Supporting Information

for

Multivalent patchy colloids for quantitative 3D self-assembly studies

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1 Additional figures

**Figure S1.** Silica protrusions grown onto a crystallite which had not been broken up during sonication. The regular spacing between the protrusions - as pointed out by the black arrows - shows that they grew at the contact areas of the silica particles in the crystal. These particles were grown as described in the *Methods* section under “Synthesis of silica particles with silica protrusions”, via the ‘anhydrous route’ with a patterning of the SCA OTMS and using core particles of 226 ± 3 nm and a polydispersity of 1.6 %. The scalebar denotes 100 nm.

**Figure S2.** Transmission Electron Microscopy (TEM) images of two different samples of patchy silica particles with titania protrusions. There is a variation in the number of protrusions per particle, with generally fewer than 12 patches. The scalebars denote 250 nm.
2 Fluted rod-like particles

The procedure for growing silica patches onto silica core particles was extended to rod-like bullet-shaped particles. Spherocylinders of high aspect ratio (L/D > 3.7) that form smectic phases at high densities.\textsuperscript{1,2} Such phases have been found experimentally for bullet-shaped particles as well.\textsuperscript{3} For low enough polydispersity in diameter, the rods are packed hexagonally within the smectic layers. This offers the possibility to pattern colloidal rods at the particle surface, creating elongated patches parallel to the rods’ long-axes.

![Figure S3](image)

**Figure S3.** Smectic crystal of rod-like particles (L = 2.07 µm, D = 0.22 µm and polydispersities $\delta_L = 9\%$ and $\delta_D = 20\%$) before (a) and after (b) sintering (5 h at 600 °C). Scale bars denote 0.5 µm and 3 µm. (c-f) A fluted rod-like particle prepared as described. Panels (c-e) are TEM micrographs of the same rod at tilt angles -30 °, 0 ° and +30 °. Scale bars denote 300 nm. Panel (f) is a surface rendering of a tomographic reconstruction of a fluted rod from the same sample.

Rod-like particles were prepared according to a modified method based on Kuijk et al.\textsuperscript{3} as described in ref. 4. The rods were left to grow for 36 hours to achieve a high aspect ratio, as needed for smectic phases most suited for the creation of long patches. The rods’ final dimensions were: a length L = 2.07 µm and a diameter D = 0.22 µm with respective polydispersities of $\delta_L = 9\%$ and $\delta_D = 20\%$ (aspect ratio L/D = 9.6). These silica rods were allowed to sediment in ethanol and the solvent was left to evaporate. A piece of the sediment was annealed for five hours at 600 °C. SEM images revealed that the smectic order in the crystal was retained after this sintering step (Fig. S3). (Rod-like particles annealed for 5 hours at 750 °C did not redisperse within two hours by sonication with the ultrasonic processor. A possible explanation is that the contact areas between rod-like particles are larger than between spherical particles, although it is also true that the rod diameter is smaller than the sphere diameters used, and thus the forces exerted by sonication are proportionally smaller as well. When annealed for 5 h at 600 °C, the rods could be dispersed fully by sonication.)
The annealed crystal was grafted with MPTMS as described previously for silica spheres: a total of 50 mg annealed rods was placed in a mixture of 8.0 mL ethanol, 0.300 mL water, 0.20 mL ammonia (aqueous, 25%) and 0.10 mL MPTMS and left in the mixture without stirring for 24 h. The colloids in the crystal were redispersed in ethanol by sonication with the ultrasonic processor. Silica was grown onto the patches through slow addition of TES to a dispersion of 0.50 mg/mL of surface-patterned rod-like particles in ethanol in the following way. First, 1 mL of water and 0.10 mL of ammonia (aqueous, 25%) were added to 8.0 mL of the sol of rods in ethanol. Subsequently, a mixture of 16 µL TES in 16 mL ethanol was added with a syringe pump at a rate of 0.72 mL/hr. An extra 1.00 mL of water was also added to the reaction mixture at the time when 8.0 mL precursor solution had been added by the syringe pump. After all TES solution had been added, the reaction mixture was left stirring for two more hours and subsequently washed three times with ethanol.

