

Supporting Information
for
Supramolecular Polymeric Vesicles Formed
by *p*-Sulfonatocalix[4]arene and Chitosan with
Multistimuli Responses

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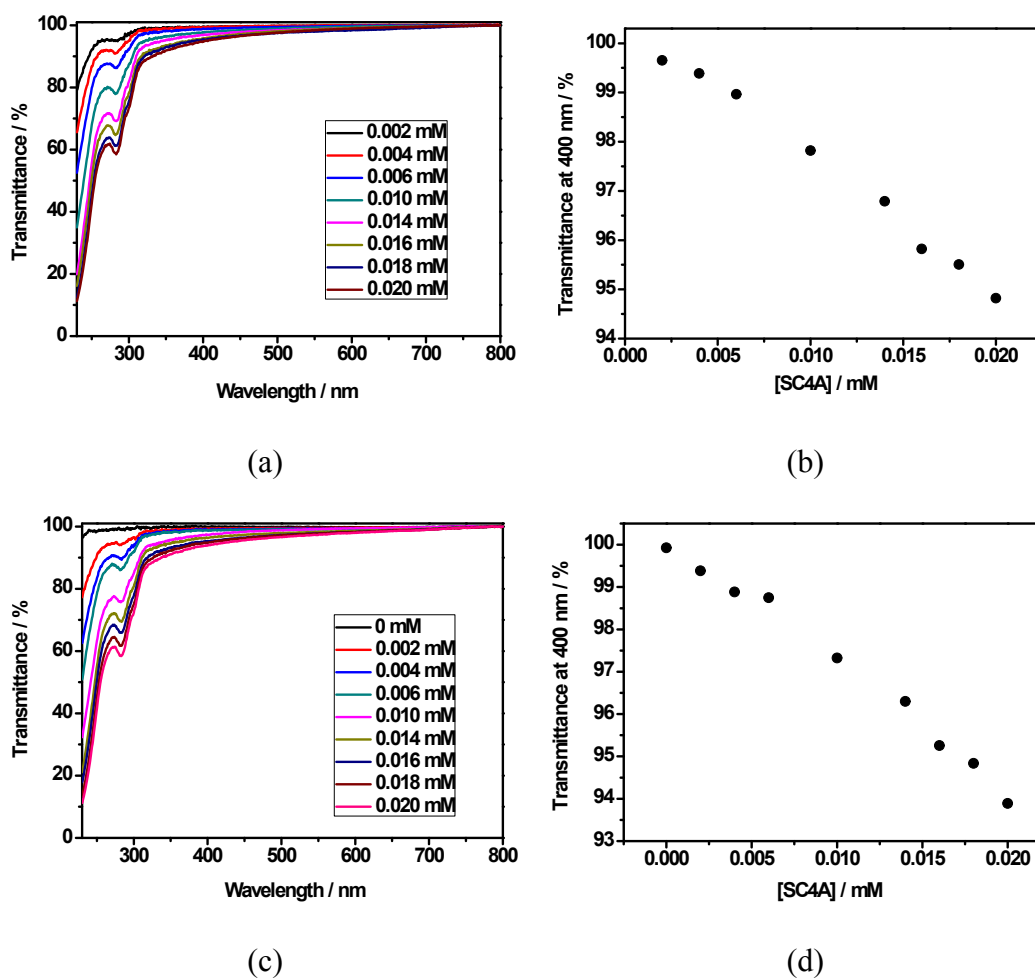


Figure S1. (a) Optical transmittance of 30 $\mu\text{g/mL}$ chitosan-0.6 solutions with SC4A of different concentrations at 25 $^{\circ}\text{C}$. (b) Dependence of the optical transmittance at 400 nm on SC4A concentration in the presence of 30 $\mu\text{g/mL}$ chitosan-0.6. (c) Optical transmittance of 30 $\mu\text{g/mL}$ chitosan-0.95 solutions with SC4A of different concentrations at 25 $^{\circ}\text{C}$. (d) Dependence of the optical transmittance at 400 nm on SC4A concentration in the presence of 30 $\mu\text{g/mL}$ chitosan-0.95.

