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Electronic Supporting Information

Self-Assembly of amphiphilic gold nanoparticles decorated with a mixed shell of oligo(*p*-phenylene vinylene)s and ethyleneoxide ligands

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Materials. All solvents were of AR quality and all chemicals were used as received.

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

Gel Permeation Chromatography (GPC). The samples were measured on a Shimadzu LC-10ADvp, using a PLgel 5 μm MIXED-C (200 – 2000000 g/mol) column in series with a PLgel 5 μm MIXED-D (200 – 400000 g/mol) column, with a Shimadzu SPD-M10Avp photo diode array detector at 420 nm and a Shimadzu RID-10Avp refractive index detector. THF was used as mobile phase (1 ml/min) and polystyrene standards were used for calibration. The samples were prepared by dissolving the nanoparticles in THF and adding a minute amount of iodine. This led to precipitation of the nanoparticles. **OPV3** and **EO4** were measured as a reference.

Langmuir-Blodgett measurements. Measurements were performed on a KSV 3000 Langmuir Blodgett trough. The size of the trough was 570 × 150 mm and the material was PTFE. Barriers were made of hydrophilic Delrin (polyacetal). The surface pressure was measured using a paper Wilhelmy plate. Langmuir isotherms were recorded by careful spreading of droplets of a 1.1 μM solution in chloroform onto the water surface (18 MΩ, pH = 7.0). Measurements were started after 15 minutes in order to evaporate the solvent. The barrier speed was 15 cm^2/min. The Langmuir-Blodgett film was made by keeping the surface pressure at 15 mN/m, while a glass plate was emerged from the water at 90 mm^2/min. The barrier compression was corrected for the barrier compression needed when no dipping experiment was performed.

UV/Vis Spectroscopy. Absorption spectra were recorded on a Perkin Elmer Lambda 40 UV/Vis Spectrometer or a Perkin Elmer Lambda 900 UV/Vis/NIR Spectrometer.

Optical Microscopy. Optical microscope images were shot on a Zeiss Axioplan 2 with a Zeiss Axiocam using dark-field set-up.

Transmission Electron Microscopy (TEM). 200 mesh carbon-coated grids were purchased from Aurion. TEM grids were prepared by applying a droplet of sample solution onto a 200 mesh carbon-coated copper grid. Excess solution was blotted away using a filter paper. The samples were analyzed at room temperature on a FEI Tecnai 20, type Sphera TEM operating with a 200 kV LaB_6 filament, equipped with a bottom mounted 1k × 1k Gatan CCD camera.

Scanning Electron Microscopy (SEM). The samples were prepared by applying a droplet of sample solution onto an amorphous silicon plate, which were extensively rinsed with isopropanol before use. After 5 minutes solution was wicked away by applying a filter paper on the corner of the sample. Measurements were carried out at room temperature with a Philips XL 20 FEG-ESEM.

Atomic Force Microscopy (AFM). Samples were analyzed at room temperature with a Digital Instruments AFM, equipped with a Nanoscope IIIa controller in tapping mode. Samples were prepared by applying a droplet of sample solution onto a highly ordered pyrolytic graphite (HOPG) substrate, which were freshly cleaved before use. After 5 minutes the solution was wicked away by applying a filter paper on the corner of the sample.

Static Light Scattering (SLS). The measurements were performed with a computerized homemade goniometer, using a step size of 2 degrees in the angular range of 30 to 106 degrees, corresponding to the scattering wavevectors of 7 to 22 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 stabilize the temperature at 294.6 ± 0.1 K during the measurements. The Rayleigh-Gans approximation was used to fit the data for different shapes:

Sphere:[1]

$$I(\Theta) = \left[\frac{3}{(qa)^3}\left(\sin(qa) - qa\sin(qa)\right)\right]^2$$

with a = radius

Ellipsoid (disk):[2]

$$I(\Theta) = \frac{9}{4\pi}\int_0^{\frac{\pi}{2}}\left[\frac{\sin(K) - K\sin(K)}{K^3}\right]^2 2\pi\sin(\phi)d\phi$$

$$K^2 = q^2\left(b^2 + \left(a^2 - b^2\right)\cos^2(\phi)\right)$$

with $a, b = c$ the radii of the ellipsoid

Cylinder:[2]

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

with $L = 2a$ and $R = b$

Dynamic light scattering (DLS). The apparatus used was similar to the one used for the SLS measurements. The detector output was sent to an ALV-5000/E Mutliple tau digital correlator, using a typical acquisition time of 90s. The obtained intensity correlation functions were fitted for all q values, using cumulant analysis:

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

By extrapolating mean decay rate $\bar{\Gamma}$ divided by q^2 to zero scattering angle, the diffusion coefficient could be obtained, and thereby the hydrodynamic radius. The relation between the diffusion constant D and the hydrodynamic radius R_h is given by:

$$D = \frac{k_b T}{6\pi\eta R_h}$$

with η the viscosity of the solvent, T the temperature and k_b Boltzmann's constant.

