Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

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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Table S1. Crystal data and structure refinement for $[Bu_4N]_2MnBr_4$ (**1**) (CCDC number: 1902826)

Parameter	Value	
Identification code	$[Bu_4N]_2MnBr_4$	
Empirical formula	2(C16H36N)Br4Mn	
Formula weight	859.49	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 12.8381(7) Å	α= 90°.
	b = 12.8997(8) Å	β= 90°.
	c = 25.0820(15) Å	γ = 90°.
Volume	4153.8(4) $Å^3$	
Z	4	
Density (calculated)	1.374 Mg/m^3	
Absorption coefficient	4.186 mm^{-1}	

F(000)	1772
Crystal size	0.280 x 0.210 x 0.150 mm^3
Theta range for data collection	2.238 to 28.385°.
Index ranges	-17<=h<=17, -17<=k<=17, -33<=l<=33
Reflections collected	140228
Independent reflections	10374 [R(int) = 0.0926]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.5105
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10374 / 26 / 360
Goodness-of-fit on F^2	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0662, wR2 = 0.1700
R indices (all data)	R1 = 0.0940, wR2 = 0.1824
Absolute structure parameter	0.055(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.586 and -0.450 e.$Å^{-3}$

Table S2. Crystal data and structure refinement for $[Ph_4P]_2MnBr_4$ (**2**) (CCDC number: 1902825)

Parameter	Value
Identification code	$[Ph_4P]_2MnBr_4$
Empirical formula	C48H40Br4MnP2
Formula weight	1053.32
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c

Unit cell dimensions	a = 11.2817(3) Å α= 90°.
	b = 19.7797(6) Å β = 92.3422(10)°.
	c = 20.5926(6) Å γ = 90°.
Volume	4591.4(2) $Å^3$
Z	4
Density (calculated)	1.524 Mg/m^3
Absorption coefficient	3.870 mm^{-1}
F(000)	2092
Crystal size	0.220 x 0.170 x 0.100 mm^3
Theta range for data collection	2.079 to 28.311°.
Index ranges	-15<=h<=15, -26<=k<=26, -27<=l<=27
Reflections collected	74530
Independent reflections	5716 [R(int) = 0.0603]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6043
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5716 / 0 / 249
Goodness-of-fit on F^2	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.0778
R indices (all data)	R1 = 0.0672, wR2 = 0.0909
Extinction coefficient	n/a
Largest diff. peak and hole	0.990 and -0.758 $e.Å^{-3}$

Table S3. Bond length [Å] of Mn-Br and C-N in $[Bu_4N]_2MnBr_4$ (**1**)

Bond type	Bond length
Mn(1)-Br(4)	2.506(2)
Mn(1)-Br(3)	2.514(2)
Mn(1)-Br(2)	2.515(2)
Mn(1)-Br(1)	2.517(2)
N(1)-C(13)	1.473(17)
N(1)-C(1)	1.504(15)
N(1)-C(5)	1.526(16)
N(1)-C(9)	1.550(16)

Table S4. Bond length [Å] of Mn-Br and P-N in $[Ph_4P]_2MnBr_4$ (**2**)

Bond type	Bond length
Mn(1)-Br(1)	2.5049(5)
Mn(1)-Br(1)#1	2.5049(5)
Mn(1)-Br(2)#1	2.5145(5)
Mn(1)-Br(2)	2.5146(5)
P(1)-C(13)	1.783(3)
P(1)-C(19)	1.787(3)
P(1)-C(1)	1.791(3)
P(1)-C(7)	1.800(3)

