Supporting Information

for

Microgel Surface Modification with Self-Assembling Peptides

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Surface-localized fibrils are observed in atomic force microscopy (AFM) images of Microgels 2, 3, and 6 after incubation with (RADA)4 (Figures S1-S3). Microgels 2, 3, and 6 contain acrylic acid (AAc) in the microgel network (5, 20, and 10% AAc, respectively). However, when microgels without AAc (Microgels 5 and 6) are incubated with (RADA)4, flocculation occurs. In the case of Microgel 5, peptide assemblies are observed between the microgels rather than associated with the microgel surface (i.e. red particles are not observed, Figure S4). Alternatively, large aggregates of Microgel 6 are seen in brightfield microscopy images of a dried aliquot (Figure S5). Stable colloidal dispersions of (RADA)4-coated microgels are not observed when AAc is not incorporated into the microgel network.

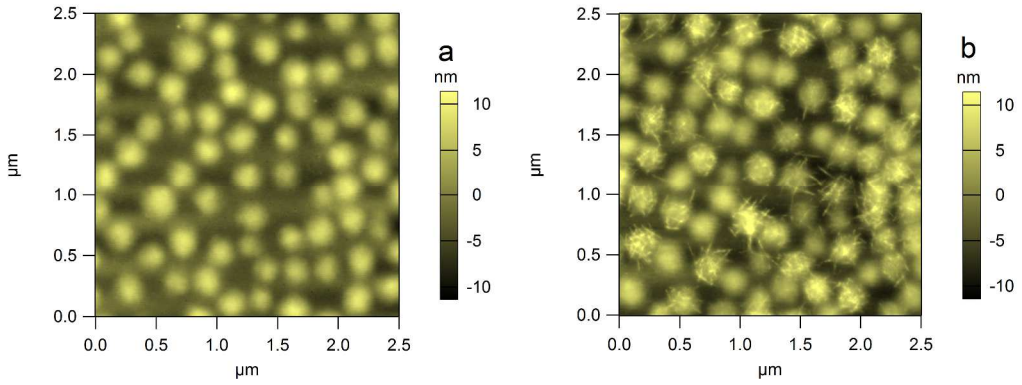

Figure S1. AFM height images of Microgel 2 (5% AAc) before (a) and after (b) coating with (RADA)4+TMR.

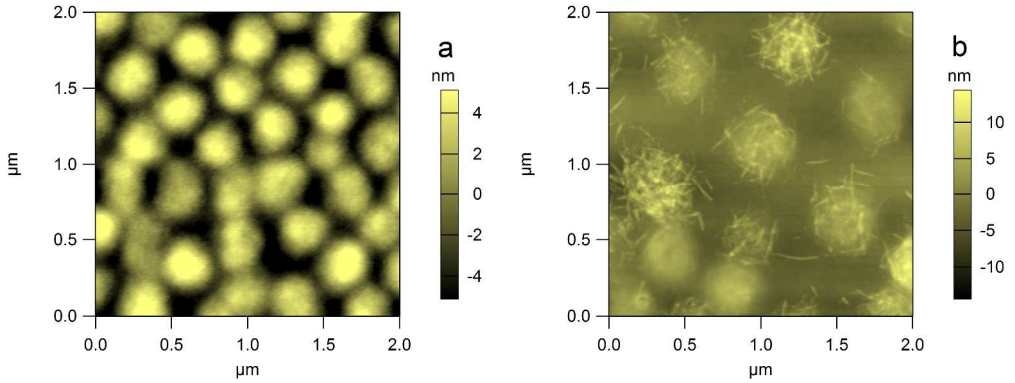

Figure S2. AFM height images of Microgel 3 (20% AAc) before (a) and after (b) coating with (RADA)4+TMR.

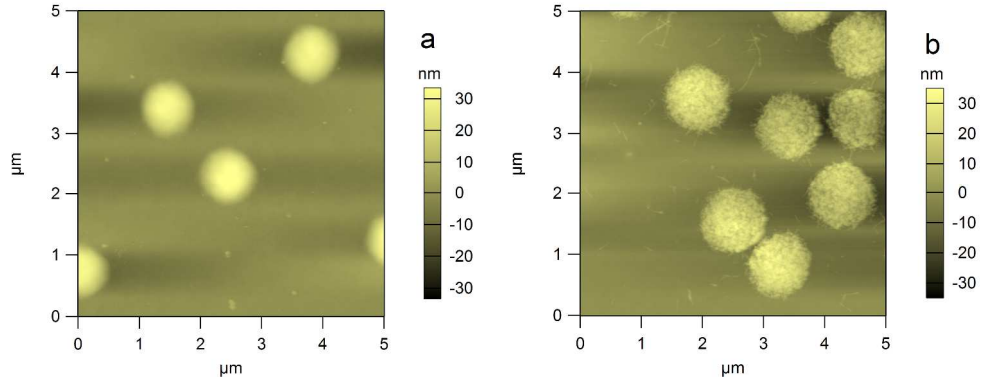

Figure S3. AFM height images of Microgel 6 (ULC, 10% AAc) before (a) and after (b) incubation with RADA+TMR.

