Supporting Information for

Photon upconversion-driven NIR photocatalysis via a $CsPbI_3$ NCs@Yb-BTC hybrid for full-spectrum solar harvesting

Xingchen Liu [a,b], Mingming Li [c], Liuliu Zhang [a,b], Ge Li [a,b], Junjie Zhou [a,b], Guijie Liang [a,b], Chunyi Zhao[d], Rui Chen[e], Zixi Yin [a,b,*], Song Wang [a,b,*]

[a] Hubei Key Laboratory of Low Dimensional Optoelectronic Materials and Devices, Hubei University of Arts and Science, Xiangyang 441053, Hubei, China.

[b] Institute of Functional Materials, Hubei University of Arts and Science, Xiangyang 441053, Hubei, China.

[c] Academy of Aerospace Solid Propulsion Technology, Xian 710025, Shaanxi, China.

[d] Anhui Province Key Laboratory of Optoelectronic Materials Science and Technology, School of Physics and Electronic Information, Anhui Normal University, Wuhu 241002, China.

[e] Xiangyang Huazhi Technology Co., Ltd., Xiangyang 441138, Hubei, China.

Experimental details

All chemicals are of analytical grade and used directly without further purification.

Synthesis of Yb-BTC and Pb@Yb-BTC microcrystals

Pure Yb-BTC was synthesized and purified using the solvothermal method based on a previous report. A mixture of 1 mmol $YbCl_3 \cdot 6H_2O$, 0.5 mmol 1,3,5-benzenetricarboxylic acid (H_3BTC), 20 mL DMF, and 10 mL deionized water was stirred at room temperature for 2 hours. The solution was then transferred to a 50 mL Teflon-lined autoclave and heated at 140 °C for 6 hours. After cooling, the solid product was isolated by filtration, washed repeatedly with DMF and ethanol, and dried at 80 °C for 12 hours.

Pb@Yb-BTC was prepared following the same procedure, with the addition of 1 mmol $Pb(NO_3)_2$ to the initial reaction mixture alongside $YbCl_3 \cdot 6H_2O$ and H_3BTC. The subsequent steps of heating, filtration, washing, and drying remained unchanged. This material served as a modified MOF template, where XPS and SEM confirmed partial Yb^{3+} substitution by Pb^{2+} without framework disruption (Fig. S1c and S3d), creating confined nucleation sites for controlled $CsPbI_3$ growth.

Synthesis of $CsPbI_3$ PQDs@Yb-BTC microcrystals

First, the Cs-OA precursor solution was prepared. 0.16 g of Cs_2CO_3 was dissolved in a mixture of 2.5 mL oleic acid and 6 mL 1-octadecene. Under a nitrogen atmosphere, the mixture was heated to

120°C with stirring for 30 min. The temperature was then raised to 150°C and maintained for 5 minutes until a clear solution was obtained. The resulting Cs-OA oleate solution was allowed to cool to room temperature and stored. It was reheated to 100°C before use.

Subsequently, $CsPbI_3$@Yb-BTC was synthesized. The prepared Cs-OA oleate solution was preheated to 100°C. In a separate vessel, PbI_2 (0.094 mmol, 0.0433 g) and the pre-synthesized Pb@Yb-BTC MOF (0.15 g) were dispersed in the mixture of oleylamine (0.5 mL), oleic acid (0.5 mL) and 2.5 mL of 1-octadecene. Under a nitrogen atmosphere, this mixture was heated to 120°C and reacted for 1 hour. Immediately afterwards, the temperature was raised to 160°C. At this point, 0.2 mL of the preheated Cs-OA oleate solution was quickly injected. The reaction proceeded for only 5 seconds before being rapidly cooled by immersing the flask in an ice-water bath. The final product was collected via centrifugation at 1000 rpm for 5 minutes. The supernatant was discarded, and the obtained solid was washed twice with an anhydrous ethanol solution and dried at 45 °C for 24 hours.