Figs. S3(c-e) display a patchy rod under three different angles; the protrusions are visible with a lighter grey shade than the core as they are thinner. They run along the length of the rods like a wing. The angle dependence (of visible protrusions upon turning the sample by 30°) shows that the protrusions are not a matter of incorrect focussing. A tomographic reconstruction of one patchy rod is shown in Fig. S3f, providing further evidence for the fluted shape.

The protrusions have a width of 56 ± 3 nm, which is similar to the height measured for silica protrusions on spherical patchy particles. The protrusions do not all run along the full lengths of the rods, presumably because the rod-like particles are slightly tapered, have a polydispersity of 20% in their diameter and/or do not have a fully smooth surface. This tapering is a result of shrinking of the emulsion droplet from which the rod grows during synthesis, since the rod consumes precursor and water from the droplet. In addition, many rods had fewer than six protrusions. Liquid crystals of the type smectic A do not necessarily have long-ranged hexagonal ordering within layers, but these rods do often have local ordering (see Fig. S3a and ref. 5). The missing protrusions are probably not due to lack of local order, but due to the relatively high polydispersity in diameter; both these issues (polydispersity and surface roughness) can be improved by seeded growth of the rods.

### 3 Additional information on dye incorporation into silica protrusions

Fig. S5a shows particles grown as the silica particles with dye-labeled silica protrusions described in Methods, but with a single MPTMS coating on the antipatch and with the equivalent amount of APTES instead of APTES-FITC. Clearly, adding APTES during patch growth causes silica growth on the antipatch, as such silica on the antipatch was not observed for a double MPTMS coating. It is likely that the positively charged amino group of APTES adheres via charge-interactions to the remaining negatively charged OH groups at the silica surface. Silica particles with dye-labeled silica protrusions grown as described in Methods, with a double MPTMS coating, only has silica grown on the patches and not on the antipatch (Fig. S5b).

Silica particles with fluorescently-labeled protrusions eventually were not used for confocal microscopy, since the protrusion height \( h \) was found not increase with core particle size (Fig. 4). Instead, silica particles with hemispherical titania protrusions were employed. For optimal use of the silica particles with titania protrusions in confocal microscopy, it was important that after infiltrating the protrusions with APTES-RITC, no dye molecules adhered to the antipatch. This was tested by grafting silica particles with MPTMS via the anhydrous method and subsequently treating overnight with APTES-RITC in a Stöber mixture in the following way: to 20 mg RITC were added 1.00 g (1.27 mL) ethanol and 20 µL APTES, after which the solution was stirred overnight. To 10.0 mL of a dispersion of the silica particles, 100 µL aqueous ammonia and 40.0 µL dye solution were added. After two washing steps with ethanol and one with CHC for index-matching, the particles displayed fluorescent rings under the confocal microscope (Fig. S5c). In conclusion, MPTMS molecules do not provide sufficient steric hindrance and/or change in hydrophilicity of the surface to prevent APTES-RITC from binding to the silica surface. Patchy silica particles with titania protrusions prepared with an OTMS coating (rather than MPTMS) via the anhydrous route did not display such a ring of dye adhered to the antipatch (Fig. 2a and Supplementary Video SV4), indicating that OTMS is sufficiently hydrophobic and/or provides sufficient steric repulsion to prevent the dye-conjugate from adhering to the silica surface.
Figure S4. Micron-sized patchy particles with silica protrusions prepared via the method of Wang et al.\textsuperscript{47} as described in Methods, with 6-10h annealing at the temperatures indicated in each panel. Few protrusions were found for annealing temperatures of 650-750 °C, while spurious silica growth was observed for 500 °C. The scalebars denote 1 µm.

4 STED Super-resolution microscopy

The presented patchy silica particles with labeled titania protrusions are only marginally suitable for super-resolution microscopy techniques, since the mismatch in refractive index between the amorphous titania protrusions (n = 1.55\textsuperscript{6}) and the Stöber silica cores (n = 1.45) precludes complete index-matching of the particles. Indeed, the improvement in resolution obtained with Stimulated Emission Depletion (STED) was only modest compared to conventional confocal microscopy (Fig. S6). Although this was not investigated in detail in this research, it is to be expected that the point spread function of the confocal microscope is affected by the locally not index-matched titania patches, thus reducing the effectiveness of the nanoscopy methodology.

