

Article



Ligand Engineering Triggered Efficiency Tunable Emission in Zero-Dimensional Manganese Hybrids for White Light-Emitting Diodes

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Abstract: Zero-dimensional (0D) hybrid manganese halides have emerged as promising platforms for the white light-emitting diodes (w-LEDs) owing to their excellent optical properties. Necessary for researching on the structure-activity relationship of photoluminescence (PL), the novel manganese bromides $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$ are reported by screening two ligands with similar atomic arrangements but various steric configurations. It is found that $(C_{13}H_{14}N)_2MnBr_4$ with planar configuration tends to promote a stronger electron-phonon coupling, crystal filed effect and concentration-quenching effect than $(C_{13}H_{26}N)_2MnBr_4$ with chair configuration, resulting in the broadband emission (FWHM = 63 nm) to peak at 539 nm with a large Stokes shift (70 nm) and a relatively low photoluminescence quantum yield (PLQY) (46.23%), which makes for the potential application (LED-1, Ra = 82.1) in solid-state lighting. In contrast, $(C_{13}H_{26}N)_2MnBr_4$ exhibits a narrowband emission (FWHM = 44 nm) which peaked at 515 nm with a small Stokes shift (47 nm) and a high PLQY of 64.60%, and the as-fabricated white LED-2 reaches a wide colour gamut of 107.8% National Television Standards Committee (NTSC), thus highlighting the immeasurable application prospects in solid-state display. This work clarifies the significance of the spatial configuration of organic cations in hybrids perovskites and enriches the design ideas for function-oriented lowdimensional emitters.

Keywords: zero-dimensional manganese bromides; steric configurations; tunable emission; white light-emitting diodes

1. Introduction

Low-dimensional organic-inorganic hybrid metal halides (OHMHs) have been widely recognized for their outstanding optical properties, including high-efficiency tunable emissions, near-unity photoluminescence quantum yields (PLQYs), and long decay lifetimes, etc., which are attributed to the strong quantum confinement at the molecular levels and the most convenient radiative recombination of photo-generated excitons [1–4]. However, the absorption peaks of most OHMHs are located in the ultraviolet (UV) region, which limits the luminous efficiency of white light-emitting diodes (*w*-LEDs) because they cannot be excited by commercial blue chips, thus hindering their industrialization in the fields of solid-state lighting and display. Remarkably, the zero-dimensional (0D) hybrid manganese halides become the preference for blue-light-excited luminescent materials since their photoluminescence excitation (PLE) bands lie in the near-ultraviolet and blue regions, while



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). exhibiting bright photoluminescence (PL) [5,6], and they possess abundant coordination modes and tunable emissions [7–11]. Whether the octahedral coordinated Mn^{2+} ions show intense broadband orange-red emission from the $[Mn_3X_{12}]^{6-}$ inorganic units [12–15], or the tetrahedral coordinated Mn^{2+} ions exhibit narrowband green emission from the $[MnX_4]^{2-}$ inorganic units, both of which are attributed to the d-d transition of Mn^{2+} and present application potential in the field of *w*-LEDs [16–19].

The inorganic units are embedded in organic matrix for OHMHs and are connected to the cations through various molecular interactions, prompting that their structure and PL behaviours can be tuned by engineering the organic cations [7,20]. Different organic cations induce the deformation of inorganic units in varying degrees, resulting in varying crystal field effects, nephelauxetic effects and concentration-quenching effects [21]. Numerous research has exposed that the effect of organic cations on the luminescence properties in 0D hybrid manganese halides. Seshadri et al., and Xia et al., investigated the relationship between structure and PL properties in hybrid manganese halides, and proposed that bulky, rigid, single-protonated cations are in favour of large Mn–Mn distance, thereby leading to high PLQYs [17,22]. Xiao et al., reported and highlighted the effect of organic components with different degrees of conjugation on the optical properties from the view of the band alignment types involving ground state and excited state [7]. Kovalenko et al., found that the PL decay can be accelerated by introducing heavy atoms (e.g., iodine, bromine) in the second coordination sphere of Mn²⁺ [6]. However, these reports ignored the role of spatial configuration of organic components on the fine-tuning PL behaviours and the correspondence between organic components and optical properties of 0D hybrid manganese halides has not been completely established.

