

Supporting information

Engineering of appropriate pore size combined with sulfonic functionalization in a Zr-MOF with reo topology for the ultra-high removal of cationic malachite green dye from an aqueous medium

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Section S1. Synthesis of the materials

Synthesis of 4-sulfonaphthalene-2,6-dicarboxylic acid (H₃SNDC) linker

2,6-naphthalenedicarboxylic acid (H₂NDC) (1 g, 4.63 mmol) was dissolved in a mixture containing 1.75 mL of oleum (SO₃ in concentrated H₂SO₄, 25 wt%) and 3.25 mL of concentrated H₂SO₄. The mixture was then introduced into a 50 mL glass flask and stirred at 130 °C for 24 h. The product was cooled to room temperature and added to 100 mL of distilled water, filtered and precipitated by 25 mL of concentrated HCl (37 wt%). Finally, the product was filtered, washed with 50 mL of concentrated HCl, and dried at 80 °C under a dynamic vacuum for 24 h to obtain a pure white solid with 80% yield, termed H₃SNDC.

Synthesis of DUT-52

A mixture of ZrCl₄ (230 mg, 0.986 mmol) and H₂NDC (216 mg, 1.000 mmol) was added to a 50 mL Pyrex vial containing DMF (20 mL) and acetic acid (1.1 mL). The mixture was then ultrasonicated in 10 min and heated at 120 °C for 48 h. Next, the solid was centrifugated, washed with DMF for 48 h (30 mL per day), and exchanged with MeOH for 48 h (30 mL per day). Finally, the product was collected, dried, and activated under vacuum at 80 °C for 24 h to obtain a white powder, namely DUT-52.

Section S2. The modelling structure of DUT-52

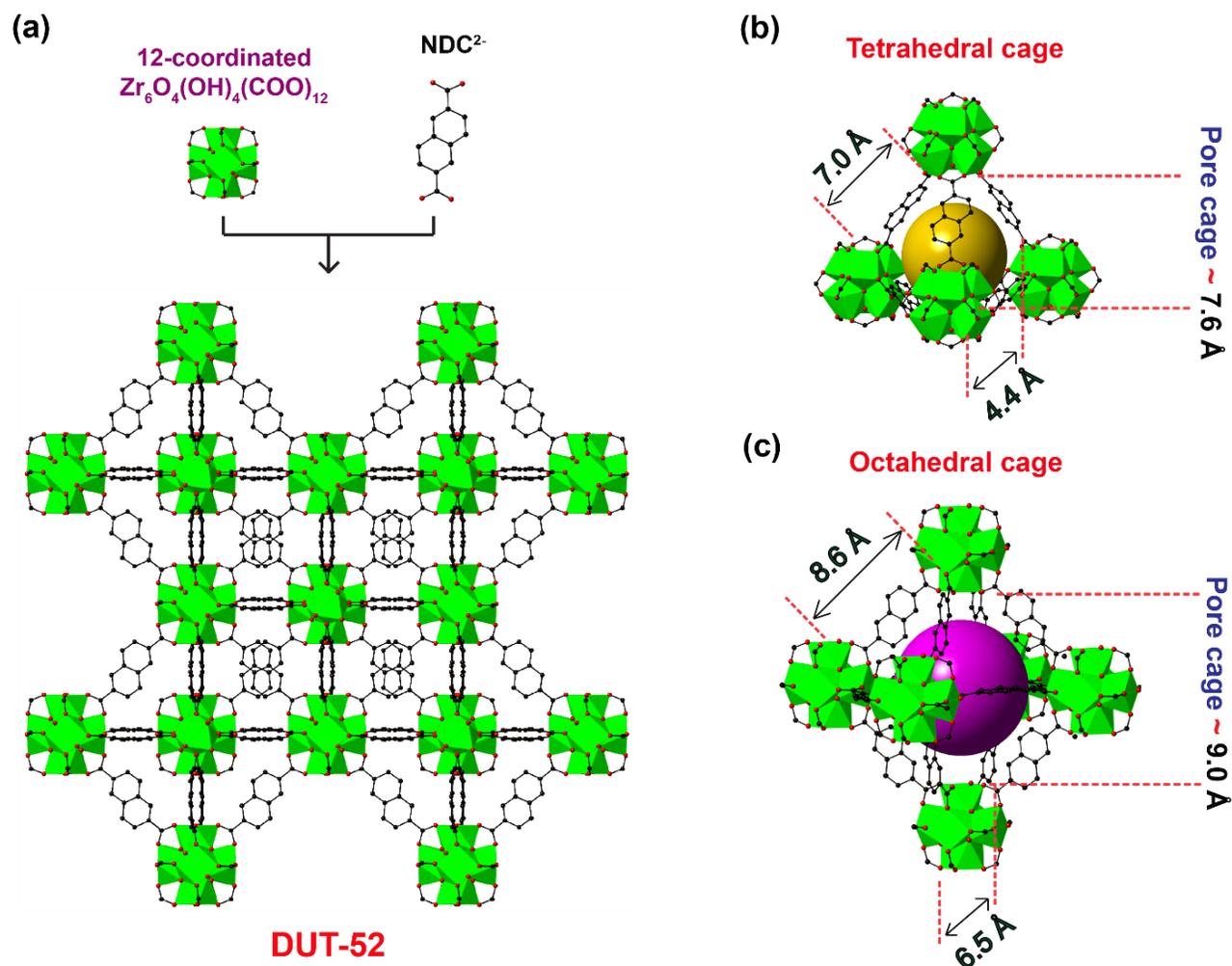


Figure S1. The structure of DUT-52 viewing along the [0 0 1] plane. Atom colors: Zr, green polyhedra; C, black; O, red; all H atoms are omitted for clarity. The pore window and cage size of the material is calculated in the CrystalMarker software.

Section S3. $^1\text{H-NMR}$ analyses of digested $\text{DMA}_{\text{C}}\text{Reo-MOF-1}$, and digested $\text{H}^+\text{CReo-MOF-1}$

