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# Turning on hotspots: Supracolloidal SERS probes made brilliant by an external activation mechanism

*Supporting Information*

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## 1 Polymer Characterization

**Table S1.** Number-average molar mass, $M_n$, weight-average molar mass, $M_w$, and dispersity value *Đ* for the star polymer used in this work as determined by size-exclusion chromatography (light-scattering detection).

| | $M_n$ (g/mol) | $M_w$ (g/mol) | *Đ* |
|---|---|---|---|
| **4-Arm-Star RAFT-PNIPAM** | 30,000 | 33,200 | 1.11 |

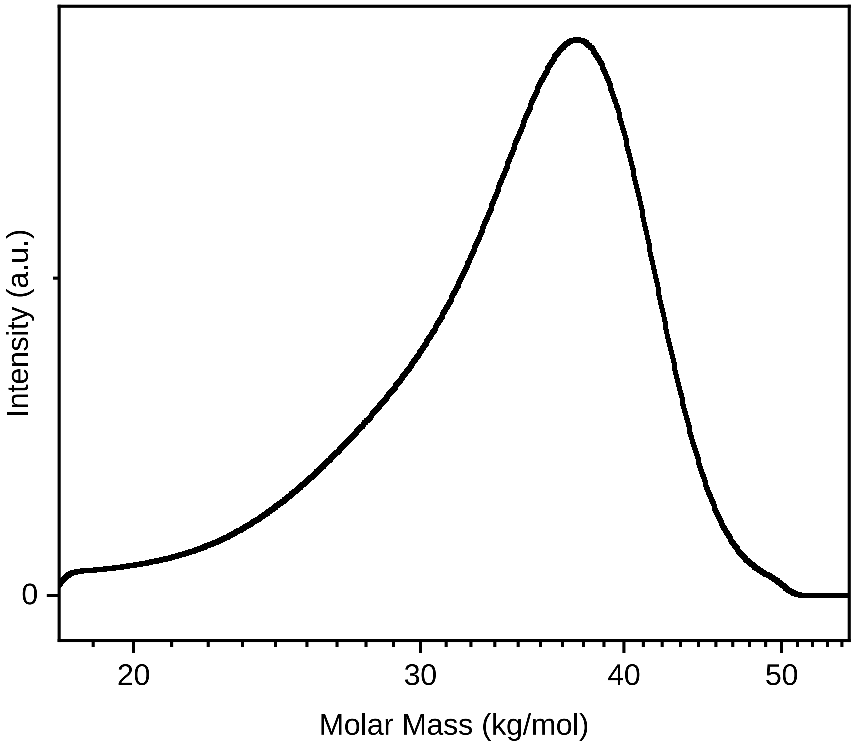



**Figure S1.** Size-exclusion chromatogram of the syntehsized poly(NIPAM) star polymer.

## 2 Nanoparticle Assembly Characterization

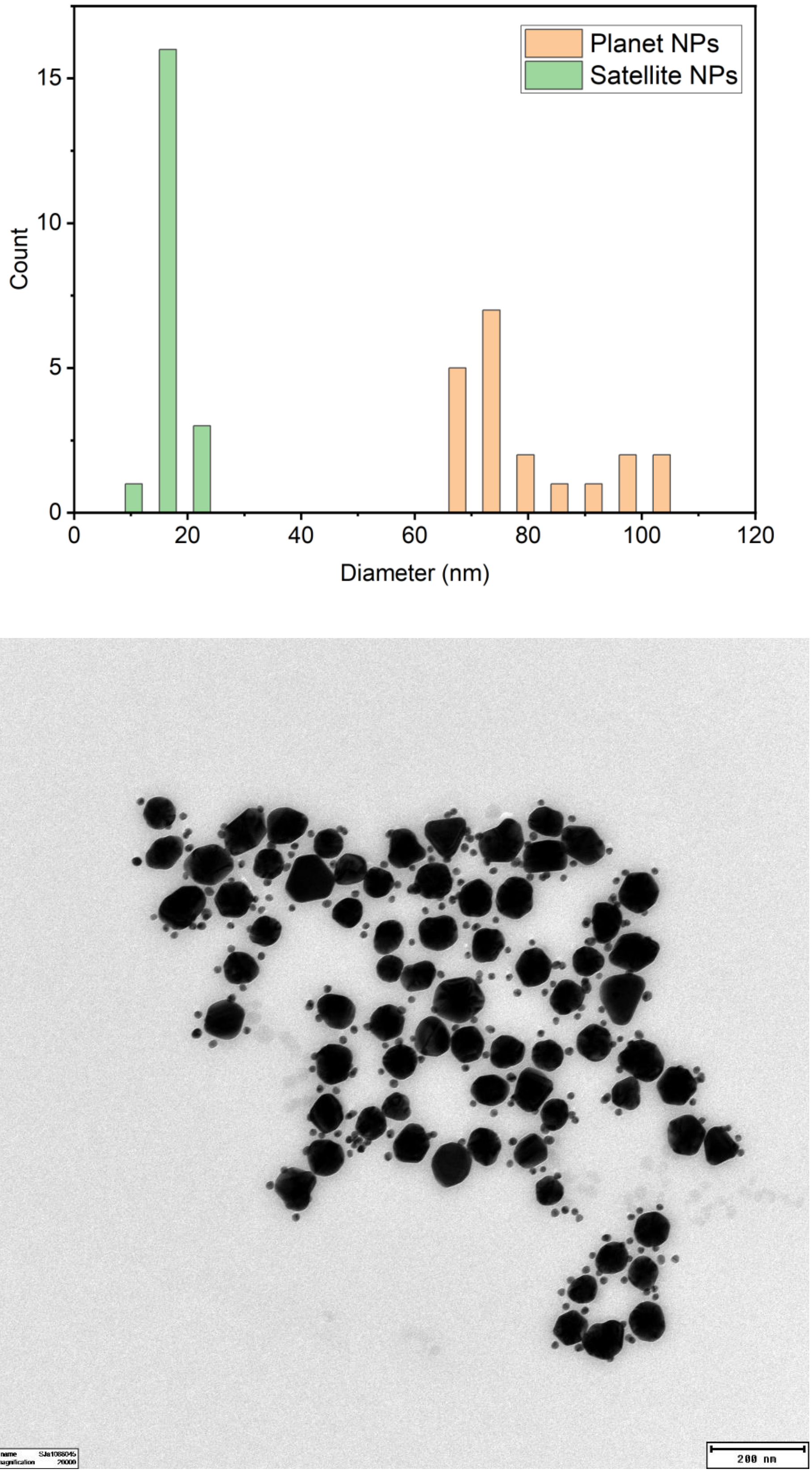
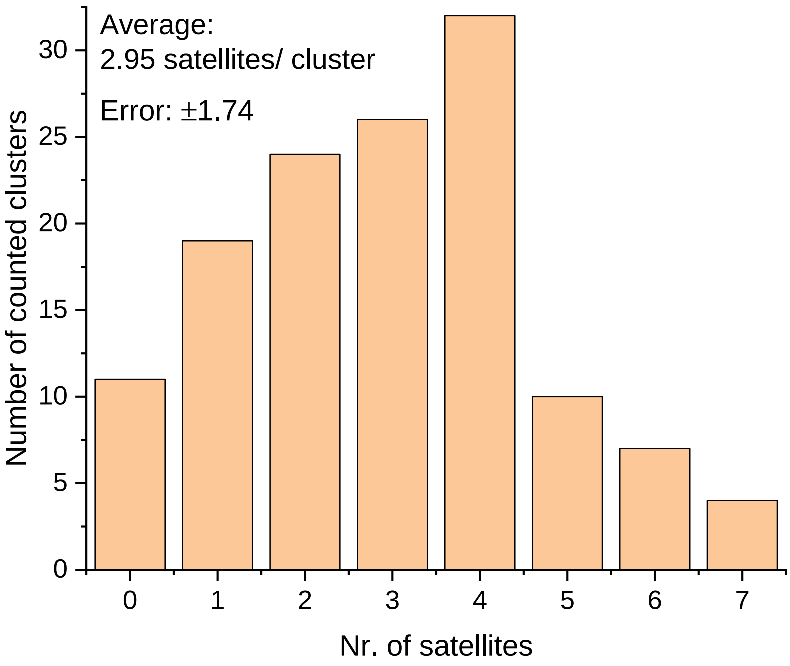



