Manganese(II) in Tetrahedral Halide Environment: Factors Governing Bright Green Luminescence

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Supporting Information

ABSTRACT: Finding narrow-band light emitters for the visible spectral region remains an immense challenge. Such phosphors are in great demand for solid-state lighting and display application. In this context, green luminescence from tetrahedrally coordinated Mn(II) is an attractive research direction. While the oxide–ligand environment had been studied for decades, much less systematic efforts have been undertaken with regard to halide coordination, especially in the form of fully inorganic halide matrices. In this study, we synthesized a series of hybrid organic–inorganic Mn(II) halides as well as a range of fully inorganic Zn halide hosts (chlorides, bromides, iodides) doped with Mn(II). In the latter, tetrahedral coordination is attained via substitutional doping owing to the tetrahedral symmetry of Zn sites. We find that the choice of the halide as well as subtle details of the crystal structure profoundly govern the photoluminescence peak positions (500–550 nm range) and emission line widths (40–60 nm) as well as radiative lifetimes (shorter for iodides) through the altered ligand-field effects and degrees of spin–orbit coupling. The photoluminescence quantum yields were as high as 70–90%. The major hurdle for the practical use of these compounds lies in their low absorption coefficients in the blue spectral regions.

INTRODUCTION

Light-emitting materials have a broad spectrum of applications including solid-state lighting, flat panel display technologies, optical data storage, radiation detection, and photovoltaics.2–5 Narrow-band green-emitting phosphors with an emission peak around 520–535 nm are central for displays and solid-state lighting technologies.6 In recent years, cadmium(II) chalcogenide (Se, S, or Te) nanocrystals (NCs), exhibiting photoluminescence (PL) full width at half maxima (fwhm) of <30 nm and PL quantum yields (QYs) of above 95%, have been used as phosphors in backlighting of displays.7 Limited RoHS compliance and steadily decreasing public and commercial acceptance of heavy-metal-containing materials motivated commercial deployment of environmentally benign indium phosphate NCs8 in spite of their considerably broader emission line width (38–40 nm) and lower stability. An emerging alternative are highly luminescent lead halide perovskite NCs (fwhm ≈ 20 nm at 520–530 nm PL peak),9 whose practical potential still needs to be thoroughly examined. Thus far, the most successful commercial phosphors are still those based on emissive rare-earth or transition-metal ions embedded into a stable crystalline host.6,10 In particular, β-SiAlON:Eu2+ (PL peak at 535 nm, fwhm ≈ 50 nm) is used in commercial LCDs,11 while other Eu2+-based compounds comprise a subject of continued research efforts.12,13

Tetrahedrally coordinated Mn(II) exhibits green emission and is thus of interest for engineering solid-state phosphors. The emission of Mn(II) and Mn(IV) in octahedral (O6) and tetrahedral (T4) crystal fields has been studied for decades.14,15 For instance, red-emissive K2SiF6:Mn4+ (octahedral coordination) has become a commercial red phosphor for white light-emitting diodes.16 In a tetrahedral field (T4) of oxide ligands,17,18 green emission of Mn(II) is characterized by a fwhm below 45 nm and can be as narrow as 26 nm.18 However, the main drawback of the oxide field is slow emission decay, typically 4–6 ms. The emission is due to intra-atomic transitions within the split energy states.19,20 The magnitude of the splitting is quantified by B, C, and Δ parameters. The B and C parameters relate to the Coloumb (electron–electron) repulsion, and Δ quantifies the strength of the crystal field (CF). In addition, the so-called nephelauxetic parameter β = B′/B, where B and B′ are the parameters for a free d-metal ion and an ion in the complex, respectively, is often used to estimate the covalency of the metal–ligand bond. The nephelauxetic effect describes the influence of the ligand on the d-orbitals expansion upon ligation. Greater orbital expansion reduces the Coulomb repulsion. The variation of

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the Δ for different ligands is known as the spectrochemical series, whereas the nephelauxetic series reflects the magnitude of B parameter reduction compared to a free ion. Scheme 1

