Electronic Supplementary Material (ESI) for RSC Advances.

"Novel hypophosphite hybrid perovskites of $[CH_3NH_2NH_2][Mn(H_2POO)_3]$ and $[CH_3NH_2NH_2][Mn(H_2POO)_{2.83}(HCOO)_{0.17}]$ exhibiting antiferromagnetic order and red photoluminescence"

by Mirosław Mączka et al.

Table S1. Experimental details.

For all structures: orthorhombic, *Pnma*, *Z*=4. Experiments were carried out with Mo *K*α radiation using an Xcalibur, Atlas. Absorption was corrected for by multi-scan methods, *CrysAlis PRO* 1.171.38.43 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. H-atom parameters were constrained.

	I	II	III
Crystal data			
Chemical formula	$CH_{13}MnN_2O_6P_3$	$CH_{13}MnN_2O_6P_3$	$C_{1.17}H_{12.84}MnN_2O_6P_{2.83}$
M_r	296.98	296.98	293.60
Temperature (K)	295	100	295
a, *b*, *c* (Å)	9.4005 (6), 13.2990 (8), 8.6191 (6)	9.2009 (6), 13.2604 (8), 8.5408 (6)	9.3938 (6), 13.3012 (8), 8.5716 (6)
V (Å^3)	1077.54 (12)	1042.04 (12)	1071.01 (12)
μ (mm^{-1})	1.67	1.73	1.66
Crystal size (mm)	0.22 × 0.18 × 0.09	0.22 × 0.18 × 0.09	0.23 × 0.19 × 0.11
Data collection			
T_{min}, T_{max}	0.838, 1.000	0.638, 1.000	0.968, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3038, 1067, 873	11095, 1037, 1014	6102, 1399, 1111
R_{int}	0.022	0.042	0.030
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.609	0.610	0.693
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.034, 0.100, 1.05	0.028, 0.083, 1.18	0.037, 0.106, 1.10
No. of reflections	1067	1037	1399
No. of parameters	69	68	68
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.36, -0.56	0.44, -0.47	0.34, -0.66

Computer programs: *CrysAlis PRO* 1.171.38.43 (Rigaku OD, 2015), *SHELXT* 2014/5 (Sheldrick, 2014), *SHELXL2018*/3 (Sheldrick, 2018).

Table S2. Selected geometric parameters (Å, º).

I		II		III	
Mn1—O3^{i}	2.163 (2)	Mn1—O3^{i}	2.1548 (17)	Mn1—O3^{i}	2.163 (2)
Mn1—O3	2.163 (2)	Mn1—O3	2.1548 (17)	Mn1—O3	2.163 (2)
Mn1—O2^{i}	2.176 (2)	Mn1—O2^{i}	2.1731 (16)	Mn1—O2^{i}	2.174 (2)
Mn1—O2	2.176 (2)	Mn1—O2	2.1731 (16)	Mn1—O2	2.174 (2)
Mn1—O1^{ii}	2.192 (2)	Mn1—O1^{ii}	2.1859 (17)	Mn1—O1^{ii}	2.1919 (19)
Mn1—O1^{iii}	2.192 (2)	Mn1—O1^{iii}	2.1859 (17)	Mn1—O1^{iii}	2.1919 (19)
P1—O3	1.470 (2)	P1—O3	1.4863 (18)	P1—O3	1.471 (2)
P1—O3^{iv}	1.470 (2)	P1—O3^{iv}	1.4864 (18)	P1—O3^{iv}	1.471 (2)
P2—O2	1.484 (2)	P2—O2	1.4986 (18)	P2—O2	1.471 (2)
P2—O1	1.493 (2)	P2—O1	1.5037 (17)	P2—O1	1.475 (2)
N2—N1	1.442 (5)	N2—N1	1.444 (4)	N2—N1	1.443 (5)
N2—C1	1.470 (6)	N2—C1	1.488 (4)	N2—C1	1.470 (5)
O3^{i}—Mn1—O3	180.00 (15)	O3^{i}—Mn1—O3	180.0	O3^{i}—Mn1—O3	180.0
O3^{i}—Mn1—O2^{i}	90.74 (9)	O3^{i}—Mn1—O2^{i}	90.59 (7)	O3^{i}—Mn1—O2^{i}	90.97 (8)
O3—Mn1—O2^{i}	89.26 (10)	O3—Mn1—O2^{i}	89.41 (7)	O3—Mn1—O2^{i}	89.03 (9)
O3^{i}—Mn1—O2	89.26 (10)	O3^{i}—Mn1—O2	89.41 (7)	O3^{i}—Mn1—O2	89.04 (9)
O3—Mn1—O2	90.74 (10)	O3—Mn1—O2	90.59 (7)	O3—Mn1—O2	90.96 (8)
O2^{i}—Mn1—O2	180.0	O2^{i}—Mn1—O2	180.0	O2^{i}—Mn1—O2	180.0
O3^{i}—Mn1—O1^{ii}	85.16 (10)	O3^{i}—Mn1—O1^{ii}	85.24 (7)	O3^{i}—Mn1—O1^{ii}	85.01 (8)
O3—Mn1—O1^{ii}	94.84 (10)	O3—Mn1—O1^{ii}	94.76 (7)	O3—Mn1—O1^{ii}	94.98 (8)
O2^{i}—Mn1—O1^{ii}	89.84 (9)	O2^{i}—Mn1—O1^{ii}	90.03 (7)	O2^{i}—Mn1—O1^{ii}	89.65 (9)
O2—Mn1—O1^{ii}	90.16 (9)	O2—Mn1—O1^{ii}	89.97 (7)	O2—Mn1—O1^{ii}	90.35 (9)
O3^{i}—Mn1—O1^{iii}	94.84 (10)	O3^{i}—Mn1—O1^{iii}	94.76 (7)	O3^{i}—Mn1—O1^{iii}	94.99 (8)
O3—Mn1—O1^{iii}	85.16 (10)	O3—Mn1—O1^{iii}	85.24 (7)	O3—Mn1—O1^{iii}	85.02 (8)

