

## Supporting Information

# A Double-walled Thorium-based Metal-Organic Framework (MOF) as a Promising Dual Functional Absorbent for Efficiently Capturing Iodine and Dyes

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## S1. Materials and Instrumentation

**Caution!** Thorium is a chemically toxic and radioactive element, so standard precautions to handle radioactive substances must be followed. Ligand H<sub>3</sub>TATAB was prepared with reference to the literature<sup>1-2</sup> with minor modifications. The other chemical reagents and solvents were all purchased commercially without further purification. The collection of PXRD data is carried out on Advance D8 Powder X-ray Diffractometer in the 2 $\theta$  range of 5 to 55° with a step size of 0.02° and a scanning rate of 3°/min using Cu–K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Thermal stability of Th-TATAB was measured from 30 °C to 800 °C under the N<sub>2</sub> atmosphere with a constant heating rate of 10 °C/min by PerkinElmer Diamond TG/DTA. Infrared (IR) spectra were determined using KBr pellets in the range of 400- 4000 cm<sup>-1</sup> on Bruker AXS TENSOR-27 FT-IR spectrometer. The solid-state UV-Vis spectra were recorded in the range of 200–1000 nm in form of solid sample on JASCO V-570 spectrometer. UV-vis absorption spectra were recorded on a Lambda35 spectrophotometer within the wavelength range 190–

600 nm. The  $^1\text{H}$  spectra was measured on a Bruker Avance II 400 Nuclear Magnetic Resonance Spectrometer. The  $\text{N}_2$  sorption isotherm measurements were carry out on a Autosorb iQ2 adsorptometer, Quantachrome Instrument at 77 K. Elemental analyses for C, H, and N were performed on a Perkin Elmer 240C automatic analyzer.

## S2. Synthesis of Ligand $\text{H}_3\text{TATAB}$ and Th-TATAB

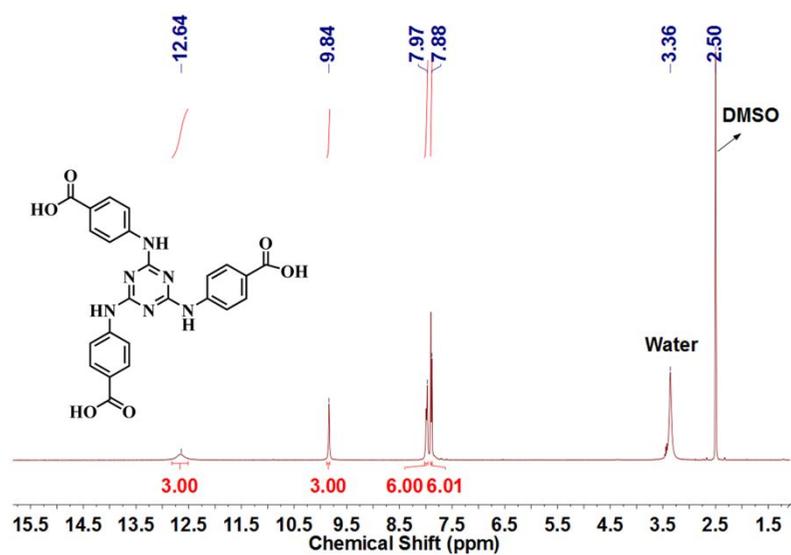
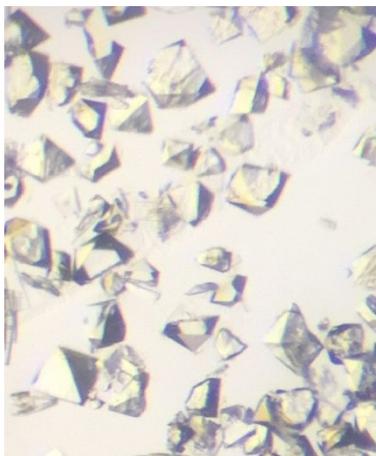


Figure S1.  $^1\text{H}$ -NMR spectrum of  $\text{H}_3\text{TATAB}$  in  $\text{DMSO-d}_6$ .

