Direct emission from quartet excited states triggered by upconversion phenomena in solid-phase synthesized fluorescent lead-free organic–inorganic hybrid compounds†

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We report, for the first time, the solid-phase gram-scale synthesis of two lead-free, zero-dimensional (0D) fluorescent organic–inorganic hybrid compounds, [Bu₄N]₂[MnBr₄] (1) and [Ph₄P]₂[MnBr₄] (2), achieved by grinding the organic and inorganic precursor salts. The solid-phase synthetic route has several advantages for modulating molecular dimensionalities. During grinding, organic cations and Mn²⁺ cations are co-crystallized together in the solid-state, forming a 0D assembly at the molecular level where each individual metal center is surrounded by organic cations. Both compounds exhibit an emission peak at 520 nm and a photoluminescence (PL) quantum yield (QY) of 47%. Here, we also report, for the first time, the upconversion phenomena which trigger different emission energies occurring in different quartet states of Mn, ⁴T₁(⁴G), ⁴T₂(⁴G), ⁴A₁(⁴G), ⁴E(⁴G), ⁴T₂(⁴D), ⁴E(⁴D), and ⁴T₁(⁴P). These optical properties are unusual phenomena which break Kasha’s rule of emission. Single particle imaging and low-temperature PL measurement are performed to obtain a deeper insight into these ground products. These results pave a new path to develop highly fluorescent non-toxic hybrid compounds with remarkable optical properties.

Introduction

Organic–inorganic hybrid materials with a general formula of ABX₃ (where A is an organic ammonium salt, B is a metal center, and X is a halide ion) have gained tremendous attention due to their attractive optoelectronic properties for various solid-state applications, such as solar cells,¹–³ sensors,⁴ quantum dots,⁵ and lasers.⁶ Among various perovskite materials, lead-halide perovskites show the highest power conversion efficiency (PCE), which is more than 23% (ref. 7), and lead-based perovskite light-emitting diodes exhibit record external quantum efficiency, more than 20%.⁷ However, since lead-containing compounds are toxic⁸–¹⁰ despite their outstanding performance, lead-based perovskites are not eco-friendly for large-scale production of solar cells¹¹–¹⁴ and solid-state lighting applications. Therefore, eco-friendly substitutes for lead-halide perovskites that can match the performance of the original perovskite material are in high demand and organic–inorganic manganese (Mn) complexes can be considered a very good alternative.¹²,¹³

Fluorescent tetrahedral manganese(II) complexes have been around for a few decades, from the first synthesis by Cotton et al. in the early 1960s.¹⁷ However, the photoluminescent properties of manganese(II) compounds have not been receiving proper attention. These Mn-based hybrid compounds have remained unsung heroes to date. The time has come to focus on these materials for solid state light-emitting devices and other optoelectronic devices. The emission in manganese complexes takes place due to d–d transition in the metal center, which is strongly correlated with the crystal field effect.¹⁸ The Mn(II) complexes possess pressure-dependent PL, which is associated with a change in configuration from four-coordinated to five or six-coordinated modes upon increasing the pressure.¹⁹ They also show excellent triboluminescence properties, where cracking of crystals generates PL.¹⁹ Typically, manganese(II) complexes with a tetrahedral configuration exhibit brilliant green emission centered at 520 nm, while octahedral Mn(II) salts exhibit orange colored emission at 605 nm.²⁰ Additionally, unlike typical perovskite crystals, where the PL depends on the crystallinity of the bulk material, the tetrahedral Mn(II) complexes are 0D fluorophores with photoluminescence properties at the molecular level.²¹ In the literature, the dimensionality has been defined in two ways: (a) morphological low-dimensional materials and (b) molecular
level low-dimensional materials. Morphological low-dimensional materials (0D, 1D, and 2D) are nanoscale materials associated with the quantum confinement effect.23 Molecular level low-dimensional materials (2D, 1D, and 0D) are defined by the connectivity (such as layers, wires, or polyhedrons) and growth of individual metal halides and are independent of their crystal size. 0D bulk materials24–26 have discrete metal centres at the molecular level where no connectivity between metal centres exists and these metal centres behave like QDs or individual metal centres.26 0D fluorophores have discrete metal centers surrounded by organic cations and exhibit quantum confinement phenomena as the size of metal center falls in the nanoregime. As the syntheses of 0D bulk crystals do not require any capping ligands, these materials will retain their high PL-QY during thin film device fabrication. Recently, 0D Cs$_2$PbBr$_6$ (ref. 26 and 27) and low-dimensional perovskites28–32 have gained tremendous attention due to their exciting optical properties. However, the toxicity of lead remains a critical problem for practical applications.

