

Supporting Information for

**A Multifunctional Eu MOF as a Fluorescent pH Sensor and
Exhibiting Highly Solvent-Dependent Adsorption and Degradation of
Rhodamine B**

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1. Materials and Methods

General Information. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. X-ray powder diffractions were measured on a Panalytical X-Pert pro diffractometer with Cu-K α radiation. Elemental analyses (C, H, N) were obtained on a PerkinElmer 240 elemental analyzer. The thermogravimetric analysis (TGA) was carried out between room temperature and 600 °C in a static N₂ with a heating rate of 10°C/min. Photoluminescence spectra were measured on Perkin Elmer LS-55 or Hitach F-7000 fluorescence spectrophotometer. Low pressure (< 800 torr) gas (N₂, CO₂ and H₂) sorption isotherms were measured using a Micrometrics ASAP 2020 surface area and pore size analyzer. Prior to the measurements, the samples were degassed for 10 h at 60 °C. Ultra-high purity (UHP grade 5.0, 99.999% purity) gases were used for all measurements. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements to prevent contamination of the samples during the degassing process and isotherm measurement. Approximately 100 mg of activated sample was used for all measurements.

1.1 Synthesis

Synthesis of UPC-5. H₄BPTC (64 mg, 0.2 mmol) and Eu(NO₃)₃•6H₂O (223 mg, 0.5 mmol) were dissolved in 50 ml of DMA-H₂O (1:1). The solution was split into 50 portions and placed in glass tubes, then 0.25ml HNO₃ (6M) was added into each tube. The sealed tubes were slowly heated to 90°C from room temperature in 5 hours, kept at 90°C for 2 days. After slowly cooled to 30°C in 13 hours, colorless block crystals of UPC-5 were separated in 49.5% yield based on H₄LBPTC. EA (%) calculated for [H₃O][Eu₃(HBPTC)₂(BPTC)(H₂O)₂]•4DMA: C, 41.78; H, 3.45; N, 3.04; found: C, 42.35; H, 3.58; N, 3.03.

Synthesis of Li-UPC-5. The crystal sample of UPC-5 was immersed in 6 ml methanol solution containing LiCl (10 mg/ml). After 12 hours, the solution was removed and fresh LiCl methanol solution was added for another 12 hours to exchange the H₃O⁺ cations. Such procedure was repeated for 3 times to completely

exchange the H_3O^+ with Li^+ to generate **Li-UPC-5**.

1.2 Crystal structure determination of UPC-5

Single-crystal X-ray diffraction was performed using an Agilent Xcalibur Eos Gemini diffractometer with Enhance (Mo) X-ray Source ($\text{MoK}\alpha$: $\lambda = 0.71073 \text{ \AA}$). Contributions to scattering from all solvent molecules were removed using the SQUEEZE routine of PLATON; structures were then refined again using the data generated.

1.3 Crystal data of UPC-5

Table S1 Crystal data and structure refinement for **UPC-5**

Compound	UPC-5
Formula	$\text{C}_{48}\text{H}_{18}\text{Eu}_3\text{O}_{26}$
Formula weight	1466.50
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/ \AA	11.6692(4)
b/ \AA	12.2365(4)
c/ \AA	13.6586(6)
$\alpha/^\circ$	65.229(4)
$\beta/^\circ$	67.518(4)
$\gamma/^\circ$	88.435(3)
Volume/ \AA^3	1615.62(10)
Z	1
$\rho/\text{g cm}^{-3}$	1.507
μ/mm^{-1}	2.947
F(000)	703.0
Crystal size/ mm^3	$0.11 \times 0.11 \times 0.1$
2 θ range for data collection	5.74 to 50
Index ranges	$-13 \leq h \leq 13, -14 \leq k \leq 14, -15 \leq l \leq 16$
Reflections collected	18053
Independent reflections	5686 [$R_{\text{int}} = 0.0480, R_{\text{sigma}} = 0.0533$]
Data/restraints/parameters	5686/0/349
Goodness-of-fit on F^2	1.064
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0324, wR_2 = 0.0847$
Final R indexes [all data]	$R_1 = 0.0412, wR_2 = 0.0894$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.85/-0.53

$${}^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, {}^b wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{0.5}.$$

1.4 Adsorption and degradation of Dye molecules

The freshly prepared sample of **Li-UPC-5** was immersed in acetone, methanol, water, isopropanol, chloroform solution containing dye molecules such as rhodamine B, methyl violet or other anionic Dye molecules to test the adsorption capacity of **Li-UPC-5**. The concentration of the Dye molecules is 0.02625 mg/ml. For the degradation experiment, the fresh **Li-UPC-5** sample was immersed in dmsol solution containing rhodamine B (0.015 mg/ml) and the suspension was stirred under natural light for given time until the color of the solution changed colorless. After each run, the solution was removed and fresh dmsol solution containing rhodamine B was added for another run.

1.5 Gas adsorption of UPC-5 and Li-UPC-5

The as-synthesized crystals of **UPC-5** or **Li-UPC-5** were soaked in methanol for 12 hours to replace dma guest molecules, such procedure was repeated three times to completely remove the dma molecules from the channels. The solvent-exchanged samples of **UPC-5** or **Li-UPC-5** were activated at 60 °C for 12 hours.

