Electronic Supplementary Material (ESI) for ChemComm.
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Supporting Information

Contents

Experimental Section

Materials and methods

All chemicals were reagent grade and used as purchased without further purification. The organic amine 2,4,6-tri(4-pyridyl)-1,3,5-triazine (TPT) was prepared according to literature procedure.[1]

Synthesis of 1: $H_2C_2O_4$ (0.39g, 3 mmol), ZnO (0.16 g, 2.00 mmol), TPT (0.037g, 0.12 mmol), H_3PO_4 (0.20 mL, 3.44 mmol), DMA (0.15 mL, 1.68 mmol) was added in order, then sealed in a Teflon-lined autoclave (20 mL) and heated to 145 °C for 7 days. Yield: ca. 47% based on TPT. Elemental analysis (%): calcd for $C_{10}H_{10}N_3O_7PZn$ (380.59): C, 31.56; H, 2.65; N, 11.04. Found: C, 31.02; H, 2.71; N, 10.94. IR before irradiation (KBr pellets, cm^{-1}): 3506(s), 3415(m), 3064(w), 2976(w), 2363(w), 1662(s), 1527(s), 1379(s), 1319(s), 1239(m), 1159(m), 1040(m), 954(s), 887(m), 806(s), 646(m), 515(s). IR after irradiation (KBr pellets, cm^{-1}): 3506(m), 3413(m), 2362(w), 1664(s), 1525(s), 1379(s), 1319(m), 1238(m), 1159(m), 1038(s), 955(s), 885(w), 804(s), 650(w), 513(s).

Synthesis of 2: The same procedure as compound **1** except to replace ZnO with MnO (0.15 g, 2.00 mmol). Yield: ca. 43% based on TPT. Elemental analysis (%): calcd for $C_{10}H_{10}N_3O_7PMn$ (370.11): C, 32.45; H, 2.72 N, 11.35. Found: C, 31.89; H, 3.51; N, 11.22. IR before irradiation (KBr pellets, cm^{-1}): 3510(s), 3352(m), 3065(w), 2927(w), 2360(m), 1660(s), 1525(s), 1379(s), 1315(s), 1239(m), 1159(m), 1043(m), 953(s), 879(s), 802(s), 648(m), 598(w), 505(s). IR after irradiation (KBr pellets, cm^{-1}): 3508(m), 3400(m), 2362(w), 1660(s), 1525(s), 1379(s), 1315(m), 1238(m), 1159(m), 1045(s), 953(s), 879(m), 802(s), 646(w), 594(w), 505(s).

Elemental analyses (C, H, and N) were measured on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). IR spectra were performed on a MAGNA-560 (Nicolet) FT-IR spectrometer with KBr pellets. The luminescence data were recorded on an FS5 Fluorescence spectrometer. The solid-state UV-Vis spectra were measured using $BaSO_4$ as a reference on a PerkinElmer Lamda-950 spectrophotometer. Electron spin resonance (ESR) spectroscopy was recorded on a JEOL JES-FA200 EPR spectrometer. X-ray photoelectron spectroscopy (XPS) was measured on Thermo ESCALAB 250Xi. Thermogravimetric (TG) analysis was measured using a powder sample with a

heating rate of 10℃ min^{-1} under N_2 atmosphere on a Rigaku standard TG-DTA analyzer. Magnetic measurements of the polycrystalline samples of **2** before and after light irradiation were carried out on a Quantum Design SQUID (MPMS-XL-7) magnetometer. Data were corrected for the diamagnetic contribution calculated from Pascal constants. Powder X-ray diffraction (PXRD) spectroscopy was performed on a Bruker D8 FOCUS diffractometer with a Cu-target tube and a graphite monochromator. Simulation of the PXRD curve was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge *via* the Internet at http://www.iucr.org. For the light irradiation experiments, a Perfect Light PLS-SXE 300 Xe lamp (320−780 nm, 300 w, at least 10 min) was equipped to prepare the colored samples of UV-vis, PXRD, ESR, XPS and magnetic susceptibilities studies.

X-ray Crystallography.

The single-crystal X-ray diffraction data of **1** and **2** was collected on a Rigaku SCX-mini diffractometer at 293(2) K with Mo-Kα radiation (λ = 0.71073 Å). SHELX-2016 software was used to solve the structure.[2] Detailed crystallographic data for **1** and **2** were summarized in Table S1, and the selected bond lengths and angles were listed in Table S2. Full crystallographic data for **1** and **2** has been deposited with the CCDC (1903597-1903598).

