Supplementary Information (SI) for Inorganic Chemistry Frontiers.

Supporting Information

Unveiling the Relationship Between the Shortest Mn-Mn Distance in Manganese Halide Hybrids and their Photoluminescence and Scintillation Properties

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EXPERIMENTAL SECTION

Materials. Manganese bromide ($MnBr_2$, >99%, Macklin), acetone (>98.0%, Xilong,), phenethyl bromide (>98.0%, Macklin), N,N-Dimethylformamide (>99.0%, Macklin), methanol (CH_3OH, ≥ 99.5%, Guangzhou Chemical Reagent), 1,7-dibromoheptane (>95.0%, BIDE), 1,8-dibromooctane (>98%, BIDE), 1,9-dibromononane (>98.0%, BIDE), 1,10-dibromodecane (>98.0%, BIDE). All reagents were used as received without further purification.

Preparation of 1,1'-(heptane-1,7-diyl)bis(1,4-diazabicyclo[2.2.2]octan-1-ium) (L_1, ted-C_7-ted) bromide. 20 mmol triethylenediamine (ted, 2.24 g) was dissolved in 25 mL of acetone. Under magnetic stirring, 10 mmol 1,7-dibromoheptane (2.58 g) was dropwise added into the ted acetone solution and stirred for several hours to obtain the white precipitate. The white precipitate was collected by filtration and washed with acetone for three times, and at last dried by vacuum. The yield is 78%.

Preparation of 1,1'-(octane-1,8-diyl)bis(1,4-diazabicyclo[2.2.2]octan-1-ium) (L_2, ted-C_8-ted) bromide. 20 mmol triethylenediamine (ted, 2.24 g) was dissolved in 25 mL of acetone. Under magnetic stirring, 10 mmol 1,8-dibromooctane (2.72 g) was dropwise added into the ted acetone solution and stirred for several hours to obtain the white precipitate. The white precipitate was collected by filtration and washed with acetone for three times, and at last dried by vacuum. The yield is 82%.

Preparation of 1,1'-(nonane-1,9-diyl)bis(1,4-diazabicyclo[2.2.2]octan-1-ium) (L_3, ted-C_9-ted) bromide. 20 mmol triethylenediamine (ted, 2.24 g) was dissolved in 25 mL of acetone. Under magnetic stirring, 10 mmol 1,9-dibromononane (2.86 g) was dropwise added into the ted acetone solution and stirred for several hours to obtain the white precipitate. The white precipitate was collected by filtration and washed with acetone for three times, and at last dried by vacuum. The yield is 83%.

Preparation of 1,1'-(decane-1,10-diyl)bis(1,4-diazabicyclo[2.2.2]octan-1-ium) (L_4, ted-C_{10}-ted) bromide. 20 mmol triethylenediamine (ted, 2.24 g) was dissolved in 25 mL of acetone. Under magnetic stirring, 10 mmol 1,10-dibromodecane (3.00 g) was dropwise added into the ted acetone solution and stirred for several hours to obtain the white precipitate. The white precipitate was collected by filtration and washed with acetone for three times, and at last dried by vacuum. The yield is 91%.

Synthesis of (ted-C_7-ted)$MnBr_4$ (compound 1), (ted-C_8-ted)$MnBr_4$ (compound 2), (ted-C_9-ted) (compound 3), and (ted-C_{10}-ted)$MnBr_4$ (compound 4) crystals. The solution volatilization method was used to prepare the compound **1** single crystals in the heating environment. 0.1 mmol $MnBr_2$ (0.0215 g) was dissolved in 1 mL N,N-

Dimethylformamide and 0.1 mmol obtained (ted-C_7-ted)$MnBr_4$ cation was dissolved in 1 mL methanol, with the aid of sonication to form clear solutions, respectively. The pre-dissolved solutions were filtered separately by using the PTFE filter head with a pore size of 0.22 µm. The above two filtered solutions were mixed in a clean glass bottle and evaporated at 328 K. After several hours, green crystals precipitated at the bottom of the solution. The yield is 90.9% based on Mn. The method of synthesizing compounds **2-4** single crystals were similar to that of compound **1** with only replacing cations ted-C_7-ted with ted-C_8-ted, ted-C_9-ted, and ted-C_{10}-ted.

LC-MS and ^{1}H-NMR analyses. Liquid chromatography-mass spectrometry (LC-MS, Thermo Fisher, UltiMate3000 ISQESI) and 600 M ^{1}H nuclear magnetic resonance spectroscopy (^{1}H-NMR, Bruker Switzerland AG, AVANCE III HD 600) were used to verify the successful synthesis of cation ted-C_7-ted, ted-C_8-ted, ted-C_9-ted, and ted-C_{10}-ted. LC-MS: The cations were prepared into 1.0 mg/mL aqueous solution, and the test was performed under the conditions of direct injection and ESI$^+$ detection mode with the Electron Spray Ionization (ESI) ion source. ^{1}H-NMR: 5-10 mg cations were dissolved in 500 µL Deuterium water.

Microscope images. Metallographic MIT500 microscope was employed to obtain the crystal photomicrographs. The glow micrograph in dark environment is obtained under 365 nm UV light irradiation.

Single-crystal X-ray diffraction (SXRD). Single crystal data were collected from a shock-cooled single crystal at 149.99(10) K on a XtaLAB Synergy R, DW system, HyPix four-circle diffractometer with a Rotating-anode X-ray tube using a mirror as monochromator and a HyPix detector. The diffractometer was equipped with a low temperature device and used Cu Kα radiation (λ = 1.54184 Å). All data were integrated with Crysalispro and a multi-scan absorption correction using SCALE3 ABSPACK was applied. The structure was solved by dual methods using SHELXT and refined by full-matrix least-squares methods against F2 by SHELXL using Olex2.

Powder X-ray diffraction (PXRD). PXRD data was collected on a Rigaku Ultima IV automated diffraction system using 1.54056 Å Cu Kα1 radiation (5-50°, 10°/min) and operating power of 40 kV/40 mA at room temperature (RT).

Thermogravimetric (TG) analysis. TG analysis carried out using a TA instruments Netzsch TG 209F1 Libra system. The samples were heated from room temperature to 800 °C at a rate of 10 °C/min, under a nitrogen flux of 20 mL/min.

Optical diffuse reflectance measurements. Optical diffuse reflectance spectrum was measured on a Hitachi UH5700 spectrophotometer using $BaSO_4$ powder as the reflectance reference. The optical bandgap was calculated by the typical Tauc method by employing the equation: $(\alpha h\nu)^n = A(h\nu - E_g)$, where α, h, ν, A, and E_g are the absorption coefficient, Plank's constant, light frequency, a constant, and band gap. The value of n here is 2 presuming that compounds **1** and **2** are direct transition semiconductor.

