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Manganese-Doped One-Dimensional Organic Lead Bromide Perovskites with Bright White Emissions

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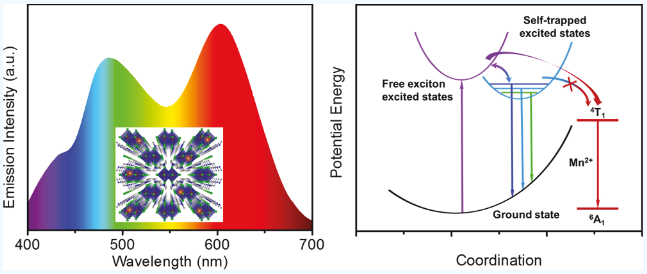
Supporting Information



ABSTRACT: Single-component white-emitting phosphors are highly promising to simplify the fabrication of optically pumped white light-emitting diodes. To achieve white emission, precise control of the excited state dynamics is required for a single-component system to generate emissions with different energies in the steady state. Here, we report a new class of white phosphors based on manganese (Mn)-doped one-dimensional (1D) organic lead bromide perovskites. The bright white emission is the combination of broadband blue emission from the self-trapped excited states of the 1D perovskites and red emission from the doped Mn^{2+} ions. Because of the indirect nature of the self-trapped excited states in 1D perovskites, there is no energy transfer from these states to the Mn^{2+} ions, resulting in an efficient dual emission. As compared to the pristine 1D perovskites with bluish-white emission, these Mn-doped 1D perovskites exhibit much higher color rendering index of up to 87 and photoluminescence quantum efficiency of up to 28%.

KEYWORDS: *metal halide perovskites, one-dimensional structure, broadband white emission, exciton self-trapping, Mn doping*

INTRODUCTION

Optically pumped white light-emitting diodes (WLEDs) have revolutionized solid-state lighting and full color display over the last decade because of their numerous advantages over conventional light sources.[1−4] To obtain pure white emission, a variety of device architectures have been developed over the years using different combinations of UV/blue light-emitting diodes (LEDs) and phosphors, including (I) a blue LED chip with a yellow phosphor or a mixture of green and red phosphors, (II) a UV LED with multiple monochromatic blue, green, and red phosphors, and (III) a UV LED with a single broadband white phosphor.[5−7] The latest approach III is highly promising, as it can not only simplify the device fabrication but also overcome a number of drawbacks associated with approaches I and II, for example, poor color rendition due to narrow emissions of phosphors, efficiency loss due to self-absorption, and the change of emission color over time due to different degradation rates of individual phosphors. However, developing highly luminescent single-component white light-emitting materials is not trivial, as it requires precise control of the excited state energy flow to generate emissions with different energies simultaneously in the steady state.[7−14] To date, the two major strategies to realizing white emission from single-component systems, codoping inorganic phosphors and utilizing the surface defects of nanocrystals, have not achieved the high performance required for real applications yet.[15−21]

Organic−inorganic hybrid metal halide perovskites have recently emerged as a new class of highly luminescent light-emitting materials.[22−32] Their exceptional structural tunability has offered numerous ways of band structure control and color tuning. Aside from narrow emissions with small full-width at half maximum (FWHM), broadband emissions with extremely large FWHM have been realized for these materials by controlling their structures and compositions. For instance, corrugated two-dimensional (2D) lead halide perovskites in the forms of bulk and nanoscale crystals have been developed to exhibit emissions across the entire visible spectrum upon UV excitation, although the photoluminescence quantum efficiencies (PLQEs) are still relatively low.[33−37] More recently, our group reported broadband-emitting one-dimensional (1D) lead bromide perovskites ($C_4N_2H_{14}PbBr_4$) with higher PLQEs,[38] as compared to those corrugated 2D perovskites. However, the stronger quantum confinement in the 1D structure leads to blueshift of the light emission, resulting in deficiency of red emission and a low color rendering index (CRI) of 66. Note

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that our 1D $C_4N_2H_{14}PbBr_4$ is a bulk crystal with a 1D structure on the molecular level, not the morphological nanoscale 1D perovskites with a three-dimensional (3D) ABX_3 structure, such as $CsPbBr_3$ nanowires/nanorods. To improve the quality of white emission with higher CRI, integrating red-emitting species in these 1D lead bromide perovskites without quenching the blue emission is desired.