References

[S1] H. L. Anderson, S. Anderson, J. K. M. Sanders, *J. Chem. Soc., Perkin Trans. 1*. **1995**, *18*, 2231.

[S2] G. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, **2015**, *71*, 3–8.

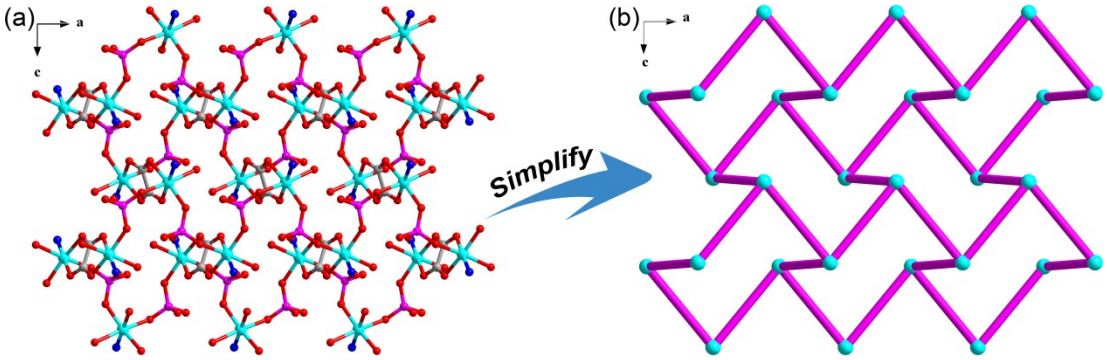

Figure S1. The inorganic-organic hybrid M-PO_4-Oxa layer: (a) The ball and stick model; (b) The topos of layer.

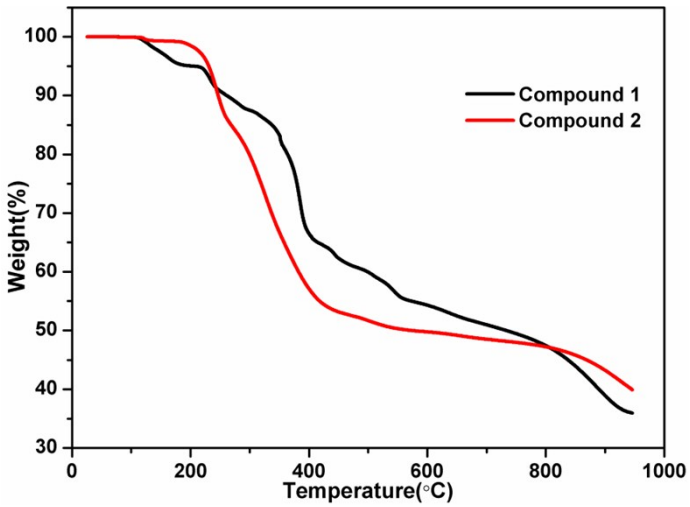

Figure S2. The TG plot of **1** and **2**.

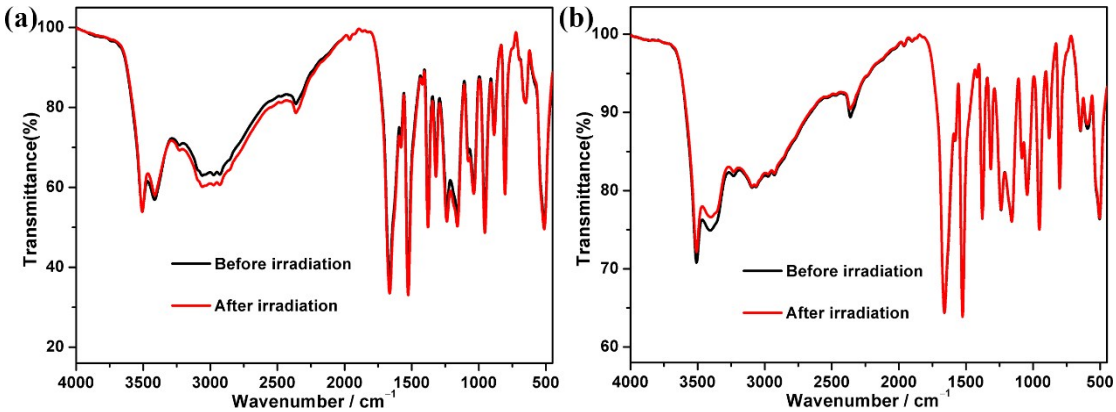

Figure S3. The IR plot of **1** and **2** before and after light irradiation.

