Supporting Information

Light-tunable DNA interactions enable spatiotemporal assembly and relaxation-driven crystallization of colloids

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1. Materials and Methods section

1.1. Materials

Krytox® LVP grease (Z273546-1EA), sodium chloride (NaCl, ≥99.0%), disodium phosphate (Na_2HPO_4, ≥98%), dipotassium phosphate (KH_2PO_4, ≥99%), sodium hydroxide (NaOH, ≥97%, pellets), hexamethyldisilazane (HMDS, 99.9%), methanesulfonyl chloride (Ms-Cl, ≥99.7%), triethylamine (TEA, ≥99.5%), Triton™ X-100 (laboratory grade), and Pluronic F-127 (MQ 200, poly(ethylene glycol)-*b*-poly(propylene glycol)-*b*-poly(ethylene glycol)) were obtained from Sigma Aldrich. Potassium chloride (KCl, 99+%) was purchased from Acros Organics. Negatively-charged, polystyrene (PS) particle 1.00 µm in diameter were purchased from Polysciences (Polybead Sulfate Microspheres) and 0.82 µm polystyrene (PS) particles were purchased from Thermo Fisher (5081A). UV glues NOA61 and NOA63 were obtained from Thorlabs. BODIPY 630/650 carboxylic acid and BODIPY TMR amine (>95%) were purchased from Lumiprobe. Poly(styrene-*b*-ethylene oxide) (PS-*b*-PEO, M_n = 1300-*b*-5600, $Đ$ = 1.10) was obtained from Polymer Source. HCl (37%) was purchased from VWR Chemicals. Methanol, toluene, diethyl ether, acetone, dichloromethane (DCM), dimethyl formamide (DMF, extra dry), and tetrahydrofuran (THF) were obtained from Biosolve. Tris(hydroxymethyl)aminomethane-ethylenediaminetetraacetic acid buffer (Tris-EDTA, TE, pH 8), phosphate-buffered saline buffer (PBS), nuclease-free water, and the sequences (DBCO-T_6C(/azobenzene/)GCG, DBCO-Cy5-T_{16}C(/azobenzene/)GCG) and DBCO-T_{10}) were purchased from IDT. The dibenzocyclooctyne (DBCO) end-group allowed coupling to the colloidal particles via Click Chemistry (see Section 1.5 and 1.7). The oligo-thymine sequence (T_6 or T_{16}) act as spacers between the self-complementary C(/azobenzene/)GCG sticky ends and the DBCO group. Water was purified using a Milli-Q system (18.2 MΩ·cm at 25 °C). All chemicals were used as received.

1.2. Preparation of PBS buffers

PBS buffers with varying ionic strengths were prepared by dissolving KCl (8 mg, 0.11 mmol), Na_2HPO_4 (58 mg, 0.41 mmol), KH_2PO_4 (10 mg, 0.06 mmol) in nuclease-free water (40 mL). NaCl (120, 160 or 320 mg; 2.1, 2.7, 5.5 mmol) were added to obtain 51, 69 and 140 mM NaCl PBS, respectively. The pH of buffers was measured and adjusted to 7.4 using concentrated aqueous HCl or NaOH solutions. F127 (1 or 3 wt%) was added depending on the experiment.

1.3. Synthesis of azido-functionalized PS-*b*-PEO (PS-*b*-PEO-N_3)

PS-*b*-PEO was end-functionalized with an azide moiety using a method previously reported by Oh *et al.*[25] First, PS-*b*-PEO (0.1 g, 0.014 mmol) was dissolved in DCM (2 mL) after which TEA (42 µL, 0.3 mmol) was added. The solution was cooled to 0 °C in an ice bath, and MsCl (24 µL, 0.3 mmol) was injected. After stirring for 2 h at 0 °C, the reaction was continued at RT for another 22 h. Afterwards, the solvent was evaporated, and the polymer was precipitated twice from MeOH + HCl (92/8, v/v%), MeOH, and diethyl ether. The solvents used for precipitation were cooled to sub-zero temperatures before use. For each precipitation step, the polymers were isolated by centrifugation at sub-zero temperatures and decantation of the solvent. After the complete precipitation procedure, the resulting mesylated block copolymer (PS-*b*-PEO-Ms) was dried under vacuum.

In the final step, the mesyl group was substituted for an azido moiety. To this end, PS-*b*-PEO-Ms was dissolved in DMF containing NaN_3 (0.01 g, 0.15 mmol). The mixture was stirred at 65 °C for 24 h, followed by the addition of excess diethyl ether, in which the PS-*b*-PEO-N_3 was precipitated. Centrifugation was used to concentrate and collect the solid. This precipitation procedure was repeated 3×, after which the resulting polymer was dried under vacuum. Successful Incorporation of the azido functionality was provided by infrared (IR) spectroscopy: $\nu = 2100$ cm^{-1} (Supporting Figure S7).

