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Supporting Information

Co-based MOF as an efficient catalyst by peroxymonosulfate activation for degradation of tetracycline: Synthesis and Performance

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Chemicals and materials

All chemical reagents and solvents were obtained from commercial sources and can be used directly without further purification. $Co(NO_3)_2$•$6H_2O$, oxone® ($KHSO_5$ · 0.5 $KHSO_4$ · 0.5 K_2SO_4, $KHSO_5$ 47%), Rhodamine B (RhB), Acid orange 7 (AO7), Methylene blue (MB), Malachite Green (MG), Eriochrome Black T (EBT), Methyl violet (MV), Congo Red (CR), tert-Butanol (TBA) were purchased from Shanghai Aladdin Biochemical Technology Co., LTD. 1,3,5-tris(4-carboxyphenyl)benzene (BTB), and 1,4-bis((1H-imidazol-1-yl)methyl)benzene (BIMB) were purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co., LTD. p-benzoquinone (p-BQ), L-Histidine (L-his) were purchased from Shanghai Maclin Biochemical Technology Co., LTD. Methanol (MeOH) was purchased from Tianjin Fuyu Fine Chemical Co., LTD. Ultrapure water was used for all experiments in this paper unless otherwise stated. The lake water was collected and filtered from South Lake Park in Changchun, China.

Characterization

X-ray single crystal diffraction data of **JLNU-11** were collected using Bruker Smart Apex III Diffractometer equipped with a Mo target (Kα, λ = 0.71073 Å) at room temperature. The structure of **JLNU-11** was analyzed by the direct method and refined by the full matrix least-squares refinements utilizing the SHELXTL-97 program package. All non-hydrogen atoms underwent anisotropic refinement. The crystal structure information of **JLNU-11** was shown in Table S1. The CIF file for **JLNU-11** had been deposited in the Cambridge Crystallography Data Centre (CCDC), and CCDC number is 2270628. Elemental analyses (C, H and N) were obtained using a PerkinElmer 2400CHN auto analyzer. The PXRD of the samples was obtained through

the Rigaku D-Max 2550 instrument using Cu-Kα radiation (λ = 1.5418 Å). Thermogravimetric analysis (TGA) was implemented on DTG-60AH analyzer. The heating temperature range was from 38 to 800℃ in nitrogen atmosphere, and the heating rate was 5 ℃ min^{-1}. FT-IR spectra were analyzed in the range of 4000 - 400 cm^{-1} on a Nicolet 380 FT-IR spectrophotometer through KBr pellets.

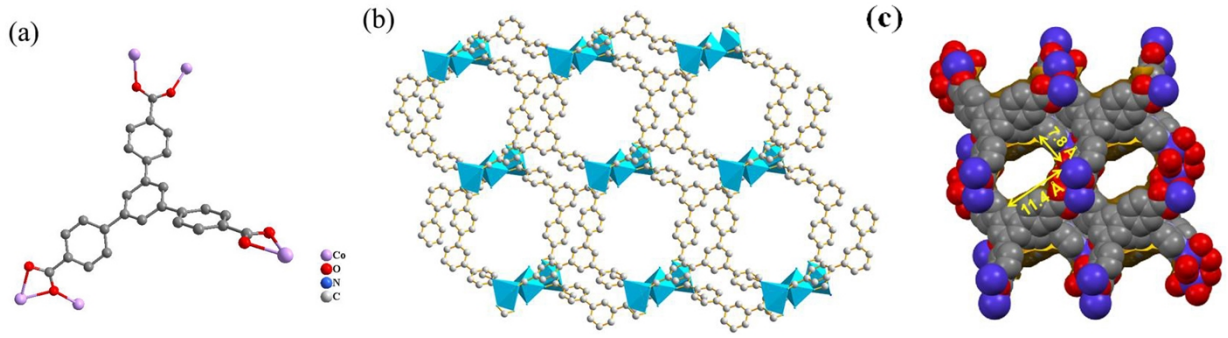

Fig. S1. (a) The coordination mode of BTB ligand. (b) The three-dimensional structure and (c) the pore stacking diagram of JLNU-11 along *a* axis

