Supporting Information

Interfacial Manganese-Doping in CsPbBr$_3$ Nanoplatelets by Employing a Molecular Shuttle

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1. Methods

1.1. Materials. All the reagents were directly used as received unless specified: PbBr$_2$ (99.998%, Alfa Aesar), Cs$_2$CO$_3$ (99.9%, Sigma-Aldrich), Manganese (II) bromide (MnBr$_2$, 98%, Sigma-Aldrich), Manganese (II) chloride (MnCl$_2$, ≥99%, Sigma-Aldrich), Manganese (II) nitrate tetrahydrate (Mn(NO$_3$)$_2$·4H$_2$O, 98%, Alfa), 1-Octadecene (ODE, 90%, Sigma-Aldrich), n-Hexane (≥ 99% GC, Carl Roth), Oleylamine (OLA, 80-90%, Acros), Oleic acid (OA, 90%, Aldrich). OLA and OA were degassed at 110 °C for one hour.

1.2. Preparation of Cs-Oleate (Cs-OA) solution. To prepare Cs-OA solution, 0.16 g of Cs$_2$CO$_3$, 0.5 mL of dried Oleic acid (OA) and 8 mL of ODE were added into a 50 ml three-neck flask. The mixture was degassed under vacuum at 120 °C for 30 min, and then the temperature was increased to 150 °C under N$_2$ atmosphere. After the solid phase was completely dissolved, the temperature was set back to 120 °C for further use.

1.3. Synthesis of CsPbBr$_3$ NPls. The CsPbBr$_3$ NPls were prepared following our previously reported literature.$^{[1]}$ In a typical synthesis of CsPbBr$_3$ NPls, 0.069 mg (0.188 mmol) of PbBr$_2$ was added into a 50 mL three-neck flask containing 0.5 mL of OA, 0.5 mL of OLA and 5 mL of ODE. The mixture was degassed under vacuum at 120 °C for 20 min and then changed to N$_2$ atmosphere. When the PbBr$_2$ was completely dissolved, the solution was cooled to room temperature. Subsequently, 0.4 mL of hot Cs-OA was injected into the solution. The mixture was heated up under an N$_2$ atmosphere. Once the temperature reached 100 °C (150 °C or 180 °C), the reaction was quenched by an ice-water bath. The product was separated by centrifugation at the speed of 8000 rpm for 5 min. The precipitate was redispersed into 10 mL of hexane. To get the final product, the hexane solution was centrifuged at 3000 rpm for 5 min, and then the precipitate was discarded.

1.4. Mn doping process in One-step two-phase post-synthetic (OPS) method. In a typical experiment, several concentrations of manganese salt in 50 µL of water was
mixed with 1 mL of as-prepared CsPbBr₃ NPs and 1 mL of hexane. Subsequently, the two-phase mixed solution was subjected to stirring at the speed of 400 rpm for 1 h at ambient conditions. Then after waiting for a minute before there is a phase separation, the hexane layer was pipetted out from the upper phase. Generally, this step is not time-sensitive, however, prolonged mixing (over days) between the two phases can destroy the NPs to some extent (see Fig. S12). Furthermore, if the stirring is continued beyond 1 hr, it takes several days (~17 days) for complete degradation of the perovskite, with negligible PL emission. Therefore, it is better to separate the phases soon after the reaction. The hexane phase was then transferred to a centrifuge tube and treated by centrifugation at the speed of 9000 rpm for 5 min. The precipitate was discarded, and the final product will be in hexane.

1.5. Mn doping process in two-step two-phase post-synthetic (TPS) method. In this method, the Mn doping process needs two steps. Firstly, 50 µL saturated aqueous solution of a manganese salt was added into 2 mL of hexane which contains 10 µL of OLA. The mixed solution was subjected to oscillation by a vortex for 30 seconds at vigorous conditions. Then, the hexane solution on the upper phase was transferred to a centrifuge tube, similar to section 1.4, and treated by centrifugation at the speed of 9000 rpm for 5 min. The hexane solution with MnX₂ on the upper phase was retained for further use, and the precipitate was discarded. Next, 1 mL of hexane with MnX₂ prepared in the first step was mixed with 1 ml as-prepared CsPbBr₃ NPs. The Mn-doped CsPbBr₃ NPs will generate immediately. The mixture could be stirred for a certain time to make sure the reaction is completed.

