**Supporting Information**

A series of Wells-Dawson and Keggin-based compounds with uncoordinated S donors as fluorescence sensors to Hg2+

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Table S1. CAT% data of n-CPE (*n* = **1**, **3**, **4**) for reduction of NO2−, H2O2, BrO3- and AA.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| CAT%  Substrate | | **1−**CPE | **3−**CPE | **4−**CPE |
| NO2− | 2 mM | 320 | 82 | 57 |
| 4 mM | 489 | 117 | 143 |
| 6 mM | 639 | 187 | 234 |
| 8 mM | 770 | 251 | 433 |
| 10 mM | 881 | 308 | 593 |
| H2O2 | 2 mM | 11 | 168 | 19 |
| 4 mM | 27 | 271 | 42 |
| 6 mM | 35 | 362. | 67 |
| 8 mM | 47 | 476. | 89 |
| 10 mM | 56 | 573 | 108 |
| BrO3- | 2 mM | 25 | 65 | 26 |
| 4 mM | 59 | 217 | 64 |
| 6 mM | 93 | 313 | 136 |
| 8 mM | 127 | 374 | 204 |
| 10 mM | 156 | 429 | 250 |
| AA | 2 mM | 328 | 2130 | 37 |
| 4 mM | 1410 | 3670 | 68 |
| 6 mM | 2220 | 4730 | 93 |
| 8 mM | 2990 | 6420 | 112 |
| 10 mM | 3770 | 7830 | 138 |

Table S2. The analytical data for **1**–, **3**– and **4**–CPE as amperometric sensors.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Response time (s) | Concentration range (mM) | Sensitivity  (μA mM–1) | Correlation coefficient | Detection limit (M) |
| Potassium nitrite | | | | | |
| **1**–CPE | 3.3 | 0.012–0.092 | 14.19 | 0.9730 | 2.6×10–5 |
| **3**–CPE | 2.3 | 0.016–0.092 | 26.54 | 0.9792 | 3.3×10–5 |
| **4**–CPE | 1.6 | 0.008–0.092 | 1.26 | 0.9937 | 2.2×10–5 |

Table S3. Selected bond distances (Å) and angles (°) for **1**-**4**.

|  |  |  |  |
| --- | --- | --- | --- |
| Compound **1** | | | |
| Zn1-N6 | 2.185(14) | Zn1-N4 | 2.249(15) |
| Zn1-N3 | 2.147(13) | Zn1-N1 | 2.217(8) |
| Zn1-N5 | 2.247(15) | Zn1-N2 | 2.189(19) |
| Zn2-O1W | 2.017(12) | Zn2-N7 | 2.091(15) |
| Zn2-N10 | 2.210(12) | Zn2-N8 | 2.183(14) |
| Zn2-N9 | 2.066(13) | Zn3-N14 | 2.051(13) |
| Zn3-N11 | 2.130(14) | Zn3-N13 | 2.125(14) |
| Zn3-O2W | 2.039(12) | Zn3-N12 | 2.078(14) |
| N6-Zn1-N4 | 95.0(6) | N3-Zn1-N5 | 94.4(5) |
| O1W-Zn2-N7 | 126.0(6) | N10-Zn2-N8 | 171.9(5) |
| N11-Zn3-N13 | 169.5(5) | N11-Zn3-O2W | 89.3(5) |
| Compound **2** | | | |
| Cd1-O1W | 2.263(16) | Cd1-N4 | 2.30(2) |
| Cd1-N3 | 2.31(2) | Cd1-N2 | 2.37(3) |
| Cd1-O6 | 2.507(17) | N1-Cd1 | 2.33(2) |
| O2W-Cd2 | 2.248(17) | Cd2-N5 | 2.219(18) |
| Cd2-N7 | 2.25(2) | Cd2-N6 | 2.32(2) |
| Cd2-N8 | 2.38(2) | Cd3-N12 | 2.32(2) |
| Cd3-N10 | 2.34(2) | Cd3-N13 | 2.35(2) |
| Cd3-N14 | 2.39(3) | Cd3-N11 | 2.43(2) |
| Cd3-N9 | 2.45(2) | N4-Cd1-N1 | 176.3(8) |
| N3-Cd1-N1 | 103.8(7) | O1W-Cd1-N2 | 165.5(8) |
| N7-Cd2-O2W | 129.3(8) | N5-Cd2-N6 | 75.8(7) |
| N7-Cd2-N6 | 109.2(7) | N12-Cd3-N10 | 164.5(7) |
| N12-Cd3-N13 | 96.2(7) | N10-Cd3-N13 | 97.1(8) |
| Compound **3** | | | |
| Cd1-N4 | 2.258(13) | Cd1-N1 | 2.322(13) |
| Cd1-N2 | 2.355(12) | Cd1-N3 | 2.388(13) |
| Cd1-Cl1 | 2.504(5) | Cd1-O22 | 2.599(11) |
| Cd2-N5 | 2.292(12) | Cd2-N8 | 2.293(13) |
| Cd2-N7 | 2.310(12) | Cd2-N6 | 2.362(13) |
| Cl1-Cd2 | 2.542(5) | O40-Cd2 | 2.670(11) |
| N1-Cd1-N2 | 73.2(4) | N1-Cd1-N3 | 166.1(4) |
| N4-Cd1-Cl1 | 146.7(4) | Cl1-Cd1-O22 | 74.6(3) |
| N5-Cd2-N8 | 110.2(5) | N5-Cd2-N6 | 74.5(5) |
| N5-Cd2-Cl1 | 85.2(4) | N6-Cd2-Cl1 | 113.2(4) |
| Compound **4** | | | |
| O6-Cd1 | 2.30(2) | Cd1-N1 | 2.29(2) |
| Cd1-N2 | 2.30(2) | Cd1-N3 | 2.30(3) |
| Cd1-N4 | 2.41(3) | Cd1-O3 | 2.48(2) |
| N1-Cd1-N2 | 76.1(8) | N1-Cd1-O6 | 95.4(8) |
| N2-Cd1-O6 | 160.9(8) | N1-Cd1-N3 | 166.4(9) |
| N2-Cd1-N3 | 100.4(8) | O6-Cd1-N3 | 91.6(8) |
| N1-Cd1-N4 | 93.0(9) | N2-Cd1-N4 | 87.3(8) |
| O6-Cd1-N4 | 110.4(8) | N3-Cd1-N4 | 73.6(9) |

Table S4. SHAPE2 analysis of different coordinate geometries in **1**-**4**.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Compound **1** | | | | | | | | |
| Zn**1** | | | | | | | | |
| HP  (D6h) | | PPY  (C5v) | **OC**  **(Oh)** | | | TPR  (D3h) | JPPY  (C5v) | |
| 24.960 | | 26.598 | **1.415** | | | 14.873 | 29.228 | |
| Zn**2** | | | | | | | | |
| PP  (D5h) | | vOC  (C4v) | **TBPY**  **(D3h)** | | | SPY  (C4v) | JTBPY  (D3h) | |
| 26.111 | | 7.120 | **1.912** | | | 5.530 | 3.366 | |
| Zn**3** | | | | | | | | |
| PP  (D5h) | | vOC  (C4v) | TBPY  (D3h) | | | **SPY**  **(C4v)** | JTBPY  (D3h) | |
| 25.666 | | 2.069 | 4.467 | | | **1.920** | 6.429 | |
| Compound **2** | | | | | | | | |
| Cd**1** | | | | | | | | |
| HP  (D6h) | | PPY  (C5v) | **OC**  **(Oh)** | | | TPR  (D3h) | JPPY  (C5v) | |
| 26.570 | | 24.541 | **2.317** | | | 14.168 | 27.169 | |
| Cd**2** | | | | | | | | |
| PP  (D5h) | | vOC  (C4v) | **TBPY**  **(D3h)** | | | SPY  (C4v) | JTBPY  (D3h) | |
| 24.568 | | 6.906 | **2.420** | | | 5.823 | 4.390 | |
| Cd**3** | | | | | | | | |
| HP  (D6h) | PPY  (C5v) | | | **OC**  **(Oh)** | TPR  (D3h) | | | JPPY  (C5v) |
| 24.603 | 25.250 | | | **2.325** | 14.215 | | | 27.852 |
| Compound **3** | | | | | | | | |
| Cd**1** | | | | | | | | |
| PP  (D5h) | | vOC  (C4v) | **TBPY**  **(D3h)** | | | SPY  (C4v) | JTBPY  (D3h) | |
| 25.797 | | 5.047 | **3.245** | | | 5.537 | 5.963 | |
| Cd**2** | | | | | | | | |
| PP  (D5h) | | vOC  (C4v) | **TBPY**  **(D3h)** | | | SPY  (C4v) | JTBPY  (D3h) | |
| 24.881 | | 5.777 | **2.708** | | | 5.329 | 6.081 | |
| Compound **4** | | | | | | | | |
| **Cd1** | | | | | | | | |
| HP  (D6h) | | PPY  (C5v) | **OC**  **(Oh)** | | | TPR  (D3h) | JPPY  (C5v) | |
| 26.937 | | 20.706 | **2.475** | | | 10.759 | 23.540 | |

The smaller the shape measure, the closer the coordination polyhedron is to the ideal shape. Abbreviations: PP-Pentagon, VOC-Vacant octahedron, TBPY-Trigonal bipyramid, SPY-Spherical square pyramid, JTBPY-Johnson-trigonal bipyramid J12, HP-Hexagon, PPY-Pentagonal pyramid, OC- Octahedron, TPR-Trigonal prism, JPPY-Johnson pentagonal pyramid J2. The bold numbers indicate the best coincidence.

