Harvesting Delayed Fluorescence in Perovskite Nanocrystals using Spin Forbidden Mn *d* states

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All-inorganic perovskite nanocrystals (NCs), although energy-efficient sources of lighting[1-4] with high defect tolerance, show several fold improvement in external quantum efficiency[5,6] upon surface processing, suggesting dominant surface trapping. Here, we introduce the concept of drip feeding of photo-excited electrons from an impurity-induced spin-forbidden state leading to Vibrationally Assisted Delayed Fluorescence (VADF) to address this major shortcoming. While electron trapping by the Mn dopant is well known, the electron detrapping from Mn^{2+} to the host conduction band through VADF is observed for the first time in a prototypical example of Mn-doped cesium lead halide ($CsPbX_3$) NCs. Raman spectroscopy and density functional theory (DFT) have been used to validate the presence and extent of Mn^{2+} coupling with specific vibrational modes of the PbX_6 (X = Cl, Br) octahedra. An increased excitonic quantum yield (QY) and delayed gated excitonic emission establish the electron back-transfer over several milliseconds signifying an efficient recombination. The formation of a magnetically coupled excitonic state also enables optical control of magnetism.

Smart electronic devices demand highly functional, cost and energy efficient solutions for various applications. A major requirement towards this goal is to reduce energy losses at all levels. In the field of lighting, energy losses mostly arise from non-radiative recombination processes like Auger recombination[7] and surface defect trapping.[8,9] Slow supply of excited state electrons from within the NCs into radiative excited states of the host NCs could greatly reduce these losses. The realization of this concept involves quick extraction of the photo-

33 excited electrons into long-lived impurity levels, slow back-transfer through finite vibrational

34 coupling of the impurity levels with the host, followed by radiative recombination of the

35 electrons. The use of spin in the pioneering work of Adaichi *et al.*[10] led the way to

36 harvesting the spin selective losses in organic molecules by thermally assisted delayed

37 fluorescence (TADF). Despite extensive use of TADF in organic molecules since then,

38 similar work has not been hitherto attempted in inorganic systems. This could be due to the

39 additional challenge of introducing a spin selective loss-pathway that is faster than other non-

40 radiative losses, while in organic molecules the spin selective (triplet) losses form the major

41 component of loss pathway. In this work, we introduce VADF in inorganic molecules

42 analogous to the TADF in organic materials. Towards this end, it is well known in

43 literature[4,11-14] that Mn doping in NCs leads to fast transfer of charge/energy from the

44 excitonic excitation, typically within a few hundred femtoseconds,[11,15] and is retained for

45 several µs to ms within the excited state of Mn. Based on the recent evidence of a charge

46 transfer state,[11] in this work we aim to deliberately play with excited state dynamics to detrap

47 these charges from the Mn and return them to the radiative excited state of the host within

48 the fluorescence lifetime of Mn to achieve our aim of VADF. It should be noted that the

49 thermally activated back and forth energy transfer from Mn levels lying above the conduction

50 band minimum has been demonstrated long back. However, two major drawbacks of this

51 technique are the absence of selection rules as well as the mandatory requirement of low

52 temperature, providing minor reduction of loss pathways (if at all) at room temperature.

53 Hence targeted hopping of electrons driven by internal selection rules, as well as the creation

54 and exploitation of an internal electron storeroom, are not only of fundamental importance

55 towards our understanding of Mn emission, but also offer a powerful strategy to increase the

56 efficiency of opto-electronic devices by reducing the overpotential and non-radiative decay

57 losses.

