

ELECTRONIC SUPPLEMENTARY INFORMATION

Hybrid Mesoporous Silica Nanocarriers with Thermovalve-Regulated Controlled Release

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(A) Schematic representation of the cuvette used on the release experiments

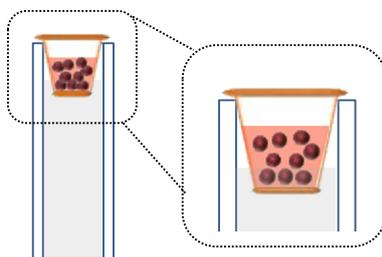


Figure S1. Schematic representation of the cuvette used on the release experiments. On the top of the cuvette stays a dialysis membrane with SRB-loaded MSN-poly nanoparticles. This membrane is in contact with the buffer solution present inside the cuvette. The SRB released from the pores diffuse across the membrane, from the top compartment to the bottom one where the fluorescence intensity of SRB is monitored.

(B) Physicochemical characterization of the MSNs

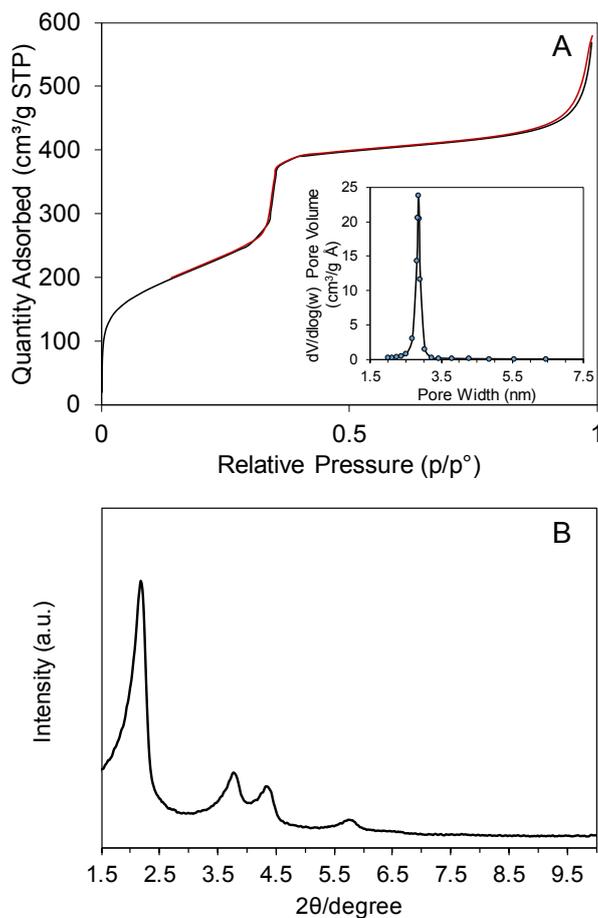


Figure S2. (A) Nitrogen sorption isotherms (adsorption – black; desorption – red) and the pore size distribution curves (inset) of the MSNs. (B) Powder X-ray diffractogram of MSNs, showing the pattern for ordered hexagonal mesopores.