Another issue with STED is related to the depletion laser, and appears when multiple dyes are used. The instrument’s depletion laser must operate at a wavelength away from the absorption wavelengths of both the dye in the cores and the dye in the protrusions, to prevent photobleaching of either component. A typical STED depletion laser wavelength is 592 nm, although some microscopes are fitted with 660 nm and 775 nm depletion lasers as well. The excitation wavelength of RITC is $\lambda_{\text{ex}} = 543$ nm (depending on solvent) which results in its photobleaching by the 592 nm laser line, hence a more suitable dye combination is FITC and DEAC-SE. For FITC $\lambda_{\text{ex}}/\lambda_{\text{em}} \approx 492$ nm/518 nm and for DEAC-SE $\lambda_{\text{ex}}/\lambda_{\text{em}} \approx 432$ nm/472 nm, leaving a window of 432-492 nm to detect the DEAC-SE emission, while both excitation wavelengths are far enough from the typical STED depletion line of
5 Modification of titania protrusions with a PALM-compatible dye

Additionally, a Photo-Activated Localization Microscopy (PALM)-compatible dye was also coupled to the amorphous titania protrusions post synthesis. For this purpose, a silane coupling agent molecule was prepared consisting of an 6-nitroveratryloxycarbonyl (NVOC)-protected amine attached to a trimethoxysilane group via a flexible C11 spacer (Fig. S7a,top; a description of the synthesis and PALM imaging is below). The obtained triethoxy silane can be efficiently tethered to silica at mild temperatures. This is particularly important for future extensions of this work to composite silicates and anisotropic particles which cannot withstand the high temperature of the van Helden synthesis.8, 9 On account of the OTMS-patterning, this silane reacts site-specifically at the protrusions. The C11 spacer helps the particles disperse in apolar solvents, as is possible in combination with OTMS on the antipatch. Introduction of the amine allows efficient coupling of various functional groups by means of isocyanates, isothiocyanates or activated esters. The NVOC protecting group can be cleaved off efficiently under mild conditions (Fig. S7a,bottom), without the need for a work-up.

Materials and methods

All chemicals for synthesis were purchased from Sigma Aldrich and used without purification, including Cage 552 (NHS ester) from Aberrior. Samples for PALM measurements were prepared by suspending 0.1 wt.water. PALM images were acquired using a Nikon N-STORM system configured for total internal reflection fluorescence (TIRF) imaging. Excitation inclination was tuned to maximize the signal-to-noise ratio. Cage 552 (protrusions) and fluorescein (core particles) were illuminated respectively by the 561 nm and 488 nm laser lines built into the microscope. UV activation with a wavelength of 405 nm was employed. Fluorescence was collected by means of a Nikon 100x, 1.4 NA oil immersion objective and passed through a quad-band pass dichroic filter (97335 Nikon). Images were acquired using of an EMCCD camera (ixon3, Andor). A minimum of 10,000 frames were acquired per image.

Synthesis of 4,5-dimethoxy-2-nitrobenzyl (4,4-dioxy-9-oxo-3,10-dioxa-8-aza-4-silahenicosan-21-yl)carbamate (14)

4,5-Dimethoxy-2-nitrobenzyl (11-hydroxyundecyl)carbamate (13) was prepared as in ref.10 This compound 13 (153 mg; 0.36 mmol) was dissolved in 10 mL chloroform. 3-(Triethoxysilyl) propyl isocyanate (107 mg; 0.43 mmol)
and a drop of the catalyst dibutyltin dilaurate were added, and the reaction mixture was refluxed overnight. After cooling to room temperature, polymer bound tris(2-aminoethyl)amine was added to scavenge the excess isocyanate. The resin was filtered off and washed with chloroform to yield the pure product 14 in quantitative yield after drying in vacuo. 1H NMR (CDCl3): $\delta = 7.71$ (s, 1H, ArH), 7.00 (s, 1H, ArH), 5.50 (s, 2H, ArCH2), 4.86 (broad s, 1H, NH) 3.97 (s, 3H, ArOCH$_3$), 3.95 (s, 3H, ArOCH$_3$), 3.82 (q, 6H, SiOCH$_2$CH$_3$) 3.29-3.04 (m, 2x2H, CH$_2$NH), 3.41-3.06 (m, 2H, CH$_2$NH), 1.73-1.47 (m, 6H, aliphatic) 1.46-1.07 (m, 14H, aliphatic), 0.89 (dt, 9H, SiOCH$_2$CH$_3$), 0.63 (m, 2H, SiCH$_2$). 13C NMR (CDCl3): $\delta$ 155.9, 153.3, 149.3, 148.0 128.2, 110.3, 108.2, 75.6, 63.4, 63.1, 58.4, 56.4, 43.3, 41.2, 32.8, 29.5, 29.5, 29.4, 29.4, 29.2, 26.8, 25.7, 18.3, 7.5. MALDI-TOF-MS calc.: m/z 673.36, found 696.4 [M+Na], 712.4 [M+K].