Photoluminescence related measurements. Photoluminescence emission (PL) and excitation (PLE) measurements (Xe lamp), and photoluminescence quantum yield (PLQY) test (λ_{ex} = 365 nm, Xe lamp) were carried out on FLS1000 spectrofluorometer (Edinburgh Instruments).

X-ray attenuation efficiency. Attenuation efficiency (%) indicates the specimen's X-rays absorption capacity and can be obtained from the following equation:[1]

$$\mathrm{AE} = (1 - e^{-t\rho d}) \times 100\%$$

where t denotes the total attenuation coefficient, which can acquire from the XCOM database of the National Institute of Standards and Technology (NIST). ρ denotes the density (g/cm^3), and d denotes the thickness (cm).

X-ray scintillation properties. The RL spectra were acquired by using an Edinburgh FLS1000 spectrofluorometer (Edinburgh Instruments) equipped with an X-ray source (TUB00153-9 series, MOXTEK with an W target and 12 W maximum power output), the same X-ray tube was used in all other experiments on scintillation performance.

The light yield of the sample is calculated via the reference method. The commercial Cerium-doped Lutetium Aluminum Garnet (LuAG:Ce) crystal was used as standard references. The sample was loaded into a cylindrical quartz vessel and subsequently placed inside the integrating sphere. The light emitted by the sample under X-ray irradiation was collected by a fiber-coupled calibration integrating sphere and its corresponding absolute photon number was obtained by an Ocean Optics portable spectrometer (QE_{pro}). The photon measured was normalized to 100% X-ray attenuation using the following formula:[1]

$$\text{RL Intensity}_{\text{normalized}} = \frac{\text{RL Intensity}_{\text{measured}}}{\text{AE}(\%)}$$

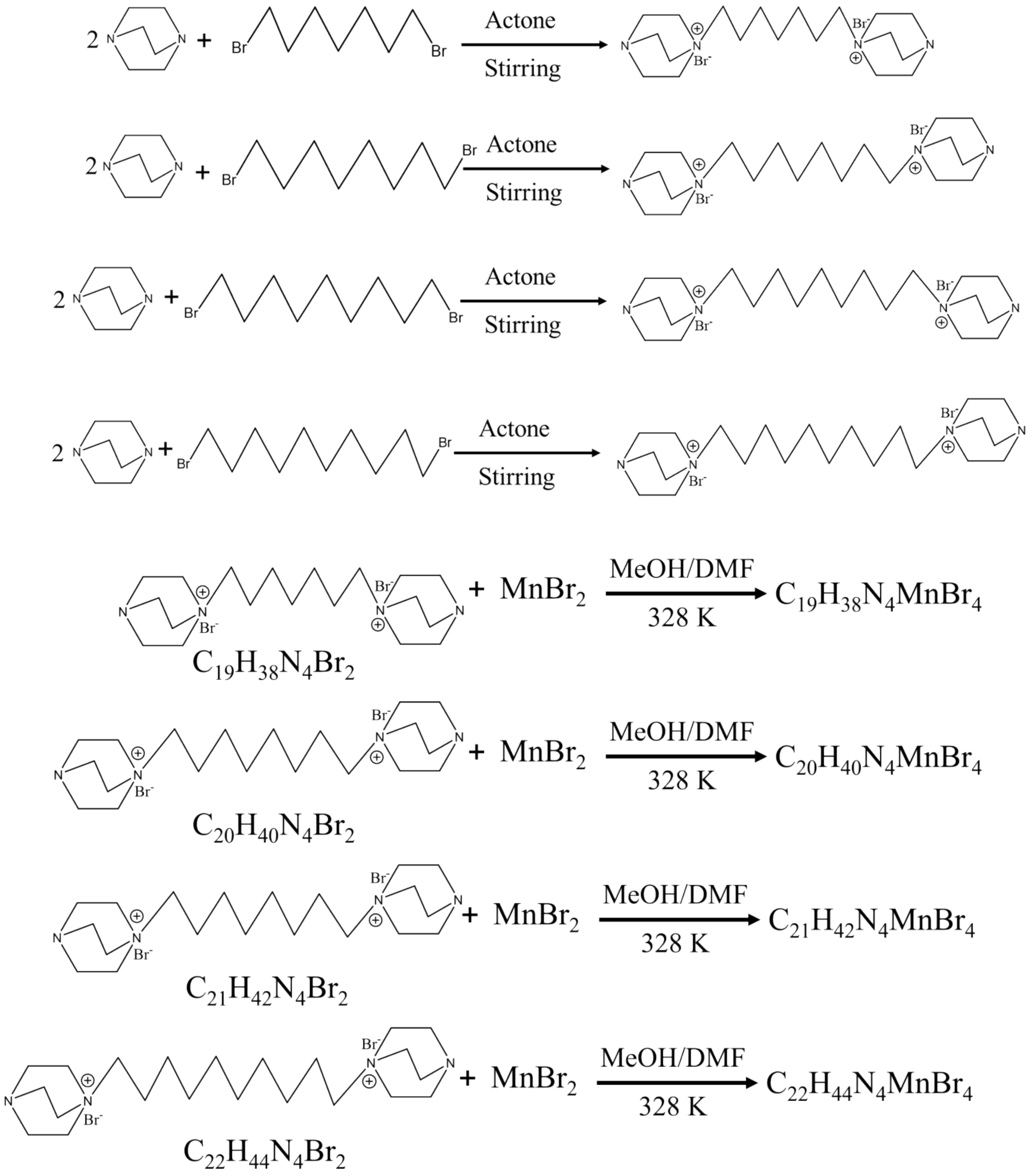
where AE(%) denotes the attenuation efficiency (%) of sample at its thickness. The light yield (LY) can be calculated as followed:[1]

$$\text{LY}_{\text{sample}} = \text{LY}_{\text{LuAG:Ce}} \times \frac{\text{RL Intensity}_{\text{normalized}}(\text{Sample})}{\text{RL Intensity}_{\text{normalized}}(\text{LuAG:Ce})}$$

the crystal samples were obtained by hydraulically pressing small single crystals into wafer, and the glass sample was obtained by in-situ melt quenching of crystals inside the quartz vessel.

Fabrication of the White light-emitting diode (WLED). First, $(\text{pe-ted})_2MnBr_4$ green phosphor and $(Sr,Ca)AlSiN_3:Eu$ commercial red phosphor (Shenzhen Looking Long Technology Co., Ltd., China) were mixed and grinded, and then blended well with UV curing adhesive. The blended phosphors were dropped on top of the InGaN blue LED chips (450 nm, 3 V, 700 mA) and dried in air to form white LEDs. The optoelectronic properties of the white LED, such as emission spectra, correlated color temperature (CCT), CIE color coordinates, external quantum efficiency (EQE), and luminous efficiency were obtained using on a LED Opto-Electronic Analyzer (ATA-500, EVERFINE Corporation, China).