Herein, we report, for the first time, a solid-state one step synthesis of 0D fluorescent organic–inorganic hybrid compounds, [Bu$_4$N]$_2$[MnBr$_4$] (1) and [Ph$_4$P]$_2$[MnBr$_4$] (2), through simple mechanical grinding with 100% yield in less than 10 minutes. The obtained materials show PL at 520 nm (2.38 eV) with brilliant green color and possess below band gap energy photon absorption capability. This type phenomenon has never explored with any 0D organic–inorganic hybrids. We have also synthesized single crystals of 1 and 2 to check the crystal structure and purity of ground products (Fig. 1). Both 1 and 2 exhibited high thermal stability. Single particle imaging and low-temperature PL measurements were also performed to gain deeper insights into their optical properties.

**Experimental section**

**Materials**

Tetrabutylammonium bromide (Bu$_4$NBr, ≥99.0%, M. Wt. 322.37), tetrphenylphosphonium bromide (Ph$_4$PBr, 97%, M. Wt. 419.29), manganese(n) bromide (MnBr$_2$, ≥99%, M. Wt. 214.75) and ethanol were purchased from Sigma-Aldrich.


**Single crystals.** Bu$_4$NBr (0.322 g, 1 mmol) and MnBr$_2$ (0.108 g, 0.5 mmol) were ground together using a mortar and pestle for 10 minutes. A light yellow powder was obtained and used for further studies. 1 showed bright green fluorescence under UV light.

Similarly, 2 was prepared using Ph$_4$PBr (0.419 g, 1 mmol) and MnBr$_2$ (0.108 g, 0.5 mmol).


**Single crystals.** Bu$_4$NBr (0.322 g, 2 mmol) and MnBr$_2$ (0.108 g, 0.5 mmol) were dissolved in ethanol (50 ml) and then stirred for 10 minutes. The solution was filtered to obtain a clear solution and kept for evaporation. After a few days, light yellow colored crystals formed. The crystals were filtered and dried under ambient conditions. The crystals exhibited bright green fluorescence under UV light. In a similar method, yellow colored crystals of 2 were synthesized using Ph$_4$PBr (0.419 g, 1 mmol) and MnBr$_2$ (0.108 g, 0.5 mmol).

CCDC 1902826 ([Bu$_4$N]$_2$MnBr$_4$) and 1902825 ([Ph$_4$P]$_2$MnBr$_4$) contain the supplementary crystallographic data for this paper.†

**Characterization**

**Powder X-ray diffraction** was performed on a D/MAX2500V/PC diffractometer, Rigaku, using a Cu-rotating anode X-ray source. Bragg’s diffraction angle (2θ) range was 10–50° and the scan rate was 2° per minute.

**X-ray photoelectron spectra (XPS)** were obtained using a K-alpha model, ThermoFisher.

The optical diffuse reflectance spectra of all the solid samples were recorded using a Cary 5000 UV-Vis-NIR Spectrophotometer (Agilent) with an integrating sphere in diffuse-reflectance mode and then they were converted to the Kubelka–Munk function, f(R).

The PL spectra of all the Mn complexes were collected in the solid state using a Cary Eclipse fluorometer (Varian). Thermogravimetric analysis (TGA) was performed using a Q500 model, TA.

Scanning electron microscopy (SEM) images were obtained using a SU8220 Cold FE-SEM, Hitachi High-Technologies.