Synthesis of $CsPbI_3$ PQDs nanocrystals

First, the Cs-OA (cesium oleate) precursor solution was preheated to 100 °C. Separately, PbI_2 (0.0433 g), oleic acid (0.5 mL), oleylamine (0.5 mL), and 2.5 mL of 1-octadecene were added to a reaction flask. The mixture was heated to 120 °C under nitrogen and maintained for 1 hour with stirring. Subsequently, the temperature was raised to 160°C and the preheated 0.2 mL Cs-OA precursor solution was swiftly injected into the reaction flask under continuous nitrogen flow. The reaction was allowed to proceed for approximately 5 seconds before the flask was immediately immersed in an ice-water bath to rapidly cool the mixture to room temperature. The crude product was then collected by centrifugation at 6000 rpm for 5 minutes. The resulting precipitate was re-dispersed in ethyl acetate and centrifuged again at 6000 rpm for 5 minutes to isolate the purified solid. Finally, this purified precipitate was dispersed in 3 mL of n-hexane, and the dispersion was centrifuged at 6000 rpm for 5 minutes. The supernatant containing the final product was collected for further use.

Structure and Optical Characterization

The XRD patterns were acquired on the D8 Advance X-ray diffractometer equipped with a Cu-Kα radiation, with data expressed in the 2θ range from 5° to 80°. XPS were acquired on the Thermo Scientific escalab 250xi system with Al Kα (1486.6 eV) as the excitation source. A Hitachi S4800 SEM (accelerating voltage 5 kV) was adopted for exploring samples’ morphology. HORIBA EX-250 instrument was applied to EDS measurement. TEM images were obtained on a HT7800 transmission electron microscope (Japan). The UV-vis absorption spectra were acquired employing a spectrophotometer UV-3700, manufactured by Shimadzu Corporation of Japan, utilizing barium sulfate ($BaSO_4$) as the reference standard. Photoluminescence (PL) spectra were procured with the aid of an F-4700 Hitachi fluorescence spectrophotometer. The excitation source employed was a picosecond pulse laser with an emission wavelength of 405 nm. Time-resolved photoluminescence spectra were acquired utilizing an FLS980 fluorescence spectrometer, which is equipped to conduct both steady-state and transient measurements.

Femtosecond transient absorption measurement

The femtosecond transient absorption setup used for this study is based on a regenerative amplified Ti:sapphire laser system from Coherent (800 nm, 35 fs, 6 mJ pulse-1, and 1 kHz repetition rate), nonlinear frequency mixing techniques and the Femto-TA100 spectrometer (Time-Tech Spectra). Briefly, the 800 nm output pulse from the regenerative amplifier was split into two parts with a 50% beam splitter. The transmitted part was used to pump a TOPAS Optical Parametric Amplifier (OPA) which generates a wavelength tunable laser pulse from 250 nm to 2.5 µm as a pump beam. The reflected 800 nm beam was split again into two parts. One part with less than 10% was attenuated with a neutral density filter and focused into a 2 mm thick sapphire window to generate a white light continuum (WLC) from 420 nm to 800 nm used for the probe beam. The probe beam was focused with an Al parabolic reflector onto the sample. After the sample, the probe beam was collimated and then focused into a fiber-coupled spectrometer with CMOS sensors and detected at a frequency of 1 kHz. The delay between the pump and probe pulses was controlled by a motorized delay stage. The pump pulses were chopped by a synchronized chopper at 500 Hz and the absorbance change was calculated with two adjacent probe pulses (pump-blocked and pump-unblocked). All experiments were performed at room temperature.

Photocatalytic test

The photocatalysis experiment was processed in multichannel photochemical reaction system (CEL-LB70, Ceaulight) with 300 mW/cm^2 Xe lamp light source. The photocatalysis under NIR irradiation and visible light was carried out using an optical filter with a wavelength (λ) greater than 800 nm and a total reflection filter, and an optical filter with $\lambda > 420$ nm, respectively. The photocatalytic activity was studied by preparing 20 mg/L Rhodamine B (RhB) as the experimental mode. 0.1 g of sample was added to 100 mL RhB solution with continuously stirring. Before the photocatalytic experiment, the reaction system was treated in the dark for 30 min to achieve the adsorption-desorption equilibrium. After light reaction for a certain time, 5 mL suspension was taken and separated by centrifugation. The concentration of RhB was determined by spectrometer. Radical trapping experiments were carried out to identify the main active species in the NIR-driven RhB degradation process over $CsPbI_3$ NCs@Yb-BTC. Isopropyl alcohol (IPA) was used as the scavenger for hydroxyl radicals (•OH), p-benzoquinone (BQ) as the scavenger for superoxide radicals ($\bullet O_2^-$), and ethylenediaminetetraacetic acid (EDTA) as the scavenger for photogenerated holes (h^+).