Herein, we screen two ligands with similar atomic arrangements but different spatial configurations to synthesize 0D manganese bromides $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$ via a simple solution-phase crystallization method. They are crystallized in different space groups and composed of [MnBr₄]²⁻ twisted tetrahedron and organic matrix with planar and chair configuration, respectively. Experimental and theoretical researches indicate that the organic cation with planar configuration tend to induce stronger electron-phonon coupling, crystal filed effect and concentration-quenching effect than chair configuration in these 0D manganese bromides, thereby finely tuning PL behaviours, including emission bandwidth, peak position, Stokes shift, lifetimes and PLQYs, as well as the luminescence mechanism was discussed by combining the Tunabe-Sugano (T-S) energy diagram. The w-LEDs devices were fabricated using the above manganese bromides as green components; it is concluded that LED-1 based on $(C_{13}H_{14}N)_2$ MnBr₄ with a high R_a of 82.1 is suitable for solid-state lighting, while LED-2 based on (C13H26N)2MnBr4 with a wide colour gamut of 107.8% NTSC holds unprecedented promising for use in solid-state displays. Our work demonstrates that the organic cations with different spatial configurations are able to trigger tunable emission in 0D Manganese hybrids, and the design principle provides a new idea for future research on white light-emitting materials.

2. Experimental

2.1. Materials and Preparation

N-Methyldiphenylamine ($C_{13}H_{13}N$, 98%, Aladdin, Shanghai, China), *N*,*N*-Dicyclohexylmethylamine ($C_{13}H_{25}N$, 98%, Aladdin, Shanghai, China), manganese bromide tetrahydrate (MnBr₂·4H₂O, 98%, Aladdin, Shanghai, China), hydrobromic acid (HBr, 40%, Aladdin, Shanghai, China) and ethanol (C_2H_5OH , 99.7%, Guangfu, Tianjin, China). MnBr₂·4H₂O needs to be heated at 120 °C for 6 h to remove the crystal water for later use.

The single-crystals of $(C_{13}H_{14}N)_2$ MnBr₄ and $(C_{13}H_{26}N)_2$ MnBr₄ were synthesized by a simple solution-phase crystallization method. First, $C_{13}H_{13}N$ (0.3665 g, 2 mmol) or $C_{13}H_{25}N$ (0.3907 g, 2 mmol) was dissolved in 1.5 mL HBr for protonation. Then MnBr₂ (0.2148 g, 1 mmol) and 5 mL C_2H_5 OH were added to the above protonated solution, and heated and stirred at 75 °C until forming a clear solution. After the solution was naturally cooled to room temperature, yellow ($C_{13}H_{14}N)_2$ MnBr₄ and green ($C_{13}H_{26}N)_2$ MnBr₄ bulky crystals were precipitated overnight. Finally, the crystals were washed several times with acetone and dried in a vacuum oven.

2.2. Characterization

Single-crystal X-ray diffraction (SCXRD) data of (C13H14N)2MnBr4 and (C13H26N)2MnBr4 were collected by using an Agilent Technologies Gemini EOS (Palo Alto, CA, USA) diffractometer at 298 K using Mo K α radiation (λ = 0.71073 Å). Powder X-ray diffraction (PXRD) data of (C13H14N)2MnBr4 and (C13H26N)2MnBr4 for Rietveld analysis was collected at room temperature with a Bruker D8 ADVANCE powder diffractometer EOS (Karlsruhe, Germany) (Cu-K α radiation) and linear VANTEC detector. The step size of 2 θ was 0.011°, and the counting time was 2 s per step. Rietveld structure refinements were performed by using TOPAS 4.2. PL, PLE spectra, PL decay curves and PLQYs were measured by an Edinburgh FLS920 fluorescence spectrometer EOS (Edinburgh, UK) with a picosecond pulsed diode laser. Temperature-dependent emission spectra were measured on the same spectrophotometer installed with a heating apparatus as the heating source. Morphology observation and elemental mappings were conducted by a scanning electron microscope (SEM, JEOL JSM-6510, EOS, Peabody, MA, USA). UV-vis absorption curves were recorded on a TU-1901 Ultraviolet spectrometer EOS (Beijing, China) at room temperature, in which BaSO₄ was used as the standard reference. CIE chromaticity coordinates were calculated using the CIE calculator software based on the emission spectra excited at 450 nm. The emission spectra, correlated colour temperature (CCT), luminous efficacy, and CIE coordinates of w-LEDs were performed on the integrating sphere spectroradiometer system (ATA-100, Everfine, EOS, Hangzhou, Cina).

