Efficient organic manganese(II) bromide green-light-emitting diodes enabled by manipulating the hole and electron transport layer†

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Lead-free, non-toxic transition metal-based phosphorescent organic–inorganic hybrid (OIH) compounds are promising for next-generation flat-panel displays and solid-state light-emitting devices. In the present study, we fabricate highly efficient phosphorescent green-light-emitting diodes (PHOLEDs) using the lead-free, non-toxic, zero-dimensional OIH compound [(H₂C==CHCH₂)(C₆H₅)₃P]₂MnBr₄ (L), which exhibits an emission peak at 516 nm and a long lifetime of 441 μs. The long lifetime indicates the phosphorescent emissive nature of L. Density functional theory calculations confirm that the narrow green emission from L is due to the highly localized electronic states of the valence and conduction bands. A flexible green-light-emitting phosphorescent substrate is successfully fabricated from L using a nylon membrane, indicating that L has a significant potential for use in flexible optoelectronic devices. By engineering the organic hole and electron transport layers, we achieve a highly efficient all-vacuum-deposited PHOLED with a current efficiency of 24.71 cd A⁻¹, a power efficiency of 20.61 lm W⁻¹, and an external quantum efficiency of 7.12%. Together, our findings will pave the way for the development of high-performance Mn(II)-based LEDs.

Introduction

Organic–inorganic hybrid (OIH) phosphorescent materials have proven to be promising materials for use in light-emitting devices,1–3 X-ray imaging,4,5 flat-panel displays, and solid-state lighting.6 In particular, Friend and co-workers first reported the fabrication of OIH lead halide perovskite-based light-emitting devices7 and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1tc02550c.

‡ Electronic supplementary information (ESI) available. CCDC 2071564. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1tc02550c.
tetrahedral and octahedral geometries, Mn(II) can also form trigonal bipyramidal \(^{24}\) and square planar geometries, \(^{25}\) which produce orange and red emissions, respectively.

Molecular-level 0D ionic hybrid Mn(II) complexes are of significant interest for use in light-emitting applications due to their high PLQY and low-cost synthesis routes. Because organic ligands separate the Mn(n) centers of the 0D Mn(n) complexes, and the tetrahedral Mn(n) centers act as the center of luminescence, the photoluminescence (PL) properties are not quenched by the aggregation effect, which generally reduces the PLQY in the solid state. Seshadri \textit{et al.} \(^{19}\) reported that the separation of the [MnBr\(_4\)]\(^{2-}\) moieties is responsible for the phosphorescence properties of \(^{1}\).

Fig. 1 Synthesis, reaction scheme, and SC structure of \(^{1}\). (a) Solvent-free mechanochemical synthesis of \(^{1}\) using a mortar and pestle. (b) Crystallization of \(^{1}\) in ethanol. (c) Stoichiometric reaction scheme for the synthesis of \(^{1}\) from its precursors. (d) Unit cell of \(^{1}\). The individual [MnBr\(_4\)]\(^{2-}\) moieties are separated by organic phosphonium cations, [[H\(_2\)C=CHCH\(_2\)](C\(_6\)H\(_5\))\(_3\)P]Br. (e) All four [MnBr\(_4\)]\(^{2-}\) moieties in the unit cell of \(^{1}\) have a large distance between the Mn(n) centers (9.671–15.443 Å). The Cambridge Crystallographic Data Centre (CCDC) number for SC \(^{1}\) is 2071564.† The separation of the [MnBr\(_4\)]\(^{2-}\) moieties is responsible for the phosphorescence properties of \(^{1}\).

