

## Supplementary Material

### Fluorescein Hydrazide Appended Metal-Organic Framework as Chromogenic and Fluorogenic Chemosensor for Mercury Ion

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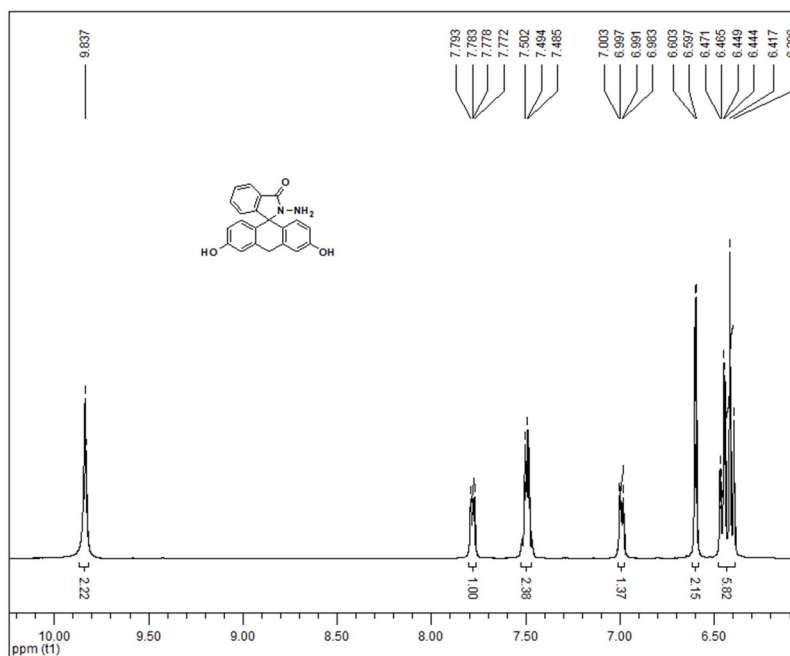
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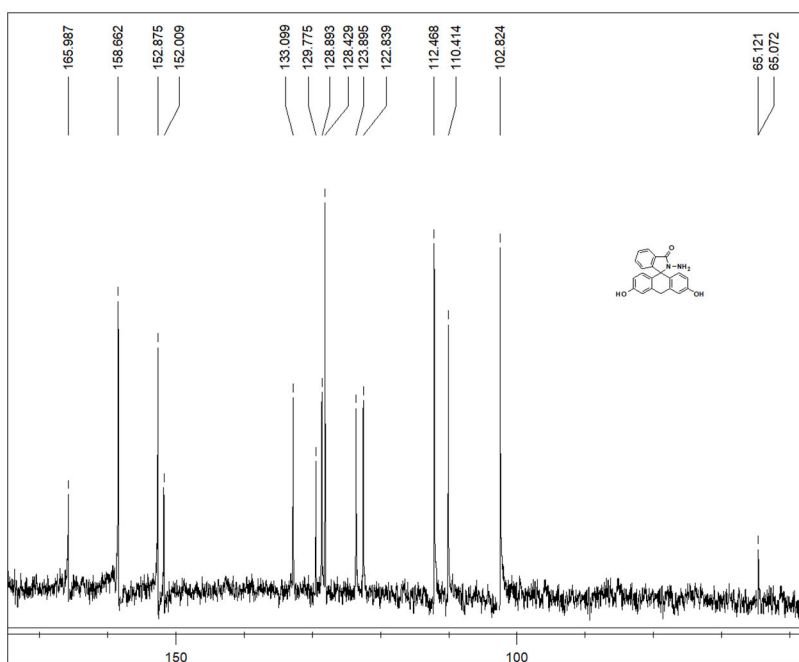
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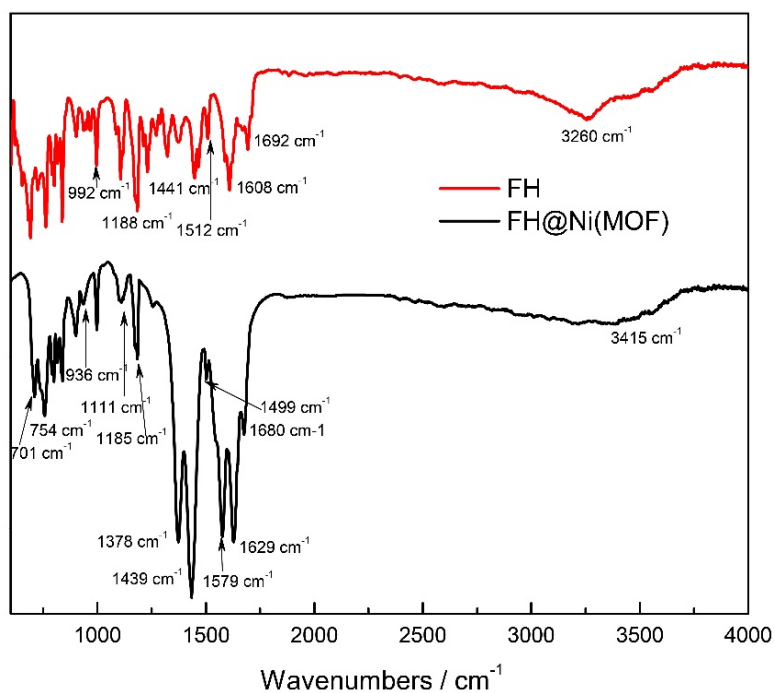
## Section S1: Characterization of FH@Ni(MOF)



