Supporting Information

Four Anderson-type $[TeMo_6O_{24}]^{6-}$-based metal-organic complexes with a new bis(pyrimidine)-bis(amide): multifunctional electrochemical and adsorption performances

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X-ray Crystallographic Study

The single-crystal X-ray diffraction data for complexes **1**–**4** were collected using a Bruker SMART APEX II with Mo Kα radiation (λ = 0.71073 Å) by ω and θ scan mode at room temperature. All the structures were solved by direct methods with the Olex2 software.[1] The final refinement was performed by full matrix least-squares techniques on F^2. All non-hydrogen atoms were refined with anisotropic temperature parameters. All hydrogen atoms were placed in geometrically idealized position as a riding mode. The selected bond distances and angles for **1**–**4** are summarized in Table S1. The CCDC numbers are 2109197-2109200.

Synthesis methods

The $(NH_4)_6[TeMo_6O_{24}]\cdot 7H_2O$ was synthesized according to the reported literature.[2] Ligand L was synthesized as follows: 4-Pyrimidinecarboxylic acid (4g), p-phenylenediamine (1.74g) and 50 ml of pyridine were added to a 250 ml distillation flask, and 10 ml of triphenyl phosphite was slowly added after stirring for 20 minutes. The mixture was refluxed for 8 h. The product was cooled at room

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temperature and stood for one day, then filtered and rinsed with ethanol to obtain a brown powder solid.

Preparation of complexes 1–4 bulk-modified carbon paste electrodes

The complex **1** bulk-modified carbon paste electrode (**1**-CPE) was fabricated by mixing 0.11 g graphite powder and 0.015 g complex **1** in an agate mortar for approximately 30 minutes to achieve a uniform mixture; then 0.10 mL paraffin oil was added and stirred with a glass rod. The homogenized mixture was packed into a 3 mm inner diameter glass tube and the tube surface was wiped with weighing paper. Electrical contact was established with a copper wire through the back of the electrode. In a similar procedure, **2**-, **3**- and **4**-CPEs were prepared with complexes **2**–**4**, respectively.

Table. S1 Selected bond distances (Å) and angles (°) for complexes **1**–**4**.

Complex **1**			
Cu(1)-O(1W)	1.982(4)	Cu(1)-O(1)	2.016(4)
Cu(1)-N(1)	2.012(4)	Cu(1)-O(3W)	1.941(4)
Cu(1)-O(2W)	2.253(4)	Cu(1)-O(14)#1	2.498(4)
O(1W)-Cu(1)-N(1)	95.46(17)	O(1W)-Cu(1)-O(2W)	88.80(17)
O(1)-Cu(1)-O(2W)	88.19(16)	N(1)-Cu(1)-O(1)	85.28(16)
N(1)-Cu(1)-O(2W)	97.37(17)	O(3W)-Cu(1)-O(1W)	88.03(18)
O(3W)-Cu(1)-O(1)	91.98(17)	O(3W)-Cu(1)-N(1)	165.51(19)
O(3W)-Cu(1)-O(2W)	96.76(18)	O(1W)-Cu(1)-O(1)	176.96(17)
O(1W)-Cu(1)-O(14)#1	98.31(16)	O(1)-Cu(1)-O(14)#1	84.68(13)
N(1)-Cu(1)-O(14)#1	85.92(15)	O(3W)-Cu(1)-O(14)#1	79.65(16)
O(2W)-Cu(1)-O(14)#1	171.88(15)		
Symmetry code for **1**: #1 -x+1, -y, -z+2			
Complex **2**			
Co(1)-O(9)#1	2.155(2)	Co(1)-O(1)	2.117(2)
Co(1)-O(3W)	2.103(2)	Co(1)-O(2W)	2.053(2)
Co(1)-N(1)	2.139(3)	Co(1)-O(1W)	2.057(2)