2.3. Computational Methods

The electronic band structure and density of state (DOS) were calculated by CASTEP based on plane-wave pseudopotential density functional theory (DFT) [23]. Perdew-Burke-Ernzerhof (PBE) functionals in the form of general gradient approximation (GGA) were used for electronic structure calculations [24]. A kinetic energy cut off value of 450 eV and a Monkhorst-pack k-point mesh spanning less than 0.03 Å⁻¹ in the Brillouin zone were chosen.

3. Results and Discussion

As shown in Figure 1a,d, two ligands with similar atomic arrangements but different spatial configurations were screened out to synthesize hybrid manganese bromides $(C_{13}H_{14}N)_2$ MnBr₄ and $(C_{13}H_{26}N)_2$ MnBr₄ with MnBr₂ via a simple solution-phase crystallization method. The crystal structures resolved by SCXRD technique show that both $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$ correspond to typical 0D "host-guest" structures. That is, central metal Mn²⁺ ions are coordinated with four Br⁻ anions to form twisted tetrahedral $[MnBr_4]^{2-}$ inorganic units and all inorganic components are periodically dispersive embedded in insulating organic cations (Figure 1c,f). Different organic cations induce the distinct packing and deformation of anions. Therefore, (C₁₃H₁₄N)₂MnBr₄ and (C₁₃H₂₆N)₂MnBr₄ are crystallized in triclinic space group P1 and monoclinic space group $P2_1/c$, respectively. As shown in Figure 1b,e, two different $[MnBr_4]^{2-}$ inorganic units exhibit different distortion degree. The distances of four Mn-Br bonds are in the range of 2.4829(13)–2.5201(13) Å and the Br–Mn–Br bond angles ranged from 103.19(5) to 117.83(6)° for $(C_{13}H_{14}N)_2MnBr_4$. However, this structural information is in the range of 2.4704(9)–2.5226(9) Å and 107.07(3) to 114.21(4) $^{\circ}$ for (C₁₃H₂₆N)₂MnBr₄. The crystallographic information files (CIFs) are shown in the Supporting Information (SI), and the main bond lengths and bond angles are shown in Table S1 and Table S2, respectively. The bond length distortion (Δd) and bond angle variance (σ^2) of individual [MnBr₄]²⁻ are calculated by the following formulas [25,26]:

$$\Delta d = 1/4 \sum_{i=1}^{4} ((d_i - d_0)/d_0)^2$$

where d_0 represents the average Mn–Br bond length and d_i are four individual lengths of Mn–Br bond.

$$\sigma^2 = 1/5 \sum_{i=1}^{6} (\theta_i - 109.47)^2$$

where θ_i refer to the individual Br–Mn–Br angles. The Δd values of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$ are 1.78×10^{-4} and 2.39×10^{-4} , respectively. The σ^2 values are 24.64 and 6.08. It is worth noting that the difference in bond length distortion is small and can be ignored, since the large distinction in the bond angle variance maybe the underlying reason for the disparate optical properties of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$.



Figure 1. (**a**,**d**) The chemical structures of organic cations $[C_{13}H_{14}N]^+$ and $[C_{13}H_{26}N]^+$. (**b**,**e**) Ball and stick models of inorganic units and structural information including bond length, bond angles and twist degrees. (**c**,**f**) Crystal structures of $(C_{13}H_{14}N)_2$ MnBr₄ and $(C_{13}H_{26}N)_2$ MnBr₄.