**Figure S2.** Histogram of Nanoparticle sizes as determined by TEM (top) and representative TEM image (bottom).




| *Nr. Satellites* | *Nr. Clusters* |
|---|---|
| *0* | *11* |
| *1* | *19* |
| *2* | *24* |
| *3* | *26* |
| *4* | *32* |
| *5* | *10* |
| *6* | *7* |
| *7* | *4* |

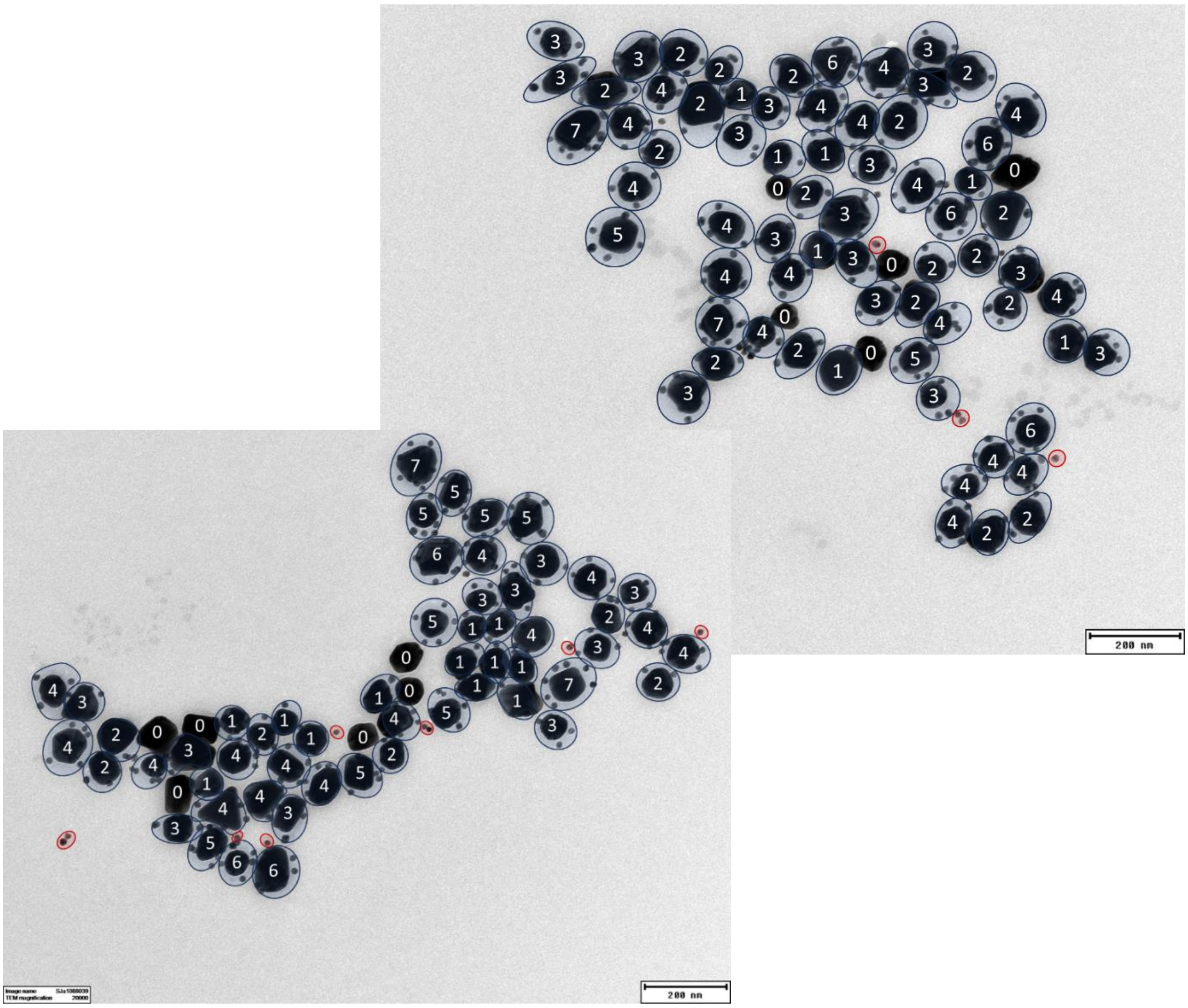



**Figure S3.** Distribution of the number of “satellite” nanoparticles per “planet” nanoparticle *via* transmission electron microscopy imaging.