Scheme S1. Schematic diagrams of the synthesis process of the cations (ted-C_7-ted)Br_2, (ted-C_8-ted)Br_2, (ted-C_9-ted)Br_2, (ted-C_{10}-ted)Br_2, 0D (ted-C_7-ted)$MnBr_4$, (ted-C_8-ted)$MnBr_4$, (ted-C_9-ted)$MnBr_4$ and (ted-C_{10}-ted)$MnBr_4$, respectively.



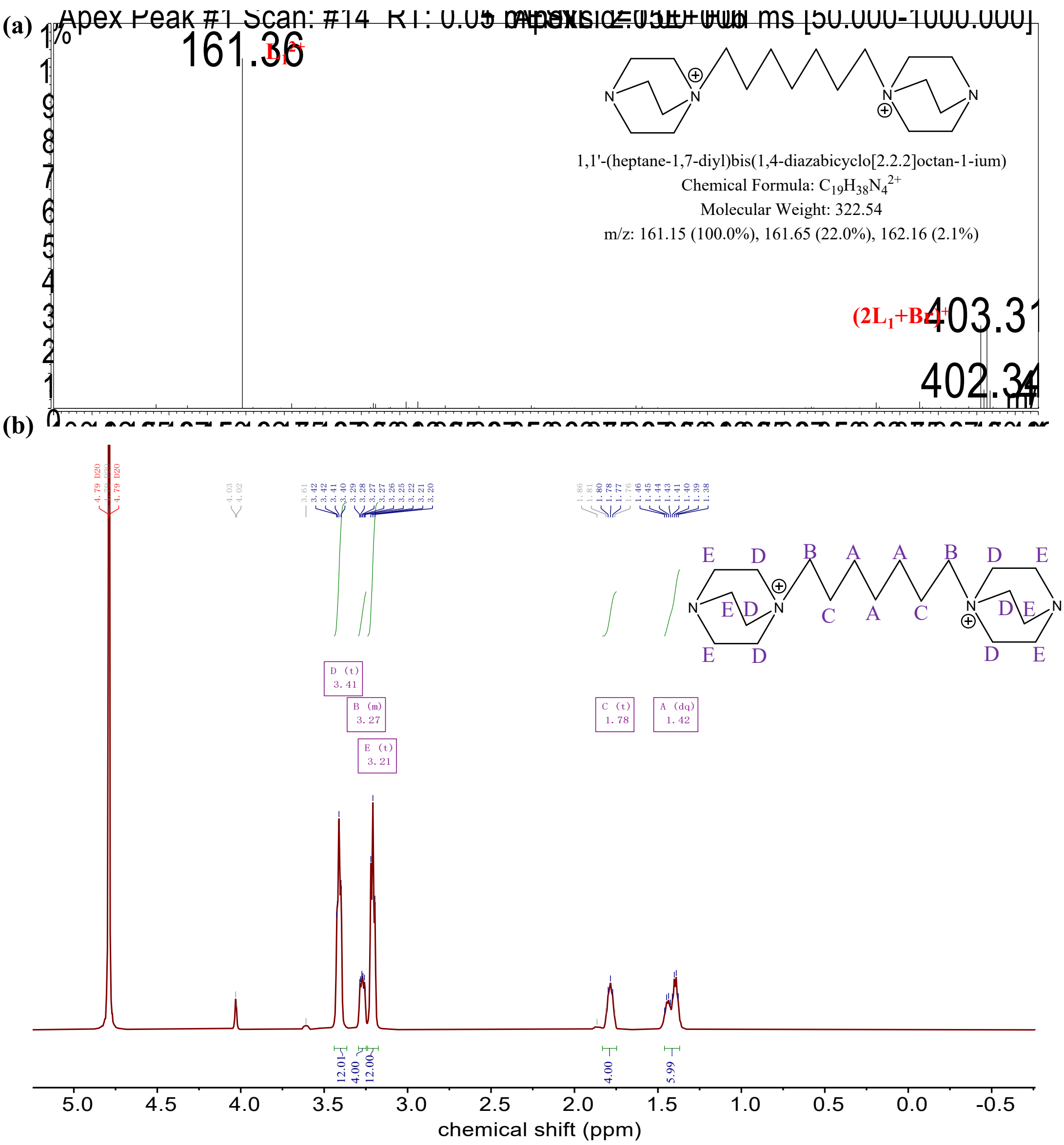


Figure S1. MS spectrum (a) and ^{1}H-NMR spectrum (b) of the cation 1,1'-(heptane-1,7-diyl)bis(1,4-diazabicyclo[2.2.2]octan-1-ium) (L_1, ted-C_7-ted) bromide, inset is the structure plot and detailed information. ^{1}H NMR (600 MHz, Deuterium Oxide) δ 3.41 (t, J = 7.8 Hz, 12H), 3.29 – 3.25 (m, 4H), 3.21 (t, J = 7.5 Hz, 12H), 1.78 (t, J = 8.3 Hz, 4H), 1.42 (dq, J = 28.4, 7.2 Hz, 6H).

