# Electronic Supplementary Information

## Ultrafast Electron Shuttling Suppresses the Energy Transfer Process in Mn-doped $CsPbCl_3$ Nanocrystals

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

### 1. Methods

#### 1.1. Materials

Cesium carbonate ($CsCO_3$), lead chloride ($PbCl_2$), manganese chloride ($MnCl_2$), 1-octadecene (ODE), oleic acid (OA), oleylamine (OLA), hexane and 4-nitro phenol (4-NP) were obtained from Sigma-Aldrich.

#### 1.2. Synthesis of undoped and Mn-doped $CsPbCl_3$ NCs

At first, a stock cesium oleate solution was prepared by adding 0.407 gm of $CsCO_3$ in 1.25ml OA and 20 ml ODE solvent and continuously stirred at 120 ˚C until complete dissolution of $CsCO_3$.

Then, 0.188 mmol of $PbCl_2$ in 0.5 ml OA, 0.5 ml OLA and 5 ml ODE were added in a 30 ml glass vial and stirred at 120 ˚C for 30 min so that complete dissolution of $PbCl_2$ occurs and a clear solution was formed. The solution temperature was raised to 165 ˚C and then 400 µl of previously prepared Cs-oleate solution was injected in one shot, leading to formation of CsPbCl3 NCs. The reaction was quenched instantly by putting the reaction vessel in an ice-water bath.

For Mn-doping, instead of 0.188 mmol of PbCl2, 0.047 mmol of PbCl2 and 0.141 mmol of MnCl2 were used (Pb: Mn feeding ratio = 1:3), and the rest of the reaction procedure is same as for the undoped CsPbCl3 NCs.

The reaction mixture for both undoped and Mn-doped CsPbCl3 NCs was then centrifuged at 10000 rpm for 10 min and the supernatant was discarded. The precipitate was dissolved in 1 ml hexane and again centrifuged at 6000 rpm for another 6 min. The supernatant was kept for further use.

### 1.3. Preparation of Mn-doped $CsPbCl_3$/4-NP nanocomposite

The Mn- CsPbCl3/4-NP nanocomposite was prepared via a post-synthetic strategy where we added the 4-NP hexane solution directly in the Mn-CsPbCl3 solution under continuous stirring.

## 2. Characterizations:

TEM images were captured by JEOL JEM 2100F (maximum acceleration voltage: 200 kV) and the images were analyzed using the imageJ Software. The steady-state UV-Vis and PL spectra were recorded by using PerkinElmer Lambda 35 UV-vis spectrophotometer and HORIBA Jobin Yvon Fluoromax-4 spectrofluorometer, respectively. Femtosecond transient absorption (TA) spectroscopic experiments were performed in a custom-built setup. Briefly, a laser pulse of ~100 fs at 1 KHz, and 800 nm output from a regenerative amplifier is split into 400 nm pump pulse (via frequency doubling using a BBO crystal) and a broadband white light probe pulse (using $CaF_2$ crystal) which are then focused and overlapped on the sample target. A motorized delay stage is placed between the pump and probe pulse. An optical chopper at a frequency of 0.5 KHz is placed in the pump arm to read out the changes in the absorbance for one pump-probe cycle. In all the experiments, we used the ~100 fs pump pulse at a very low fluence, typically ~6 $\mu J/cm^2$, in order to minimize the effect of multiexciton generation, exciton-exciton annihilation, etc.

## 3. Results and Discussions:

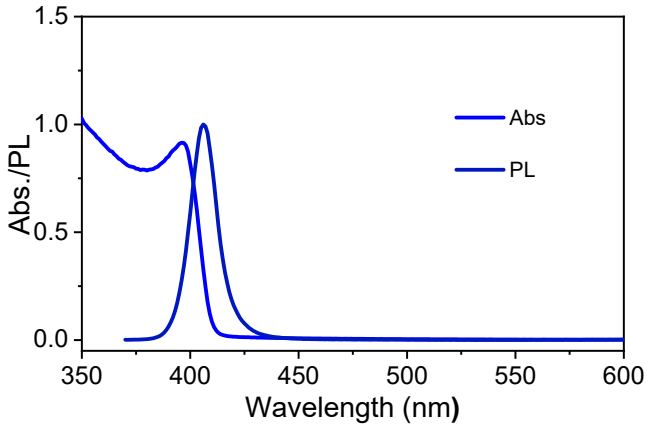


Figure S1. Steady state UV-vis absorption and PL spectra of the undoped CsPbCl3 (Un-PNC), having a PL quantum yield of ~4.7%.

