

**Electronic Supplementary Information**

**Realizing Both Selective Adsorption and Efficient Regeneration  
by Adsorbents with Photo-Regulated Molecular Gates**

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## Experimental section

### Materials synthesis.

**Preparation of MCM-41.** MCM-41 silica particles were synthesized as follows.<sup>1</sup> Typically synthesis, 3.5 mL of NaOH (2 M) solution was mixed with 480 mL of distilled water. The solution was heating to 80 °C with stirring after 1.0 g of template cetyltrimethylammonium bromide (CTAB) was added. When the solution became homogeneous, 5 mL of tetraethyl orthosilicate (TEOS) was added dropwise, giving rise to a white slurry. After 2 h, the resulting product was filtered, washed with distilled water, and dried at 80 °C for 12 h, which leads to the formation of as-synthesized MCM-41.

**Synthesis of 7-allyloxy coumarin.** The compound 7-allyloxy coumarin was obtained as follows. Under dry N<sub>2</sub>, 1.08 mL of 3-bromo-1-propene (12.5 mmol) was added dropwise to a stirred mixture of 7-hydroxy coumarin (0.81 g, 5 mmol) and anhydrous K<sub>2</sub>CO<sub>3</sub> (1.04 g, 7.5 mmol) in 150 mL of acetone. The resulting mixture was then boiled under reflux for 12 h and the K<sub>2</sub>CO<sub>3</sub> filtered off and washed with fresh acetone. The solvent was removed in vacuo and the resulting cream-yellow crystals recrystallized from methanol.

**Synthesis of 7-[(3-triethoxysilyl)propoxy] coumarin.** The compound 7-[(3-triethoxysilyl)propoxy] coumarin (TPC) used as gate molecules was synthesized as follows.<sup>2</sup> After bubbling of dry N<sub>2</sub> to the toluene solution (0.22 mL) of 7-allyloxy coumarin (0.202 g, 1 mmol) and triethoxysilane (2.94 g, 1.22 mmol) for 10 min, 0.05 mL of the toluene solution (2 mM) of Pt (dvs) [platinum(0)-1,3-divinyl-1,1,3,3-tetramet-hydisiloxane complex] (Aldrich) was added, and the resulting solution was stirred for 12 h at 50 °C. After removal of the solvent under the reduced pressure, the obtained oil was used directly in the modification of MCM-41.

**Preparation of Coumarin-Modified MCM-41 Samples.** As-synthesized MCM-41 (0.4 g) was suspended in a solution containing 4 mL of *n*-hexane and certain weight of TPC under stirring at room temperature for 15 min.<sup>3</sup> The amounts of coumarin substituents used in grafting procedure were 0.01, 0.02, 0.03, and 0.04 g respectively. *n*-Hexane was evaporated by a rotary evaporator at 80 °C for 2 h and dried under vacuum at 150 °C for 12 h. Then the obtained samples with surfactant were refluxed in 100 mL of ethanol containing 1 mL of HCl (1 M) at 80 °C for 4 h. This process was carried out twice to ensure the complete removal of

surfactant from the pores of MCM-41. The obtained solid was filtered off, washed with ethanol and water, and finally dried at 80 °C for 12 h. The materials grafted with different amounts of coumarin derivatives were denoted as CM-1, CM-2, CM-3, and CM-4, corresponding to the data of TG analyses. In addition, template-free MCM-41 was employed for grafting. The template of as-prepared MCM-41 was extracted by acidic alcohol solution in advance. Then MCM-41 (0.24 g) was suspended in a solution containing 4 mL of *n*-hexane and 0.02 g of TPC under stirring at room temperature for 15 min. The obtained solid was filtered off, washed with ethanol and water, and finally dried at 80 °C for 12 h. The obtained reference sample is denoted as CM'-2.

### **Characterization.**

X-ray diffraction (XRD) patterns of the materials were recorded using a Bruker D8 Advance diffractometer with monochromatic Cu K $\alpha$  radiation in the  $2\theta$  range from 1° to 6° and 10° to 80° at 40 kV and 40 mA. Transmission electron microscopy (TEM) images were taken on a JEM-2010 UHR electron microscope operated at 200 kV. N<sub>2</sub> adsorption-desorption isotherms were measured using ASAP 2020 at -196 °C. The temperature selected to perform the degasification step was 80 °C, and the degasification time was 4 h. The Brunauer-Emmett-Teller (BET) surface area was calculated using adsorption data in a relative pressure ranging from 0.04 to 0.20. The total pore volume was determined from the amount adsorbed at a relative pressure of about 0.99. The pore size distribution of the mesoporous materials was calculated from the adsorption branch by using the Barrett–Joyner–Halenda (BJH) method. Fourier transform infrared (IR) spectra of the samples diluted with KBr were carried out on a Nicolet Nexus 470 spectrometer with a spectra resolution of 2 cm<sup>-1</sup>. Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were carried out in a N<sub>2</sub> flow from room temperature to 800 °C on a TG209F1 apparatus. Diffuse reflectance UV-vis spectroscopy were obtained with a UV-2401PC spectrophotometer, and BaSO<sub>4</sub> was used as an internal standard. <sup>1</sup>H (nuclear magnetic resonance) (NMR, 300 MHz) were measured on a Bruker AVANCE 400 spectrometer in CDCl<sub>3</sub>. The dye content of the treated solutions was determined using a Lambda 35 spectrometer (Pekin-Elmer). The molecular size estimation was carried out using Materials Studio (Accelrys).

