Supplementary Material (ESI) for *CrystEngComm*

Four Keggin-type polyoxometalate-based complexes derived from bis(pyrazine)-bis(amide) ligands for sensing multiple analytes and adsorbing dye molecules

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X-ray Crystallographic Study

Single crystal X-ray diffraction analysis data for **1-4** were carried out using a Bruker SMART APEX II CCD diffractometer equipped with Mo-Kα monochromatic radiation (λ = 0.71073 Å) by ω and θ scan mode. 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 Hydrogen atoms were placed in geometrically idealized position as a riding mode. In **1**, the instruction "ISOR" was used to refine atoms O3, O16, O17, O18, O22, O23, O24, O4W and O7W. In **2**, the instruction "ISOR" was used to refine atoms O2W, O12, C12, N4, C14 and O4. In **3**, the instruction "ISOR" was used to refine atoms O9, O11, O2W and O3W. The instruction "RIGU" was used to refine atoms O1, C9, N4, O19, C5, C6, N3, C8 and C2. The instruction "DFIX" was used to refine the distance of Si1 and O14. In **4**, the instruction "ISOR" was used to refine atoms O15, O15A, O18A, O18, O5, O12, O16, O10A, O21 and O10. Data collection, cell refinement and data reduction for complexes **1-4** were performed in Table 1. Selected bond distances and angles were summarized in Table S1. The CCDC numbers are 1998300-1998301, 2061293-2061294.

Preparation of complexes 1-4 bulk-modified carbon paste electrode (1-, 2-, 3-, 4-CPEs)

Complexes **1-4** modified carbon paste electrodes **(1-, 2-, 3-, 4-CPEs)** was prepared as follows: graphite powder (0.10 g) and complexes **1-4** (0.01 g) were mixed and ground together in an agate mortar for approximately 45 minutes to get a homogeneous mixture, and then 0.05mL paraffin oil was added and the mixture was stirred with a glass rod. The uniform mixture was packed into a 3 mm inner diameter glass tube and the tube

surface was wiped with weighing paper. The electrical contact was established with copper wire through the back of the electrode.

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

Complex **1**			
Cu(1)-O(1)	1.958(6)	Cu(2)-O(1W)	2.454(11)
Cu(1)-O(1)#2	1.958(6)	Cu(2)-O(2)#3	1.968(7)
Cu(1)-O(4)#2	2.367(6)	Cu(2)-O(2)	1.968(7)
Cu(1)-O(4)	2.367(6)	Cu(2)-N(2)	1.966(10)
Cu(1)-N(1)#2	1.971(7)	Cu(2)-N(2)#3	1.966(10)
Cu(1)-N(1)	1.971(7)	Cu(2)-O(1W)#3	2.454(11)
O(1)#2-Cu(1)-O(1)	180	N(1)#2-Cu(1)-O(4)	89.7(3)
O(1)-Cu(1)-O(4)	94.0(3)	N(1)-Cu(1)-N(1)#2	180
O(1)-Cu(1)-O(4)#2	86.0(3)	O(2)-Cu(2)-O(1W)	86.8(4)
O(1)#2-Cu(1)-O(4)#2	94.0(3)	O(2)#3-Cu(2)-O(1W)	93.2(4)
O(1)#2-Cu(1)-O(4)	86.0(3)	O(2)#3-Cu(2)-O(2)	180
O(1)#2-Cu(1)-N(1)	97.7(3)	N(2)#3-Cu(2)-O(1W)	88.4(4)
O(1)#2-Cu(1)-N(1)#2	82.3(3)	N(2)-Cu(2)-O(1W)	91.6(4)
O(1)-Cu(1)-N(1)#2	97.7(3)	N(2)#3-Cu(2)-O(2)#3	82.5(3)
O(1)-Cu(1)-N(1)	82.3(3)	N(2)-Cu(2)-O(2)#3	97.5(3)
O(4)#2-Cu(1)-O(4)	180	N(2)-Cu(2)-O(2)	82.5(3)
N(1)-Cu(1)-O(4)#2	89.7(3)	N(2)#3-Cu(2)-O(2)	97.5(3)
N(1)#2-Cu(1)-O(4)#2	90.3(3)	N(2)-Cu(2)-N(2)#3	180
N(1)-Cu(1)-O(4)	90.3(3)		

