Electronic Supplementary Material (ESI) for Chemical Communications


# Supporting Information

# Pickering emulsion templated soft capsules by self-assembling cross-linkable ferritin-polymer conjugates

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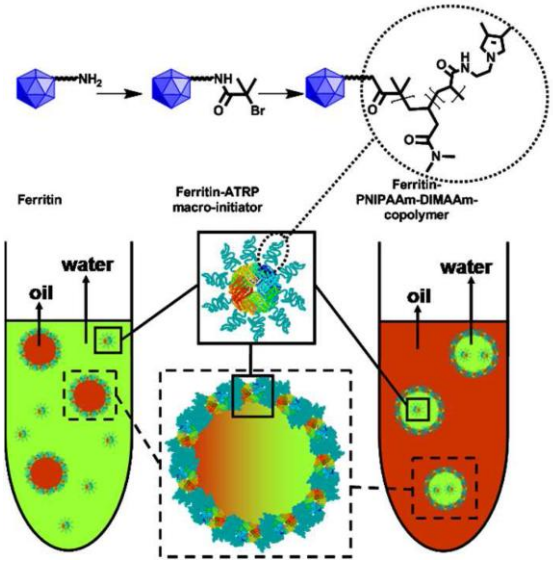
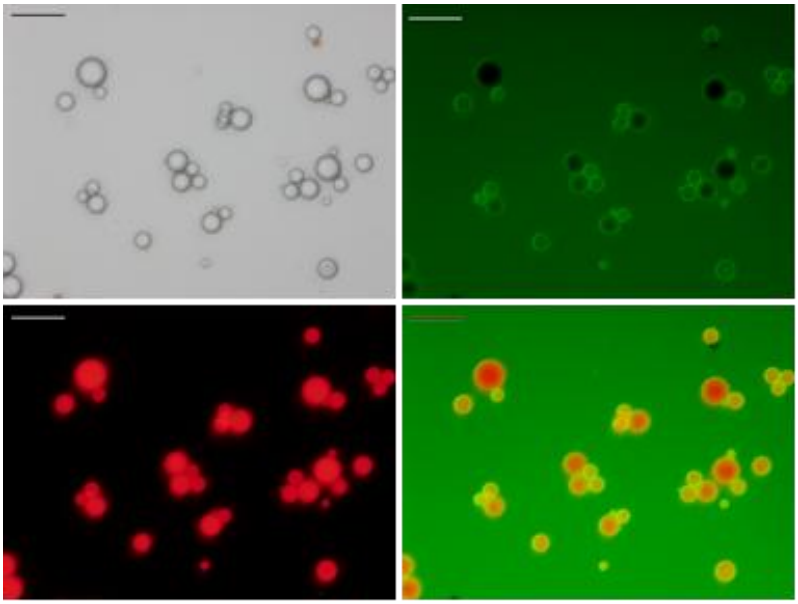
## SI 1: Experimental and Materials.




The synthesis of the Ferritin-PNIPAAm-DMIAAm was performed as described in previous work (ref. 22) with a ratio of initiator to monomer of 1:1000 and the relative amount of NIPAAm/DMIAAm used was 95/5. Emulsions were prepared by vortexing the polar and apolar phase at 2000 rpm for 1 hour. UV irradiation of the emulsion was carried out with a 400W UV lamp (Panacol 400F), with emitting light with λ: 315-400 nm and cooling the sample with an ice-bath. For the preparation of the emulsions, Milli-pore water was used and Benzotrifluoride (98%) and Toluene (HPLC-grade) were purchased from