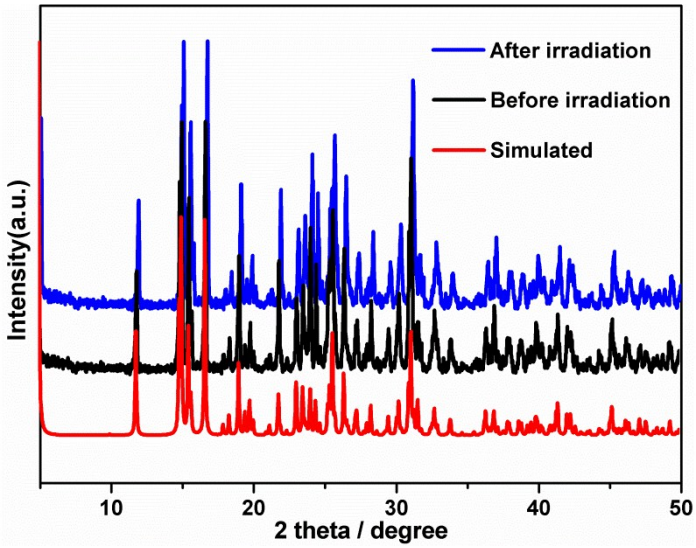

Figure S4. The PXRD plot of **1**.

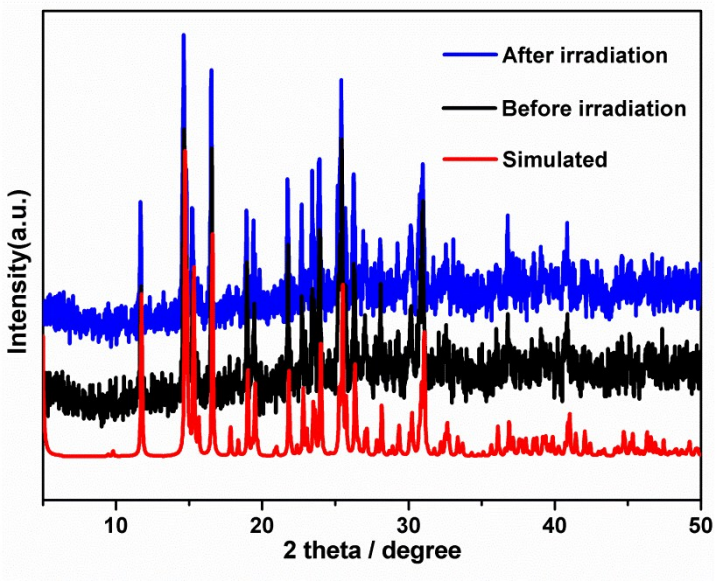

Figure S5. The PXRD plot of **2**.

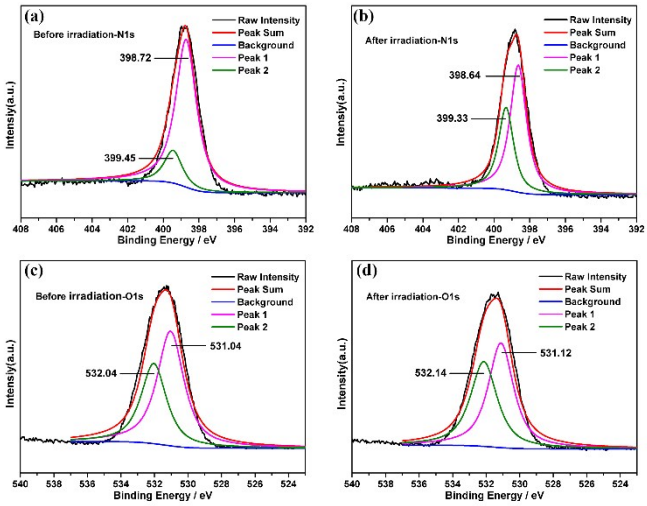

Figure S6. The XPS spectra for **1**: (a) Before light irradiation of N1s; (b) After light irradiation of N1s; (c) Before light irradiation of O1s; (d) After light irradiation of O1s.

