Supplementary Materials

26-Ring-Channel Structure Constructed from Bimetal Phosphite Helical Chains

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Figure S1. ORTEP drawing of the asymmetric unit in NTHU-5

Figure S2. The structure of NTHU-5

Figure S3. 26R unit in NTHU-5

Figure S4. Hydrogen bonds in NTHU-5

Figure S5. TGA curves for NTHU-5 (black line) and Ga analogue of NTHU-5 (red line)

Figure S6. Calculated and observed power XRD patterns for NTHU-5

Figure S7. IR spectra of NTHU-5 (top one) and Ga analogue of NTHU-5 (bottom one)

Figure S8. The photoluminescence of NTHU-5

Figure S9. The solid state NMR for NTHU-5

Figure S10. The solid state NMR for Ga analogue of NTHU-5

Figure S11. Magnetic susceptibility of the Fe analogue of NTHU-5.

Table S1. Results of ICP-AES and elemental analysis

Table S2. Crystallographic Data for NTHU-5, Ga analogue of NTHU-5 and Fe analogue of NTHU-5

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{C}_4\text{H}_9\text{NH}_3]_2[\text{GaFZn}_2(\text{HPO}_3)_4]$

Table S4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{C}_4\text{H}_9\text{NH}_3]_2[\text{GaFZn}_2(\text{HPO}_3)_4]$

Table S5. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$) for $[\text{C}_4\text{H}_9\text{NH}_3]_2[\text{GaFZn}_2(\text{HPO}_3)_4]$

Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{C}_4\text{H}_9\text{NH}_3]_2[\text{AlFZn}_2(\text{HPO}_3)_4]$

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Figure S1. ORTEP drawing of the asymmetric unit in NTHU-5

Figure S2. The structure of NTHU-5 (a) view along [001] and (b) connectivity between two helical chains

Figure S3. 26R unit in NTHU-5 (a) consecutive 26Rs along [001]; (b) and (c) are two 4_2 -symmetry-related 26Rs

Donor	--- H....Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
N(1)	-- H(3) .. O(3)	[13554.01]	0.8472	2.0551	2.8449	154.87
N(1)	-- H(4) .. O(2)	[]	1.0036	1.9254	2.9003	163.11

Figure S4. Hydrogen bonds in NTHU-5

Weight loss	calcd (%) 2 C ₄ H ₁₁ N + HF	observed (%)
NTHU-5 [C ₄ H ₉ NH ₃] ₂ [AlFZn ₂ (HPO ₃) ₄]	25.78	25.2
Ga analogue of NTHU-5 [C ₄ H ₉ NH ₃] ₂ [GaFZn ₂ (HPO ₃) ₄]	24.17	22.5

Figure S5. TGA curves for NTHU-5 (black line) and Ga analogue of NTHU-5 (red line)

Figure S6. Calculated and observed power XRD patterns for NTHU-5 : (a) Calculated pattern, (b) Observed pattern without heating, (c) Observed pattern after sample heated at 200 °C for 2 h and (d) Observed pattern after sample heated at 210 °C for 2 h

Figure S7. IR spectra of NTHU-5 (top one) and Ga analogue of NTHU-5 (bottom one)

Figure S8. The photoluminescence of NTHU-5

Figure S9. The solid state NMR for NTHU-5

Figure S10. The solid state NMR for Ga analogue of NTHU-5.

Figure S11. Magnetic susceptibility of the Fe analogue of NTHU-5.

Table S1. Results of ICP-AES and elemental analysis

	NTHU-5 [C ₄ H ₉ NH ₃] ₂ [AlFZn ₂ (HPO ₃) ₄]	Ga analogue of NTHU-5 [C ₄ H ₉ NH ₃] ₂ [GaFZn ₂ (HPO ₃) ₄]	Fe analogue of NTHU-5 [C ₄ H ₉ NH ₃] ₂ [FeFZn ₂ (HPO ₃) ₄]
%Zn found (calcd.) ^a	19.58 (20.28)	18.45 (19.02)	18.65 (19.41)
%M found (calcd.) ^a	3.95 (4.18) for Al	9.58 (10.14) for Ga	7.74 (8.29) for Fe
%P found (calcd.) ^a	18.93 (19.21)	17.61 (18.02)	18.02 (18.39)
%C found (calcd.) ^b	14.66 (14.90)	13.81 (13.97)	13.88 (14.26)
%H found (calcd.) ^b	4.12 (4.38)	3.89 (4.10)	4.05 (4.19)
%N found (calcd.) ^b	4.21 (4.34)	3.95 (4.07)	3.98 (4.16)

^a Zinc, Aluminum, Gallium, Iron and Phosphorous content were measured by ICP-AES.

^b Carbon, Hydrogen and Nitrogen content were measured by elemental analysis.

