

# Highly Sensitive Adsorption and Detection of Iodide in Aqueous Solution by a Post-Synthesized Zirconium-Organic Framework

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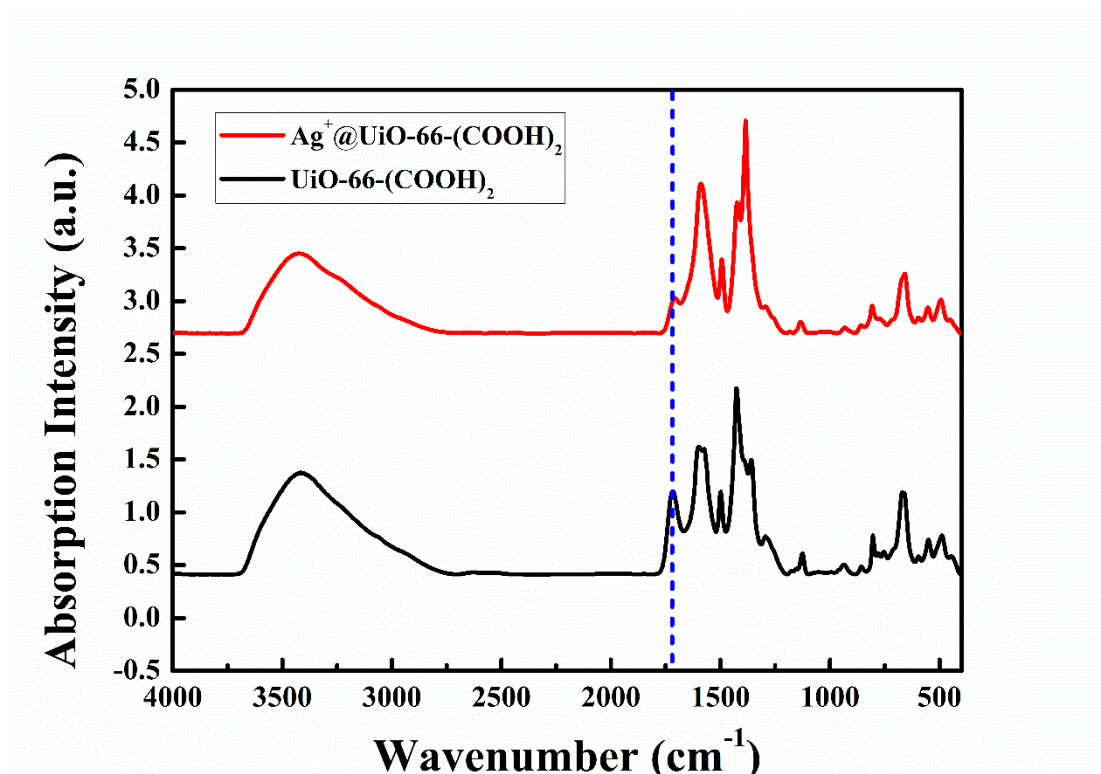


Figure S1. FT-IR spectra of UiO-66-(COOH)<sub>2</sub> and Ag<sup>+</sup>@UiO-66-(COOH)<sub>2</sub>.