O2^{i}—Mn1—O1^{iii}	90.16 (9)	O2^{i}—Mn1—O1^{iii}	89.97 (7)	O2^{i}—Mn1—O1^{iii}	90.35 (9)
O2—Mn1—O1^{iii}	89.84 (9)	O2—Mn1—O1^{iii}	90.03 (7)	O2—Mn1—O1^{iii}	89.65 (9)
O1^{ii}—Mn1—O1^{iii}	180.0	O1^{ii}—Mn1—O1^{iii}	180.0	O1^{ii}—Mn1—O1^{iii}	180.0
O3—P1—O3^{iv}	118.0 (2)	O3—P1—O3^{iv}	116.93 (16)	O3—P1—O3^{iv}	117.7 (2)
O2—P2—O1	117.05 (13)	O2—P2—O1	116.36 (10)	O2—P2—O1	116.72 (12)
P2—O1—Mn1^{v}	127.35 (13)	P2—O1—Mn1^{v}	124.84 (10)	P2—O1—Mn1^{v}	127.76 (11)
P2—O2—Mn1	130.98 (14)	P2—O2—Mn1	128.71 (10)	P2—O2—Mn1	131.42 (12)
P1—O3—Mn1	156.37 (18)	P1—O3—Mn1	154.85 (12)	P1—O3—Mn1	156.62 (16)
N1—N2—C1	116.3 (4)			N1—N2—C1	115.8 (3)

Symmetry code(s): (i) -*x*+1, -*y*+1, -*z*+1; (ii) *x*+1/2, *y*, -*z*+3/2; (iii) -*x*+1/2, -*y*+1, *z*-1/2; (iv) *x*, -*y*+3/2, *z*; (v) -*x*+1/2, -*y*+1, *z*+1/2.

