



## Supporting Information

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Neutral MOF Anion Receptor: Radical-Promoted Precise Anion Recognition

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Supporting Information

## **Neutral MOF Anion Receptor: Radical-Promoted Precise Anion Recognition**

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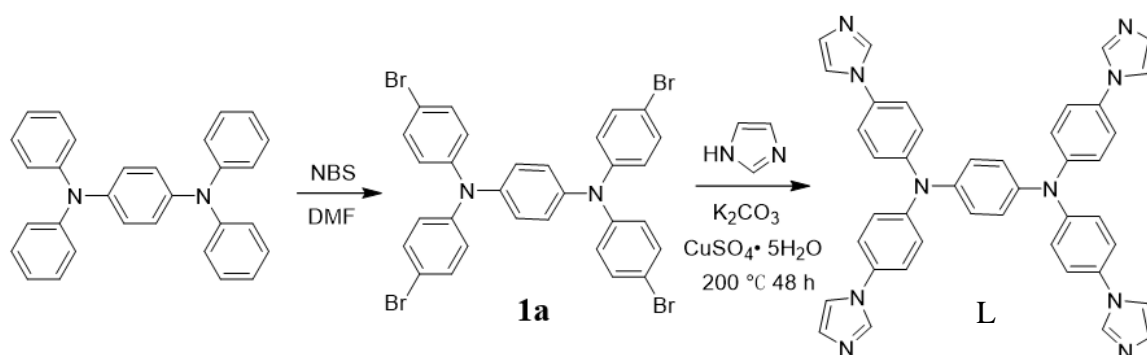
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## 1. Materials and general methods

All the reagents were purchased from Adamas Reagent, Ltd. and used as received without further purification. X-ray powder diffraction were collected by a Bruker AXSD8 Discover powder diffractometer at 40 kV, 40 mA for Cu K $\lambda$  ( $\lambda = 1.5406 \text{ \AA}$ ). The simulated powder patterns were calculated by Mercury 1.4. Infrared Spectra (IR) were measured by a Bruker VERTEX70 spectrometer in the 600-4000  $\text{cm}^{-1}$  region. The analyses of concentrations of  $\text{ReO}_4^-$  in the solution was carried out by ThermoFisher iCap7600 ICP-OES instruments. X-ray photoelectron spectra (XPS) were collected by Thermo Scientific ESCALAB 250 Xi spectrometer.

## 2. Synthesis of L



Synthesis of  $\text{N}^1,\text{N}^1,\text{N}^4,\text{N}^4$ -Tetrakis(4-bromophenyl)benzene-1,4-diamine (**1a**): A solution of  $\text{N}^1,\text{N}^1,\text{N}^4,\text{N}^4$ -Tetraphenylbenzene-1,4-diamine (0.7g, 1.70 mmol) in dimethylformamide (DMF; 5 mL) was cooled to  $0^\circ\text{C}$ . A solution of N-bromo succinimide (NBS, 1.33 g, 7.47 mmol) in DMF (5 mL) was added dropwise, and the temperature was maintained below  $5^\circ\text{C}$ . After addition, the reaction mixture was stirred for 12 h under room temperature. The reaction mixture was then poured into water (500 mL) and filtered, and the residue was washed with methanol for three times. Then, the precipitate was filtered off and dried in vacuum oven at  $50^\circ\text{C}$  to afford the pure product **1a** as a white powder (1.12 g, 93% yield).  $^1\text{H NMR}$ (400 MHz,  $\text{CDCl}_3$ )  $\delta$  [ppm]: 7.49 (d,  $J = 8.8$  Hz, 8H), 7.19 (d,  $J = 8.8$  Hz, 8H), 7.14 (s, 4H).

Synthesis of  $\text{N}^1,\text{N}^1,\text{N}^4,\text{N}^4$ -tetrakis(4-(1H-imidazol-1-yl)phenyl)benzene-1,4-diamine (L): A sample of **1a** (1.1 g, 1.52 mmol), imidazole (2.2 g, 32.3 mmol),  $\text{K}_2\text{CO}_3$  (2.2 g, 15.9 mmol),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.256 g, 1.04 mmol) were mixed and heated at  $200^\circ\text{C}$  for 48 h. Then the reaction mixture was cooled to ambient temperature, and washed several times with water. The remaining solid residue was brought to dryness to give pale green solid L (0.98 g, 1.45 mmol, 95%).  $^1\text{H NMR}$ (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  [ppm]: 8.35 (d,  $J = 8.8$  Hz, 4H), 7.98 (d,  $J = 8.8$  Hz, 4H), 7.65 (s, 4H), 7.31 (s, 8H), 7.20 (s, 8H), 7.17 (s, 4H).

