Supporting Information

$Co\{P_4Mo_6\}$-based Compound as Electrochemical Sensor for Highly Sensitive Detection of Cr(VI)

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Instrumentation and Characterization

All reagents and solvents used in this study were obtained commercially and employed without additional purification. Powder X-ray diffraction (PXRD) analysis was conducted using a Rigaku D-max 2550 diffractometer with CuKα radiation (λ = 1.5418 Å). For electrochemical measurements, a CHI 760E Electrochemical Workstation was utilized, employing a three-electrode configuration consisting of a Hg/HgO reference electrode. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo ESCALAB 250 spectrometer. The surface morphology and elemental distribution of the synthesized materials were examined using scanning electron microscopy (SEM, SU-8000) coupled with elemental mapping, while the microstructure was further analyzed via transmission electron microscopy (TEM, JEM-2010).

Electrochemical Measurements

The electrochemical properties of LLXY-110 were investigated using a three-electrode system on a CHI760E electrochemical workstation. Experiments were conducted in either 0.5 M H_2SO_4 (pH = 0-4) or 0.1 M HAc-NaAc buffer solutions (pH = 5). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were employed to characterize the materials. EIS measurements were performed over a frequency range of 100 kHz to 0.1 Hz. Additionally, differential pulse voltammetry (DPV) was used to assess the electrochemical detection performance within a potential window of −0.2 V to 0.6 V and an amplitude of 50 mV.

The detection limits for both materials were determined based on the signal-to-noise ratio (S/N = 3). To evaluate reproducibility, the relative standard deviation (RSD) was calculated from 30 consecutive blank measurements. Finally, detection sensitivity was derived from the linear regression of Cr(VI) concentration versus peak current.