1.4. Surface-immobilization of PS-*b*-PEO-N_3 onto spherical PS particles

Micron-sized PS particles were functionalized via a method based on a procedure previously described by Oh et al. An aqueous solution of PS-*b*-PEO-N_3 (86 µL, 0.58 mM) was mixed with a dispersion of PS particles (150 µL, 2.6 wt%) in a 1.5 mL glass vail and placed in a thermomixer at 250 rpm at RT. This was followed by the dropwise addition of THF (125 µL). A solution of BODIPY 630/650 in toluene (1 µL, 0.1 mg/mL) was added when fluorescent particles were required. The suspension was left under gentle agitation for 1 h, after which water (1 mL) was added to lower the THF concentration. Subsequently, the temperature was raised to 60 °C to evaporate the THF. The surface-functionalized particles were washed by centrifugation and redispersion in water (3×) and finally redispersed in water (98 µL, resulting solid content = 4 wt%).

1.5. Synthesis of azo-DNA and non-azoDNA coated particles (respectively azoDCP and DCP)

A dispersion of the azide functionalized particles (as prepared in Section 1.4, 35 µL, 4 wt%) was transferred to a 1.5 mL conical centrifuge tube and diluted with a PBS buffer (400 µL, 0.1 wt% Triton™ X-100). Subsequently, a solution containing DBCO-T_6CGCG or DBCO-T_6C/azobenzene/GCG (10 µL, 300 µM) was added. The tube was placed in a thermomixer and agitated at 55 °C and 900 rpm for 48 h. The DNA functionalized particles were washed using double distilled water (2×) and TE buffer (2×) and finally redispersed in TE buffer (resulting solid content = 2 wt%).

1.6. Synthesis of patchy PTPM-PS colloids

A dispersion of spherical PS particles (130 µL, 3.4 wt%, ø = 1.00 µm) was diluted with water (8 mL) in a 10 mL glass vial. Ammonia (30 µL) was added while the mixture was magnetically stirred (300 rpm). Next, TPM (60 µL) was injected and the reaction mixture was left stirring at RT for 2.5 h.

The obtained dispersion was divided equally over two 15 mL conical centrifuge tubes and water (2 mL) and SDS (0.3 mL, 4 wt% aqueous solution) was to each tube. The contents were homogenized at RT by placing the tubes in a thermomixer. While shaking, $CHCl_3$ (0.3 mL) was added to each tube. Shaking was continued at RT for 30 min. Subsequently, the temperature was increased to 60 °C and the caps of the tubes were removed to allow the $CHCl_3$ to evaporate. After shaking at 60 °C for 30 min, AIBN was added (6 mg to both tubes) and the tubes were closed. The temperature was increased to 75 °C and mixing was continued for 4 h to polymerize the added TPM. After polymerization, mixing was continued overnight at RT.

Finally, the particles were washed by centrifugation (2 min, 200 *g*) and redispersion cycles (3×). The particles were stored in water (solid content = 1.3 wt%). The anisotropic particle morphology was confirmed using scanning electron microscopy (SEM) (see Supporting Figure S5).

1.7. Synthesis of azoDNA-PTMP-PS patchy particles

Similar to the DNA immobilization procedure described for the spherical particles, the PS patch was first grafted with PS-*b*-PEO-N_3 followed by DNA coupling via Click Chemistry.

To selectively immobilize the azido-functionalized polymer onto the PS patch, PTPM-PS particle dispersion (160 µL, 1.3 wt%), ethanol (160 µL) and a solution of PS-*b*-PEO-N_3 (100 µL, 0.58 mM) were added in a 1.5 mL conical centrifuge tube and mixed using a thermomixer operating at RT and 250 rpm. Next, toluene (2 µL) containing BODIPY TMR amine was added. This solution was prepared by dissolving BODIPY TMR amine (1 mg) in DMSO (10 µL) and adding toluene (1 mL). Addition of toluene caused partial precipitation of the BODIPY derivative. The saturated toluene solution was used to swell the patchy particles. After addition, the suspension was left in the thermomixer (250 rpm, RT) for 1 h. Afterwards, the lid of the centrifuge tube was opened and the toluene was allowed to evaporate during an additional hour of agitation. The particles were washed with water with centrifugation and redispersion cycles (3×) and finally redispersed in water (resulting solid content = 2 wt%).