Symmetry codes: #2 -x,-y+1,-z+1; #3 -x,-y+2,-z+2

Complex **2**			
Cu(1)-O(1)#1	1.935(9)	Cu(2)-O(2)	1.934(9)
Cu(1)-O(3)	1.941(9)	Cu(2)-O(4)#2	1.949(9)
Cu(1)-O(6)	2.548(10)	Cu(2)-O(7)	2.457(9)
Cu(1)-N(1)#1	2.003(11)	Cu(2)-N(2)	1.977(12)
Cu(1)-N(11)	1.979(11)	Cu(2)-N(6)#2	1.992(12)
Cu(1)-O(5)	2.463(10)	O(2)-Cu(2)-O(7)	81.6(3)
O(1)#1-Cu(1)-O(6)	82.3(4)	O(2)-Cu(2)-N(2)	83.0(4)
O(1)#1-Cu(1)-N(1)#1	83.4(4)	O(2)-Cu(2)-N(6)#2	97.4(4)
O(1)#1-Cu(1)-N(11)	97.6(4)	O(4)#2-Cu(2)-O(7)	106.8(4)
O(3)-Cu(1)-O(6)	95.8(4)	O(4)#2-Cu(2)-N(2)	95.3(4)
O(3)-Cu(1)-N(1)#1	97.0(4)	O(4)#2-Cu(2)-N(6)#2	82.7(4)
O(3)-Cu(1)-N(11)	82.4(4)	N(2)-Cu(2)-O(7)	101.9(4)
N(1)#1-Cu(1)-O(6)	110.1(4)	N(2)-Cu(2)-N(6)#2	168.9(5)
N(11)-Cu(1)-O(6)	82.2(4)	N(6)#2-Cu(2)-O(7)	89.1(4)
N(11)-Cu(1)-N(1)#1	167.6(4)	O(2)-Cu(2)-O(4)#2	171.6(4)
O(1)#1-Cu(1)-O(3)	178.1(4)		
Symmetry codes: #1 x, -y+3/2, z+1/2; #2 x, -y+1/2, z-1/2			
Complex **3**			
Co(1)-O(1W)#2	2.059(13)	Co(1)-N(1)	2.131(11)
Co(1)-O(1W)	2.059(13)	Co(1)-O(1)	1.95(3)
Co(1)-N(1)#2	2.131(11)	Co(1)-O(1)#2	1.95(3)
O(1W)#2-Co(1)-O(1W)	86.5(9)	N(1)#2-Co(1)-N(1)	179.0(6)
O(1W)#2-Co(1)-N(1)#2	88.0(4)	O(1)-Co(1)-O(1W)	102.0(11)
O(1W)-Co(1)-N(1)	88.0(4)	O(1)-Co(1)-O(1W)#2	170.3(11)

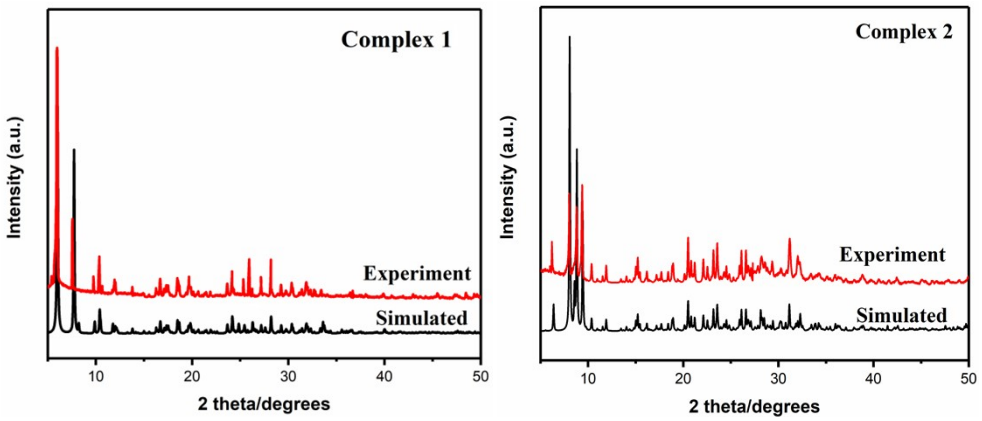
O(1W)-Co(1)-N(1)#2	92.7(4)	O(1)-Co(1)-N(1)#2	96.4(8)
O(1W)#2-Co(1)-N(1)	92.7(4)	O(1)-Co(1)-N(1)	82.8(8)

Symmetry codes: #2 -x, y, -z+1

Complex **4**

Cu(1)-O(1)	1.952(14)	Cu(1)-N(1)#2	1.962(18)
Cu(1)-O(2)#2	1.948(14)	Cu(1)-N(2)	1.958(18)
Cu(1)-O(3)	2.345(14)	O(2)#2-Cu(1)-N(1)#2	83.6(7)
O(1)-Cu(1)-O(3)	88.3(6)	O(2)#2-Cu(1)-N(2)	96.8(7)
O(1)-Cu(1)-N(1)#2	96.3(7)	N(1)#2-Cu(1)-O(3)	100.7(6)
O(1)-Cu(1)-N(2)	84.0(7)	N(2)-Cu(1)-O(3)	87.8(7)
O(2)#2-Cu(1)-O(1)	175.6(6)	N(2)-Cu(1)-N(1)#2	171.5(7)
O(2)#2-Cu(1)-O(3)	87.5(6)		

