

Electronic Supplementary Information

**Selective adsorption and efficient regeneration *via* smart adsorbents
possessing thermo-controlled molecular switches**

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General methods

Chemicals

N-isopropylacrylamide (NIPAM; TCI, 97%) was recrystallized twice from a toluene/hexane solution (v/v = 50:50) and dried under vacuum prior to use. 2,2'-azobis(2-methylpropionitrile) (AIBN; Sigma-Aldrich, 98%) was recrystallized twice from methanol and dried under reduced pressure before use. Cetyltrimethylammonium bromide (CTAB; Sigma-Aldrich, 99%), tetraethylorthosilicate (TEOS; Sigma-Aldrich, 98%), (3-mercaptopropyl)trimethoxysilane (MPTMS; Sigma-Aldrich, 95%), tetrahydrofuran (THF; Aladdin, 99%), and ethanol (Aladdin, $\geq 99.9\%$) were used directly without any further purification. Deionized water was generated by a Milli-Q integral pure and ultrapure water purification system and used in all experiments.

Synthesis of thiol-functionalized mesoporous silica (SH@MS)

The support SH@MS was synthesized following a previously described method with some modifications.¹ The template CTAB (1.0 g, 2.74 mmol) was dissolved in a mixture of H₂O (480 mL) and NaOH solution (2 M, 3.5 mL). The obtained solution was heated to 80 °C. After the temperature stabilized, TEOS (5 mL, 2.57×10^{-2} mol) was added dropwise to the solution for 10 min, then added dropwise with MPTMS (0.5 mL, 2.64×10^{-3} mol) to the solution. The mixture was then stirred vigorously at 80 °C for 2 h. The resulting solid was filtered and washed with excessive H₂O and ethanol. Finally, the sample was dried under vacuum to yield the as-synthesized SH@MS, whose pores were occluded by the template CTAB. To remove the surfactant template (CTAB), 1.0 g of as synthesized SH@MS was refluxed for 24 h in a solution of 3 mL of HCl (2 M) and 100 mL of ethanol followed by washing with deionized water and ethanol extensively. The resulting template-free SH@MS material was placed under high vacuum to remove the remaining solvent in the mesopores.

Synthesis of TRP-functionalized mesoporous silica (TRP@MS)

The materials SH@MS (0.2 g) was dispersed in THF (5 mL), followed by addition of NIPAM (0.15 g) and AIBN (1.0 mg) in a Schlenk tube with a stir bar. After the mixture was sealed and deoxygenated by bubbling argon for 30 min, the mixture subsequently stirred for 12 h at 0 °C in the dark. Then, the Schlenk tube was placed in an oil bath preheated to 65 °C for 12 h for polymerization. After that, the

product was soaked in a large number of THF for 12 h to remove unreacted monomers and any detachable polymer. The obtained solid was collected by centrifugation and washed with ethanol several times and dried under vacuum, leading to the formation of TRP@MS.

Characterization

^{13}C cross polarization magic angle spinning NMR (^{13}C CP MAS) spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz). Differential scanning calorimetry (DSC) was performed using a DSC Q100 from TA instruments under nitrogen with 2 °C/min ramping rate from 20 to 50 °C. The samples were dispersed in deionized water and the resulting slurries were sealed in the sample pans. UV-vis spectra were collected on the SHIMADZU UV-2600 in the region of 200-800 nm. Particle size measurements were carried out by dynamic light scattering (DLS) using a Malvern Instrument Zetasizer nano series instrument in water at temperatures ranging from 20 to 50 °C, where the intensity weighted mean hydrodynamic size (Z-average) were obtained from analysis of the autocorrelation function. At least 3 measurements at 20~50 °C were made for each sample with an equilibrium time of 5 min before starting the measurement.