quaternary organic ammonium cation is essential for the development of efficient Mn(n)-based luminescent materials\(^{19}\) that can be used for the fabrication of high-performance PHOLEDs\(^{26\text{–}30}\). Vacuum-based deposition is an effective technique for fabricating PHOLEDs and other electronic devices. Vacuum-processed films tend to have a higher density, higher transition temperature, and better thermal stability. In addition, they also offer a larger number of horizontally oriented molecules, strengthening the optical and electrical properties of the films, while multi-stacked films with exceptional reproducibility can be easily fabricated using vacuum processing.\(^{31\text{–}35}\)
In this work, we demonstrate the solution-processed synthesis of green-light-emitting OIH \([\text{H}_2\text{C} = \text{CHCH}_2\text{(C}_6\text{H}_3)_3\text{P}]_2\text{MnBr}_4\) single crystals (SCs) (denoted as 1) and their powdered form synthesized by solvent-free mechanochemical grinding (Fig. 1a and b). We explore the effect of the organic ligands on the optical properties of 1 using both experimental and computational methods. We find that large cationic organic ligands create a clear separation between Mn···Mn, thus enhancing the PL characteristics of the individual tetrahedral Mn(n) centers. A pinhole-free smooth and dense large-area tetrameric Mn(n) [1]-filled nylon membrane (15 × 10 cm²) is employed as a light-emitting flexible substrate for potential solid-state light-emitting applications. We also explore different hole transport layers (HTLs) and electron transport layers (ETLs) for the fabrication of high-performance green-light-emitting PHOLEDs using 1 as the active light-emitting layer. The champion device exhibits a high external quantum efficiency (EQE) of 7.12%@100 cd m⁻² and a peak brightness of 4885 cd m⁻². Our results provide a significant clue to develop desired phosphorescent zero dimensional hybrid materials for highly-efficient phosphorescent green-light-emitting diodes.

Experimental methods

Materials

\(\text{MnBr}_2\), \([\text{H}_2\text{C} = \text{CHCH}_2\text{(C}_6\text{H}_3)_3\text{P}]_2\text{MnBr}_4\) hole transport layers (HTLs), electron transport layers (ETLs), emitting layers (EMLs) and solvents were purchased from Merck and used without further purification, unless otherwise specified. Nylon membrane was bought from Sterlitech Corporation.

Synthetic procedure

**Synthesis of \([\text{H}_2\text{C} = \text{CHCH}_2\text{(C}_6\text{H}_3)_3\text{P}]_2\text{MnBr}_4\) powder.** In a typical synthesis, \(\text{MnBr}_2\) (0.042 g, 0.2 mmol) and \([\text{H}_2\text{C} = \text{CHCH}_2\text{(C}_6\text{H}_3)_3\text{P}]_2\text{Br}\) (0.152 g, 0.4 mmol) were ground together using 1 ml of ACN for 10 minutes. The solid product exhibited bright green phosphorescence under UV light.

**Synthesis of \([\text{H}_2\text{C} = \text{CHCH}_2\text{(C}_6\text{H}_3)_3\text{P}]_2\text{MnBr}_4\) (1) SCs.** \(\text{MnBr}_2\) (0.042 g, 0.2 mmol) and \([\text{H}_2\text{C} = \text{CHCH}_2\text{(C}_6\text{H}_3)_3\text{P}]_2\text{Br}\) (0.152 g, 0.4 mmol) were ground and dissolved in 10 ml of ethanol by sonication for 5 min and subjected to slow evaporation at room temperature. After a few days, XRD-quality light yellow SCs were observed. The SCs have been used for the fabrication of PHOLEDs.

**Fabrication of a phosphorescent flexible nylon membrane using 1.** First, 1 (1 g, 1.03 mmol) was dissolved in 5 ml of ACN via sonication and then dropcasted onto a nylon membrane with an active area of 15 × 10 cm². It was dried under ambient conditions for 12 hours. The nylon membrane containing 1 produced bright green phosphorescence under a UV lamp (365 nm).