**Pre-treatment of silica particles with titania protrusions**

Silica particles with OTMOS coating and rhodamine-labeled titania protrusions were prepared as described in Methods. The protrusions were further infiltrated with amorphous silica in the following way. Patchy particles were dispersed in ethanol (5.0 g/L). To 30 mL of this dispersion, 0.30 mL ammonia solution (25%) and 3.8 $\mu$L TEOS were added. The reaction was allowed to proceed for 6 h under gentle tumbling of the reaction vial, after which the particles were washed 3 times with ethanol.

**Coupling of 14 to silica-infiltrated titania protrusions**

A suspension of silica beads coated with OTMOS and with titania protrusions, dispersed in ethanol, were allowed to
Figure S7. Super-resolution imaging using PALM. (a,top) Structure formula of 4,5-dimethoxy-2-nitrobenzyl (4,4-diethoxy-9-oxo-3,10-dioxo-8-aza-4-silahenicosa-21-yl)carbamate (compound 14), which was selectively coupled to titania protrusions. (a,bottom) UV-light deprotection of 14. (b) TEM and (c) PALM micrograph of a silica particle with an FITC labeled core (depicted in blue) and Cage 552-labeled titania/silica protrusions (depicted in green) in a carbonate buffer.

sediment by centrifuging 3 minutes at 4000 rpm. The supernatant was replaced by chloroform. This procedure was repeated 3 times and after the last time the sediment was transferred to 1 mL of a 10 wt.% solution of NVOC-silane 14 in chloroform. The reaction mixture was stirred overnight at room temperature under an argon atmosphere. The obtained product was allowed to sediment by centrifuging 3 minutes at 4000 rpm, the supernatant was removed and the pellet was resuspended in 3 mL of chloroform. This procedure was repeated 6 times and after the last step, the pellet was dried in vacuo.

Palm imaging
The NVOC-groups were deprotected/uncaged by illumination with UV light (354 nm) in chloroform for 60 minutes. The amines of the silane were then conjugated with Cage 552, an N-hydroxysuccinimide ester activated rhodamine analogue for PALM.11,12 The Cage 552 was directly added to this reaction mixture and allowed to react overnight at room temperature while stirring (Fig. S7a). The resulting particles were imaged by PALM (Fig. S7b,c). These images likely still suffer from refractive index mismatch due to the presence of titania in the protrusions, however future research can use the silica particles with silica protrusions prepared with an OTMS patterning via the anhydrous route. It is possible to couple benzene-1,3,5-tricarboxamide (BTA) to the deprotected silane instead of Cage 552.10,13,14 BTAs attached to colloids have been shown to induce colloidal assembly,13 which opens up the way to supramolecular patch-patch interactions for these patchy particles, similar to refs. 15, 16.

6 Supporting calculation
The following is a rough calculation of the dependence of patch height as a function of core particle diameter. Suppose $R$ is the average particle diameter, $r$ the average patch diameter and $H$ the average patch height. We may model a patch as a cylinder of volume $\pi r^2 H$. For a total silica content $M$ of seed particles in the reaction mixture, the number of silica particles $N$ in the reaction mixture is $N = M/(\frac{4}{3} \pi R^3 \rho)$, with $\rho$ the density of silica. Given the total volume $V$ of silica that can be formed from the added amount of TES, the volume $v$ of a protrusion is then
Equating the volume of the cylinder to $v$, we arrive at $H = \frac{\rho V}{9M \pi \tau}$. From Figure 4, we see that as the particle radius triples from $\sim 350$ nm to 1050 nm ($R \rightarrow 3R$), the patch width (anhydrous method) approximately doubles from 60 nm to 120 nm ($r \rightarrow 2r$). Thus, $H \rightarrow \frac{9}{4}H$, and the patch height is expected to increase with particle diameter. The model is not completely accurate however, since at small heights the volume of the protrusion is closer to a hemisphere of volume $v = \frac{4}{3} \pi r^3$.

