Supporting information to

Surfaces with Dual Functionality through Specific Coimmobilization of Self-Assembled Polymeric Nanostructures

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Contents:

1. Azide containing polymersomes

$PMOXA_6$-*b*-$PDMS_{43}$-*b*-$PMOXA_6$ copolymer based polymersomes with different ratios (0 % to 10 %) of azide-terminated $PMOXA_7$-*b*-$PDMS_{40}$-*b*-$PMOXA_7$ copolymers were limited in their size distribution by extrusion through 200 nm and further size exclusion on Sepharose 2B.

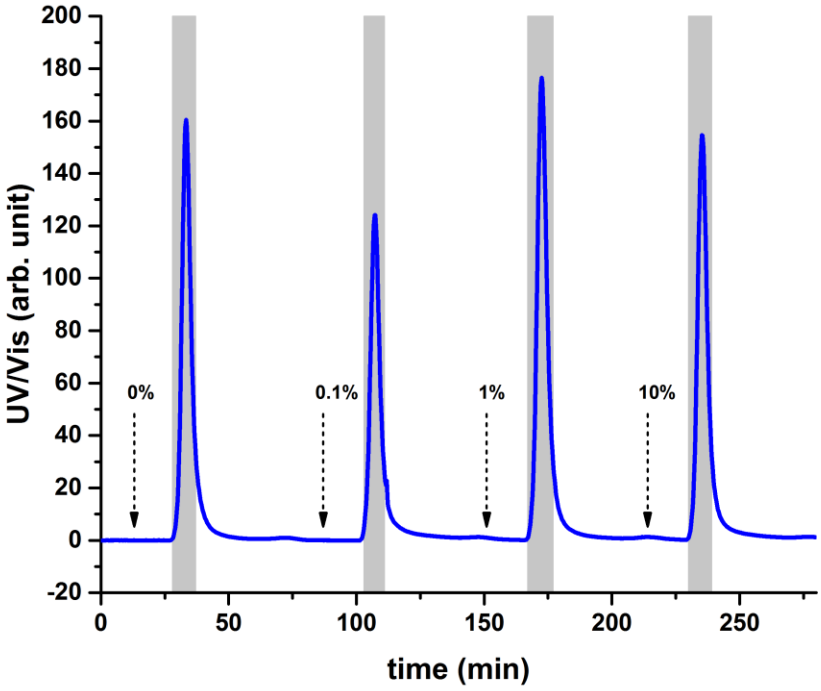

Figure S1. Size exclusion chromatograms (UV-Vis absorption at 280 nm) of polymersomes prepared from block copolymer mixtures of 0.0, 0.1, 1.0, and 10 mol% of azide functionalized polymer with respect to hydroxy functionalized ones. Injection volumes were 880, 850, 860, and 860 µL respectively. Arrows indicate the time of injection. The polymersomes were eluted in PBS and collected as a single fraction indicated by the grey areas.