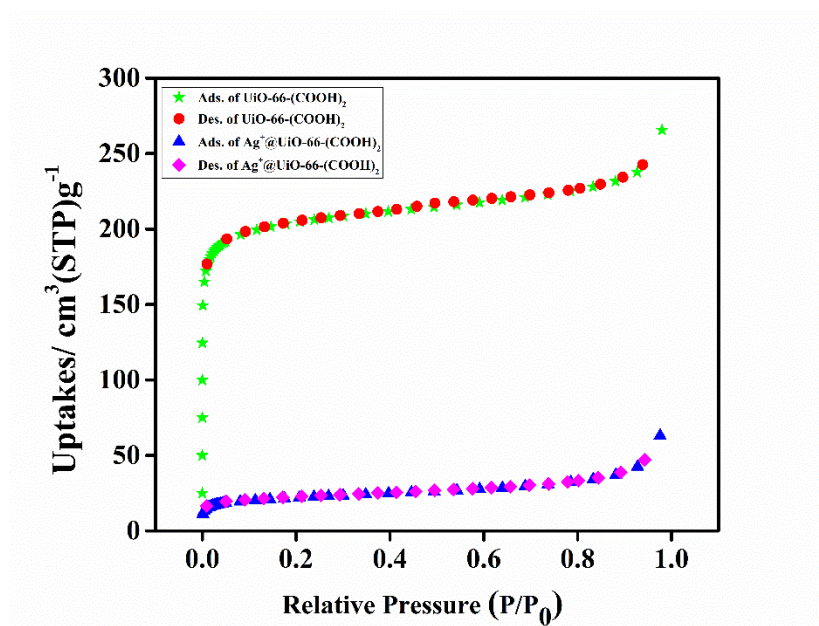


Figure S2. N<sub>2</sub> adsorption-desorption isotherms of UiO-66-(COOH)<sub>2</sub> and Ag<sup>+</sup>@UiO-66-(COOH)<sub>2</sub> at 77 K.

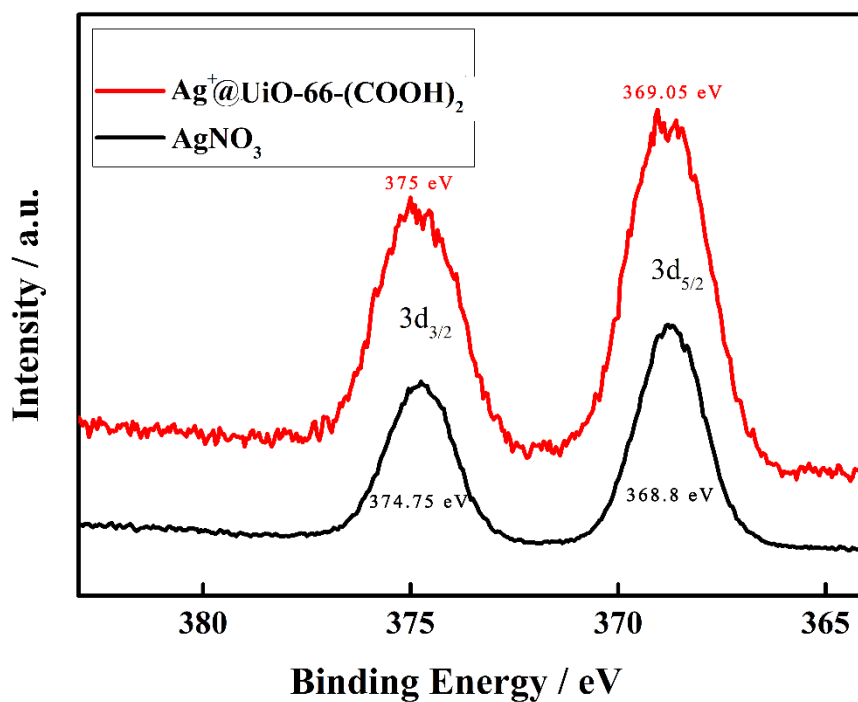


Figure S3. Survey XPS spectra of Ag<sup>+</sup>@UiO-66-(COOH)<sub>2</sub> and AgNO<sub>3</sub>.

