Supporting information

Efficient modulation of photoluminescence by hydrogen bonding interactions among inorganic $[MnBr_4]^{2-}$ anions and organic cations

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Experimental Section

Materials

N-butyl-N-methylpyrrolidinium bromide ([P14]Br) (99%) and N-butyl-N-methylpiperidinium bromide ([PP14]Br) (99%) were purchased from Lanzhou Yulu Fine Chemical Co., LTD (Lanzhou, China); manganese bromide tetrahydrate ($MnBr_2{\cdot}4H_2O$) (99.0%) was purchased from ACRO Chem Co., LTD (Shanghai, China); acetonitrile (99.0%) was purchased from Sinopham Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals were used without further purification. Polyacrylonitrile (PAN) was purchased from Macklin Biochemical Co., Ltd. (Shanghai, China).

Synthesis

Growth of $[A]_2[MnBr_4]$ (A = $[P14]^+$ for **1**, $[PP14]^+$ for **2**) crystals. A mixture of $[A]$Br (A = $[P14]^+$ for **1**, $[PP14]^+$ for **2**) and $MnBr_4{\cdot}4H_2O$ with the stoichiometric molar ratio of 2:1 in acetonitrile was loaded into a 20 mL glass bottle. The glass bottle was closed and heated at 100 °C for 3 days, and then cooled to room temperature naturally, resulting in a pale yellow solution with many transparent green block-like crystals.

Characterization methods

Single crystal X-ray diffraction (SCXRD). A suitable single crystal was carefully selected under an optical microscope and glued to a thin glass fiber. The single-crystal X-ray diffraction data were collected on a SuperNova CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 100(2) K. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXL-2016 program package.[1] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to C atoms were located at geometrically calculated positions and were not refined. CCDC 1910341 for compound **1** and CCDC 1910342 for compound **2** contain the supplementary crystallographic data for the two structures.

Powder X-ray diffraction (PXRD). PXRD was measured on a Rigaku Miniflex-II diffractometer with Cu $K\alpha$ radiation (λ = 1.54178 Å) in the angular range of 2θ= 3-65° with a scan speed of 2°/min. The simulated PXRD patterns are based on single-crystal X-ray diffraction data using the Mercury program.[2]

Elemental analysis (EA). EA was performed using a German Elementary Vario EL III instrument. Elemental analysis: calcd. (%) for **1**: C: N: 4.25% C: 32.80% H: 6.11%; Found for **1**: N: 4.14%,C: 32.73%,H: 6.10%; calcd. (%) for **2**: C: 34.96% N: 4.07% H: 6.45%; Found for **2**: C: 35.22% N:

4.04% H: 6.45%.

Thermogravimetric analysis (TGA). TGA was performed on a NETZSCH STA 449F3 unit at a heating rate of 10 K·min^{-1} under N_2 atmosphere.

Photophysical properties. PL (photoluminescence), PLE (photoluminescence excitation) and TRPL (time-resolved photoluminescence) were recorded on an Edinburgh FL980 UV/V/NIR fluorescence spectrometer. Quantum yields were measured by Edinburgh FLS 1000 UV/V/NIR fluorescence spectrometer.

Preparation of the 1-PAN composites.

0.70 g compound **1** were dissolved in 2 mL of dimethysulfoxide (DMSO) to obtain the clear solution; 0.2 g PAN were then placed into the above solution and stirred at 40 ^{0}C for 4 h to produce a light brown viscous liquid. A certain amount of the above-mentioned viscous liquid was taken with a dropper and added into a 500 mL beaker filled with 200 mL of water one by one. The settled balls were obtained at the bottom of the beaker and filtered to get the balls. The balls were dried in a 40 °C oven overnight to get the balls with green luminescence. And the mass ratio of PAN and **1** was the key to determine whether **1**-PAN could be formed as the ball. The minimum concentration of PAN for fluorescent ball formation should be 0.1 g/ml with the minimum ratio of 7:2 between **1** and PAN.

