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Electronic Supplementary Information

Insitu $CsPbBr_3$ Architecture Engineered in the Electrospun Fibers and Its Ultrafast Charge Transfer Dynamics

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Experimental Section

Chemicals and reagents

Cesium bromide (CsBr 99.98 % trace metals basis), lead (II) bromide ($PbBr_2$, 99.99 % trace - metals basis), *N,N*-dimethylformamide (DMF, 99.8%), and PVDF-HFP (MW 4,00,000 g/mol) were procured from Sigma-Aldrich and used without further purification.

Preparation of $CsPbBr_3$@PVDF-HFP fiber.

$CsPbBr_3$@ PVDF-HFP fiber was prepared by electrospinning method. 12 wt % (1.2 g) of PVDF-HFP granules was dissolved in 10 ml of anhydrous DMF by stirring for 1 h at room temperature to form homogeneous solution. Then 73 mg (0.02 mM) of $PbBr_2$ and 42 mg (0.02 mM) of CsBr were added in the above PVDF-HFP solution and stirred for another an hour. The resulting homogeneous solution was filled in a syringe (5 ml) and kept in the holder of electrospinning machine. The holder was connected to stainless steel needle and aluminium foil wrapped drum collector. The flow rate was maintained to 0.3 ml h^{-1} and the potential was fixed at 12 kV across a typical collector distance of 15 cm. The as-prepared fibers were kept in an oven at 60 °C for overnight to remove the solvent and then used for other characterizations.

Synthesis of $CsPbBr_3$ NCs

NC-$CsPbBr_3$ were synthesized after following previously reported synthetic method of Kovalenko and co-workers with slight modification.[1-3]

Characterization:

The optical absorption spectra were acquired from Shimadzu UV-2600 UV-vis spectrophotometer. Fluorescence measurements were carried using Edinburgh FS5 spectrofluorometer instrument. The photoluminescence decay lifetimes were estimated by time-correlated single-photon counting (TCSPC) using a Deltaflex Modular Fluorescence Lifetime System (HORIBA Scientific) with nano-LED pulsed diode light source. The instrument response function (IRF) was recorded using ludox (colloidal silica) solution up to ~200 ps. X-ray diffraction (XRD) patterns of the prepared samples were recorded using Rigaku Smart Lab diffractometer operating at 9 kW (200 mA; 45 kV) using Cu–kα (λ=1.54Å) as the incident radiation. The prepared fibers were fixed over glass slide to make film and directly used for XRD measurements. TEM and HRTEM images were acquired from JEOL JEM 210 Transmission Electron Microscope operating at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopic (XPS) measurements of fiber sample were performed with a PHI 5000 Versaprobe II XPS system with an AlKα source and a charge neutralizer at room temperature, maintaining a base pressure of about 6×10^{-10} mbar and an energy resolution of 0.6 eV. Optical images of fibers were noticed with an optical microscope (Olympus BX53F microscope). PLQY was measured with a Horiba Jobin Yvon Fluromax-4 spectrometer using the integrating sphere (HORIBA Quanta Phi) as a quantum yield accessory.

Femtosecond pump probe spectroscopy experimental setup:

The experimental setup for the requisition of transient absorption data employs a Ti : Sapphire regenerative amplifier-based femtosecond laser system (Astrella, Coherent systems, central wavelength ~800 nm, energy per pulse ~5 mJ) and Helios Fire spectrometer. The pulse beam from the main laser head with repetition rate of 1 kHz is split into two components, *viz.* pump and probe beam using a dichroic beam splitter (R:T = 90:10). The reflected component i.e. the pump beam can be tuned to any required excitation wavelength (within the predefined system limits, 250 - 1200 nm) with the help of Optical Parametric Amplifier (OperA SOLO). The pump intensity can be modulated using variable neutral density filter. The other component namely, the probe beam is guided through a computer control-based delay stage onto a CaF_2 window to generate white light continuum. The pump beam is chopped using a synchronized chopper at 500Hz in order to compute the absorbance change in the two consecutive probe pulses which can be defined as $\Delta A = (A^{probe})_{pump\ on} - (A^{probe})_{pump\ off}$.