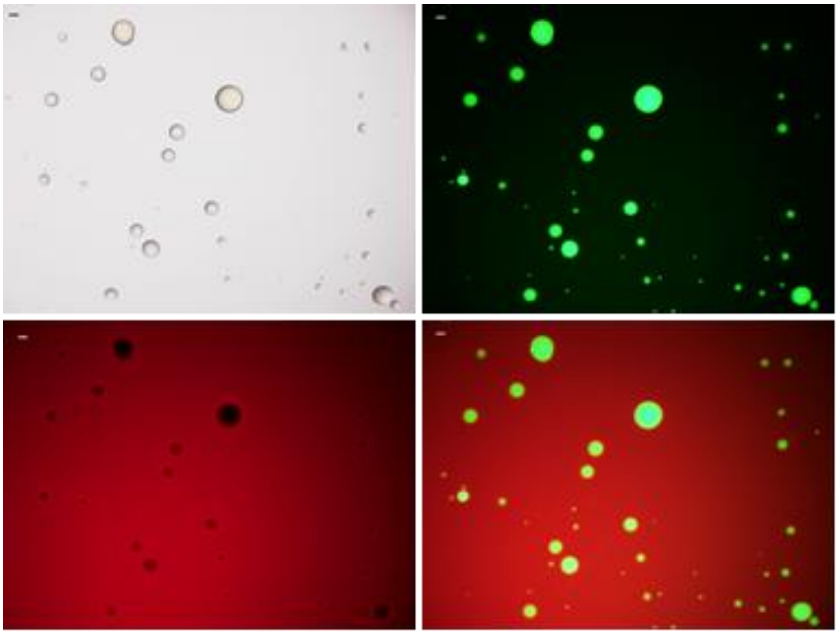
Sigma Aldrich and used as received. The fluorescent dyes Nile Red and amino-Fluorescein were also purchased from Sigma Aldrich and used without further purification. For the optical and fluorescence microscope images a Keyence BZ-8100E was used with excitation-mode for Texas Red ($\lambda_{excitation}$: 589 nm) and GFP ($\lambda_{excitation}$: 475 nm) for visualization of the Nile Red and Fluorescein-co-monomer, respectively, both purchased from Sigma Aldrich and used as obtained. TEM-imaging was done by dipping a carbon coated copper grid into an emulsion and after approximately one minute, the excess liquid was removed with filtration paper and allowed further in air at room temperature. The analysis was performed on a ZEISS LIBRA®120 PLUS electron microscope, operating at 80 kV. Scanning Force Microscopy images were taken on a Veeco Instruments Scanning Force Microscope operating on Nanoscope software.

**SI 2: Optical and fluorescence microscopy images of cross-linked o/w emulsions.**



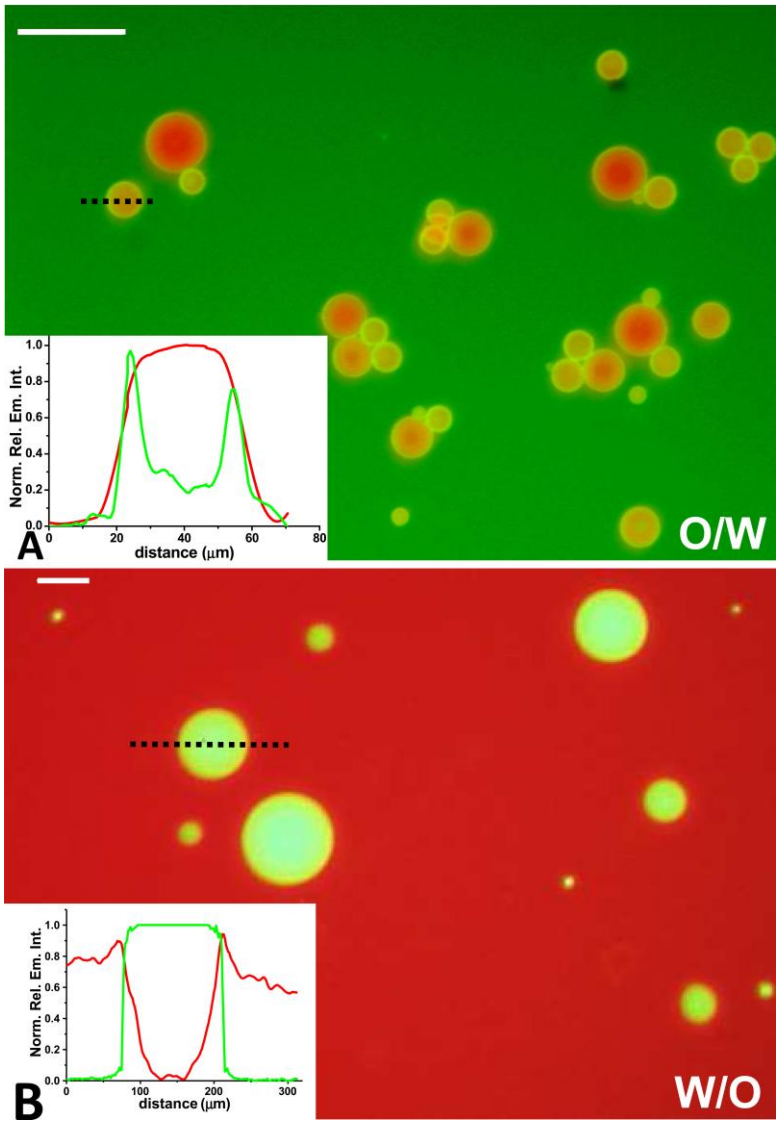
Optical and Fluorescence microscopy images from which the overlay image in Fig. 2A of the manuscript is composed of 10 µL BTF+Nile Red (0.01mM) in 1000 µL water+Fluorescein (0.01 mM) with ~10 mg $ml^{-1}$ Fer-NIPAAm-DMIAAm, cross-linked. Measurements were performed at room temperature, scale bars represent 100 µm.