Scheme 1. Energy States Splitting and Optical Transitions in Tetrahedrally Coordinated MnII Ion

and Table S1 illustrate the energy states splitting for Mn in Td environment.21,22 A spectrally narrow, i.e., 25−60 nm in fwhm, green emission peaked at 500−550 nm originates from the lowest 4T1 → 6A1 transition. The excitation spectra in the blue and near-ultraviolet (near-UV) features several bands, corresponding to two groups of transitions: 6A1 → 4G and 4A1 → 4D. In addition, interatomic Mn−Mn interaction can further modify the energy states. The Mn(II) emission in the octahedral environment is known to be in the red region, foremost due to the weaker ligand field, as compared to the Td coordination. In addition, the distance between O−Mn(II) atoms had been reported to adjust the PL peak position in the orange-red region.23 The d−d transition of Mn 2+ in the field, as compared to the

EXPERIMENTAL SECTION

The list of chemicals is available in the Supporting Information. Synthesis of Organic−Inorganic Hybrids. Hybrid phosphors were obtained from MnX2 and organic cation halide precursor solutions in ethanol, methanol, or dimethylformamide. In addition, some compounds were obtained in a reaction of MnCO3 with organic cation in aqueous hydrohalic acids. For example, for the preparation of Bmippip2MnCl4, BmippipCl (0.4 mmol, 0.0767 g) and MnCl2 (0.2 mmol, 0.0252 g) were dissolved in 1.5 mL of MeOH with stirring. The solution was filtered through a 0.2 μm PTFE filter. For single-crystal growth, the crude solution was then slowly concentrated at 50 °C or placed into an anisotropic evaporation chamber with dichloromethane. In a typical synthesis from a hydrohalic acid, N-benzyl-N,N,N-trimethyl chloride (1 mmol, 0.1875 g) and MnCO3 (0.5 mmol, 0.0575 g) were dissolved in aqueous HCl (6 mmol, 0.53 mL) at 70 °C. Single crystals were grown by slow evaporation of the filtered precursor solution at room temperature. Synthesis of Fully Inorganic Mn-Doped Hosts. Na2ZnBr4 and Li2ZnBr4 were prepared as follows. Dry ABr (A = Na or Li) and

Figure 1. Various compounds, studied in this work, featuring tetrahedral coordination of Mn(II). Mn ions are introduced either in the form of dopant (ZnX4, A2ZnX4, A3ZnX5) or as anion in organic−inorganic hybrids (Cat)3MnX4.

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ZnBr$_2$ mixed at a molar ratio of 2:1 was loaded in a Pyrex ampule and sealed under vacuum. The ampule was placed in a quartz tube and heated to the melting point (326 and 347 °C for Li$_2$ZnBr$_4$ and Na$_2$ZnBr$_4$, respectively) at a heating rate of 50 °C/h. Samples were kept at this temperature for 12 h and cooled to room temperature at a rate of 10 °C/h. Samples were kept 10−20 °C above the melting point for 1−2 h and then cooled to room temperature at a rate of 50 °C/h.

Characterization. Powder X-ray diffraction (XRD) patterns were collected in transmission (Debye−Scherer geometry) with a STADI P diffractometer (STOE Cie GmbH), equipped with a silicon strip MYTHEN 1K Detector (Fa. DECTRIS) with a curved Ge (111)-Monochromator (Cu $K\alpha$ = 1.54056 Å). For the measurement, a grounded powder was placed between the adhesive tape. Single-crystal XRD measurements were conducted on Oxford Xcalibur S diffractometer equipped with a Saphire 3 CCD detector and a molybdenum (Mo $K\alpha$ = 0.71073 Å) sealed tube as an X-ray source. The data were processed with Oxford Diffraction CrystAlis Pro software; structure solution and refinement were performed with SHELXL and SHELXL, respectively, imbedded in the Olex2 package.$^{11,14}$ The crystal structure of the synthesized compound was solved with direct methods, light elements (C, N) were located in the difference Fourier map, most of the positions of the cations were refined as rigid groups, and hydrogen atoms were placed at calculated positions.