## 3. Synthesis of ECUT-300

A mixture of L (10 mg) and Co (NO<sub>3</sub>)<sub>2</sub> (15 mg) in 3 mL DMF and 1 mL acetonitrile in the presence of 250  $\mu$ L HCl (concentrated hydrochloric acid) was sealed in a Teflon lined Parr autoclave. The solution was heated at 120 °C for 3 days followed by decreasing to room temperature within 2 days. After filtration, block crystals of ECUT-300 were collected as a pure phase. The yield is 67% based on L. Element analysis: Exp. C/53.07%, H/5.06%, N/14.85%, Calc. C/53.06%, H/5.09%, N/14.73%.

#### 4. Synthesis of ECUT-300-L

**ECUT-300-L** was obtained through exposing the samples of ECUT-300 under xenon lamp under ambience for 1 h. Element analysis: Exp. C/53.04%, H/5.05%, N/14.67%, Calc. C/53.06%, H/5.09%, N/14.73%.

#### 5. X-ray Crystallography

X-ray diffraction data were collected on a Bruker diffractometer at 300 K using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The data reduction included a correction for Lorentz and polarization effects, with an applied multiscan absorption correction (SADABS). The crystal structure was solved and refined using the SHELXTL program suite. Direct methods yielded all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms. The SQUEEZE subroutine of the PLATON software suite was used to remove the scattering from the highly disordered guest molecules. CCDC 2260550-2260552 contains the supplementary crystallographic data of these materials, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

#### 6. ReO<sub>4</sub><sup>-</sup> uptake experiments

ReO<sub>4</sub><sup>-</sup> mother solution was prepared by dissolving 1.44 g NH<sub>4</sub>ReO<sub>4</sub> in 1000 mL deionized water to create an 1000 mg/L (ppm) NH<sub>4</sub>ReO<sub>4</sub> solution. All the adsorption experiments were conducted at 298 K.

#### 7. ReO<sub>4</sub><sup>-</sup> adsorption kinetics

In kinetics experiments, the ReO<sub>4</sub><sup>-</sup> solution with initial concentration of 50 ppm was used. The dose of adsorbent is 10 mg, while the used volume of solution is 20 mL.

#### 8. ReO<sub>4</sub><sup>-</sup> adsorption isotherms

In isotherm experiments, the ReO<sub>4</sub><sup>-</sup> solution with initial concentration of 100-500 ppm was used. The dose of adsorbent is 10 mg, while the used volume of solution is 20 mL and the contact time is 2 h.

The adsorption amount,  $Q_e$  (mg/g), was calculated by the difference of the  $\text{ReO}_4^-$  equilibrium concentration before and after adsorption (see equation 1):

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

where  $c_0$  (mg/L) and  $c_e$  (mg/L) are the initial concentration and equilibrium concentration of  $\text{ReO}_4^-$  in the solutions, respectively;  $V$  (mL) is the volume of testing solution and  $m$  (mg) is the amount of sorbent.

## 9. Selectivity

In selective adsorption experiments, a binary mixed solution contains both  $\text{ReO}_4^-$  and other ion ( $\text{NaNO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{NaH}_2\text{PO}_4$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$ ) with respectively 1:1, 1:10, 1:100, and 1:1000 ratio. The dose of adsorbent is 10 mg, while the solution is 20 mL.

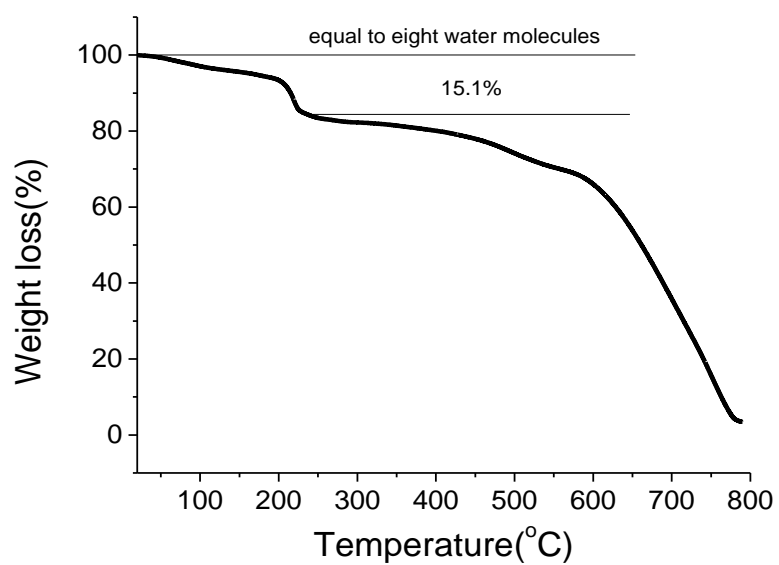
$K_d$  value and selectivity ( $S$ ) is calculated from the following two equations,