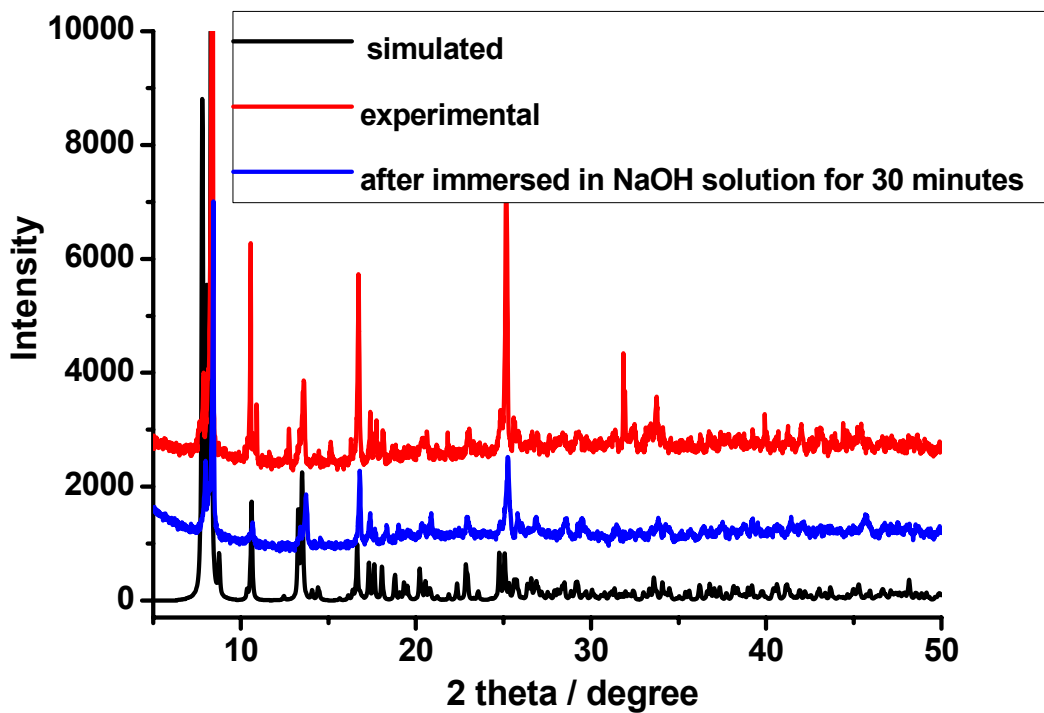
1.6 A typical procedure for the adsorption experiments of Rhodamine B

Li-UPC-5 (20 mg) was added into a 4 mL acetone solution of Rhodamine B (26.3 mg·L⁻¹) at room temperature for 3 h. The solution was centrifuged and the solution was diluted to the appropriate concentrations and analyzed by UV-Vis absorption spectroscopy. The amount of adsorbed RHB was calculated from the following mass balance equation:

$$Q_{ad} = \frac{(C_0 - C_{ad})V}{m}$$

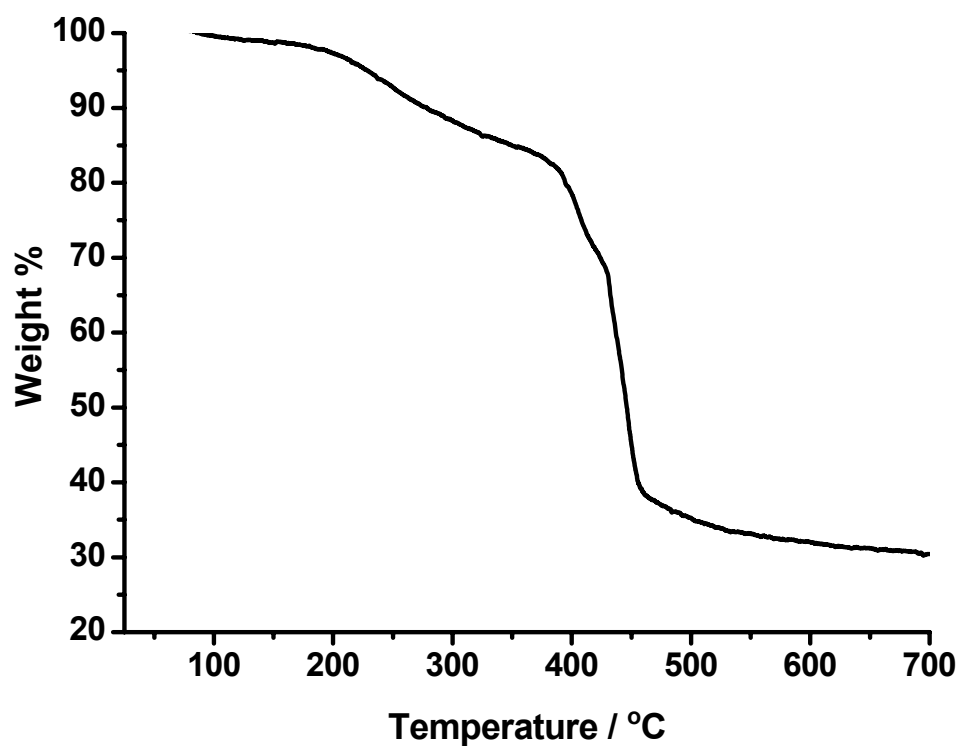
where Q_{ad} (mg/g) is the amount of adsorbed RHB by adsorbent **Li-UPC-5**, C_0 is the initial concentration of RHB in the acetone (mg/L), C_{ad} is the concentration of RHB after adsorption (mg/L), V is the volume of the solution (L), and m is the mass of adsorbent **Li-UPC-5** (g).