**PL QY (PLQY)** was experimentally determined using an FP-8500ST spectrophluorometer (Jasco International). PLQY was evaluated using an integrating sphere and the following equation was used:23

\[
\text{QY} \% = \frac{S_2}{S_0 - S_1} \times 100
\]

$S_1$ = area scattered from the sample, $S_2$ = area emitted from the sample, $S_0$ = area from incident light. $S_0$ was measured with nothing in the sample holder.

Fourier-transform infrared (FTIR) spectra were collected using an FTIR spectrometer (670-IR, Varian) with an attenuated total reflection detector.

PL single particle imaging of all the powder samples was performed using an LSM 780 NLO (manufacturer: Carl Zeiss),
The focus of the samples was adjusted mechanically using 10× air and 100× oil objective lenses. The laser wavelength used in this study was 405 nm. The detection range was 420–700 nm (8.9 nm).

Single crystal X-ray diffraction analyses of 1 and 2 were performed at the Western Seoul Center of the KBSI. A crystal was picked up with Paratone oil and mounted on a Bruker D8 Venture PHOTON 100 CMOS diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.7107 Å) radiation source at 25 °C. The goniometer equipped with the diffractometer is a KAPPA four circle goniometer with φ, ω and 2θ axes around which the crystal was rotated. The unit cell parameters were determined by collecting the diffracted intensities from 24 frames measured in two different crystallographic zones and using the method of difference vectors. Data collection and integration were carried out with a SMART APEX2 (Bruker, 2012) and SAINT (Bruker, 2012). Absorption correction was performed by the multi-scan method implemented in the Vienna simulation package (VASP).24,25 We used the generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhof (PBE) functional augmented by including Hubbard-U corrections (GGA + U) based on Dudarev’s approach.26 In Dudarev’s approach, the Coulomb and exchange interactions are specified by the $U_{\text{eff}}$ parameter. The core–valence interaction is described by the projector-augmented wave method. We have also considered the Tkatchenko–Scheffler method27 for dispersion correction. Plane wave functions were expanded with an energy cutoff of 520 eV and Brillouin zone sampled using a 4×4×4 gamma centered k-mesh. The value of $U_{\text{eff}} = 3.7$ eV is used for Mn atoms to treat strong correlation Mn-3d electrons.28 Structure optimization was performed on a full unit cell of 1 and 2 containing 444 and 380 atoms, respectively. The full unit cell and all atoms are fully relaxed using the conjugate-gradient method until the absolute values of the Hellmann–Feynman forces were converged to within 0.0025 eV Å⁻¹.

### Results and discussion

The syntheses of [Bu₄N][MnBr₄] (1) and [Ph₃P]₂[MnBr₄] (2) were performed by simple hand grinding using a mortar and pestle. During this process, the crystalline structure of MnBr₂ was broken by means of thermal energy provided by grinding, and the vacant sites were coordinated by two more Br atoms from the organic precursor. Dinegative charges in tetrahedral [MnBr₄]²⁻ are neutralized by two ammonium cations in 1 and two phosphonium cations in 2 producing isolated 0D photoluminescent particles surrounded by large organic moieties.41 Photographs of different stages of the synthesis are provided in Fig. S1† and the SEM images of 1 and 2 are shown in Fig. S2 and S3.† The method is extremely cost efficient and time saving. For lead-halide perovskites, the 0D perovskite preparation methodologies demand precise control of the reaction conditions and involve tedious processes which are too long to perform.42 Even then, it is unavoidable to have different 2D and 3D phases. Conversely, solid state synthesis employed in our work results in 100% yield of 0D materials within 10 minutes and less control is required. Additionally, they have better reproducibility, since their PL depends solely on the coordination environment of the metal center.43 Such a methodology is of paramount importance for low-cost fabrication of solid state light-emitting devices. Phase purities of 1 and 2 were confirmed by powder X-ray diffraction (XRD) analysis (Fig. 2a). Single crystals of both 1 and 2 were grown through solution assisted synthesis, where ethanolic solutions of precursors were slowly evaporated over 5 days until the crystals of 1 and 2 were obtained. According to single crystal XRD measurements (Tables S1 and S2†), 1 has an orthorhombic crystal structure with the P2₁2₁2₁ space group, while 2 has a monoclinic crystal structure with the C2/c space group. All the bond lengths of 1 and 2 are tabulated in Tables S3 and S4† respectively. The unit cells of 1 and 2 are shown in Fig. S4 and S5.† The metal centers of both compounds have distorted tetrahedral geometry, with bond lengths between 2.505 Å and 2.517 Å. The Mn²⁺ cations in 1 and 2 possess tetrahedral geometry, with C–N bond lengths between 1.437 Å and 1.550 Å for 1 and C–P bond lengths between 1.783 Å and 1.800 Å for 2 (Tables S3 and S4†). Powder XRD patterns of
both complexes well-match the single crystal XRD spectra of the corresponding compounds, with slightly varying intensities, due to non-uniform crystallinity of the powder samples. We have performed the PXRD measurements of all the precursor salts, MnBr$_2$, Bu$_4$NBBr and Ph$_4$PBr, to confirm the purity of the synthesized products (Fig. S6†). Pure MnBr$_2$ has a strong PXRD peak at 5.72° which is absent in 1 and 2. The PXRD peaks of organic precursor salts Bu$_4$NBBr and Ph$_4$PBr are also absent in 1 and 2. Thus we confirmed that there was no impurity of precursor salts in the synthesized compounds.