X-ray diffraction (XRD) patterns of samples were recorded with an X-ray diffractometer (Japan Rigaku D/MAX- γ A) using Cu K α radiation. Transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) analysis were performed using an FEI Tecnai G2 F30 S-Twin electron microscope operated at 300 kV. Scanning electron microscope (SEM) images were collected on a Hitachi New Generation SU8010 field emission scanning electron microscope. N₂ adsorption-desorption isotherms were measured using ASAP 2020 analyzer at -196 °C. The samples were degassed at 80 °C for 12 h prior to analysis. The Brunauer-Emmett-Teller (BET) surface area was calculated using adsorption data in a relative pressure ranging from 0.05 to 0.3. The total pore volume was determined from the amount adsorbed at a relative pressure of about 0.99. The pore diameter was calculated from the adsorption branch by using the Barrett-Joyner-Halenda (BJH) methods. Fourier transform infrared (IR) spectra of the samples were carried out on a Nicolet Nexus 470 spectrometer with KBr wafer. The elemental analysis (C, H, N, and S) was performed by a Vario Micro Cube elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany). Thermogravimetric (TG) analysis curves were obtained from the use of a thermobalance analyzer (STA-499C, NETZSCH). The

sample was heated from room temperature to 800 °C with a heating rate of 10 °C/min under a flow of nitrogen (10 mL/min).

Adsorption experiments

An adsorbent was weighted precisely and added to a cuvette, followed by the addition of dye solution (coomassie brilliant blue or methylene blue). Adsorption was conducted statically at 25 and 45 °C until the equilibrium was reached. The dye concentration was determined using a UV-vis spectrophotometer at appropriate time intervals.^{2,3} 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/water solution at 25 and 45 °C. 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

- S1. S. Giri, B. G. Trewyn, M. P. Stellmaker and V. S. Y. Lin, *Angew. Chem. Int. Ed.*, 2005, **44**, 5038-5044.
- S2. X. Zhuang, Y. Wan, C. Feng, Y. Shen and D. Zhao, *Chem. Mater.*, 2009, **21**, 706-716.
- S3. K. Y. Ho, G. McKay and K. L. Yeung, *Langmuir*, 2003, **19**, 3019-3024.

Table S1 Textual properties and elemental compositions of MS, SH@MS, and TRP@MS.

| Sample | S_{BET} (m ² /g) | V_{p} (cm ³ /g) | D_{p} (nm) | Elemental composition (wt%) | | | |
|---------------|---|--|------------------------|------------------------------------|----------|----------|----------|
| | | | | C | H | N | S |
| MS | 1143 | 1.16 | 2.9 | 3.04 | 1.73 | 0.06 | 0.12 |
| SH@MS | 889 | 0.87 | 2.3 | 1.19 | 2.79 | 0.08 | 3.91 |
| TRP@MS | 642 | 0.58 | 1.9 | 19.34 | 3.77 | 1.81 | 3.12 |

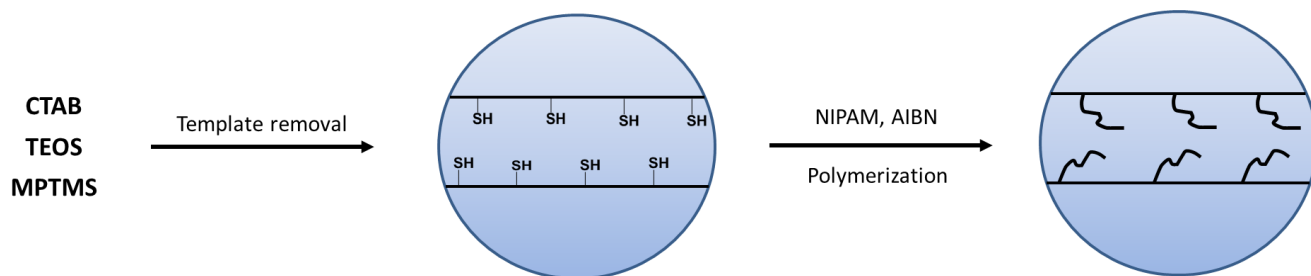


Fig. S1 Schematic synthetic process of the adsorbent TRP@MS.

