Electronic Supplementary Material (ESI) for CrystEngComm

Solvent-free synthesis of new manganese phosphate-oxalate hybrid solids

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Physical measurements:

The thermogravimetric analyses were performed on a Mettler Toledo TGA/SDTA 851e analyzer in a flow of N_2 with a heating rate of 10 ºC/min. IR spectra (KBr pellets) were recorded on an ABB Bomen MB 102 spectrometer. Powder X-ray diffraction (XRD) data were obtained using a Rigaku D/MAX-rA diffractometer with Cu-Kα radiation (λ = 1.5418 Å). The photoluminescent spectra were measured on a Perkin-Elmer LS 55 luminescence spectrometer equipped with a 450 W xenon lamp.

Synthesis

Synthesis of Mn(2,2'-bpy)(H_2PO_4)(C_2O_4)$_{0.5}$ (1): A mixture of $Mn(H_2PO_4)_2{\cdot}2H_2O$ (0.569 g), $H_2C_2O_4{\cdot}2H_2O$ (0.378 g), and 2,2'-bipyridine (0.312 g) was sealed in a Teflon-lined stainless steel autoclave and heated at 150 °C for 7 d. The autoclave was subsequently allowed to cool to room temperature. Rod-like crystals were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (15.3 % yield based on manganese).

Synthesis of Mn(phen)(H_2PO_4)(C_2O_4)$_{0.5}$ (2): A mixture of $Mn(H_2PO_4)_2{\cdot}2H_2O$ (0.569 g), $H_2C_2O_4{\cdot}2H_2O$ (0.504 g), and 1,10-phenanthroline·H_2O (0.401 g) was sealed in a Teflon-lined stainless steel autoclave and heated at 150 °C for 14 d. The autoclave was subsequently allowed to cool to room temperature. Rod-like crystals were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (52.4 % yield based on manganese).

Synthesis of (4,4'-H_2bpy)$_{0.5}$·Mn(H_2PO_4)(C_2O_4) (3): A mixture of $Mn(H_2PO_4)_2{\cdot}2H_2O$ (0.569 g), $H_2C_2O_4{\cdot}2H_2O$ (0.252 g), and 4,4'-bipyridine (0.312 g) was sealed in a

Teflon-lined stainless steel autoclave and heated at 150 °C for 14 d. The autoclave was subsequently allowed to cool to room temperature. Prism-like crystals were recovered by filtration, washed with distilled water, and finally dried at ambient temperature (30.3 % yield based on manganese).

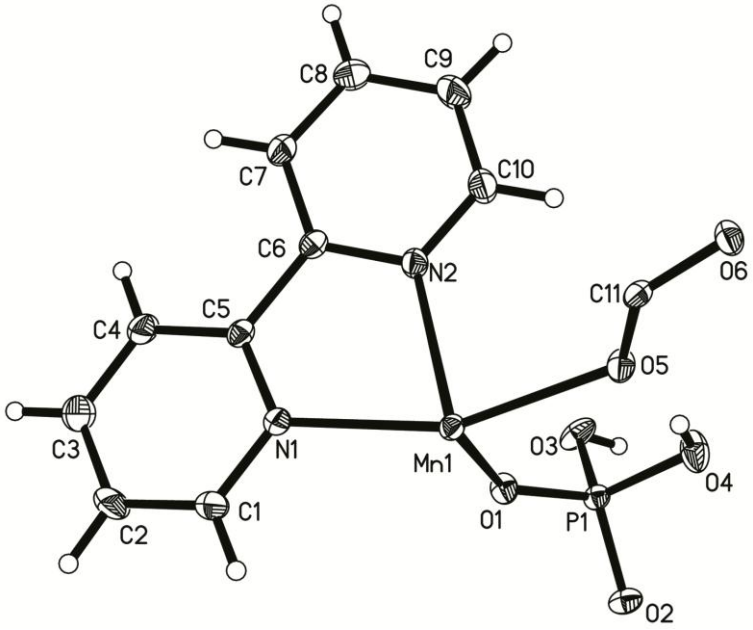

Figure S1. ORTEP plot of the asymmetric unit of compound **1**, showing the labeling scheme and the 30% probability displacement ellipsoid.