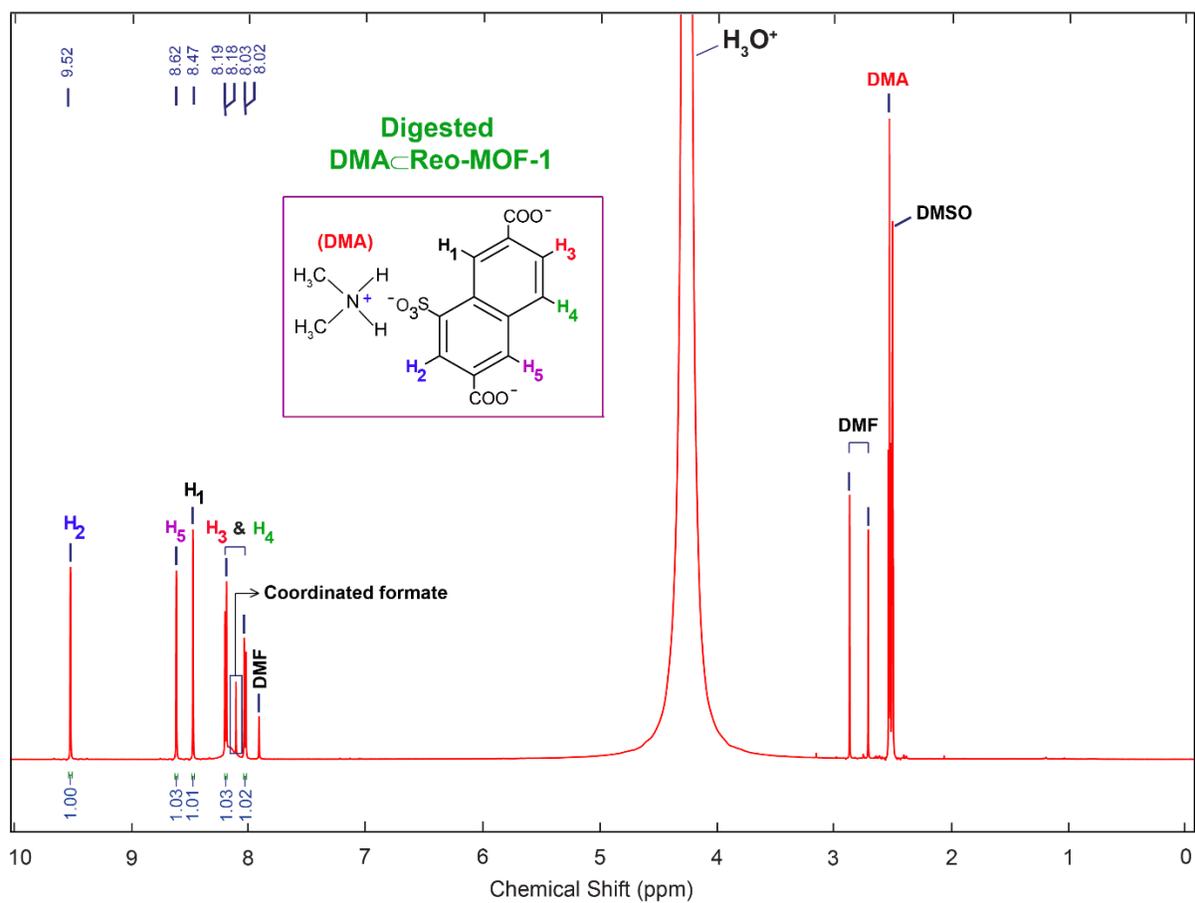


Figure S2. $^1\text{H-NMR}$ analysis of digested $\text{DMA}_{\text{C}}\text{Reo-MOF-1}$.

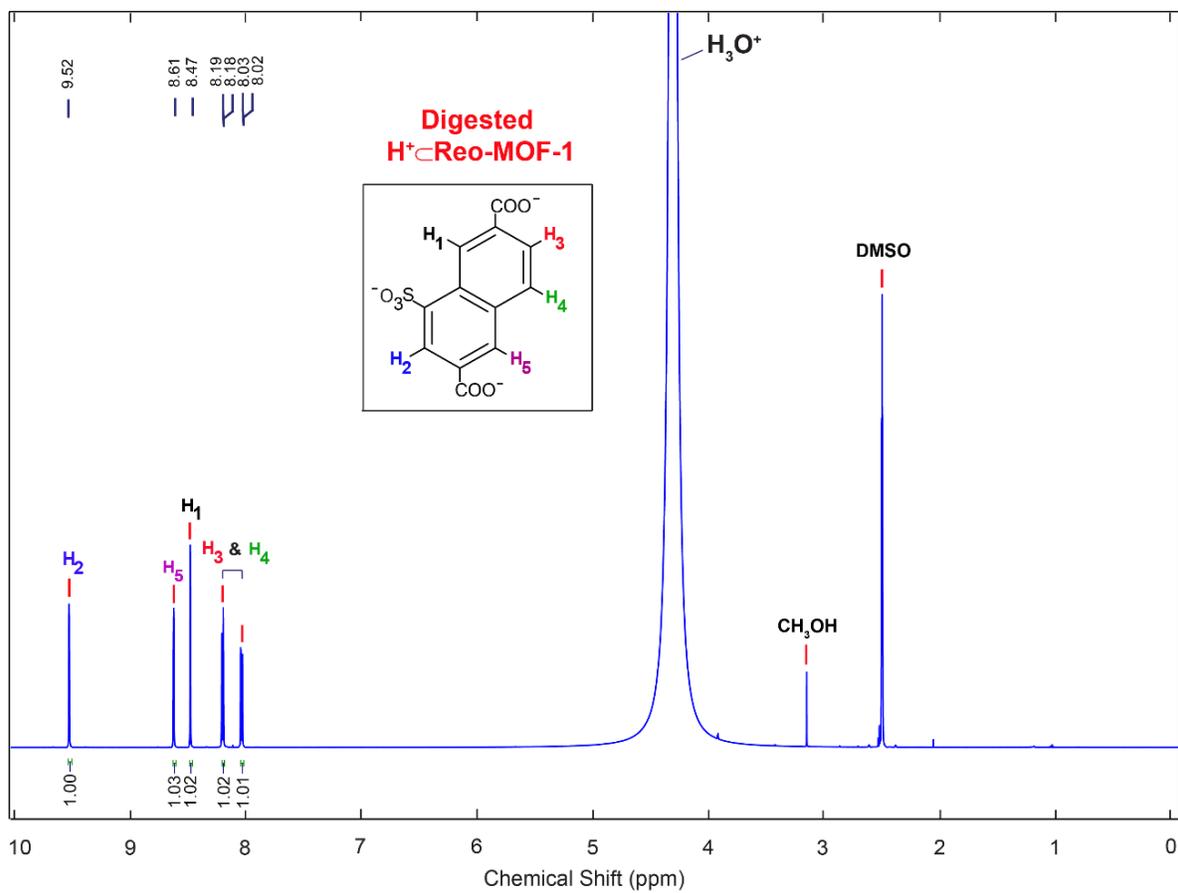


Figure S3. 1H -NMR analysis of digested $H^+Reo-MOF-1$.

Section S4. Powder X-ray diffraction patterns (PXRD)

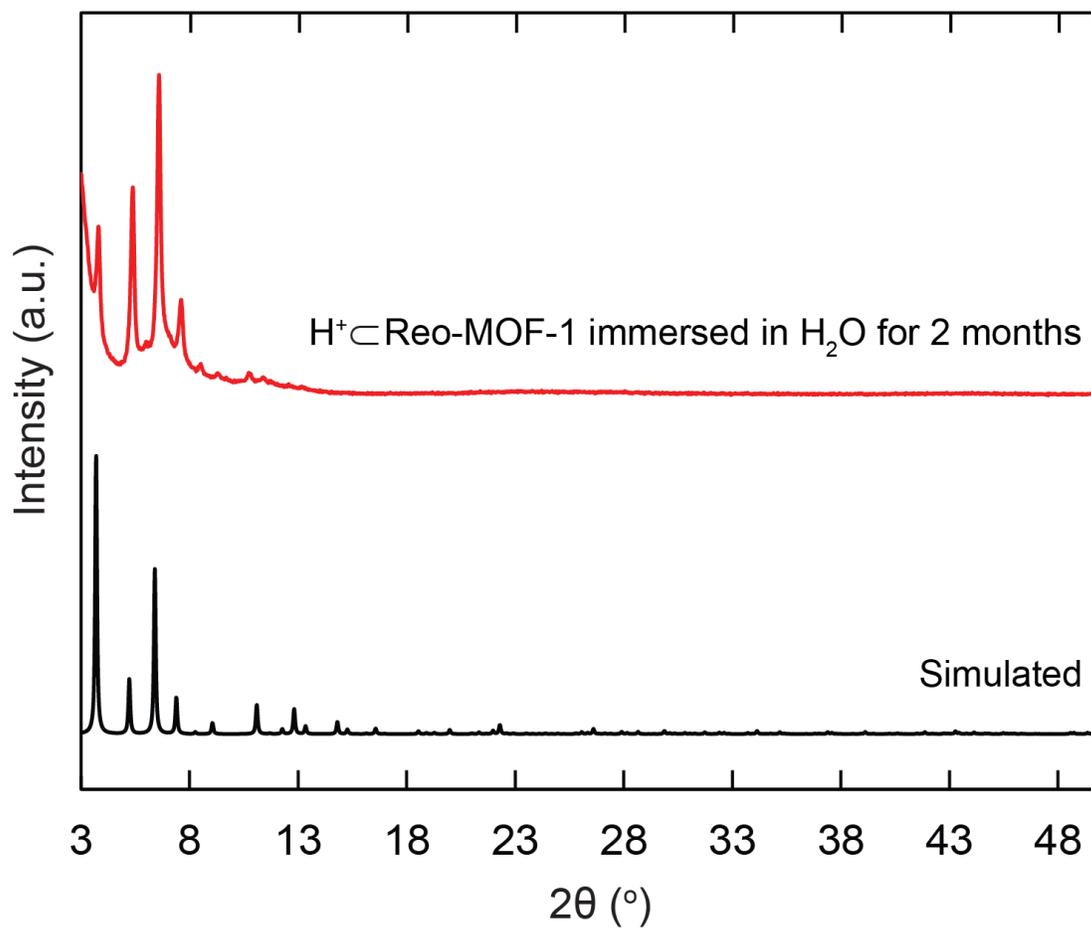


Figure S4. PXRD patterns of simulated structure with reo topology (black) in comparison with H⁺ Reo-MOF-1 soaked in water for 2 months.