Table S2. Crystallographic Data for NTHU-5, Ga analogue of NTHU-5 and Fe analogue of NTHU-5

	NTHU-5	Ga analogue of NTHU-5	Fe analogue of NTHU-5
empirical formula	$[\text{C}_4\text{H}_9\text{NH}_3]_2[\text{AlFZn}_2(\text{HPO}_3)_4]$ $\text{C}_8\text{H}_{28}\text{N}_2\text{Zn}_2\text{AlFP}_4\text{O}_{12}$	$[\text{C}_4\text{H}_9\text{NH}_3]_2[\text{GaFZn}_2(\text{HPO}_3)_4]$ $\text{C}_8\text{H}_{28}\text{N}_2\text{Zn}_2\text{GaFP}_4\text{O}_{12}$	$[\text{C}_4\text{H}_9\text{NH}_3]_2[\text{FeFZn}_2(\text{HPO}_3)_4]$ $\text{C}_8\text{H}_{28}\text{N}_2\text{Zn}_2\text{FeFP}_4\text{O}_{12}$
formula weight	644.92	687.66	673.79
temperature(K)	293 (2)	293 (2)	293 (2)
wavelength (Å)	0.71073	0.71073	0.71073
crystal system	tetragonal	tetragonal	tetragonal
space group	$I 4_1/acd$	$I 4_1/acd$	$I 4_1/acd$
unit cell dimensions (Å)	$a = 31.013 (1)$ $c = 9.8348(8)$	$a = 31.0722(6)$ $c = 9.8995(4)$	$a = 31.212 (5)$ $c = 9.954(3)$
volume (Å ³)	9459 (1)	9557.8(5)	9697(4)
Z, calculated density (g/cm ³)	16, 1.811	16, 1.912	16, 1.846
Absorption coefficient	2.398 mm ⁻¹	3.440 mm ⁻¹	2.878 mm ⁻¹
F(000)	5248	5536	5456
Crystal size (mm ³)	0.25 x 0.025 x 0.025	0.5 x 0.03 x 0.02	0.2 x 0.025 x 0.025
Theta range for data collection	1.31 to 28.33	1.31 to 28.30	1.30 to 17.47
Index ranges	$-30 \leq h \leq 41,$ $-41 \leq k \leq 41, -13 \leq l \leq 12$	$-36 \leq h \leq 41,$ $-36 \leq k \leq 41, -13 \leq l \leq 13$	$-26 \leq h \leq 26,$ $-26 \leq k \leq 26, -8 \leq l \leq 8$
Reflections collected	33207	33739	11351
Independent reflections	2955 [R(int) = 0.0234]	2983 [R(int) = 0.0301]	773 [R(int) = 0.0521]
Completeness to theta = 28.33	99.9 %	100.0 %	99.1 %
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	2955 / 3 / 137	2983 / 3 / 137	773 / 3 / 138
Goodness-of-fit on F ²	0.933	0.873	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0547, wR2 = 0.1497	R1 = 0.0462, wR2 = 0.1153	R1 = 0.0772, wR2 = 0.1827
R indices (all data)	R1 = 0.1166, wR2 = 0.1706	R1 = 0.0897, wR2 = 0.1274	R1 = 0.1127, wR2 = 0.2275
Largest diff. peak and hole	0.727 and -0.481 e. ⁻³	0.837 and -0.527 e. ⁻³	1.093 and -0.923 e. ⁻³

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{C}_4\text{H}_9\text{NH}_3]_2[\text{GaFZn}_2(\text{HPO}_3)_4]$

	x	y	z	U(eq) ^a
Ga(1)	7500	5578(1)	0	21(1)
Zn(1)	5527(1)	5306(1)	-716(1)	32(1)
P(1)	5120(1)	5588(1)	-3500(2)	36(1)
P(2)	6534(1)	5261(1)	-317(1)	28(1)
F(1)	7615(1)	5115(1)	-1250	29(1)
O(1)	5156(1)	5590(1)	-1980(4)	46(1)
O(2)	5458(1)	4680(1)	-781(4)	41(1)
O(3)	5342(1)	5475(2)	1089(4)	48(1)
O(4)	6895(1)	5585(1)	-493(4)	32(1)
O(5)	7393(1)	6019(1)	1356(3)	27(1)
O(6)	6120(1)	5445(1)	-859(4)	47(1)
N(1)	5896(2)	5610(2)	3327(5)	51(2)
C(1)	5864(7)	6129(6)	3446(17)	199(10)
C(2)	5911(10)	6446(7)	4597(19)	620(40)
C(3)	5873(10)	6894(7)	3970(40)	420(20)
C(4)	5757(12)	6660(20)	2660(30)	660(30)

^aU(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table S4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{C}_4\text{H}_9\text{NH}_3]_2[\text{GaFZn}_2(\text{HPO}_3)_4]$

	x	y	z	U(eq)
H(1)	5205	6003	-4050	80
H(2)	6694	4978	-1195	80
H(3)	5740	5563	2592	80
H(4)	5786	5513	4072	80
H(5)	6165	5502	3164	80

Table S5. Selected bond lengths (Å) and angles (°) for [C₄H₉NH₃]₂[GaFZn₂(HPO₃)₄]