O(1)-Co(1)-O(9)#1	87.81(8)	O(1)-Co(1)-N(1)	83.31(9)
O(3W)-Co(1)-O(9)#1	170.66(9)	O(3W)-Co(1)-O(1)	84.39(9)
O(3W)-Co(1)-N(1)	98.46(10)	O(2W)-Co(1)-O(9)#1	82.46(9)
O(2W)-Co(1)-O(1)	95.42(9)	O(2W)-Co(1)-O(3W)	93.14(10)
O(2W)-Co(1)-O(1W)	86.60(10)	O(2W)-Co(1)-N(1)	168.13(10)
O(1W)-Co(1)-O(9)#1	99.83(10)	O(1W)-Co(1)-O(1)	172.30(10)
O(1W)-Co(1)-O(3W)	88.08(10)	O(1W)-Co(1)-N(1)	96.23(10)
N(1)-Co(1)-O(9)#1	85.70(9)		
Symmetry code for **2**: #1 -x+1, -y, -z+2			
Complex **3**			
Ni(1)-O(7)#1	2.122(4)	Ni(1)-O(2W)	2.071(4)
Ni(1)-O(1)	2.071(4)	Ni(1)-O(3W)	2.012(5)
Ni(1)-O(1W)	2.027(4)	Ni(1)-N(1)	2.079(5)
O(2W)-Ni(1)-O(7)#1	172.18(17)	O(2W)-Ni(1)-N(1)	96.4(2)
O(1)-Ni(1)-O(7)#1	87.92(16)	O(1)-Ni(1)-O(2W)	85.42(17)
O(1)-Ni(1)-N(1)	84.80(19)	O(3W)-Ni(1)-O(7)#1	82.94(18)
O(3W)-Ni(1)-O(2W)	93.58(19)	O(3W)-Ni(1)-O(1)	95.25(18)
O(3W)-Ni(1)-O(1W)	85.3(2)	O(3W)-Ni(1)-N(1)	170.0(2)
O(1W)-Ni(1)-O(7)#1	98.5(2)	O(1W)-Ni(1)-O(2W)	88.1(2)
O(1W)-Ni(1)-O(1)	173.6(2)	O(1W)-Ni(1)-N(1)	95.8(2)
N(1)-Ni(1)-O(7)#1	87.03(19)		
Symmetry code for **3**: #1 -x+1, -y, -z+2			
Complex **4**			
Zn(1)-O(1)	2.176(3)	Zn(1)-O(8)#1	2.290(3)
Zn(1)-O(3W)	2.081(4)	Zn(1)-O(2W)	2.001(3)
Zn(1)-O(1W)	2.054(3)	Zn(1)-N(1)	2.113(4)
O(1)-Zn(1)-O(8)#1	85.07(12)	O(3W)-Zn(1)-O(1)	84.94(13)
O(3W)-Zn(1)-O(8)#1	168.77(13)	O(3W)-Zn(1)-N(1)	100.04(15)
O(2W)-Zn(1)-O(1)	93.21(13)	O(2W)-Zn(1)-O(8)#1	78.75(13)

O(2W)-Zn(1)-O(3W)	96.71(15)	O(2W)-Zn(1)-O(1W)	88.64(14)
O(2W)-Zn(1)-N(1)	162.47(16)	O(1W)-Zn(1)-O(1)	174.88(16)
O(1W)-Zn(1)-O(8)#1	99.99(15)	O(1W)-Zn(1)-O(3W)	90.10(16)
O(1W)-Zn(1)-N(1)	96.42(14)	N(1)-Zn(1)-O(1)	83.22(14)
N(1)-Zn(1)-O(8)#1	83.84(14)		

Symmetry code for **4**: #1 -x+1, -y, -z+2

Table S2. Selected hydrogen-bonding distance (Å) and angles (°) for complexes **1**–**4**.

Complex **1**				
D-H···A	D-H	H···A	D···A	D-H···A
O1W-H1WA···O11	0.85	1.92	2.699(6)	152
O1W-H1WB···O8	0.85	1.92	2.756(6)	167
O2W-H2WA···O9	0.89	1.99	2.849(6)	163
O3W-H3WA···O6	0.90	2.12	2.680(6)	120
Complex **2**				
D-H···A	D-H	H···A	D···A	D-H···A
O1W-H1WA···O7	0.85	1.86	2.709(3)	175
O1W-H1WB···O5	0.85	2.03	2.814(3)	153
O3W-H3WB···O14	0.85	1.99	2.812(3)	161
Complex **3**				
D-H···A	D-H	H···A	D···A	D-H···A
O1W-H1WA···O14	0.85	1.88	2.716(6)	167
O1W-H1WB···O12	0.85	2.00	2.819(7)	161
O2W-H2WB···O10	0.91	1.97	2.851(6)	165
O3W-H3WA···O11	0.85	1.96	2.683(6)	142
Complex **4**				
D-H···A	D-H	H···A	D···A	D-H···A
O1W-H1WA···O9	0.85	1.87	2.702(4)	168
O1W-H1WB···O10	0.85	2.00	2.782(5)	152

