

Supporting Information

Microfluidic droplet-facilitated hierarchical assembly for dual cargo loading and synergistic delivery

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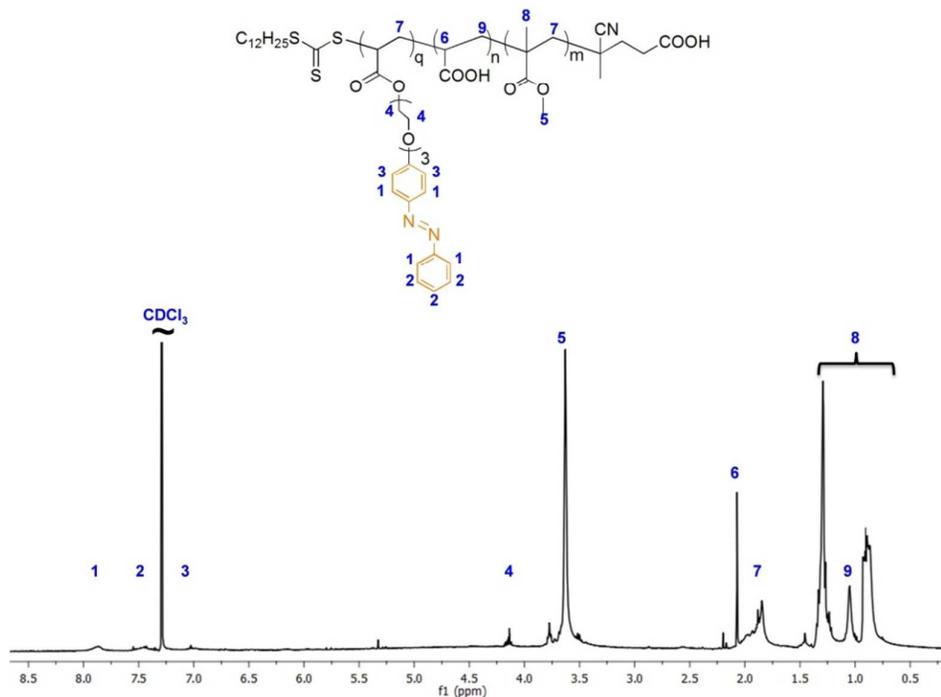


Figure S1. Chemical structure and ^1H NMR spectrum of polymer **P1**: poly(methyl methacrylate)-*block*-poly(acrylic acid), containing pendant azobenzene groups.

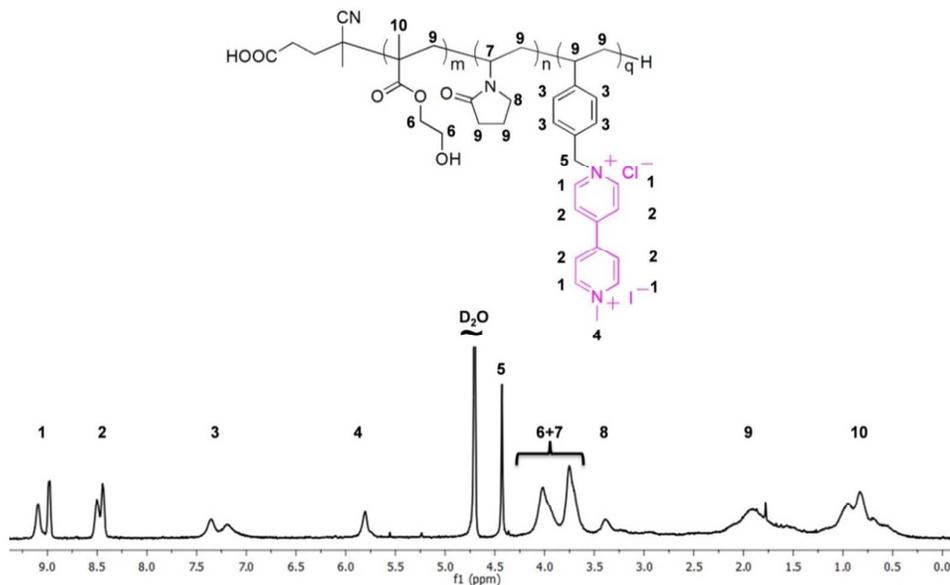


Figure S2. Chemical structure and ^1H NMR spectrum of polymer **P2**: poly(*N*-vinylpyrrolidone)-*co*-poly(hydroxyethyl methacrylate)-*co*-poly(MV-styrene), containing pendant viologen groups.