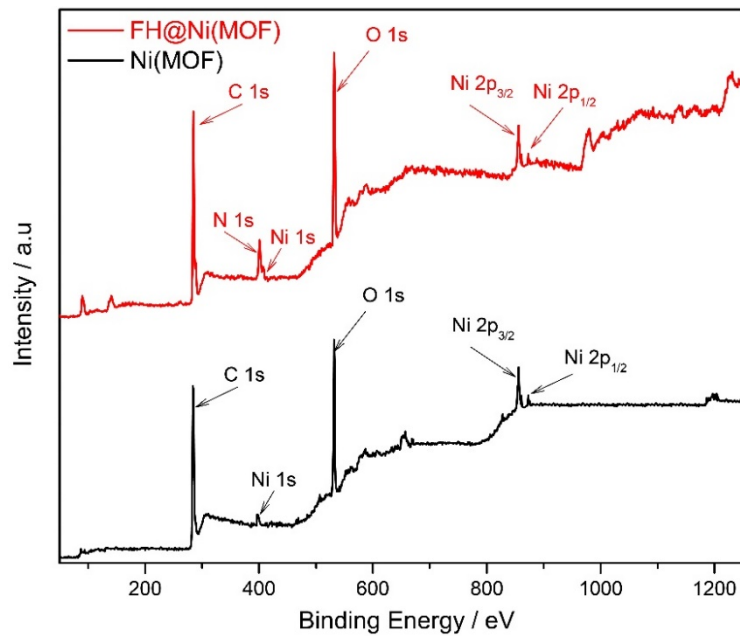
**Figure S1.** <sup>1</sup>H NMR spectrum of FH in DMSO-*d*<sub>6</sub> solution at 400 MHz.



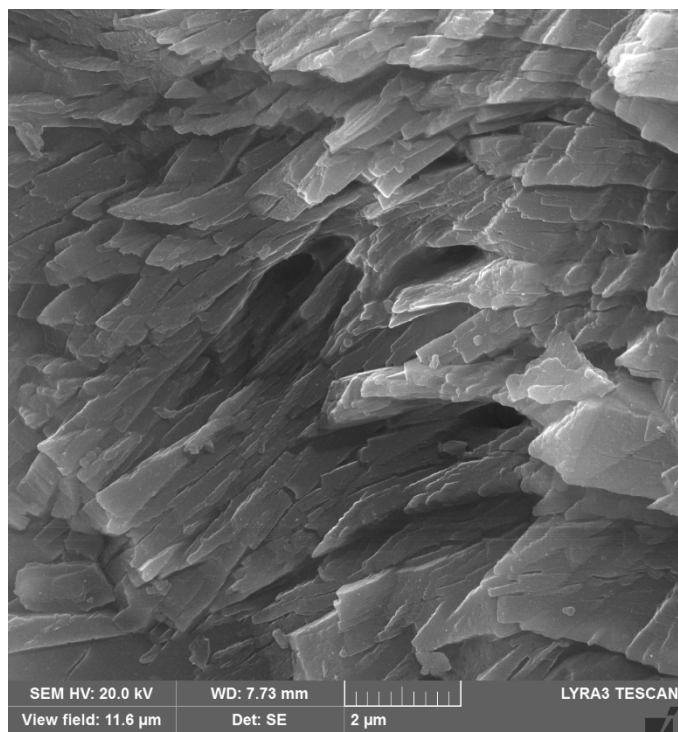
**Figure S2.** <sup>13</sup>C NMR spectrum of FH in DMSO-*d*<sub>6</sub> solution at 200 MHz.



