

Video Article

Synthesis and Characterization of Supramolecular Colloids

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Abstract

Control over colloidal assembly is of utmost importance for the development of functional colloidal materials with tailored structural and mechanical properties for applications in photonics, drug delivery and coating technology. Here we present a new family of colloidal building blocks, coined supramolecular colloids, whose self-assembly is controlled through surface-functionalization with a benzene-1,3,5-tricarboxamide (BTA) derived supramolecular moiety. Such BTAs interact via directional, strong, yet reversible hydrogen-bonds with other identical BTAs. Herein, a protocol is presented that describes how to couple these BTAs to colloids and how to quantify the number of coupling sites, which determines the multivalency of the supramolecular colloids. Light scattering measurements show that the refractive index of the colloids is almost matched with that of the solvent, which strongly reduces the van der Waals forces between the colloids. Before photo-activation, the colloids remain well dispersed, as the BTAs are equipped with a photo-labile group that blocks the formation of hydrogen-bonds. Controlled deprotection with UV-light activates the short-range hydrogen-bonds between the BTAs, which triggers the colloidal self-assembly. The evolution from the dispersed state to the clustered state is monitored by confocal microscopy. These results are further quantified by image analysis with simple routines using ImageJ and Matlab. This merger of supramolecular chemistry and colloidal science offers a direct route towards light- and thermo-responsive colloidal assembly encoded in the surface-grafted monolayer.

Video Link

The video component of this article can be found at <http://www.jove.com/video/53934/>

Introduction

Mesostructured colloidal materials find widespread application in science and technology, as model systems for fundamental studies on atomic and molecular materials^{1,2}, as photonic materials^{3,4}, as drug delivery systems^{5,6}, as coatings⁷ and in lithography for surface patterning^{8,9}. Since lyophobic colloids are metastable materials that eventually aggregate irreversibly due to the omnipresent van der Waals interactions, their manipulation into specific target structures is notoriously difficult. Numerous strategies have been developed to control colloidal self-assembly including the use of additives to tune the electrostatic^{10,11} or depletion interactions^{12,13}, or external triggers such as magnetic¹⁴ or electric¹⁵ fields. A sophisticated alternative strategy to achieve control over the structure, dynamics and mechanics of these systems is their functionalization with molecules interacting through specific and directional forces. Supramolecular chemistry offers a comprehensive toolbox of small molecules exhibiting site-specific, directional and strong yet reversible interactions, which can be modulated in strength by solvent polarity, temperature and light¹⁶. Since their properties have been studied extensively in bulk and in solution, these molecules are attractive candidates to structure soft materials into exotic phases in a predictable manner. Despite the clear potential of such an integrated approach to orchestrate colloidal assembly via supramolecular chemistry, these disciplines have rarely interfaced to tailor the properties of mesostructured colloidal materials^{17,18}.

A solid platform of supramolecular colloids must fulfill three main requirements. Firstly, coupling of the supramolecular moiety should be done under mild-conditions to prevent degradation. Secondly, surface forces at separations larger than direct contact should be dominated by the tethered motifs, which means that uncoated colloids should nearly exclusively interact via excluded-volume interactions. Therefore, the physico-chemical properties of the colloids should be tailored to suppress other interactions inherent in colloidal systems, such as van der Waals or electrostatic forces. Thirdly, characterization should allow for an unequivocal attribution of the assembly to the presence of the supramolecular moieties. To meet these three prerequisites, a robust two-step synthesis of supramolecular colloids was developed (**Figure 1a**). In a first step, hydrophobic NVOC-functionalized silica particles are prepared for dispersion in cyclohexane. The NVOC group can be easily cleaved, yielding amine-functionalized particles. The high reactivity of amines enables straightforward post-functionalization with the desired supramolecular moiety using a wide range of mild reaction conditions. Herein, we prepare supramolecular colloids by functionalization of silica beads with stearyl alcohol and a benzene-1,3,5-tricarboxamide (BTA) derivative²⁰. The stearyl alcohol plays several important roles: it makes the colloids organophilic and it introduces short-range steric repulsions which aids to reduce the nonspecific interaction between colloids^{21,22}. van der Waals forces are further reduced because of the close match between the refractive index of the colloids and the solvent²³. Light- and thermoresponsive short-range attractive surface forces are generated by incorporation of *o*-nitrobenzyl protected BTAs²⁰. *O*-nitrobenzyl moiety is a photo-cleavable