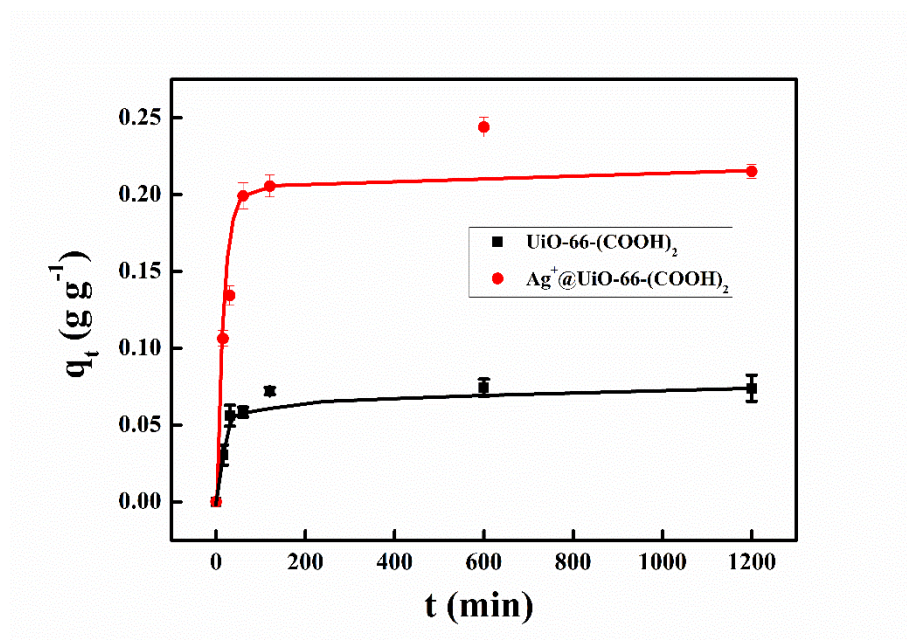


Figure S4. The effect of contact time on the  $I^-$  adsorption on  $UiO-66-(COOH)_2$  and  $Ag^+@UiO-66-(COOH)_2$  at room temperature.

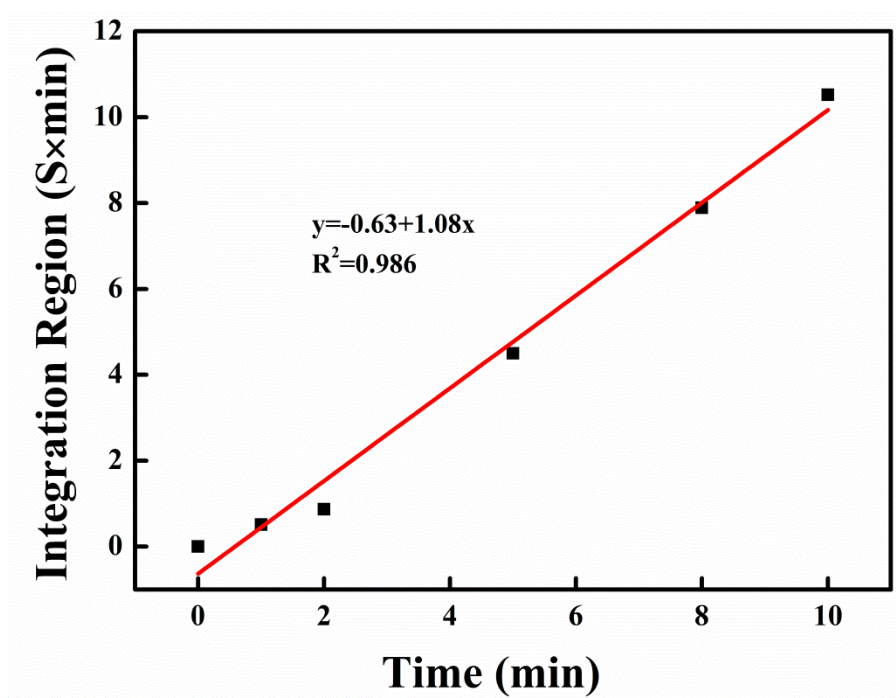


Figure S5. Standard curve of iodide in aqueous solution by ion chromatography.

