Supplementary Information

Reversible Color Switching in Dual Emitting Mn(II) Doped CsPbBr₃ Perovskite Nanorods: Dilution Versus Evaporation

Shyamal Kumar Mehetor,^{+,¥} Harekrishna Ghosh,^{+,¥} Biswajit Hudait,[¥] Niladri Sekhar Karan,[⊥] Animesh Paul,[§] Sujoy Baitalik^{*§} and Narayan Pradhan^{*¥}

[¥]School of Materials Sciences, Indian Association for the Cultivation of Science, Kolkata 700032, India

[⊥]Department of Chemistry, Asutosh College, Kolkata 700026

[§]Inorganic Chemistry Section, Department of Chemistry, Jadavpur University, Kolkata 700032, India

⁺Authors S.K.M. and H.G. contributed equally

Experimental Section

Materials. Lead (II) bromide (PbBr₂) was purchased from Loba chemie India and Cesium carbonate (Cs₂CO₃, 99%) was purchased from Spectrochem India. Manganese (II) bromide tetrahydrate (MnBr₂.4H₂O), 1-octadecene (ODE, technical grade, 90%), Oleylamine (OLA) (technical grade, 70%) and oleic acid (OA) (technical grade, 70%) were purchased from Sigma-Aldrich and Hydrobromic acid (HBr, 47%), were purchased from Spectrochem. All the solvents were purchased from Finar India. All chemicals were used without further purification.

Methods

Preparation of Cs-oleate Stock Solution. To prepare Cs-oleate solution, in a 50 ml three neck round bottom flask, 0.8 mmol (260.60 mg) Cs_2CO_3 was taken along with 18 ml ODE and 2 ml oleic acid. The solution was purged with N₂ at 120 °C for 1 hour. Then the solution temperature was raised to 150 °C under N₂ flow and heated for another 15-20 minutes. The solution turns bright yellow indicating dissolution of the Cs_2CO_3 and formation of Cs-oleate. This Cs-oleate solution was stored in a deaerated vial. While required, this solution was heated at 80 °C temperature to transform to liquid form and injected to the reaction system.

Synthesis of Mn doped CsPbBr₃ nanorods. Synthesis of Mn doped CsPbBr₃ nanorods was carried out in two steps. First CsPbBr₃ was prepared, purified and then dispersed in hexane (or toluene). Next, appropriate amount of MnBr₂ was added and the solution was stirred vigorously to obtain Mn (II) doped CsPbBr₃ nanorods.

In a typical reaction, 0.42 mmol of $PbBr_2$ (154.1 mg) and 9 ml ODE were loaded in a 50 ml round bottom flask and degassed at 120 °C for 1 hour by purging nitrogen gas with stirring. Then, 1 ml of dried oleylamine (OLA) and 1 ml of dried oleic acid (OA) were injected into the reaction flask.

S2

It was kept under heating condition for 15 more minutes. Then the reaction mixture was allowed to cool down at room temperature. Then 0.8 ml pre-heated stock Cs-oleate solution was injected swiftly and stirring was continuing for further twenty minutes.

Next, 6 ml of crude solution was centrifuged with (10 % of volume) ethyl acetate for 30 minutes at 3500 rpm speed. Resulting precipitate was dispersed in 4 ml of hexane and transferred to a three neck round bottom flask along with 0.035 mmol (0.01 g) of MnBr₂.4H₂O and the mixture was stirred under degassing condition at room temperature. Within 10 minutes, blue emission of Mn containing CsPbBr₃ solution turned transient violet to pink and finally to orange red under UV (365 nm) irradiation, indicating formation of Mn (II) doped CsPbBr₃ nanorods. This Mn doped CsPbBr₃ solution was further evaporated to ~ 2 ml of concentrated solution and treated as original C₀ solution.

For dilution and concentration dependent study, 2 ml of this as synthesized nanorods solution(which was considered as C_0) was diluted by adding calculated amount of same solvent and again solution was concentrated by purging nitrogen gas. For solvent dependent study, different solvents were added in place of hexane or toluene.

Synthesis of OLA-HBr stock solution: 5 ml of OLA and 0.5 ml of HBr were loaded in a 25 ml three neck round bottomed flask. Then the solution was heated and purged with nitrogen gas (Purity 99.99%) for 1 hour at 120 °C. Then solution was collected and stored in a deaerated 20 ml vial fitted with screw type septa. While cooled down, it solidified, this was heated to 80°C for further use. For the OLA-HBr experiment, 20 μ l of prepared OLA-HBr solution was diluted in 1 ml of hexane and this diluted OLA-HBr solution was used for further experimental purpose.

S3

Dilution Study using OLA-HBr: For dilution study using OLA-HBr, calculated amount of diluted OLA-HBr was added to the one of the diluted samples (60 µl of stock in 3 ml doped nanorod solution) where absorbance is within measurable range and mixed well, then UV-Vis and PL spectra was measured. Then half of the cuvette solution was removed and equal amount of same solvent was added and UV-Vis and PL spectra was measured. Further two more measurements were carried out in similar fashion.