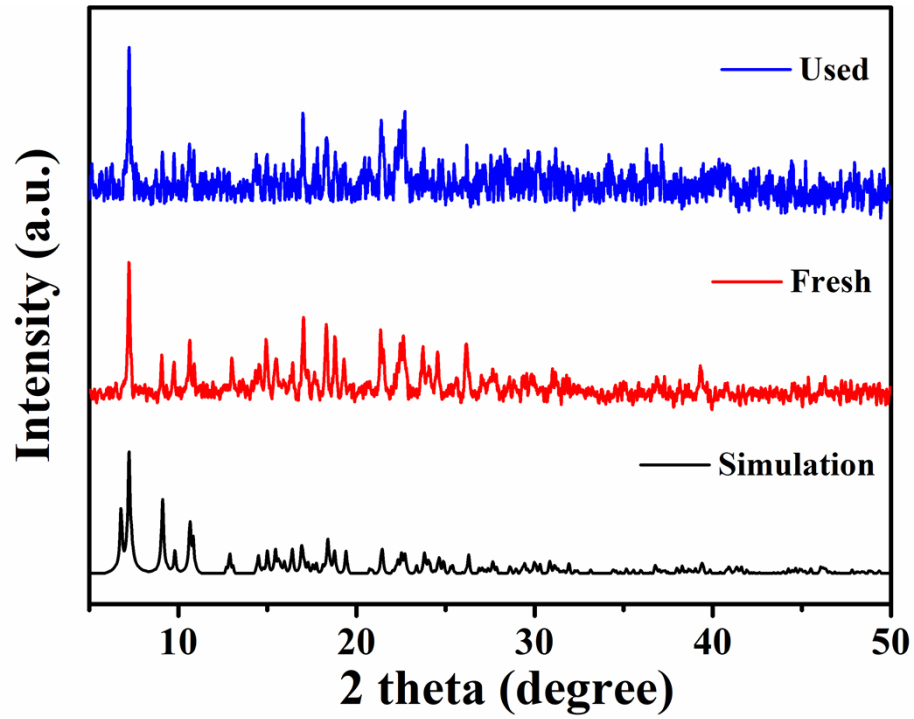

Fig. S2. Powder X-ray diffraction patterns of JLNU-11: simulation(black), . experimental (red) and after reaction (blue).

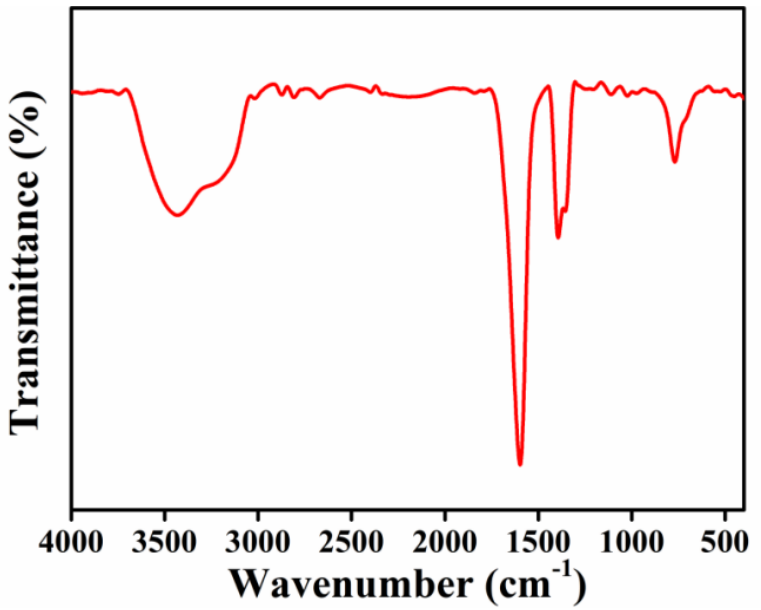

Fig. S3. FTIR spectra of **JLNU-11**.