**Figure S3:** FTIR spectrum of FH and FH@Ni(MOF)

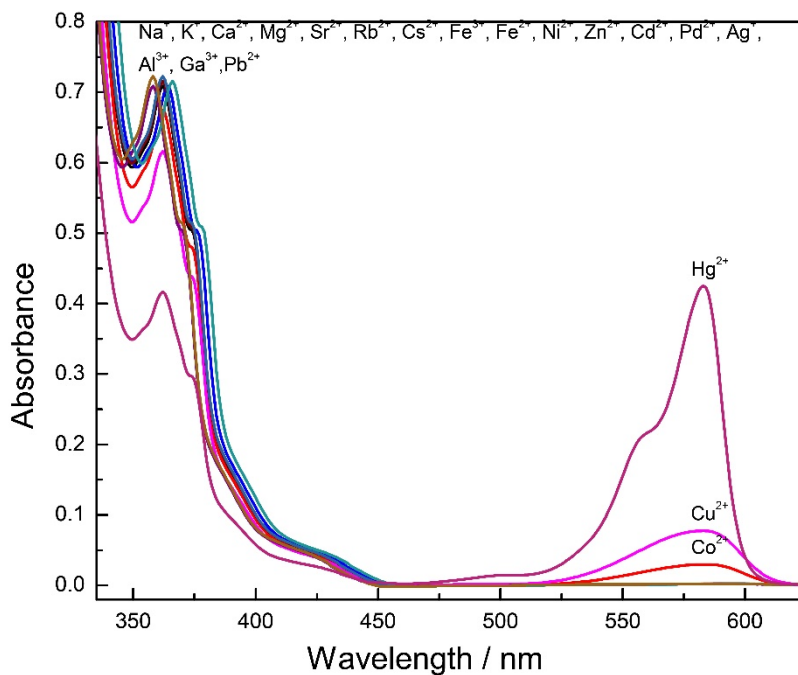


**Figure S4:** XPS spectrum of FH and FH@Ni(MOF)

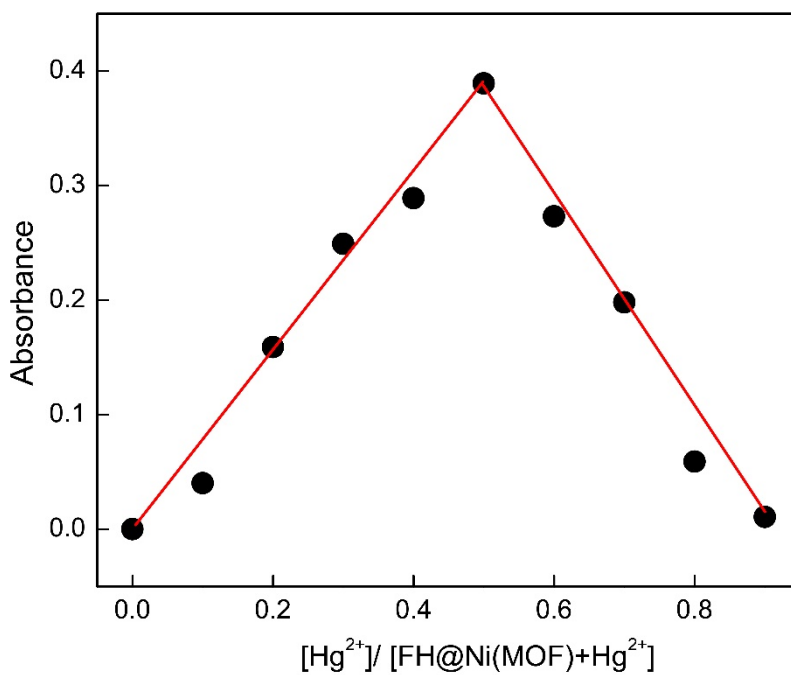


**Figure S5:** SEM of FH@Ni(MOF)

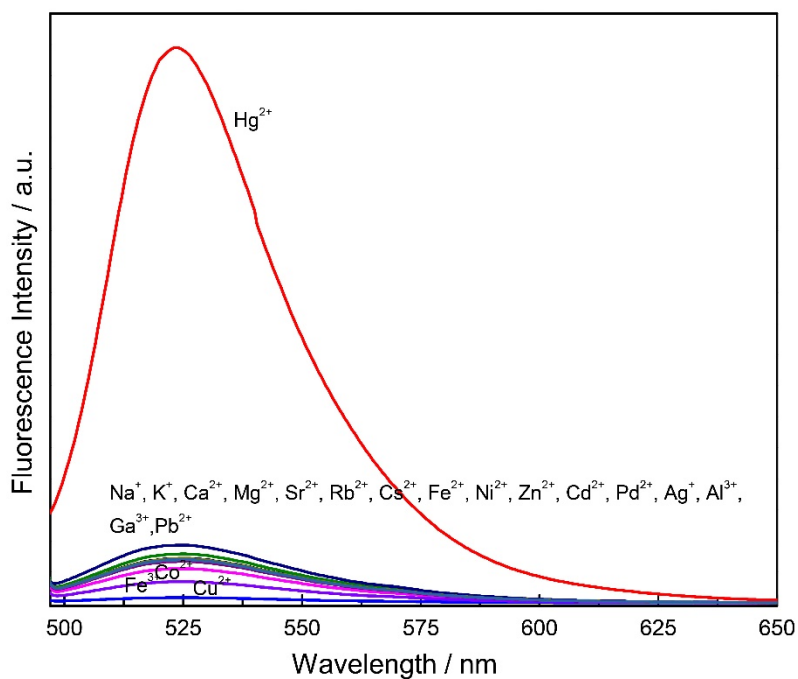
## Section S2: Optical Sensing properties of FH@Ni(MOF)



