SUPPORTING INFORMATION for

Dissipative disassembly of colloidal microgel crystals driven by a coupled cyclic reaction network

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Materials

The merocyanine photoacid: (3H-indolium, 2-[(1E)-2-(2-hydroxyphenyl)ethenyl]-3,3-dimethyl-1-(3-sulfopropyl)-, inner salt) was synthesized as reported previously [Ref. 8 in Manuscript: Y. Liao *et al.*, *J. Am. Chem. Soc.*, 2011, **133**, 14699–14703].

All of the other chemicals are purchased from Sigma Aldrich and used without any further purification. *N*-Isopropylacrylamide (NIPAM) (97 %), styrene (>99 %), sodium dodecyl sulfate (SDS) (98 %), *N*,*N'*-methylenebis(acrylamide) (MBA) (99 %), Nile red (98 %), 2-(*N*-morpholino)ethanesulfonic acid (99 %), 4-(2-hydroxyethyl)-1-piperazineethanesulfonicacid (HEPES) (98 %), *N*-hydroxysuccinimide (NHS) (98 %), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC) (98 %), *N, N*-dimethylethylenediamine (DMEDA) (99 %), potassium peroxodisulfate (KPS) (>99 %).

Experimentals

Zeta potential measurements are carried out using a Zetasizer Nano ZS from Malvern Instruments at 25 °C. The samples are prepared by diluting 10 µL of particle dispersions with 1 mL of the corresponding aqueous solution. The pH is set using automatic titration via MPT-2 autotitrator from Malvern Instruments. Every data point represents an average value of three measurements. Each measurement consists of a set of runs, which is performed until convergence (max. 100 runs). The zeta potential is determined from the electrophoretic mobility based on the Helmholtz-Smoluchowski relationship.

Confocal laser scanning microscopy is performed on a Leica TCS SP8. Fluorescently labelled particles are used to visualize and analyze the core-shell microgel's structure. The sample chamber is the well of a 96-well microplate with a glass bottom. The Nile red labelled PS-cores are excited with $\lambda = 561$ nm and the resulting emission is detected at the range $\lambda = 640 – 750$ nm. In order to monitor the phase transition between the colloidal crystalline and the liquid state, 100 µL of the microgel sample and 5 µL of the 0.2 mM photoacid solution are filled in one well. The sample is irradiated with the integrated UV diode laser with pulses of $\lambda_{em} = 405$ nm (730 mW). The pulses last 5 s each except for the first pulse that lasts 130 s. This is necessary to overcome the initial buffer capacity of the microgels, see manuscript for discussion. After each pulse, the system is monitored at a scanning speed of 400 Hz, an area size of 23.75 µm x 23.75 µm and a penetration depth of approximately 55 µm until the crystalline structure is reassembled.

Transmission electron microscopy is carried out using a Zeiss Libra 120 operating at 120 kV in zero-loss energy-filter mode. 10 µL core-shell microgel dispersions in 1 mL deionized water are dried on carbon-coated copper grids (Electron Microscopy Sciences) at room temperature before imaging.

Dynamic light scattering measurements are performed with a laser light scattering spectrometer (ALV/DLS/SLS-5000) equipped with an ALV-5000/EPP multiple digital time correlator and laser goniometry system ALV/CGS-8FS/N025 with a helium-neon laser (Uniphase 1145P, output power of 22 mW and wavelength of $\lambda = 632.8$ nm) as a light source.

pH measurements over time are carried out using a Titrando 905 from Metrohm. The pH and its changes upon photoacid generation are detected and recorded automatically. To initiate the pH switch, the aqueous photoacid solution at a concentration of 0.2 mM is exposed to an array of LEDs with $\lambda_{em} = 400 – 500$ nm ($\lambda_{max} = 450$ nm) and output power of 13 W.

Synthesis of polystyrene (PS) core particles: The fluorescent core particles are synthesized by emulsion polymerization of styrene initiated with 0.1 wt% of KPS. 5 mg (0.016 mmol) of the fluorescent marker Nile Red, are dissolved in 13.5 g (129.6 mmol) styrene. The organic solution is transferred into a two-necked round bottom flask. 0.025 g (0.087 mmol) of SDS and 1.50 g (13.3 mmol) of NIPAM are dissolved in 45 mL of deionized water and added to the organic solution. (NIPAM is added here to achieve better surface compatibility for the subsequent condensation of the NIPAM microgel shell.) While degassing the emulsion with argon, it is heated up to a temperature of 80 °C and the KPS, pre-dissolved in 5 mL deionized water, is added to initiate the polymerization. The reaction is allowed to proceed for 24 hours at 80 °C. To remove SDS residuals the redispersed particles were dialysed in deionized water for 24 - 72 h.