The phase purity and crystallinity of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$ powders were monitored by PXRD, and the results are shown in Figure S1. All peaks were indexed by triclinic cell (*P*1) and monoclinic cell (*P*2₁/*c*) with parameters close to those obtained from a single crystal experiment, respectively. Therefore, these structures were considered as a starting model for Rietveld refinement, as shown in Figure 2a,b, which were performed using TOPAS 4.2. The refinement results were stable and gave low R-factors. The main parameters of processing and refinement of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$ were listed in Table S3. The elemental mapping images (Figure 2c,d) indicate that the elements N, Br and Mn are evenly distributed on the above manganese bromides.

As shown in Figure S2b,c, the manganese bromides of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$ with yellow-green body colour exhibit bright yellow-green fluorescence under a 365 nm UV lamp, and the corresponding CIE coordinates are depicted in Figure S2a. To further reveal their PL properties, the PLE and PL spectra of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$ are initially investigated in Figure 3a,b. Both manganese bromides exhibit similar excitation bands attributed to the d–d transition of tetrahedrally coordinated Mn^{2+} centres and can be excited by blue light, but they possess distinct emission spectra. $(C_{13}H_{14}N)_2MnBr_4$ displays a broadband emission peaked at 539 nm with a full width at half maximum (FWHM) of 63 nm and the Stokes shift of 70 nm, which is wider than most 0D hybrid manganese halides [19,27,28]. In contrast, the emission peak of $(C_{13}H_{26}N)_2MnBr_4$ appears at 515 nm, with a FWHM of 44 nm and the Stokes shift of 47 nm. Meanwhile, we synthesized the powder chlorides of $(C_{13}H_{14}N)_2MnCl_4$ and $(C_{13}H_{26}N)_2MnCl_4$ using the above two ligands and they exhibit the same effect and difference on their PL properties as

 $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$ (Figure S3). We consider that the essence for the PL difference may be caused by the different spatial configuration of organic components in above manganese bromides. The ligand $C_{13}H_{13}N$ contains two planar benzene rings with little steric hindrance. However, the twelve carbon atoms are not in the same plane for $C_{13}H_{25}N$, so that there is a larger steric hindrance. Proceeding from $(C_{13}H_{14}N)_2MnBr_4$ to $(C_{13}H_{26}N)_2MnBr_4$, the increasing cation volume and the steric hindrance not only shrink the free space for the atom movement or the cation/anion rotation, but also inhibit the lattice distortion [29,30]. Therefore, $(C_{13}H_{14}N)_2MnBr_4$, resulting in a broadband emission with large Stokes shift.



Figure 2. Rietveld refinements of PXRD patterns for (**a**) $(C_{13}H_{14}N)_2MnBr_4$, (**b**) $(C_{13}H_{26}N)_2MnBr_4$. SEM images and EDS elemental mapping images showing the homogeneous distribution of N, Mn and Br in compounds for (**c**) $(C_{13}H_{14}N)_2MnBr_4$ and (**d**) $(C_{13}H_{26}N)_2MnBr_4$.



Figure 3. Normalized PLE and PL spectra of (**a**) $(C_{13}H_{14}N)_2MnBr_4$ and (**b**) $(C_{13}H_{26}N)_2MnBr_4$. (**c**) Temperature-dependent PL spectra of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$ under 450 nm excitation in the range from 80 to 300 K. (**d**) FWHM² fitting curves of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$ as a function of 1/(2kT). Time-resolved PL decay curves of (**e**) $(C_{13}H_{14}N)_2MnBr_4$ and (**f**) $(C_{13}H_{26}N)_2MnBr_4$ at 298 K and 80 K.

Figure 3c depicts the temperature-dependent PL spectra of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$ in the range of 80–300 K. The PL intensity decreases with the increasing temperature, which is consistent with the PL quenching behaviour caused by thermally activated non-radiative recombination. Meanwhile, the emission peak positions have a blue-shift. It is speculated that the reason for this phenomenon is that the thermally induced lattice expansion weakens the crystal field strength, or reduces the energy loss due to the spin-spin coupling between localized neighbouring Mn^{2+} ions [16]. Furthermore, the FWHM versus temperature (Figure 3d) can reveal the origin of the PL differences in above manganese bromides. The Huang-Rhys factor *S* defines the degree of electron–phonon coupling; it can be solved by the following equation [18,31,32]:

