Supporting Information

Energy Transfer Mediated Rabi Splitting in Ag@$CsPbCl_3$ Nanohybrids

Abhishek Kumar, Eeshani Bora and Tushar Debnath

Nano Physical Spectroscopy Group, Department of Chemistry, School of Natural Sciences, Shiv Nadar Institution of Eminence, Delhi NCR, Uttar Pradesh 201314, India

Email: tushar.debnath@snu.edu.in, debnathtushar@gmail.com

1. Results and discussion

Calculation

1.1 Concentrations calculation for $CsPbCl_3$ NCs[1]:

Molar extinction coefficients of $CsPbCl_3$ NCs with a size of 9 nm,

$$\varepsilon = \frac{N_A \mu_i d^3}{1000 ln10}$$

$$\varepsilon = \frac{6.022 \times 10^{23} Mol^{-1} \times 1.88 \times 10^5 \, cm^{-1} \times (9 \times 10^{-7} cm)^3}{1000 ln10}$$

$$\varepsilon = 3.6 \times 10^7 \, M^{-1} cm^{-1}$$

Apply Beer–Lambert:

$$c = \frac{A}{\varepsilon \, l}$$

$$c = \frac{A}{3.6 \times 10^7 \times M^{-1} cm^{-1} \times 1 \, cm} \times 10^9$$

$$c(nM) = A \times 27.93$$

A	c (nM)
0.22	6.1
0.25	6.9
0.34	9.4
0.41	11.4

0.67	18.6

1.2 Concentrations calculation for Ag NPs with a size of 4.5 nm[2]:

As per the reported literature,[2] the molar extinction co-efficient of Ag NPs of ~4.5 nm is

$\varepsilon = 4.65 \times 10^7\ M^{-1}cm^{-1}$

Apply Beer–Lambert:

$$c = \frac{A}{\varepsilon\, l}$$

$$c = \frac{0.29}{4.65 \times 10^7 \times M^{-1}cm^{-1} \times 1\ cm} \times 10^9$$

$$c(nM) = 6.2$$

Symbol	**Meaning**	**Units**
ε	Molar extinction coefficient	$M^{-1}cm^{-1}$
N_A	Avogadro's number = 6.022×10^{23}	mol^{-1}
$ln\ 10$	Natural log of 10 = 2.302585	—
μ_i	Intrinsic absorption coefficient (material absorption per unit length)	cm^{-1}
d	Characteristic nanocrystal dimension (edge or effective diameter)	cm
d^3	Nanocrystal volume term	cm^3
1000	Litre to cm^3 conversion factor	—
A	Absorbance	—
c	Concentration	M

l	length of path	cm

1.3 Calculation for g_c

The experimental lower plexciton (E_-), as shown below, can be best fit by considering the single exciton coupling strength (normalized with respect to the added CPCl concentration) of $g_0 = 0.084\,\frac{eV}{\sqrt{nM}}$.

$$E_- = \frac{\tilde{E}_x + \tilde{E}_p}{2} - \sqrt{{g_c}^2 + \frac{(\tilde{E}_x - \tilde{E}_p)^2}{4}}$$

From the real part:

$$E_- = \frac{E_x + E_p}{2} - \sqrt{{g_c}^2 + \frac{(E_x - E_p)^2}{4}}$$

$$E_- = \frac{3.107 + 3.024}{2} - \sqrt{{g_c}^2 + \frac{(3.107 - 3.024)^2}{4}}$$

$$E_- = 3.065 - \sqrt{{g_c}^2 + 0.00172}$$

$$E_- \cong 3.065 - g_c$$

$[CPCl]$	$g_c \cong \sqrt{[CPCl]}\ 0.084\frac{eV}{\sqrt{nM}}$
6.1 nM	0.207 eV
6.9 nM	0.220 eV
9.4 nM	0.257 eV
11.4 nM	0.283 eV

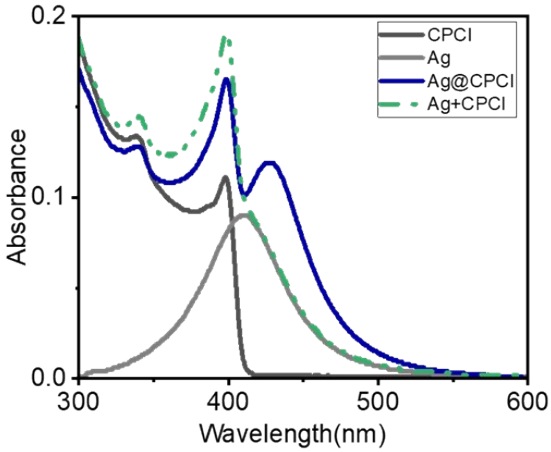

Figure S1. UV–vis absorption spectra of CPCl NCs, Ag NPs and the Ag@CPCl NCs. The green dashed line indicates the physical addition of the two spectra between CPCl NCs and Ag NPs, which clearly indicates absorption broadening due to plasmonic red shift.