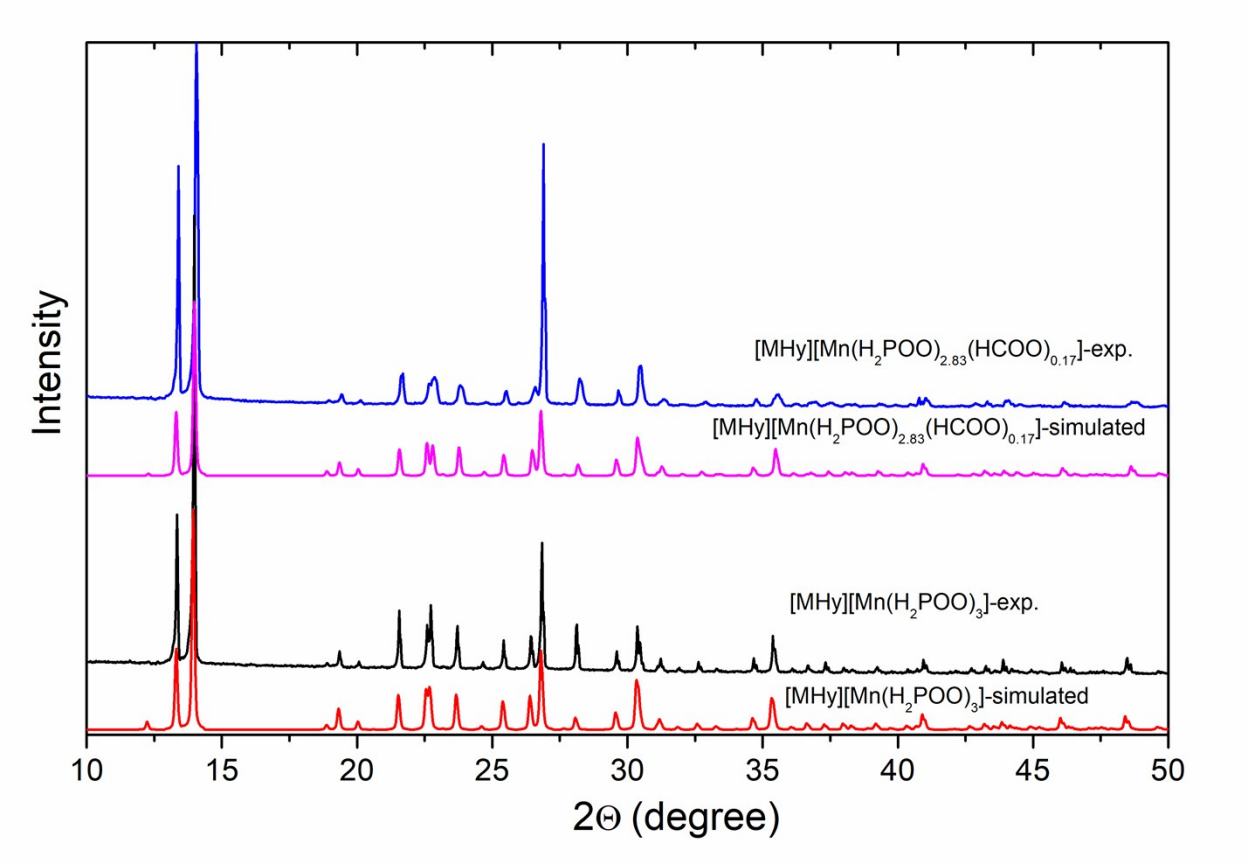

Figure S1. Room-temperature powder XRD pattern for the obtained samples together with the calculate ones based on the RT single crystal structure.

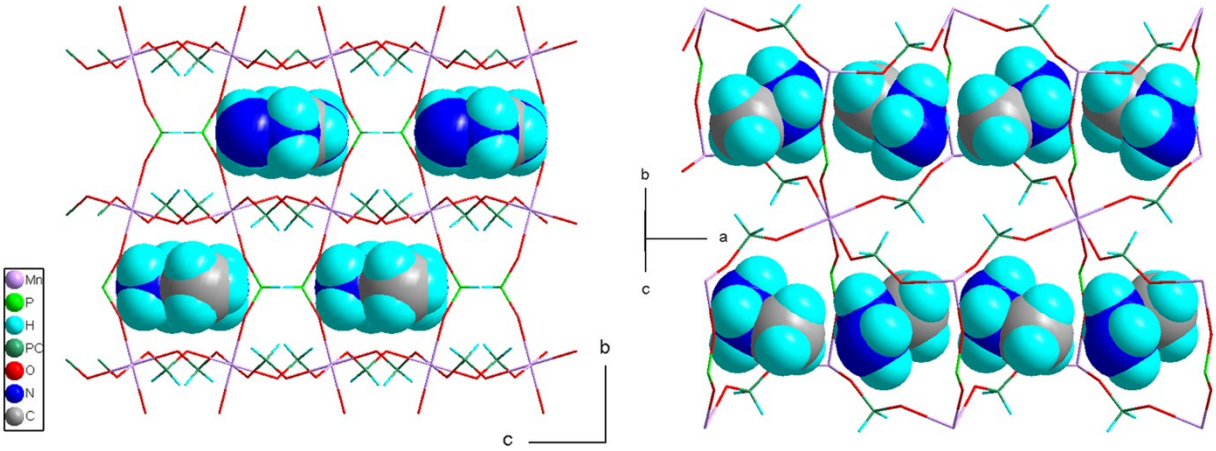

Figure S2. The position of MHy^{+} cations in the structure of $[MHy][Mn(H_2POO)_3]$. Unlike in $[MHy][Mn(HCOO)_3]$ formate, the cations are distributed in the windows expanding along orthorhombic *a*-direction.

