

Electronic Supplementary Information

Dual-responsive supramolecular colloidal microcapsules from cucurbit[8]uril molecular recognition in microfluidic droplets

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Additional data related to this publication is available at the University of Cambridge data repository (<http://dx.doi.org/10.17863/CAM.11810>)

Dynamic light scattering (DLS) characterisation

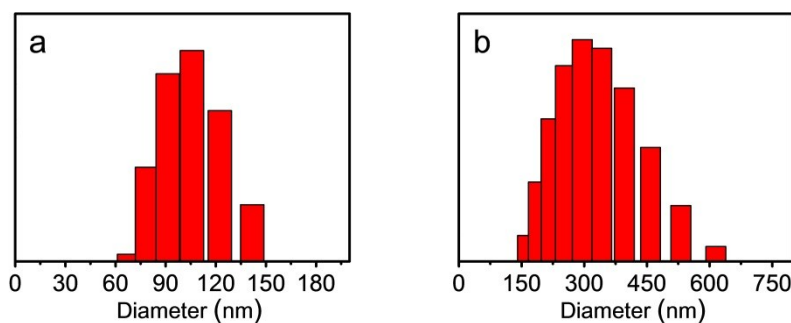


Fig. S1. DLS of (a) the template P(St-co-StMV) colloidal particles in neutral aqueous solution ($\bar{\phi}$ = 100 nm, PDI = 0.05) and (b) the colloidal particles (MCP) after surface grafting with NIPAM ($\bar{\phi}$ = 322 nm, PDI = 0.08).

Fourier transform infrared (FTIR) spectra characterisation

Spectrum (a) in Fig. S2 reports the FT-IR of the template PSt-co-PStMV colloidal particles. The characteristic absorption peaks at 1600, 1493, 1452, 757, and 697 cm^{-1} are attributed to the polystyrene (PS) segment, with the absorptions at 3100-2820 cm^{-1} are ascribed to the C-H stretch next to nitrogen. Those characteristic absorption peaks confirmed the formation of the P(St-co-StMV) colloidal particles. Spectrum (b) reports the FT-IR of the MV-bearing colloidal particles (MCP). The absorption at the areas of 1660-1780 cm^{-1} originate from the amide C=O stretch, and the absorption at 3300-3700 cm^{-1} are ascribed to the amide N-H stretch from PNIPAM segment.

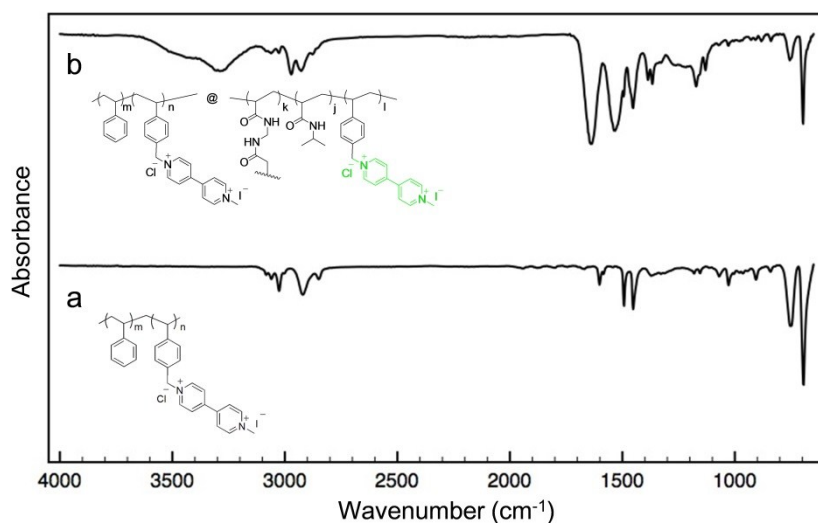


Fig. S2. Fourier transform infrared (FTIR) spectra of (a) the template PSt-co-PStMV colloidal particles and (b) MV-bearing colloidal particles (MCP)

Schematic illustration

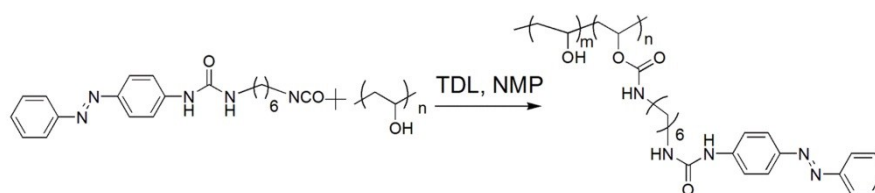


Fig. S3 Schematic illustration of the preparation of azobenzene functionalised poly(vinyl alcohol) (AP).