Results and discussion

**Synthesis and physical characterizations**

In a typical synthesis method, light-pink \(\text{MnBr}_2\) and white quaternary phosphonium salt, \([\text{H}_2\text{C} = \text{CHCH}_2\text{(C}_6\text{H}_3)_3\text{P}]_2\text{Br}\) were ground at a 1:2 molar ratio for 10 minutes in a mortar using a pestle (Fig. 1a). A small amount of acetonitrile was used for smoother grinding. The color of the product became yellowish-green following the reaction \(\text{MnBr}_2 + 2[\text{H}_2\text{C} = \text{CHCH}_2\text{(C}_6\text{H}_3)_3\text{P}]_2\text{Br}\) (Fig. 1c). The ground powder exhibited bright green phosphorescence under an ultraviolet (UV) lamp (365 nm). To investigate the SC structure in detail, the ground powder was dissolved in ethanol and exposed to slow evaporation to promote crystallization (Fig. 1b). After a few days, light yellow X-ray diffraction SCs appeared inside the beaker. The SCs were isolated by filtration and dried in the air. The X-ray crystal structure has the stoichiometric formula \([\text{H}_2\text{C} = \text{CHCH}_2\text{(C}_6\text{H}_3)_3\text{P}]_2\text{MnBr}_4\) (to the best of our knowledge, this is the first time this SC has been synthesized. The SC structure contains cationic allyltriphenylphosphonium and an anionic tetrameric manganese[n] complex, \([\text{MnBr}_4]^{2-}\). The Mn(n) center is surrounded by four bromide ions forming a tetrahedral geometry. A perspective view of 1 is presented in Fig. 1d, and important crystallographic parameters are listed in Tables S1 and S2 (ESI†). The crystal lattice is monoclinic with \(P2_1/n\) symmetry and the unit cell contained four molecules (Fig. 1d). The Mn(1)–Br(3), Mn(1)–Br(4), Mn(1)–Br(1), and Mn(1)–Br(2) were 2.5077(14), 2.5079(14), 2.5093(13), and 2.5164(13). The Br(3)–Mn(1)–Br(4), Br(3)–Mn(1)–Br(1), Br(4)–Mn(1)–Br(1), Br(3)–Mn(1)–Br(2), Br(4)–Mn(1)–Br(2), and Br(1)–Mn(1)–Br(2) angles are 108.95(5), 105.90(5), 110.87(5), 111.25(5), 108.22(5), and 111.62(5), respectively. In the unit cell of 1, the Mn···Mn distances fall within the range of 9.671–15.443 Å (Fig. 1e). To assess the crystal structure of the mechanochemically synthesized 1 powder, the powder X-ray diffraction (XRD) patterns for the powder sample and simulated XRD patterns of SC 1 were compared (Fig. S1, ESI†). The XRD patterns for both samples were similar, indicating that both the SCs and powder had a similar structure. The absence of additional peaks confirmed the 100% conversion of the precursor salts to 1. The thermal stability of 1 was then analyzed using thermogravimetric analysis (TGA) (Fig. S2, ESI†). The TGA spectrum of 1 exhibited a two-step decomposition at 273 °C and 590 °C. The first decomposition temperature was ascribed to the loss of the organic components and the second to the degradation of \(\text{MnBr}_2\). The high thermal stability of 1 was attributed to the three phenyl rings in the organic phosphonium cation.

X-Ray photoelectron spectroscopy (XPS) measurements were carried out to explore the surface chemical composition of 1 (Fig. S3, ESI†). Mn in 1 exhibited two XPS peaks at 651.82 eV and 640.30 eV, which corresponded to 2p_{3/2} and 2p_{1/2}, respectively. The sharp peaks without any satellite peak indicated the presence of Mn(n) in \([\text{MnBr}_4]^{2-}\) and the absence of any MnO impurities. The Br 3d spectrum of 1 exhibited one peak at 67.12 eV, which suggested one type of Br in the form of \([\text{MnBr}_4]^{2-}\). A P 2p peak appeared at 131.17 eV. The absence of any broad peak in the P XPS spectrum in the higher energy region indicated no surface chemisorption of oxygen or the oxidation of P. The C 1s spectrum exhibited one broad peak with small shoulder peaks for C–C bonding at 282.73 eV and C–P bonding at 283.67 eV.
Typically, OIH Mn complexes have tetrahedral and octahedral geometries that produce green and red phosphorescence, respectively, under UV light. It is well-known that tetrahedral Mn2+ has the quartet excited states 4T1(4G), 4T2(4G), 4A1/4E(4G), 4T2(D), 4E(D), and 4T1(P), whereas octahedral Mn2+ exhibits the quartet excited states 4T1g(G), 4T2g(G), 4A1gE, 4Eg(D), 4T2g(D), and 4T1g(P). Because our synthesized compound 1 had a tetrahedral Mn2+ center, it exhibited six different absorption bands at 472, 451, 435, 390, 375, and 361 nm, corresponding to 4T1(4G), 4T2(4G), 4A1/4E(4G), 4T2(D), 4E(D), and 4T1(P), respectively (Fig. 2a and b). The PL excitation (PLE) spectrum exhibited six bands at 472, 452, 434, 390, 375, and 361 nm, thus corresponding well with the absorbance bands (Fig. 2c). The PL peak for 1 was observed at 516 nm with a narrow full width at half maximum (FWHM) of 45 nm (Fig. 2c), indicating that the emission was generated collectively from individual Mn2+ centers. Generally, the optical properties of materials are directly influenced by their sizes at the nanoscale. As the SCs of 1 are bulk in nature, the PL emission did not depend on the size of the particles. The powdered form of 1 exhibited a bright green emission under UV light (Fig. S4, ESI†). Because all of the Mn2+ centers were separated by large organic molecules (Fig. 1e), complex 1 exhibited a quantum confinement effect with a high PLQY of 48%.