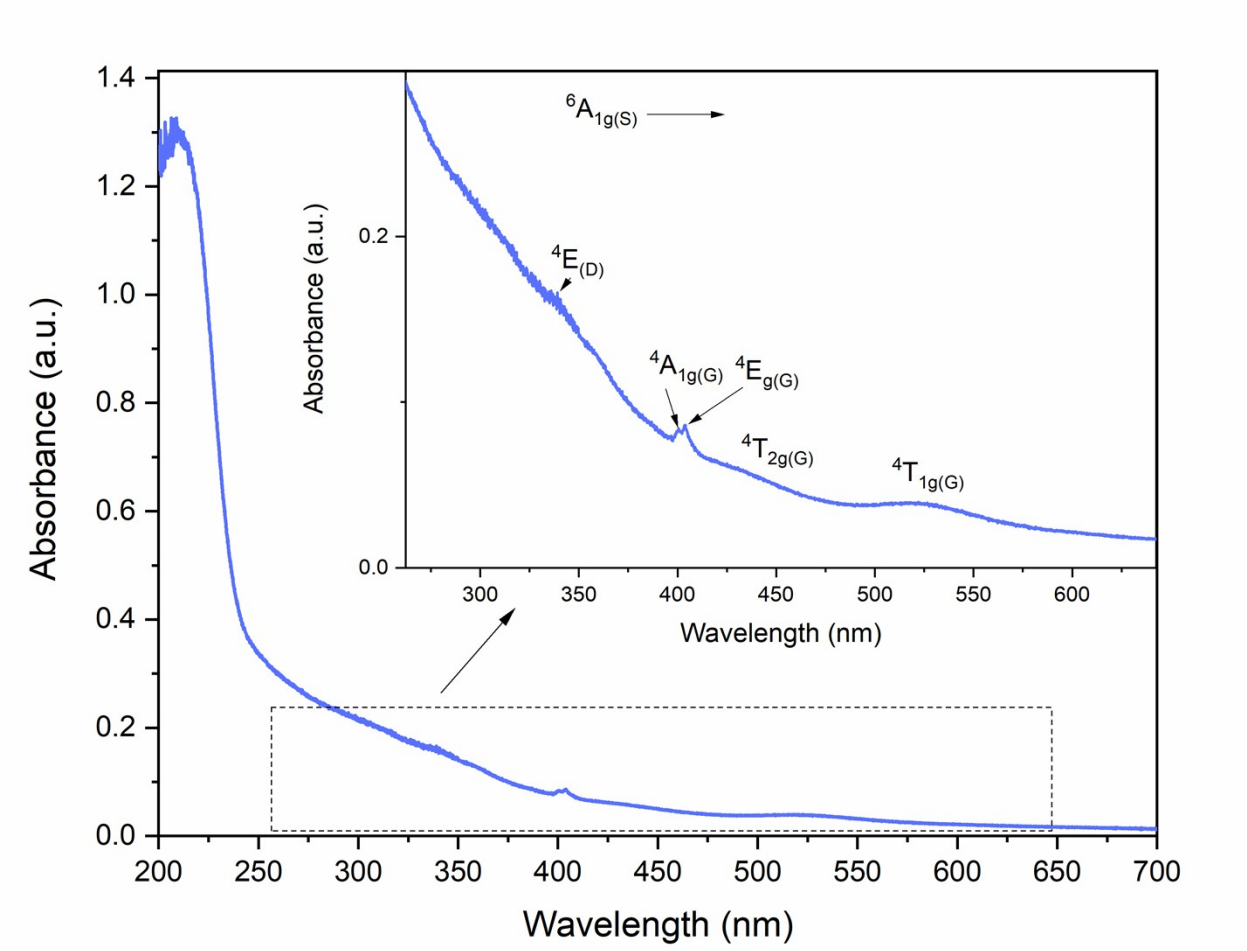

Figure S3. Absorption spectrum of [MHy][$Mn(H_2POO)_3$] recorded at 300 K.