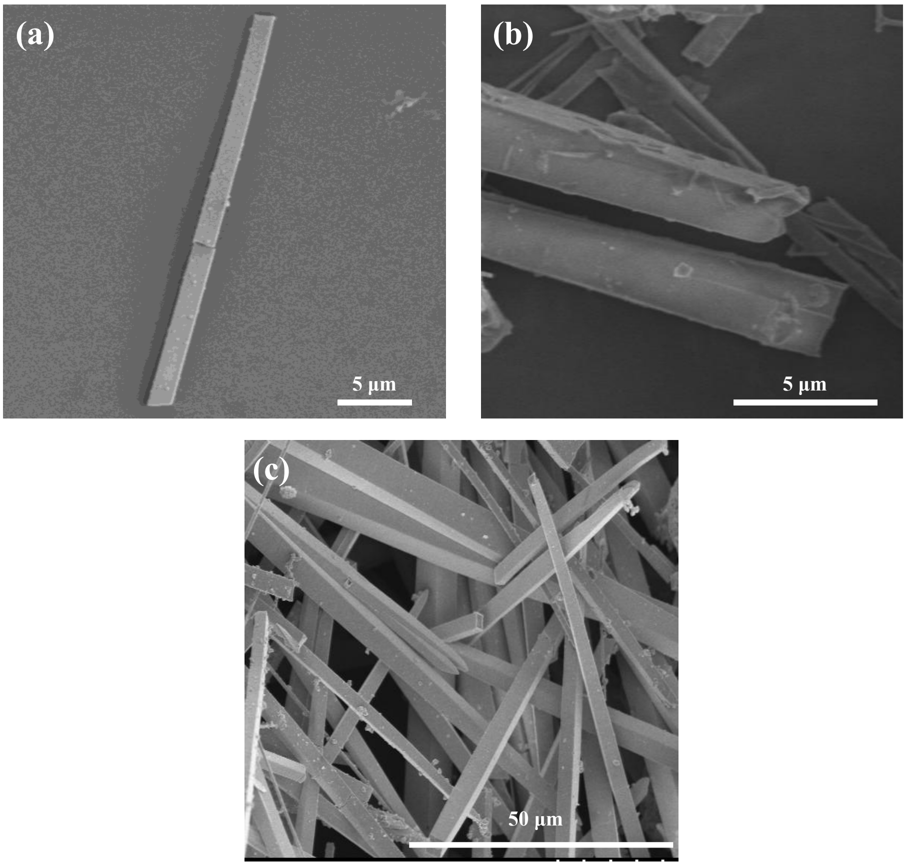

Fig. S1. SEM image of (a) pure Yb-BTC, (b) $CsPbI_3$ NCs@Yb-BTC and (C) Pb@Yb-BTC.

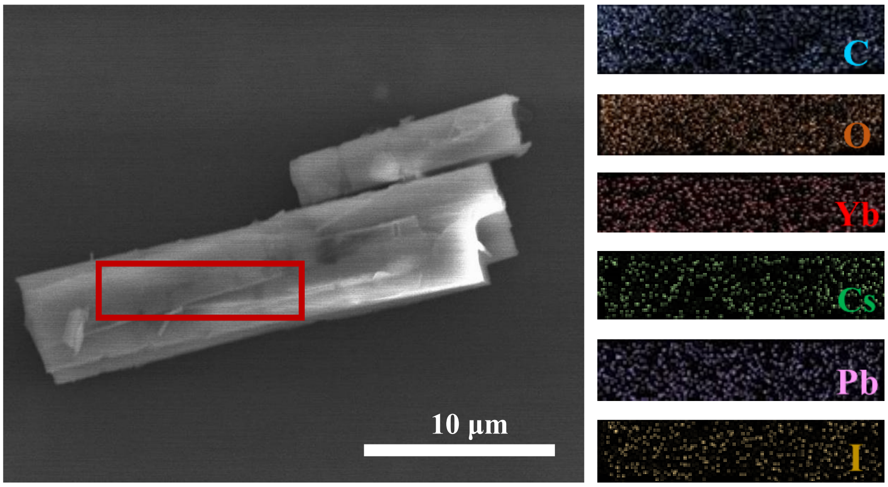

Fig. S2 The elemental mapping diagrams of CsPbI$_3$ NCs@Yb-BTC.