58 For the charge detrapping study with vibrational assistance we chose Mn-doped perovskite

59 NCs as a prototype due to the anomalous properties observed in this class of materials.[12-14,16]

60 For example, despite extensive efforts spanning over a hundred papers, Mn emission has not

61 been observed in hosts with lower band gaps (E_g), such as $CsPb(Cl/Br)_3$ and $CsPbBr_3$

62 NCs[4,9,13,14,16-18] and the complete absence of excitonic emission has been elusive in all

63 materials. This has been attributed to reasons like the disparity of M-Br (M =Pb, Mn) bond

64 dissociation energies,[4] clustering of Mn atoms,[19] surface defects,[9] and lattice instabilities

65 arising from size mismatch of the anion and cation.[13] However, when the E_g of the NCs is

66   higher, for example, in nanoplatelets of $CsPbBr_3$,[16] irrespective of the composition, Mn

67   emission has been observed. Secondly, the absence of Mn emission occurs in perovskites

68   with E_g that is in resonance or near resonance with the Mn excitation energy (500 nm).[11] In

69   this work, we study the Mn excitation and emission mechanism for Mn-doped perovskite

70   NCs with specific emphasis on the coupling of Mn with the host, leading to back transfer of

71   photo-excited electrons to the host and hence an improved QY giving rise to an intrinsically

72   new class of materials.

73   Fig. 1a shows the steady-state photoluminescence (PL) spectra of undoped (P1-P6) and Mn-

74   doped (MP1-MP6) NCs of $CsPb(Cl/Br)_3$ at room temperature; the compositions are given in

75   Table S1 and the corresponding absorption spectra are shown in Fig. S1 of the supplementary

76   information (SI). Similar to earlier reports, Br-incorporation into the NCs shifts the exciton

77   PL towards lower energy both in undoped and Mn-doped NCs. In addition, Mn-doped

78   samples with larger E_g show broad emission at 590 nm (2.1 eV), arising from the spin

79   forbidden $^4T_1$ to $^6A_1$ transition. We further characterized the samples with other methods

80   with typical results being shown for P3 and MP3, wherein both excitonic and Mn emission

81   peaks are observed. Femtosecond transient absorption measurements on P3 and MP3,

82   reported in Fig. 1b, show similar photobleaching with a noticeable absence of the fast

83   component (~200 - 400 fs) that is characteristic of Mn doping,[11] in spite of a Mn emission

84   peak at 590 nm (2.1 eV). This could be the signature of a very efficient fast charge transfer,

85   taking place in less than 100 fs (resolution limit of the setup) followed by a back-electron

86   transfer on much longer timescales. Further, the lifetimes of the excitonic emission in Mn-

87   doped and undoped samples shown in Fig. 1c show that while the nanosecond components of

88   P3 and MP3 are similar, MP3 also has a long-lived component for the excitonic emission,

89   that is absent in the undoped counterpart. We observe that the lifetime of the Mn emission,

90   shown in the inset of Fig. 1c, exactly matches that of the long-lived excitonic emission.

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Fig. 1. Stationary and transient optical properties of perovskite NCs. *a) Steady-state PL emission for undoped and Mn-doped CsPb(Cl/Br)₃ perovskite NCs b) Differential transmission (ΔT/T) decay profiles for P3 and MP3 NCs at their respective band edge absorption energies. Pump photon energy is at 400nm c) Lifetime of excitonic emission for P3 and MP3; inset shows comparison of lifetime of long-lived band edge emission with Mn emission for MP3. Excitation energy is at 365 nm.*

In order to understand the coupling of the Mn states with the host, we calculate the electronic band structure of 12.5% Mn-doped CsPbBr₃ using *ab initio* DFT as shown in Fig. 2a. The orbital character is extracted based on a projection onto atomic wavefunctions of Mn 3d (red), Pb 6p (green) and Br 4p (blue), and the intermediate colors indicate the degree of hybridization between these three states. It is interesting to note that the bottom of the conduction band is pulled considerably lower in energy due to spin-orbit coupling, resulting in the Mn levels being buried deep within the conduction band, unlike the situation in II-VI semiconductors. We also note that there are signatures of significant electronic coupling between Mn 3d and Pb 6p states, especially in the vicinity of the R point in the Brillouin zone. However, conservation of momentum (k) restricts the electron back transfer to the Γ point in the absence of vibrational assistance.