O2W-H2WA···O6	0.86	1.94	2.700(4)	147
O3W-H3WB···O11	0.85	1.99	2.809(5)	161

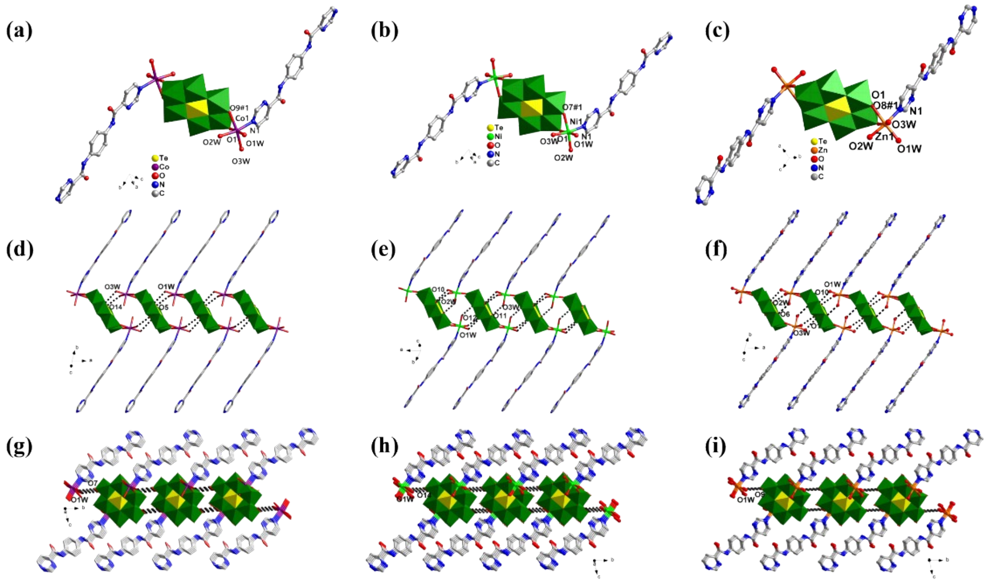


Fig. S1. (a-c) The dinuclear units of complexes **2**–**4** (Symmetry codes: #1 -x+1, -y, -z+2); (d-f) The 1D chain structure of **2**–**4** linked by hydrogen bonds; (g-i) The 2D supramolecular layer of **2**–**4**.

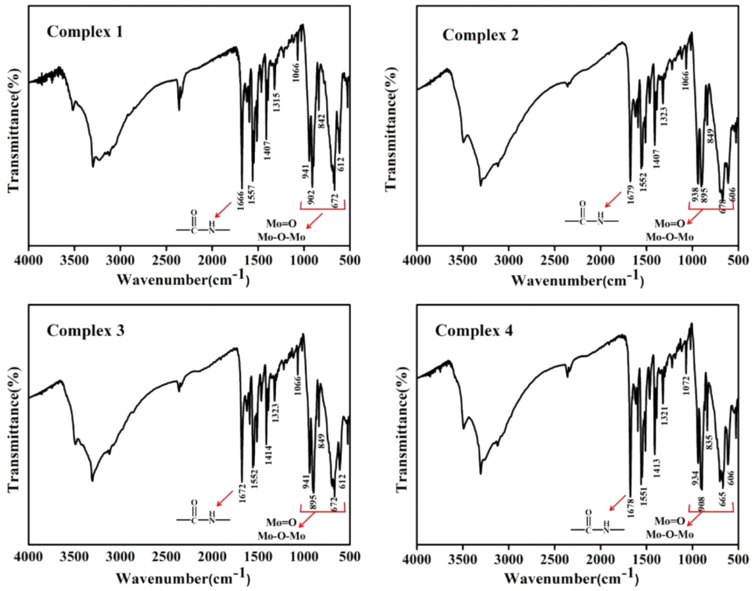


Fig. S2. The IR spectra of complexes **1**–**4**.

