Supporting Information

Enhancing Photoluminescence Efficiencies of Hybrid Manganese Halides Through Rational Structural Design Strategy

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Experimental Section

Materials

All chemicals were purchased and used without any further purification: 1-(2-Dimethylaminoethyl)-4-methylpiperazine (DMAEMP, 98%, Macklin), 1-propyl-2,3-dimethylimidazolium chloride ([PDMIm]Cl, 99%, Licp), 1-methyl-piperazine (MP, 99%, Aladdin), N,N'-dimethyl-piperazine (DMP, 98%, Aladdin), 1-ethyl-piperazine (EP, 98%, Aladdin), manganese chloride tetrahydrate ($MnCl_2·4H_2O$) (Aladdin), ethanol absolute (99.7%, SCR), hydrochloric acid (36%, SCR), N,N-Dimethylacetamide (DMA) (99%, SCR).

Synthesis of [DMAEMP]$MnCl_4$. A mixture of 0.1 g $MnCl_2·4H_2O$, 0.094 g DMAEMP, 5 mL ethanol absolute and 0.5 mL hydrochloric acid was added into a 25 mL glass bottle followed by 15 min stirring for sufficient dispersion. The glass bottle was then sealed and heated at 80 °C for 5 day. After 5 day, green crystals of [DMAEMP]$MnCl_4$ were isolated after vacuum filtration, and washed with ethanol three times. The colorless crystals of [DMAEMP]$MnCl_4$ were obtained with a yield of 67% based on $MnCl_2·4H_2O$. Elemental analysis calculated for $C_{16}N_4H_{30}MnCl_4$: C, 29.21%, N, 11.36%, H, 6.26%; found: C, 29.26%; N, 11.28%, H, 6.29%.

Synthesis of [PDMIm]$_2$$MnCl_4$. Single crystals of [PDMIm]$_2$$MnCl_4$ were grown from ethanol solution with [PDMIm]Cl and $MnCl_2·4H_2O$ as raw materials. The stoichiometric mixture of $MnCl_2·4H_2O$ (0.198 g) and [PDMIm]Cl (0.349 g) was dissolved in 5 mL of ethanol solution and heated to 100 °C under continuous stirring, forming a colorless solution, which was slowly cooled to room temperature. One day later the target compound was obtained. The colorless crystals of [PDMIm]$_2$$MnCl_4$ were obtained with a yield of 61% based on $MnCl_2·4H_2O$. Elemental analysis calculated for $C_{16}N_4H_{30}MnCl_4$: C, 40.44 %, N, 11.79 %, H, 6.36 %; found: C, 40.52 %, N, 11.83 %,

H, 6.24 %.

Synthesis of $[MP]_2MnCl_4 \cdot 2Cl$. A mixture of 0.1 g $MnCl_2 \cdot 4H_2O$, 0.133 g MP, 5 mL ethanol and 0.5 mL hydrochloric acid was added into a 25 mL glass bottle followed by 15 min stirring for sufficient dispersion. The glass bottle was then sealed and heated at 80 °C for 5 days. After 5 days, slight green crystals of $[MP]_2MnCl_4 \cdot 2Cl$ were isolated after vacuum filtration, and washed with ethanol. The colorless crystals of $[MP]_2MnCl_4 \cdot 2Cl$ were obtained with a yield of 42% based on $MnCl_2 \cdot 4H_2O$. Elemental analysis calculated for $C_{16}N_4H_{30}MnCl_4$: C, 25.45%, N, 11.87%, H, 5.98 %; found: C, 25.39%, N, 11.92%; H, 6.03%.

Synthesis of $[DMP]MnCl_4$. A mixture of 0.1 g $MnCl_2 \cdot 4H_2O$, 0.111 g DMP, 5 mL ethanol and 0.5 mL hydrochloric acid was added into a 25 mL glass bottle followed by 15 min stirring for sufficient dispersion. The glass bottle was then sealed and heated at 80 °C for 5 days. After 5 days, slight green crystals of $[DMP]MnCl_4$ were isolated after vacuum filtration, and washed with ethanol three times. The colorless crystals of $[DMP]MnCl_4$ were obtained with a yield of 31% based on $MnCl_2 \cdot 4H_2O$. Elemental analysis calculated for $C_{16}N_4H_{30}MnCl_4$: C, 23.03%; N, 8.95%; H, 5.15%; found: C, 22.97%; N, 9.11%; H, 5.02%.

Synthesis of $[EP]MnCl_4$. A mixture of 0.1 g $MnCl_2 \cdot 4H_2O$, 0.112 g EP, 5 mL ethanol absolute and 0.5 mL hydrochloric acid was added into a 25 mL glass bottle followed by 15 min stirring for sufficient dispersion. The glass bottle was then sealed and heated at 80 °C for 5 days. After 5 day, slight green crystals of $[EP]MnCl_4$ were isolated after vacuum filtration, and washed with ethanol. The colorless crystals of $[EP]MnCl_4$ were obtained with a yield of 45% based on $MnCl_2 \cdot 4H_2O$. Elemental analysis calculated for $C_{16}N_4H_{30}MnCl_4$: C, 23.03%; N, 8.95%; H, 5.15%; found: C, 23.01%; N, 8.99%; H, 5.12%.

Characterizations

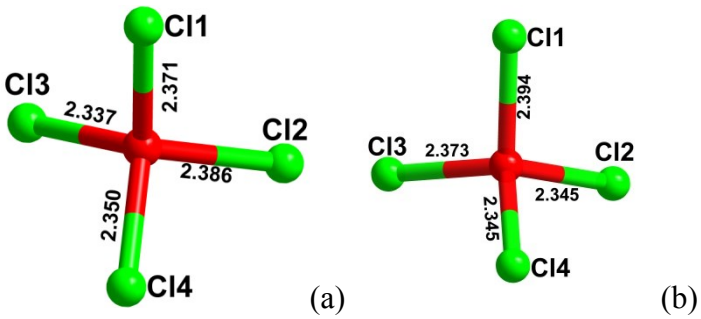
Single crystal X-Ray diffraction (SCXRD): A Bruker D8 diffractometer with Mo *Kα* radiation (λ = 0.71073Å) was utilized for single crystal X-ray diffraction. The APEX3 software was used for data reduction and multi-scans absorption correction. SHELXTL software was applied to solve crystal structure using direct methods. And the structure was refined by the full matrix method based on F^2 using the package SHELXTL-97. All nonhydrogen atoms of the structure were refined with anisotropic thermal parameters. Symmetry analysis on the model using PLATON revealed that no obvious space group change was needed.