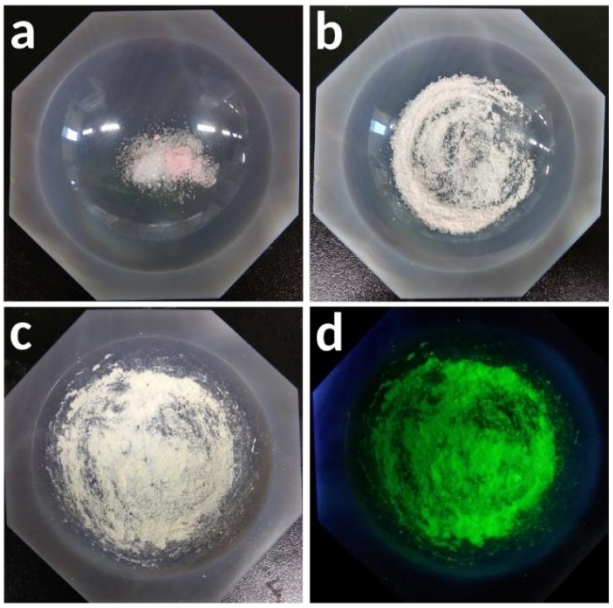

Fig. S1. Photography images of **1** at different stages of synthesis: (a) two precursors before grinding; (b) two precursors after mixing for 5 min; (c) final product after grinding for 10 min; (d) final product under 365 nm UV irradiation.

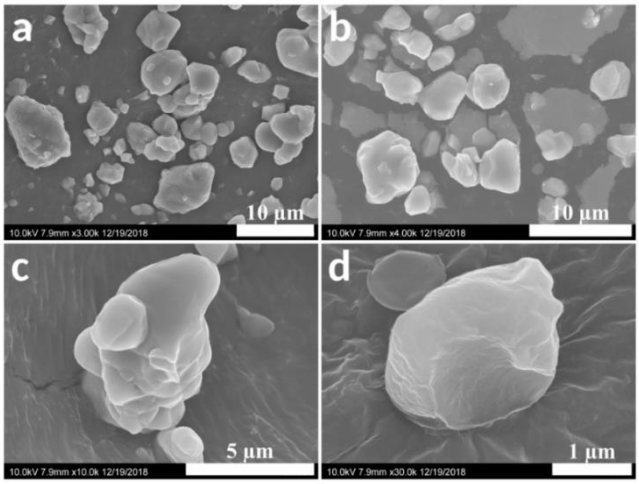

Fig. S2. SEM images of **1** at low magnification with particle distribution (a-b), and single particle images at high magnification (c-d).

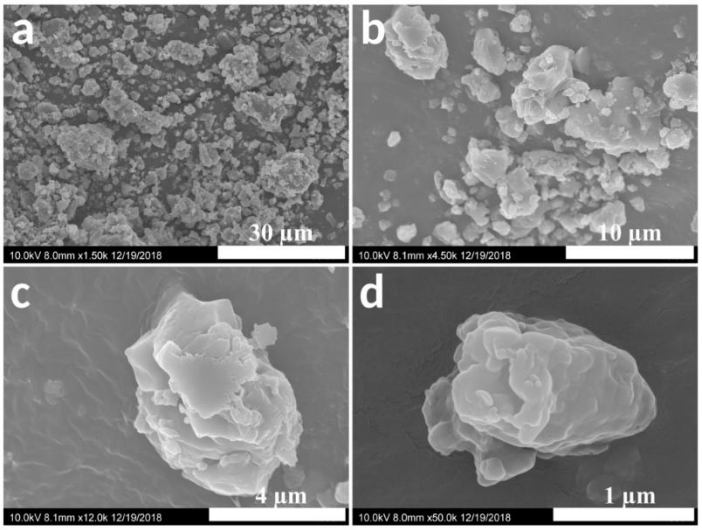

Fig. S3. SEM images of **2** at low magnification with particle distribution (a-b), and single particle images at high magnification (c-d).