group that blocks the formation of hydrogen bonds between adjacent BTAs when incorporated on the amides in the discotics (**Figure 1b**). Upon photocleavage by UV-light, the BTA in solution is able to recognize and interact with identical BTA molecules through a 3-fold hydrogen bond array, with a binding strength that is strongly temperature dependent¹⁷. Since the van der Waals attractions are minimal for stearyl coated silica particles in cyclohexane as well as light- and temperature-independent, the observed stimuli-responsive colloidal assembly must be BTA-mediated.

This detailed video demonstrates how to synthesize and characterize supramolecular colloids and how to study their self-assembly upon UV-irradiation by confocal microscopy. In addition, a simple image analysis protocol to distinguish colloidal singlets from clustered colloids and to determine the amount of colloids per clusters is reported. The versatility of the synthetic strategy allows to readily vary particle size, surface coverage as well as the introduced binding moiety, which opens up new avenues for the development of a large family of colloidal building blocks for mesostructured advanced materials.

Protocol

1. Synthesis of Core-shell Silica Particles

Note: Silica particles are synthesized according to the following procedure, which is based on the Stöber method^{24,25}.

1. Synthesis of fluorescent silica seeds

1. Dissolve 105 mg (0.27 mmol) of fluorescein-isothiocyanate in 5 ml of ethanol.
2. Add 100 μ l of (3-aminopropyl) triethoxysilane (APTES, 0.43 mmol) to the previous solution.
3. Sonicate the solution during 5 min and let it react overnight under an argon atmosphere at room temperature while stirring. The dye-functionalized APTES complex is used without purification.
4. In a 1 L round-bottom flask mix 2.5 ml of the dye-functionalized APTES with 25 ml of ammonia (25% in water) and 250 ml of ethanol.
5. Add 10 ml of tetraethylorthosilicate (TEOS) under the meniscus of the previous reaction mixture with the help of a glass pipette while stirring with a magnetic stirrer.
6. Similarly, after 5 hr, add another 1.75 ml of TEOS and stir the mixture overnight under an argon atmosphere.
7. Pour the dispersion into several 45 ml tubes.
8. Centrifuge the tubes (350 x g, 30 min), remove the supernatant and add 30 ml of fresh ethanol in each tube. Sonicate the new dispersions for 3 min, and centrifuge again to remove the supernatant. Repeat these washing steps 3 times.
9. Keep the fluorescent seeds in ethanol in a concentration of about 13.6 mg/ml and in the dark (avoid exposure to light).
10. Prepare non-fluorescent seeds following the same procedure omitting the addition of the fluorescent dye.

Note: Following this procedure, seeds of about 100 nm in radius are obtained.

2. Synthesis of core-shell silica particles

1. Fill a 1 L round-bottom flask with 51 ml of ethanol, 17 ml of deionized water, 3.4 ml of ammonia (25% in water) and 4 ml of the seed dispersion (54.4 mg of fluorescent seeds approximately).
2. Fill a plastic syringe with 5 ml of TEOS and 10 ml of ethanol.
3. Fill a second plastic syringe with 1.34 ml of ammonia (25% in water), 3.4 ml of deionized water and 10.25 ml of ethanol.
4. Connect both syringes to the round-bottom flask with plastic tubing.
5. Equip the flask with an argon flow and a magnetic stirrer. The argon inlet has to be next to the outlet of the second syringe to avoid contact between ammonia gases from the TEOS droplets to prevent secondary nucleation.
6. Add the content of both syringes at the same time at 1.7 ml/hr using peristaltic pumps while stirring the mixture. Ensure to obtain free falling droplets to avoid gliding on the walls and therefore secondary nucleation.
7. Stop the addition after 7 hr to obtain core-shell particles of approximately 300 nm in radius.
8. Pour the content of the flask into several 45 ml tubes.
9. Centrifuge the tubes (350 x g, 30 min), remove the supernatant and add 30 ml of fresh ethanol in each tube. Sonicate the new dispersion for 3 min, and centrifuge again to remove the supernatant. Repeat these washing steps 3 times.
10. Keep the core-shell particles in ethanol and in the dark (avoid exposure to light).
11. Prepare non-fluorescent silica particles following the same procedure but using the non-fluorescent seeds.