Incorporating Mn^{2+} ions into inorganic crystal lattices and metal halide perovskites has been demonstrated as an effective approach to introducing a low-energy emission peaked at around 600 nm from an internal $^4T_1$ to $^6A_1$ transition of the Mn^{2+} ions.[39−46] Herein, we report the synthesis and characterization of Mn-doped 1D lead bromide perovskites with bright white emissions. The white emission is realized by combining blue emission from the indirect self-trapped excited states of the 1D perovskites and red emission from the doped Mn^{2+} ion. In these Mn-doped 1D perovskites, the excited state energy flows from the direct free exciton excited states to both the self-trapped excited states and Mn^{2+} ions simultaneously. Because of the indirect nature of the self-trapped excited states, no direct energy transfer from these states to the Mn^{2+} ions is expected. In other words, independent multiple excited states are realized in these materials that produce efficient dual emission. The excited state dynamics present in these materials with self-trapped excited states is significantly different from those in conventional Mn-doped inorganic crystals and 3D metal halide perovskites, where efficient energy transfer from the free exciton excited states to Mn^{2+} ions often quenches the high-energy emission with only low-energy Mn^{2+} luminescence, even at a low Mn^{2+} doping concentration. The emissions of these Mn-doped 1D perovskites possess much improved CRI of up to 87 and a PLQE of up to 28%, as compared to those of the pristine 1D perovskites of 66 and 12%, respectively.

■ RESULTS AND DISCUSSION

A series of Mn-doped 1D lead bromide perovskites were prepared via a facile one-pot synthesis method,[47,48] as shown in Figure 1a. In a typical reaction, dimethyl ethylene ammonium bromide salt ($C_4N_2H_{14}Br_2$), $PbBr_2$, and $MnBr_2$ are fully dissolved in dimethyl sulfoxide to prepare a clear precursor solution, which was injected to a vigorously stirred acetone and stirred for 10 minutes at room temperature. The colloidal white solution was then centrifuged to remove the supernatant and afford Mn-doped 1D lead bromide perovskites in a high yield (∼80%). By simply changing the $MnBr_2$ concentration in the precursor solutions, 1D lead bromide perovskites with various Mn^{2+} doping concentrations were prepared. More details of synthesis can be found in the Supporting Information. X-ray fluorescence (XRF) and powder X-ray diffraction (XRD) were used to characterize the composition and structure of these Mn-doped 1D perovskites. The Mn^{2+} doping concentrations were characterized from the semiquantitative XRF measurements by comparing the content of Mn and Pb. The Mn-doped 1D perovskites with various doping concentrations were determined as $C_4N_2H_{14}Pb_{0.992}Mn_{0.008}Br_4$ (**Mn08**), $C_4N_2H_{14}Pb_{0.987}Mn_{0.013}Br_4$ (**Mn13**), and $C_4N_2H_{14}Pb_{0.970}Mn_{0.030}Br_4$ (**Mn30**). Figure 1b shows the XRD patterns of the pristine and Mn-doped 1D perovskites. The almost identical powder XRD patterns suggest that there is no detectable phase change or separation resulting from the doping of Mn^{2+} ions. Thermogravimetric analysis shows that the incorporation of Mn^{2+} ions slightly enhances the thermal stability of the doped 1D perovskites, which do not decompose until about 300 °C (Figure S1).

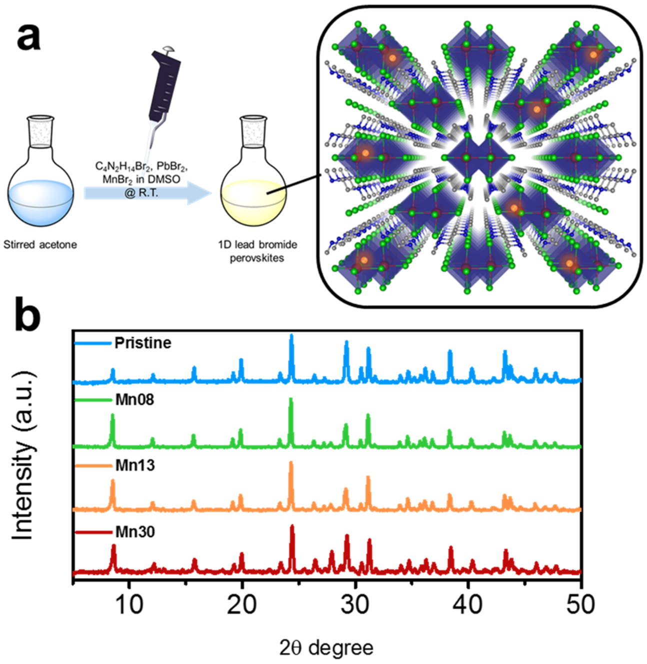

Figure 1. (a) One-pot synthesis of Mn-doped 1D lead bromide perovskites. (b) Powder XRD patterns of the pristine and Mn-doped 1D lead bromide perovskites.