Photoluminescence emission and excitation steady-state spectra were recorded with a FluoroMax-Plus-P (Horiba Jobin Yvon) equipped with a 150 W Xe lamp. Absolute quantum yields of the powders were measured using a Quantaurus-QY (Hamamatsu) spectrometer with an integrating sphere in a quartz Petri dish. The relative uncertainty of the PLQY measurement is ±3%.

Photoluminescence decay was measured with a FluoroMax-Plus-P equipped with a pulsed Xe lamp (3 μs). Decay curves were measured as a PL peak intensity over time. The temporal window size was 5 μs; each data point is accumulated over 100 lamp flashes.

Attenuation coefficient estimation was obtained from the transmission spectra of a single crystal through two parallel facets, recorded on a Jasco V500 spectrometer. The crystal was positioned into an opaque diaphragm with a hole of the crystal size. The diaphragms were used to calibrate baselines of the spectrometer according to the sample’s sizes. Reflection and scattering losses were taken into account by the measurement of specular and diffuse reflection spectra in the integrating sphere with an aluminum foil of the corresponding size as a reference. The spectral attenuation coefficient $\mu_l$ of a crystal with dimension $l$ was estimated from the optical density $\tau$ according to the equation

$$\mu_l = \tau/l, \text{[cm}^{-1}]$$

To analyze Mn−Br distances in the host lattice of ternary metal halides, density functional theory (DFT) was used as implemented in the Vienna Ab Initio Simulation Package (VASP) code. The projector augmented wave (PAW) potentials for atoms were used. For the generalized gradient approximation (GGA), the Perdew−Burke−Ernzerhof exchange-correlation functional (PBE) was used.$^{43−45}$ A 112-atom supercell (2 × 2 × 1) of each compound containing one Mn on Zn site was used for the calculations. Atomic positions were optimized while keeping the lattice parameters constant until the forces on atoms were smaller than 0.01 eV/Å. A gamma-centered automatic k-point mesh with 2 × 2 × 2 density was used.

### RESULTS AND DISCUSSION

**Organic−Inorganic Hybrids.** Organic−inorganic Mn(II) halides can be prepared from the corresponding aqueous hydrohalic acid solution of manganese halide and organic cation or from the solution of cation halide and manganese halide in polar organic solvents (methanol, ethanol, acetonitrile, N-methylformamide, N,N-dimethylformamide, dimethyl sulfoxide). To display the trends in emission properties, we have selected three manganese(II) halide complexes with benzyl-1-trimethylammonium (Bz(Me)$_3$N)$^+$ cation (Figure 2).

![Photographs of (Bz(Me)$_3$N)$_2$MnX$_4$ under visible light and UV excitation (365 nm).](image)

Figure 2. (a−c) PLE (empty) and PL (shaded, exc. 360 nm) of three hybrid compounds: (Bz(Me)$_3$N)$_2$MnX$_4$ (X = Cl, Br, I). (d) Emission decay curves for (Bz(Me)$_3$N)$_2$MnX$_4$ (X = Cl, Br, I). (e) PLQY dependence on the excitation wavelength for (Bz(Me)$_3$N)$_2$MnX$_4$ (X = Cl, Br, I). (f) Photographs of (Bz(Me)$_3$N)$_2$MnX$_4$ under visible light and UV excitation (365 nm).

