

SUPPLEMENTARY INFORMATION:

Experiments

Synthesis of gold nanorods: The synthesis and surface functionalization of gold nanorods were carried out as described in the literature³⁶. For the synthesis of gold nanorods, seed solution and growth solution were prepared as described below.

Seed Solution. In a 30 mL glass vial, 364 mg of CTAB (hexadecyltrimethylammonium bromide) was dissolved in 5mL of water upon slight heating with a heat gun (up to 30-35 °C). In a separate glass vial, 1 mg of H_{AuCl}₄.3H₂O is dissolved in 5 mL of water at room temperature. These two solutions were mixed together right after their preparation and 0.6 mL of 0.01M ice-cold aqueous solution of NaBH₄ was added at once upon vigorous stirring (1200 rpm). After the color changed from greenish-yellow to brown; the mixture was stirred for an additional two minutes.

Growth Solution. In a 1L Erlenmeyer flask, 18.22g of CTAB was dissolved in 250mL of water upon slight heating. After the complete dissolution of CTAB, 12.5mL of 0.004M AgNO₃ solution was added and mixed gently. In separate flask, 98.5 mg of H_{AuCl}₄.3 H₂O was dissolved in 250 mL of H₂O and added to the mixture of CTAB and AgNO₃. After an additional three minutes, 3.5 mL of 0.0788 M aqueous solution of ascorbic acid was added to the above mixture. The flask was hand-stirred until the mixture became colorless (typically 3-5 seconds). At this point, 0.8 mL of seed solution was added to the entire growth solution and the mixture was stirred for 30 seconds. After that the flask containing the growth solution was placed into an oil bath at 27 °C and kept without stirring. A reddish-brown color slowly developed within 10 minutes. Investigation of the growth solution by TEM showed that the growth of nanorods is

complete within 30 minutes and no change in size of the rods occurs after that. The rods prepared under these conditions are typically 10 nm in diameter and 45 nm in length.

Surface functionalization of gold nanorods with binary SAMs: The surface functionalization of gold nanorods with mixed thiols was carried out by the drop wise addition of tetrahydrofuran (THF) solution of an equimolar amount of 3-mercaptopropanoic acid and 1-octanethiol into the rod solution. In a typical experiment, 2.5g of 3-mercaptopropanoic acid and 3.4g of 1-octanethiol was dissolved in 30 mL of THF. The THF solution of mixed thiols was introduced into the nanorod solution drop wise upon vigorous stirring. The mixture was then allowed to stir at 27 °C for 12 h. After 12h, a new portion of 100mL of pure THF was added and the mixture was stirred for an additional 2 h. The mixture was then centrifuged at 4000 rpm for 10 min. The precipitate of nanorods was collected by washing with pure THF (light sonication was applied when necessary). The residual CTAB and mixture of thiols were removed by multiple rounds of centrifugation (4-5 rounds). The final product was dissolved in a 50/50 mixture of THF and DFM for further STEM characterization.

Scanning Tunneling Microscopy (STM) experiments were carried out with a Veeco Multimode IIIa Scanning Probe Microscope. The STM samples were prepared by dropping a concentrated solution onto Au (111) thermally evaporated on mica substrates (Molecular Imaging, AZ). Pt-Ir mechanically cut tips were used (Veeco, CA). The tip speed used varied from 0.17 $\mu\text{m/s}$ to 2.9 $\mu\text{m/s}$. The bias voltage varied from 500 mV to 1000 mV and the current varied from 400pA to 700 pA. Imaging gains varied from 0.4 to 0.7 for the integral and proportional.

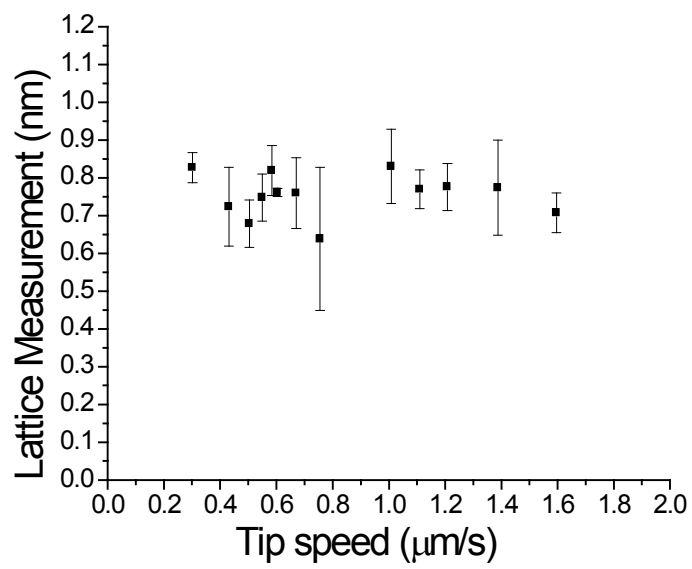


Figure SI1: Plot of the average stripe width for a single nanorod imaged at multiple tip-speeds. The little to no dependence of the stripe width over the imaging speed confirms that the observed features are indeed intrinsic to the sample, and are not imaging artifacts.

