

Efficient NIR-II luminescence of inorganic Er-Yb alloyed nanocrystals for optical communication

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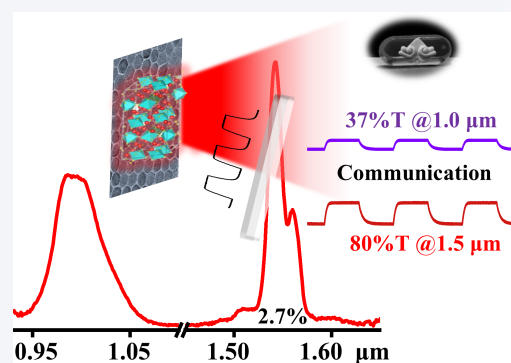
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ABSTRACT: Zero-dimensional metal halides have emerged as a promising class of luminescent materials, attracting significant interest due to their unique electronic structures and fascinating optical characteristics. The photoluminescence (PL) properties of inorganic ternary $\text{Cs}_3\text{Er}_x\text{Yb}_{1-x}\text{Cl}_6$ nanocrystals (NCs) were investigated. These alloyed NCs emit dual-band near-infrared (NIR) PL, featuring a sharp NIR-II emission at 1543 nm alongside an NIR-I emission around 987 nm, which originate from the rare earth Er^{3+} and Yb^{3+} ions, respectively. $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs exhibit efficient NIR-II PL with a quantum yield of 2.7% and a lifetime of 157 μs . The enhanced NIR-II PL can be attributed to highly localized excitons, fast energy transfer from Yb^{3+} to Er^{3+} ions and passivation of nonradiative defect states in the Er-Yb alloyed NCs. Given their good penetrability of the NIR-II PL from Er^{3+} ions, a single-component NIR phosphor-converted light-emitting diode (pc-LED) fabricated using $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs demonstrates their potential for future applications in optical communication.

KEYWORDS: near-infrared luminescence, rare earth chloride nanocrystals, exciton dynamics, Er-Yb alloying, optical communication



1 Introduction

Zero-dimensional (0D) metal halides have attracted considerable attention for their applications in light-emitting diodes (LEDs), photodetectors, X-ray imaging, and information encryption [1–5]. As emerging luminescent materials, they exhibit a good lattice tolerance, high stability, unique electronic structure with fascinating photoelectric characteristics [6–9]. Rare earth elements, owing to their f-f/d inner-shell levels, could give the metal halide

nanocrystals (NCs) more abundant optical properties spanning from the ultraviolet, visible, near-infrared (NIR), and even to middle-infrared regions [10–13]. A series of 0D ternary metal halide Cs_3LnCl_6 (Ln: Y, Ce, Gd, Er, Tm, Yb, Eu, Tb) NCs had been synthesized, and their photoluminescence (PL) would be tuned by varying the Ln cations within the isolated $[\text{LnCl}_6]^{3-}$ units [14–16]. LED based on Cs_3EuCl_6 NCs was fabricated and exhibited a pure red PL emission with the FWHM of 18 nm at 617 nm [17]. An effective thermally boosting energy transfer of Sb-doped Cs_3TbCl_6 NCs made exciton highly localized on $[\text{TbCl}_6]^{3-}$ octahedron, producing a narrow-band green PL and a sensitive X-ray imaging [18]. Cs_3TmCl_6 NCs presented a broadband blue PL emission, and were considered as the phosphor converter to fabricate the white LED [19].

Beyond these excellent visible-light PL characteristics, rare earth ions can also emit NIR PL with longer wavelengths, offering advantages such as low thermal effects, excellent penetration depth,

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and non-invasiveness [20–24]. There are wide applications in food analysis, medical health, bio-remote sensing, and communication [25–29]. Zhang's group used a fabricated NIR phosphor-converted LED (pc-LED) as a light source, and its NIR PL around 800 nm could penetrate certain barriers to realize the optical communication [30]. In this work, we successfully synthesized a series of inorganic ternary rare earth chloride $\text{Cs}_3\text{Er}_x\text{Yb}_{1-x}\text{Cl}_6$ NCs. These NCs would emit the NIR PL at 1543 and 987 nm, corresponding to the Yb^{3+} and Er^{3+} ions' emissions, respectively. The energy transfer dynamics in the alloyed NCs was investigated through a combination of theoretical calculations, time-resolved PL (TR-PL), temperature-dependent PL, and femtosecond transient absorption (TA) spectroscopy. Capitalizing on the high-performance NIR-II emission at 1543 nm, we fabricated an NIR pc-LED based on $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs, highlighting their potential as promising candidates for non-invasive detection and optical communication.

2 Experimental

2.1 Materials

The experimental materials are cesium acetate ($\text{Cs}(\text{OAc})$, 99.99%, Aladdin), ytterbium acetate ($\text{Yb}(\text{OAc})_3$, 99.99%, Shanghai Yuanye Bio-Technology Co, Ltd), erbium acetate ($\text{Er}(\text{OAc})_3$, 99.99%, Shanghai Yuanye Bio-Technology Co, Ltd), chlorotrimethylsilane (TMSCl , 98%, Alfa Aesar), 1-octadecene (90%, Aladdin), oleylamine (OLA, 80%, Aladdin), oleic acid (OA, 85%, Aladdin), toluene (99.5%, Sinopharm Chemical Reagent Co., Ltd, China), n-hexane (97%, Aladdin). All chemicals were used as received without further purification.