Powder X-ray diffraction (PXRD): A Rigaku MiniFlex Ⅱ diffractometer equipped with a Cu *K*α radiation was used for powder X-ray diffraction (PXRD) at room temperature. Collection 2θ range from 5° to 60° and step size is 5°/min.

Thermogravimetric analysis (TGA): Thermogravimetric analysis (TGA) measurement was implemented on a Netzsch STA 449C thermal analyser with a heating rate of 20 K/min from 35 K to 800 K under N_2 atmosphere.

Photoluminescent property characterizations: The PL spectra were performed on an Edinbergh FLS980 fluorescence spectrometer. The photoluminescence quantum efficiency (PLQE) was achieved by incorporating an integrating sphere into the FLS980 spectrofluorometer. The PLQE was calculated based on the equation: $\eta_{QE} = I_S/(E_R\text{-}E_S)$, which I_S represents the luminescence emission spectrum of the sample, E_R is the spectrum of the excitation light from the empty integrated sphere (without the sample), and E_S is the excitation spectrum for exciting the sample. The time-resolved decay data were carried out using the Edinburgh FLS980 fluorescence spectrometer with a picosecond pulsed diode laser. The average lifetime was obtained by exponential fitting.

Fabrication of colorful Phosphors and white LED. The white LEDs were fabricated by integrating the green [DMAEMP]$MnCl_4$ phosphor, commercial red phosphor of $K_2SiF_6:Mn^{4+}$ (Shenzhen looking long Technology Co., Ltd, China), commercial blue phosphor of $BaMgAl_{10}O_{17}:Eu^{2+}$ (Shenzhen looking long Technology Co., Ltd, China) and UV chip (365 nm, 3V, 300 mA, Shenzhen looking long Technology Co., Ltd, China). The phosphors were thoroughly mixed using an epoxy resin and the obtained mixture was coated on the LED chip. The electrical photoelectric properties, such as, the emission spectrum, color temperature (CCT), color rendering index (R_a) and CIE color coordinate of the LED were collected using an integrating sphere spectroradiometer system (EVERFINE HAAS-2000). The as-fabricated white LEDs were operated at 3 V in varied drive currents from 20 to 120 mA.



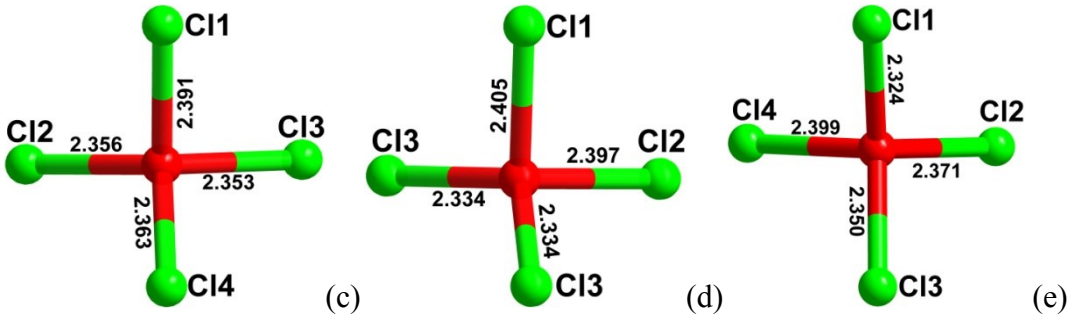
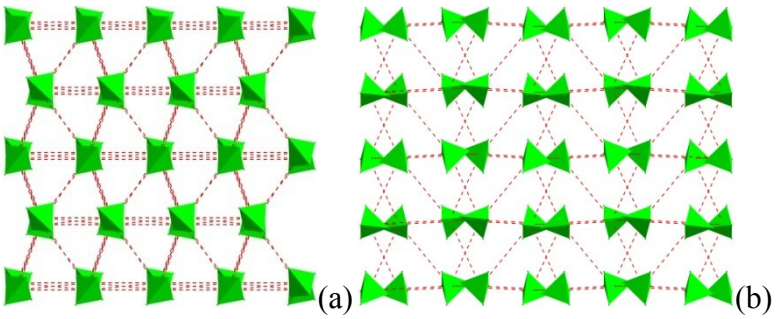


Fig. S1. The detailed coordination configurations of $[MnCl_4]^{2-}$ tetrahedrons in compounds [DMAEMP]$MnCl_4$ (a), $[PDMIm]_2MnCl_4$ (b), $[MP]_2MnCl_4{\cdot}2Cl$ (c), [DMP]$MnCl_4$ (d) and [EP]$MnCl_4$ (e).



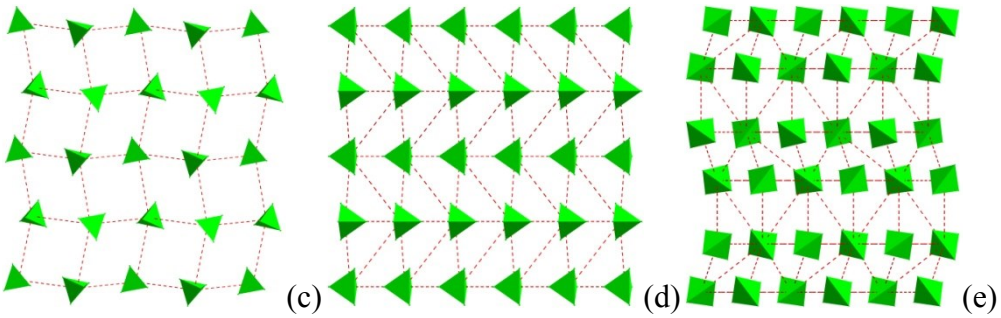


Fig. S2. The stacking manner of $[MnCl_4]^{2-}$ tetrahedrons in compounds $[DMAEMP]MnCl_4$ (a), $[PDMIm]_2MnCl_4$ (b), $[MP]_2MnCl_4{\cdot}2Cl$ (c), $[DMP]MnCl_4$ (d) and $[EP]MnCl_4$ (e). The green polyhedron represent the $[MnCl_4]^{2-}$ units.