The vibrational coupling between the host and the Mn dopant atoms depends on the phonon band structure, which is calculated from density functional perturbation theory (DFPT) and is

112   shown in Fig. 2b. The phonon branches are color coded according to the elemental

113   contributions to the relevant mode, in a way analogous to the projections performed for the

114   electronic band structure.   Significant coupling of the Mn and Pb atoms (as observed from

115   the intermediate colors) is observed in the frequency range of 90 to 135 cm^{-1}, corresponding

116   to the modes b_1 to b_{11} (marked in Fig. 2b) at the Γ point. In contrast, similar phonon

117   dispersion calculations on Mn doped $CsPbCl_3$ shown in Fig. 2c, (look at the analogous modes

118   c_1 to c_{15} in the range of 100 to 150 cm^{-1}) demonstrate a very weak coupling of the Mn modes

119   with the host, as shown by the predominantly blue color of the phonon modes at the Γ point.

120   While it is evident that the interatomic vibrational interactions of Mn doped $CsPbBr_3$

121   demonstrate the effect of Mn on the host phonon modes, it is important to see the coupling of

122   these phonon modes with the electronic states. In order to investigate this, atoms were

123   displaced along the eigenvectors of these modes, and the resulting effect on the electronic

124   band structure was observed. As an example, in Fig. S2 in the Supporting Information, we

125   show the perturbed electronic band structure after displacing the atoms according to the

126   vibrational mode b_5 and standardising with respect to the Cs 5s core level. Perceptible

127   changes in the band structure upon perturbation confirm the existence of a strong electron-

128   phonon coupling.

129

Fig. 2. Electronic and Vibrational Coupling Between Atoms: a) Electronic band structure of the conduction band, for Mn-doped CsPbBr₃. Red, green and blue colors indicate Mn 3d, Pb 6p and Br 4p like character, respectively, while intermediate colors indicate the degree of hybridization between these states. The Fermi level E_F is taken as the top of the valence band. b) Part of the phonon spectrum, as calculated from DFT, for 12.5% Mn-doped CsPbBr₃. The branches are colored according to their weights on the different atoms in the unit cell, as shown in the RGB color triangle. c) Part of the phonon spectrum, as calculated from DFT, for 12.5% Mn-doped CsPbCl₃. The branches are colored according to their weights on the different atoms in the unit cell, as shown in the RGB color triangle. d) Temperature dependent Raman spectra for MP3 perovskite NCs.

These theoretical predictions are further verified by Raman spectroscopy, wherein similar modes were observed. Temperature dependent Raman studies on MP3 show a sharpening of the 132 cm^{-1} [Pb-Br stretching mode (Transverse Optical phonon) in the octahedron[20,21]] and 365 cm^{-1} (second order combination mode of Transverse Optical phonon and Longitudinal Optical phonon[22]) peaks on the Mn-doped samples compared to the undoped counterpart, as shown in Fig. S3. This 132 cm^{-1} peak is strongly coupled to the Mn^{2+} states as shown by the Raman spectra in this range in Fig. 2d. The width of the Raman peak, which is inversely proportional to the phonon lifetime, is observed to have a non-monotonic temperature dependence, suggesting a temperature driven back-transfer.[20]

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Fig. 3. Experimental proof of VADF: a) Schematic of gated emission b) Room temperature gated PL emission for Mn-doped CsPb(Cl/Br)₃ perovskite NCs (MP1 to MP5) c)Temperature dependent Gated PL emission for MP3 NCs. d) Temperature dependent Gated PL area ratio of band edge emission (closed circles) vs total emission for Mn-doped CsPb(Cl/Br)₃ perovskite NCs and inverse of FWHM of 132 cm⁻¹ peak from Raman spectra of MP3 (open circles). e) Absorption spectra for smaller size of MP3 (MP3 LT) in comparison with MP3 and MP1 f) Intensity of delayed excitonic emission as a function of temperature for different sizes of MP3 along with MP1. g) Comparison of PLQY for the drop casted films of undoped and Mn-doped CsPb(Cl/Br)₃ perovskite NCs.