(C) NMR characterization of MSN-APTES

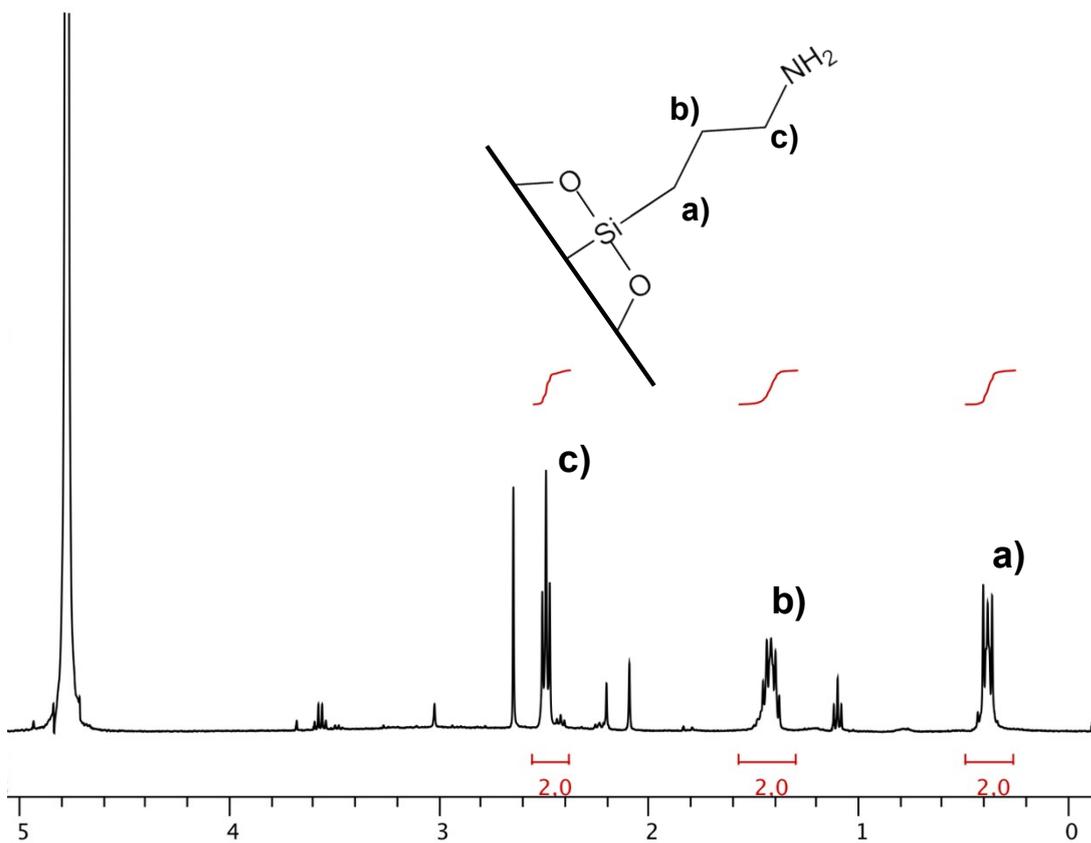


Figure S3. Solution ¹H-NMR (at pH=13) of MSN-APTES, with peaks assigned for the propyl chain APTES, showing surface modification of the nanoparticles.

(D) Determination of the amount of RAFT agent on the MSNs

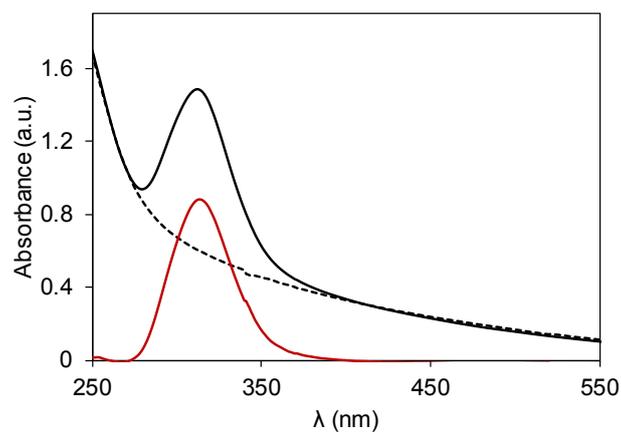


Figure S4. The amount of RAFT agent at the MSNs surface was calculated from the absorption spectrum represented in red, obtained by subtracting the light scattering contribution (measured for the unlabeled MSNs, black dashed curve), from the absorption spectrum of MSN-RAFT (black solid curve).