2.2 Synthesis methods

The $\text{Cs}_3\text{Er}_x\text{Yb}_{1-x}\text{Cl}_6$ ($x = 0, 0.06, 0.25, 0.50$, and 1) NCs were prepared by variable temperature hot injection. 0.70 mmol $\text{Cs}(\text{OAc})$, 0.5x mmol $\text{Er}(\text{OAc})_3$ and 0.5(1-x) mmol $\text{Yb}(\text{OAc})_3$ were added in a mixture of oleic acid (2.8 mL), oleylamine (0.65 mL) and 1-octadecene (10 mL), which was heated to 110 °C under vacuum for 60 min. The reaction mixture was heated through a temperature gradient of 6 °C·min⁻¹ under a nitrogen atmosphere, and TMSCl (0.4 mL) was swiftly injected at 175 °C. The reaction mixture continued to 190 °C, and immediately cooled to room temperature in an ice-water bath. The reaction mixture was then decanted into a centrifugal tube and centrifuged at 10,000 rpm for 10 min. The supernatant was removed. The precipitate was washed in 10 mL toluene and centrifuged at 10,000 rpm for 10 min. The supernatant was discarded. The precipitate was redispersed in 5 mL hexane with sonication and centrifuged at 5000 rpm for 10 min, and colloidal $\text{Cs}_3\text{Er}_x\text{Yb}_{1-x}\text{Cl}_6$ NCs were obtained by discarding the bottom precipitate.

2.3 Structural characterizations

X-ray diffraction (XRD) was performed on an Ultima IV-185 diffractometer equipped with $\text{Cu K}\alpha$ X-ray ($\lambda = 1.542 \text{ \AA}$) tubes, and the acquisition was done for every 0.04° increment over the Bragg angle range of 10°–60°. Transmission electron microscopy (TEM) measurements were performed by using the JEOL JEM-F200.

2.4 PL spectroscopy

For colloidal NCs, steady-state optical absorption measurement was performed by using the absorbance and fluorescence spectrometer

(Duetta, Horiba Scientific). The PL excitation, NIR PL emission, absolute PL quantum yield (QY), time-resolved PL, and temperature-dependent PL measurements were recorded on the PL spectrometer (FLS1000, Edinburgh Instruments). For night vision, PL of NIR pc-LED was detected by a InGaAs array detector (short-wave infrared GH-SW320-U2, Shanxi Guohui Optoelectronic). The spectral range is 900–1700 nm. In the optical communication, the input TTL signals from the signal generator (Rigol, DG4102) was loaded to the fabricated NIR pc-LED. After transmitting different barriers, NIR PL from NIR pc-LED was collected by a InGaAs photodiode, and the output photoelectric signal was recorded by an oscilloscope (Tektronix, MDO3052).

2.5 Ultrafast transient absorption spectroscopy

TA experiments were operated by using a home-made femtosecond pump-probe setup. Laser pulses (800 nm, 50 fs pulse length, 1 kHz repetition rate) were generated by a Ti: sapphire femtosecond laser source (Hurricane, Spectra-Physics). An optical parametric amplifier was used to change the laser wavelength. For the probe, we used the super-continuum generation from a thin CaF_2 plate. The mutual polarization between pump and probe beams was set to the magic angle (54.7°) by placing a Berek compensator in the pump beam. The kinetic of the different scans stay the same showing no sign of degradation. Excitation power and spot size measurements were used to determine the excitation fluence (pump wavelength: 280 nm; pump fluence: 6.2×10^{14} photons·pulse⁻¹·cm⁻²). During the measurement, colloidal NCs were contained in 1 mm cuvette.

2.6 Theoretical calculation

First-principles calculations were performed using the Vienna *ab initio* simulation package (VASP). The generalized gradient approximation (GGA), as implemented in the Perdew–Burke–Ernzerhof (PBE) functional, was chosen to describe the exchange-correlation interaction of electrons. The projector augmented wave (PAW) method was employed to describe the exchange-correlation potential and energy. The energy cutoff for the planewave basis was set to be 600 eV. The Brillouin zones (BZs) were sampled using a $1 \times 2 \times 3$ k-point grid mesh for the geometry optimization. Convergence criteria of 10^{-3} eV for total energy and $0.02 \text{ eV}\cdot\text{\AA}^{-1}$ for the force were adopted for self-consistent calculations and geometry optimization.

3 Results and discussion

3.1 Structural characterizations of the Er-Yb alloyed NCs

The inorganic ternary rare earth chloride $\text{Cs}_3\text{Er}_x\text{Yb}_{1-x}\text{Cl}_6$ NCs were prepared by the variable hot injection [31–34]. Cs_3ErCl_6 NC presents a 0D monoclinic structure with C12/c1 space group, where the $[\text{ErCl}_6]^{3-}$ octahedra units are isolated by the surrounding Cs^+ ions completely (Fig. 1(a)). XRD feature of the Cs_3ErCl_6 NCs reveals that there is a high crystallinity and a single pure phase (Fig. 1(b)). XRD data can be refined using the black calculated line, and the lattice parameters of Cs_3ErCl_6 NCs are given in Table S1 of the Electronic Supplementary Material (ESM). Figure 1(c) shows the XRD patterns of $\text{Cs}_3\text{Er}_x\text{Yb}_{1-x}\text{Cl}_6$ NCs with the different Er-Yb alloyed ratio ($x = 0, 0.06, 0.25, 0.50$, and 1) from bottom to top. Both of them have a pure phase, confirming the absence of undesired secondary phases. Moreover, there is almost no shift of