### Adsorption test.

Two dyes were used as adsorbates for selective adsorption study. Methylene blue (MB) was considered as smaller molecules, and the Coomassie brilliant blue (CBB) as large molecules. The contents of guest molecules in aqueous solutions were both  $25 \text{ mg}\cdot\text{L}^{-1}$ . Adsorption experiments were performed in the quartz cuvette directly in the cell holder of UV-vis spectrophotometer under ambient conditions. In a typical adsorption experiment, 2 mg of the adsorbent was statically dispersed in the aqueous solution (3 mL) containing  $25 \text{ mg}\cdot\text{L}^{-1}$  of guest molecules, until the adsorption equilibrium was reached. The contents of guest molecules in the treated solutions were determined at regular intervals using the UV-vis spectrophotometer. For comparison, another portion of samples were irradiated with UV light for 180 min (wavelength  $>310 \text{ nm}$ ) using a xenon lamp (CEL-HXUV300) equipped with a filter. After photo-irradiation, the samples were used for the same adsorption experiments as above. The dye concentration was detected using a UV-vis spectrophotometer at appropriate time intervals. The adsorption amount ( $Q_e$ ) was determined according to formula (1).

$$Q_e = \frac{(c_i - c_e)V}{m} \quad (1)$$

Where  $c_i$  is the initial concentration,  $c_e$  is the residual or equilibrium concentration,  $V$  is the volume of liquid phase, and  $m$  is the mass of adsorbent.

Desorption was carried out by using saturated adsorbents in the mixture of ethanol solution. The dye concentration was measured at appropriate time intervals by UV-vis spectrophotometer and the desorption amount ( $Q_d$ ) was determined according to formula (2).

$$Q_d = \frac{c_d V}{m Q_e} \times 100\% \quad (2)$$

Where  $c_d$  is the desorption equilibrium concentration.

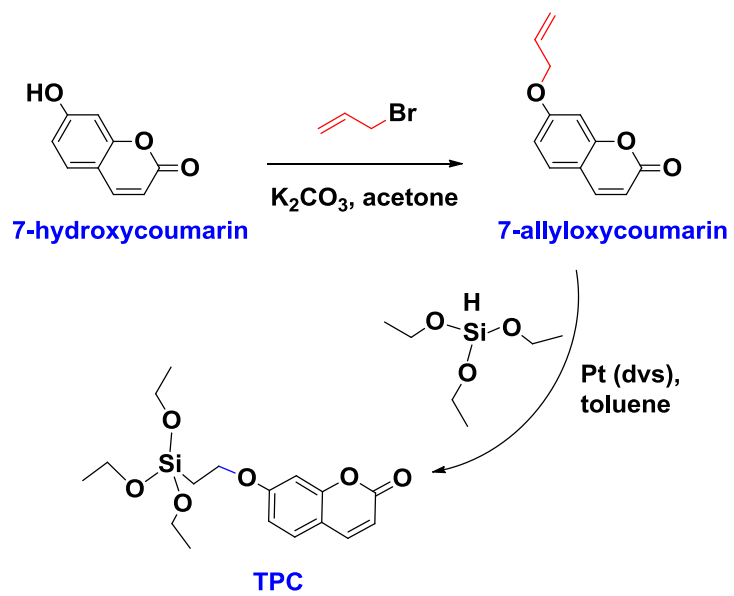
### References

- 1 Q. Cai, Z. S. Luo, W. Q. Pang, Y. W. Fan, X. H. Chen and F. Z. Cui, *Chem. Mater.*, 2001, **13**, 258.
- 2 S. W. Ha, C. E. Camalier, G. Beck and J. K. Lee, *Chem. Commun.*, 2009, **20**, 2881.
- 3 N. K. Mal, M. Fujiwara and Y. Tanaka, *Nature*, 2003, **421**, 350.

