Electronic Supplementary Information

Self-assembly of colloidal molecules that respond to light and magnetic field

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Experimental procedures

Materials and instruments

All chemicals used in this study were purchased from Alfa Aesar (Karlsruhe, Germany), Sigma-Aldrich Chemie (Taufkirchen, Germany), or TCI Europe (Zwijndrecht, Belgium) and used without further purification. *β*-CD was kindly donated by Wacker Chemie (Burghausen, Germany). Solvents were dried according to conventional methods before use. Moisture sensitive reactions were carried out in oven-dried glassware under inert atmosphere.

Analytical thin layer chromatography was performed on Merck silica gel 60 F254 plates. Visualization of the compounds was achieved either under UV-light of 254 nm with a dual wavelength UV lamp (254 and 366 nm) (CAMAG, Muttenz, Switzerland) or by staining with basic permanganate solution.

For column chromatography, silica gel 60 (230−400 mesh) was used. NMR spectra were recorded on a Bruker AV300 (300 MHz), Bruker AV400 (400 MHz), or Agilent DD2 (600 MHz) spectrometer. Chemical shifts were referenced to internal standards.

UV/vis- and OD600 measurements were conducted using a JASCO V-650 double-beam spectrophotometer (JASCO Labor- and Datentechnik GmbH, Gross-Umstadt) at 25 °C using 1 mL low-volume disposable PMMA cuvettes (Brand GmbH & CO KG, Wertheim). The spectrometer was controlled by Spectra Manager version 2.08.04 (Jasco Labor- and Datentechnik GmbH, Gross-Umstadt). The samples were dissolved in an appropriate solvent and measured against the same solvent. Data analysis was carried out using OriginPro 9.1G (OriginLab Corp., Northampton, MA).

Optical and fluorescence microscopy were performed using an Olympus CKX41 microscope. For fluorescence excitation, an X-Cite 120Q source from Lumen Dynamics was used. Fluorescence images were obtained using suitable filters. Images were recorded using an Olympus XC-30 camera controlled by Stream Essentials (v. 1.9). Insertion of scale bars and image corrections were carried out with ImageJ (v. 1.51).
Scanning electron microscopy SEM with a field emission gun (Schottky-type) was used to investigate the particle size and morphology. The multiple areas per sample were analyzed in an Auriga CrossBeam workstation from Zeiss without additional treatments at an acceleration voltage of 3 kV with a working distance of 2 mm.

Transmission electron microscopy TEM investigations were performed using a Zeiss Libra 200FE with in-column energy filter (Carl Zeiss AG, Oberkochen, Germany) equipped with a Gatan US 4000 CCD camera (Gatan GmbH, München, Germany). For size measurements ImageJ 1.45s (National Institutes of Health, Bethesda, MD) was used. TEM samples were prepared by immersing the copper grid in the nanoparticle solution for 20 s. Grids were dried under ambient conditions overnight.

Photoswitching experiments were performed using two different light sources, a Rayonet photochemical reactor (The Southern New England Ultraviolet Company) equipped with 16 RPR-3500 lamps (365 nm) for *E*→*Z*-isomerization and a LSC-G HighPower-LED emitting at 520 nm for Z→E-isomerization.

Preparation of vinyl-functionalized silica particles

Silica particles were obtained from micro particles GmbH as a dry powder. They were obtained with an average diameter of 6.65 µm, a standard deviation of 0.28 µm and a coefficient of variance of 4.2. Prior to functionalization, 25 mg of the particles were stirred in boiling conc. hydrochloric acid (3.0 mL) for 7 h, collected by centrifugation (10.000 rpm, 5 min) and washed in Milli Q water (3x), abs. ethanol (1x) and dry toluene (3x). The particles were then dispersed in 4.0 mL dry toluene and n octenyl trichlorosilane (0.6 mL) was added. The dispersion was stirred overnight at rt under inert atmosphere. The particles were purified by centrifugation (10.000 rpm, 5 min) and redispersion in dry toluene (3x) and dry DMF (3x) and stored at 4 °C until use.

Sandwich microcontact printing

PDMS stamps were prepared from Sylgard 184 (10:1 prepolymer and cross-linker) dropcasted on a pre-patterned silicon wafer and heated in an oven at 80 °C for 3 nights. The PDMS stamps were cut into pieces of 1.5 x 2.0 cm and oxidized in the ozonizer for 55 min. The stamps were washed in abs. ethanol for 5 min to remove uncured PDMS oligomers and stored in water before printing (max. 30 min after oxidation). A monolayer of the vinyl-functionalized silica particles was prepared by spreading the particle dispersion on a glass slide, while toluene was evaporated. Two oxidized PDMS stamps were incubated with 200 µL of ink solution (ATRP-TAD initiator (8.6 mg, 25 µmol) in 1.0 mL of dry ACN) for 1 min. Next, the stamps were dried by an argon stream. The first inked stamp was used to lift up the particles from the monolayer, by gently pressing it on the glass slide. The second inked stamp was pressed onto the first stamp with particles sticking on the surface. As a result, the particles are sandwiched between the two stamps. The stamps were fixed with some pressure in a special squeezer for 15 min at 80 °C. Finally, the particles were detached from the stamps by sonification in abs. ethanol for 20 min. The particles were purified by centrifugation (10.000 rpm, 5 min) and redispersion in abs. ethanol (1x), ACN (1x) and DMF (3x; centrifugation at 10.000 rpm, 10 min).

