Supplementary Information (SI) for Nanoscale.

Electronic Supporting Information for

Hot carrier harvesting at the interface of $CsPbI_3$ nanocrystals

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Experimental section

Chemicals used

Caesium carbonate (Cs_2CO_3, ~99%), lead acetate trihydrate [$Pb(OAc)_2 \cdot 3H_2O$, ≥99%], 1,3-diiodo-5,5-dimethylhydantoin (DIDMH, ≥96%), 1-octadecene (ODE, technical grade, ~90%), oleic acid (OA, technical grade, ~90%), oleylamine (OAm, technical grade, ~70%), hexane (≥99%), and methyl acetate (~99%) were obtained from Sigma-Aldrich. The chemicals were utilized in their original form without undergoing any additional purification.

Synthesis of $CsPbI_3$ nanocrystals

For the synthesis of $CsPbI_3$ NCs, a reported three-precursor hot-injection method was followed with slight modifications.[1-2]

(i) **Caesium Oleate (Cs-oleate) preparation**

To prepare Cs-oleate, 21.7 mg (0.067 mmol) of Cs_2CO_3 and 112 μL of OA were mixed thoroughly with 1 mL of ODE in a 25 mL two-neck round-bottom flask. The mixture was heated at 120 °C for 1 hour under a nitrogen atmosphere to ensure complete dissolution and removal of any residual moisture and oxygen. After that, the temperature was raised to 150 °C and retained for 15 minutes to complete the reaction. The resulting product was then collected while hot using an air-tight glass syringe and stored in a deaerated vial.

(ii) **Synthesis of colloidal nanocrystal**

In a 25 mL three-neck round-bottom flask, 72 mg of lead acetate (0.188 mmol), 1 mL of OAm, 5 mL of ODE, 1 mL of OA, and 214.5 mg of DIDMH (0.564 mmol) were mixed. The resultant mixture was subsequently heated to 120 °C for 1 hour under a nitrogen atmosphere, allowing the complete dissolution of the solid components and resulting in a clear, deep red solution. The temperature was then raised to 210 °C, and 0.5 mL of pre-heated Cs-oleate (>100 °C) synthesized in the previous step, was quickly injected into the reaction mixture. The reaction was quenched within 5 seconds of the hot injection by immersing the flask in an ice bath. The bright red crude product was centrifuged at 4000 rpm for 5 minutes, and the precipitate, containing larger particles and impurities, was discarded. 15 mL of methyl acetate was added to the remaining supernatant, followed by another centrifugation at 4400 rpm for 10 minutes to isolate the desired nanocrystals. The supernatant was discarded, and the precipitate was redispersed in 2 mL hexane. The bright red colloidal suspension was collected in an oxygen-free vial at around ~4 °C for future optical studies.

Instrumentation

Steady-state absorption and fluorescence spectra

Steady-state absorption and fluorescence spectra were recorded using a double-beam UV-visible spectrophotometer (V-730, Jasco) and a Shimadzu fluorimeter, respectively.

Transmission electron microscopy (TEM)

TEM/HRTEM images were obtained using a JEOL electron microscope (~200 kV, JEM-2100).

Powder X-ray diffraction spectra

The powder XRD data were recorded using a Bruker Davinci D8 advanced diffractometer with Cu-Kα radiation (λ = 1.5418 Å) as X-ray source.

TCSPC, FCS and Femtosecond upconversion studies

Time-resolved emission spectra were acquired using the Edinburgh OB-920 time-correlated single-photon counting (TCSPC) system. A vertically polarized picosecond pulsed diode laser (~375 nm excitation wavelength) with a ~90 ps instrument response function (IRF) was employed for excitation. Emission decay profiles were recorded at the magic angle using an MCP photomultiplier tube (PMT) detector.

FCS measurements were conducted using an inverted confocal fluorescence microscope (MicroTime 200, PicoQuant). The setup features an inverted microscope equipped with a 60x water immersion objective lens optimized for FCS. Detailed descriptions of the FCS instrumentation and data fitting procedures can be found in our recent publications.[3–5]

Femtosecond fluorescence upconversion measurements were carried out in a FluoMax fluorescence upconversion spectrometer (IB Photonics Ltd.). The setup utilized ~820 nm and ~880 nm fundamental pulses, with a repetition rate of ~80 MHz, generated by a mode-locked Ti:Sapphire oscillator (Spectra-Physics). A nonlinear BBO crystal was employed to generate the second harmonic pulses from fundamentals, generating ~410 nm and ~440 nm pulses which were used for the excitation. The frequency-doubled beam was separated from the gate/fundamental beam using a dichroic mirror and attenuated using a neutral density filter to reduce photobleaching and multiexciton generation in the NCs. The NC dispersion was placed in a 1 mm path-length quartz cuvette and excited with the attenuated 410 nm and 440 nm light. The time delay between the fluorescence and gate beam was introduced by adjusting the path difference in the delay line. Fluorescence photons were upconverted by mixing with the fundamental pulses in a nonlinear Sum Frequency Generation (SFG) crystal. The upconverted signal was directed through a monochromator to a photomultiplier tube for detection.