To avoid any possible optical damage to the sample, the sample is stirred magnetically at all times during the experiment. The spectral data obtained is chirped corrected during the analysis to eliminate the group velocity dispersion effects.

Optical studies:

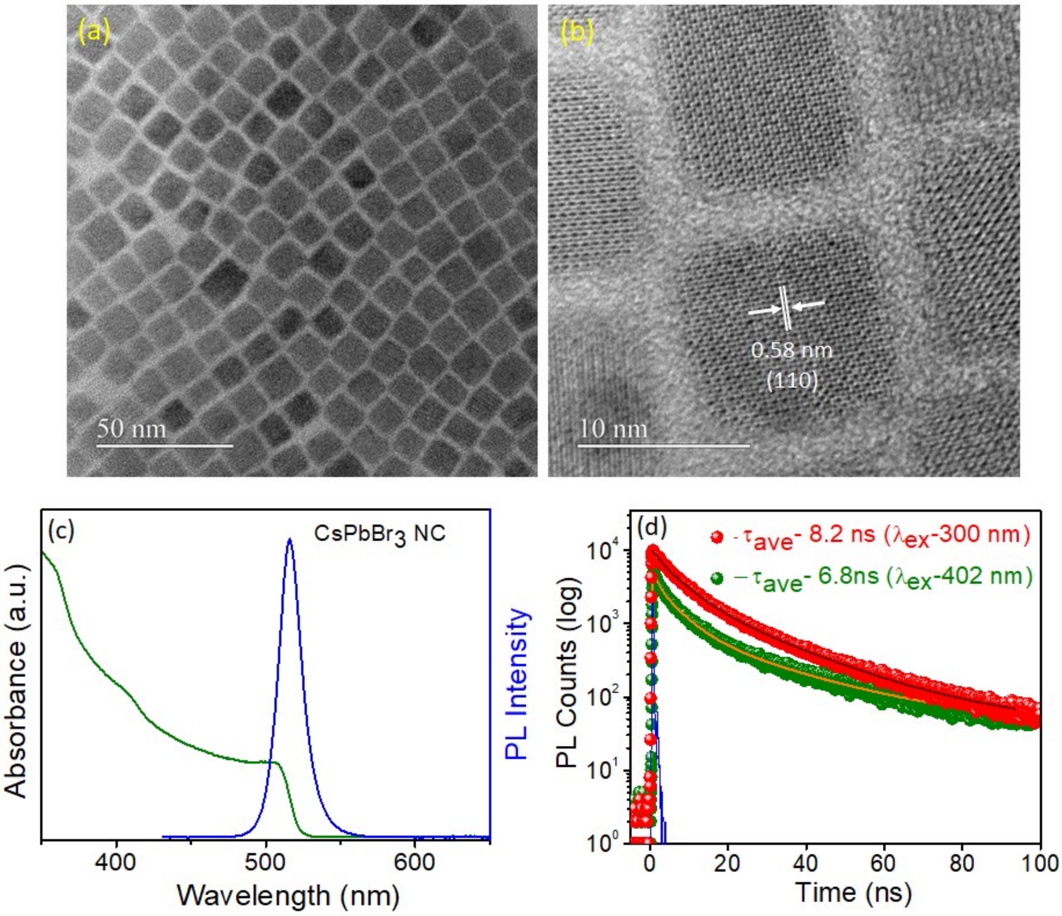
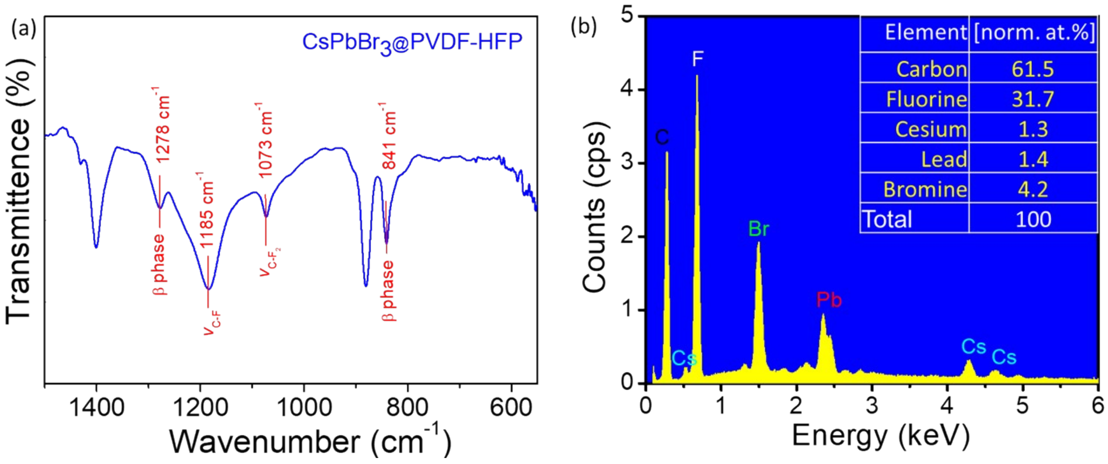