Finally, the most direct evidence of the delayed excitonic fluorescence is furnished, and can be quantified, by measuring the gated emission (schematic shown in Fig. 3a), wherein excitonic luminescence obtained after a delay of 150 μs is measured. Typical gated emission spectra at room temperature for various halide ion concentrations are shown in Fig. 3b. From the figure, it is apparent that irrespective of the E_g, all the samples show Mn emission in the gated fluorescence. Additionally, there is a substantial excitonic emission along with the Mn

165   emission, specifically in low E_g materials like MP5.   This delayed excitonic emission could

166   either be due to delayed host excitation with energy provided by the non-radiative Mn decay

167   or due to electron back-transfer from Mn leading to electron drip-feeding. While both

168   mechanisms are interesting from a fundamental perspective, the electron drip-feeding could

169   lead to far-reaching consequences as it would couple selectively to the radiative pathways

170   leading to decrease in energy loss pathways. The presence of Mn-coupled host phonon

171   modes in the Raman spectra and the DFT calculations indeed suggests that there is significant

172   phonon assistance to mediate charge transfer between the Mn and the host. Further, even

173   though the Mn excitation is almost in resonance with the E_g of the sample P6, the Mn

174   emission is much lower in energy and hence is unlikely to be capable of affecting delayed

175   excitation.

176   In order to provide convincing proof of the mechanism at play, we study the delayed

177   excitonic fluorescence using gated emission as a function of temperature as well as quantum

178   confinement. Typical spectra for Mn-doped sample (MP3) is shown in Fig. 3c, while the

179   ratio of the area under the gated excitonic emission to the total area for varying halide ion

180   concentrations as a function of temperature are shown in Fig. 3d. It should be noted here that

181   in the absence of Mn, this is observed to be a flat line with no gated excitonic intensity.

182   Though an increase in the area of the steady state excitonic feature as a function of

183   temperature can be observed due to trapping and detrapping of charge carriers by defect

184   states, this does not lead to an increase in the delayed excitonic feature. However, in the

185   presence of Mn, due to back transfer from Mn states, the area under the gated excitonic

186   emission peak increases with increasing temperature, possibly due to the low thermal energy,

187   up to a certain maximum temperature determined by the E_g of the material. For temperatures

188   above this maximum, we see a decrease in the intensity of the delayed excitonic emission,

189   with the intensity finally becoming zero at sufficiently high temperatures. The observation of

190   state specific back transfer and activation barriers, which is also supported by the Raman

191   spectroscopy study in Fig. 2, suggests the presence of real population kinetics, like an

192   electron transfer. In order to compare this with the phonon lifetime as obtained from Raman

193   spectra, we have also plotted the inverse of the full width at half maximum (FWHM) for a

194   typical sample MP3, within the same plot. We observe that the phonon lifetime increases and

195   reaches a maximum at the same temperature (123 K for MP3) as that of the optical signature.

196   Further, with increasing temperature, this temperature-driven phonon assistance remains high

197   until the gated excitonic emission reaches zero. This behavior of the lifetime suggests that

198 phonon assistance and gated excitonic emission could respectively be in a cause-effect

199 relation in a thermally activated phonon assisted electron transfer, further supporting the

200 possible existence of an electron drip-feeding mechanism.

201 Additional confirmation of the mechanism is obtained by reducing the size of the NCs,

202 wherein the E_g increases due to quantum confinement which also allows a relaxation of the

203 phonon selection rules. Smaller MP3 LT NCs (12 nm as seen from TEM in Fig. S5a) show a

204 higher E_g (3.15 eV) compared to the 16 nm MP3 (E_g = 2.87 eV) as shown in Fig. 3e. The

205 absorption spectrum of MP1 (E_g = 3.10 eV) is also shown in the figure for comparison. The

206 area ratios of the delayed excitonic emission as a function of temperature for MP3, MP3 LT

207 and MP1 are compared in Fig. 3f. The similarity of the plots for MP3 and MP3 LT shows

208 that the phonon assistance increases as expected in the smaller sized NCs, due to the

209 relaxation of the phonon selection rules.