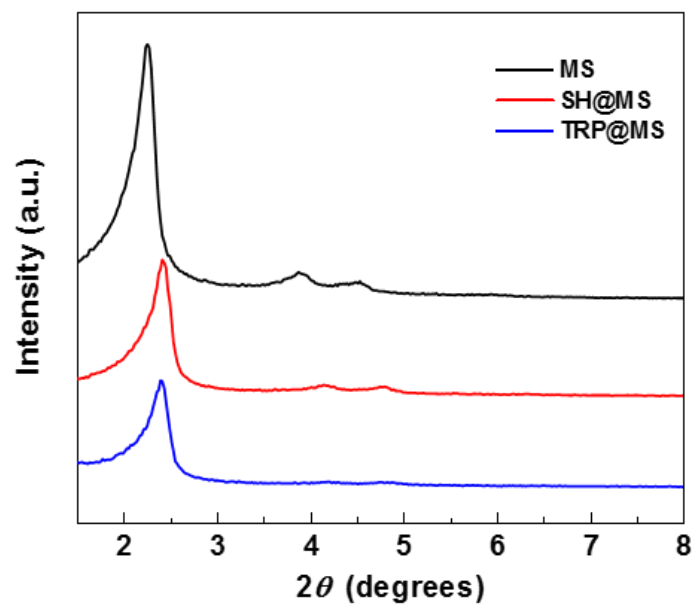


Fig. S2 Low-angle XRD patterns of the samples MS, SH@MS, and TRP@MS.

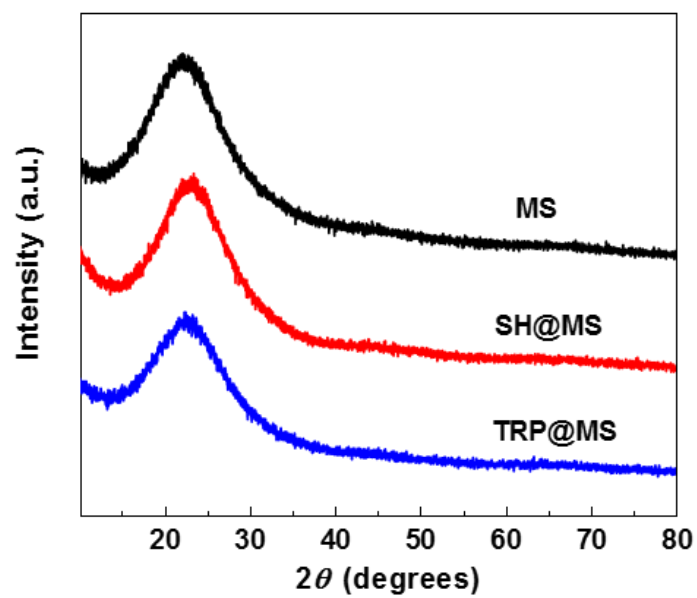


Fig. S3 Wide-angle XRD patterns of the samples MS, SH@MS, and TRP@MS.

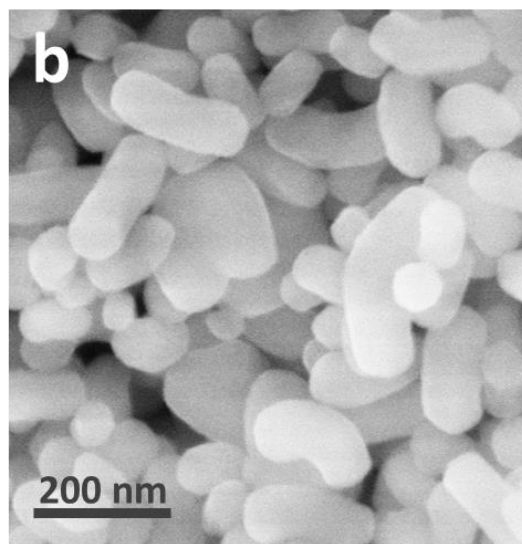
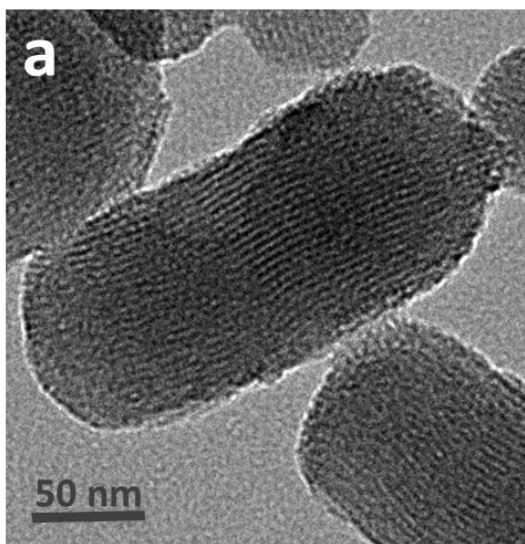


Fig. S4 (a) TEM and (b) SEM images of the sample TRP@MS.