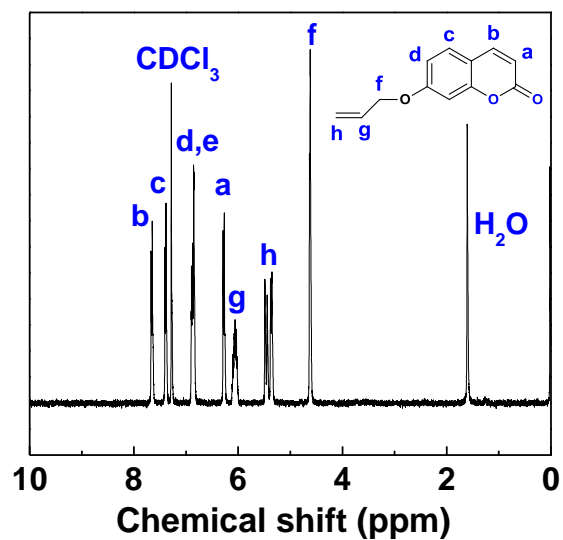
**Table S1.** Physicochemical properties of different samples.

Sample	Grafted amount <sup>a</sup> (wt %)	$S_{\text{BET}}^b$ (m <sup>2</sup> g <sup>-1</sup> )	$D_p^c$ (nm)	$V_p^d$ (cm <sup>3</sup> g <sup>-1</sup> )
MCM-41	0	1010	2.67	0.83
CM-1	0.3	989	2.61	0.79
CM-2	1.0	971	2.52	0.70
CM-3	2.1	955	2.43	0.68
CM-4	5.6	952	2.32	0.63

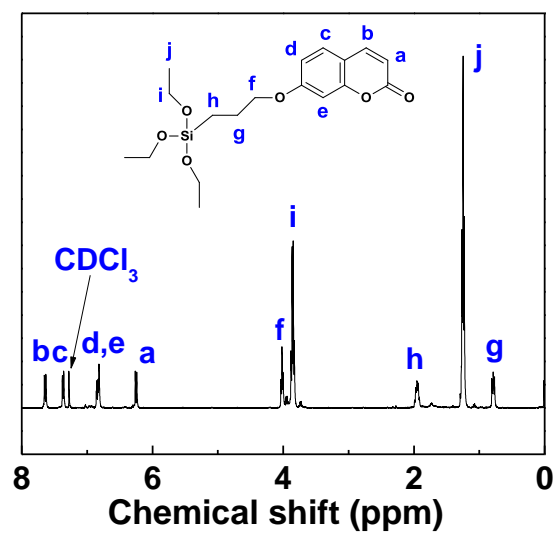
<sup>a</sup> The grafted amount was calculated according to TG data. <sup>b</sup> The BET surface area was calculated using adsorption data in relative pressures ranging from 0.04 to 0.20. <sup>c</sup> The pore size distribution was calculated from the adsorption isotherm by using the BJH method. <sup>d</sup> The pore volume was determined from the amount adsorbed at a relative pressure of about 0.99.



**Fig. S1** The synthetic process of the compound TPC used for grafting.

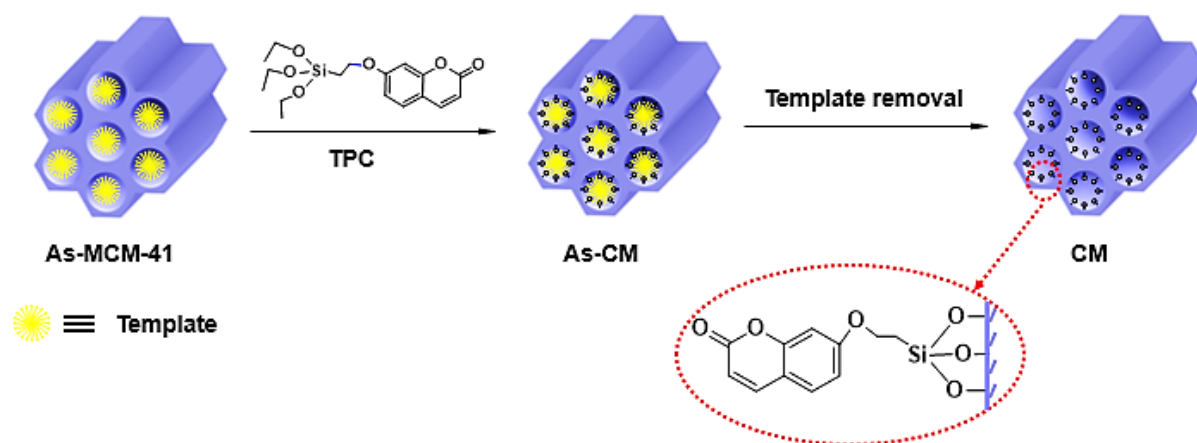


**Fig. S2** <sup>1</sup>H NMR spectrum of 7-allyloxy coumarin recorded at 400 MHz. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ ppm 4.55-4.65 (m, 2H), 5.30-5.37 (m, 1H), 5.40-5.50 (m, 1H), 5.95-6.10 (m, 1H), 6.24 (d, 1H), 6.80 (d, 1H), 6.86 (dd, 1H), 7.37 (d, 1H), 7.64 (d, 1H).