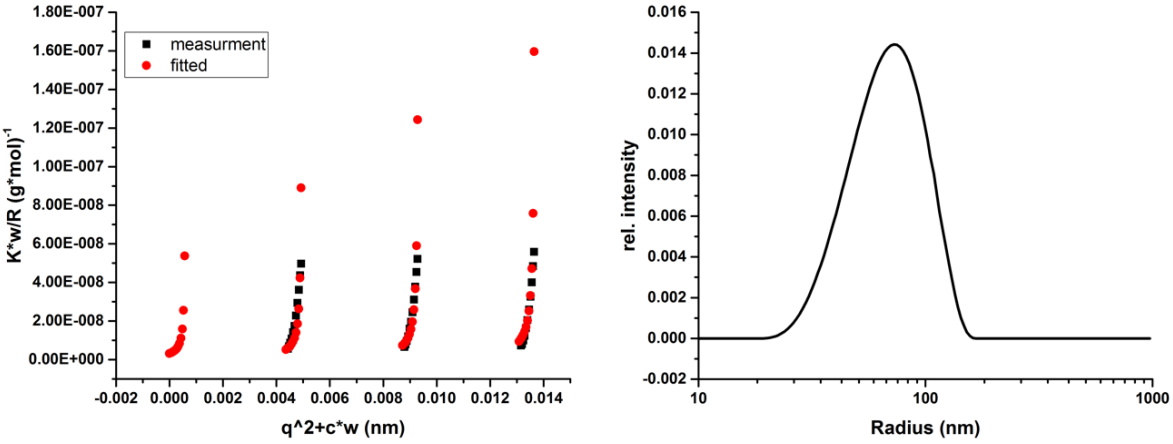

Figure S2. LS data of self-assembled structures containing 1 mol% azide-terminated polymers. The extruded solutions containing polymersomes were diluted with filtered (Millex-LCR syringe filters, hydrophilic, polytetrafluoroethylene - PTFE, 0.45 µm; Millipore) PBS buffer to obtain the desired polymer concentrations; 0.3, 0.2, and 0.1 mg mL^{-1}. Left: Zimm plot with obtained SLS data acquired every 10° between 40 and 110°. Right: DLS of the 0.1 mg mL^{-1} solution of polymersomes recorded at 90°.