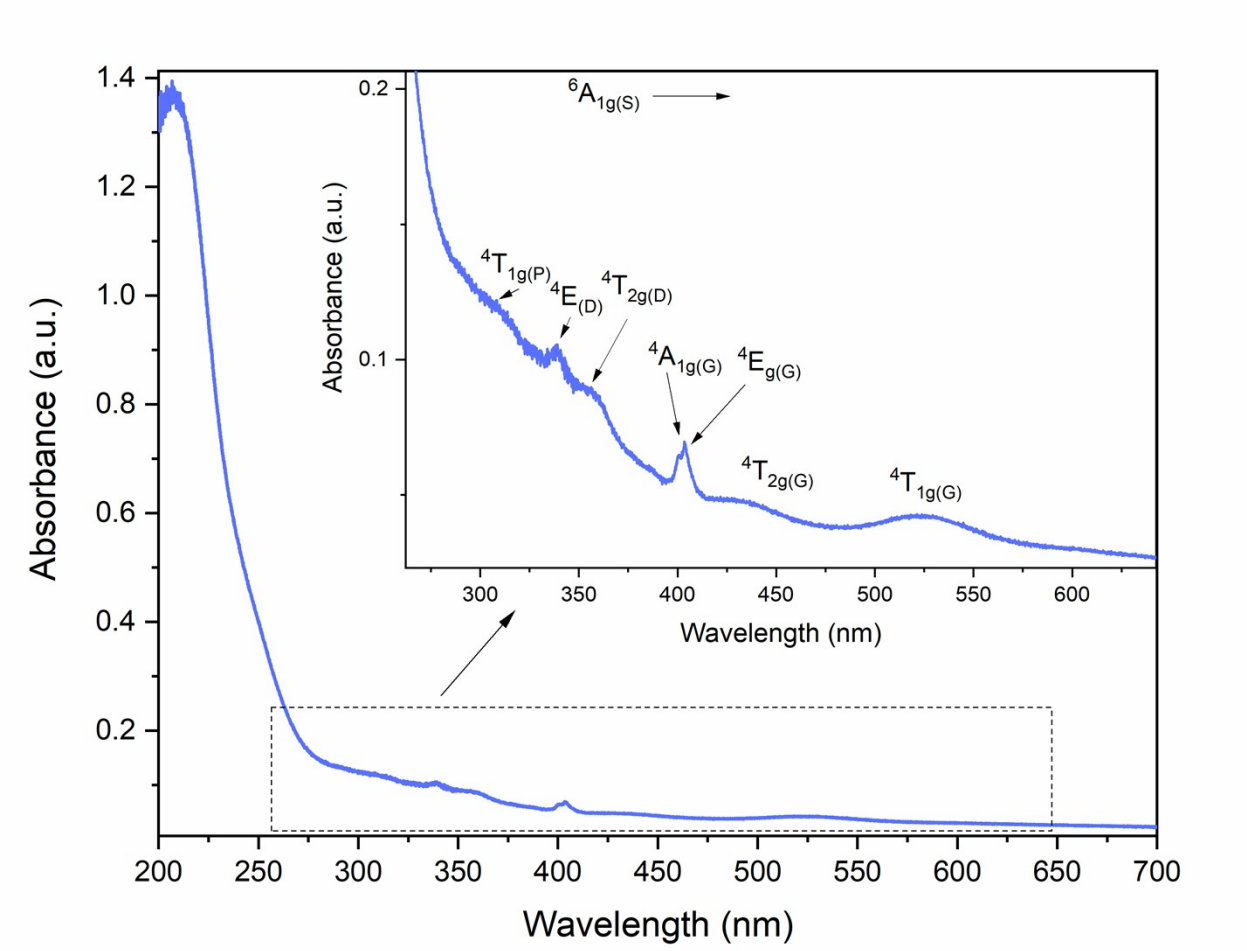

Fig S4. Absorption spectrum of $[MHy][Mn(H_2POO)_{2.83}(HCOO)_{0.17}]$ recorded at 300 K.

