Supporting Information

Perovskite photocatalysis: realizing long-lived charge-separated states at the interface of $CsPbBr_3$ nanocrystals and functionalized ferrocene molecules

Siddharth Singh, Diksha Mittal[#], Vinithra Gurunarayanan[#], Ankita Sahu, Ramesh Ramapanicker, and Vishal Govind Rao[*]

Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, 208016, UP, India

Corresponding Author

* Vishal Govind Rao, Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, 208016, UP, India; orcid.org/0000-0003-1205-3006; E-mail: vgrao@iitk.ac.in

[#]Both authors contributed equally to the manuscript.

Synthesis of Ferrocenyl Surfactants (FcS)

The general procedure for synthesizing FcS1, FcS2, and FcS4 and their detailed characterization has been discussed before[1], and just a brief outline is presented here. 3-ferrocenyl propanoic acid (1 equivalent) and dichloromethane (10 mL) were mixed until complete dissolution and cooled in an ice bath. To the solution, EDC.HCl (1-ethyl-3-[3-dimethylaminopropyl] carbodiimide) (1.5 equivalent) and HOBt (1-Hydroxybenzotriazole) (1.5 equivalent) was added and stirred for 1 hour. C-protected peptide fragment was added as H-Gly-OMe (1equiv) for FcS1, H-Gu (OMe) γ-OMe (1 equivalent) for FcS2, and H_2- Lys (OMe) (0.5 equivalent) for FcS4. Upon N, N-diisopropylethylamine (1.5 equivalent) addition, the reaction mixture was stirred at room temperature for 36 hours and diluted with 20 mL of dichloromethane. The desired C-protected FcS was extracted from the reaction solution and purified by washing and evaporating the solvent and column chromatography. Deprotection of the products was done using LiOH (1.2 equivalent for FcS1 and FcS4 and 2.2 equivalent for FcS2) in aqueous methanol. After 6-12 hours, the resulting solution was neutralized with aqueous $KHSO_4$. The organic layer was extracted with the help of ethyl acetate and dried over Na_2SO_4. The solvent was evaporated, and the residue was washed and then purified using silica gel column chromatography with a solution of methanol and chloroform (1:4) for elution.

Double Reciprocal Analysis and K_{app} Calculation

Double reciprocal analysis of the emission quenching data was done with the help of the Benesi-Hildebrand method, originally used for assessing binding constants using absorbance data.[2] The association constant (K_{app}) between the adsorbed quencher molecules (Q) and the nanocrystals was estimated using the following Equation 1:

$$\frac{1}{\Delta F} = \frac{1}{\Delta F_{max}} + \frac{1}{K_{app}\Delta F_{max}[Q]} \quad (1)$$

Here, ΔF represents the change in fluorescence intensity with respect to the initial intensity (0 nM FcS) upon successive addition of FcS, ΔF_{max} is the maximum change in fluorescence intensity with the addition of FcS which was calculated as the difference between the intensity at 0 nM FcS and 293 nM FcS addition, and [Q] is the concentration of the quencher species (FcS). The equation is y = mx + c; hence, a linear relationship can be drawn between 1/ΔF and 1/[Q].

Structural Analysis of $CsPbBr_3$ NCs

Size distribution of $CsPbBr_3$ NCs with and without the addition of ferrocenyl surfactants was determined from their respective TEM images using Image J software. The average size of bare CsPbBr3 NCs was evaluated as 9.36 nm and 8.82 nm, 9.24 nm, 9.46 nm, and 9.38 nm, upon the addition of 293 nM Fc, FcS1, FcS2, and FcS4, respectively.

