Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

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

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Experimental Section

Materials

All reagents were obtained from commercial sources and used without further purification. PNIPAM-NHS (M_n ~ 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 μmoL), $ZrCl_4$ (12 mg, 52 μmol), and benzoic acid (190 mg, 1.6 mmol) were dissolved in DMF (1 mL), and the mixture was kept still standing at 120 ºC 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 ºC 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 ºC 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 ºC for 24 h. The crystal was collected by centrifuging (10,000 rpm, 40 ºC, 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.

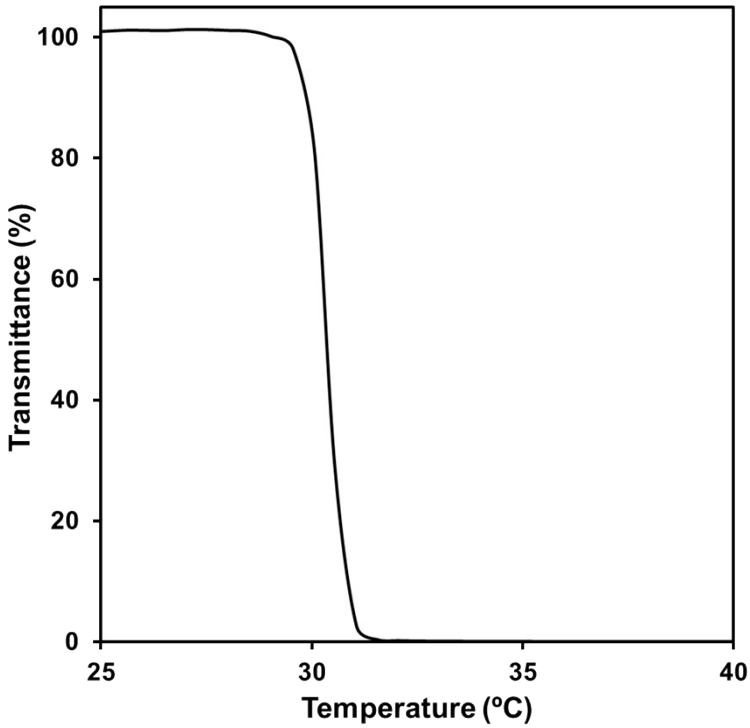

Fig. S1 Thermoresponsiveness of PNIPAM-NHS (15 g/L in water).

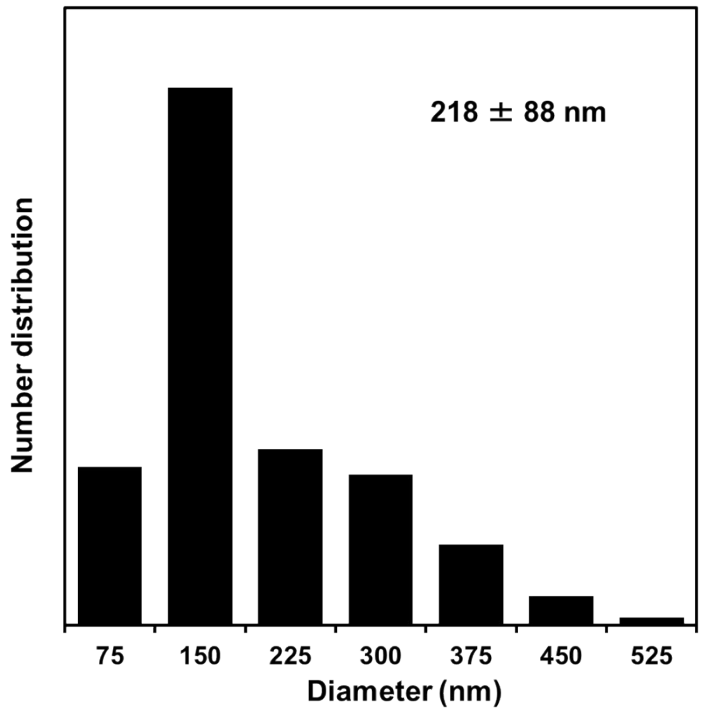

Fig. S2 DLS histogram of **UiO-66-PNIPAM**.