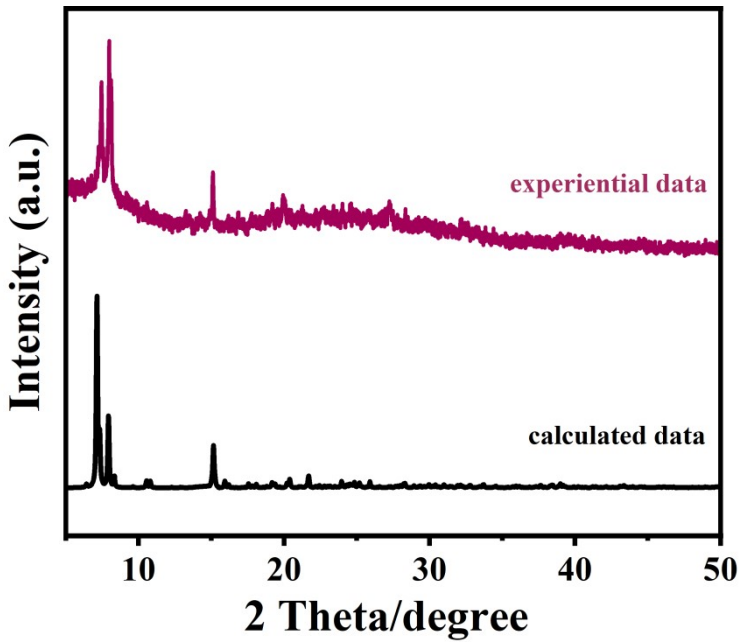

Fig. S1 XRD pattern of LLXY-110

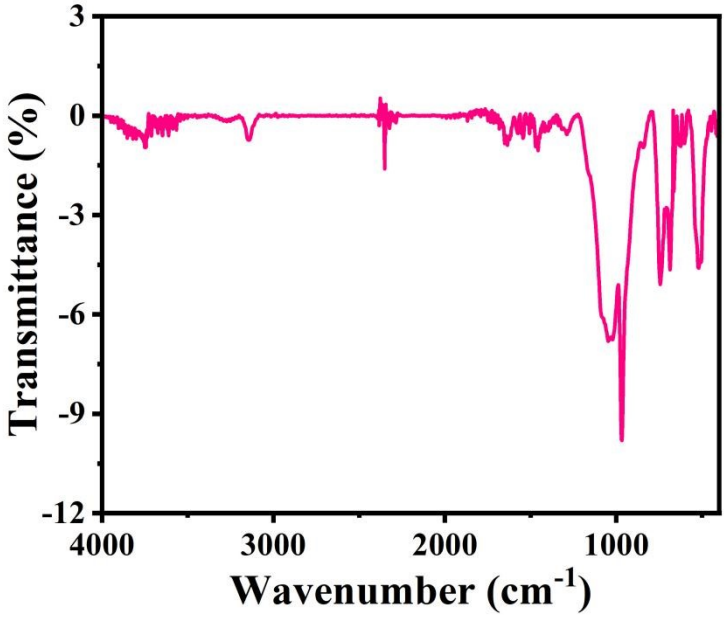

Fig. S2 Infrared spectra of LLXY-110

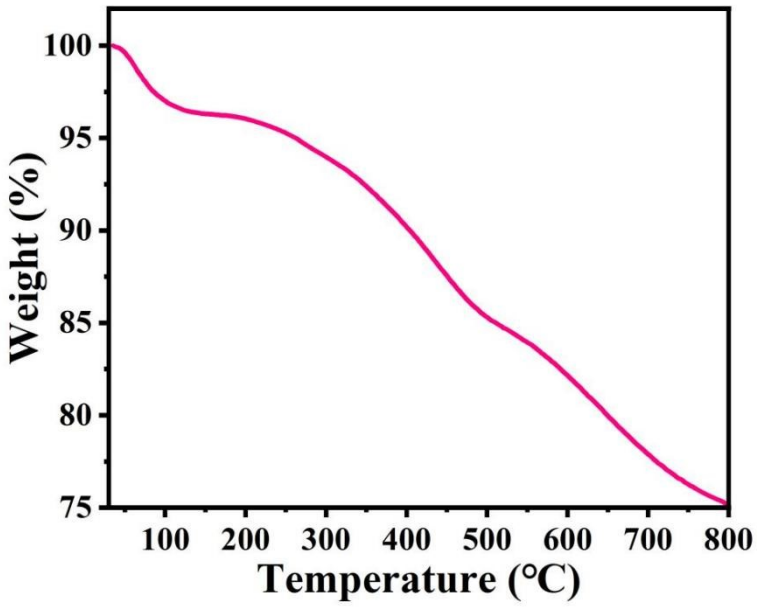

Fig. S3 TGA curves of LLXY-110

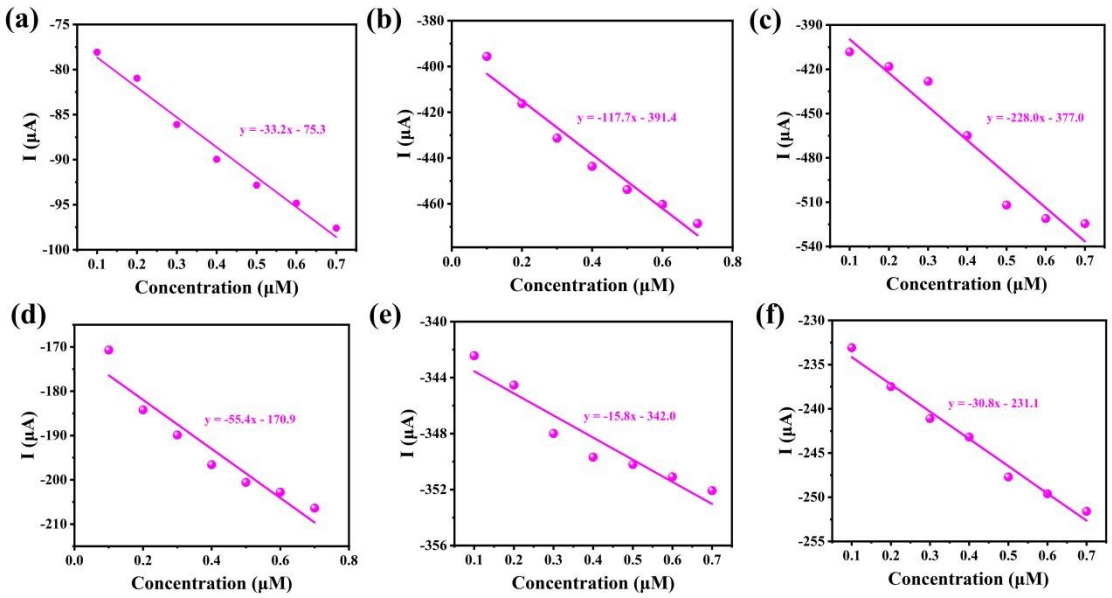

Fig. S4 The linear relationship corresponding toLLXY-110: AB(1:4) at different pH: (a) pH = 0 (b) pH = 1 (c) pH = 2 (d) pH = 3 (e) pH = 4 (f) pH = 5 with varying Cr(VI) concentrations

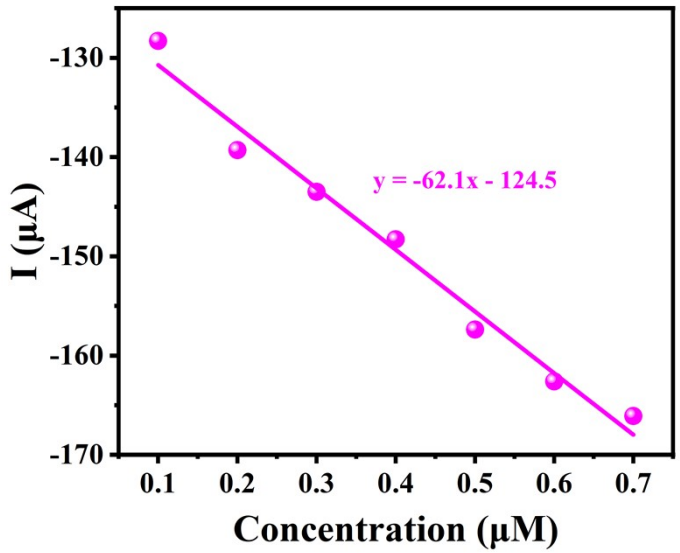

Fig. S5 The linear relationship corresponding toLLXY-110: AB(1:4) in acidified lake water with varying Cr(VI) concentrations

Table S1 Crystallographic data sheets for LLXY-110

Parameters	LLXY-110
Identification code	2463462
Empirical formula	$C_{30}H_{48}N_{12}O_{62}CoP_8Mo_{12}$
Formula weight	3026.77
