Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Investigating the Luminescence Mechanism of Mn-doped $CsPb(Br/Cl)_3$ Nanocrystals

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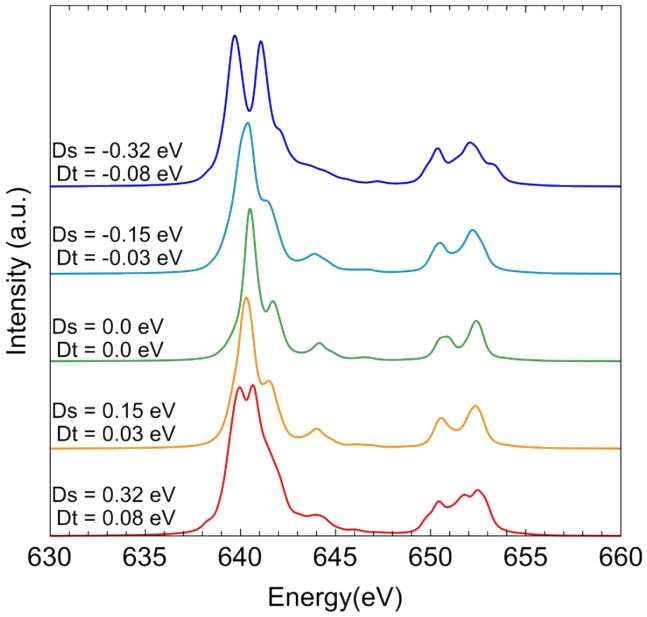

Figure S1. Calculated Mn $L_{3,2}$-edge XANES spectra from Mn^{2+} in a D_{4h} field. The 10Dq parameter is fixed to 0.5 eV, the Dt and Ds parameters are labelled on the figure. When Dt = Ds = 0 eV, an octahedral field is regained. D_{4h} symmetry occurs when octahedral bonding experiences Jahn-Teller distortion, i.e. when the bond length along the z-direction is longer or shorter than the bond lengths in x- and y-directions. When Dt, Ds > 0 the z-direction bond is longer than the x,y-bonds, when Dt,Ds < 0 the z-direction bond is shorter. These calculated spectra are used as a qualitative indication of what we may expect in a XANES measurement if the Mn local environment is distorted from octahedral symmetry.

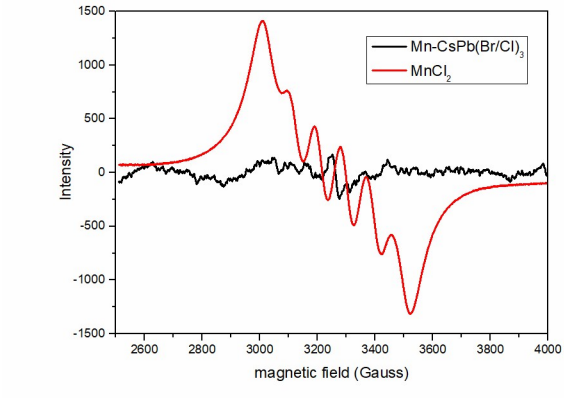

Figure S2. EPR spectra of Mn doped $CsPb(Br/Cl)_3$ NCs and commercial $MnCl_2$.

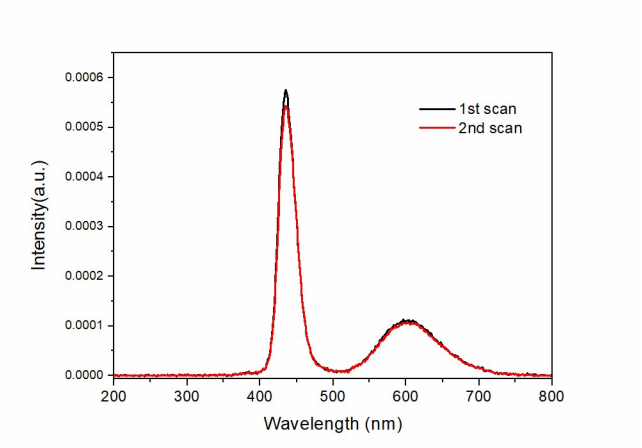

Figure S3. XEOL spectra of Mn-doped $CsPb(Br/Cl)_3$ acquired at E_{ex}=640 eV on the same spot at the beginning of X-ray irradiation (1st scan) and after continuous X-ray irradiation for a duration of 3 min (2nd scan).