Section S5. Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) curves

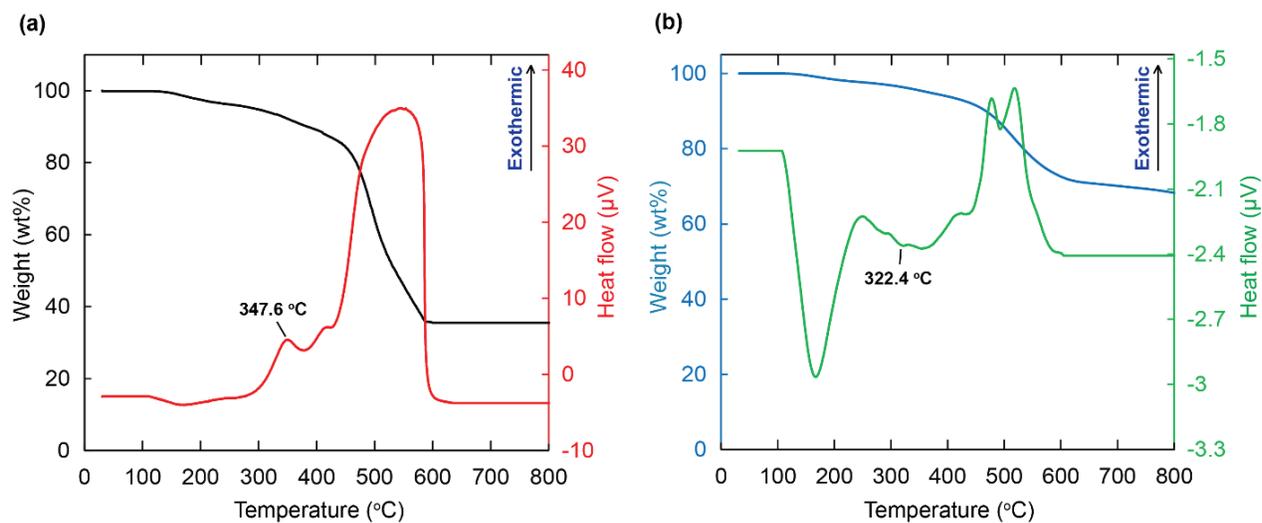


Figure S5. TGA-DSC curves of DMA^cReo-MOF-1 in dry air (a), and in argon (b).

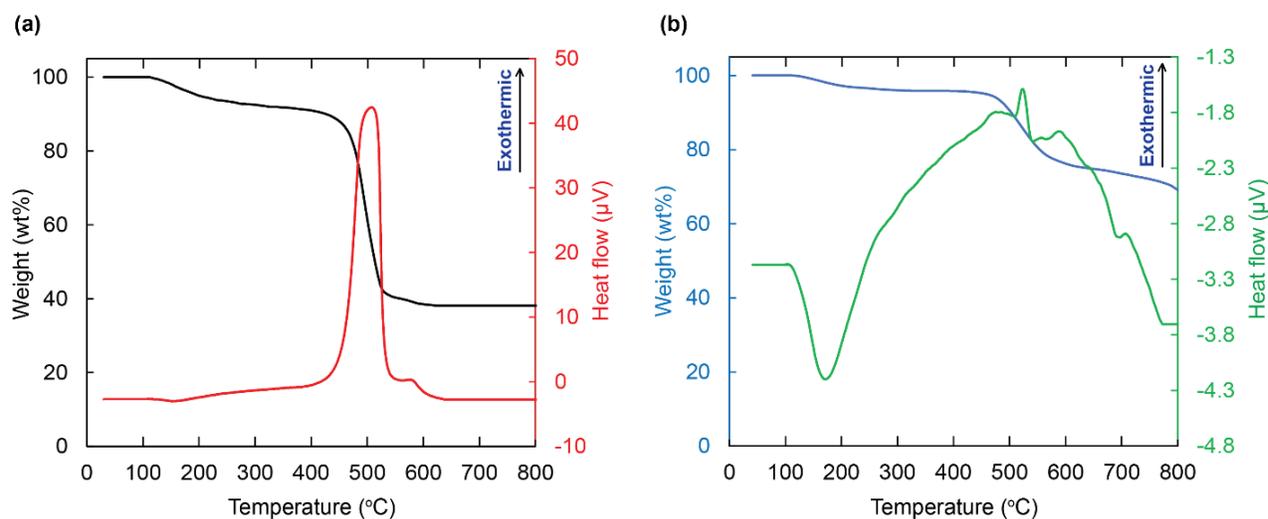


Figure S6. TGA-DSC curves of H⁺Reo-MOF-1 in dry air (a), and in argon (b).