To prepare the film, a small amount of the viscous liquid was taken and spun on a spinner at the speed of 1000 min/rap; then a green luminous film was obtained after heating the film overnight in the oven at 40 °C. The light brown viscous liquid was laid as a belt fashion in the glass dish, and then the glass dish was placed in a 40 °C oven overnight. Finally, the liquid was cured as a flexible belt with green light PL. The light brown viscous can also be used as writable slurry for fluorescent letter.

Fabrication of colorful Phosphors and white LED. The phosphors with orange light emission and yellow light emission were obtained by mixing compound **1** with commercial nitride red phosphor at the mass ratios of 5:1 and 12:1, respectively. Under the same conditions, the phosphors with variable colours from green to red could be obtained by mixing compound **1** with commercial nitride red phosphor with varied ratios. The obtained yellow phosphor was loaded on the blue bulb to achieve the desirable white LED.

All the above fabrications have a good reproducibility under the same experimental conditions.

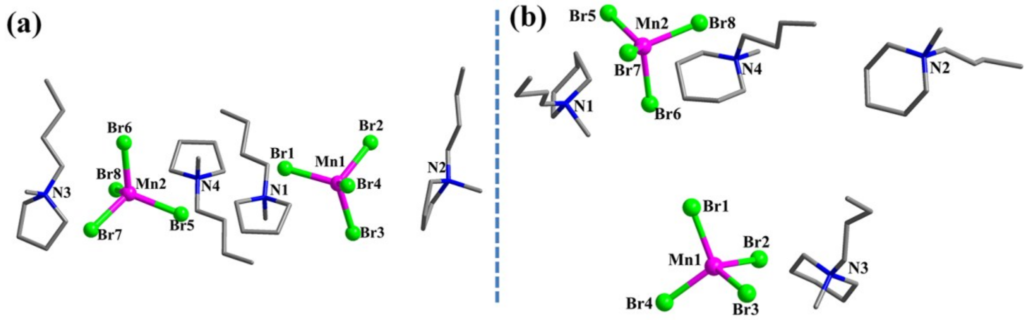

Fig. S1 The asymmetric units of **1** (a) and **2** (b); H atoms are removed for clarity.

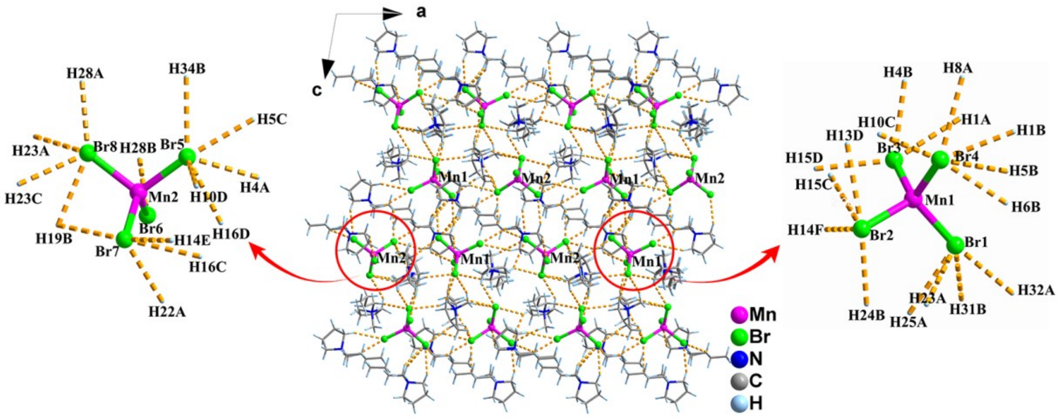

Fig. S2 Structural diagrams of **1**. Packing of the structure of **1** viewed along the *b*-axis (middle); highlighted hydrogen bonds for Mn(2)Br_4 (left) and Mn(1)Br_4 (right).