Symmetry codes: #2 x-1/2, -y+3/2, z-1/2



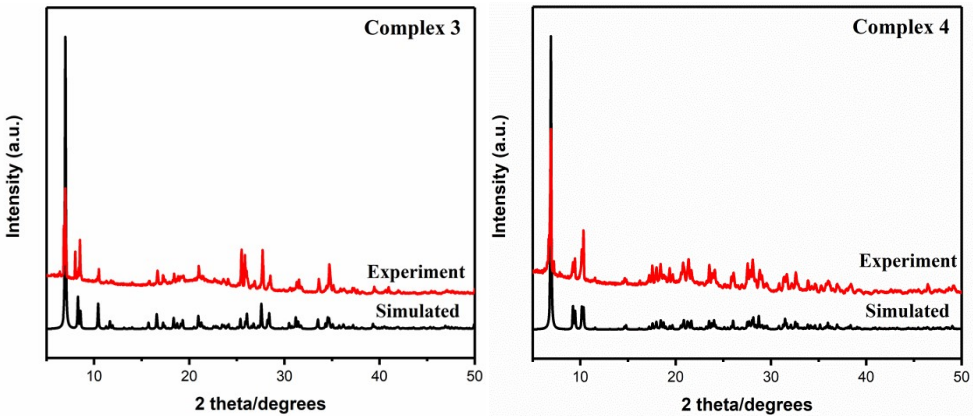


Fig. S1 The PXRD patterns of complexes **1-4.**

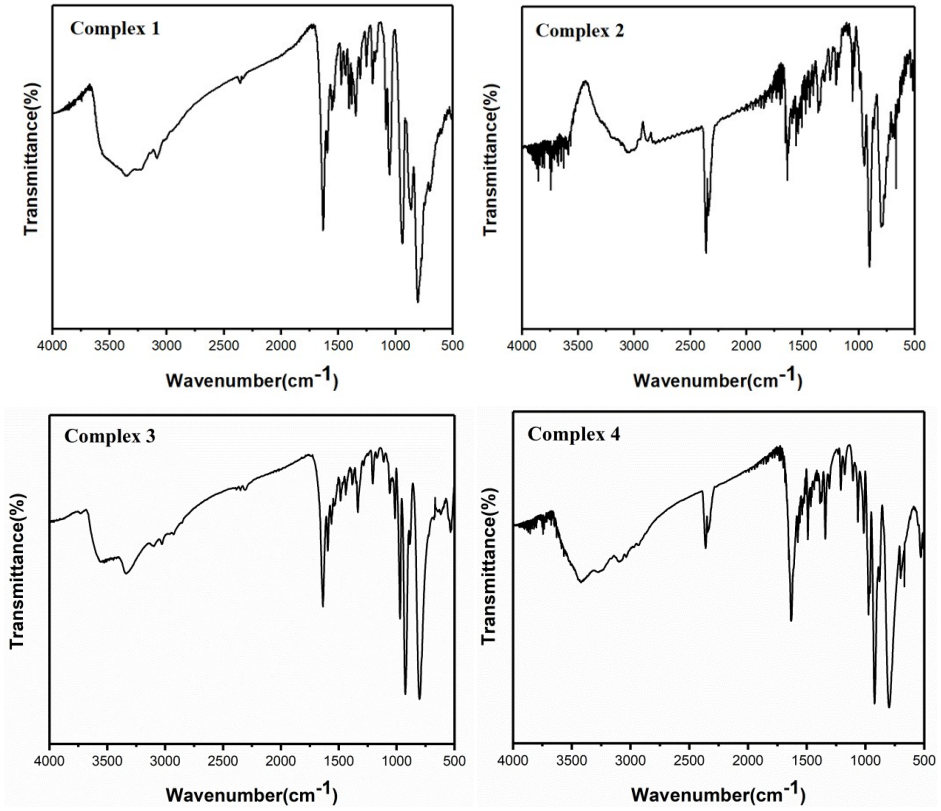
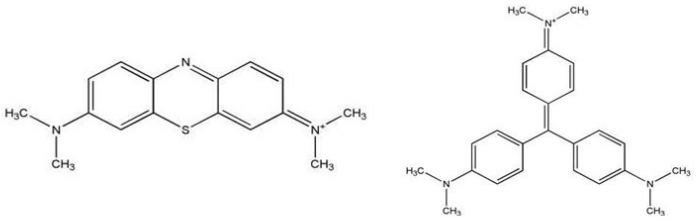


Fig. S2 The IR spectra of complexes **1-4**.