The optical properties of the as-prepared Mn-doped 1D perovskites were fully characterized. The inset of Figure 2a shows the images of the pristine and Mn-doped 1D perovskites. All of the samples are white powders under ambient light but show a wide range of "cold" to "warm" white emissions under UV irradiation (365 nm) depending on the Mn^{2+} doping concentration. The little-to-no change of the absorption spectra in Figure 2a suggests that the light absorption is primarily by the host 1D perovskites with minimum contributions from the doped Mn^{2+} ions. The photoluminescence spectra of the pristine and Mn-doped 1D perovskites upon UV excitation at 355 nm are also shown in Figure 2a. In the pristine 1D perovskites, a dual emission is recorded with a high-energy narrow band (peaked at ∼390 nm) from the free exciton excited states and a low-energy broadband (peaked at ∼485 nm) from the self-trapped excited states. In the Mn-doped 1D perovskites, the near UV emission at ∼390 nm is significantly quenched with an additional broadband emission peaked at ∼605 nm, which is attributed to the ligand field transition ($^4T_1$ to $^6A_1$) of Mn^{2+} ions. Interestingly, the blue emission from the self-trapped excited states remains relatively unchanged. By combining the self-trapped broadband blue emission from the 1D perovskites and the strong red emission from the Mn^{2+} ions with the characteristic d−d transition, bright white emissions have been realized in these Mn-doped 1D perovskites. It is worthwhile to mention that this class of materials are almost free from the self-reabsorption issue that many other phosphors suffer (e.g., 3D materials) because of the effective large stokes shift. Figure 3b shows the corresponding CIE coordinates of the emissions from the pristine and Mn-doped 1D perovskites. By controlling the Mn^{2+} doping concentration, the CRI of these 1D perovskites can be increased from 66 to 87, and the correlated color temperature (CCT) reduced from 24 154 K to 2459 K. The great color tunability of these Mn-doped 1D

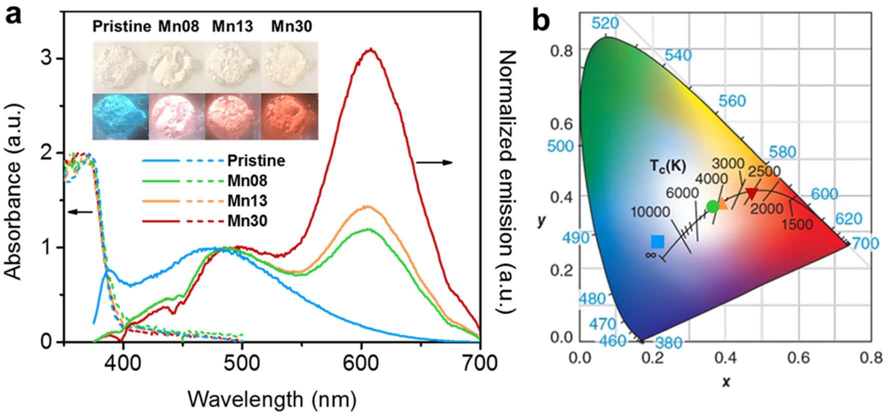

Figure 2. (a) Absorption (dashed line) and emission (solid line) spectra of the pristine and Mn-doped 1D lead bromide perovskites, the inset shows the images of the pristine and Mn-doped 1D lead bromide perovskites under ambient light (top) and UV light (365 nm, bottom). (b) CIE coordinates of the emissions of the pristine and Mn-doped 1D lead bromide perovskites upon UV excitation: pristine (blue rectangle), **Mn08** (green circle), **Mn13** (orange triangle), and **Mn30** (red nabla).