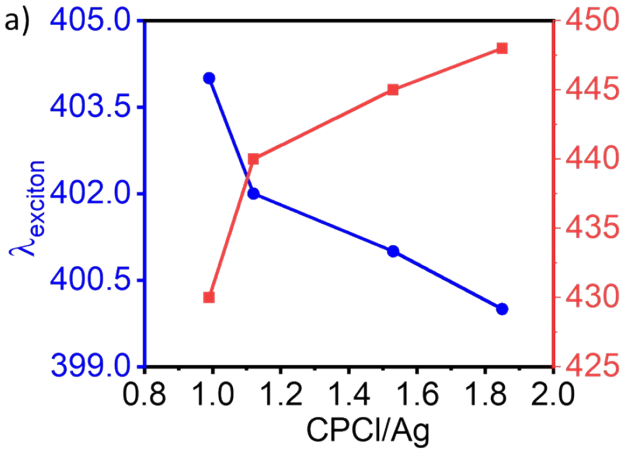

Figure S2. a) The shift in the exciton and plasmon peak position in wavelength in nm.

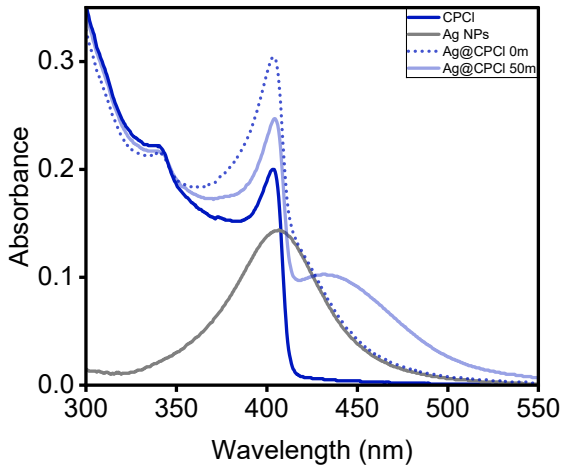

Figure S3. The hexane diluted UV–vis absorption spectrum of Ag@$CsPbCl_3$ NCs immediate after mixing of $CsPbCl_3$ and Ag (noted at Ag@CPCl 0m) and after 50 min of mixing (noted at Ag@CPCl 50m). Here $CsPbCl_3$ is first diluted in hexane and Ag is added afterward.

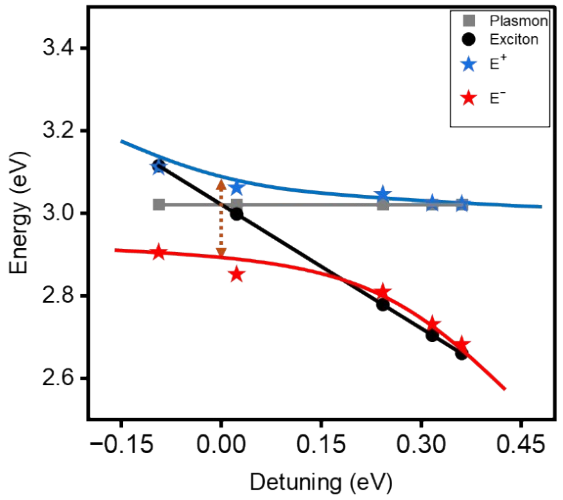

Figure S4. Dispersion curve of plexciton with upper (E^+) and lower (E^-) polariton branches as a function of detuning energy. Red and blue stars indicate experimental data of upper and lower polaritons. The solid red and blue lines are eye guidelines. The grey data points and line present the plasmon energy of the pure Ag NPs, while the black data points and line indicate the CPX (X=Cl/Br) exciton resonance. The dashed double headed arrow at zero detuning show the Rabi splitting energy.

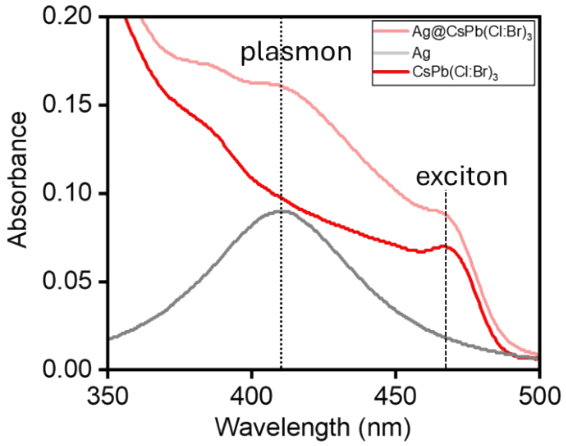

Figure S5. UV–vis absorption spectra of $CsPb(Cl:Br)_3$ and $Ag@CsPb(Cl:Br)_3$ NCs, showing the exciton resonance at 470 nm (for both) and the plasmon resonance at 410 nm (for the later). The plasmon resonance in $Ag@CsPb(Cl:Br)_3$ NCs show negligible shift from the bare plasmon resonance of Ag NPs, due to negligible exciton-plasmon spectral overlap.