Methylene blue (MB^+) **Gentian violet (GV^+)**

Scheme S1 Chemical structures of MB and GV.

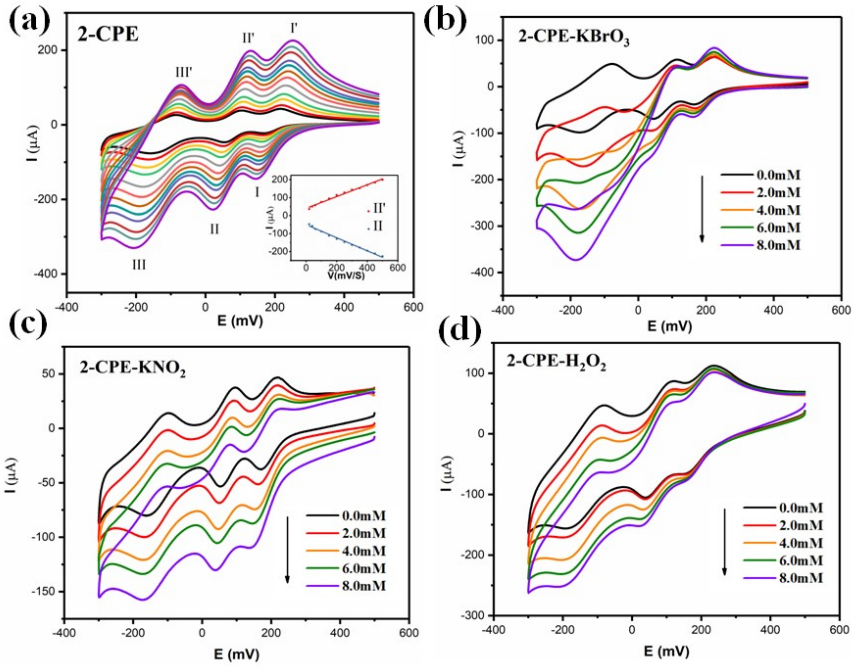


Fig. S3 (a) Cyclic voltammograms of the **2**-CPE in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution at different scan rates (from inner to outer: 20, 40, 60, 100, 150, 200, 250, 300, 350, 400, 450, 500 mV s^{-1}); Inset: the plots of peak currents vs. scan rates. The cyclic voltammograms of **2**-CPE in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 electrolyte solution including (b) $KBrO_3$, (c) KNO_2 and (d) H_2O_2 (scan rate: 60 mV s^{-1}).

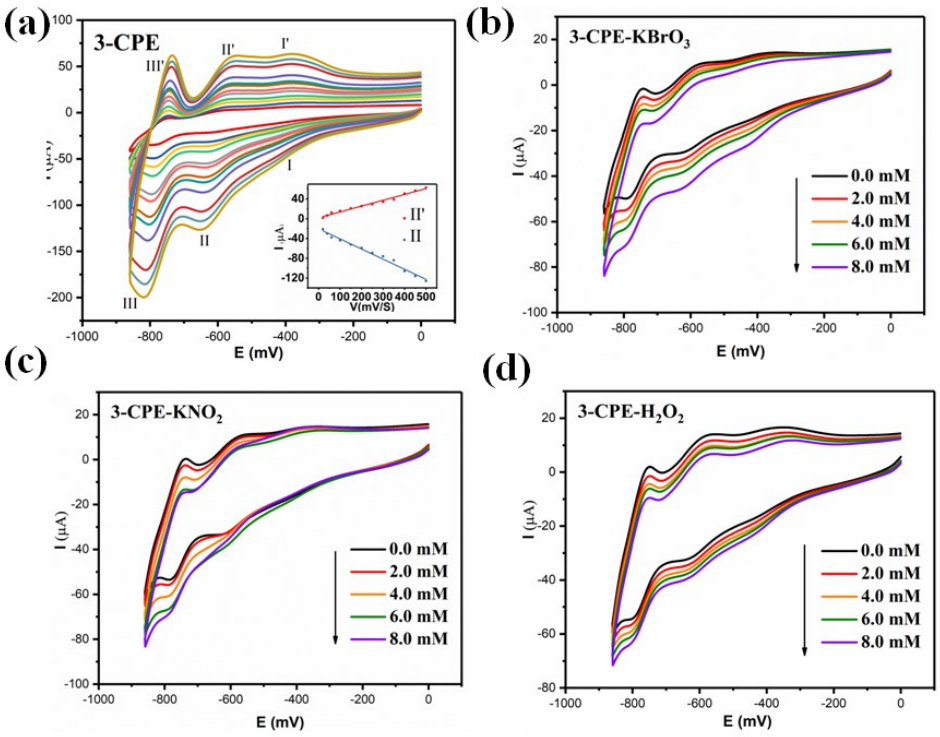


Fig. S4 (a) Cyclic voltammograms of the **3**-CPE in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution at different scan rates (from inner to outer: 20, 40, 60, 100, 150, 200, 250, 300, 350, 400, 450, 500 mV s^{-1}); Inset: the plots of peak currents vs. scan rates. The cyclic voltammograms of **3**-CPE in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 electrolyte solution including (b) $KBrO_3$, (c) KNO_2 and (d) H_2O_2 (scan rate: 60 mV s^{-1}).