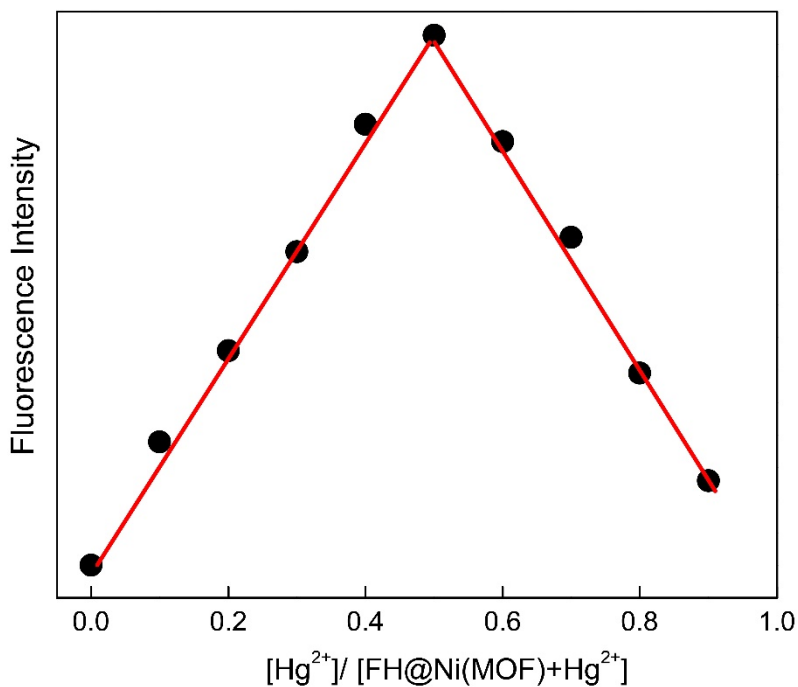
**Figure S6.** Change in the UV-vis spectrum of FH@Ni(MOF) in water upon addition of 200  $\mu\text{L}$  of different metal cations ( $10^{-2}$  M).



**Figure S7.** Job's plot for FH@Ni(MOF) with Hg<sup>2+</sup> in water.



**Figure S8.** Change in the fluorescence emission spectrum of FH@Ni(MOF) in water upon addition of 200  $\mu\text{L}$  of different metal cations ( $10^{-2}$  M).



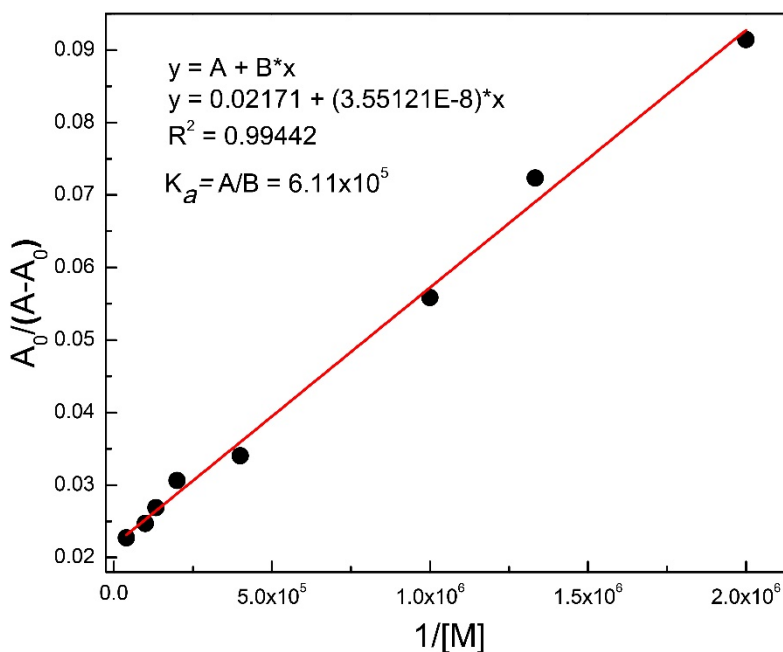
**Figure S9.** Job's plot for FH@Ni(MOF) with  $\text{Hg}^{2+}$  in water.