7 Additional information on titania polymorph characterization by SAED

We first verified that the titania protrusions indeed consist of titania by performing energy dispersive X-ray diffraction (EDX) on the particle core (Fig. S8a) and selectively on a protrusion (Fig. S8b). The EDX pattern taken when the beam was aimed at the core particle does not show any X-rays from titanium atoms. On the other hand, the EDX spectrum procured at a protrusion has the characteristic peaks from the K$\alpha$ and K$\beta$ energy levels of the titanium ions.

Figure S8. EDX spectra from a patchy silica particle (OTMS patterned) with titania protrusions taken (a) at the particle core, and (b) at the protrusion.

Figure S9. Patchy particles with titania protrusions of the same batch (a) annealed for 2 h at 400 $^\circ$C, and (b) infiltrated with APTES-RITC and annealed for 2 h at 500 $^\circ$C. Scale bars: 500 nm and 200 nm.

Diffraction patterns satisfy the Bragg’s law $2dsin(\theta) = m\lambda$, with $m$ an integer] for small angles, i.e. assuming $R \ll L$:

$$d \cdot R = \lambda \cdot L$$

with $d$ the lattice spacing in the crystal, $R$ the radius of the diffraction ring, $\lambda$ the wavelength of the electrons and $L$ the distance between sample and detector. Once the “camera constant” $\lambda L$ is known, the lattice spacings can be
derived by measuring the radii of the diffraction rings $R$ in a diffraction pattern. An electron diffraction pattern of gold was used as a calibration to determine the camera constant for the instrument (electron microscope and detector) used. By measuring the radius of the diffraction rings in Fig. 3, we arrived at the lattice spacings $d$ in table S1. The spacings agree with those of the anatase phase to within the error bars. The rutile phase has a first diffraction ring at 3.247 Å: this value lies outside the error margin of the observed first ring. The phase diffraction rings of brookite are rather similar to those of anatase, but brookite has a strong diffraction ring at 2.9 Å, which is absent in the present spectra. Therefore, we believe that the titania patches of the patchy particles were converted to anatase titania by annealing two hours at 500 °C. The lattice spacings calculated from the diffraction rings for particles annealed for 8h at 500 °C and 2h at 900 °C are close to anatase as well, but the fact that the diffraction patterns consist of spots rather than rings indicating an increased crystal size affects the measurement uncertainty.

**Figure S10.** Dark field TEM images of particles with titania protrusions annealed at 1100 °C, under various angles. Different protrusions lit up brightly under various azimuthal angles of the incident beam as the crystal planes satisfied Bragg’s law with respect to the detector. The scale bars denote 0.5 µm.
Table S1. Table of the lattice spacings found from the diffraction rings of patchy particles with titania protrusions annealed at 500 °C for 2 h, and comparative data from JCPDS card no. 21-1272. The second ring is a composite ring due to three very similar lattice spacings. ‘Too faint’ indicates that individual spots could still be seen, but that it was unclear which formed a ring together.
Additional figure on patch number distributions

Figure S11. (a) Confocal image of a dilute dispersion of patchy particles (core particle diameter 1085 nm and polydispersity 1%) and (b) computer rendering of the tracked image. In the computer rendering, the core particle’s surface is drawn, making the core particles appear larger than in the confocal image, since only the seeds inside the core particles are fluorescently labeled. (c) Computer rendering of the tracked 3D data stack of sample A from Supplementary Video SV4. (d) Distance $r$ of all protrusions to their closest core particle of diameter $\sigma = 1085$ nm. A distance of $r = 1.5\sigma/2$ was used as a cut-off to identify a number of spurious protrusions determined by the tracking algorithm. These protrusions were not counted towards the angle histogram in Fig. 5f.
9 Additional information on self-assembly by solvophobic interactions