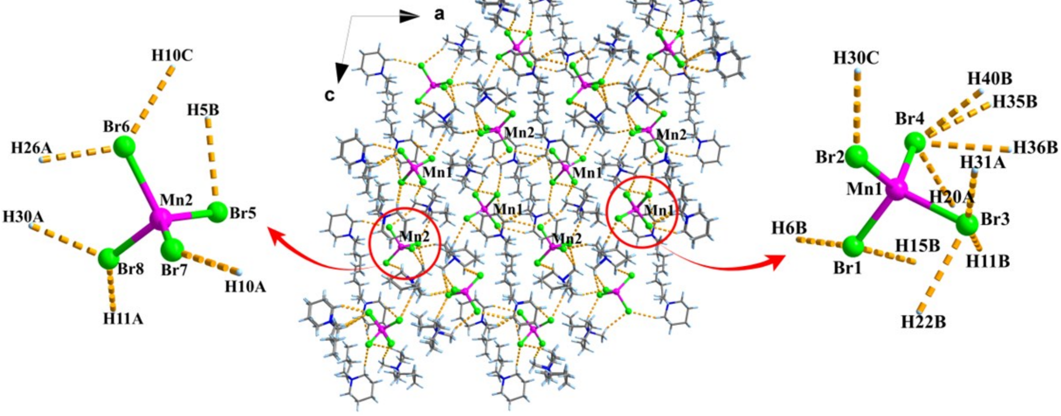

Fig. S3 Structural diagrams of **2**. Packing of the structure of **2** viewed along the *b*-axis (middle); highlighted hydrogen bonds for Mn(2)Br_4 (left) and Mn(1)Br_4 (right).

Table S1 Crystallographic data and refinement details for compounds **1** and **2**.

Crystal	$[P14]_4[MnBr_2]_2$ (**1**)	$[PP14]_4[MnBr_2]_2$ (**2**)
Empirical formula	$C_{18}H_{40}Br_4MnN_2$	$C_{20}H_{44}Br_4MnN_2$
Formula weight	659.10	687.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a/Å	17.0484(3)	32.1617(6)

b/Å	10.30830(10)	10.0012(2)
c/Å	29.8192(4)	34.9081(6)
β/°	100.0370(10)	101.273(2)
V/Å^3	5160.22(13)	11011.8(4)
Z	8	16
T/K	100	100
F(000)	2616	5488
ρ_{calcd}/g cm^{-3}	1.697	1.658
μ/mm^{-1}	11.440	10.748
Measured refls.	21648	40982
Independent refls.	8682	10219
No. of parameters	459	708
R_{int}	0.0402	0.0555
R_1 (I> 2$\sigma(I)$)^a	0.0433	0.0791
wR (I> 2$\sigma(I)$)^b	0.1065	0.1392
GOF	1.015	1.011

[a] $R_1 = \sum\|F_o|-|F_c\|/\sum|F_o|$, [b] $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table S2 Hydrogen bonding data for compound **1**.

D-H---A	d(D-H) (Å)	d(H---A) (Å)	d(D---A) (Å)	< (DHA) (°)
C(1)-H(1A)---Br(3)#1	0.99	3.09	3.853(5)	135.2
C(1)-H(1B)---Br(4)	0.99	2.98	3.796(5)	140.3
C(4)-H(4A)---Br(5)	0.99	2.96	3.917(5)	161.9
C(4)-H(4B)---Br(3)#1	0.99	3.04	3.833(5)	138.0
C(5)-H(5A)---Br(4)#2	0.98	3.08	4.034(5)	164.0
C(5)-H(5B)---Br(4)	0.98	3.13	3.957(5)	143.4
C(5)-H(5C)---Br(5)	0.98	2.98	3.893(5)	156.5
C(6)-H(6B)---Br(4)	0.99	2.98	3.876(5)	150.5
C(10)-H(10C)---Br(4)	0.99	2.97	3.735(5)	135.0
C(10)-H(10D)---Br(5)#1	0.99	3.04	3.815(5)	136.0
C(11)-H(11C)---Br(4)	0.99	3.12	3.710(5)	119.3
C(13)-H(13C)---Br(2)#3	0.99	2.86	3.823(5)	163.5
C(14)-H(14E)---Br(7)#1	0.98	3.13	4.110(5)	178.6
C(14)-H(14F)---Br(2)#3	0.98	3.02	3.824(5)	140.4
C(15)-H(15C)---Br(2)	0.99	2.99	3.937(5)	161.0
C(15)-H(15D)---Br(3)#3	0.99	3.03	3.939(4)	153.7
C(16)-H(16C)---Br(7)#1	0.99	3.11	3.928(5)	140.9
C(16)-H(16D)---Br(5)#1	0.99	3.12	4.066(5)	159.3
C(19)-H(19B)---Br(7)#4	0.99	3.08	3.862(5)	136.7
C(19)-H(19B)---Br(8)#4	0.99	3.08	3.878(5)	138.7
C(22)-H(22A)---Br(7)	0.99	2.91	3.700(5)	137.6
C(23)-H(23C)---Br(8)#4	0.98	3.07	3.794(5)	132.0
C(24)-H(24B)---Br(2)#5	0.99	2.92	3.892(5)	169.1

