Electronic Supplementary Material (ESI) for Nanoscale.

Enabling the Synthesis of Homogeneous or Janus Hairy Nanoparticles through Surface Photoactivation

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1. Experimental Procedures

1.1 Materials

Uranyl acetate (2 wt% in deionized water), Ammonium hydroxide (NH4OH, Acros Organics, 28–30% solution), Hydrogen peroxide solution (H_2O_2, 30%), Ethanol abs. (EtOH, VWR, 99.9%). 3-amino- propyltriethoxysilane (APTES, 99%), Tetraethylorthosilicate (TEOS, 99%), Toluene (99.8%), Acetonitrile (99.5%), Dichloromethane (CH_2Cl_2, 99.8%), Acetone (ACS reagent), Hydrochloric acid (HCl, ACS reagent 37%), Potassium hydroxide (KOH, pellets), Poly (ethylene glycol) methyl ether methacrylate (PEGMEMA, M_n 500), Lauryl methacrylate (LMA) were purchased from Sigma Aldrich. Silicon dioxide microparticles (1.0 micron, 99.9%) were purchased from Alfa Aesar. Deionized water was obtained from Milli-Q purification system (Millipore). 3-(trimethoxysilyl) propyl 3-[bis(2,4,6-trimethyl- benzoyl) phosphinyl]-2-methyl-propionate (TEMSI^2-BAPO) was synthetized via a stable bis(mesitoyl)phosphane intermediate as reported elsewhere.[1]

1.2 Synthesis of silica nanoparticle cores

Monodisperse 50nm-sized silica nanoparticles were synthetized using a one-pot hydrolysis-condensation procedure of TEOS in ethanol with ammonia hydroxide as catalyst based on a modified Stöber approach[2]. In a typical procedure 145 ml of absolute ethanol and 10 ml of ammonia solution are added in 250 ml round-bottom flask. The flask is sealed with a silicon septum and heated to 60 °C. When the temperature is stable 5 ml of TEOS are added and the solution is kept at to 60 °C under continuous stirring at 700 rpm overnight. After hydrolysis-condensation, the obtained nanoparticles are washed 5 times with absolute ethanol by centrifugation/redispersion cycles. For each step, the particles were collected after 30 minutes of centrifugation at a relative centrifugal force of 15400 g. At each vial, containing about 60 mg of nanoparticles, 30 ml of washing solvent were added to redisperse the particles. Finally, the purified particles are dried in a vacuum oven under reduced pressure at 60 °C.

1.3 Functionalization of silica nanoparticle with TMESI^2-BAPO: photoactive nanoparticles (I)

Purified and dried 50nm-sized silica nanoparticles were dispersed in 125 ml of toluene by sonication (final concentration 17.5 g/l). Then, 0.2 ml of TMESI^2-BAPO were added to the reaction mixture. The colloidal suspension was transferred in a round-bottom flask and sealed. After 48 hours of stirring at room temperature, the particles were collected by centrifugation and washed four times in toluene, two times in acetone by centrifugation/redispersion cycles. For each step, the particles were collected after 30 minutes of centrifugation at a relative centrifugal force of 15400 g. At each vial, containing about 60 mg of nanoparticles, 30 ml of washing solvent were added to redisperse the particles. After purification, the particles were dried under reduced pressure. Finally, the functionalized photoactive nanoparticles were dispersed and stored in acetonitrile with a concentration of 15 g/l. Please note that all the steps were conducted in a UV-protected environment.

1.4 Preparation of the aminated microscaffold NH_2-MSs (V)

Commercially available silica microparticles (1μm in diameter) were cleaned with wet chemical treatment (RCA-SC1) to remove contaminants and activate the silanols on the silica surface. Silica microparticles (1 g) were added to 100 ml hydrogen peroxide (30%), 100 ml ammonia hydroxide (28-30%) and 100 ml deionize water. The mixture was sonicated and stirred for 1 hour at 70 °C in an open round-bottom flask. The particles were then collected by centrifugation and washed 5 times with absolute ethanol by centrifugation/redispersion cycles. Afterwards, APTES was added to the cleaned particles (500mg) in 30 ml of absolute ethanol in a sealed flask (5 vol% of in ethanol). The mixture was stirred at room temperature for 24 hours. APTES functionalized particles (NH_2-MSs (V)) were collected by centrifugation, washed 5 times with absolute ethanol by centrifugation/redispersion cycles. For each step, the particles were collected after 10 minutes of centrifugation at a relative centrifugal force of 5000 g. At each vial, containing about 500 mg of nanoparticles, 30 ml of washing solvent were added to redisperse the particles. After purification, the particles were dried under reduced pressure.