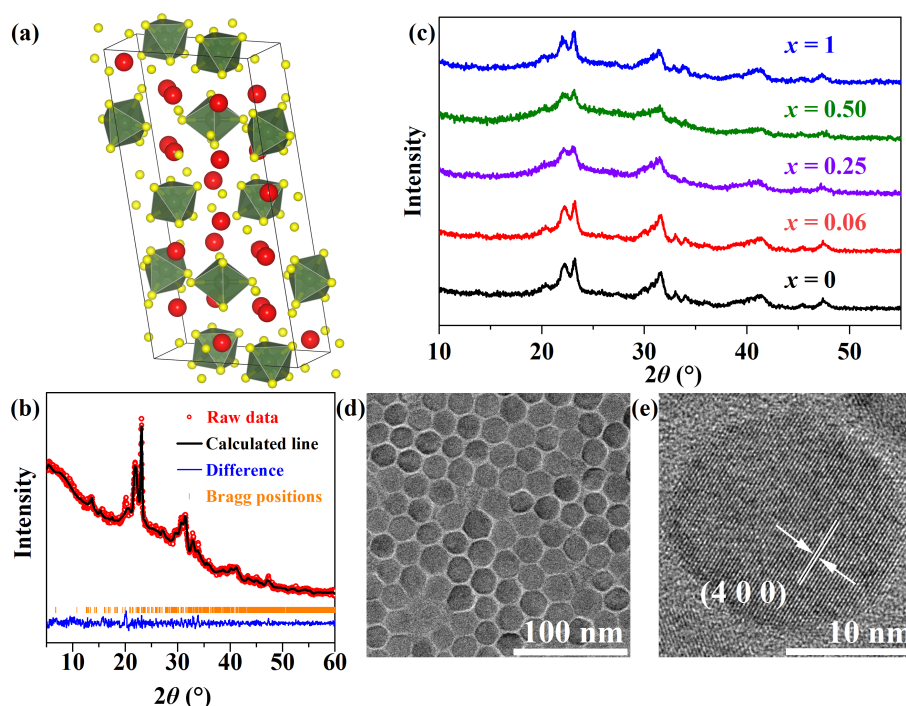


Figure 1 Structural characterizations: (a) Crystal structure and (b) XRD pattern of Cs_3ErCl_6 NCs. (c) XRD patterns of $\text{Cs}_3\text{Er}_{1-x}\text{Yb}_x\text{Cl}_6$ ($x = 0, 0.06, 0.25, 0.50$, and 1) NCs. (d) TEM and (e) HRTEM images of $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs.

the diffraction peaks, due to similar trivalent ionic radius of rare earth Er^{3+} and Yb^{3+} ions. It is indicated that the crystal structure of the NCs would not be broken by Er-Yb alloying. XRD characterization and refinement parameters of Cs_3YbCl_6 NCs are also given in Fig. S1 and Table S2 in the Electronic Supplementary Material (ESM). There exhibited a high monodispersity and quasi-spherical shape uniformity for $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs clearly in the TEM image of Fig. 1(d). The NCs average size were ~ 18.7 nm (Fig. S2 in the ESM).

A high-resolution TEM (HRTEM) image of individual NC confirms a high crystallinity and the lattice spacing value is ~ 2.8 Å, corresponding to the (400) lattice plane (Fig. 1(e)). In addition, the inductively coupled plasma optical emission spectrometer (ICP-OES) measurements were carried out, the actual amounts of Er^{3+} and Yb^{3+} ions are similar to the feed ratio in Table S3 in the ESM.

3.2 Optical properties of $\text{Cs}_3\text{Er}_x\text{Yb}_{1-x}\text{Cl}_6$ NCs

As shown in Fig. 2, the optical characteristics of $\text{Cs}_3\text{Er}_x\text{Yb}_{1-x}\text{Cl}_6$ NCs were investigated by ultraviolet-visible (UV-vis) absorption, NIR PL emission, and TR-PL spectra. Cs_3ErCl_6 and Cs_3YbCl_6 NCs present a direct band structure with the band gap $E_g = 5.8$ eV (Fig. S3 in the ESM). There is little absorption change for all alloyed $\text{Cs}_3\text{Er}_x\text{Yb}_{1-x}\text{Cl}_6$ NCs, and they are still the direct band structure (Fig. 2(a)). Upon UV light excitation at 280 nm, $\text{Cs}_3\text{Er}_{1-x}\text{Yb}_x\text{Cl}_6$ NCs can emit a dual PL combining an NIR-I emission centered at 987 nm and a sharp NIR-II emission at the fiber-optic communication wavelength of 1543 nm (Fig. 2(b)), originating from the f-band Laporte forbidden transition ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ and ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ of Yb^{3+} and Er^{3+} ions, respectively. There emits a strong NIR-I PL for Cs_3YbCl_6 NCs, and its intensity can be quenched gradually with the Yb amount decreasing in the alloyed NCs. Meanwhile, Cs_3ErCl_6 NCs would merely emit a weak NIR-II PL, implying that many defect trapping induced nonradiative recombination would occur. It is interesting that the Er-Yb alloying can enhance the sharp

NIR-II PL of Er^{3+} ions rather than quench the PL with the Er amount decreasing. In $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs, a little Er amount ($x = 0.06$) in the alloyed NCs presents the strongest NIR-II PL (Fig. S4 in the ESM), indicating that there exists the energy transfer from ${}^2\text{F}_{5/2}$ and ${}^4\text{I}_{13/2}$ states and it is conducive to the Er^{3+} ions' emission. The absolute NIR-II PLQY of $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs at around 1543 nm is up to 2.7% (Fig. S5 in the ESM), further improving the NIR-II PL ten-fold than that of our previous reported $\text{Cs}_2\text{NaEr}_{0.5}\text{Sb}_{0.5}\text{Cl}_6$ NCs [33], and the entire NIR PLQY is 4.9%.