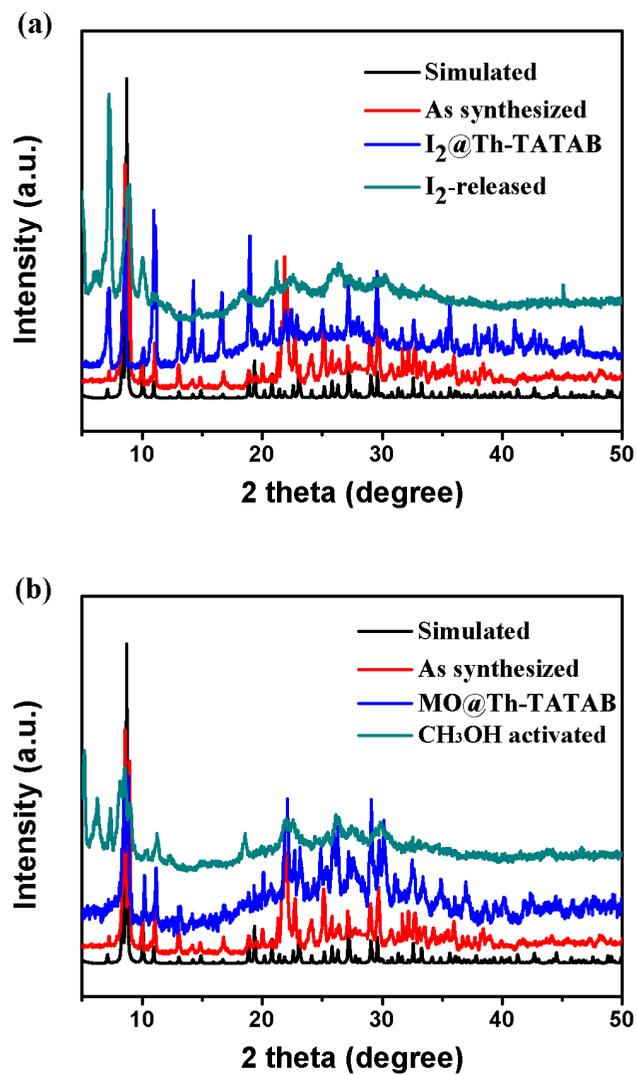
## S3. The photograph of crystals of Th-TATAB



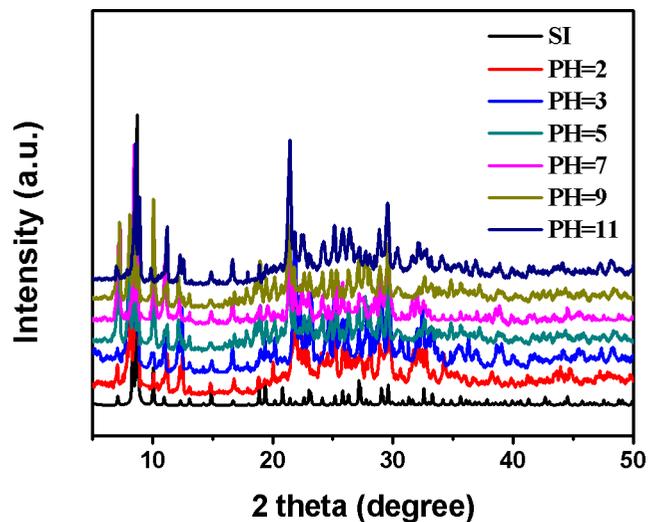
**Figure S2.** The photograph of crystals of Th-TATAB.

#### **S4. Powder X-ray Diffraction Analyses**

The powder X-ray diffraction data of the compounds Th-TATAB was obtained and compared with the simulated single-crystal diffraction data (Fig S3). The corresponding compound is considered as pure phase owing to the basic agreement of the peak positions. The different intensity may be due to the preferred orientation of the powder samples. The peak positions in the powder XRD of  $I_2@Th-TATAB$  and  $MO @Th-TATAB$  are basically consistent with that of the compound Th-TATAB, indicating that the host framework after adsorbing the iodine and dye is retained, but the absorption peaks of  $I_2@Th-TATAB$  are significantly broadened (Fig S3 and S4).