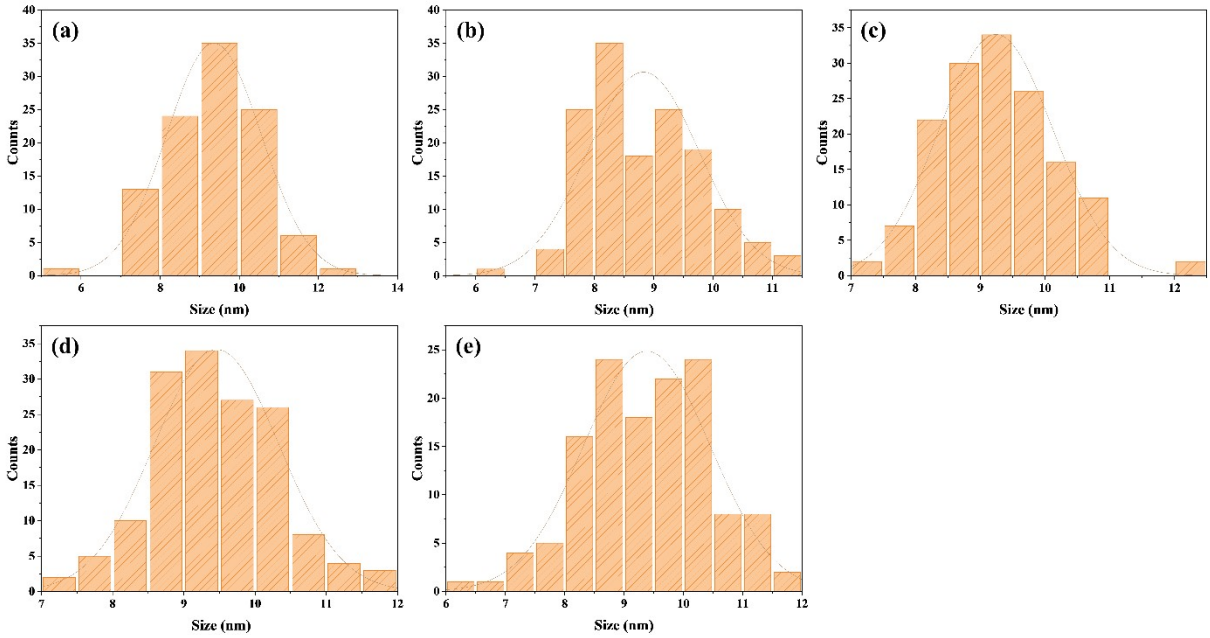

Fig. S1: Average size distribution of $CsPbBr_3$ NCs (a) without any ferrocenyl surfactant (average size of 9.36 nm) and with (b) Fc (average size of 8.82 nm), (c) FcS1 (average size of 9.24 nm), (d) FcS2 (average size of 9.46 nm), and (e) FcS4 (average size of 9.38 nm).

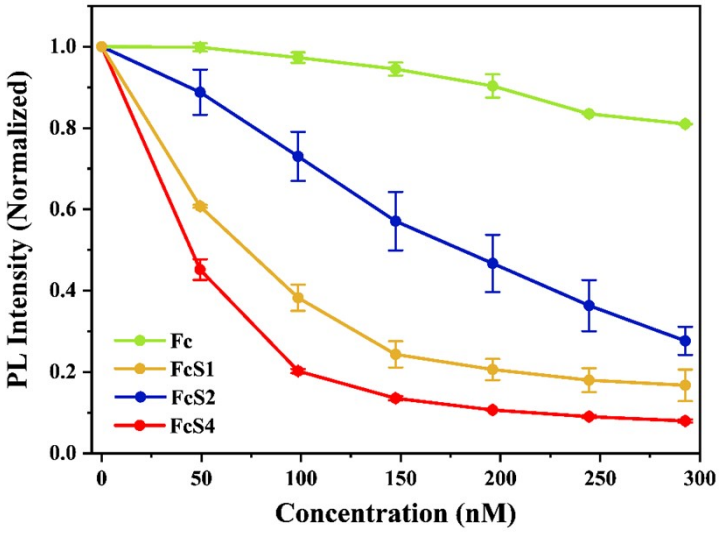

Fig. S2: Relative $CsPbBr_3$ photoluminescence (PL) intensity in the presence of ferrocenyl surfactants with different concentrations.

XPS Error Analysis

Table S1: Possible error in peak positions and accuracy of peak fitting method as evaluated in coefficient of determination (COD). As the COD values are close to 1 for all the cases, near-perfect fits are obtained following the Gaussian model.

Sample	**Model**	**Peak**	**Peak position with error (eV)**	**COD Value**
$CsPbBr_3$	Gaussian	Pb $4f_{7/2}$	138.07762 ± 0.00331	0.99882
		Pb $4f_{5/2}$	142.93252 ± 0.00346	
		Br $3d_{5/2}$	67.94349 ± 0.01086	0.99796
		Br $3d_{3/2}$	68.93729 ± 0.02113	
$CsPbBr_3$ + FcS1	Gaussian	Pb $4f_{7/2}$	138.08458 ± 0.00215	0.99903
		Pb $4f_{5/2}$	142.93437 ± 0.00389	
		Br $3d_{5/2}$	67.9904 ± 0.01365	0.99757
		Br $3d_{3/2}$	69.00879 ± 0.02226	
$CsPbBr_3$ + FcS2	Gaussian	Pb $4f_{7/2}$	138.14842 ± 0.00326	0.99888
		Pb $4f_{5/2}$	142.9991 ± 0.00493	
		Br $3d_{5/2}$	68.03 ± 0.01125	0.99768