TR-PL spectra were also performed to explore the energy transfer dominant NIR-II PL enhancement of the Er-Yb alloyed NCs. The NIR PL decay dynamics at 987 and 1543 nm can be bi-exponentially fitted, as shown in Figs. 2(c) and 2(d). The average lifetime of Cs_3YbCl_6 NCs is 29.1 μs . With the Yb amount decreasing, the NIR-I PL lifetime of Yb^{3+} ions would be reduced to 3.7 μs in the $\text{Cs}_3\text{Er}_{0.50}\text{Yb}_{0.50}\text{Cl}_6$ NCs (Fig. 2(c)). Both the shorter lifetime and the weaker NIR PL of the Yb^{3+} ions illustrate that its radiative transition can be suppressed of ${}^2\text{F}_{5/2}$ state and the energy prefers to transfer to ${}^4\text{I}_{13/2}$ of the Er^{3+} ions. Energy transfer efficiency η_{ET} from Yb^{3+} to Er^{3+} ions can be evaluated by $\eta_{\text{ET}} = 1 - \tau_x/\tau_0$ [35], where τ_x and τ_0 are the average PL lifetimes of the alloyed and Cs_3YbCl_6 NCs at 987 nm, respectively. $\eta_{\text{ET}} = 43.3\%$ in $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs, and it can reach up to 87% as x increased to 0.5. A highest energy transfer could not produce a strongest NIR-II PL in the Er-Yb alloyed NCs.

Then, the NIR-II PL decay dynamics of the Er^{3+} ions can be inquired. The average lifetime of Cs_3ErCl_6 NCs at 1543 nm is 25.3 μs (Fig. 2(d)). It can be prolonged to 157.0 μs in $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs. However, more Er^{3+} ions in the alloyed NCs presents a shorter lifetime, accompanying with a weaker NIR-II PL. It originates from the enhanced nonradiative recombination of ${}^4\text{I}_{13/2}$ states, and excessive Er^{3+} ions cause concentration quenching. The longer NIR-II PL lifetime reveals there is an excellent crystallization environment for the Er^{3+} ions, indicating that the Er-Yb alloying

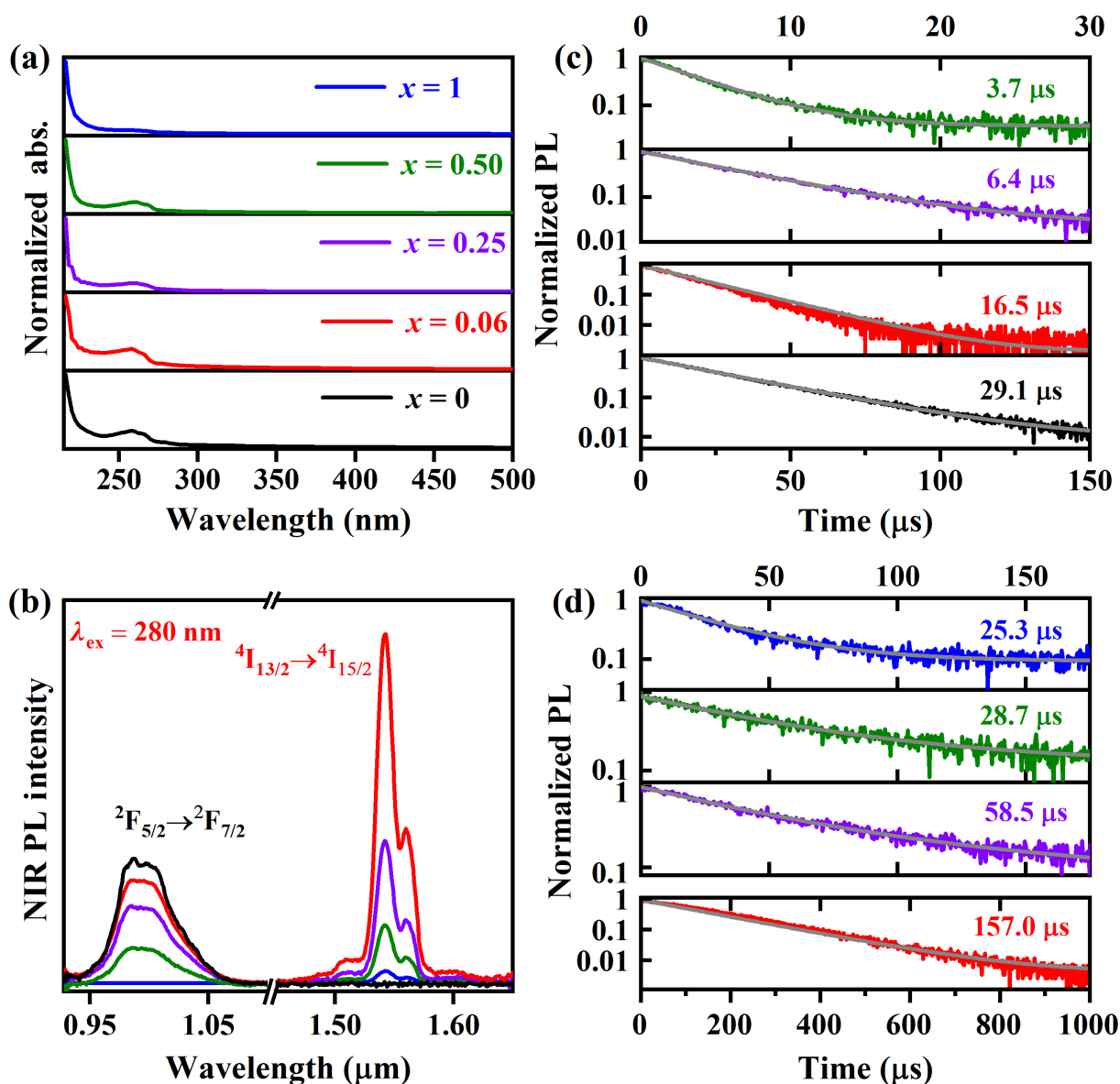


Figure 2 Optical properties of $\text{Cs}_3\text{Er}_x\text{Yb}_{1-x}\text{Cl}_6$ NCs: (a) Absorption spectra and (b) NIR PL spectra at UV light excitation. TR-PL spectra of (c) Yb and (d) Er ions in the NCs and their corresponding fitting curves (gray line).

would passivate the nonradiative defect trapping states. To achieve a higher NIR-II PL of $\text{Cs}_3\text{Er}_x\text{Yb}_{1-x}\text{Cl}_6$ NCs, it needs an excellent crystallization environment, and to balance the relationship between energy transfer and concentration quenching of the Er^{3+} ions.