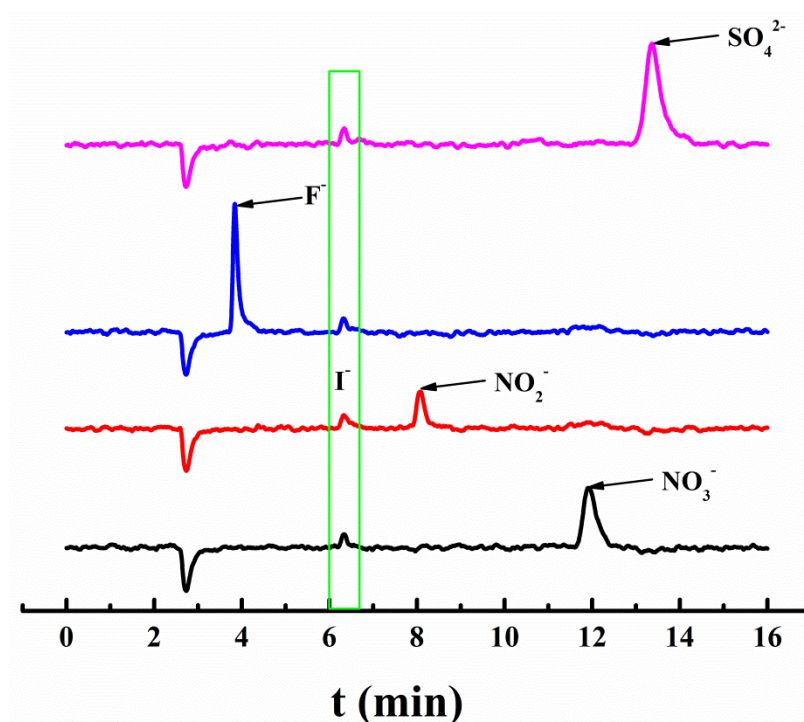


Figure S6. Ion chromatography of binary mixture containing  $\text{I}^-$  and other competing anions.

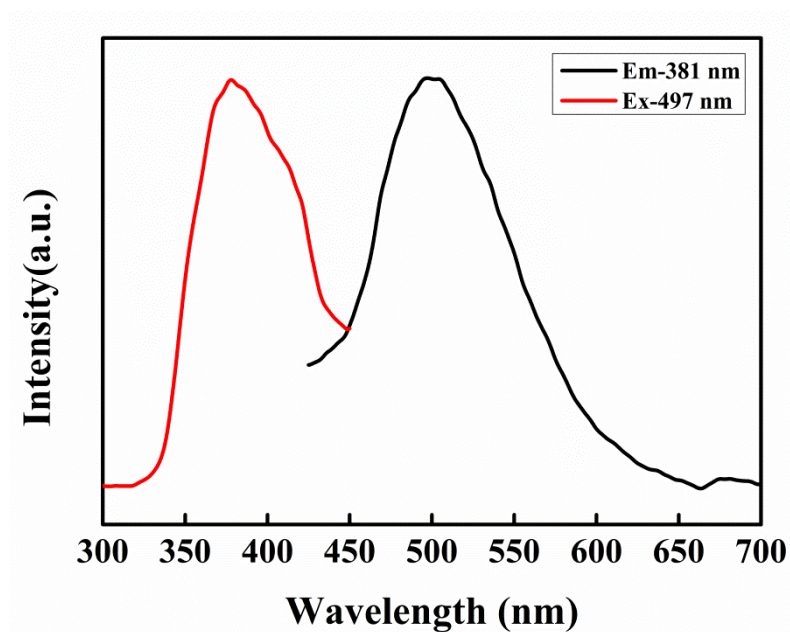
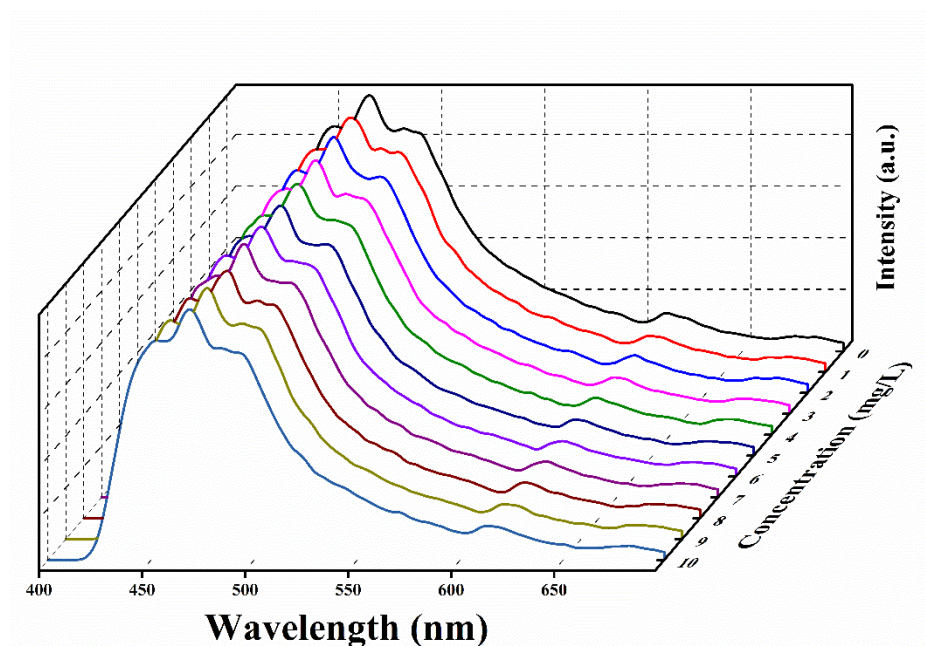