2. XRD of UPC-5



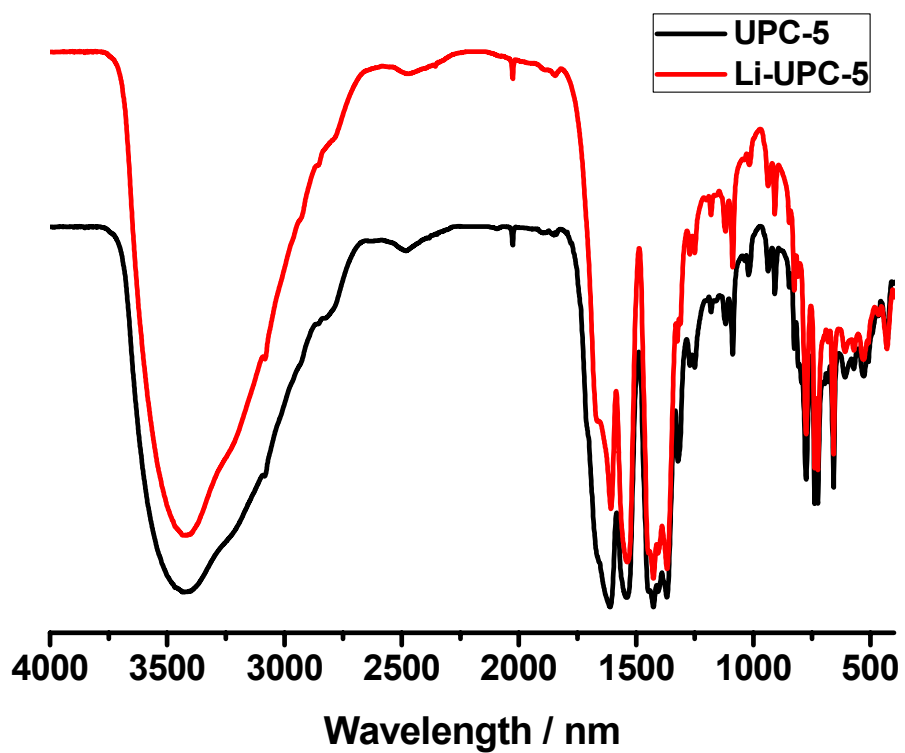
Supplementary Figure 1. XRD of UPC-5, simulated, experimental, and after immersed in NaOH solution (pH = 10) for half an hour. XRD measurement revealed that UPC-5 is stable in the aqueous solution at pH = 10.

3. The TG curve of UPC-5



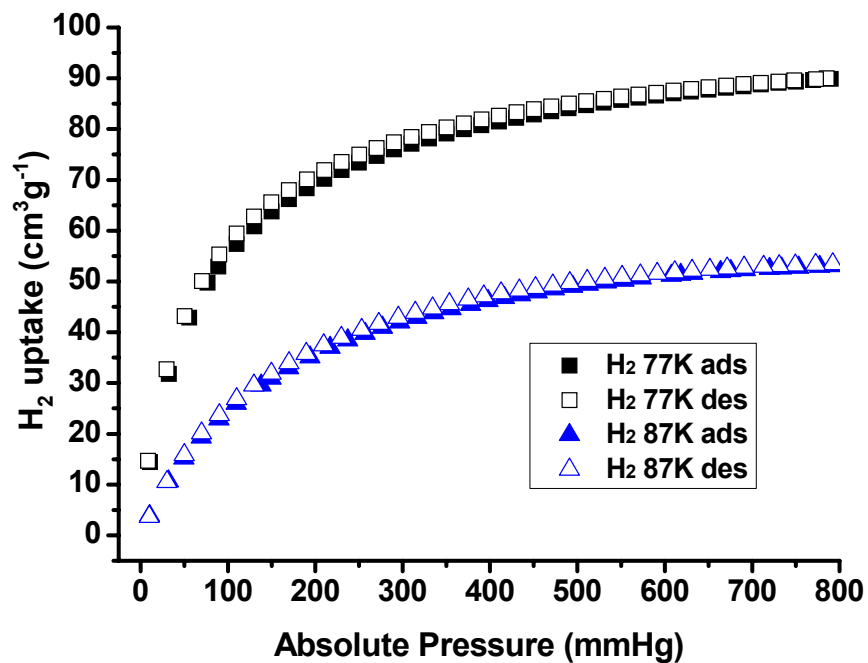
Supplementary Figure 2. TG curve of UPC-5. Based on the TGA, UPC-5 can be stable up to 380 °C, and after 380 °C, UPC-5 starts to decompose.