FTIR spectra characterisation

Fig. S4(a) shows the FTIR spectra of poly(vinyl alcohol). The broad peak observed between 3550 and 3100 cm^{-1} is attributed to the O-H stretch from the intermolecular and intramolecular hydrogen bonds from poly(vinyl alcohol). The vibrational band observed at 2939 cm^{-1} arises from the C-H stretch from the alkyl groups. (b) in Fig. S4 shows the FTIR spectra of the azobenzene functionalised poly(vinyl alcohol) (AP). The absorption at 1730 cm^{-1} originates from stretching of the carbonyl groups. Moreover, the weakened signal between 3550 and 3100 cm^{-1} indicates the decrease of OH fraction.

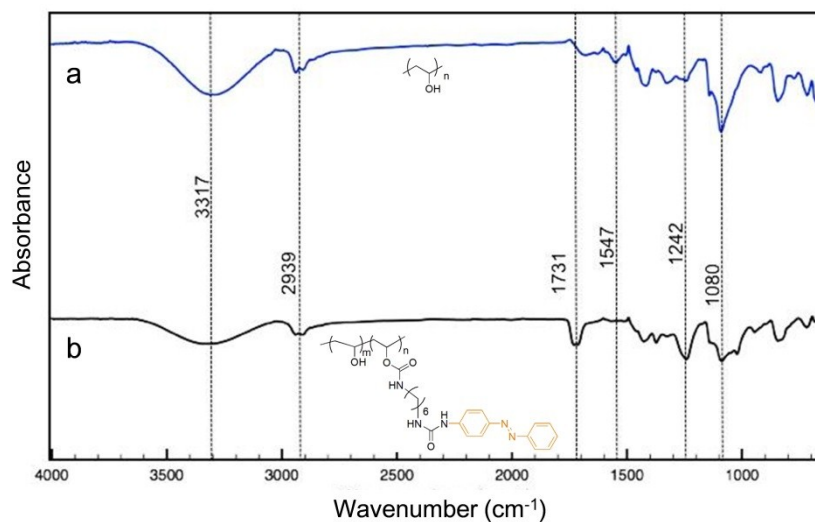


Fig. S4. FTIR spectra of (a) poly(vinyl alcohol) and (b) azobenzene functionalised poly(vinyl alcohol) (AP)

^1H NMR spectrum characterisation

^1H NMR analysis showed the polymer structure contained 2.5 mol% azobenzene guests in the final polymer

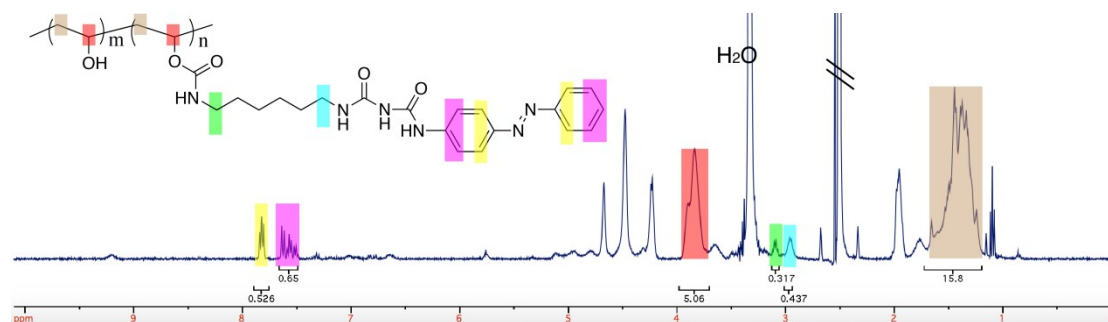


Fig. S5 ^1H NMR spectrum of polymer AP.