210

211 *Fig. 4. Schematic of Phonon coupling: Visual analogy of phonon coupling for Mn-doped*
212 *CsPbBr$_3$, CsPbCl$_3$ perovskite NCs and for Mn doped CdSe quantum dots.*

213 In summary, Fig. 4 symbolically depicts the two key players of this mechanism, vibrational

214 coupling and the energy barrier for transfer to and from the Mn ion. The energy barrier is

215 largely controlled by spin-orbit coupling, as the Mn energy levels are pushed deeper into the

216   CB due to the spin-orbit coupling. However, the critical mechanism in these cases is the

217   vibrational coupling. For $CsPbBr_3$, at room temperature, the coupling is efficient and hence

218   we observe photons arising out of the back transfer. This coupling is further strengthened at

219   low temperatures, leading to more efficient back transfer as shown in the visual analogy in

220   Fig. 4. In contrast, materials like mixed halides and chlorides show progressively weaker

221   coupling, leading to back transfer only at lower temperature. This selective back transfer is

222   favoured when the lifetimes of the relevant phonon modes have increased, as observed from

223   Raman spectroscopy and DFT calculations. However, in the case of most II-VI quantum dots

224   (including quantum confined CdSe wherein thermally driven energy back transfer has been

225   shown only in cases where the E_g is lower than the Mn transition energy), the coupling is not

226   possible at any temperature and do not observe back transfer from the Mn atom.

227   Additionally, quantum confinement is not expected to change the coupling between the Mn

228   and the host which is consistent with our experimental observations. This is fundamentally

229   different than the case of CdSe[24] which is driven by the thermal back transfer as well as

230   quantum confinement and does not provide the additional advantage of selective drip-feeding

231   to the radiative states.

232   Finally, from a device perspective, Mn doping has been acknowledged to be superior due to

233   the lack of self-absorption,[23] but with a broad non-tunable emission at 590 nm (2.1 eV). By

234   using Mn as a storehouse of charges, all these advantages will be transferred to the excitonic

235   features in addition to the tunability and the sharpness of the excitonic emission peak. This

236   shutdown of the non-radiative channels increases the QY of the sharp tunable excitonic

237   feature in the doped samples. In addition, the absence of self-absorption due to electron drip-

238   feeding should retain high QY even on highly concentrated NC films. It should be noted that

239   even though the solution QYs of the undoped NCs is about 30% for P5 (Fig. S4), the same is

240   reduced substantially in NC films (< 10%) due to self-absorption as shown in Fig. 3g (green

241   circles). However, the excitonic emission in Mn doped NCs is substantially greater (> 50%

242   for MP6) due to absence of self-absorption. In conclusion, electron drip-feed leading to

243   delayed excitonic emission adds an additional handle to increase and maintain a high QY

244   with low losses. The immediate fallout of this is the reduction of overpotential losses and/or

245   non-radiative loss leading to more efficient devices with Mn doping.

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Methods:

Undoped (P1-P6) and Mn-doped (MP1-MP6) CsPb (Cl/Br)$_3$ NCs with varying Cl to Br ratios were synthesized by direct hot injection method using a mixture of lead halide, manganese halide and cesium oleate precursors according to literature reports[25] (see supplementary information (SI) for details). After purification, NCs were characterized by TEM images of the Mn-doped NCs shown in Fig. S5b; these indicate the existence of a monodisperse highly crystalline and cubic morphology, similar to that of the undoped perovskite NCs. X-ray diffraction (XRD) (Fig. S6 in SI) shows high crystallinity along with retaining the cubic structure. Elemental analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES) shows less than 5% Mn within the NCs. The E_gs were obtained from the absorption spectra and are shown in Fig. S1. Room temperature steady state and gated PL spectra were collected by exciting the sample dispersed in hexane at 365 nm and low temperature PL measurements were obtained by drop casting the purified NCs on a glass slide. The QY was obtained on drop-casted thin films using an integrating sphere. These drop casted NCs were also used to perform temperature-dependent Raman spectroscopy.