$$FWHM = 2.36\hbar\omega\sqrt{S \cosh\left(\frac{\hbar\omega}{2kT}\right)}$$

where ω is the phonon frequency, $\hbar\omega$ is the maximum phonon energy, k is the Boltzmann constant, S is Huang-Rhys factor, and $coth(x) = \frac{e^x + e^{-x}}{e^x - e^{-x}} = 1 + \frac{2}{e^{2x} - 1}$. When $\frac{\hbar\omega}{kT}$ is small enough, $e^{\frac{\hbar\omega}{kT}} - 1 \approx \frac{\hbar\omega}{kT}$, it can be obtained the following equation:

$$FWHM^{2} = 5.57(\hbar\omega)^{2}S\left(1 + \frac{2}{e^{\frac{\hbar\omega}{kT}} - 1}\right) = 5.57(\hbar\omega)^{2}S\left(1 + \frac{1}{\frac{\hbar\omega}{2kT}}\right)$$

Further written as:

$$FWHM^2 = a + \frac{b}{\frac{1}{2kT}}$$

where $a = 5.57 \times S \times (\hbar\omega)^2$ and $b = 5.57 \times S \times (\hbar\omega)$.

The obtained *S* factor is 2.89 and phonon energy $\hbar\omega$ phonon is 44.26 meV for $(C_{13}H_{14}N)_2MnBr_4$, while for $(C_{13}H_{26}N)_2MnBr_4$, it corresponds to S = 0.77, $\hbar\omega = 75.85$ meV. The higher *S* factor indicates that there is a stronger electron-phonon coupling in $(C_{13}H_{14}N)_2MnBr_4$, which is favourable for the formation of broadband emission with large Stokes shift.

In addition, the crystal field strength plays a key role in affecting the PL properties of manganese bromides. Previous references reported that the crystal field strength is related to the polyhedral distortion, and the increasing distortion leads to strong crystal field splitting and low position of the lowest 3d excited energy levels, resulting in the red-shift of the emission band [33–36]. The σ^2 values of (C₁₃H₁₄N)₂MnBr₄ and (C₁₃H₂₆N)₂MnBr₄ are 24.64 and 6.08, respectively, as calculated above, indicating that the larger bond angle distortion contributes to a red-shift of the emission peak from 515 nm to 539 nm.

To verify the electronic transition process, we measured the lifetimes excited at 450 nm and monitored at 539 nm and 515 nm, respectively. As shown in Figure 3e,f, the PL decay curves can be fitted with a single order exponential equation:

$$I(t) = I_0 + A \exp\left(-t/\tau\right)$$

where I(t) and I_0 are the luminescence intensity at time t and $t \gg \tau$, respectively. A is a constant, and τ is the decay time for an exponential component. At 298 K, the lifetimes are on millisecond scale, and the values are determined to be 0.245 ms and 0.370 ms, respectively, which are close to the previously reported lifetimes of hybrid manganese bromides, demonstrating that these emissions belong to the d–d transition $({}^{4}T_{1}-{}^{6}A_{1})$ of Mn^{2+} [17,37,38]. At 80 K, the lifetimes are prolonged, but the variation tendency of $(C_{13}H_{14}N)_2MnBr_4$ is greater than that of $(C_{13}H_{26}N)_2MnBr_4$, which may be because that $(C_{13}H_{14}N)_2MnBr_4$ has more vibration options. In addition, PLQY is also affected by the spatial configuration of organic cations in these manganese bromides. Figure S4 shows that the $[C_{13}H_{14}N]^+$ cations containing benzene ring planar configuration generate a short average distance between the nearest $[MnBr_4]^{2-}$ is 8.5934 Å, while the chair configuration of $[C_{13}H_{26}N]^+$ cations with

greater steric hindrance produce a longer Mn–Mn average distance is 9.6703 Å. Accordingly, the concentration-quenching effect of $(C_{13}H_{26}N)_2$ MnBr₄ is weakened, resulting in PLQYs of 46.23% and 64.60% for $(C_{13}H_{14}N)_2$ MnBr₄ and $(C_{13}H_{26}N)_2$ MnBr₄, respectively.