$$K_d = \frac{V}{m} \frac{(C_0 - C_e)}{C_e} \times 10^3 \quad (2)$$

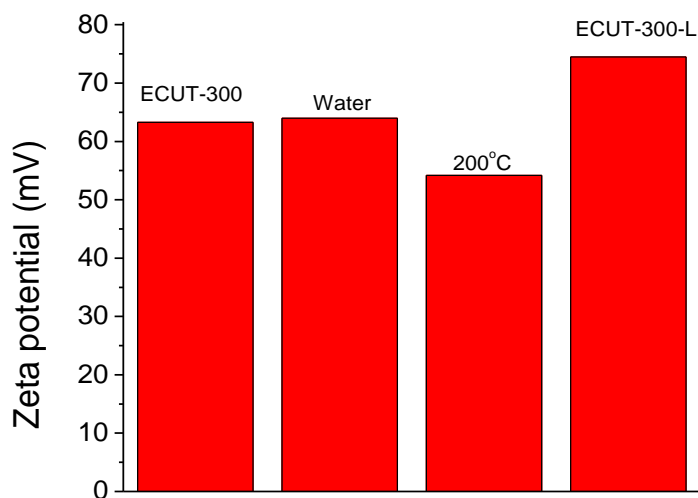
$$S = \frac{K_d^U}{K_d^M} \quad (3)$$

where the unit for  $K_d$  value is mL/g.

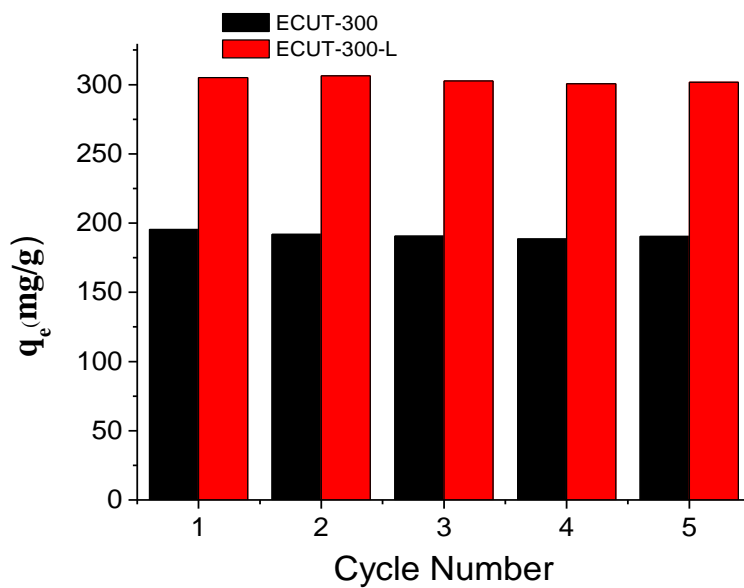
## 10. Additional Figures and Tables



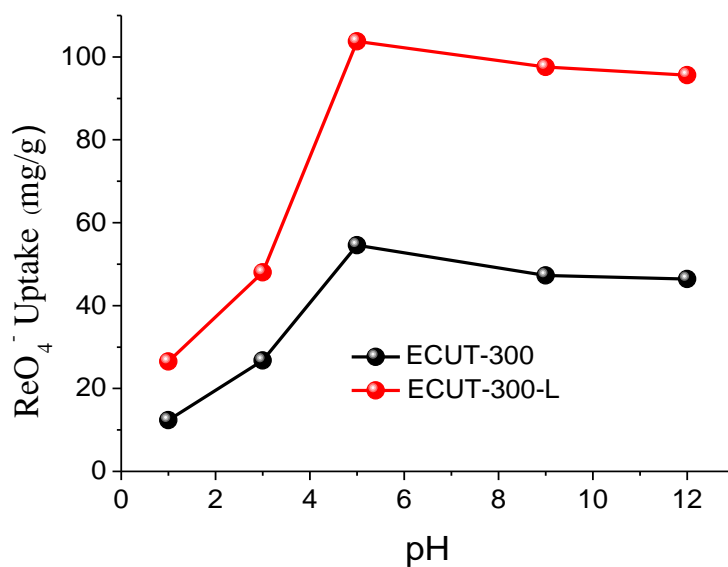
**Figure S1.** The TG plot of ECUT-300.