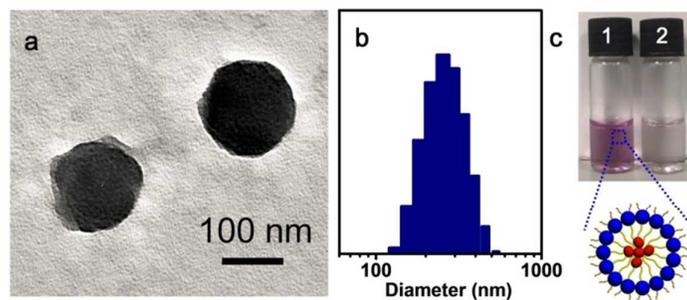


Figure S3 (a) Transmission electron micrograph (TEM) of **P1** micelles and (b) size distribution by dynamic light scattering (DLS) measurement. (c) Photograph of vials containing: a suspension of Nile Red-containing **P1** micelles (left:vial 1) and insoluble Nile Red only (right:vial 2).

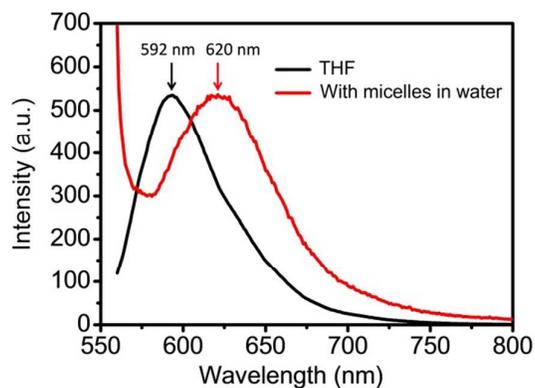


Figure S4 Fluorescence spectra of Nile Red in tetrahydrofuran (THF) and within micelles in water.

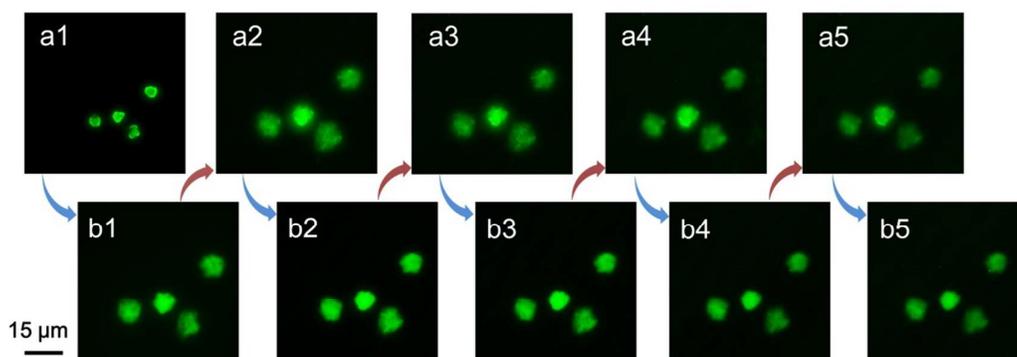


Figure S5 Fluorescence images of microcapsules after five cycles of (a:1-5) dehydration and (b:1-5) rehydration, all cycles are 1 h in length. (Blue arrows represent hydration and red arrows represent dehydration of the microcapsules)

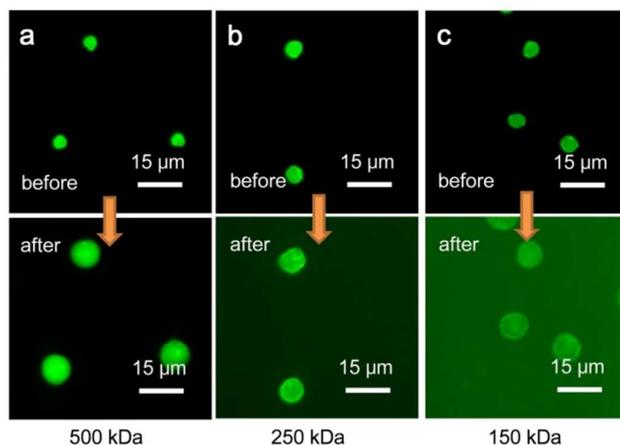


Figure S6 Fluorescence images of microcapsules loaded with (a) 500 kDa, (b) 250 kDa, and (c) 150 kDa FITC-dextran before and after 3 hours rehydration in water.

