

Electronic Supplementary Information for:

Disk Micelles from Amphiphilic Janus Gold Nanoparticles

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General methods

Nuclear Magnetic Resonance spectroscopy (NMR). ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 at 25.0 °C on a Varian Mercury Vx (400 MHz). Additionally ^1H - ^1H COSY and HETCOR experiments were carried out to assign all peaks. Chemical shifts (δ) are given in ppm relative to tetramethylsilane, which was used as internal standard. Abbreviations used are s = singlet, t = triplet and m = multiplet.

Infrared spectroscopy (IR). Infrared spectra were run on a Perkin Elmer Spectrum One UATR FT-IR spectrophotometer.

Gas chromatography - mass spectroscopy (GC-MS). GC-MS analysis was performed on a Shimadzu GCMS-QP5000 Gas Chromatography Mass Spectrometer equipped with a Zebron ZB-5 column with a length of 15 m, a thickness of 0.1 μm and a diameter of 0.25 mm.

Optical spectroscopy. UV-vis measurements were performed on a Perkin Elmer Lambda 40 UV/Vis Spectrometer equipped with a Peltier Temperature Programmer model 1 (PTP-1) or a Perkin Elmer Lambda 900 UV/Vis/NIR Spectrometer. Fluorescence measurements were performed on a Perkin Elmer LS-50B Luminescence Spectrometer.

Optical Microscopy. Dark-field optical microscope images were shot on a Zeiss Axioplan 2 equipped with a Zeiss AxioCam.

Scanning Electron Microscopy (SEM). Measurements were carried out at room temperature with a Philips XL30 FEG-ESEM. The samples were drop-cast on glass

substrates coated with indium tin oxide (ITO), which were mounted on aluminum stubs with double-sided carbon tape.

Transmission Electron Microscopy (TEM). Samples were prepared by applying a droplet of sample solution onto 200 mesh carbon coated copper grids, which were purchased from Aurion. Excess solution was blotted away using a filter paper. The samples were analysed at room temperature on a FEI Tecnai 20, type Sphera TEM operating with a 200 kV LaB6 filament, equipped with a bottom mounted 1k x 1k Gatan CCD camera.

Atomic Force Microscopy (AFM). Measurements were carried out at room temperature with an AFM (Digital Instruments) equipped with a Nanoscope IIIa controller (Digital Instruments) in the Tapping Mode. Glass substrates were cleaned intensively by rinsing with acetone and ethanol followed by drying under nitrogen flow. The samples were drop-cast from water and dried in a vacuum oven overnight.

Langmuir monolayers. The Langmuir isotherms were recorded using a KSV 3000 computer controlled system equipped with a temperature controlled removable Minithrough constructed from a solid piece of PTFE. A 0.5 mM solution of 1:3 **C10/EO4-Au** Janus gold nanoparticles in chloroform was spread on water by using a microliter syringe. Subsequently, the system was compressed with a compression rate of 10 mm/min. at room temperature.

Static Light Scattering (SLS). The SLS measurements were performed with a computerised homemade goniometer, using a step size of 1 degree in the angular range of 25 to 100 degrees, corresponding to the scattering wavevectors of 6 to 20 μm^{-1} . The scattered intensity was measured using a single mode optical fiber with a collimating lens in combination with an ALV/SO-SIPD single photon detector, using a 5 s integration time per angle. A temperature controller was used to stabilise the temperature at 293.0 ± 0.1 K during the measurements. The data points were fit using the Rayleigh-Gans approximation for a cylinder of length $L=2a$ and radius b :¹

$$I(q) \propto \int_0^{2\pi} \left[\frac{\sin(qa \cos(\phi))}{qa \cos(\phi)} \frac{J_1(qb \sin(\phi))}{qb \sin(\phi)} \right]^2 \sin(\phi) d\phi$$

Caution is required when obtaining size information from this fit because of the relatively low refractive index of gold, compared to the solvent refractive index. Therefore the size was obtained by dynamic light scattering, although the size obtained by SLS perfectly agreed with the size obtained by DLS ($R = 285 \pm 20$ nm, $L = 0 - 8$ nm)).