### Section S3: Determination of the Rate Constant:

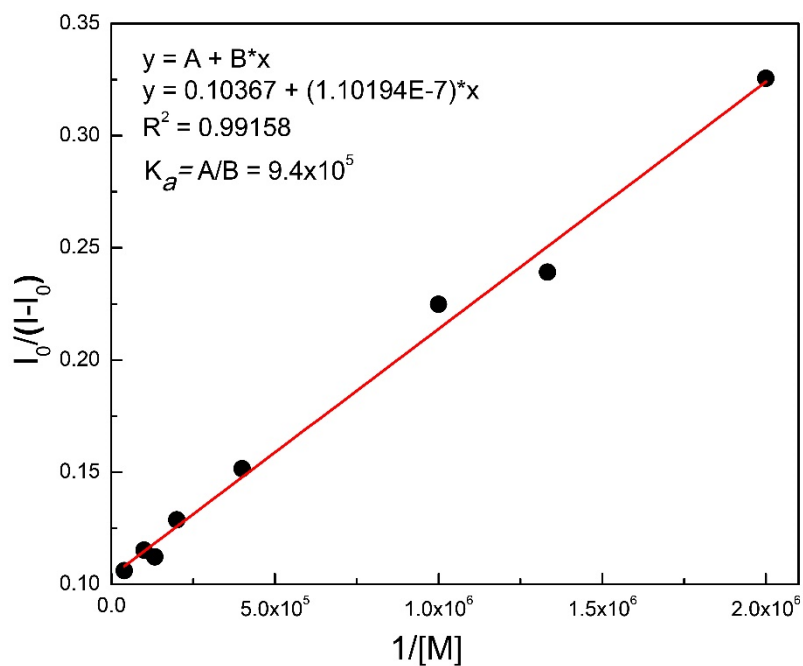
The rate constant was calculated using the following equation.<sup>1</sup>

$$F_0/(F - F_0) = [a/(b - a)][(1/K_s[M]) + 1].$$

Where  $F_0$  is the absorbance or fluorescence intensities of the free host (here FH@Ni(MOF)),  $F$  is the absorbance or fluorescence intensities of the host-guest complex,  $a$  and  $b$  are constants,  $K_s$  is the rate constant and  $M$  is the concentration of the guest (here  $\text{Hg}^{2+}$ ). When  $F_0/(F - F_0)$  is plotted against the reciprocal of the concentration of the guest (here hydrazine)  $[M]^{-1}$ , the rate constant is given by the ratio intercept/slope.



**Figure S10.** Linear regression curve of FH@Ni(MOF) obtained by plotting absorbance  $A_0/(A-A_0)$  as a function of  $1/[\text{Hg}^{2+}]$  in aqueous system.



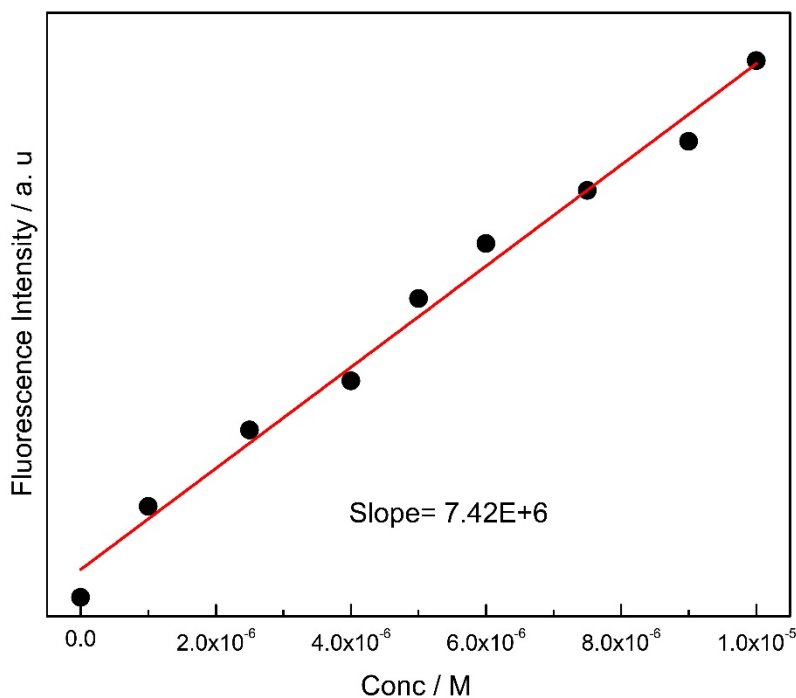
**Figure S11.** Linear regression curve of FH@Ni(MOF) obtained by plotting emission  $I_0/(I-I_0)$  as a function of  $1/[\text{Hg}^{2+}]$  in aqueous system. ( $\lambda_{\text{ex}} = 460 \text{ nm}$ )