Synthesis of PS-core-PNIPAM-shell colloids: The core-shell microgels are prepared by surfactant seeded precipitation polymerization of comonomers around the fluorescent labelled PS-cores. NIPAM (2,3 g; 20,3 mmol), MBA (23 mg; 0,15 mmol) and AAc (177 µL; 184 mg; 2,55 mmol) are dissolved in water (95 mL). 5 mL of the PS-particle despersion were added and heated up to 70 °C while the mixture was stirred. KPS (50 mg; 0,37 mmol) dissolved in water (5 mL) was added after the emulsion was stirred for 15 min at 70 °C. After 2 h of stirring at 70 °C the reaction was stopped by contact with air. The mixture was directly filtered at a temperature above the LSCT of the polyNIPAM shell. The purification of the microgels was carried out via dialysis in water for 24 - 72 h.

Post-modification via *1-Ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC)/N-Hydroxy-succinimide (NHS)*: The prepared anionic PS-core P(NIPAM-*co*-AAc)-shell microgels were functionalized via EDC-NHS coupling. 20 mL of the anionic core-shell microgel were mixed with solutions of NHS (307 mg ; 2,67 mmol) in 5 mL 2-(N-morpholino)-ethanesulfonic acid (MES)-buffer (100 mM; pH = 4,5) and EDC (205 mg; 1,07 mmol) in 5 mL MES-buffer (100 mM; pH = 4,5) and carefully stirred (50 rpm) for 15 min at 25 °C. A solution of *N*,*N*-dimethylethylenediamine (292 µL, 2,71 mmol) in 5 mL 4-(2-hydroxyethyl)-1-

piperazineethanesulfonic acid (HEPES)-buffer (100 mM; pH = 7,0) was added. The mixture was stirred at 25 °C for 24 h. The resulting microgels were adjusted to their starting volume via centrifugation with following decantation and addition of deionised water. After particle redispersion, the residual reactants were removed via dialysis in water for 24 - 72 h.

Digital image processing: Particles are tracked based on a method originally proposed by Grier et al. [J.C. Crocker and D.G. Grier, Methods of digital video microscopy for colloidal studies, *Journal of Colloid and Interface Science* **179**:298-310 (1996)]. Briefly: images are filtered using a band-pass filter constructed as the difference of an image convolved with a narrow Gaussian kernel and another with a broader box-car kernel. The resulting image is thresholded (typically at 50-70% of the intensity range of the filtered image) and the local peaks are identified. An accurate location is estimated as the statistical first momentum of the intensity distribution in a circle of user defined radius around the previously identified peaks. These positions are then recorded for further processing.
Overall order is visualized by calculating a self-convolution of the original images (for centrosymmetric images this is equivalent to autocorrelation), of which the absolute values are displayed within a window of +/- 100 pixels around the center peak.
The corresponding software is written in Python, an interpreted scripting language and available online. The basic image processing functions are part of the ImageP package [T. Haraszti: ImageP: image processing add-ons to Python and numpy. 2017 2009, https://launchpad.net/imagep].

Order parameters are estimated using the method published in [A.E. Larsen and D.G. Grier, Melting of metastable crystallites in charge-stabilized colloidal suspensions, *Physical Review Letters* **76(20)**:3862-3865 (1996)]. Briefly, iterating through all positions, the $N = 6$ closest neighbours are selected within a 50 pixel radius (if there are less, then N is modified accordingly). An order parameter (Ψ_N) is calculated as the absolute value of the average of the complex $exp(\, i\, N\, \Theta)$ values, where Θ is the relative angle of the neighbour from the center. For visualizing time evolution the average of the order parameters (of all identified particles) is plotted as the function of time.