C(28)-H(28A)---Br(8)	0.99	2.96	3.820(5)	146.0
C(28)-H(28B)---Br(6)#6	0.99	3.04	3.852(5)	139.8
C(31)-H(31B)---Br(1)	0.99	3.12	4.061(5)	158.7
C(32)-H(32A)---Br(1)	0.98	3.05	3.987(5)	161.5
C(34)-H(34B)---Br(5)	0.99	3.13	3.816(5)	127.4

Symmetry transformations used to generate equivalent atoms: #1 -*x*+1, *y*+1/2, -*z*+1/2; #2 -*x*+1, *y*-1/2, -*z*+1/2; #3 -*x*+1, -*y*+1, -*z*; #4 -*x*, -*y*+1, -*z*+1; #5 *x*, -*y*+3/2, *z*+1/2; #6 -*x*, *y*-1/2, -*z*+1/2

Table S3 Hydrogen bonding data for compound **2**.

D-H---A	d(D-H) (Å)	d(H---A) (Å)	d(D---A) (Å)	< (DHA) (°)
C(1)-H(1B)---Br(6B)#1	0.99	3.06	3.537(18)	110.7
C(2)-H(2A)---Br(4B)#1	0.99	3.11	3.81(2)	129.0
C(5)-H(5B)---Br(5)	0.99	3.09	3.962(18)	148.1
C(6)-H(6B)---Br(1)#1	0.99	2.89	3.866(15)	168.4
C(6)-H(6B)---Br(1B)#1	0.99	3.03	3.993(16)	164.8
C(10)-H(10A)---Br(7)#2	0.98	3.11	4.064(15)	164.4
C(10)-H(10A)---Br(7B)#2	0.98	2.98	3.903(17)	156.9
C(10)-H(10B)---Br(6B)#1	0.98	2.99	3.78(2)	139.3
C(10)-H(10C)---Br(6)	0.98	3.05	4.012(17)	166.6
C(10)-H(10C)---Br(6B)	0.98	3.10	4.074(18)	177.1
C(11)-H(11A)---Br(8)#3	0.99	2.98	3.931(13)	161.3
C(11)-H(11B)---Br(3)#4	0.99	2.95	3.812(11)	145.4
C(11)-H(11B)---Br(3B)#4	0.99	2.64	3.559(13)	155.2
C(15)-H(15A)---Br(5B)#5	0.99	2.96	3.942(16)	171.3
C(15)-H(15B)---Br(1)#4	0.99	3.07	3.955(12)	149.9
C(15)-H(15B)---Br(1B)#4	0.99	3.13	3.987(13)	145.2
C(20)-H(20A)...Br(4)#5	0.98	2.88	3.83(2)	162.7
C(20B)-H(20D)...Br(4B)#7	0.98	2.90	3.80(2)	153.2
C(22)-H(22A)---Br(1B)#2	0.99	3.03	3.70(2)	125.5
C(22)-H(22B)---Br(3)#2	0.99	3.03	3.85(2)	140.3
C(25)-H(25B)---Br(1B)#6	0.99	3.14	4.000(18)	146.3
C(26)-H(26A)---Br(6)#6	0.99	2.76	3.722(16)	163.8
C(26)-H(26A)---Br(6B)#6	0.99	2.87	3.853(18)	175.3
C(30)-H(30A)---Br(8)#6	0.98	2.94	3.794(13)	146.9
C(30)-H(30A)---Br(8B)#6	0.98	2.94	3.688(13)	134.0
C(30)-H(30C)---Br(2)	0.98	3.04	3.981(12)	160.6
C(30)-H(30C)---Br(2B)	0.98	2.98	3.934(17)	164.0
C(31)-H(31A)---Br(3)#6	0.99	3.00	3.60(2)	120.2
C(35)-H(35B)---Br(4)#7	0.99	2.98	3.87(2)	150.7

