to allow comparison across the literature. The refractive index of the medium was taken as 1.44, an average value between 1.427 (cyclohexane) and 1.459 (OA). The reported PLQY of the UCNPs donor \((\Phi_D)\) was in the range of 0.005-0.1\%,\(^9\) while \( \Phi_D = 0.01\% \) was also assumed for the UCNPs to allow comparison across the literature.\(^10,11\)

The rate of FRET \((\kappa_T)\) is calculated from the lifetime of the donor in absence of the acceptor, Förster distance, and the average UCNPs-QDs separation distance, according to Eq. (S4):\(^12\)

\[ \kappa_T = \frac{1}{\tau_D} \times \left( \frac{R_0}{r} \right)^6 \]  

(S4)

Taking into account an average separation distance between the donor and the acceptor of 3 nm (Ln ions in the center of the particle) and \( \tau_D \) values reported in Table 1 in the manuscript (9.4 µs, 9.0 µs and 28.9 µs for Tm\(^{3+}\), Ho\(^{3+}\) and Er\(^{3+}\), respectively), it is possible to retrieve \( \kappa_T \) values of 2.7×10\(^5\) s\(^{-1}\), 2.9×10\(^5\) s\(^{-1}\) and 3.4×10\(^4\) s\(^{-1}\) for the FRET processes from the Tm\(^{3+}\), Ho\(^{3+}\) and Er\(^{3+}\) donors, respectively.

It has however to be remarked that in the studied systems the donor units are the emitting lanthanide ions (Tm\(^{3+}\), Ho\(^{3+}\) and Er\(^{3+}\)) that are homogeneously distributed into the UCNPs and therefore lie at various distances from the surface of the QDs acceptor depending on the size of the nanoparticle. According to the Förster’s model, predictions of the FRET efficiency on dependence of the distance \( r \) between the donor/acceptor pair, can be quantified by the following equation:\(^7\)
\[
\eta = \frac{R_0^6}{R_0^6 + r^6} \quad (S5)
\]

As shown in Fig. S6, the FRET efficiencies estimated by the Förster model (taking the reliable value of $\kappa^2 = 2/3$) can reach ~70% for the Tm$^{3+}$ and Ho$^{3+}$ to CsPbBr$_3$ QDs, and ~50% for Er$^{3+}$ to CsPbBr$_3$ QDs when the Ln$^{3+}$ are located in the center of the UCNPs. Ln$^{3+}$ closer to the acceptors will exhibit higher FRET efficiencies. These results suggest that higher energy transfer from the UCNPs to the CsPbBr$_3$ QDs may be achieved for smaller donor sizes.

Fig. S8 FRET efficiency as a function of separation distance between the donor/acceptor pair: (a) Tm$^{3+}$ to CsPbBr$_3$ QDs, (b) Ho$^{3+}$ to CsPbBr$_3$ QDs and (c) Er$^{3+}$ to CsPbBr$_3$ QDs.

Fig. S9 (a) Thermal stability tests of the CsPbBr$_3$ QDs and BaYF$_5$: Yb, Tm/CsPbBr$_3$ composite films versus thermal treatment time at 80 °C under ambient pressure, (b) humidity stability tests. Exposure to moisture was realized by spraying deionized water onto the sample’ surface.
Interestingly, the BaYF$_5$: Yb, Tm/CsPbBr$_3$ composite sample exhibited a sharp increase in PL intensity in the first two hours upon thermal annealing at 80 °C followed by a decrease, while the PL intensity was still enhanced by 42% after 5 h thermal treatment. On the contrary, an obvious thermal quenching of PL intensity was observed in the pristine CsPbBr$_3$ QDs sample and only 68% of the initial signal was left. It was also found that both the pristine CsPbBr$_3$ QDs and the BaYF$_5$: Yb, Tm/CsPbBr$_3$ composite displayed a slight red shift (1-2 nm) of emission, suggesting that the CsPbBr$_3$ QDs were growing during the thermal annealing process. Similar PL phenomena were also observed in the bare CsPbBr$_3$ QDs by Yuan et al.$^{13}$

The PL changes observed in the BaYF$_5$: Yb, Tm/CsPbBr$_3$ composite are probably a result of the two competing processes: the increase of nonradiative recombination centers and the shortening of the distance between the energy donors and acceptors, which will lead to PL quenching and enhancement, respectively. Only the first process occurred in the pristine CsPbBr$_3$ QDs. The increase of the nonradiative recombination centers is likely arising from the partial loss of surface bonding ligands during the thermal treatment, followed by the formation of surface energy states and subsequent PL quenching.$^{13}$ On the other hand, the evaporation of cyclohexane is likely to favor a shorter distance between the energy donors and acceptors which will improve the FRET efficiency. Therefore, the PL intensity of the BaYF$_5$: Yb, Tm/CsPbBr$_3$ composite was enhanced due to the increased energy transfer efficiency from the energy donors to the acceptors. In the BaYF$_5$: Yb, Tm/CsPbBr$_3$ composite, the latter process dominated in the first two hours and then became weaker, accompanied with the PL enhancement and subsequent quenching.

The pristine CsPbBr$_3$ QDs and BaYF$_5$: Yb, Tm/CsPbBr$_3$ composite films were subjected to cycles of water spraying followed by natural drying (30 minutes in air) to investigate the stability to humidity of the materials and their PL performances. As shown in Fig. S8, the BaYF$_5$: Yb, Tm/CsPbBr$_3$ composite showed a serious PL intensity drop compared with the pristine CsPbBr$_3$ QDs upon water exposure. However, after 30 minutes drying, 87% and 81% of the original intensities were recovered after three cycles for the pristine CsPbBr$_3$ QDs and the BaYF$_5$: Yb, Tm/CsPbBr$_3$ composite, respectively. Further, the exciton peak positions of the two samples stayed the same. The PL quenching is probably associated with the desorption of the capping ligands on the surface of the nanoparticles or surface decomposition, followed by the occurrence of new surface trap states.$^{14}$ The BaYF$_5$: Yb, Tm/CsPbBr$_3$ composite is more sensitive to moisture compared with the pristine CsPbBr$_3$ QDs. In the BaYF$_5$: Yb, Tm/CsPbBr$_3$ composite, partial UCNPs detachment from the surface of the CsPbBr$_3$ QDs, owing to the desorption of the surface bonding ligands, or enhanced lanthanide vibrational quenching, could related to the reduced FRET efficiency and PL intensity in the presence of water.
References