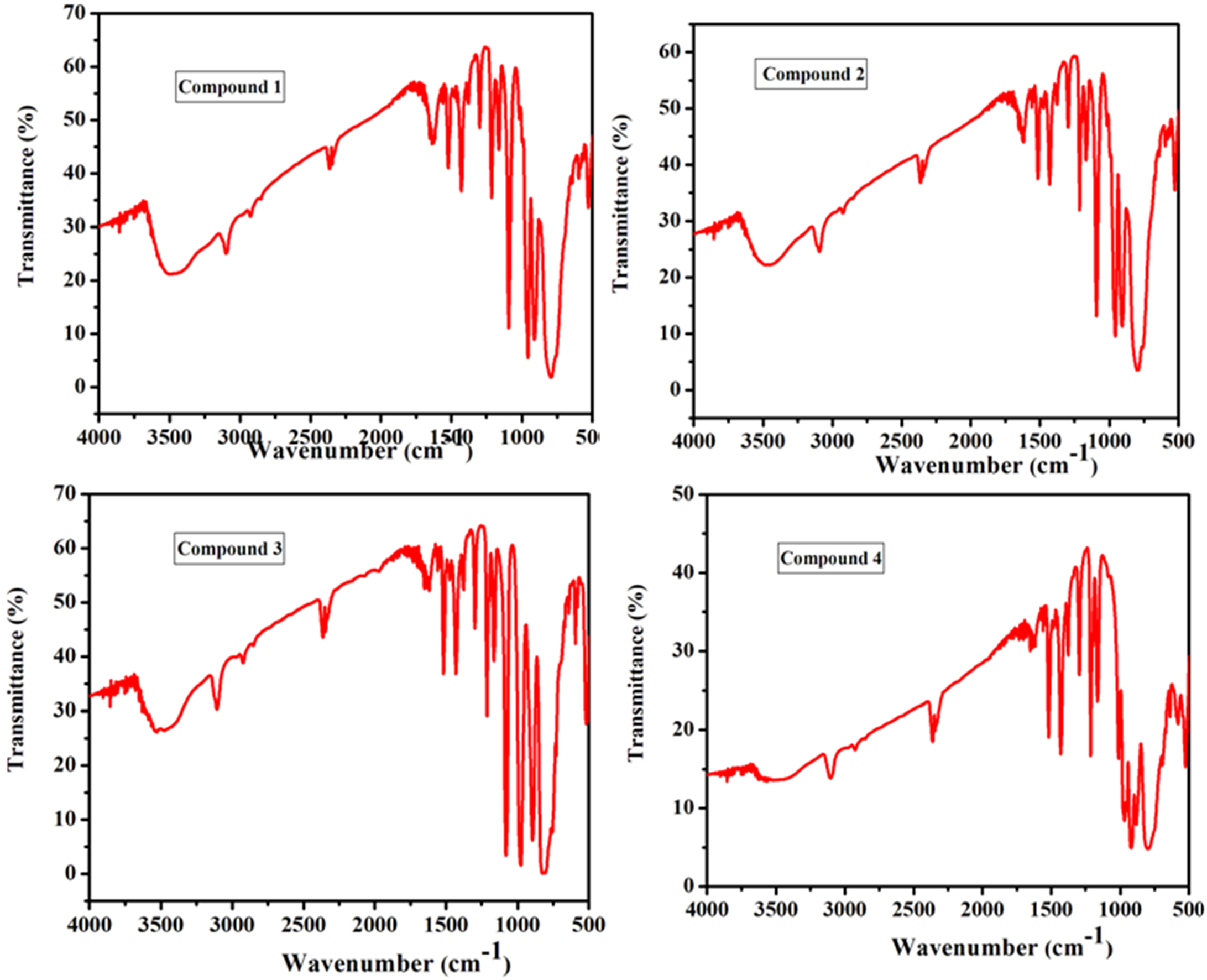
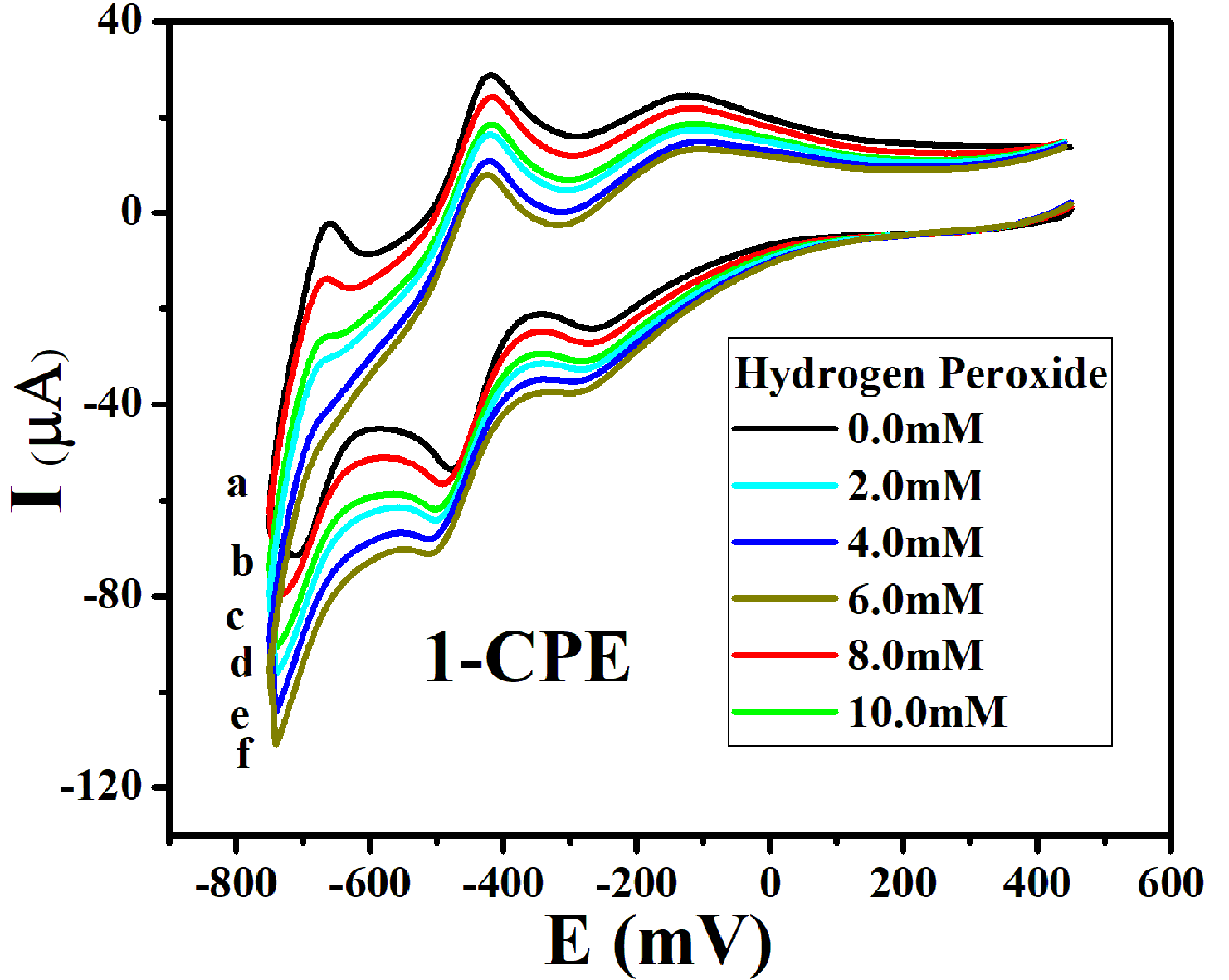
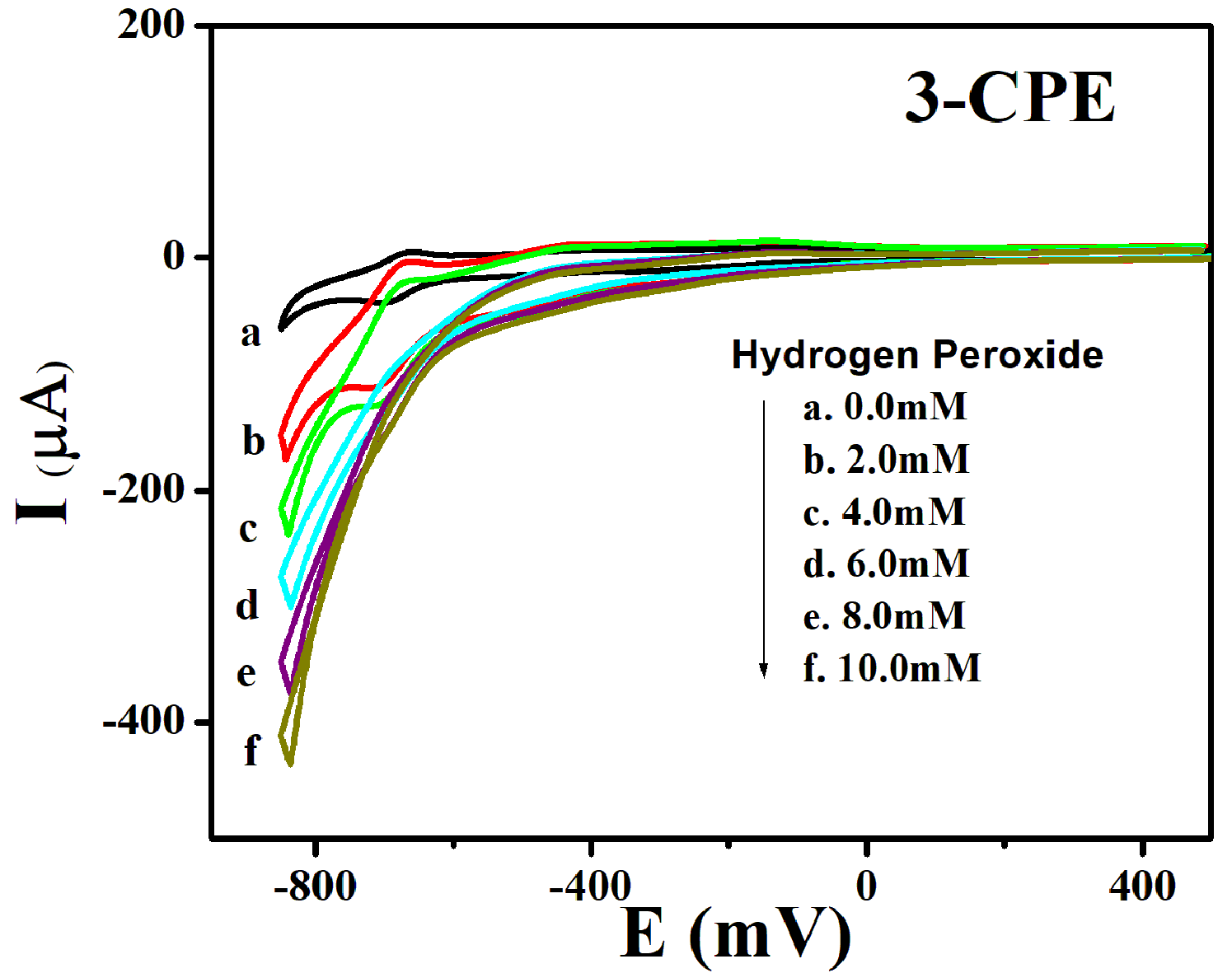
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Figure S1. The IR spectra of **1-4**.