Growth of polymer brushes

HEA (1.29 g, 11.07 mmol), AAPA (0.36 mg, 830 µmmol, 7.5 mol%; for AAPA functionalized brushes) and NBDA (15 mg, 50 µmol, 0.5 mol%) were added to a Schlenk tube under argon atmosphere. ATRP-TAD initiator printed particles in 1.0 mL of dry DMF were added. Additionally, a solution (0.25 mL) of Cu(II)Br_2 (5 mg, 22 µmol) and Tris[2-(dimethylamino)ethyl]amine (36 mg, 110 µmol) in DMF (10 mL) was added. The tube was subjected to three freeze/thaw cycles with intermediate argon purges in liquid nitrogen. After adding ascorbic acid (6 mg, 35 µmol) the tube was heated at 65 °C for 36 h. The particles were collected by centrifugation and redispersed in DMF (3x), ACN (2x), DCM (1x) and DMF again. Prior to assembly experiments, additional purification in Milli Q water (3x) was carried out. The concentration of the polymer particles was around 0.7 mg/mL after purification. The concentration varied depending on the stamp size and quality of the monolayer.

Synthesis of CD functionalized magnetite nanoparticles

Magnetite nanoparticles functionalized with per-6-deoxy-per(carboxylpropyl)thio-β-cyclodextrin were synthesized by co-precipitation.[1] The synthesis was carried out under argon atmosphere. Ferrous sulfate heptahydrate (0.69 g, 2.50 mmol) and ferric chloride hexahydrate (1.35 g, 5.00 mmol) were dissolved in 60 mL of degassed Milli Q water. The solution was stirred vigorously, followed by a quick addition of NH3 solution (25%, 15 mL). The colour of the solution changed from orange to black due to the formation of a black precipitate. Under vigorous stirring the solution was heated to 60 °C for 1 h. Afterwards, the reaction mixture was cooled

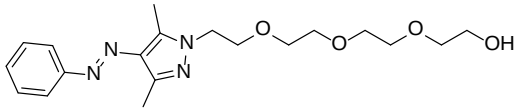
down to room temperature and the formed iron oxide nanoparticles were washed with Milli Q water until the pH of the solution became neutral (pH 7). The concentration was defined by removing the solvent of 1 mL nanoparticle solution in vacuum and weighing the residue. The volume required for 10 mg of nanoparticles was sonicated for 30 min. A solution of per-6-deoxy-per(carboxylpropyl)thio-β-cyclodextrin in Milli Q water (35 mg, 0.02 mmol, 3 mL, pH adjusted to pH = 10 by dropwise addition of NH3 solution (25%)) was added. The solution was sonicated for 3 h and the nanoparticles were washed twice with Milli Q water to remove the ligand excess. The solution was filtered two times through syringe filters (Rotilabo® filters, pore size: 0.2 µm) before experiments. The functionalized nanoparticles were characterized by TEM (see Fig. S9), dynamic light scattering (hydrodynamic diameter 35-45 nm) and zeta potential measurements (zeta potential -37 mV).

Assembly, magnetic manipulation and light-response

Janus particles and magnetite nanoparticles were each dispersed in Milli Q water by centrifugation and redispersion for at least three times. Concentrations around 1 mg/mL for the magnetic nanoparticles and 0.7-1.0 mg/mL for the silica Janus particles were used. The particles were sonicated for 3 min and then mixed in different proportions. A droplet of the particle mixture was analysed by light and fluorescence microscopy on a thin glass slide. For magnetic manipulation, a strong neodymium magnet was held close to the droplet and moved around it. This resulting movement of the particle assembly was recorded directly by the microscope. For light-responsive assembly and disassembly, the particle mixture was irradiated by UV light (365 nm) for 3 h. The mixture was sonicated for 2 min after 1 h, 2h, and 3h. A small droplet of the particle mixture was analysed by using light microscopy on a thin glass slide. Next, the particle mixture was irradiated for 2 h with green light (520 nm) and sonicated for 2 min after 1 h and 2 h. A droplet of the mixture was analysed using light microscopy on a thin glass slide. Irradiation experiments were repeated for three cycles.

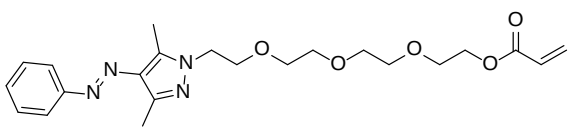
Synthesis of AAPA

AAP-TEG



To a stirred solution of the AAP core[2] (2.51 g, 12.55 mmol, 1 eq.) in 150 ml of dry acetonitrile, containing K_2CO_3 (8.67 g, 62.75 mmol, 5 eq.) and catalytic amounts of LiBr, tosylated tetraethyleneglycol (2.99 g, 15.11 mmol, 1.2 eq.) dissolved in acetonitrile (50 mL) was added and the reaction mixture was refluxed for 3 days under argon. It was then allowed to cool to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in DCM (120 mL), washed with water (100 mL) and brine (3 × 100 mL). The organic phase was dried over $MgSO_4$ and concentrated. The residue was purified by silica gel column chromatography (eluent, DCM/methanol 95:5) to afford the title compound. **Yield:** 4.21 g (11.19 mmol, 89%) as red oil. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.83 – 7.73 (m, 2H), 7.51 – 7.40 (m, 2H), 7.40 – 7.30 (m, 1H), 4.22 (t, *J* = 5.4 Hz, 2H), 3.86 (t, *J* = 5.4 Hz, 2H), 3.72 – 3.64 (m, 2H), 3.64 – 3.48 (m, 10H), 2.61 (s, 3H), 2.50 (s, 3H) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 153.66, 142.51, 140.58, 135.00, 129.43, 128.98, 121.84, 72.57, 70.78, 70.67, 70.60, 70.40, 69.96, 61.74, 49.11, 14.15, 10.02 ppm. **MS (m/z):** (ESI, MeOH) Calculated for $[C_{19}H_{28}N_4O_4Na]^+$: 399.2003, found 399.2017.