1.5 Synthesis of hydrophilic homogeneous hairy nanoparticles (II)

In a typical procedure, 5 mL of BAPO functionalized silica nanoparticles in acetonitrile (~ 65 mg) are dispersed in water-PEGMEMA solution (5 vol %), sonicated and transferred in a lab-made UV-reactor. It consists of a round-bottom flask with three necks for argon inlet and outlet and optical fiber connection through the main neck. The optical fiber is adjusted at 3 cm from the level of the liquid and connected to a light source (LC8 Lightning cure, Hamamatsu Photonics, Hamamatsu, Japan equipped with a Mercury-Xenon lamp with a spectral range distribution from a wavelength of 250 nm to visible light). The flask was covered with aluminum foil and immersed in a bath of water at room temperature to prevent any overheating. The mixture was purged with argon for 20 min under gentle stirring prior light exposure. Then, the light source was activated with an intensity of 120 $mWcm^{-2}$ (UVA) for 1 hour to induce the photopolymerizaton. Finally, the polymer-grafted nanoparticles were collected by centrifugation, washed seven times with ethanol. For each step, the particles were collected after 30 minutes of centrifugation at a relative centrifugal force of 15400 g. At each vial, containing about 60 mg of nanoparticles, 30 ml of washing solvent were added to redisperse the particles. After purification, the particles were dried under reduced pressure.

1.6 Synthesis of amphiphilic Janus hairy nanoparticles (IV)

In a typical procedure, 5 mL of BAPO functionalized silica nanoparticles in acetonitrile (~ 65 mg) were added in 20 mL of deionized water containing 3 g of amino functionalized microscaffolds (V). The pH of the mixture was adjusted to 5 with few μl of HCl (10^{-2} M) sonicated and stirred for 1 hour to promote the nanoparticle assembly on the positively charged microscaffolds. Then, the mixture was centrifuged at low speed (5000 g for 10 minutes) to collect the nanoparticles-microscaffold assembly and remove the unattached nanoparticles (which were removed as supernatant and replaced with the same amount of water a pH of 5). The collected assemblies were transferred in 25 ml of deionized water – PEGMEMA solution and adjusting the pH to 5. The mixture was transferred in the abovementioned UV-reactor and purged with argon for 20 min.

The mixture was light irradiated to promote the *grafting-from* of PEGMEMA under the same condition of the homogeneous nanoparticles synthesis. After 1 hour, few µl of KOH (10^{-2} M) were added and the mixture was sonicated to promote disassembly of the nanoparticle-microscaffold structures. The microscaffols were removed by low speed centrifugation (5000 g for 10 minutes) and partially grafted nanoparticles (intermediate Janus hairy nanoparticles, III) were collected in the supernatant liquid. The intermediate Janus hairy nanoparticles were purified by centrifugation/redispersion cycles with water, acetonitrile.. For each step, the particles were collected after 30 minutes of centrifugation at a relative centrifugal force of 15400 g. At each vial, containing about 60 mg of nanoparticles, 30 ml of washing solvent were added to redisperse the particles. After purification, the particles were redispersed in 25 ml CH_2Cl_2. The nanoparticles in CH_2Cl_2 were transferred in the UV-reactor with 2.5 vol% of LMA monomer. The UV-reactor was immerged in a water bath with a small amount of ice to keep the mixture slightly below room temperature and avoid CH_2Cl_2 evaporation. Similarly to the first grafting, the mixture purged with argon and light-irradiated for 1 hour. The amphiphilic Janus particles (IV) were washed seven times by centrifugation/redispersion cycles with CH_2Cl_2. For each step, the particles were collected after 30 minutes of centrifugation at a relative centrifugal force of 15400 g. At each vial, containing about 60 mg of nanoparticles, 30 ml of washing solvent were added to redisperse the particles. After purification, the particles were dried under reduced pressure.