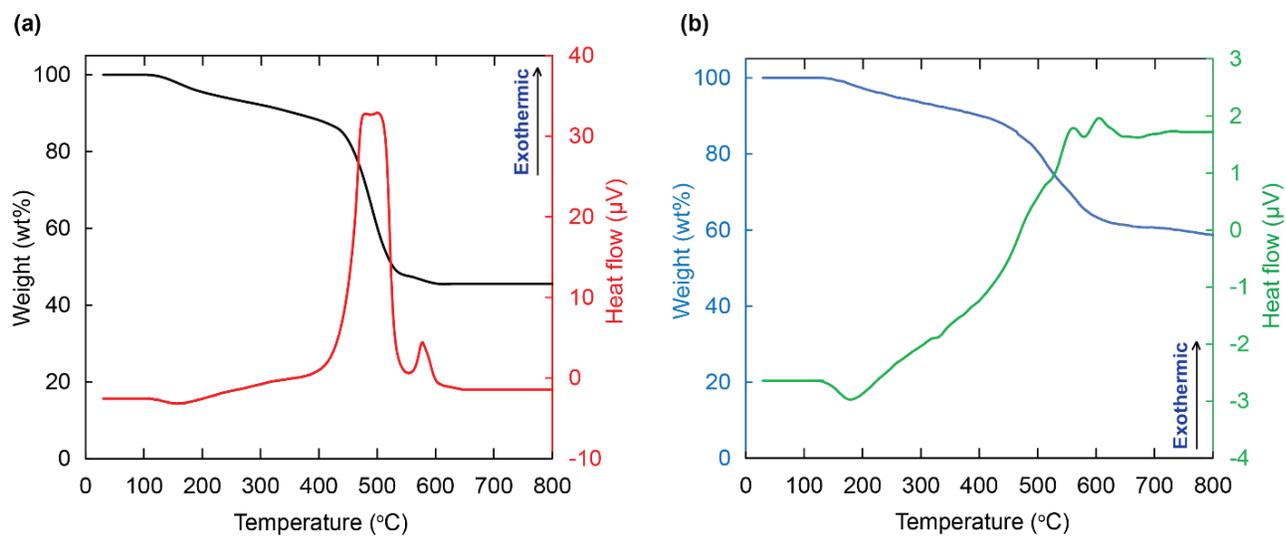
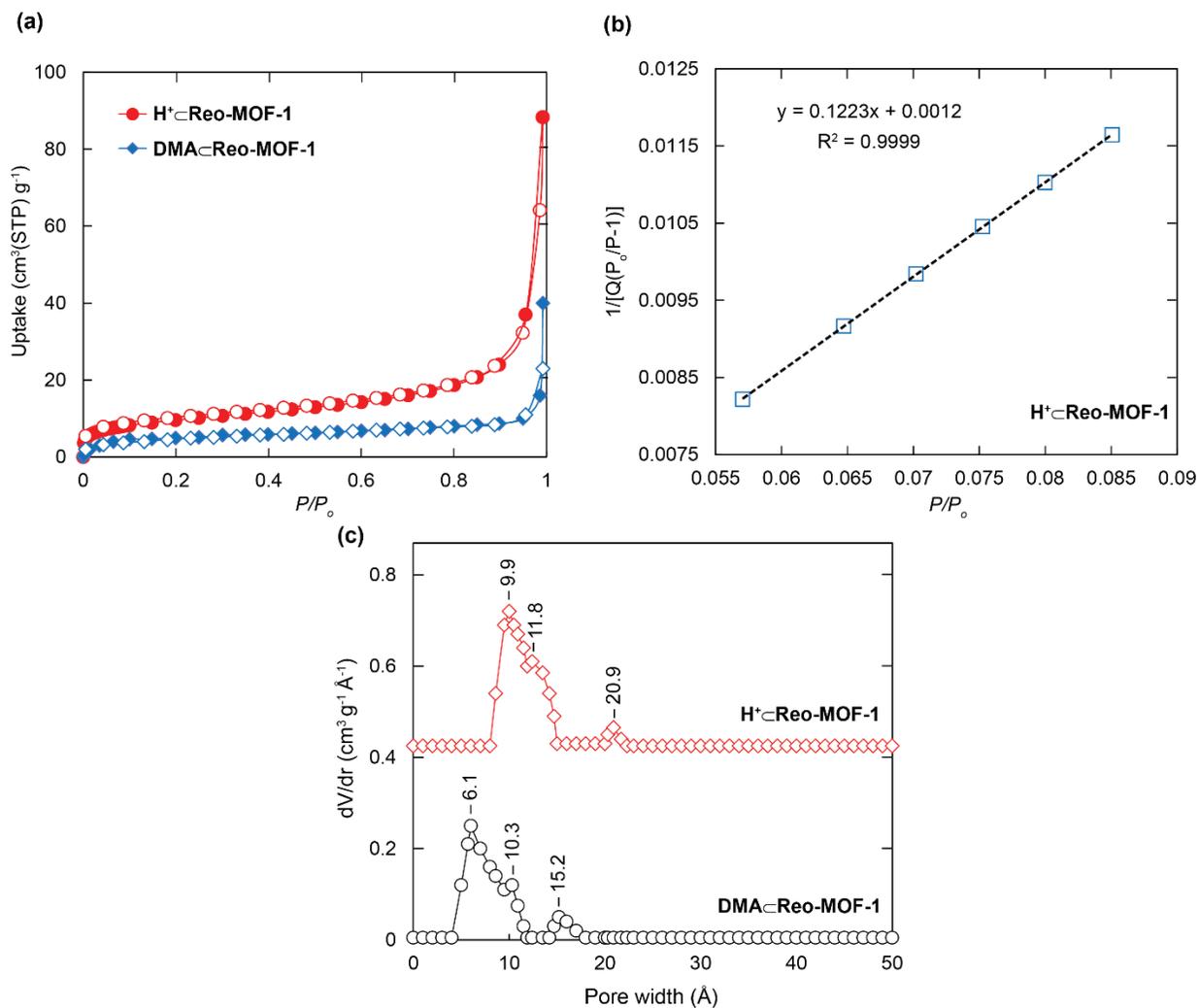


Figure S7. TGA-DSC curves of MG_cReo-MOF-1 in dry air (a), and in argon (b).

Section S6. N₂ adsorption measurement at 77 K



(d)

P/P ₀ range	0.057 – 0.085
Correlation coefficient	0.9999
C	102.92
Q _m (cm ³ g ⁻¹ STP)	8.0970
Molecular cross-sectional area (S / nm ²)	0.1620
BET surface area (m ² g ⁻¹)	35.252

Figure S8. N₂ isotherm and pore size distribution of DMAcReo-MOF-1 and H⁺CReo-MOF-1 at 77 K.

Section S7. Scanning electron microscopy (SEM) and energy-dispersive X-ray mapping (EDX-mapping) analysis

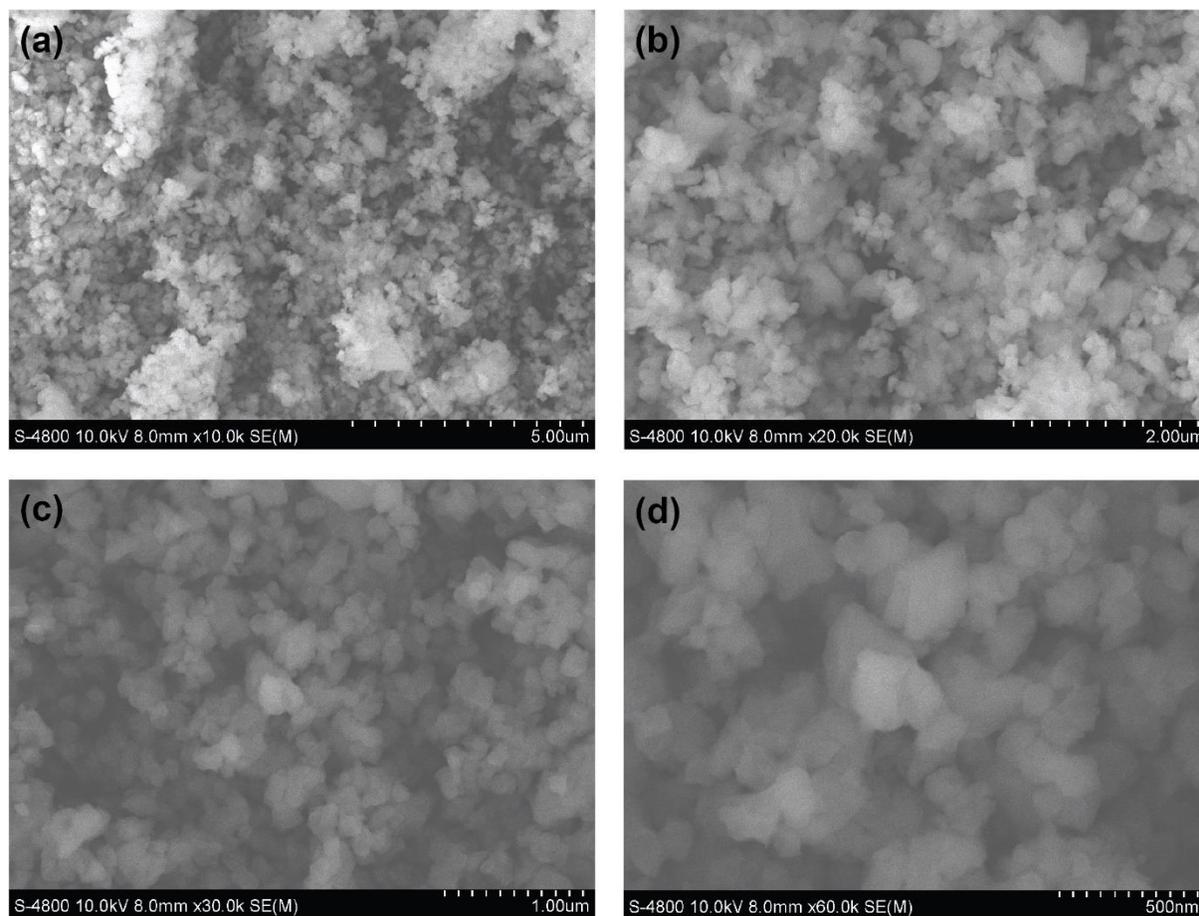
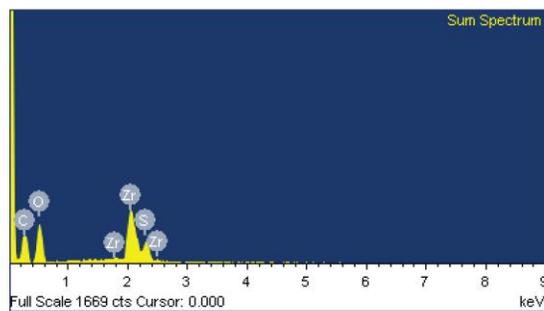


Figure S9. SEM images of H⁺@Reo-MOF-1 at different scale bars of 5.00 μm, 2.00 μm, 1.00 μm and 500 nm, respectively.