3.3 Theoretical analysis on the electronic properties

We conducted first-principal calculations to gain a deep understanding on the electronic properties of the inorganic ternary rare earth chloride [36–39]. Figure 3 presented calculated electronic band structures, projected density of states (PDOS) and conduction band minimum (CBM)/valence band maximum (VBM) projected charge densities. Cs_3ErCl_6 and $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ exhibit direct band gaps with the energy of 5.8 eV in Figs. 3(a) and 3(b). Both CBM and VBM are at the Γ point. The introduction of Yb atoms has negligible effects on the type and energy of the band gap, which is consistent with the experimental results. Figures 3(c) and 3(d) present PDOS for Cs_3ErCl_6 and $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$, the CBM and

VBM are both primarily contributed by Er and Cl atoms, respectively. The A-site Cs cation exerts a minimal influence on the CBM and VBM [40, 41]. The projected real-space charge densities of the CBM and VBM for Cs_3ErCl_6 , $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ and Cs_3YbCl_6 are shown in Figs. 3(e) and 3(f), and Fig. S6(c) in the ESM, respectively. The charge of the CBM and VBM evenly distributed around Er/Yb and its associated Cl atoms in Cs_3ErCl_6 or Cs_3YbCl_6 . As depicted in Fig. 3(f), the charge of the CBM in $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ concentrated distributed around the small amount Er atom rather than the Yb atom, and the photogenerated carriers are localized on the isolated $[\text{ErCl}_6]^{3-}$ octahedra, showing a highly localized charge distribution [42, 43]. It can be responsible for the enhanced NIR-II PL in $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$.

3.4 Photophysical mechanism of NIR-II PL enhancement

In order to gain more insight into the photophysical mechanism of $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs, the temperature-dependent NIR-II PL of the Er^{3+} ions were further analyzed. With the temperature being