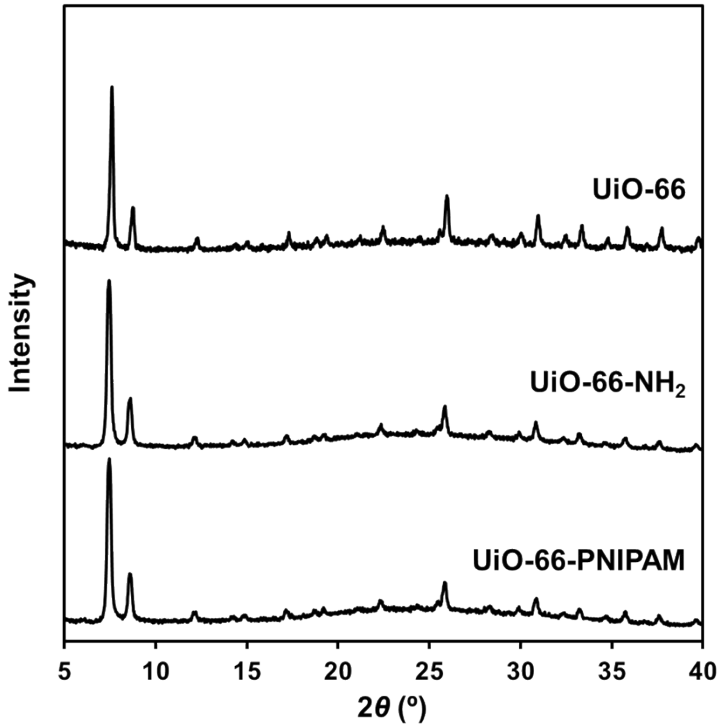

Fig. S3 XRD patterns of UiO-66, **UiO-66-NH_2**, and **UiO-66-PNIPAM**.

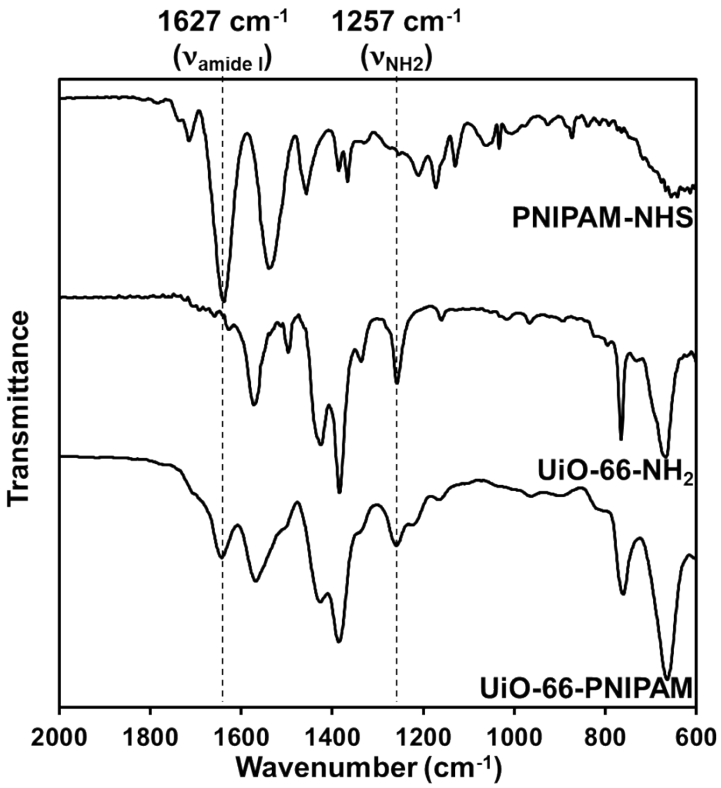

Fig. S4 FT-IR spectra of **UiO-66-NH_2**, and **UiO-66-PNIPAM**.