		Br $3d_{3/2}$	69.029 ± 0.02012	
$CsPbBr_3$ + FcS4	Gaussian	Pb $4f_{7/2}$	138.2067 ± 0.00308	0.99904
		Pb $4f_{5/2}$	143.08295 ± 0.00715	
		Br $3d_{5/2}$	68.13156 ± 0.0181	0.9979
		Br $3d_{3/2}$	69.16759 ± 0.02893	

Here, to calibrate the XPS spectrum, we have used the carbon C1s peak (284.8 eV) as a reference. Calibrating the XPS spectrum by adjusting the peak positions with reference to the C1s peak also rectified the instrument-related peak position error.

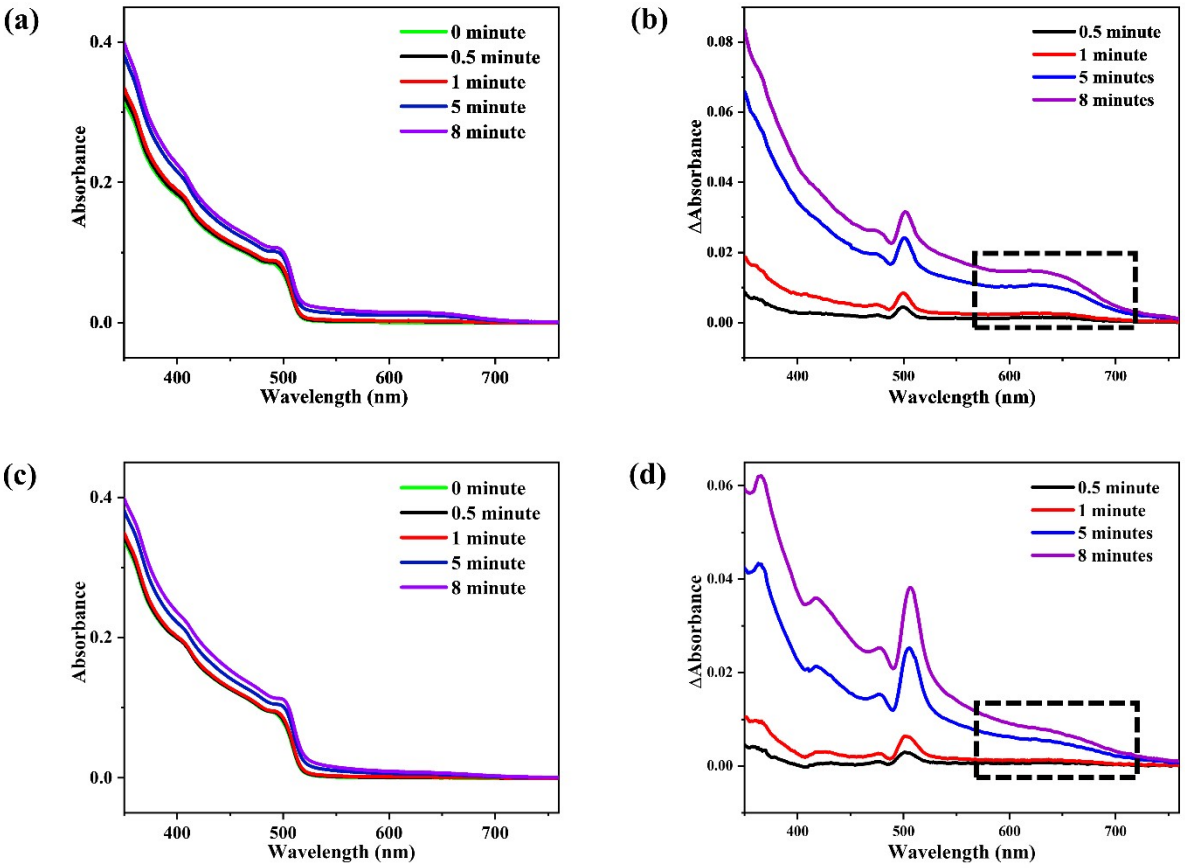

Fig. S3: Steady-state photolysis of $CsPbBr_3$ NCs and FcS solution with visible light ($\lambda > 400$ nm). (a) Absorption spectra of ~10 nM $CsPbBr_3$ and 100 µM FcS2 were recorded at regular time intervals upon visible light exposure. (b) The difference absorption spectra of $CsPbBr_3$ and FcS2 solution were recorded at regular intervals. The highlighted region indicates a peak at ~620 nm with time, confirming the formation of Fc^+ species. (c) Absorption spectra of ~10 nM $CsPbBr_3$ and 100 µM FcS4 were recorded at regular intervals upon visible