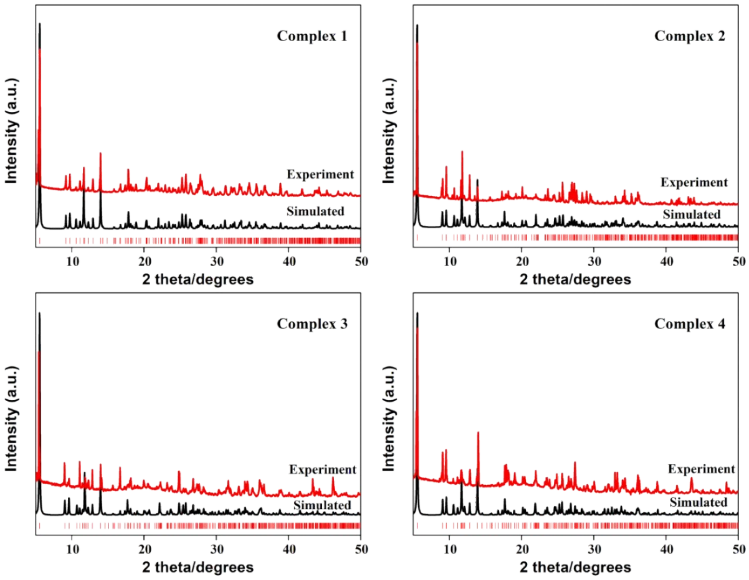


Fig. S3. Powder X-ray diffraction patterns of complexes **1**–**4**.

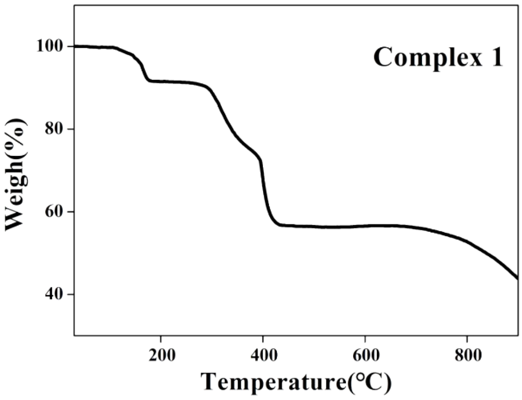


Fig. S4. The TG curve of the complex **1**.

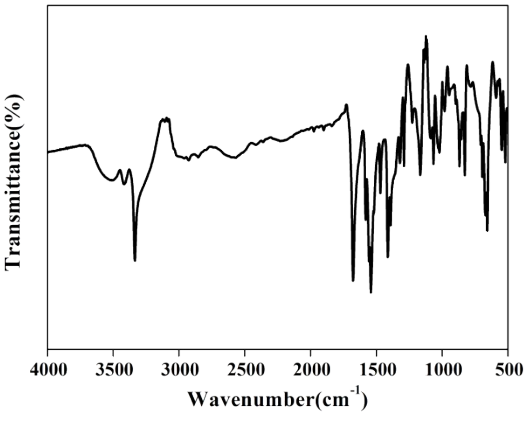


Fig. S5. The IR spectrum of L ligand.