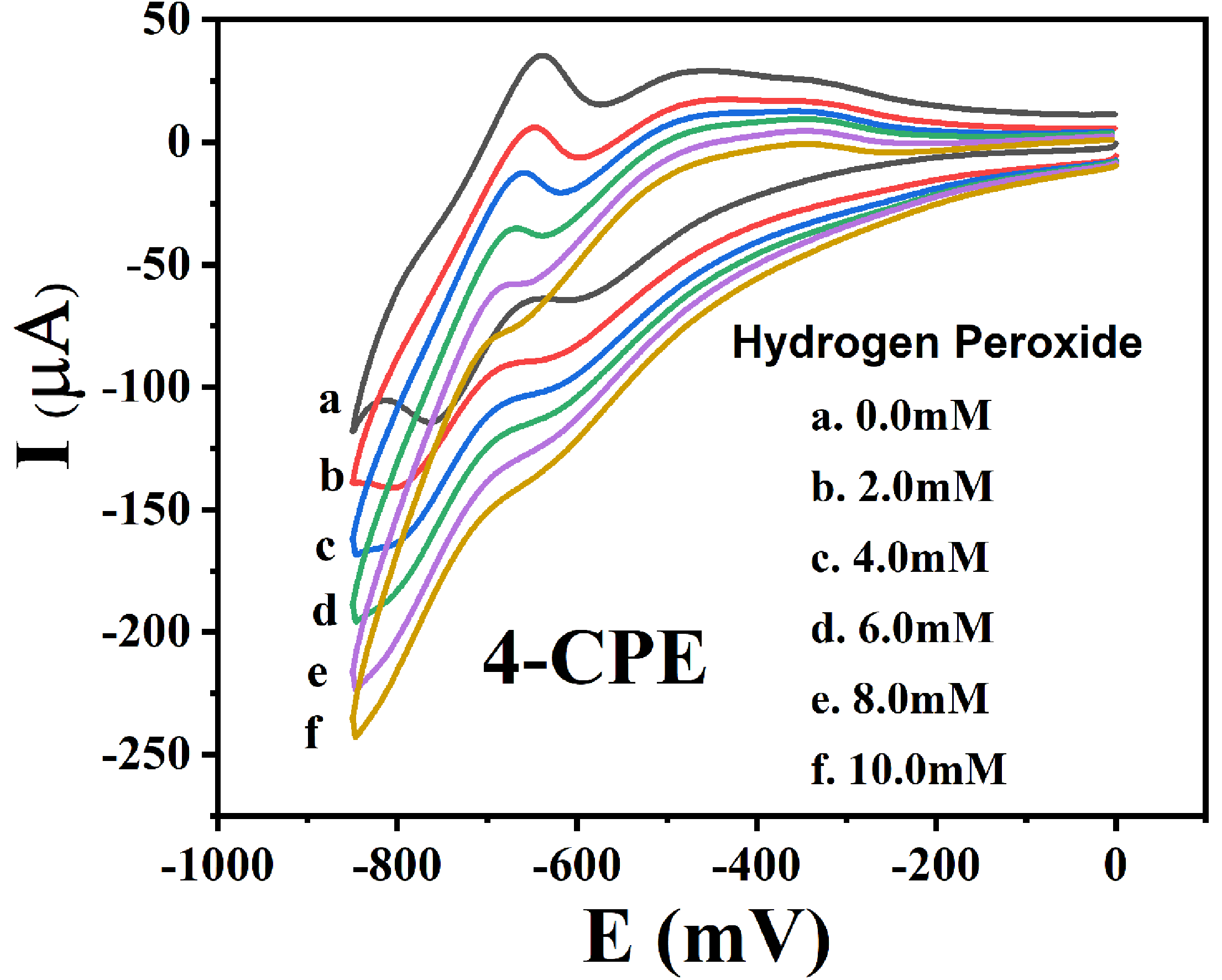
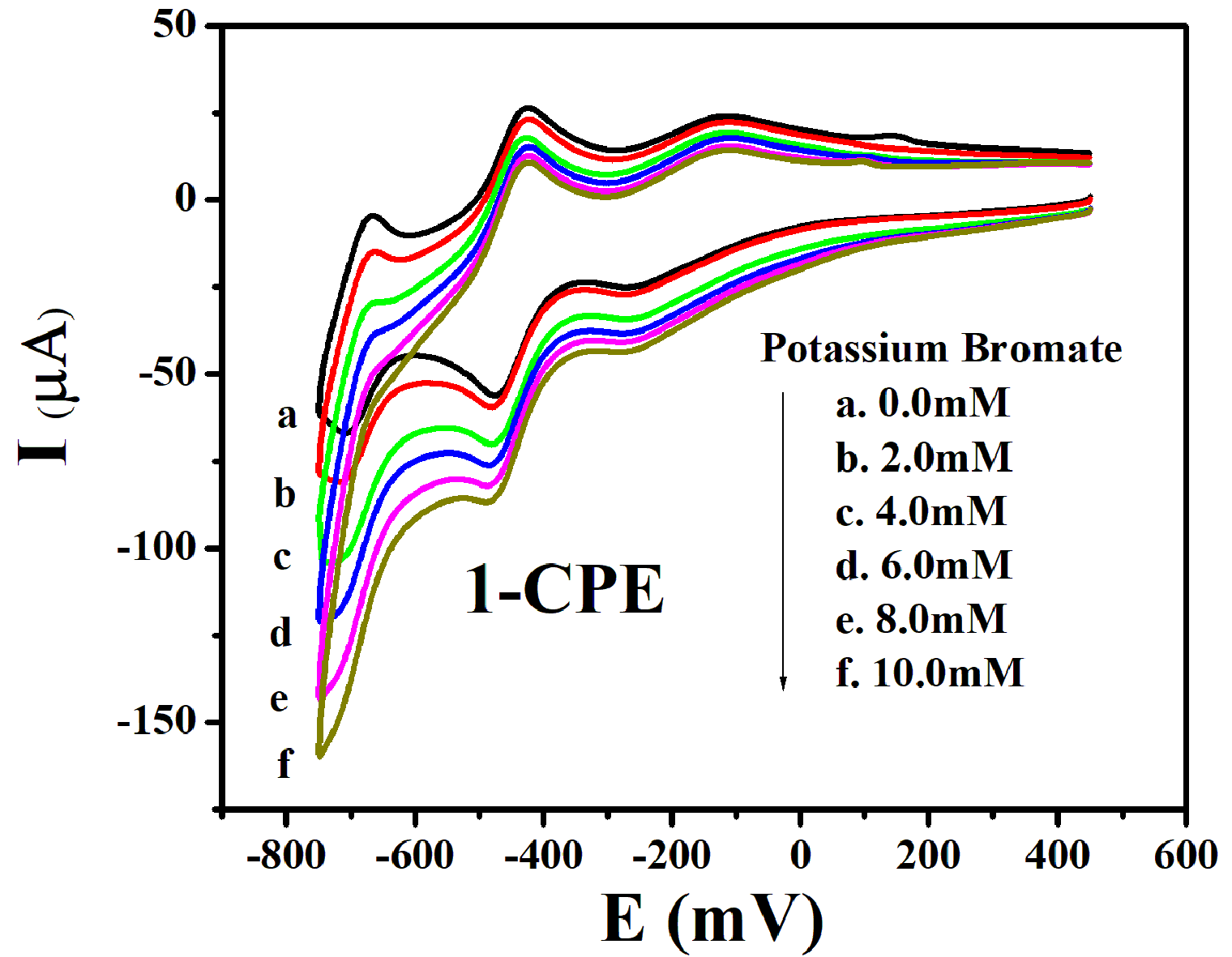
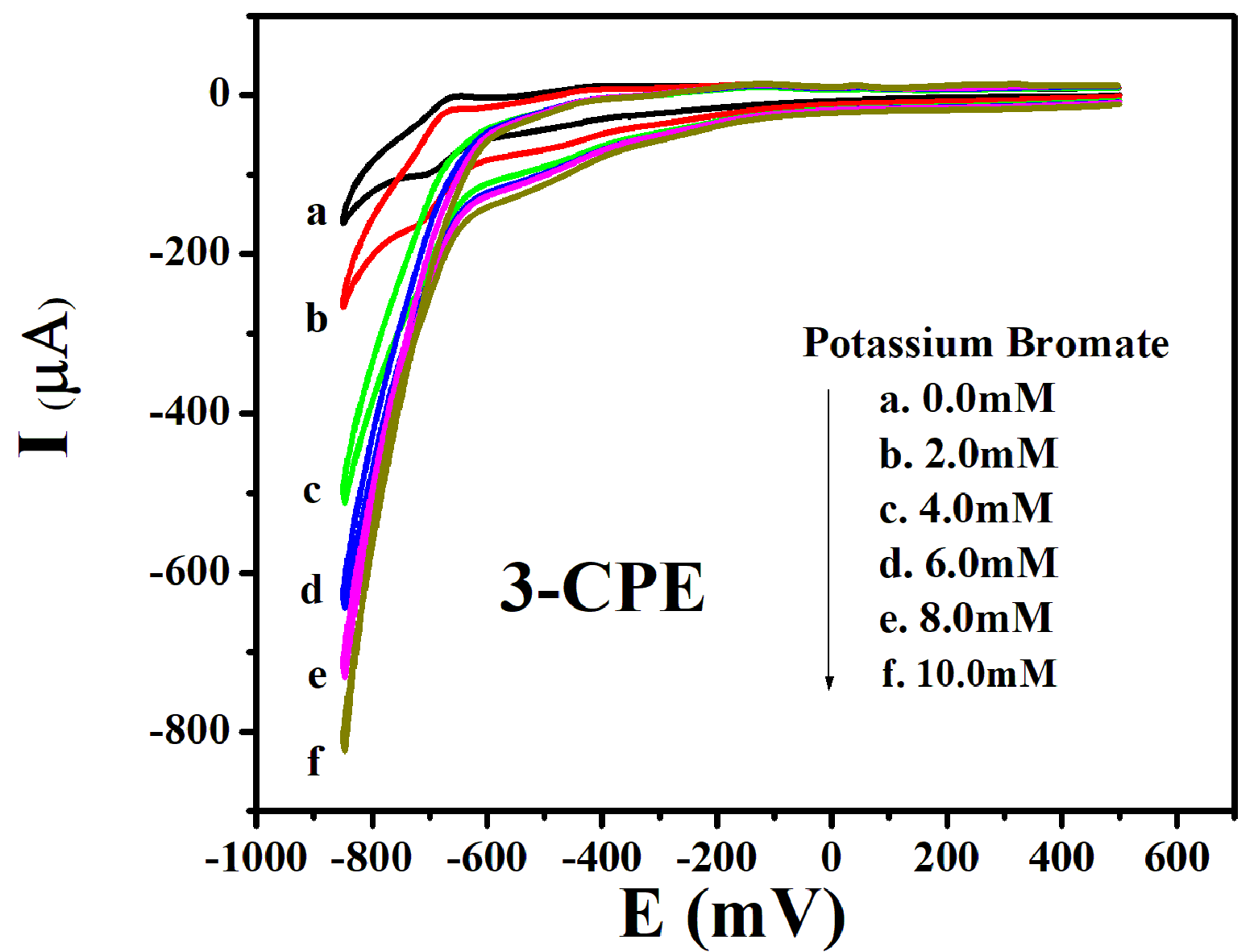


Figure S2. Cyclic voltammograms of **1**–, **3**– and **4**–CPE in 0.1 M H2SO4 + 0.5 M Na2SO4 aqueous solution containing 0 (a); 2 (b); 4 (c); 6 (d); 8 (e) and 10 (f) mM H2O2. Scan rate: 200 mV·s-1.