2. Characterization

2.1. Transmission electron microscopy (TEM). Scanning transmission electron microscopy in high-angle annular dark-field mode was performed with a probe corrected FEI Titan Themis operating at 300 kV (Department of Chemistry, LMU Munich). TEM specimen was prepared on a carbon-coated Cu grid by dropping 10 µL of dilute colloidal dispersions on each sample.
2.2. *Electron Paramagnetic Resonance (EPR) spectroscopy.*

The presence of Mn in the doped NPls is determined by an EPR spectroscopy from ADANI Spinscan X (2020 model). The conditions are used as following: 20mW, 200μT-mod. Amplitude, 70mT-range, 150s-scanTime, 9.4506 GHz. To prepare samples for the EPR measurement, first the prepared Mn-doped NPls (via OPS method) was precipitated with an anti-solvent (ethyl acetate) and collected after centrifugation, which would remove the undoped Mn ions in the solution. To get a sufficient amount of samples for measurements, 10 typical batches (NPls in 10 ml hexane) of the two doping concentrations were made and collected together. The solid sample was then filled into the quartz tube for EPR measurement. The EPR signals of the empty tube were first taken as the baseline.

2.3. *Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).*

The amount of Mn-doping in the NPls is determined by ICP-OES measurement from Varian Vista RL simultaneous spectrometer with autosampler. To prepare samples for the ICP-OES measurement, first the prepared Mn-doped NPls (4M and 7M) (via OPS method) were precipitated with an anti-solvent ethyl acetate and collected after centrifugation, which would remove the undoped Mn ions in the solution. To get a sufficient amount of samples for measurements, 5 typical batches (NPls in 10 ml hexane) of the two doping concentrations were made and collected together. Then the solid doped NPls were dissolved in 400 μL aqua regia (freshly made and stirred for over 30 min) under strong sonication, which were further diluted to 20 ml aqueous solutions. The samples were filtrated before measured in the ICP-OES equipment.

2.4. *UV-Vis absorption and Photoluminescence (PL) spectroscopy.* The absorption spectra were measured by a Cary 5000 UV-Vis-NIR spectrophotometer. A Horiba Jobin Yvon Fluorolog-3 FL3-22 spectrometer with a 450W Xe lamp was used to acquire the photoluminescence spectra.
2.5. *Time-resolved fluorescence spectroscopy.* A homemade device with a white light laser (NKT SuperK Extreme EXR-20), extended with an EXTEND-UV box, was used to perform the time-resolved fluorescence measurements. The samples were excited with 350 nm laser. The signal was detected with a Princeton Instruments monochromator fiber connected to a low-noise Avalanche Photodiode from Excelitas.

2.6. *Femtosecond transient absorption spectroscopy.* A custom-built transient absorption setup from Newport was used for the ultrafast transient absorption measurement, similar to our earlier work.[2] A femtosecond multi-pass Ti: Sapphire regenerative amplifier laser system (Libra HE+, Coherent Inc.) produces ~100 fs laser pulse having 1 kHz repetition rate at 800 nm. A fraction of this laser pulse is frequency doubled using a β-barium borate (BBO) crystal to produce the pump beam at 400 nm for the sample excitation. Another fraction of the laser pulse (~1 μJ) is used to generate the white-light probe pulse by focusing part of the initial 800-nm beam through a 2-mm-thick motorized CaF₂ crystal. The pump and the probe pulses are spatially and temporally overlapped at the sample, with the pump pulse passing through at 0.5 kHz chopper to read out the changes in probe transmission for every pump-probe cycle. A motorized optical delay line is placed in the probe arm to offer a time delay between the two pulses. The NPLs dispersed in hexane were kept in a 2-mm cuvette for the pump-probe experiment. The average number of excitons were kept low enough (<<1) to avoid the multi-exciton phenomenon.