Dynamic Light Scattering (DLS). The apparatus used for the DLS measurements was similar to the one used for SLS measurements. The detector output was sent to an ALV-5000/E Multiple tau digital correlator, using a typical acquisition time of 300s. The obtained intensity correlation functions were fit for all q values, using cumulant analysis:

$$g^{(2)}(\tau) - 1 = \beta e^{-2\bar{\Gamma}\tau} \left(1 + \frac{\mu_2 \tau^2}{2} \right)^2 \quad \text{where} \quad g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle^2}$$

By measuring the slope of the mean decay rate $\bar{\Gamma}$ vs q^2 close to zero scattering angle, the diffusion coefficient could be obtained, and thereby the hydrodynamic radius. Since the height of the micelles was determined to be around 8 nm by SAXS, the mean radius could be found by using the relation:²

$$R_h = \frac{3}{2} R \left(\sqrt{1 + \left(\frac{h}{2R} \right)^2} + \frac{2R}{h} \ln \left(\frac{h}{2R} + \sqrt{1 + \left(\frac{h}{2R} \right)^2} \right) - \frac{h}{2R} \right)^{-1}$$

with R_h the hydrodynamic radius, R the radius and h the height of the disk.

Small Angle X-Ray Scattering (SAXS). Small-Angle X-ray Scattering (SAXS) measurements were performed at the Dutch-Belgian BM26B beamline at the ESRF in Grenoble (France).³ An X-ray photon energy of 10 keV and two different sample-to-detector distances (8 m and 1.5 m, respectively) were used, in order to explore a wide q range ($0.35 \text{ nm}^{-1} < q < 2.9 \text{ nm}^{-1}$, where q is the modulus of the scattering vector $q = 1.014E \sin \theta$, E the energy of the X-rays and θ the scattering angle). The SAXS images were recorded using a 2D multiwire gas filled detector.⁴ The 2D images were

radially averaged in order to obtain the 1D intensity $I(q)$ vs q profiles. The beam centre and the q range calibrations were determined using Silver Behenate powder and a wet rat tail collagen fiber.⁵ The liquid samples were contained in 2 mm borosilicate capillaries. Standard data reduction procedures, i.e. subtraction of the empty capillary contribution, correction for the sample absorption etc. were applied. Calibration of the scattered intensity on an absolute scale was performed using a Lupolen sample as a secondary standard calibrant.⁶

The analysed amphiphilic Janus gold nanoparticle aggregates could be considered as aggregates showing a fractal-like structure over a length scale of 8 nm up to 300 nm or more. These mass fractals are built up from aggregated gold nanoparticles with a gold core radius R . The SAXS intensity $I(q)$ scattered on an absolute scale by a collection of uniform spherical objects can be written as:

$$I(q) = (\Delta\rho)^2 N_p F(q)^2 S(q)$$

where N_p is the number density of spheres, $\Delta\rho$ the electron density difference between the spheres and the solvent, $F(q)$ the sphere form factor and $S(q)$ the interparticle structure factor which takes into account the correlation between the spherical objects forming the aggregate. The form factor for a sphere is given by:

$$F(q) = \frac{4\pi}{3} R^3 \left(3 \frac{\sin(qR) - (qR) \cos(qR)}{(qR)^3} \right)$$

For a mass fractal of spheres with radius R characterised by a fractal dimension D , $S(q)$ can be described by the following empirical expression:⁷

$$S(q) = 1 + \frac{1}{(qR)^D} \frac{D\Gamma(D-1)}{[1 + (q\xi)^{-2}]^{(D-1)/2}} \times \sin[(D-1) \tan^{-1}(q\xi)]$$

where $\Gamma(D-1)$ is the gamma function with argument $(D-1)$,⁸ D the fractal dimension ($1 \leq D \leq 3$), and ξ the so-called cut-off distance.

Synthesis of 2-{2-[2-(2-Methoxyethoxy)-ethoxy]-ethoxy}-ethyl-5-[1,2]dithiolan-3-ylpentanoate (EO4)

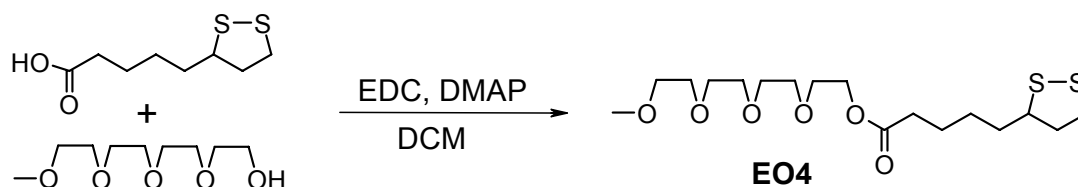


Fig. S1 Synthesis of **EO4**.