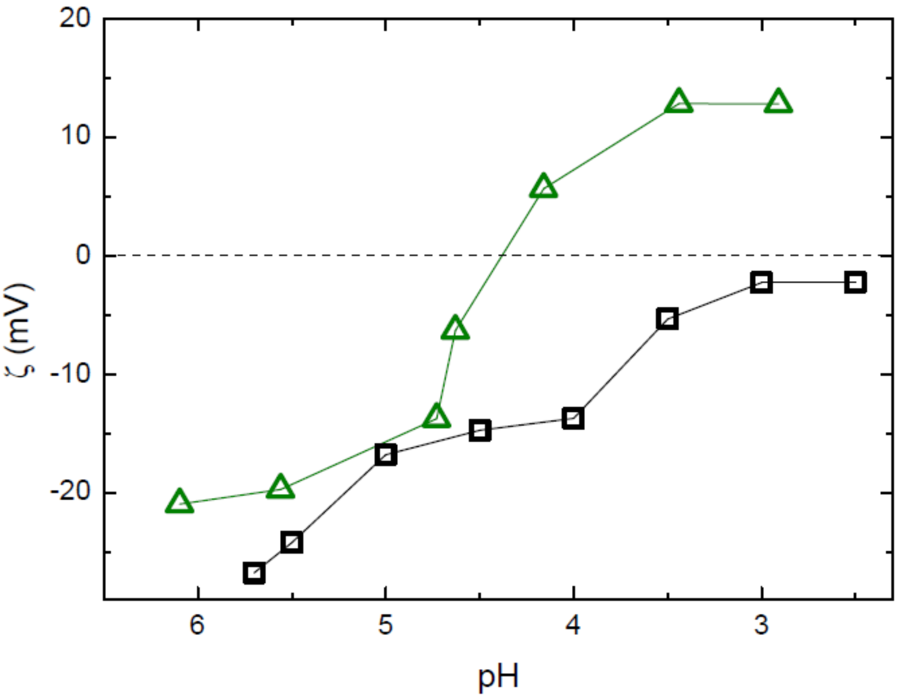

Figure S1: Equilibrium ζ-potential of the anionic P(NIPAM-co-AAc) (black squares) and the polyampholyte (green triangles) core-shell microgels at various pH. The IEP of the polyampholyte microgel system is at pH 4.5.

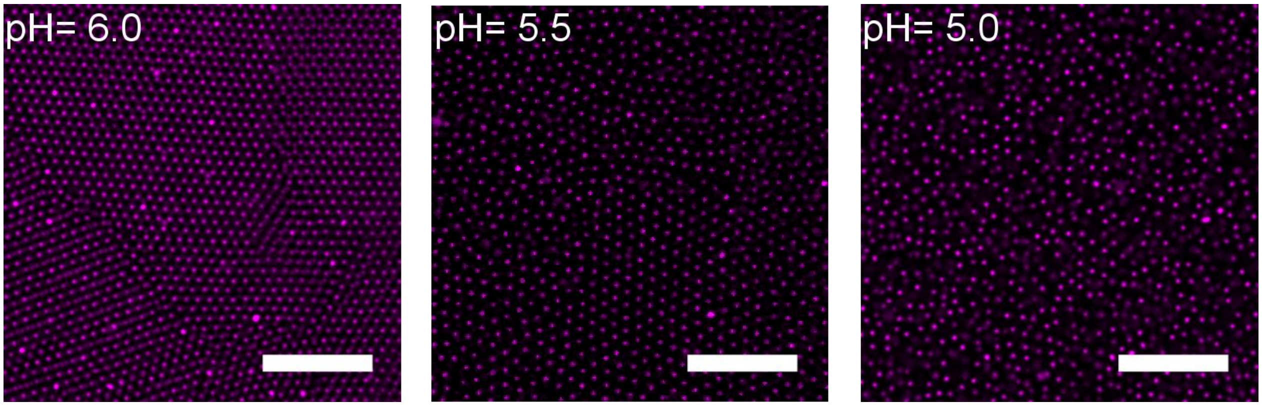

Figure S2: Confocal images of the polyampholyte core-shell microgels at different static pH, which are tuned by dialysing the colloids against the desired pH solution. The colloidal behaviour correlates well with the dynamic laser activation experiments, with the crystalline state at pH_{static} = 6.0, the semi crystalline state at pH_{static} = 5.5 and the liquid state at pH_{static} = 5.0. Scale bars represent 10 µm.