**Elemental mapping of
H⁺@Reo-MOF-1**

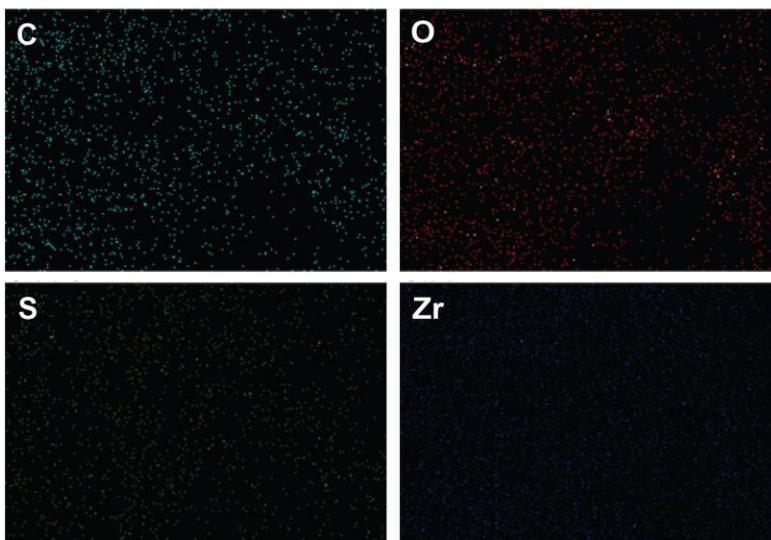
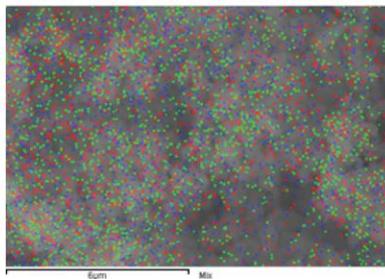


Figure S10. Elemental mapping by SEM-EDX of H⁺@Reo-MOF-1.

Section S8. Transmission electron microscopy (TEM) analysis

H⁺Reo-MOF-1 before adsorption

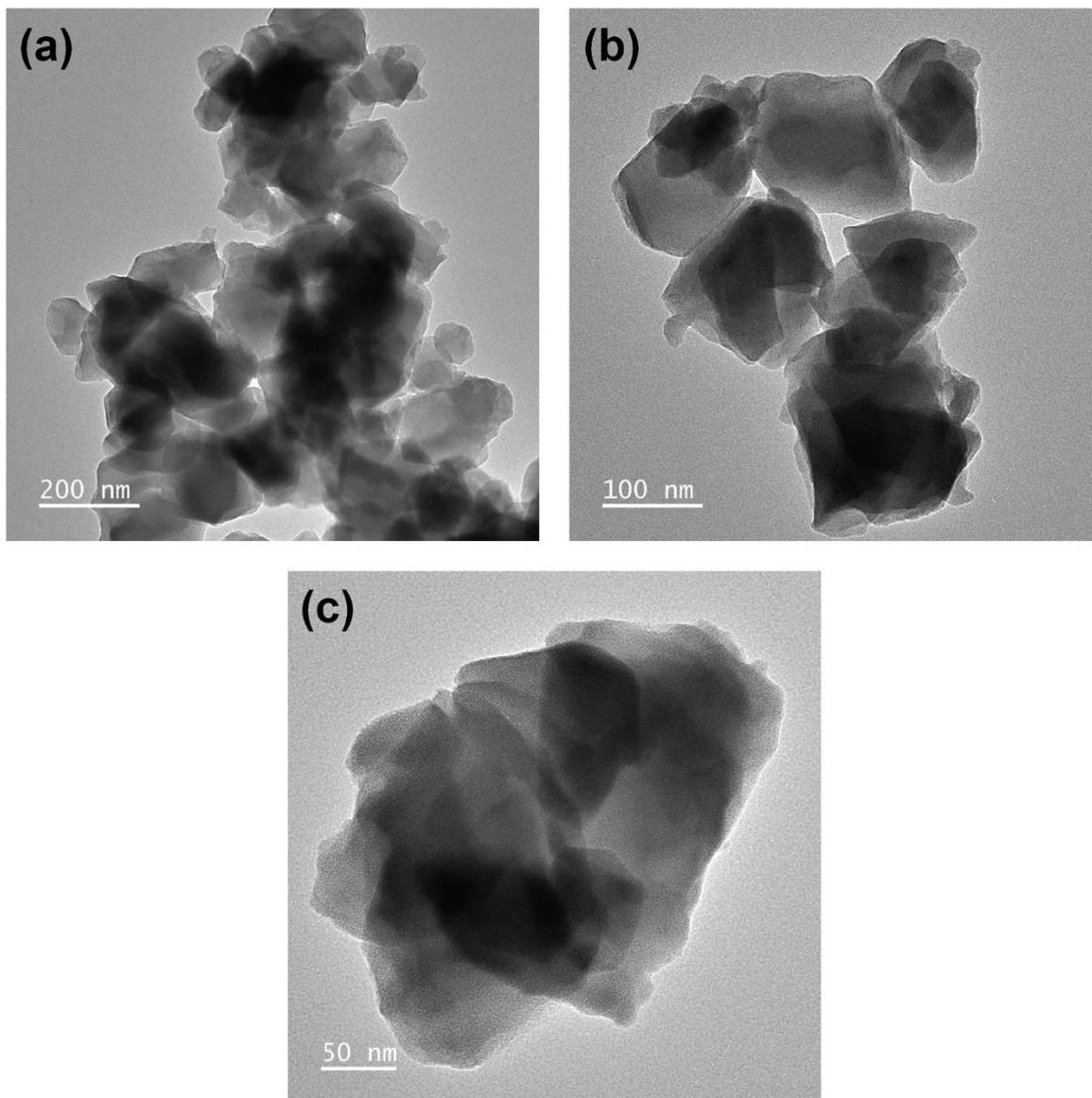


Figure S11. TEM images of H⁺Reo-MOF-1 before adsorption of MG at different scale bars of 200, 100, and 50 nm, respectively.