2. Functionalization of Silica Colloids

1. Synthesis of NVOC-functionalized colloids

1. Disperse 10 mg of core-shell silica particles in 1 ml of ethanol together with 12 mg (0.03 mmol) of the NVOC-C11-OH molecule and 31 mg (0.11 mmol) of stearyl alcohol in a 50 ml round-bottom flask (resulting in a 20/80 NVOC-C11-OH/stearyl alcohol molar ratio).
2. Sonicate the mixture for 10 min to ensure that all molecules are dissolved and the particles are well dispersed.
3. Add to the mixture a magnetic stirrer bar and evaporate the ethanol with a steady stream of argon at room temperature. Before proceeding, ensure that there is no ethanol left, otherwise it could react with the silanol groups of the particles. To check whether the ethanol is completely evaporated pay attention to the temperature of the bottom of the flask. If it feels cold, ethanol is not yet completely evaporated.
4. Heat the flask up to 180 °C for 6 hr under continuous stirring and under a steady stream of argon²².
5. Let the flask cool down to room temperature.
6. Add 3 ml of CHCl_3 into the flask and sonicate for 5 min (or until all the solid content has been dissolved or dispersed).
7. Centrifuge the dispersion (2,600 x g, 4 min), remove the supernatant and add fresh CHCl_3 . Sonicate the new dispersion for 3 min, and centrifuge again to remove the supernatant. Repeat these washing steps 6 times.

8. Dry the particles at 70 °C *in vacuo* overnight and store them in a desiccator.

2. Synthesis of BTA-colloids

1. Disperse 10 mg of particles functionalized with a 20/80 molar ratio of NVOC-C11-OH/stearyl alcohol in 3 ml of CHCl₃.
2. Irradiate the dispersion in a UV-oven ($\lambda_{\text{max}}=354$ nm) for 1 hr to cleave the NVOC group. Ensure that the deprotection is homogeneous on the surface of the particles by stirring the dispersion gently with a magnetic stirrer while deprotecting. This yields the amine-functionalized particles (**Figure 1a**).
3. Dissolve 9 mg of the benzene-1,3,5-tricarboxamide derivative (BTA, 0.01 mmol), 8.7 μ l of *N,N*-diisopropylethylamine (DIPEA, 0.05 mmol) and 5.2 mg of (benzotriazol-1-yloxy)tripyrrolidinophosphonium hexafluorophosphate (PyBOP, 0.01 mmol) in 1 ml of CHCl₃.
4. Add the solution to the amine-functionalized particle dispersion and stir overnight at room temperature and under an argon atmosphere.
5. Centrifuge the dispersion (2,600 x g, 4 min), remove the supernatant and add 3 ml of fresh CHCl₃. Sonicate the new dispersion for 3 min, and centrifuge again to remove the supernatant. Repeat these washing steps 6 times.
6. Dry the particles at 70 °C *in vacuo* for 48 hr and store them in a desiccator.

3. Static Light Scattering Measurements (SLS)

Note: Use non-fluorescent particles, since the fluorescent core absorbs light of the same wavelength as the incident laser light of conventional light scattering equipment.