Temperature/K	273(2)
Crystal system	monoclinic
Space group	*C2/c*
a/Å	16.9079(8)
b/Å	24.1648(9)
c/Å	22.4364(11)
α/°	90
β/°	98.053(2)
γ/°	90
Volume/Å^3	9076.6(7)
Z	4
ρ_{calc}g/cm^3	2.215
μ/mm^{-1}	2.023
F(000)	5836.0
Crystal size/mm^3	0.230 × 0.180 × 0.110
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.612 to 50.126
Index ranges	-20 ≤ h ≤ 20, -27 ≤ k ≤ 28, -26 ≤ l ≤ 26
Reflections collected	47752
Independent reflections	8038 [Rint = 0.0743, Rsigma = 0.0503]
Data/restraints/parameters	8038/68/514
Goodness-of-fit on F^2	1.096
Final R indexes [I>=2σ(I)]	R_1 = 0.0783, wR_2 = 0.1981
Final R indexes [all data]	R_1 = 0.0953, wR_2 = 0.2110
Largest diff. peak/hole / e Å^{-3}	2.79/-1.78

$wR_1 = \sum||F_0|-|F_c||/\sum|F_0|$. $wR_2=\{\sum[w(F_0^2-F_c^2)_2]/\sum[w(F_0^2)^2]\}^{1/2}$