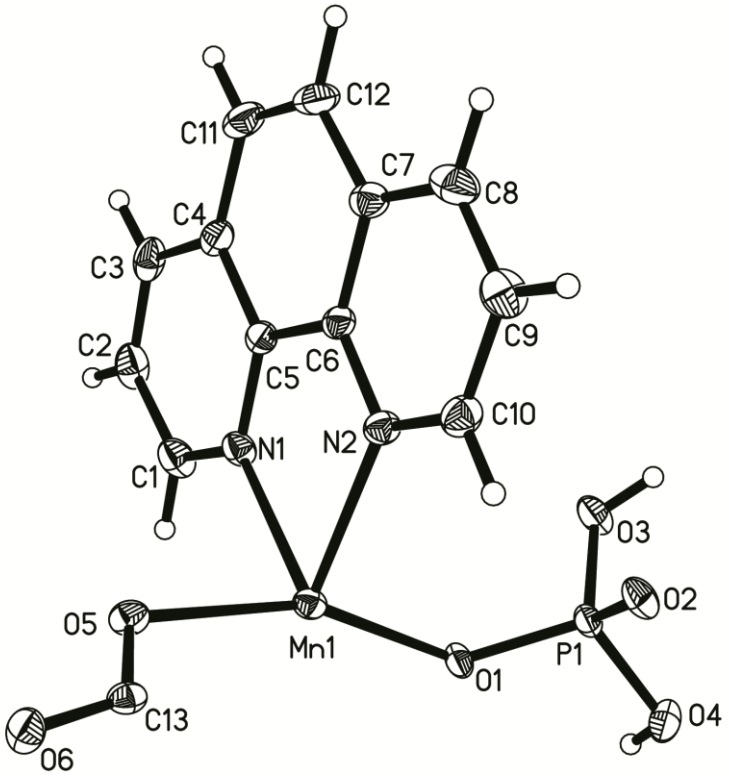

Figure S2. ORTEP plot of the asymmetric unit of compound **2**, showing the labeling scheme and the 30% probability displacement ellipsoid.

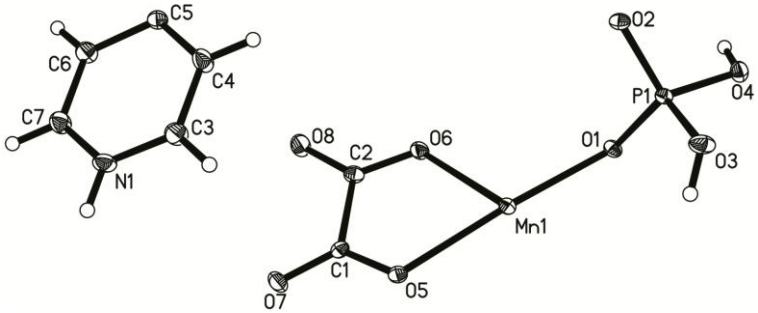

Figure S3. ORTEP plot of the asymmetric unit of compound **3**, showing the labeling scheme and the 30% probability displacement ellipsoid.

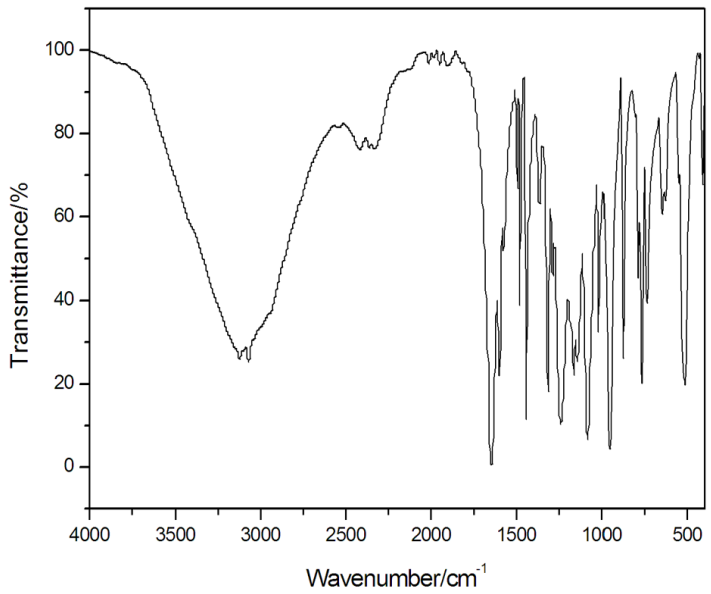

Fig. S4. IR spectrum of compound **1**.