Synthesis of AAP acrylate



Triethylamine (4.57 mL, 33 mmol, 3 eq.) was added to a solution of AAP-TEG (4.14 g, 11 mmol, 1 eq.) in dry DCM (50 mL). To this, a solution of acryloylchloride (2.7 mL, 33 mmol, 3 eq.) in dry DCM (20 mL) was added dropwise at 0 °C. Afterwards the solution was allowed to warm to room temperature and was stirred for 18 h. Water was added (75 mL) and the layers were separated. The organic layer was washed with brine (3 × 75 mL), dried with $MgSO_4$ and concentrated under reduced pressure. Purification via column chromatography (DCM/methanol 98:2) yielded the desired compound. **Yield:** 4.2 g (9.76 mmol, 89%) as red oil. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.76 – 7.64 (m, 2H), 7.44 – 7.34 (m, 2H), 7.34 – 7.25 (m, 1H), 6.34 (dd, *J* = 17.3, 1.5 Hz, 1H), 6.06 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.75 (dd, *J* = 10.4, 1.5 Hz, 1H), 4.28 – 4.11 (m, 4H), 3.79 (t, *J* = 5.4 Hz, 2H), 3.66 – 3.59 (m, 2H), 3.58 – 3.44 (m, 8H), 2.55 (s, 3H), 2.44 (s, 3H) ppm. **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 166.27, 153.71, 142.58, 140.64, 131.15, 129.43, 129.02, 128.37, 121.87, 70.92, 70.73, 70.67, 70.06, 69.22, 63.77, 49.20, 14.26, 10.06 ppm. **MS (m/z):** (ESI, MeOH) Calculated for $[C_{22}H_{30}N_4O_5Na]^+$: 453.2108, found 453.2103.

Synthesis of TAD ATRP initiator

The triazolindione (TAD) ATRP Initiator was synthesized according to the literature.[3,4]

Synthesis of NBD acrylate

The NBD acrylate (NBDA) was synthesized according to the literature.[4]

Control experiments – Sandwich microcontact printing

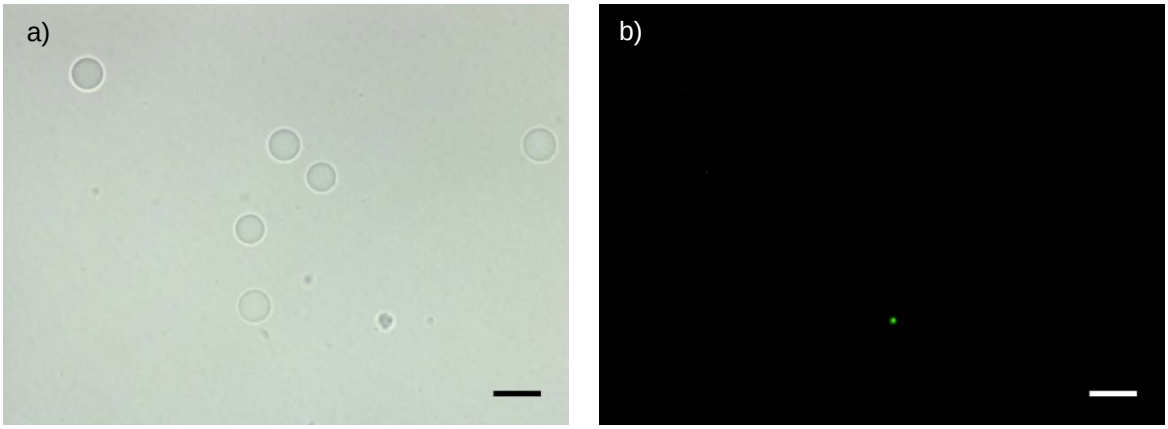


Fig. S1 a) Light microscopy of silica microparticles printed without ATRP-TAD initiator on both sides by sandwich microcontact printing, followed by a PNBDA-PHEA copolymerisation. Stamps were only incubated with acetonitrile. b) Fluorescence microscopy of the same particles. Scale bar: 10 µm.