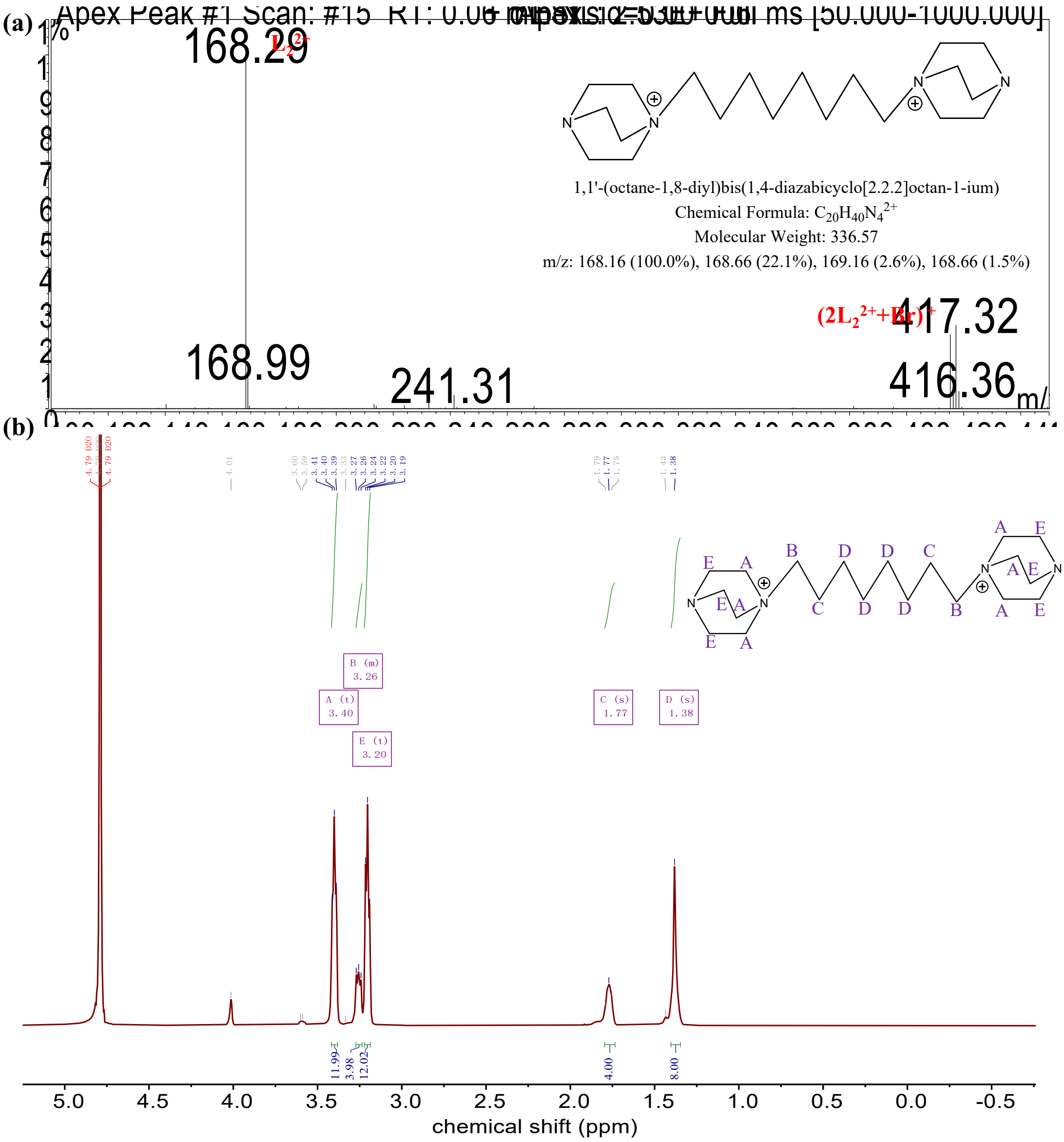


Figure S2. MS spectrum (a) and ^{1}H-NMR spectrum (b) of the cation of 1,1'-(octane-1,8-diyl)bis(1,4-diazabicyclo[2.2.2]octan-1-ium) (L_2, ted-C_8-ted) bromide, inset is the structure plot and detailed information. ^{1}H NMR (600 MHz, Deuterium Oxide) δ 3.40 (t, *J* = 7.4 Hz, 12H), 3.27 – 3.24 (m, 4H), 3.20 (t, *J* = 7.6 Hz, 12H), 1.77 (s, 4H), 1.38 (s, 8H).

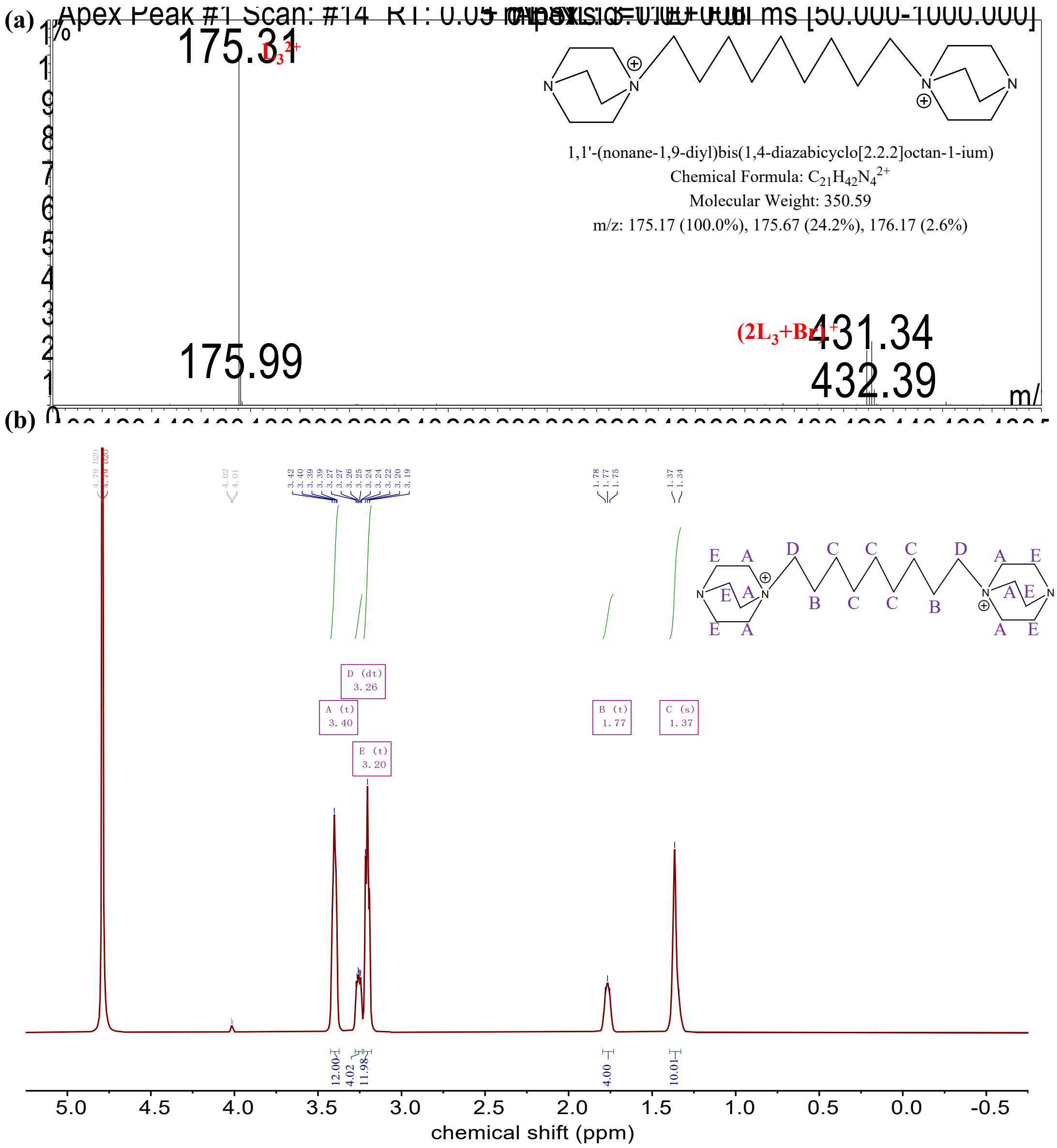


Figure S3. MS spectrum (a) and ^{1}H-NMR spectrum (b) of the cation of 1,1'-(nonane-1,9-diyl)bis(1,4-diazabicyclo[2.2.2]octan-1-ium) (L_3, ted-C_9-ted) bromide, inset is the structure plot and detailed information. ^{1}H NMR (600 MHz, Deuterium Oxide) δ 3.40 (t, *J* = 7.5 Hz, 12H), 3.27 – 3.23 (m, 4H), 3.20 (t, *J* = 7.5 Hz, 12H), 1.76 (t, *J* = 8.6 Hz, 4H), 1.34 (d, *J* = 25.6 Hz, 12H).