H⁺Reo-MOF-1 after desorption

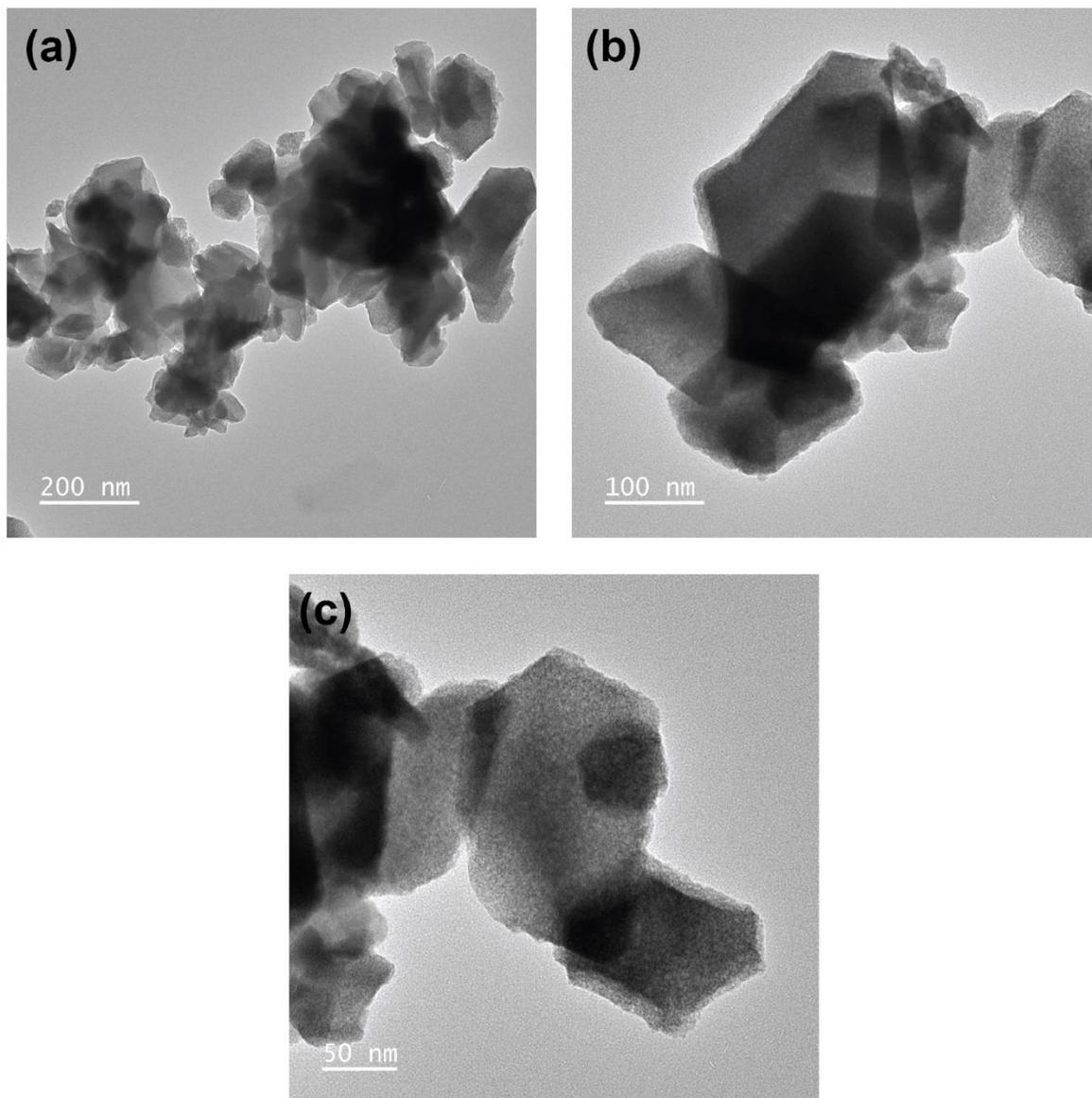


Figure S12. TEM images of H⁺Reo-MOF-1 after desorption of MG at different scale bars of 200, 100, and 50 nm, respectively.

Section S9. Adsorption studies

Adsorption isothermal models

The nonlinear forms of the Langmuir and Freundlich are represented by the equations (1) and (2):

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (\text{S1})$$

$$q_e = K_F \cdot C_e^{1/n} \quad (\text{S2})$$

Where C_e (mg L^{-1}) and q_e (mg g^{-1}) are the MG concentration and adsorption capacity at equilibrium, respectively, q_m (mg g^{-1}) is the theoretical maximum capacity of the MG adsorption. K_L (L mg^{-1}) and K_F ($\text{mg g}^{-1} (\text{L g}^{-1})^{1/n}$) display the constants of Langmuir and Freundlich, respectively. $1/n$ value symbolizes the adsorption capacity index of Freundlich isotherm.

The nonlinear types of the Temkin and Dubinin–Radushkevich (DR) are described by the equations (3) and (4):

$$q_e = \frac{RT}{\beta} \ln(k_T C_e) \quad (\text{S3})$$

$$q_e = q_m \cdot e^{-K_{DR} \cdot \varepsilon^2} \quad (\text{S4})$$

Where R is the gas constant, β and k_T are the constant of adsorption heat and the constant of Temkin, respectively, and T is the adsorption temperature. ε is a constant, K_{DR} and C are the constant of DR isotherm and the adsorption energy per adsorbent molecule, respectively.

The separation factor (R_L) is utilized by equation (5):

$$R_L = \frac{1}{1 + K_L C_o} \quad (\text{S5})$$

Where C_o and K_L are the initial concentration of MG and the constant of Langmuir, respectively.

Adsorption kinetics

The pseudo first order, pseudo second order, and intra-particle diffusion models are displayed by the equations (6), (7), and (8):

$$q_t = q_e \cdot (1 - e^{-k_1 t}) \quad (\text{S6})$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (\text{S7})$$

$$q_t = k_i t^{1/2} + c \quad (\text{S8})$$

Where q_t (mg g^{-1}) and q_e (mg g^{-1}) are the MG uptake amounts at t and equilibrium time, respectively. k_1 (min^{-1}), k_2 ($\text{g mg}^{-1} \text{min}^{-1}$), and k_i ($\text{g mg}^{-1} \text{min}^{-1}$) are the rate constants of pseudo first order, pseudo second order, and intra-particle diffusion models, and c is the constant indicating the thickness of the boundary layer.

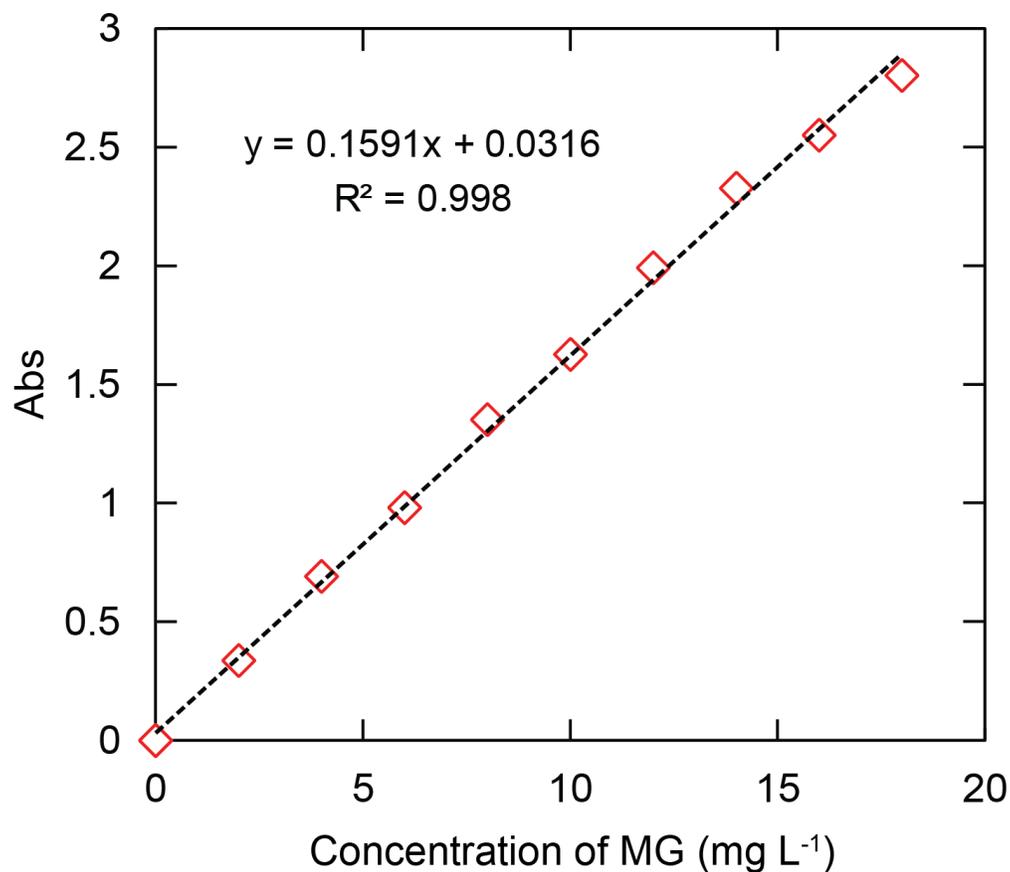


Figure S13. The relationship between the absorbed intensity (red dots) of MG and different concentrations of 0 - 18 mg L^{-1} by linear fitting.