1.7 Thermogravimetric analysis (TGA)

Thermogravimetric analyses were performed to measure the amount of polymer grafted on the. All the experiments were conducted on a thermal analyzer STA 449 F1 Jupiter (NETZSCH GmbH & Co) with few mg of sample loaded in alumina crucible and heated from room temperature to 600 °C with a heating rate of 10 K min^{-1} under inert helium atmosphere. The polymer fractions were evaluated by subtracting the total mass loss of BAPO functionalized nanoparticles to the total mass loss of the grafted particles (mass losses were evaluated between 140 and 535 °C). These polymer fractions along with the remaining masses at high temperature were used to evaluate the average polymer per unit area in mg of polymer per m^2 of nanoparticles surface as described elsewhere.[3]

1.8 Electrokinetic measurements

The pH-dependent electrokinetic measurements via electrophoresis of the particles in dispersion were carried out with a Zetasizer Nano ZS from Malvern Instruments Ltd. and an MPT-2 autotitrator. For the measurements, the particles were suspended in a solution of 10^{-3} M KCl in water (0.42 mg ml^{-1}). The pH of the prepared suspensions was controlled by adding either 0.1 M KOH or HCl aqueous solutions. Three measurements were recorded for each sample at each pH value.

1.9 Scanning electron microscopy (SEM)

All scanning electron microscopy images were acquired using a field emission SUPRA 40 (Carl Zeiss) scanning electron microscope from Carl Zeiss NTS GmbH, operating at 3 keV in the secondary electron mode.

1.10 Transmission electron microscopy (TEM)

All transmission electron microscopy investigations were conducted on JEOL 2010 FEG (JEOL Ltd.) with an acceleration voltage of 200 kV. The images were generally acquired with an ORIUS SC 200 (2k x 2k) camera for conventional imaging and with Gatan UltraScan 4000 (4k x 4k) camera for low electron dose imaging (below 15 $e^-/Å^2$). Samples for negative stain CTEM were prepared by depositing a drop of colloid (3 mg ml^{-1}) on carbon coated TEM grids (glow discharged). After 1 minute, the liquid in excess was blotted with filter paper. Immediately after, the grid was washed twice with deionized water by rapidly blotting the water drop from the grid. Then the sample was stained with a drop of uranyl acetate solution (2 wt%). After 30 seconds, the liquid in excess was blotted away with filter paper and washed twice with deionized water as above. Finally, another drop of uranyl acetate solution was deposited on the grid. After 30 seconds the liquid was blotted and the grid was dried under a flux of nitrogen.

Samples for cryogenic TEM were prepared by depositing a drop of colloid (3 mg ml^{-1}) on 200 mesh holey-carbon-coated grids. The grids were blotted with filter paper and frozen by rapidly plunging into liquid ethane. By doing so, a thin film (few hundreds nm) of amorphous ice embedding the nanoparticles was generated. The grids were mounted in a nitrogen-cooled sample holder Gatan 626 and inserted in the microscope by using a dedicated cooled transfer station. All observations were carried out at a temperature of about -180 °C in low dose conditions.

Liquid-cell TEM experiments were performed in a Poseidon 210 liquid flow sample holder (Protochips Inc.) loaded with microfabricated E-chips with thin silicon nitride amorphous windows. The E-chips (EPB 55 DM – bottom chip; EPT 55 W – top chip) were rinsed in acetone first and then ethanol (2 min each) to remove the protective coating layers. After being dried with a gas duster, the E-chips were plasma cleaned for 1 minute to enhance the silicon nitride membranes hydrophilicity and to remove any organic contaminants. After having loaded the bottom E-chip inside the sample holder, a drop of the colloidal solution was deposited on it. Then, the system was sealed with the top E-Chip with the silicon nitride windows facing the colloid. After the assembly, the vacuum seal was tested with a turbo pumping station (Pfeiffer Vacuum Technology AG, Germany). During the LCTEM analysis, low electron dose conditions were used along with a flux deionized water (300 µl h^{-1}) by means of a programmable syringe pump (Harvard Apparatus, USA). The image processing was carried out using Gatan Microscopy Suite (GMS3) and ImageJ software.

1.11 Dynamic light scattering (DLS)

A Zetasizer Nano ZS (Malvern Instruments, UK) was used for the determination of the hydrodynamic diameters using plastic cells for aqueous suspensions. The device is equipped with a 633 nm laser and with non-invasive backscatter (NIBS) technology to increase the particle size sensitivity. For each sample, three experiments (100 measurements each experiment) were run. For each collection of date, the poly dispersity index (PDI) is herein defined as the square of the ratio between the standard deviation and the mean hydrodynamic diameter.