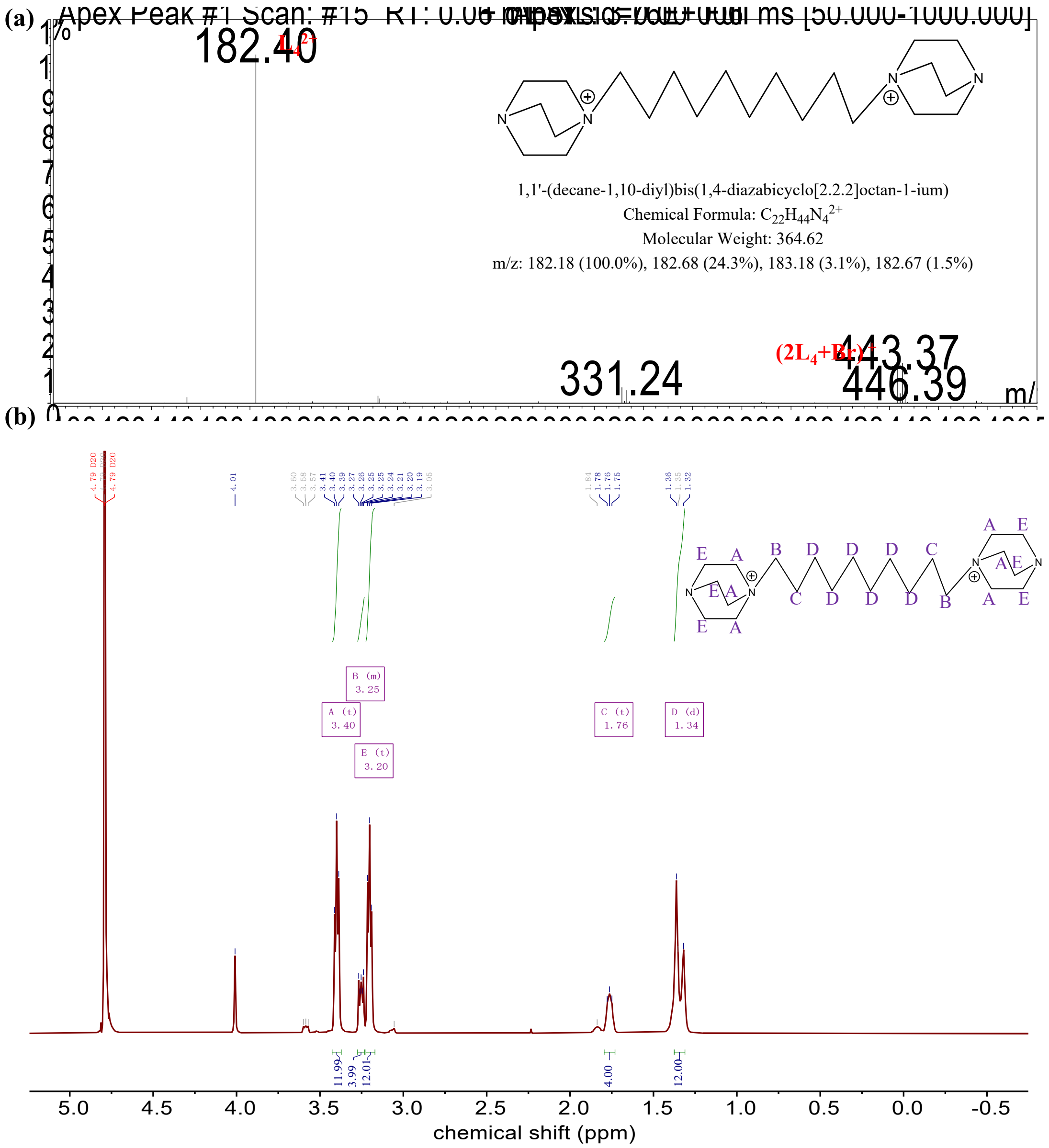


Figure S4. MS spectrum (a) and ^{1}H-NMR spectrum (b) of the cation of 1,1'-(decane-1,10-diyl)bis(1,4-diazabicyclo[2.2.2]octan-1-ium) (L_4, ted-C_{10}-ted) bromide, inset is the structure plot and detailed information. ^{1}H NMR (600 MHz, Deuterium Oxide) δ 3.40 (t, *J* = 7.2 Hz, 12H), 3.26 (dt, *J* = 11.7, 3.7 Hz, 4H), 3.20 (t, *J* = 7.5 Hz, 12H), 1.77 (t, *J* = 8.4 Hz, 4H), 1.37 (s, 10H).

