Supporting Information: General Route Towards Chemically Anisotropic Colloids

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Click Chemistry on Spherical particles.

Preparation of spherical, azide functionalized polystyrene particles.

The overall synthetic strategy towards particles which can participate in Click Chemistry reactions is shown in Figure 1. The first step is the synthesis of cross-linked polystyrene colloids (CPs) using a straightforward emulsion polymerization of styrene with divin ylbenzene as cross-linker. In the next step (**i**) these seed particles were used to grow a chlorinated shell around these particles (as discussed in the main article). The surface chlorine groups are then converted into azides by a nucleophilic substitution reaction with sodium azide (**ii**).

Scheme S1. Schematic overview of the synthesis of azide functionalized colloids.
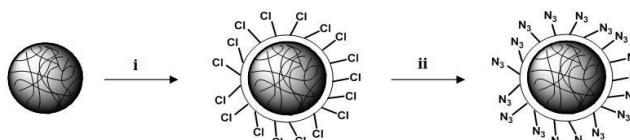
The preparation of the cross-linked polystyrene colloids was carried out as in reference 1 and resulted in monodispers particles which could directly be used in the second step. A chlorinated and cross-linked shell was grown around the polystyrene seeds.

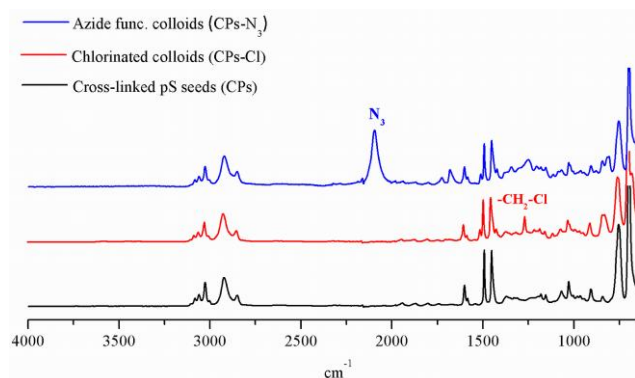

Figure S1. IR spectra of cross-linked polystrene particles, chlorinated particles (red) and azide functionalized particle (blue).
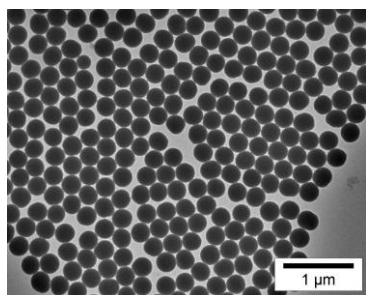

Figure S2. Transmission electron microscope picture of chlorinated cross-linked polystyrene particles.

Successful incorporation of the chlorine functionality was given by both IR analysis (Figure S1) and XPS (Figure S3) as also discussed in the main article.
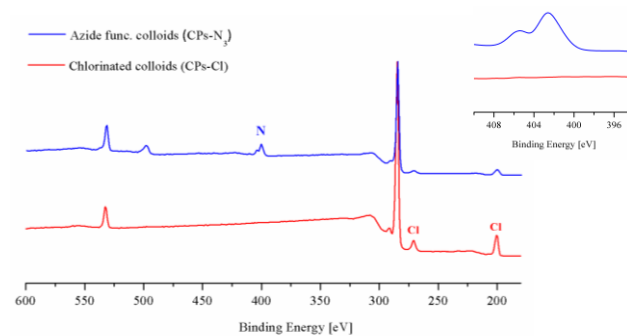

Figure S3. XPS spectra of chlorinated particles (red), azide functionalized particles (blue) and enlargement of the nitrogen signal.