3. *Result and discussion*

3.1. *Possible Mechanism of Mn-incorporation into the NPLs as a function of thickness.*

To understand the underlying mechanism of Mn incorporation into the NPLs as a function of the thickness of parent NPLs, we performed a detailed investigation of the stability of the undoped and doped NPLs prepared at 100 and 180 °C, by probing the PL
spectra. As shown in Fig. S10-12, the undoped NPls prepared at 100 °C is only stable for a few days (<10 days), while the one prepared at 180 °C is stable for more than 10 days, as the PL spectra remain unchanged on the 10th day. The same phenomenon has also been observed for the corresponding Mn-doped NPls. Here the intensity of the Mn PL for the doped NPls obtained from the Un-100 NPls (named Mn-100) drops significantly at the 10th day while that for the Mn-180 NPls remains quite similar to day 1, albeit a slight blue shift in the Mn PL is observed for both Mn-100 and Mn-180 NPls (see section 3.2). One possible reason for the better stability of the NPls prepared at a higher reaction temperature (180 °C) corresponds to thicker NPls (5 ML) due to better surface passivation. This directs that most of the ligands (both OA and OLA) are engaged towards the surface passivation of the NPls prepared at a higher reaction temperature. As revealed in the main text, the post-synthetic method developed in this work is based on the shuttling effect of the OLA, which is liable for the MnX2- transport at the water-hexane interface. Due to better surface passivation, the number of available shuttling ligands is limited in the hexane solution, leading to low incorporation of Mn-ion into the 5 ML NPls prepared at 180 °C.

Conversely, the NPls prepared at 100 °C showed lower stability due to poorer surface passivation. This not only leads to additional availability of the shuttling ligands in the solution but also opens more room for Mn-ion incorporation through poorer surface passivation, eventually leads to more Mn-ion incorporation into the NPls (i.e. Mn-100). The additional available OLA ligand plays the shuttling role, which can be verified from the fact that if the amount of OLA is increased in the hexane solution (as described in Fig. 2a), the incorporation of Mn-ion into the NPls increases (see Fig. S6). As a result, one can conclude that the amount of the Mn-ion incorporation into the NPls in the post-synthetic method described in this work depends on the number of available shuttling ligands (here OLA) in the nonpolar solvent. Moreover, as Mn-100 (7M) NPls are less passivated compared to Mn-180 (7M) NPls, this indicates the organic ligand may plays an essential role in the energy transfer process in the two system, as described later.
One should also note that, a small side band along with the main exciton PL peak is observed in some of the samples (Fig. S5, S8, S9). Most probably, these are due to formation of different size/thickness NPls, which forms possibly due to different solvent mixture used in the post-synthetic doping.

3.2. Mn PL tunability as a function of NPls thickness.

The atomic like Mn PL in the doped NCs or NPls is supposed to appear ~600 nm (2.1 eV), independent of the host NCs/NPls. However, it is also reported the Mn PL peak position tunability upto ~55 nm, starting from ~585 nm to ~640 nm, in perovskite nanocrystals[4]. The atomic like $^4T_1-^6A_1$ Mn PL peak position tunability depends on a few factors [5]:

1) ligand field strength,
2) Mn – Mn interaction,
3) doping induced lattice contraction effect in the crystal field strength, etc.

In the present investigation, the Mn PL peak position appears ~618 nm for the Mn-180 (7M) NPls. On a closer inspection suggests the Mn PL peak position blue-shifted upon reduction of the parent NPls thickness; for example, the Mn PL appears at ~608 nm and ~605 nm for Mn-150 (7M) and Mn-100 (7M) NPls, respectively (see Fig. 3b). On the contrary, the Mn PL peak position is independent of Mn amount for a particular thickness, e.g. it always appears ~618 nm for all Mn-180 NPls (see Fig. 1g), indicating the Mn – Mn interaction and doping induced lattice contraction may not be the underlying reason for Mn PL position tunability in the present case. We believe the Mn PL peak position tunability in the present case may be related to the ligand field strength. Here the Mn-dopant in the NPls with a lower thickness (e.g. Mn-100 NPls) faces a higher ligand field interaction from the surrounding shuttle ligands due to additional available shuttle ligands. This eventually leads to more splitting of the $^4T_1-^6A_1$ energy, causing the blue shift from Mn-180 to Mn-100 NPls.