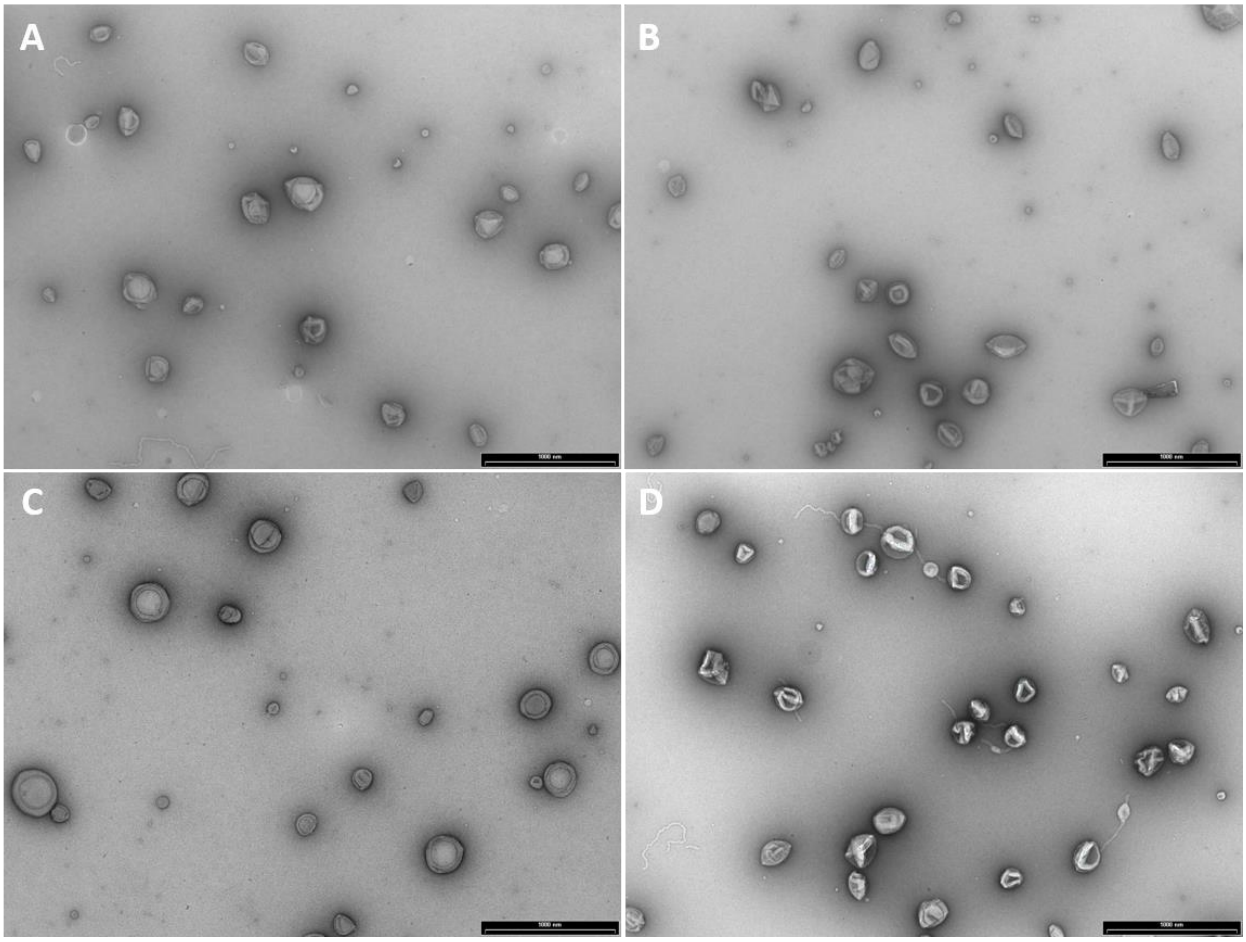

Figure S3. TEM images of polymersomes with different ratios of azide-terminated polymers: A) 0.0 mol% N_3, B) 0.1 mol% N_3, C) 1.0 mol% N_3, D) 10 mol% N_3. Scale bars: 1 µm.

2. Methacrylate containing nanoassemblies

Methacrylate nanoassemblies were self-assembled from methacrylate-terminated PMOXA-*b*-PDMS-*b*-PMOXA containing traces (approximately 0.5 mol%) of SRB labeled PMOXA-*b*-PDMS-*b*-PMOXA polymers. The nanostructures were characterized by DLS and TEM. The polymersomes have a diameter of 182 ± 96 nm and the micelles of 82 ± 50 nm according to number PSD. The higher polydispersity compared to the azide-exposing polymersomes can also be seen in the TEM images where larger polymersomes coexist with smaller particles. This is because the methacrylate nanostructures have been used without further treatment to cap their size by extrusion or SEC.

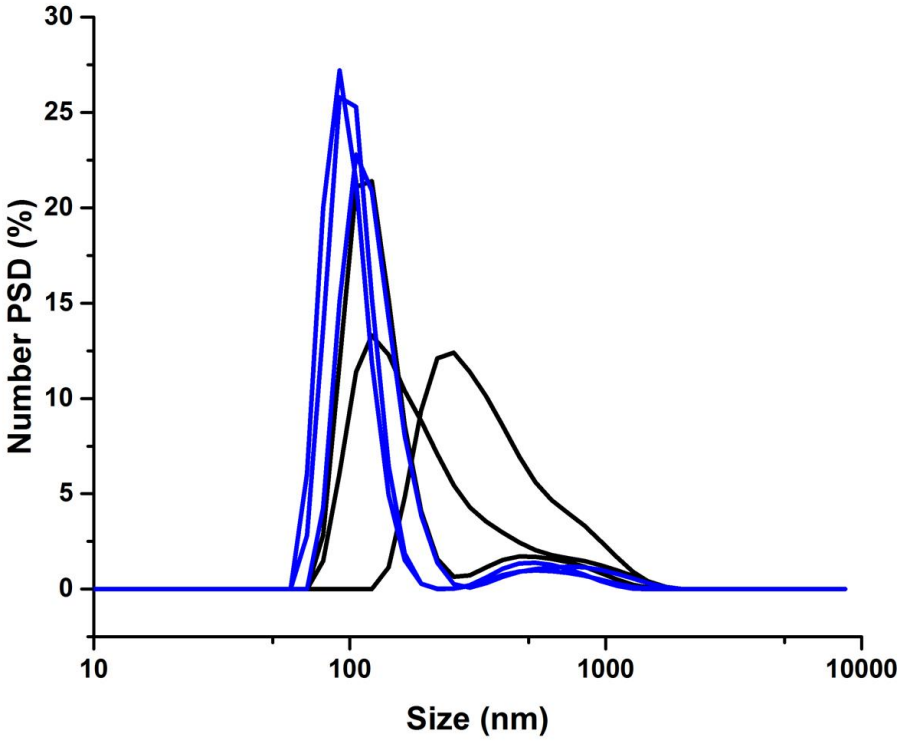

Figure S4. DLS of two separately, but identically prepared methacrylate solutions of polymersomes, which were self-assembled from methacrylate terminated $PMOXA_{19}$-*b*-$PDMS_{67}$-*b*-$PMOXA_{19}$ block copolymer. The number average PSD of each measurement is shown and results in a diameter of 182 ± 96 nm. Each color represents one identically prepared sample of which three measurements were done.