Tetraethylene glycol monomethyl ether (3.0 g, 14.4 mmol) and thioctic acid (3.57 g, 17.3 mmol) were dissolved in 75 mL freshly distilled dichloromethane (DCM). The mixture was stirred for 15 minutes at 0 °C under an argon atmosphere. Then a solution of N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide (EDC) (4.14 g, 21.6 mmol) and 4-(dimethylamino)-pyridine (DMAP) (0.53 mg, 4.3 mmol) in 15 mL dichloromethane was added and stirring was continued at 0 °C for another 15 minutes. After stirring an additional 24 hours at room temperature the reaction was completed. The reaction mixture was washed with NH_4Cl (sat), NaHCO_3 (sat) and NaCl (sat), dried over MgSO_4 and evaporated *in vacuo*. Purification by column chromatography on silica gel (DCM) gave pure **EO4** (5 g, 88%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25°C, TMS): δ 1.36 (m, 2 H, 13), 1.55 (m, 4 H, 12 and 14), 1.79 (m, 1 H, 16), 2.23 (t, $J = 7.3$ Hz, 2 H, 11), 2.34 (m, 1 H, 16), 2.96 - 3.09 (m, 2 H, 17), 3.25 (s, 3 H, 1), 3.45 (m, 2 H, 8), 3.53 (m, 12 H, 2 - 7), 3.57 (m, 2 H, 15), 4.10 (t, $J = 4.8$ Hz, 2 H, 9).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25°C, TMS): δ 24.51 (1C, 12), 28.60 (1C, 13), 33.81 (1C, 11), 34.49 (1 C, 14), 38.39 (1 C, 17), 40.11 (1 C, 16), 56.20 (1 C, 15), 58.91 (1 C, 1), 63.34 (1 C, 9), {69.03, 70.40, 70.44, 70.48, 70.50, 71.83} (7 C, 2 - 8), 173.22 (1C, 10).

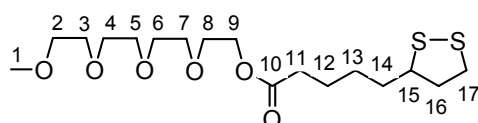


Fig. S2 Numbering of the protons and carbon atoms of **EO4**.

IR (UATR): ν (cm^{-1}): 2920, 2869 (C-H stretch); 1732 (C=O stretch); 1455, 1420, 1381, 1350, 1283, 1247, 1177; 1104 (C-O-C stretch); 1040, 989, 944, 852, 732.

GC-MS (FW = 396.57): m/z 396.

General procedure for the synthesis of gold nanoparticles. Solutions of 300 mg $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 10 mL deionised water and 1.04 g tetra-*n*-octylammonium bromide in 20 mL toluene were shaken in a separatory funnel. The yellow water layer became colourless and the colourless toluene layer became red as the Au^{3+} was phase-transferred. The water layer was removed, the resulting solution was stirred vigorously in a round-bottom flask and a freshly prepared solution of 288 mg NaBH_4 in 5 mL deionised water was added all at once after which the solution darkened. After 2 hours of stirring the water was removed by extraction. An excess of solution (*circa* 1 mmol) containing the two different ligands, pre-mixed in the desired ratio in 10 mL toluene, were exchanged with the tetraoctylammonium bromide-capped gold nanoparticles by stirring for 2 hours. Subsequently the toluene was evaporated *in vacuo*. The black residue was redissolved in dichloromethane (DCM) and remaining unbound ligands were removed by preparative size-exclusion chromatography (Bio-Beads S-X1) with DCM as eluent.