1. Functionalize 10 mg of non-fluorescent silica particles with stearyl alcohol only (no NVOC-C11-OH) following the procedure described in section 2.1.
2. Prepare 500 μ l of a dispersion of 0.033 mg/ml of non-functionalized particles in water and another one of 2 mg/ml of the stearyl alcohol-coated particles in cyclohexane.
3. Sonicate both dispersions for at least 20 min to ensure that the particles are well dispersed.
4. Measure the scattered intensity of both dispersions, the solvents and the reference solvent from 30° to 120° in steps of 5°.
5. Plot the intensity of the sample (I_{sample}) as a function of q
(Equation 1) $q = 4\pi n_{\text{solvent}} \sin(\theta/2)/\lambda_0$
with the scattering angle θ , the refractive index of the solvent n_{solvent} and the wavelength of the laser λ_0 .
6. Fit the data to the following equation using software (e.g., Origin)
(Equation 2) $I_{\text{sample}} = CP(qR)$
where C is a constant and the form factor $P(qR)$ is given by
(Equation 3) $P(qR) = 9 \left(\frac{\sin(qR) - qR \cos(qR)}{(qR)^3} \right)^2$
wherein the average radius of the spherical colloids is R .
7. Extract R from the fits for each dispersion.
8. Calculate the Rayleigh Ratio (R_θ), which is an absolute measure for the intensity of the scattered light, according to the following equation, for each θ .
(Equation 4) $R_\theta = \frac{I_{\text{sample}} - I_{\text{solvent}}}{I_{\text{reference}}} R_{\text{reference}} \frac{n_{\text{solvent}}^2}{n_{\text{reference}}^2}$
with the intensity of the sample, the solvent and the reference, I_{sample} , I_{solvent} and $I_{\text{reference}}$ respectively, the refractive index of the solvent and the reference n_{solvent} and $n_{\text{reference}}$, correspondingly, and the Rayleigh Ratio of the reference $R_{\text{reference}}$. Here use toluene as a reference, such that $n_{\text{water}} = 1.332$, $n_{\text{toluene}} = 1.497$, $n_{\text{cyclohexane}} = 1.426$; $R_{\text{toluene}} = 2.74 \times 10^{-3} \text{ m}^{-1.26}$.
9. Compute the average refractive index of the colloids (n_{colloids}) from R_θ and Equation 5.
(Equation 5) $R_\theta = (n_{\text{colloids}}^2 - n_{\text{solvent}}^2)^2 \frac{\pi^2 N v_{\text{particle}}^2}{\lambda_0^4} P(qR) S(q)$
with the number of particles per volume N , the volume of a particle v_{particle} given by $v_{\text{particle}} = 4/3\pi R^3$, and assuming that the structure factor $S(q) \sim 1$, which is the limit of non-interacting particles.

4. Quantification of the Number of Active Sites Per Particle

Note: Use small particles of 13 nm in radius (with a larger surface-to-volume ratio).

1. Functionalize small commercially available particles with a 20/80 molar ratio of NVOC-C11-OH/stearyl alcohol following the procedure described in Section 2.1.
2. Disperse 20 mg of the small, functionalized particles in 1 ml CHCl₃ and irradiate the dispersion in a UV-oven ($\lambda_{\text{max}}=354$ nm) for 1 hr to cleave the NVOC group. Stir the dispersion gently with a magnetic stirrer bar while deprotecting. In this manner the colloids do not sediment and their surface remains exposed to the UV light, hence ensuring homogeneous deprotection.
3. Spin down the resulting amine-functionalized particles (3,400 x g, 10 min) and remove the supernatant.
4. Dry the particles at 70 °C for 2 hr.
5. Dissolve 0.50 mg of succinimidyl 3-(2-pyridyldithio)propionate (SPDP, 0.0016 mmol) in 200 μ l of dimethylformamide (DMF).
6. Add the SPDP solution to the 20 mg of the dried amine-functionalized particles and vortex the system for 30 min. Within this time, all available primary amines on the colloids have reacted with the SPDP.
7. Wash the particles with 1 ml of DMF for 6 times (or until no free SPDP is detected in the supernatant by UV-Vis spectroscopy at $\lambda=375$ nm). In the last washing step try to remove as much supernatant as possible.
8. Dissolve 0.53 mg of dithiothreitol (DTT, 0.0034 mmol) in 50 μ l of DMF. Add the DTT solution to the particles and vortex the dispersion for 30 min. Within this time the pyridine-2-thione group is cleaved.