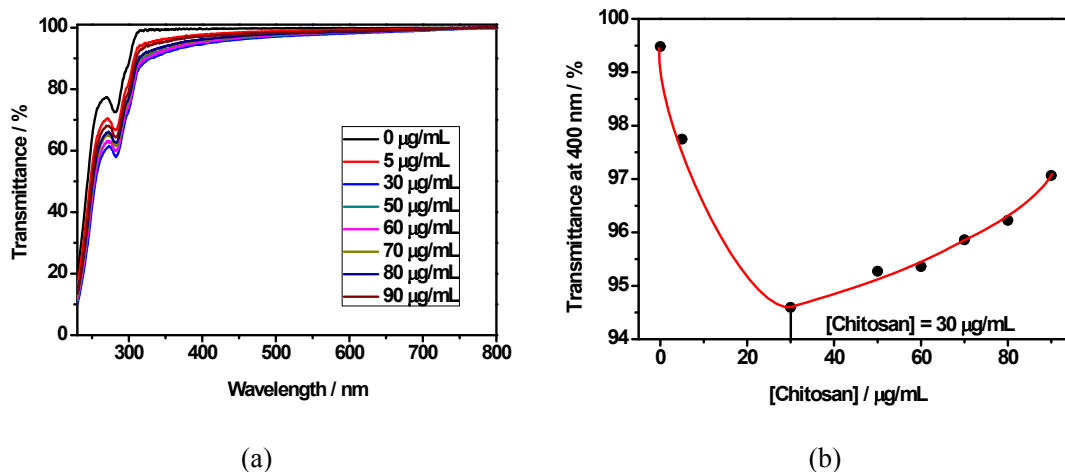


Figure S2. (a) Optical transmittance of SC4A (0.02 mM) by increasing the concentration of chitosan-0.6 from 0 µg/mL to 90 µg/mL at 25 °C in aqueous solution at pH 5.3. (b) Dependence of the optical transmittance at 400 nm on the concentration of chitosan-0.6 with a fixed SC4A concentration of 0.02 mM.

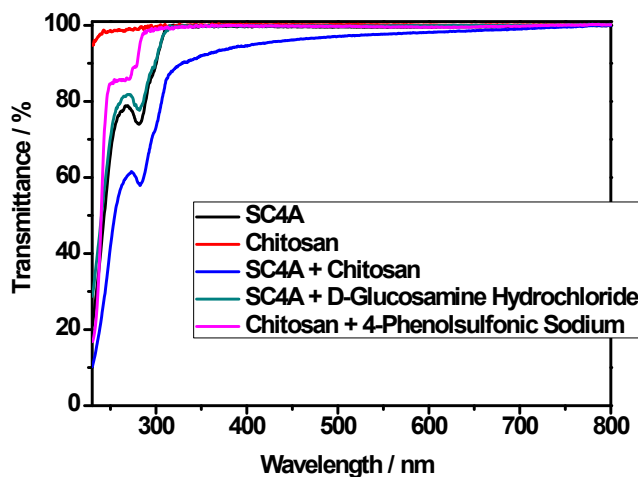


Figure S3. Optical transmittances of SC4A, chitosan, SC4A+chitosan, SC4A+D-glucosamine hydrochloride, and chitosan+4-phenolsulfonic sodium at 25 °C in aqueous solution at pH 5.3. [SC4A] = 0.02 mM, [chitosan-0.6] = 30 µg/mL, [4-phenolsulfonic sodium] = 0.02 mM.

phenolsulfonic sodium] = 0.08 mM, and [D-glucosamine hydrochloride] = 22 $\mu\text{g}/\text{mL}$.