C(36)-H(36B)---Br(4)#7	0.99	3.07	3.93(3)	147.0
C(40)-H(40B)---Br(4)#7	0.98	2.88	3.81(3)	158.4
C(34B)-H(34C)---Br(8B)#2	0.99	2.43	3.24(3)	138.9
C(35B)-H(35C)---Br(8B)#2	0.99	2.92	3.40(3)	111.2
C(37B)-H(37C)---Br(2B)#6	0.99	2.84	3.74(3)	151.7

Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z+1/2, #2 -x+1/2,y-1/2,-z+3/2, #3 x,y-1,z, #4 -x,-y+1,-z+1, #5 -x+1/2,-y+3/2,-z+1, #6 x,-y+1,z-1/2, #7 -x+1/2,-y+1/2,-z+1, #8 x-1/2,y-1/2,z.

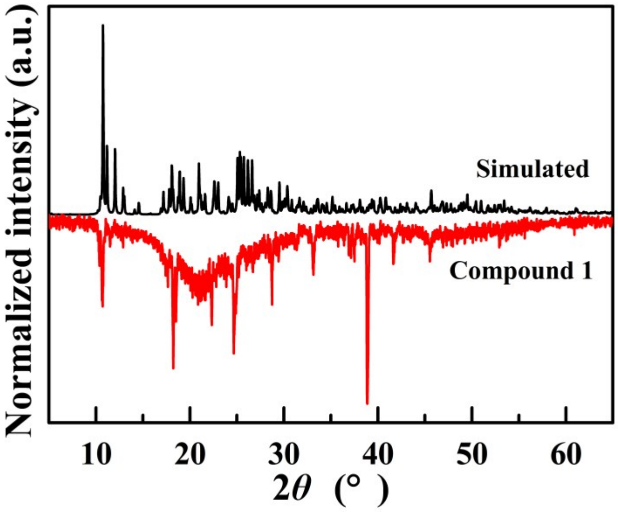

Fig. S4 The powder X-ray diffraction (PXRD) pattern of **1** compared to that simulated from single-crystal X-ray data of **1**.

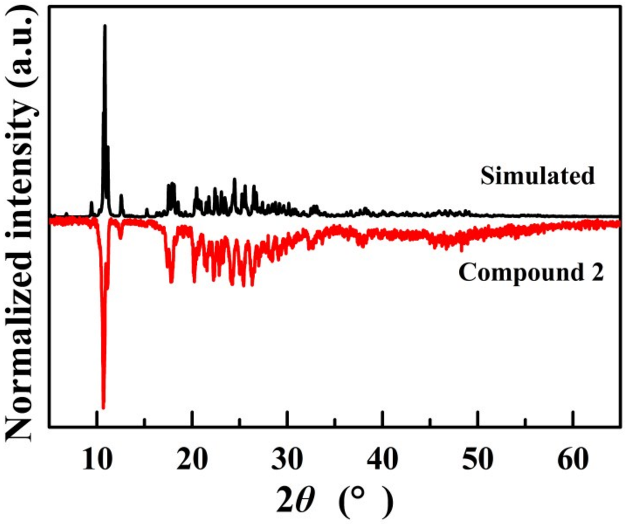

Fig. S5 The powder X-ray diffraction (PXRD) pattern of **2** compared to that simulated from single-crystal X-ray data of **2**.