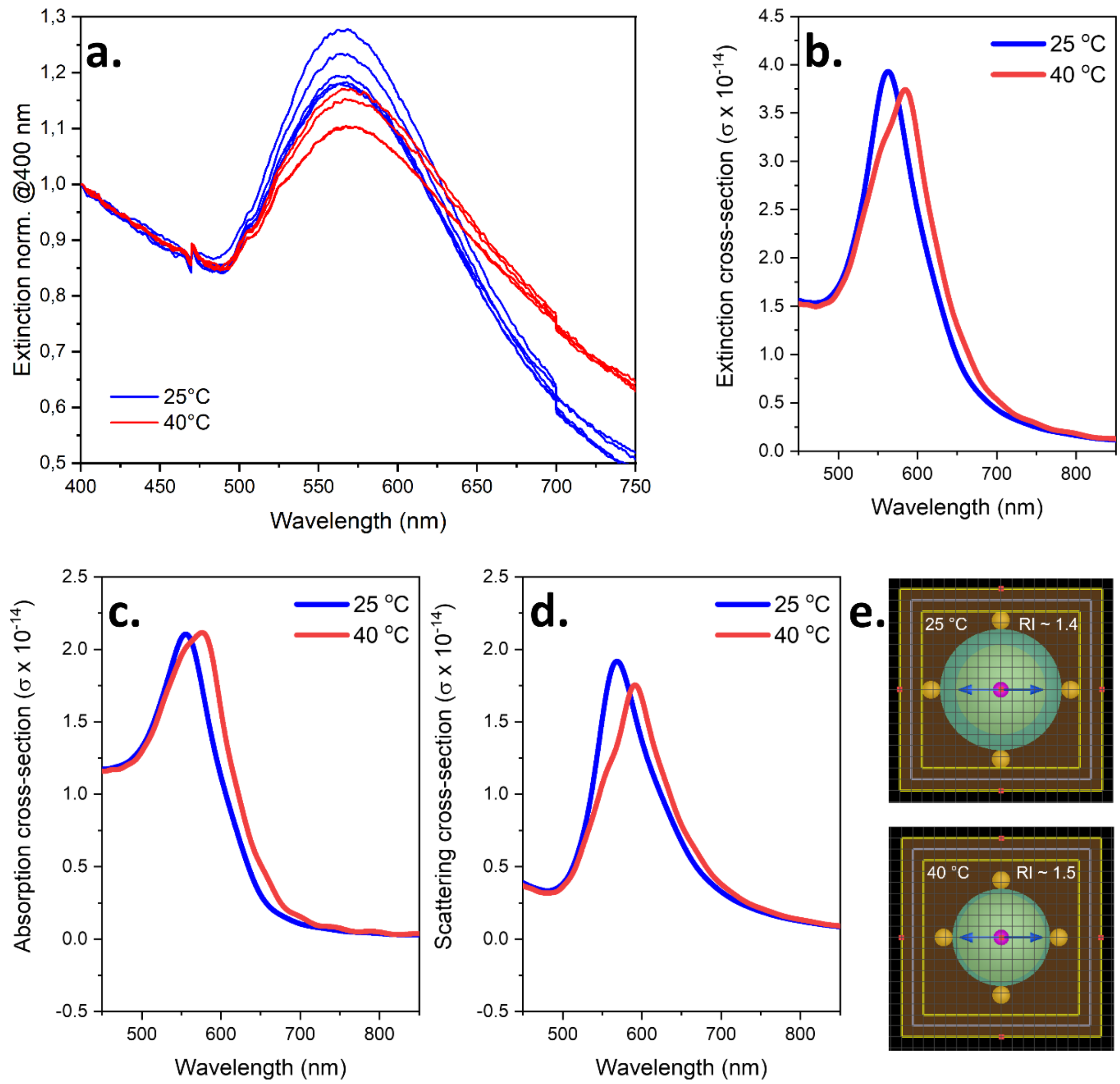



**Figure S4.** (a.) Experimental extinction spectra for the assembled structures at different temperatures. (b.) Simulated extinction spectra for the assembled structure at different temperatures. (c., d.) Contribution of absorption and scattering to the simulated extinction spectra. (e.) Simulation geometry and parameters.