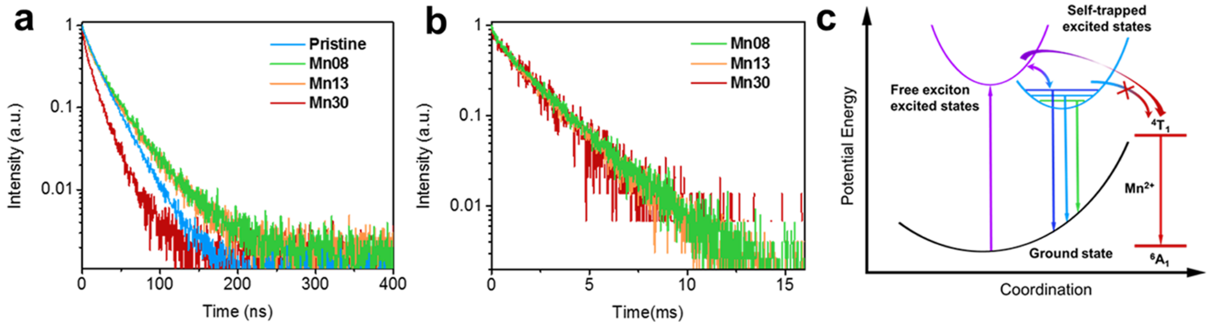

Figure 3. Photoluminescence decay profiles of the pristine and Mn-doped 1D lead bromide perovskites monitored at 450 nm (a) and 650 nm (b). Proposed energy diagram and excited state dynamics of Mn-doped 1D lead bromide perovskites (c): the straight and curved arrows represent optical and energy relaxation/transfer transitions, respectively.

Table 1. Photophysical Properties of the Pristine and Mn-Doped 1D Lead Bromide Perovskites at Room Temperature

sample	λ_{em} (nm)	PLQE (%)	lifetime (ns)@450 nm	lifetime (ms)@650 nm	CIE	CRI	CCT (K)
pristine	389, 475	10−12	22.6	N/A	(0.21, 0.27)	66	24 154
Mn08	484, 605	20−22	28.2	2.0	(0.37, 0.37)	87	4286
Mn13	484, 605	25−28	26.9	1.9	(0.39, 0.37)	85	3767
Mn30	486, 608	20−22	15.3	1.9	(0.47, 0.40)	78	2459

perovskites would allow for the development of optically pumped WLEDs with different photometric properties for various applications. The PLQEs of these Mn-doped 1D perovskites in the form of microscale crystals were determined (Figure S2), with the highest value of ∼28% for the sample (**Mn13**) containing 1.3% Mn^{2+} doping, representing a significant improvement over that of the pristine 1D perovskites of ∼12%. A lager amount of Mn^{2+} doping results in a decrease in PLQE, which is likely attributed to the surface or internal defects from excessive doping. Such a phenomenon has been observed in other Mn-doped systems, such as Mn-doped $CsPbCl_3$.[42]

Time-resolved photoluminescence measurements were carried out to gain an insight into the excited state dynamics of these Mn-doped 1D perovskites with multiple excited states, including free exciton excited states, self-trapped excited states, and Mn^{2+} transition states. Figure 3a, b shows the luminescent decay profiles monitored at two different emission peaks, with fittings in Figure S3. The emission decay profiles collected at 450 nm are primarily from the contributions of the self-trapped excited states and a little amount of the free exciton excited states, which are in equilibrium at room temperature.[38] It is found that the 450 nm emissions of **Mn08** and **Mn13** have a longer lifetime of ∼27 ns than that of the pristine 1D perovskites of ∼22 ns, which is likely due to the influence of the Mn^{2+} doping on the competitive kinetics between the radiative and nonradiative decays. As suggested by previous studies,[43,44] a small amount of Mn^{2+} dopants may remove the preexisting structural defects accounting for the nonradiative decays. With further increase of the doping concentration to 3%, the lifetime of the 450 nm emission deceases to ∼15 ns, which could be attributed to two reasons. First, the internal or surficial defects by excessive Mn^{2+} ions may speed up the nonradiative relaxation process. Second, the higher doping concentration leads to higher energy transfer from the free exciton excited states to the Mn^{2+} ions, also resulting in enhanced nonradiative decay of the free exciton excited states. The decay profiles of emissions from Mn^{2+} ions at 650 nm are shown in Figure 3b. The lifetimes for the emissions of the three Mn-doped 1D perovskites were calculated to be identical at ∼1.9 ms. Such extremely long lifetimes confirm their origination from the spin-forbidden ligand field transition ($^4T_1$ to $^6A_1$) of the doped Mn^{2+} ions. Unlike typical Mn-doped inorganic crystals and metal halide perovskites with only direct band-edge emission and Mn^{2+} emission, this new class of Mn-doped 1D perovskites could have emissions from the direct free exciton and indirect self-trapped excited states, as well as Mn^{2+} ions. The major photophysical properties of Mn-doped 1D perovskites are summarized in Table 1.