To investigate the emissive behaviour of 1, a time-resolved PL (TRPL) experiment was carried out. Compound 1 exhibited a long lifetime of 441 µs, which was indicative of the phosphorescent emissive nature of 1 (Fig. 2d). This long lifetime was attributed to the 4A1g(G) → 4T1(4G) emission, which has been previously reported for tetrabromide manganese(n) complexes. To employ the phosphorescence of 1 within a flexible substrate, we dissolved 1 in acetonitrile, dropcast it onto a nylon membrane, and then dried it overnight (Fig. 3a). The fabricated nylon membrane exhibited bright green phosphorescence under UV light and excellent flexibility (Fig. 3b and c).
Fig. 3d displays the scanning electron microscopy (SEM) images of bare nylon, showing a compact arrangement of nylon wires, and Fig. 3e shows the polycrystalline powder of 1. Following the dropcasting of 1 onto the nylon membrane, a smooth flexible substrate was fabricated (Fig. 3f). This flexible substrate has significant potential for use in a range of light-emitting applications.

To assess the optical properties, density functional theory calculations were conducted on the relaxed structures of 1, with the electronic band structure (Fig. 4a), the projected density of states (PDOS) (Fig. 4b), and the decomposed charge densities (Fig. 4c and d) calculated. The PDOS analysis confirmed that the Br-4p and Mn-3d states primarily contributed to the valence bands while the conduction bands consisted of the C-2p and Br-4p and Mn-3d states primarily contributed to the valence bands. The PDOS of the Mn d-orbitals was very narrow, indicating extremely localized 3d states. The aromatic rings in the phenyl groups of the phosphonium cations formed the antibonding π states in the CB, as shown in the decomposed charge density plots (Fig. 4d). The electronic band structure of 1 is displayed in Fig. 4a, revealing the low dispersion of both the valence and conduction bands.

The highly localized electronic states were confirmed by the fltness of both the conduction and valence bands, where intermolecular coupling is negligible. A similar phenomenon has also been reported for the 0D organic metal halides of tin and lead. These calculations suggest that the individual $\text{[MnBr}_4\text{]}^{2-}$ units were responsible for the measured PL properties. In the SC structure, all of the $\text{[MnBr}_4\text{]}^{2-}$ units were separate and exhibited the quantum confinement effect, leading to the production of bright green phosphorescence under UV light. Although the organic phosphonium cation contributed to the conduction band minimum (CBM), the exciton's localization occurred within the $\text{[MnBr}_4\text{]}^{2-}$ unit, and this was attributed to the strong Coulomb binding energy between the electrons and holes. This led to a strong Mn$^{2+}$ d–d transition. The experimental PL bandgap and the calculated bandgap were 2.62 eV and 2.07 eV, respectively, with a small difference due to the well-known bandgap error in Perdew–Burke–Ernzerhof calculations.