To react the surface-immobilized azido groups with DBCO-terminated DNA sequences, the PS-*b*-PEO-N_3 functionalized particles (100 µL, 1.3 wt%) were centrifuged (500*g*, 3 min) and the supernatant was replaced by a 140 mM NaCl PBS buffer containing 1 wt% F127 (400 µL). After redispersion of the particles, a DBCO-Cy5-T_{16}C/azobenzene/GCG solution (5 µL, 300 µM) was added. In addition to the DNA sequence used for the isotropic PS particles, these DNA strands are labelled with a fluorophore (Cyanine5), close to the DBCO. To balance this additional bulky group and prevent undesired interactions, 10 additional thymine bases are added to the spacer before the sticky end. The obtained dispersion was agitated using a thermomixer at 55 °C and 900 rpm for 48 h. The DNA functionalized particles were washed with water (2×) and TE buffer (1×) by means of centrifugation and redispersion cycles. The particles were finally redispersed in TE buffer (resulting solid content = 1.3 wt%).

1.8. Microscopy set-ups allowing simultaneous temperature and light stimulation

1.8a. Microscope observation and temperature control

Nikon microscope (Fig1, Fig2, Fig3, Fig7, S2 and S3, and movies SM1, SM2, SM5, SM6, SM7 and SM8)

Samples were observed using a TiE Nikon inverted fluorescence microscope, equipped with a PerfectFocus (PFS) module to maintain the imaged plane constant while changing the temperature of the sample. The PFS continuously corrects the drift in Z resulted from small thermal deformation of the sample's environment. The observation was performed using a Nikon 60× air extra-long working distance objective (~2 mm WD) in order to decouple thermally the sample and the microscope. The images were acquired on a camera Andor Zyla sCMOS on the side port position or an Imaging Source camera (DMK 33UX250) on the front port position for the DLP experiments. A lab-made transparent ITO-based slide heater, piloted by a temperature controller (TC200, Thorlabs, interfaced through python), controlled the temperature of the samples.

Leica Microscope (Fig4, Fig5 and Fig6 and movies SM3 and SM4)

Samples were observed used a Leica SP8 inverted confocal microscope, equipped with 4 excitation lasers (405, 488, 552, 638 nm). Objectives with different magnifications and immersion liquids were used (10×, 20× dry; 63× water or glycerol; 100× oil). Confocal images were acquired using a 12 kHz resonance of a field of view (FOV) scanner in combination with a hybrid (HyD) or photomultiplier tube (PMT) detector. Brightfield and widefield fluorescent imaging was performed using a dedicated digital camera. The temperature of the samples was controlled using a VaHeat micro heating stage (Interherence). This set-up comprises a control unit that is connected to a microscopy slide containing commercially available smart substrates. This substrate is made of microscopy-grade glass (thickness = 170 µm) and contains a ITO coated area (5 × 5 mm) flanked by two electrodes. Applying an electrical current over the electrodes results in rapid (ms) resistive heating up to 100 ºC with a 0.1 ºC precision.

1.8b. Wide field UV and blue irradiation – Nikon microscope (Conditions for Fig1, Fig2, Fig3, S2 and S3, and movies SM1 and SM2)

To study the light response of the azoDCP under un-patterned illumination, the samples were installed on the stage of a TiE Nikon inverted fluorescence microscope equipped with a LED bright field light source for which the red, green and blue LED can be selectively activated during the experiments. On the light sensitive samples, only the red LED was used to image the sample while the blue LED (peaked around 450 nm) was used to switch the azobenzene back to the *trans* rich state. An additional LED (Thorlabs M365LP1, λ = 365 nm) was installed on the BF path in order to illuminate homogeneously the sample plane through the microscope condenser in order to switch the azobenzene to the *cis* conformation. This configuration allows exposing a large part of the sample with the desired blue and UV intensity. The illumination conditions were calibrated using a power meter (Thorlabs PM100D) equipped with a microscope slide photodiode power sensor (Thorlabs S170C) covered with a 300 µm pinhole placed in the sample plane of the microscope. The intensity calibrations were performed in order to truly estimate the light intensity received by the particles, taking into account the presence of glass and ITO in the optical path.

1.8c. UV and blue patterned irradiation – Nikon microscope (conditions for Fig7 and movies SM7 and SM8)

The local control of the UV and blue irradiation was performed by creating patterns of UV and blue light on the sample plane. The patterns were created by a DLP (DLi4110 Streaming Development Kit with the DLP9500UV DMD chip) illuminated with two LEDs (Thorlabs M365LP1, λ = 365 nm and M450LP2, λ = 450 nm). The structured light was send through the left video port of a TiE Nikon microscope and through the microscope objective. Spatial and temporal patterns were created in PowerPoint, while the illumination conditions were controlled by a python code. Images were acquired with an Imaging Source camera (DMK 33UX250) on the front port position. The light intensity at the sample plane was calibrated for both wavelengths using a power meter (Thorlabs PM100D) equipped with a microscope slide photodiode power sensor (Thorlabs S170C) placed in the sample plane of the microscope.