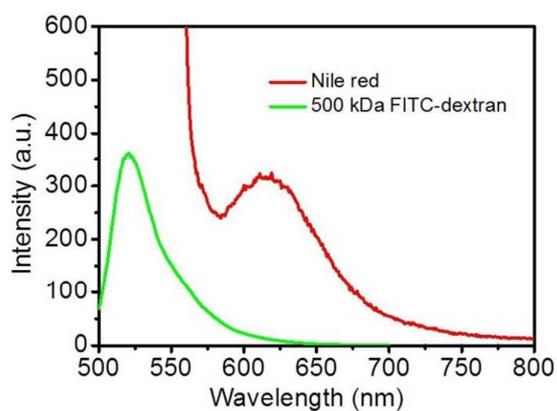


Figure S7 Fluorescence spectra of cargo released from microcapsules after exposure to 1-adamantylamine solution. Green: 500 kDa FITC-dextran and Red: Nile Red .

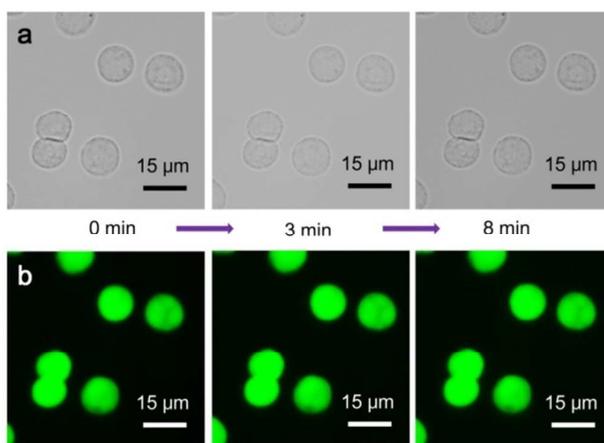


Figure S8 (a) Transmission and (b) fluorescence micrographs of encapsulated 500 kDa FITC-dextran cargo upon rehydration without UV exposure (cf. Figure 6b-d).