Another thing also needs to be considered: upon Mn-halide saturated aqueous solution addition, a certain amount of Mn-halide shuttled to hexane via OLA, all of
which (i.e. Mn-OLA complex) indeed does not lead to doping in the NPls. As a result, the doping process still may continue after several days, even after separating the two phases. This observation apparently can be seen from the blue-shift in the Mn PL spectra after 10 days, presented in Fig. S10-12. For example, although at day 0, the Mn PL peak appears at ~620 nm for Mn-180 (7M) NPls, after 10 days, the Mn PL peak shifted to ~600 nm. Presumably, over time surface doping increases in the NPls from the surrounding Mn-OLA complex, leading to a more ligand field interaction (i.e. higher splitting of the $^4T_1\rightarrow^6A_1$ energy), causing the blue shift in the Mn PL. However, a detailed investigation is necessary to have a clear understanding of such doping mechanism and the resultant Mn PL tunability.

### 3.3. Estimation of the energy transfer efficiency and time.

To estimate the energy transfer efficiency, we model the bleaching dynamics (in Fig. 4b and Fig. S15) with bi-exponential functions where the longer time constant corresponds to energy transfer process. From the fitted time constants, we computed the rate of the bleach recovery process for Un-100 ($\gamma_{Un}$) and Mn-100 (7M) ($\gamma_{Mn}$) NPls which is $4.93 \times 10^8$ s$^{-1}$ and $52.1 \times 10^8$ s$^{-1}$ respectively. By using the following formula, we then estimated the energy transfer efficiency ($\eta$) which is ~91% for the 7M Mn-doped NPls prepared at 100 °C $^{[6]}$:

$$\eta = 1 - \frac{\gamma_{Un}}{\gamma_{Mn}}$$

Similarly, the energy transfer efficiency of the 7M Mn-doped NPls prepared at 180 °C is estimated to be ~73%.

Furthermore, to estimate the time constant for the energy transfer process, we plotted the difference between the two transients at the bleaching wavelength (after normalizing at a longer time delay ~ns) in Fig. 4b (inset) and Fig. S15 for both Mn-100 (7M) and Mn-180 (7M). Exponential fitting of the difference transients yields exciton-to-dopant energy transfer time for Mn-100 (7M) and Mn-180 (7M) NPls to be ~168 ps and ~311 ps, respectively, again suggesting the energy transfer process is more efficient
in Mn-100 (7M) NPls than Mn-180 (7M) NPls.

Moreover, by recalling the PL lifetime measurement (Fig. 4, Fig. S13 and Table S2, S3), we found the undoped NPls prepared at a lower temperature (Un-100) has higher exciton lifetime than the one prepared at a higher temperature, Un-180 (4 ns vs. 3.1 ns). This indicates the non-radiative exciton relaxation decreases in the Un-100 NPls due to reduced interaction with ligands (less surface passivated). Therefore, the exciton can transfer the energy more efficiently to the Mn-dopant in the Mn-100 NPls than the Mn-180 NPls. In short, the organic ligands act as a non-radiative center for exciton trapping and thereby reduced the energy transfer efficiency.
Figure S1. Electron diffraction pattern of CsPbBr$_3$ NPs recorded at a camera length of 600 mm. The lattice plane distances of the visible reflections are consistent with orthorhombic CsPbBr$_3$ in [001] orientation along the beam. [7]

Figure S2. a) Overview and b, c) High-resolution STEM-HAADF images of Mn-doped CsPbBr$_3$ NPs obtained from 4M of MnBr$_2$ in water. The parent CsPbBr$_3$ NPs were prepared at 180 °C.
**Figure S3.** EPR spectrum of the blank tube, undoped CsPbBr$_3$ NPls, 2M and 7M Mn-doped CsPbBr$_3$ NPls. The parent NPls were prepared at 180 °C.

**Figure S4.** The absorption and PL spectra obtained upon the post-synthetic doping (the OPS strategy) in the presence of MnCl$_2$ in water and Mn(NO$_3$)$_2$ in water. A saturated solution of Mn-ion in water was used for both cases, which were directly added to the undoped NPls solutions. The parent NPls were prepared at 100 °C. The doping process was viable only in the presence of halide-ion (i.e. MnCl$_2$), as can be confirmed through the appearance of the Mn-related broad PL ~610 nm, which was absent for the Mn(NO$_3$)$_2$ case.