 opacity stacking aids in crystallization. The cation bulkiness favors the crystallization of manganese in isolated MnX$_4$ units. (Bz(Me)$_3$N)$_2$MnBr$_4$ and (Bz(Me)$_3$N)$_2$MnI$_4$ are isostructural.
and feature one asymmetric unit of MnX₄, whereas (BzMe₃N)₂MnCl₄ comprises two inequivalent MnCl₄ units. The PL excitation (PLE) spectra of all three compounds contain bands that are corresponding to the transitions described above (Scheme 1). In the region between 300 and 500 nm there are two distinct groups of bands, corresponding to 6A₁ → 4G (360, 375, and 390 nm for Cl, Br, I, respectively) and 6A₁ → 4D (450, 460, and 475 nm) transitions. Emission spectra feature only one emission peak (Figure 2a−c). Generally, the emission and excitation wavelengths of Mn in such hybrids depend on the ligand field splitting: the energy splitting decreases from Cl to I, according to spectrochemical series. The adequate assignment of PLE lines is still rather unrealistic. To simplify the description of optical properties, we have adopted the difference between the strongest excitation peak around 450 nm (6A₁ → 4T₂) and the emission peak (4T₁ → 6A₁), E[4T₂] − E[4T₁] as a measure for the magnitude of the splitting. In this case, larger E[4T₂] − E[4T₁] values correspond to a stronger field. In addition, from lighter to heavier halide, spin−orbit coupling (SOC) gains importance. Figure 2d shows how SOC influences the decay time of the emission: τ is longest in chlorides (≈4 ms) and fastest in iodides (≈40 μs). In comparison, Mn²⁺ in a Td oxide environment exhibits radiative lifetimes above 5 ms. The PLQYS are highest when excited within the lowest energy PLE bands (around 450 nm) and decrease from chloride to iodide (Figure 2e). Spectral dependence of PLQY generally follows the PLE spectrum, as expected. However, optical absorption at PLE/PLQY minima is still significant (Figure 8), pointing to the background absorption by nonemissive impurity species such as degradation products (molecular halides, trihalide anions, etc.). Organic−inorganic manganese tetrahalide hybrids can be prepared with a wide variety of cations. Optical properties of the resulting complexes cover the spectral range between 505 and 547 nm. All of these complexes are bright with PLQYS from 30% to 90% (at 450 nm excitation).

### Table 1. Optical Properties (peak position, FWHM, PLQY) of the Organic−Inorganic Manganese(II) Tetrahalide Hybrids

| cation   | halide | peak position, nm | fwhm, nm | fwhm, meV | PLQY, % | E[4T₂] − E[4T₁], meV |
|----------|--------|-------------------|----------|-----------|---------|-----------------------|
| Et₄N     | Cl     | 518               | 53.1     | 246       | 75      | 36                    |
| n-Pr₄N  | Cl     | 512               | 49.8     | 236       | 81      | 35                    |
| Br(ε-Bu)₃N | Cl     | 522               | 57.5     | 262       | 60      | 39                    |
| Ph(Me)₃N | Cl     | 522               | 55.1     | 251       | 89      | 36                    |
| Ph₃P     | Cl     | 517               | 55.8     | 260       | N/A     | 39                    |
| Et(PH)₃P | Cl     | 520               | 55.8     | 257       | 66      | 38                    |
| Br(Me)₂N | Cl     | 547               | 71.8     | 299       | 78      | 51                    |
| (PPh₃)₂N | Cl     | 544               | 62.4     | 262       | N/A     | 51                    |
| Et₄N     | Br     | 516               | 49.1     | 229       | 86      | 34                    |
| n-Pr₄N  | Br     | 511               | 47.8     | 227       | N/A     | 33                    |
| Br(ε-Bu)₃N | Br     | 520               | 53.5     | 246       | 68      | 36                    |
| Ph(Me)₃N | Br     | 520               | 49.2     | 226       | 76      | 35                    |
| Ph₃P     | Br     | 516               | 48.3     | 225       | N/A     | 34                    |
| Me(PH)₃P | Br     | 507               | 40.5     | 196       | 74      | 30                    |
| Et(PH)₃P | Br     | 510               | 43.6     | 208       | 45      | 32                    |
| Br(Me)₂N | Br     | 516               | 48.7     | 227       | 63      | 34                    |
| K[crypt-222] | Br | 504               | 39.4     | 193       | N/A     | 31                    |
| Et₄N     | I      | 535               | 52       | 226       | 62      | 32                    |
| n-Pr₄N  | I      | 531               | 54       | 238       | N/A     | 31                    |
| Ph(Me)₃N | I      | 540               | 55.3     | 236       | N/A     | 31                    |
| Br(Me)₂N | I      | 537               | 49.8     | 215       | 33      | 30                    |

The strength of the crystal field is reflected in the difference between optical bands E[4T₂] and E[6A₁]. *b* PLQY measured with 450 nm excitation.