Ga(1)-F(1)	1.9312(16)	Ga(1)-O(4)#2	1.943(3)
Ga(1)-F(1)#1	1.9314(16)	Ga(1)-O(5)	1.946(3)
Ga(1)-O(4)	1.943(3)	Ga(1)-O(5)#2	1.946(3)
Zn(1)-O(6)	1.898(4)	Zn(1)-O(3)	1.949(4)
Zn(1)-O(1)	1.917(4)	Zn(1)-O(2)	1.956(4)
P(1)-O(1)	1.509(4)	P(2)-O(6)	1.509(4)
P(1)-O(2)#3	1.518(4)	P(2)-O(4)	1.517(4)
P(1)-O(3)#4	1.531(4)	P(2)-O(5)#5	1.532(4)
P(1)-H(1)	1.4242	P(2)-H(2)	1.3321
Ga(1)-F(1)-Ga(1)#6	133.3(2)	P(2)-O(4)-Ga(1)	132.7(2)
P(1)-O(1)-Zn(1)	133.9(3)	P(2)#5-O(5)-Ga(1)	128.9(2)
P(1)#3-O(2)-Zn(1)	129.6(2)	P(2)-O(6)-Zn(1)	135.7(2)
P(1)#7-O(3)-Zn(1)	125.6(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -y+5/4,x-1/4,z+1/4 #2 -x+3/2,y,-z #3 x,-y+1,-z-1/2

#4 -x+1,y,z-1/2 #5 -y+5/4,-x+5/4,-z+1/4 #6 y+1/4,-x+5/4,z-1/4

#7 -x+1,y,z+1/2

Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{C}_4\text{H}_9\text{NH}_3]_2[\text{AlFZn}_2(\text{HPO}_3)_4]$

	x	y	z	U(eq) ^a
Al(1)	2500	5557(1)	0	20(1)
Zn(1)	533(1)	5307(1)	699(1)	32(1)
P(1)	124(1)	4412(1)	1514(2)	36(1)
P(2)	1543(1)	5253(1)	284(2)	27(1)
F(1)	2376(1)	5124(1)	-1250	27(1)
O(1)	166(2)	5600(2)	1959(5)	47(1)
O(2)	464(2)	4681(2)	787(5)	41(1)
O(3)	336(2)	5464(2)	-1101(5)	48(1)
O(4)	1917(1)	5557(1)	528(4)	28(1)
O(5)	2392(1)	5992(1)	-1292(4)	24(1)
O(6)	1129(1)	5452(2)	788(5)	47(1)
N(1)	903(2)	5597(2)	-3336(6)	49(2)
C(1)	1463(4)	6496(6)	960(20)	145(7)
C(2)	1111(5)	6810(6)	580(30)	207(11)
C(3)	634(7)	6691(12)	700(30)	530(40)
C(4)	760(20)	6642(14)	2190(30)	600(30)

^aU(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table S7. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{C}_4\text{H}_9\text{NH}_3]_2[\text{AlFZn}_2(\text{HPO}_3)_4]$

	x	y	z	U(eq)
H(1)	1594	4884	1081	80
H(2)	191	4015	1000	80
H(3)	798	5595	-2540	80
H(4)	735	5561	-4199	80
H(5)	1119	5433	-3104	80

Table S8. Selected bond lengths (Å) and angles (°) for [C₄H₉NH₃]₂[AlFZn₂(HPO₃)₄]

Al(1)-F(1)	1.860(2)	Al(1)-O(4)	1.882(4)
Al(1)-F(1)#1	1.860(2)	Al(1)-O(5)#2	1.883(4)
Al(1)-O(4)#2	1.882(4)	Al(1)-O(5)	1.883(4)
Zn(1)-O(6)	1.902(4)	Zn(1)-O(3)	1.935(5)
Zn(1)-O(1)	1.913(5)	Zn(1)-O(2)	1.955(5)
P(1)-O(1)#3	1.508(5)	P(2)-O(6)	1.510(5)
P(1)-O(2)	1.524(5)	P(2)-O(4)	1.513(4)
P(1)-O(3)#4	1.534(5)	P(2)-O(5)#5	1.539(4)
P(1)-H(2)	1.3457	P(2)-H(1)	1.3955
Al(1)-F(1)-Al(1)#6	137.4(3)	P(2)-O(4)-Al(1)	133.7(3)
P(1)#3-O(1)-Zn(1)	133.3(3)	P(2)#5-O(5)-Al(1)	130.2(3)
P(1)-O(2)-Zn(1)	129.8(3)	P(2)-O(6)-Zn(1)	135.6(3)
P(1)#4-O(3)-Zn(1)	126.8(3)		

Symmetry transformations used to generate equivalent atoms:

#1 $y-1/4, -x+3/4, z+1/4$ #2 $-x+1/2, y, -z$ #3 $x, -y+1, -z+1/2$
#4 $-x, -y+1, -z$ #5 $-y+3/4, -x+3/4, -z-1/4$ #6 $-y+3/4, x+1/4, z-1/4$