Patchy particles with an OTMS-grafted silica core particle and dyed titania patches were dispersed in low-polar solvents to attempt to induce patch-patch attractive interactions. Such interactions are expected, since the titania protrusions do not possess a hydrophobic grafting and can stick due to solvophobic and van der Waals interactions. The solvents opted for were low-polar solvents, since the grafted silica can be charge-stabilized in these solvents: cyclohexyl chloride (CHC, static \( \varepsilon = 7.6, n_D = 1.46 \) and \( \rho = 0.993 \) at \( 25^\circ C \)) and 1,2-dichloroethane (DCE, static \( \varepsilon = 10.7, n_D = 1.44 \) and \( \rho = 0.862 \) g/cm\(^3\) at \( 25^\circ C \)). The conductivity of deionized CHC was 20 pS/cm, corresponding to a Debye length of 11 \( \mu m \). The patchy particles formed gels in both solvents within the time needed (~10 minutes) to cure the glue (Fig. 7a-b). The gel in deionized CHC was easily broken up into a fluid of clusters upon turning the capillary upside down for confocal microscopy (Fig. 7a), while the gels in non-deionized CHC and DCE did not break up under the same conditions.

Zeta potentials were measured (as described in Methods for OTMS-grafted silica particles and for titania particles in both CHC and DCE, and the results are displayed in Fig. S12.

10 Supporting videos

Video SV1a Tilt series of a sub-micron sized patchy silica particle with MPTMS grafting and titania protrusions.
Video SV1b Tilt series of a micron sized patchy silica particle with MPTMS grafting and titania protrusions.
Video SV2 Tomographic reconstruction of the patchy particle in SV1a.
Video SV3 Surface rendering of the patchy silica particle with titania protrusions in SV1a, as derived from the surface rendering in SV2.
Video SV4 Confocal 3D data stack of sample A, patchy particles in dodecanol. The FITC-labeled silica cores are depicted in green, RITC-labeled titania protrusions in red.
Video SV5 Confocal 3D data stack of patchy particles in CHC. The FITC-labeled silica cores are depicted in green, RITC-labeled titania protrusions in red.
Video SV6 Confocal 3D data stack of patchy particles in DCE. The FITC-labeled silica cores are depicted in green, RITC-labeled titania protrusions in red.
Video SV7 Confocal time series of silica particles and RITC-dyed titania in CHC. The FITC-labeled silica cores are depicted in green and the RITC-labeled titania in red. The movie plays at 4.4x real time.
Video SV8 Confocal time series of silica particles and RITC-dyed titania in DCE. The FITC-labeled silica cores are depicted in green and the RITC-labeled titania in red. The movie plays at 4.4x real time.

In the low-polar solvent dodecanol (Supplementary Video SV4), the patchy particles also form a gel structure, however interactions in the system were more difficult to analyze experimentally due to the high melting point of dodecanol. A pair correlation function for the protrusions (Fig. S13) shows a maximum at the protrusion width, \( d = 255 \) nm. This shows that protrusions are on average touching other protrusions, possibly indicating selective patch-patch interactions, but the analysis does not exclude patch-core interactions.

11 Supporting references

1. Veerman, J. A. C. & Frenkel, D. Phase diagram of a system of hard spherocylinders by computer simulation. Physical Review A 41, 3237-3244 (1990).
2. Bolhuis, P. and Frenkel, D. Tracing the phase boundaries of hard spherocylinders. The Journal of Chemical Physics 106, 666-687 (1997).
Figure S12. Zeta potentials measured for OTMS-grafted 1085 nm ± 5 nm (p.d. 1%) silica particles and (non-dyed) titania particles in CHC and DCE. The voltages used were 10-20 V as higher voltages resulted in multiple peaks. For conversion of electrophoretic mobilities to zeta potentials, the Hückel limit was assumed. Titania concentration is 1.1 mg/mL. The OTMS-silica concentration was adjusted by dilution until a slight scattering was observed by eye.

Figure S13. Pair correlation function for protrusions, calculated from particle tracking on the structure in Supplementary Video SV4. The protrusion width for these patch particles is $w = 255 \text{ nm} \pm 2 \text{ nm}$ (p.d. = 54 nm).

3. Kuijk, A., van Blaaderen, A. and Imhof, A. Synthesis of monodisperse, rodlike silica colloids with tunable aspect ratio. *Journal of the American Chemical Society* 8, 2346-2349 (2011).

4. Peng, B, Soligno, G., Kamp, M., de Nijs, B., de Graaf, J., Dijkstra, M., van Roij, R., van Blaaderen, A. and Imhof, A. Site-specific growth of polymers on silica rods. *Soft Matter* 10, 9644-9650 (2014).