The FT-IR spectrum of 1 exhibits characteristic peaks of saturated hydrocarbon, with symmetric/asymmetric C–H stretching at 2871 cm$^{-1}$/2958 cm$^{-1}$ and C–H and H–C–H bending at 1376/1485 cm$^{-1}$ (Fig. 2b). 2 possesses weak peaks for aromatic C–H/C=C stretching at 3055/1585 cm$^{-1}$ and C–H bending at 1107 cm$^{-1}$. Both compounds exhibit only characteristic vibrations, with no sign of impurities. The thermal stability and possible phase transitions were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Fig. 2c shows the thermal stability curves of 1 and 2. The decomposition of 1 starts after 220 °C, with two-step weight drops until complete decomposition above 700 °C. A DSC measurement in the stability range of 1 has a melting peak onset above 60 °C during the first forward scan, with the melting point at 100 °C. However, no phase transitions occur for the reverse and second forward scans (Fig. 2d). This indicates that 1 undergoes phase transition above 60 °C, and starts to irreversibly melt above 100 °C. On the other hand, 2 has excellent stability up to 400 °C, with melting and crystallization peaks in both forward and reverse DSC scans. Melting occurs above 270 °C, while 2 is completely stable below 270 °C. This additional robustness might be inherent due to the tetraphenyl phosphate cation, which is more constrained in its structure due to the presence of four aromatic rings in the moiety. We have tried to measure the melting points of 1 and 2 to confirm the purity of the samples. From DSC and TGA measurements, we found that the organic component of both compounds melted first without decomposition. The DSC curves reveal that the melting of the organic component in 1 and 2 occurred at 100 °C and 278 °C, respectively, and the TGA curves show that the first decompositions of 1 and 2 occurred at 220 °C and 410 °C, respectively. The first decompositions of 1 and 2 are associated with the loss of the organic part and the second weight loss centered at around 630 °C is attributed to the evaporation of MnBr$_2$. As these samples undergo decomposition before melting, it is difficult to measure the melting points of 1 and 2. Previously the Mitzi group also reported this type of phenomenon where the decomposition of organic–inorganic perovskites occurred before melting.†