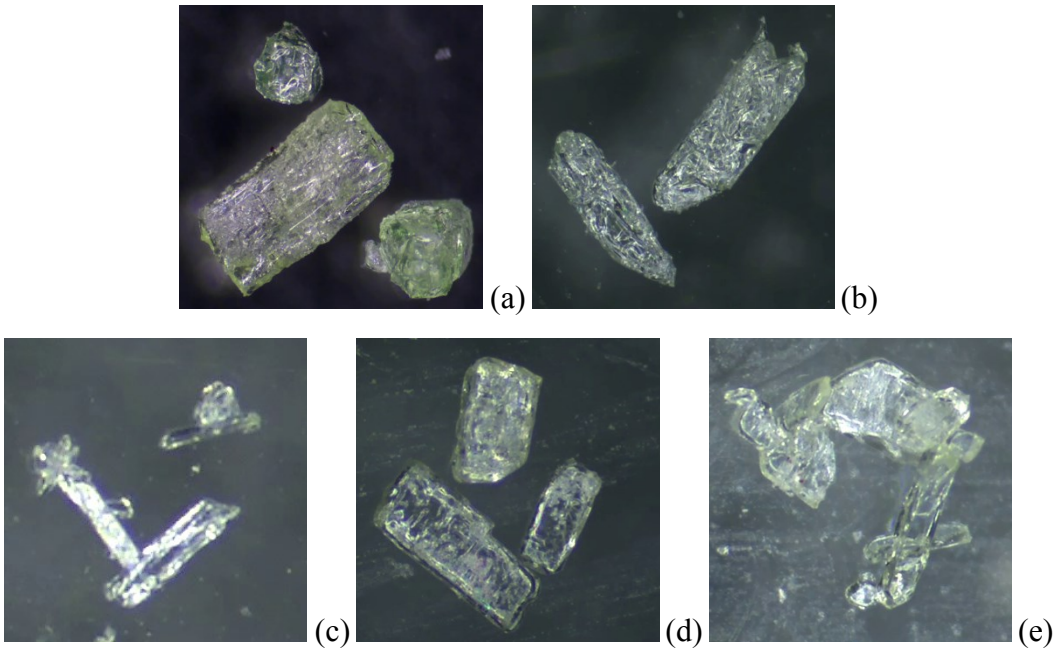


Fig. S3. The photo images of bulk crystals in compounds $[DMAEMP]MnCl_4$ (a), $[PDMIm]_2MnCl_4$ (b), $[MP]_2MnCl_4{\cdot}2Cl$ (c), $[DMP]MnCl_4$ (d) and $[EP]MnCl_4$ (e).

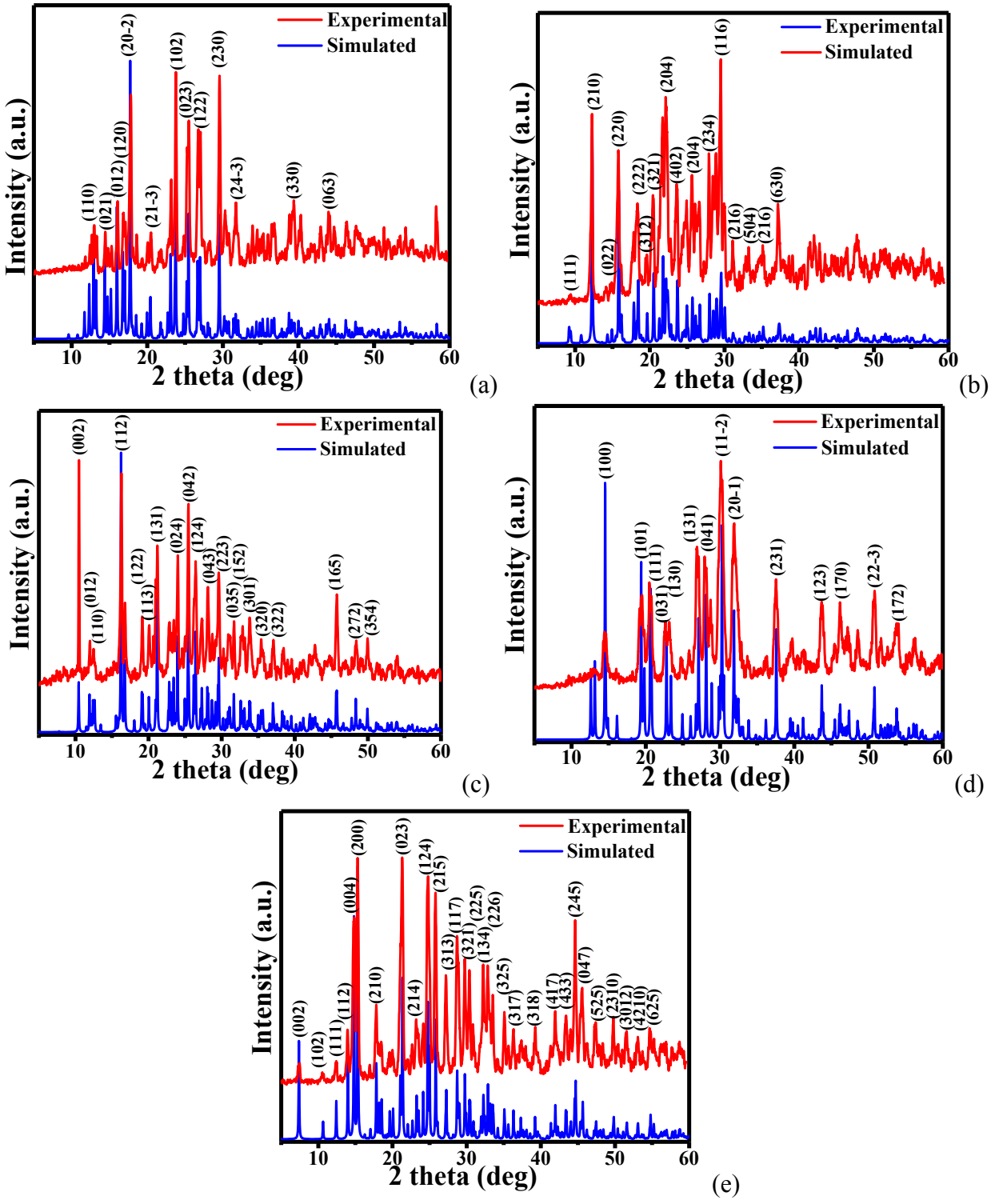


Fig. S4. The simulated and experimental PXRD patterns of $[DMAEMP]MnCl_4$ (a), $[PDMIm]_2MnCl_4$ (b), $[MP]_2MnCl_4 \cdot 2Cl$ (c), $[DMP]MnCl_4$ (d) and $[EP]MnCl_4$ (e).