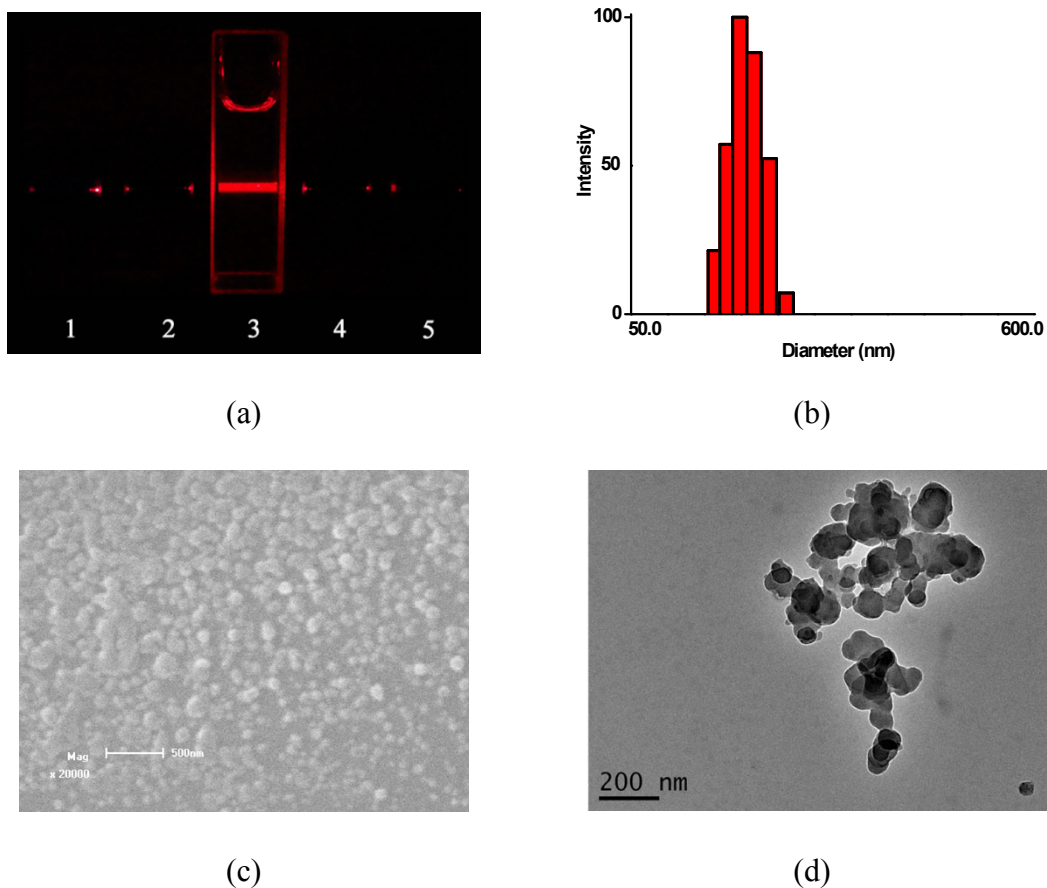
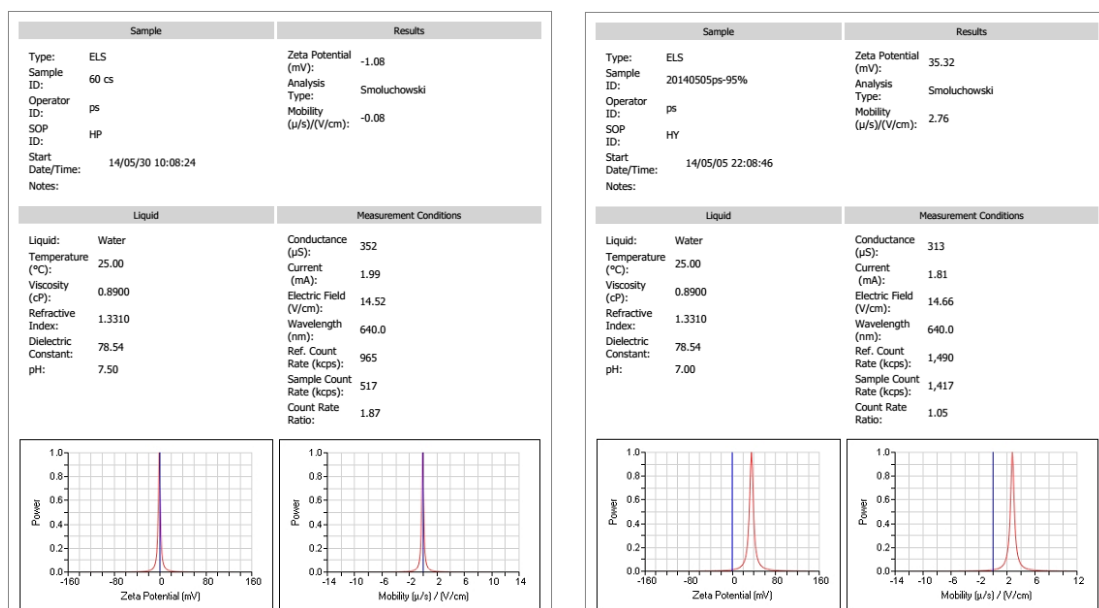