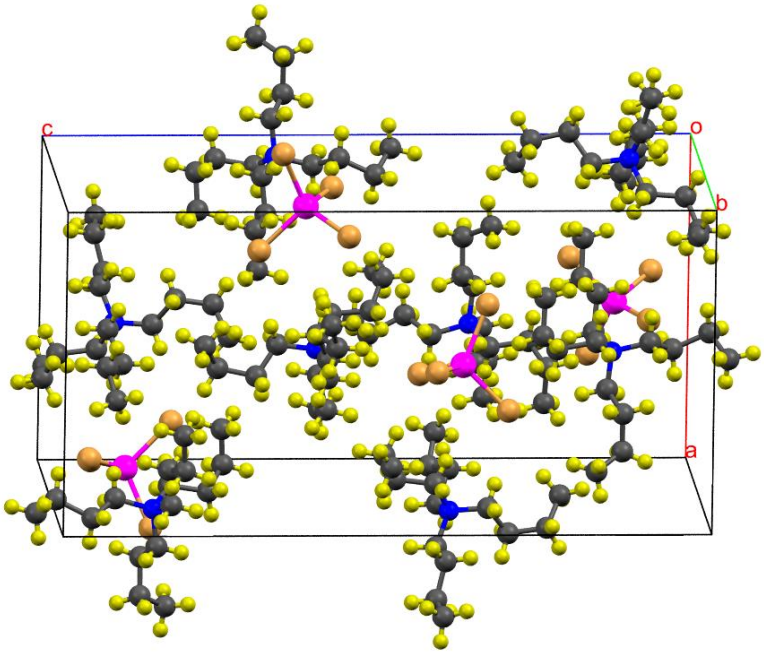

Fig. S4. Unit cell of **1**. Pink: Mn, Yellow: H, Blue: N, Orange: Br

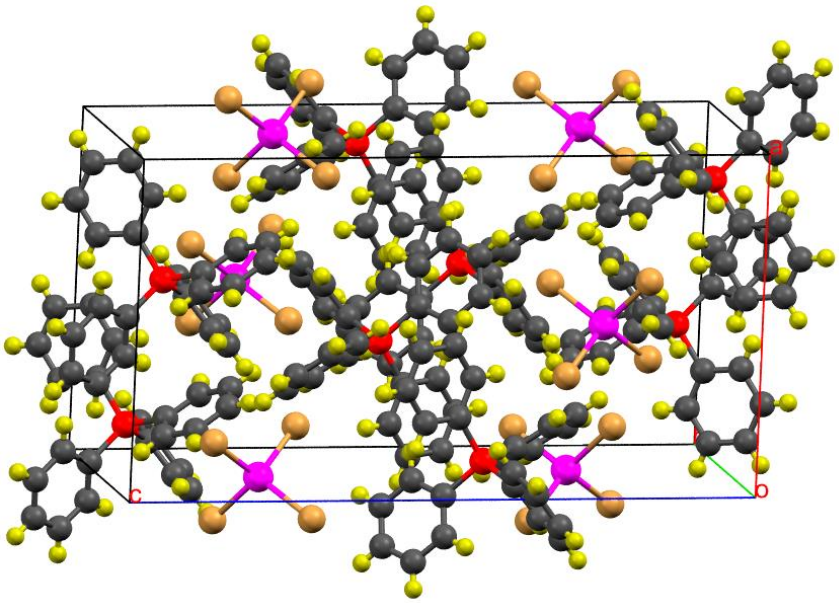

Fig. S5. Unit cell of **2**. Pink: Mn, Yellow: H, Blue: N, Orange: Br, Red: P.