**SI 3: Optical and fluorescence microscopy images of cross-linked w/o emulsions.**



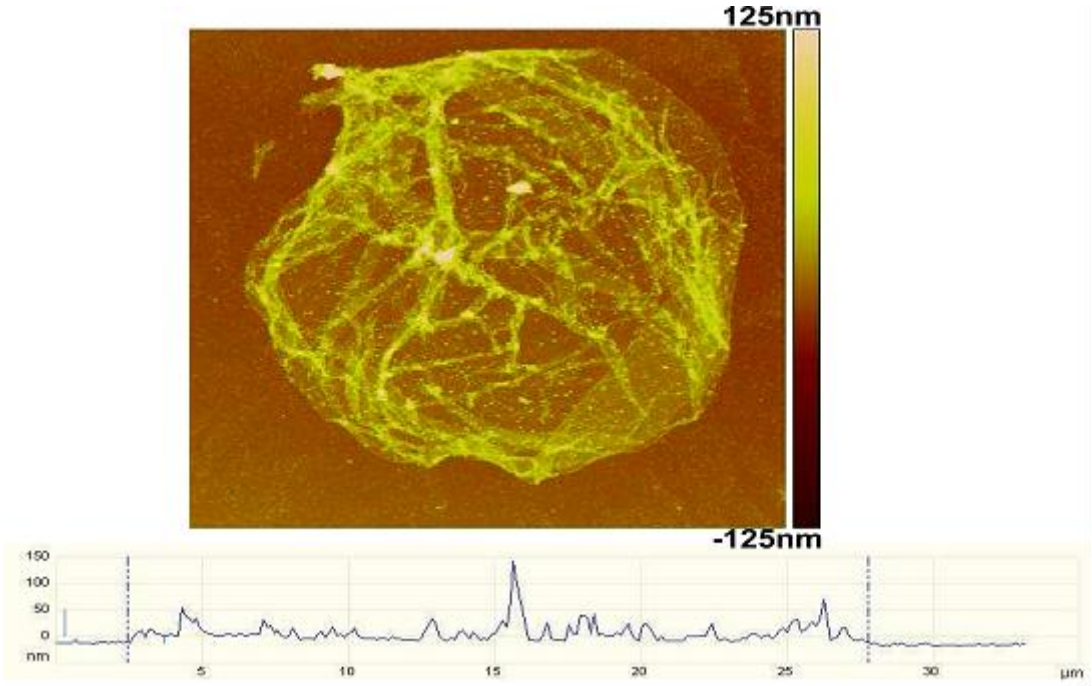
Optical and Fluorescence microscopy images from which the overlay image in Fig. 2B of the manuscript is composed of 10 µL water+Fluorescein (0.01 mM) with ~400 mg $ml^{-1}$ Fer-NIPAAm-DMIAAm, in 1000 µL Toluene+Nile Red (0.01mM), cross-linked. Measurements were performed at room temperature, scale bars represent 100 µm.