Typically for the relaxation mediated colloidal crystallization (Figure 7b-c and Supporting Movie SM8), an initial patterned blue illumination was progressively increased over 24 min (up to 0.55 $mW \cdot cm^{-2}$), followed by additional short illumination steps applied after 87, 135, and 159 min (with durations of 5, 4, and 2 min, respectively) to selectively melt undesired crystallites while allowing the selected domains to grow during the intervening dark relaxation periods.

1.8.d. UV and blue patterned irradiation – Leica microscope (conditions for Fig4, Fig5 and Fig6 and movies SM3 and SM4)

A Mightex Polygon1000 digital micromirror device (DMD, DSI-K2-000) was mounted to the Leica microscope (section 1.8b) by making use of a Multiport Illuminator (MPI-D-100). High power LEDs of 455 nm (BLS-LCS-0455-03-22) and 365 nm (BLS-LCS-0365-04-2) were connected to a beam combiner (LCS-BC25-0409) which was linked to the DMD via a light guide (see Figure S4 for details). The two LEDS were triggered by a LED driver (BLS-1000-2) via a control module (BLS-IO04-US). DMD patterns were programmed via Polyscan2 software (Mightex). The light intensities for both 365 and 455 nm LED light were calibrated and measured using a power meter (Thorlabs PM100D) equipped with a microscope slide photodiode power sensor (Thorlabs S170C) placed in the sample plane of the microscope.

1.9. Pre-treatment of capillaries

To minimize undesired sticking of the azoDNA functionalized particles to the glass surface during assembly experiments, the capillaries used as sample cells were chemically modified. Capillaries (0.1 × 2 × 50 mm) were used whole or cut in half using a diamond cutter, followed by sonication in acetone for 15 min. The capillaries were dried with a stream of nitrogen and placed upright in a 4 mL vial which contained HMDS (200 µL). The vail was left open for 2 days, after which the HMDS was evaporated. During evaporation, the bare capillary glass surface is coated with the HDMS, rendering it hydrophobic. The hydrophobized capillaries were subsequently transferred to a 4 mL vial containing an aqueous 10 wt% F127 solution. Exposure to F127 causes physical absorption of the triblock copolymers via hydrophobic interactions with their hydrophobic poly(propylene glycol) middle block. The capillaries were left submerged in the Pluronic solution for at least one day after which they were stored in a 1 wt% F127 solution until used for sample preparation.

1.10. Preparation of microscopy samples to study light-mediated manipulation of azoDCP and Janus azoDCP

A pre-treated capillary (as prepared in Section 1.10, stored in 1 wt% F127, 15 mm) was dried using a stream of nitrogen. One end was sealed with Krytox® LVP grease and the capillary was filled with azoDNA (patchy) colloid dispersion. After being completely filled, the other end of the capillary was sealed with Teflon grease. The capillary was fixated onto the bottom side of a heating stage substrate (VaHeat; see section 1.8 for elaborate description) by using UV glue.

Alternatively, capillaries were fully loaded with the particles suspension, placed on a glass slide and sealed at both ends using UV curable glue. During the polymerization of the glue under UV, the colloidal suspensions were protected with aluminum foil to prevent UV irradiation on the photo-switches. Then the sample were kept horizontally in an oven at 75 °C in the dark for at least 2 h in order to let the azobenzene relax to their ground state. Finally, the glass slides were fitted to a lab-made ITO-based stage heater for further measurements (see section 1.8a).

1.11. Preparation of microscopy samples to confine particles in wells (conditions for Fig 7 and S6 and movies SM7 and SM8)

In order to keep a given set of particles in the field of the microscope, and to prevent their diffusion out, we prepared SU8 wells on coverslips to be used as the bottom part of an experimental chamber. The absence of spatial confinement of the particles lead to a visible decrease of the concentration of particles out or the illuminated field, and their aggregation at the periphery of the illuminated spot. First 50 mm x 45 mm coverslips were immersed in a Hellmanex solution at 2 vol% at 35 °C for 40 min. They were then rinsed twice and sonicated in MilliQ water before being dried under N_2 flow and stored in a clean environment. Then a layer of SU8 3025 was deposited on a clean 1.5 coverslip by spin coating (3 s at 500 rpm then 30 s at 1000 rpm) followed by a soft cure at 95°C was performed for 40 min. Then the coverslips were placed on the microscope stage (DLP illumination 1.8c) in order to perform maskless lithography (4× objective, 8.35 $mW \cdot cm^{-2}$ of UV for 40 s which corresponds to 335 $mJ.cm^{-2}$). The coverslips were then post-baked for 1 min at 65 °C then 5 min at 95 °C. To recover the final pattern, the coverslips was immersed in 2 baths of SU8 developer for a few minutes before being finally rinsed with IPA and dried under Nitrogen. The obtained patters were in the order of 50 µm tall (Supporting Figure S6) and were used as the bottom part of a 150 µm thick sample chamber. Just before loading this cell with with azoDCP suspended in a PBS buffer, the cell was treated with 15 min O_2 plasma and hydrophobized with vapors of HDS overnight.