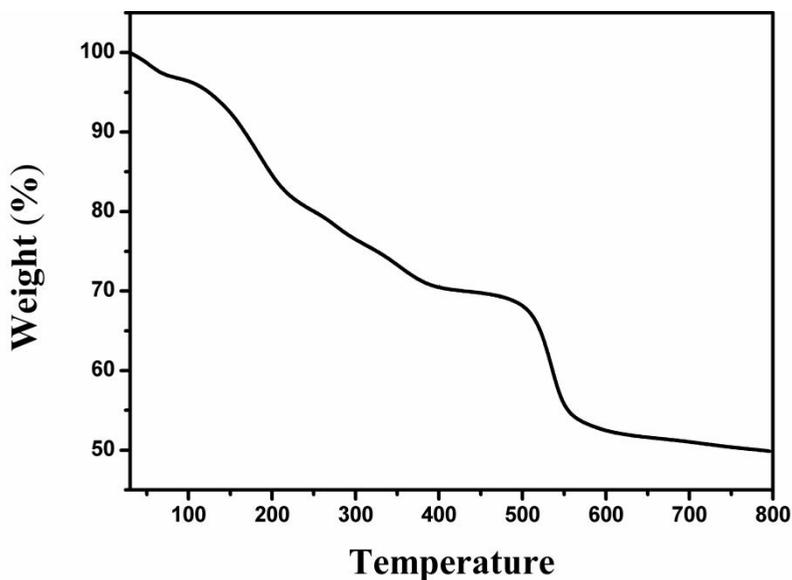
**Figure S3.** (a) PXRD of the simulated, as-synthesized,  $I_2@Th-TATAB$  and  $I_2$ -released; (b) PXRD of the simulated, as-synthesized,  $MO@Th-TATAB$  and samples activated with methanol.



**Figure S4.** PXRD patterns of Th-TATAB after being soaked 24h in aqueous solutions at PH=2-11.

#### **S5. Thermogravimetric analysis.**

TGA analysis (Figure S5) suggests that the framework of Th-TATAB is stable before 400 °C. Before 400 °C, the weight loss is assigned to the elimination of coordination water molecule, free water molecules and DMF from the pores. At 500 °C, the collapse of the structure is observed, and the finally relative plateau corresponds to thorium oxide (ThO<sub>2</sub>).