5. Kuijk, A., Byelov, D. V., Petukhov, A. V., van Blaaderen, A. & Imhof, A. Phase behavior of colloidal silica rods. *Faraday Discussions* 159, 181-199 (2012).

6. Demirörs, A. F., van Blaaderen, A. and Imhof, A. A general method to coat colloidal particles with titania. *Langmuir* 26, 9297-9303 (2010).

7. Lin, J., Siddiqui, J. A. and Ottenbrite, R.I M. Surface modification of inorganic oxide particles with silane coupling agent and organic dyes. *Polymers for Advanced Technologies* 12, 285-292 (2001).
8. van Helden, A. K., Jansen, J. W. and Vrij, A. Preparation and characterization of spherical monodisperse silica dispersions in nonaqueous solvents. *Journal of Colloid and Interface Science* **81**, 354 - 368 (1981).

9. van Helden, A. K. and Vrij, A. Static light scattering of concentrated silica dispersions in apolar solvents. *Journal of Colloid and Interface Science* **78**, 312 - 329 (1980).

10. Vilanova, N., de Feijter, I., Teunissen, A. J. P. and Voets, I. K. Light induced assembly and self-sorting of silica microparticles. *Scientific Reports* **8**, 1271 (2018).

11. Belov, V. N., Mitronova, G. Y., Bossi, M. L., Boyarskiy, V. P., Hebisch, E., Geisler, C., Kolmakov, K., Wurm, C. A., Willig, K. I. and Hell, S. W. Masked rhodamine dyes of Five Principal Colors Revealed by Photolysis of a 2-Diazo-1-Indanone Caging Group: Synthesis, Photophysics, and Light Microscopy Applications. *Chemistry – A European Journal* **20**, 13162-13173 (2014).

12. Aloi, A., Vargas Jentzsch, A., Vilanova, N., Albertazzi, L., Meijer, E. W. and Voets, I. K. Imaging Nanostructures by Single-Molecule Localization Microscopy in Organic Solvents *Journal of the American Chemical Society* **138**, 2953-2956 (2016).

13. de Feijter, I., Albertazzi, L., Palmans, A. R. A. and Voets, I. K. Stimuli-Responsive Colloidal Assembly Driven by Surface-Grafted Supramolecular Moieties. *Langmuir* **31**, 57-64 (2015).

14. Vilanova, N., de Feijter, I. and Voets, I. K. Synthesis and Characterization of Supramolecular Colloids. *Journal of Visual Experiments* **110**, 53934 (2016).

15. Benyettou, F., Zheng, X., Elacqua, E., Wang, Y., Dalvand, P., Asfari, Z., Olsen, J.-C., Han, D. S., Saleh, N., Elhabiri, M., Weck, M. and Trabolsi, A. Redox-Responsive Viologen-Mediated Self-Assembly of CB[7]-Modified Patchy Particles *Langmuir* **32**, 7144-7150 (2016).

16. Elacqua, E., Zheng, X. and Weck, M. Light-Mediated Reversible Assembly of Polymeric Colloids. *ACS Macro Letters* **6**, 1060-1065 (2017).

17. Powder Diffraction File, Card No.21-1272. Joint Committee on Powder Diffraction Standards. Swarthmore, United States of America.

18. Williams, J.W. The dieconstant constants of binary mixtures. X. The electric moments of simple derivatives of cyclohexane an of dioxan. *Journal of the Americal Chemical Society* **52**, 1831-1837 (1930).

19. Crowe, R. W. & Smyth, Charles P. The dielectric and polymorphic behavior of cyclohexanol, cyclohexanone, chlorocyclohexane and cyclohexane1,2. *Journal of the Americal Chemical Society* **73**, 5406-541 (1951).

20. Rodríguez, S., Lafuente, C., Cea, P., Royo, F. M. & Urieta, J. S. Densities and viscosities of binary mixtures of some cyclic ethers + chlorocyclohexane at 298.15 and 313.15 K. *Journal of Chemical & Engineering Data* **42**, 1285-1289 (1997).

21. Corradini, F., Marchetti, A., Tagliazucchi, M.& Tassi, L. Static dielectric constants of 1,2-dichloroethane + 2-methoxyethanol + 1,2-dimethoxyethane ternary liquid mixtures from -10 to 80 °C. *Fluid Phase Equilibria* **124**, 209-220 (1996).