Schematic illustration

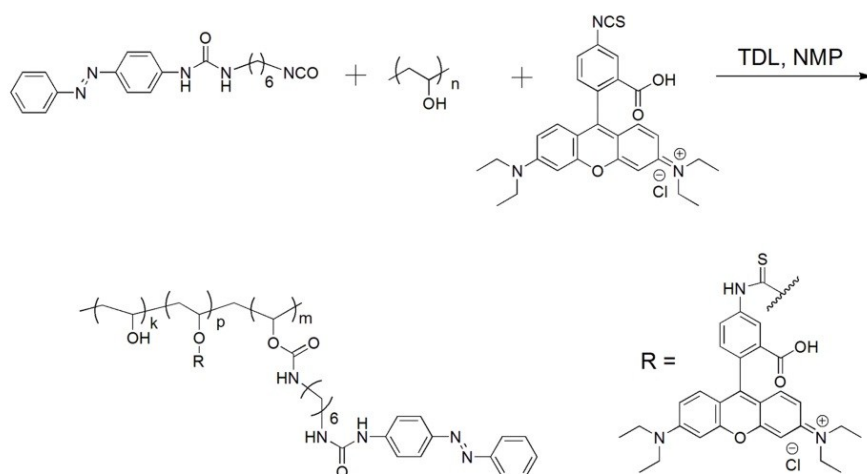


Fig. S6 Schematic illustration of the preparation of Rhodamine B-labelled AP.

Optical microscopy image

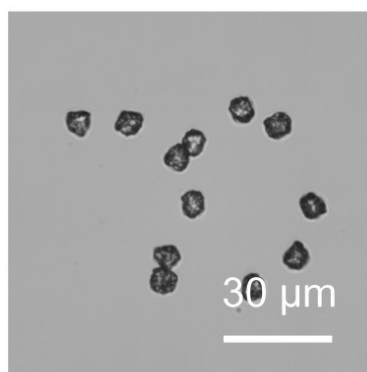


Fig. S7 Optical microscopy image of dried supramolecular colloidal microcapsules.

Ultraviolet absorption spectroscopy

Exposure of AP solution ($[\text{azobenzene}] = 15 \times 10^{-6} \text{ M}$) at 350 nm for 10 minutes leads to a decrease of the absorbance around 378 nm because of *trans* to *cis* isomerization.

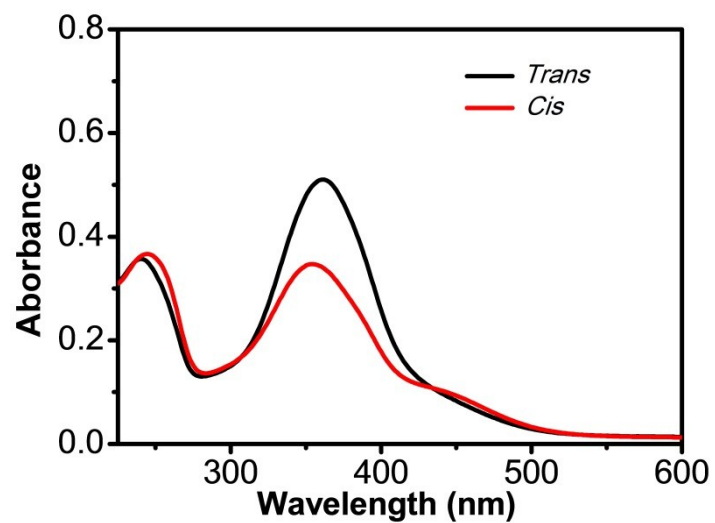


Fig. S8 UV-visible absorption spectra of AP, before and after illumination with UV-light (350 nm, 10 mins). This leads to a decrease of the peak at 378 nm, attributed to *trans-cis* photoisomerization.

Optical microscopy image

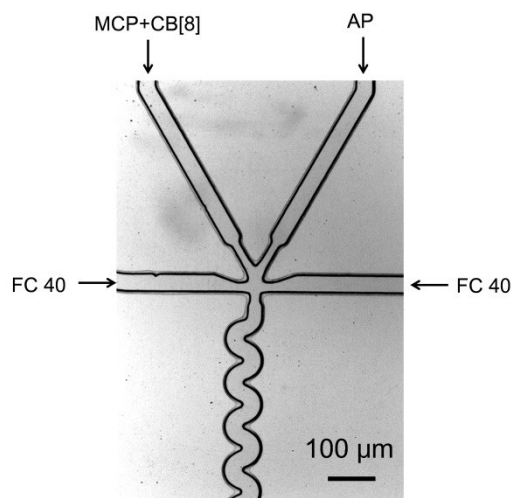


Fig. S9 Optical microscopy image of the microfluidic device used to generate supramolecular colloidal microcapsules.