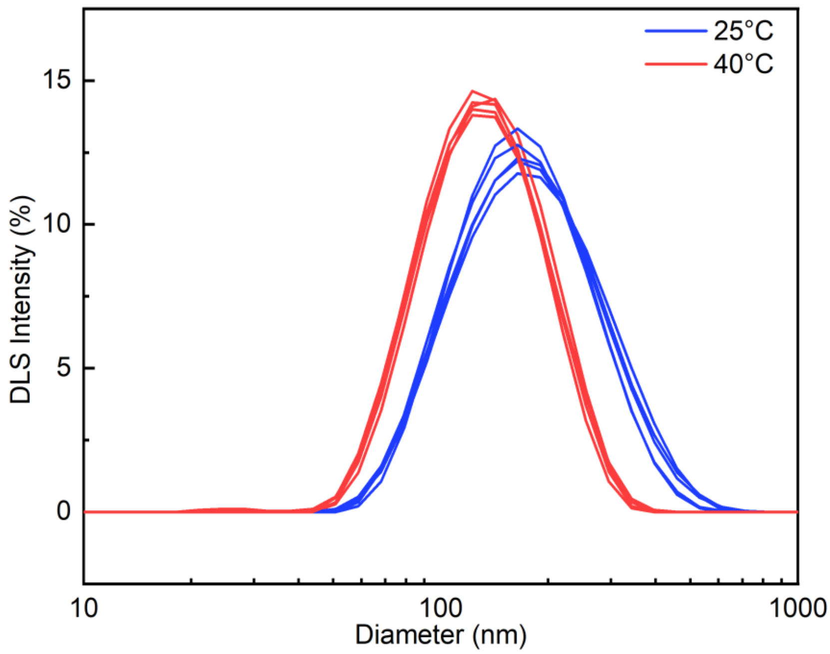



**Figure S5.** DLS intensity distribution at different temperatures.

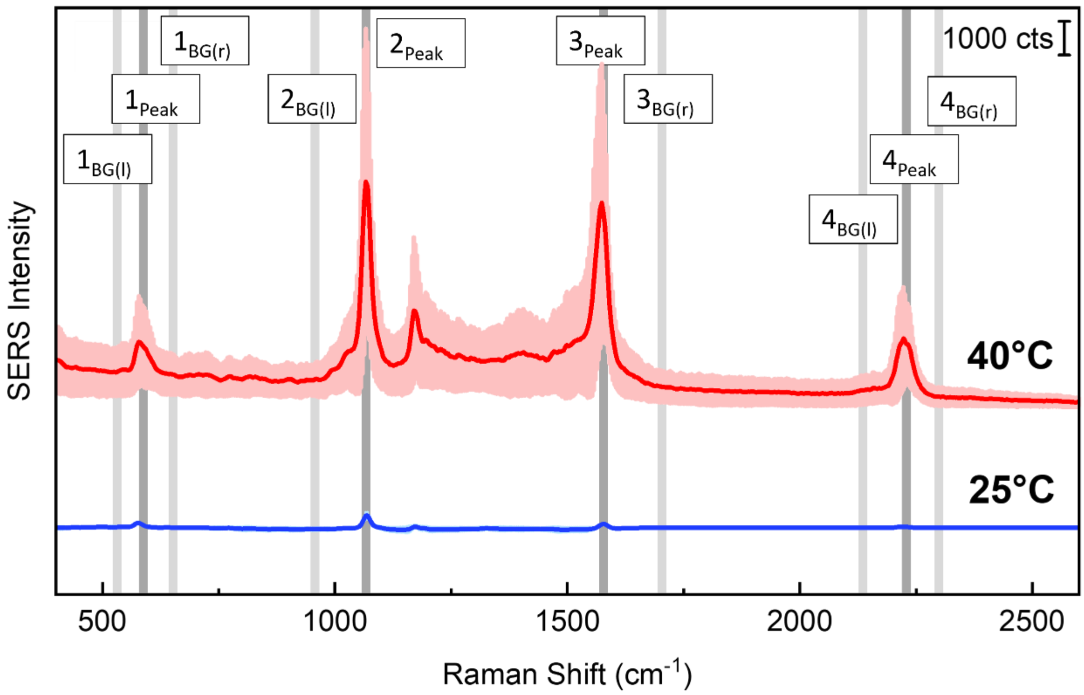



**Figure S6.** Peak heights from SERS Spectra and calculation of the heating-induced intensity increase.

**Table S2.** Extracted values of peak heights from the measured SERS spectra.

| | | 40°C | | 25°C | | |
|---|---|---|---|---|---|---|
| | X | Y | Peak height | Y | Peak height | Intensity ratio |
| $1_{BG(l)}$ | 534 | 2293 | 916 | 1166 | 126 | 7 |
| **$1_{Peak}$** | **max ~578** | **3151** | | **1272** | | |
| $1_{BG(r)}$ | 651 | 2177 | | 1125 | | |
| $2_{BG(l)}$ | 901 | 2025 | 5871 | 1070 | 371 | 16 |
| **$2_{Peak}$** | **max ~1067** | **7896** | | **1441** | | |
| **$3_{Peak}$** | **max ~1574** | **7246** | **5581** | **1182** | 190 | 29 |
| $3_{BG(r)}$ | 1721 | 1665 | | 992 | | |
| $4_{BG(l)}$ | 2102 | 1458 | 1627 | 968 | 25 | 66 |
| **$4_{Peak}$** | **max ~2226** | **3022** | | **988** | | |
| $4_{BG(r)}$ | 2291 | 1332 | | 958 | | |

**Calculation of shell thickness above LCST of poly(NIPAM)**

The literature-known density of poly(NIPAM) ($d_P$ = 1.1 g/cm$^3$)[1] is assumed, as the polymer is dense above the LCST. A spherical shell is assumed where the shell thickness $t$ equals