FTIR data (cm^{-1}): 3070 (s, ν(C-H)), 1650 (vs, ν(C=O)), 1480 (m, δ(C-H)), 1440 (s, ν(C-C)), 1310 (s, ν(C-O)), 1240 (s, ν(C–N)), 1080 (s, ν_{as}(P–O)), 1020 (m, ν_{as}(P–O)), 955 (s, ν_{as}(P–O)), 876 (s, ν_{s}(P–O)), 766 (s, ν_{s}(P–O)), 513 (s, δ(P–O))

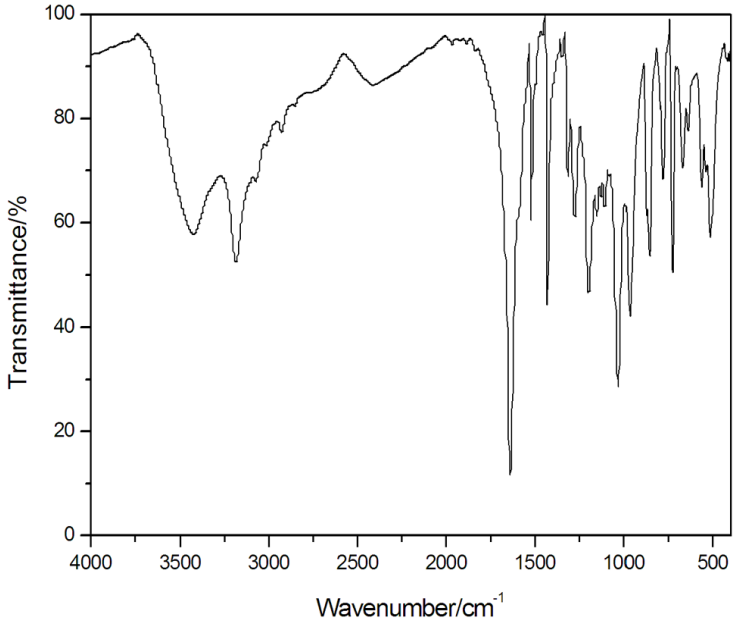

Fig. S5. IR spectrum of compound **2**.

FTIR data (cm^{-1}): 3420 (m, ν(OH) , 3180 (ν(C-H)), 1640 (vs, ν(C=O)), 1520 (m, ν(C-C)), 1430 (s, ν(C-C)), 1310 (m, ν(C-O)), 1200 (m, ν(C–N)) , 1030(s, ν_{as}(P–O)), 964 (s, ν_{as}(P–O)), 854 (s, ν_{s}(P–O)), 781(m, ν_{s}(P–O)) , 725(s, ν_{s}(P–O)) , 515 (m, δ(P–O))

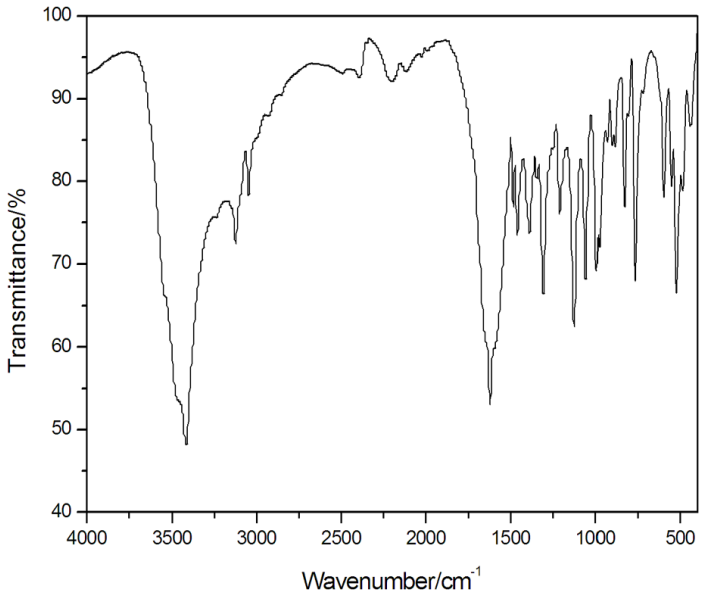

Fig. S6. IR spectrum of compound **3**.