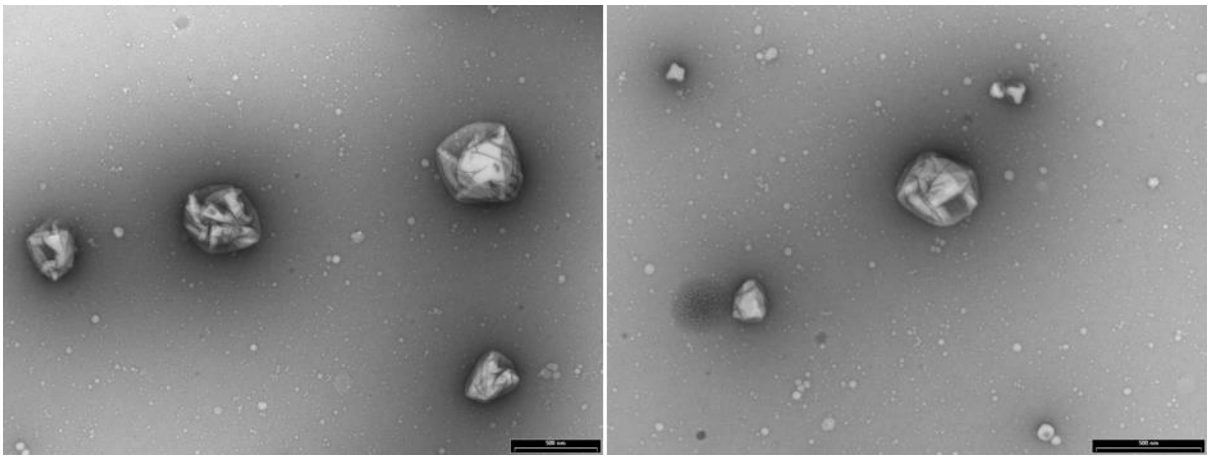

Figure S5. TEM micrographs of the same sample of methacrylate polymersomes, stained by uranyl acetate, scale bars: 500 nm.

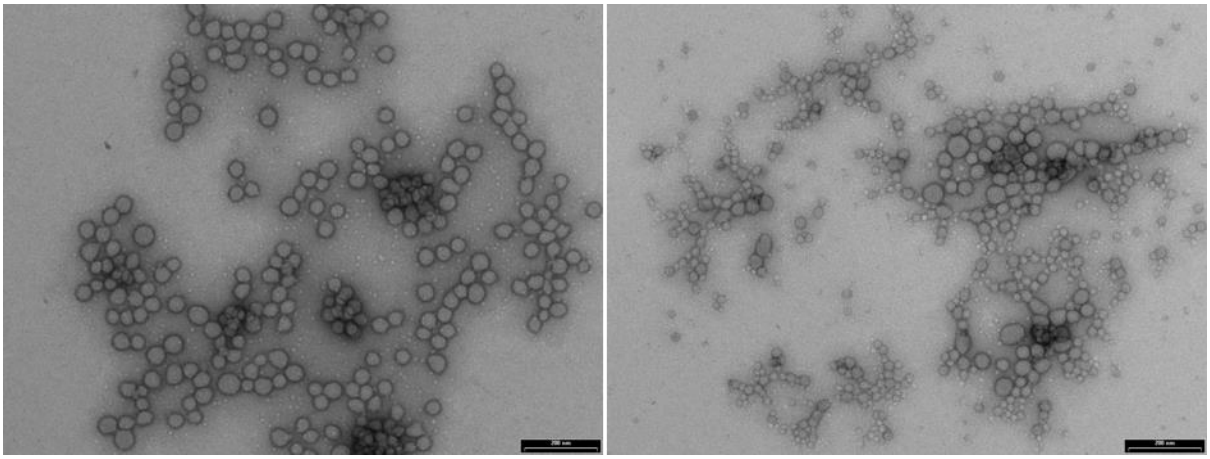

Figure S6. TEM micrographs of the same sample of methacrylate micelles, stained by uranyl acetate, scale bar: 200 nm.