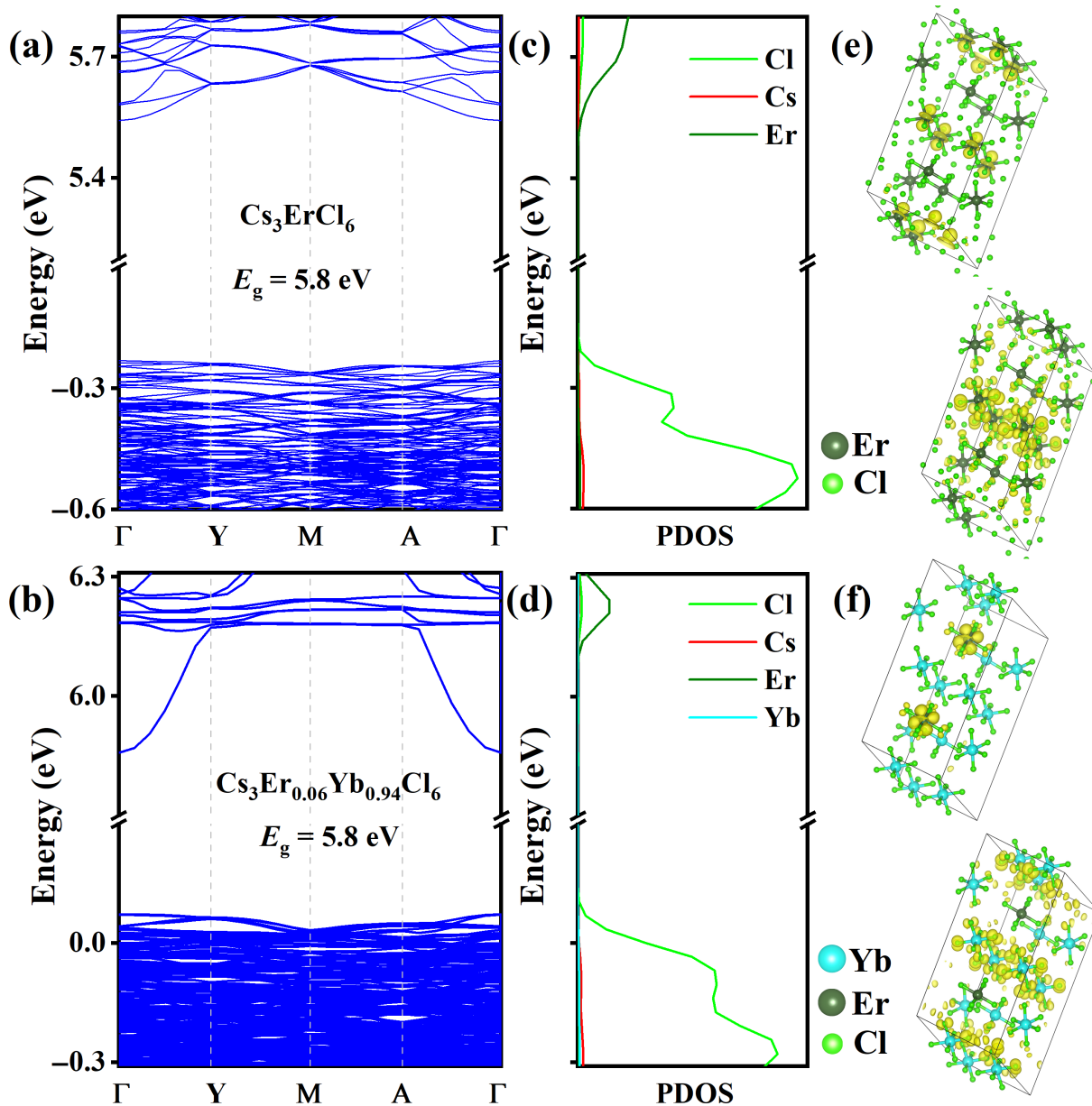


Figure 3 (a) and (b) Electronic band structures, (c) and (d) PDOS, and (e) and (f) CBM/VBM (upper/lower panel) projected charge density maps of ((a), (c), and (e)) Cs_3ErCl_6 and ((b), (d), and (f)) $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$. In (e) and (f), Cs atoms are not depicted in the schematic representations for the purpose of clarity.

increased from 80 to 500 K, NIR-II PL can be gradually quenched (Fig. 4(a)), suggesting that the lattice vibration is expanded and nonradiative recombination increases. At the low temperature of 80 K, characteristic PL peak of the Er^{3+} ions is slightly blue-shifted from 1543 to 1536 nm. It can be attributed that the crystal lattice undergoes a little contraction, resulting in the slightly strengthened crystal field [44–47]. The exciton binding energy (E_b) can be calculated by the following formula [48]

$$I(T) = \frac{I_0}{1 + A \exp\left(-\frac{E_b}{k_b T}\right)} \quad (1)$$

where k_b is the Boltzmann constant, I and I_0 is the integrated intensity at different temperature (T) and 0 K, respectively. For Cs_3ErCl_6 NCs, there is an exciton binding energy $E_b = 71.7$ meV (Fig. S7 in the ESM). It is much larger than the thermal ionization

energy at room temperature (≈ 26 meV) [49–51], suggesting a relatively high energy barrier to retard thermal quenching. E_b of $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs can be improved to 184.5 meV in Fig. 4(b). The large exciton binding energy is favorable for the stabilization and survival of localized excitons at high temperature, which is easy to achieve a high PL efficiency [52–54]. To understand the exciton-phonon coupling, temperature-dependent full width at half maximum (FWHM) can be quantitatively analyzed by the following formula [55]

$$\text{FWHM} = 2.36\sqrt{S\hbar\omega} \sqrt{\coth\left(\frac{\hbar\omega}{2k_b T}\right)} \quad (2)$$

where S is Huang–Rhys parameter, $\hbar\omega$ is phonon energy. Generally, a large S corresponds to a stronger tendency to form the self-trapped excitons (STEs) and leads to a larger coordinate difference between free exciton state and STEs [56, 57]. As shown