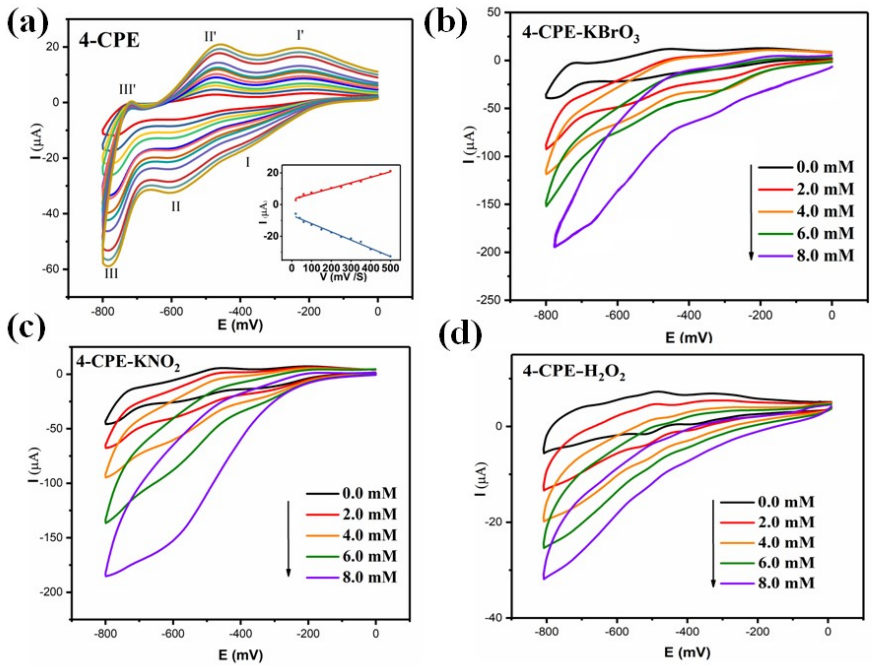


Fig. S5 (a) Cyclic voltammograms of the **4**-CPE in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution at different scan rates (from inner to outer: 20, 40, 60, 100, 150, 200, 250, 300, 350, 400, 450, 500 mV s^{-1}); Inset: the plots of peak currents vs. scan rates. The cyclic voltammograms of **4**-CPE in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 electrolyte solution including (b) $KBrO_3$, (c) KNO_2 and (d) H_2O_2 (scan rate: 60 mV s^{-1}).

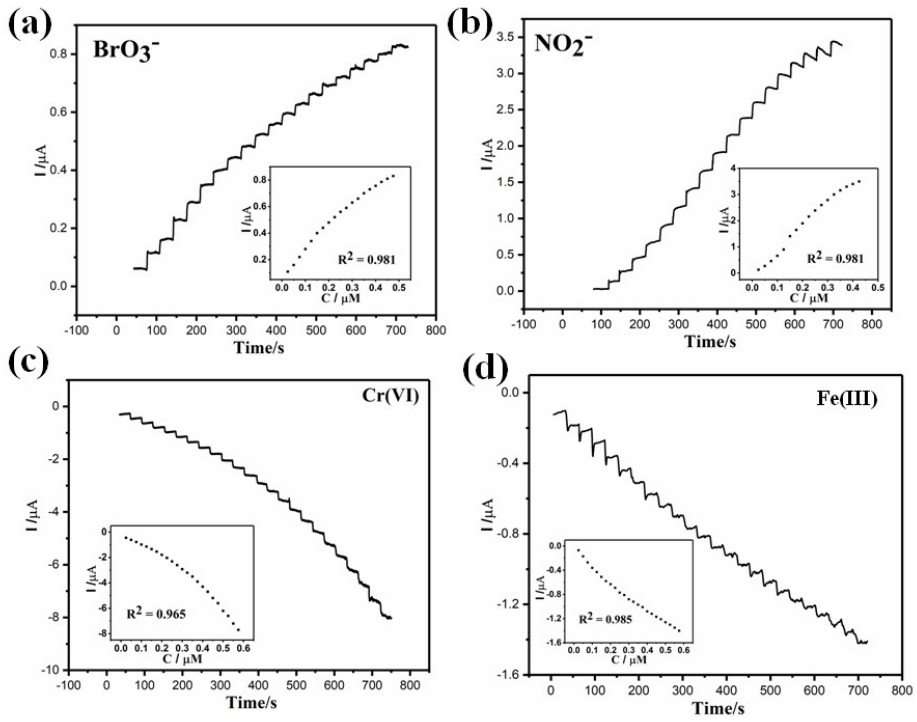


Fig. S6 Amperometric response for the **2**–CPE on successive addition of 0.1 mM BrO_3^- (a), NO_2^-(b), Cr(VI) (c) and Fe(III) (d) to 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution per 30 s interval. The inset: the steady-state calibration curve for current versus nitrite concentration.