Fig. S1 (a,b) HR-TEM images pristine CsPbBr$_3$ NCs, (c) Optical absorption and steady state PL spectra of CsPbBr$_3$ NCs, the sample was excited at 420 nm and (d) Time-correlated single photon counting (TCSPC) study of CsPbBr$_3$ NCs after exciting the sample at 300 and 402 nm and the emission monitored at 516 nm, (laser pulse (IRF) blue line).

EDS analysis:



Element	[norm. at.%]
Carbon	61.5
Fluorine	31.7
Cesium	1.3
Lead	1.4
Bromine	4.2
Total	100

Fig. S2. (a) FT-IR analysis and (b) EDS pattern of CsPbBr$_3$@PVDF-HFP fiber.

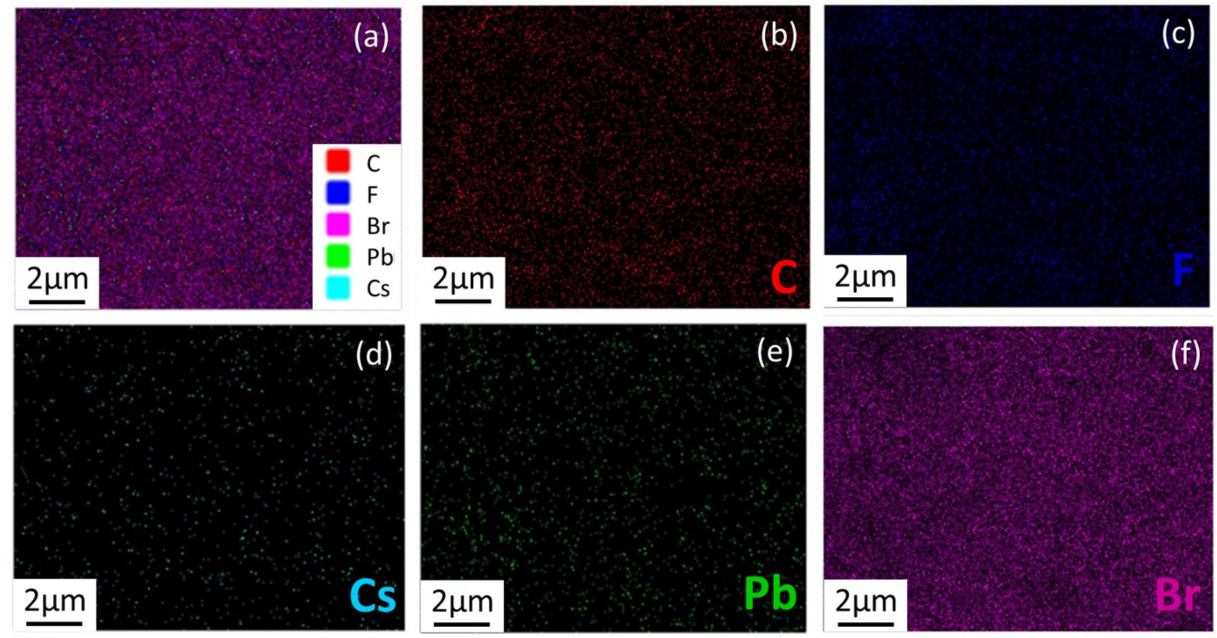


Fig. S3 (a-f). EDS elemental mapping of $CsPbBr_3$@PVDF-HFP fiber.

Photoluminescence Quantum Yield (PLQY) measurement:

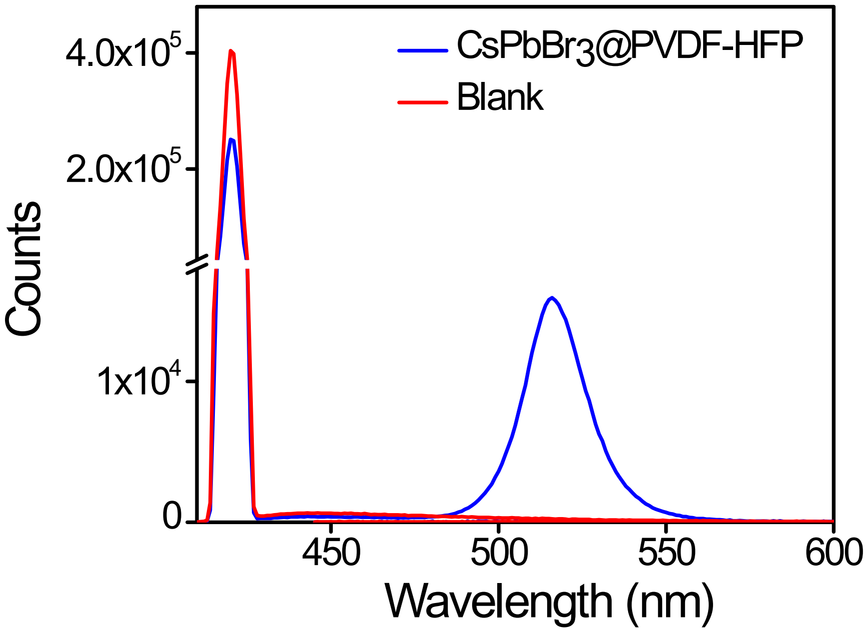


Fig. S4. PLQY measurement of $CsPbBr_3$@PVDF-HFP fiber and the sample was excited at 420 nm.

Table S1: Absorbance and emission values obtained from the $CsPbBr_3$@PVDF-HFP fiber and blank.

Blank		**Sample+ Blank**		**PLQY (%)**
Absorbance	Emission	Absorbance	Emission	
1390000	23965.4	858240.7	186108.2	30.7

Low temperature TA studies:

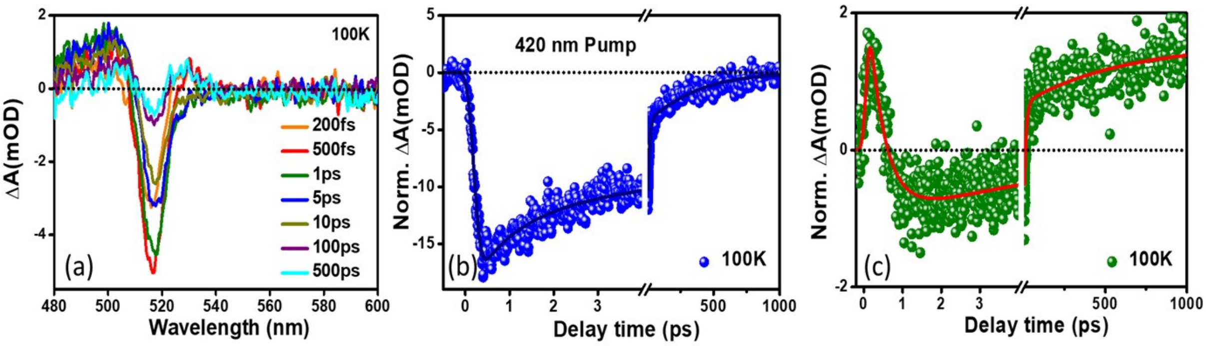


Fig. S4. (a) TA spectra of $CsPbBr_3$@PVDF-HFP fiber at 100 K under 300 nm pump excitation and (b) corresponding bleach and bi-exciton kinetics monitored at 514 and 530 nm, probe wavelength, respectively.

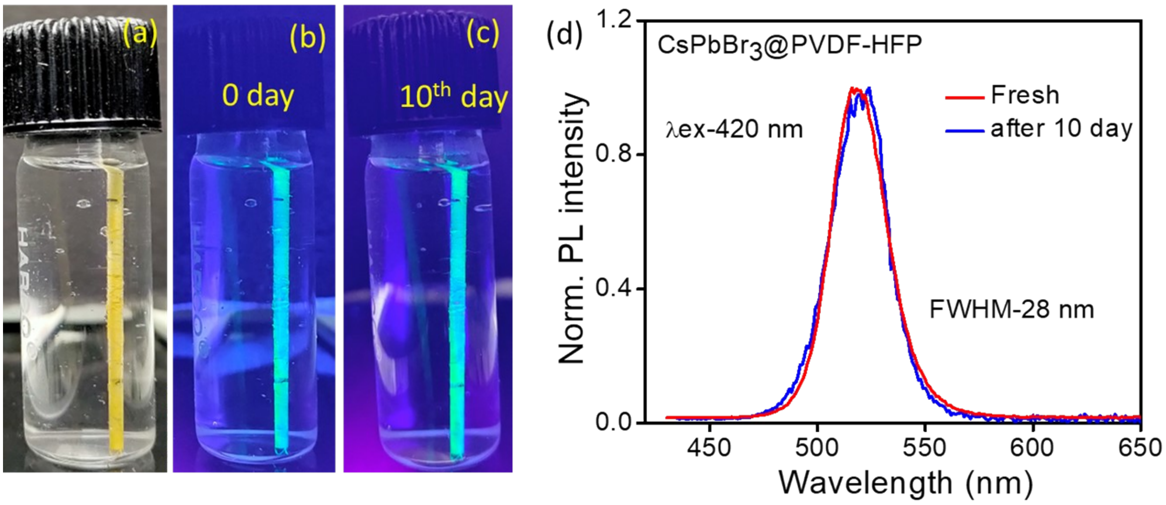


Fig. S5 Photographic images of CsPbBr$_3$@PVDF-HFP in water: (a) day light and under UV light (λ_{ex}-365 nm) on (b) 0 day, (c) more than 10 days of storage and (d) corresponding normalized PL spectra excited at 420 nm.

Table S2: Fitting parameters for the kinetics monitored at bleach position after exciting the samples at 420 nm laser pulse.

System	**λ (nm)**	τ_{g1}	τ_{g2}	τ_1	τ_2	τ_3
CsPbBr$_3$ NCs	514	<150 fs (72%)	0.73 ±0.08 ps (28%)	85 ± 5 ps (-56%)	350 ±12 ps (-28%)	>1 ns (-16%)
CsPbBr$_3$@PVDF-HFP fibers	516	<150 fs (68%)	0.7 ± 0.05 ps (32%)	72±11 ps (-52%)	220 ±15 ps (-33%)	>1 ns (-15%)

Table S3: Fitting parameters for the kinetics monitored at biexciton maximum position after exciting the samples at 420 nm laser pulse.