The excited state dynamics of these Mn-doped 1D perovskites can be therefore depicted as in Figure 3c. Upon UV photoabsorption, the system is excited to the direct free exciton excited states, which can undergo energy relaxation/transfer to both the indirect self-trapped excited states and Mn^{2+} ions simultaneously. The dual emission from the self-trapped excited states and Mn^{2+} ions suggests that these two energy transfer processes are likely competitive with similar time scales. The same excitation of indirect self-trapped emission and Mn^{2+} emission (Figure S4) confirms their identical origin from the free exciton excited states by direct band absorption. Higher Mn^{2+} doping concentration would lead to enhanced energy transfer from the free exciton excited states to the Mn^{2+} ions. Unlike the self-trapped excited states creating a thermal equilibrium with the free exciton excited states in the pristine 1D perovskites, the Mn^{2+} ions possess no back energy transfer to the free exciton excited states in the Mn-doped 1D perovskites because of the large energy offset. This perfectly explains why the deep blue emission from the free exciton excited states is significantly quenched. On the other hand, the energy transfer from the self-trapped excited states to the Mn^{2+} ions is not allowed, although the transitions from the self-trapped excited states to the ground state have larger energy difference with blue emission than that of Mn^{2+} ions with red emission. This is because the self-trapped excited states are indirect transient states with unpopulated ground states that could block electron exchange in Dexter energy transfer.[12] Overall, multiple excited states coexist in these Mn-doped 1D perovskites to generate white emissions in the steady state, which are indeed similar to the previously reported co-doped systems, such as Mn and Cu codoped ZnSe quantum dots.[17] Here, the intrinsic indirect self-trapped excited states of the host material replace one of the doping ions, thereby significantly simplifying the material preparation process. To further prove the proposed mechanism and that there is no direct energy transfer from the self-trapped excited states to Mn^{2+} ions, we have measured the emission of **Mn13** (Figure S5) and the decay lifetimes at 77 K (Figure S6). A much higher intensity of the emission from the indirect self-trapped excited states than that of the emission from Mn^{2+} ions is observed. This is not surprising, as there is no thermally activated equilibrium between the free exciton and self-trapped excited states at low temperature, suspending the back energy transfer from the self-trapped excited states to the free exciton excited states that will be quenched by the Mn^{2+} ions. Also, the emission from the self-trapped excited states has much higher PLQE with longer lifetime at 77 K than at room temperature. Moreover, the emission intensity decreases without the change of spectral shape upon the increasing of temperature from room temperature to 80 °C, which is likely due to the enhanced nonradiative decay. The emission intensity recovers after cooling from 80 °C to room temperature, indicating a very good thermostability of the doped 1D perovskites (Figure S7).

■ CONCLUSIONS

In conclusion, we have applied a simple one-pot synthesis to prepare highly luminescent Mn-doped 1D organic lead bromide perovskites. The structural characterizations using XRD confirmed that the host 1D perovskite structure is nearly intact after doping the Mn^{2+} ions. Bright white emissions have been achieved in these new rare earth-free phosphors, by combining the self-trapped blue emission from the 1D perovskites and the red emission from the doped Mn^{2+} ions. This new approach of combining indirect band emission and dopant emission paves a way to develop highly efficient white light-emitting materials with potential applications in solid-state lighting and display. This work shows our capability of directing the excited state energy flow in a complex system with multiple excited states to achieve desired photophysical properties. Investigation of the excited state kinetics in these new materials using ultrafast spectroscopies is underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b12456.

Syntheses and characterizations of the Mn-doped 1D lead bromide perovskites (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Mueller-Mach, R.; Mueller, G. O. White Light Emitting Diodes for Illumination. *Light-Emitting Diodes: Research, Manufacturing, and Applications IV*, 2000; Vol. *3938*, pp 30−41.

(2) Žukauskas, A.; Shur, M. S.; Gaska, R. Light-Emitting Diodes: Progress in Solid-State Lighting. *MRS Bull.* **2001**, *26*, 764−769.

(3) Seo, J. H.; Lee, S. J.; Koo, J. R.; Shin, H. S.; Lee, K. H.; Yoon, S. S.; Kim, Y. K. White Organic Light-Emitting Diodes for Emotion Solid-State Lighting. *J. Nanosci. Nanotechnol.* **2012**, *12*, 4215−4218.

(4) De Almeida, A.; Santos, B.; Paolo, B.; Quicheron, M. Solid State Lighting Review—Potential and Challenges in Europe. *Renewable Sustainable Energy Rev.* **2014**, *34*, 30−48.