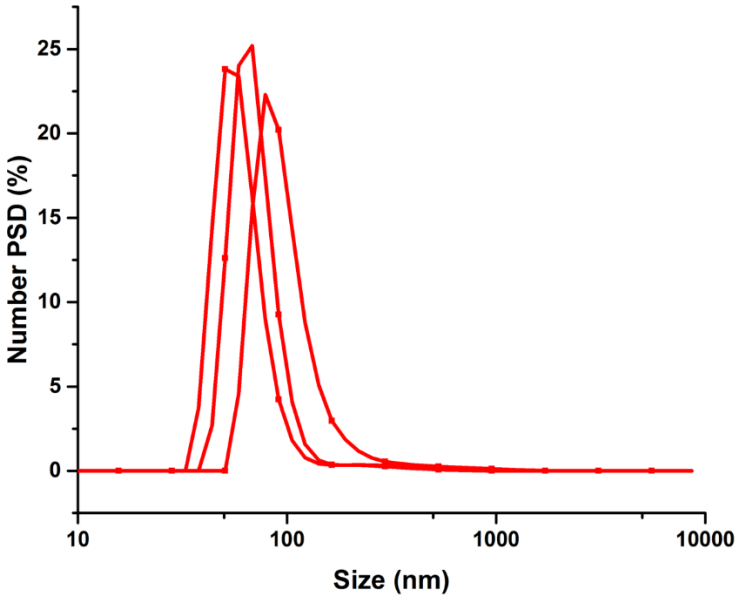

Figure S7. DLS of a solution of methacrylate micelles self-assembled by $PMOXA_{25}$-*b*-$PDMS_{54}$-*b*-$PMOXA_{25}$. The number average PSD of three measurements of the same sample are displayed and result in an average diameter of 82 ± 50 nm.

3. DBCO functionalized surface

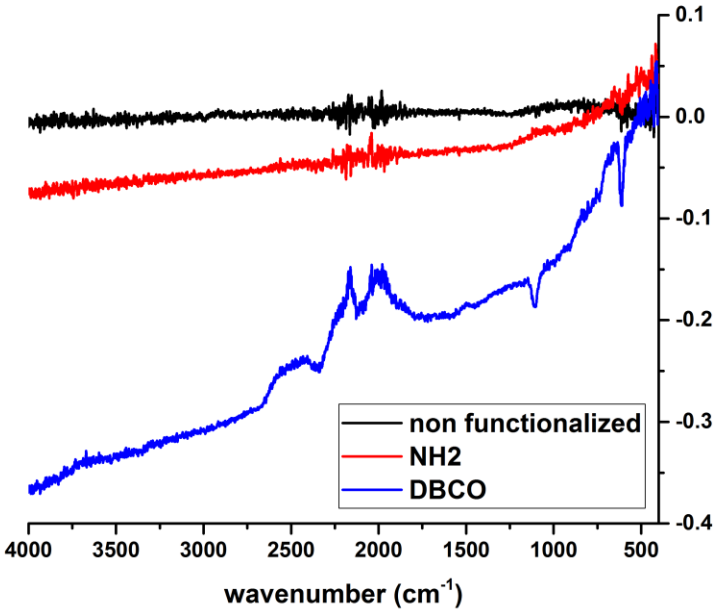

Figure S8. ATR-FTIR of silica wafers during the different functionalization steps.

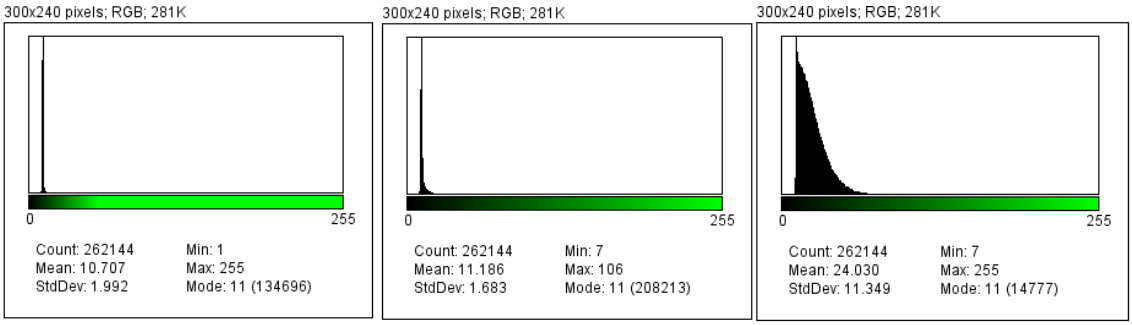

Figure S9: Intensity histograms from left to right: non functionalized surface, NH_2 functionalized surface and DBCO functionalized surface.