1.12 Small angle X-ray scattering (SAXS)

Experiments were performed on suspensions of hydrophilic HHPs (**II**) and amphiphilic JHPs (**IV**) in water at concentrations ranging from 0.2 to 3 mg/cm^3. The data were collected at the Laboratoire Léon Brillouin (LLB) of the CNRS-CEA in Saclay (France) from a Xeuss 2.0 laboratory beamline from Xenocs. Data reduction was achieved by subtracting from each spectrum, the one measured for pure water. Absolute calibration was achieved by taking water as reference, leading to the coherent differential scattering cross section of particles per volume unit, S, as a function of the scattering vector q. For all spectra, a non-linear minimization of the objective function $\chi^2 = \frac{1}{N}\sum_{i=1}^{N}((S_i - S_{ci})/\Delta S_i)^2$ was employed, where S_i and S_{ci} are the measured and computed values of the *i*th data point. For all the spectra, the S_{ci} values (Equation 1) are computed using the scattering function $P_1(q)$ of one particle made of a spherical core surrounded by a homogeneous spherical corona (Equation 2)

$$S_{\mathrm{ci}}(q) = S_{c\to 0} \times \frac{1}{P_1(0)} \int P_1(k)\mathcal{R}(q,k)dk \quad (1)$$

$$P_1(q) = \iint \left[\left(\tilde{b}_{H_2O} - \tilde{b}_c\right)(r+\epsilon)^3 \mathcal{A}\left(q(r+\epsilon)\right) - \left(\tilde{b}_c - \tilde{b}_{SiO_2}\right) r^3 \mathcal{A}(qr)\right]^2 p(r,\bar{r},\sigma_r)p(\epsilon,\bar{\epsilon},\sigma_\epsilon)drd\epsilon \quad (2)$$

where $\mathcal{R}(q,k)$ is the resolution function of the apparatus, $\mathcal{A}(x) = 3j_1(x)/x$ with $j_1(x)$ as the spherical Bessel function of the 1st kind of order 1, r the radius of the core, ϵ the thickness of the corona, $p(x,\bar{x},\sigma_x)$ the Gaussian distribution function centered on $\bar{x}$ with standard deviation σ_x and $\tilde{b}_{H_2O}$, $\tilde{b}_c$, $\tilde{b}_{\mathrm{SiO}_2}$ the scattering length densities of solvent, polymer corona and core, respectively. Data fitting was fulfilled by fixing values for $\tilde{b}_{H_2O}$ and for $\tilde{b}_{\mathrm{SiO}_2}$. Also, σ_r/r and σ_ϵ/ϵ were kept equal. Using this model, minimum values of χ^2 less than 1 are obtained for all spectra, although higher values are obtained for Janus than for homogeneous particles. This means that the theoretical curve passes through all data points within error bars and that, as far as the minimum of χ^2 is concerned, an alternative model could not be better.

2. Results and Discussion

2.1 Small angle X-ray scattering (SAXS)

Small angle X-ray scattering allows the characterization of nanoscale systems in terms of nanoparticle structural information and nanoparticle assemblies, making use of the electron density variations of a sample to generate contrast.[4] SAXS characterizations on polymer-grafted nanoparticles have been reported previously.[5][6] For these systems, similarly to LTEM, X-ray scattering enables to interrogate the nanoparticles in realist environments such as in water. This is possible in a nondestructive manner and at the same time providing more statistically meaningful information since scattering intensities are averaged over macroscopic sample volumes (i.e. millions of particles). Both hydrophilic HHPs (**II**) and amphiphilic JHPs (**IV**) were investigated by collecting their SAXS spectra for different concentration ranging from 0.2-3.0 mg ml^{-1}. In Figure S10, an example of results is reported in terms of coherent differential scattering section S and scattering vector *q*. Both the measured (S_i, reported in points) and computed (S_{ci}, reported in full lines) spectra are reported. The S_{ci} values are computed using the scattering function $P_1(q)$ of one particle made of a spherical core surrounded by a spherical corona. Parameters of the scattering function such as radius of the core r, thickness of the polymeric corona ϵ and the relative standard deviations

σ_ϵ and σ_r were determined by non-linear optimization using the mean weighted least square deviation as estimator χ^2. Complete SAXS data are reported in Table S1-S3. We found silica particles cores radius slightly smaller than 25 nm. Similarly, the thickness of the swollen polymeric corona was found to have a thickness of 23.6 ± 6 nm and 23.8 ± 9 nm for homogeneous and Janus nanoparticles respectively. Interestingly, these results are very close to what was obtained from cryo and liquid cell TEM.

