Nanosol SERS/RRS aptamer assay of trace cobalt (II) by covalent organic framework BtPD-loaded nanogold catalytic amplification

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Fig. S1 Absorption spectra of the catalytic system
A: a: 0.067 mg/mL HAuCl₄+0.67 mmol/L HCl +3 mmol/L CH₂O₃Na; b-g: a+0.044, 0.089, 0.134, 0.179, 0.223, 0.268 μg/mL BtPD.
B: a: 0.067 mg/mL HAuCl₄+0.67 mmol/L HCl+3 mmol/L CH₂O₃Na; b-g: a+0.044, 0.089,
0.134, 0.179, 0.223, 0.268 μg/mL AuBtPD.

C: 0.067 mg/mL HAuCl₄ + 0.67 mmol/L HCl + 3 mmol/L CH₃CO₂Na; b-g: a=0.065, 0.129, 0.194, 0.259, 0.323, 0.388 μg/mL AuNPs.

D: a: 0.064 mg/mL HAuCl₄ + 0.67 mmol/L HCl + 3 mmol/L CH₃CO₂Na + 0.179 μg/mL AuBtPD + 16 nmol/L Apt₃Co; b-g: a=0.033, 0.167, 0.333, 0.5, 0.667, 1 nmol/L Co²⁺.
**Fig. S2 Conditions optimization**

**A:** HAuCl₄ concentration: HAuCl₄ + 0.67 mmol/L HCl + 3 mmol/L CHO₂Na + 0.179 μg/mL AuBtPD + 16 nmol/L Apt₇Co + 0.667 nmol/L Co²⁺.

**B:** Influence of CHO₂Na concentration: CHO₂Na + 0.064 mg/mL HAuCl₄ + 0.67 mmol/L HCl + 0.179 μg/mL AuBtPD + 16 nmol/L Apt₇Co + 0.667 nmol/L Co²⁺.

**C:** Influence of HCl concentration: HCl + 0.064mg/mL HAuCl₄ + 3 mmol/L CHO₂Na + 0.179 μg/mL AuBtPD + 16 nmol/L Apt₇Co + 0.667 nmol/L Co²⁺.

**D:** Influence of AuBtPD concentration: AuBtPD + 0.064 mg/mL HAuCl₄ + 0.67 mmol/L HCl + 3 mmol/L CHO₂Na + 16 nmol/L Apt₇Co + 0.667 nmol/L Co²⁺.

**E:** Influence of Apt₇Co concentration: atp₇Co + 0.064 mg/mL HAuCl₄ + 0.67 mmol/L HCl + 3 mmol/L CHO₂Na + 0.179 μg/mL AuBtPD + 16 nmol/L Apt₇Co + 0.667 nmol/L Co²⁺.

**F:** Influence of water bath temperature: 0.064 mg/mL HAuCl₄ + 0.67 mmol/L HCl + 3 mmol/L CHO₂Na + 0.179 μg/mL AuBtPD + 16 nmol/L Apt₇Co + 0.667 nmol/L Co²⁺.

**G:** Influence of water bath time: 0.064 mg/mL HAuCl₄ + 0.67 mmol/L HCl + 3 mmol/L CHO₂Na + 0.179 μg/mL AuBtPD + 16 nmol/L Apt₇Co + 0.667 nmol/L Co²⁺.

**H:** Influence of the added volume of trisodium citrate: 0.064 mg/mL HAuCl₄ + 0.67 mmol/L HCl + 3 mmol/L CHO₂Na + 0.179 μg/mL AuBtPD + 16 nmol/L Apt₇Co + 0.667 nmol/L Co²⁺.
Fig. S3 RRS intensity of COF

a: 0.1 mg/mL AuBtPD; b: 0.1 mg/mL BtPD.