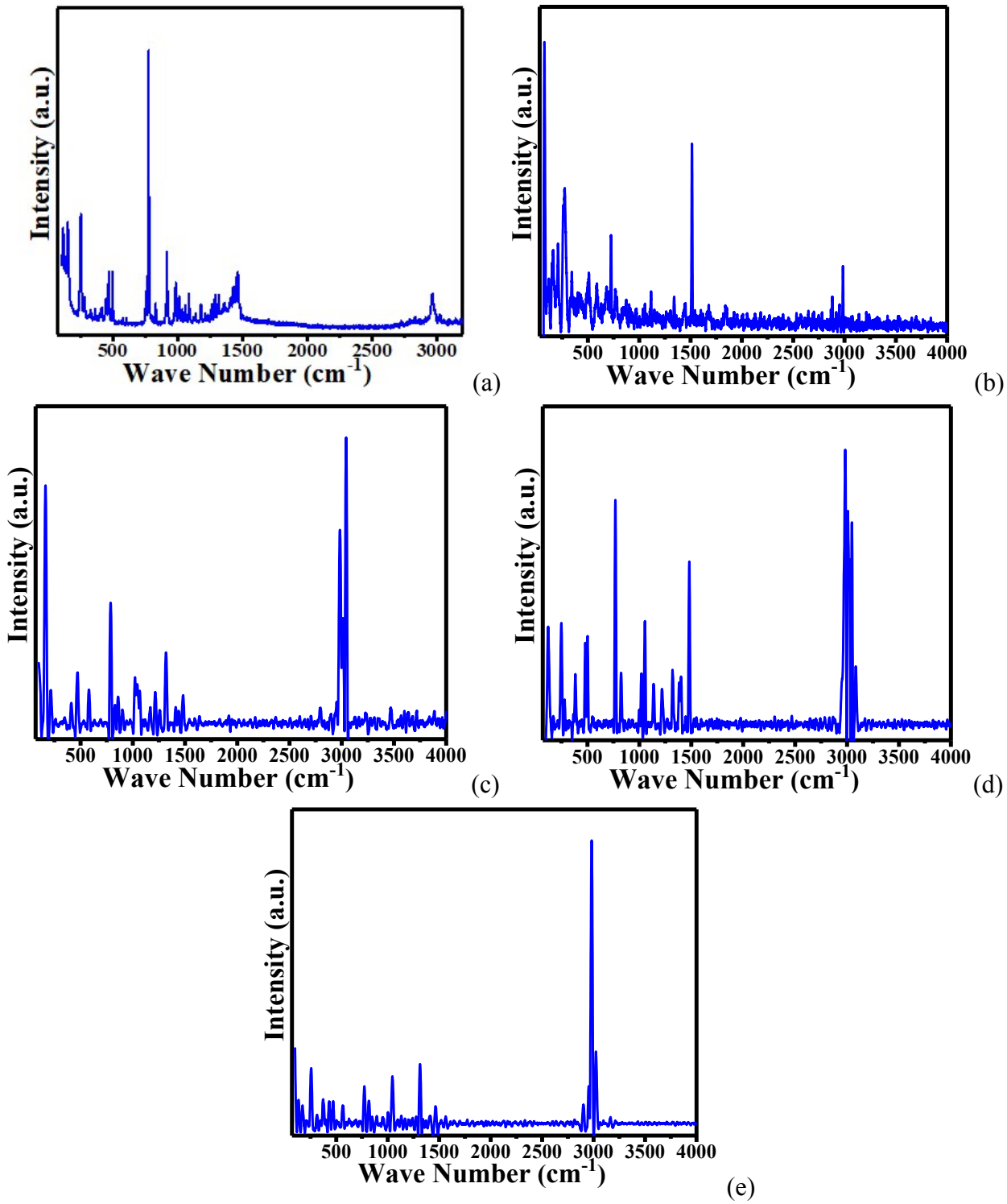


Fig. S5. Raman spectrum of [DMAEMP]$MnCl_4$ (a), $[PDMIm]_2MnCl_4$ (b), $[MP]_2MnCl_4{\cdot}2Cl$ (c), [DMP]$MnCl_4$ (d) and [EP]$MnCl_4$ (e).

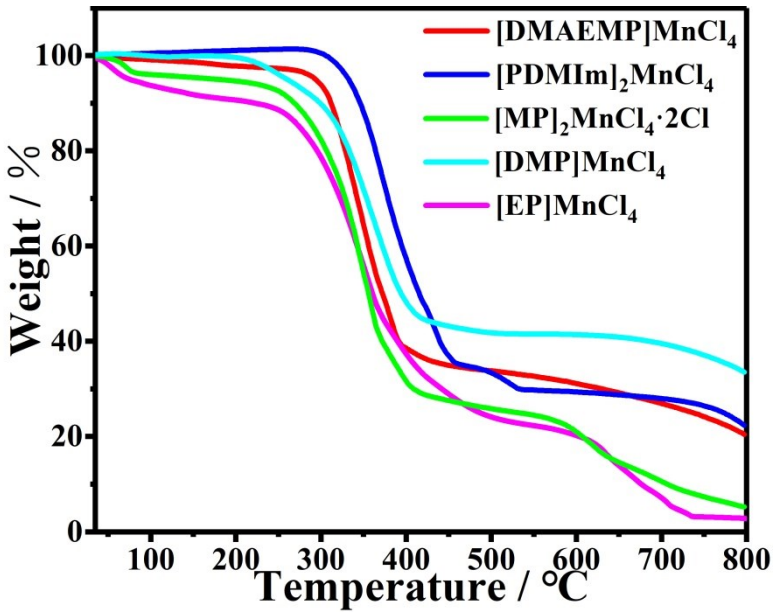


Fig. S6. The thermogravimetric analyses (TGA) curves for $[DMAEMP]MnCl_4$, $[PDMIm]_2MnCl_4$, $[MP]_2MnCl_4{\cdot}2Cl$, $[DMP]MnCl_4$ and $[EP]MnCl_4$