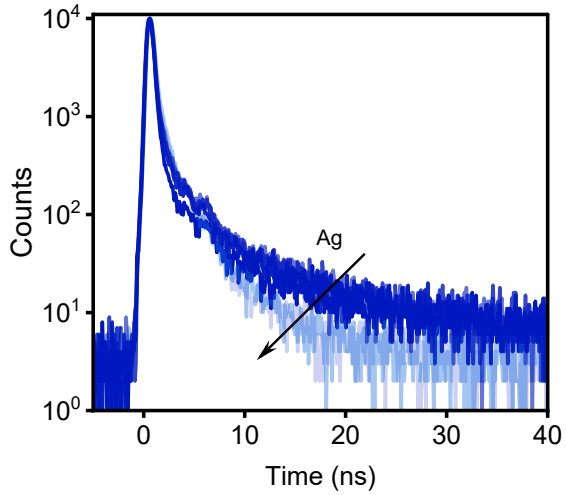

Figure S6. Time resolved PL decay traces of pure CPCl NCs and Ag@CPCl NCs with varying CPCl-to-Ag ratio.

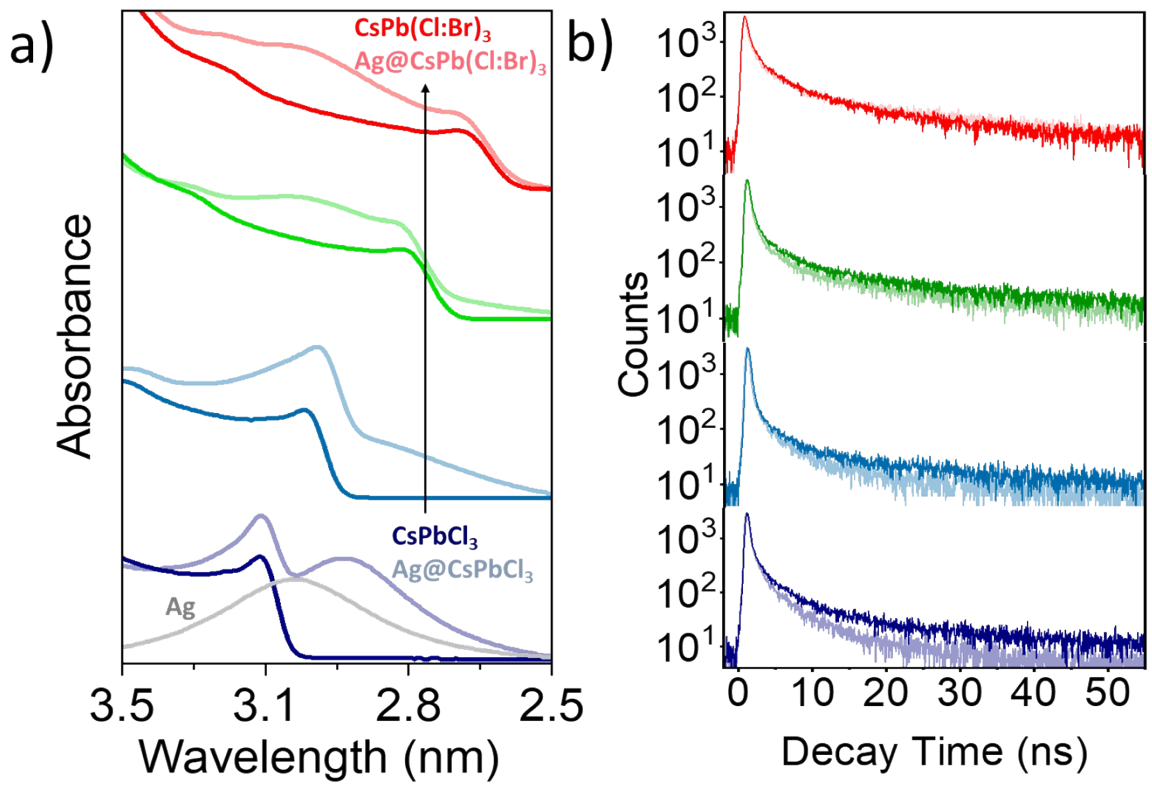

Figure S7. a) UV–vis absorption, b) time-resolved PL decay traces of different CsPb(Cl/Br)3 NCs without and with Ag-incorporation. Both absorption and PL emission red shifts on increasing Br content into the parent CPCl NCs. Clearly, the absorption broadening and the PL quenching efficiency reduces gradually in the Ag incorporated samples on increasing the Br content.

