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Experimental Section

Materials. HAuCl_4 , tetradecylammonium bromide, sodium borohydride, and dodecanethiol were obtained from Sigma-Aldrich and used as obtained. 10,12-Tricosadiynoic acid (TRCDA) and 10,12-Docosadiynedioic acid (DOCDA) were purchased from Alfa Aesar (Karlsruhe, Germany). The compounds were purified by dissolving the solid in chloroform (CHCl_3) and filtration of the resulting solution through a 0.45 μm Nylon filter. The purified solid was obtained by evaporation of the solvent. Chloroform and toluene were HPLC grade (Frutarom Ltd). The TRCDA and DOCDA were dissolved in chloroform at a concentration of 2 mM. The various molar fractions were prepared by mixing the appropriate amounts of parent solutions of each compound. The water subphase used in the Langmuir trough was doubly purified by a Barnstead D7382 water purification system (Barnstead Thermolyne Corporation, Dubuque, IA), yielding 18.3 $\text{m}\Omega$ resistivity. The PH of water was 7.

Synthesis of Colloidal Gold Nanoparticles The synthesis of the dodecanthiol stabilized Au NPs was according to the Brust procedure^[1] followed a slightly changes^[2] based upon a two-phase (toluene-water) reduction of HAuCl_4 in the presence of the stabilizing ligand. Briefly, 100 mg HAuCl_4 were dissolved in 10 ml water and transferred to 40 ml toluene by mixing with 500 mg of tetradecylammonium bromide. A volume of 0.0147 ml of dodecanethiol was added to the solution while stirring vigorously. Finally, 200 mg of NaBH_4 dissolved in 1 ml of water was added. After 10 min the entire solution was dark brown, indicating the formation of Au NPs. The solution was stirred overnight to ensure that the reaction was complete. The organic phase was washed with 2M H_2SO_4 and with water in a separated funnel. The organic phase was then evaporated *in vacuum* to near dryness. The resultant dodecanethiol-capped gold NPs were precipitated by addition of ethanol (60 mL). Subsequently, the gold NPs were washed three times with ethanol and once with 2-propanol and finally dried in vacuum to yield 34.9 mg of Au NPs as a black wax, which was easily dissolved in chloroform to give 3.12 mg/ml. The Au NPs were

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characterized using ultraviolet-visible (uv-vis) spectroscopy and TEM. The average diameter of the particles was approximately 3 nm.

Surface-pressure/area isotherms and preparation of substrates for Microscopy experiments: All surface-pressure/area isotherms were measured using a computerized Langmuir trough (model 622/D1, Nima Technology Ltd, Coventry, U.K.). The surface pressure was monitored using a 1-cm-wide filter paper as a Wilhelmy plate. For each isotherm experiment, the desired amount of TRCDA or DOCDA with gold NP mixture in chloroform were spread on the water subphase and equilibrated for 15 min allowing for solvent evaporation prior to compression. Compressions were carried out at a constant barrier speed of $8 \text{ cm}^2 \text{ min}^{-1}$. The resulting films at the desired surface pressures were transferred horizontally onto freshly cleaved mica (for AFM measurements) and onto 400 mesh copper Formvar/carbon grids (Electron Microscopy Sciences, Hatfield, PA, USA) for TEM. Ultraviolet ozone cleaning system (T10x10/GES/E UVCOS.INC Montgomeryville PA) was used for plasma etching of the films deposited on mica to eliminate the organic layer.

Brewster angle microscopy (BAM): A Brewster angle microscope (NFT, Gottingen, Germany) mounted on a Langmuir film balance was used to observe the microscopic structures *in situ*. The light source of the BAM was a frequency doubled Nd:YAG laser with a wavelength of 532 nm and 20-70 mW primary output power in a collimated beam. The BAM images were recorded with a CCD camera. The scanner objective was a Nikon superlong working distance objective with a nominal 10x magnification and diffraction-limited lateral resolution of $2 \mu\text{m}$. The images were corrected to eliminate side-ratio distortion originating from a non-perpendicular line of vision of the microscope.

Atomic Force Microscopy (AFM): AFM measurements were performed at ambient conditions using a Digital Instrument Dimension 3100 mounted on an active anti-vibration table. A $100 \mu\text{m}$ scanner was used. Microfabricated Si oxide NSC11/50

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type Ultrasharp with integrated pyramidal . The 512 x 512 pixel images were taken in tapping mode with a scan size of up to 5 μm at a scan rate of 1 Hz.

Transmission electron microscopy (TEM): TEM images were recorded on a Jeol JEM-1230 TEM (JEOL LTD, Tokyo, Japan) operating at 120 kV.

- [1] M. Brust , M. Walker, D. Bethell, D. Schiffrin, R. Whyman, *J. Chem. Soc., Chem. Commun.* **1994**, 801-802.
- [2] K. Norgaard, M. J. Weygand, K. Kjaer, M. Brust, T. Bjornholm, *Faraday Discuss* **2004**, 125, 221-233; discussion 293-309.