Absorption Spectra

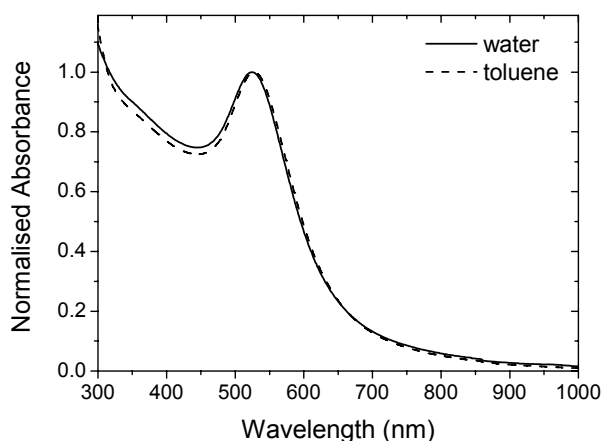
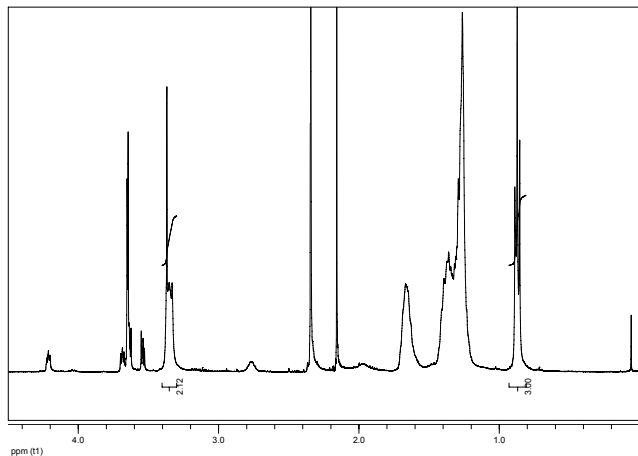


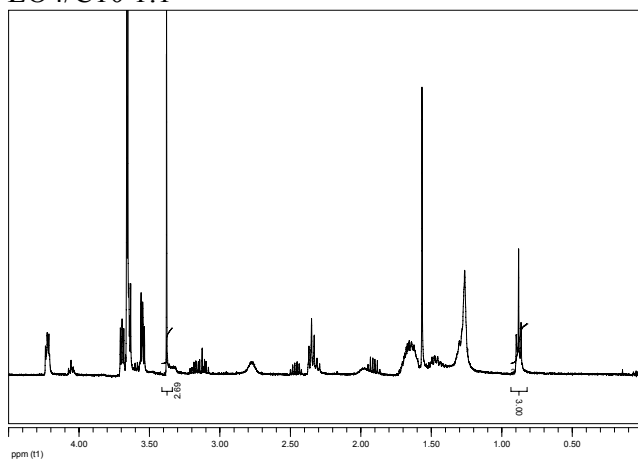
Fig. S3 Normalised UV-vis absorption spectra of **EO4-Au** nanoparticles in toluene and water.

NMR Spectra

EO4/C10 3:1



EO4/C10 1:1



EO4/C10 1:3

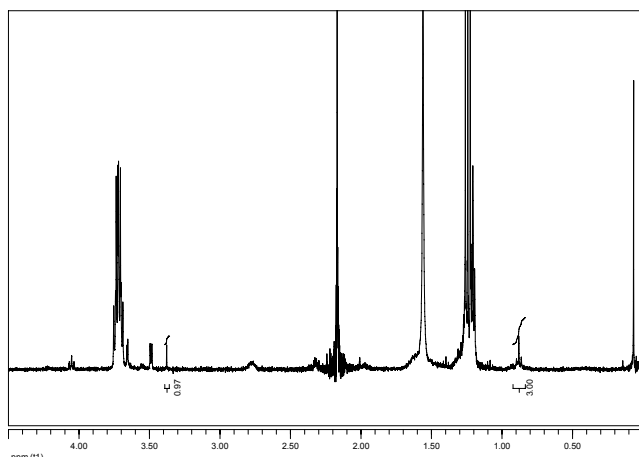


Fig. S4 ^1H -NMR spectra of the gold nanoparticles containing different ratios of EO4/C10 ligands.