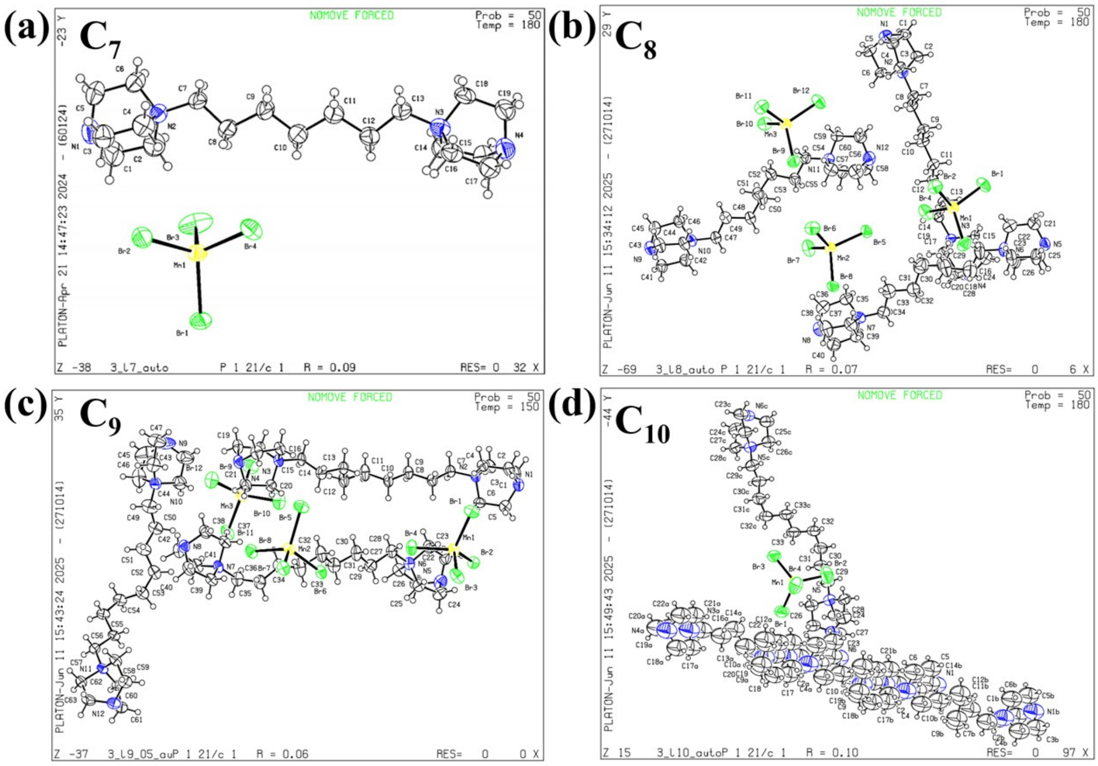


Figure S5. Crystal-structure diagram of (a) compound **1**, (b) compound **2**, (c) compound **3** and (d) compound **4**, respectively.

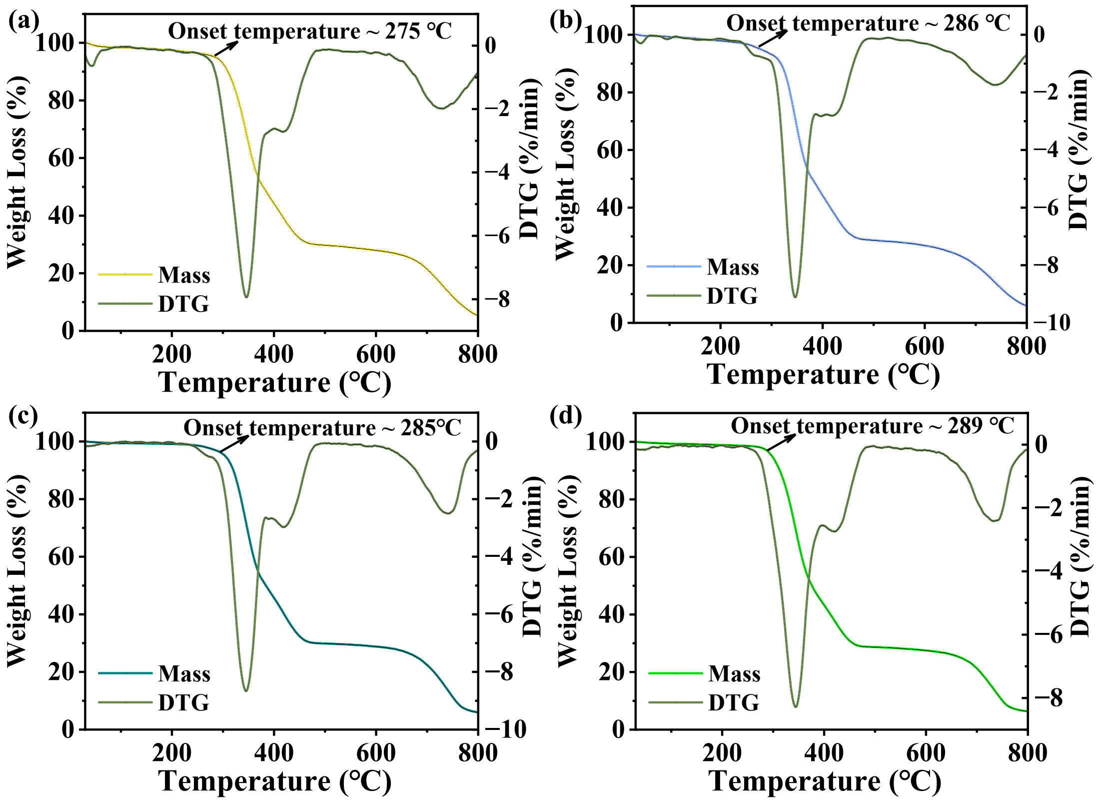


Figure S6. Thermogravimetric (TG) and derivative thermogravimetry (DTG) analysis of (a) compound **1**, (b) compound **2**, (c) compound **3** and (d) compound **4**, respectively.