1.12. Writing/erasing patterns with azoDNA colloids– Leica microscope

Typically, the sample (as prepared in Section 1.10, 1 wt% azoDNA colloids dispersed in 69 mM NaCl PBS and 1 wt% F127) was brought to a temperature below the T_m causing aggregation of the particles. Next, the full illumination area, as defined by the DMD device, was exposed to UV light (λ = 365 nm, 1.1 $mW \cdot cm^{-2}$) while using a 20× dry objective. Next, simultaneous illumination with blue (λ = 455 nm, 5.3 $mW \cdot cm^{-2}$) and the UV light was used to generate a light pattern. An arbitrary pattern could be generated by assigning inverse binary bitmap images to the blue and UV light source of the DMD. The images associated with the different wavelengths of light were projected onto azoDNA colloids

dispersion in an alternating fashion, with a dwell time of 500 ms. The illumination sequence was repeated for a total of 4 min to fully transfer the illumination pattern to the azoDNA colloids. After ceasing light exposure for 30 s, the full DMD area was illuminated with UV light (4 min) to fully erase the colloidal pattern. After 2 min of DMD inactivity, patterning could be reinitiated. Writing and erasing the patterns was repeated a least 5 times. The process was followed by taking confocal microscopy images (581,3 × 581,3 μm, 1024 × 1024 pixels) every 30 s using a 20× dry objective.

1.13. Manipulating the 2D-crystallization of azoDNA colloids

Typically, the sample (as prepared in Section 1.10, 0.1 wt% azoDNA colloids dispersed in 69 mM NaCl PBS and 3 wt% F127) was placed on a hotplate at 55 °C for 1 h, slightly above T_m. Next, the sample was placed on the heating stage (temperature set-point = 49 °C), resulting in the formation of a small 2D crystallites. One of the formed crystallites was selected for further growth or manipulation by local illumination with blue light (≈ 5 mW·cm^{-2}). The other crystallites in the field of view were selectively disassembled by local UV illumination (≈ 2.4 mW·cm^{-2}). A 63× dry objective was used to apply patterns and to visualize the particles. For brightfield imaging, a long pass filter (590 nm, FGL590S, Thorlabs) was placed between the light source and the sample.