Fluorescence-probe studies. The critical aggregation concentration (CAC) was determined by using pyrene as polarity probe.⁹ Above the CAC pyrene is solubilised within the hydrophobic domain of the aggregate, whereas it is molecularly dissolved in water below this concentration. Upon dilution, the aggregates break up and the (0,0) transition band shifts from 338 nm to 335 nm in the excitation spectrum. Furthermore, the intensity ratio between the first and the third vibronic band in the emission spectrum (I_3/I_1) increases. Additionally, the turbidity was measured at an absorption of $\lambda = 700$ nm. Plotted against the logarithm of the concentration, a critical aggregation concentration (CAC) of approximately 0.02 μM was determined (Figure S4).

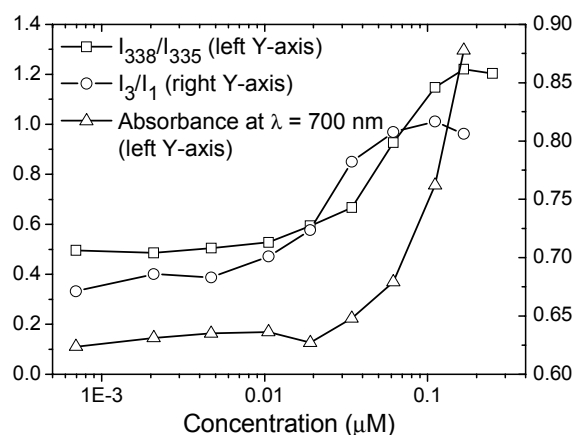


Fig. S5 Fluorescent probe studies on aggregates of 1:3 **C10/EO4-Au** Janus nanoparticles (0.25 μM in water). Shown are excitation ($\lambda_{\text{em}} = 390$ nm, I_{338}/I_{335} , $\square$), emission ($\lambda_{\text{ex}} = 339$ nm, I_3/I_1 ,

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○) and absorption data (A_{700} , Δ) at different concentrations. A pyrene concentration of 5×10^{-7} M has been used in all experiments.

Microscopy pictures

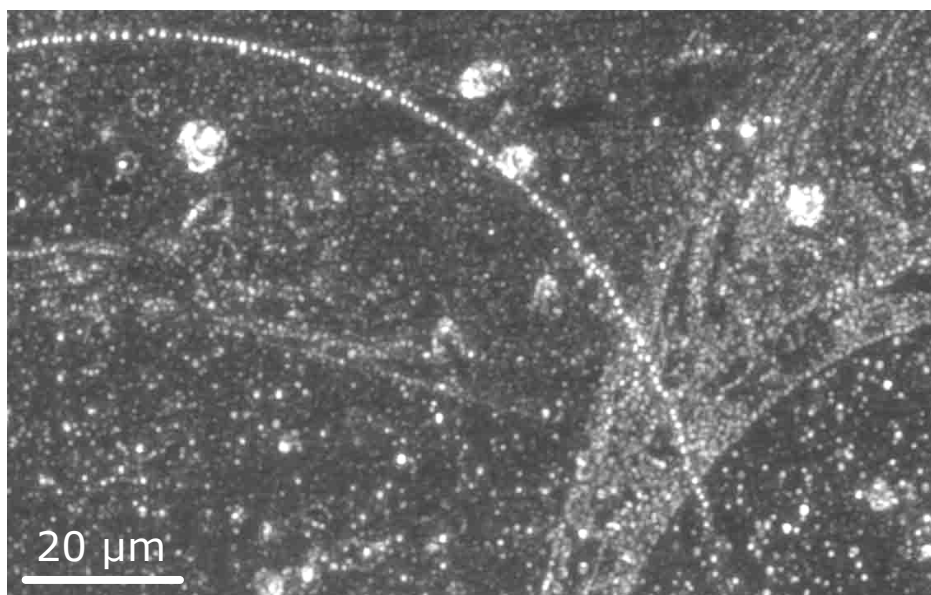


Fig. S6 Dark-field optical microscopy image of a solution between two glass plates (0.25 μM in water) of disk-shaped aggregates of 1:3 **C10/EO4-Au** Janus nanoparticles.