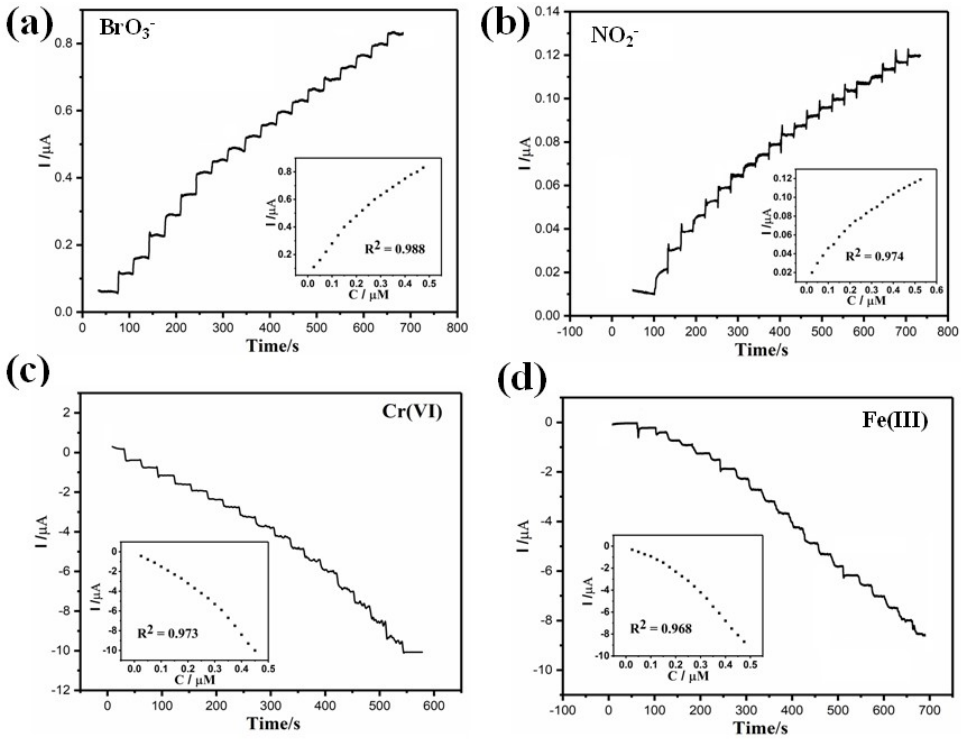


Fig. S7 Amperometric response for the **3**–CPE on successive addition of 0.1 mM BrO_3^- (a), NO_2^-(b), Cr(VI) (c) and Fe(III) (d) to 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution per 30 s interval. The inset: the steady-state calibration curve for current versus nitrite concentration.