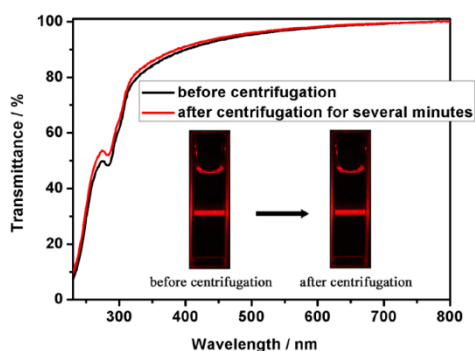
Figure S4. (a) Tyndall effect of free SC4A (1), free chitosan (2), SC4A+chitosan (3), SC4A+D-glucosamine hydrochloride (4), and chitosan+4-phenolsulfonic sodium (5). (b) DLS data of the SC4A+chitisan assembly. (c) SEM, and (d) high-resolution TEM images of the SC4A+chitisan assembly. [SC4A] = 0.02 mM, [chitosan-0.6] = 30 $\mu\text{g}/\text{mL}$, [4-phenolsulfonic sodium] = 0.08 mM, and [D-glucosamine hydrochloride] = 22 $\mu\text{g}/\text{mL}$.



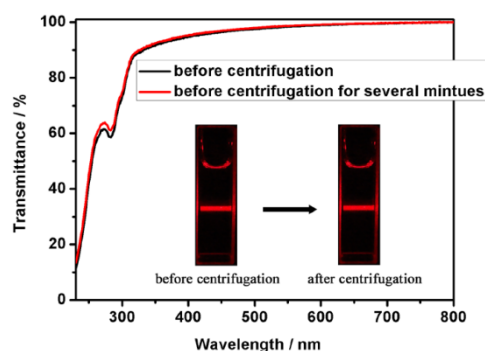
(a)

(b)

Figure S5. Zeta potential measurement of the SC4A+chitosan assembly at 25 °C in aqueous solution at pH 5.3. (a): [SC4A] = 0.02 mM, [chitosan-0.6] = 30 $\mu\text{g}/\text{mL}$; (b): [SC4A] = 0.02 mM, [chitosan-0.95] = 30 $\mu\text{g}/\text{mL}$.

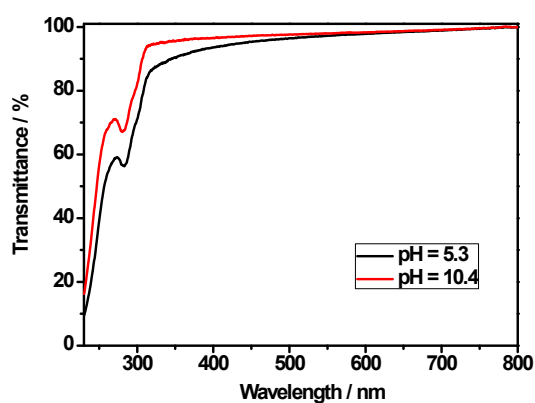


(a)

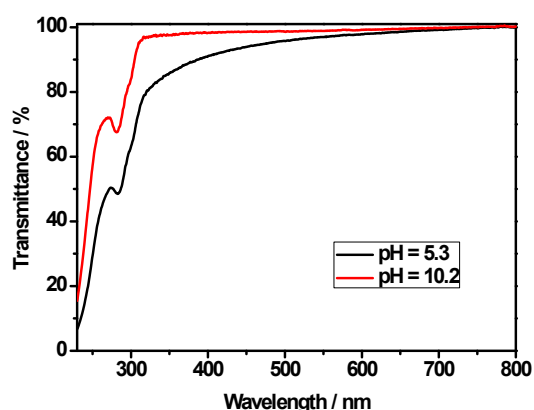


(b)