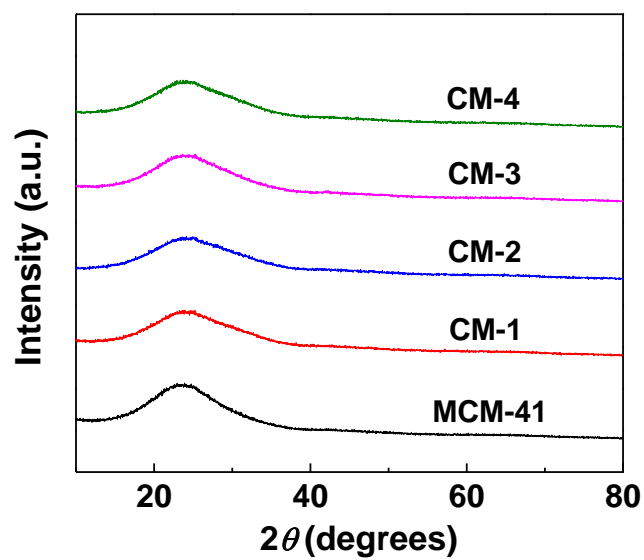


**Fig. S3** <sup>1</sup>H NMR spectrum of 7-[(3-triethoxysilyl) propoxy] coumarin recorded at 400 MHz. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ ppm 0.75-0.80 (m, 2H), 1.24 (t, 9H), 1.92-1.97 (m, 2H), 3.84 (q, 6H), 4.01 (t, 2H), 6.22-6.26 (m, 1H), 6.80-6.83 (m, 2H), 7.33-7.37 (m, 1H), 7.60-7.65 (m, 1H).