Fitting of femtosecond time resolved PLs (TRPLs)

In femtosecond TRPL fitting, reconvolution is essential for accurately estimating lifetimes. The measured fluorescence decay is influenced by the instrument response function (IRF), which must be accounted for during analysis. Reconvolution involves fitting the measured decay using a model that incorporates the excitation lamp profile, ensuring the extracted lifetime values remain unaffected by the system’s temporal broadening effects. This process is especially critical for short lifetimes, as it effectively separates instrumental effects, which are most pronounced in the initial time regime, from the true fluorescence decay.

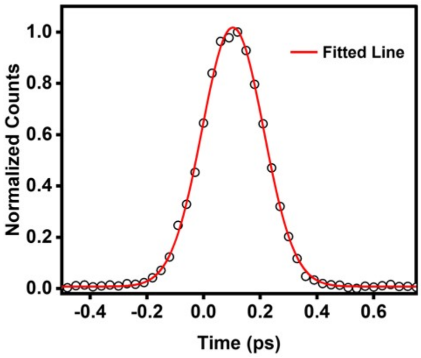

Fig. Excitation lamp profile of our femtosecond upconversion set-up recorded at Raman scattering wavelength, fit nicely to a Gaussian function with FWHM ~0.3 ps.

To characterize the excitation lamp profile, we recorded the Raman scattering of ethanol and subsequently determined the full width at half maximum (FWHM) by fitting it with a Gaussian function (above figure). During lifetime fitting, we supplied the fitted lamp profile and its FWHM into the fitting software. Igor Pro software was used for the fitting.

Assumptions adopted for extracting the intrinsic charge transfer timescale of the NC-NMA complex

It may be noted that the complexation reaction occurs on the timescale of a few hundred microseconds, whereas charge transfer within the complex is completed in <1 ps**.** With an 80 MHz laser repetition rate of our Ti-sap laser, each NC attached to NMA experiences more than 10,000 excitation cycles, all these cycles consistently recording a charge transfer timescale of <1 ps. When the NC detaches from NMA, it experiences a similar number of excitation cycles before recomplexing. However, free NCs do not contribute to the <1 ps component, as within this timeframe, a free NMA molecule at an optimal distance cannot diffuse to the NC surface for charge transfer. Diffusion is inherently slow, and any diffusion-controlled process would lead to a significantly longer quenching timescale (>a few ns). Therefore, the <1 ps charge transfer component is intrinsic and entirely independent of cumulative effects from multiple complexation-dissociation cycles

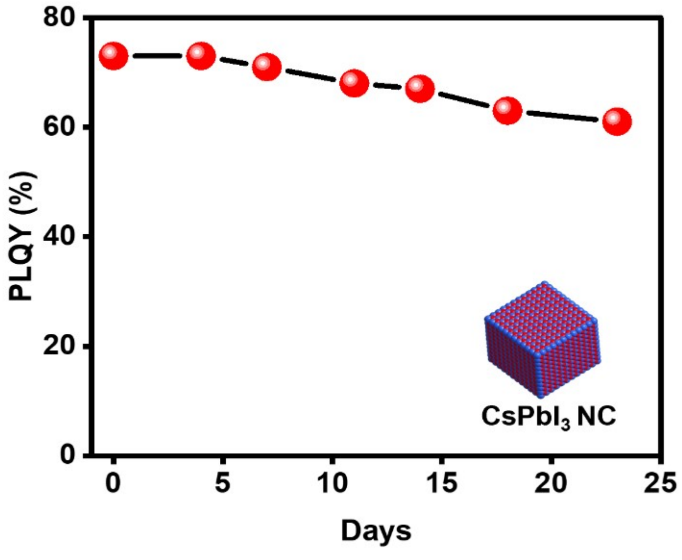

Fig. S1 PLQY of $CsPbI_3$ NCs as a function of storage time (in days).