Figure S7. Excitation and emission spectra of  $\text{Ag}^+@ \text{UiO-66-(COOH)}_2$  in aqueous solution.





**Figure S8.** Emission spectra of UiO-66-(COOH)<sub>2</sub> upon the addition of different concentration of I<sup>-</sup>.

**Table S1.** Kinetics parameters for I<sup>-</sup> adsorption on Ag<sup>+</sup>@UiO-66-(COOH)<sub>2</sub>.

| Concentration | k <sub>2</sub>    | Q <sub>e</sub> | R <sup>2</sup> |
|---------------|-------------------|----------------|----------------|
| 500 mg/L      | 0.898 (g/(g·min)) | 221.2 mg/g     | 0.995          |

**Table S2.** The Langmuir isotherm model parameters for I<sup>-</sup> adsorption on Ag<sup>+</sup>@UiO-66-(COOH)<sub>2</sub>.

| Materials                                   | K <sub>L</sub> | q <sub>m</sub> | R <sup>2</sup> |
|---|----------------|----------------|----------------|
| UiO-66-(COOH) <sub>2</sub> @Ag <sup>+</sup> | 11.81 (L/g)    | 235.5 mg/g     | 0.970          |

**Table S3.** Comparison of the iodide adsorption in different adsorbents.

| Adsorbent                                   | Adsorption capacity (mg/g) | Equilibrium time | Ref.      |
|---|----------------------------|------------------|-----------|
| MIL-101(Cr)-SO <sub>3</sub> Ag              | 244.2                      | 24 h             | [1]       |
| Nano Cu <sub>2</sub> O/Cu-C                 | 41.2                       | 10 min           | [2]       |
| 25%-Ag@MIL-101                              | 2.14                       | 2 h              | [3]       |
| Mg/Al/Bi MMO                                | 202.2                      | 12 h             | [4]       |
| 1.0%-Ag@Cu <sub>2</sub> O                   | 25.38                      | 2 h              | [5]       |
| Al <sub>2</sub> O <sub>3</sub> carbon fiber | 46.15                      | 2 h              | [6]       |
| MIL-101(Cr)@Ag                              | 57                         | 10 min           | [7]       |
| Ag <sup>+</sup> @UiO-66-(COOH) <sub>2</sub> | 235.5                      | 20 h             | This work |

**Table S4.** Comparison of the iodide sensing on different fluorescent probes.

| Probes  | Linear range            | LOD       | Ref.      |
|---|-------------------------|-----------|-----------|
| <b>Gold nanoclusters</b>                        | 1–100 $\mu\text{M}$     | 0.056 ppm | [8]       |
| <b>Thymine</b>                                  | 0.01–1000 $\mu\text{M}$ | 0.64 ppb  | [9]       |
| <b>Cz-TPM</b>                                   | 100–800 $\mu\text{M}$   | 1.10 ppm  | [10]      |
| <b>OTf</b>                                      | 0–50 $\mu\text{M}$      | 0.025 ppm | [11]      |
| <b>Cd-MOF</b>                                   | 0–25 $\mu\text{M}$      | 0.088 ppm | [12]      |
| <b>IPF</b>                                      | 1–10 $\mu\text{M}$      | 0.11 ppm  | [13]      |
| <b>Ag<sup>+</sup>@UiO-66-(COOH)<sub>2</sub></b> | 0.72–7.2 $\mu\text{M}$  | 0.58 ppm  | This work |