Fig. S4 SERS Intensity of different batches

0.064 mg/mL HAuCl4 + 0.67 mmol/L HCl + 3 mmol/L CHO2Na + 0.179 μg/mL AuBtPD + 16nmol/L Apt + 1 nmol/L Co2+.
| functional group     | IR peak(cm$^{-1}$) BtPD | IR peak(cm$^{-1}$) AuBtPD |
|----------------------|-------------------------|--------------------------|
| O–H                  | 3367                    | 3247                     |
| C= N                 | 1697                    | 1662                     |
| benzene ring         | 1622                    | 1574                     |
| C= C                 | 1497                    | 1383                     |
| C– N                 | 1346                    | 1270                     |
| C– C                 | 1251, 1149              | 1077                     |
| C– H                 | 971                     | 952                      |
| –NH$_2$              | 838                     | 836                      |
| Coexisting substances | Tolerance limit (times) | Relative error (%) | Coexisting substances | Tolerance limit (times) | Relative error (%) |
|-----------------------|------------------------|--------------------|-----------------------|------------------------|--------------------|
| K⁺                    | 500                    | 5.6                | Ca²⁺                  | 1000                   | -7.8               |
| Cl⁻                   | 500                    | 6.3                | PO₄³⁻                 | 10                     | -3.3               |
| Fe³⁺                  | 100                    | -8.7               | Al³⁺                  | 10                     | -6.6               |
| Zn²⁺                  | 1000                   | -2.4               | NH₄⁺                  | 100                    | -5.1               |
| Cu²⁺                  | 50                     | -3.2               | Cr³⁺                  | 1000                   | 4.4                |
| Fe²⁺                  | 1000                   | 6.4                | Hg²⁺                  | 50                     | 7.2                |
| Mg²⁺                  | 100                    | -4.6               | NO₃⁻                  | 1000                   | 4.3                |
| Na⁺                   | 1000                   | -8.4               | NO₂⁻                  | 1000                   | 5.2                |
| SO₄²⁻                 | 50                     | -6.1               | Ba²⁺                  | 100                    | -6.9               |
| Pb²⁺                  | 500                    | -5.8               | Cd²⁺                  | 50                     | 7.6                |

| Coexisting substances | Tolerance limit (times) | Relative error (%) | Coexisting substances | Tolerance limit (times) | Relative error (%) |
|-----------------------|------------------------|--------------------|-----------------------|------------------------|--------------------|
| K⁺                    | 500                    | 8.8                | Ca²⁺                  | 1000                   | 2.3                |
| Cl⁻                   | 500                    | 5.4                | PO₄³⁻                 | 10                     | -8.5               |
| Fe³⁺                  | 500                    | -7.3               | Al³⁺                  | 10                     | -8.7               |
| Zn²⁺                  | 1000                   | -3.5               | NH₄⁺                  | 500                    | -6.1               |
| Cu²⁺                  | 50                     | -8.4               | Cr³⁺                  | 1000                   | 3.3                |
| Fe²⁺                  | 1000                   | 9.2                | Hg²⁺                  | 50                     | 5.7                |
| Mg²⁺                  | 100                    | 1.5                | NO₃⁻                  | 1000                   | 6.3                |
| Na⁺                   | 1000                   | -3.7               | NO₂⁻                  | 1000                   | 1.6                |
| SO₄²⁻                 | 50                     | -1.2               | Ba²⁺                  | 100                    | -6.6               |
| Pb²⁺                  | 500                    | -1.6               | Cd²⁺                  | 100                    | 5.8                |
### Table S4 Results of RRS method

| Sample     | Measurement value (nmol/L) | Average (nmol/L) | Added Co²⁺ (nmol/L) | Measurement value after adding (nmol/L) | Recovery (%) | RSD (%) |
|------------|----------------------------|------------------|---------------------|----------------------------------------|--------------|---------|
| river      | 3.56, 3.40, 3.57, 3.81, 3.65 | 3.60             | 0.5                 | 4.13, 3.96, 4.34, 3.84, 4.39           | 106          | 4.14    |
| waste      | 15.04, 14.87, 15.34, 14.50, 14.72 | 14.89           | 0.5                 | 15.10, 15.20                          | 91           | 2.14    |
| tap water  | 1.27, 1.28, 1.06, 1.10, 1.17 | 1.18             | 0.5                 | 1.36, 1.84, 1.52, 1.84, 1.70           | 94           | 8.39    |

### Table S5 Results of SERS method

| Sample     | Measurement value (nmol/L) | Average (nmol/L) | Added Co²⁺ (nmol/L) | Measurement value after adding (nmol/L) | Recovery (%) | RSD (%) |
|------------|----------------------------|------------------|---------------------|----------------------------------------|--------------|---------|
| river      | 3.92, 3.55, 3.55, 3.74, 3.63 | 3.68             | 0.5                 | 4.24, 4.16, 4.16, 4.44, 3.92            | 101          | 4.24    |
| waste      | 15.50, 15.36, 14.25, 14.62 | 14.79           | 0.5                 | 15.24, 14.96                          | 92           | 4.06    |
| tap water  | 1.25, 1.39, 1.10, 1.14, 1.24 | 1.22             | 0.5                 | 1.72, 1.72, 1.58, 1.86, 1.70           | 99           | 9.22    |