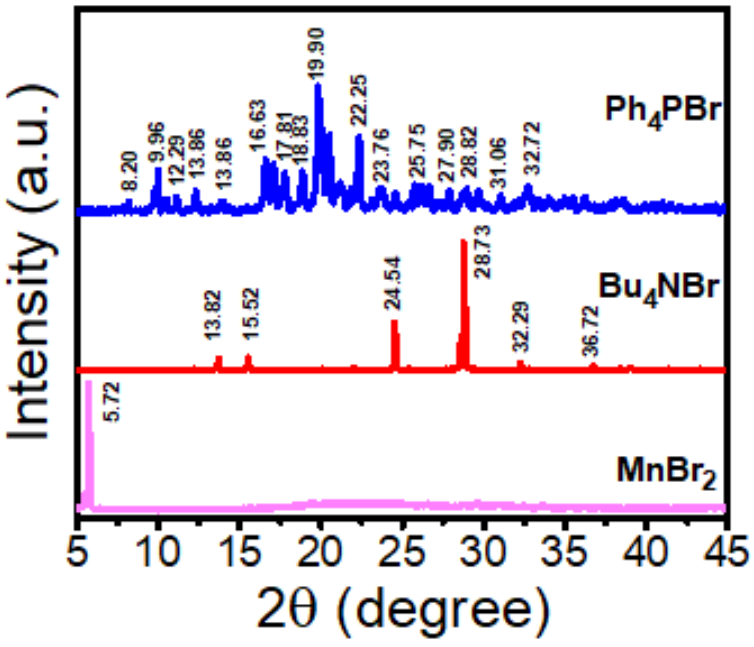

Fig. S6. PXRD of $MnBr_2$, Bu_4NBr and Ph_4PBr

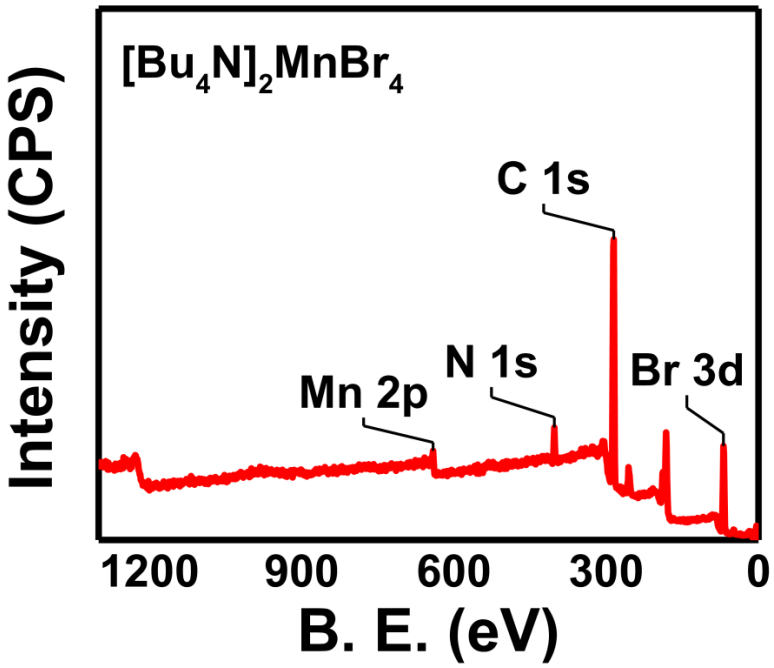

Fig. S7. Wide scan XPS survey data of **1** at ambient environment.

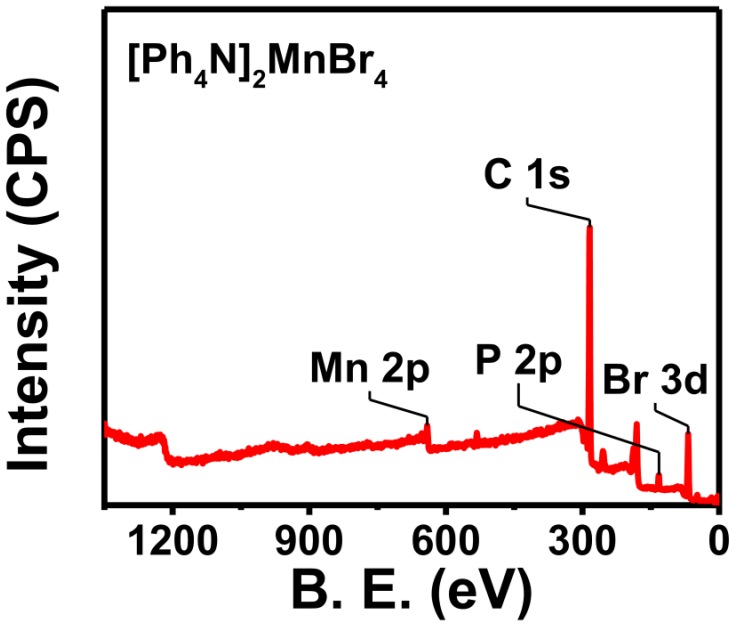

Fig. S8. Wide scan XPS survey data of **2** at ambient environment.