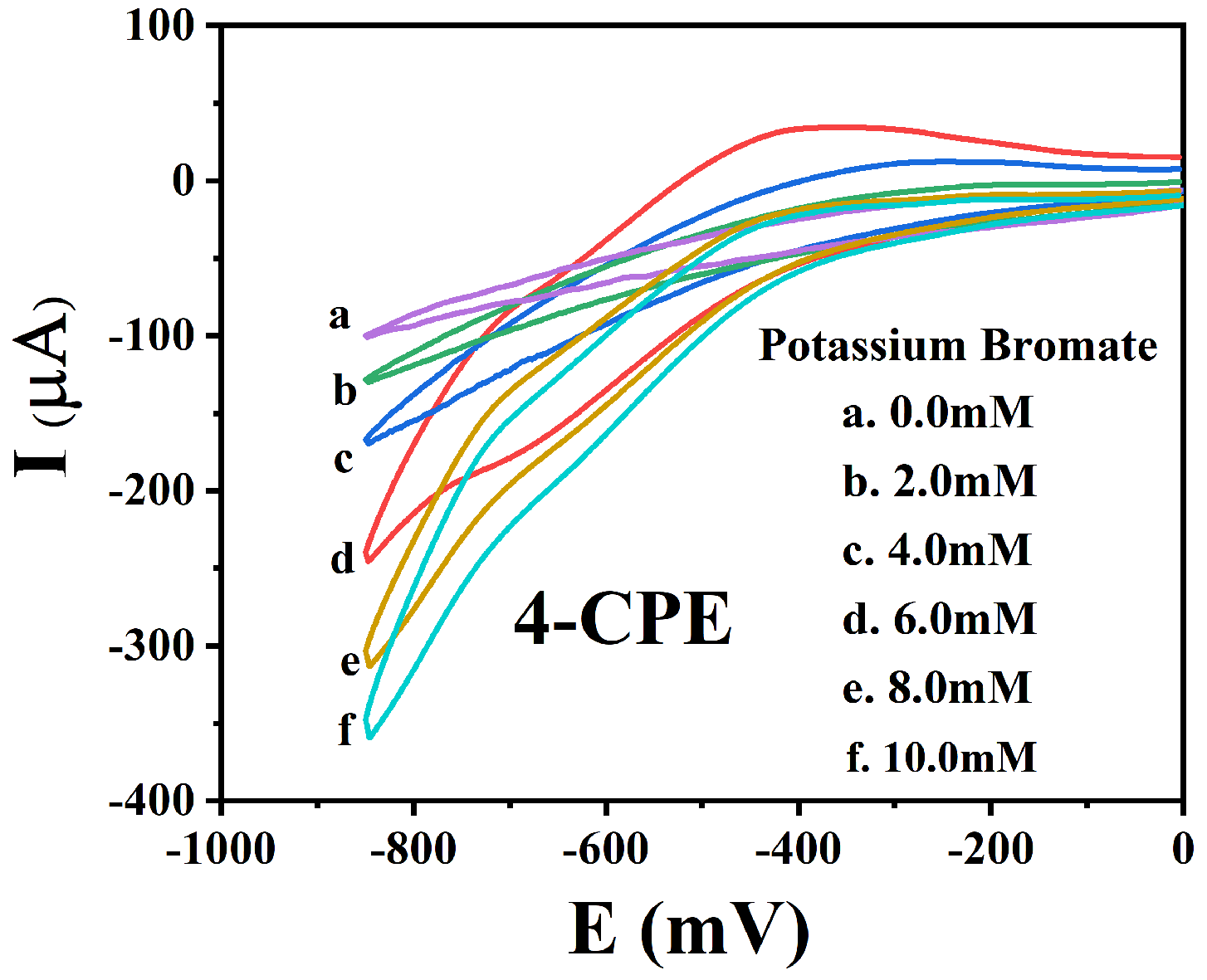
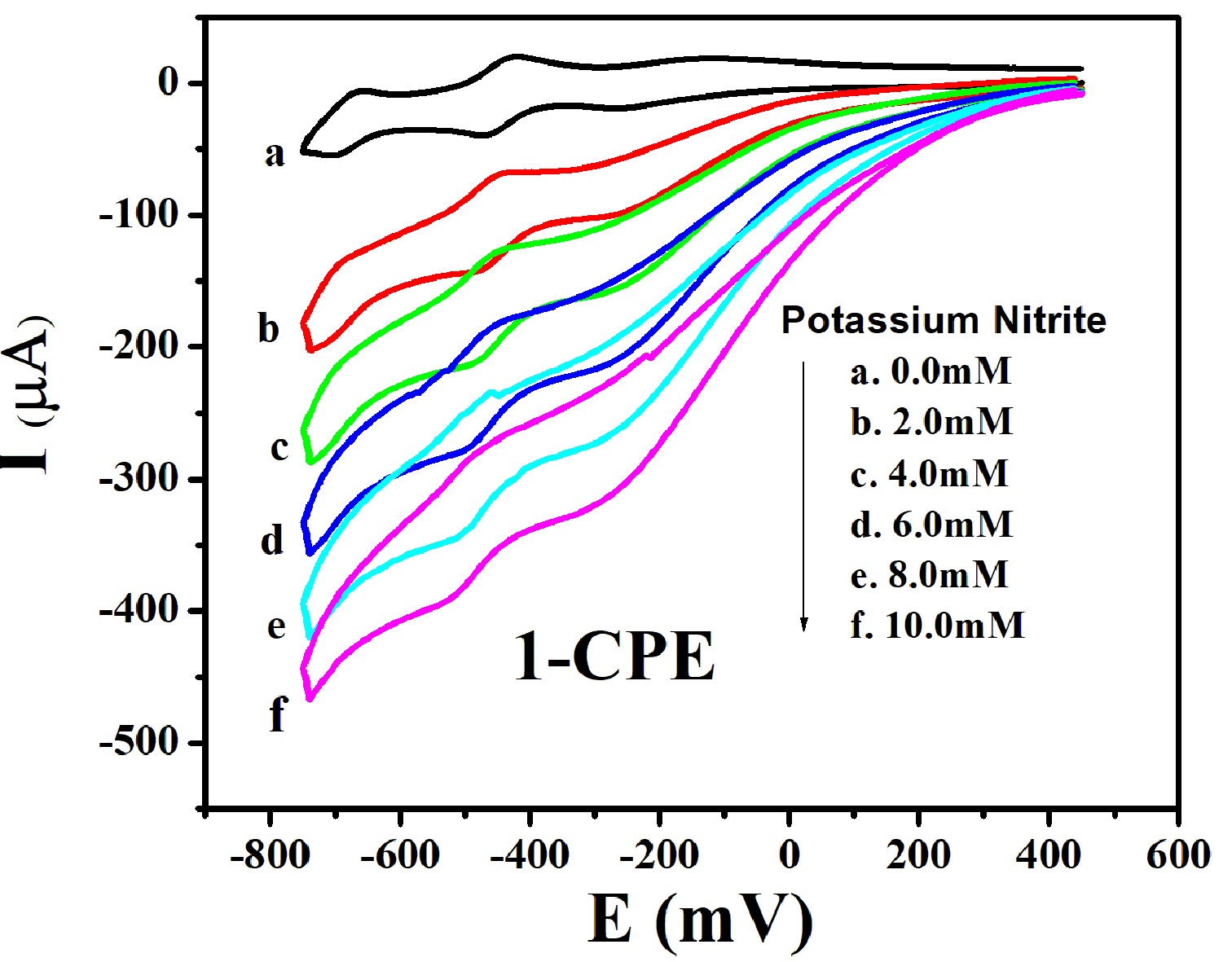
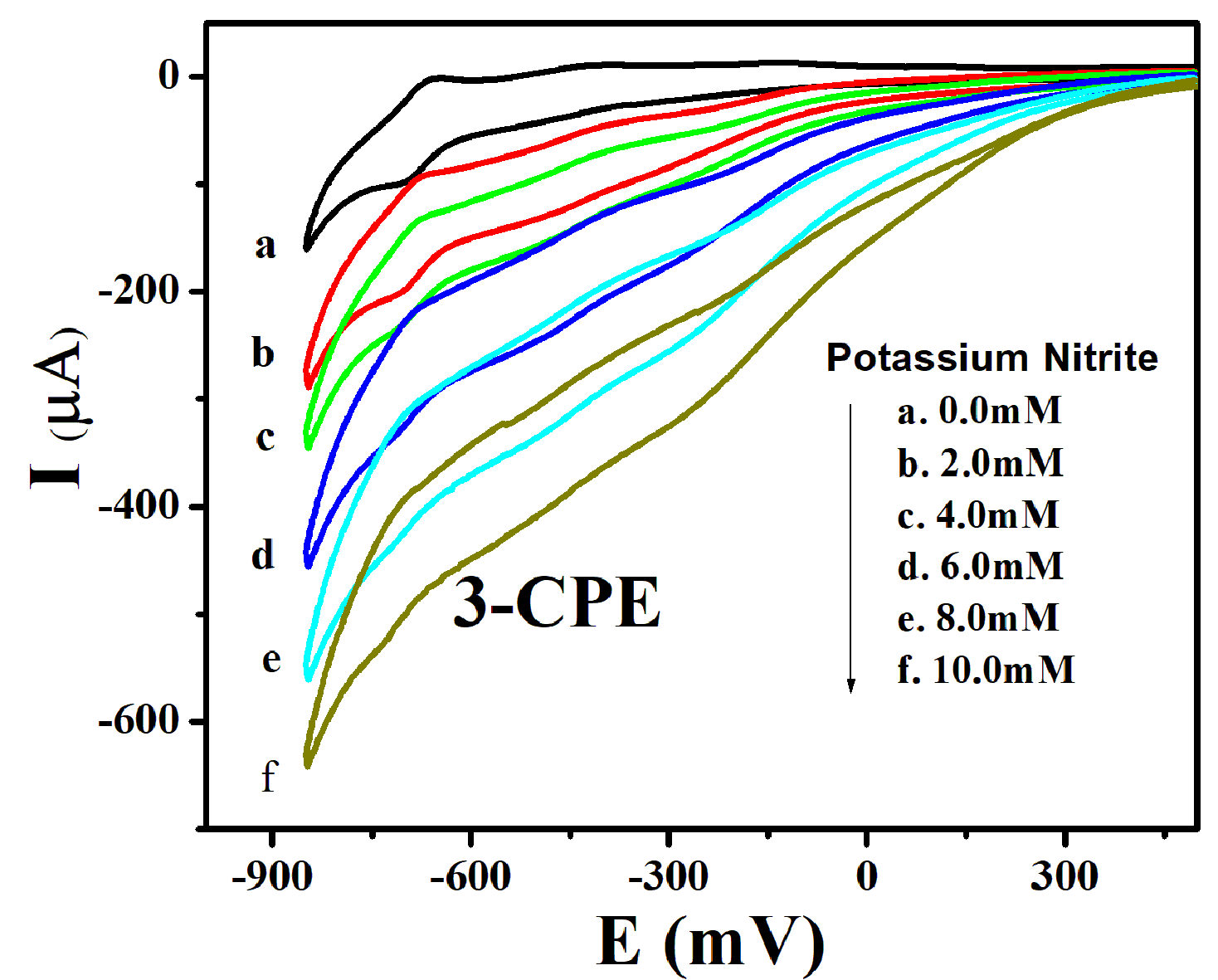


Figure S3. Cyclic voltammograms of **1**–, **3**– and **4**–CPE in 0.1 M H2SO4 + 0.5 M Na2SO4 aqueous solution containing 0 (a); 2 (b); 4 (c); 6 (d); 8 (e) and 10 (f) mM BrO3-. Scan rate: 200 mV·s-1.