Further analysis of SAXS data can be done using with those obtained from thermogravimetric analysis (TGA). Basically, this technique gives access to the weight fraction w_i of each chemical species *i* (e.g. PEGMEMA, PLMA and the silica core). Let us denote $x_i$and ρ_i the volume fraction and mass density, respectively. Then, the system of linear equations: $\rho = \sum_i x_i\rho_i$, $w_i\rho = x_i\rho_i, \sum x_i = 1$ provides volume fractions x_i of each chemical species, the average mass density ρ of the particles. The employed scattering function $P_1(q)$ considers that an 'average polymer' participates to the polymer corona. This polymer is PEGMEMA for homogeneous nanoparticles, but for Janus nanoparticles it is averaged between PEGMEMA and PLMA. Therefore, it is possible to write: $w_{pol} = \sum_j w_j$, $x_{pol} = \sum_j x_j$, $k_j = x_j/\sum_j x_j$, $\rho_{pol} = \sum_j k_j\rho_j$, $\tilde{b}_{pol} = \sum_j k_j\tilde{b}_j$ where the subscript "pol" is for the average polymer and "j" for the a given polymer species. Furthermore, the calculated scattering lengths of the corona $\tilde{b}_c$, account for the average polymer and the embedded solvent. That is, $\tilde{b}_c = \tilde{b}_{pol}\phi_{pol} + \tilde{b}_c(1-\phi_{pol})$, where ϕ_{pol} is the volume fraction occupied by the average polymer inside the swollen corona. Thus, from the scattering density of the corona, it is possible to calculate the ϕ_{pol} for the homogeneous ($\phi_{pol}^{HHP-\boldsymbol{II}}$ of 0.192 ± 0.001) and Janus ($\phi_{pol}^{JHP-\boldsymbol{IV}}$of 0.5 ± 0.01) hairy nanoparticles. Since Janus nanoparticles have a polymer corona partially made of swollen PEGMEMA and of collapsed PLMA, the ($\phi_{pol}^{JHP-\boldsymbol{IV}}$ for Janus should lie between 0.192 (corresponding to the swollen PEGMEMA corona of homogeneous nanoparticles) and 1 (corresponding to bulk polymer). Therefore, the value of 0.5 ± 0.01 found for Janus nanoparticles is coherent with the morphology of the system. Additionally, if our methodology is correct, we should be able to calculate the $\phi_{pol}^{JHP-\boldsymbol{IV}}$for Janus particles using only the TGA measurements and the $\phi_{pol}^{HHP-\boldsymbol{II}}$ for homogeneous particles. Indeed, accordingly to our assumptions, $\phi_{pol}^{JHP-\boldsymbol{IV}} = \phi_{pol}^{HHP-\boldsymbol{II}} \times k_{PEGMEMA} + 1 \times k_{PLMA}$ is equal to 0.508 and therefore it is in good agreement with the value determined from the SAXS contrast of the corona for Janus nanoparticles (i.e. 0.5 ± 0.01).

3. Supplementary images and tables

Table S1. Resulting from data-fitting using scattering function $P_1(q)$ for homogeneous hairy nanoparticles at different concentrations. Confidence intervals on parameters are smaller than 1%))

C (mg cm^{-3})	$S_{q\to 0}$ (cm^{-1})	r (nm)	ϵ (nm)	$\sigma_r/r = \sigma_\epsilon/\epsilon$ (-)	$\tilde{b}_c$ (cm^{-2})	χ^2 (-)
0.2	28.4	24.5	24.3	0.116	9.71	0.29
0.9	109	24.7	24.3	0.113	9.70	0.40
1.6	191	24.6	23.6	0.116	9.71	0.48
2.3	280	23.2	23.2	0.117	9.71	0.50
3.0	352	23.0	23.0	0.116	0.69	0.49

Table S2. Resulting from data-fitting using scattering function $P_1(q)$ for Janus hairy nanoparticles at different concentrations. Confidence intervals on parameters are smaller than 1%))