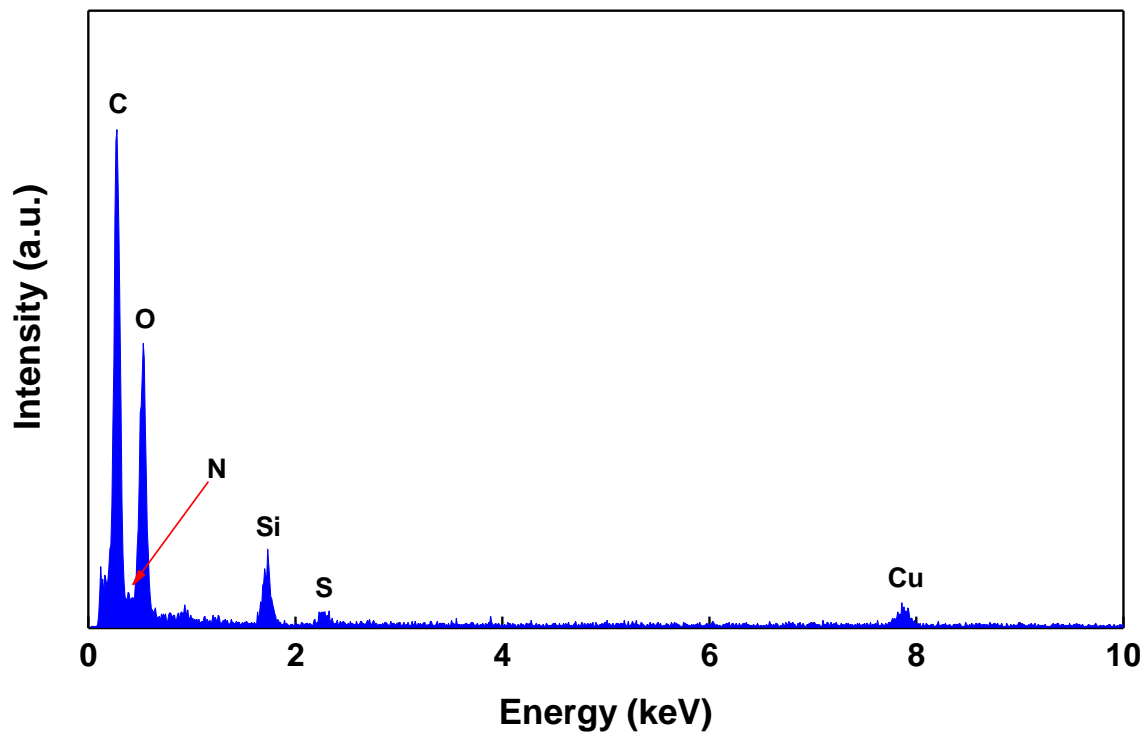


Fig. S5 EDX spectrum of the sample TRP@MS. The element Cu was originated from the Cu grid used in the measurement.