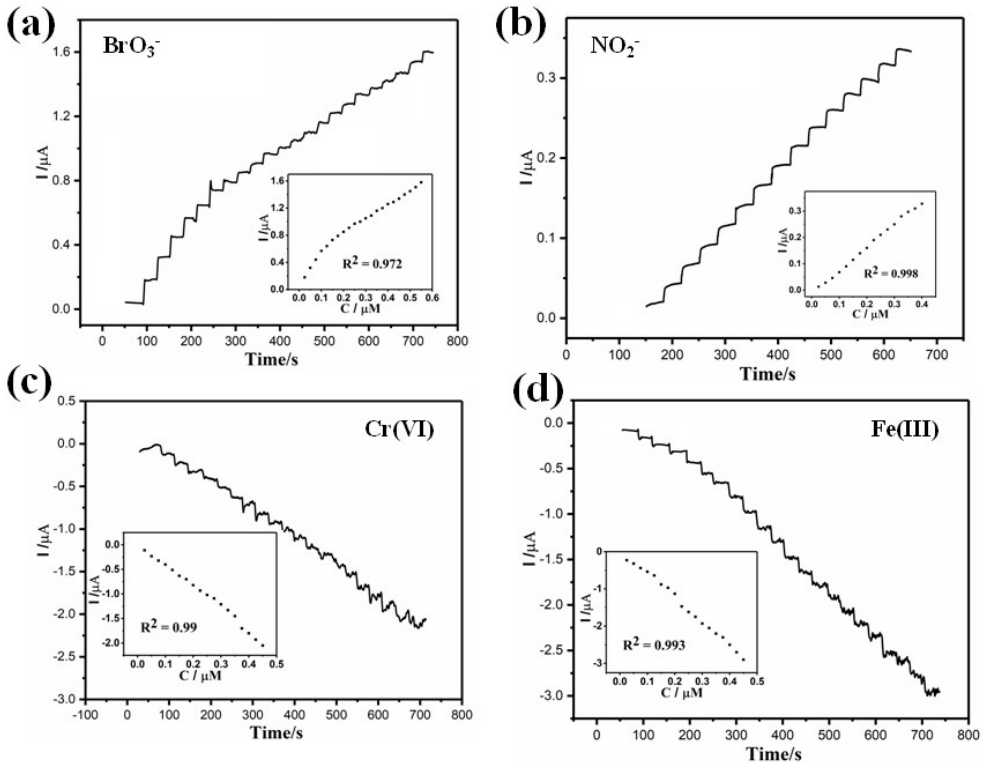


Fig. S8 Amperometric response for the **4**–CPE on successive addition of 0.1 mM BrO_3^- (a), NO_2^-(b), Cr(VI) (c) and Fe(III) (d) to 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution per 30 s interval. The inset: the steady-state calibration curve for current versus nitrite concentration.

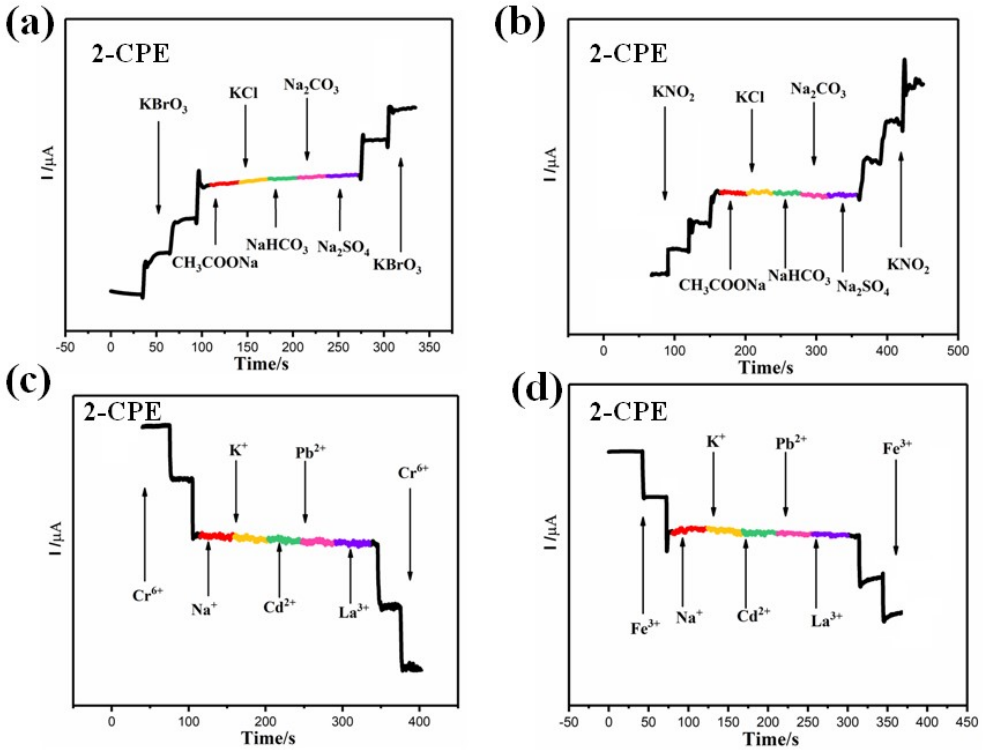


Fig. S9 Current response of **2**-CPE for BrO_3^- (a), NO_2^-(b), Cr(VI) (c) and Fe(III) (d) and other interfering ions in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 electrolyte.