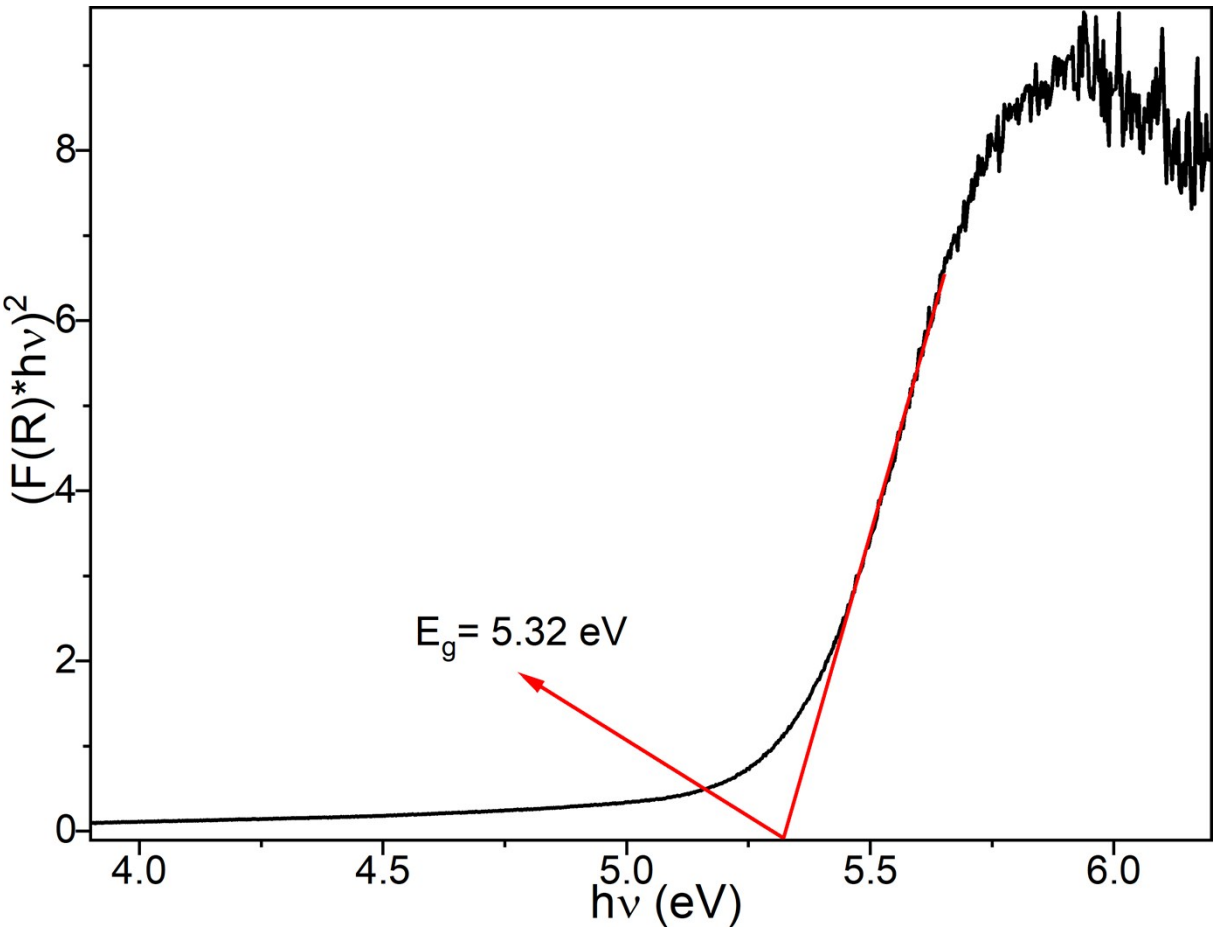

Figure S5. The energy band gap of [MHy][$Mn(H_2POO)_3$] determined using Kubelka – Munk function.

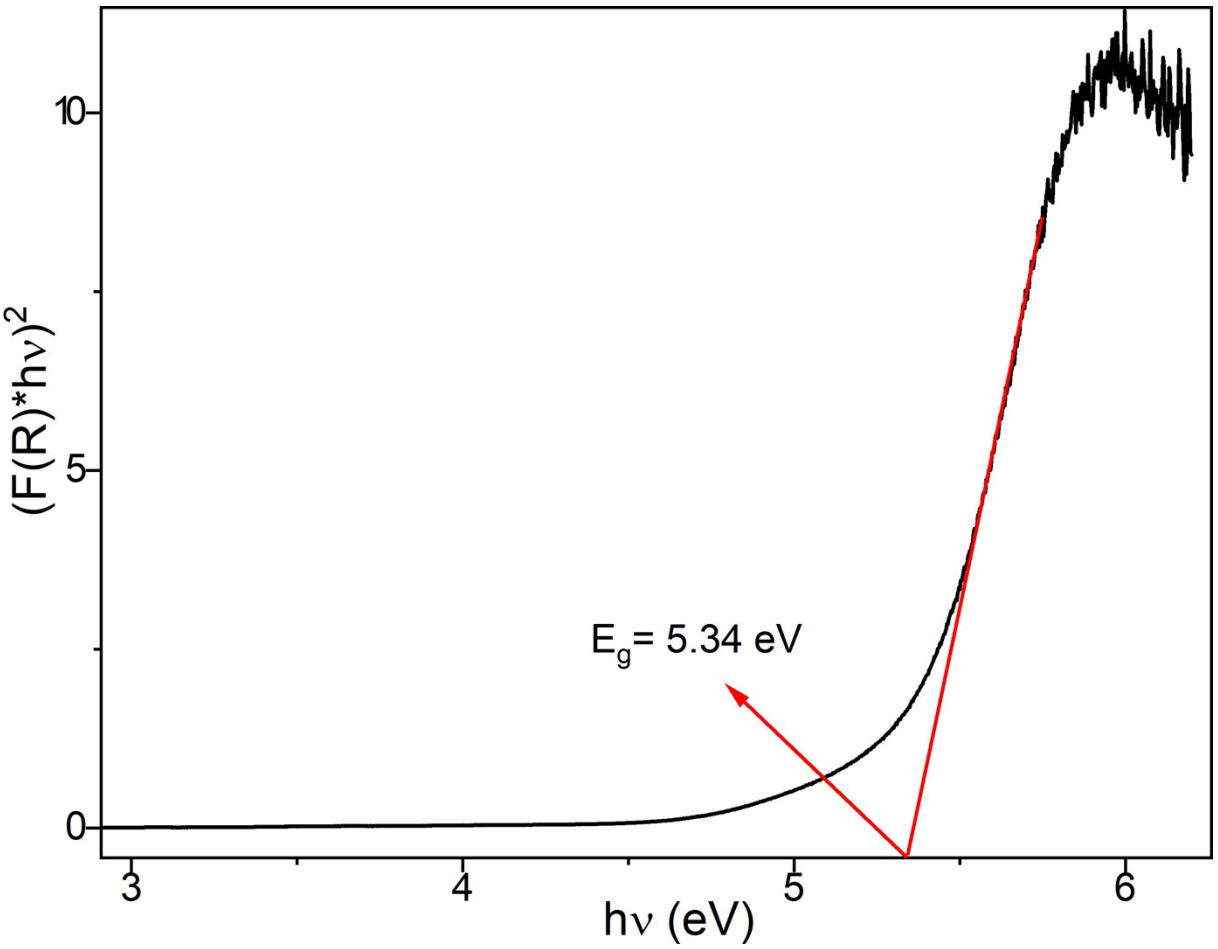

Figure S6. The energy band gap of $[MHy][Mn(H_2POO)_{2.83}(HCOO)_{0.17}]$ determined using Kubelka – Munk function.