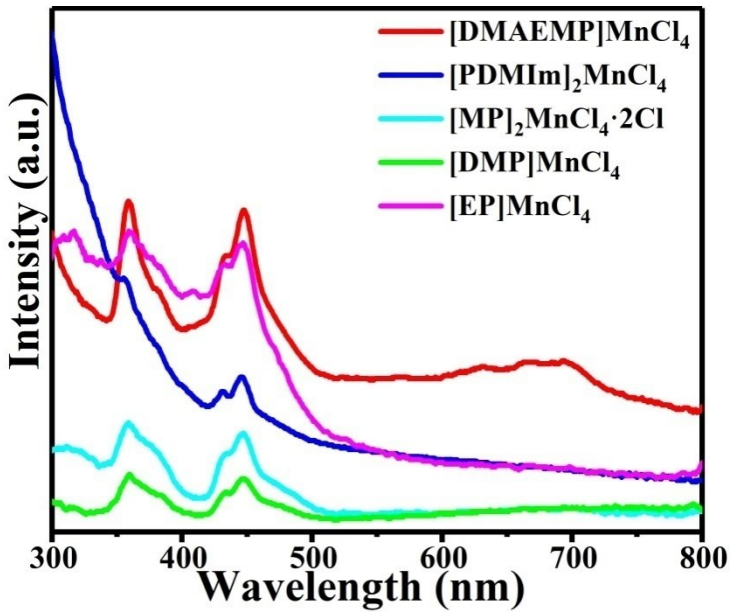


Fig. S7. The solid state absorption optical spectra of $[DMAEMP]MnCl_4$, $[PDMIm]_2MnCl_4$, $[MP]_2MnCl_4{\cdot}2Cl$, $[DMP]MnCl_4$ and $[EP]MnCl_4$ at 300 K.

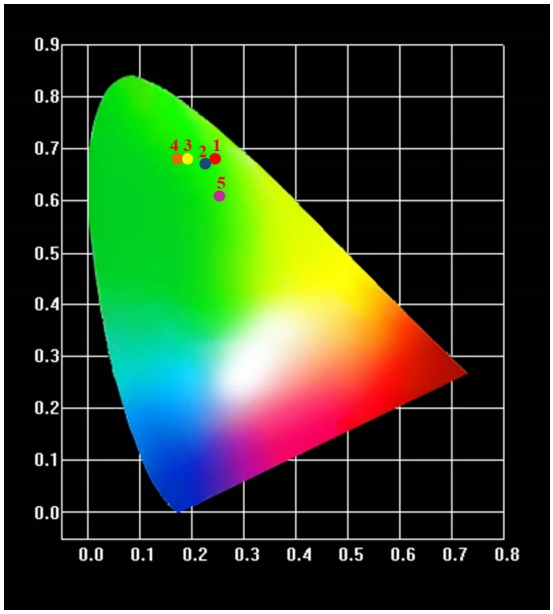


Fig. S8. The CIE chromaticity coordinates of $[DMAEMP]MnCl_4$ (**1**), $[PDMIm]_2MnCl_4$ (**2**), $[MP]_2MnCl_4{\cdot}2Cl$ (**3**), $[DMP]MnCl_4$ (**4**) and $[EP]MnCl_4$ (**5**).

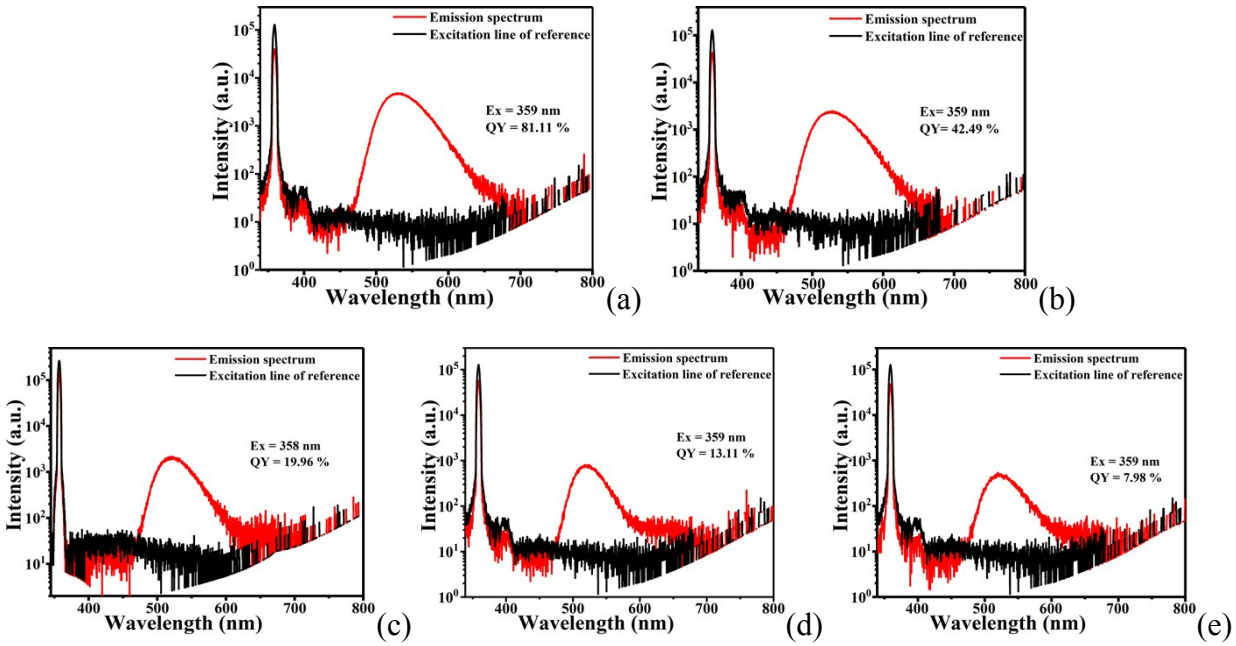


Fig. S9. The PLQYs of $[DMAEMP]MnCl_4$ (a), $[PDMIm]_2MnCl_4$ (b), $[MP]_2MnCl_4{\cdot}2Cl$ (c), $[DMP]MnCl_4$ (d) and $[EP]MnCl_4$ (e).

Table S1. Comparison of photoluminescence parameters of green light emitting 0D hybrid manganese halides.