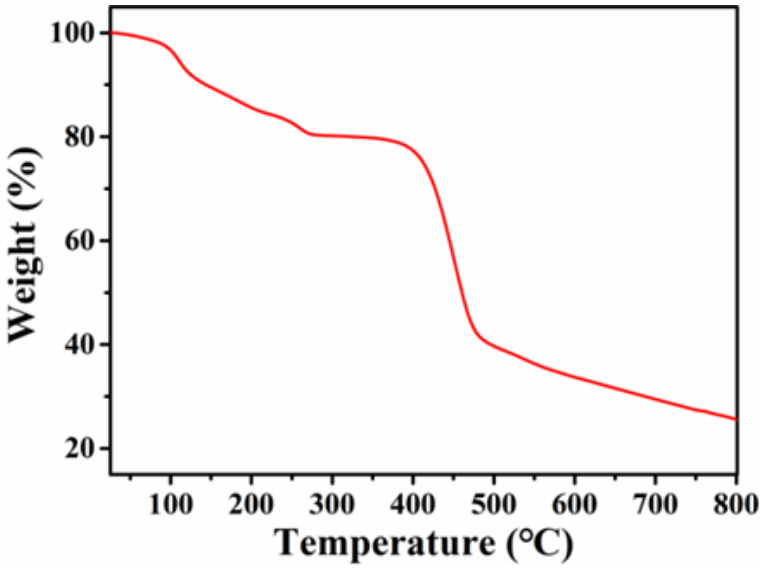

Fig. S4. TGA curve of **JLNU-11**.

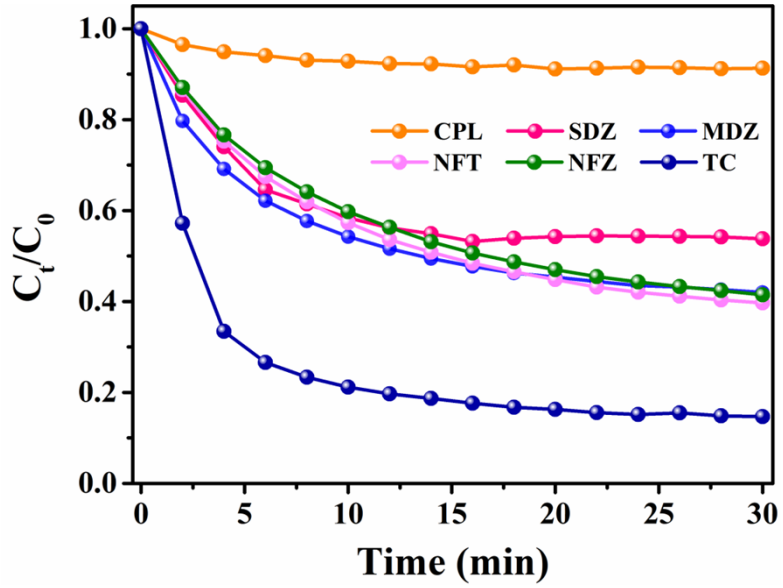

Fig. S5. Degradation curve of different antibiotics by JLNU-11/PMS system, experimental conditions: [JLNU 11] = 0.08 g/L, [PMS] = 0.12 g/L, [pollution] = 20 mg/L.