light irradiation. (d) Difference absorption spectra of $CsPbBr_3$ and FcS4 solution. The highlighted region indicates a peak at ~620 nm with time, confirming the formation of Fc^+ species. However, an increase in the overall absorbance is observed with time, which indicates scattering by $CsPbBr_3$ NCs in the presence of native oleylamine and oleic acid ligands upon the addition of FcS2 and FcS4. This arises due to the binding equilibrium between the two species, possibly allowing enhanced binding of FcS species to the $CsPbBr_3$'s surface.[3,4]

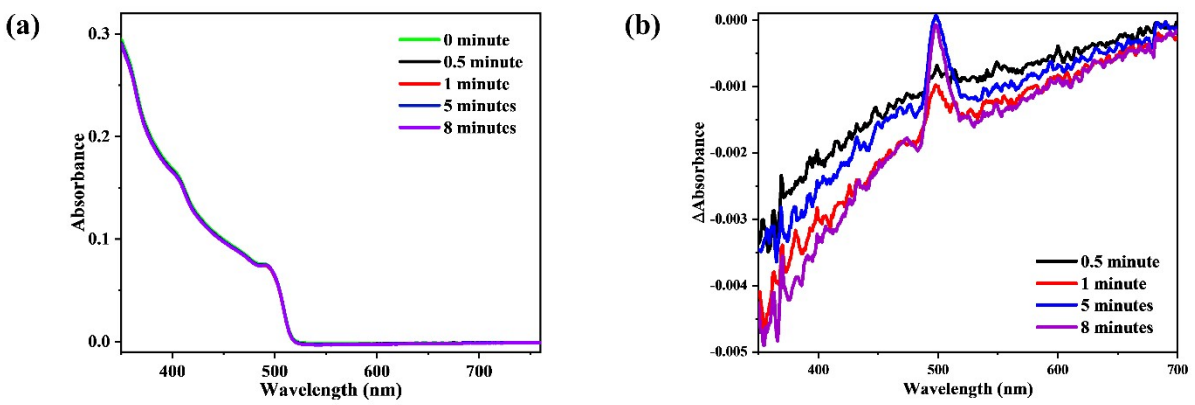

Fig. S4: Control experiment for charge transfer between $CsPbBr_3$ NCs and FcS1 in the dark. (a) Absorption spectra of ~10 nM $CsPbBr_3$ and 100 µM FcS1 solution were recorded at regular intervals without visible light exposure. No significant change in absorption can be seen in the region where Fc^+ absorbs. (b) The difference absorption spectra of $CsPbBr_3$ and FcS1 solution in the zoomed region of 350-700 nm show no peak formation corresponding to Fc^+.