System	λ (nm)	bi-exciton		single exciton		
		Growth τ_g^1	decay τ_d^1	growth	recovery	
NC-CsPbBr$_3$	524	τ_g^1 = <150fs (53%)	τ_d^1 = 0.280 ± 0.04 ps (-69%)	τg^2 =5.2 ± 0.5 ps (-31%)	τ_r^1 = 76 ±6 ps (43 %)	τ_r^2 => 200 ± 11ps (4 %)
CsPbBr$_3$@ PVDF-HFP fibers	524	τ_g^1 = <150fs (50%)	τ_d^1 = 0.250±0.05 ps (-65%)	τ_g^2 = 3.5 ±0.7 ps (-35%)	τ_r^1 = **76**± 8 **ps** (46 %)	τ_r^2 => 220 ±15 ps (4 %)

Table S4: Fitting parameters for the kinetics monitored at bleach position after exciting the samples at 300 nm laser pulse.

System	λ (nm)	growth		recovery			
		τ_{g1}	τ_{g2}	τ_1	τ_2	τ_3	τ_4
NC-CsPbBr$_3$	506	<150fs (72%)	1.2±0.06ps (28%)	5.8±0.6 ps (-16%)	52.7 ± 6 ps (-45%)	300 ± 13ps (-19%)	>1ns (-20%)
CsPbBr$_3$@PVDF-HFP fibers	514	<150fs (100%)		2.2±0.8 ps (-15%)	43.7±8 ps (-40%)	250 ±25 ps (-19%)	>1ns (-26%)

Table S5: Kinetics fitting parameters for bi-excitonic peak position after exciting the samples at 300 nm laser pulse.

System	**λ nm**	**bi-exciton**		**single exciton**			
		Growth τ_{g1}	**decay τ_{d1}**	**growth**	**recovery**		
NC-$CsPbBr_3$	524	0.220±0.008 ps (68.1%)	0.410 ±0.002 ps (-74.6%)	3.2±0.2 ps (-25.4%)	19.8±1.5ps (24.5%)	102 ±11 ps (6.45%)	>1ns (0.95%)
$CsPbBr_3$@PVDF-HFP fibers	528	< 150 fs (72.2 %)	250±0.005 fs (-71.3%)	1.8±0.5 ps (-28.7%)	25.2 ±2.2 ps (15.5%)	125± 15ps (10.5%)	>1ns (1.8%)

Table S6: Kinetic fitting parameters at excitonic bleach position for $CsPbBr_3$@PVDF-HFP fibers at different temperature under 420 nm pump excitation.

Lattice Temp (K)	τ_{g1}	τ_{g2}	τ_1	τ_2	τ_3
300	<150fs (65%)	0.62±0.008ps (35%)	60 ±5 ps (-43.2 %)	200±22ps (-28.6%)	>1ns (-28.2%)
100	<150fs (94.6%)	0.24±0.004ps (5.4%)	6.8 ±1.5 ps (-50.4%)	30±24ps (-37.2%)	180 ±33ps (-12.4%)
5	<150fs (96.6%)	0.21±0.005 ps (3.2%)	4.2±1.3 ps (-58.5%)	22±18 ps (-34.1%)	100±35 ps (-7.4%)

Table S7: Kinetic fitting parameters at the bi-exciton position for NP-$CsPbBr_3$ deposited over a glass substrate at different temperature under 420 nm pump excitation.

Lattice Temp. (K)	**(bi-exciton)**		**single exciton**		
	Growth τ_{g1}	**decay** τ_{d1}	**growth**	**Recovery**	
300	<150fs (71.8%)	0.240 ±0.002ps (-74.83%)	3 ±1.2ps (-25.17%)	43 ±5ps (18.9%)	105±28 ps (5.85%)
100	<150fs (70.95%)	0.300 ±0.006ps (-71.5%)	2.4±1.1ps (-28.5%)	28 ±8ps (26.89%)	
5	< 150 fs (83.4%)	0.320±0.008 ps (-84.2%)	2.5±1.45 ps (-15.8%)	21±3.5 ps (16.6%)	

Notes and references

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