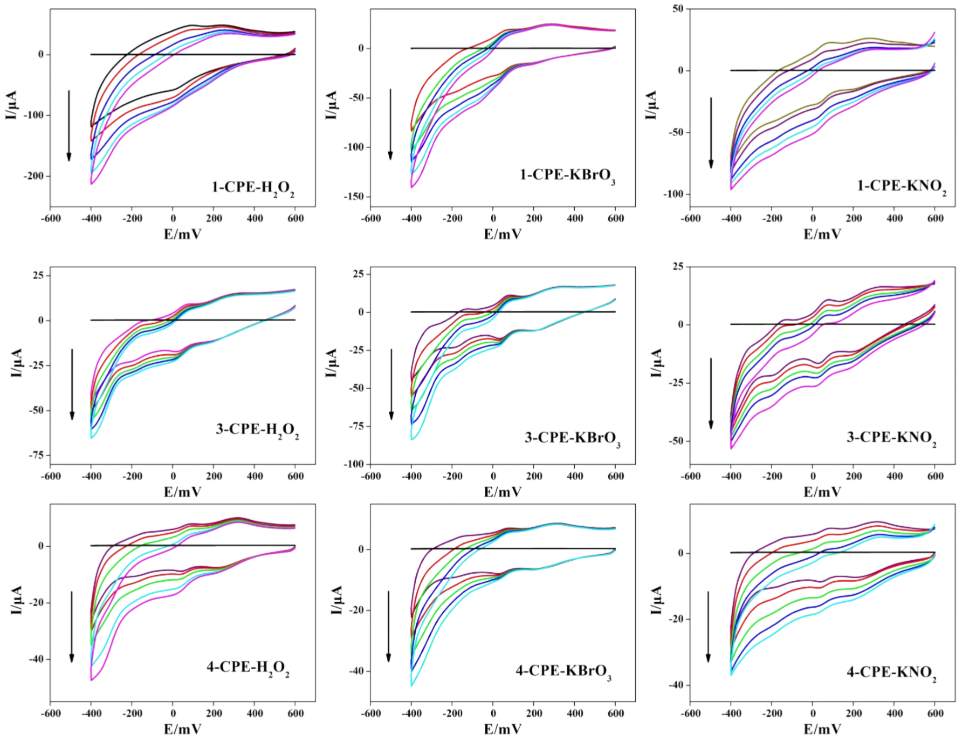


Fig. S6. The cyclic voltammograms of **1-**, **3-**, **4-**CPE in electrolyte solution containing H_2O_2, BrO_3^- and NO_2^- (Scan rate: 60 mV·s^{-1}).

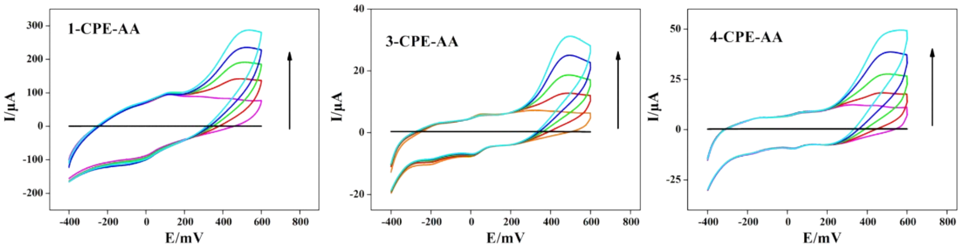


Fig. S7. The cyclic voltammograms of **1-**, **3-**, **4-**CPE in electrolyte solution containing AA (Scan rate: 60 mV·s^{-1}).

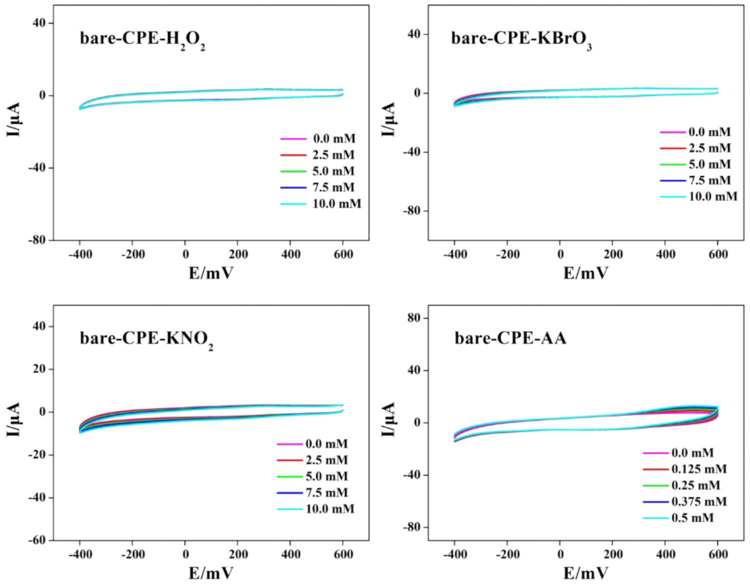


Fig. S8. The cyclic voltammograms of the bare-CPE in electrolyte solution containing H_2O_2, $KBrO_3$, KNO_2 and AA.