FTIR data (cm^{-1}): 3420 (vs, ν(O-H)), 3120 (w, ν(C-H)), 3050 (w, ν(C-H)), 1620 (vs, ν(C=O)), 1460 (m, ν(C-C)), 1390 (m, δ(C–H), 1300 (m, ν(C-O)), 1210 (w, ν(C–N)), 1120 (s, ν_{as}(P–O)), 1050 (m, ν_{as}(P–O)), 995(m, ν_{as}(P–O)), 827 (m, ν_{s}(P–O)), 766 (s, ν_{s}(P–O)), 596 (m, δ(P–O)), 523 (s, δ(P–O))

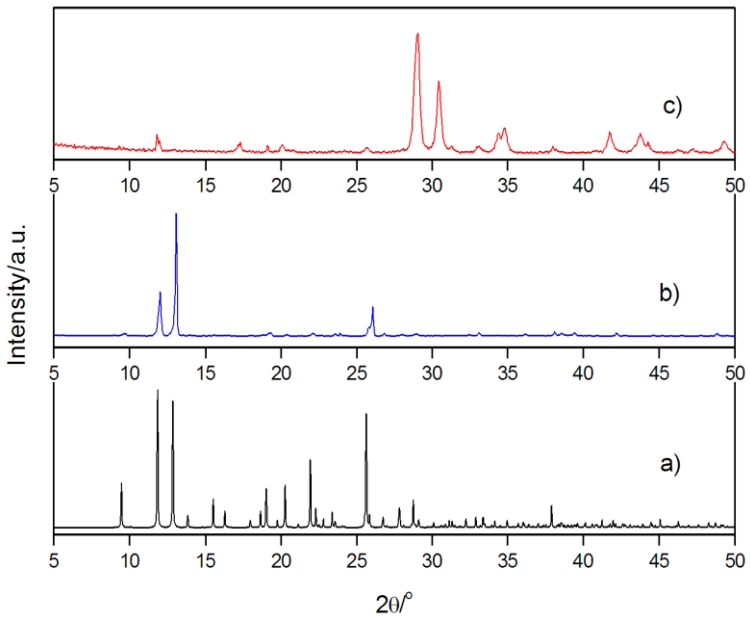

Fig. S7. (a) Simulated and (b) experimental powder XRD patterns of compound **1** and (c) the as-synthesized sample upon treatment at 700 ºC for 1 h.

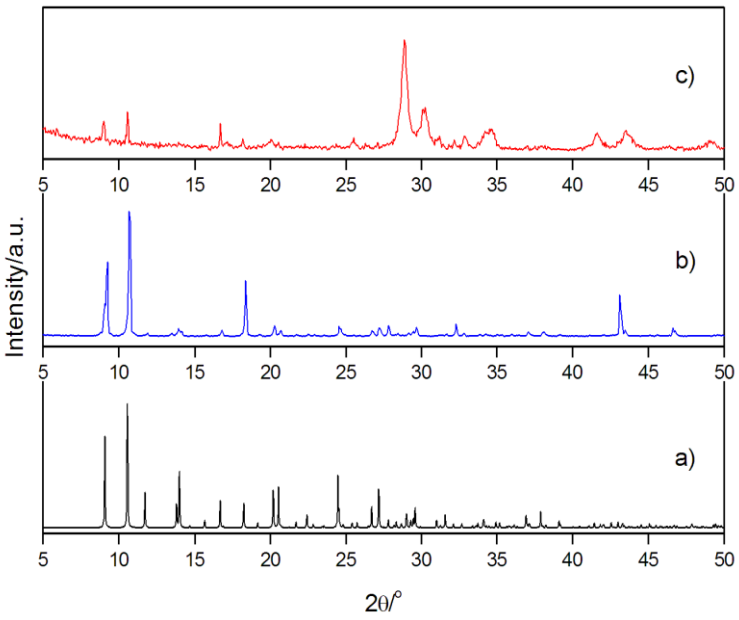

Fig. S8. (a) Simulated and (b) experimental powder XRD patterns of compound **2** and (c) the as-synthesized sample upon treatment at 700 ºC for 1 h.