Material	Emission	PLQY	FWHM	Lifetime	Ref.
$[Ph_4P]_2MnBr_4$	516 nm	98 %	·····	0.355 ms	1
$(TMPEA)_2MnBr_4$	520 nm	98 %	·····	0.096 ms	2
$(ETPP)MnBr_4$	517 nm	95 %	51 nm	0.318 ms	3
$(PD)_2MnBr_4$	521 nm	95 %	42 nm	0.263 ms	4
$LMnCl_4$	530 nm	92.3	·····	1.54 ms	5
$(TPA)_2MnBr_4$	512 nm	89.2 %	·····	·····	6
$(BTMA)_2MnBr_4$	518 nm	88.8 %	46 nm	0.33 ms	7
$(BTMA)_2MnBr_4$	516 nm	88.5 %	48 nm	·····	8
$(TBA)_2MnBr_4$	515 nm	85.1 %	47 nm	0.443 ms	9
$(PD)_2MnCl_4$	520 nm	82 %	·····	0.384 ms	10
$[DMAEMP]MnCl_4$	525 nm	81.11 %	54 nm	3.26 ms	This work
$[P14]MnBr_4$	520 nm	81 %	55 nm	0.358 ms	11
$(Bmpy)_2MnBr_4$	528 nm	80.1 %	64 nm	0.326 ms	12
$(MPip)MnCl_4$	530 nm	79.4 %	60 nm	0.715 ms	13
$(TEA)_2MnBr_4$	516 nm	78.9 %	·····	·····	7
$(Bz(Me)_3N)_2MnCl_4$	547 nm	78 %	71.8nm	3.79 ms	14
$(BTMA)_2MnBr_4$	514 nm	72.3 %	·····	0.236 ms	15
$(btmdme)_2MnCl_4$	516 nm	71.3 %	·····	·····	7
$(EMMIm)_2MnCl_4$	536 nm	70.8	·····	3.90 ms	16
BA_2MnI_4	550 nm	68 %	·····	0.0211 ms	17
$(Bz(Me)_3N)_2MnBr_4$	516 nm	63 %	48.7nm	0.34 ms	14
$DIPA_2MnBr_4$	525 nm	62 %	62.9 nm	1.44 ns	18
$[PP14]MnBr_4$	527 nm	55 %	64 nm	0.361 ms	11
$(IPTMA)_2MnBr_4$	497 nm	52.6 %	·····	·····	19
$[Py]_2MnBr_4$	525 nm	51.4 %	·····	·····	20
$(Bmpy)_9[Pb_3Br_{11}](MnBr_4)_2$	528 nm	49.8 %	67 nm	0.114 ms	21
Cs_3MnBr_5	520 nm	49 %	42 nm	0.29 ms	22

$(TPP)_2MnCl_4$	517 nm	48 %	·····	1.97 ms	23
$[Bu_4N]_2MnBr_4$	520 nm	47 %	·····	0.35 ms	24
$[Ph_4P]_2MnBr_4$	520 nm	47 %	·····	0.35 ms	24
$[(btz)_2(MnCl_4)]\cdot 2H_2O$	530 nm	43.2 %	·····	·····	25
$[MMPrIm]MnCl_4$	521 nm	42.49 %	·····	3.527 ms	This work
$(Mor)_2MnCl_4$	520 nm	39 %	·····	3.36 ms	26
$(KC)_2MnBr_4$	520 nm	38.5 %	·····	0.35 ms	27
$(Bz(Me)_3N)_2MnI_4$	537 nm	33 %	49.8 nm	0.045 ms	14
$[(btz)_2(MnBr_4)]\cdot 2H_2O$	525 nm	26.2 %	·····	·····	25
$(HEP)_3MnBr_5$	519 nm	25.5 %	·····	0.049 ms	2
$[MP]_2MnCl_4\cdot 2Cl$	516 nm	19.96 %	48 nm	2.89 ms	This work
$(PLD)_2MnBr_4$	520 nm	19 %	42 nm	3.97 ns	28
$[PRD]MnBr_4$	525 nm	16 %	·····	0.73 ns	29
$[PRD]MnI_4$	550 nm	15 %	·····	0.19 ns	29
$[DMP]MnCl_4$	516 nm	13.11 %	43 nm	0.787 ms	This work
$(3MP)_2MnBr_4$	523 nm	13 %	·····	0.019 ms	2
$[ASN]_2[MnBr_4]$	525 nm	13 %	54 nm	·····	30
$(N\text{-}EPD)_2MnBr_4$	515 nm	12 %	·····	0.188 ms	10
$(3AMP)MnBr_4\cdot H_2O$	514 nm	9.5 %	·····	0.025 ms	2
$[EP]MnCl_4$	518 nm	7.98 %	56 nm	1.40 ms	This work
$(DMA)_2MnBr_4$	520 nm	7.8 %	·····	0.081 ms	2
$(KC)_2MnCl_4$	518 nm	7.8 %	·····	2.79 ms	27
$[PRD]MnI_4$	540 nm	4.4 %	·····	0.51 ns	29

Ph_4P=Tetraphenylphosphonium, TMPEA=trimethylphenylammonium, ETPP=ethylenebis-triphenylphosphonium, PD=pyridine, L=1-(cyclopentyl)-4-aza-1-azonia-bicyclo[2.2.2]octane, TPA=tetrapropylammonium, BTMA=Benzyltrimethyl ammonium, TBA= tetraethylammonium, P14=N-butyl-N-methylpyrrolidinium, Bmpy=1-buty-1-methylpyrrolidinium, MPip=N-methylpiperidinuium, TEA=tetraethylammonium, $Bz(Me)_3N$=N-benzyl-N,N,N-trimethylammonium, btmdme=N-((1H-Benzotriazol-1-yl)methyl) -N,N-dimethylethanaminium, BA=n-butylamine, [EMMIm]=1-ethyl-2,3-dimethylimidazolium chloride, DIPA=Diisopropylammonium, PP14=N-butyl-N-methylpiperidinium, IPTMA = isopropyl-trimethylammonium, Py=pyrrolidinium, TPP=tetraphenylphosphonium, Bu4N=Tetrabutylammonium, Btz=benzothiazole, Mor=morpholine, KC=K(dibenzo-18-crown-6), HEP=heptamethylenimine, PLD=pyrrolidine, PRD=pyrrolidine, 3MP=methylpiperidinium, ASN=5-azonia-spiro[4,4]nonane, N-EPD=N-ethyl pyridine, 3AMP=3-aminomethylpiperidinium, DMA=dimethylammonium.

Table S2. Summary of the photophysical properties for title hybrid manganese halides at 300 K.

	λ_{em}/nm	FWHM/nm	Lifetime/ms	Φ/%
Compound **1**	525	54	3.26	81.11
Compound **2**	521	56	3.53	42.50
Compound **3**	516	48	2.89	19.96
Compound **4**	516	43	0.79	13.11
Compound **5**	526	56	1.40	7.98

λ_{em} represent the of maximum emission wavelengths and Φ is PLQY.

Table S3. Separation distances (Å) of Mn···Mn for neighboring $[MnCl_4]^{2-}$ tetrahedrons in the title hybrid manganese halides.