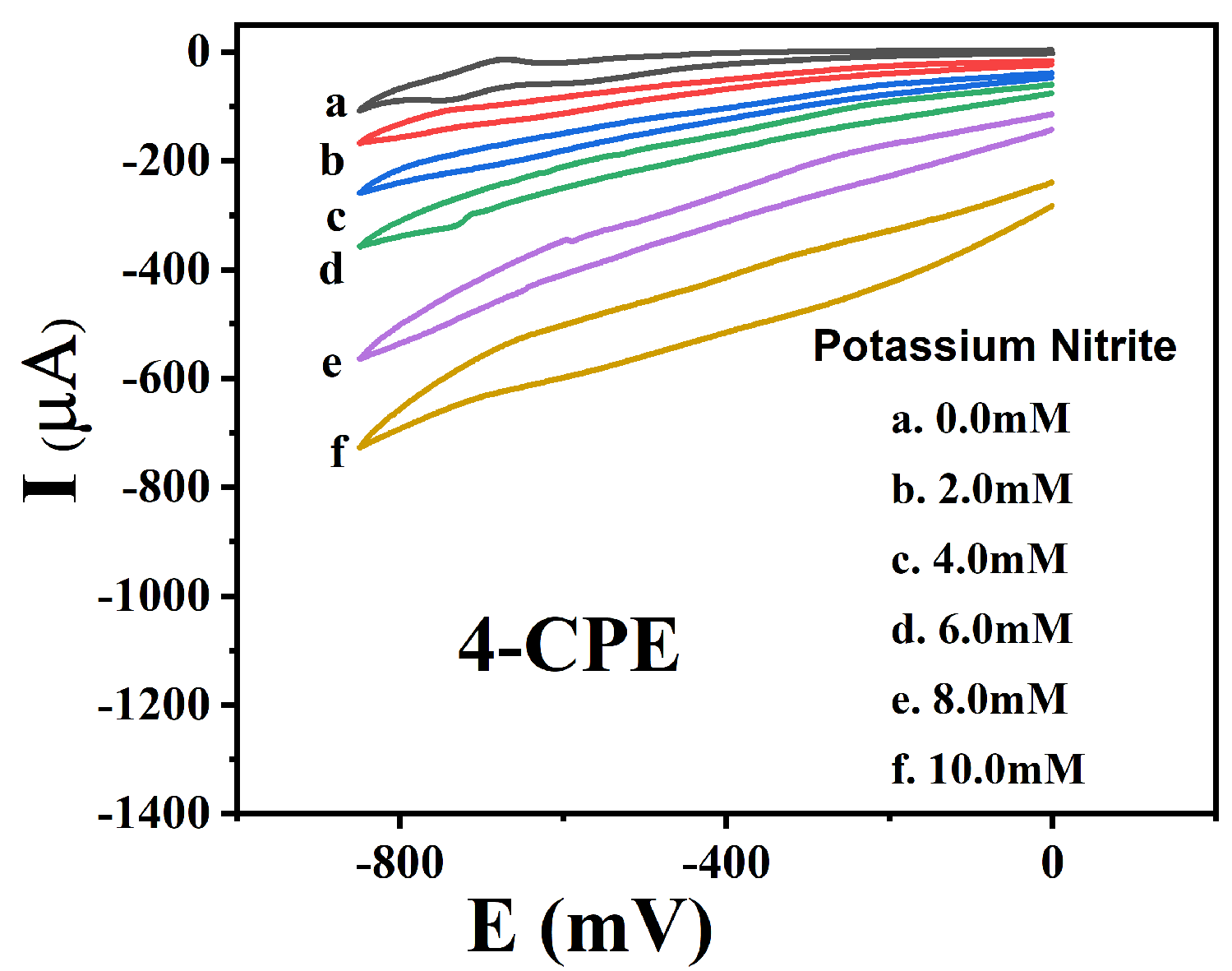
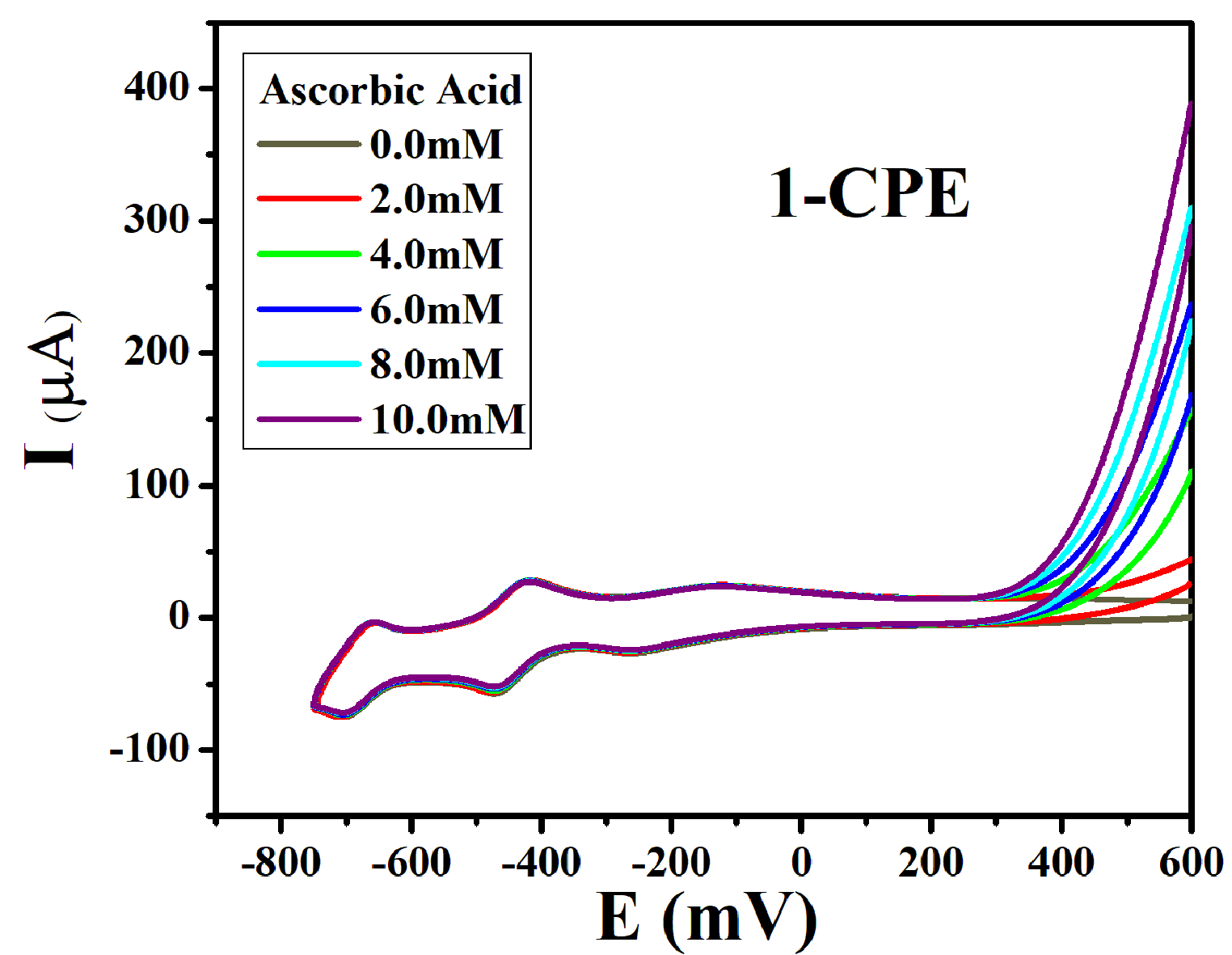
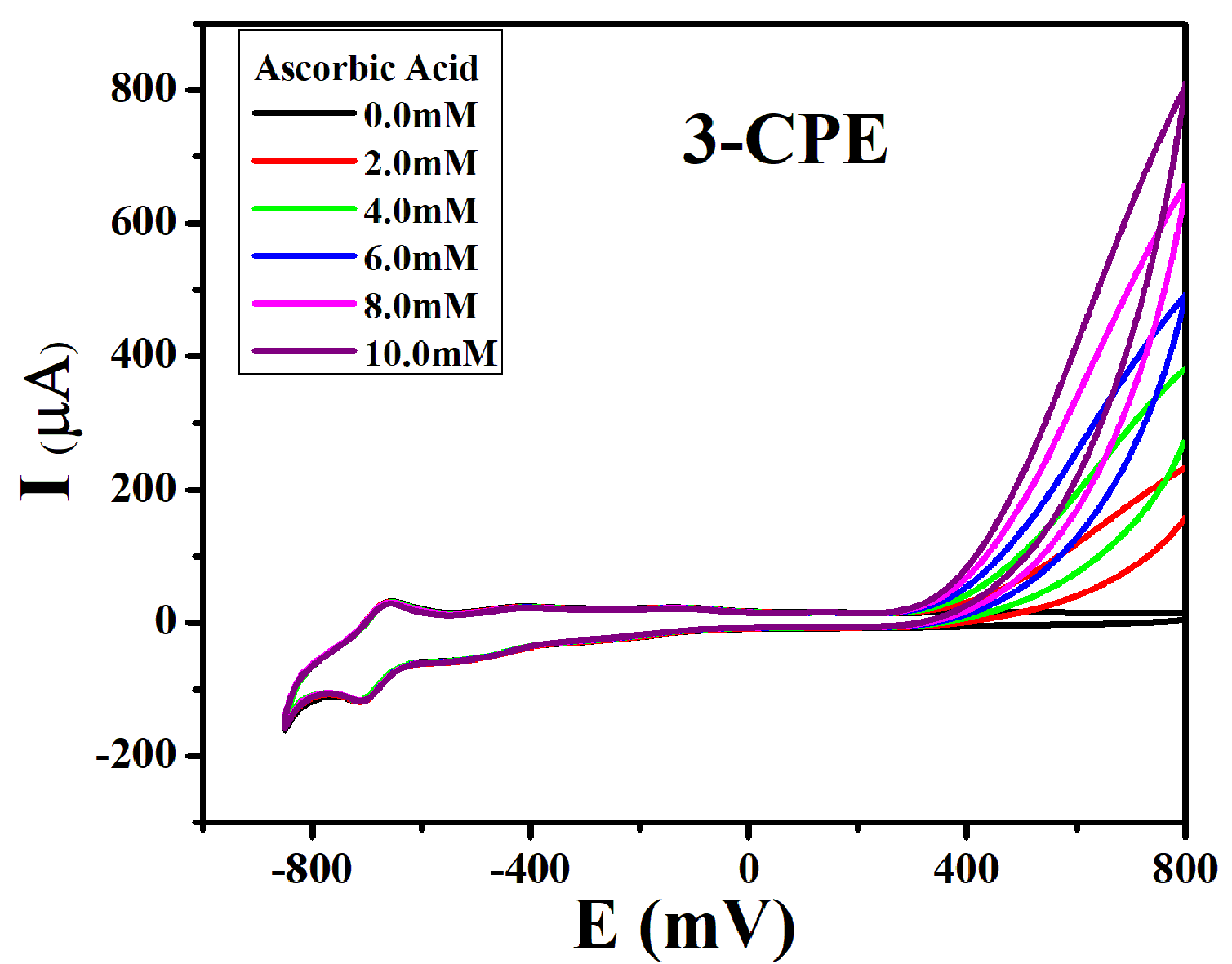


Figure S4. Cyclic voltammograms of **1**–, **3**– and **4**–CPE in 0.1 M H2SO4 + 0.5 M Na2SO4 aqueous solution containing 0 (a); 2 (b); 4 (c); 6 (d); 8 (e) and 10 (f) mM NO2-. Scan rate: 200 mV·s-1.





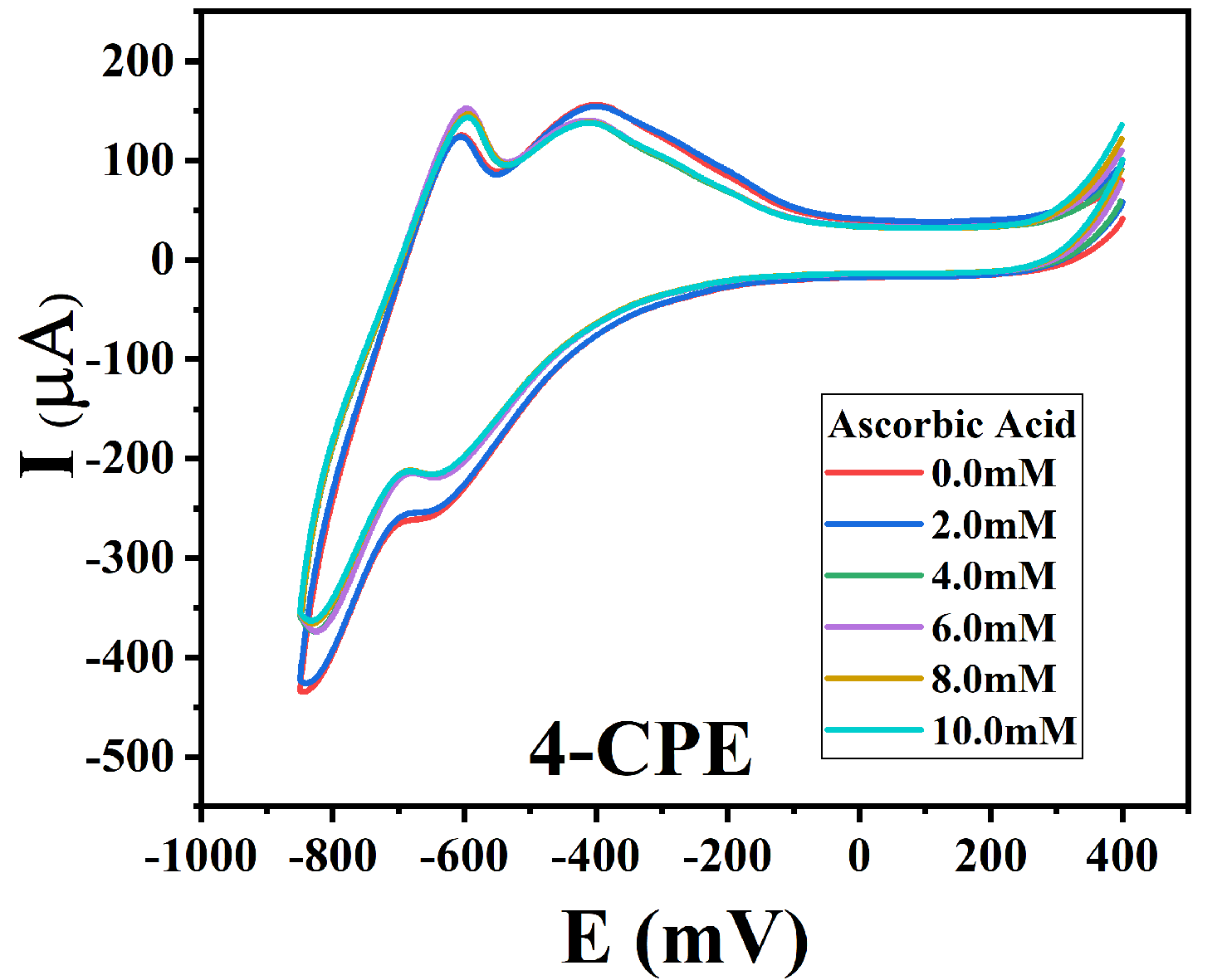


Figure S5. Cyclic voltammograms of **1**–, **3**– and **4**–CPE in 0.1 M H2SO4 + 0.5 M Na2SO4 aqueous solution containing 0 (a); 2 (b); 4 (c); 6 (d); 8 (e) and 10 (f) mM AA. Scan rate: 200 mV·s-1.

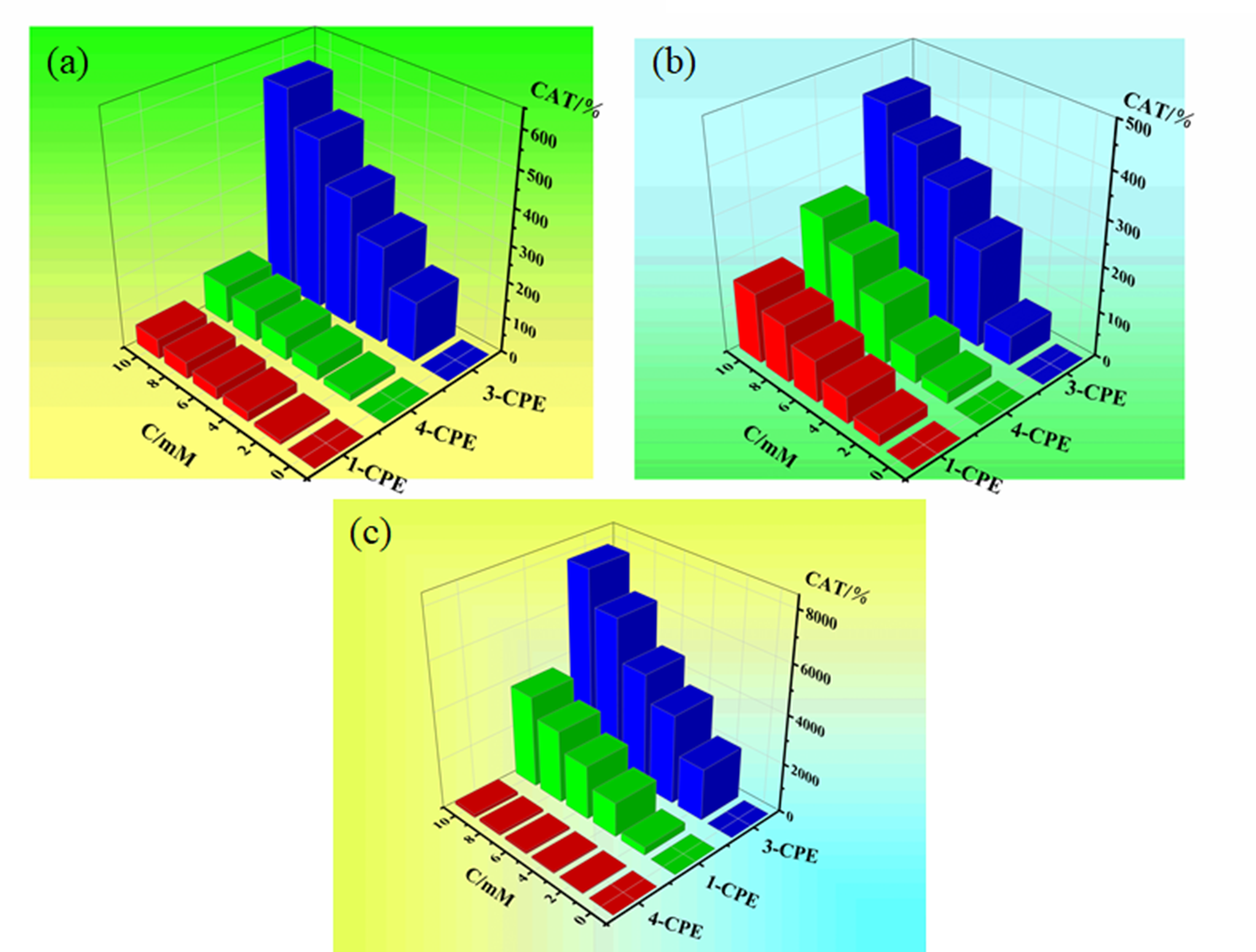


Figure S6. Chart of the CAT *vs.* concentration of H2O2 (a), BrO3- (b) and AA (c) for **1**−, **3**− and **4**−CPEs (scan rate of 200 mV·s-1).