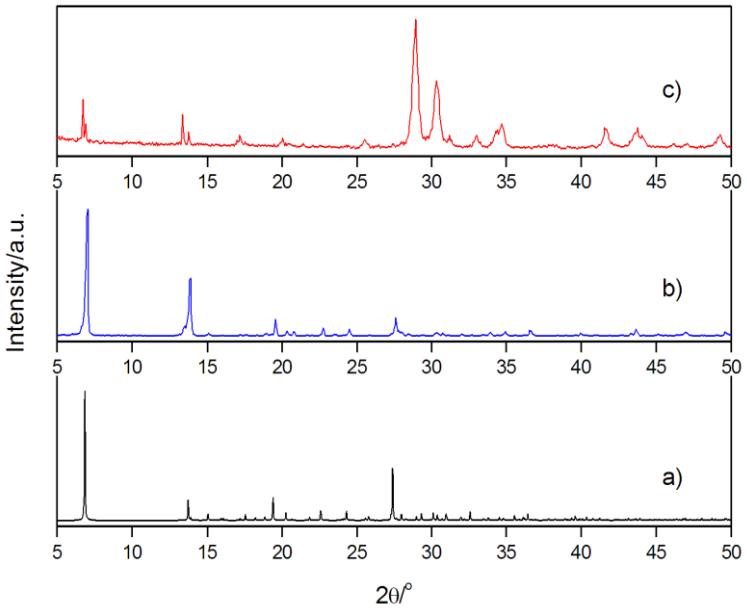

Fig. S9. (a) Simulated and (b) experimental powder XRD patterns of compound **3** and (c) the as-synthesized sample upon treatment at 700 ºC for 1 h.

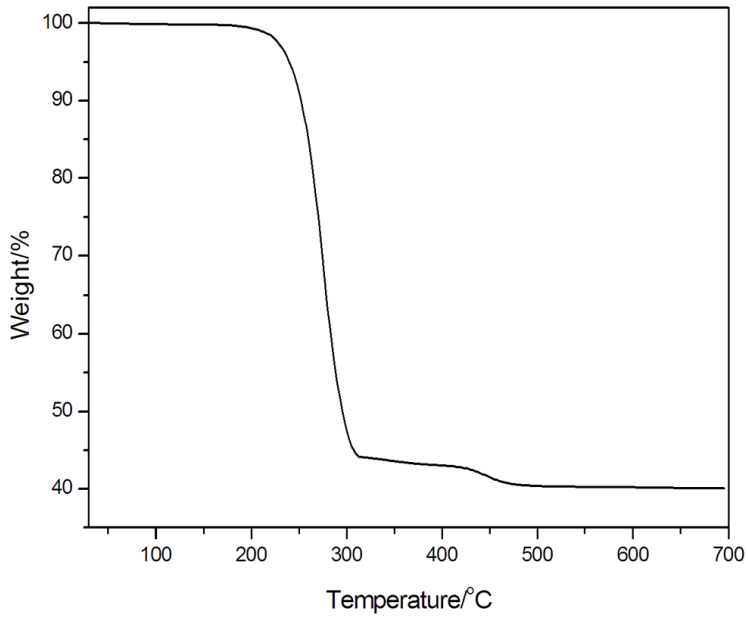

Fig. S10. TGA curve of compound **1** in a flow of air with a heating rate of 10 °C/min.