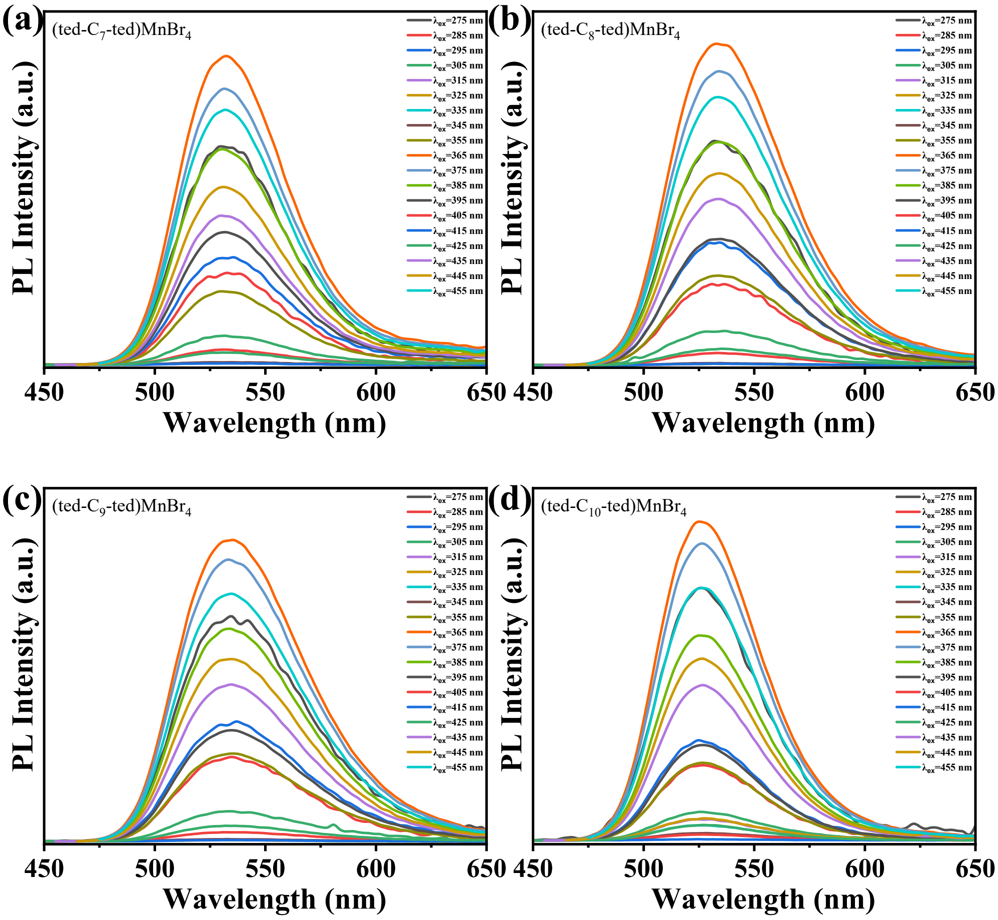


Figure S7. Excitation-wavelength-dependent PL spectra of (a) compound **1**, (b) compound **2**, (c) compound **3** and (d) compound **4**, respectively.

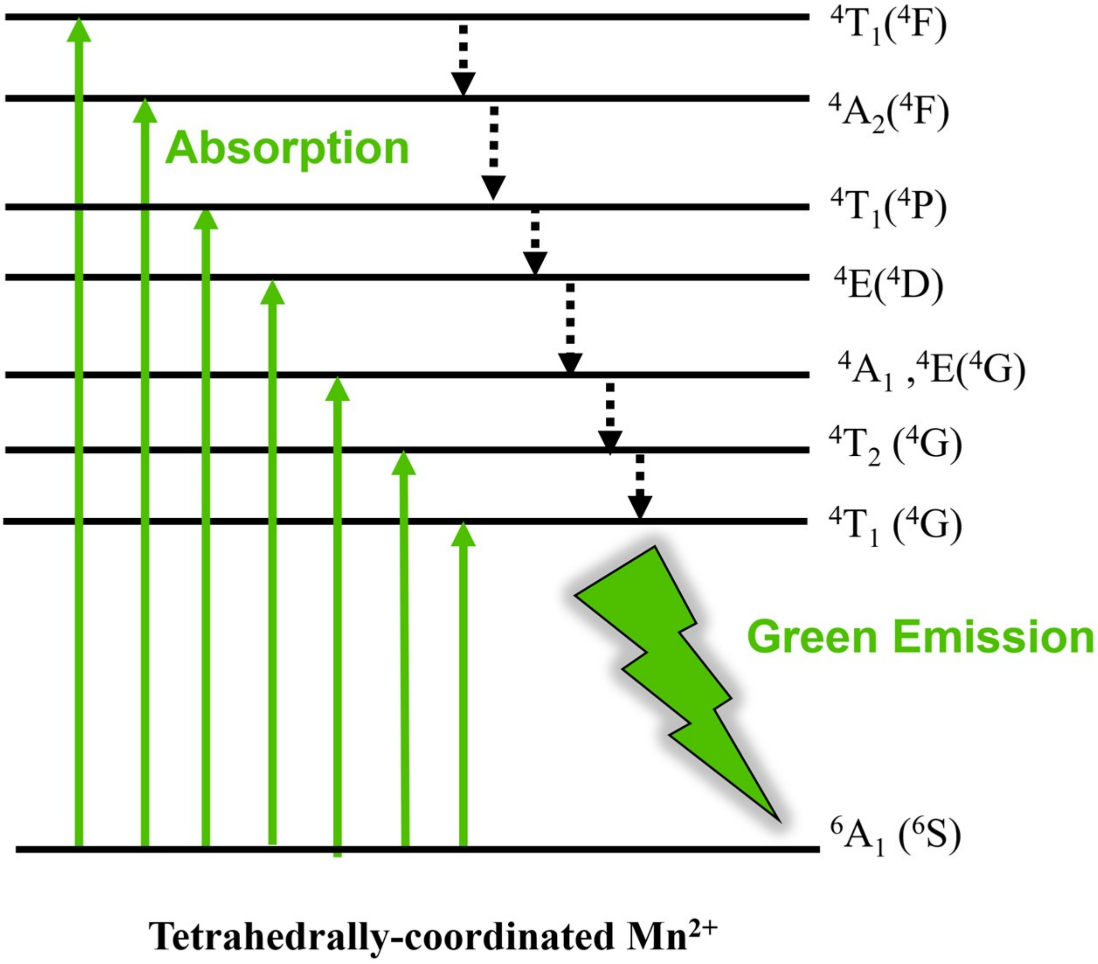


Figure S8. Schematic diagram showing the energy adsorption, migration, and emission process in tetrahedrally coordinated Mn^{2+} ion.