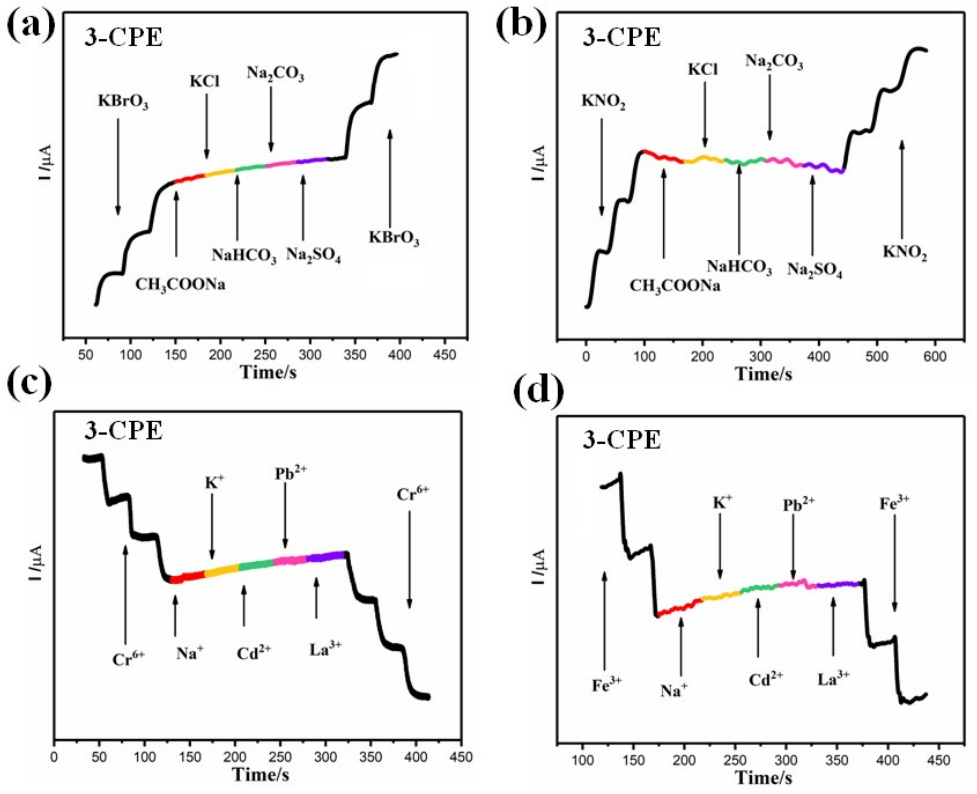


Fig. S10 Current response of **3**-CPE for BrO_3^- (a), NO_2^-(b), Cr(VI) (c) and Fe(III) (d) and other interfering ions in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 electrolyte.

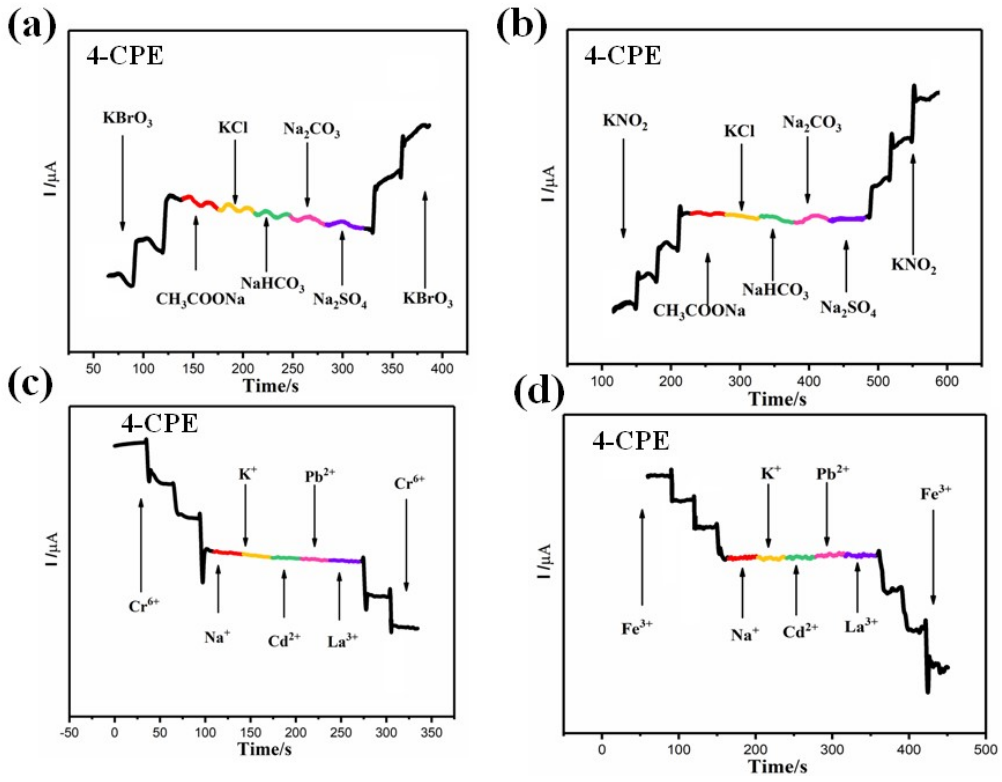


Fig. S11 Current response of **4**-CPE for BrO_3^- (a), NO_2^-(b), Cr(VI) (c) and Fe(III) (d) and other interfering ions in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 electrolyte.

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.