Figure S6. (a) Optical transmittance of SC4A+chitosan-0.95 assembly before and after centrifugation for several minutes at 2500 r/min in aqueous solution at pH 5.3. Inset: Tyndall effect of SC4A+chitosan-0.95 assembly before and after centrifugation. (b) Optical transmittance of SC4A+chitosan-0.6 assembly before and after centrifugation for several minutes at 2500 r/min in aqueous solution at pH 5.3. Inset: Tyndall effect of SC4A+chitosan-0.6 assembly before and after centrifugation. [SC4A] = 0.02 mM, [chitosan-0.95] = 30 $\mu\text{g/mL}$, [chitosan-0.6] = 30 $\mu\text{g/mL}$.



(a)



(b)

Figure S7. Optical transmittance of SC4A+chitosan solution under acidic and

alkaline conditions. (a): [SC4A] = 0.02 mM, [chitosan-0.6] = 30 $\mu\text{g/mL}$; (b): [SC4A] = 0.02 mM, [chitosan-0.95] = 30 $\mu\text{g/mL}$.

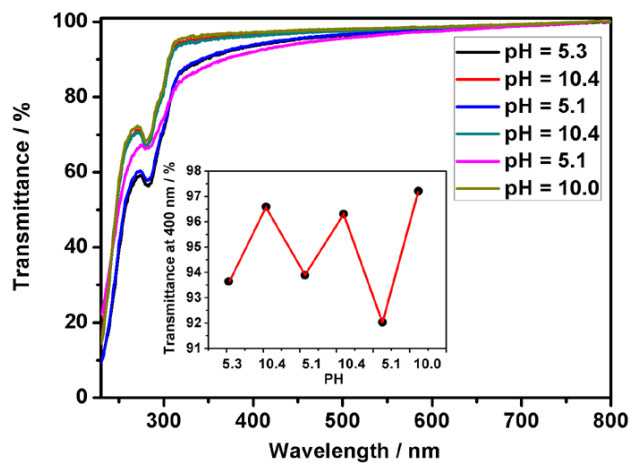
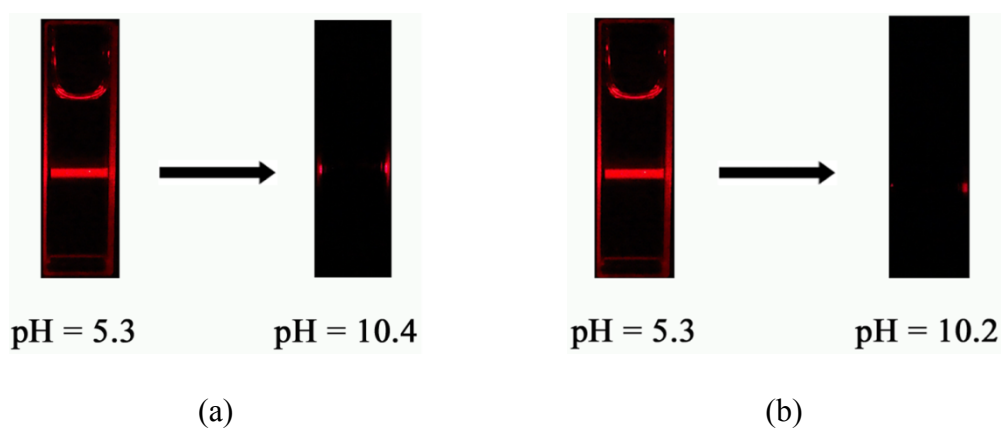


Figure S8. Optical transmittance of SC4A+chitosan-0.6 solution observed upon several cycles under acidic and alkaline conditions. Inset: the optical transmittance changes at 400 nm. [SC4A] = 0.02 mM, [chitosan-0.6] = 30 $\mu\text{g/mL}$.