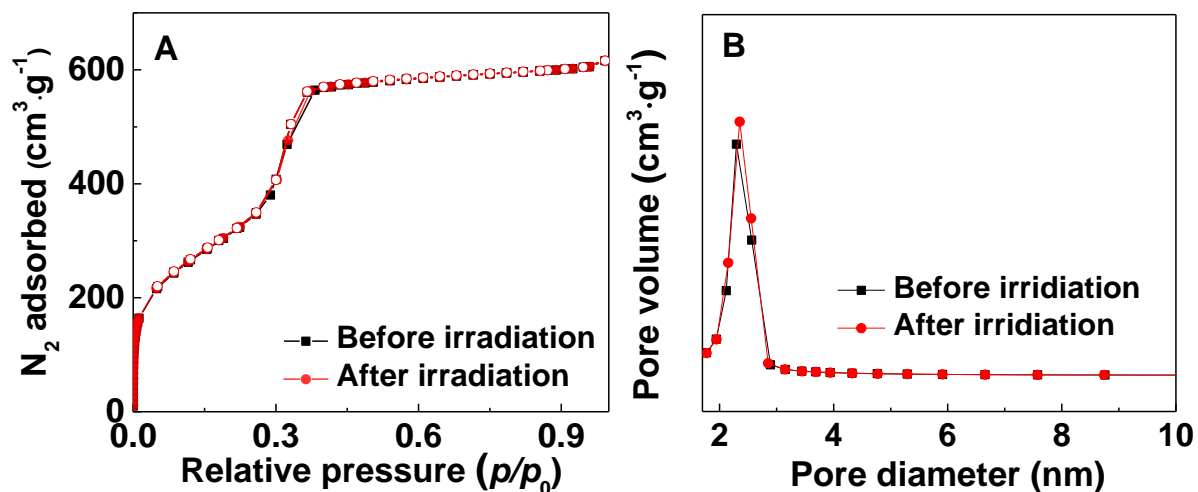




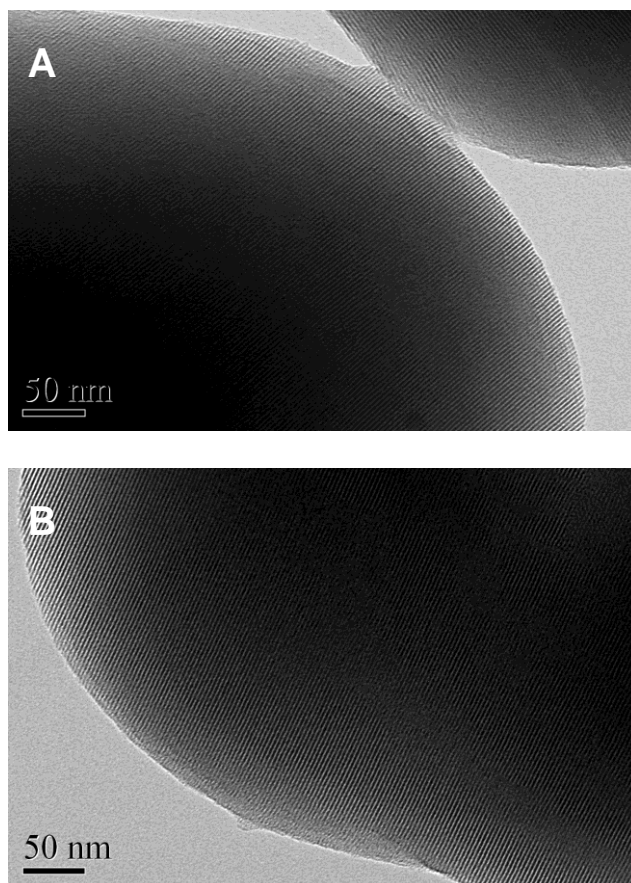
**Fig. S4** The synthetic process of coumarin-modified mesoporous silica MCM-41.



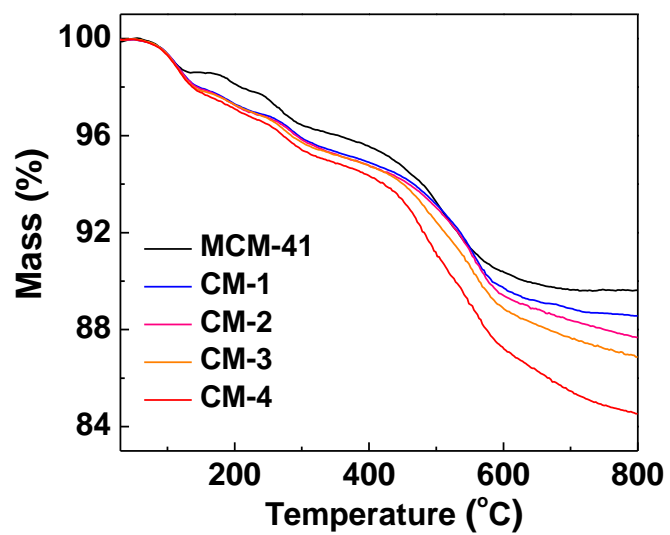
**Fig. S5** Wide-angle XRD patterns of MCM-41, CM-1, CM-2, CM-3, and CM-4 grafted with increasing amount of coumarin substituents.



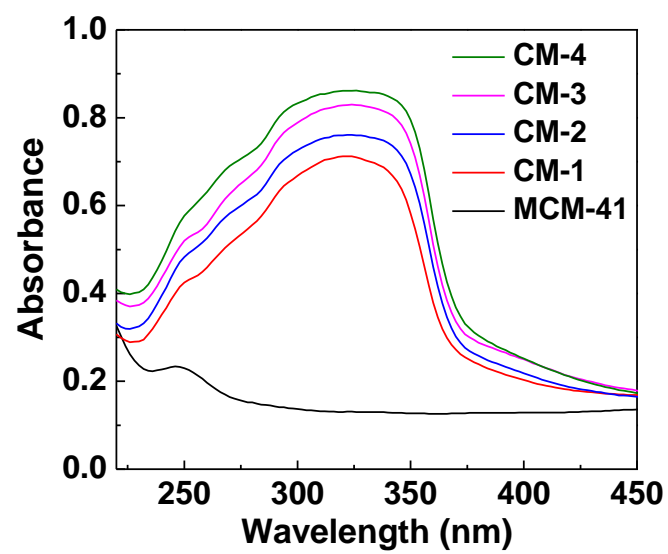
**Fig. S6** (A) N<sub>2</sub> adsorption-desorption isotherms and (B) pore size distributions of the sample CM-2 before and after UV irradiation (> 310 nm).



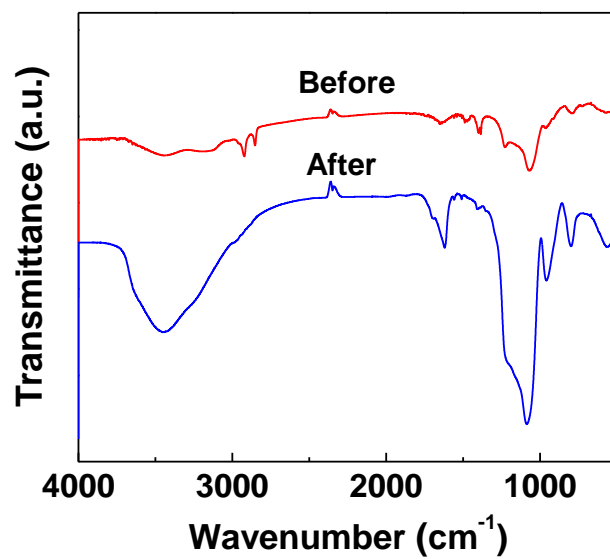
**Fig. S7** TEM images of (A) pristine mesoporous silica MCM-41 and (B) the smart adsorbent CM-2.