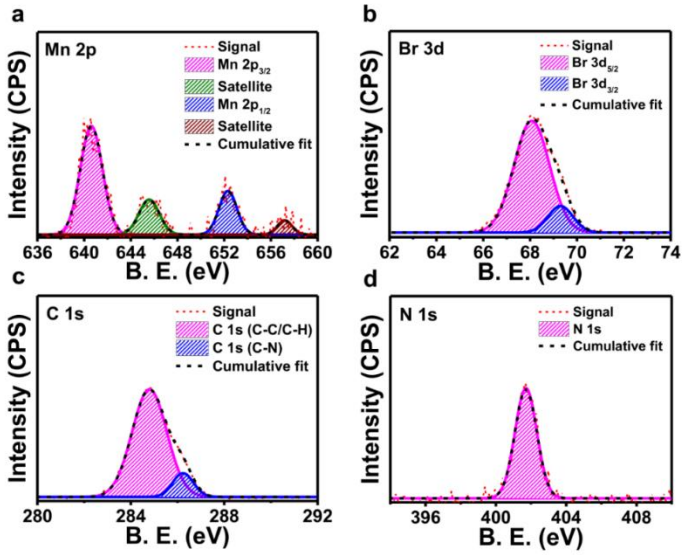

Fig. S9. High resolution XPS scans of $[Bu_4N]_2MnBr_4$ for (a) Mn 2p, (b) Br 3d, (c) C 1s, and (d) N 1s.

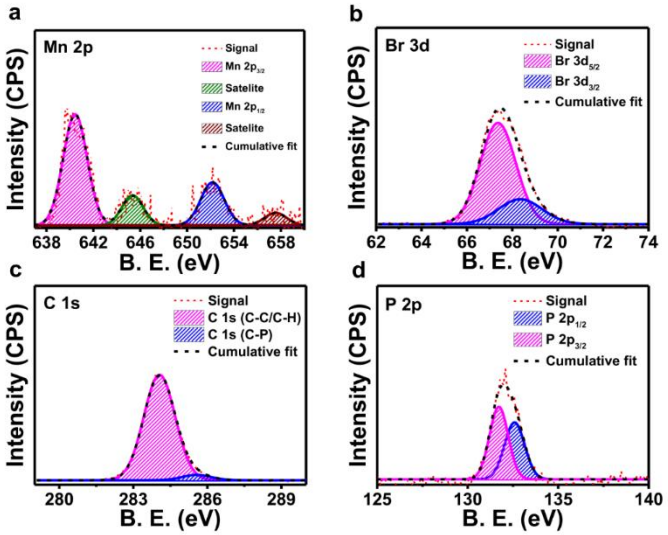

Fig. S10. High resolution XPS scans of $[Ph_4P]_2MnBr_4$ for (a) Mn 2p, (b) Br 3d, (c) C 1s, and (d) P 2p.

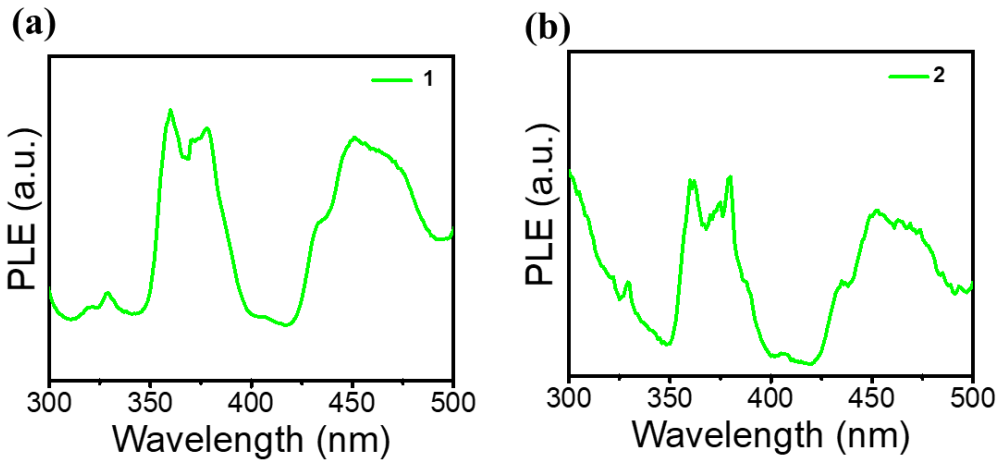

Fig. S11. Photoluminescence Excitation (PLE) spectra of (a) **1** and (b) **2**.