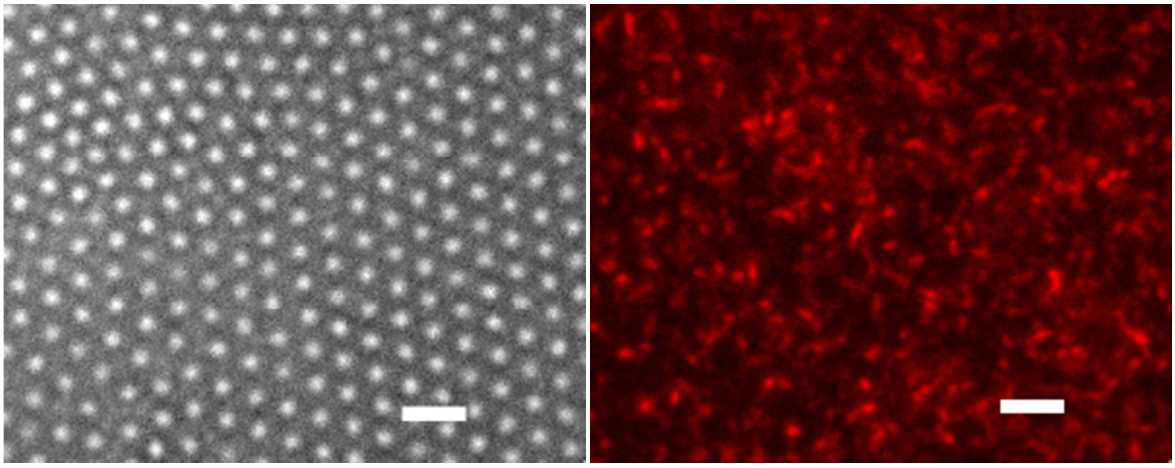

Figure S4. Representative microscopy images of Microgel 5 following incubation with (RADA)4+TMR and dialysis: (a) brightfield and (b) fluorescence following excitation with green light (scale bar=2 μm).

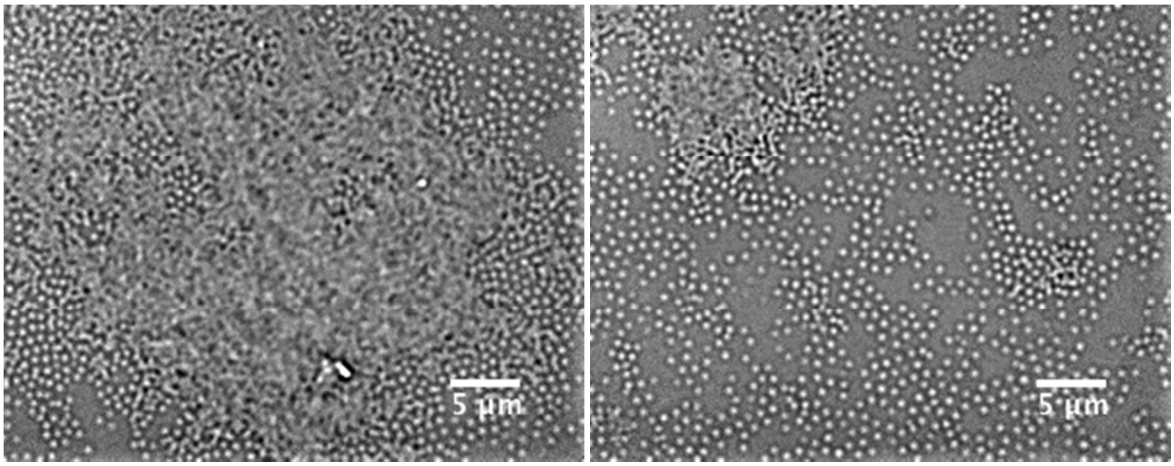

Figure S5. Representative brightfield microscopy images of Microgel 6 after incubation with (RADA)4 and dialysis.

Microgel 1 was coated with (RADA)4C with or without co-assembly of a tetramethylrodamine-modified (RADA)4 (TMR). Following dialysis, the thiol of the cysteine residue was conjugated to 5-iodoacetamidofluorescein (5-IAF). Aliquots of each were centrifuged to form pellets (Figure S6). Without any fluorophores, the pellet is colorless (far right). When TMR is incorporated into the peptide shell a pink pellet results (middle right). Likewise, a yellow pellet is observed following conjugation of 5-IAF. When both TMR and 5-IAF are present an orange pellet can be seen (far left). These results suggest the successful

conjugation of 5-IAF to (RADA)4C, and the inclusion of TMR into the peptide shell, demonstrating the ability to modify the shell both during and after shell assembly.