SEM of particle oligomers

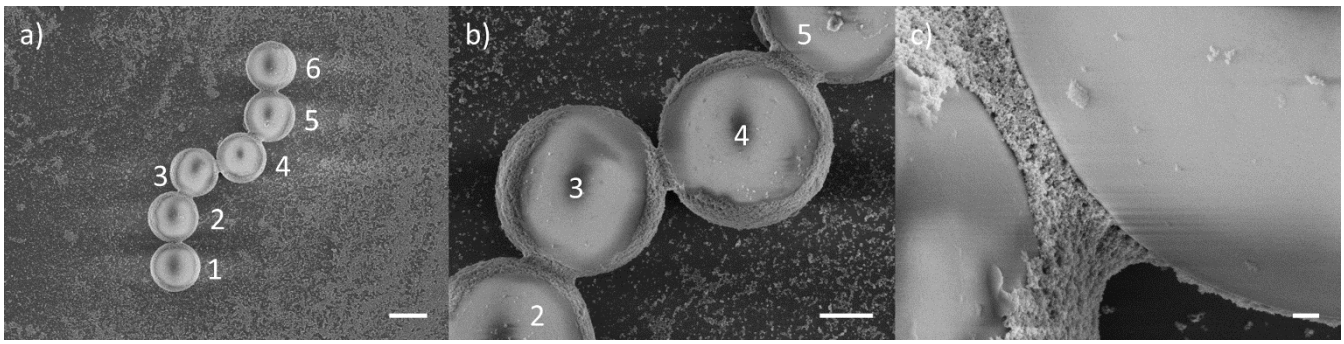


Fig. S2 SEM of PAAPA-PNBDA-PHEA-copolymerized microparticles with the CD MNPs at 2000-fold magnification. Scale bar: 5 µm; b) SEM of particles 3 and 4 at 7000-fold magnification. Scale bar: 2 µm; c) Zoom-in at 35.000-fold magnification. Scale bar: 200 nm.

Control experiments – Supramolecular interaction

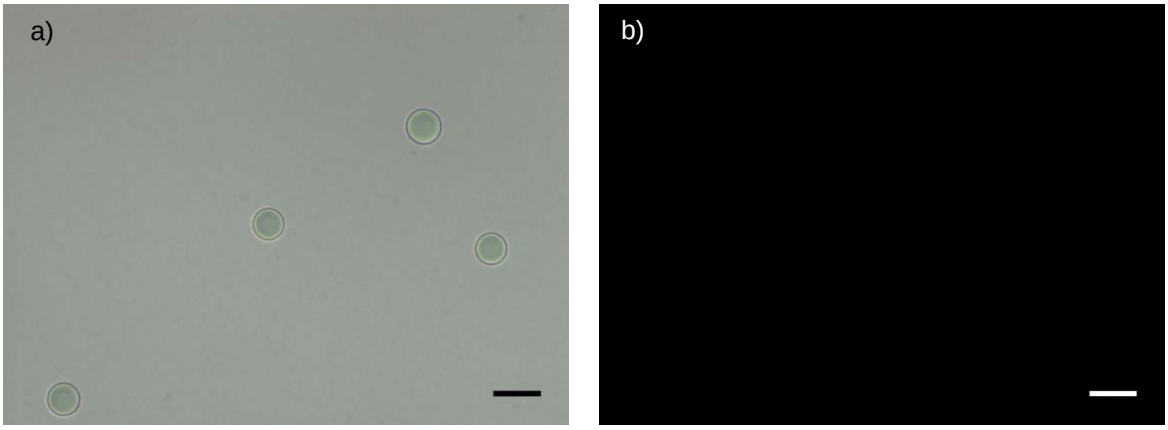


Fig. S3 a) Light microscopy of silica microparticles printed without ATRP-TAD initiator on both sides by sandwich microcontact printing, followed by a PNBDA-PHEA copolymerization. Stamps were only incubated with acetonitrile, mixed with CD MNPs in Milli Q water. b) Fluorescence microscopy of the same particles. Scale bar: 10 µm.

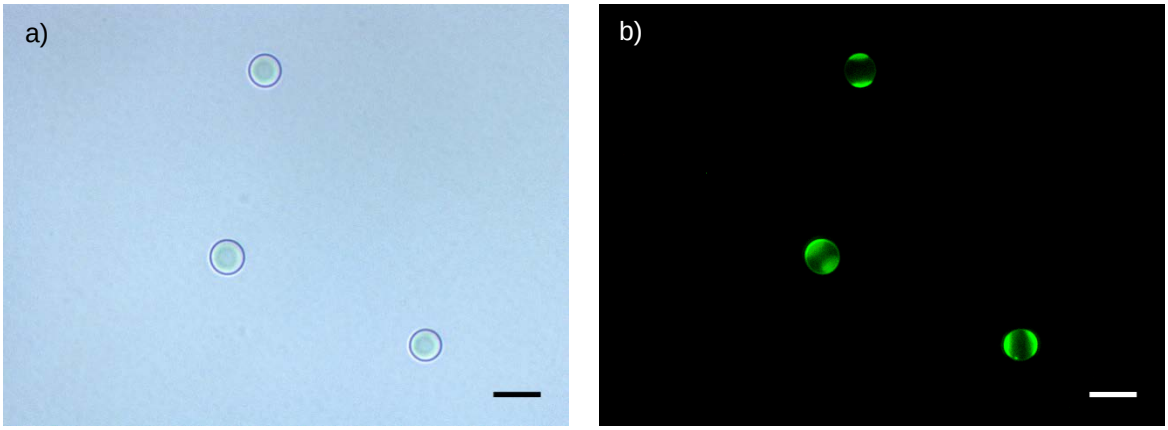


Fig. S4 a) Light microscopy of silica microparticles printed with ATRP-TAD initiator on both sides by sandwich microcontact printing, followed by a PNBDA-PHEA copolymerisation, mixed with CD MNPs in Milli Q water. b) Fluorescence microscopy of the same particles. Scale bar: 10 µm.