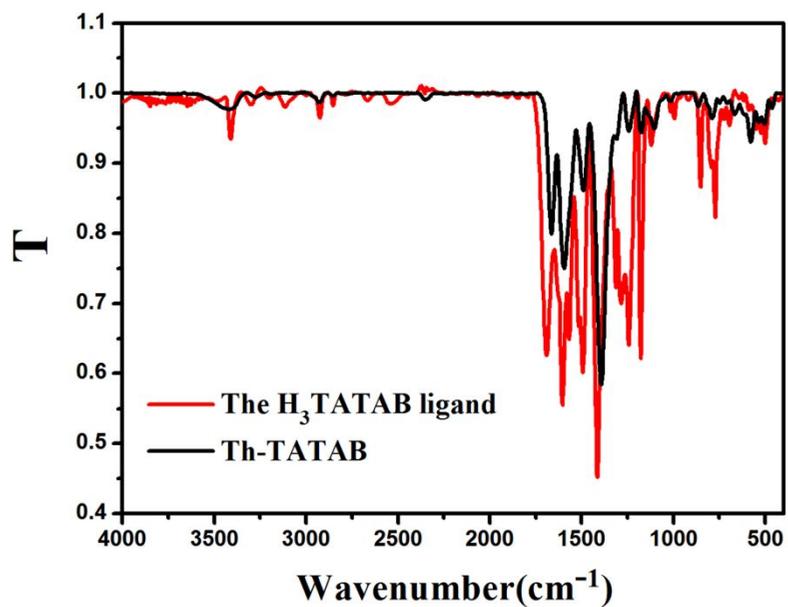


**Figure S5.** The TGA curve of Th-TATAB

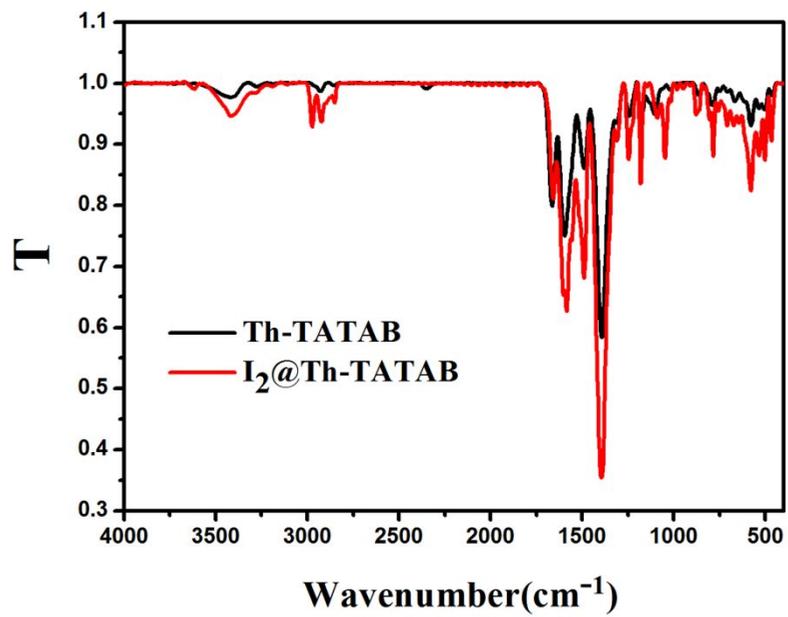
## S6. IR spectra

The synthesized ligand H<sub>3</sub>TATAB and thorium compounds Th-TATAB were characterized by IR spectra as shown in Fig S6. For Th-TATAB, the peaks at 1659 cm<sup>-1</sup> and 1594 cm<sup>-1</sup> can be attributed to the C=O asymmetric stretching vibrations. The C=C and C=N bands on benzene ring and triazine in-plane are observed at about 1486 cm<sup>-1</sup>. Strong absorption peaks at 1383 cm<sup>-1</sup> correspond to the C=O symmetric stretching vibrations. A broad band is observed around 3400 cm<sup>-1</sup> and attributed to stretching vibration of O-H from H<sub>2</sub>O. Compared with the infrared spectra of the ligand H<sub>3</sub>TATAB, the C=O asymmetric and symmetric stretching vibrations of Th-TATAB shifted from 1689 and 1417 cm<sup>-1</sup> to 1659 and 1383 cm<sup>-1</sup>, which red shifted by 30 and 34 cm<sup>-1</sup>, respectively. It can be concluded that the thorium center is coordinated with the carboxyl oxygen atoms from the ligand

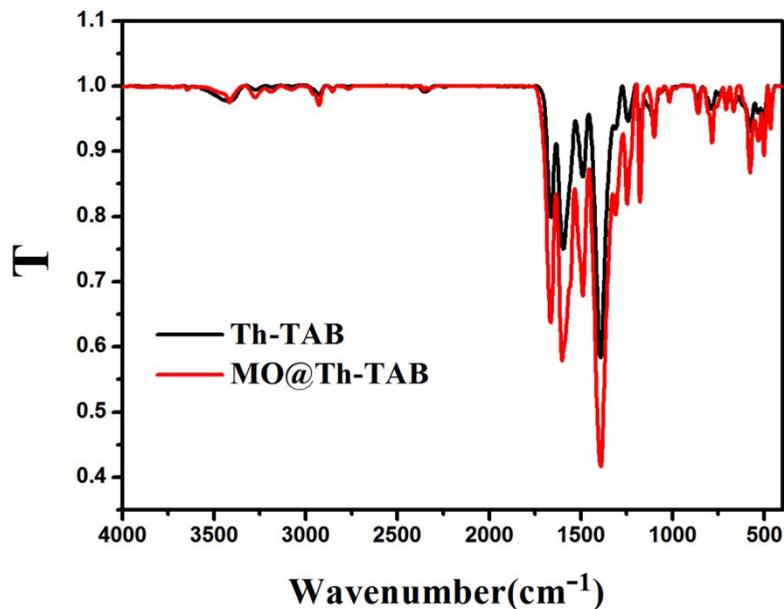
H<sub>3</sub>TATAB. When comparing the infrared spectra of Th-TATAB, it can be seen that the iodine-loaded and MO-loaded networks exhibits significantly enhanced benzene and triazine ring vibrations (Fig S7 and S8).



**Figure S6.** Infrared spectra of ligand H<sub>3</sub>TATAB and Th-TATAB.



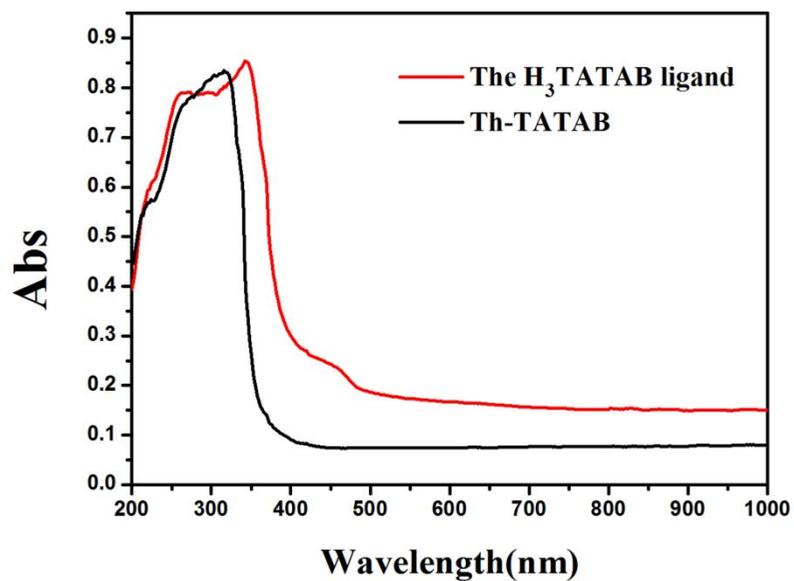
**Figure S7.** Infrared spectra of Th-TATAB and  $\text{I}_2@$ Th-TATAB.