4. IR spectra of UPC-5 and Li-UPC-5

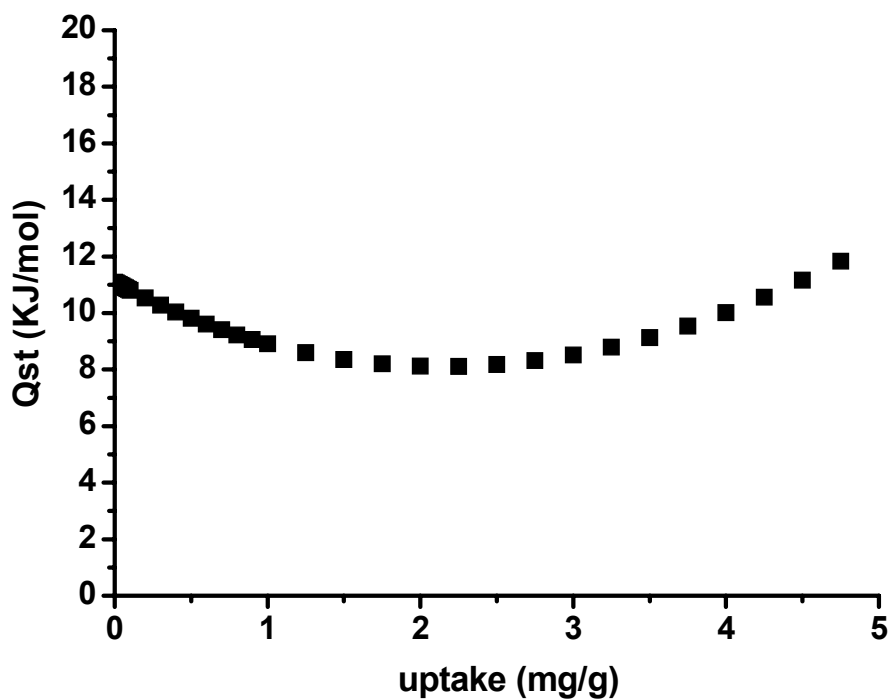


Supplementary Figure 3. IR spectra of UPC-5 and Li-UPC-5.

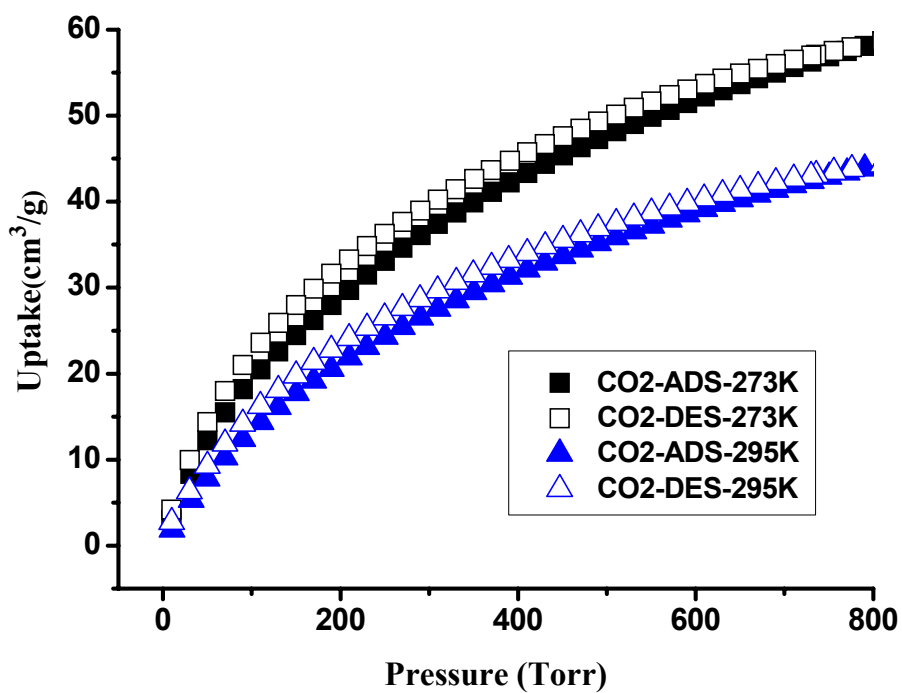
5. The gas adsorption of UPC-5 and Li-UPC-5



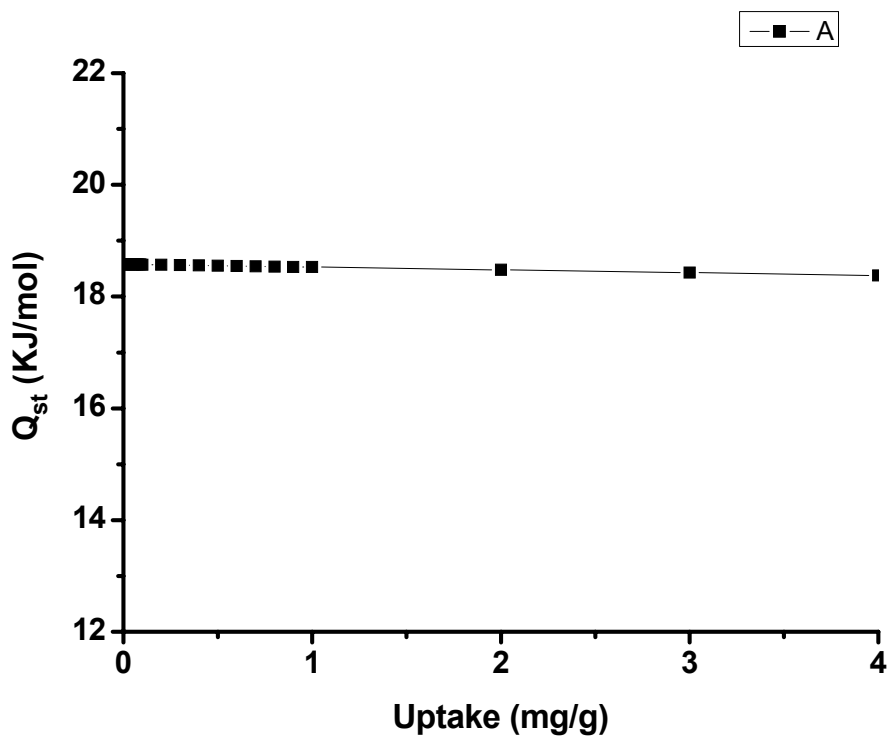
Supplementary Figure 4. H₂ adsorption isotherms of UPC-5.