Table S2 Bond Lengths for LLXY-110

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mo1	O13	1.680(8)	Co1	O4	2.152(7)
Mo1	O11	1.924(8)	Co1	O12[1]	2.165(6)
Mo1	O12	1.963(6)	Co1	O12	2.165(6)
Mo1	O27	2.058(8)	P1	O27	1.513(10)
Mo1	O1	2.098(7)	P1	O29	1.518(11)
Mo1	O2	2.302(7)	P1	O28	1.528(9)
Mo1	Mo6	2.5747(15)	P1	O30	1.552(12)
Mo2	O14	1.680(9)	P2	O21	1.519(10)
Mo2	O3	1.928(8)	P2	O20	1.520(11)
Mo2	O4	1.963(7)	P2	O19	1.521(11)
Mo2	O28	2.062(8)	P2	O22	1.552(13)
Mo2	O1	2.096(7)	P3	O24	1.493(11)
Mo2	O2	2.284(8)	P3	O26	1.496(14)
Mo2	Mo3	2.5752(13)	P3	O23	1.522(11)
Mo3	O15	1.682(9)	P3	O25	1.560(19)
Mo3	O3	1.931(8)	P4	O6	1.535(8)
Mo3	O4	1.973(7)	P4	O31	1.538(9)
Mo3	O19	2.050(8)	P4	O10	1.540(9)
Mo3	O5	2.088(7)	P4	O2	1.546(8)
Mo3	O6	2.307(8)	C1	C2	1.4200
Mo4	O16	1.686(8)	C1	N1	1.4200
Mo4	O7	1.938(8)	C2	N2	1.4200
Mo4	O8	1.972(7)	N2	C3	1.4200
Mo4	O21	2.062(8)	C3	N1	1.4200
Mo4	O5	2.080(7)	N1	C4	1.38(2)
Mo4	O6	2.305(8)	C4	C5	1.52(2)
Mo4	Mo5	2.5928(15)	C5	C5[2]	1.51(4)
Mo5	O17	1.662(10)	C6	N4	1.4200
Mo5	O7	1.941(9)	C6	N3	1.4200
Mo5	O8	1.966(7)	N3	C8	1.4200
Mo5	O23	2.063(9)	N3	C9	1.48(2)
Mo5	O9	2.105(8)	C8	C7	1.4200
Mo5	O10	2.272(8)	C7	N4	1.4200
Mo6	O18	1.667(8)	C9	C10	1.42(3)
Mo6	O11	1.916(8)	C10	C11	1.43(3)
Mo6	O12	1.968(7)	C11	C12	1.412(10)
Mo6	O24	2.053(8)	C12	N5	1.42(4)
Mo6	O9	2.093(8)	C14	C15	1.4200

Mo6	O10	2.312(8)	C14	N6	1.4200
Co1	O8	2.147(6)	C15	N5	1.4200
Co1	O8[1]	2.148(6)	N5	C13	1.4200
Co1	O4[1]	2.152(7)	C13	N6	1.4200