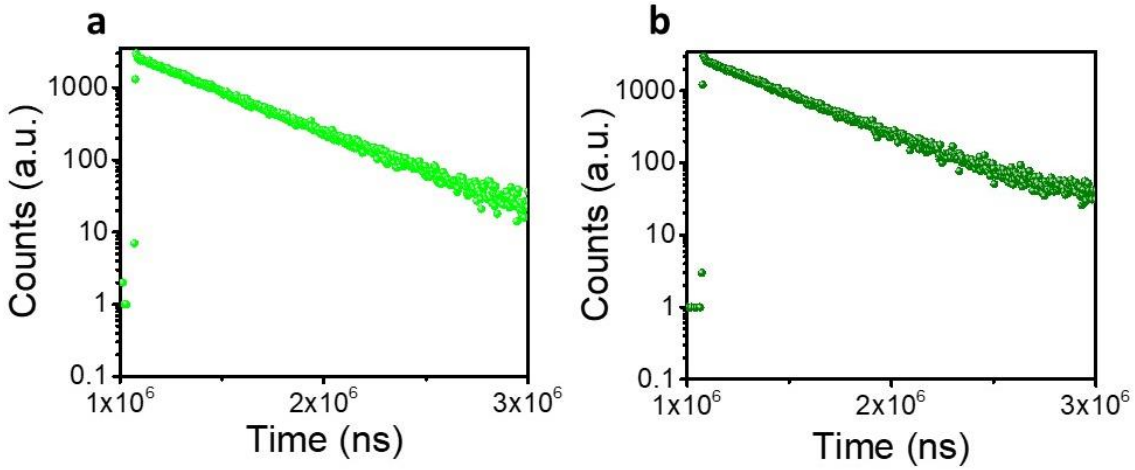

Fig. S12. Time resolved photoluminescence spectroscopy. (a) **1** and (b) **2**. Excitation and emission wavelengths are 472 nm and 520 nm, respectively.

Table S5. Absorbance maxima and quartet states of **1** and **2**.

Compound	Absorbance maxima (nm)	Energy (cm^{-1})	Quartet States
1	472	21186.44	$^4T_1(^4G)$
	450	22222.22	$^4T_2(^4G)$
	434	23041.47	$^4A_1(^4G)$, $^4E(^4G)$
	400	25000	$^4T_2(^4D)$
	368	27173.91	$^4E(^4D)$
	347	28818.44	$^4T_1(^4P)$
2	472	21186.44	$^4T_1(^4G)$
	450	22222.22	$^4T_2(^4G)$
	422	23696.68	$^4A_1(^4G)$, $^4E(^4G)$
	403	24813.9	$^4T_2(^4D)$
	370	27027.03	$^4E(^4D)$
	341	29325.51	$^4T_1(^4P)$

Table S6. Excitation wavelength/energy and emission wavelength/energy of compound **1**

Excitation wavelength (nm)/ Energy (eV)	2×Energy of photons (eV)	Two photons energy (cm^{-1})	Emission wavelength (nm)/ Energy (eV)
640/1.93	3.86	31129.03	574/2.16, 597/2.07, 607/2.04
660/1.87	3.74	30161.29	546/2.27, 573/2.16, 597/2.07, 604/2.05, 609/2.03
680/1.82	3.64	29354.84	546/2.27, 574/2.16, 597/2.07, 607/2.04
710/1.74	3.48	28064.52	545/ 2.27, 554/2.23, 574/2.16, 597/2.07, 605/2.04
730/1.69	3.38	27258.06	425/2.91, 450/2.75, 525/2.36
740/1.67	3.34	26935.48	431/2.87, 470/2.63, 546/2.27
760/1.63	3.26	26290.32	457/2.71, 493/2.51, 569/2.17
780/1.58	3.16	25483.87	476/2.60, 514/2.41, 588/2.10
800/1.55	3.1	25000	501/2.47, 534/2.32, 609/2.03
820/1.51	3.02	24354.84	518/2.39, 556/2.22