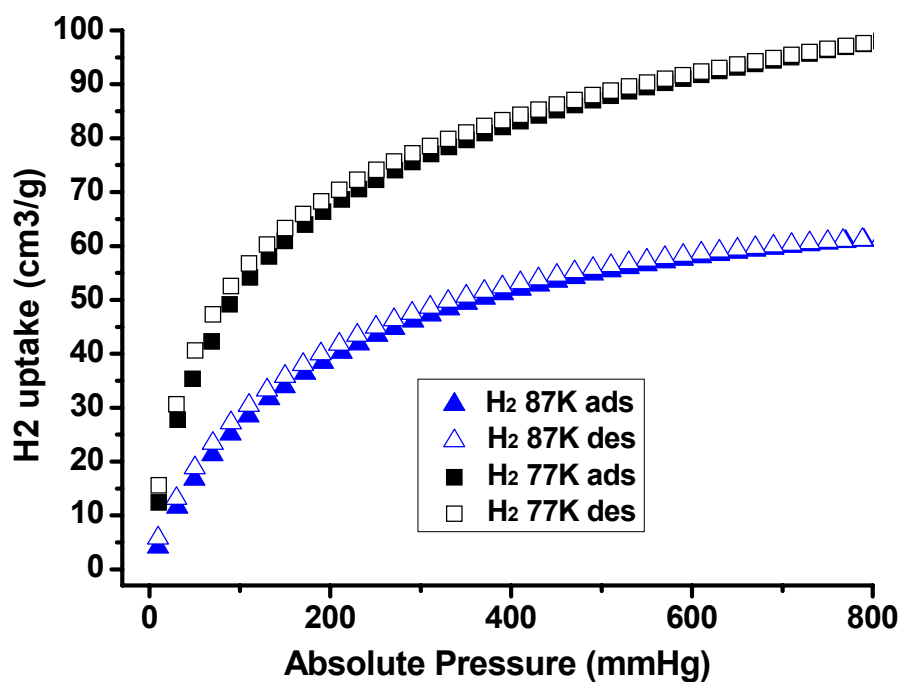
Supplementary Figure 5. The Q_{st} of H₂ for UPC-5.



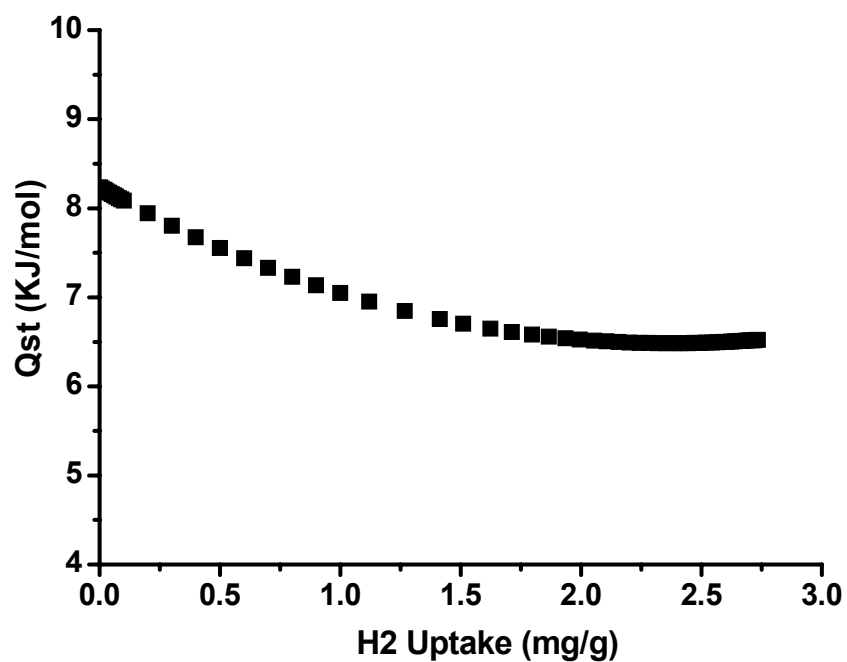
Supplementary Figure 6. CO₂ adsorption isotherms of UPC-5.



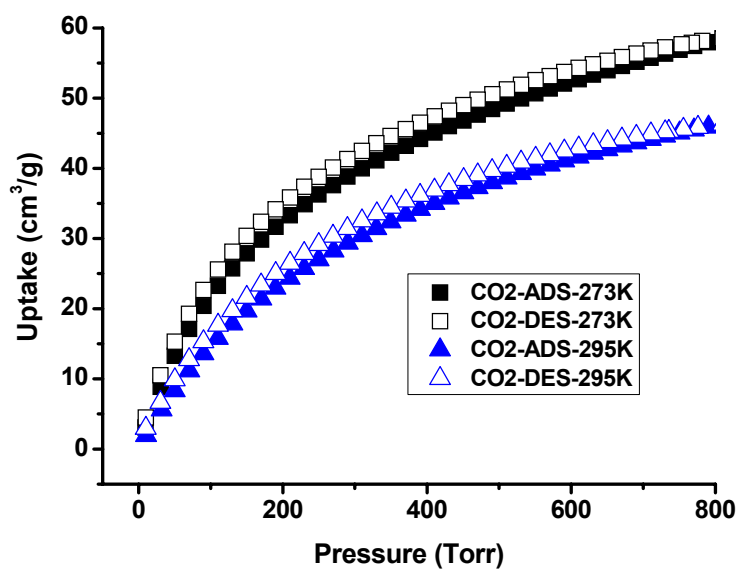
Supplementary Figure 7. The Q_{st} of CO₂ for UPC-5.