	[DMAEMP]$MnCl_4$	$[PDMIm]_2MnCl_4$	$[MP]_2MnCl_4 \cdot 2Cl$	[DMP]$MnCl_4$	[EP]$MnCl_4$
d(Mn-Mn)/Å	7.727	8.478	8.047	6.112	6.188
d(Mn-Mn)/Å	8.346	8.478	8.047	6.945	6.62
d(Mn-Mn)/Å	8.551	8.923	8.265	8.019	7.943
d(Mn-Mn)/Å	9.757	8.923	8.265	8.097	8.001
d(Mn-Mn)/Å	9.578	9.323	8.695	9.213	8.494
d(Mn-Mn)/Å	9.996	9.417	8.695	9.29	8.461
d(Mn-Mn)/Å	10.978	9.417	9.32	9.769	8.601
d(Mn-Mn)/Å	10.978	10.064	9.32	9.797	8.914
d_{ave}(Mn-Mn)/Å	9.49	9.12	8.58	8.40	7.90
PLQY	81.11%	42.49%	19.96%	13.11%	7.98%

Table S4. Crystal data and structural refinements for the title compounds **1**-**3**.

Compound	[DMAEMP]$MnCl_4$ (**1**)	$[PDMIm]_2MnCl_4$ (**2**)	$[MP]_2MnCl_4{\cdot}2Cl$ (**3**)
chemical formula	$C_9N_3H_{23}MnCl_4$	$C_{16}N_4H_{30}MnCl_4$	$C_{10}N_4H_{28}MnCl_6$
fw	370.04	478.15	472
Space group	*P* $2_1/c$ (No.14)	*Pbca* (No.61)	$P2_12_12_1$ (No.19)
a/Å	9.9960(2)	16.387(4)	8.04650(10)
b/Å	14.3562(2)	15.292(4)	15.39100(10)
c/Å	15.3780(3)	18.810(5)	16.93960(10)
V(Å^3)	1723.35(5)	4714(2)	2097.86(3)
Z	4	8	4
D_{calcd} (g·cm^{-3})	1.426	1.339	1.494
Temp (*K*)	296(2)	296(2)	296(2)
μ (mm^{-1})	11.815	1.021	12.136
F (000)	764	1976	972
Reflections collected	10246	29234	48524
Unique reflections	3461	4148	4312
Reflections ($I>2\sigma(I)$)	3042	3964	4189
GOF on F^2	1.042	1.068	1.036
R_1,wR_2 ($I > 2\sigma(I)$)[a]	0.0351/0.0962	0.0563/0.1634	0.0246/0.0609
R_1,wR_2 (all data)	0.0417/0.1083	0.0602/0.1667	0.0260/0.0620

[a] $R_1 = \Sigma\left\|F_0\right|-\left|F_c\right\| / \Sigma\left|F_0\right|$, $wR_2 = [\Sigma(F_o^2 - F_c^2) / \Sigma w(F_0)^2]^{1/2}$

Table S5. Crystal data and structural refinements for the title compounds **4**-**5**.

Compound	[DMP]$MnCl_4$ (**4**)	[EP]$MnCl_4$ (**5**)
chemical formula	$C_6N_2H_{16}MnCl_4$	$C_6N_2H_{16}MnCl_4$
fw	312.95	312.95
Space group	$P2_1/m$ (No.11)	*Pbca* (No.61)
a/Å	6.1119(2)	11.5561(2)
b/Å	14.5023(5)	9.7596(2)
c/Å	6.9450(2)	23.9095(5)
V(Å^3)	615.56(3)	2696.58(9)
Z	2	8
D_{calcd} (g·cm^{-3})	1.688	1.542
Temp (*K*)	296(2)	296(2)
μ (mm^{-1})	16.393	14.969
F (000)	318	1272
Reflections collected	1958	8628
Unique reflections	1057	2659
Reflections ($I>2\sigma(I)$)	976	2391
GOF on F^2	1.047	1.007
R_1,wR_2 ($I > 2\sigma(I)$)[a]	0.0417/0.1188	0.0390/0.1054
R_1,wR_2 (all data)	0.0442/0.1232	0.0437/0.1194

[a] $R_1 = \Sigma\left\|F_0\right|-\left|F_c\right\| / \Sigma\left|F_0\right|$, $wR_2 = [\Sigma(F_o^2 - F_c^2) / \Sigma w(F_0)^2]^{1/2}$

Table S6. Selected bond lengths (Å) and bond angles (°) for [DMAEMP]$MnCl_4$.

Mn(1)-Cl(1)	2.3712(8)	Mn(1)-Cl(3)	2.3369(7)
Mn(1)-Cl(2)	2.3859(8)	Mn(1)-Cl(4)	2.3503(8)
Cl(1)-Mn(1)-Cl(2)	111.19(4)	Cl(3)-Mn(1)-Cl(2)	111.73(3)
Cl(3)-Mn(1)-Cl(1)	108.47(3)	Cl(3)-Mn(1)-Cl(4)	111.06(3)
Cl(4)-Mn(1)-Cl(1)	112.63(3)	Cl(4)-Mn(1)-Cl(2)	101.70(3)

Table S7. Selected bond lengths (Å) and bond angles (°) for $[PDMIm]_2MnCl_4$.

Mn(1)-Cl(1)	2.395(17)	Mn(1)-Cl(3)	2.373(6)
Mn(1)-Cl(2)	2.35(3)	Mn(1)-Cl(4)	2.35(3)
Mn(1)-Cl(1A)	2.33(3)	Mn(1)-Cl(3A)	2.32(3)
Mn(1)-Cl(2A)	2.340(11)	Mn(1)-Cl(4A)	2.374(6)
Cl(2)-Mn(1)-Cl(1)	108.9(10)	Cl(2)-Mn(1)-Cl(4)	105.5(18)
Cl(2)-Mn(1)-Cl(3)	111.1(12)	Cl(1)-Mn(1)-Cl(4)	116.0(12)
Cl(1)-Mn(1)-Cl(3)	105.5(6)	Cl(3)-Mn(1)-Cl(4)	110.0(10)
Cl(3A)-Mn(1)-Cl(1A)	116.2(17)	Cl(3A)-Mn(1)-Cl(2A)	107.0(17)
Cl(1A)-Mn(1)-Cl(2A)	102.0(13)	Cl(3A)-Mn(1)-Cl(4)	112.5(12)
Cl(1A)-Mn(1)-Cl(4)	114.6(14)	Cl(2A)-Mn(1)-Cl(4)	102.6(15)
Cl(3A)-Mn(1)-Cl(2)	103.3(19)	Cl(1A)-Mn(1)-Cl(2)	102.9(14)
Cl(1A)-Mn(1)-Cl(3)	112.3(15)	Cl(2A)-Mn(1)-Cl(3)	114.8(8)
Cl(3A)-Mn(1)-Cl(4A)	110.4(9)	Cl(1A)-Mn(1)-Cl(4A)	110.4(8)
Cl(2A)-Mn(1)-Cl(4A)	110.4(9)	Cl(2A)-Mn(1)-Cl(1)	108.3(8)
Cl(2)-Mn(1)-Cl(4A)	113.3(13)	Cl(3)-Mn(1)-Cl(4A)	107.0(4)
Cl(3A)-Mn(1)-Cl(1)	109.8(11)	Cl(4A)-Mn(1)-Cl(1)	110.8(6)

Table S8. Selected bond lengths (Å) and bond angles (°) for $[MP]_2MnCl_4 \cdot 2Cl$.