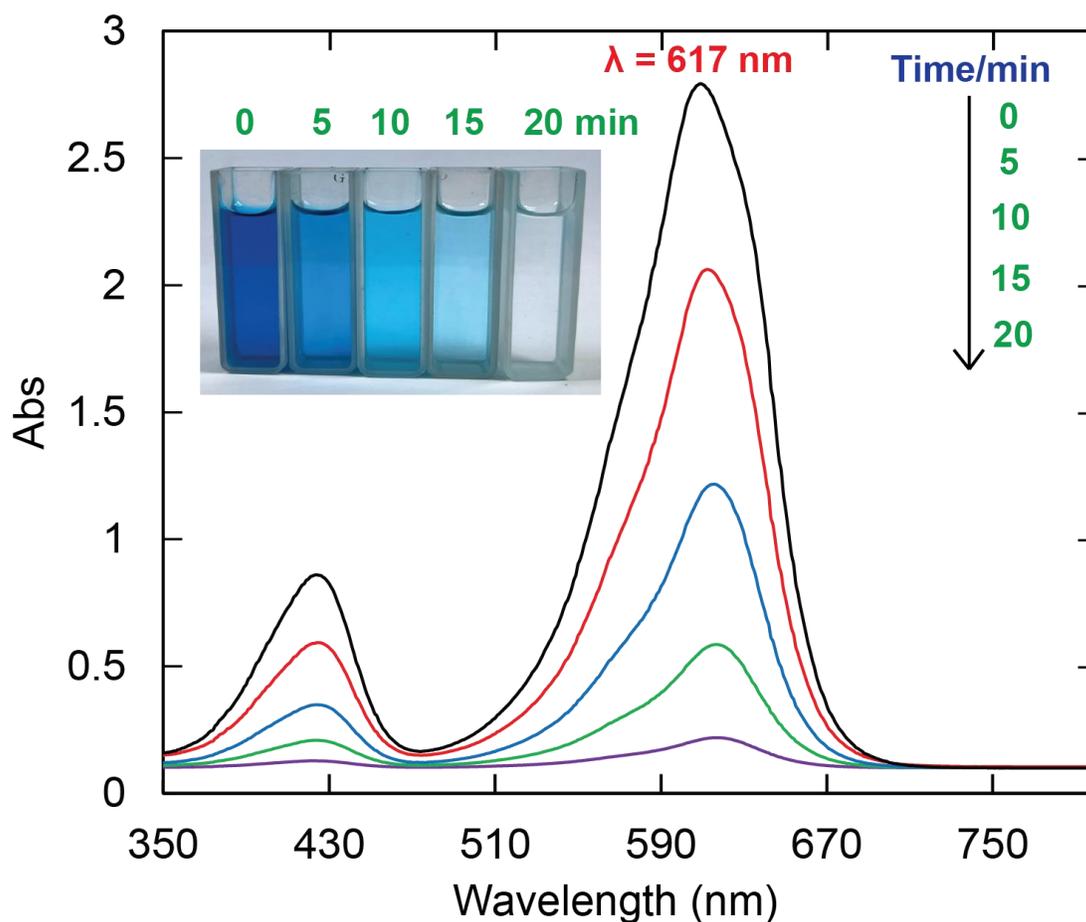


Figure S14. UV-Vis spectra of MG dye after absorbed onto H⁺@Reo-MOF-1 at the intervals of 0, 5, 10, 15 and 20 min, respectively. Herein, 5 mg H⁺@Reo-MOF-1 was introduced into 100 mL of MG solution (18 mg L⁻¹) and stirred at room temperature with the mentioned intervals.

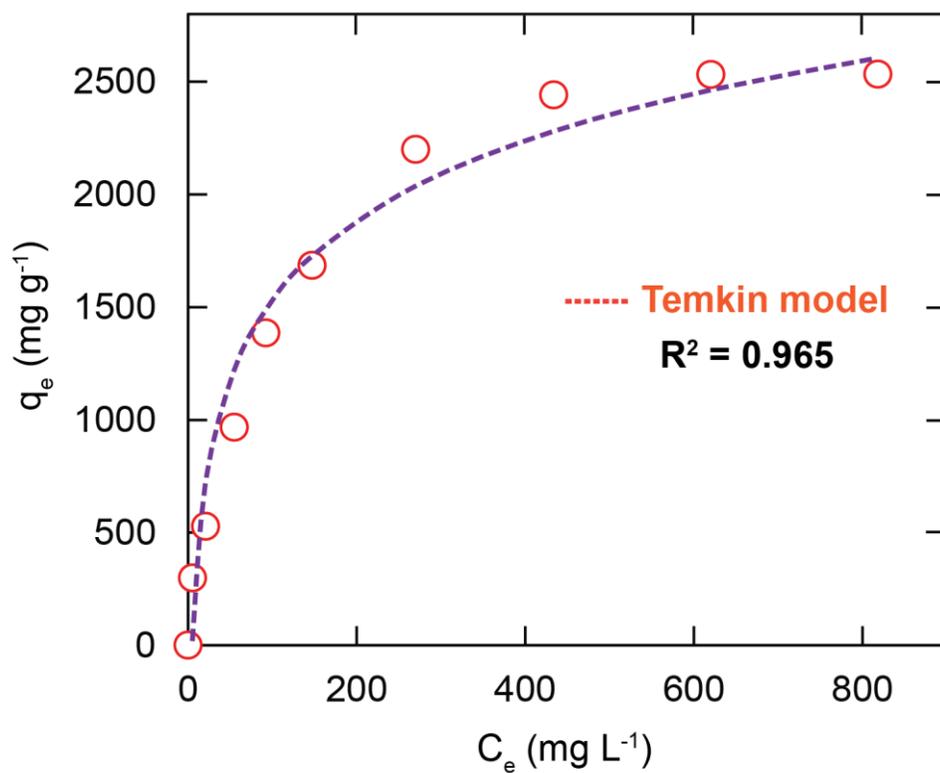


Figure S15. Data fitting with the Temkin adsorption isotherm model of the MG adsorption onto H⁺CReo-MOF-1.

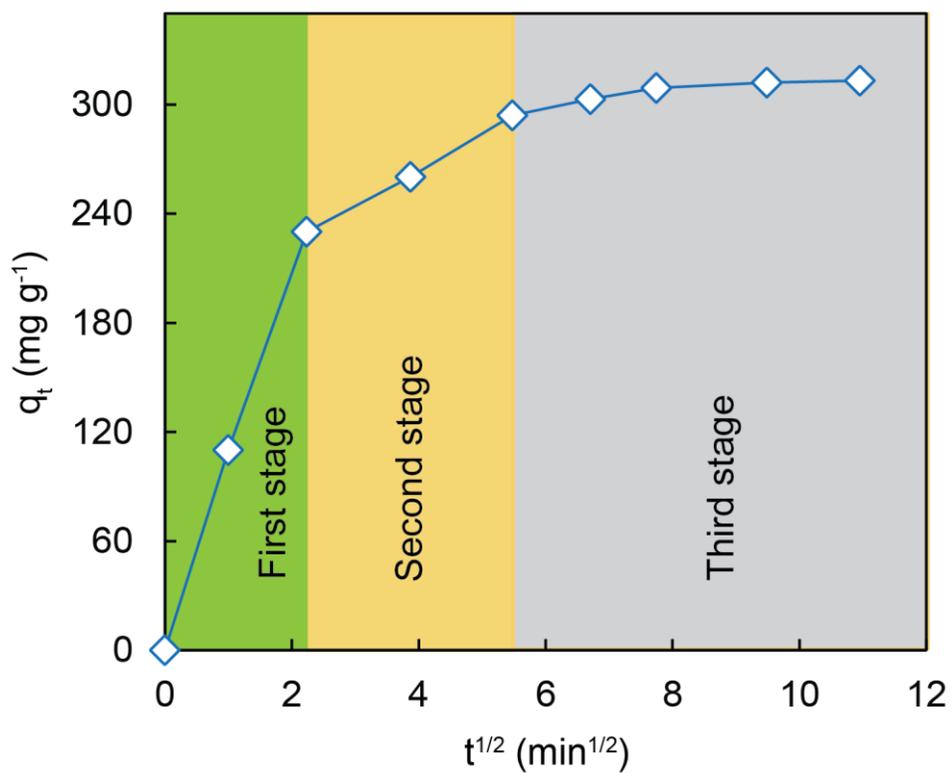


Figure S16. Data fitting with the intra-particle diffusion model of the MG adsorption onto H⁺Reo-MOF-1.