Particles are monodispers and spherical as can be observed from the transmission electron microscope picture from these particles (Figure S2). With these particles at hand we moved on to the final reaction step. Following Breed *et al.*,[3] attempts were carried out to perform the substitution reaction with sodium azide in an aqueous environment. However, this resulted in very low chlorine conversions. Increasing the number of equivalents of sodium azide significantly was not possible due to salt induced aggregation of the colloids. To circumvent this problem, DMF was chosen as solvent. Both particle core and chlorinated shell are cross-linked to prevent the particles from dissolving. DMF is known for its poor ability to solvate anions.[4] Therefore, dissolving sodium azide in DMF results in a 'naked', i.e., not hydrated azide ions. These ions are highly reactive. The reaction in DMF resulted in high chlorine conversions as was shown with IR spectroscopy (Figure S1) which showed disappearance of the -CH_2-Cl signal at 1266 cm^{-1} and the appearance of a strong –N_3 vibration at 2096 cm^{-1}. XPS (Figure S3) showed similar results: the chlorine signals significantly decreased after the reaction. The fact that not the complete signal disappears can be explained by the fact that a part of the chlorine groups are buried just under the particle surface and cannot be reached by the azide anion. The spectrum also shows a splitted nitrogen signal at 401 and 406 eV. This peak splitting indicates the presence of two nitrogen species and reflects the differently charged nitrogen atoms in an azide group.[5]

Click Chemistry on azide functionalized particles.

In the previous section it was shown that the azide functionality could be introduced on the surface of polystyrene colloids. This opens the way to surface modification with Click Chemistry. Due to the high instability of the azide containing particles in water, the modification reactions were carried out in DMF. The reason for this instability in water is a little puzzling, as one expects the azide functionalized colloids to be stable in water due to the hydrophilic character (resonance structures with charge separation) of the azides. Cu(PPh$_3$)$_3$Br in combination

Scheme S2. Synthetic strategy of the surface modification of spherical colloids via Click Chemistry.
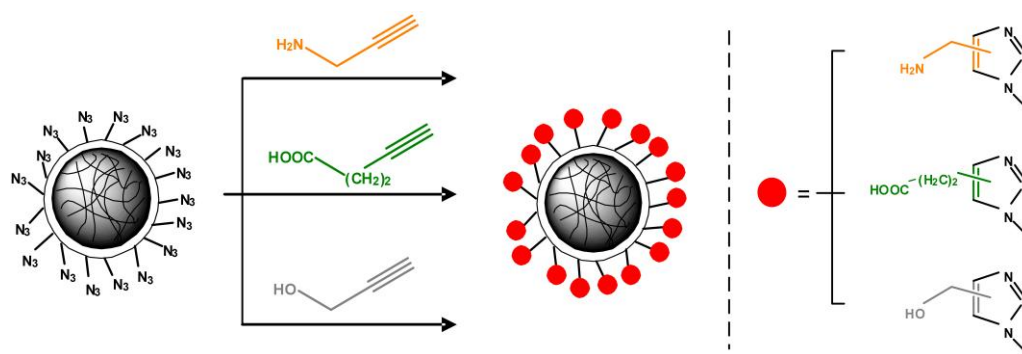
with DIPEA was used as a catalytic system, because this system is soluble in the reaction medium. Three alkyne precursors with different types of functional groups (pentynoic acid = COOH, propargyl alcohol = OH and propargyl amine = NH₂) were used as model molecules for surface modification. Schematically the reactions are depicted in Scheme S2.The particles obtained after Click Chemistry reactions were analyzed using IR spectroscopy. The obtained spectra are depicted in Figure S4. Regardless of the functionality present on the alkyne precursor, the IR spectra show no azide signal (2096 cm^{-1}) anymore. This is a clear indication that most free azides have reacted to form the triazole moiety (Figure S5). The signal of the triazole group itself is hard to detect although in all three spectra a new signal appeared around 1650 cm^{-1} which is possibly caused by this group.
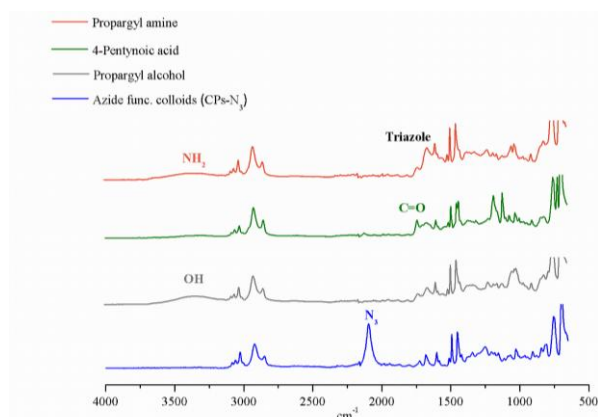