Fully Inorganic Alkali Zinc Halides Doped with Manganese. We have prepared and analyzed Mn-doped zinc halides and several alkali metal zinc halides (Figure 3). They were synthesized by melting the mixtures of the respective metal halides. With ZnBr₂ as a host, high MnBr₂ loadings of up to 15 wt % can be achieved without any evidence of multiple phases in powder X-ray diffraction (PXRD, Figure S1). In a CsBr−ZnBr₂ system, all compounds melt congruently, which results in the formation of a pure Cs₂ZnBr₄ phase (Figure S2a,b). In the case of K₂ZnBr₄ and Rb₂ZnBr₄, impurity peaks at small 2θ might remain unassigned and are attributed to a rather technical purity of the precursors (Figure S2c,d). In Li₂ZnBr₄ and Na₂ZnBr₄ we have observed identical groups of peaks that belong to unreacted ZnBr₂ and ABr (Figure S2e,f) due to incongruent melting of these ternary phases. Both Cs₂ZnI₄ and Cs₃ZnI₅ form as pure phases.
In the case of K2ZnI4 and Rb2ZnI4, unknown impurity phases can be seen (Figure S3c,d). Among olivine structures, only Li2ZnI4 was obtained as a pure phase (Figure S3e) and the formation of Na2ZnI4 has not been observed; the reaction mixture contained unreacted NaI and ZnI2 (Figure S3f). All of the doped phosphors exhibit bright characteristic Mn emission at room temperature, and the deeper color of the doped samples reflects the increase in Mn concentration (Figure 4a−c).

Mn-containing ZnBr2 and ZnI2 exhibit a bright green emission that peaked at 515 and 545 nm, respectively; with a very similar line broadening (196 and 199 meV). Ternary halides as hosts allow for tuning the luminescence over a wider region. A2ZnBr4 crystallize in three distinct crystal structures, stable at room temperature, all with Td symmetry around Zn. Na2ZnBr4 and Li2ZnBr4 crystallize in olivine-Mg2SiO4 orthorhombic structure type, whereas Cs2ZnBr4 and Rb2ZnBr4 are isostructural to the Cs2CuCl4 orthorhombic structure type. K2ZnBr4 is found in a lower symmetry monoclinic polymorph. In addition, for Cs, another ternary phase exists with Cs3ZnBr5 stoichiometry, which consists of alternating CsZnBr and CsBr layers (Figure 1). In ternary iodides, Li2ZnI4 and Na2ZnI4 crystallize in olivine structure, whereas both K and Rb homologues exist in monoclinic structure. Only Cs2ZnI4 has the same structure as its bromide counterpart.

Figure 4d and 4e summarizes the optical properties of the binary and ternary hosts doped with 2 wt % of Mn. Compounds with olivine structure (Li2ZnBr4, Na2ZnBr4, K2ZnI4) systematically show the emission peak shifted toward higher energies: 506−514 nm for bromides and 530 nm for iodide. For comparison, K, Rb, and Cs counterparts emit above 520 nm (bromides) and above 540 nm (iodides). Higher peak energies correspond to a stronger ligand field, which is corroborated by sharper PLE peaks. The narrowest fwhm is observed for olivine-type hosts (177 meV for Na2ZnBr4, Figure 4b). For monoclinic structures (K2ZnBr4, K2ZnI4, and Rb2ZnI4), the fwhm is is higher (195−210 meV). Cs2CuCl4-type Rb2ZnBr4, Cs2ZnBr4, and Cs2ZnI4 exhibit the emission with the highest fwhm ranging between 210 and 240 meV. Among all cesium-based compounds, the phase with excess cesium halide (Cs2ZnX4) shows narrower emission at a lower wavelength. To test the PLQY dependence on Mn concentration, we have chosen the compounds in the CsBr−ZnBr2 system. From 0.3 to 2 wt % of Mn, the PLQY increased almost seven times. We have also estimated the equilibrium Mn−halide distances in the host lattice (for the case of A2ZnBr4) using DFT calculations. The calculated distances are summarized in Table 2. Generally, metal−ligand distances are larger in olivine-type structures and shorter in orthorhombic structures.