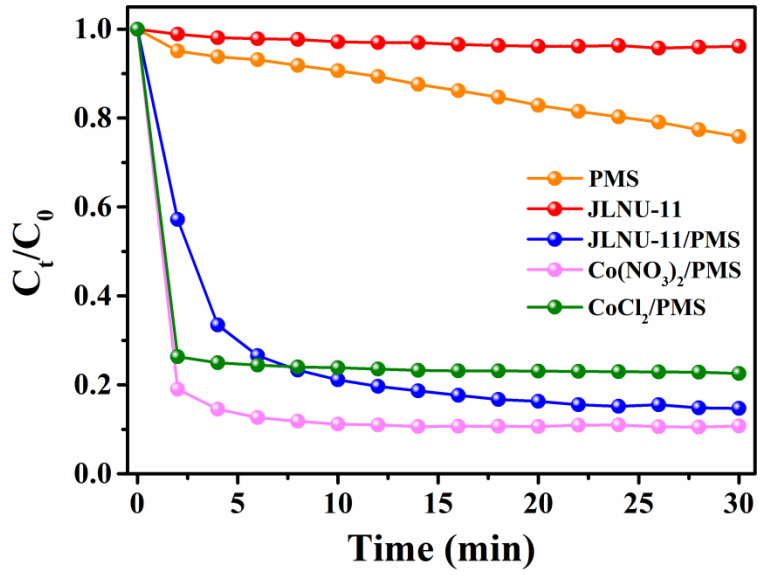

Fig. S6. Degradation curve of different catalysts, experimental conditions: [JLNU-11] = 0.08 g/L, [$Co(NO_3)_2$ or $Co(Cl)_2$] = 0.08 g/L, [PMS] = 0.12 g/L, [TC] = 20 mg/L