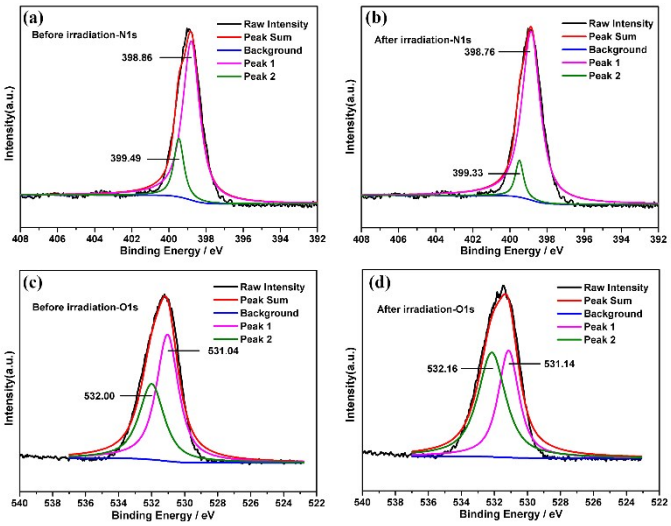

Figure S7. The XPS spectra for **2**: (a) Before light irradiation of N1s; (b) After light irradiation of N1s; (c) Before light irradiation of O1s; (d) After light irradiation of O1s.

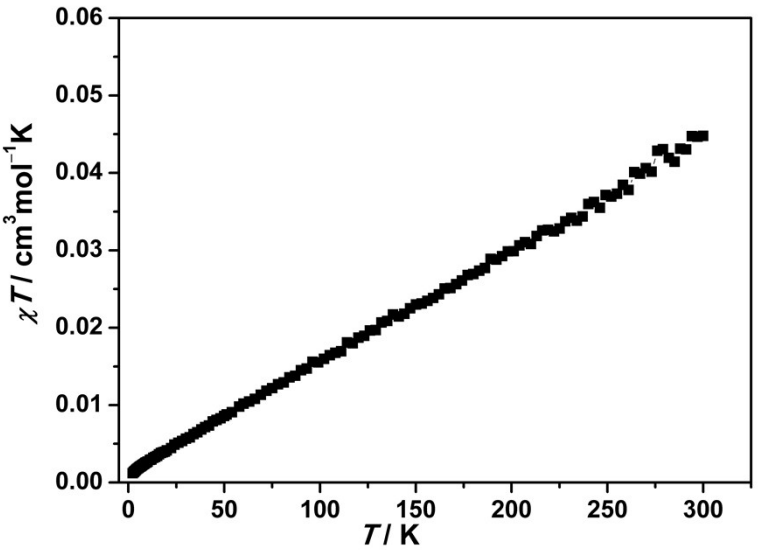

Figure S8. Temperature-dependent susceptibilities of **1** under a dc magnetic field of 1000 Oe after light irradiation.

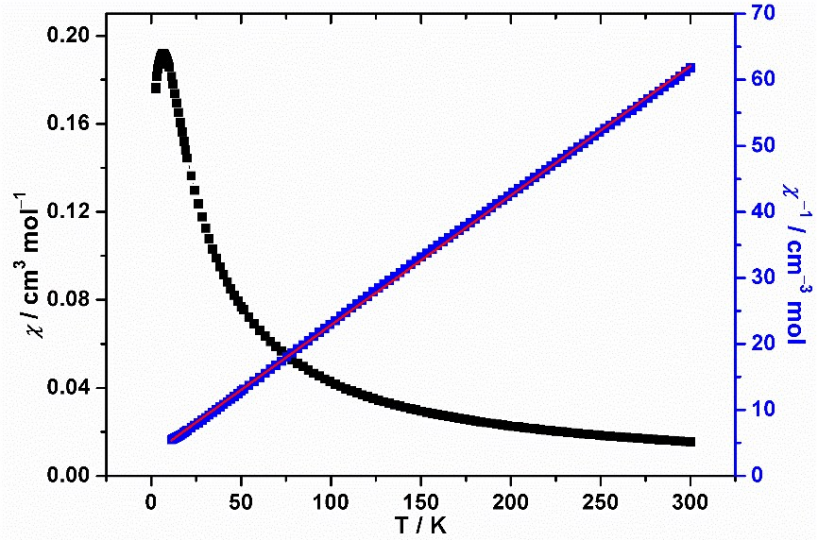

Figure S9. Plots of χ vs. T (black line) and χ^{-1} vs. T (blue line) for **2** (red solid line for the Curie-Weiss fitting).