Table 2. Equilibrium Mn−Br distances (Angstroms) Calculated by DFT in Five A2ZnBr4 Hosts

| compound   | d1    | d2    | d3    | d4    | d_{average} |
|------------|-------|-------|-------|-------|-------------|
| Li2ZnBr4   | 2.378 | 2.386 | 2.380 | 2.378 | 2.380       |
| Na2ZnBr4   | 2.383 | 2.381 | 2.383 | 2.384 | 2.383       |
| K2ZnBr4    | 2.363 | 2.363 | 2.380 | 2.382 | 2.372       |
| Rb2ZnBr4   | 2.373 | 2.377 | 2.355 | 2.355 | 2.365       |
| Cs2ZnBr4   | 2.354 | 2.386 | 2.354 | 2.374 | 2.367       |

Limitations and Prospects of Mn Green Emission: Decay Rates, PL Peak Position, fwhm, and Absorption Coefficient. Assessment of the practical utility of a novel phosphor for applications such as LCD displays and lighting requires knowledge of the following optical parameters: emission decay rate, PL peak position, fwhm, absorption coefficient, and PLQY. As can be noticed from Figure 2a−c, the widths of the excitation and emission bands are notably different: characteristic Mn2+ PLE bands (fwhm = 10−30 nm)
are narrower than the PL band (fwhm = 40–60 nm). This is often attributed to the difference in the chemical bonding in the ground and excited states. The observable variability in these parameters can be rationalized by considering energy level splittings of the Mn$^{2+}$ in a tetrahedral halide crystal field, in particular, by focusing on the strength of the crystal field ($\Delta$) and covalency ($B$) of the Mn–ligand bond as two primary factors. To illustrate the splitting of the energy states as a function of $\Delta$, a Tanabe–Sugano (TS) correlation diagram is used (Figure 5). The field strength increases from left to right.

![Figure 5. Phenomenological model of the Tanabe–Sugano diagram for a d$^3$ (Mn$^{2+}$) ion. Colored areas show relative locations of tetrahedral and octahedral Mn$^{2+}$ fields.]

On the basis of this general theory of d-ions emission, the strength of the crystal field defines the position of the Mn$^{2+}$ emission peak: in the weaker field, the $^4T_2$ and $^4A_2$ levels are separated stronger and hence emission occurs at higher energies (506–520 nm). As the crystal field increases, the emission peak shifts to lower energies (525–545 nm). The d-energy levels are also influenced by the electron–phonon coupling. A general intuition from the TS diagram would be that higher slopes shall correspond to greater sensitivity to the crystal–phonon coupling and hence higher homogeneous broadening of the transition. This argument fully explains the trends in organic–inorganic chlorides and bromides (Figure 6a). However, in the case of iodide, being the weakest ligand in the halide series, crystal field strength arguments fail to predict correctly the optical properties. Although the experimental splitting between the states still follows the TS diagram (the smallest values of $E[4T_2] - E[4A_2]$ for iodides: 30–32 meV), the PL peak position shifts to the red and the fwhm is broader (Figure 6a). This can be explained by the Mn–I bond having a more covalent nature and iodine having a higher nephelauxetic effect. “Covalent” in this context refers to the degree of mixing between the d orbitals of Mn and orbitals of the ligands. As a result, all energy states in tetraiodomanganates, including those that do not depend on the crystal field splitting, e.g., $^4A_2$, $^4E(G)$, $^4E(D)$, shift toward lower energies ($B' < B$). This effect is responsible for tetrahedral Mn$^{2+}$ orange emission (ca. 575–580 nm) in ZnS host.50 In general, the ordering of the ligands in the spectrochemical series and nephelauxetic series is opposite: free ion $< I^- < Br^- < Cl^- < S^{2-}$ $< F^- < O^{2-}$ vs free ion $< F^- < O^{2-} < Cl^- < Br^- < I^- < S^{2-}$.51 For the case of weak tetrahedral fields, Coulomb repulsion of d electrons has a higher contribution and the nephelauxetic effect is, therefore, more pronounced. In other words, a more ionic Mn–ligand bonding renders the states involved in the optical transitions more localized on Mn ions and thus less sensitive to the electron–phonon coupling. This can explain an observation of the narrowest spectral width for Mn$^{2+}$ $T_d$ emission (fwhm = 17.5 nm) in the strongest crystal field of oxides.52,53