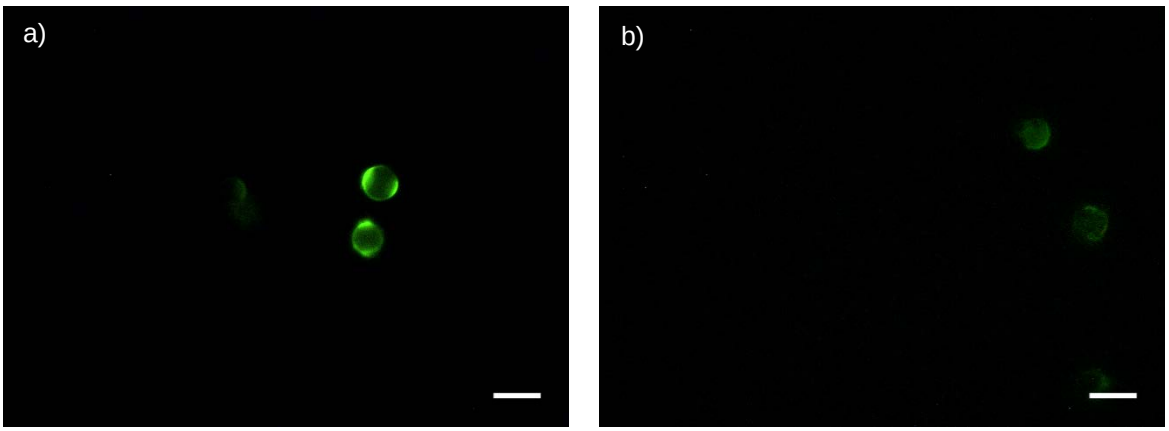


Fig. S5 a) Fluorescence microscopy of silica microparticles printed with ATRP-TAD initiator on both sides by sandwich microcontact printing, followed by a PNBDA-PHEA copolymerisation, mixed with undecorated NPs in Milli Q water. b) Fluorescence microscopy of silica microparticles printed with ATRP-TAD initiator on both sides by sandwich microcontact printing, followed by a PAAPA-PNBDA-PHEA copolymerisation, mixed with undecorated NPs in Milli Q water. Scale bar: 10 µm.

Overview pictures

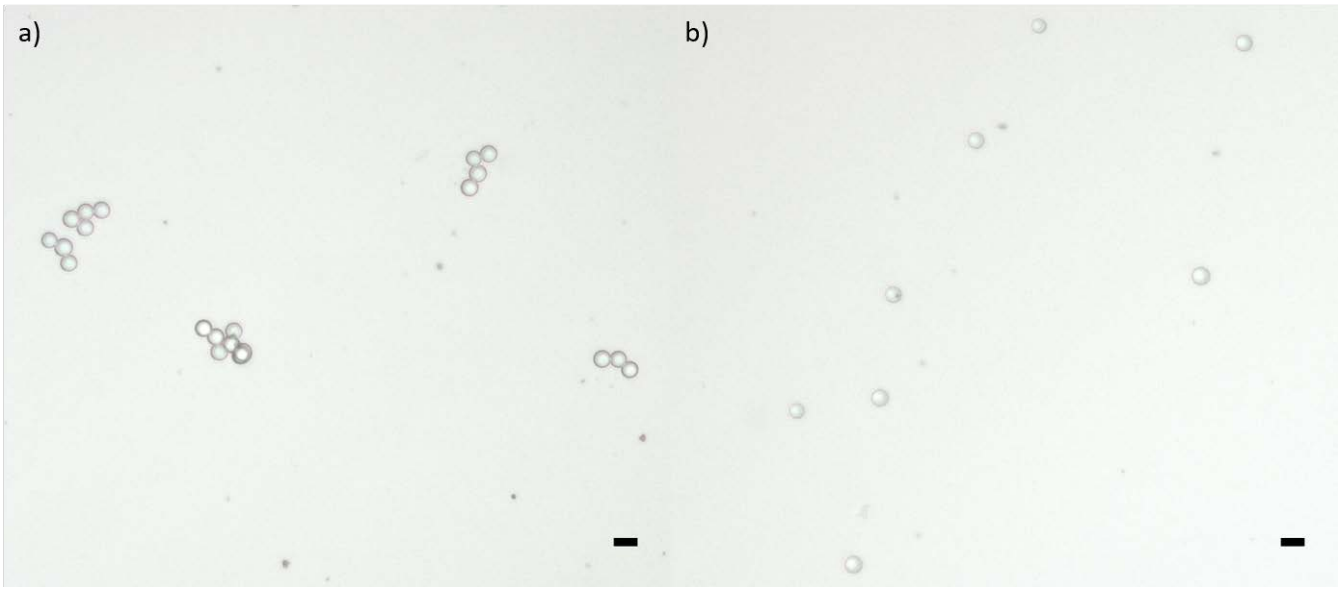


Fig. S7 Overview pictures of light-responsive self-assembly of Janus particle oligomers at lower magnification after mixing (a) and after UV irradiation (b); scale bar = 10 µm.

UV/vis spectrum of AAP-TEG

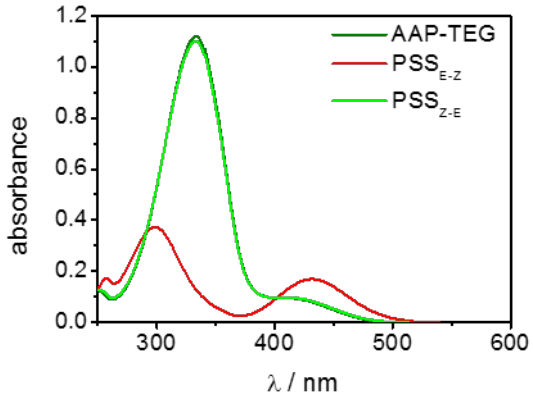


Fig. S8 UV/Vis-spectrum of AAP-TEG with a concentration of c = 35 µmol in water.