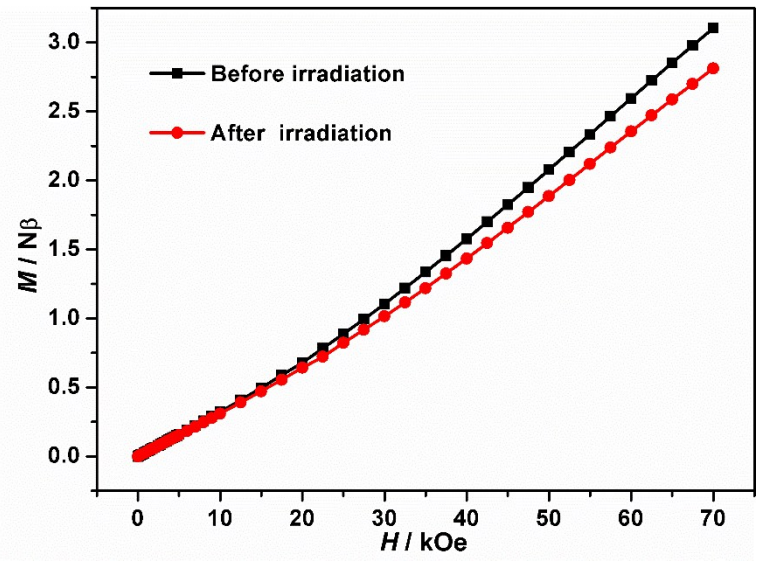

Figure S10. Isothermal magnetization curve of **2** at 2 K before and after light irradiation.

Table S1. Crystallographic data for **1** and **2** at 293K

	1		**2**	
Formula	$C_{10}H_{10}N_3O_7PZn$		$C_{10}H_{10}N_3O_7PMn$	
*M*r (g·mol^{-1})	380.55		370.12	
Space group	*Pnma*		*Pnma*	
Crystal system	Orthorhombic		Orthorhombic	
a (Å)	7.5480(5)		7.5670(5)	
b (Å)	35.339(8)		36.064(2)	
c (Å)	9.6434(6)		9.6567(6)	
V (Å^3)	2572.3(6)		2635.2(3)	
Z	8		8	
F(000)	1536		1496	
Dc (gcm^{-3})	1.965		1.866	
μ (mm^{-1})	2.077		1.165	
R_{int}	0.0372		0.0572	
	-8≤h≤8		-9≤h≤8	
limiting indices	-42≤k≤25		-42≤k≤20	
	-11≤l≤7		-8≤l≤11	
Collected reflections	5689		7716	
Unique reflections	2307		2361	
GOF on F^2	1.064		1.041	
R_1, wR_2 [$I>2\sigma(I)$]	0.0431	0.0730	0.0575	0.1498
R_1, wR_2 [all data]	0.0665	0.0806	0.0778	0.1652