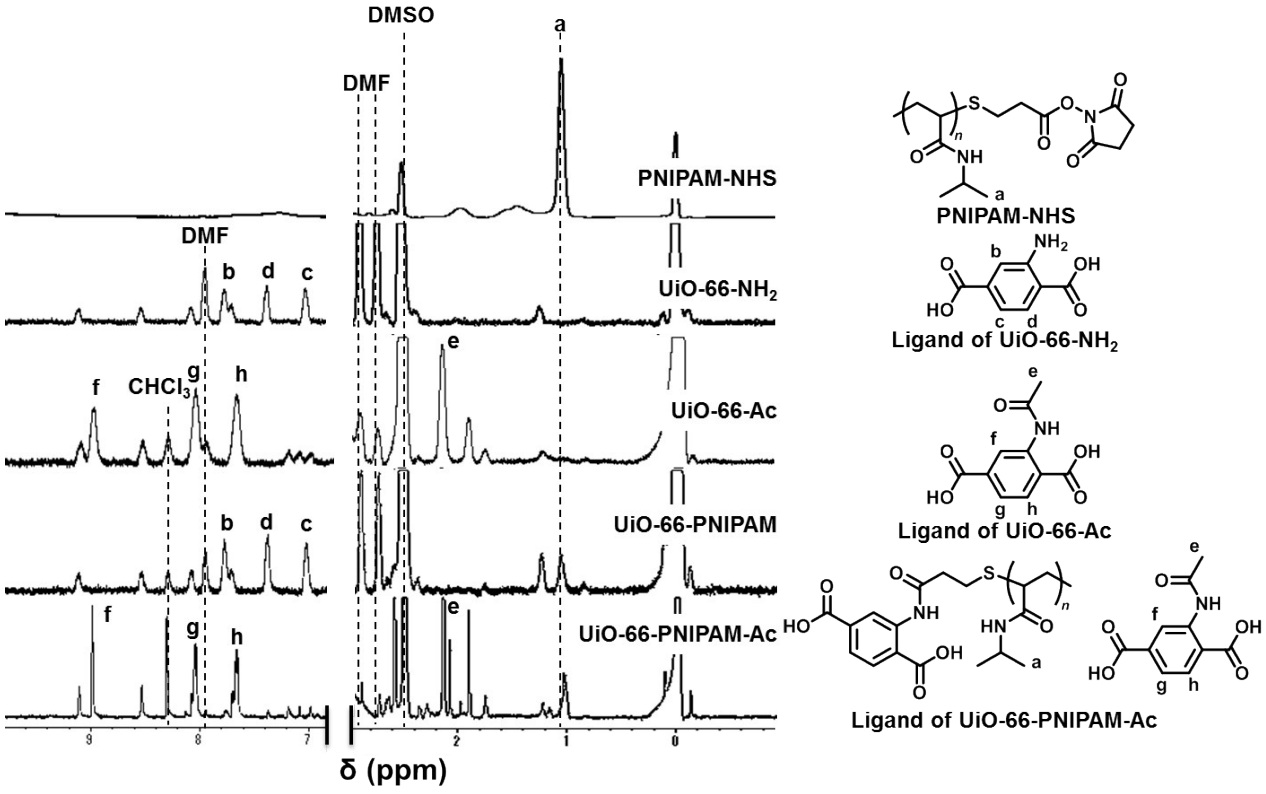

Fig. S5 ^{1}H NMR spectra change upon acetylation of **UiO-66-NH$_2$** and **UiO-66-PNIPAM**.