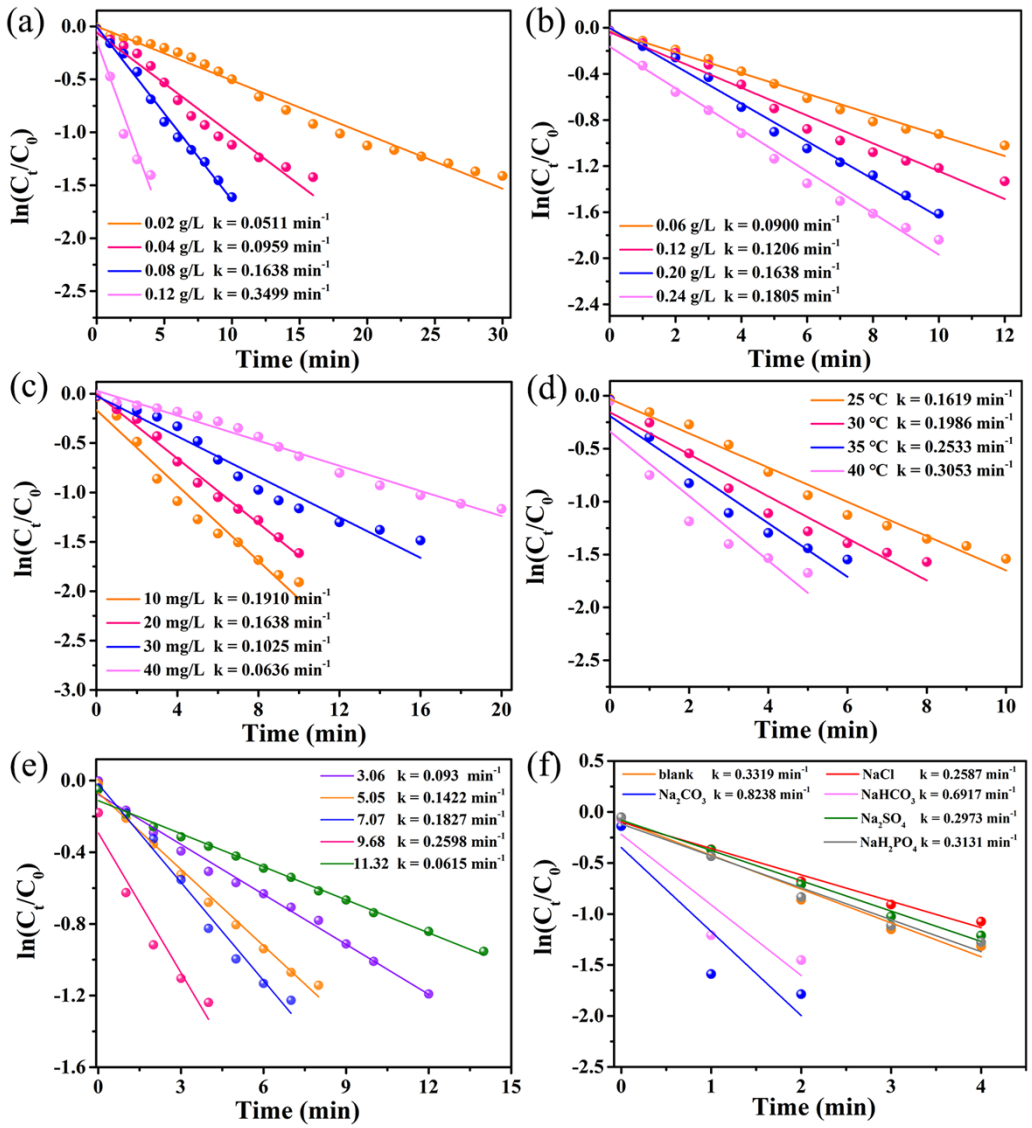

Fig. S7. Reaction rate constants: (a) JLNU-11dose; (b) PMS concentration; (c) TC concentrations; (d) temperatures; (e) pH and (f) anions.

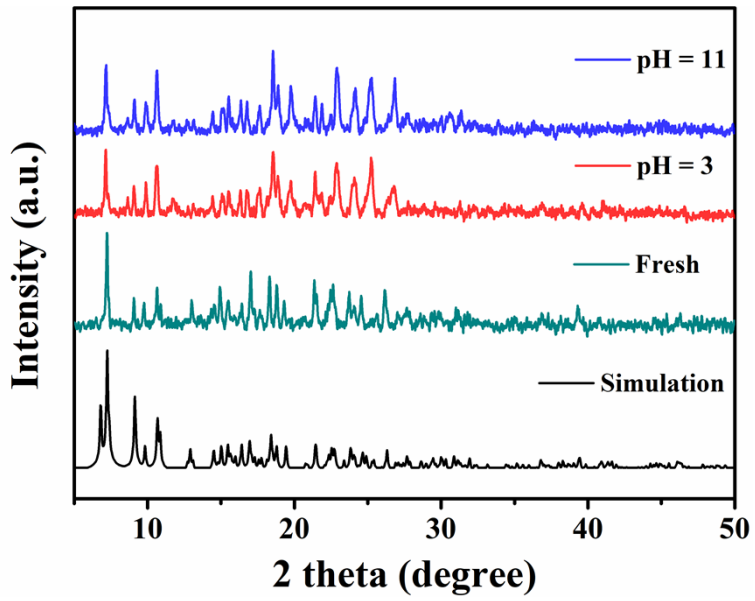

Fig. S8. Powder X-ray diffraction patterns of JLNU-11: simulation(black), . fresh (green), pH=3 (red) and pH=11(blue).