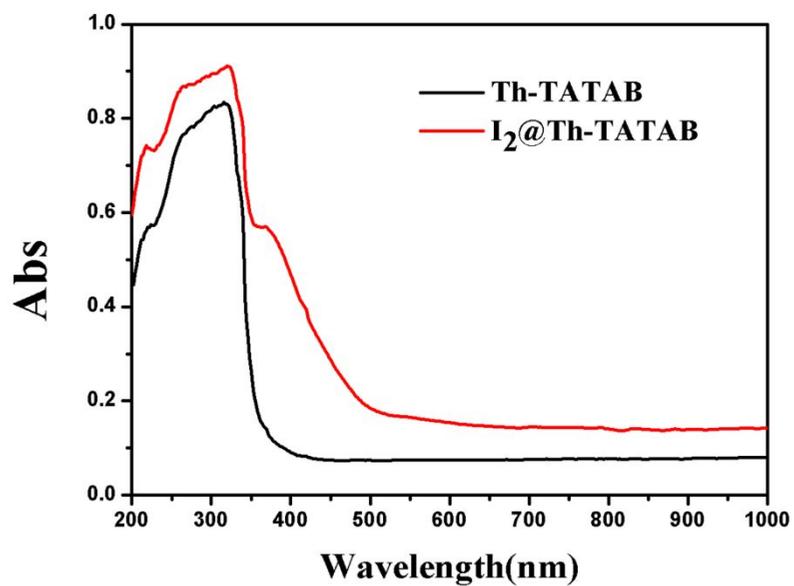
**Figure S8.** Infrared spectra of Th-TATAB and MO@Th-TATAB.

### S7. The solid-state UV-Vis absorption spectra

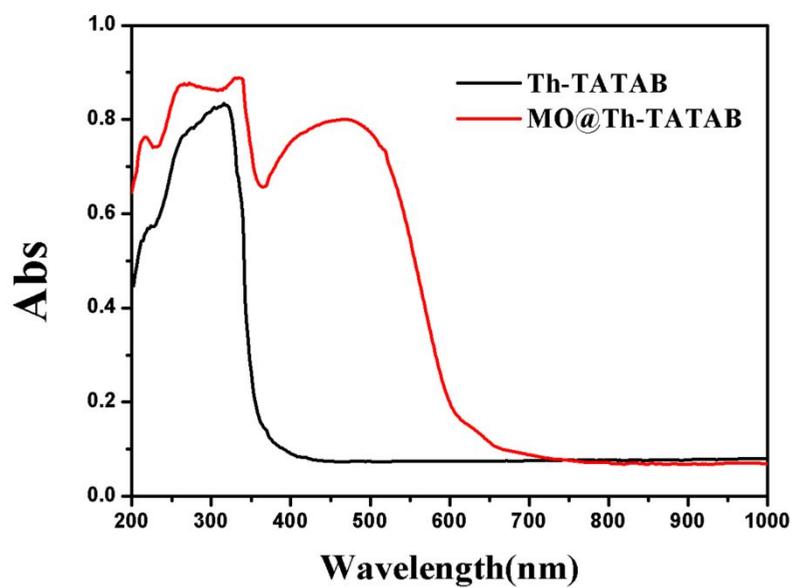
The absorbance spectra for ligand H<sub>3</sub>TATAB and compound Th-TATAB were collected. As shown in Fig S9, for ligand H<sub>3</sub>TATAB, the three absorption peaks appearing at about 221, 259 and 341 nm can be attributed to the  $\pi \rightarrow \pi^*$  transition of the ligand; for Th-TATAB, the absence of the bands at about 221, 259 nm are associated with the  $\pi \rightarrow \pi^*$  transition of the ligand, while absorption peaks at 341 nm correspond to the ligand-to-metal transition (LMCT). Compared with the UV-Vis spectrum of the complex, the absorption band of I<sub>2</sub>@Th-TATAB is significantly broadened (Fig S10). Moreover, the band centered around 350 nm is characteristic for a charge transfer complex involving iodine I<sub>2</sub> [see for instance the same observation reported by R.J. Session *et al.* Chem. Phys. Letters 242