9. Determine the absorbance of the free pyridine-2-thione liberated in the supernatant at $\lambda=293$ nm with a microvolume UV-Vis spectrophotometer.
10. Construct a calibration curve to determine the extinction coefficient ϵ ($\sim 12.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) of the pyridine-2-thione in DMF by measuring the absorbance of a dilution series of different known amounts of SPDP with an excess of DTT.
11. Calculate the concentration of pyridine-2-thione, C_{p2t} , which is cleaved from the particles using the Lambert-Beer law:
(Equation 6) $Abs = C_{p2t} \epsilon l$
with the molar concentration of pyridine-2-thione C_{p2t} , the extinction coefficient ϵ and the path length l .
12. Calculate the number of active sites (amines) per particle with the following equation
(Equation 7) $amine\ groups/particle = \frac{[pyridine-2-thione] M_{particle}}{V_{total} M_{total}}$
with the mass of one particle $M_{particle}$ that is $M_{particle} = 4/3 \pi R^3 \rho$, with $\rho = 1.295 \text{ g/cm}^3$, the total weighted mass of particles M_{total} (20 mg) and the total volume V_{total} (50 μl). This equation assumes that all available amines react with the SPDP and the DTT reduces all SPDP molecules attached to the particles.

5. Monitor Colloidal Assembly by Confocal Microscopy

Note: Use core-shell silica particles (with a fluorescent core and a non-fluorescent shell).

1. Prepare 400 μl of a dispersion of 0.1 wt% of BTA-functionalized particles in cyclohexane and sonicate the sample for 20 min.
2. Irradiate the sample vial in the UV oven ($\lambda_{max} = 354$ nm) to cleave off the *o*-nitrobenzyl group of the BTA. Take 25 μl aliquots at different times of irradiation, for example from 0 up to 30 min, to monitor the clustering process.
3. Place the different aliquots on different glass slides with the help of a spacer and close the chambers with a cover slip (chamber size is 13 mm diameter \times 0.12 mm height). After closing the chamber, turn the cover slip upside down to let the particles sediment and adsorb onto the glass, which facilitates the imaging.
4. Take several images of each sample with the confocal microscope as soon as possible after sample preparation for each irradiation time.

6. Image Analysis

1. Quantification of the number of singlets with ImageJ

Note: All commands used to write the script are described in the ImageJ manual:

<http://imagej.nih.gov/ij/docs/guide/user-guide.pdf>

1. Smooth the confocal images to remove isolated pixels from the edges and fill small holes running the "Smooth" function.
2. Given that only the cores are fluorescent, dilate the bright areas until the edge of the particles that belong to the same cluster touch and particles merge. Do this using the "Dilate" filter. With particles with approximately 180 nm shell thickness, and pictures with a resolution of 0.02 $\mu\text{m}/\text{pixel}$, two dilation steps are enough.
3. Convert the images into a binary picture running the "Make binary" function.
4. Set the scale by running the tool "Set Scale...", distance=1 known=0.02 pixel=1 unit= μm for pictures taken with a resolution of 0.02 $\mu\text{m}/\text{pixel}$ for instance.
5. Apply a threshold size to discriminate noise and out-of-focus particles from in-of-focus particles. For instance, with pictures taken with a resolution of 0.02 $\mu\text{m}/\text{pixel}$, all areas smaller than 0.2 pixels are ruled out. Do this using the "Analyze particles...", "size=0.2-Infinity" command.
6. Create an all.jpg image and an all.txt file with the size of all bright areas in the image (clusters and singlets) by using the commands "results", "_all.txt" and "JPEG", "all".
7. Assume that all bright areas between 0.2 and 0.7 pixels in size and with a circularity ($\text{circularity} = 4 \pi \text{Area}/\text{Perimeter}^2$) between 0.7 and 1.0 are singlets running the command "Analyze particles...", "circularity=0.7-1.0".
8. Create a singlets.jpg image and a singlets.txt file with the information of all bright areas that are singlets by using the commands "results", "_singlets.txt" and "JPEG", "singlets".