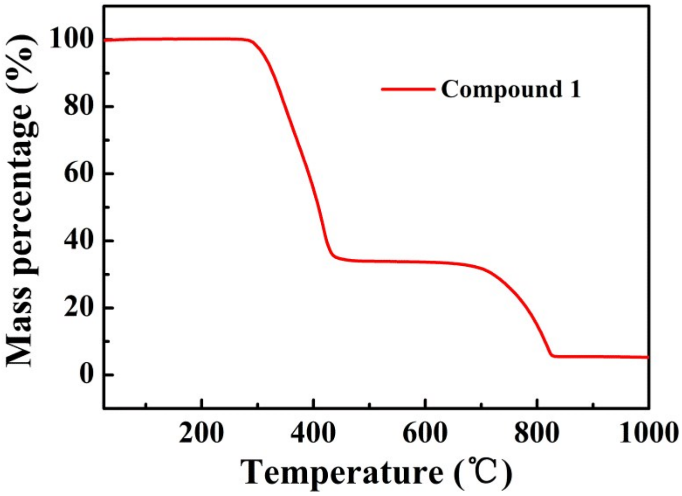

Fig. S6 Thermogravimetric curve for **1**.

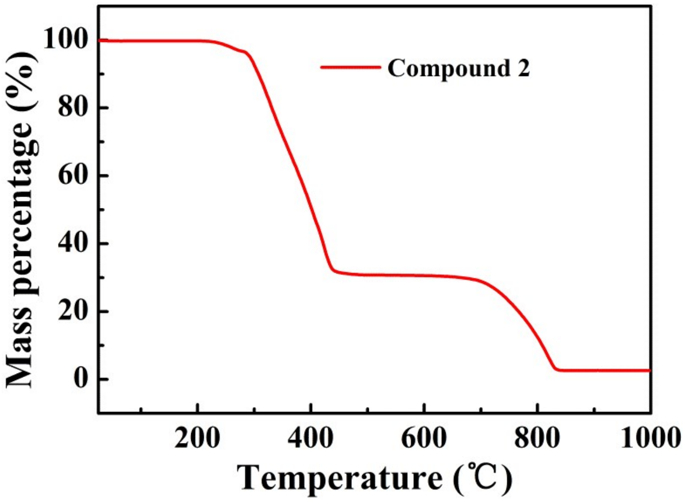

Fig. S7 Thermogravimetric curve for **2**.

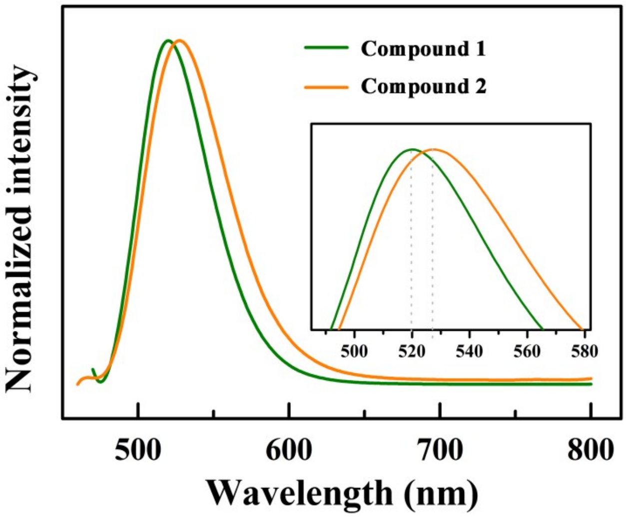

Fig. S8 The emission spectra for compounds **1** and **2**.