**Figure S9.** The solid-state UV-Vis spectra of ligand H<sub>3</sub>TATAB and Th-TATAB.



**Figure S10.** Solid-state UV-Vis spectra of Th-TATAB and I<sub>2</sub>@Th-TATAB.



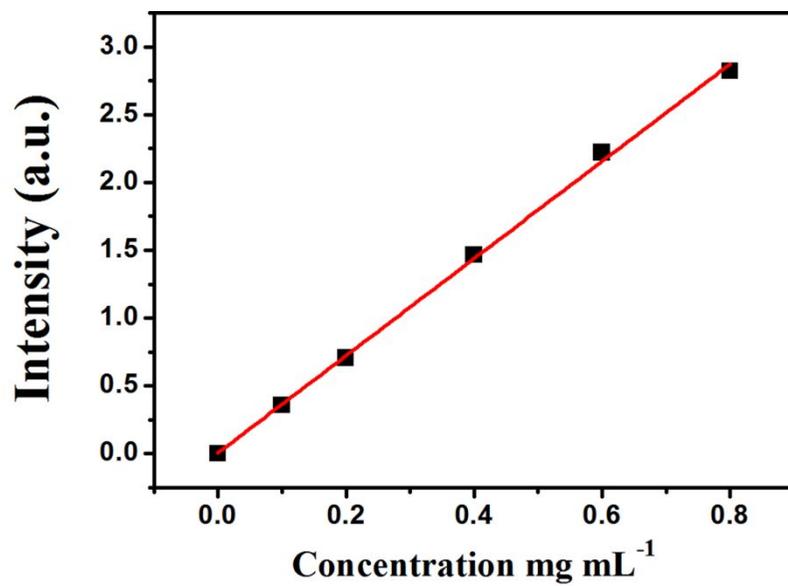
**Figure S11.** Solid-state UV-Vis spectra of Th-TATAB and MO@Th-TATAB.

### **S8. Capture and Release of Iodine experiments.**

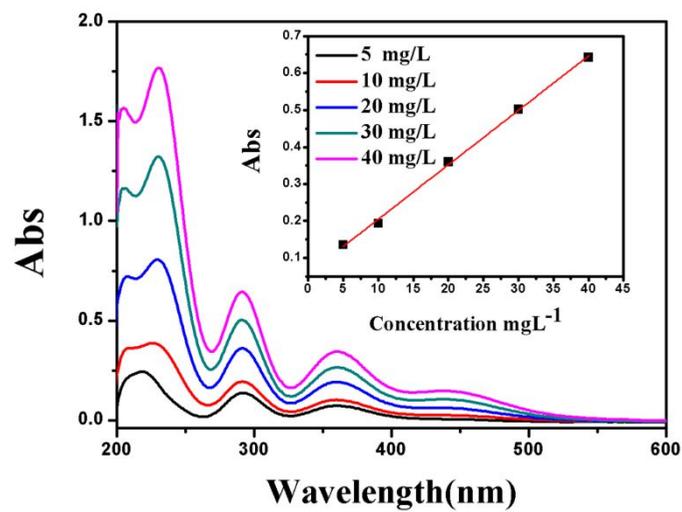
pseudo- second -order equation :<sup>3</sup>

$$\frac{t}{Q_t} = \frac{1}{Q_e^2 k_2} + \frac{t}{Q_e}$$

where  $Q_e$  (mg/g) is the equilibrium adsorption amount,  $Q_t$  (mg/g) is the adsorption amount of the adsorbent at any time  $t$ , and  $k_2$  represents the pseudo-second-order rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ ).