Figure S4. IR spectra of azide functionalized particles before (blue) and after surface modification with propargyl alcohol (grey), 4-pentynoic acid (green) or propargyl amine (orange) using Click Chemistry.
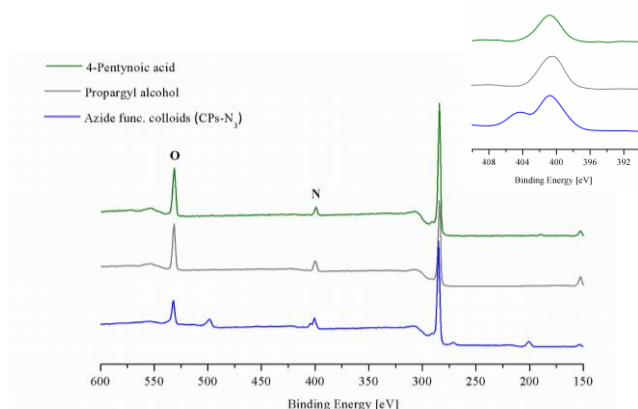

Figure S5. XPS spectra of azide functionalized particles (blue) and the particles after Click reaction with propargyl alcohol (gray) and 4-pentynoic acid (green) and enlargement of the nitrogen signal.

On top of this, all three spectra contain the IR-signals corresponding to the functionality of the specific alkyne precursor which was added. XPS analysis was carried out on the particles functionalized with 4-pentynoic acid and propargyl alcohol (Figure S5).In both cases an increase in the oxygen content (543 eV) was observed, which was expected if carboxylic and hydroxyl functionalities are added to the surface (the oxygen signal present before Click Chemistry can be attributed to sulfate or sulfonate groups produced by the initiator system). Besides this enrichment in oxygen, the splitted nitrogen signal in the azide functionalized particles is merged into one signal after reaction. This indicates that the free azides have participated in the reactions [4] and together with all other evidence from IR and XPS it can be concluded that the alkyne precursors can indeed be coupled to the colloids.

As mentioned before, the colloids with azide functionalities were highly unstable in water. After Click Chemistry the azide groups are converted to triazoles and hydrophilic groups are added to the surface of the particles. In principle the water stability should therefore increase. To test this, small drops of the particles in DMF before and after Click reactions were added to relatively large volumes of water. The result is shown in Figure S6. The particles after surface modification showed indeed increased water stability compared to the azide functionalized particles. This is again extra proof that we really managed to change the surface properties of these particles.
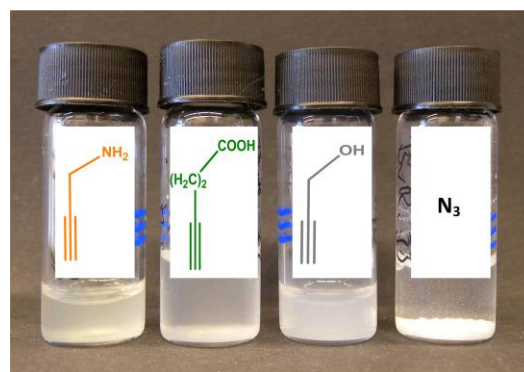

Figure S6. Stability of DMF dispersion in water before and after surface modification.