To further reveal the photo-physical properties of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2$ MnBr₄ composed of organic moleties with different spatial configurations. The theoretical calculations involving electronic band structure and densities of states (DOS) are conducted based on the density functional theory. As shown in Figure 4a,b, the calculated band gap of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$ are 2.54 eV and 2.80 eV, respectively, which are coincide with the observed optical absorption spectra (Figure S5). It is worth noting that the (C13H14N)2MnBr4 has a lower conduction band level compared to (C13H26N)2MnBr4, resulting from the higher degree of conjugation of organic component, which is also responsible for the red-shift of the emission peak of $(C_{13}H_{14}N)_2MnBr_4$. Both the frontier orbitals are flat and dispersion-less, indicating that the photoelectrons are localized for above manganese bromides. This is because that the isolated $[MnBr_4]^{2-}$ tetrahedrons separated by bulky organic cations have weak interactions, resulting in spatial confinement and electronic confinement effects. Figure 4c,d show the DOS projected onto the constituent elements in $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$. The valence band maximum (VBM) states and the conduction band minimum (CBM) states are mainly composed of Mn 3d and Br 3p orbitals, indicating that the electronic transition process related to luminescence occurs within the [MnBr₄]²⁻ inorganic units, and the VBM- and CBM-associated charge densities (Figure S6) also confirm this mechanism.

Figure 4. Electronic energy band structures of (**a**) $(C_{13}H_{14}N)_2MnBr_4$ and (**b**) $(C_{13}H_{26}N)_2MnBr_4$. The total and orbital projection of partial density of states of (**c**) $(C_{13}H_{14}N)_2MnBr_4$ and (**d**) $(C_{13}H_{26}N)_2MnBr_4$.

According to the electron transition process, we employ the T-S energy diagram to visualize the effect of spatial configuration of organic ligands on PL behaviours. It is well known that the Mn^{2+} ions possess the outermost electron configuration of $3d^5$, and the original five degenerate d orbitals of free Mn^{2+} are split into multiple energy levels under the electrostatic field effect generated by ligands. In the tetrahedral field, the ground

state is denoted as ⁶A₁, the excited states of ⁴F, ⁴P, ⁴D and ⁴G correspond to the excited energy levels in the UV (200-400 nm) and blue (400-500 nm) regions, respectively [6,7]. The electrons located at the ground state are transferred to different excited states under excitation, and then transferred to the lowest excited state energy level ${}^{4}T_{1}$ through nonradiative relaxation, and finally the electrons return to the ground state with the release of photons. In the T-S energy diagram, the strength of the crystal field is represented by the abscissa (Δ) and the energy difference between excited states ${}^{4}T_{2}$ and ${}^{4}T_{1}$. The stronger the crystal field strength, the more obvious the splitting of ${}^{4}T_{2}$ and ${}^{4}T_{1}$, making the larger values of E $[{}^{4}T_{2}]$ -E $[{}^{4}T_{1}]$. In view of this, the luminescent mechanism is depicted in Figure 5. $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$ are arranged in the region of strong crystal field and weak crystal field, respectively. $(C_{13}H_{14}N)_2MnBr_4$ occupies a wider range on the abscissa than $(C_{13}H_{26}N)_2MnBr_4$, due to the larger electron-phonon coupling coefficient for $(C_{13}H_{14}N)_2MnBr_4$, resulting in the crystal field strength varies greatly with lattice vibrations. Reflected on the vertical coordinates, it is shown that $(C_{13}H_{14}N)_2MnBr_4$ has a larger ΔE than $(C_{13}H_{26}N)_2$ MnBr₄, that is, $(C_{13}H_{14}N)_2$ MnBr₄ exhibits a broadband emission with a large Stokes shift.

Figure 5. Tanabe–Sugano energy-level diagram of Mn²⁺ ions in tetrahedral crystal field.