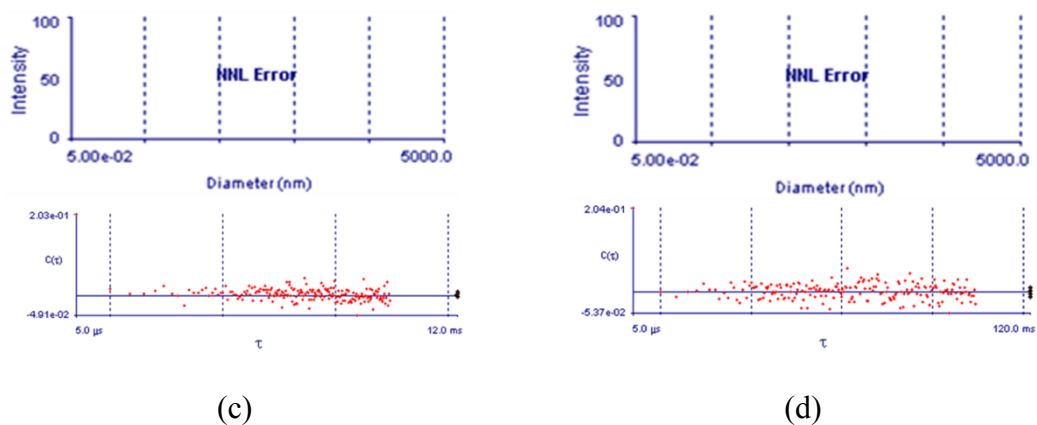


Figure S9. (a) Tyndall effect of SC4A+chitosan-0.6 solution under acidic and alkaline conditions. (b) Tyndall effect of SC4A+chitosan-0.95 solution under acidic and alkaline conditions. (c) DLS data of SC4A+chitosan-0.6 solution under alkaline condition. (d) DLS data of SC4A+chitosan-0.95 solution under alkaline condition. [SC4A] = 0.02 mM, [chitosan-0.6] = 30 $\mu\text{g/mL}$, [chitosan-0.95] = 30 $\mu\text{g/mL}$.

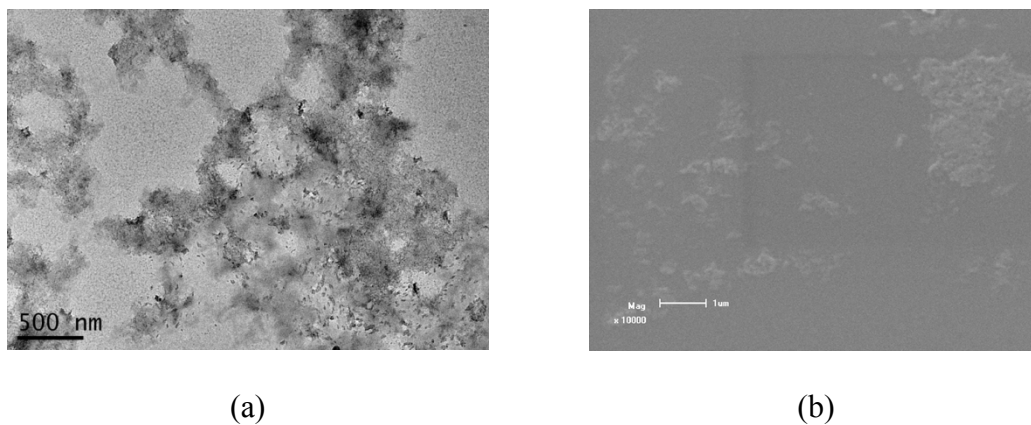


Figure S10. (a) High-resolution TEM, and (b) SEM images of SC4A+chitosan-0.6 solution under alkaline condition. [SC4A] = 0.02 mM, [chitosan-0.6] = 30 $\mu\text{g/mL}$. The scale bar of SEM image is 1 μm .