Theoretically, a tetrahedral fluoride environment could result in an even narrower emission line width. However, finding a proper matrix poses a problem: due to the smallest ionic radii of F$^−$ among halides (1.33 vs 1.81 Å for Cl), structures with tetrahedral coordination are scarce. For example, ZnF$_2$ has a rutile structure that features $O_6$ coordination of Zn. The covalency argument also explains why Mn$^{2+}$ in $T_d$ oxide or Mn$^{4+}$ in $O_6$ fluoride field display longer decay times (few milliseconds):54 higher mixing of states in a more covalent case helps to relax the forbidden nature of the transition.

The nephelauxetic effect is also present in the compounds with the same halide composition (e.g., A$_2$ZnBr$_4$). It has been previously demonstrated from ab initio calculations for a d$^3$-metal impurity in A$_2$NaBX$_4$ hosts (A = K, Cs, B = Sc, Y) that the $B$ parameter and $\Delta$ depend on the metal–ligand distance, which in turn reflects the covalency of the bond.55 For A$_2$ZnBr$_4$:Mn compounds, the fwhm and PL peak positions appear to correlate with the average equilibrium Mn–Br distance (from Table 2, Figure 6b).

![Figure 6. (a) Dependence of the fwhm on the crystal field strength (represented by the difference between optical bands $E[^4T_2]$ and $E[^4A_2]$) in organic–inorganic hybrid Mn(II) chlorides, bromides, and iodides. (b) Dependence of the fwhm (shaded circles) and PL (open circles) on the equilibrium Mn–Br bond distance in fully inorganic A$_2$ZnBr$_4$ compounds.]

The PL peak position and energy states splitting relate also to the distance between manganese atoms.51,23 This can be exemplified by comparing the Mn–Mn distance distribution in two compounds: Bmpip$_2$MnCl$_4$ and (Bz(Me)$_2$N)$_2$MnCl$_4$ (Figure 7a). In (Bz(Me)$_2$N)$_2$MnCl$_4$, the smallest Mn–Mn distance is 8.5 Å, whereas for Bmpip$_2$MnCl$_4$ it is 9.1 Å (Tables S3 and S4, CCDC 1936177 and CCDC 1936170). The
emission of Bmpip$_2$MnCl$_4$ is centered around 513 nm, and the $E[{}^4T_2] - E[{}^4T_1]$ splitting is 38 meV. In comparison, a much larger splitting of 51.3 meV in the case of (Bz(Me)$_3$N)$_2$MnCl$_4$ could originate from the smaller Mn–Mn interatomic distance (Figure 7b).

In addition, the larger fwhm of the 547 nm peak can be attributed to two symmetrically inequivalent MnCl$_4$ units present in the structure.

One of the concerns related to the forbidden nature of the transition is the slower emission decay as compared to, for instance, semiconductor quantum dot phosphors. We have found that tetrabromomanganates(II), a bromoalkyl derivative of manganese(II) (green), and their bromoalkyl derivatives (blue). (d) Chemical formulas of the cations used for comparison.

Figure 7. (a) Mn–Mn distance distribution in two tetrachloride compounds, Bz(Me)$_3$N$_2$MnCl$_4$ and Bmpip$_2$MnCl$_4$, calculated from crystal structure files measured with single-crystal X-ray diffraction (CCDC 1936177 and CCDC 1936170). (b) PL spectra (exc. 360 nm) of Bz(Me)$_3$N$_2$MnCl$_4$ and Bmpip$_2$MnCl$_4$. (c) Emission decay for tetraalkylphosphonium, tetraalkylammonium tetrabromomanganates-(II) (green), and their bromoalkyl derivatives (blue). (d) Chemical formulas of the cations used for comparison.