Characterization of magnetite nanoparticles

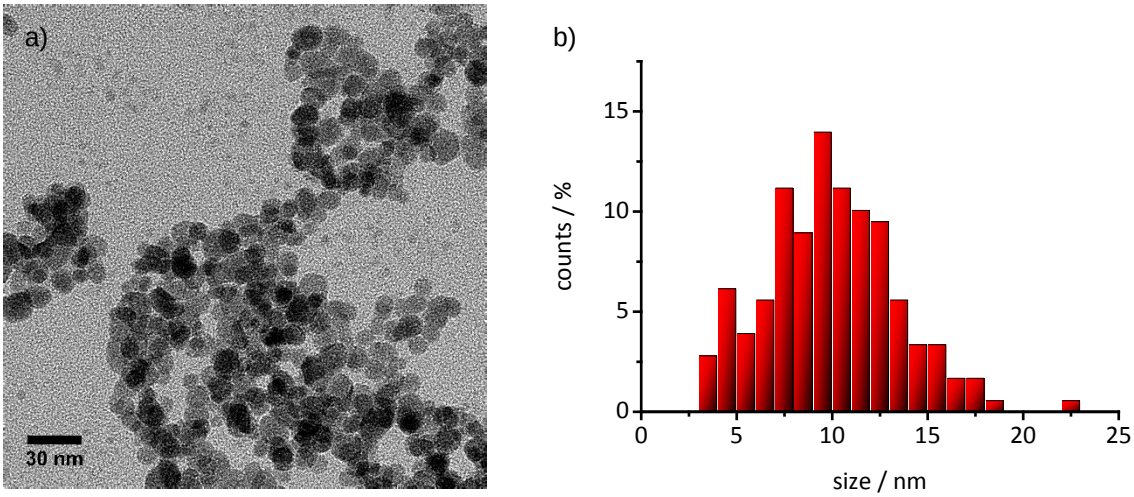


Fig. S9 a) TEM image of CD MNPs; b) size distribution of the CD MNPs.

References

1 A. Samanta and B. J. Ravoo, *Angew. Chem. Int. Ed.,* 2014, **53**, 12946.

2 L. Stricker, E.-C. Fritz, M. Peterlechner, N. L. Doltsinis and B. J. Ravoo, *J. Am. Chem. Soc.,* 2016, **138**, 4547.

3 S. Billiet, K. De Bruycker, F. Driessen, H. Goossens, V. Van Speybroeck, J. M. Winne and F. E. Du Prez, *Nat. Chem.,* 2014, **6**, 815.

4 O. Roling, K. De Bruycker, B. Vonhören, L. Stricker, M. Körsgen, H. F. Arlinghaus, B. J. Ravoo and F. E. Du Prez, *Angew. Chem. Int. Ed.,* 2015, **54**, 13126.

NMR spectra of AAP-TEG

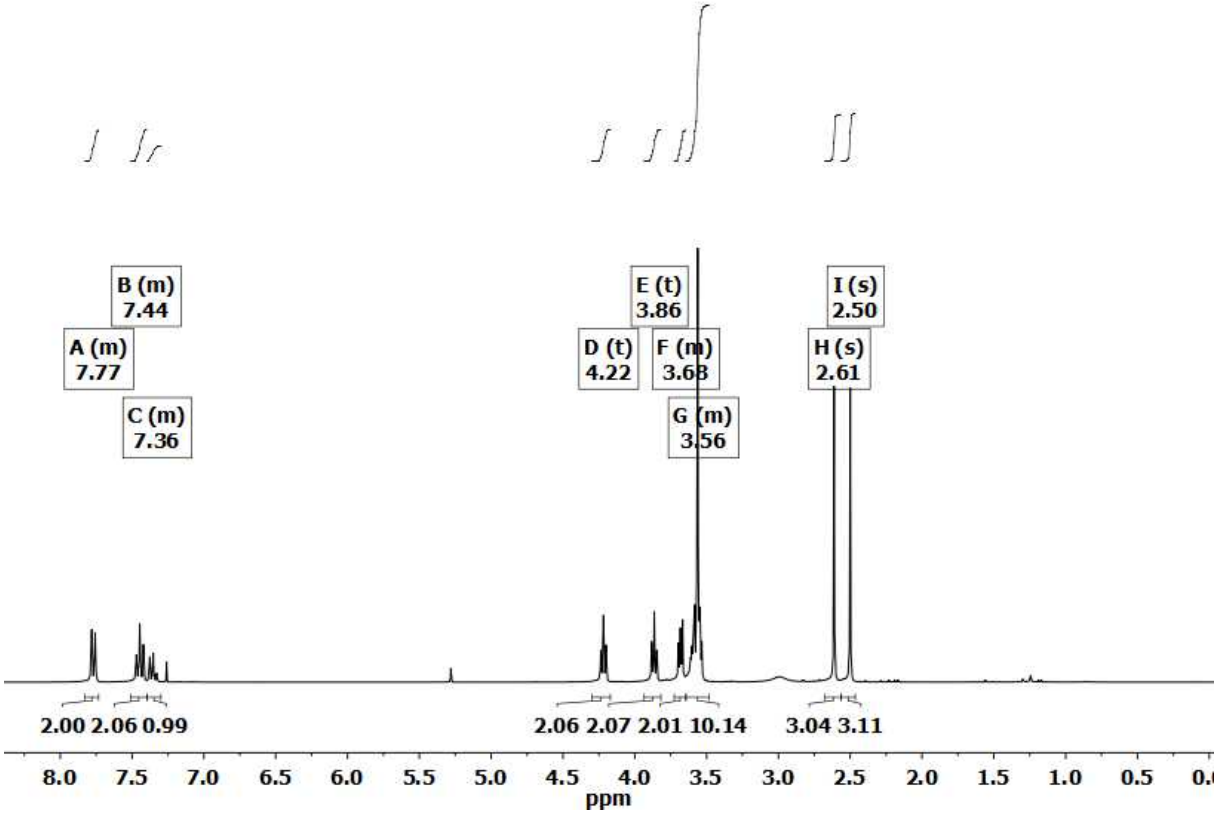


Fig. S10 ^{1}H-NMR of AAP-TEG.