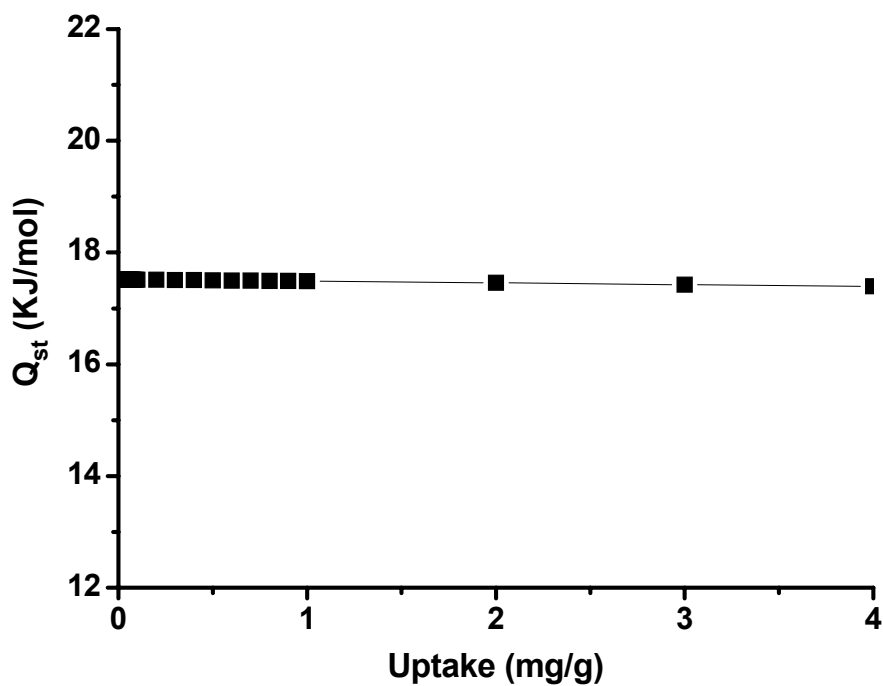
Supplementary Figure 8. H₂ adsorption isotherms of Li-UPC-5.



Supplementary Figure 9. The Q_{st} of H₂ for Li-UPC-5.

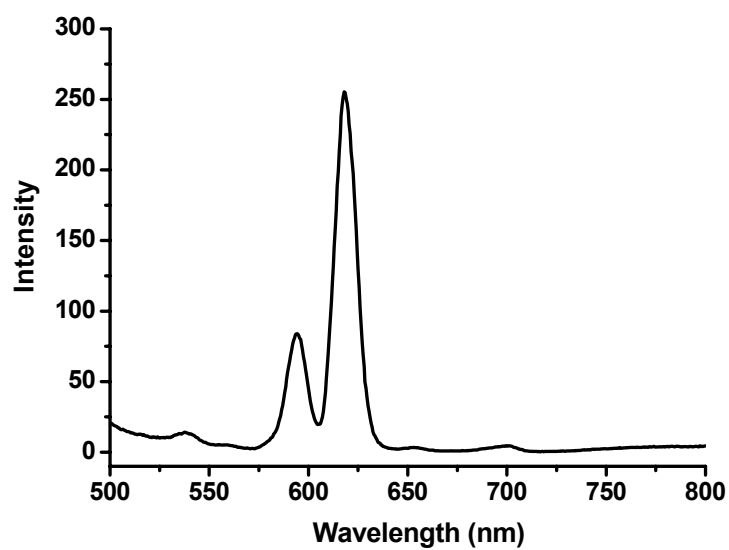


Supplementary Figure 10. CO₂ adsorption isotherms of Li-UPC-5.

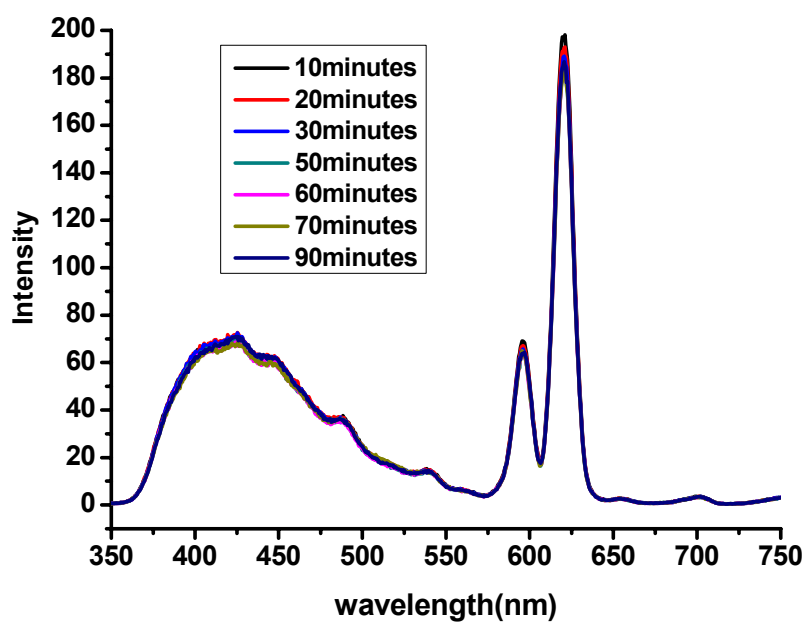


Supplementary Figure 11. The Q_{st} of CO₂ for Li-UPC-5.