Mn(1)-Cl(1)	2.3913(7)	Mn(1)-Cl(3)	2.3516(7)
Mn(1)-Cl(2)	2.3550(6)	Mn(1)-Cl(4)	2.3620(7)
Cl(3)-Mn(1)-Cl(2)	115.89(3)	Cl(3)-Mn(1)-Cl(1)	103.30(3)
Cl(3)-Mn(1)-Cl(4)	109.26(3)	Cl(2)-Mn(1)-Cl(1)	106.64(2)
Cl(2)-Mn(1)-Cl(4)	112.69(3)	Cl(4)-Mn(1)-Cl(1)	108.39(3)

Table S9. Selected bond lengths (Å) and bond angles (°) for $[DMP]MnCl_4$.

Mn(1)-Cl(1)	2.4050(13)	Mn(1)-Cl(3)	2.3336(8)
Mn(1)-Cl(2)	2.3973(13)	Mn(1)-Cl(3) #1	2.3336(8)
Cl(3)-Mn(1)-Cl(3)#1	120.79(5)	Cl(3)-Mn(1)-Cl(1)	105.18(3)
Cl(3)-Mn(1)-Cl(2)	110.62(3)	Cl(3)#1-Mn(1)-Cl(1)	105.18(3)
Cl(3)#1-Mn(1)-Cl(2)	110.62(3)	Cl(2)-Mn(1)-Cl(1)	102.51(5)

Table S10. Selected bond lengths (Å) and bond angles (°) for $[EP]MnCl_4$.

Mn(1)-Cl(1)	2.3243(8)	Mn(1)-Cl(3)	2.3497(8)
Mn(1)-Cl(2)	2.3709(8)	Mn(1)-Cl(4)	2.3987(8)
Cl(1)-Mn(1)-Cl(2)	112.10(4)	Cl(2)-Mn(1)-Cl(4)	106.41(3)
Cl(1)-Mn(1)-Cl(3)	119.30(3)	Cl(3)-Mn(1)-Cl(2)	106.97(3)
Cl(1)-Mn(1)-Cl(4)	104.84(3)	Cl(3)-Mn(1)-Cl(4)	106.37(3)

Table S11. Hydrogen bonding data for [DMAEMP]$MnCl_4$.

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA)(°)
N(2)-H(2)···N(1)	0.91	2.48	2.9205(1)	110
N(3)-H(3)···Cl(2)	0.91	2.32	3.1711(1)	156
C(2)-H(2A)···Cl(3)	0.96	2.76	3.7109(1)	173
C(3)-H(3A)···Cl(3)	0.97	2.79	3.7347(1)	164
C(4)-H(4A)···Cl(2)	0.97	2.77	3.7225(1)	168
C(8)-H(8B)···Cl(4)	0.97	2.79	3.5476(1)	135

Table S12. Hydrogen bonding data for $[PDMIm]_2MnCl_4$.

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA)(°)
C(2)-H(2)···Cl(3)	0.93	2.76	3.5804(10)	147
C(3)-H(3C)···Cl(3A)	0.96	2.77	3.4625(9)	130
C(5)-H(5A)···Cl(4A)	0.97	2.74	3.6747(10)	162
C(5)-H(5A)···Cl(4)	0.97	2.81	3.7430(10)	162
C(5)-H(5B)···Cl(2A)	0.97	2.76	3.6661(10)	155
C(5)-H(5B)···Cl(2)	0.97	2.66	3.5562(9)	153
C(9)-H(9)···Cl(4A)	0.93	2.68	3.5369(9)	154
C(9)-H(9)···Cl(4)	0.93	2.76	3.5830(10)	148
C(13)-H(13B)···Cl(4A)	0.96	2.83	3.7842(10)	174

Table S13. Hydrogen bonding data for $[MP]_2MnCl_4 \cdot 2Cl$.

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA)(°)
N(1)-H(1)···Cl(6)	0.91	2.10	3.0019(1)	173
N(2)-H(2A)···Cl(1)	0.90	2.43	3.1823(1)	141
N(2)-H(2B)···Cl(4)	0.90	2.54	3.2351(1)	134
N(3)-H(3)···Cl(5)	0.91	2.19	3.0730(1)	164
N(4)-H(4A)···Cl(5)	0.90	2.31	3.0990(1)	147
N(4)-H(4B)···Cl(6)	0.90	2.28	3.0949(1)	151
C(2)-H(2D)···Cl(5)	0.97	2.82	3.4656(1)	125
C(3)-H(3A)···Cl(6)	0.97	2.64	3.3997(1)	135
C(6)-H(6A)···Cl(3)	0.97	2.74	3.7029(1)	175
C(8)-H(8A)···Cl(5)	0.96	2.75	3.6638(1)	158
C(9)-H(9A)···Cl(6)	0.97	2.72	3.4676(1)	134

Table S14. Hydrogen bonding data for $[DMP]MnCl_4$.

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(DHA)(°)
N(1)-H(1)···Cl(1)	0.91	2.72	3.3928(1)	132
N(1)-H(1)···Cl(2)	0.91	2.65	3.3884(1)	139
C(1)-H(1B)···Cl(3)	0.97	2.74	3.6364(10)	154
C(2)-H(2B)···Cl(3)	0.97	2.79	3.6419(1)	147

Table S15. Hydrogen bonding data for [EP]$MnCl_4$.

D-H···A	**d(D-H) (Å)**	**d(H···A) (Å)**	**d(D···A) (Å)**	**<(DHA)(°)**
N(1)-H(1D)···Cl(2)	0.90	2.33	3.1991(1)	162
N(1)-H(1E)···Cl(3)	0.90	2.73	3.3349(1)	125
N(1)-H(1E)···Cl(4)	0.90	2.55	3.2656(1)	137
N(2)-H(2C)···Cl(4)	0.91	2.36	3.2176(1)	158
C(5)-H(5A)···Cl(2)	0.97	2.79	3.7102(1)	159

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