The previous results show that at the chemical level the modifications have worked. However, for these reactions to be useful it is of course necessary that the particles stay intact during the whole procedure. Usually this is not an issue, because most reported reactions are carried out in water. In this case both introduction of azides and subsequent Click Chemistry reactions are performed in DMF at elevated temperature. The cross-linking of the particles should be high enough to prevent dissolution of the particles (linear polystyrene can be dissolved in DMF). TEM was used to check if the particles survived the reactions. As an

example, Figure S7 showed that the particles after modification with propargyl alcohol were still present and that they remained spherical. Both on the chemical as on the colloidal level the surface modifications were therefore successful.
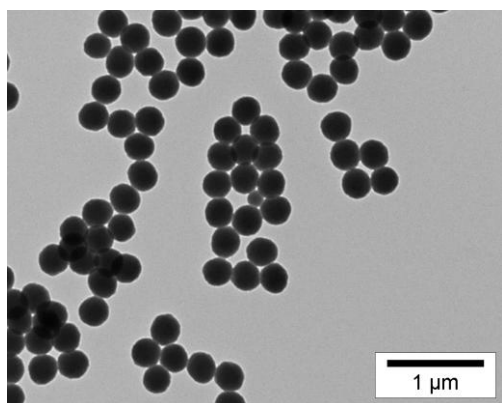

Figure S7. TEM image after Click reaction with propargyl alcohol.

Experimental details for conversion of chlorine groups to azides on spherical particles.

The CPs-Cl particles are first transferred from water to DMF by centrifugation and redispersion (3 times). The solid content was maintained at 5% during this process. 32 mg NaN_3 was weighed into a reaction tube and 5 mL of the DMF-dispersion was added. The mixture was heated for 24 hours at 70°C. After this, the emulsion is washed with DMF to remove excess NaN_3. Conversion of the chlorine functionality to azides was confirmed by FT-IR (ATR) and XPS. The same reaction was also carried out in an aqueous environment.

Experimental details for Click Chemistry on spherical azide functionalized particles.

25 mg of $Cu(PPh_3)_3Br$ was introduced in a 25 mL round bottom flask equipped with stir bar. 4 mL DMF is added to dissolve the catalyst. To this solution, 52 μL DIPEA and an alkyne precursor is added (either directly or from a stock solution of the precursor in DMF. If a shock solution is used the amount of DMF used to dissolve the catalyst is reduced to keep to total reaction volume equal). Finally, 1 mL of the CPs-N_3 dispersion (in DMF, solid content = 1%) is added. The reaction is allowed to run for 24 hours under gentle stirring at 70°C (flask is equipped with water cooler). After the reaction, the particles are washed with DMF. FT-IR (ATR) and XPS were used to show successful surface modification.