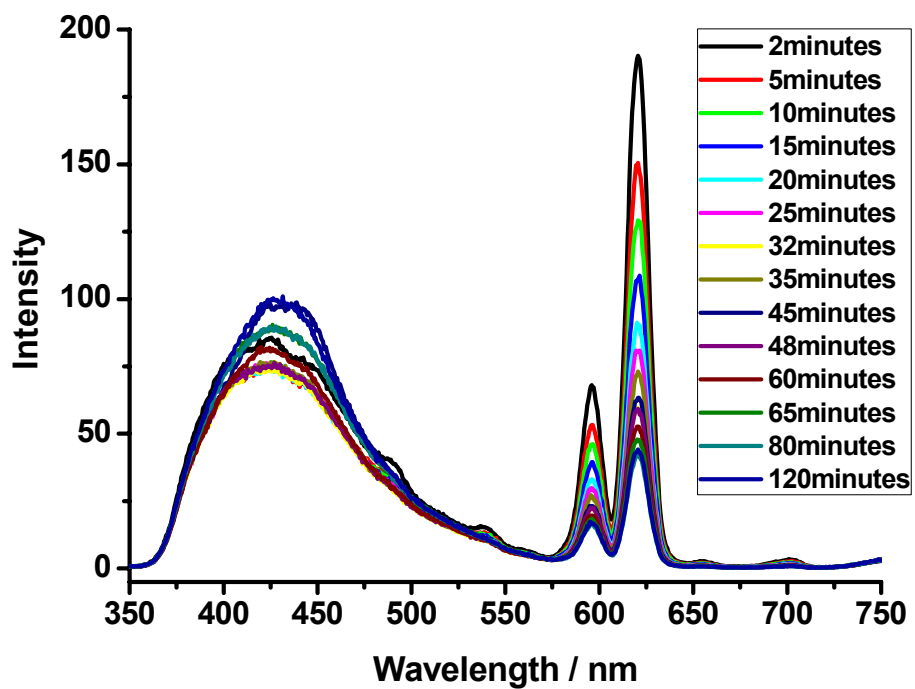
6. Photoluminescence spectra of UPC-5.



Supplementary Figure 12. Solid-state photoluminescence spectra of UPC-5.

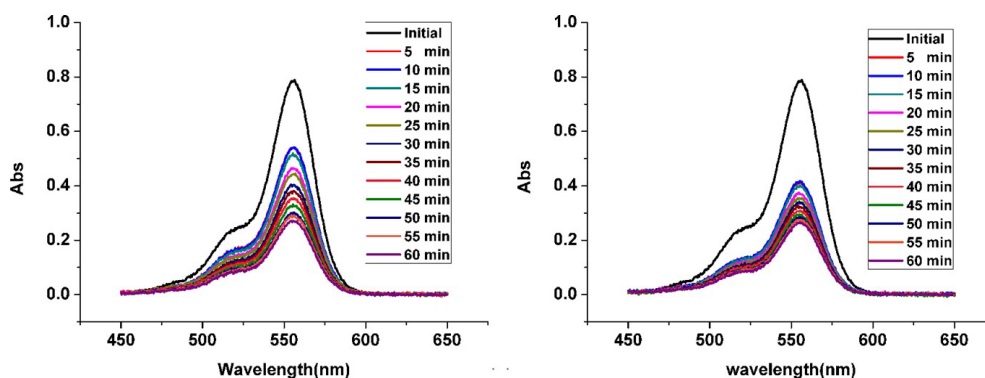


Supplementary Figure 13. Time-dependent emission spectra of UPC-5 suspended in water.

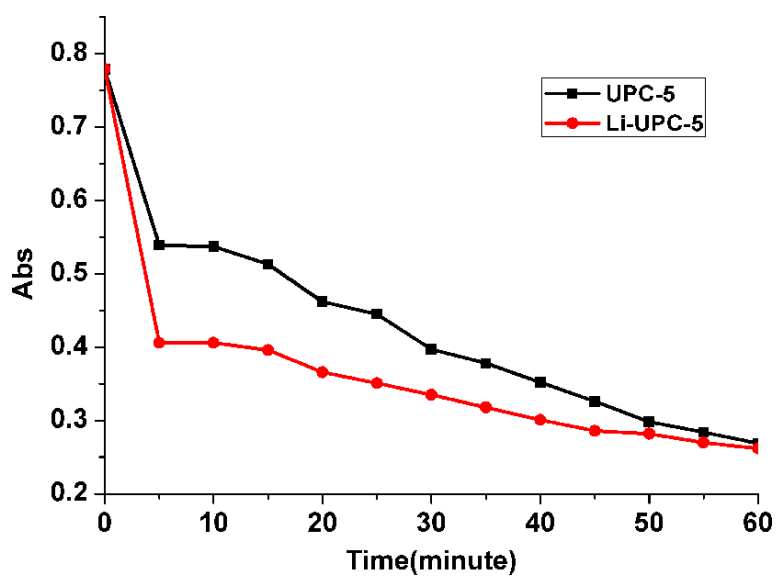


Supplementary Figure 14. Time-dependent emission spectra of UPC-5 suspended in water after adding 1d NaOH.