C (mg cm^{-3})	$S_{q\to 0}$ (cm^{-1})	r (nm)	ϵ (nm)	$\sigma_r/r = \sigma_\epsilon/\epsilon$ (-)	$\tilde{b}_c$ (cm^{-2})	χ^2 (-)
0.2	53.5	24.5	24.3	0.124	9.68	0.32
0.9	198	24.8	22.7	0.116	9.64	0.39
1.6	355	24.8	23.0	0.117	9.64	0.57
2.3	528	24.7	24.6	0.118	9.67	0.80
3.0	700	24.7	24.5	0.117	9.67	1.03

Table S3. Physical constants for the different chemical species, $\tilde{b}_X$ is the scattering length density for X-ray (http://sld-calculator.appspot.com); ρ is the mass density.

Chemical species	$\tilde{b}_X$ (10^{10}cm^{-2})	ρ (g cm^{-3})
H_2O	9.47	1.0
SiO_2	16.30	1.90
PEGMEMA	10.67	1.15
PLMA	8.55	0.9

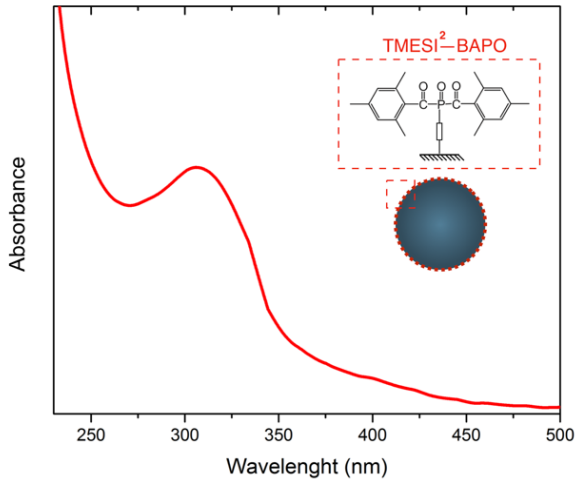

Figure S1. UV-Vis spectrum of photoactive silica nanoparticles functionalized with BAPO photoinitiator. The spectrum was collected in acetonitrile with a particle concentration of 0.15 mg ml^{-1}

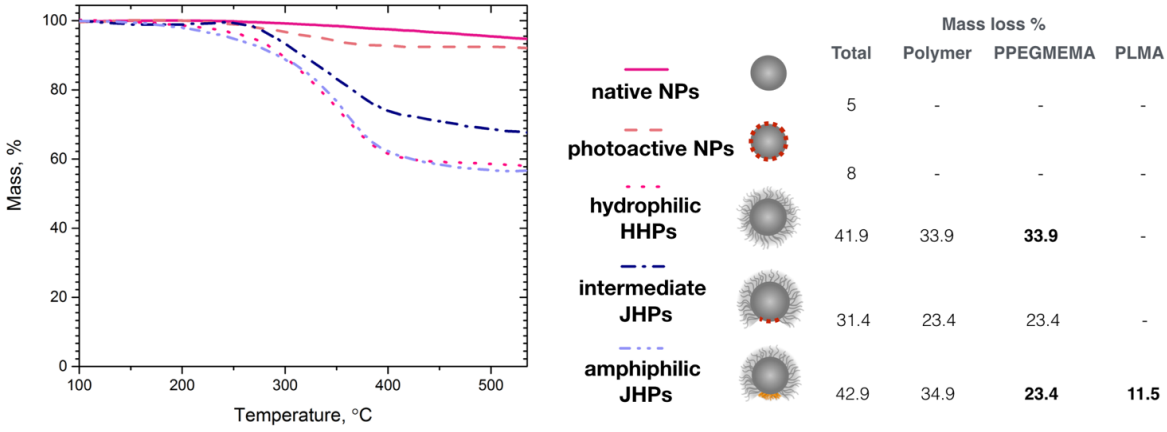

Figure S2. Thermogravimetric analysis curves for (——) native silica nanoparticles; (– –) BAPO functionalized photoactive NPs; (- - -) hydrophilic HHPs; (– - –) intermediate JHPs ; (– - - –) Amphiphilic JHPs. The polymer mass losses were calculated by considering the total weight loss for each step of the synthesis.