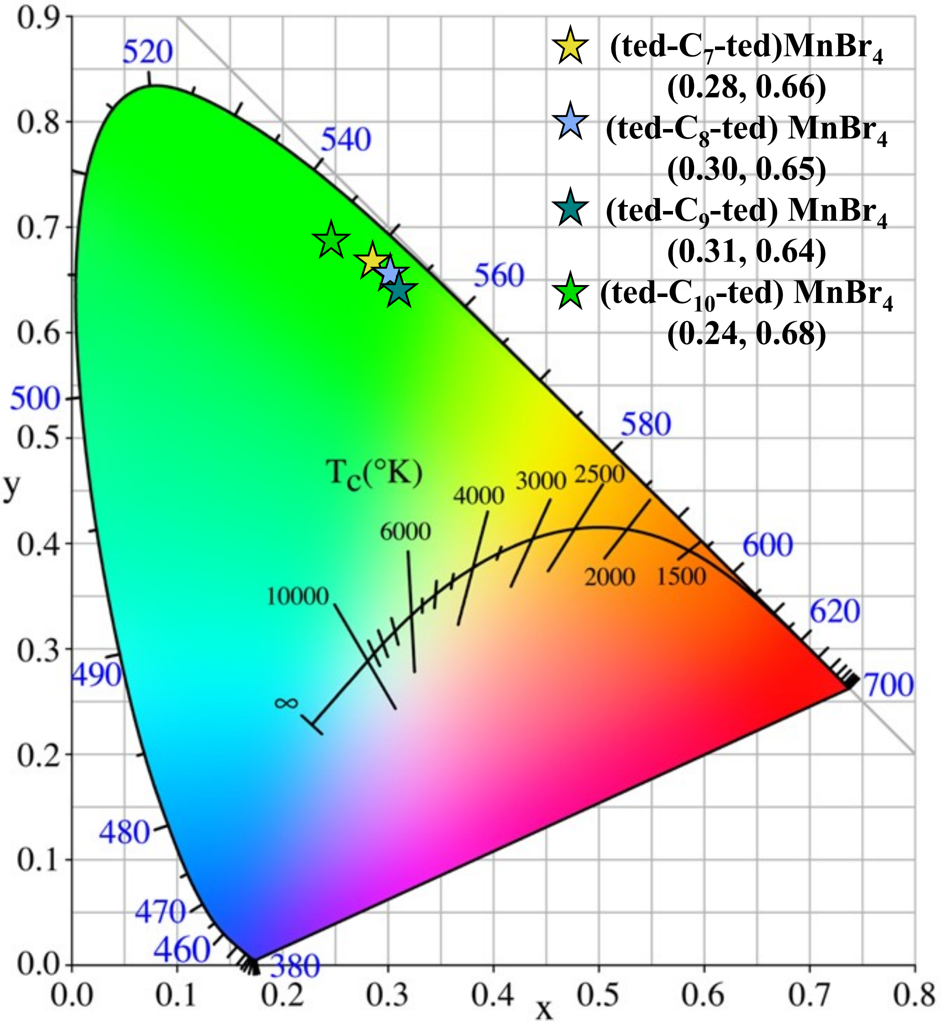


Figure S9. The Commission Internationale de l'Eclairage (CIE) chromaticity coordinates of compounds **1**-**4**, respectively. (yellow denote compound **1**; light blue denote compound **2**; dark cyan denote compound **3**; green denote compound **4**).

Table S1. Crystal data and structure refinement for compounds **1-4**.

Compound	(ted-C_7-ted)$MnBr_4$	(ted-C_8-ted)$MnBr_4$	(ted-C_9-ted)$MnBr_4$	(ted-C_{10}-ted)$MnBr_4$
Empirical formula	$C_{19}H_{38}Br_4MnN_4$	$C_{20}H_{40}Br_4MnN_4$	$C_{21}H_{42}Br_4MnN_4$	$C_{22}H_{44}Br_4MnN_4$
Formula weight	697.11	711.14	725.16	739.19
Temperature [K]	180.00(10)	180.00(10)	150.00(10)	179.99(10)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group (number)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/c$ (14)	$P2_1/c$ (14)
a [Å]	11.7423(4)	14.8046(7)	18.40270(19)	10.1580(6)
b [Å]	13.7327(5)	34.8846(13)	11.66512(16)	28.8285(11)
c [Å]	16.2406(6)	17.0954(6)	40.1595(5)	10.2760(4)
α [°]	90	90	90	90
β [°]	93.819(3)	112.379(5)	101.1121(11)	95.380(5)
γ [°]	90	90	90	90
Volume [Å^3]	2613.04(17)	8164.0(6)	8459.40(18)	2996.0(2)
Z	4	12	12	4
ρ_{calc} [gcm^{-3}]	1.772	1.736	1.708	1.639
μ [mm^{-1}]	6.635	6.372	10.555	9.946
F(000)	1380	4236	4332	1476
Radiation	Mo K_α (λ=0.71073 Å)	Mo K_α (λ=0.71073 Å)	Cu K_α (λ=1.54184 Å)	Cu K_α (λ=1.54184 Å)
2θ range [°]	4.57 to 61.25 (0.70 Å)	4.35 to 61.47 (0.70 Å)	4.48 to 132.89 (0.84 Å)	6.13 to 133.50 (0.84 Å)
Index ranges	$-16 \le h \le 12$ $-18 \le k \le 19$ $-20 \le l \le 20$	$-20 \le h \le 16$ $-47 \le k \le 47$ $-24 \le l \le 24$	$-21 \le h \le 21$ $-13 \le k \le 8$ $-47 \le l \le 47$	$-11 \le h \le 12$ $-34 \le k \le 33$ $-12 \le l \le 9$
Reflections collected	27377	50503	99178	28146
Independent reflections	6704 R_{int} = 0.0505 R_{sigma} = 0.0579	19549 R_{int} = 0.0608 R_{sigma} = 0.0905	14648 R_{int} = 0.0626 R_{sigma} = 0.0322	5139 R_{int} = 0.0830 R_{sigma} = 0.0483
Data / Restraints / Parameters	6704/156/253	19549/486/784	14648/0/811	5139/624/247
Goodness-of-fit on F^2	1.115	0.981	1.088	1.115
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0933 wR_2 = 0.1734	R_1 = 0.0729 wR_2 = 0.1818	R_1 = 0.0639 wR_2 = 0.1600	R_1 = 0.1049 wR_2 = 0.2730
Final *R* indexes [all data]	R_1 = 0.1436 wR_2 = 0.1913	R_1 = 0.1516 wR_2 = 0.2176	R_1 = 0.0758 wR_2 = 0.1680	R_1 = 0.1323 wR_2 = 0.2937
Largest	1.75/-1.01	2.55/-1.24	2.03/-0.54	1.14/-0.62

peak/hole [$e\text{Å}^{-3}$]	

Table S2. Selected bond length of compound **1**.

Atom–Atom	Length [Å]
Br1–Mn1	2.5140(14)
Br2–Mn1	2.5070(15)
Br3–Mn1	2.4850(16)
Br4–Mn1	2.4932(16)

Table S3. Selected bond length of compound **2**.

Atom–Atom	Length [Å]
Br1–Mn1	2.4975(14)
Br2–Mn1	2.4959(14)
Br3–Mn1	2.4983(15)
Br4–Mn1	2.5030(15)
Br5–Mn2	2.5007(14)
Br6–Mn2	2.4994(13)
Br7–Mn2	2.4903(14)
Br8–Mn2	2.5253(13)
Br9–Mn3	2.4885(15)
Br10–Mn3	2.5044(14)
Br11–Mn3	2.5043(13)
Br12–Mn3	2.4909(15)

Table S4. Selected bond length of compound **3**.

Atom–Atom	Length [Å]
Br1–Mn1	2.5213(12)
Br2–Mn1	2.5053(11)
Br3–Mn1	2.4804(12)
Br4–Mn1	2.4911(12)
Br5–Mn2	2.5057(13)
Br6–Mn2	2.5007(13)
Br7–Mn2	2.5289(13)
Br8–Mn2	2.4993(12)
Br9–Mn3	2.4835(13)
Br10–Mn3	2.4874(13)
Br11–Mn3	2.5271(14)
Br12–Mn3	2.4993(14)

Table S5. Selected bond length of compound **4**.

Atom–Atom	Length [Å]
Br1–Mn1	2.492(2)
Br2–Mn1	2.482(3)
Br3–Mn1	2.498(2)
Br4–Mn1	2.485(2)