For a sphere, the hydrodynamic radius is simply the radius of the sphere, for a thin disc R_h can be found using[3]:

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

with R the radius and h the height of the disk. For a cylindrical object, the diffusion constant can be written as[4]:

$$D = \frac{k_b T}{3\pi\eta L}\left[\ln(\frac{L}{d})+0.312+0.565\frac{d}{L}-0.1\frac{d^2}{L^2}\right]$$

with *L* the length of the cylinder and *d* its diameter.

Contact angle measurement. The contact angles were determined by using a Data Physics OCA 20. Static contact angles were measured using an ellipsoidal fit.

General procedure for the synthesis of EO4/OPV3-Au Janus nanoparticles

300 mg of $HAuCl_4 \cdot 3H_2O$ (0.76 mmol) was dissolved in 10 mL ultrapure water (18 MΩ, pH = 7.0) and added to a solution of 1.04 g of tetra-*n*-octylammonium bromide (**TOAB**) (1.9 mmol) in 20 mL of toluene in a separatory funnel and shaken. The yellow water layer hereby became colorless and the toluene layer turned orange. The water layer was removed and the resulting solution was stirred vigorously in a round-bottom flask, while adding a freshly prepared solution of 288 mg of $NaBH_4$ (6.0 mmol) in 5 mL of ultrapure water at once. The solution immediately darkened and started to bubble. After 2 hours of stirring, the water was removed by extraction. To 10 mL (half of the total solution) of tetra-*n*-octylammonium bromide capped gold nanoparticles (**TOAB-Au**) in toluene, the desired ratio of **EO4** and **OPV3** ligands were added as a solution of a total of 0.035 mmol in 2 mL of toluene. After stirring for one hour, small amounts of precipitation were filtered off using a paper filter. The excess of ligands used were removed using preparative size-exclusion chromatography (Biobeads S-X1) with toluene as eluent.

IR (UATR): ν (cm^{-1}): 2925, 2873 (C-H stretch); 1734 (C=O stretch); 1463, 1421, 1379, 1350, 1244, 1199, 1119, 1042, 965, 856, 802.

For further characterisation of the different hybrid nanoparticles see TEM images and UV-vis spectra (*vide infra*).

Injection of EO4/OPV3-Au Janus nanoparticles into water.

The right ratio of **EO4/OPV3-Au** Janus nanoparticles were dissolved in tetrahydrofuran (THF) yielding a 37 μM solution. 20 μL of this solution was into 3 mL of ultrapure water (18 MΩ, pH = 7.0).