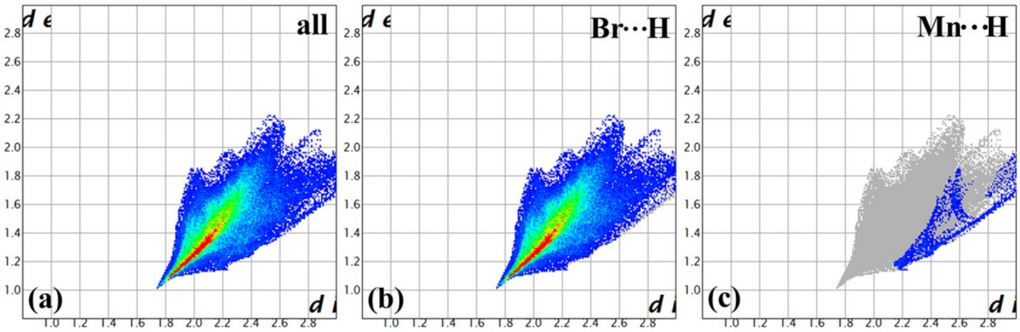

Fig. S9 The 2D fingerprint plots for $[MnBr_4]^{2-}$ anion in compound **1** resolved into different types of intermolecular interactions.

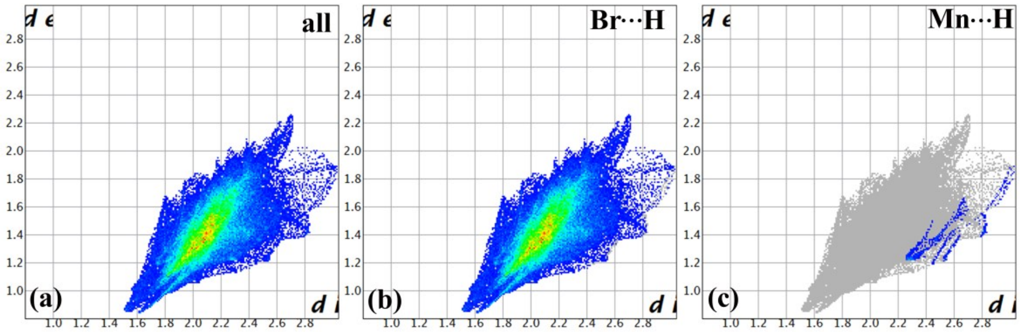

Fig. S10 The 2D fingerprint plots for $[MnBr_4]^{2-}$ anion in compound **2** resolved into different types of intermolecular interactions.

Table S4 Comparison of the photoluminescent data of title compounds and the reported ones.

Compound	***QY***	**λ_{em} (nm)**	**Ref.**
[Pyrrolidinium][$MnBr_3$]	58.5%	680	3
[PPh_4]$_2$[$MnBr_4$]	98%	522	4
[Diisopropylammonium]$_2$[$MnBr_4$]	62.2%	525	5
[Pyrrilidinium]$MnCl_3$	53.6%	640	6
[$C_{10}H_{16}N$]$_2$[$MnBr_4$]	72.26%	514	7
(2-methylimidazolium)$MnCl_3(H_2O)$	/	613	8
(3-pyrrolinium)$MnCl_3$	28.22%	635	9
$[(CH_3)_3NH]_3(MnBr_3)(MnBr_4)$	41.96%	507, 609	10
[Mn(dppeO_2)$_3$][$MnBr_4$]	28.9%	594	11
(Hmpy)$MnCl_3$ (Hmpy = N-methylpyrrolidinium)	54.54%	632	12
$C_{11}H_{21}Cl_3MnN_2$	35.8%	639	13
$C_{11}H_{22}Cl_4MnN_2$	92.3%	530	13
[P14]$_2$[$MnBr_4$]	80.89%	520	This work

$[PP14]_2[MnBr_4]$	54.53%	527	This work

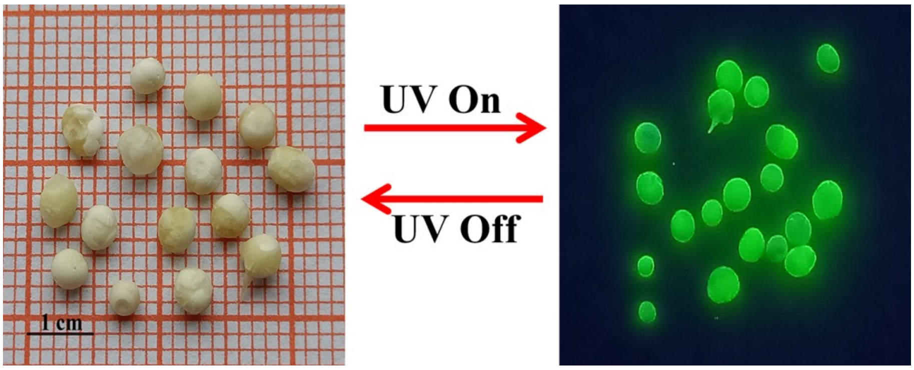

Fig. S11 The photos of the balls made by mixing compound **1** and **PAN**.