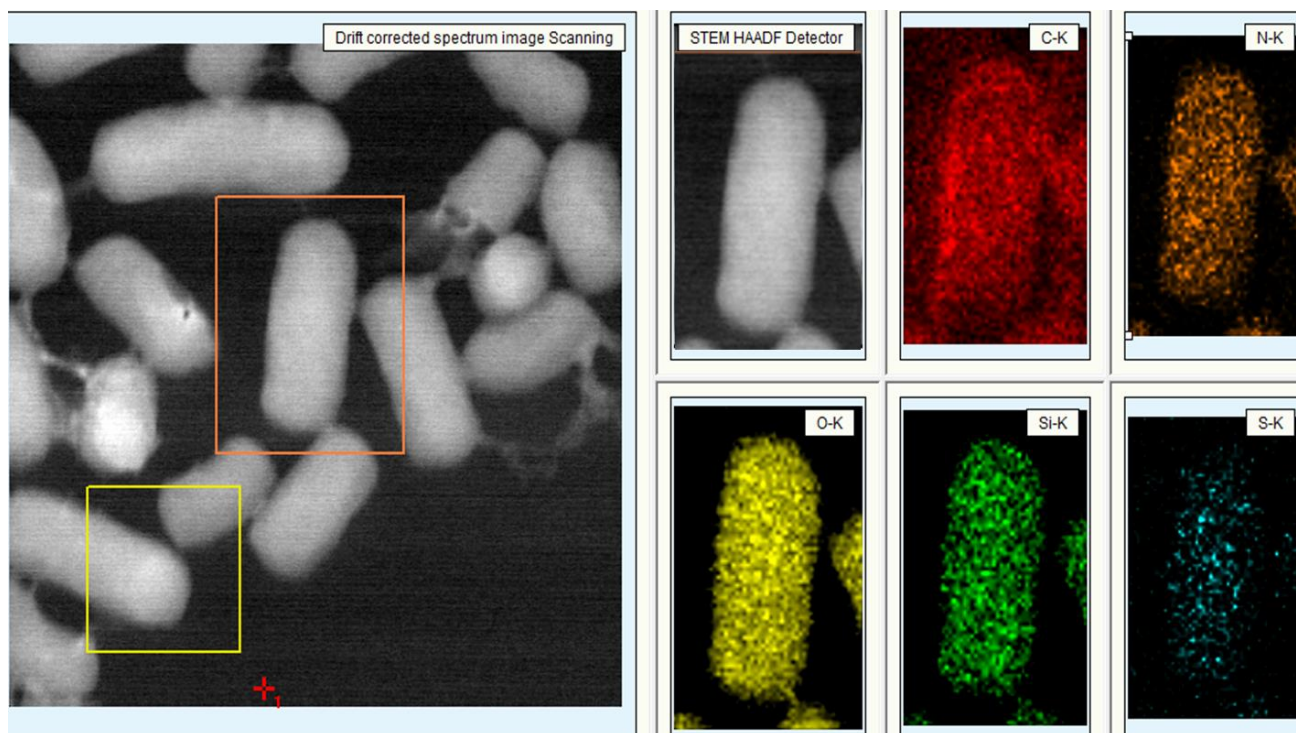


Fig. S6 HAADF STEM and STEM-EDX mapping images of C, N, O, Si, and S elements of TRP@MS.

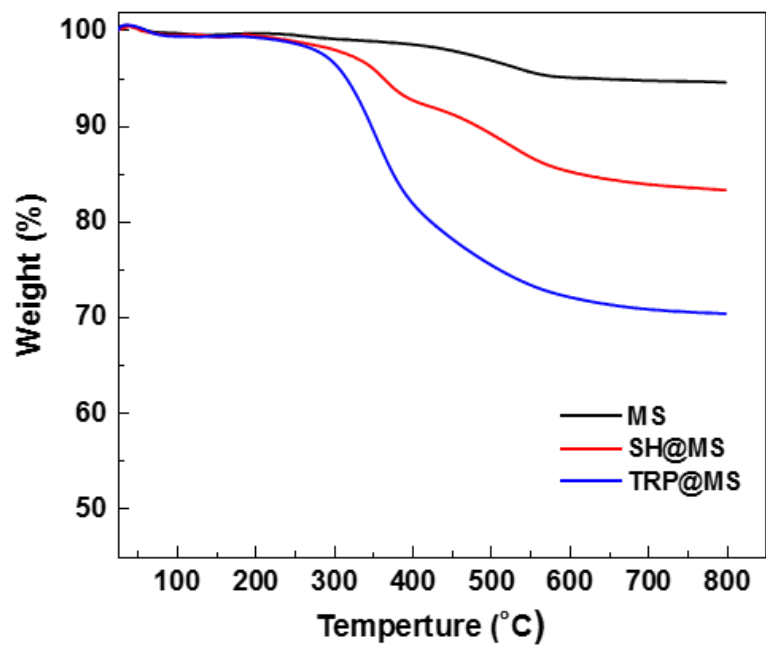


Fig. S7 TG curves of the samples MS, SH@MS, and TRP@MS.