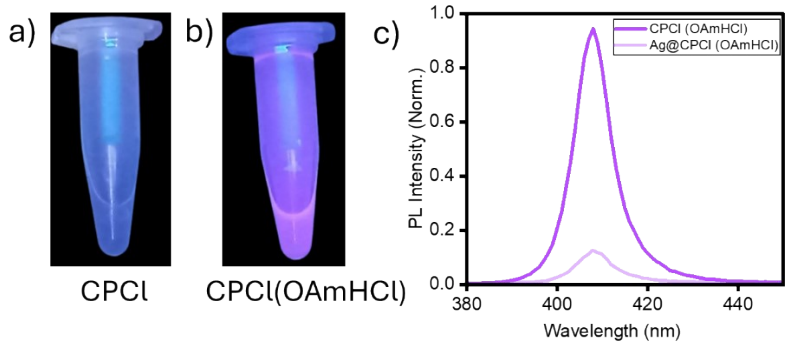

Figure S8. a) Untreated and b) OAmHCl treated CPCl under UV-light excitation. Blue-violet fluorescence is clearly visible from the treated sample due to efficient surface passivation. c) PL spectra of OAmHCl treated CPCl without and with Ag.

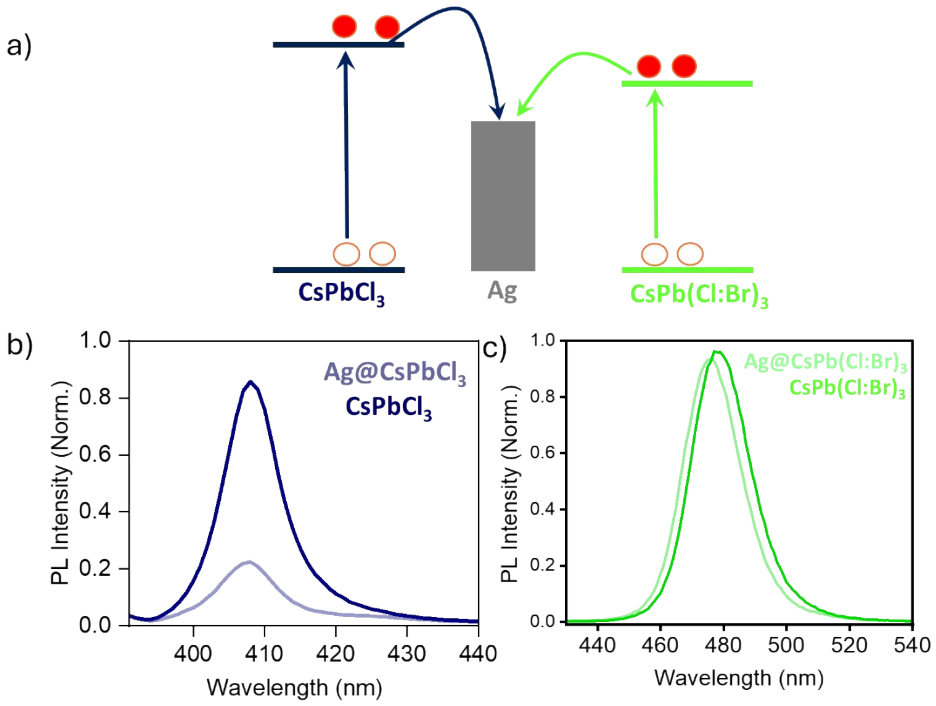

Figure S9. a) Schematic of thermodynamic band alignment of $CsPbCl_3$, $CsPb(Cl:Br)_3$ and Ag Fermi energy, showing feasibility of electron transfer process from perovskite to Ag domain. PL spectra of b) $CsPbCl_3$ and c) $CsPb(Cl:Br)_3$ without and with Ag.

References.

1) J. Maes, L. Balcaen, E. Drijvers, Q. Zhao, J. D. Roo, A. Vantomme, F. Vanhaecke, P. Geiregat, and Z. Hens. Light Absorption Coefficient of CsPbBr3 Perovskite Nanocrystals. *J. Phys. Chem. Lett.* **2018**, *9*, 3093−3097.
2) D. Paramelle, A. Sadovoy, S. Gorelik, P. Free, J. Hobleya and D. G. Fernig. A rapid method to estimate the concentration of citrate capped silver nanoparticles from UV-visible light spectra. *Analyst* **2014**, *139*, 4855.