(5) McKittrick, J.; Shea-Rohwer, L. E. Review: Down Conversion Materials for Solid-State Lighting. *J. Am. Ceram. Soc.* **2014**, *97*, 1327−1352.

(6) Lin, C. C.; Liu, R.-S. Advances in Phosphors for Light-Emitting Diodes. *J. Phys. Chem. Lett.* **2011**, *2*, 1268−1277.

(7) Roushan, M.; Zhang, X.; Li, J. Solution-Processable White-Light-Emitting Hybrid Semiconductor Bulk Materials with High Photoluminescence Quantum Efficiency. *Angew. Chem., Int. Ed.* **2012**, *51*, 436−439.

(8) Wang, M.-S.; Guo, G.-C.; Chen, W.-T.; Xu, G.; Zhou, W.-W.; Wu, K.-J.; Huang, J.-S. A White-Light-Emitting Borate-Based Inorganic−Organic Hybrid Open Framework. *Angew. Chem., Int. Ed.* **2007**, *46*, 3909−3911.

(9) Park, S.; Kwon, J. E.; Kim, S. H.; Seo, J.; Chung, K.; Park, S.-Y.; Jang, D.-J.; Medina, B. M.; Gierschner, J.; Park, S. Y. A White-Light-Emitting Molecule: Frustrated Energy Transfer between Constituent Emitting Centers. *J. Am. Chem. Soc.* **2009**, *131*, 14043−14049.

(10) Ni, W.-X.; Li, M.; Zheng, J.; Zhan, S.-Z.; Qiu, Y.-M.; Ng, S. W.; Li, D. Approaching White-Light Emission from a Phosphorescent Trinuclear Gold(I) Cluster by Modulating Its Aggregation Behavior. *Angew. Chem., Int. Ed.* **2013**, *52*, 13472−13476.

(11) Yang, Q.-Y.; Lehn, J.-M. Bright White-Light Emission from a Single Organic Compound in the Solid State. *Angew. Chem., Int. Ed.* **2014**, *53*, 4572−4577.

(12) Han, M.; Tian, Y.; Yuan, Z.; Zhu, L.; Ma, B. A Phosphorescent Molecular "Butterfly" that undergoes a Photoinduced Structural Change allowing Temperature Sensing and White Emission. *Angew. Chem., Int. Ed.* **2014**, *53*, 10908−10912.

(13) Behrh, G. K.; Serier-Brault, H.; Jobic, S.; Gautier, R. A Chemical Route Towards Single-Phase Materials with Controllable Photoluminescence. *Angew. Chem., Int. Ed.* **2015**, *54*, 11501−11503.

(14) Xie, Z.; Chen, C.; Xu, S.; Li, J.; Zhang, Y.; Liu, S.; Xu, J.; Chi, Z. White-Light Emission Strategy of a Single Organic Compound with Aggregation-Induced Emission and Delayed Fluorescence Properties. *Angew. Chem., Int. Ed.* **2015**, *54*, 7181−7184.

(15) Bowers, M. J.; McBride, J. R.; Rosenthal, S. J. White-Light Emission from Magic-Sized Cadmium Selenide Nanocrystals. *J. Am. Chem. Soc.* **2005**, *127*, 15378−15379.

(16) Guo, C.; Luan, L.; Xu, Y.; Gao, F.; Liang, L. White Light-Generation Phosphor $Ba_2Ca(BO_3)_2$: $Ce^{(3+)}$, $Mn^{(2+)}$ for Light-Emitting Diodes. *J. Electrochem. Soc.* **2008**, *155*, J310−J314.

(17) Panda, S. K.; Hickey, S. G.; Demir, H. V.; Eychmüller, A. Bright White-Light Emitting Manganese and Copper Co-Doped ZnSe Quantum Dots. *Angew. Chem., Int. Ed.* **2011**, *50*, 4432−4436.

(18) Rosson, T. E.; Claiborne, S. M.; McBride, J. R.; Stratton, B. S.; Rosenthal, S. J. Bright White Light Emission from Ultrasmall Cadmium Selenide Nanocrystals. *J. Am. Chem. Soc.* **2012**, *134*, 8006−8009.

(19) Krause, M. M.; Mooney, J.; Kambhampati, P. Chemical and Thermodynamic Control of the Surface of Semiconductor Nanocrystals for Designer White Light Emitters. *ACS Nano* **2013**, *7*, 5922−5929.