The incorporation and/or conjugation of fluorophores were further investigated by measuring the fluorescence intensities of fluorescence images of dried microgel aliquots as a result of excitation with green, blue, or violet light. We expect to observe an increase in fluorescence intensity upon exposure to: green light when TMR is present, blue light when 5-IAF is present, and violet light with CAz is present. The average and standard deviation of five locations on each sample are presented in Table S1. Overall, higher fluorescence is observed when TMR is incorporated or a fluorophore is conjugated to an amino acid residue (cysteine for 5-IAF or propargyl for CAz) when compared to unmodified Microgel 1, confirming the presence of the fluorophores.

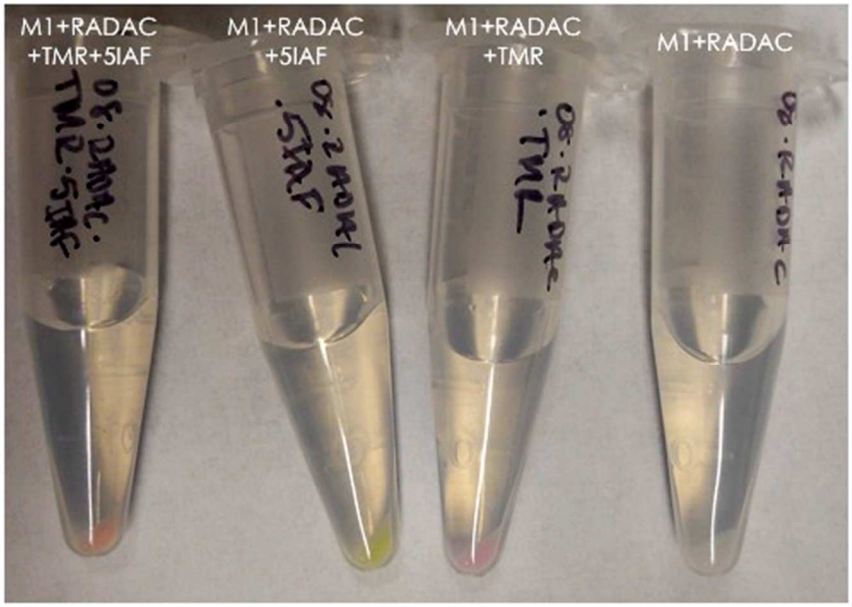

Figure S6. Microgel 1+(RADA)4C pellets following centrifugation.

Table S1. Average Fluorescence Intensities of (RADA)4-Coated Microgel 1 Images

	Microgel 1	+5IAF	+RADA +TMR	+RADA +TMR +5IAF	+RADAC +TMR	+RADAC +5IAF	+RADAC +TMR +5IAF	+RADAPr	+RADAPr +CAz*
Green Ex	103±0	104±0	193±15	194±48	412±52	108±3	471±42	103±0	104±0
Blue Ex	103±0	106±1	104±0	103±0	105±1	169±18	146±14	103±0	104±0
UV Ex	108±1	N/A	N/A	N/A	N/A	N/A	N/A	105±0	229±20

*Following CuAAC reaction with $CuSO_4$, ascorbic acid, and THPTA

AFM images reveal fibrils of (RADA)4Pr on the surface of Microgel 1 (Figure S7), demonstrating that the propargyl group does not interfere with surface assembly.

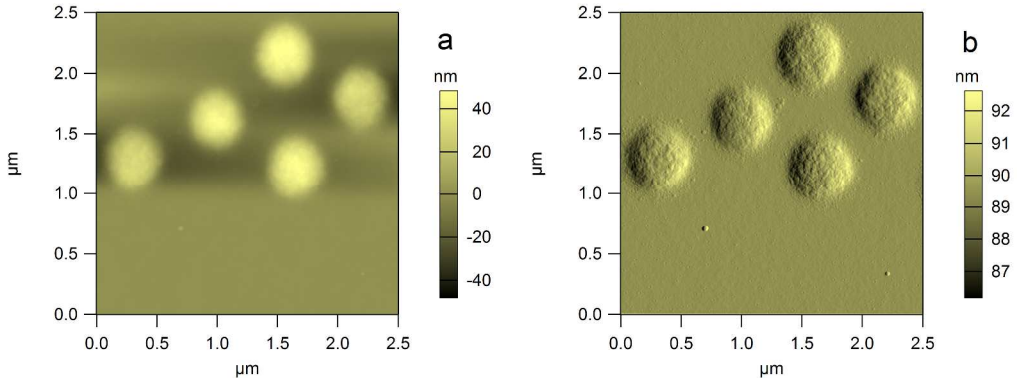

Figure S7. AFM height (a) and amplitude (b) images of Microgel 1+(RADA)4Pr