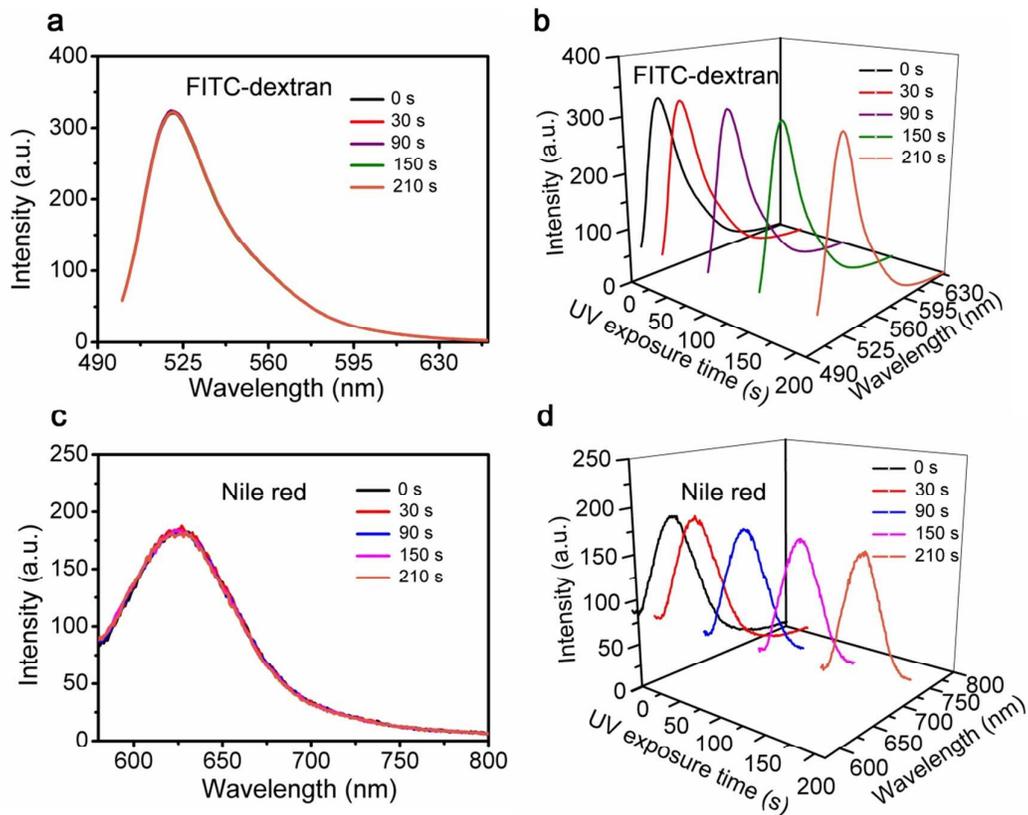


Figure S9 (a) Fluorescence spectra and (b) the 3D distribution of 500 kDa FITC-dextran in water, after ultraviolet light irradiation of 0s, 30s, 90s, 150s, and 210s, respectively. (c) Fluorescence spectra and (d) the 3D distribution of Nile Red in **P1** micelles, after ultraviolet light irradiation of 0s, 30s, 90s, 150s, and 210s, respectively.

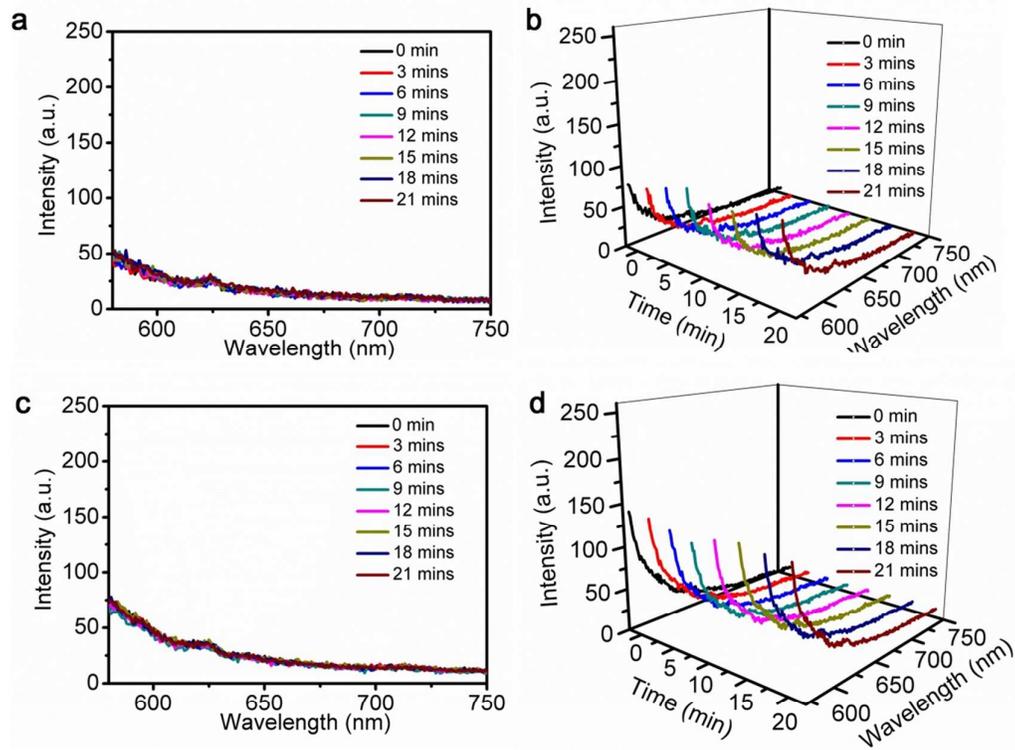


Figure S10 (a) Fluorescence spectra (b) the 3D distribution of the released Nile Red in micelles as a function of the rehydration time (without 3 min UV exposure). (c) Fluorescence spectra (d) the 3D distribution of the released Nile Red in micelles as a function of the rehydration time with 3 min UV exposure.