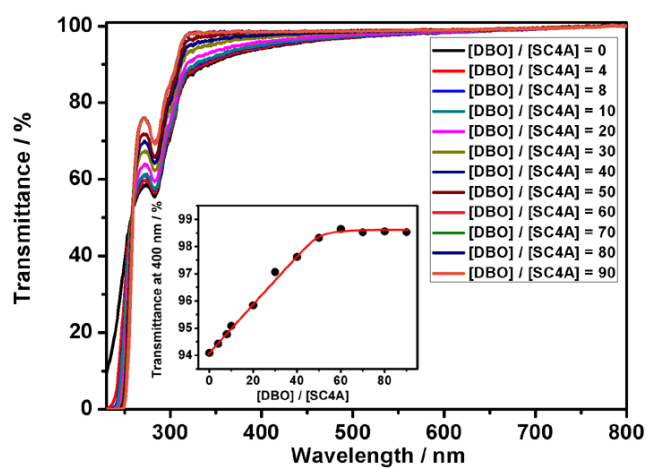
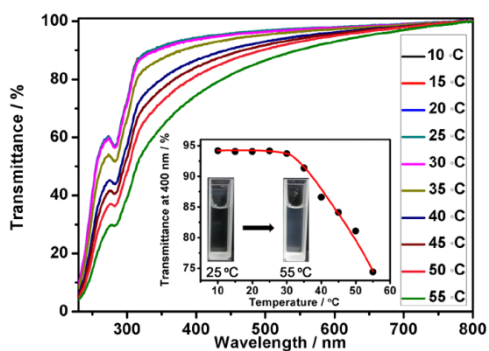
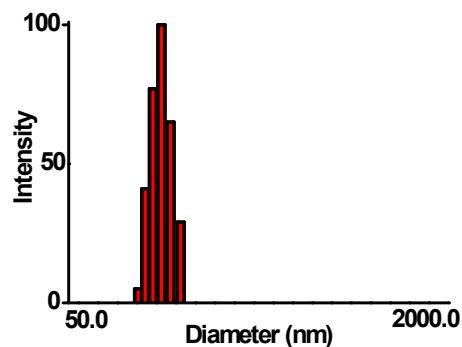


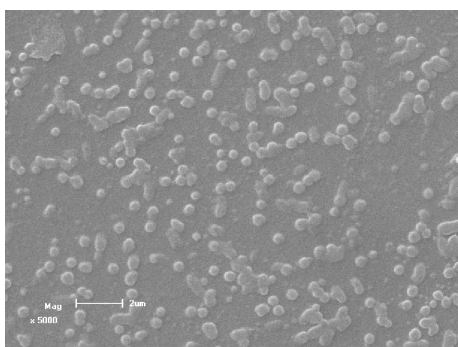
Figure S11. Optical transmittance of SC4A+chitosan-0.6 solution at different concentrations of DBO. Inset: dependence of the optical transmittance at 400 nm on DBO concentration with a fixed SC4A concentration of 0.02 mM. [chitosan-0.6] = 30 $\mu\text{g/mL}$.



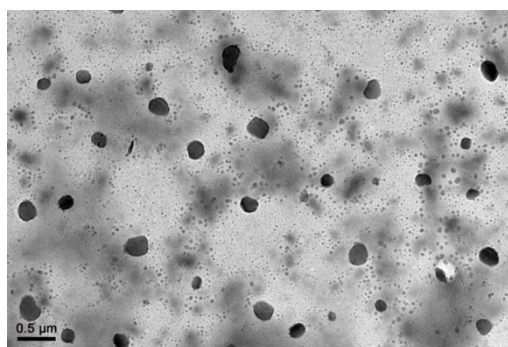
(a)



(b)



(c)



(d)

Figure. S12 (a) Optical transmittance of SC4A+chitosan-0.6 assembly with temperature ascending from 10 to 55 °C. Inset: dependence of the optical transmittance at 400 nm on temperature, and the corresponding turbidity photos at 25 and 55 °C. DLS data (b), SEM (c), and high-resolution TEM (d) images of SC4A+chitosan assembly at 55 °C. [SC4A] = 0.02 mM, [chitosan-0.6] = 30 μg/mL.

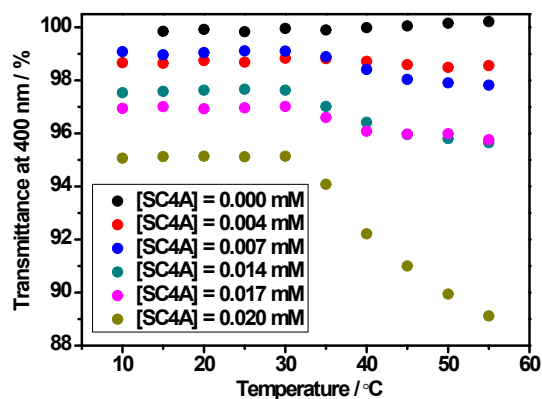


Figure S13. Dependence of the optical transmittance at 400 nm on temperature in the presence of different concentrations of SC4A with a fixed chitosan-0.6 concentration of 30 $\mu\text{g/mL}$.