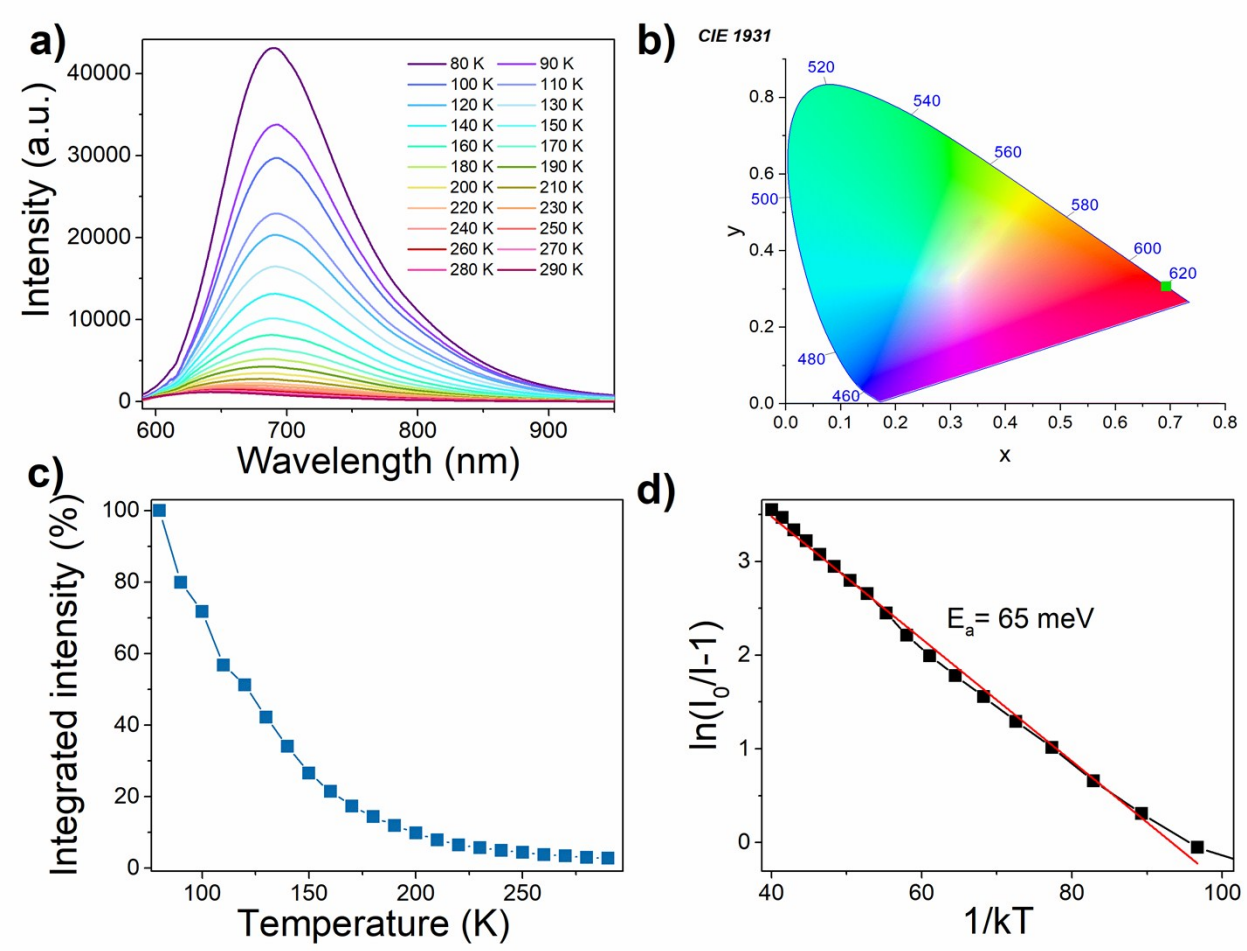

Figure S7. a) The temperature-dependent emission spectra of $[MHy][Mn(H_2POO)_{2.83}(HCOO)_{0.17}]$ excited at 266 nm, b) CIE coordinate at 80 K, c) integrated emission intensity as a function of temperature and d) activation energy of the thermal quenching.