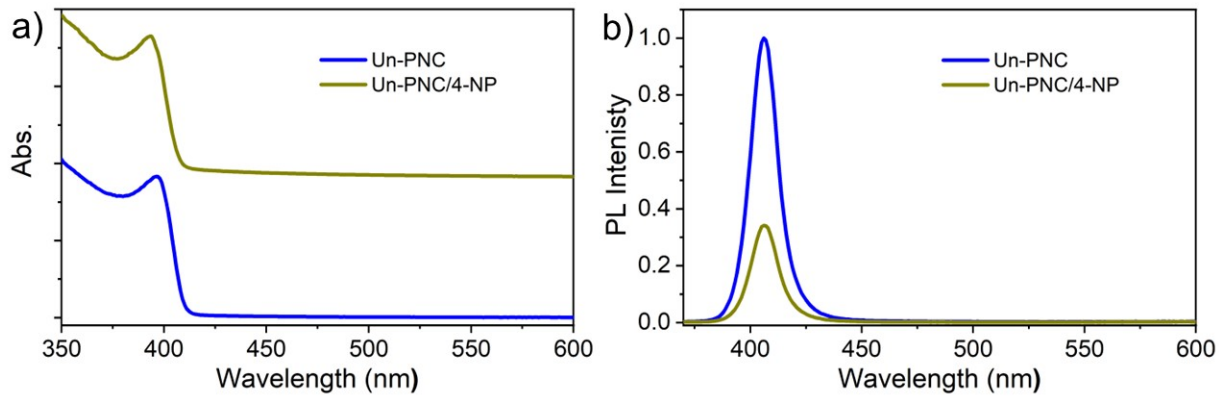


Figure S2. a) UV-vis absorption and b) PL spectra of Un-PNC in the absence and presence of the 4-NP molecule.

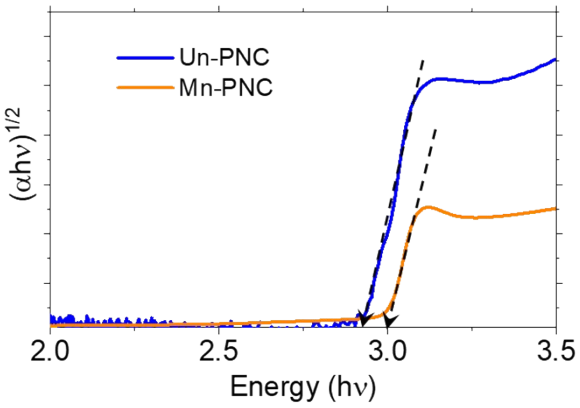


Figure S3. Tauc plot of Un-PNC and Mn-PNC, calculated from their respective absorption spectra. The bandgap (Eg) of Un-PNC = 2.93 eV and Eg of Mn-PNC = 3.0 eV.

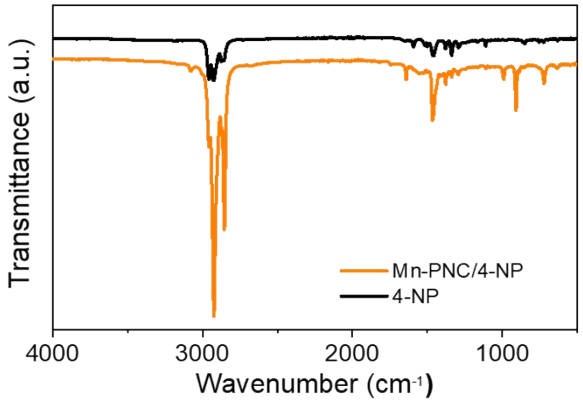


Figure S4. FTIR spectra of the 4-NP molecule and Mn-PNC/4-NP nanocomposite in the 4000 – 500 $cm^{-1}$ range.