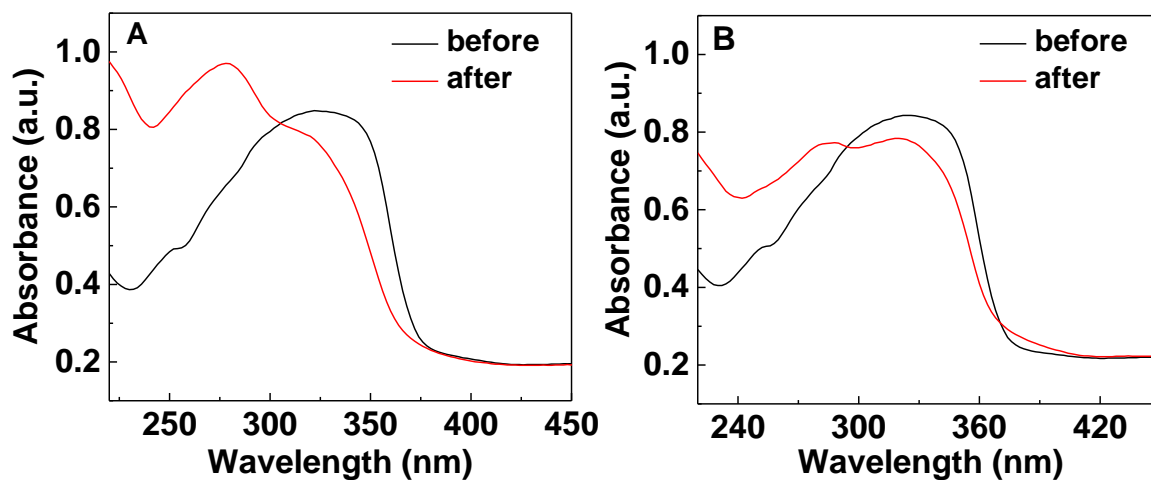
**Fig. S8** TG curves of MCM-41 before and after introduction of molecular gates.