**Figure S5.** The PL spectra obtained upon the post-synthetic doping in the presence of a) MnBr$_2$ in water and b) MnCl$_2$ in water, however, without any ligand in hexane in the two-step method (the TPS strategy). (Inset) The upper phase in hexane remains transparent for both cases, indicating no MnX$_2$ transportation from water to hexane. The solutions under the UV-irradiation show typical blue luminescence due to the undoped NPls. The PL spectra contain only the exciton PL, but no Mn PL at ~610 nm.
is observed. The parent NPls were prepared at 100 °C. This observation further supports the shuttling role of the OLA ligand.

**Figure S6.** PL spectra for the Mn-doped CsPb(Cl/Br)₃ NPls, synthesized using three different OLA amounts in the hexane during the two-step method (TPS). A saturated aqueous solution of MnCl₂ was used for all the cases, directly added to the different OLA in hexane solutions. The parent NPls were prepared at 100 °C. Clearly, upon increasing the OLA amount, not only the incorporation of the Mn²⁺ increases (Mn PL intensity increases) but also the incorporation of the Cl⁻ increases, as can be seen from the blue-shift of the exciton peak. This further supports the shuttle behavior of the OLA for MnX₂ transport at the water-hexane interface.
Figure S7. Time-dependent absorption and PL spectra of Mn-doped CsPbBr$_3$ NPs obtained at (a) 180 °C and (b) 100 °C from the OPS method. The corresponding PL emission photographs under the UV-irradiation are also shown on the right side. A saturated solution of MnBr$_2$ in water was used for both cases.
Figure S8. Time-dependent absorption and PL spectra of Mn-doped CsPbBr\textsubscript{3} NPls obtained at 100 °C from the OPS method. The corresponding PL emission photographs under the UV-irradiation are also shown on the right side. The concentration of the MnBr\textsubscript{2} in water was 4 M.
Figure S9. MnBr$_2$ concentration-dependent absorption and PL spectra of Mn-doped CsPbBr$_3$ NPs obtained at 100 °C from the OPS method. The corresponding PL emission photographs under the UV-irradiation are also shown at the inset. The doping reaction time was 2 h for each case.
Figure S10. The stability of (a) the CsPbBr$_3$ and (b-d) the Mn-doped CsPbBr$_3$ NPls over the first 10-days in terms of the PL spectra. The parent NPls were prepared at 100 °C. A saturated solution of MnBr$_2$ in water was used for all the cases. The reaction time for the OPS doping process in (b), (c) and (d) are 4, 30 and 60 min, respectively.
Figure S11. The stability of (a) the CsPbBr$_3$ and (b-d) the Mn-doped CsPbBr$_3$ NPls over the first 10-days in terms of the PL spectra. The parent NPls were prepared at 180 °C. A saturated solution of MnBr$_2$ in water was used for all the cases. The reaction time for the OPS doping process in (b), (c) and (d) are 4, 30 and 60 min, respectively. Clearly, the NPls are more stable than those prepared from the NPls prepared at 100 °C, as shown in Fig. S10.
**Figure S12.** a) The stability of the Mn-doped CsPbBr$_3$ NPls stored in the dark on Day10 and its comparison with Day0 in terms of the PL spectra. This indicates ambient humidity does not have any significant role in the perovskite stability if they are separated from the aqueous environment after 1 hr stirring. b) PL spectra of Mn-doped CsPbBr$_3$ NPls stored in the glove box, without separating the hexane phase from the aqueous phase, on Day0 and Day10. Here, the NPls itself destroyed to some extend by the aqueous environment, giving rise to PL from other thickness/phase. Therefore, prolonged (in days) mixing of aqueous solution with the NPls can degrade the perovskites, even if they were stored in the glove box. The parent NPls were prepared at 180 °C. A saturated solution of MnBr$_2$ in water was used along with 1 hr reaction time (stirring).

**Figure S13.** Time-resolved PL decay traces ($\lambda_{ex} = 365$ nm) of undoped and Mn-doped CsPbBr$_3$ NPls (with various concentrations of MnBr$_2$ in water) at the exciton position obtained at 180 °C during the parent NPl synthesis.
Figure S14. Femtosecond transient absorption spectra of (a, c) undoped-180 and -100 and (b, d) Mn-doped-180 and -100 (7M) CsPbBr\textsubscript{3} NPls at different time intervals between 1 ps and 1 ns, respectively, after photoexcitation with a 400 nm pump pulse (excitation photon density $\sim$10\textsuperscript{13} cm\textsuperscript{-2}).