2. Process the information with Matlab

1. Read the singlet .txt file and calculate the average size of a singlet per picture (A_{singlet}).
2. Use the average size of a singlet to compute the number of particles per cluster ($A_{\text{doublet}}=2A_{\text{singlet}}$, $A_{\text{triplet}}=3A_{\text{singlet}}$...) and the total number of particles in the picture from the other all.txt file.
3. Calculate the fraction of particles in singlets for each exposure time: $f_{\text{singlets}} = \text{number singlets}/\text{total particles}$
4. Calculate the fraction of doublets, triplets, etc.: $f_{\text{doublets}} = 2 \times \text{number of doublets}/\text{total particles}$, etc.

Representative Results

Given that the two-step procedure used to synthesize the supramolecular colloids (**Figure 1a**), couples the BTA- derivatives (**Figure 1b**) in a second step at room temperature and in mild-reaction conditions, its stability is ensured.

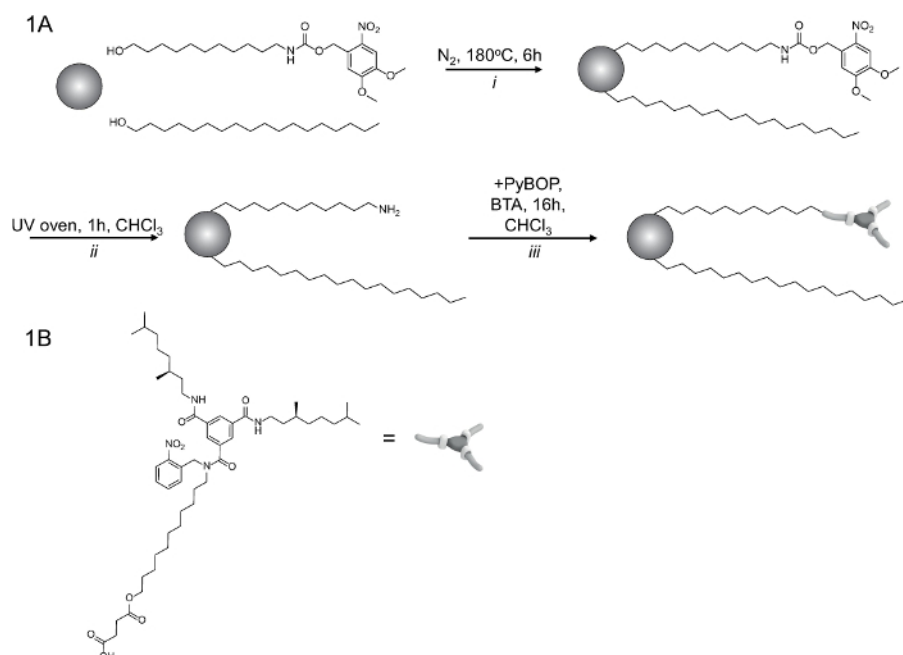


Figure 1. Scheme of the synthesis of supramolecular colloids. **A)** Coupling of the stearyl alcohol and the NVOC-protected alkyl chain to the silica colloids, followed by amine deprotection upon irradiation by UV-light in a UV-oven and subsequent coupling of the BTA molecule. **B)** Structure of the benzene-1,3,5-tricarboxamide (BTA) derivative used. [Please click here to view a larger version of this figure.](#)

By fitting the static light scattering (SLS) data, the refractive index of bare and stearyl alcohol-coated colloids are obtained. We find $n_{\text{silica}} = 1.391$ and $n_{\text{silica@stearyl alcohol}} = 1.436$ (**Figure 2**). This clearly shows that surface functionalization has an impact on the refractive index of the colloids. The chemical composition of the monolayer of stearyl alcohol coated colloids and the BTA-colloids is highly similar since the molar fraction of BTA is at most 0.2. Therefore, we assume that the refractive index of the BTA-colloids is close to $n_{\text{silica@stearyl alcohol}} = 1.436$.