4. Immobilized azide containing vesicles

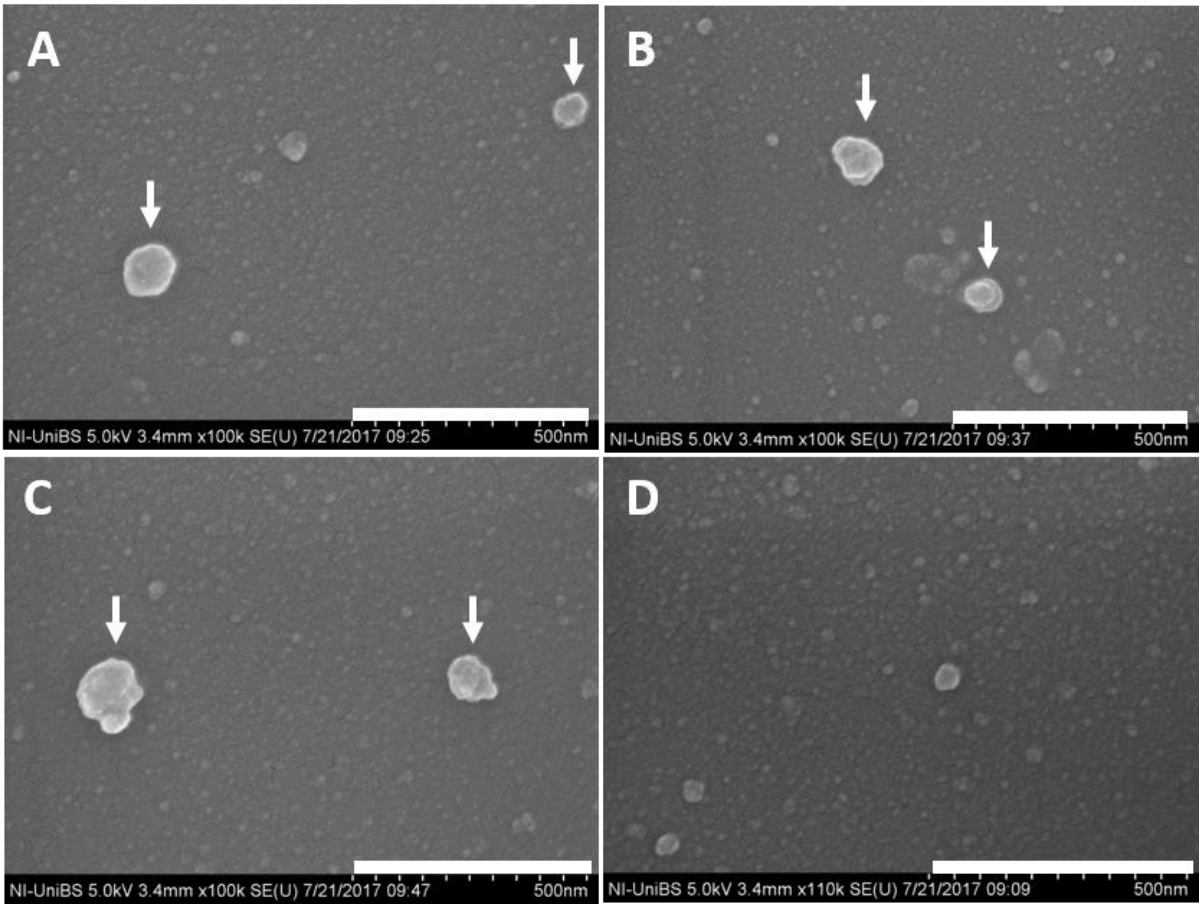

Figure S10. SEM images of immobilized, bodipy free, platinum sputtered polymersomes with different ratios of azide-terminated polymers A) 0.1 % B) 1.0 % C) 10 % D) 0.0 % on DBCO functionalized silica wafers. Scale bars: 500 nm. The arrows indicate immobilized vesicles.