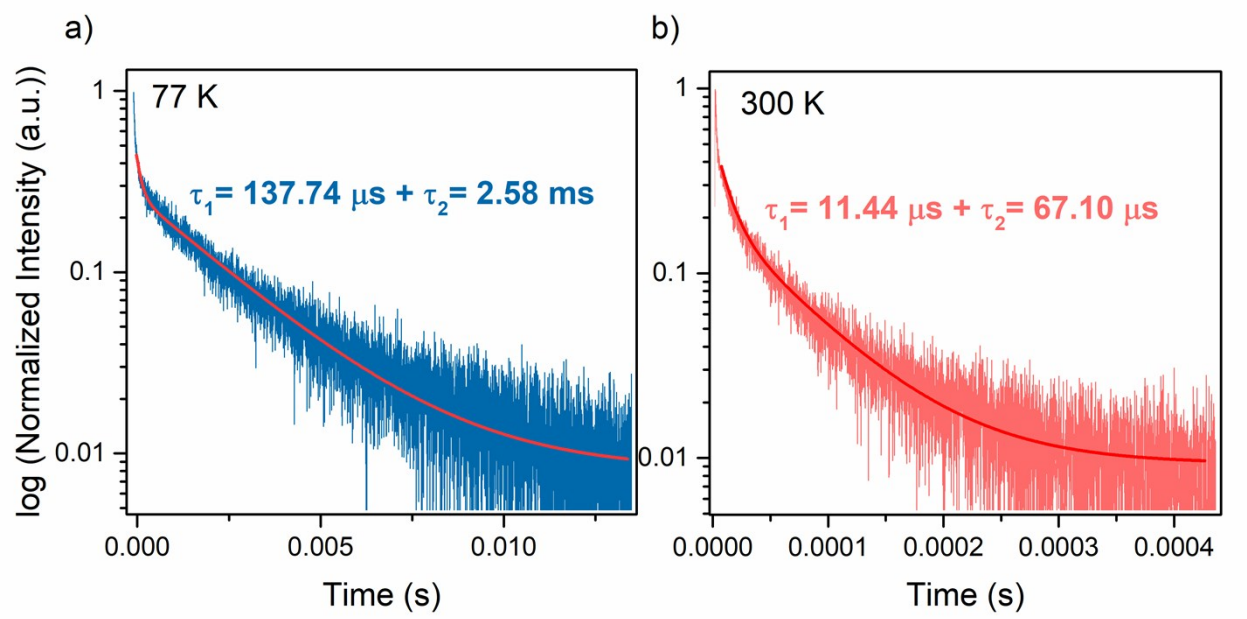

Figure S8. Emission decay curves of [MHy][$Mn(H_2POO)_{2.83}(HCOO)_{0.17}$] at a) 77 K and b) 300 K.

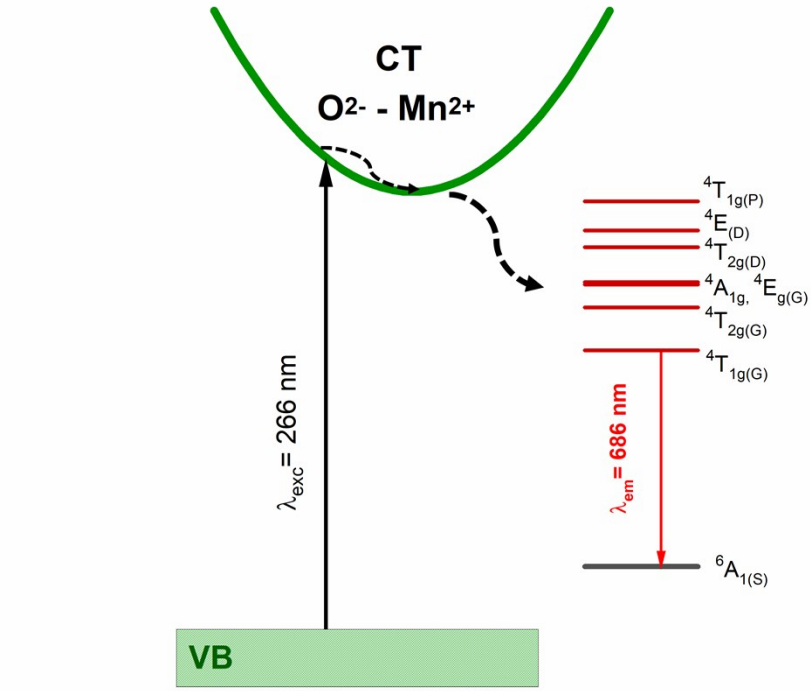

Figure S9. Schematic illustration of possible luminescence mechanism of Mn^{2+} in hypophosphites compounds, where dashed arrows indicate nonradiative processes.