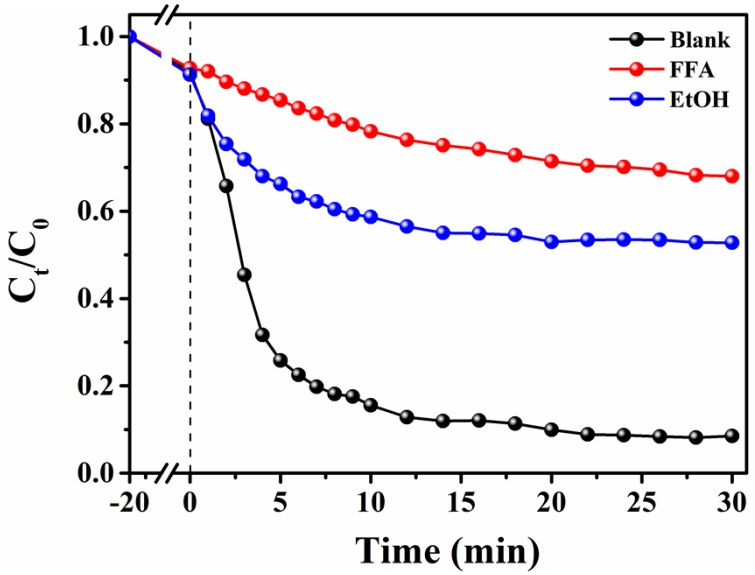

Fig. S9. Effects of different quenchers (EtOH and FFA) on TC degradation, experimental conditions: [JLNU-11] = 0.08 g/L, [PMS] = 0.20 g/L

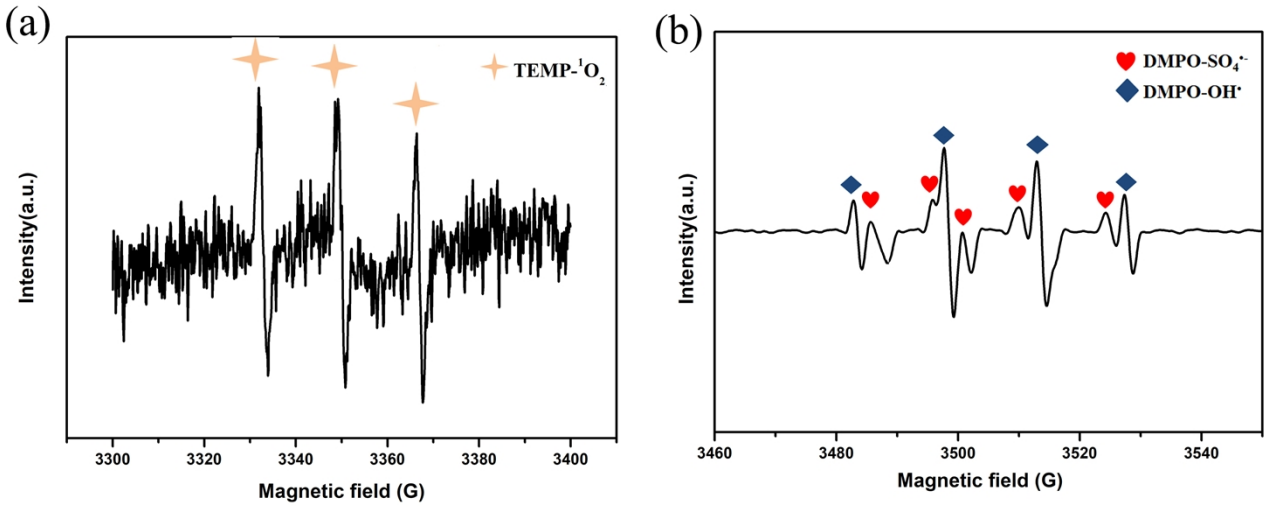

Fig. S10. The ESR signals of (a) TEMP-$^1O_2$ and (b) DMPO- $SO_4^{\bullet-}$/•OH