2. Supporting figures

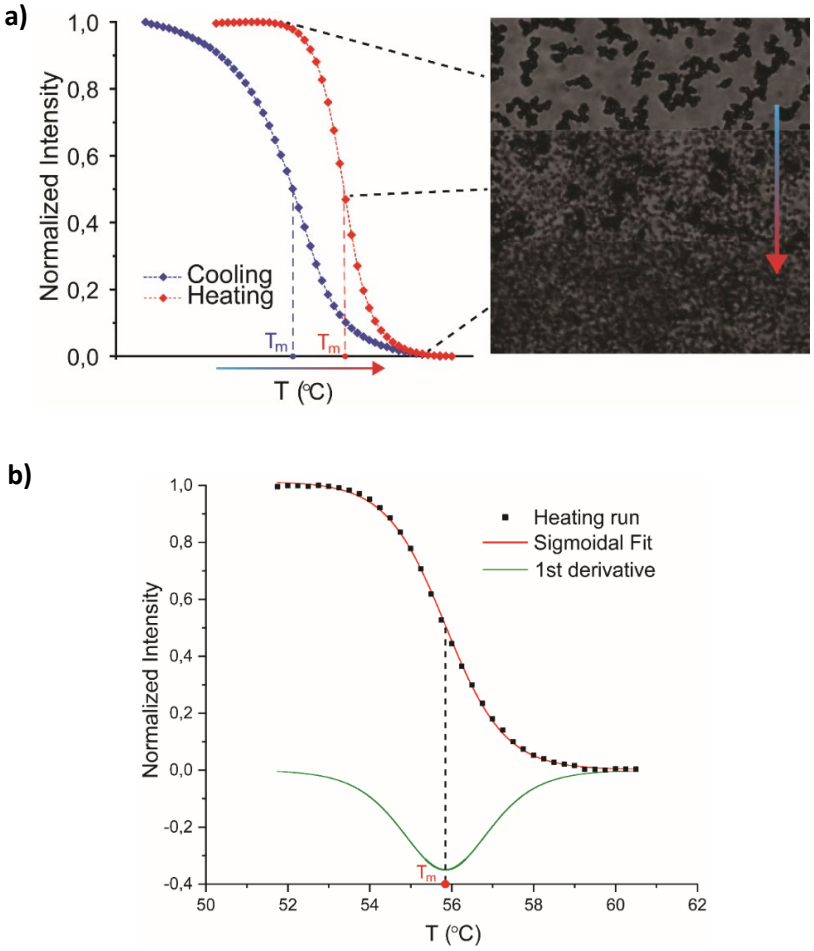


Figure S1: Melting temperature (T_m) determination from optical microscopy derived melting curves. (a) Representative example of (left) melting curves obtained by normalizing the intensity of optical microscopy images from a heating (red) and cooling (blue) cycle of spherical DNA functionalized particles. (right) Optical microscopy images showing the disassembly of colloidal aggregates of increasing the temperature. **(b)** Determination of the T_m after fitting a sigmoidal function (red) to the experimental heating curve. T_m is defined as the temperature where the first derivative of this fit (green) is minimal.

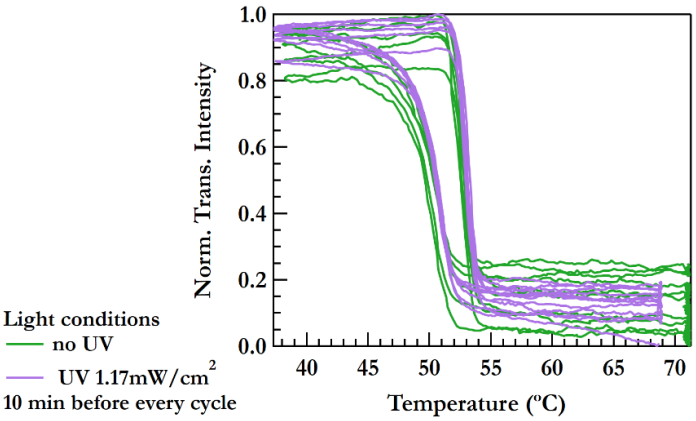


Figure S2: Effect of UV light on no-azoDCP. Temperature cycles on 0.82 µm PS particles decorated with the no-azoDNA sticky-end CGCG, dispersed in PBS [NaCl] = 150 mM, pH 7.4. The temperature cycles are performed under no light (in green) or under UV irradiation (in purple, 1.17 mW·cm^{-2}) (Light illumination setup: see Section 1.8b). The melting properties of the no-azoDCP are not modified by exposure to UV or Blue light. The variations are simply a consequence of fluctuation of the particles concentration in the capillary.

Illuminating the no-azoDCP with either blue (λ = 455 nm) or UV (λ = 365 nm) light did not significantly alter the T_m (± 0.2 °C). Although this result was anticipated based on the absence of any photo-switching entities, this blank experiment proves that the immobilized DNA sequences do not damaged under the used illumination conditions. DNA degradation would lead to a decreasing number of sticky ends that can form inter-particles bonds and would therefore be accompanied by a decrease in T_m. Evidently, the lack of degradation is beneficial for the repetitive and reversible switching behavior of these particles.

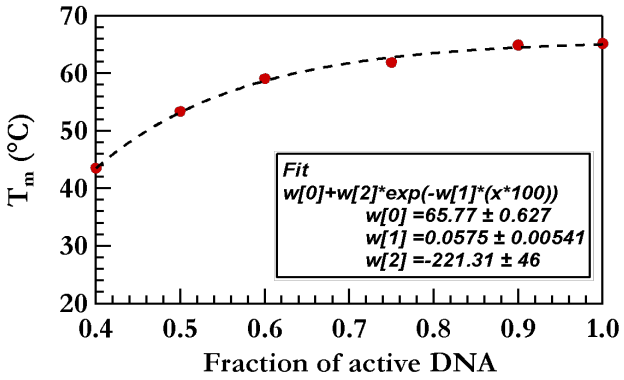


Figure S3: Calibration curve for T_m = f([sticky DNA coverage]). Melting temperature of 0.82 µm polystyrene particles coated with DNA strands, suspended in a PBS buffer, [NaCl] = 150 mM. The DNA coating is composed of a mixture of azoDNA and non-sticky DNA strands composed of a polyT strands. An exponential fit of the data is reported as a dashed line. The DNA particles are prepared following the protocol reported in the experimental section 1.5. The azoDNA and polyT DNA, both DBCO terminated, are mixed at a prescribed ratio in an Eppendorf tube prior being added to the suspension of azide PS particles. Considering an identical reactivity for both strands (same functional group, same size), we can consider that the composition of the DNA coating grafted on the particles is identical to the composition of the DNA strand mixture.