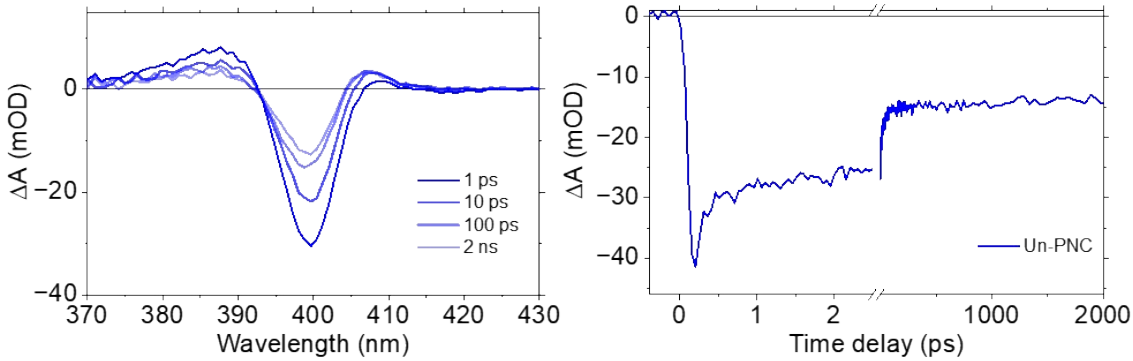


Figure S5. TA spectra and kinetics (at the bleach maxima) of the Un-PNC upon resonant excitation with a 100-fs pump pulse.

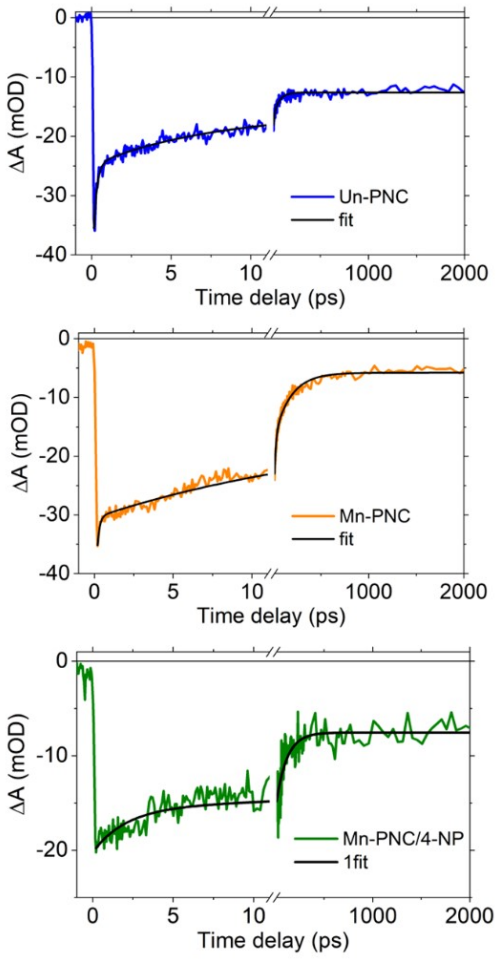


Figure S6. TA transient and their multi-exponential fitting for the Un-PNC, Mn-PNC and Mn-PNC/4-NP nanocomposite.

Table S1. Multiexponential fitting parameters of the bleaching transients of the Un-PNC, Mn-PNC and Mn-PNC/4-NP nanocomposite.

| | $\tau_1$ (%) | $\tau_2$ (%) | $\tau_3$ (%) | $\tau_4$ (%) |
|---|---|---|---|---|
| Un-PNC | 368 fs (42) | 19 ps (25) | - | >1 ns (33) |
| Mn-PNC | 140 fs (40) | 15 ps (25) | 175 ps (21) | >1 ns (14) |
| Mn-PNC/4-NP | - | 2 ps (24) | 110 ps (42) | >1 ns (34) |