The surface chemistry of 1 and 2 was analyzed by X-ray photoelectron spectroscopy (XPS) measurements (Fig. S7–S10†). Mn 2p spectrum of 1 possesses two peaks at 641 eV and 652 eV, corresponding to 2p$_{3/2}$ and 2p$_{1/2}$, respectively (Fig. S9a†). The peaks are sharp, and those associated only with Mn(II) species are present in the sample. It also contains satellite peaks at 646 eV and 657 eV. The Br 3d spectrum for 1 exhibits characteristic peaks of bromine at 68 eV and 69.5 eV for 3d$_{5/2}$ and 3d$_{3/2}$, respectively (Fig. S9b†), and an N 1s peak appears at 402 eV (Fig. S9d†). The deconvolution of the broad peak in the C 1s spectrum of 1 in Fig. S9c† reveals the presence of two different carbon environments, (i) C atoms bound to another C atom with lower binding energy of 1s electrons (285 eV) and (ii) C atoms bound to a more electronegative N atom with slightly higher 1s electron binding energy (286.5 eV). The XPS spectra of Mn 2p and Br 3d for 2 are identical to the XPS spectra of 1 (Fig. S9a and b†). Similarly, the C 1s spectrum possesses one broad peak with small shoulder peaks for C–C bonding at 284 eV and C–P bonding at 286 eV (Fig. S10c†). The peaks in the P 2p spectrum of 2 are deconvoluted into two peaks at 132 eV and 133 eV for 2p$_{3/2}$ and 2p$_{1/2}$, respectively (Fig. S10d†).

To analyze the photochemical properties, solid-state diffuse reflectance (SSDR) analysis and PL measurements were carried out. Fig. 3a and b show the absorbance plot, the Kubelka–Munk (K–M) function vs. wavelength (nm), for 1 and 2, respectively, whereas Fig. 3c and d show the zoomed in absorbance plots of 1 and 2. The absorbance spectrum of 1 exhibits peaks centered at 472, 450, 434, 400, 368, and 347 nm, which correspond to transitions from the ground state $^4A_2S$ of tetrahedral Mn(II) to the excited states of $^4T_1(G)$, $^4T_2(G)$, $^4A_1(G)$, $^4E(G)$, $^4T_2(D)$, $^4E(D)$, and $^4T_1(P)$, respectively. These excited states are well-known in the Mn$^{2+}$ system (d$^5$) which exhibits several excited states in the Tanabe–Sugano diagram. PL excitation (PLE) measurements have also been carried out due to low absorption of 1 and 2, and PLE gives better information on absorption properties due to improved signal-to-noise ratio compared to conventional absorption measurements in transmission geometry. PLE also supported the corresponding electronic transitions of both 1 and 2 (Fig. S11†). For 2, the absorption peaks appeared at 472, 450, 422, 403, 370, and 341 nm. The PL emission caused by above band gap energy photons for both 1 and 2 is at 2.38 eV with a full width at half maximum of 40 nm, which implies the dependence of the emission wavelength not on the organic cation, but on the tetrahedral Mn center. Therefore, interchanging different organic cations with relatively similar sizes would not alter the photoluminescence properties of the Mn center. This idea can be developed further by modifying the physical properties of the photoluminescent compound, such as thermal stability and wettability, while maintaining the same photoluminescence properties.

In our synthesized compounds, we rule out the possibility of a self-trapped exciton (STE) which was generally observed in low dimensional perovskite materials.48 In the absence of lattice defects, the STE appears through the formation of transient lattice defects by a “self-trapping” process.47 In the case of STE formation, the FWHM is very broad [generally more than 100 nm] for a single emission peak47–49 while two emission peaks appear in a wide region (in the case of white light-emitting perovskite).50,51 In our synthesized 0D-[Mn$_2$NPh]$_2$MnBr$_4$ crystal, the FWHM is only 40 nm which rules out the self-trapped exciton state phenomena within [MnBr$_4$]$^{2–}$. Both ground products, 1 and 2, exhibit a PL-QY of 47%. We also rule out the possibility of surface trap-states because the time resolved PL (TRPL) spectra of 1 and 2 reveal a single exponential
decay channel (Fig. S12†). If there are defect states in 1 and 2, then the TRPL decay curve should exhibit multiple decay channels. The average life times for both compounds are calculated to be 350 μs. Previously, a similar type of organic–inorganic hybrid perovskite also exhibited an average life time in the microsecond range.15,52 Thus we confirm that the Mn$^{2+}$ emission is a spin-forbidden transition.