## References

- Zhao, X.; Han, X.; Li, Z.; Huang, H.; Liu, D.; Zhong, C. Enhanced removal of iodide from water induced by a metal-incorporated porous metal–organic framework. *Appl. Surf. Sci.* **2015**, *351*, 760–764.
- Zhang X, Gu P, Li X, Zhang G, Efficient adsorption of radioactive iodide ion from simulated wastewater by nano Cu<sub>2</sub>O/Cu modified activated carbon. *Chem. Eng. J.* **2017**, *322*, 129–139.
- Mao P, Qi B, Liu Y, Zhao L, Jiao Y, Zhang Y, Jiang Z, Li Q, Wang J, Chen S, Yang Y, Ag-II doped MIL-101 and its adsorption of iodine with high speed in solution. *J. Solid State Chem.* **2016**, *237*, 274–283.
- Lee S-H, Takahashi Y, Selective immobilization of iodide onto a novel bismuth-impregnated layered mixed metal oxide: Batch and EXAFS studies. *J. Hazard. Mater.* **2020**, *384*, 121223.
- Mao P, Liu Y, Jiao Y, Chen S, Yang Y, Enhanced uptake of iodide on Ag@Cu<sub>2</sub>O nanoparticles. *Chemosphere*, **2016**, *164*, 396–403.
- Rong J, Zhao Z, Jing Z, Zhang T, Qiu F, Xu J, High-specific surface area hierarchical Al<sub>2</sub>O<sub>3</sub> carbon fiber based on a waste paper fiber template: preparation and adsorption for iodide ions. *J. Wood Chem. Technol.* **2017**, *37*, 485–492.
- Wan J, Li Y, Jiang Y, Yin Y, Silver-doped MIL-101(Cr) for rapid and effective capture of iodide in water environment: exploration on adsorption mechanism. *J. Radioanalytical Nuclear Chem.* **2021**, *328*, 1041–1054.
- Wang M, Wu Z, Yang J, Wang G, Wang H, Cai H, Au<sub>25</sub>(SG)<sub>18</sub> as a fluorescent iodide sensor, *Nanoscale* **2012**, *4*: 4087–4090.
- Dai R, Wang X, Wang Z, Mu S, Liao J, Wen Y, Lv J, Huang K, Xiong X, A sensitive and label-free sensor for melamine and iodide by target-regulating the formation of G-quadruplex. *Microchem. J.* **2019**, *146*, 592–599.
- Dang Q, Wan H, Zhan X, Carbazolic porous framework with tetrahedral core for gas uptake and tandem detection of iodide and mercury, *ACS Appl. Mater. Interfaces* **2017**, *9*, 21438–21446.
- Salomón-Flores M, Hernández-Juárez C, Bazany-Rodríguez I, Barroso-Flores J, Martínez-Otero D, López-Arteaga R, Valdés-Martínez J, Dorazco-González A, Efficient fluorescent chemosensing of iodide based on a cationic meso-tetraarylporphyrin in pure water. *Sens. Actuators B* **2019**, *281*, 462–470.
- Singha D, Majee P, Mondal S, Mahata P, Luminescent cadmium based MOF as selective and sensitive iodide sensor in aqueous medium. *J. Photochem. Photobiol. A* **2018**, *356*, 389–396.
- Chen Z, Sun R, Feng S, Wang D, Liu H, Porosity-induced selective sensing of iodide in aqueous solution by a fluorescent imidazolium-based ionic porous framework, *ACS Appl. Mater. Interfaces* **2020**, *12*, 11104–11114.