**Fig. S9** UV-vis spectra of MCM-41 before and after introduction of molecular gates.

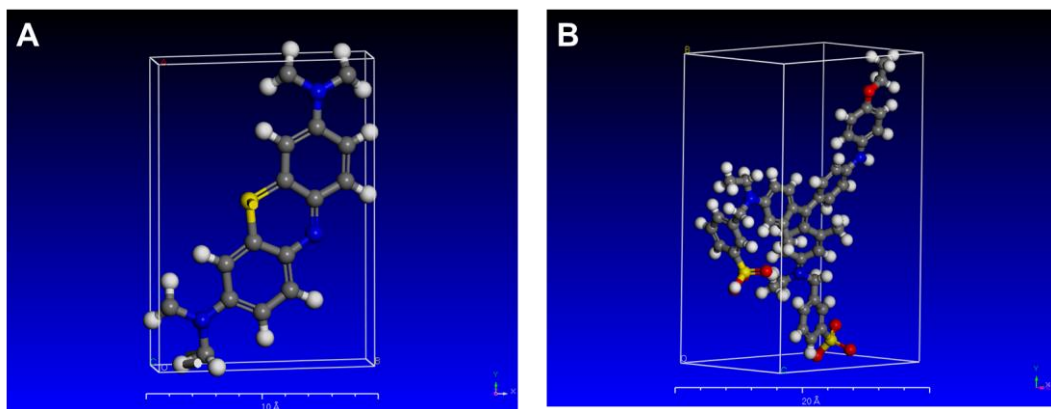


**Fig. S10** IR spectra of the sample CM-2 before and after the removal of template.

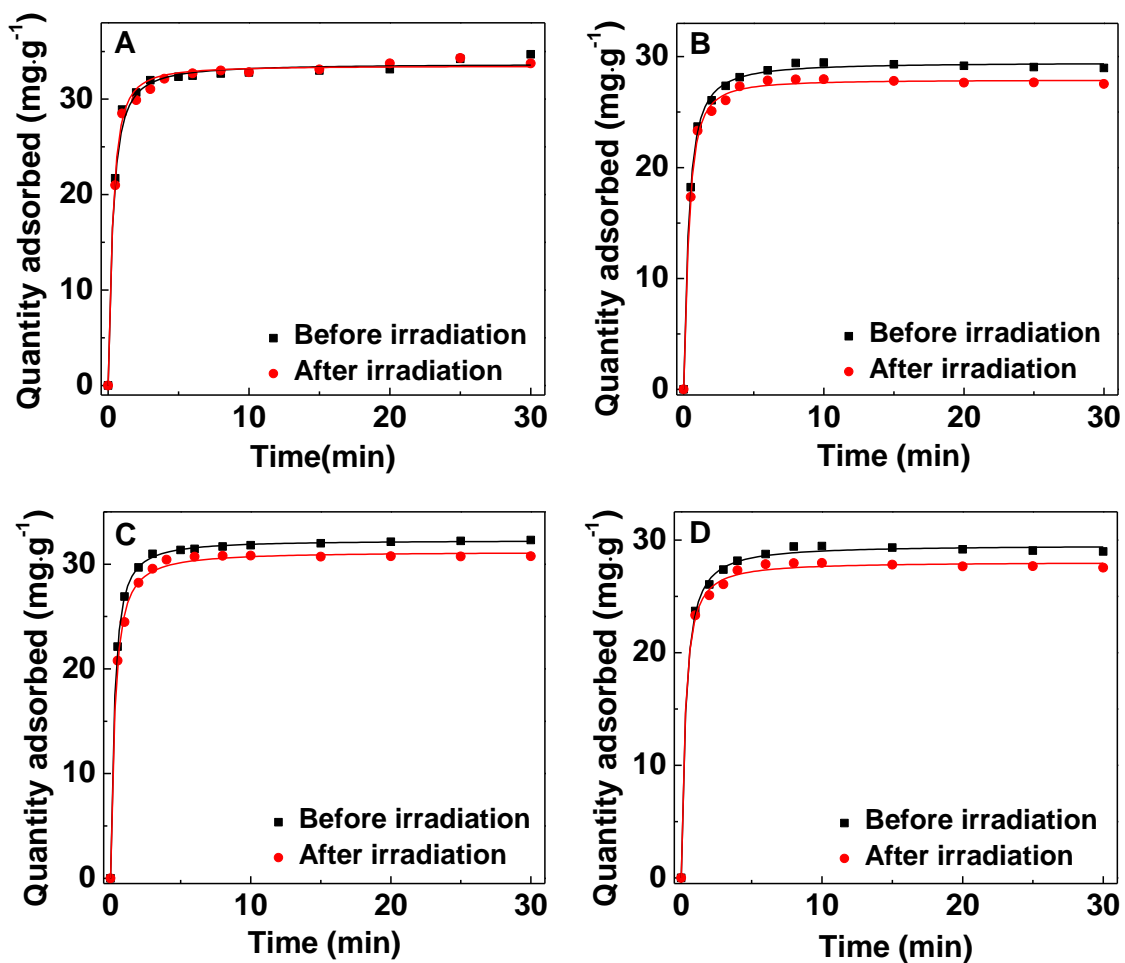


**Fig. 11** UV-vis spectra of the samples (A) CM-2 and (B) CM'-2 before and after UV irradiation for 240 min.

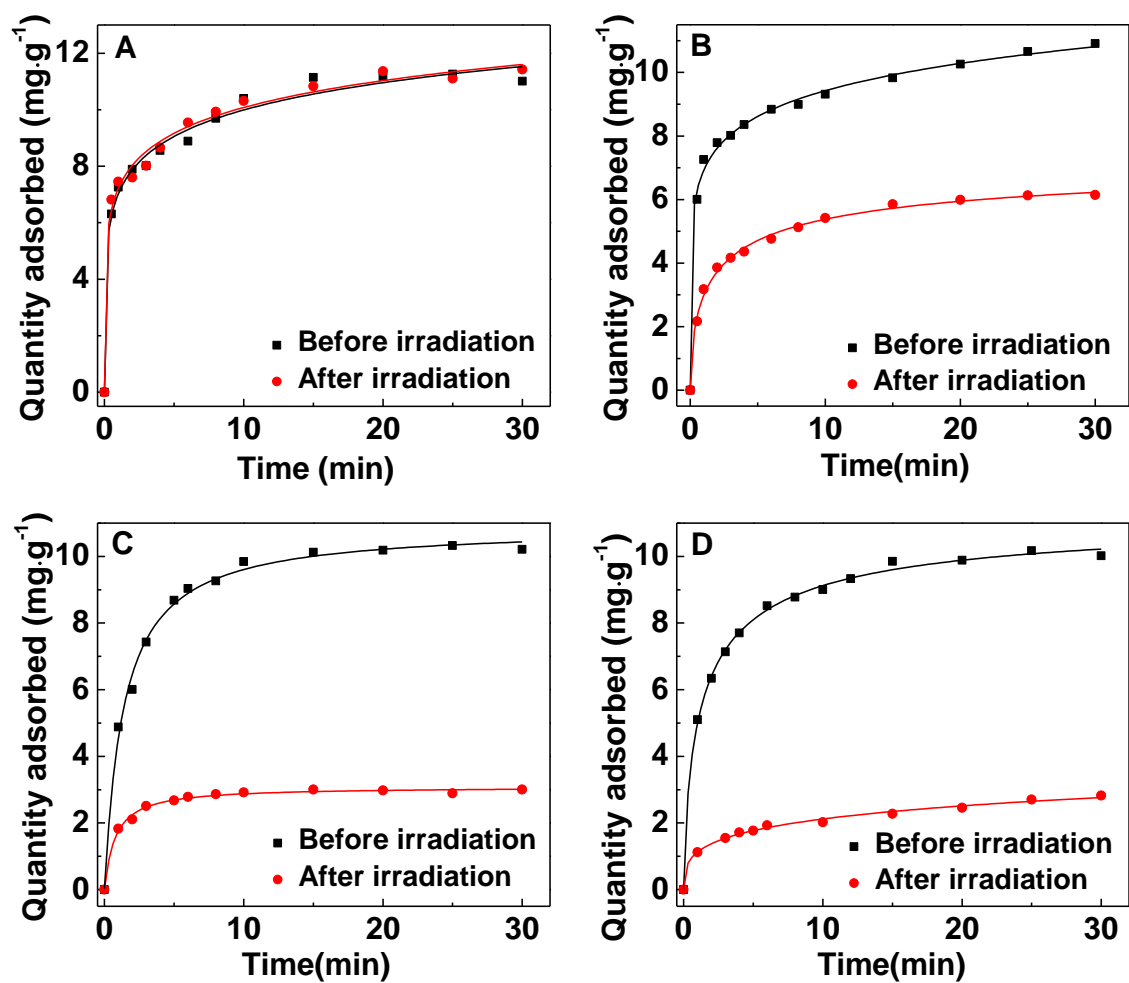




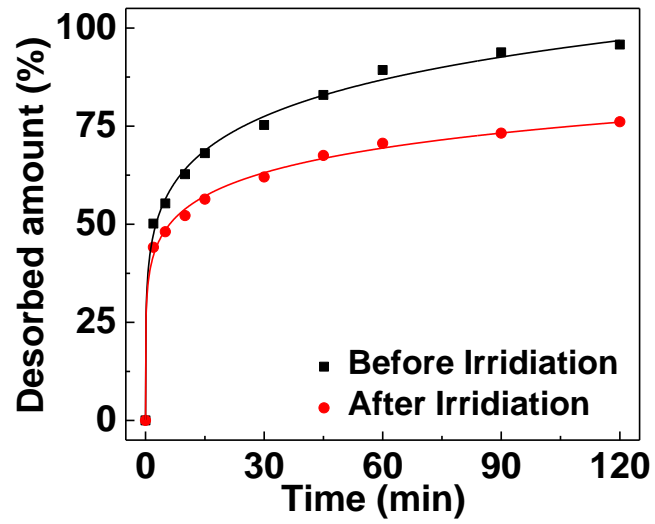
**Fig. S12** The molecular structure of dye molecules (A) methylene blue (MB) and (B) Coomassie brilliant blue (CBB).



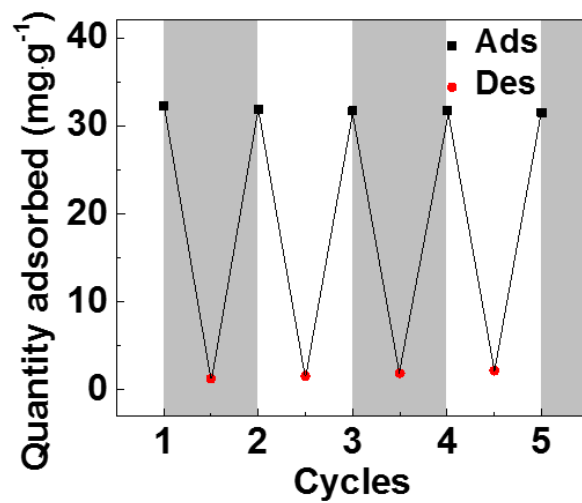
**Fig. S13** Adsorption curves of MB before and after irradiation with UV light (wavelength >310 nm) of samples (A) MCM-41, (B) CM-1, (C) CM-3, and (D) CM-4.



**Fig. S14** Adsorption curves of CBB before and after irradiation with UV light (wavelength >310 nm) of samples (A) MCM-41, (B) CM-1, (C) CM-3, and (D) CM-4.



**Fig. 15** Desorption curves of MB on the smart adsorbent CM-2 before and after irradiation.



**Fig. 16** Adsorption-desorption cycle curves of CM-2. Adsorption and desorption was conducted with the molecular gate closed and opened, respectively.