To further evaluate their practical applications, the *w*-LEDs (LED-1 and LED-2) were encapsulated by coating (C13H14N)2MnBr4/(C13H26N)2MnBr4 and KSF:Mn4+ red phosphors on a commercial InGaN blue chip (450 nm), respectively. As shown in Figure 6, LED-1 presents the standard white-light emission with a relatively high colour-rendering index (CIR) of Ra = 82.1, and a CIE chromaticity coordinate of (0.3211, 0.3206). LED-2 presents a cool white-light emission with a wide colour gamut of 107.8% NTSC in the CIE 1931 colour space, and a CIE chromaticity coordinate of (0.3037, 0.3297). It is concluded that $(C_{13}H_{14}N)_2MnBr_4$ is more suitable for solid-state lighting, while $(C_{13}H_{26}N)_2MnBr_4$ is unprecedentedly promising as a narrow-band green emitter for solid-state displays. The emission spectra of LED-1 and LED-2 under different drive current different current (20-120 mA) in Figure S7 suggests that the w-LEDs possess excellent colour stability. Of course, we also evaluated the thermal quenching behaviour of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$. As shown in Figure S8, the PL intensity decreases with increasing temperature. The PL intensity of (C₁₃H₁₄N)₂MnBr₄ and (C₁₃H₂₆N)₂MnBr₄ at 373 K remain around 79.86% and 84.84% of that at room temperature, respectively, suggesting that the above manganese bromides have relatively good thermal stability.

Figure 6. Emission spectrum of *w*-LEDs based on (**a**) $(C_{13}H_{14}N)_2MnBr_4$ and (**b**) $(C_{13}H_{26}N)_2MnBr_4$. The insets show the photographs of *w*-LEDs in the daylight (top) and working at 20 mA (bottom). (**c**) CIE 1931 colour coordinates of fabricated LED-1 (orange dotted line), LED-2 (red dotted line) and the NTSC standard (black dotted line).

4. Conclusions

In summary, the two new 0D manganese bromides were developed by using organic cations with different spatial configuration. $(C_{13}H_{14}N)_2MnBr_4$ exhibits a broadband emission peaked at 539 nm with a FWHM of 63 nm and a Stokes shift of 70 nm, while $(C_{13}H_{26}N)_2MnBr_4$ shows a narrowband emission peaked at 515 nm with a FWHM of 44 nm and a Stokes shift of 47 nm, which is ascribed to that the ligand of $C_{13}H_{13}N$ with planar configuration induces a stronger electron-phonon coupling (S = 2.89) and crystal field strength $(\sigma^2 = 24.64)$ than the ligand of $C_{13}H_{25}N$ with chair configuration. DFT calculations reveal that $(C_{13}H_{14}N)_2MnBr_4$ possesses a narrower bandgap compared to $(C_{13}H_{26}N)_2MnBr_4$, resulting in the red-shift of the emission peak of $(C_{13}H_{14}N)_2MnBr_4$. Moreover, the steric effect of organic cations on PL behaviours in manganese halides is comprehensively reflected in T-S energy diagram. The as-fabricated white LED-1 based on $(C_{13}H_{14}N)_2MnBr_4$ with a high CIR of Ra = 82.1 is suitable for solid-state lighting, while the as-fabricated white LED-2 based on $(C_{13}H_{26}N)_2MnBr_4$ with a wide colour gamut of 107.8% NTSC in the CIE 1931 colour space presents an unprecedentedly promising utility for solid-state display.

Supplementary Materials: The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/nano12183142/s1, Figure S1: PXRD patterns and standard diffraction pattern of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$; Figure S2: CIE chromaticity diagrams of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$; Figure S2: CIE chromaticity diagrams of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$; Figure S2: CIE chromaticity diagrams of $(C_{13}H_{14}N)_2MnBr_4$ and the photographs with UV off and on; Figure S3: Normalized PLE and PL spectra and time-resolved PL decay curves of $(C_{13}H_{14}N)_2MnCl_4$ and $(C_{13}H_{26}N)_2MnBr_4$; Figure S6: VBM- and CBM-associated charge densities of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$; Figure S7: PL spectra of the w-LED devices under different current (20-120 mA); Figure S8: Temperature-dependent PL spectra of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$; Tables S1 and S2: The bond length (Å) and the bond angles (°) of $(C_{13}H_{14}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$ and $(C_{13}H_{26}N)_2MnBr_4$.

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