Table S1. The detailed crystal parameters of **JLNU-11**

Identification code	JLNU-11
CCDC Number	2270628
Empirical formula	$C_{68}H_{44}Co_3N_4O_{14}$
Formula weight	1317.86
Temperature/K	296.15
Crystal system	triclinic
Space group	*P-1*
a/Å	12.174(3)
b/Å	11.1597(4)
c/Å	13.317(3)
α/°	80.136(3)
β/°	81.546(4)
γ/°	83.025(4)
Volume/Å^3	1958.6(8)
Z	1
ρ_{calc} g/cm^3	1.117
μ/mm^{-1}	0.683
F(000)	673.0
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection/°	3.334 to 51.594
Index ranges	-14 ≤ h ≤ 13, -15 ≤ k ≤ 15, -16 ≤ l ≤ 12
Reflections collected	11626
Independent reflections	7475 [R_{int} = 0.0542, R_{sigma} = 0.1164]
Data/restraints/parameters	7475/0/403
Goodness-of-fit on F^2	0.920
Final R indexes [I>=2σ (I)]	R_1 = 0.0550, wR_2 = 0.1245
Final R indexes [all data]	R_1 = 0.1115, wR_2 = 0.1488
Largest diff. peak/hole / e Å^{-3}	0.59/-0.52

Table S2. Selected bond distances (Å) for **JLNU-11**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	O2[1]	2.223(3)	C5	C22	1.381(6)
Co1	O2[2]	2.223(3)	C5	C29	1.395(6)
Co1	O3[3]	2.011(3)	C6	C7	1.403(5)
Co1	O3	2.011(3)	C6	C24	1.385(6)
Co1	O4	2.120(3)	C7	C10	1.388(5)
Co1	O4[3]	2.120(3)	C8	C11	1.378(5)
Co2	O1	2.022(3)	C8	C12	1.394(5)
Co2	O2[2]	2.092(3)	C9	C17	1.407(5)
Co2	O5[2]	2.296(3)	C10	C16	1.381(6)
Co2	O6[4]	2.026(3)	C11	C19	1.487(5)
Co2	N1	2.066(4)	C11	C21	1.395(6)
O1	C2	1.270(5)	C12	C14	1.396(5)
O2	C19	1.300(5)	C13	C17	1.405(5)
O3	C2	1.256(5)	C14	C27	1.397(6)
O5	C19	1.261(5)	C15	C16	1.396(6)
O6	C25	1.259(6)	C15	C24	1.392(6)
N1	C23	1.317(5)	C16	C17	1.492(5)
N1	C26	1.381(6)	C18	C20	1.370(6)
O7	C25	1.252(5)	C18	C22	1.397(5)
N2	C23	1.335(6)	C20	C25	1.499(6)
N2	C31	1.352(6)	C20	C28	1.383(6)

N2	C32	1.484(6)	C21	C27	1.375(6)
C1	C3	1.388(5)	C26	C31	1.346(7)
C1	C13	1.378(5)	C28	C29	1.381(6)
C1	C14	1.489(5)	C30	C32	1.529(7)
C2	C6	1.497(6)	C30	C33	1.360(7)
C3	C4	1.392(5)	C30	C34	1.357(7)
C4	C5	1.487(5)	C33	C34[5]	1.378(7)
C4	C9	1.388(5)			

[1]1-X,2-Y,1-Z; [2]-1+X,+Y,1+Z; [3]-X,2-Y,2-Z; [4]-1+X,1+Y,+Z; [5]-X,1-Y,1-Z

Table S3. Selected bond angles (°) for **JLNU-11**.

Atom	Atom	Atom	Angles (˚)	Atom	Atom	Atom	Angles (˚)
O2[1]	Co1	O2[2]	180.0	C22	C5	C29	117.4(4)
O3	Co1	O2[2]	93.56(11)	C29	C5	C4	122.1(4)
O3[3]	Co1	O2[1]	93.56(11)	C7	C6	C2	121.5(4)
O3[3]	Co1	O2[2]	86.44(11)	C24	C6	C2	119.6(4)
O3	Co1	O2[1]	86.44(11)	C24	C6	C7	118.7(4)
O3[3]	Co1	O3	180.0	C10	C7	C6	120.3(4)
O3	Co1	O4	94.49(12)	C11	C8	C12	120.5(4)
O3[3]	Co1	O4	85.51(12)	C4	C9	C17	121.7(4)
O3[3]	Co1	O4[3]	94.49(12)	C16	C10	C7	120.9(4)
O3	Co1	O4[3]	85.51(12)	C8	C11	C19	120.5(4)
O4[3]	Co1	O2[2]	89.46(11)	C8	C11	C21	119.1(4)
O4[3]	Co1	O2[1]	90.54(11)	C21	C11	C19	120.3(4)
O4	Co1	O2[2]	90.54(11)	C8	C12	C14	120.8(4)