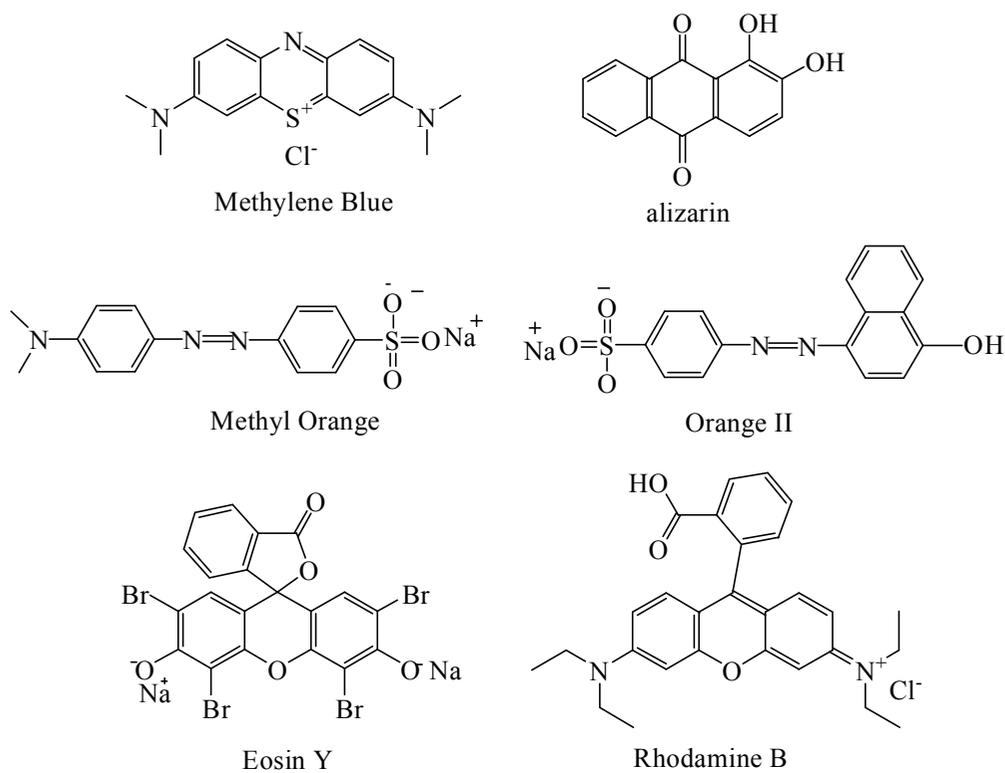


**Figure S12.** Calibration plot of standard iodine by UV-Vis spectra in cyclohexane solution.



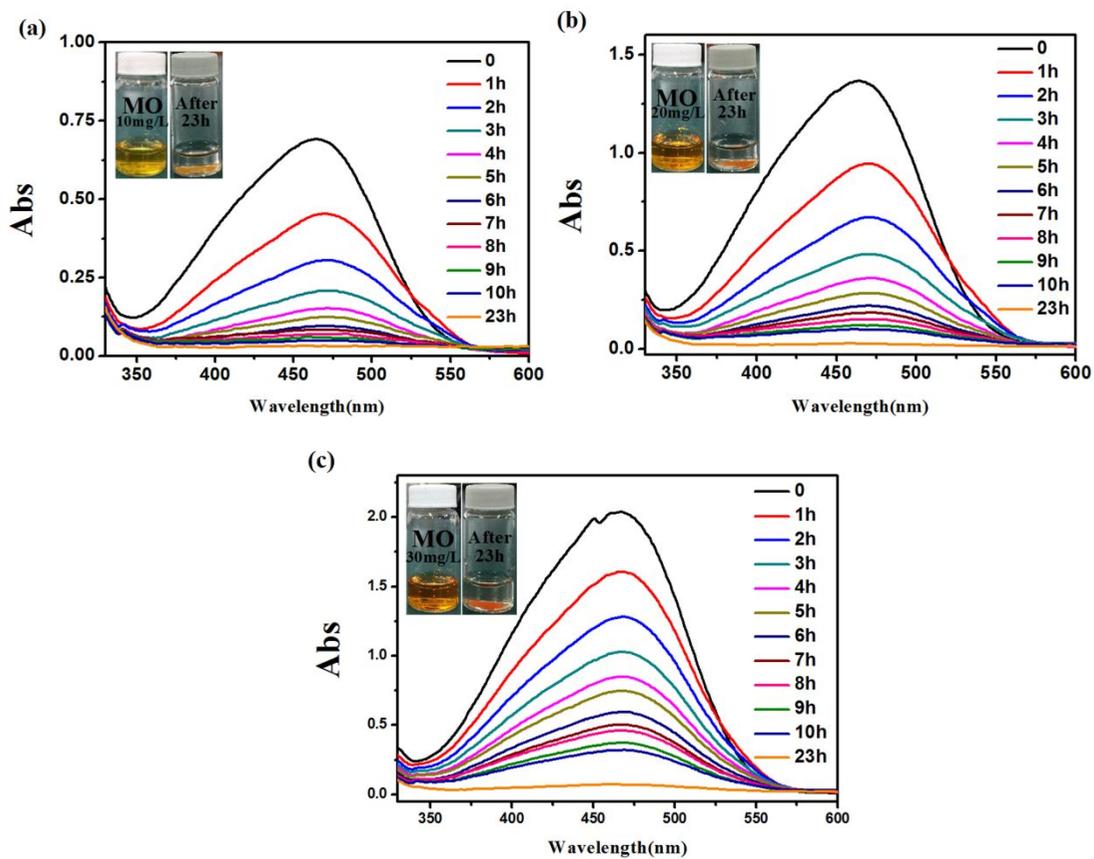
**Figure S13.** Calibration plot of standard iodine by UV-Vis spectra in ethanol solution.