[1]1/2-X,1/2-Y,1-Z; [2]-X,1-Y,2-Z

Table S3 Bond Angles for LLXY-110

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O13	Mo1	O11	104.9(4)	O18	Mo6	O9	97.7(4)
O13	Mo1	O12	102.8(4)	O11	Mo6	O9	155.8(3)
O11	Mo1	O12	95.0(3)	O12	Mo6	O9	86.1(3)
O13	Mo1	O27	96.8(4)	O24	Mo6	O9	84.8(4)
O11	Mo1	O27	86.7(4)	O18	Mo6	O10	169.9(4)
O12	Mo1	O27	159.2(3)	O11	Mo6	O10	83.5(3)
O13	Mo1	O1	98.1(4)	O12	Mo6	O10	80.6(3)
O11	Mo1	O1	156.1(3)	O24	Mo6	O10	78.6(3)
O12	Mo1	O1	85.9(3)	O9	Mo6	O10	72.7(3)
O27	Mo1	O1	84.3(3)	O18	Mo6	Mo1	100.1(3)
O13	Mo1	O2	170.3(4)	O11	Mo6	Mo1	48.0(3)
O11	Mo1	O2	83.3(3)	O12	Mo6	Mo1	49.00(19)
O12	Mo1	O2	81.4(3)	O24	Mo6	Mo1	133.3(3)
O27	Mo1	O2	78.2(3)	O9	Mo6	Mo1	134.2(2)
O1	Mo1	O2	73.3(3)	O10	Mo6	Mo1	89.2(2)
O13	Mo1	Mo6	99.8(3)	O8	Co1	O8[1]	180.0(3)
O11	Mo1	Mo6	47.8(2)	O8	Co1	O4[1]	84.7(3)
O12	Mo1	Mo6	49.2(2)	O8[1]	Co1	O4[1]	95.3(3)
O27	Mo1	Mo6	134.1(3)	O8	Co1	O4	95.3(3)
O1	Mo1	Mo6	134.24(19)	O8[1]	Co1	O4	84.7(3)
O2	Mo1	Mo6	89.5(2)	O4[1]	Co1	O4	180.0(4)
O14	Mo2	O3	105.4(4)	O8	Co1	O12[1]	84.0(3)
O14	Mo2	O4	102.1(4)	O8[1]	Co1	O12[1]	96.0(3)
O3	Mo2	O4	95.7(3)	O4[1]	Co1	O12[1]	95.5(3)
O14	Mo2	O28	96.0(4)	O4	Co1	O12[1]	84.5(3)
O3	Mo2	O28	86.5(4)	O8	Co1	O12	96.0(3)
O4	Mo2	O28	160.5(3)	O8[1]	Co1	O12	84.0(3)
O14	Mo2	O1	96.6(4)	O4[1]	Co1	O12	84.5(3)
O3	Mo2	O1	156.9(4)	O4	Co1	O12	95.5(3)
O4	Mo2	O1	86.5(3)	O12[1]	Co1	O12	180.0
O28	Mo2	O1	84.2(3)	O27	P1	O29	111.2(6)
O14	Mo2	O2	169.4(3)	O27	P1	O28	114.1(5)