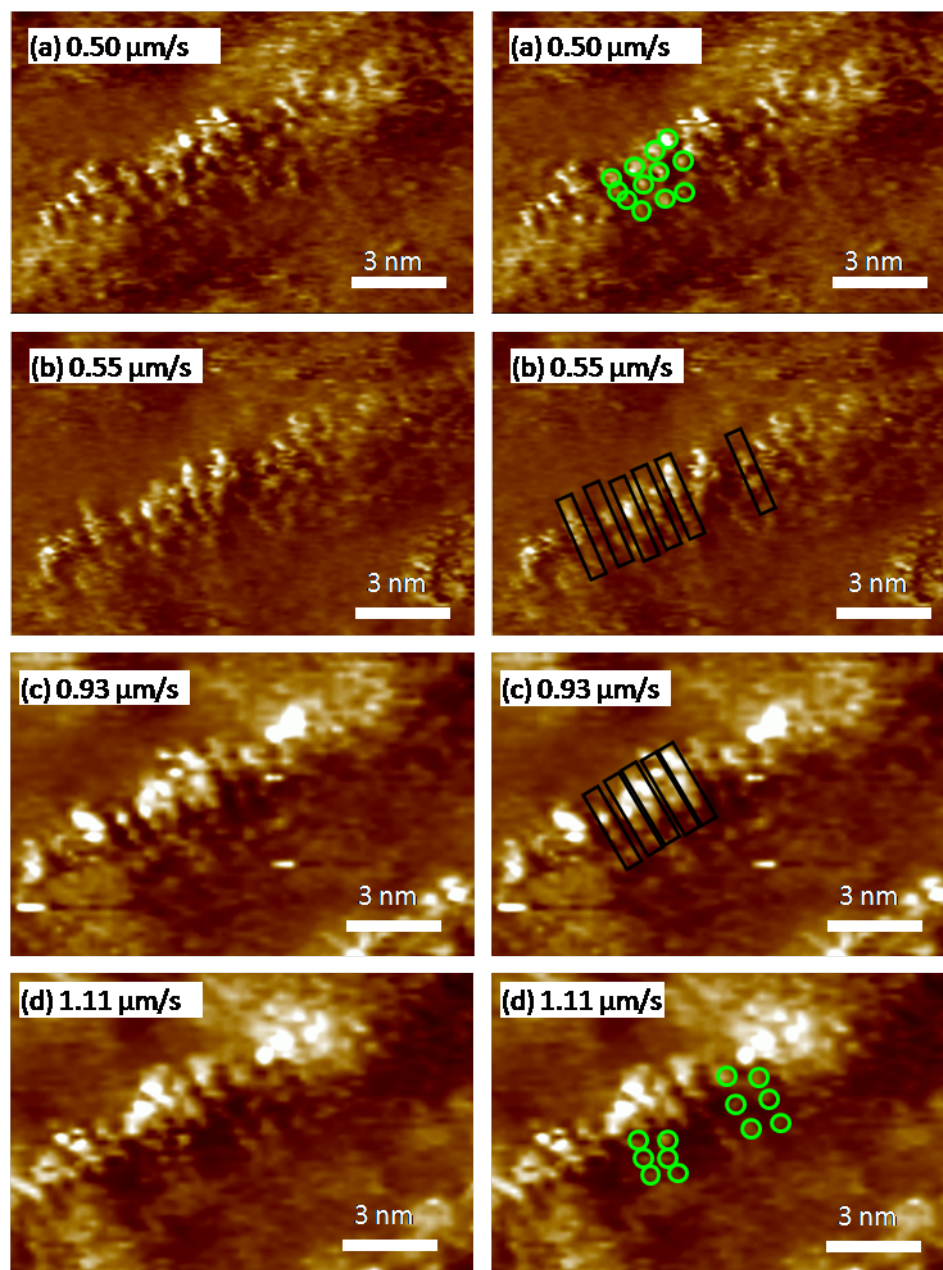


Figure SI2: Representative images of the same nanorod from the series of measurements carried out in Fig S11. In (a) and (d) individual end groups are observed (marked out by the green circles); in (b) and (c) stripe-like structures are observed (marked out by the black boxes). The left images are pristine images; the right images are marked with green circles and black boxes for eye guidance. The above series show that the “stripes” are composed of individual end groups.

Simulations

Figure SI3 demonstrates that our simulations find no dependence of the striped phase on the length of the cylinders. This confirms that 1) there is no effect of the periodic boundary conditions; and 2) there are no finite size effects when using short cylinders in simulations.