Section S10. The stability of H⁺Reo-MOF-1 during the adsorption and desorption process of MG

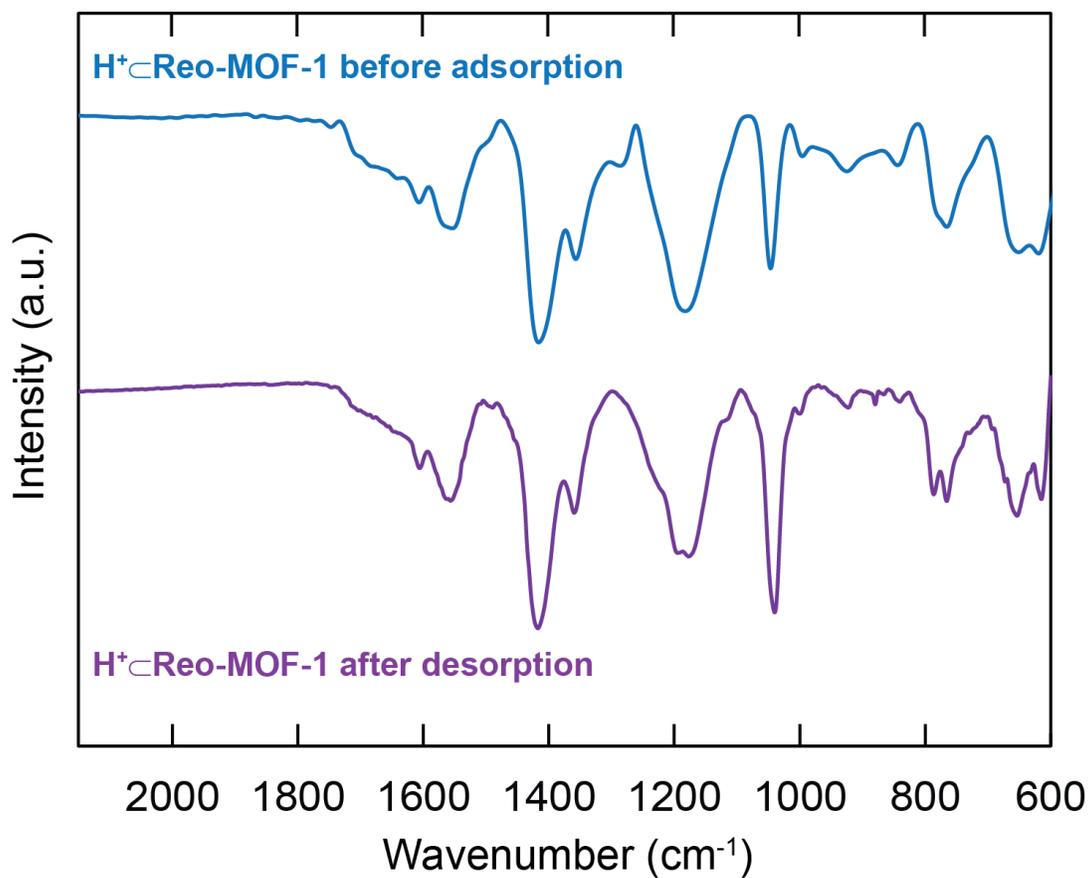


Figure S17. FT-IR spectrum of H⁺Reo-MOF-1 before adsorption of MG (blue) in comparison with FT-IR spectrum of H⁺Reo-MOF-1 after desorption of MG (purple).

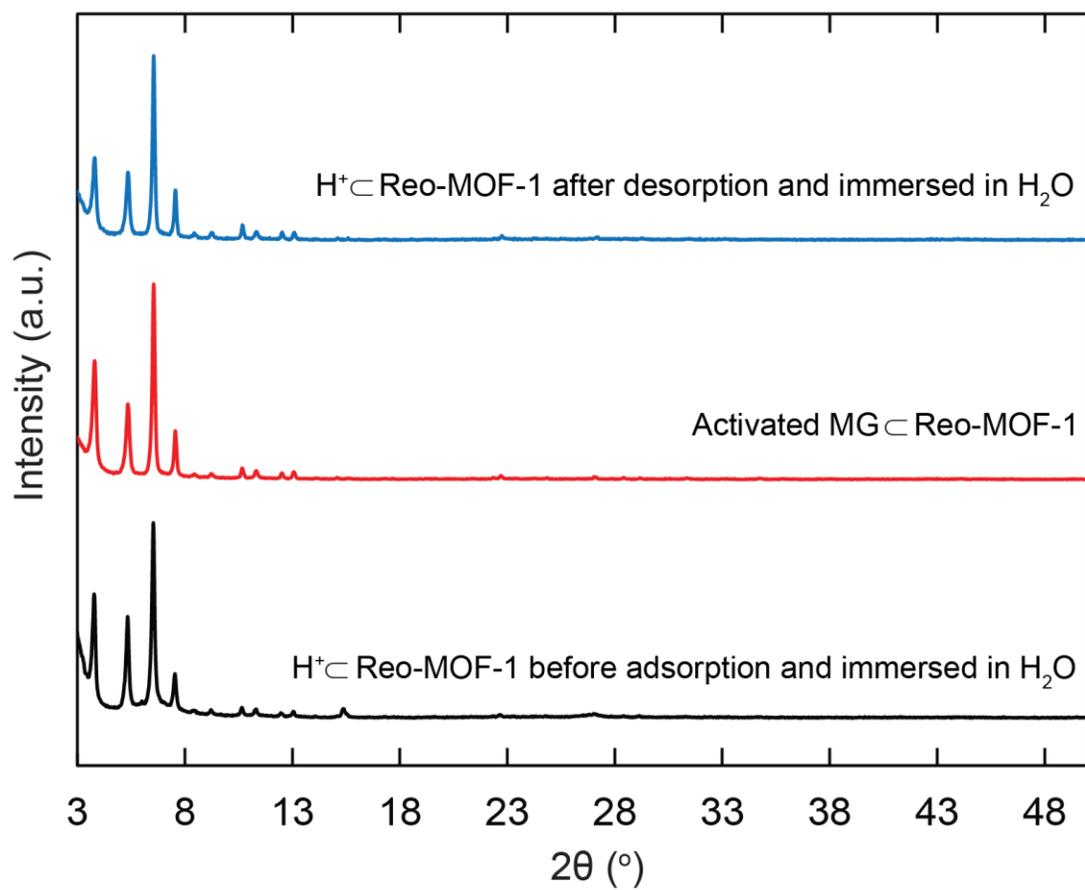


Figure S18. PXRD pattern of H⁺ Reo-MOF-1 before adsorption of MG and immersed in water (black), and activated MG Reo-MOF-1 (red) as compared to the experimental pattern from the subjecting H⁺ Reo-MOF-1 after desorption of MG.