O4	Co1	O2[1]	89.46(11)	C1	C13	C17	121.6(4)
O4[3]	Co1	O4	180.00(16)	C12	C14	C1	120.3(4)
O1	Co2	O2[1]	100.28(12)	C12	C14	C27	117.7(4)
O1	Co2	O5[1]	160.31(11)	C27	C14	C1	121.9(4)
O1	Co2	O6[4]	99.98(13)	C24	C15	C16	120.7(4)
O1	Co2	N1	94.04(14)	C10	C16	C15	118.5(4)
O2[1]	Co2	O5[1]	60.04(11)	C10	C16	C17	120.7(4)
O6[4]	Co2	O2[1]	143.94(14)	C15	C16	C17	120.6(4)
O6[4]	Co2	O5[1]	97.46(13)	C9	C17	C16	119.7(4)
O6[4]	Co2	N1	97.33(15)	C13	C17	C9	117.5(4)
N1	Co2	O2[1]	110.61(13)	C13	C17	C16	122.6(4)
N1	Co2	O5[1]	92.73(14)	C20	C18	C22	120.1(4)
C2	O1	Co2	126.2(3)	O2	C19	C11	120.0(4)
Co2[5]	O2	Co1[5]	117.22(13)	O5	C19	O2	118.6(4)
C19	O2	Co1[5]	139.8(3)	O5	C19	C11	121.4(4)
C19	O2	Co2[5]	94.8(2)	C18	C20	C25	120.0(4)
C2	O3	Co1	141.8(3)	C18	C20	C28	119.0(4)
C19	O5	Co2[5]	86.6(3)	C28	C20	C25	120.9(4)
C25	O6	Co2[6]	100.6(3)	C27	C21	C11	120.3(4)
C23	N1	Co2	126.0(3)	C5	C22	C18	121.6(4)
C23	N1	C26	104.0(4)	N1	C23	N2	112.2(4)
C26	N1	Co2	127.6(3)	C6	C24	C15	120.5(4)
C23	N2	C31	107.2(4)	O6	C25	C20	119.2(4)
C23	N2	C32	126.5(4)	O7	C25	O6	119.9(4)
C31	N2	C32	126.0(4)	O7	C25	C20	120.9(5)
C3	C1	C14	120.1(4)	C31	C26	N1	110.1(5)
C13	C1	C3	119.2(4)	C21	C27	C14	121.4(4)

C13	C1	C14	120.6(4)	C29	C28	C20	120.8(4)
O1	C2	C6	117.9(4)	C28	C29	C5	121.0(4)
O3	C2	O1	125.5(4)	C33	C30	C32	119.1(5)
O3	C2	C6	116.4(4)	C34	C30	C32	123.7(5)
C1	C3	C4	121.5(4)	C34	C30	C33	117.2(5)
C3	C4	C5	121.3(4)	C26	C31	N2	106.4(5)
C9	C4	C3	118.4(3)	N2	C32	C30	112.9(4)
C9	C4	C5	120.2(4)	C30	C33	C34[7]	121.5(5)
C22	C5	C4	120.4(4)	C30	C34	C33[7]	121.3(5)

[1]-1+X,+Y,1+Z; [2]1-X,2-Y,1-Z; [3]-X,2-Y,2-Z; [4]-1+X,1+Y,+Z; [5]1+X,+Y,-1+Z; [6]1+X,-1+Y,+Z; [7]-X,1-Y,1-Z