**Phosphorescent OLED fabrication and performance evaluation**

Organic–inorganic hybrid compounds have weak ionic bonding that easily breaks in polar solvents, causing the compounds to lose their bright phosphorescence properties. To avoid this issue, we adopted the high-vacuum evaporation deposition process for fabricating high-performance PHOLEDs. We fabricated all-vacuum-deposited PHOLEDs with various HTLs, including 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC), tris(4-carbazoyl-9-ylphenyl)amine (TCTA), $N,N'$-di(1-naphthyl)-$N,N'$-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB), and $N,N'$-bis(3-methylphenyl)-$N,N'$-diphenylbenzidine (TPD), emitting layers (ETLs), and emitting layers (EMLs). Atomic force microscopy (AFM) images of the fabricated PHOLEDs (Devices 1–10) are presented in Fig. 5a, revealing the low dispersion of both the valence and conduction bands.
EMLs, and ETLs, and 1 are displayed in Fig. 7. In addition, the electroluminescence performance of all of the devices is shown in Table 1. The atomic force microscopy (AFM) images shown in Fig. 5b–d reveal that the surface roughness values of the mCP:TPBi:1, TCTA:TPBi:1, and TCTA:TmPyPB:1 films were 0.88, 0.70, and 0.74 nm, respectively. This indicates that the doped mCP:TPBi mixed host has a higher surface roughness compared to doped TCTA:TPBi and TCTA:TmPyPB. Lower RMS led to a better contact at the interface and in turn lower $V_{on}$ was observed. Furthermore, devices with different concentrations of (1) and mCP as the host were fabricated to optimise the doping concentration; devices with a 25 wt% concentration of 1 produced the highest EQE (Fig. 7c). Devices 1–4 were fabricated with a configuration of ITO/PEDOT:PSS/TAPC (30 nm)/EML:25 wt% Mn(II) (30 nm)/TPBi (40 nm)/LiF (1 nm)/Al (120 nm).

mCP was used as the host for Device 1 due to its low electron injection barrier and effective host-to-guest energy transfer. TPBi was used along with mCP as mixed hosts in Device 2 to

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Fig. 6 Chemical structures of the organic molecules used in the fabrication of PHOLEDs and the corresponding energy-level diagram. (a) Molecular structure of the HTL materials, 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC), tris(4-carbazoyl-9-ylphenyl)amine (TCTA), N,N’-di(1-naphthyl)-N,N’-diphenyl-(1,1’-biphenyl)-4,4’-diamine (NPB), and N,N’-bis[3-methylphenyl]-N,N’-diphenylbenzidine (TPD), and the ETL materials, 2,2’,2”-(1,3,5-benzinetriyl)-tris(1-phenyl-1H-benzimidazole) (TPBi), bathocuproine (BCP), and 1,3,5-tri(m-pyridin-3-yl)phenyl]benzene (TmPyPB). (b) Energy-level diagram of the HTL and ETL materials.
achieve a balanced charge transport with the EML. Although TPBi and TmPyPB have similar LUMO levels, they have different HOMO (deeper in the case of TmPyPB which also acts as the hole blocking layer) and carrier mobility values leading to different EQEs. Similarly, BCP has a wider injection barrier for electrons and has different electron mobility values. Based on the current density–voltage–luminance (J–V–L) curves (Fig. 7a), it was observed that both Devices 1 and 2 exhibited high turn-on voltages (V_{on}) of 4.7 and 4.5 V with EQE values of 2.26 and 3.03% respectively. The high V_{on} was due to the high injection barrier from the HTL to the EML. Therefore, Device 3 was fabricated with TCTA in the place of mCP in the EML. As expected, this device exhibited a low V_{on} of 3.4 V with an intense green emission and a high EQE of 4.12%. In addition, Device 3 exhibited a high brightness of 1376 cd m^{-2}. Device 4 was fabricated using TmPyPB and TCTA as mixed hosts, producing a low V_{on} of 3.5 V and a high EQE of 3.81%, with a luminance of 908 cd m^{-2}. Furthermore, we also fabricated devices with different HTL and ETL materials to evaluate the performance of 1 as a green emitter. Device 7, with a configuration of ITO/PEDOT:PSS/TPD (30 nm)/TAPC (10 nm)/TCTA:TPBi:25 wt% Mn(II) (30 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (120 nm) exhibited the strongest performance with a high EQE of 5.19% and a brightness of 2399 cd m^{-2}.