#### Section S4: Determination of the detection limit<sup>2</sup>

The detection limit was calculated based on the fluorescence quenching titration experiments. The fluorescence emission spectrum of FH@Ni(MOF) was measured five times from which the standard deviation of the blank measurement was achieved. To gain the slope, the fluorescence intensity at 523 nm was plotted as a concentration of the analytes. So the detection limit was calculated with the following equation:

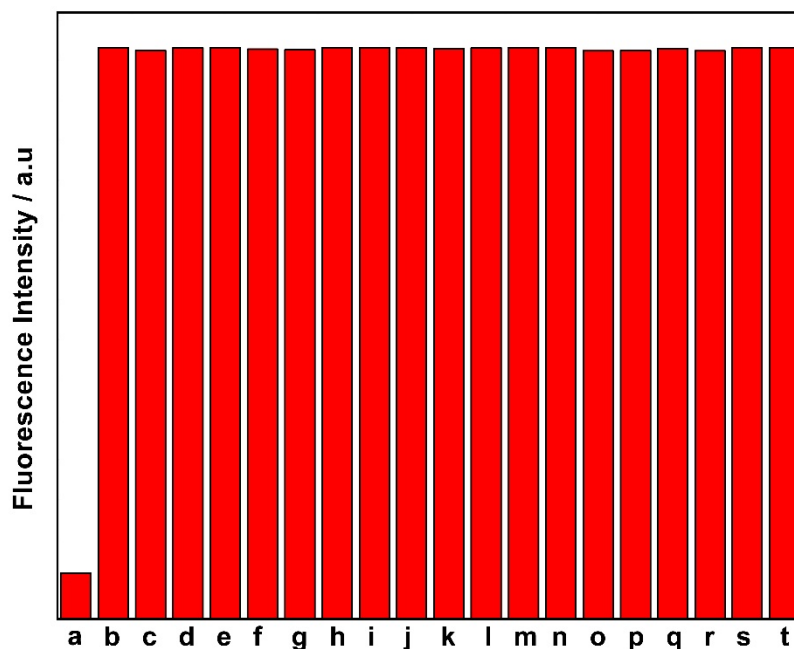
$$\text{Detection limit} = 3\sigma/k$$

Where  $\sigma$  is the standard deviation of blank measurement,  $k$  is the slope between the normalized fluorescence intensity versus analytes concentrations.



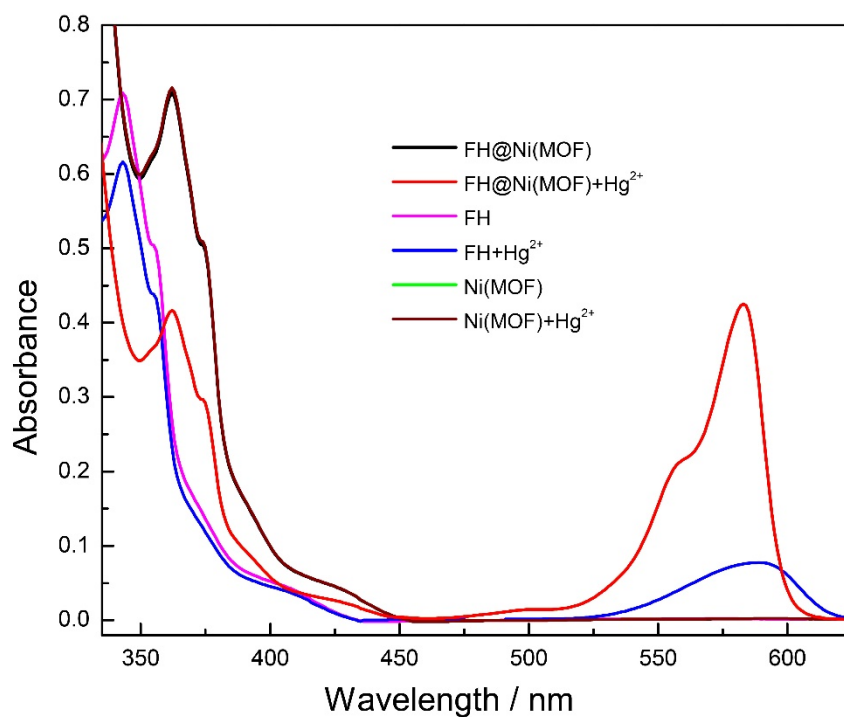
**Figure S12.** Linear region of fluorescence intensity ( $\lambda_{\text{ex}} = 460$  nm and  $\lambda_{\text{em}} = 523$  nm) for FH@Ni(MOF) suspensions in water upon incremental addition of  $\text{Hg}^{2+}$  solutions.