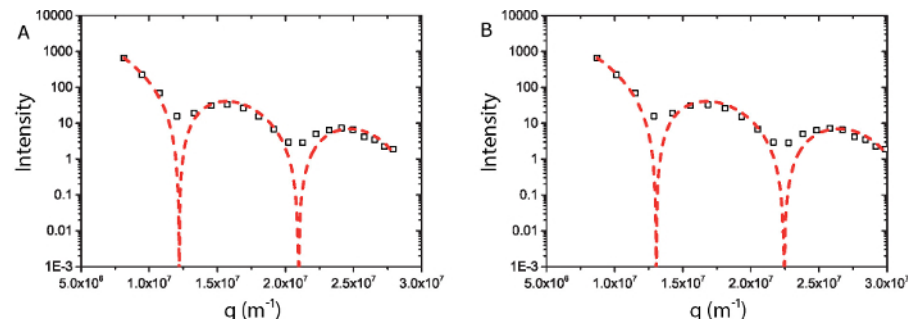


Figure 2. Static light scattering measurements of silica colloids. Intensity of scattered light as a function of the detection angle θ for **A)** bare silica particles in water and **B)** stearyl alcohol-coated particles in cyclohexane. Dashed lines are the fits to the experimental data points. [Please click here to view a larger version of this figure.](#)

Using the reaction scheme shown in **Figure 3**, small particles functionalized with a 20/80 NVOC-C11-OH/stearyl alcohol molar ratio result in 1 amine per 46.4 nm² on their surface. This number can in turn be correlated to the number of supramolecular moieties that can be coupled, which we refer to as the multivalency of the particles.

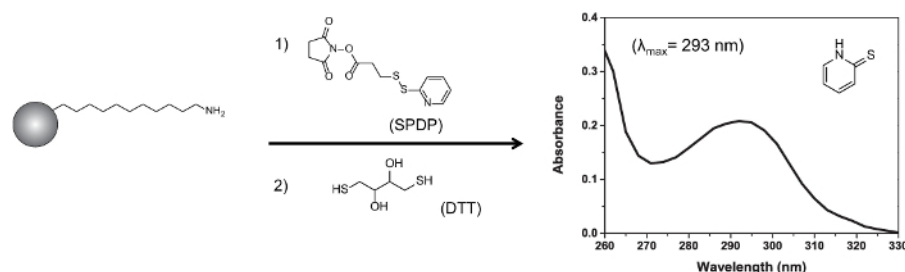


Figure 3. Assessment of the amount of active sites per particle. Procedure followed to determine the amount of amines per particle: amine-functionalized colloids are reacted with SPDP. Hereafter, DTT is added to the system to cleave off the pyridine-2-thione group, which can be detected by photospectrometry at its absorption maximum $\lambda_{\text{max}} = 293$ nm in DMF. [Please click here to view a larger version of this figure.](#)

In the confocal images, most of the supramolecular colloids of the dispersion before irradiation with UV light are singlets (**Figure 4**, top). Interestingly, upon irradiation, an evolution from the singlet state to the clustered state is observed (**Figure 4** middle and bottom). Image analysis is used to monitor the aggregation in a more quantitative manner. A sharp decrease in the number of singlets from 80% down to 9% is observed upon UV-irradiation within the first 5 minutes.