Table S7. Excitation wavelength/energy and emission wavelength/energy of compound **2**

Excitation wavelength (nm)/ Energy (eV)	2×Energy of photons (eV)	Two photons energy (cm^{-1})	Emission wavelength (nm)/ Energy (eV)
640/1.93	3.86	31129.03	574/2.16, 597/2.07, 607/2.04
660/1.87	3.74	30161.29	546/2.27, 573/2.16, 597/2.07, 604/2.05, 609/2.03
680/1.82	3.64	29354.84	546/2.27, 574/2.16, 597/2.07, 607/2.04
710/1.74	3.48	28064.52	543/2.28, 553/2.24, 574/2.17, 597/2.07, 605/2.04
730/1.69	3.38	27258.06	420/2.95, 450/2.75, 525/2.36
740/1.67	3.34	26935.48	431/2.87, 470/2.63, 546/2.27
760/1.63	3.26	26290.32	457/2.71, 493/2.51, 571/2.17
780/1.58	3.16	25483.87	476/2.60, 514/2.41, 588/2.10
800/1.55	3.1	25000	501/2.47, 534/2.32, 609/2.03
820/1.51	3.02	24354.84	518/2.39, 556/2.22, 627/1.97

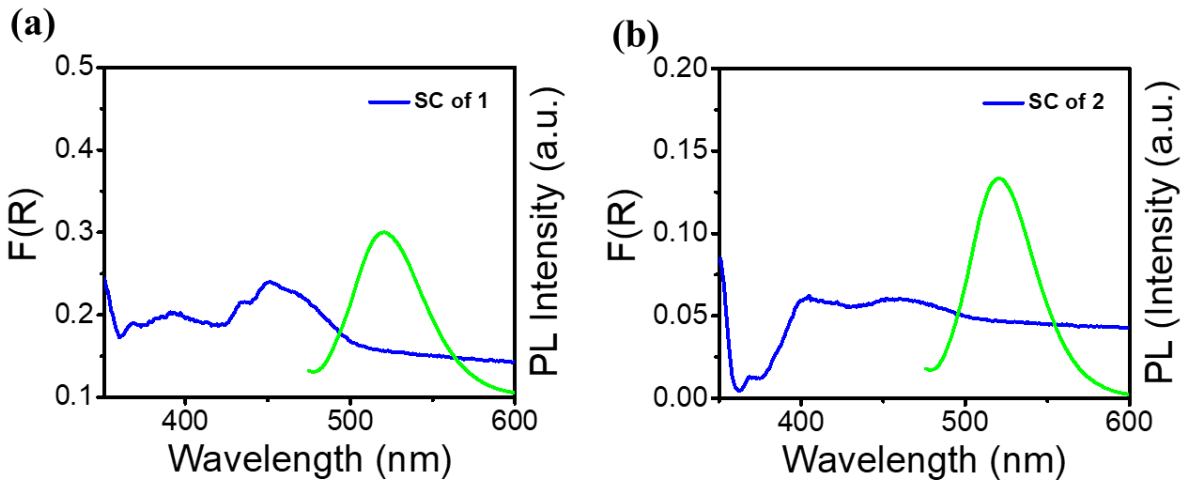

Fig. S13. Photophysical characterizations. Solid-state diffusion reflectance and PL spectra of single crystals (a) **1** and (b) **2** (Excitation wavelength: 380 nm). Blue line: diffuse reflectance spectra and green line PL spectra.