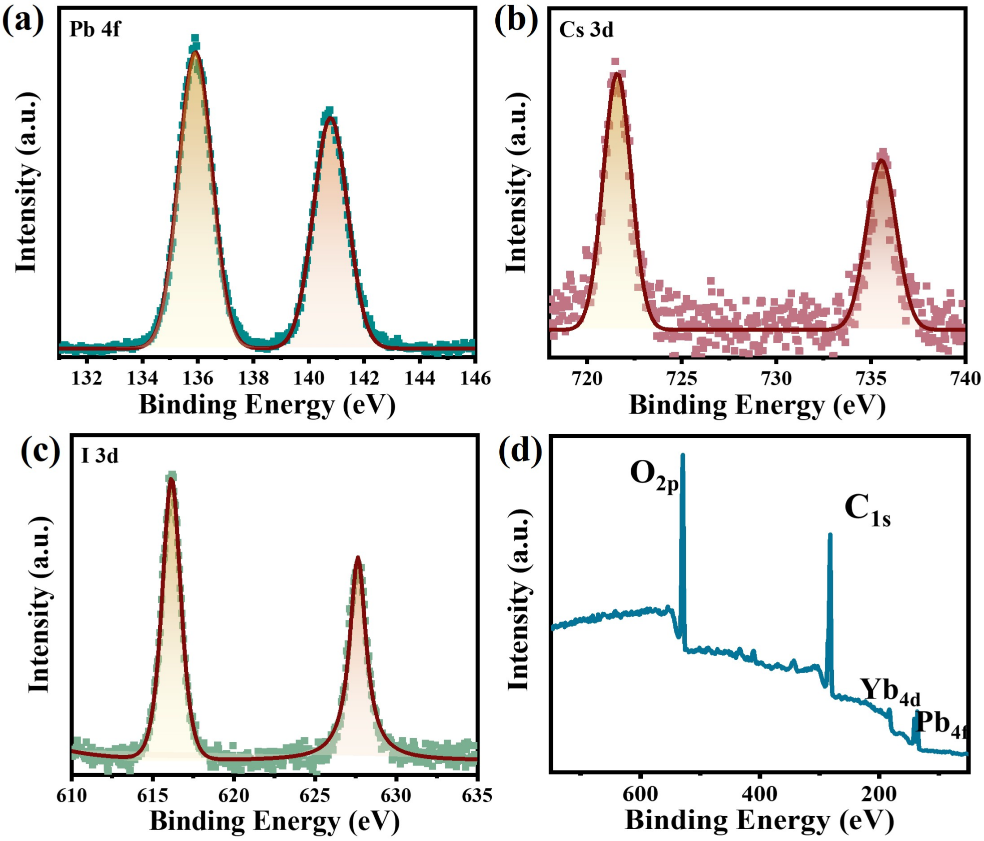

Fig. S3 The high-resolution XPS profiles of (a) Pb 4f, (b) Cs 3d, (c) I 3d in CsPbI$_3$ NCs@Yb-BTC. (d) The XPS survey spectra of Pb@ Yb-BTC.

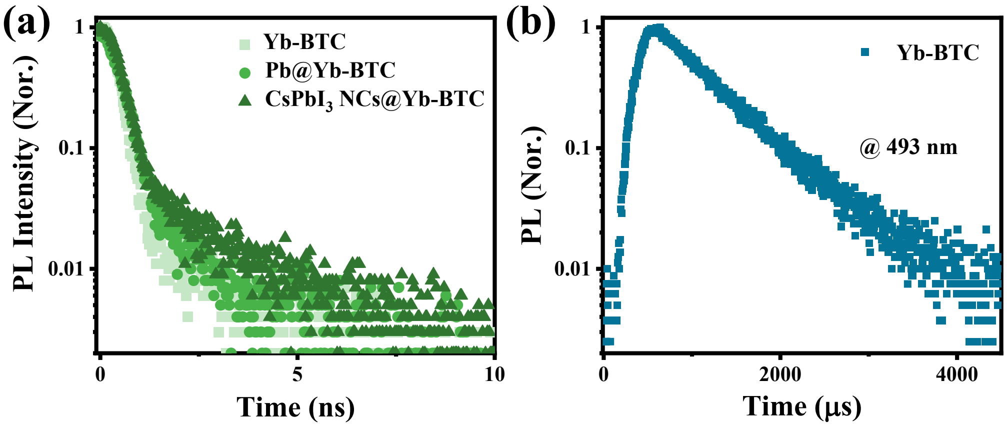

Fig. S4 (a) Normalized PL kinetics collected around 550 nm in Yb-BTC, Pb@ Yb-BTC, and $CsPbI_3$ NCs@Yb-BTC under 400 nm excitation. (b) Upconversion PL kinetic of Yb-BTC collected at 493 nm under 980 nm excitation.