O3	Mo2	O2	83.8(3)	O29	P1	O28	108.0(6)
O4	Mo2	O2	81.9(3)	O27	P1	O30	108.8(7)
O28	Mo2	O2	79.1(3)	O29	P1	O30	105.6(7)
O1	Mo2	O2	73.7(3)	O28	P1	O30	108.7(6)
O14	Mo2	Mo3	99.9(3)	O21	P2	O20	111.7(7)
O3	Mo2	Mo3	48.2(2)	O21	P2	O19	114.4(5)
O4	Mo2	Mo3	49.30(19)	O20	P2	O19	106.2(7)
O28	Mo2	Mo3	134.5(3)	O21	P2	O22	105.8(8)
O1	Mo2	Mo3	135.0(2)	O20	P2	O22	109.1(8)
O2	Mo2	Mo3	90.15(18)	O19	P2	O22	109.5(8)
O15	Mo3	O3	105.4(4)	O24	P3	O26	107.2(11)
O15	Mo3	O4	101.8(4)	O24	P3	O23	115.5(5)
O3	Mo3	O4	95.2(3)	O26	P3	O23	109.0(12)
O15	Mo3	O19	98.0(4)	O24	P3	O25	108.5(10)
O3	Mo3	O19	85.6(4)	O26	P3	O25	106.7(14)
O4	Mo3	O19	159.2(4)	O23	P3	O25	109.6(9)
O15	Mo3	O5	98.0(4)	O6	P4	O31	109.1(5)
O3	Mo3	O5	155.6(4)	O6	P4	O10	109.5(4)
O4	Mo3	O5	86.4(3)	O31	P4	O10	108.0(6)
O19	Mo3	O5	84.6(3)	O6	P4	O2	109.8(4)
O15	Mo3	O6	171.0(3)	O31	P4	O2	110.8(5)
O3	Mo3	O6	82.8(3)	O10	P4	O2	109.7(4)
O4	Mo3	O6	80.7(3)	Mo2	O1	Mo1	113.2(3)
O19	Mo3	O6	78.7(3)	P4	O2	Mo2	125.0(4)
O5	Mo3	O6	73.4(3)	P4	O2	Mo1	125.4(5)
O15	Mo3	Mo2	99.7(3)	Mo2	O2	Mo1	99.5(3)
O3	Mo3	Mo2	48.1(2)	Mo2	O3	Mo3	83.7(3)
O4	Mo3	Mo2	48.97(19)	Mo2	O4	Mo3	81.7(3)
O19	Mo3	Mo2	133.3(3)	Mo2	O4	Co1	134.9(3)
O5	Mo3	Mo2	134.43(19)	Mo3	O4	Co1	135.6(3)
O6	Mo3	Mo2	88.51(18)	Mo4	O5	Mo3	114.0(3)
O16	Mo4	O7	105.3(4)	P4	O6	Mo4	125.6(5)
O16	Mo4	O8	102.3(4)	P4	O6	Mo3	125.9(4)
O7	Mo4	O8	95.2(3)	Mo4	O6	Mo3	98.6(3)
O16	Mo4	O21	96.4(4)	Mo4	O7	Mo5	83.9(3)
O7	Mo4	O21	87.1(4)	Mo5	O8	Mo4	82.4(2)
O8	Mo4	O21	159.7(3)	Mo5	O8	Co1	134.7(3)
O16	Mo4	O5	97.0(3)	Mo4	O8	Co1	135.0(4)
O7	Mo4	O5	156.5(4)	Mo6	O9	Mo5	113.5(4)
O8	Mo4	O5	87.0(3)	P4	O10	Mo5	126.2(4)

O21	Mo4	O5	83.1(3)	P4	O10	Mo6	125.4(4)
O16	Mo4	O6	170.0(4)	Mo5	O10	Mo6	99.9(3)
O7	Mo4	O6	83.6(3)	Mo6	O11	Mo1	84.2(3)
O8	Mo4	O6	81.1(3)	Mo1	O12	Mo6	81.8(2)
O21	Mo4	O6	79.2(3)	Mo1	O12	Co1	135.3(4)
O5	Mo4	O6	73.6(3)	Mo6	O12	Co1	134.9(3)
O16	Mo4	Mo5	100.7(3)	P2	O19	Mo3	135.1(6)
O7	Mo4	Mo5	48.1(3)	P2	O21	Mo4	135.4(5)
O8	Mo4	Mo5	48.7(2)	P3	O23	Mo5	133.7(6)
O21	Mo4	Mo5	134.8(3)	P3	O24	Mo6	134.2(6)
O5	Mo4	Mo5	134.77(19)	P1	O27	Mo1	136.6(5)
O6	Mo4	Mo5	88.6(2)	P1	O28	Mo2	135.5(5)
O17	Mo5	O7	105.2(4)	C2	C1	N1	108.0
O17	Mo5	O8	102.1(4)	N2	C2	C1	108.0
O7	Mo5	O8	95.3(3)	C2	N2	C3	108.0
O17	Mo5	O23	97.2(5)	N2	C3	N1	108.0
O7	Mo5	O23	86.5(4)	C4	N1	C3	122.8(13)
O8	Mo5	O23	159.4(4)	C4	N1	C1	128.8(13)
O17	Mo5	O9	96.5(4)	C3	N1	C1	108.0
O7	Mo5	O9	157.3(4)	N1	C4	C5	111.4(17)
O8	Mo5	O9	86.5(3)	C5[2]	C5	C4	114(2)
O23	Mo5	O9	84.2(4)	N4	C6	N3	108.0
O17	Mo5	O10	169.3(4)	C8	N3	C6	108.0
O7	Mo5	O10	84.5(3)	C8	N3	C9	124.3(15)
O8	Mo5	O10	81.1(3)	C6	N3	C9	127.6(15)
O23	Mo5	O10	78.6(4)	C7	C8	N3	108.0
O9	Mo5	O10	73.4(3)	C8	C7	N4	108.0
O17	Mo5	Mo4	100.5(3)	C6	N4	C7	108.0
O7	Mo5	Mo4	48.0(2)	C10	C9	N3	111.3(18)
O8	Mo5	Mo4	48.92(19)	C9	C10	C11	110(2)
O23	Mo5	Mo4	134.0(3)	C12	C11	C10	112(3)
O9	Mo5	Mo4	134.6(2)	C11	C12	N5	115(3)
O10	Mo5	Mo4	89.3(2)	C15	C14	N6	108.0
O18	Mo6	O11	105.6(4)	C14	C15	N5	108.0
O18	Mo6	O12	102.5(4)	C12	N5	C15	125(7)
O11	Mo6	O12	95.1(3)	C12	N5	C13	127(7)
O18	Mo6	O24	97.6(4)	C15	N5	C13	108.0
O11	Mo6	O24	85.7(4)	N6	C13	N5	108.0
O12	Mo6	O24	158.9(3)	C13	N6	C14	108.0