Instrumentations and Sample Preparation

Absorption, Photoluminescence (PL) and Photoluminescence excitation (PLE) Measurement. UV-Vis spectra were recorded with Agilent-Cary 60 UV-Vis spectrophotometer. PL and PLE spectra were measured using a Horiba Jobin Yvon Fluromax-4 spectrofluorometer. For PL measurements excitation wavelength was fixed at 360 nm and for PLE measurement emission wavelength was fixed at 605 nm. For all the measurements, the purified sample was diluted with hexane or corresponding solvent and measured in a quartz micro-cuvette. For PL measurement, primary wavelength was also adjusted to minimum (< 1mm) using specially designed sample holder chamber.

PL Excited State Decay Measurement. CsPbBr₃ exciton emission lifetime measurements were carried out by using time correlated single photon counting set up on a Hamamatsu MCP photomultiplier (R3809) and was analysed by using IBH DAS6 software in Horiba Jobin-Yvon. The samples were excited with 370 nm laser source Mn phosphorescence lifetime was measured on DeltaFlex-01-DD system and the samples were excited with 370 nm spectral LED. The luminescence decay data were analysed by using Ez Time software in DeltaFlex-01-DDsystem.

S4

The following expression was used to analyze the experimental time-resolved fluorescence decays, P(t)

$$P(t) = A + \sum_{i}^{n} B_{i} exp(-t/\tau_{i})$$

Here, *n* is the number of discrete emissive species, *A* is a baseline correction (dc offset), and B_i and τ_i are the pre-exponential factors and excited-state fluorescence lifetimes associated with the *i*th component, respectively.

PLQY Measurements: Photoluminescence quantum yields (PLQY) were measured using the integrated radiation sphere coupled with Horiba jobin yvon Fluoromax-4 spectrometer.

Transmission Electron Microscopy (TEM). TEM, HRTEM and HAADF-STEM images were taken on JEOL-JEM-200F transmission electron microscope using 200 kV electron source. Specimens were prepared by drop casting a very small amount of nanocrystals solution in hexane/toluene on a carbon coated copper grid and the grid was dried in air and stored in a desiccator.

X-ray Diffraction (XRD). XRD were measured on Bruker D8 Advance power diffractometer using Cu K α (λ = 1.54 Å) as the incident radiation. For XRD sample preparation, solution of the nanocrystals was drop casted on glass slide to make a film over it and immediately measured.

Supporting Figures:



Figure S1. TEM images of Mn (II) doped CsPbBr₃ nanorods obtained from as prepared hexane solution in different resolutions.



Figure S2. TEM images of Mn (II) doped CsPbBr₃ nanorods obtained from 4 times dilution of as prepared hexane solution in different resolutions.



Figure S3. TEM images of Mn doped CsPbBr₃ nanorods obtained from 8 times dilution of as prepared hexane solution (2 ml) in different resolutions.



Figure S4. Histogram of the length of the Mn(II) doped nanorods.



Figure S5. Powder X-ray diffraction patterns of the Mn(II) doped CsPbBr₃ nanorods.



Figure S6. Dilution protocol has been shown in histogram. As synthesized doped nanorods was taken as a whole in 2ml and successive dilutions were carried out (see inset). Data presented in Figure 4a and 4b are obtained from this experiment and similar manner dilution. Optical spectra in Figure 4b are obtained from second dilution.



Figure S7. EDS data of the samples in hexane. (a) 8 times diluted sample of orginal 2 ml Mn (II) doped nanorods.(b) original 2ml Mn(II) doped nanorods concentrated sample. Composition in the 2 ml solution is provided in the experimental section. As Mn concentration was low, the EDS spectra was enlarged and the data in the table is as obtained from the measurement.



Figure S8. Successive (a) absorbance and (b) PL spectra obtained with stepwise dilutions from undoped CsPbBr₃ solution in hexane. Here C0 is initial concentrated sample then C1 to C6 is the successive diluted samples.

| sample | T ₁ (ns) | B ₁ (%) | X ² |
|----------------|---------------------|--------------------|----------------|
| C ₀ | 1.791 | 100 | 1.1510 |
| C ₁ | 2.320 | 100 | 1.2159 |
| C ₂ | 3.655 | 100 | 1.1927 |
| C ₃ | 4.025 | 100 | 1.1297 |
| C ₄ | 5.150 | 100 | 1.2557 |

Table S1. Fitting parameters for excitonic emission decay plots.

Table S2. Fitting parameters for dopant emission decay plots.

| sample | T ₁ (ms) | T ₂ (ms) | B ₁ (%) | B ₂ (%) | X ² |
|----------------|---------------------|---------------------|--------------------|--------------------|-----------------------|
| Co | 0.165 | 0.360 | 26.98 | 73.02 | 1.0522 |
| C ₁ | 0.331 | | 100 | | 1.1893 |
| C ₂ | 0.383 | | 100 | | 1.0440 |
| C ₃ | 0.395 | | 100 | | 1.1365 |
| C ₄ | 0.435 | | 100 | | 1.0912 |