Ab initio density functional theory (DFT)[26,27] calculations were performed using the Quantum ESPRESSO[28] package, with a plane wave basis set and ultrasoft pseudopotentials, and spin orbit effects were incorporated using fully relativistic pseudopotentials. Phonon calculations were performed by DFPT.[29] The Brillouin zone was sampled with a Monkhorst-Pack mesh[30] of 8✕8✕8 k-points for the primitive unit cell of CsPbBr$_3$. A large unit-cell where one of 8 Pb atoms was substituted by Mn, was constructed to reduce the Mn concentration down to 12.5%, but we note that this concentration is still substantially higher than < 5% Mn in the experimental samples, as determined from inductively coupled plasma optical emission spectroscopy.   Further details of the experimental synthesis and theoretical calculations are given in the SI.

References

1   Zhou, Q. *et al.* In situ fabrication of halide perovskite nanocrystal embedded polymer composite films with enhanced photoluminescence for display backlights. *Adv. Mater.* **28**, 9163-9168 (2016).

2   Nedelcu, G. *et al.* Fast anion-exchange in highly luminescent nanocrystals of cesium lead halide perovskites ($CsPbX_3$, X= Cl, Br, I). *Nano Lett.* **15**, 5635 (2015).

3   Song, J. *et al.* Quantum dot light emitting diodes based on inorganic perovskite cesium lead halides ($CsPbX_3$). *Adv. Mater.* **27**, 7162-7167 (2015).

4   Liu, W. *et al.* Mn^{2+}-Doped lead halide perovskite nanocrystals with dual-color emission controlled by halide content. *J. Am. Chem. Soc.* **138**, 14954-14961 (2016).

5   Li, J. *et al.* 50 Fold EQE improvement up to 6.27% of solution processed all inorganic perovskite $CsPbBr_3$ QLEDs via surface ligand density control. *Adv. Mater.* **29**, 1603885 (2017).

6   Tan, Z.-K. *et al.* Bright light-emitting diodes based on organometal halide perovskite. *Nat. Nanotechnol.* **9**, 687 (2014).

7   Chernenko, A. *et al.* Auger recombination of excitons in semimagnetic quantum dot structure in a magnetic field. *Phys. Rev. B* **72**, 045302 (2005).

8   Krause, M. M., Mooney, J. & Kambhampati, P. Chemical and thermodynamic control of the surface of semiconductor nanocrystals for designer white light emitters. *ACS Nano* **7**, 5922-5929 (2013).

9   Pinchetti, V. *et al.* Trap-mediated two-step sensitization of manganese dopants in perovskite nanocrystals. *ACS Energy Lett.* **4**, 85-93 (2018).

10   Uoyama, H., Goushi, K., Shizu, K., Nomura, H. & Adachi, C. Highly efficient organic light-emitting diodes from delayed fluorescence. *Nature* **492**, 234 (2012).

11   Gahlot, K. *et al.* Transient species mediating energy transfer to spin forbidden Mn d states in II-VI semiconductor quantum dots. *ACS Energy Lett.* **4**, 729-735 (2019).

12   Parobek, D. *et al.* Exciton-to-dopant energy transfer in Mn-doped cesium lead halide perovskite nanocrystals. *Nano Lett.* **16**, 7376-7380 (2016).

13   Van der Stam, W. *et al.* Highly emissive divalent-Ion-doped colloidal $CsPb_{1-x}M_xBr_3$ perovskite nanocrystals through cation exchange. *J. Am. Chem. Soc.* **139**, 4087-4097 (2017).