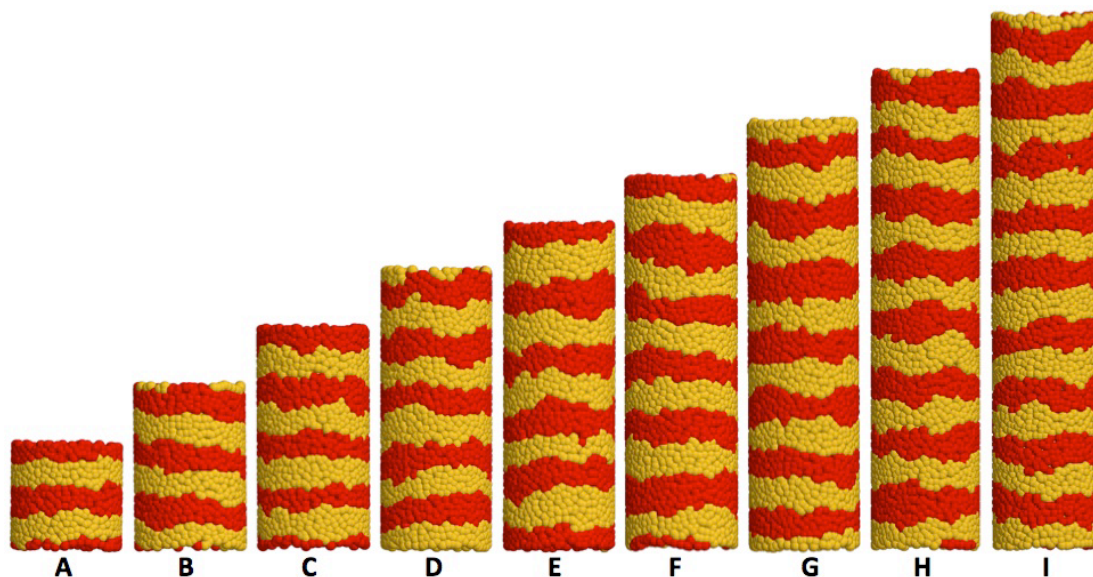


Figure SI3: Effect of cylinder length on phase-separated pattern formed in mixtures of long (7-bead, yellow) and short (4-bead, red) surfactants grafted on the cylinder surface. The lengths of the cylinders are A. 10, B. 15, C. 20, D. 25, E. 30, F. 35, G. 40, H. 45, I. 50. The radius of the cylinder is 5 in all cases.

Figure S14 shows that the rings are equilibrium structures since they do not depend upon initial conditions provided that the surfactant system remains the same.

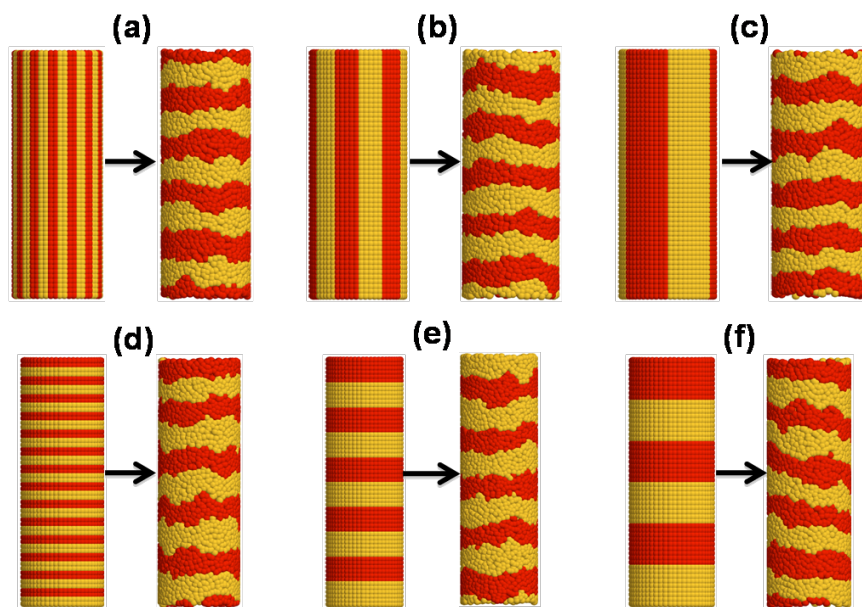


Figure SI4: Phase separation in mixtures of long (7-bead, yellow) and short (4-bead, red) surfactants grafted on an example cylindrical surface, starting from different striped configurations. The stripe widths in (a) – (c) are commensurate with the circumference and those in (d) – (e) are commensurate with the length of the cylinder. All initial conditions with the same surfactant system produce the identical equilibrium ring structure.