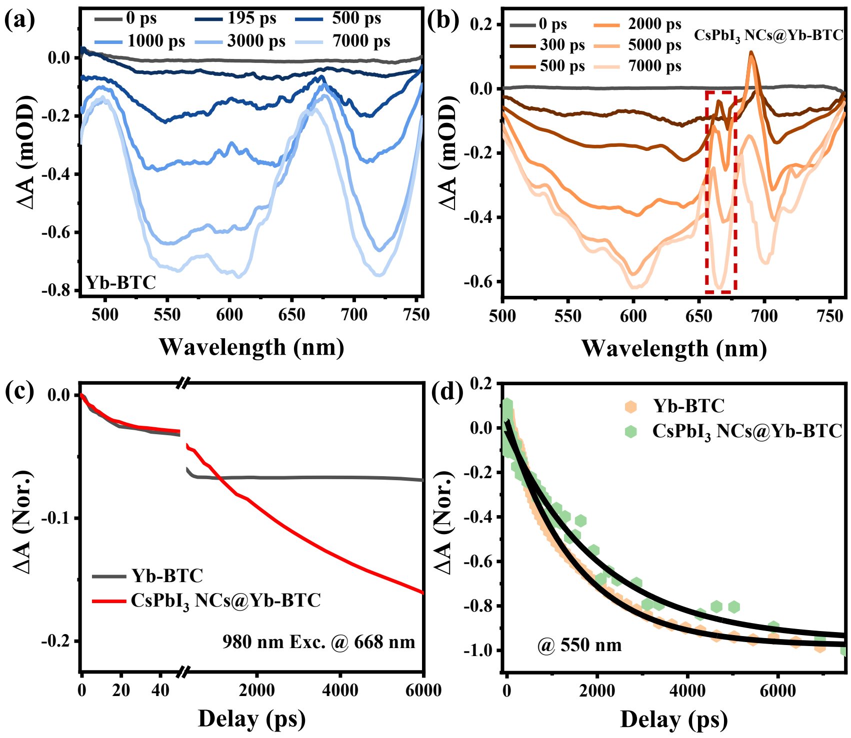

Fig. S5 TA spectra of (a) Yb-BTC and (b) $CsPbI_3$ NCs@Yb-BTC and at indicated delay times under 980 nm excitation. (c) Normalized TA kinetics of Yb-BTC and $CsPbI_3$ NCs@Yb-BTC probed at 668 nm. (d) Normalized TA kinetics of Yb-BTC and $CsPbI_3$ NCs@Yb-BTC probed at 550 nm under 980 nm excitation.

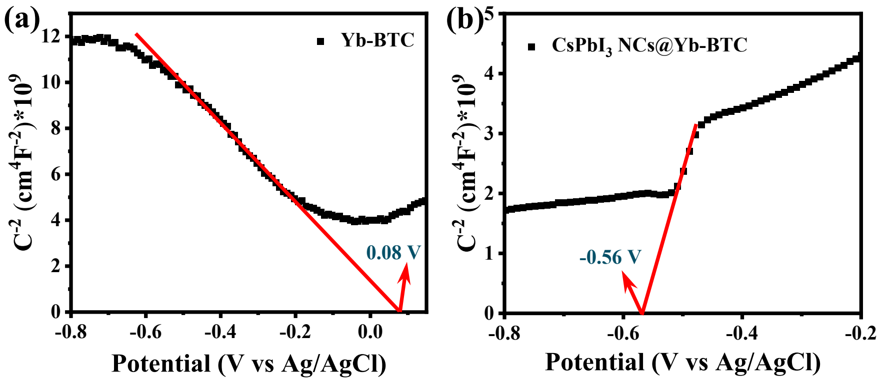

Fig. S6 The Mott-Schottky plots of (a) Yb-BTC and (b) $CsPbI_3$ NCs@Yb-BTC.