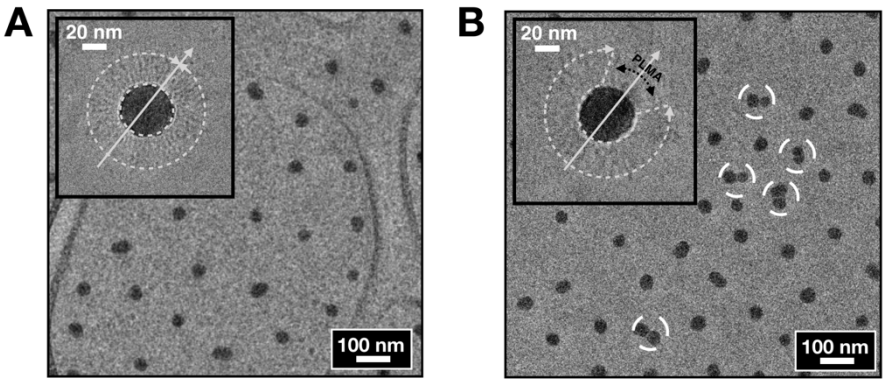

Figure S3. Cryo-TEM micrographs showing the spatial distribution of hydrophilic HHPs **II** (A) and amphiphilic JHPs **IV** (B). Magnification of the swollen polymer coronas are shown in the insets. In (B) interacting nanoparticles are indicated by white circles.

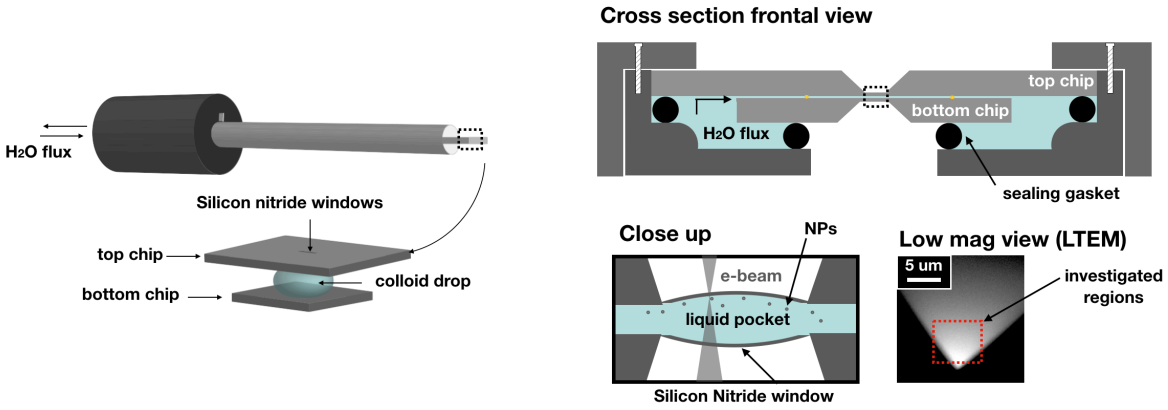

Figure S4. Liquid phase transmission electron microscopy analysis: Sample holder for liquid-phase TEM and illustration of the microfabricated liquid-cell used in the experiments.