**S9. Dye adsorption experiments measurements.**

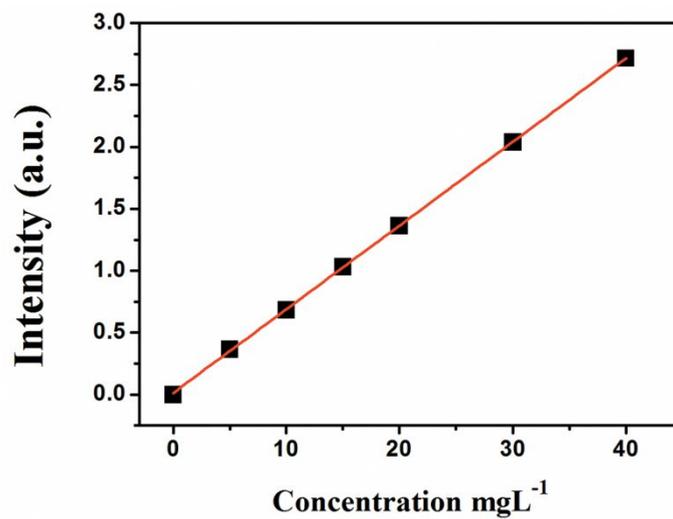


**Fig S14.** Structures of the dye molecules used in the dye adsorption experiment.

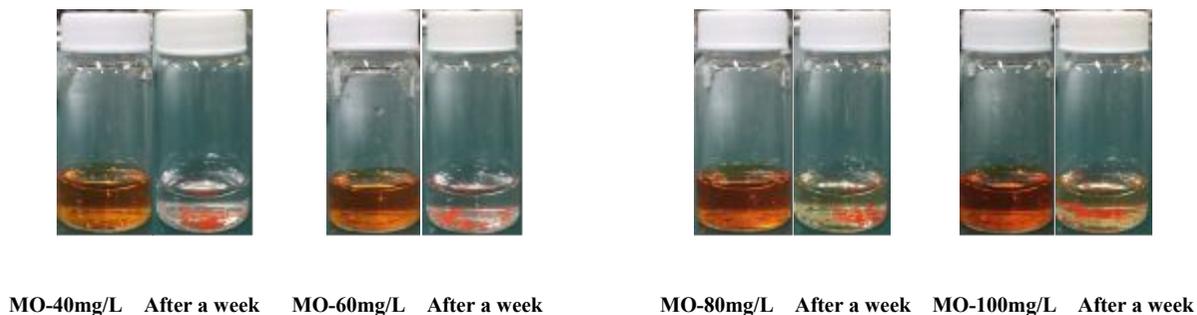
**Effect of initial concentrations on adsorptive removal of methyl orange.**



**Fig S15.** UV-Vis spectra of MO as a function of time at different initial concentrations (10, 20, 30  $\text{mgL}^{-1}$ ). The insets show the color changes of the dye solution before and 23 h after adsorption.



**Fig S16.** Calibration curves for dyes MO ( $R^2 = 0.9999$ )



**Fig S17.** The photographs showing the colours of the MO dye solutions before and after adsorption

## References

1. Xi-Sen, W.; Shengqian, M.; Daofeng, S.; Sean, P.; Hong-Cai, Z., A mesoporous metal-organic framework with permanent porosity. **2006**, *128*, 16474-16475.
2. Fang, Q. R.; Yuan, D. Q.; Sculley, J.; Li, J. R.; Han, Z. B.; Zhou, H. C., Functional mesoporous metal-organic frameworks for the capture of heavy metal ions and size-selective catalysis. *Inorg. Chem.* **2010**, *49*, 11637-11642.
3. El-Khaiary, M. I.; Malash, G. F.; Ho, Y. S. J. D., On the use of linearized pseudo-second-order kinetic equations for modeling adsorption systems. **2010**, *257*, 93-101.