Table S1. Polymersomes were mixed with Bodipy prior immobilization to be able to visualize them on the surface by airyscan CLSM. Several images of immobilized polymersomes were taken for each sample. The round fluorescent dots were counted by analyze particles on Fiji by ImageJ. The number of immobilized polymersomes per area of the image was calculated.

Azide ratio	**0.1 mol%**	**1 mol%**	**10 mol%**	**0 mol%**
Polymersomes per 100 µm²	40.7	4.4	31.3	1.6
	33.5	5.3	23.6	1.2
	43.5	9.4	26.3	1.2
	36.8	37.0	6.1	0.9
	46.8	44.1	13.9	2.7
Average ± standard deviation	40.3 ± 4.7	20.0 ± 17	20.2 ± 9.1	1.5 ± 0.6

5. Coimmobilization of azide containing vesicles with methacrylate-exposing nanostructures

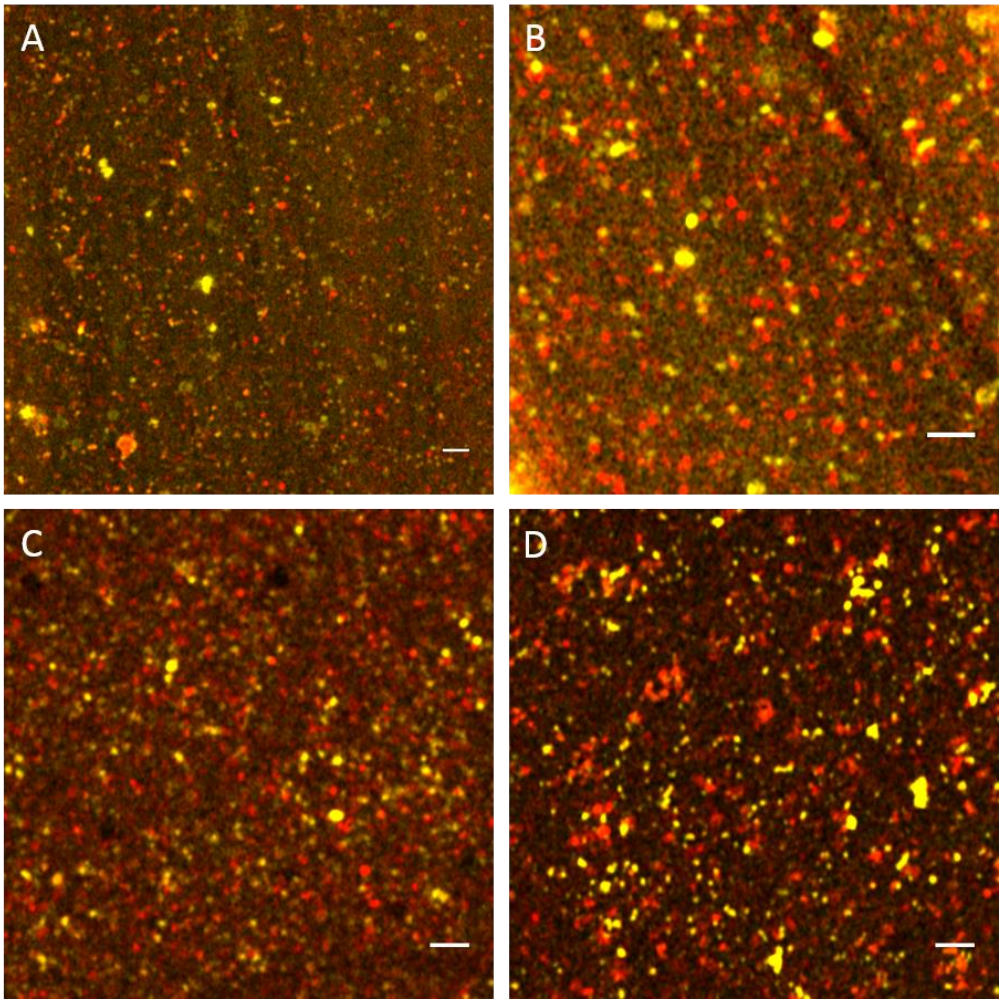

Figure S11. Coimmobilization of azide functionalized polymersomes (containing bodipy, red) and SRB labeled methacrylate functionalized nanoassemblies (yellow): A-B) polymersomes and C-D) micelles. Scale bars: 2 μm.