a)

b)

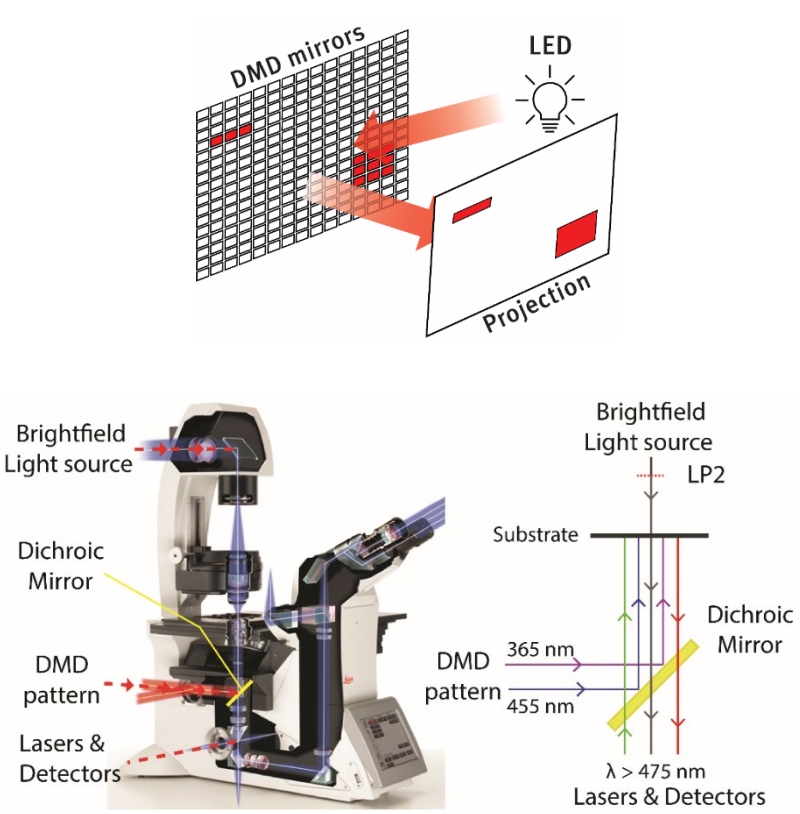


Figure S4: Microscopy – Digital mirror device (DMD) set-up for spatially resolved light-triggered manipulation. (a) Schematic representation of the principle underlying pattern formation using a DMD device. Adapted from Mightexbio.com). **(b)** Overview of (left) the different light paths in a DMD-equipped confocal microscope (Leica SP8). The placement of a long pass dichroic mirror (LP 475 nm) makes it possible to combine DMD patterns with confocal and brightfield imaging. (right) different wavelengths of light, originating from DMD patterns, lasers, brightfield or fluorescence that either reflect on or pass through the dichroic mirror. A LP filter (LP2) needs to be placed between the light source and the sample to prevent interference of the lower wavelengths (white light) with the responsive materials while imaging in brightfield mode.

