Supplement Information

A Metal Phosphite Containing 24-Ring Channels with 10-ring windows**

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Inductively coupled plasma (ICP) analysis: this work was carried on T. T. A. ICP9000 (N+M) to confirm the metal ion and phosphorus contents. ICP analysis the single crystals reveals that in the framework of Cr-NKU-24 the mass ratio of Al and Cr element is 88:12. It means that 9.1% Al atoms were substituted by Cr atoms.

Table S1. Crystal data for Cr-NKU-24.

Table S2. Selected bond distances (Å) and angles (°) for Cr-NKU-24.

Figure S1. Simulated and as-synthesis XRD patterns a) as-synthesis pattern of Cr-NKU-24; b) simulated one from the single crystal data of Cr-NKU-24.

Figure S2. Perspective view of a single 24-ring viewed along b axis direction, which consists of six building units. (Color code yellow: Zn, cyan: Al, red: P, blue: O)

Figure S3. FT-IR spectra of Cr-NKU-24.

Figure S4. TG curve of Cr-NKU-24 (under N₂ flew).

Figure S5. Solid-state UV-vis spectra of (1)Cr-NKU-24 (2)NKU-24

Figure S6. 10-ring windows of Cr-NKU-24 along three directions

Table S 1. Crystal data for Cr-NKU-24

Formula	C ₁₂ H ₄₀ N ₂ Al _{0.57} Cr _{0.10} O ₁₆ P ₄ Zn ₂
CCDC	619171
Formula weight	743.57
T(K)	293(2)
Wavelength(Å)	0.71073
Crystal system,	Hexagonal
space group	<i>P</i> 6 ₃ <i>mc</i> (No. 186)
a (Å)	15.269(2)
b (Å)	15.269(2)
c (Å)	10.336(3)
α (°)	90
β (°)	90
γ (°)	120
V (Å ³)	2086.8(8)
Z	3
ρ _{calx} (Mg/m ³)	1.775
μ (mm ⁻¹)	2.080
<i>F</i> (000)	1151
Crystal size (mm)	0.20×0.14×0.10
θ range (°)	1.54 to 25.01
Limiting indices	-9≤ <i>h</i> ≤18, -18≤ <i>k</i> ≤17, -12≤ <i>l</i> ≤12
Reflections collected / unique	10509/1347[R _{int} =0.0409]
Completeness to theta = 26.39	100.0 %
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	1374 / 133 / 158
Goodness-of-fit on <i>F</i> ²	1.143
Final R indices [I>2σ(I)]	R1=0.0486, wR2=0.1405
R indices (all data)	R1=0.0565, wR2=0.1518
Largest diff. peak and hole (e.Å ⁻³)	0.918 and -1.090

$$^a R = \sum \| |F_o| - |F_c| \| / \sum |F_o|; ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$$

Table S 2. Selected bond distances (Å) and angles (°) for Cr-NKU-24

Zn1—O5	1.915(1)	P1—O1	1.490(1)
Zn1—O3 ⁱ	1.936(1)	O3—P2	1.516(1)
Zn1—O1 ⁱⁱ	1.955(1)	O5—P2	1.516(1)
Zn1—O1 ⁱ	1.955(1)	O4—P2	1.510(1)
Cr1—O2 ⁱⁱⁱ	1.867(1)	N1—C4	1.440(3)
Cr1—O2 ^{iv}	1.866(1)	C4—C5	1.506(2)
Cr1—O2	1.867(1)	C5—C6	1.522(3)
Cr1—O4	1.897(1)	C6—C1	1.531(3)
Cr1—O4 ^{iv}	1.896(1)	C1—C2	1.521(2)
Cr1—O4 ⁱⁱⁱ	1.896(1)	C2—C3	1.521(3)
P1—O2	1.476(1)	C3—C4	1.511(3)
P1—O1 ^v	1.490(1)		
O5—Zn1—O3 ⁱ	101.56(5)	O4 ^{iv} —Cr1—O4 ⁱⁱⁱ	89.27(2)
O5—Zn1—O1 ⁱⁱ	107.90(4)	O2—P1—O1 ^v	112.83(6)
O3 ⁱ —Zn1—O1 ⁱⁱ	114.41(4)	O2—P1—O1	112.83(7)
O5—Zn1—O1 ⁱ	107.90(4)	O1 ^v —P1—O1	111.87(6)
O3 ⁱ —Zn1—O1 ⁱ	114.41(4)	O4—P2—O5	109.57(5)
O1 ⁱⁱ —Zn1—O1 ⁱ	109.96(5)	O4—P2—O3	116.88(6)
O2 ⁱⁱⁱ —Cr1—O2 ^{iv}	92.57(4)	O5—P2—O3	113.29(7)
O2 ⁱⁱⁱ —Cr1—O2	92.54(4)	P2—O3—Zn1 ^{vii}	139.35(8)
O2 ^{iv} —Cr1—O2	92.57(4)	P2—O5—Zn1	142.88(6)
O2 ⁱⁱⁱ —Cr1—O4	89.04(4)	P2—O4—Cr1	134.85(5)
O2 ^{iv} —Cr1—O4	177.67(3)	P1—O1—Zn1 ^{vii}	120.11(7)
O2—Cr1—O4	89.04(4)	P1—O2—Cr1	167.73(9)
O2 ⁱⁱⁱ —Cr1—O4 ^{iv}	177.62(4)	N1—C4—C5	96.12(10)
O2 ^{iv} —Cr1—O4 ^{iv}	89.10(3)	C4—C5—C6	109.66(11)
O2—Cr1—O4 ^{iv}	89.07(4)	C5—C6—C1	107.39(18)
O4—Cr1—O4 ^{iv}	89.24(3)	C(6)—C(1)—C(2)	108.2(7)
O2 ⁱⁱⁱ —Cr1—O4 ⁱⁱⁱ	89.07(2)	C1—C2—C3	107.92(14)
O2 ^{iv} —Cr1—O4 ⁱⁱⁱ	89.10(2)	C2—C3—C4	110.18(16)
O2—Cr1—O4 ⁱⁱⁱ	177.62(4)	C3—C4—N1	96.09(14)
O4—Cr1—O4 ⁱⁱⁱ	89.24(2)		

Symmetry codes:

- (i) 1-x, 1-y, -0.5+z; (ii) y, x, -0.5+z; (iii) 1-y, 1+x-y, z; (iv) -x+y, 1-x, z;
(v) -x+y, y, z; (vi) 1-y, 1-x, z; (vii) 1-x, 1-y, 0.5+z.

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