To investigate the upconversion (UC) phenomena that occurred in 1 and 2, we performed low photon energy absorption analyses on 1 and 2 by measuring the fluorescence emission from the samples while exciting them with low energy photons. In order to excite an electron with below band gap energy photons from the ground to the excited state, several photons with lower energy than the band gap of a material are absorbed simultaneously. The band gap of 1 and 2 is 2.62 eV (472 nm). To observe the low energy photon absorption, the compounds were excited in the range between 640 and 820 nm with increments of 20 nm. When the ground products were excited at 640–710 nm, both 1 and 2 showed a similar emission pattern, with peaks between 550 and 609 nm (Fig. 3e and f).

However, when excited with an energy below 730 nm down to 820 nm, the materials exhibit distinctive emission peaks that shift toward higher wavelengths as the excitation wavelength increases (Fig. 3g and h). These emissions are a result of the quartet excited states of Mn.

Quantitatively, we verified the two photon absorption phenomena from the UV and PL spectra. Fig. 3a–d reveal that 1 and 2 have an absorbance minimum at 3.41 eV (363 nm). This minimum is a turning point for emission caused by below band gap energy photons. We observed two distinct emissive features depending on the energy of photons. The photons with an energy of 1.93 eV to 1.74 eV (640 nm to 710 nm) produced similar PL spectra in the range of 550–610 nm, and the photons with an energy of 1.69 eV to 1.51 eV (730–820 nm) produced PL spectra spanning from 450 nm to 600 nm. The absorbance minimum (3.41 eV) of 1 and 2 falls within $2 \times 1.74 \text{ eV}$ to $2 \times 1.69 \text{ eV}$. The emissions occurred in 1 and 2 following this condition: $h\nu/\lambda_{\text{abs}} \leq 2E_p$ where $h$, $c$, $\lambda_{\text{abs}}$, and $E_p$ are the Planck constant, speed of light in a vacuum, absorbance wavelength and incident photon energy, respectively. Whether it is 2 or 3 photon absorption phenomena, we need to consider two different regions of the PL spectrum. If 3 photon absorption occurs with photons having an energy between 1.69 eV and 1.51 eV (730 nm to 820 nm), then the electron will gain energy between $5.07 \text{ eV} (3 \times 1.69 \text{ eV})$ and $4.53 \text{ eV} (3 \times 1.51 \text{ eV})$ which are above the absorption minimum energy of 3.41 eV and the gained energy could produce the same transitions as observed with the photons having an energy between 4.13 and 3.41 eV. However, we did not observe such emissions. Thus we confirmed the two photon absorption phenomena ruling out the 3 photon absorption phenomena. The different emission energy levels indicate a violation of Kasha’s rule for photon emission. This type of phenomenon was never observed in Mn complexes. These exciting optical properties could be used to fabricate optical devices that distinguish different energy photons. In 1950, Kasha stated that the emitting level of a given multiplicity is the lowest excited level of that multiplicity where the term multiplicity is defined as $(2S + 1)$ and $S$ is the total spin angular momentum of the level. This rule is widely known as Kasha’s rule. If $2S + 1 = 1$, 2, 3, 4, these states are denoted as singlet, doublet, triplet and quartet, respectively. According to Kasha’s rule, emission will occur from the vibrational ground state of the lowest excited singlet level and the triplet state in the cases of fluorescence and phosphorescence, respectively.
2 exhibit emission upon exciting with below band gap energy photons and the emission peak positions change with the energy of excited photons. This phenomenon indicates that the emission occurs not only from the lowest excited state but also from the other excited states. If emission occurs from the lowest excited state to the ground state, then we should observe the same peak positions as found in previously reported CsPbBr₃ NCs.²³