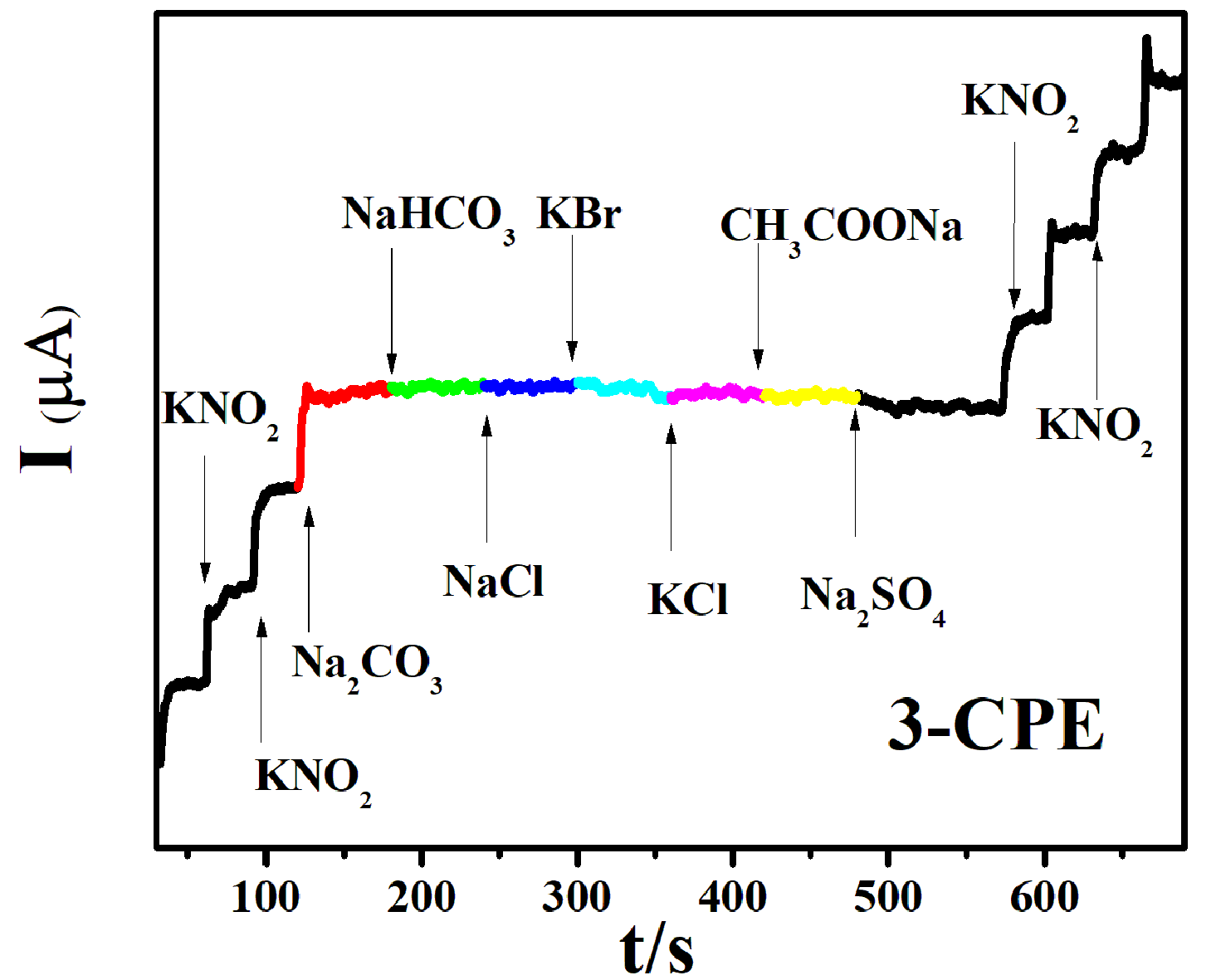


Figure S7. Amperometric current responses of **3**−CPE in aqueous solution upon addition of various inorganic ions.

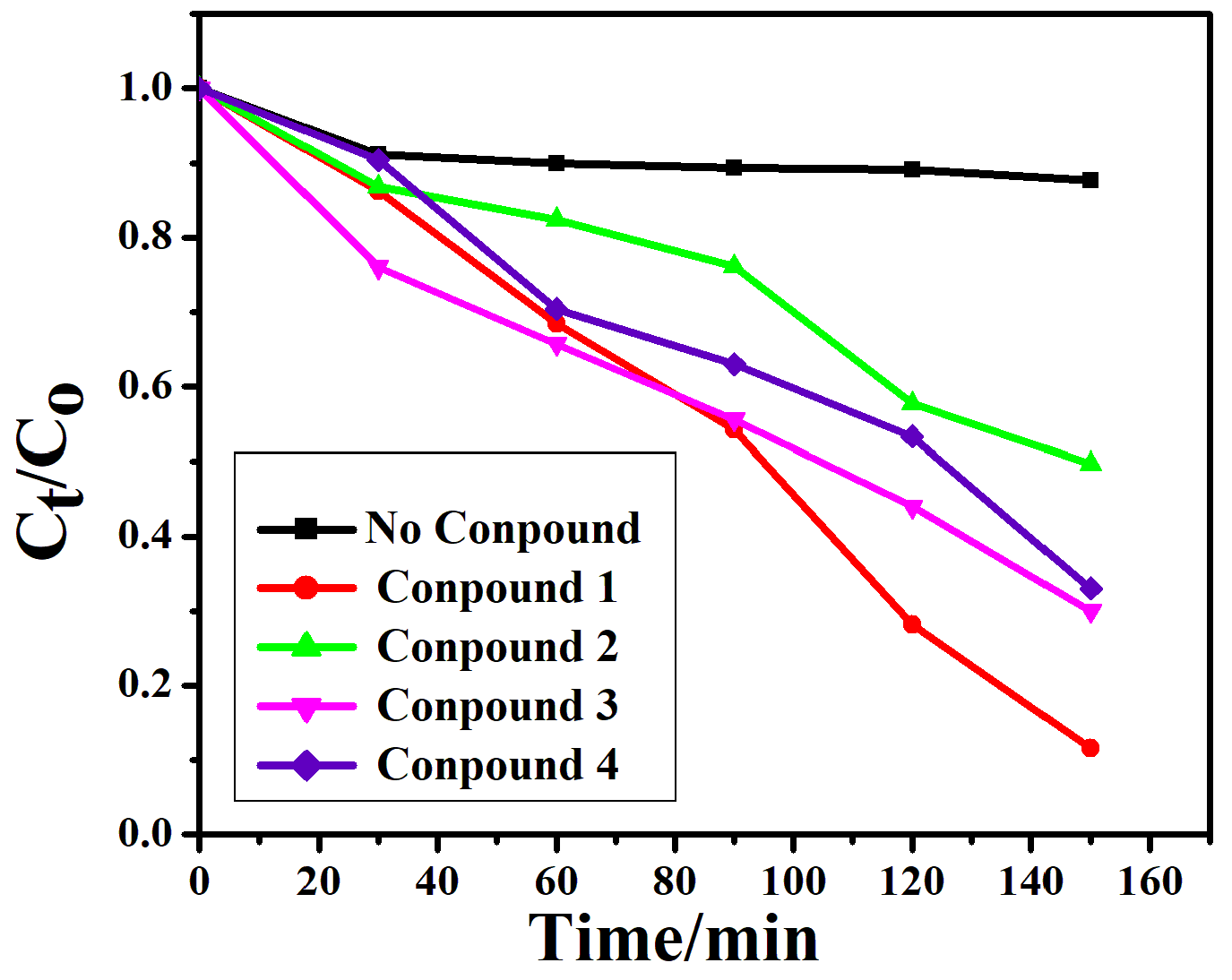


Figure S8. The conversions of MB with **1-4** as the catalysts.

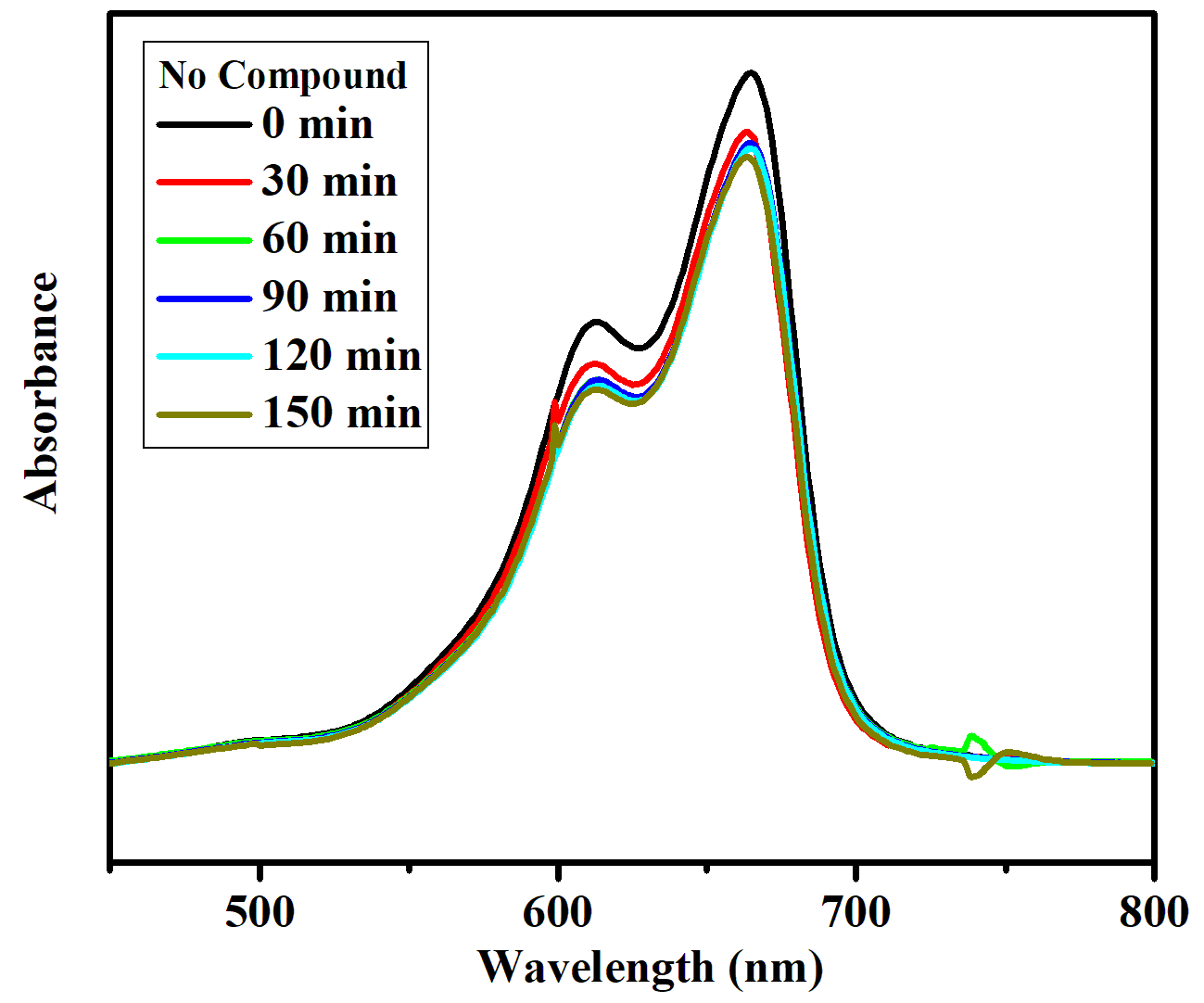
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Figure S9. Absorption spectra of the MB solution during the decomposition reaction under UV irradiation without catalyst.