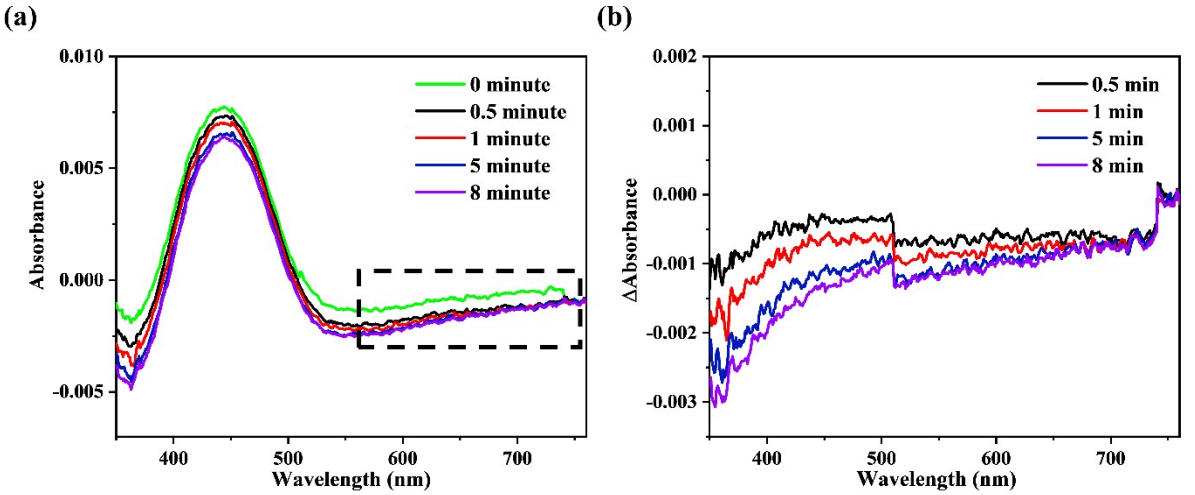

Fig. S5: Charge transfer study upon direct irradiation of FcS1. (a) Absorption spectra of 100 µM FcS1 solution were recorded at regular time intervals upon visible light irradiation (λ > 400 nm). No significant peak formation can be observed in the highlighted region of interest. (b) Difference absorption spectra of the same show no peak formation in the region where Fc^+ absorbs.

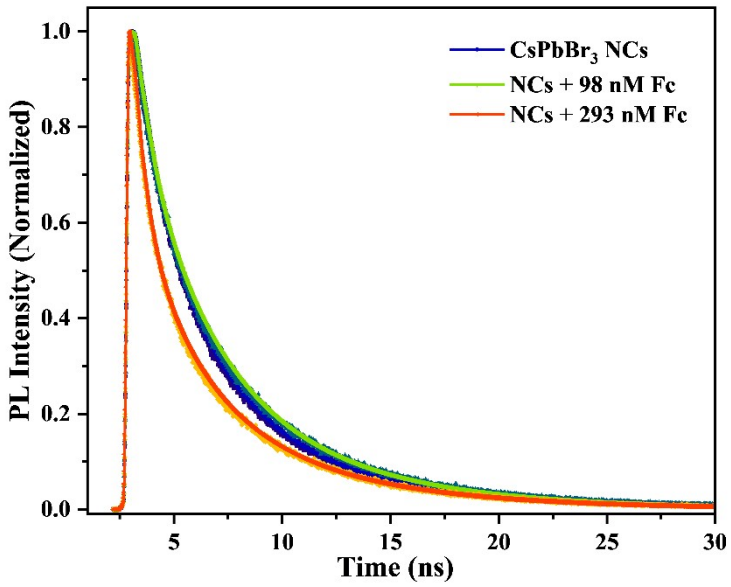

Fig. S6: Photoluminescence decay of $CsPbBr_3$ NCs with the addition of two different concentrations of Fc. The sample was excited using a 375 nm diode laser.

Table S2: Parameters for the kinetic analysis of photoluminescence decay corresponding to Fig. S5 and Fig. 6a-c of the main manuscript.

Sample	**a_1**	**a_2**	**a_3**	**τ_1 (ns)**	**τ_2 (ns)**	**τ_3 (ns)**	**τ_{av}(ns)**
$CsPbBr_3$ NCs + 0 nM Fc	0.31	0.60	0.09	0.97	3.74	9.56	4.97
NCs + 98 nM Fc	0.28	0.52	0.20	0.74	3.49	7.90	5.27
NCs + 293 nM Fc	0.46	0.35	0.19	0.51	2.75	7.06	4.82
$CsPbBr_3$ NCs + 0 nM FcS1	0.30	0.64	0.06	1.08	3.96	11.25	5.09
NCs + 98 nM FcS1	0.51	0.40	0.09	0.51	2.21	6.29	3.30
NCs + 293 nM FcS1	0.53	0.41	0.06	0.44	1.72	5.03	2.28
$CsPbBr_3$ NCs + 0 nM FcS2	0.33	0.61	0.06	1.00	3.86	11.31	5.08
NCs + 98 nM FcS2	0.40	0.50	0.10	0.59	3.00	8.08	4.39
NCs+ 293 nM FcS2	0.53	0.39	0.08	0.47	2.17	6.30	3.21
$CsPbBr_3$ NCs + 0 nM FcS4	0.29	0.58	0.13	1.03	3.58	8.99	5.15
NCs + 98 nM FcS4	0.56	0.36	0.08	0.35	1.34	4.16	2.08
NCs + 293 nM FcS4	0.58	0.35	0.07	0.22	0.67	1.98	0.92

Tri-exponential fitting of the decay data has been done using the following equation 2:

$$y = a_1 e^{-\frac{t}{\tau_1}} + a_2 e^{-\frac{t}{\tau_2}} + a_3 e^{-\frac{t}{\tau_3}} \quad (2)$$

τ_{av} is the average lifetime from the tri-exponential fit calculated using the following equation 3:

$$\tau_{av} = \sum_{i=1}^{3} a_i \tau_i^2 \Big/ \sum_{i=1}^{3} a_i \tau_i \quad (3)$$

References:

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