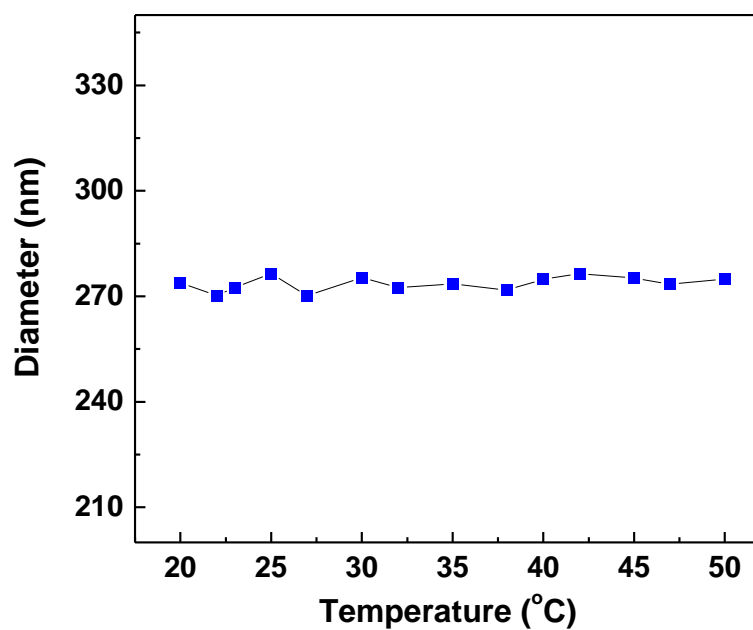


Fig. S8 Plot of diameter as a function of temperature for the aqueous solution of TRP@MS by using DLS.

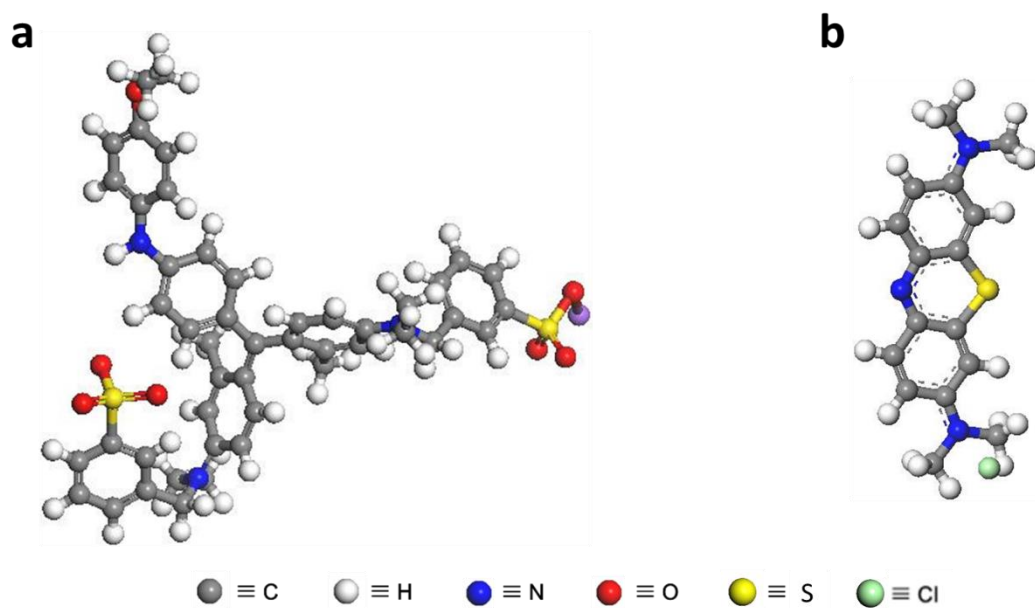


Fig. S9 The molecular structure of guest molecules (a) Coomassie brilliant blue (CBB) and (b) methylene blue (MB).