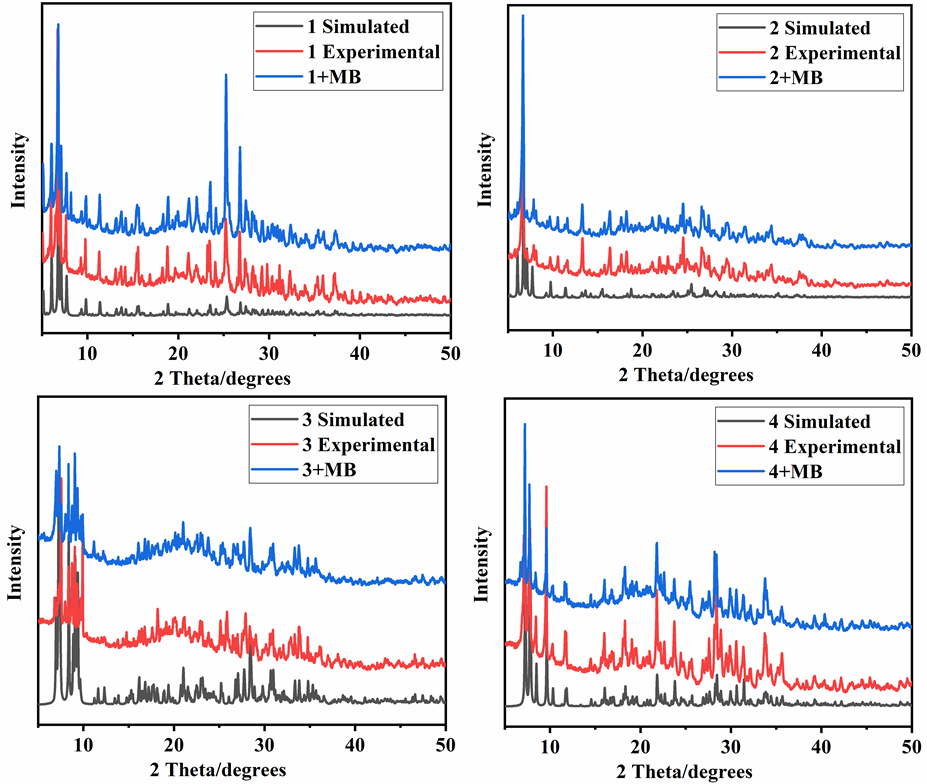
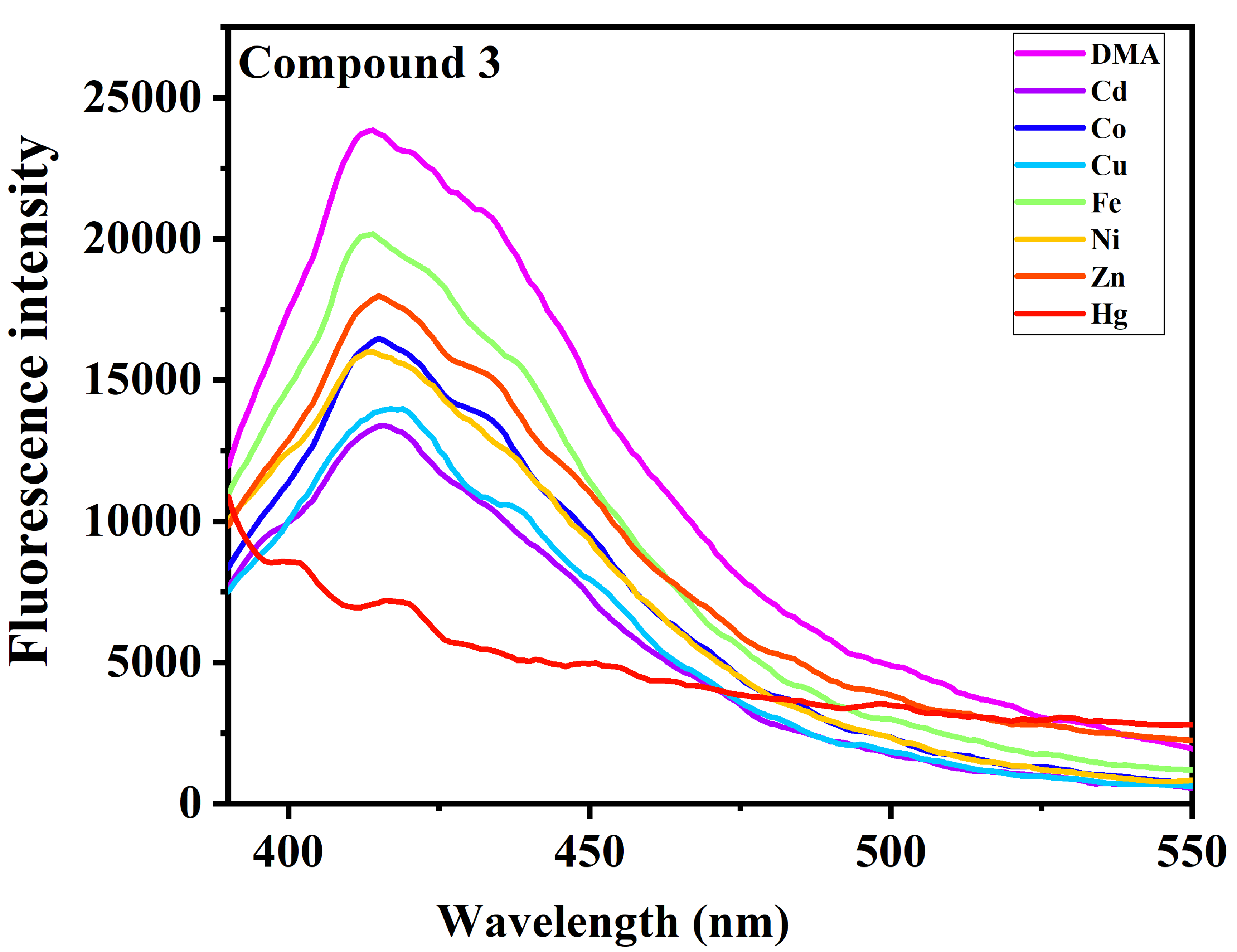


Figure S10. The simulative, experimental and recycled after photocatalysis powder X-ray diffraction patterns for compounds **1**−**4**.



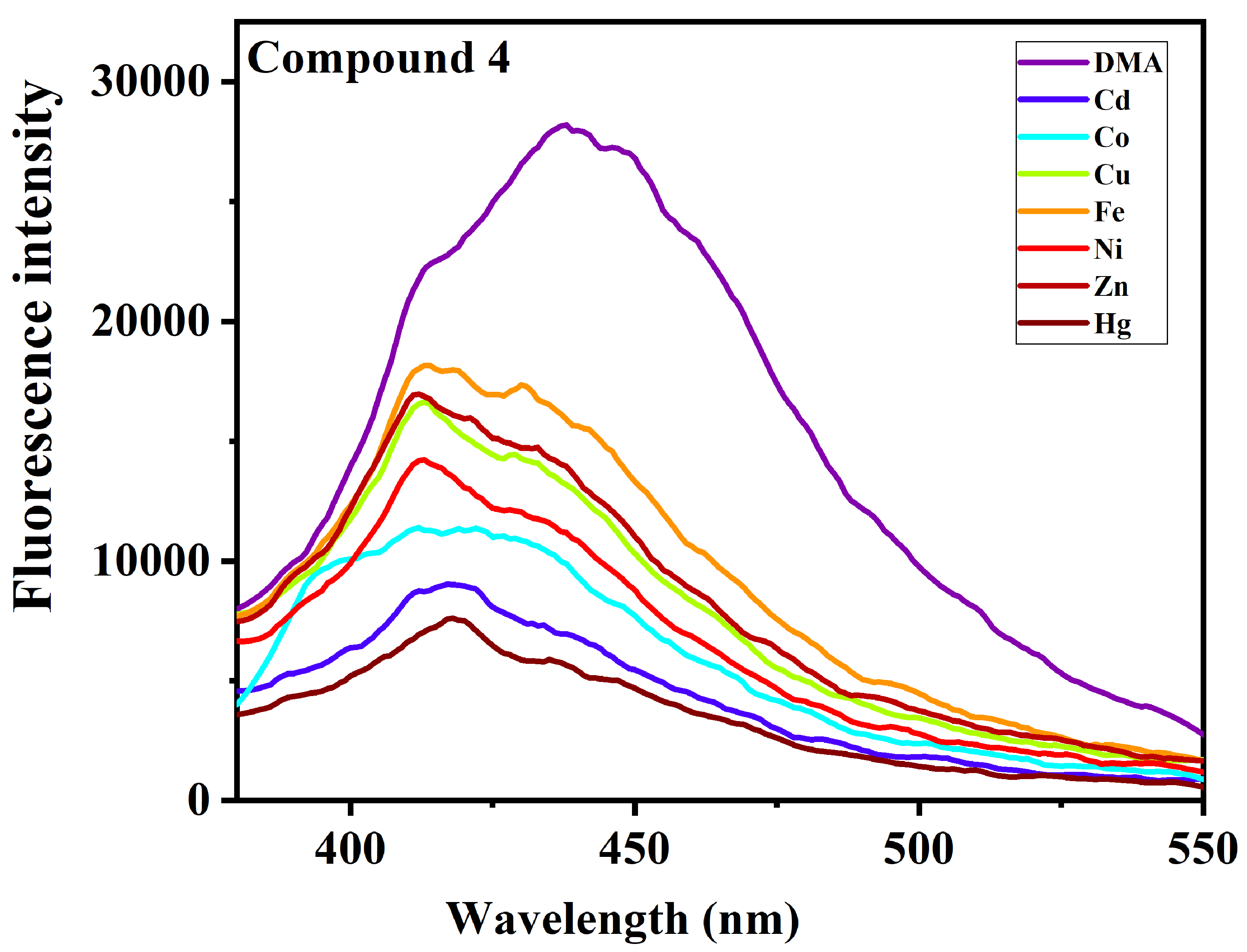
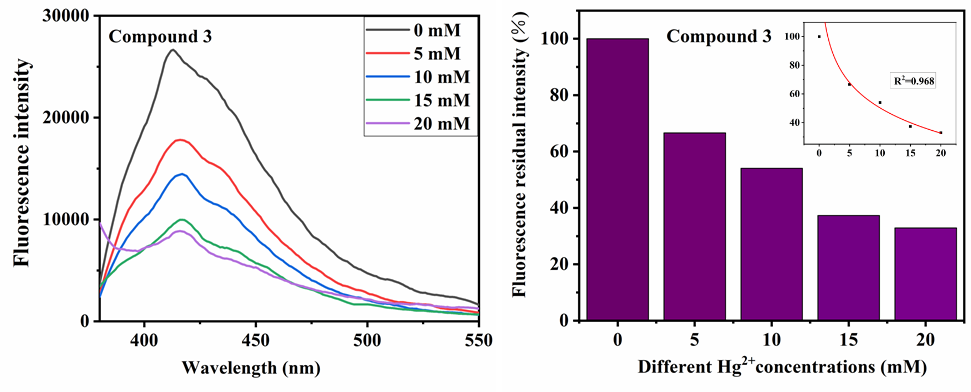


Figure S11. Fluorescence intensity of **1** and **2** suspension with the addition of different metal ions (excited at 380 nm).