Figure S15. (a) The comparison of transient traces at the bleaching maxima of the undoped and Mn-doped CsPbBr\textsubscript{3} NPls was obtained at 180 °C. Note the break in the time axis between 10 and 10.1 ps. A significant faster bleaching recovery is observed upon Mn-doping (which is even faster for Mn-100 NPls, Figure 4b), indicating the
energy transfer process between the exciton and the Mn$^{2+}$ ion. (b) The difference between the two transients (ΔΔA) in (a), after normalizing at a longer time (~ns). The solid red line in (b) represents the exponential fit.
**Table S1.** Average Mn and Pb amount and corresponding Mn to Pb ratio in the 4M and 7M Mn-doped CsPbBr$_3$ NPLs, as determined from the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) measurements. The parent NPLs were prepared at 180 °C.

| Sample       | Mn-Avr. [μg/ml] | Mn Amount [μmol/ml] | Pb-Avr. [μg/ml] | Pb Amount [μmol/ml] | Ratio [%]  |
|--------------|-----------------|---------------------|-----------------|---------------------|------------|
| Mn-180 (4M)  | 0.136325        | 0.00248143          | 12.353          | 0.05961873          | 4.1621715  |
| Mn-180 (7M)  | 0.3275          | 0.00596127          | 15.505          | 0.07483108          | 7.96629601 |

**Table S2.** Exponentially fitted time constants (along with the error and their respective amplitude) for the undoped and several concentrations of the Mn-doped NPLs for the time-resolved PL decay traces. The standard deviations on the error of the average lifetime are also shown. The parent NPLs were prepared at 100 °C.

| $C_{\text{MnBr}_2}$ (M) | $\tau_1$ ns          | $\tau_2$ ns          | $\tau_{av}$ ns |
|--------------------------|----------------------|----------------------|----------------|
| 0                        | 2.9 ± 0.05 (76%)     | 7.6 ± 0.3 (24%)      | 4.0 ± 0.18     |
| 2                        | 1.8 ± 0.02 (93%)     | 6.5 ± 0.47 (7%)      | 2.1 ± 0.32     |
| 4                        | 1.5 ± 0.01 (96%)     | 6.4 ± 0.41 (4%)      | 1.7 ± 0.28     |
| 7                        | 0.8 ± 0.01 (100%)    |                      | 0.8            |

**Table S3.** Exponentially fitted time constants (along with the error and their respective amplitude) for the undoped and several concentrations of the Mn-doped NPLs for the time-resolved PL decay traces. The standard deviations on the error of the average lifetime are also shown. The parent NPLs were prepared at 180 °C.

| $C_{\text{MnBr}_2}$ (M) | $\tau_1$ ns          | $\tau_2$ ns          | $\tau_{av}$ ns |
|--------------------------|----------------------|----------------------|----------------|
| 0                        | 2.5 ± 0.03 (87%)     | 6.8 ± 0.41 (13%)     | 3.1 ± 0.27     |
|   | Value          | Standard Deviation | Percentage |
|---|--------------|-------------------|------------|
| 2 | 1.9 ± 0.02   | 91%               | 2.3 ± 0.22 |
| 4 | 1.7 ± 0.02   | 94%               | 1.9 ± 0.23 |
| 7 | 1.1 ± 0.01   | 100%              | 1.1        |

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**Author contributions**

L. W., Q. Z. and H. H. proposed the idea of interface chemistry. L. W. Y. W. and H. H. performed the synthesis and steady-state measurements. M. D. performed the STEM-HAADF measurements. L. W. and T. D. performed the time-resolved experiments. Y. W. performed the ICP-OES and EPR experiments. L. W., Y. W., J. F. and T. D. discussed the final figures and outline of the manuscript. T. D. wrote the manuscript with input from L. W., Y. W., M. K., A. D., M. C., M. D., Q. Z., J. F., H. H. All authors contributed towards the interpretation of the results and the discussions.