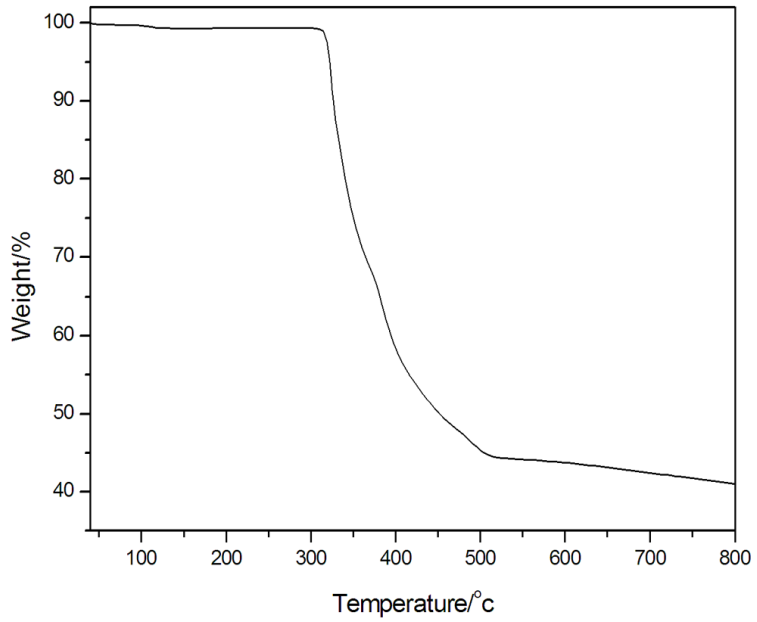

Fig. S11. TGA curve of compound **2** in a flow of air with a heating rate of 10 °C/min.

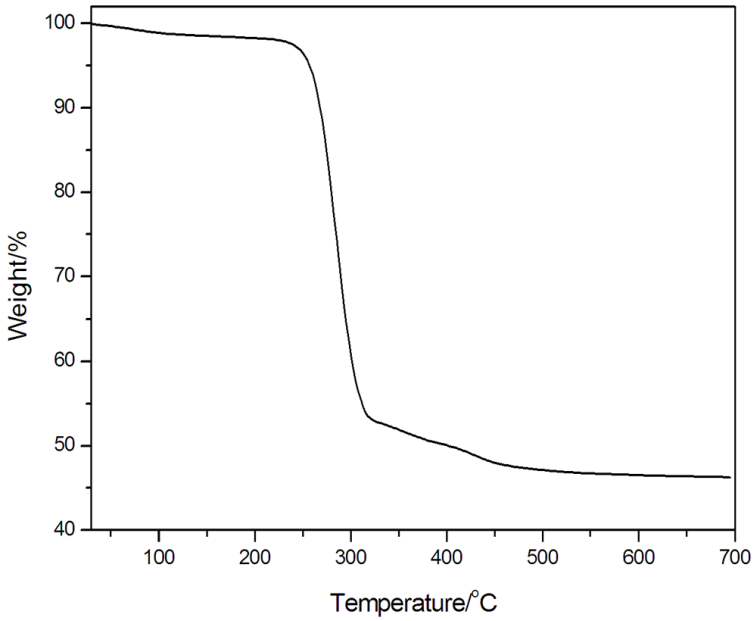

Fig. S12. TGA curve of compound **3** in a flow of air with a heating rate of 10 °C/min.

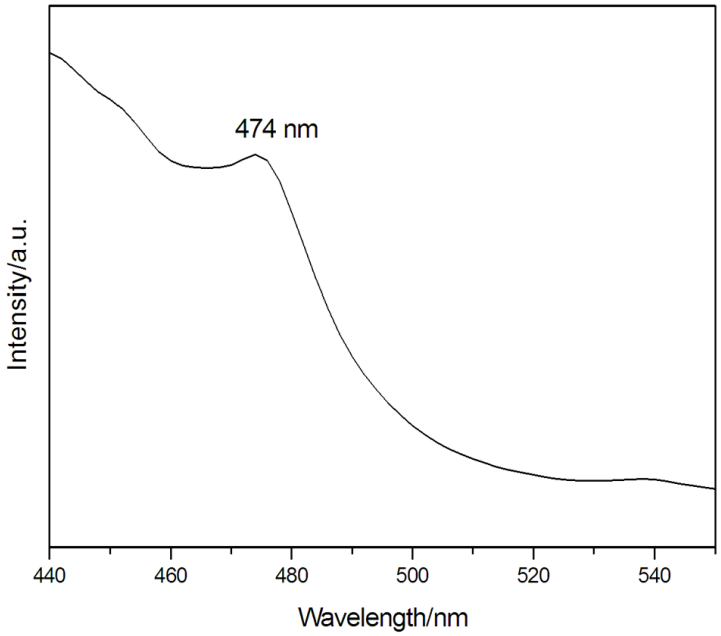

Fig. S13. Solid state photoluminescent spectrum of compound **1** at room temperature.