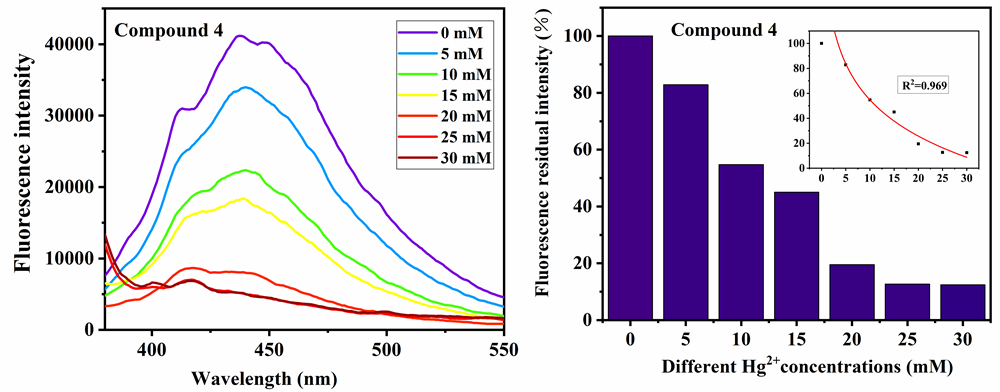
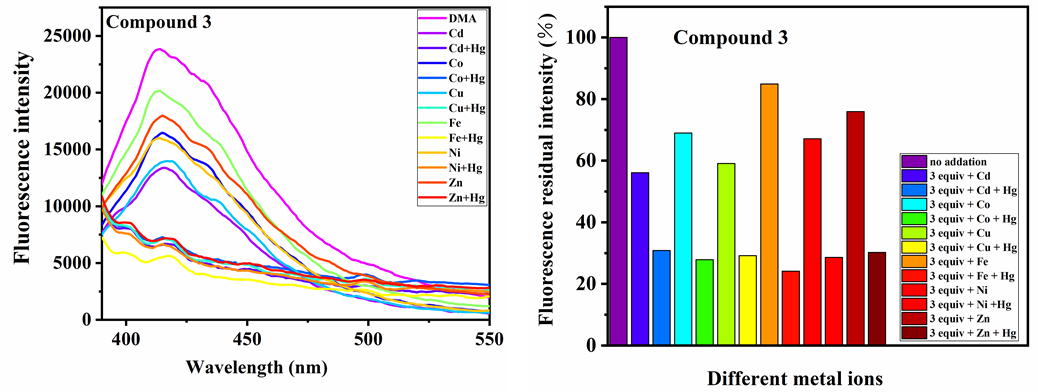


Figure S12. Fluorescence intensity of **3** and **4** with gradually increased Hg2+ (left), the right histogram reflects fluorescence residual intensity’s change (Inserted plot showing a fluorescence change after adding Hg2+).



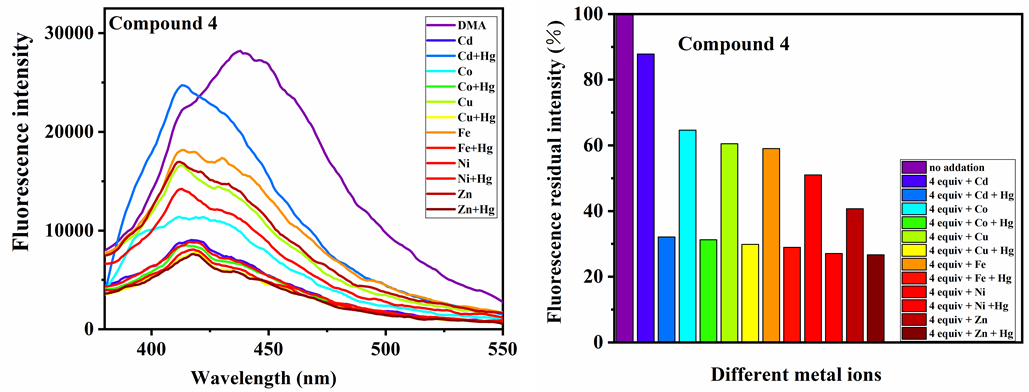


Figure S13. Fluorescence intensity of **3** and **4** at about 420 nm in suspension at room temperature upon the addition of Hg2+ or Hg2+ + Mn+ ions (excited at 380 nm).

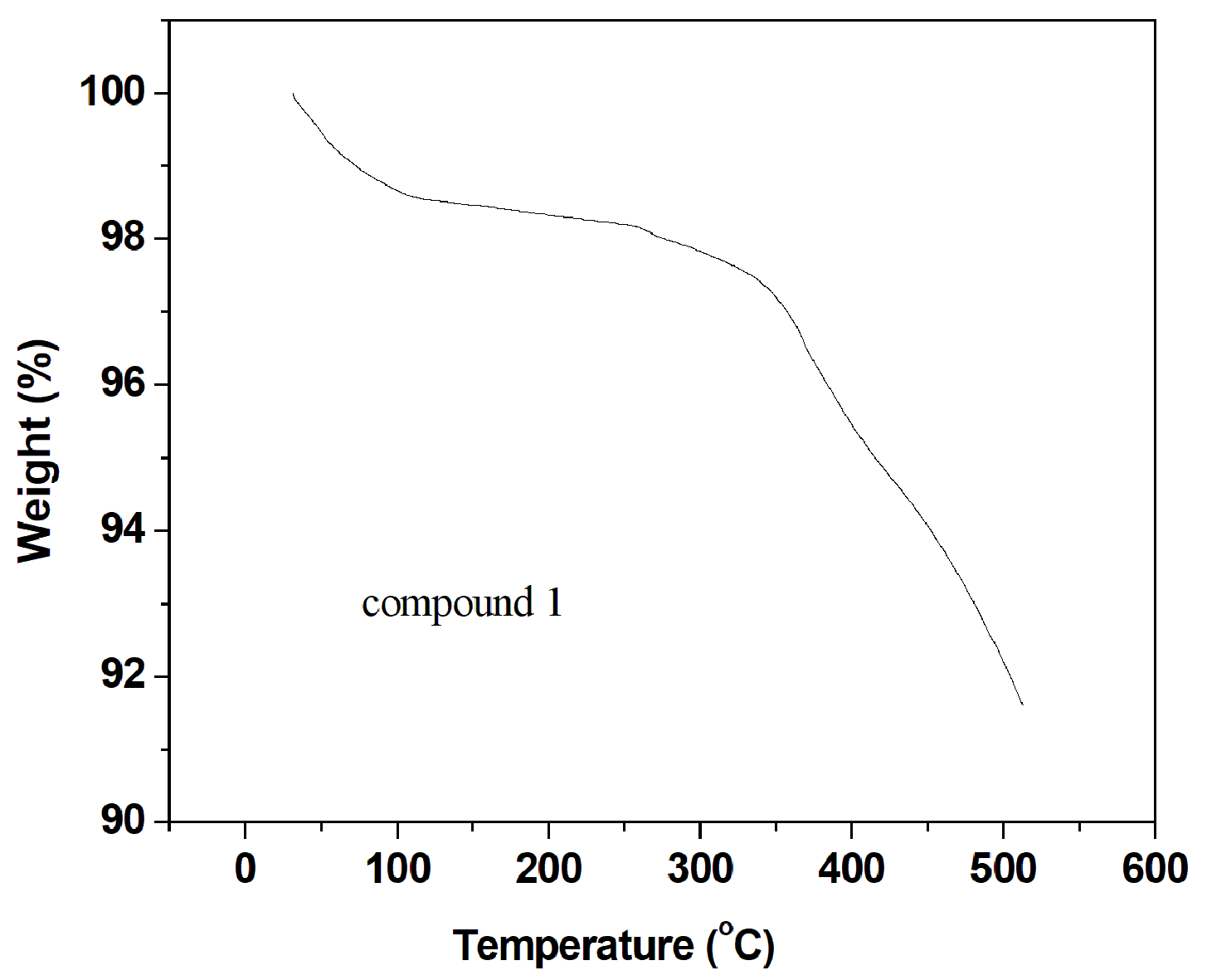
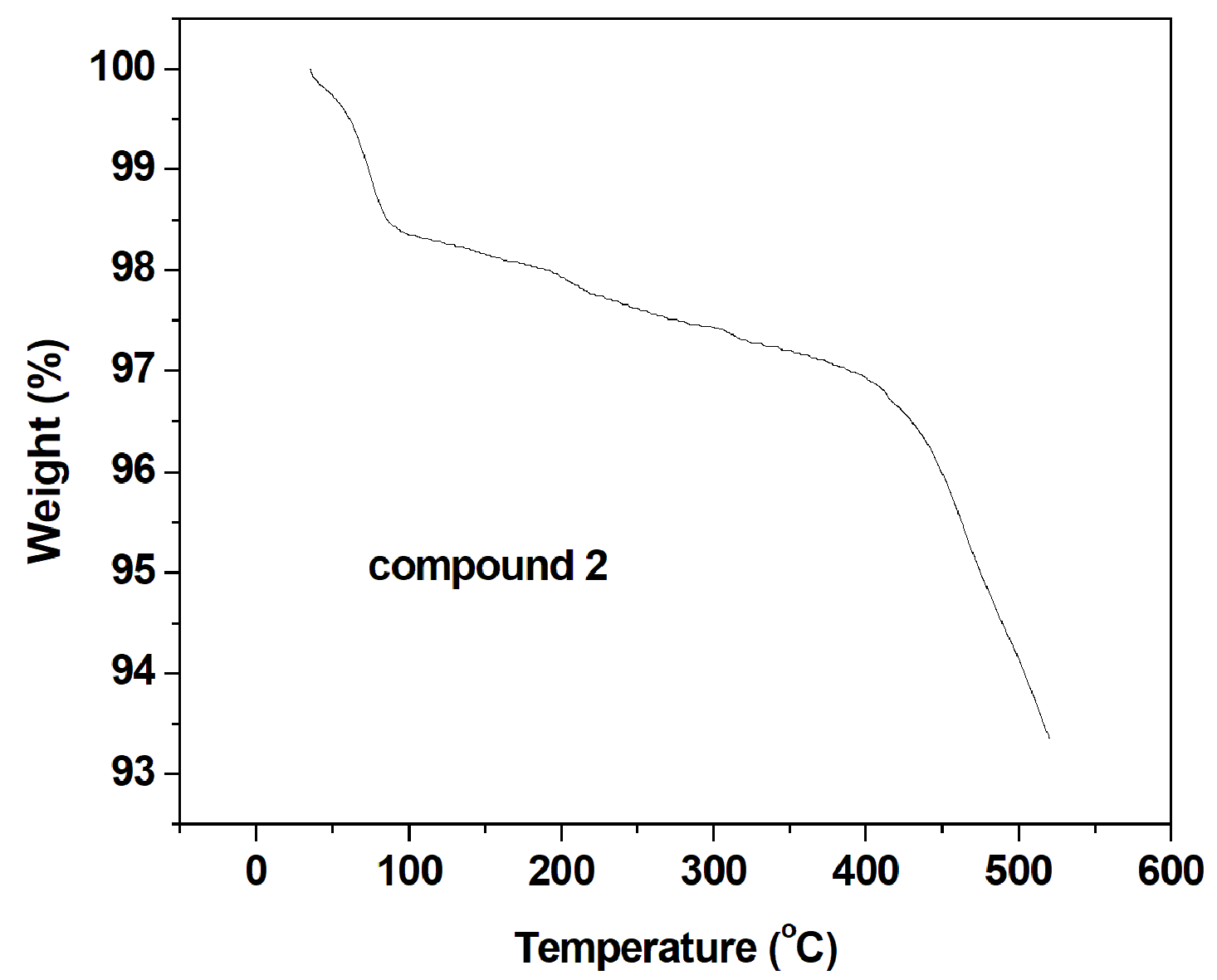
 

Figure S14. The TG curves of **1** and **2**.

**Thermalgravimetric analyses.** The TGA experiments were performed under N2 atmosphere with a heating rate of 10°C⋅min-1 in the temperature range of 40−500 °C for **1** and **2**, shown in figure S1. In the TG curve for **1**, the weight loss of 2.65% (calc. 2.74%) from 40 to 300 °C corresponds to the loss of crystal water molecules. The first weight loss step of TG curves of **2** below 300 °C (3.39%) correspond to the loss of water molecules (calc. 3.69%). In **1** and **2**, the four and thirteen water molecules were highly disordered and could not be modeled properly, thus the *SQUEEZE* routine of *PLATON* was applied to remove the contributions to the scattering from the solvent molecules. The reported refinements are of the guest-free structures using the \*.hkp files produced by using the *SQUEEZE* routine. The TG results further confirm the rationality of *SQUEEZE* routine.