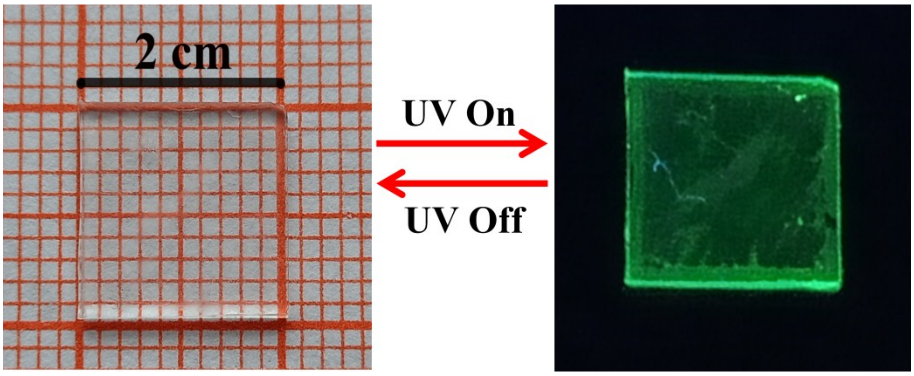

Fig. S12 The photos of the film made by mixing compound **1** and **PAN**.

References:

1 G. M. Sheldrick, *Acta Crystallogr. Sect. C* 2015, **71**, 3-8.
2 http://www.ccdc.cam.au.uk/mercury/
3 Y. Zhang, W. Q. Liao, D. W. Fu, H. Y. Ye, C. M. Liu, Z. N. Chen and R. G. Xiong, *Adv. Mater.* 2015, **27**, 3942–3946.
4 L. J. Xu, C. Z. Sun, H. Xiao, Y. Wu and Z. N. Chen, *Adv. Mater.* 2016, 1605739.
5 C. Jiang, N. Zhong, C. Luo, H. Lin, Y. Zhang, H. Peng and C. G. Duan, *Chem. Commun.* 2017, **53**, 5954-5957.
6 Y. Zhang, W. Q. Liao, D. W. Fu, H. Y. Ye, Z. N. Chen and R. G. Xiong, *J. Am. Chem. Soc.* 2015, **137**, 4928-4931.
7 X. W. Cai, Y. Y. Zhao, H. Li, C. P. Huang and Z. Zhou, *J. Mol. Struct.* 2018, **1161**, 262-266.
8 Q. Guo, W. Y. Zhang, C. Chen, Q. Ye and D. W. Fu, *J. Mater. Chem. C* 2017, **5**, 5458-5464.
9 H. Y. Ye, Q. Zhou, X. Niu, W. Q. Liao, D. W. Fu, Y. Zhang, Y. M. You, J. Wang, Z. N. Chen and R. G. Xiong, *J. Am. Chem. Soc.* 2015, **137**, 13148-54.
10 Z. Wei, W. Q. Liao, Y. Y. Tang, P. F. Li, P. P. Shi, H. Cai and R. G. Xiong, *J. Am. Chem. Soc.* 2018, **140**, 8110-8113
11 Y. Wu, X. Zhang, L. J. Xu, M. Yang and Z. N. Chen, *Inorg. Chem.* 2018, **57**, 9175-9181.
12 X. F. Sun, P. F. Li, W. Q. Liao, Z. X. Wang, J. X. Gao, H. Y. Ye and Y. Zhang, *Inorg. Chem.* 2017, **56**, 12193-12198.
13 Z. X. Wang, P. F. Li, W. Q. Liao, Y. Tang, H. Y. Ye and Y. Zhang, *Chem. Asian J.* 2016, **11**, 981-985.