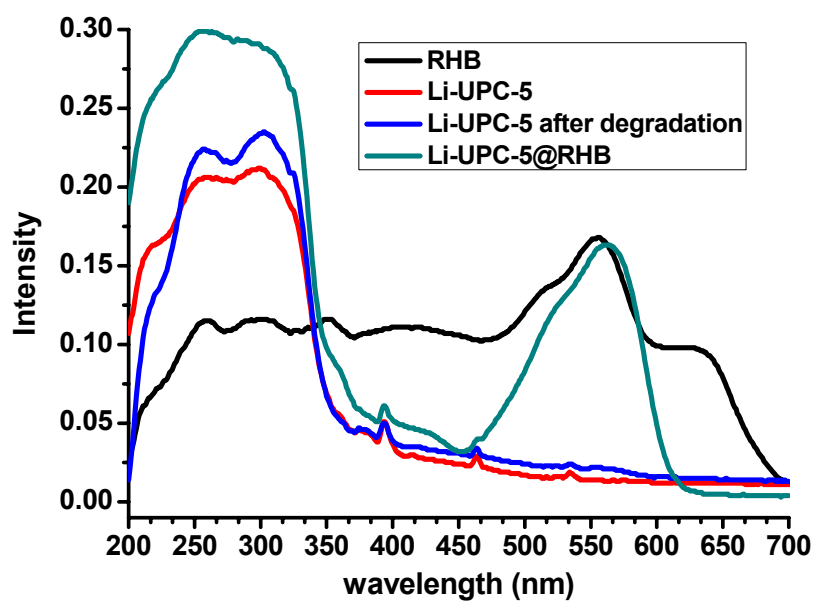
7. UV-vis spectra of UPC-5 and Li-UPC-5.



Supplementary Figure 15. A time-dependent UV-vis spectra of the solution containing Rhodamine B after adsorbed by **UPC-5** (left) and **Li-UPC-5** (right).

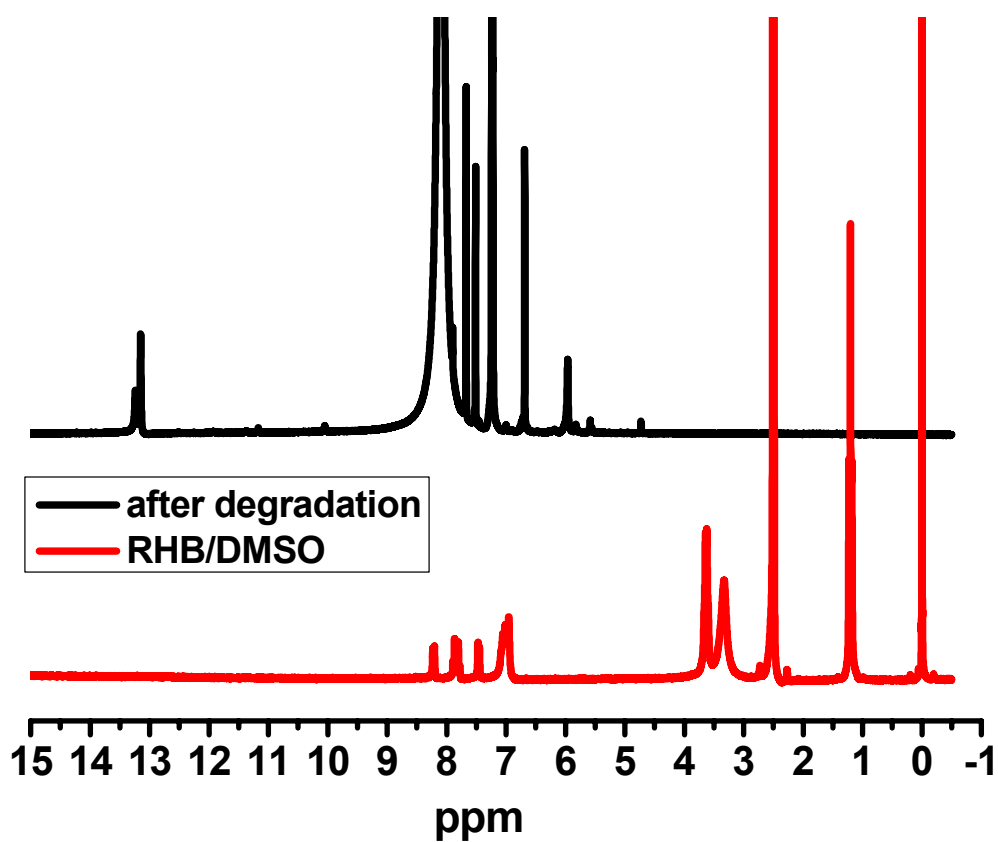


Supplementary Figure 16. Absorbance changes of **UPC-5** and **Li-UPC-5** with time at 557 nm, showing the dye adsorption features for **Li-UPC-5** improve and occur faster than that for **UPC-5**.



Supplementary Figure 17. UV-vis spectra of the solid RHB, Li-UPC-5 before and after the degradation, and RHB@Li-UPC-5.

8. ^1H NMR spectra for before and after the degradation of RHB



Supplementary Figure 18. ^1H NMR spectra for before and after the degradation. The peaks at ~ 3.5 and ~ 1.0 ppm for $-\text{CH}_2\text{CH}_3$ group disappear, while new peaks at ~ 13 ppm, which should be assigned to the proton of carboxylate group, appear after the degradation.