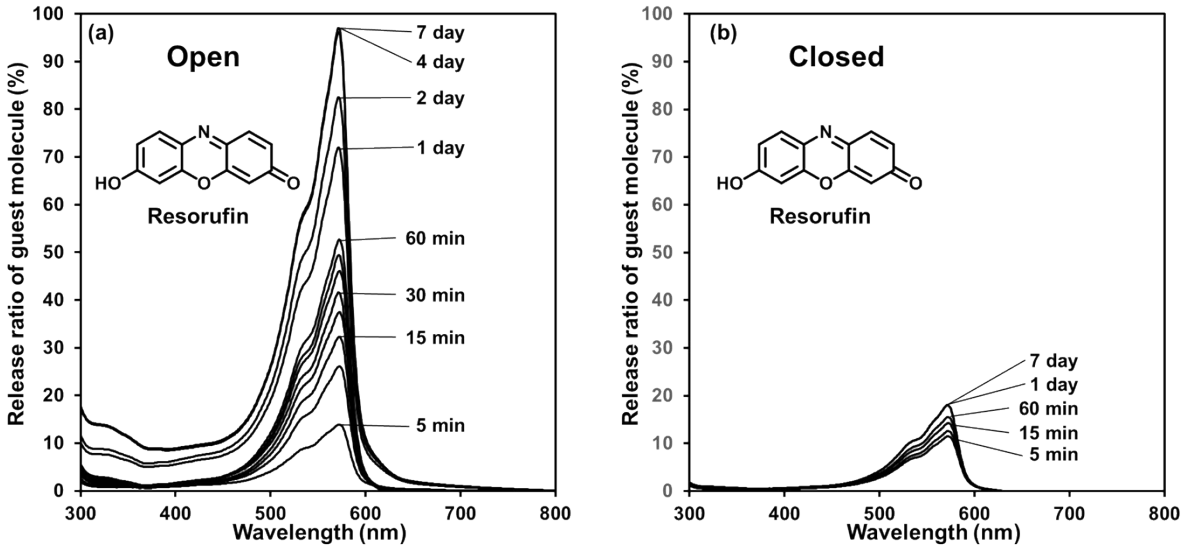

Fig. S6 Time-course UV-Vis spectra upon release of resorufin from **UiO-66-PNIPAM** in (a) open state (25 °C) and (b) closed state (40 °C).

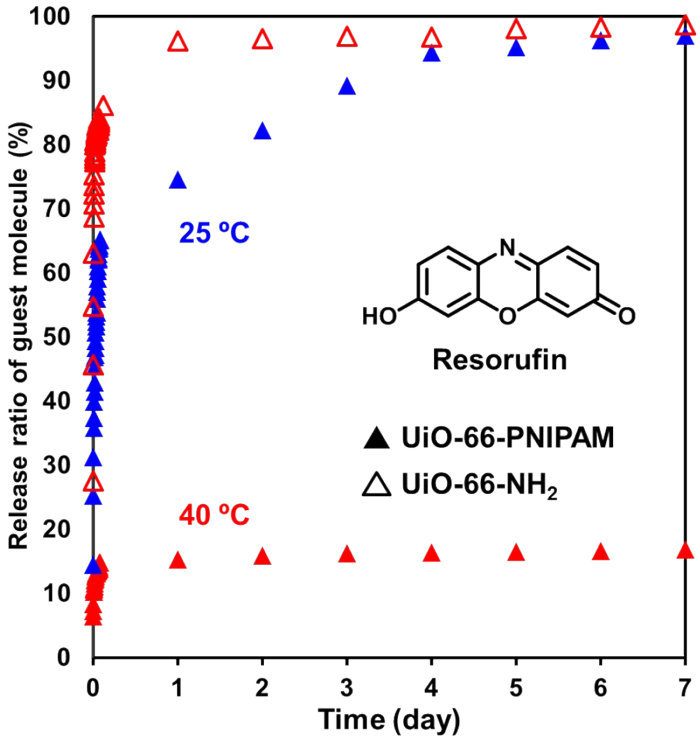

Fig. S7 Release behavior of resorufin from pristine **UiO-66-NH_2** (open triangle, 40 ºC) and **UiO-66-PNIPAM** (filled triangle, 25 ºC and 40 ºC). The release ratio was determined from the absorbance at 572 nm.