(20) Yuan, X.; Ma, R.; Zhang, W.; Hua, J.; Meng, X.; Zhong, X.; Zhang, J.; Zhao, J.; Li, H. Dual Emissive Manganese and Copper Co-Doped Zn−In−S Quantum Dots as a Single Color-Converter for High Color Rendering White-Light-Emitting Diodes. *ACS Appl. Mater. Interfaces* **2015**, *7*, 8659−8666.

(21) Teunis, M. B.; Lawrence, K. N.; Dutta, P.; Siegel, A. P.; Sardar, R. Pure White-Light Emitting Ultrasmall Organic−Inorganic Hybrid Perovskite Nanoclusters. *Nanoscale* **2016**, *8*, 17433−17439.

(22) Tan, Z.-K.; Moghaddam, R. S.; Lai, M. L.; Docampo, P.; Higler, R.; Deschler, F.; Price, M.; Sadhanala, A.; Pazos, L. M.; Credgington, D.; Hanusch, F.; Bein, T.; Snaith, H. J.; Friend, R. H. Bright Light-Emitting Diodes Based on Organometal Halide Perovskite. *Nat. Nanotechnol.* **2014**, *9*, 687−692.

(23) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX3, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, *15*, 3692−3696.

(24) Pathak, S.; Sakai, N.; Rivarola, F. W. R.; Stranks, S. D.; Liu, J.; Eperon, G. E.; Ducati, C.; Wojciechowski, K.; Griffiths, J. T.; Haghighirad, A. A.; Pellaroque, A.; Friend, R. H.; Snaith, H. J. Perovskite Crystals for Tunable White Light Emission. *Chem. Mater.* **2015**, *27*, 8066−8075.

(25) Sichert, J. A.; Tong, Y.; Mutz, N.; Vollmer, M.; Fischer, S.; Milowska, K. Z.; Cortadella, R. G.; Nickel, B.; Cardenas-Daw, C.; Stolarczyk, J. K.; Urban, A. S.; Feldmann, J. Quantum Size Effect in Organometal Halide Perovskite Nanoplatelets. *Nano Lett.* **2015**, *15*, 6521−6527.

(26) Stranks, S. D.; Snaith, H. J. Metal-Halide Perovskites for Photovoltaic and Light-Emitting Devices. *Nat. Nanotechnol.* **2015**, *10*, 391−402.

(27) Yuan, Z.; Shu, Y.; Xin, Y.; Ma, B. Highly Luminescent Nanoscale Quasi-2D Layered Lead Bromide Perovskites with Tunable Emissions. *Chem. Commun.* **2016**, *52*, 3887−3890.

(28) Li, X.; Wu, Y.; Zhang, S.; Cai, B.; Gu, Y.; Song, J.; Zeng, H. CsPbX3 Quantum Dots for Lighting and Displays: Room-Temperature Synthesis, Photoluminescence Superiorities, Underlying Origins and White Light-Emitting Diodes. *Adv. Funct. Mater.* **2016**, *26*, 2435−2445.

(29) Sessolo, M.; Gil-Escrig, L.; Longo, G.; Bolink, H. J. Perovskite Luminescent Materials. *Top. Curr. Chem.* **2016**, *374*, 52.

(30) Zhang, Y.; Liu, J.; Wang, Z.; Xue, Y.; Ou, Q.; Polavarapu, L.; Zheng, J.; Qi, X.; Bao, Q. Synthesis, Properties, and Optical Applications of Low-Dimensional Perovskites. *Chem. Commun.* **2016**, *52*, 13637−13655.

(31) Kim, Y.-H.; Cho, H.; Lee, T.-W. Metal Halide Perovskite Light Emitters. *Proc. Natl. Acad. Sci. U.S.A.* **2016**, *113*, 11694−11702.

(32) Zhou, C.; Tian, Y.; Wang, M.; Rose, A.; Besara, T.; Doyle, N. K.; Yuan, Z.; Wang, J. C.; Clark, R.; Hu, Y.; Siegrist, T.; Lin, S.; Ma, B. Low-Dimensional Organic Tin Bromide Perovskites and Their Photoinduced Structural Transformation. *Angew. Chem., Int. Ed.* **2017**, *56*, 9018−9022.

(33) Dohner, E. R.; Hoke, E. T.; Karunadasa, H. I. Self-Assembly of Broadband White-Light Emitters. *J. Am. Chem. Soc.* **2014**, *136*, 1718−1721.

(34) Dohner, E. R.; Jaffe, A.; Bradshaw, L. R.; Karunadasa, H. I. Intrinsic White-Light Emission from Layered Hybrid Perovskites. *J. Am. Chem. Soc.* **2014**, *136*, 13154−13157.