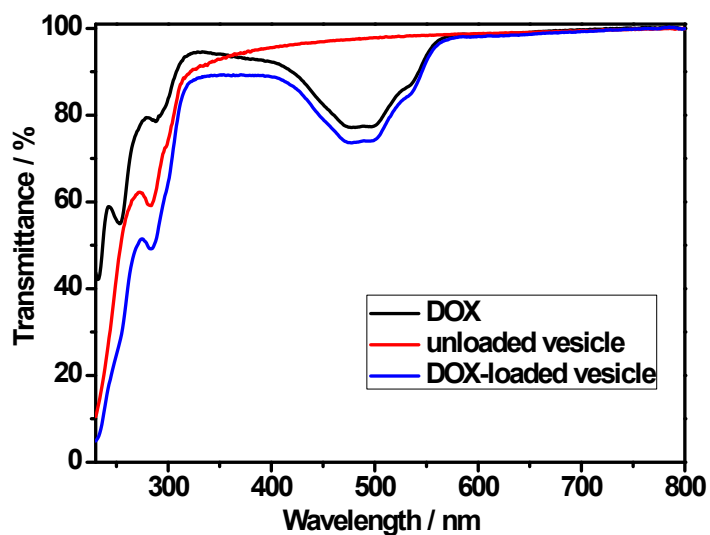
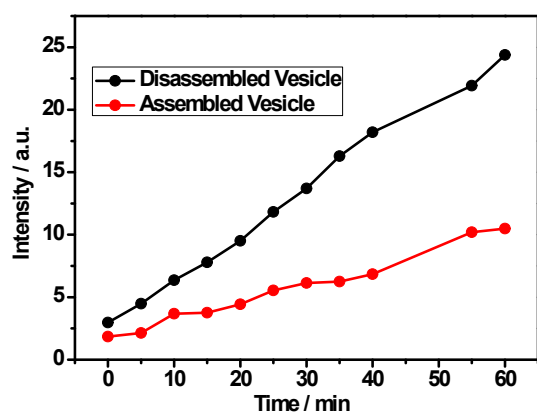
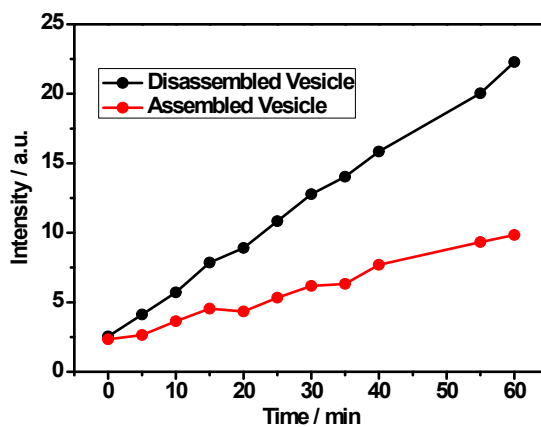


Figure S14. Optical transmittances of DOX, unloaded vesicles, DOX-loaded vesicle at 25 $^{\circ}\text{C}$ in aqueous solution at pH 5.3. $[\text{SC4A}] = 0.02 \text{ mM}$, $[\text{chitosan-0.6}] = 30 \mu\text{g/mL}$.



(a)



(b)

Figure S15. (a) Dependence of the fluorescence intensity of DOX outside of dialysis bag at 600 nm on time. $[SC4A] = 0.02$ mM, $[chitosan-0.95] = 30$ $\mu\text{g/mL}$. (b) Dependence of the fluorescence intensity of DOX outside of dialysis bag at 600 nm on time. $[SC4A] = 0.02$ mM, $[chitosan-0.6] = 30$ $\mu\text{g/mL}$. $\lambda_{\text{ex}} = 500.0$ nm, band width (ex and em): 10.0 nm.