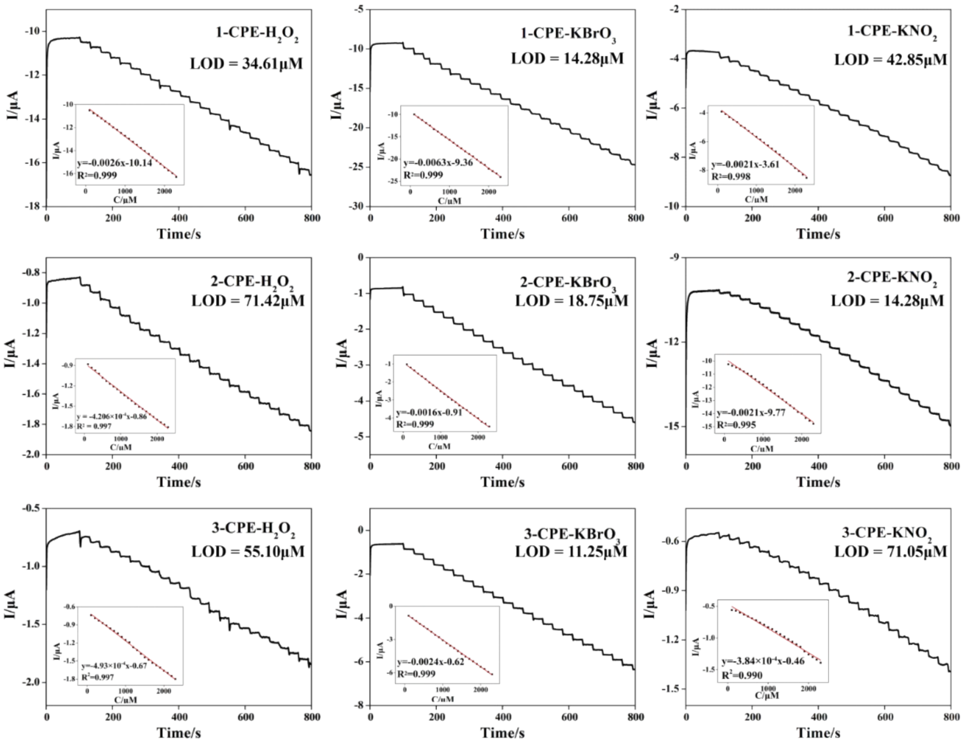


Fig. S9. Current response of **1~3-**CPEs when H_2O_2, $KBrO_3$ and KNO_2 are continuously added to electrolyte solution. The applied potential was -0.2V. (Inset: linear relationship between concentrations of the substrate and response current).

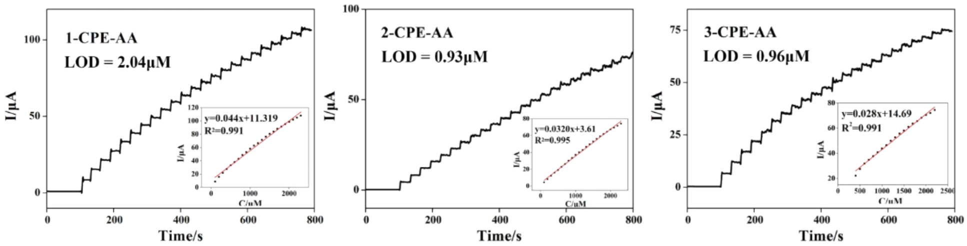


Fig. S10. Current response of **1~3**-CPEs when AA are continuously added to electrolyte solution. The applied potential was 0.5V. (Inset: linear relationship between concentrations of the substrate and response current).

Table S3 Parameters for AA, H_2O_2, potassium bromate and potassium nitrite determination using **1~4**-CPEs.