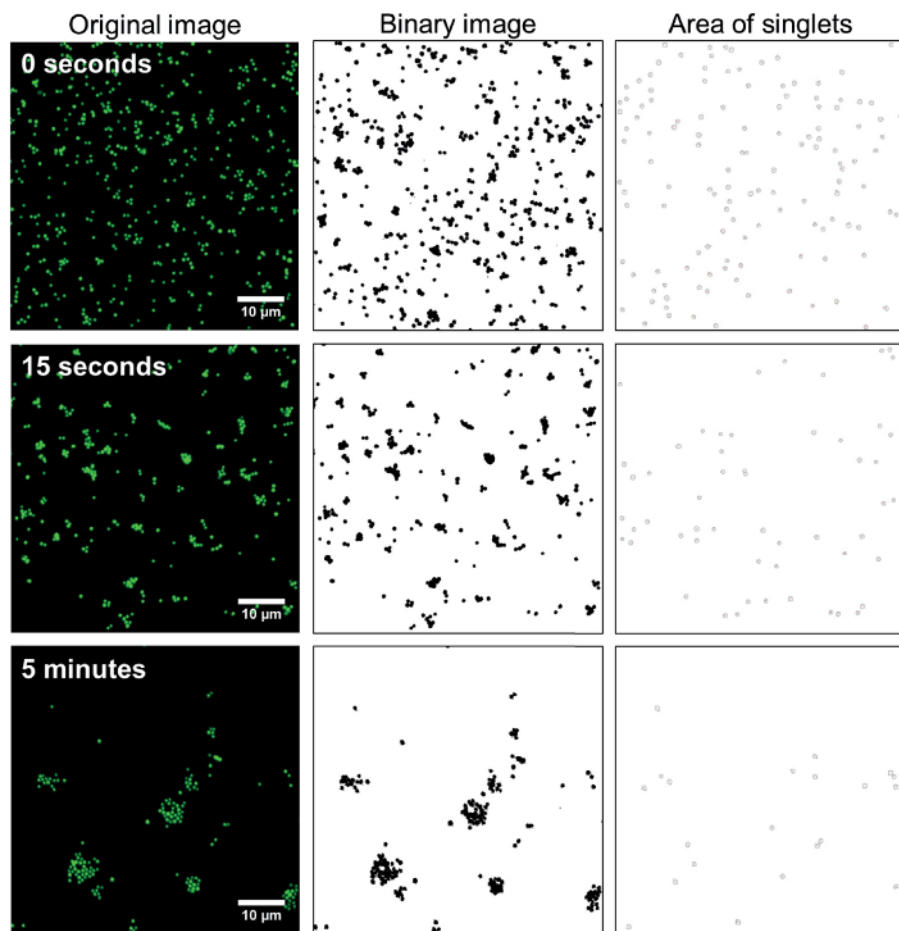


Figure 4. Image processing procedure. Original confocal microscopy images, binary images and the area of singlets for samples deprotected for (top) 0 min, (middle) 15 sec and (bottom) 5 min. The scale bar represents 10 µm. [Please click here to view a larger version of this figure.](#)

Discussion

When cyclohexane, with a refractive index of 1.426, is used as a solvent to disperse the BTA-colloids, van der Waals interactions are very weak, since the refractive indices of colloids and solvent are nearly the same. Note that the concentration of functionalized colloids used for the SLS experiments in cyclohexane is much higher compared to the bare silica colloids in water. This is necessary to obtain a sufficiently strong scattering due to the low contrast as the refractive indices are almost matched. Trace amounts of water in the cyclohexane samples are immediately detected, albeit indirectly, by non-negligible clustering due to capillary forces. Therefore, it is of utmost importance to ensure that the colloids are free of water during all synthesis steps by drying them *in vacuo* for long periods of time as described in the protocol.

Given that the method used to quantify the amines analyses the amount of pyridine-2-thione cleaved from the particles, it circumvents artifacts due to scattering of the particles that could be faced using other techniques such as NMR. Assuming equal surface density for small and large particles, the detected amine density for the small particles corresponds to approximately 24,350 amines per big colloids of 300 nm in radius. Interestingly, the introduced approach allows to regulate the multivalency of the supramolecular colloids by simply changing the NVOC-C11-OH / stearyl alcohol molar ratio during the first functionalization step. Such variation in the multivalency can be further quantified by the same amine quantification procedure.

The successful dispersion of the colloids in singlets before light activation, observed by confocal microscopy, is in line with very weak van der Waals interactions and negligible hydrogen-bonding in cyclohexane prior to photocleavage of the protective *o*-nitrobenzyl group. Hence, photo-induced clustering can be readily attributed to the supramolecular moieties. This is crucial as we aim to direct clustering via supramolecular forces. Cleavage of the *o*-nitrobenzyl group by UV-light indeed allows for BTAs anchored onto different colloids to interact, hence promoting colloidal self-assembly as confirmed by the formation of clusters.

In conclusion, we have demonstrated a straightforward method to couple BTA-derivatives onto silica particles in a controlled manner. The behavior of the resulting supramolecular colloids is successfully governed by the attractive interactions between surface-grafted molecules, namely intermolecular hydrogen-bonding interactions. This methodology can readily be extended to synthesize a broad range of different

supramolecular colloids decorated with other types of supramolecular moieties. Hence, the protocol described herein paves the way for the development of a new family of building blocks to form mesostructured colloidal materials.

Disclosures

The authors have nothing to disclose.

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