To study the stability of the immobilized polymersomes, the surfaces were washed with ethanol after immobilization of polymersomes.

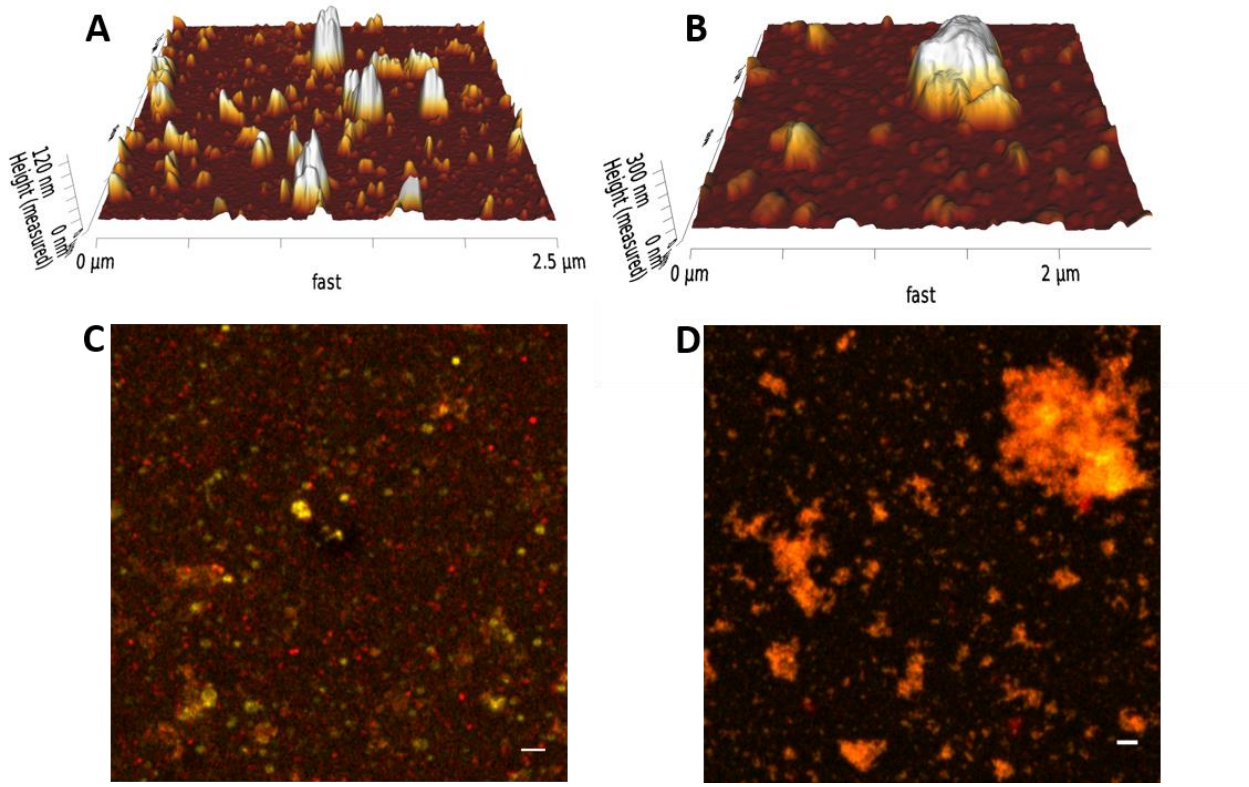

Figure S12. A) AFM of coimmobilized azide and methacrylate functionalized polymersomes. B) AFM image of the same surface after ethanol treatment. C) CLSM micrograph of coimmobilized azide and methacrylate functionalized polymersomes. D) CLSM micrograph of the same surface after ethanol treatment. Scale bars (C and D): 2 µm.