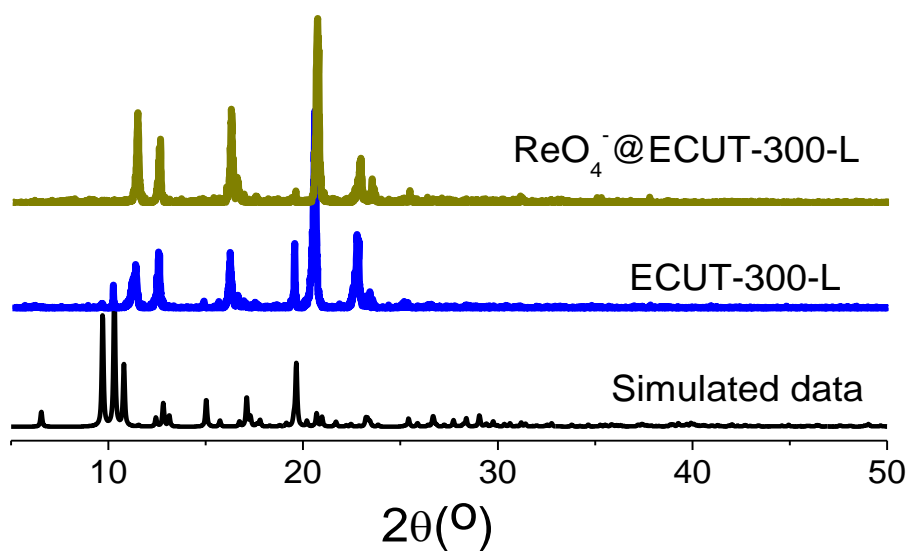
**Figure S2.** The Zeta potential of these samples at pH=5.



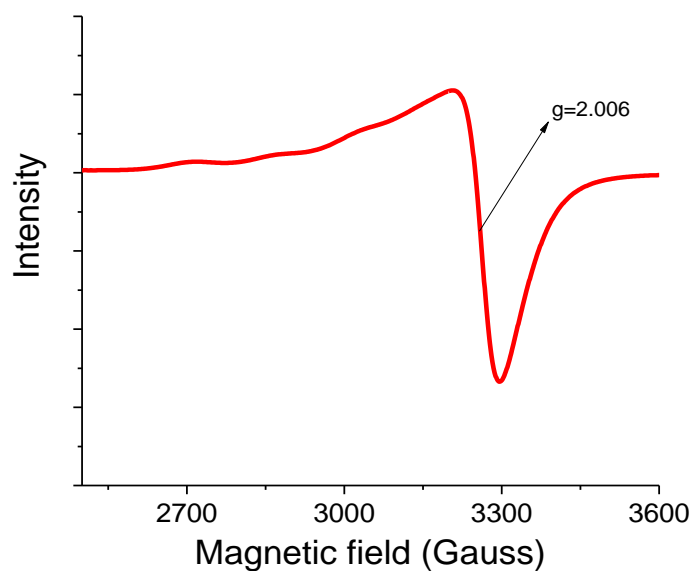
**Figure S3.** The adsorption-desorption cycle.



**Figure S4.** The pH effect on  $\text{ReO}_4^-$  uptake.

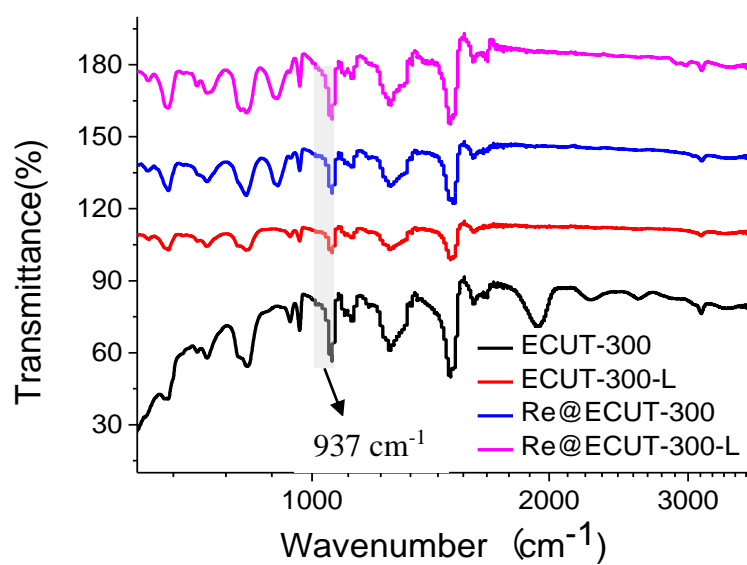


**Figure S5.** A comparison of PXRD patterns between ECUT-300-L and  $\text{ReO}_4^-$  loading samples.



**Figure S6.** EPR of ECUT-300-L samples after loading  $\text{ReO}_4^-$ .





**Figure S7.** A comparison of IR among ECUT-300, ECUT-300-L, and corresponding ReO<sub>4</sub><sup>-</sup> loaded samples.