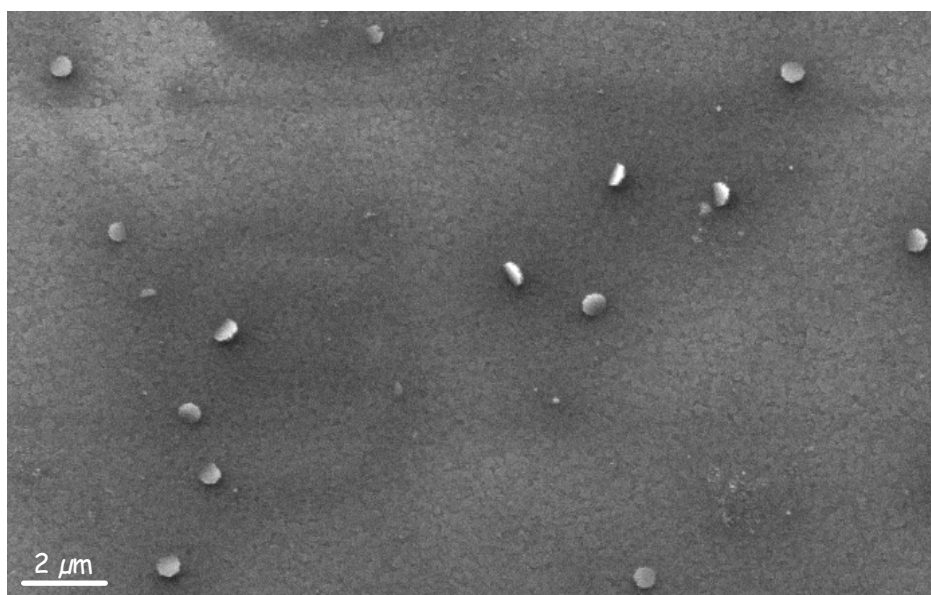


Fig. S7 SEM image of a dried film of disk-shaped aggregates of 1:3 **C10/EO4-Au** Janus nanoparticles drop-cast on indium tin oxide-coated glass from a 0.25 μM solution in water.