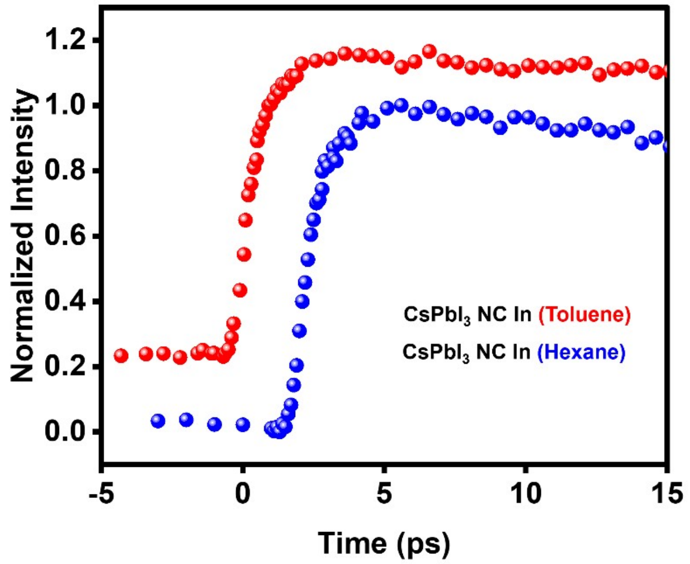

Fig. S2 Femtosecond time-resolved PL spectra of NCs in toluene (red) and hexane (blue) were recorded at an emission wavelength of ~670 nm, following excitation at ~410 nm. The similar growth kinetics observed in both solvents suggest that HC cooling timescales are essentially independent of the dispersion medium.

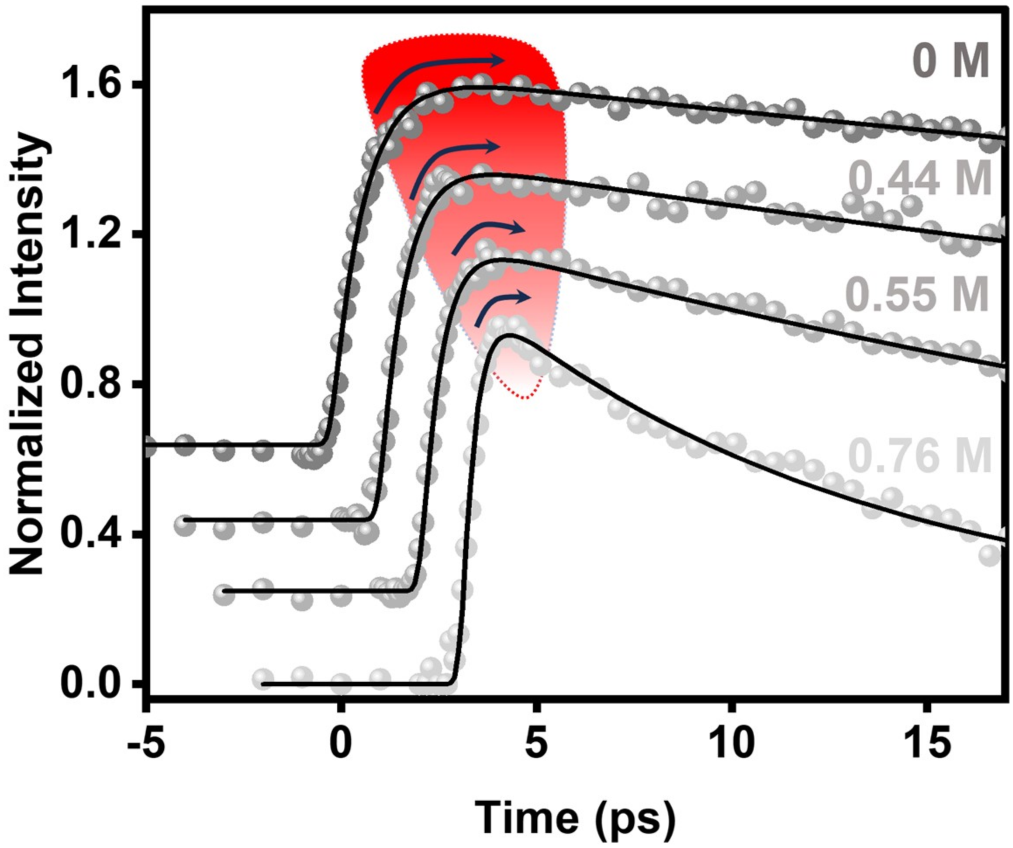

Fig. S3 Femtosecond time-resolved PLs (traces) of $CsPbI_3$ NCs dispersed in hexane, monitored at ~670 nm under varying NMA concentrations (λ_{ex} ~410 nm). The initial growth timescale, attributed to HC cooling, decreases from ~800 fs (without NMA) to ≤300 fs (at ~0.76 M NMA), indicating the extraction of partially relaxed HCs. This observation is in analogy with Fig. 5A, implying changing solvent from toluene to hexane does not alter the HC extraction kinetics.

References

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