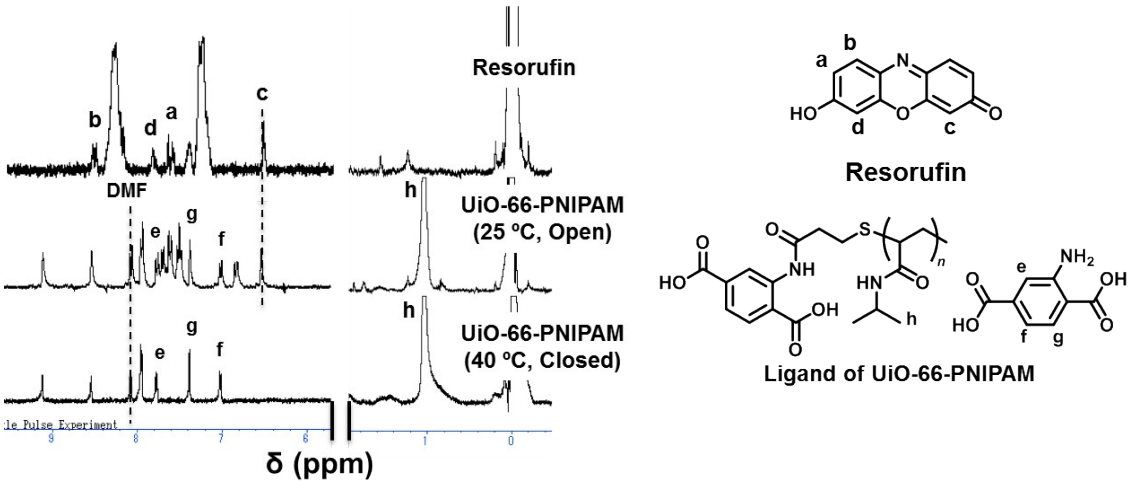

Fig. S8 ^{1}H NMR spectra of digesting solution of **UiO-66-PNIPAM** treated with resorufin water solution (50mM) at 40 ºC.

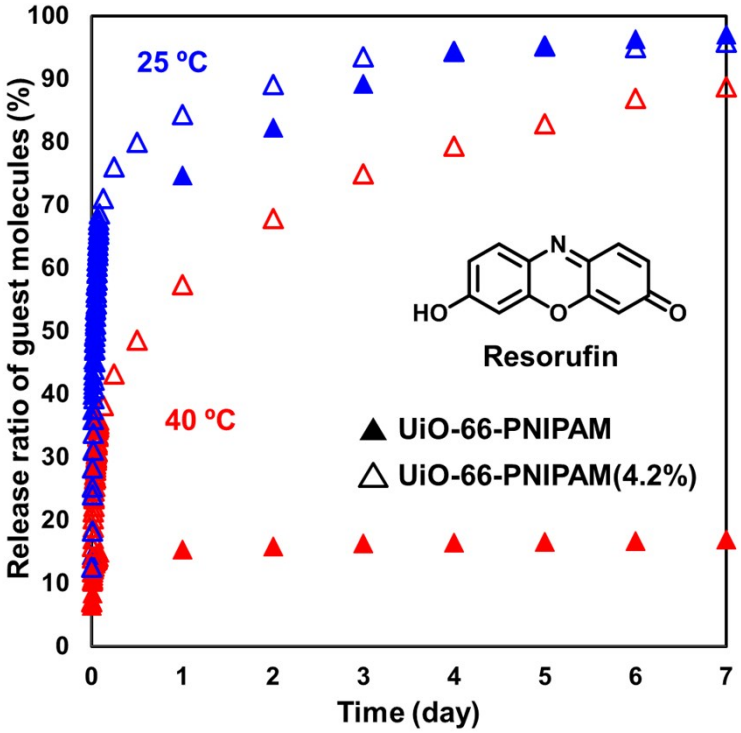

Fig. S9 Release behavior of resorufin from **UiO-66-PNIPAM** (filled triangle) and **UiO-66-PNIPAM(4.2)** (open triangle) at 25 ºC and 40 ºC. The release ratio was determined from the absorbance at 572 nm.