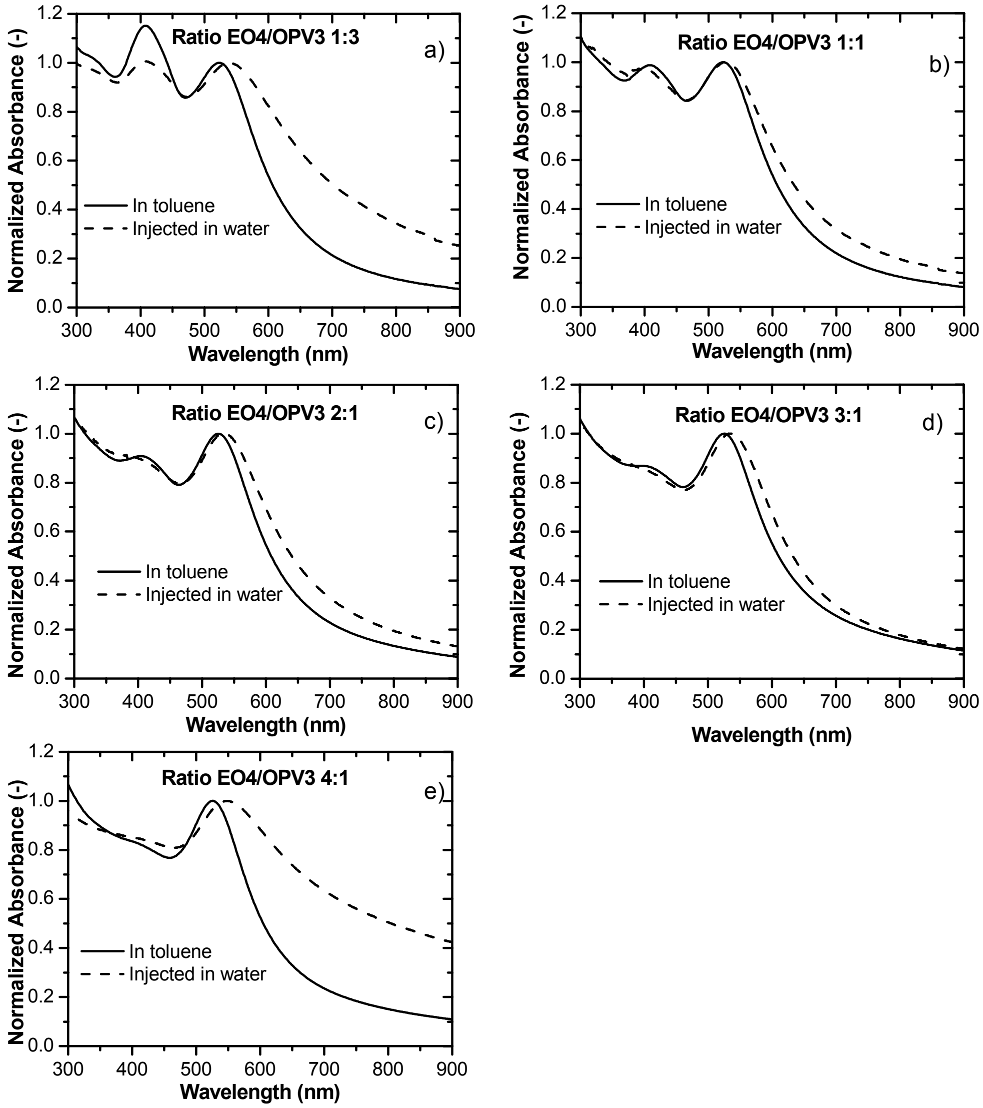

Fig. S1 (a-e) Absorption spectra of the different ratios of **EO4/OPV3-Au** Janus nanoparticles in toluene (solid lines) and after injection into water (dashed lines).

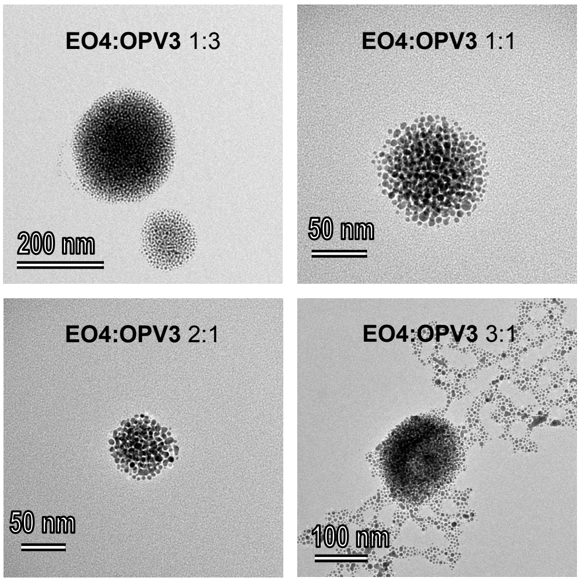

Fig. S2 TEM images of the different ratios of **EO4/OPV3-Au** Janus nanoparticles deposited from water (0.25 µM).

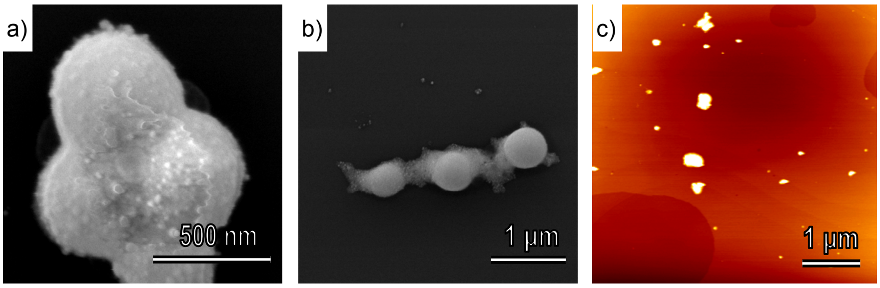

Fig. S3 (a-c) Microscopy images of aggregates of **4:1 EO4/OPV3-Au** Janus nanoparticles deposited from water (0.25 µM). a,b) SEM images on amorphous silicon. c) AFM height image on highly ordered pyrolytic graphite (HOPG).

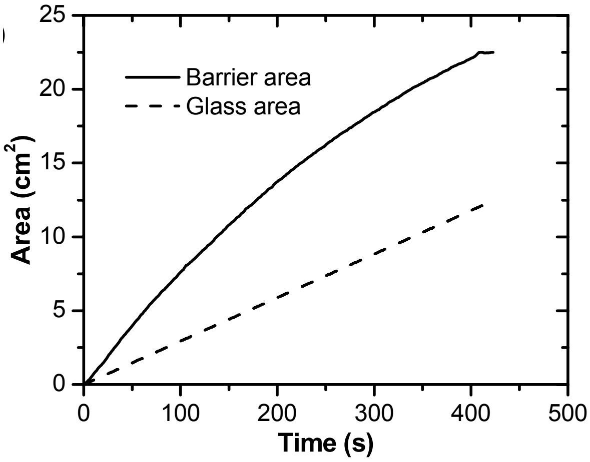

Fig. S4 Upward dip experiment; the area the barriers compressed to stabilize the pressure at 15 mN/m (solid line) and the area of the glass emerged from the water surface (dashed line).

References

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