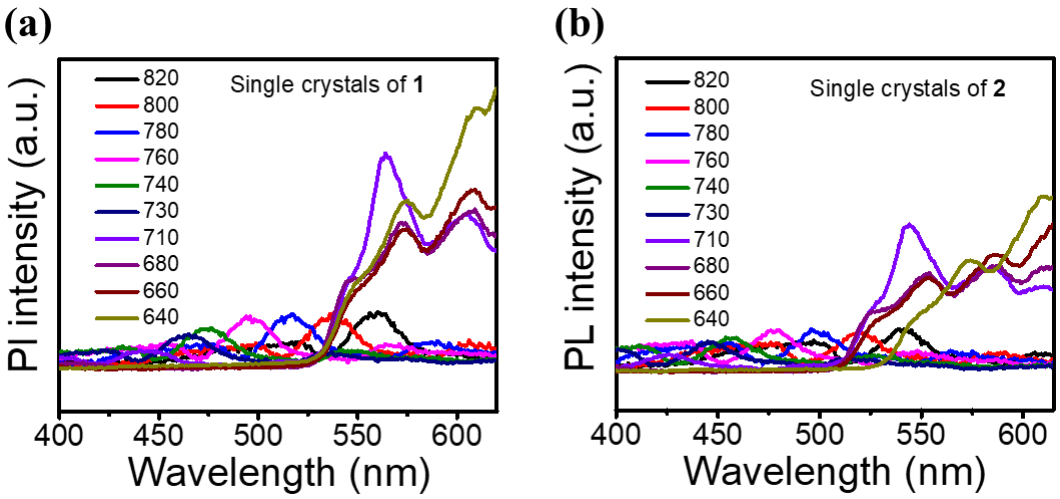

Fig. S14. PL spectra of single crystals excited between 640-820 nm. (a) **1** (b) **2.**

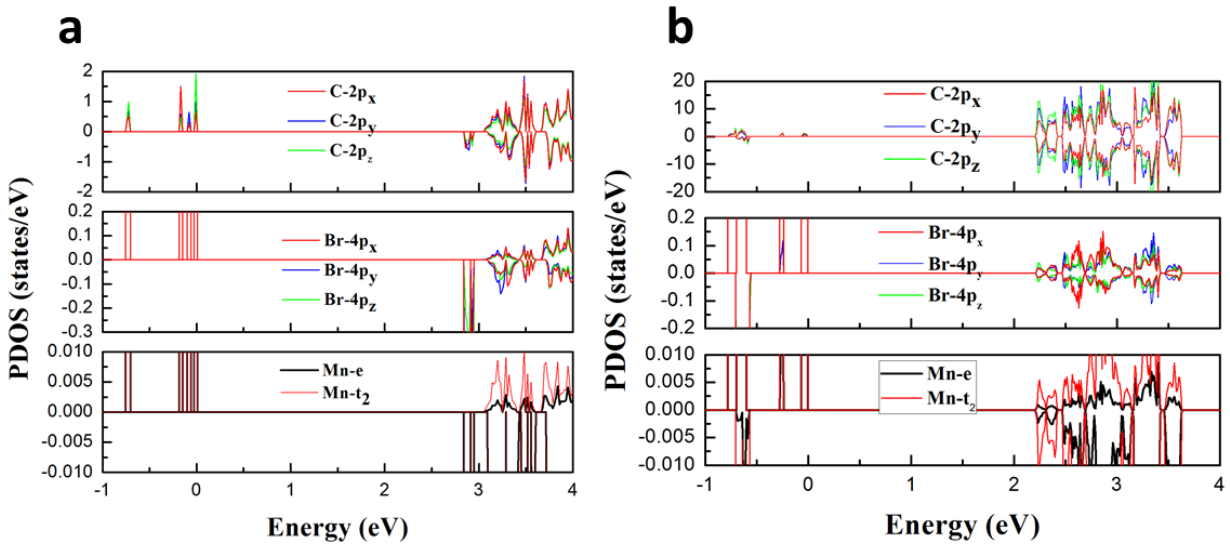

Fig. S15. Projected density of states for C-2p, Br-4p and Mn-3d orbitals of (a) **1** and (b) **2**. Fermi level is set to zero.