(35) Hu, T.; Smith, M. D.; Dohner, E. R.; Sher, M.-J.; Wu, X.; Trinh, M. T.; Fisher, A.; Corbett, J.; Zhu, X.-Y.; Karunadasa, H. I.; Lindenberg, A. M. Mechanism for Broadband White-Light Emission from Two-Dimensional (110) Hybrid Perovskites. *J. Phys. Chem. Lett.* **2016**, *7*, 2258−2263.

(36) Yuan, Z.; Zhou, C.; Messier, J.; Tian, Y.; Shu, Y.; Wang, J.; Xin, Y.; Ma, B. A Microscale Perovskite as Single Component Broadband Phosphor for Downconversion White-Light-Emitting Devices. *Adv. Opt. Mater.* **2016**, *4*, 2009−2015.

(37) Cortecchia, D.; Yin, J.; Bruno, A.; Lo, S.-Z. A.; Gurzadyan, G. G.; Mhaisalkar, S.; Brédas, J.-L.; Soci, C. Polaron Self-Localization in White-Light Emitting Hybrid Perovskites. *J. Mater. Chem. C* **2017**, *5*, 2771−2780.

(38) Yuan, Z.; Zhou, C.; Tian, Y.; Shu, Y.; Messier, J.; Wang, J. C.; van de Burgt, L. J.; Kountouriotis, K.; Xin, Y.; Holt, E.; Schanze, K.; Clark, R.; Siegrist, T.; Ma, B. One-Dimensional Organic Lead Halide Perovskites with Efficient Bluish White-Light Emission. *Nat. Commun.* **2017**, *8*, 14051.

(39) Bhargava, R. N.; Gallagher, D.; Hong, X.; Nurmikko, A. Optical-Properties of Manganese-Doped Nanocrystals of Zns. *Phys. Rev. Lett.* **1994**, *72*, 416−419.

(40) Pradhan, N.; Sarma, D. D. Advances in Light-Emitting Doped Semiconductor Nanocrystals. *J. Phys. Chem. Lett.* **2011**, *2*, 2818−2826.

(41) Sharma, V. K.; Guzelturk, B.; Erdem, T.; Kelestemur, Y.; Demir, H. V. Tunable White-Light-Emitting Mn-Doped ZnSe Nanocrystals. *ACS Appl. Mater. Interfaces* **2014**, *6*, 3654−3660.

(42) Liu, W.; Lin, Q.; Li, H.; Wu, K.; Robel, I.; Pietryga, J. M.; Klimov, V. I. Mn^{2+}-Doped Lead Halide Perovskite Nanocrystals with Dual-Color Emission Controlled by Halide Content. *J. Am. Chem. Soc.* **2016**, *138*, 14954−14961.

(43) Parobek, D.; Roman, B. J.; Dong, Y.; Jin, H.; Lee, E.; Sheldon, M.; Son, D. H. Exciton-to-Dopant Energy Transfer in Mn-Doped

DOI: 10.1021/acsami.7b12456
ACS Appl. Mater. Interfaces 2017, 9, 40446−40451

Cesium Lead Halide Perovskite Nanocrystals. *Nano Lett.* **2016**, *16*, 7376−7380.

(44) Liu, H.; Wu, Z.; Shao, J.; Yao, D.; Gao, H.; Liu, Y.; Yu, W.; Zhang, H.; Yang, B. $CsPb_xMn_{1-x}Cl_3$ Perovskite Quantum Dots with High Mn Substitution Ratio. *ACS Nano* **2017**, *11*, 2239−2247.

(45) Mir, W. J.; Jagadeeswararao, M.; Das, S.; Nag, A. Colloidal Mn-Doped Cesium Lead Halide Perovskite Nanoplatelets. *ACS Energy Lett.* **2017**, *2*, 537−543.

(46) 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.* **2017**, *2*, 1014−1021.

(47) McLaurin, E. J.; Fataftah, M. S.; Gamelin, D. R. One-Step Synthesis of Alloyed Dual-Emitting Semiconductor Nanocrystals. *Chem. Commun.* **2013**, *49*, 39−41.

(48) Yazdanparast, M. S.; Webb, M. T.; McLaurin, E. J. Single-Step Synthesis of Hyperbranched, Luminescent Mn^{2+}-Doped $ZnSe_{1-x}S_x$ Nanocrystals Using Dichalcogenide Precursors. *J. Mater. Chem. C* **2016**, *4*, 6907−6913.