The origin of the upconversion by photons with energy between 1.93 eV and 1.74 eV (640–710 nm) has been explained using the Tanabe–Sugano diagram of the Mn²⁺ ion which has five unpaired d electrons. We have plotted the energy level diagram (Scheme 1) for the quartet states of the Mn²⁺ ion in [MnBr₄]²⁻, relative to the energy of the ⁶A₁ ground state vs. Δ (cm⁻¹) qualitatively (Table S5†). The free Mn²⁺ ion has ⁴G, ⁴P and ⁴D terms which further split into closely spaced [⁴T₁(⁴G), ⁴T₂(⁴G), ⁴A₁(⁴G), ⁴E(⁴G)], [⁴T₁(⁴P)] and [⁴T₂(⁴D), ⁴E(⁴D)], respectively in the presence of a ligand field. The energy level diagram reveals that three absorption bands, ⁴T₁(⁴G), ⁴T₂(⁴G), and ⁴A₁(⁴G)/⁴E(⁴G), exist in the range 21 000 to 24 000 cm⁻¹ (Table S5†). The next three absorption bands, ⁴T₂(⁴D), ⁴E(⁴D), and ⁴T₁(⁴P), appear in the range 25 000 to 29 000 cm⁻¹ (Table S5†).

When the energy of exciting photons was between 1.93 eV and 1.74 eV (640–710 nm), the energy of electrons reached between 31 129.03 and 28 064.52 cm⁻¹ due to two photon absorption phenomena (Tables S6 and S7†). This amount of energy is sufficient to reach above or equal to ⁴T₁(⁴D), ⁴E(⁴D), and ⁴T₁(⁴P) quartet states. The emission occurred from these associated levels.

In another case, when the energy of exciting photons was between 1.69 eV and 1.51 eV (730–820 nm) were from the corresponding ⁴T₁(⁴G), ⁴T₂(⁴G), and ⁴A₁(⁴G)/⁴E(⁴G) states. It is to be mentioned that these states are below the ⁴T₁(⁴D), ⁴E(⁴D), and ⁴T₁(⁴P) quartet states. As the emission occurred from different quartet states, the nature of the emission feature changed dramatically.

The energy of different quartet excited states ⁴T₁(⁴G), ⁴T₂(⁴G), ⁴A₁(⁴G), ⁴E(⁴G), ⁴T₂(⁴D), ⁴E(⁴D), and ⁴T₁(⁴P) lies within 21 186.44 (472 nm – 28 818.44 cm⁻¹ (341 nm)], [energy difference, ∆E = 7632 cm⁻¹] for ¹ and 21 186.44 cm⁻¹ (472 nm) – 29 325.51 cm⁻¹ (341 nm)] [∆E = 8139.07 cm⁻¹] for ² whereas the emission energies lie within 23 529.41 cm⁻¹ (425 nm) – 16 420.36 cm⁻¹ (609 nm) [∆E = 7109.05 cm⁻¹] for ¹ and 23 809.52 cm⁻¹ (420 nm) – 15 948.96 cm⁻¹ (627 nm) [∆E = 7860.56 cm⁻¹] for ² (Tables S6 and S7†) and this indicates that the energy difference is quite high between the lowest and highest excited states. Generally, the energy difference of different vibrational states of the same excited states is much smaller than the emission energy difference of different excited states and the emissive nature of different vibrational states of the same excited states should be similar. In our case, we observed two distinct emissive features. Thus we rule out the possibility of emission from different vibrational states of the same excited states by considering the emissive nature and emissive energy difference in our synthesized compounds. From all the above phenomena, we conclude that ¹ and ² exhibit anti-Kasha’s emission.

We collected the diffuse reflectance spectra, PL spectra and PLQY of solution grown single crystals and compared them with the optical properties of mechanochemically synthesized materials. Both materials synthesized by grinding and solution processing exhibited the same diffuse reflectance spectra and PLQY (Fig. S13†). PLQYs of single crystals of ¹ and ² are 54% and 79%, respectively. These values are higher than those of the powders synthesized by the grinding method, due to the higher crystallinity of single crystals. Single crystals of ¹ and ² also exhibit the same upconversion characteristics (Fig. S14†).