(E) SRB emission correction and diffusion

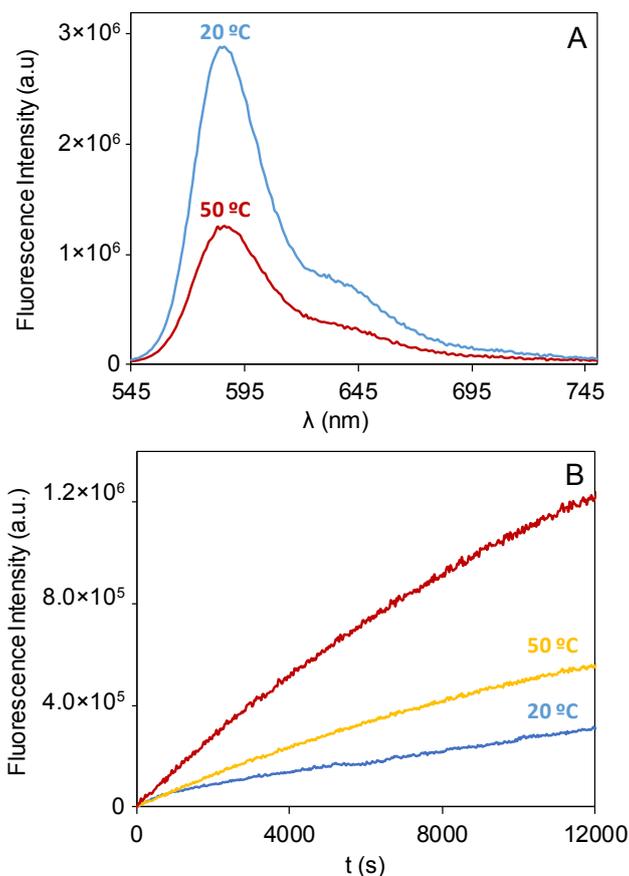


Figure S5. (A) Fluorescence emission spectra of SRB obtained at 20 °C (blue line) and 50 °C (red line), using 520 nm as excitation wavelength. Correction for the quantum yield difference at the two temperatures is performed by dividing the fluorescence intensity at 585 nm obtained at 50 °C by the value at 20 °C. (B) Diffusion profile of free SRB in PBS (pH=7, 10^{-6} M), obtained during 3h20min at 20 °C (blue curve), and at 50 °C (yellow curve). The curve obtained at 50 °C was corrected for the quantum yield difference (red curve).

(F) Determination of the molar absorptivity of SRB in PBS

Five solutions with a known concentration of SRB in PBS (pH=7) were prepared to obtain the calibration curve shown below. The molar absorptivity at 565 nm is $\varepsilon = 7.25 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$.

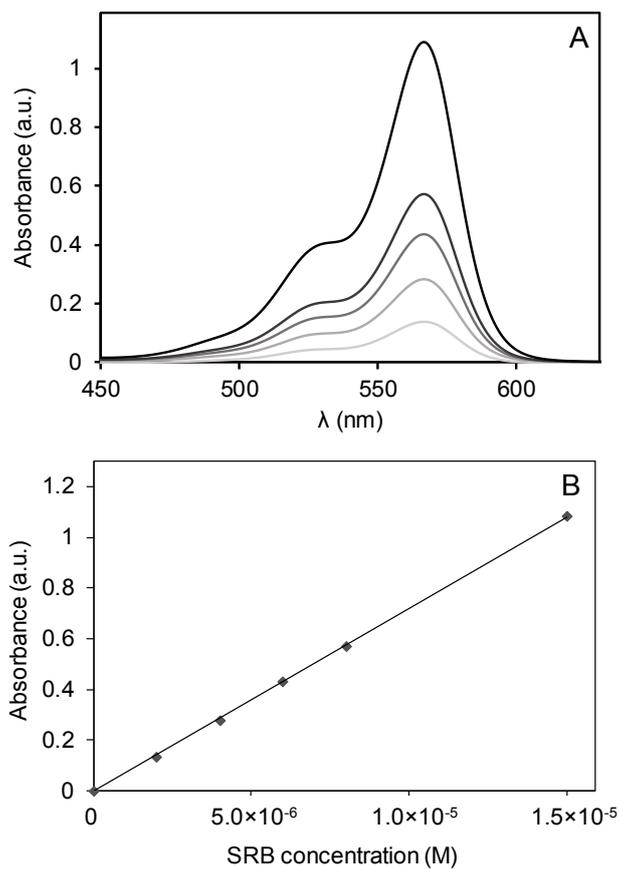


Figure S6. (A) Absorbance spectra of SRB solutions in PBS (pH=7) with a known concentration of SRB and (B) the corresponding calibration curve.