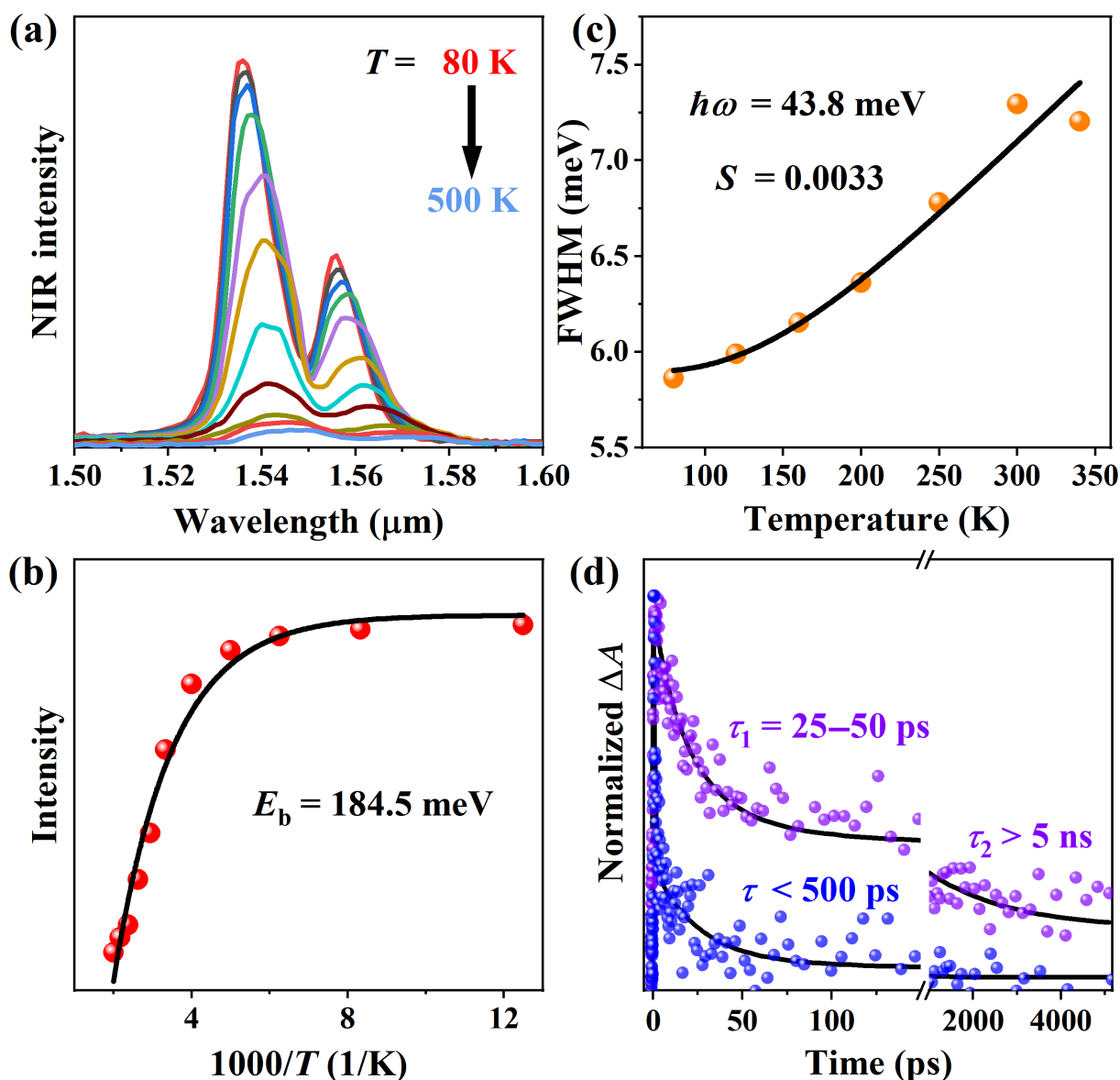


Figure 4 (a) Temperature-dependent NIR-II PL spectra of $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs ranging from 80 to 500 K. The relationship of the integral (b) intensity or (c) FWHM at $1.54 \mu\text{m}$ vs. temperature, respectively. (d) PIA decay dynamics of Cs_3ErCl_6 (blue) and $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ (purple) NCs in the femtosecond TA measurement.

in Fig. 4(c), it is obtained that $S = 0.0033$ and $\hbar\omega = 43.8 \text{ meV}$ for the Er^{3+} ions. In $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs, Huang–Rhys parameter is between 0 and 1, illustrating there is a much weaker exciton-phonon coupling interaction. The photogenerated excitons are bound to isolated $[\text{ErCl}_6]^{3-}$ units to form highly localized excitons, rather than the STEs in the alloyed NCs, consistent with the above theoretical calculation results. The highly localized exciton is one of the keys determining factors for the efficient NIR-II PL in the Er-Yb alloyed NCs.

Femtosecond TA measurement was also performed to further explore the exciton dynamics of the inorganic ternary rare earth chloride NCs. There is a broad photoinduced absorption (PIA) feature in the TA spectrum of Cs_3ErCl_6 NCs. PIA dynamics can be fitted by a single-exponential decay with a fast lifetime of $\tau < 500 \text{ ps}$ (Fig. 4(d)). The fast process with several hundred picoseconds is attributed to a nonradiative defect trapping. In the $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs, there are two decay components: $\tau_1 = 25\text{--}50 \text{ ps}$ and $\tau_2 > 5 \text{ ns}$. The ultrafast process corresponds to exciton energy transfer from

the Yb^{3+} to Er^{3+} ions, which is beneficial to the enhanced NIR-II PL of Er^{3+} ions. The emerging slow process demonstrates the existence of localized excitons in the alloyed NCs [58], which is consistent with the above discussions. The dynamics of several hundred picoseconds disappears in $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs, indicating that the Er-Yb alloying can effectively passivate the non-radiative defect trapping state.

3.5 Applications

Given the exceptional NIR optical properties of $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs, the stability testing has been conducted. The Er-Yb alloyed NCs remain unchanged after three weeks (Fig. S8 in the ESM), and show almost no PL quenching after exposure to air for 3 months (Fig. S9 in the ESM). Utilizing the excellent optical performance and admirable stability, a NIR pc-LED was fabricated considering $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs as a single-component phosphor, in which the polymethyl methacrylate (PMMA) blended with the alloyed NCs was excited by a 280 nm commercial UV-LED chip (Fig. S10 in the

ESM). As-fabricated high performance NIR pc-LED based on $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs can be considered as an emitter to achieve the optical communication, as shown in Fig. 5(a).

After loading the square-wave electric signals to the UV-chip, NIR PL of $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs can be modulated. Compared to

the input signals, the output NIR PL recording by an InGaAs photodiode (PD) has no obvious distortion at the different frequencies of 10, 50, and 100 Hz in Fig. 5(b). Furthermore, many barriers including the card or bacon are placed before the PD device. NIR emitter based on Cs_3YbCl_6 NCs merely transmits 37%