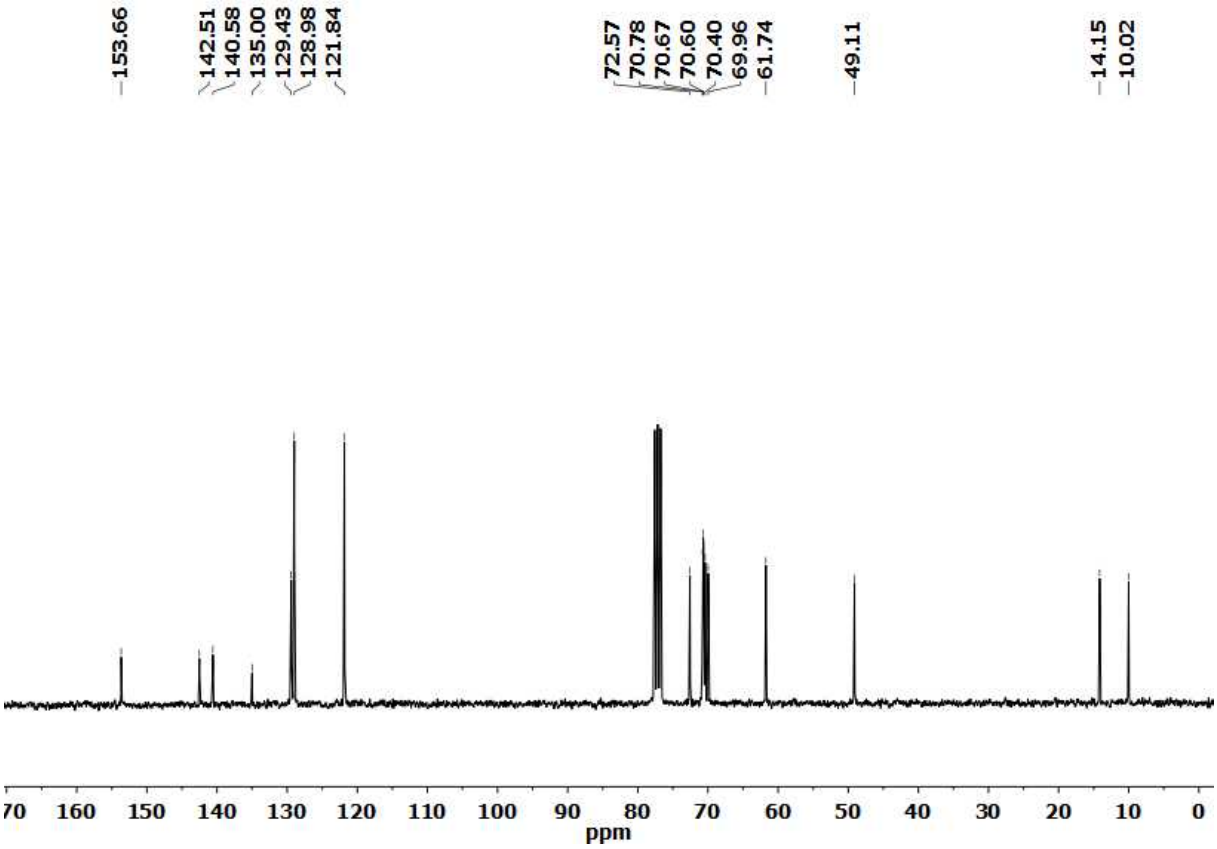


Fig. S11 ^{13}C-NMR of AAP-TEG.