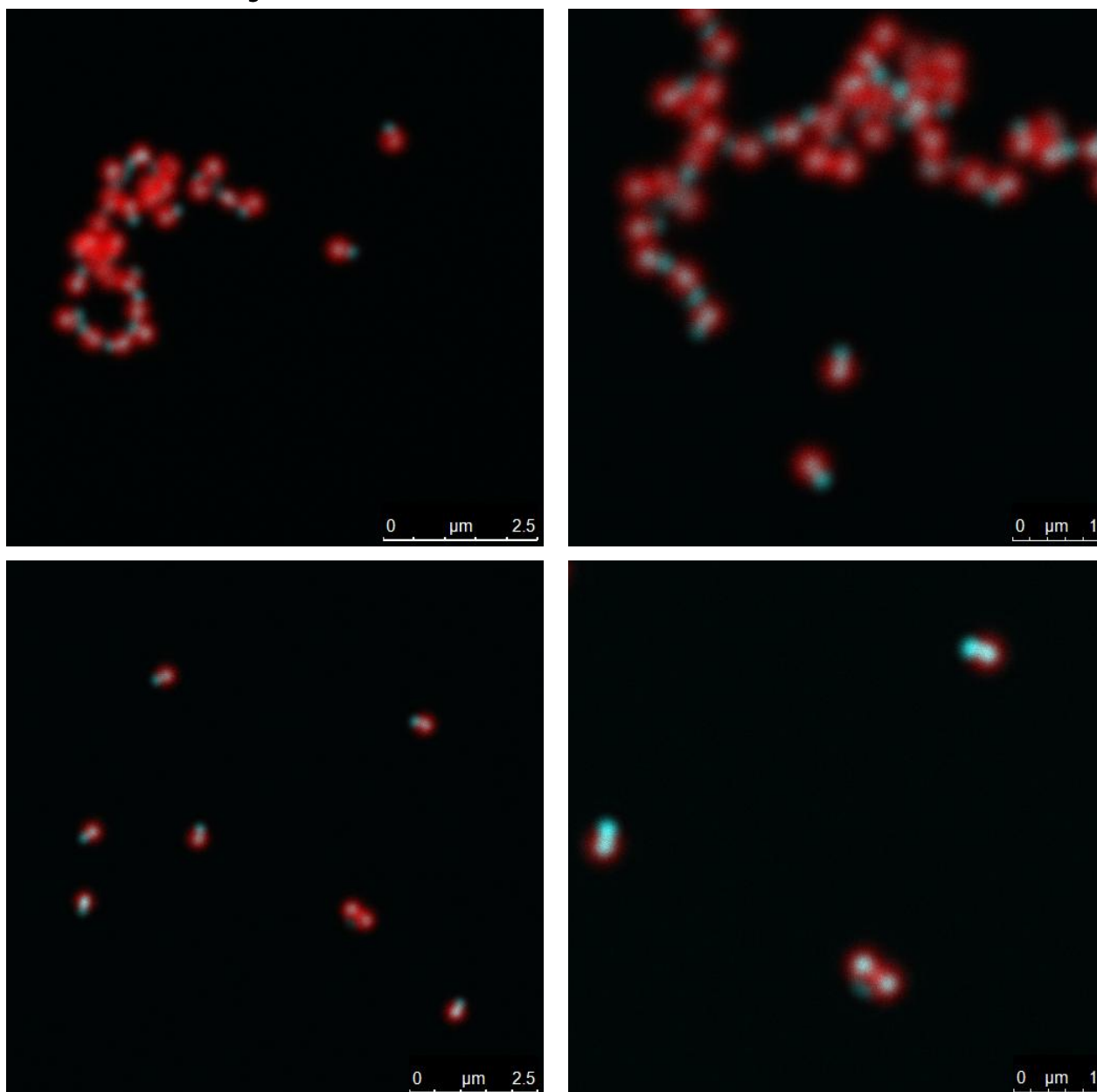**Additional confocal images of fluoresceinamine functionalized dumbbells.**

Figure S8. Confocal images of anisotropic particles after reaction of the chlorinated patch with fluoreseceinamine. Image captured by combining two imaging channels, with one recording in reflection mode (cyan) and the other is fluorescence mode (red).

References

(1) Kraft, D.J.; Vlug, W.S.; Van Kats, C.M.; Van Blaaderen, A.; Imhof, A.; Kegel, W.K. *J. Am. Chem. Soc.* **2009**, *131*, 1182-1186

(2) Maurer, M.K.; Lednev, I.K.; Asher, S.A. *Adv. Func. Mater.* **2005**, *15*, 1401-1406

(3) Breed, D.R.; Thibault, R.; Xie, F.; Wang, Q.; Hawker, C.J.; Pine, D.J. *Langmuir*, **2009**, *25*, 4370-4376

(4) Fox, M.A.; Whitesell, J.K. *Organic Chemistry*, 3rd ed., Jones and Bartlett publishers, Sudbury, **2003**, pp. 373-375

(5) Haensch, C.; Hoeppener, S.; Schubert, U.S. *Nanotechnology*, **2008**, *19*, 1-7