14   Guria, A. K., Dutta, S. K., Adhikari, S. D. & Pradhan, N. Doping Mn^{2+} in lead halide perovskite nanocrystals: successes and challenges. *ACS Energy Lett.* **2**, 1014-1021 (2017).

15   Chen, H.-Y., Chen, T.-Y. & Son, D. H. Measurement of energy transfer time in colloidal Mn-doped semiconductor nanocrystals. *J. Phys. Chem. C* **114**, 4418-4423 (2010).

16   Parobek, D., Dong, Y., Qiao, T. & Son, D. H. Direct hot-injection synthesis of Mn-doped $CsPbBr_3$ nanocrystals. *Chem. Mater.* **30**, 2939-2944 (2018).

17   Huang, G. *et al.* Postsynthetic doping of $MnCl_2$ molecules into preformed $CsPbBr_3$ perovskite nanocrystals via a halide exchange driven cation exchange. *Adv. Mater.* **29**, 1700095 (2017).

18   Xu, K. & Meijerink, A. Tuning exciton–Mn^{2+} energy transfer in mixed halide perovskite nanocrystals. *Chem. Mater.* **30**, 5346-5352 (2018).

19   De Siena, M. C., Sommer, D. E., Creutz, S. E., Dunham, S. T. & Gamelin, D. R. Spinodal decomposition during anion exchange in colloidal Mn^{2+}-doped $CsPbX_3$ (X= Cl, Br) perovskite nanocrystals. *Chem. Mater.* (2019).

20   Yin, J. *et al.* Intrinsic lead ion emissions in zero-dimensional Cs_4PbBr_6 nanocrystals. *ACS Energy Lett.* **2**, 2805-2811 (2017).

21   Liao, M., Shan, B. & Li, M. In situ Raman spectroscopic studies of thermal stability of all-inorganic cesium lead halide ($CsPbX_3$, X= Cl, Br, I) perovskite nanocrystals. *J. Phys. Chem. Lett.* **10**, 1217-1225 (2019).

22   Calistru, D. M., Mihut, L., Lefrant, S. & Baltog, I. Identification of the symmetry of phonon modes in $CsPbCl_3$ in phase IV by Raman and resonance-Raman scattering. *J. Appl. Phys.* **82**, 5391-5395 (1997).

23   Pandey, A. & Sarma, D. D. Recent advances in manganese doped II VI semiconductor quantum dots. *Z. Anorg. Allg. Chem.* **642**, 1331-1339 (2016).

332 24 Beaulac, R., Archer, P. I., van Rijssel, J., Meijerink, A. & Gamelin, D. R. Exciton storage by
333 Mn^{2+} in colloidal Mn^{2+}-doped CdSe quantum dots. *Nano Lett.* **8**, 2949-2953 (2008).
334 25 Protesescu, L. *et al.* Nanocrystals of cesium lead halide perovskites ($CsPbX_3$, X= Cl, Br, and
335 I): novel optoelectronic materials showing bright emission with wide color gamut. *Nano Lett.*
336 **15**, 3692-3696 (2015).
337 26 Kohn, W. & Sham, L. J. Self-consistent equations including exchange and correlation effects.
338 *Phys. Rev. A* **140**, A1133 (1965).
339 27 Hohenberg, P. & Kohn, W. Inhomogeneous electron gas. *Phys. Rev. B* **136**, B864-B871
340 (1964).
341 28 Giannozzi, P. *et al.* QUANTUM ESPRESSO: a modular and open-source software project for
342 quantum simulations of materials. *J. Phys.: Condens. Matter* **21**, 395502 (2009).
343 29 Baroni, S., de Gironcoli, S., Dal Corso, A. & Giannozzi, P. Phonons and related crystal
344 properties from density-functional perturbation theory. *Rev. Mod. Phys.* **73**, 515-562 (2001).
345 30 Monkhorst, H. J. & Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **13**,
346 5188 (1976).

347