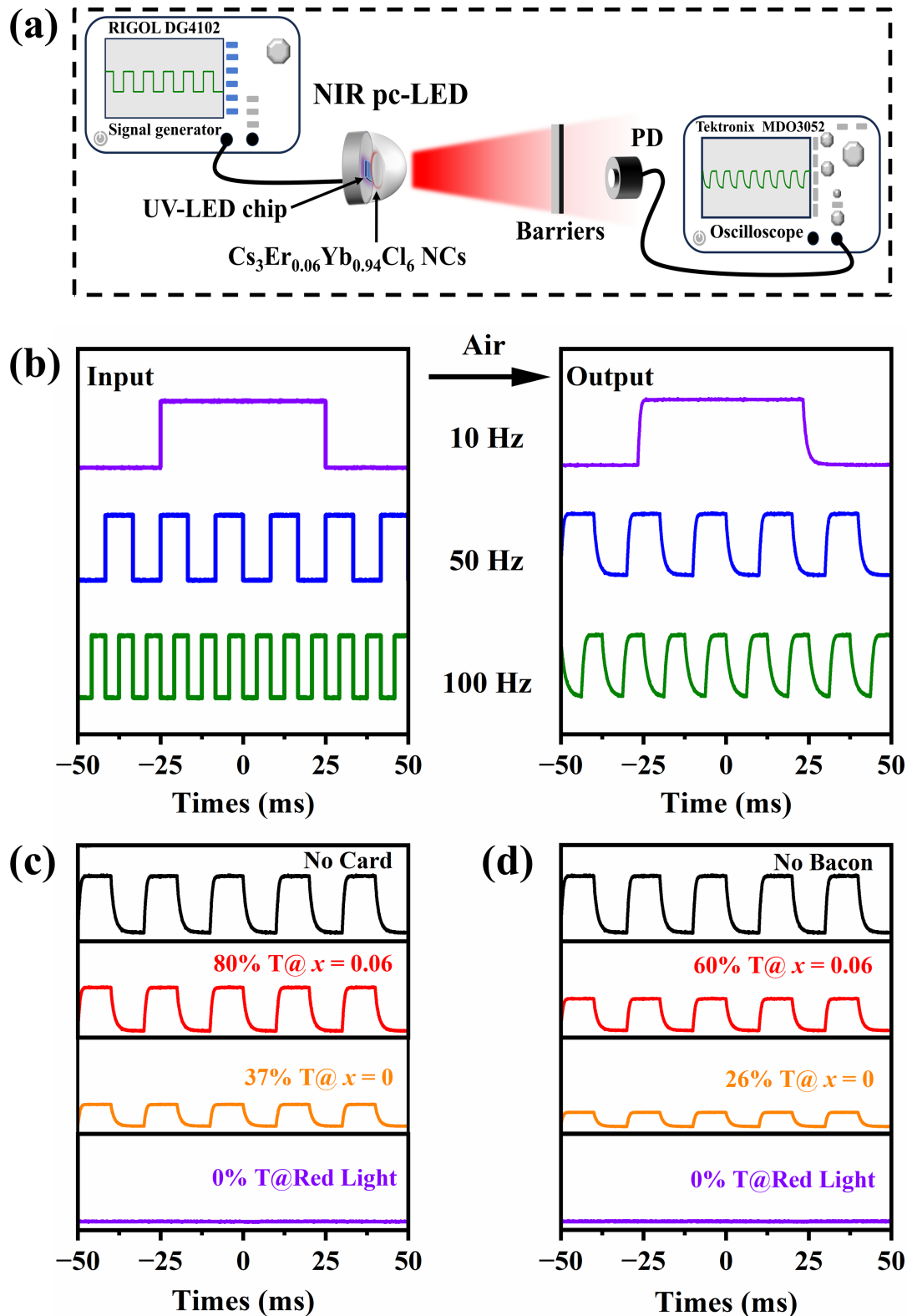


Figure 5 (a) Schematic of optical communication. (b) Input and output signal information of $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs at different frequencies. Attenuation of output signal intensity when using (c) a 1 mm card or (d) a 3 mm bacon slice as the barrier in red, NIR-I and NIR-II communication.

NIR-I PL with a significant PL attenuation through the barrier of 1 mm thick card, and the red light cannot transmit the barrier certainly. In comparison, there is 80% PL of $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs can transmit and exhibits a little NIR-II PL loss (Fig. 5(c)). NIR-II emitter still presents a good penetrability when the barrier changes to 3 mm thick bacon in Fig. 5(d). Herein, it is demonstrated that the Er-Yb alloyed NCs is more suitable for optical communication. A non-invasive detection based on $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs was constructed, as shown in Fig. S11 in the ESM.

4 Conclusions

In summary, a series of inorganic ternary $\text{Cs}_3\text{Er}_x\text{Yb}_{1-x}\text{Cl}_6$ ($x = 0, 0.06, 0.25, 0.50$, and 1) NCs were synthesized. The optimized $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs demonstrated a remarkable 27-fold enhancement in NIR-II PL at 1543 nm of Er^{3+} ions with a PLQY of 2.7% and a lifetime of 157 μs . It is revealed by temperature-dependent PL and theoretical analysis that the exceptional performance originates from a large exciton binding energy, weak exciton-phonon coupling and reduced nonradiative recombination in $\text{Cs}_3\text{Er}_{0.06}\text{Yb}_{0.94}\text{Cl}_6$ NCs. The enhanced NIR-II PL is primarily attributed to highly localized excitons, efficient energy transfer from Yb^{3+} to Er^{3+} ions, and passivation of nonradiative defect trapping states. This work not only provides profound insight into the photophysics of rare earth halide NCs, but also paves a novel avenue for designing high-performance NIR emitters for advanced photonic applications. Ultimately, a single-component NIR-II pc-LED fabricated using these NCs, owing to its good penetrability, validates their practical potential in optical communication.

Electronic Supplementary Material: Supplementary material (XRD patterns and their refinement parameters; ICP-OES results; size distribution histogram; PL spectra; Tauc plots; NIR PLQY results; theoretical calculations; temperature-dependence PL spectra; stability tests; photograph of the fabricated NIR-II pc-LED; non-invasive detection; upconversion PL measurement; and comparison of different metal halide NCs) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908846>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

R. X. W.: Conceptualization, funding acquisition, investigation, project administration, supervision, writing – original draft, writing – review & editing. F. J. G.: Data curation, investigation, methodology, visualization, writing – original draft. Z. L. H.: Formal analysis, investigation, validation, visualization. Z. X. W.: Data curation, investigation, methodology, software. P. G. H.: Conceptualization, funding acquisition, investigation, project administration, resources, writing – review & editing. B. L.: Funding acquisition, investigation, validation, writing – review & editing. R. Z.: Investigation, resources. J. F. Z.: Funding acquisition, validation, writing – review & editing. X. Y. M.: Conceptualization, funding acquisition, project administration, supervision, writing – review & editing. C. B. Q.: Funding acquisition, resources, writing – review & editing. L. T. X.: Conceptualization, funding acquisition, project administration, supervision, writing – review & editing. All the authors reviewed and contributed to this paper.

Use of AI statement

None.

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