(G) Fluorescence release studies for MSN-POLY

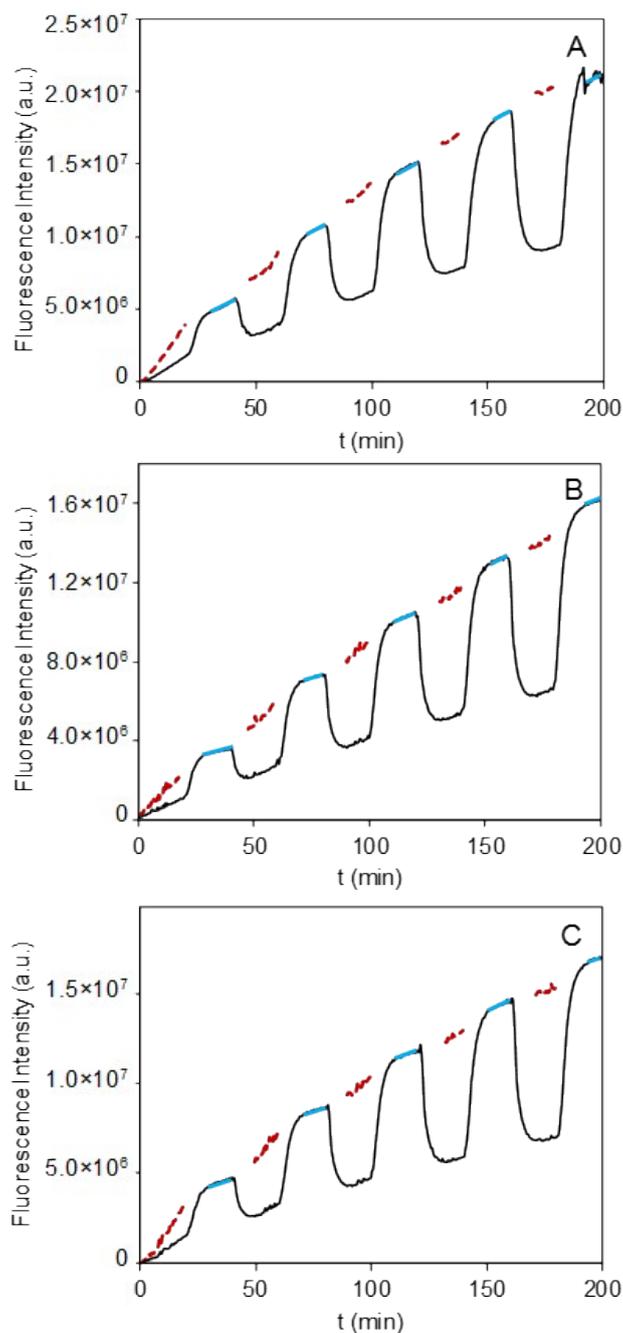


Figure S7. Fluorescence intensity obtained from fluorescence release studies for (A) MSN-POLY1, (B) MSN-POLY2 and (C) MSN-POLY3 in PBS buffer, measured continuously during 3h20 at $\lambda_{\text{emi}} = 585$ nm and using $\lambda_{\text{exc}} = 565$ nm excitation (solid line). The studies were performed with heating - cooling cycles of 20 minutes. The fluorescence intensities measured at 50 °C were corrected with RF (dashed red lines). The release rates at 20 °C and 50 °C are represented in blue and red, respectively.