Similarly, Device 9 with TmPyPB as the ETL (replacing TPBi) but otherwise having a similar configuration to that of Device 3 exhibited excellent performance as a PHOLED with an exceptional EQE and a current efficiency (CE) of 5.68% and 19.81 cd A^{-1}, respectively. Based on the above results, a champion device with the architecture of ITO/PEDOT:PSS/TPD (30 nm)/TAPC (10 nm)/TCTA:TPBi:25 wt% Mn(II) (30 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (120 nm) was fabricated, producing a remarkably low V_{on} and a high EQE of 3 V and 7.12%, respectively, with an outstanding brightness of 4885 cd m^{-2} (Fig. 8). This represents the highest reported brightness and lowest V_{on} for a PHOLED based on Mn(II) complexes as an emitter (Table S4, ESI†).

The green emissions of the fabricated PHOLEDs were investigated using Commission Internationale de L’Eclairage (CIE) chromaticity coordinates (x, y) (Table 1). All of the devices
exhibited stable and similar color coordinates, indicating that the emissions arose from the 1 dopant. The optimal device (Device 10) produced the most vigorous green emission with color chromaticity coordinates of (0.28, 0.62) (Fig. S6, ESI†) and FWHM of 45 nm. The device lifetime was measured using the configuration of the champion device (Fig. S7, ESI†). The devices exhibited an exceptional operational lifetime with EQE > 65% after 100 hours and excellent reproducibility (Fig. S8, ESI†). Of the 15 devices fabricated for the reproducibility test, 9 had an EQE of ~6%. These findings support the potential use of 1 as a solid-state light emitter in PHOLEDs for practical applications.

Finally, we have also shown the results of solution-processed PHOLEDs for comparison. We have fabricated the PHOLED through a solution process and the device shows a higher turn on voltage of 4.2 V, lower brightness of 1301 cd m\(^{-2}\) as well as lower EQE of 3.77% (Fig. S9 and Table S5, ESI†) than that fabricated using the high-vacuum evaporation deposition process. This is because compound 1 has weak ionic bonding between organic and inorganic parts and loses its phosphorescence properties in polar solvents during device fabrication.

**Conclusion**

We reported for the first time the synthesis of lead-free, green-light-emitting compound 1 using both a solution process and mechanochemical grinding. The SC structure was determined using SC XRD analysis. Each \([\text{MnBr}_4]\) \(^2-\) unit in 1 behaves like a quantum dot at the molecular level, exhibiting quantum confinement and narrow green emission. The bright green phosphorescence of 1 under UV light prompted us to fabricate a green-light-emitting flexible nylon membrane filled with 1 for potential use in light-emitting applications. We also investigated the use of various HTLs, EMLs, and ETLs to produce highly efficient all-vacuum-deposited green LEDs with a narrow green emission using the lead-free, environmentally benign tetrabromide Mn(II) complex (1). The optimal device had an architecture of ITO/PEDOT:PSS/TPD (30 nm)/TAPC (10 nm)/TCTA:TPBi:25 wt% Mn(II) (30 nm)/TmPyPB (40 nm)/LiF (1 nm)/Al (120 nm), exhibiting a very low \(V_{on}\) and high EQE of 3 V and 7.12%, respectively, with an excellent brightness of 4885 cd m\(^{-2}\) due to the smooth surface of the device and balanced charge injection. This is the highest brightness and lowest \(V_{on}\) for PHOLEDs with an ionic hybrid Mn(II) complex as the emitter. Our approach thus demonstrates the feasibility of low-cost, highly efficient PHOLEDs for potential light-emitting applications.

**Author contributions**


**Conflicts of interest**

There are no conflicts to declare.
Acknowledgements

This work was supported by the National Research Foundation (NRF) of Korea (grant no. 2021R1A2B5B01001796, 2019R1I1A1A01048852, 2021R1F1A1062528, and 2021R1A4A5031805) and the Technology Innovation Program (grant no. 20013597) funded by the Ministry of Trade, Industry & Energy.

Notes and references