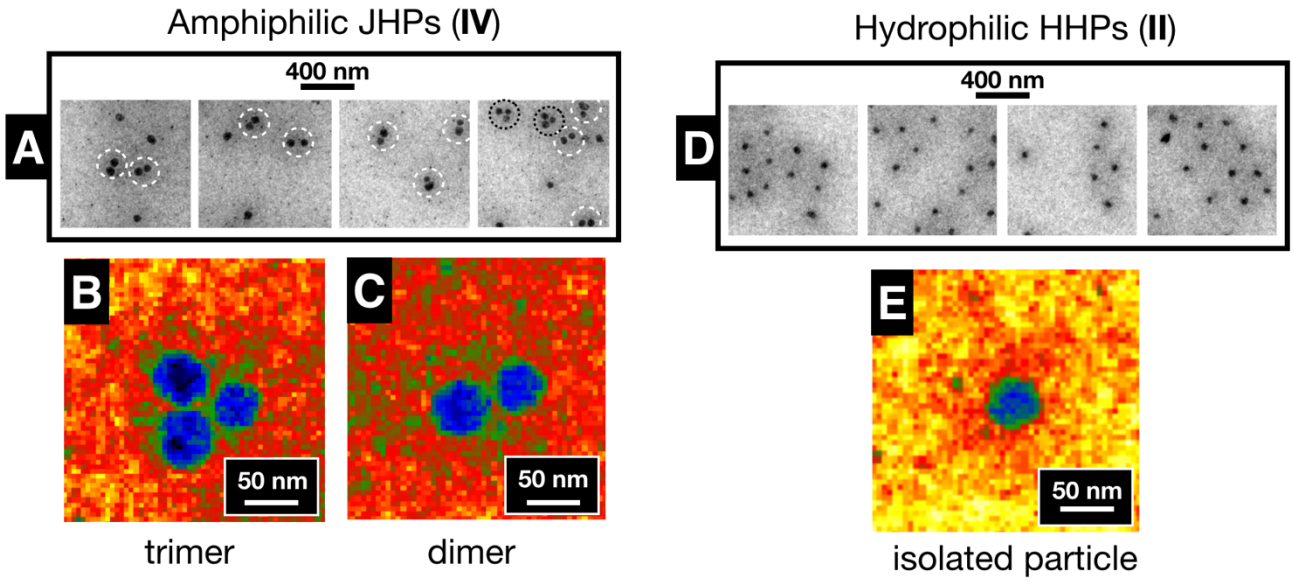

Figure S5. Liquid phase transmission electron microscopy analysis showing the spatial distribution of the amphiphilic JHPs (A) with assemblies in dimers (white circles) and trimers (black circles). Magnifications in false colours of nanoparticle assemblies in trimers and dimers are reported in (B) and (C) respectively. Spatial distribution of the hydrophilic HHPs (D) with magnification in false colours of a non-interacting particle.

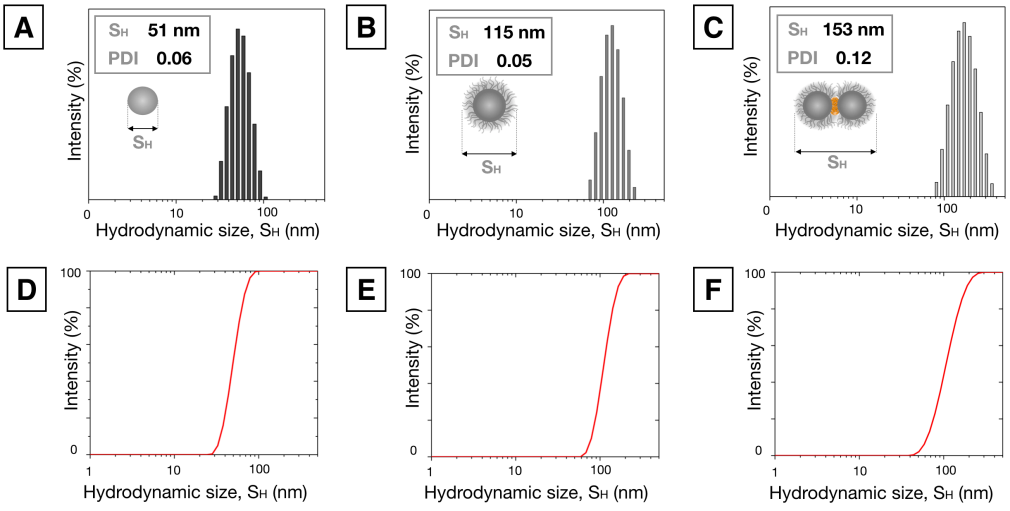

Figure S6. Hydrodynamic size distributions determined by dynamic light scattering for native silica nanoparticles (A), hydrophilic HHPs (B) and amphiphilic JHPs (C) nanoparticle suspensions in water, and their respective cumulative distributions (D), (E), (F).

4. Acknowledgements

This research was supported in part by a Marie Skłodowska-Curie Research and Innovation Staff Exchange (RISE) Fellowship (Mat4Treat, proposal no. 645551) within the H2020-MSCARISE-2014 European Community Call. The "*Laboratoire des Solides Irradiés*" (UMR 7642) gratefully acknowledge the support of the French Research Agency (ANR) for the "*Programme d'investissement d'avenir*" Equipex TEMPOS (ANR-10-EQPX-50) for the liquid cell sample holder. The authors acknowledge Marie-Claude Clochard for her guidance in the chemical synthesis and the fruitful discussions, Eric Larquet and Pierre-Damien Coureux for help in cryogenic TEM measurements.

5. References

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