Electronic Supplementary Information

Metal-Organic Framework Tethering PNIPAM for ON-OFF Controlled Release in Solution

Shunjiro Nagata, Kenta Kokado*, Kazuki Sada*

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Experimental Section

Materials

All reagents were obtained from commercial sources and used without further purification.

PNIPAM-NHS ($M_n \sim 2,000$) were purchased from Sigma-Aldrich.

Measurements. $^1$H (500 MHz) NMR measurements were recorded on a Bruker Biospin AVANCE DRX500 instrument, using 0.05% tetramethylsilane (TMS) as an internal standard. Size exclusion chromatography (SEC) at room temperature was carried out on a SHIMADZU LC-9A system (SHODEX KD-805 column) with a SPD-10AVP UV-Vis Detector using chloroform as an eluent, after calibration with the standard polystyrene samples. UV-Vis spectra and turbidity were recorded on a JASCO V-570 spectrophotometer with a JASCO ETC-50ST temperature controller. Powder X-ray diffraction (XRD) patterns were obtained by Bruker AXS D8 ADVANCE. Scanning electron microscope (SEM) images were obtained by using a JEOL JSM-7400F. Transmitting electron microscope (TEM) images were acquired by using a JEOL JEM-2100F. Fourier transform infrared (FTIR) spectra were observed with a JASCO FTIR-4100 SK spectrometer with a ZnSe prism kit PKS-ZNSE for ATR technique. Dynamic light scattering (DLS) measurement was conducted by a Beckman-Coulter Delsa Nano HC.

Synthesis of UiO-66-NH$_2$

In an autoclave vial, 2-amino-benzenedicarboxylic acid (11 mg, 61 $\mu$moL), ZrCl$_4$ (12 mg, 52 $\mu$mol), and benzoic acid (190 mg, 1.6 mmol) were dissolved in DMF (1 mL), and the mixture was kept still standing at 120 °C for 24 h. After cooling to room temperature, the crystal was collected by centrifuging (2,000 rpm, 3 min), with repeating wash by DMF and methanol.
Synthesis of UiO-66-PNIPAM

In a 5mL screw vial, UiO-66-NH$_2$ (60 mg) and 0.1 M PNIPAM-NHS solution (500 μL) in chloroform were mixed, and the mixture was kept still standing at 60 °C for 24 h. After cooling to room temperature, the crystals were collected by filtration and repeatedly washed by chloroform and methanol. The modification rate was determined by $^1$H NMR after digestion of the crystal by HF aq.

Modification of UiO-66-NH$_2$ by acetic anhydride

In a 5mL screw vial, UiO-66-NH$_2$ (10 mg) and 0.4 M acetic anhydride solution (2 mL) in chloroform were mixed, and the mixture was kept still standing at 60 °C for 48 h. After cooling to room temperature, the crystals were collected by centrifuging (10,000 rpm, 5 min), and immersed in chloroform for 3 days to remove the residual acetic anhydride. Finally, the crystal was collected by centrifuging (10,000 rpm, 5 min). The modification rate was determined by $^1$H NMR after digestion of the crystal by HF aq.

Guest loading of UiO-66-PNIPAM

In a 5mL screw vial, UiO-66-PNIPAM (10 mg) was immersed in 50 mM guest solution (1 mL), and it was kept standing at 25 °C for 24 h. The crystal was collected by centrifuging (10,000 rpm, 40 °C, 5 min) and washed by water, and this cycle was repeated 10 times. The amount of whole guest was determined by $^1$H NMR after digestion of the crystal by HF aq.
**Fig. S1** Thermoresponsiveness of PNIPAM-NHS (15 g/L in water).

**Fig. S2** DLS histogram of UiO-66-PNIPAM.
Fig. S3 XRD patterns of UiO-66, UiO-66-NH$_2$, and UiO-66-PNIPAM.

Fig. S4 FT-IR spectra of UiO-66-NH$_2$, and UiO-66-PNIPAM.
Fig. S5 $^1$H NMR spectra change upon acetylation of UiO-66-NH$_2$ and UiO-66-PNIPAM.

Fig. S6 Time-course UV-Vis spectra upon release of resorufin from UiO-66-PNIPAM in (a) open state (25 °C) and (b) closed state (40 °C).
Fig. S7 Release behavior of resorufin from pristine UiO-66-NH$_2$ (open triangle, 40 ºC) and UiO-66-PNIPAM (filled triangle, 25 ºC and 40 ºC). The release ratio was determined from the absorbance at 572 nm.

Fig. S8 $^1$H NMR spectra of digesting solution of UiO-66-PNIPAM treated with resorufin water solution (50mM) at 40 ºC.
Fig. S9 Release behavior of resorufin from UiO-66-PNIPAM (filled triangle) and UiO-66-PNIPAM(4.2) (open triangle) at 25 °C and 40 °C. The release ratio was determined from the absorbance at 572 nm.

Fig. S10 $^1$H NMR spectra of digesting solution of UiO-66-NH$_2$ and UiO-66-PNIPAM treated with PPIX water solution (50mM).
Fig. S11 Release behavior of resorufin from reloaded UiO-66-PNIPAM until 3 times at 25 ºC and 40 ºC. The release ratio was determined from the absorbance at 572 nm.

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