NMR spectra of AAP acrylate

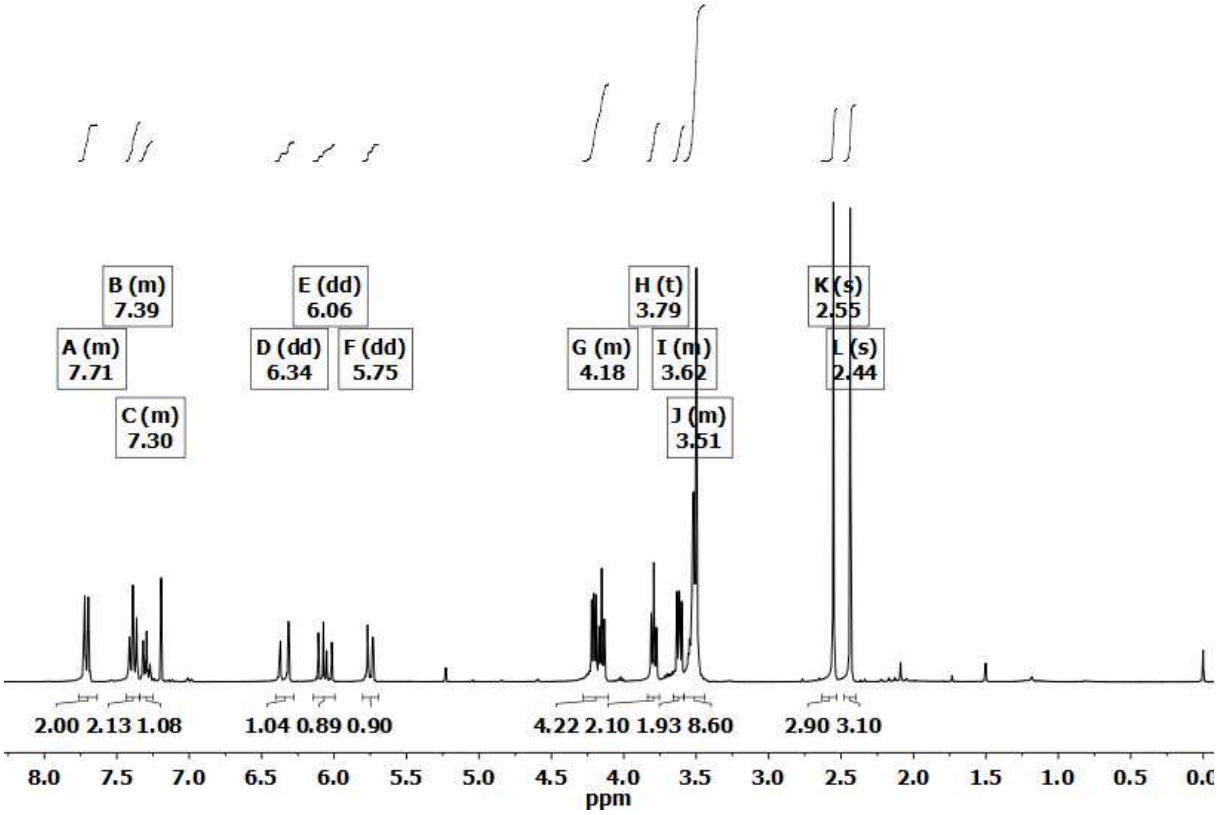


Fig. S14 ^{1}H-NMR of AAP acrylate.

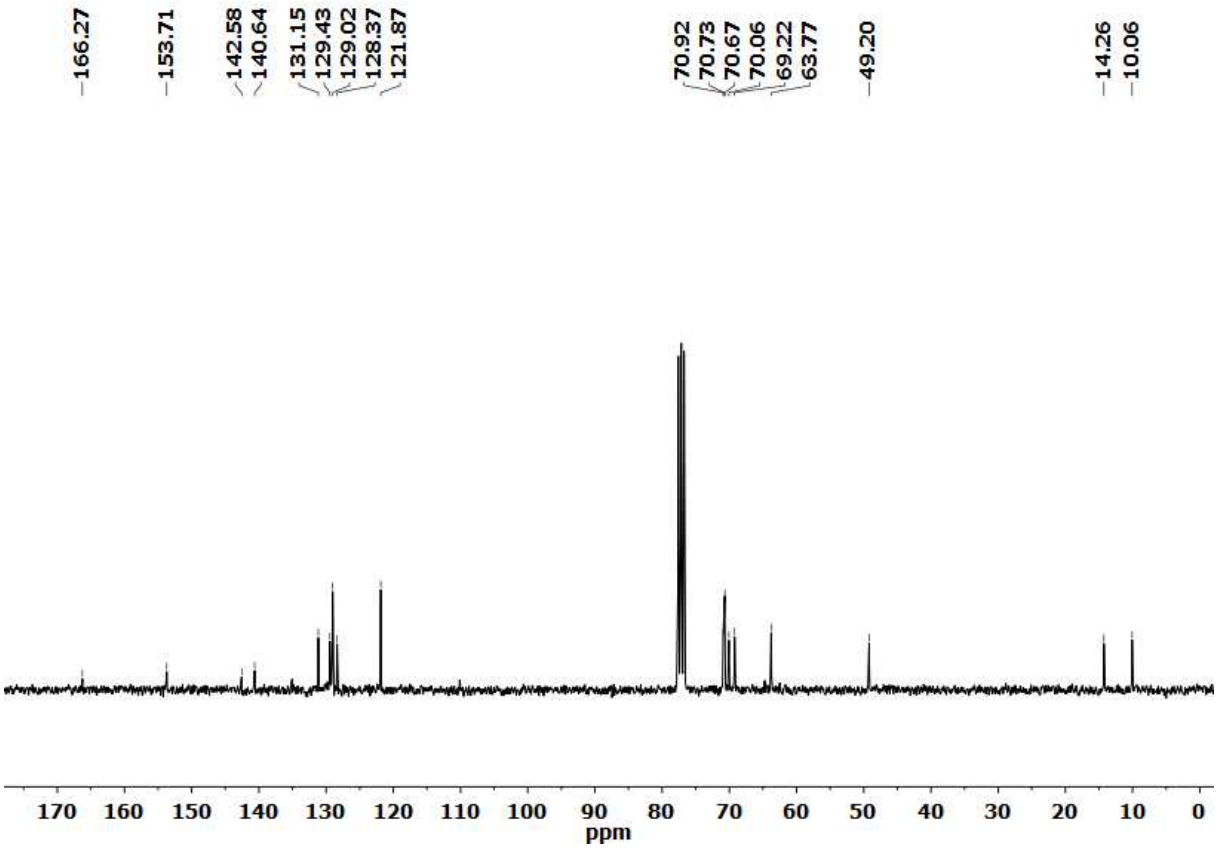


Fig. S15 ^{13}C-NMR of AAP acrylate.