Material		**1**-CPE	**2**-CPE	**3**-CPE	**4**-CPE
Detection limit (μmol L^{-1})	AA	2.04	0.93	0.96	0.90
	H_2O_2	34.61	71.42	55.1	31.12
	BrO_3^-	14.28	18.75	11.25	6.12
	NO_2^-	42.85	14.28	71.05	36.99
Sensitivity (μA μM^{-1})	AA	0.044	0.032	0.028	0.033
	H_2O_2	2.6×10^{-3}	4.2×10^{-4}	4.9×10^{-4}	9.6×10^{-4}
	BrO_3^-	6.3×10^{-3}	1.6×10^{-3}	2.4×10^{-3}	4.9×10^{-3}
	NO_2^-	2.1×10^{-3}	2.1×10^{-3}	3.8×10^{-4}	8.1×10^{-3}
Linear Range (μmol L^{-1})	AA	100-2300	100-2300	100-2300	100-2300
	H_2O_2	100-2300	100-2300	100-2300	100-2300
	BrO_3^-	100-2300	100-2300	100-2300	100-2300
	NO_2^-	100-2300	100-2300	100-2300	100-2300

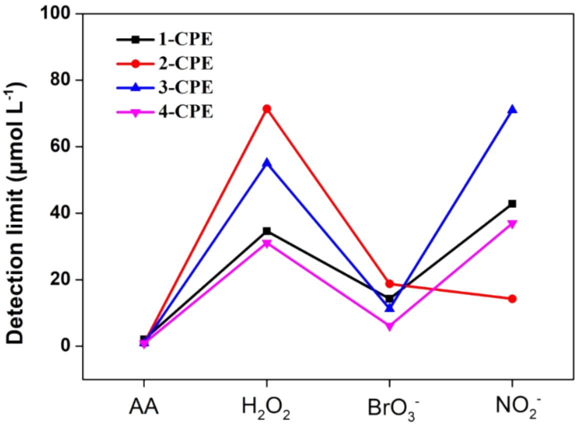


Fig. S11. Line graph of detection limits of **1~4**-CPEs for AA, H_2O_2, $KBrO_3$ and KNO_2.

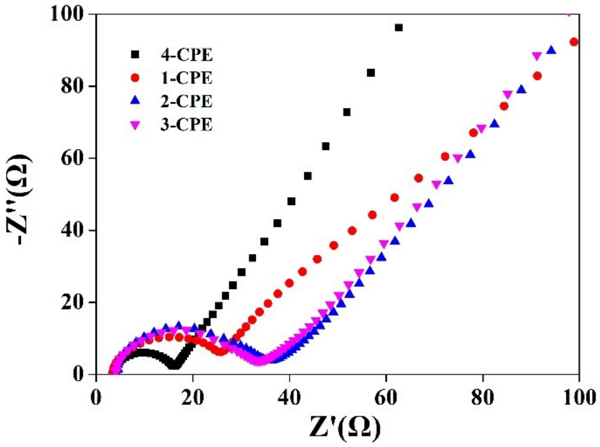
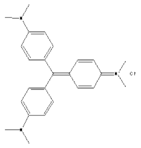
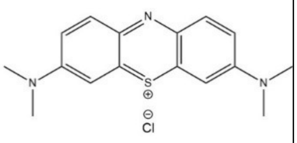
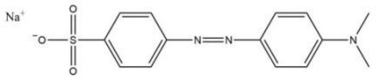


Fig. S12. The electrochemical impedance spectroscopy of **1**~**4**-CPEs.

Table S4 The charges and sizes of the selected organic dyes.

Name	GV	MB	MO
Structure			
Colour	Violet	Blue	Orange
Charge	+1	+1	-1
X(Å)	4.00	4.00	5.31
Y(Å)	12.97	12.97	7.25
Z(Å)	13.74	13.74	17.39