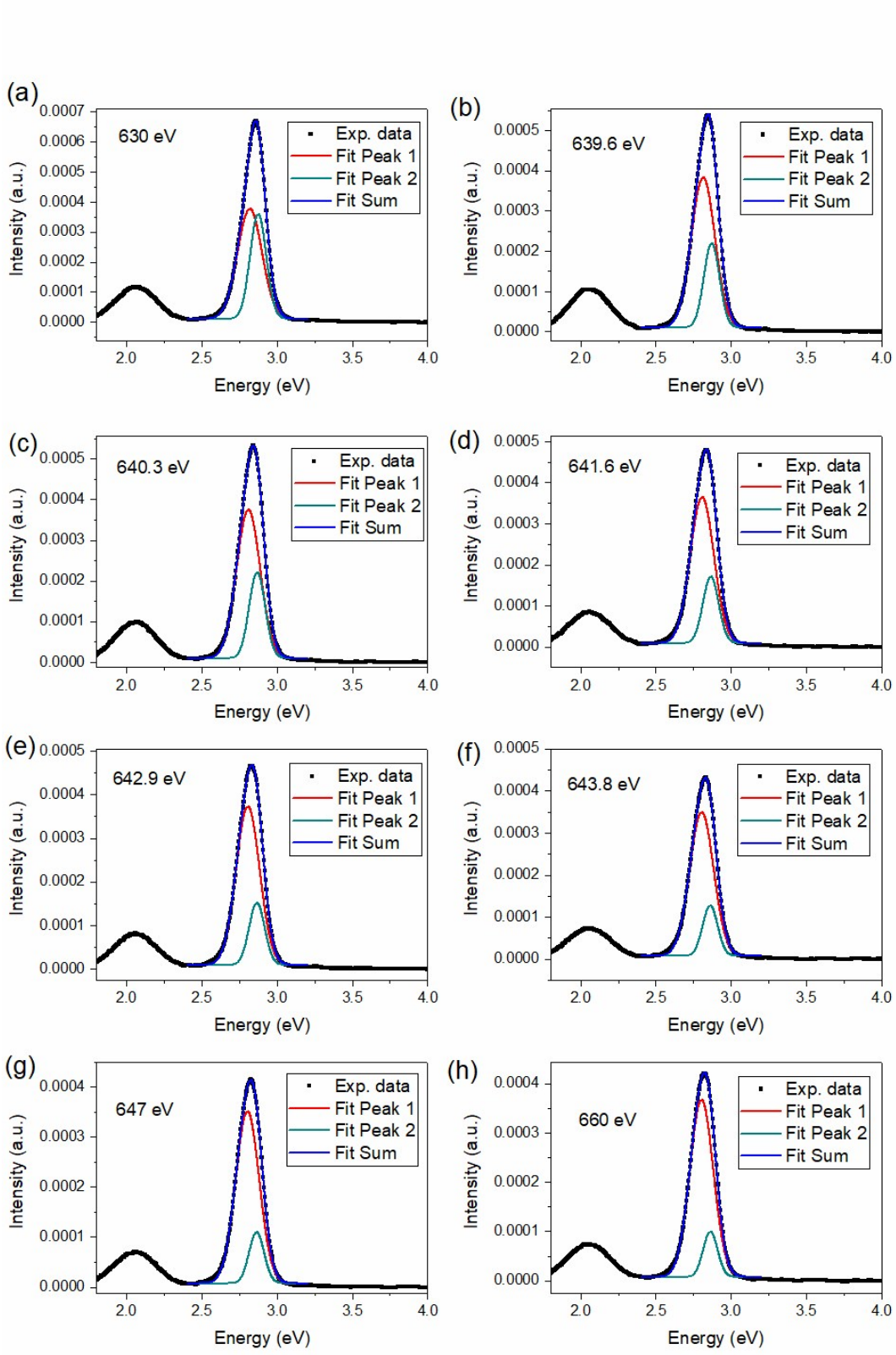

Figure S4. Fitting results of the blue emission in each XEOL spectrum.

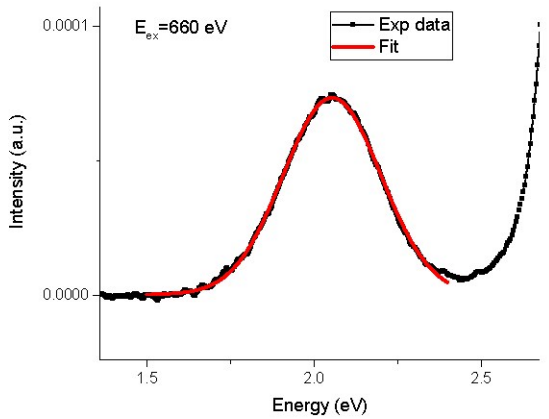

Figure S5. Fitting result of the orange emission in XEOL of Mn-doped $CsPb(Br/Cl)_3$ at E_{ex}=660 eV.

X-ray attenuation length calculation

X-ray attenuation length was calculated using the online X-ray attenuation length calculator (http://henke.lbl.gov/optical_constants/atten2.html). Three compounds were calculated, which are $CsMnBr_3$, $CsPbBr_3$, and the doped $CsPbBr_3$, respectively. To obtain the values of attenuation length within a chosen excitation energy range, the densities of the compounds are required. For pure compounds, the densities were calculated based on their corresponding crystal structure. To mimic the doped perovskite, we start with a cubic $CsPbBr_3$ unit cell, expand it four times, and substitute one Pb with one Mn. It can be seen in Figure S4 that the two compounds containing Mn both exhibit a decrease in attenuation length at the Mn L_3-edge threshold, but the change is much less significant in the doped perovskite. Note that the doped structure used in this calculation actually has a Mn concentration of 25%, further reduce the Mn concentration will make the difference below and above the Mn L_3-edge nearly negligible.

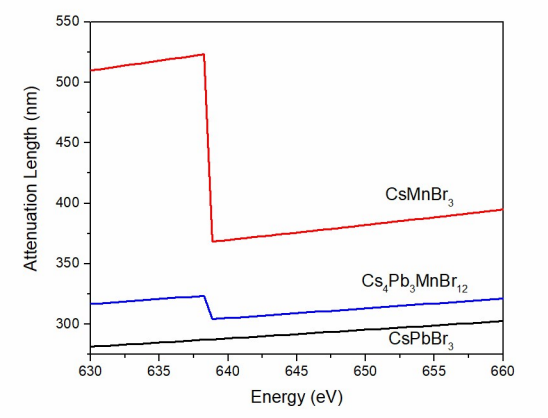

Figure S6. Comparison of attenuation lengths among $CsMnBr_3$, $CsPbBr_3$, and a $CsPbBr_3$-like structure with Mn substitution.