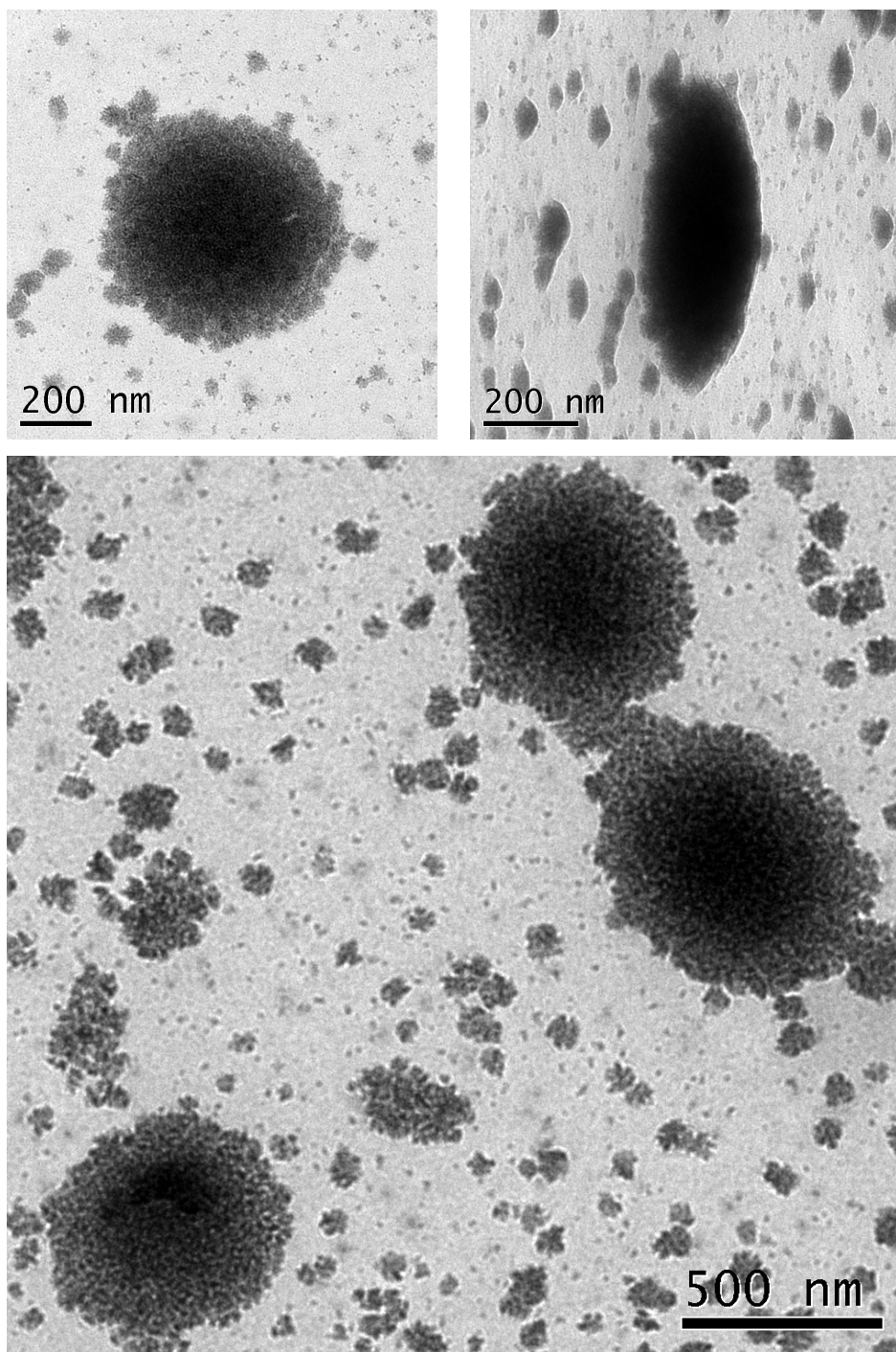


Fig. S8 TEM images of a disk-shaped aggregate of 1:3 **C10/EO4-Au** Janus nanoparticles at tilt angles of 0° and 70° , respectively (top) and an overview (bottom).

Langmuir

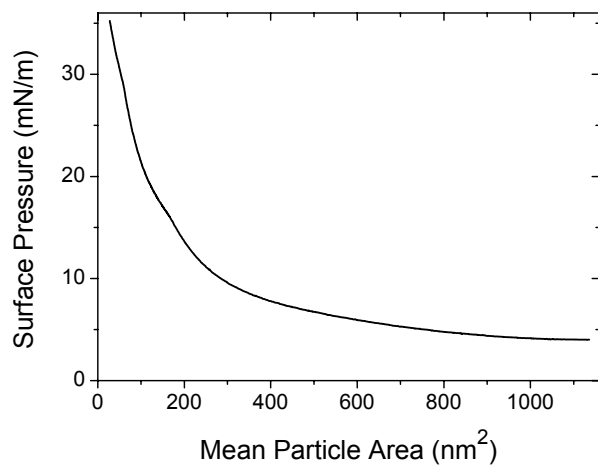


Fig. S9 Langmuir isotherm of 1:3 **C10/EO4-Au** Janus nanoparticles.

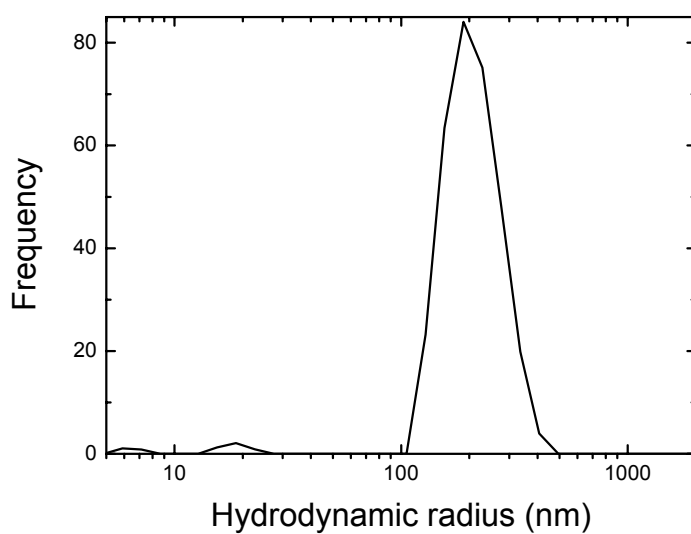


Fig. S10 CONTIN distribution function for the DLS measurements on aggregates of 1:3 **C10/EO4-Au** Janus nanoparticles (0.25 μM in water) for the smallest angle measured (22.5° scattering angle).

References

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