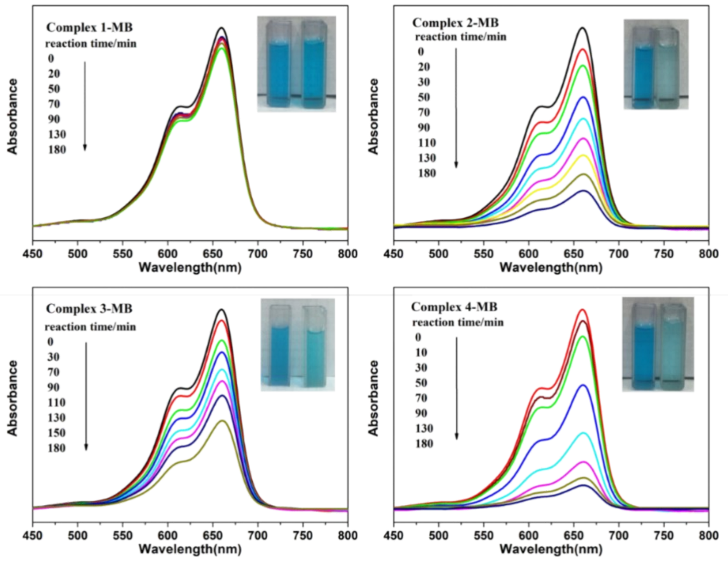


Fig. S13. UV/vis spectra of the MB in the presence of complexes **1**–**4**.

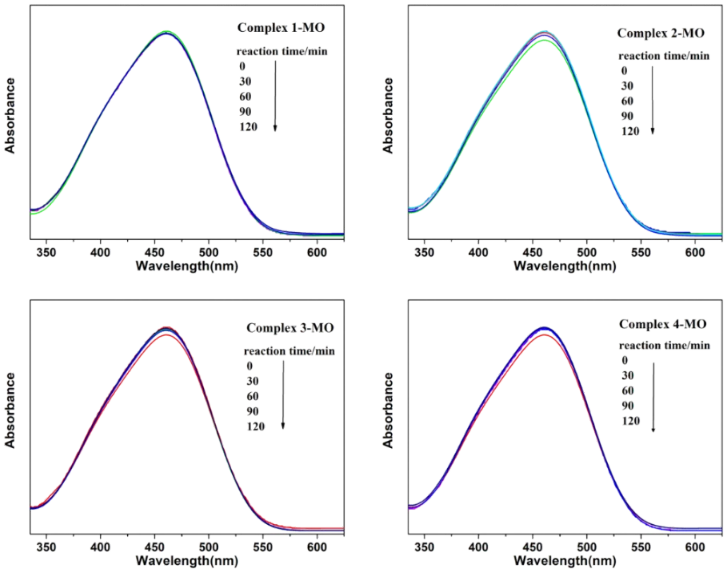


Fig. S14. UV/vis spectra of the MO in the presence of complexes **1**–**4**.

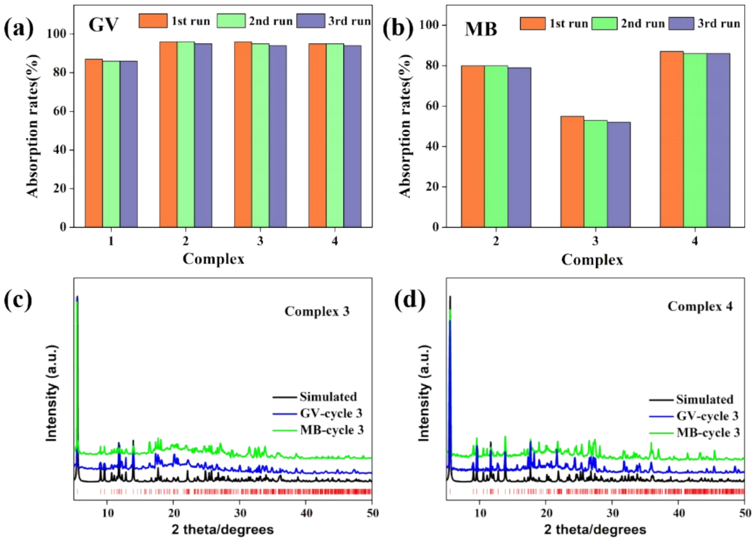


Fig. S15. (a-b) Three cycles of adsorption test of complexes **1**–**4** for GV and MB. (c-d) PXRD patterns of complexes **3**–**4** after three cycles of adsorption test.

Notes and references

S1. O.V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.

S2. Z. X. Zhang, T. Murayama, M. Sadakane, H. Ariga, N. Yasuda, N. Sakaguchi, K. Asakura, W. Ueda, *Nat Commun*, 2015, **6**, 7731.