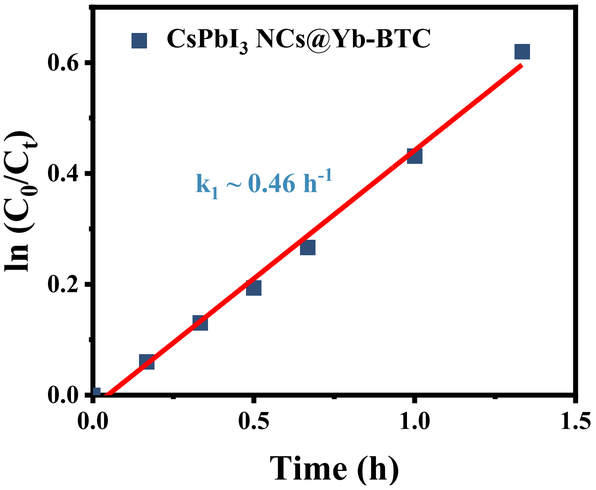

Fig. S7 Photocatalytic kinetic fit plots of $CsPbI_3$ NCs@Yb-BTC under NIR light irradiation. The photocatalytic reaction process can be fitted by the first-order kinetic equation: $\ln(C_0/C_t) = k_1t$.

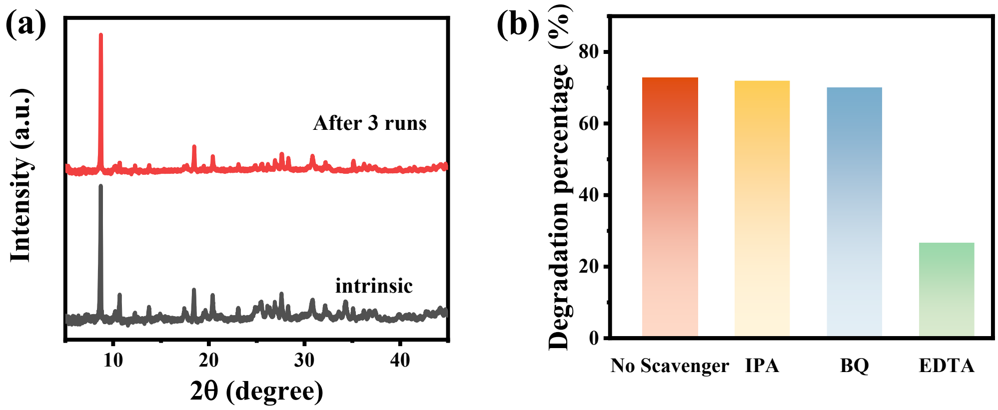

Fig. S8 (a) XRD patterns of $CsPbI_3$ NCs@Yb-BTC before and after cycling tests. (b) Reactive species trapping experiments for the NIR-driven RhB degradation over $CsPbI_3$ NCs@Yb-BTC photocatalyst

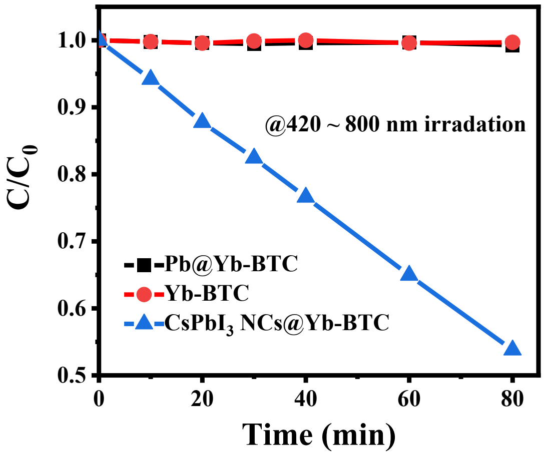

Fig. S9 Photocatalytic degradation of RhB over pure Yb-BTC, Pb@Yb-BTC and $CsPbI_3$ NCs@Yb-BTC under visible light irradiation.

Table S1. Single-exponential fitting parameters for the kinetics of Yb-BTC and $CsPbI_3$ NCs in $CsPbI_3$ NCs@Yb-BTC shown in Fig. 3c, where τ is the fitting PL lifetimes (μs).

Wavelength	493 nm	668 nm
τ (μs)	669	794

Table S2. Single-exponential fitting parameters for the kinetics of Yb-BTC in Yb-BTC and $CsPbI_3$ NCs@Yb-BTC shown in Fig. S5d, where τ_1 is the fitting lifetimes (ps).

Sample (@ 550 nm)	**Yb-BTC**	**$CsPbI_3$ NCs@Yb-BTC**
τ_1 (ps)	**1505**	**2071**