	Blank Readings	Hg <sup>2+</sup>
1	Fluorescence Intensity	14.2862
2	Fluorescence Intensity	14.1745
3	Fluorescence Intensity	14.2356
4	Fluorescence Intensity	14.3421
5	Fluorescence Intensity	14.2928
6	Fluorescence Intensity	14.3143
Standard Deviation ( $\sigma$ )		0.06023
Slope (m)		7.42E+6
Detection limit ( $3\sigma/m$ )		0.024 $\mu$ M / 5.0 ppb

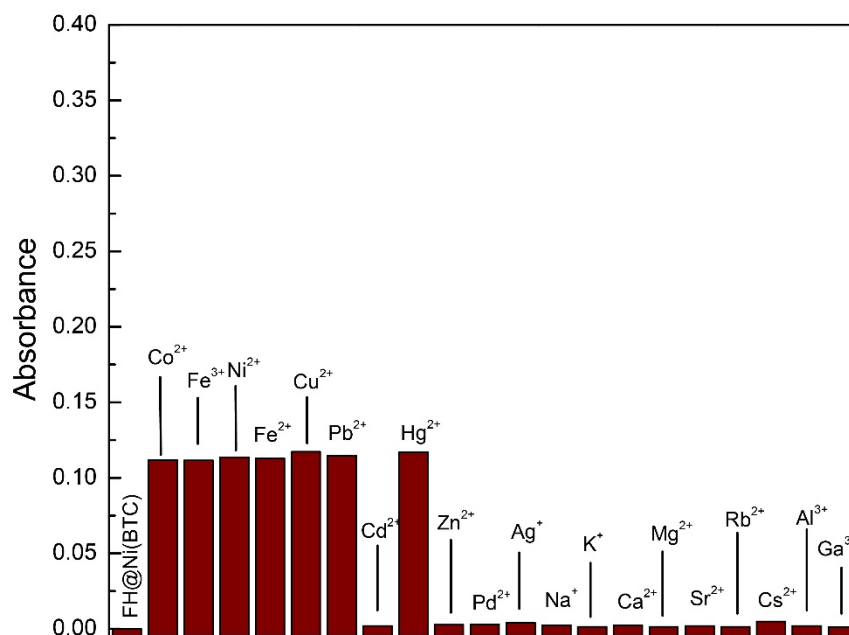


**Figure S13.** Competitive metal ion selectivity of FH@Ni(MOF): Bars indicate the fluorescence intensity (460 nm excitation, 523 nm emission). Salts of various metal ions ( $10^{-2}$  M) were added to FH@Ni(MOF) and Hg<sup>2+</sup> ( $10^{-2}$  M) (a) FH@Ni(MOF) only, (b) Ag<sup>+</sup> + Hg<sup>2+</sup>, (c) Pb<sup>2+</sup> + Hg<sup>2+</sup>, (d) Zn<sup>2+</sup> + Hg<sup>2+</sup>, (e) Mg<sup>2+</sup> + Hg<sup>2+</sup>, (f) Fe<sup>3+</sup> + Hg<sup>2+</sup>, (g) K<sup>+</sup> + Hg<sup>2+</sup>, (h) Co<sup>2+</sup> + Hg<sup>2+</sup>, (i) Al<sup>3+</sup> + Hg<sup>2+</sup>, (j) Fe<sup>2+</sup> + Hg<sup>2+</sup>, (k) Na<sup>+</sup> + Hg<sup>2+</sup>, (l) Cd<sup>2+</sup> + Hg<sup>2+</sup>, (m) Sr<sup>2+</sup> + Hg<sup>2+</sup>, (n) Rb<sup>+</sup> + Hg<sup>2+</sup>, (o) Pd<sup>2+</sup> + Hg<sup>2+</sup>, (p) Ni<sup>2+</sup> + Hg<sup>2+</sup>, (q) Fe<sup>3+</sup> + Hg<sup>2+</sup>, (r) Ga<sup>3+</sup> + Hg<sup>2+</sup>, (s) Cs<sup>+</sup> + Hg<sup>2+</sup>, (t) Ca<sup>2+</sup> + Hg<sup>2+</sup> in water.