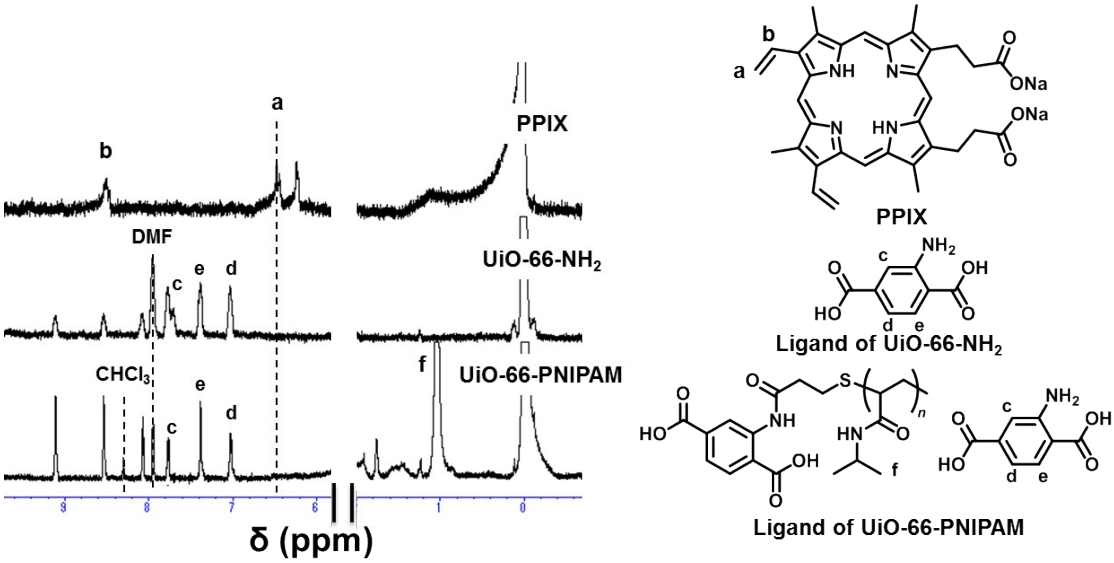

Fig. S10 ^{1}H NMR spectra of digesting solution of **UiO-66-NH$_2$** and **UiO-66-PNIPAM** treated with **PPIX** water solution (50mM).

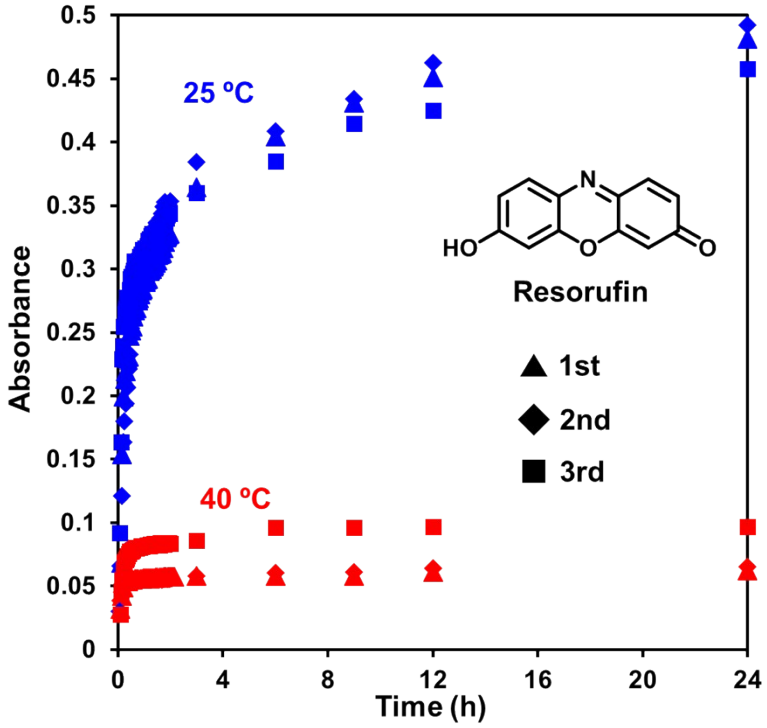

Fig. S11 Release behavior of resorufin from reloaded **UiO-66-PNIPAM** until 3 times at 25 ºC and 40 ºC. The release ratio was determined from the absorbance at 572 nm

Acknowledgement

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