**SI 4: Fluorescence microscopy overlay images of cross-linked o/w and w/o emulsions with fluorescence intensity profile.**



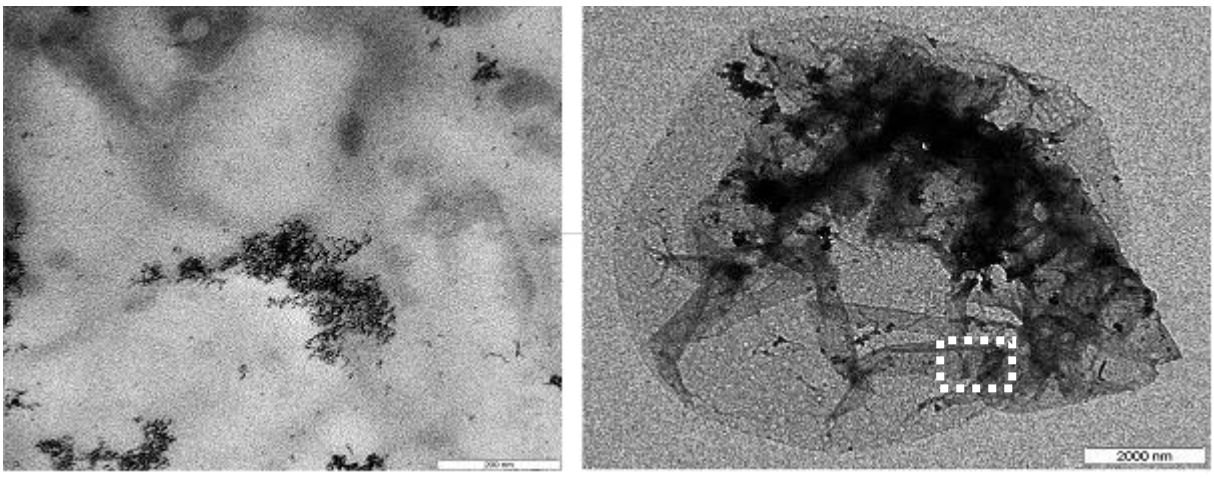

Fluorescent microscopy overlay images of emulsion of **A**) 10 μL BTF+Nile Red (0.01mM) in 1000 μL water+Fluoresceine (0.01 mM) with ~10 mg $ml^{-1}$ Fer-NIPAAm-DMIAAm, cross-linked; with inset the emission intensity profile across a capsule (black dotted line), the red line corresponds to the Nile Red emission and the green to Fluoresceine; **B**) 10 μL water+Fluoresceine (0.01mM) with ~400 mg $ml^{-1}$ Fer-NIPAAm-DMIAAm, in 1000 μL Toluene+Nile Red (0.01 mM), cross-linked; with inset the emission intensity profile across a capsule (black dotted line). Measurements were performed at room temperature, scale bar represents 100 μm.

**SI 5: Cross-section of the SFM height image of a soft matter ferritin-polymer capsule.**




The cross-section of the SFM height image (Fig. 4B) of the capsule shows a variation in height. There where the wrinkles are, the height can extend upto 150 nm. The relatively flat areas are very thin, and with a measured thickness of about 15 nm, means that the shell of the capsule is only 7.5 nm thick (in the dry state) which is averaged over the ferritin and polymer combined.

**SI 6: Soft capsule shown by TEM and an enlargement of the shell to observe the iron-cores of the proteins.**




An enlargement of the shell structure of the capsule is shown. It is seen that some locations have a high density of iron-cores (on top of the wrinkles) and areas where there are only a few iron-cores surrounded by low contrast areas depicting the polymer layer. The low density areas indicate that the ferritin particles have long polymer chains attached to them.