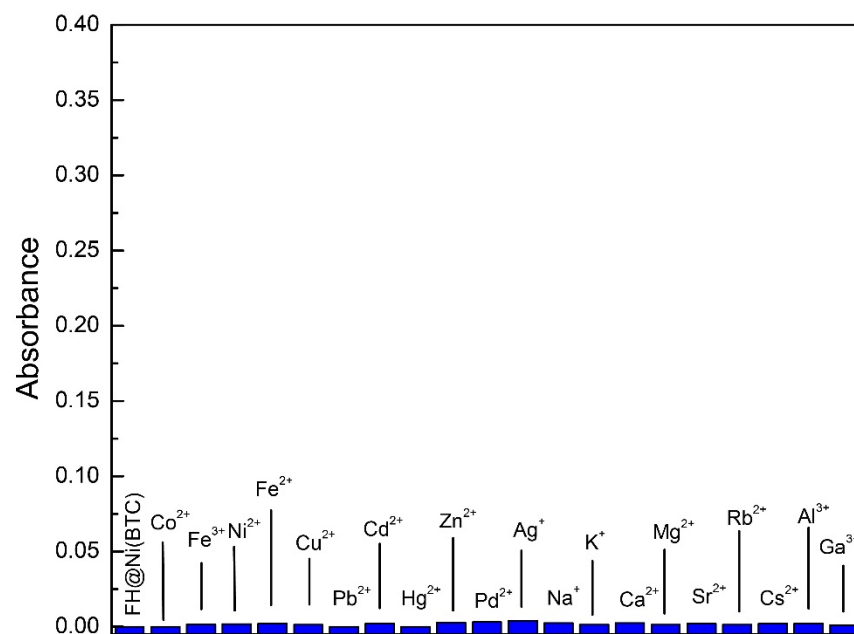
## Section S5: Comparison of Absorbance of FH, Ni(MOF), and FH@Ni(MOF) with metal ions



**Figure S14.** Change in the UV-vis spectrum of FH@Ni(MOF), FH, and Ni(MOF) in water upon addition of  $\text{Hg}^{2+}$  ( $10^{-2}$  M).

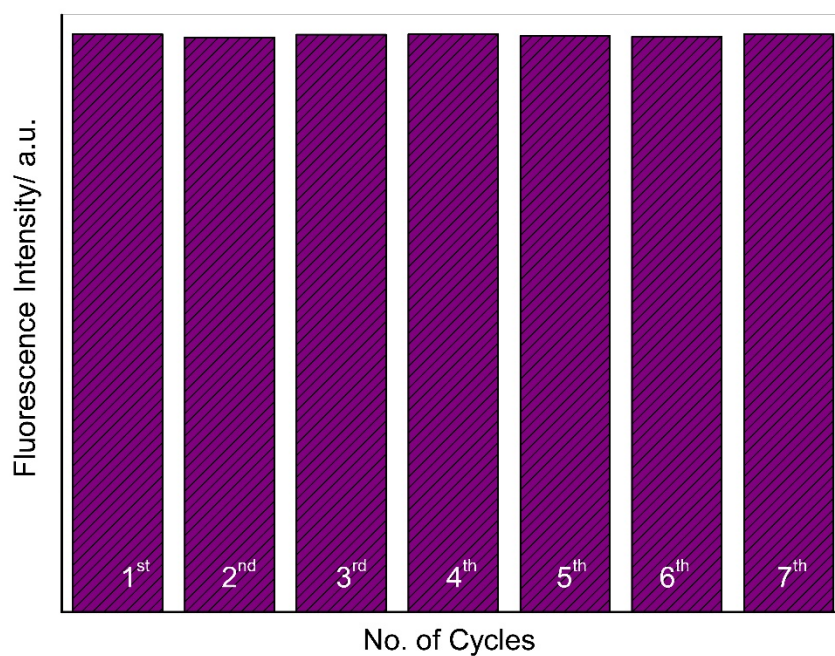


**Figure S15.** Change in the UV-vis absorbance of FH in water upon addition of 200  $\mu\text{L}$  of different metal cations ( $10^{-2}$  M).



**Figure S16.** Change in the UV-vis absorbance of Ni(MOF) in water upon addition of 200  $\mu\text{L}$  of different metal cations ( $10^{-2}$  M).

## Section S6: Recyclability of FH@Ni(MOF)



**Figure S17.** Bar diagram depicting the recyclability of FH@Ni(MOF) on addition of the Hg<sup>2+</sup> up to 7 cycles.

## Section S7: References

1. S. Fery-Forgues, M.-T. Le Bris, J.-P. Guett, B. Valeur, *J. Phys. Chem.* **1988**, 92, 6233-6237.
2. Lv, R.; Wang, J.; Zhang, Y.; Li, H.; Yang, L.; Liao, S.; Gu, W.; Liu, X. *J. Mater. Chem. A* **2016**, 4, 15494-15500.