Another limitation that comes from the forbidden nature of the optical transitions is a relatively low absorption coefficient. To estimate the absorption, we have chosen two organic–inorganic hybrid compounds, for which crystals of sufficient quality and size (4–7 mm) could be isolated: (Bz-(Me)$_3$N)$_2$MnBr$_4$ and (Bz(Me)$_3$N)$_2$MnI$_4$. Light absorption was deduced from the transmission spectra by subtracting the reflectivity. By dividing the spectral optical depth $τ_j$ (at 450 nm for bromide and 475 nm for iodide) by the dimension of the crystal, we obtained the directional attenuation coefficient $μ_τ$ (Figure 8a and 8b): 0.5 cm$^{-1}$ for bromide and 55 cm$^{-1}$ (128 cm$^{-1}$·M$^{-1}$) for iodide. A higher absorption coefficient correlates well with the faster emission in iodides. However, these values are still very low when compared to the organic dyes (e.g., fluorescein, $λ_{400} = 92 230$ cm$^{-1}$·M$^{-1}$) or direct band-gap semiconductors (e.g., InP, $λ_{400} = 30 861$ cm$^{-1}$).

**CONCLUSIONS**

We prepared and summarized the properties of various halides with tetrahedral coordination of Mn(II): organic–inorganic manganese(II) tetrhalide hybrids and Mn(II)-doped fully inorganic ternary halides. Thus far, research efforts around Mn-based green emitters for display and lighting applications have focused on oxide matrixes. A concerted effort is urgently needed for unveiling the potential Mn(II) in solid-state halides. The tetrahedral halide ligand environment, in particular, iodide and bromide, brings about its advantages over oxides: faster emission decay of 0.05–0.5 ms (vs 4–7 ms in oxides or oxynitrides), larger PLQY of up to 90%, and facile low-temperature synthesis (vs 1000–1500 °C for oxides). Emission and excitation spectra can be fine tuned by the crystal field splitting parameters. The latter are adjustable by both the halide composition as well as the distance between manganese atoms. The emission decay is accelerated by four times in organic–inorganic hybrids with the additional halide atom in the second coordination sphere of Mn. We propose that the two effects, namely, crystal field strength and nephelauxetic effect, compete in the Cl, Br, and I series and have opposite trends: the PL broadening and red shift in the case of Cl originates from strong crystal field splitting, whereas the same effect in I is attributed to the higher covalency of the Mn–I bond. The entirety of the experimental results on the structure–property relationship allows drawing the following...
conclusions as to how engineerable the PL characteristics can be. In particular, weaker fields and less covalent Mn–ligand bonds cause emission that is narrower yet slower (5–10 ms) and less efficient. The major practical hurdle for this class of phosphors concerns low absorption in the blue region due to the forbidden nature of the transition (Laporte rule). Overcoming this limitation requires new materials design strategies, which may include sensitization or enhancement of the SOC effect.

**ASSOCIATED CONTENT**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.9b03782.

Crystallographic data for [(Bz(Me)3N)2MnCl4 (CCDC 1936177)] (CIF)

Crystallographic data for [(Bz(Me)3N)2MnI4 (CCDC 1936176)] (CIF)

Crystallographic data for Bmpip2MnCl4 (CCDC 1936170) (CIF)

Crystallographic data for [(n-PrBrMe2N)2MnBr4 (CCDC 1936114)] (CIF)

Materials: Energy levels for Mn2+ in tetrahedral halide environment; photoluminescence quantum yield (Φ), total life-time τtot and radiative life-time τr calculated according to the formula τr = τtot/Φ for several organic–inorganic hybrid manganese halides; XRD patterns of ZnBr2 with different Mn mass loading (%) demonstrating that up to 15% of Mn(II) can be accommodated without additional phases appearing, and close-up of the (224) diffraction peak of ZnBr2 depicting a very small shift corresponding to the increase of the unit cell size due to Mn incorporation; measured and simulated XRD patterns for ternary alkaline zinc bromides with 2% Mn mass loading; crystal data and structure refinement for (Bz(Me)3N)2MnCl4; crystal data and structure refinement for Bmpip-MnCl4; crystal data and structure refinement for (n-PrBrMe2N)2MnBr4; crystal data and structure refinement for (Bz(Me)3N)2MnI4 melting points of fully inorganic tertiary zinc halides (PDF)

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Notes

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