[1]1/2-X,1/2-Y,1-Z;[2]-X,1-Y,2-Z

Table S4 The comparative table of different P_4Mo_6-based materials for Cr(VI) detection

Materials	LODs (nM)	Sensitivity ($\mu A \cdot \mu M^{-1}$)	Ref
LLXY-110	0.09	228	This Work
$(H_2bib)_6[Co(Hbib)_2(H_2O)_5][Co(P_4Mo_6O_{31}H_7)_2]_2 \cdot 15H_2O$	11.0	124.29	[1]
$[Co^{II}_2(H_2O)_4Na^{I}_2][Co^{II}(Hbpe)][Na^{I}(bpe)_{1.5}]\{Co^{II}[P_4Mo^{V}_6O_{31}H_6]_2\} \cdot 9H_2O$	30	0.11	[2]
$[Co^{II}(H_2O)_4Na^{I}_3][Co^{II}(Hbpe)][Co^{II}(bpe)]\{Co^{II}[P_4Mo^{V}_6O_{31}H_6]_2\} \cdot 9H_2O$	27	0.14	[2]
$\{[Cd(H_2O)_2]_2[Cd(btmbp)]_2\}\{Cd(P_4Mo_6O_{31}H_7)_2\} \cdot 20H_2O$	4.17	226.32	[3]
$((H_3DETA)_4\{Ni[Mo_6O_{12}(PO_4)_2(OH)_3(HPO_4)_2]_2\} \cdot 3H_2O$	500	0.023	[4]
$[Na_{0.5}Cu_{5.5}(H_2O)_2(btmbp)_4][Mn(H_2O)_3]_2\{Mn[H_6P_4Mo_6O_{31}]_2\} \cdot 10H_2O$	0.95	330.5	[5]
$[Cu^{I}(BBTZ)]_4[Mn^{II}(H_2O)_3]_2[Cu^{II}(P_4Mo^{V}_6O_{31}H_7)_2] \cdot H_3PO_4 \cdot 3H_2O$	1.59	111.08	[6]
$Na^{I}_2(H_2BBTZ)[Na^{I}(H_2O)(BBTZ)]_2[Mn^{II}(H_2O)_2]_2[Mn^{II}(P_4Mo^{V}_6O_{31}H_6)_2] \cdot 2H_2O$	2.91	119.87	[6]
$[Co_2L_2(H_2O)_8(TeMo_6O_{24}) \cdot H_2O$	0.412	3.98	[7]
$(H_2bib)_2[Cd(H_2O)]_2[Na(H_2O)_{0.5}][Cd(P_4Mo_6O_{31}H_{6.5})_2] \cdot 13H_2O$	18.41	122.49	[8]
$[Cd^{II}_2(dm4bt)_4][GeW_{12}O_{40}]$	210	7.17	[9]

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