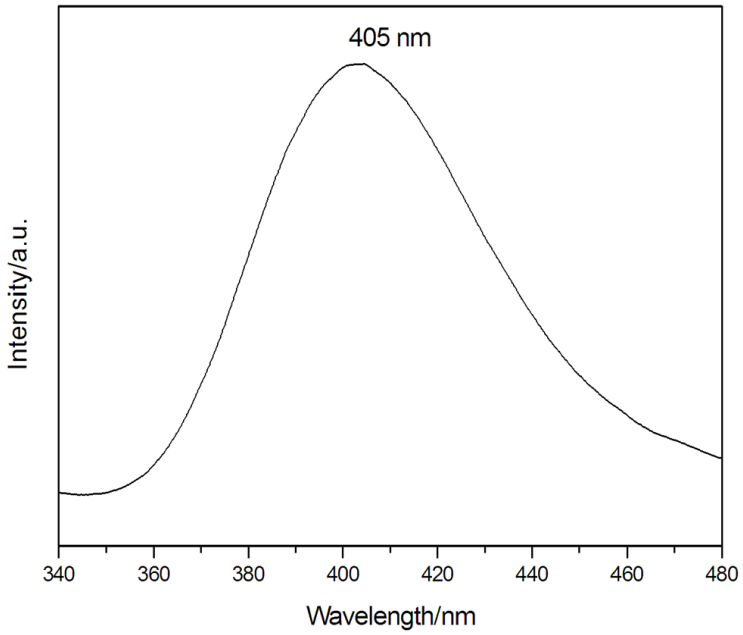

Fig. S14. Solid state photoluminescent spectrum of compound **2** at room temperature.

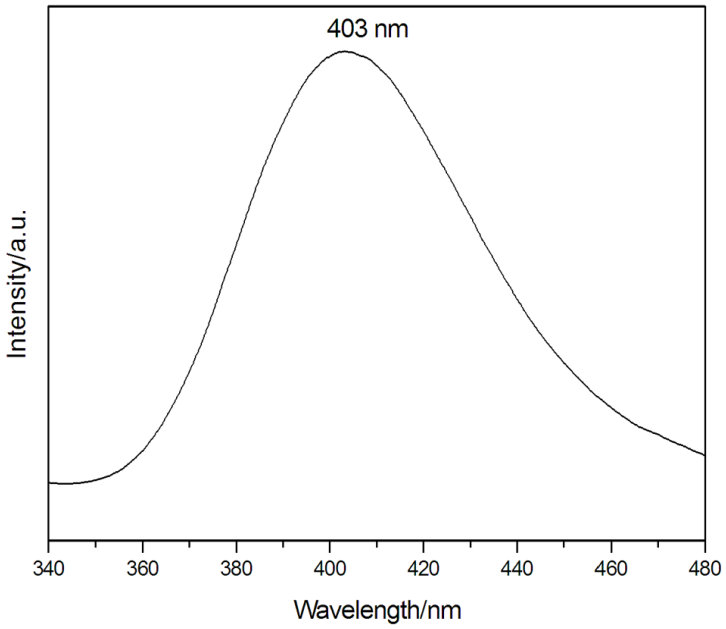

Fig. S15. Solid state photoluminescent spectrum of compound **3** at room temperature.

Table 1. Hydrogen bonds information for compounds **1**-**3**

D-H···A[a]	d(D-H)(Å)	d(H···A)(Å)	d(D···A) (Å)	<(DHA) (deg)
Compound **1**				
O3-H1···O2#1	0.82	1.87	2.674(3)	165.9
O4-H2···O5	0.82	1.88	2.693(3)	171.6
Compound **2**				
O3-H1···O2#2	0.82	1.71	2.524(2)	173.3
O4-H2···O5#3	0.82	1.89	2.683(3)	161.8
Compound **3**				
N1-H3···O8#4	0.86	1.81	2.666(3)	177.3

[a] Symmetry transformations used to generate equivalent atoms: #1 -x, -y+1, -z+1; #2 -x+1, -y+1, -z+1; #3 -x+1, -y, -z+1; #4 x-1, y, z.