Table S2. Selected bond lengths (Å) and angles (°) for **1** and **2** at 293K

1			
C(1)-O(6)	1.249(5)	C(9)-C(10)#2	1.384(5)
C(1)-O(5)	1.253(5)	C(9)-C(10)	1.384(5)
C(1)-C(1)#1	1.551(8)	C(10)-C(11)	1.381(6)
C(2)-N(1)	1.337(6)	C(11)-N(2)	1.330(6)
C(2)-C(3)	1.369(6)	N(1)-Zn(1)	2.081(4)
C(3)-C(4)	1.385(5)	O(1)-P(1)	1.515(3)
C(4)-C(5)	1.390(6)	O(1)-Zn(1)	2.085(2)
C(4)-C(7)	1.470(6)	O(2)-P(1)	1.566(3)
C(5)-C(6)	1.373(6)	O(3)-P(1)	1.488(3)
C(6)-N(1)	1.342(5)	O(3)-Zn(1)#3	2.078(3)
C(7)-N(4)	1.336(5)	O(4)-P(1)	1.588(3)
C(7)-N(3)	1.340(5)	O(5)-Zn(1)#1	2.109(3)
C(8)-N(3)#2	1.341(4)	O(6)-Zn(1)	2.146(3)
C(8)-N(3)	1.341(4)	O(7)-Zn(1)	2.211(3)
C(8)-C(9)	1.470(8)		
O(3)-P(1)-O(1)	114.16(15)	O(1)-Zn(1)-O(5)#1	87.00(11)
O(3)-P(1)-O(2)	106.98(17)	O(3)#4-Zn(1)-O(6)	89.96(11)
O(1)-P(1)-O(2)	111.10(16)	N(1)-Zn(1)-O(6)	101.25(13)
O(3)-P(1)-O(4)	110.16(17)	O(1)-Zn(1)-O(6)	165.13(12)
O(1)-P(1)-O(4)	108.92(17)	O(5)#1-Zn(1)-O(6)	78.28(11)
O(2)-P(1)-O(4)	105.14(15)	O(3)#4-Zn(1)-O(7)	175.64(11)
O(3)#4-Zn(1)-N(1)	87.76(12)	N(1)-Zn(1)-O(7)	88.84(13)
O(3)#4-Zn(1)-O(1)	93.03(10)	O(1)-Zn(1)-O(7)	89.90(10)
N(1)-Zn(1)-O(1)	93.42(12)	O(5)#1-Zn(1)-O(7)	90.08(12)
O(3)#4-Zn(1)-O(5)#1	93.30(11)	O(6)-Zn(1)-O(7)	88.03(11)
N(1)-Zn(1)-O(5)#1	178.84(13)		

Symmetry codes: #1: -x, -y, -z+1; #2: x, -y+1/2, z; #3: x+1/2, y, -z+3/2; #4: x-1/2, y, -z+3/2.

2

C(1)-O(7)#1	1.241(6)	C(9)-C(10)	1.378(7)
C(1)-O(6)	1.259(5)	C(9)-C(10)#2	1.378(7)
C(1)-C(1)#1	1.548(10)	C(10)-C(11)	1.370(8)
C(2)-N(4)	1.329(7)	C(11)-N(3)	1.333(7)
C(2)-C(3)	1.387(7)	Mn(1)-O(4)#3	2.133(3)
C(3)-C(6)	1.370(7)	Mn(1)-O(3)	2.151(3)
C(4)-N(4)	1.335(6)	Mn(1)-O(6)	2.191(3)
C(4)-C(5)	1.372(7)	Mn(1)-O(7)	2.210(3)
C(5)-C(6)	1.385(7)	Mn(1)-N(4)	2.212(4)
C(6)-C(7)	1.481(6)	Mn(1)-O(5)	2.229(4)
C(7)-N(1)	1.314(6)	O(1)-P(1)	1.585(3)
C(7)-N(2)	1.335(6)	O(2)-P(1)	1.567(3)
C(8)-N(1)	1.345(5)	O(3)-P(1)	1.504(3)
C(8)-N(1)#2	1.345(5)	O(4)-P(1)	1.486(3)
C(8)-C(9)	1.468(10)		

O(4)#3-Mn(1)-O(3)	91.91(13)	O(3)-Mn(1)-O(5)	91.44(13)
O(4)#3-Mn(1)-O(6)	91.35(13)	O(6)-Mn(1)-O(5)	92.29(14)
O(3)-Mn(1)-O(6)	86.56(12)	O(7)-Mn(1)-O(5)	89.38(13)
O(4)#3-Mn(1)-O(7)	88.50(13)	N(4)-Mn(1)-O(5)	88.45(15)
O(3)-Mn(1)-O(7)	162.10(12)	O(4)-P(1)-O(3)	114.86(19)
O(6)-Mn(1)-O(7)	75.54(12)	O(4)-P(1)-O(2)	107.17(19)
O(4)#3-Mn(1)-N(4)	87.93(14)	O(3)-P(1)-O(2)	111.0(2)

O(3)-Mn(1)-N(4)	93.32(14)	O(4)-P(1)-O(1)	110.14(19)
O(6)-Mn(1)-N(4)	179.26(15)	O(3)-P(1)-O(1)	108.20(19)
O(7)-Mn(1)-N(4)	104.58(14)	O(2)-P(1)-O(1)	105.0(2)
O(4)#3-Mn(1)-O(5)	175.20(13)		

Symmetry codes: #1: -x+2, -y, -z+1; #2: x, -y+1/2, z; #3: x+1/2, y, -z+3/2; #4: x-1/2, y, -z+3/2.