$$t_{40} = r_{tot} - r_C = \left[\frac{3V_{tot}}{4\pi}\right]^{\frac{1}{3}} = \left[\frac{3}{4\pi}(V_P + V_C)\right]^{\frac{1}{3}}$$

The volume of the polymer canopy $V_P$ can be calculated from the surface area of the core nanoparticle $A_C$, Avogadro number $N_A$, along with the known molar mass $M_n$, the radius of the central particle $r_C$ and an estimated grafting density $\sigma$.

$$V_P = \frac{A_C \sigma M_n}{N_A d_p}$$

Combining these formulas gives a final expression for the thickness of the polymer layer, which equals the approximate planet–satellite distance in the compacted state:

$$t_{40} = \left[3{r_C}^2\left(\frac{1}{3}r_C + \frac{\delta M}{N_A d_p}\right)\right]^{\frac{1}{3}} - r_C$$

With a grafting density of 0.1 nm$^{-1}$ estimated based on previous results,[2] a distance of $t_{40}$ = 4 nm was calculated.

## 3 References

(1) Schild, H. G. Poly(N-Isopropylacrylamide): Experiment, Theory and Application. *Progress in Polymer Science* **1992**, *17* (2), 163–249. https://doi.org/10.1016/0079-6700(92)90023-R.

(2) Tang, Q.; Rossner, C.; Vana, P.; Müller, M. Prediction of Kinetically Stable Nanotheranostic Superstructures: Integral of First-Passage Times from Constrained Simulations. *Biomacromolecules* **2020**, *21* (12), 5008–5020. https://doi.org/10.1021/acs.biomac.0c01184.