Single particle images in Fig. 4a and b obtained by confocal laser scanning microscopy indicate that each particle exhibits bright green PL at 520 nm upon irradiation with a 405 nm laser beam. The normalized single-point emissions from both compounds are shown in Fig. 4c. The emission peak position of a single particle is the same as that of the powder sample, ruling out shape dependent PL emission. To check the emission behavior with respect to temperature, we obtained emission spectra at 295 and 77 K. Both compounds exhibit blue-shifted PL wavelengths at 77 K as compared to 295 K and these PL peaks are reversibly interchanged with temperature. The blue shifts for ¹ and ² are 15 nm (520 to 505 nm) and 5 nm (520 nm to 515 nm), respectively. Thus, ² can be used for temperature sensitive solid state light-emitting device applications due to its small PL peak shift with temperature.

We have performed DFT calculations to corroborate the experimental photophysical properties of ¹ and ². The projected density of states (PDOS) and the decomposed charge densities of both compounds have been calculated from the relaxed structures. Fig. 5 shows the calculated PDOS for ¹ and ². At the band edges, it is evident from the PDOS for ¹ that the orbital

![Scheme 1](image-url) Qualitative energy level diagram for the quartet states of the free Mn²⁺ ion and the Mn²⁺ ion in [MnBr₄]²⁻. Energies are set to the ground state ⁶A₁ as zero.
contribution to the valence band stems primarily from MnBr4 (Br-4p and Mn-3d states), while that to the conduction band arises from C-2p and Mn-3d states (also see Fig. S15† for clarity). The calculated PDOS of 2 reveals valence and conduction band edges derived from MnBr4 (Br-4p and Mn-3d states) and Ph4P (C-2p and P-3p states), respectively. From the PDOS plots, we observe that the exchange splitting of Mn-3d levels is quite different, even though Mn2+ is tetrahedrally coordinated to four Br/C0 ions in both compounds. This is attributed to the presence of different organic cations in 1 and 2. 1 contains four n-butyl groups and 2 contains four aromatic benzene rings having π electrons. These aromatic rings in Ph4P+ form antibonding π states in the conduction band of 2.† This antibonding π states are evident in the decomposed charge density plots in Fig. 6. In Fig. S15† it is seen that the empty Mn-3d state of 2 is also located within the Ph4P dominated conduction band.

For both compounds, several empty bands with higher energy than that of the conduction band edge are formed by C-2p, Mn-3d, and Br-4p orbitals. Br-4s and Mn-4s orbitals show no contributions to both the conduction and valence bands in both compounds. N-2p and P-3p orbitals contribute to the valence band of 1 and 2, respectively, but these states are far away from the band edges. In Fig. S15† it is seen that in both compounds the Mn t2 and e bands are very narrow, implying an extremely localized 3d state. Even though the Mn-3d (t2 and e) levels are overlapped with C-2p states in conduction band minima, the excited electrons in both compounds prefer to be localized at MnBr4 due to the strong Coulomb binding between the electrons and holes.† This leads to Mn2+ d–d transition induced PL. The calculated band gaps for 1 and 2 are about 2.95 eV and 2.2 eV, respectively, and the experimentally measured absorption and PL bandgaps are around 2.62 eV and 2.38 eV, respectively. The small differences between the calculated and experimentally measured results for both compounds are due to the challenges in the excited state calculations using DFT-PBE (well-known band-gap error of the semi-local exchange-correlation functional).

Conclusions

Solid-state mechanochemical synthesis to obtain lead-free and highly fluorescent 0D organic–inorganic hybrid compounds, 1 and 2, has been reported, for the first time, along with their solution-processed single crystals. 1 and 2 do not follow the well-known Kasha rule which states that electronic transition occurs from the lowest excited state of a given multiplicity. So far, this breakdown was not observed in any 0D hybrid material. Both compounds show excellent thermal stability. 2 exhibits slight changes in the PL peak position with temperature. This will pave the way for designing temperature sensitive solid state
lighting devices which will withstand temperature variation. The ground products exhibit emission phenomena upon excitation with above and below band gap photons. These phenomena have not been explored as yet. While lead-containing organic–inorganic perovskites are in great demand, the toxicity of lead hinders their practical application. In this context, this work provides a general green and cost-effective synthetic route to design and synthesize non-toxic low-dimensional organic–inorganic hybrid compounds with intriguing optical properties.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