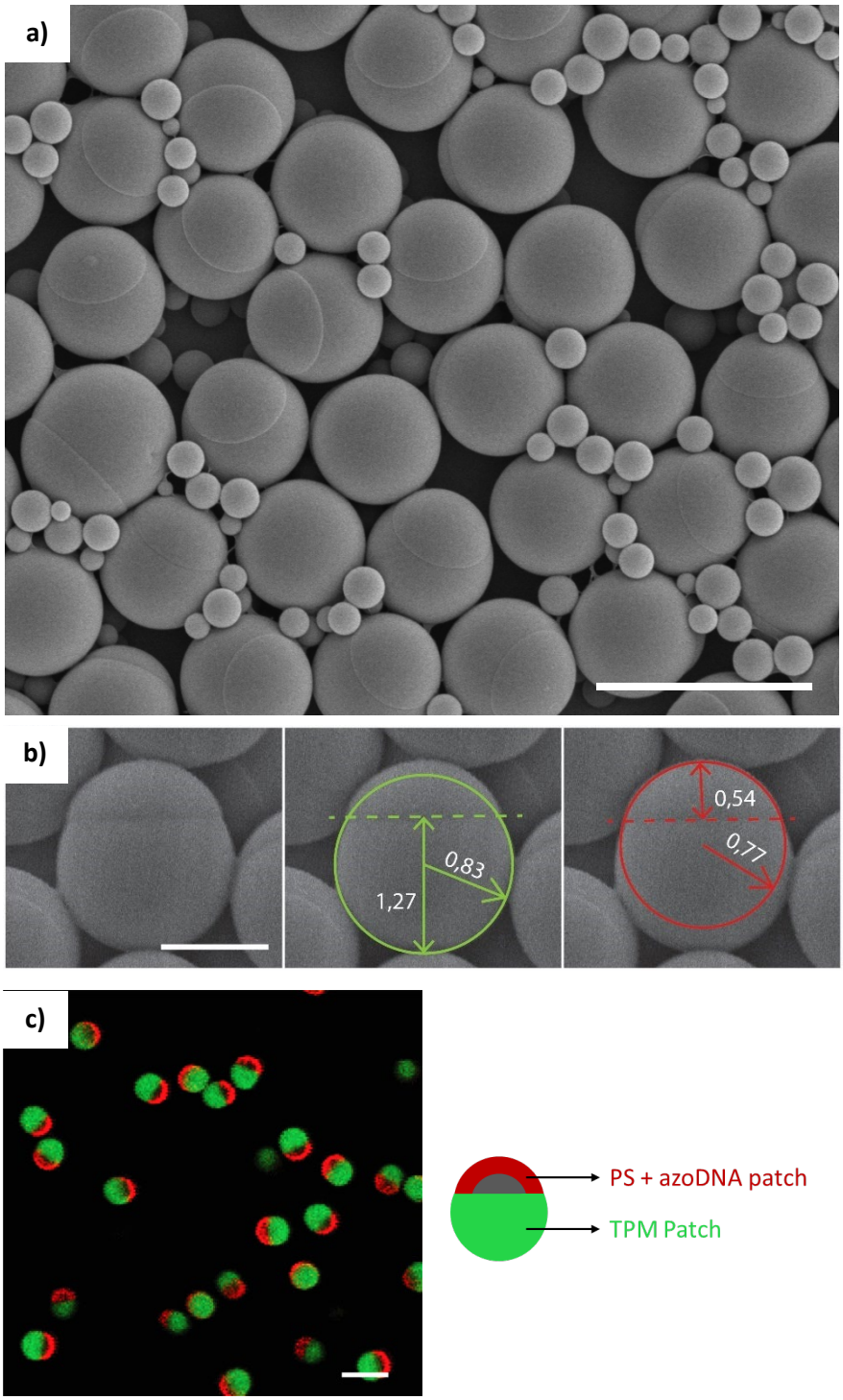


Figure S5: Microscopy analysis of (azoDNA-)PTMP-PS patchy particles. (a) Scanning electron microscopy (SEM) image of crude patchy PTPM-PS colloids. The small spherical particles represent secondary nucleation which were quantitatively removed by repetitive centrifugation and redispersion cycles (see Section 1.6). Scale bar = 3 µm. **(b)** High magnification SEM image of particles shown in panel a with the corresponding radii and heights of the TPM (green) and PS (red) patches in micrometers. Scale bar = 1 µm. **(c)** Confocal microscopy image of fluorescently labeled patchy azoDNA colloids. The green lobe corresponds to the TPM patch (label: BODIPY TMR). The red colored patch corresponds to the azoDNA-functionalized PS patch. The fluorescent signal from the PS patch originates from a Cy5 label that was incorporated in the immobilized DNA strands (see Section 1.7). Scale bar = 3 µm.

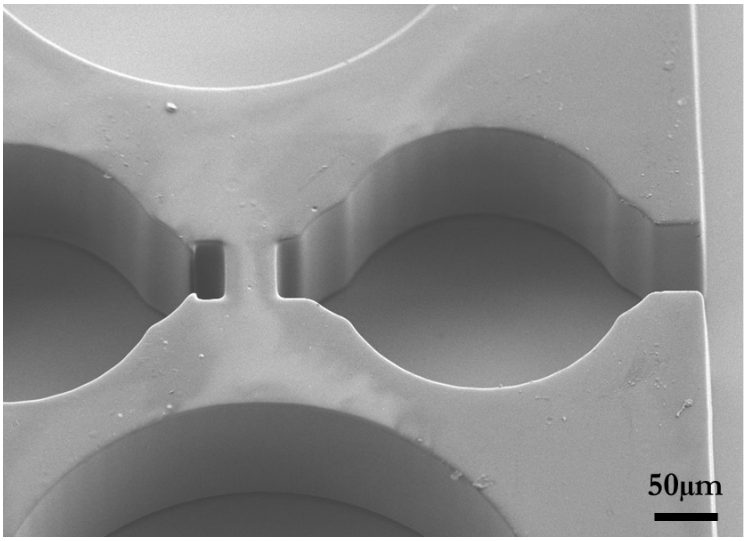


Figure S6: SU8 patterned wells on coverslip. Scanning electron microscopy image of a typical SU8 patterned well on coverslip to confine spatially colloidal particles and prevent their diffusion out of the field of view of the microscope during long experiments under various light conditions

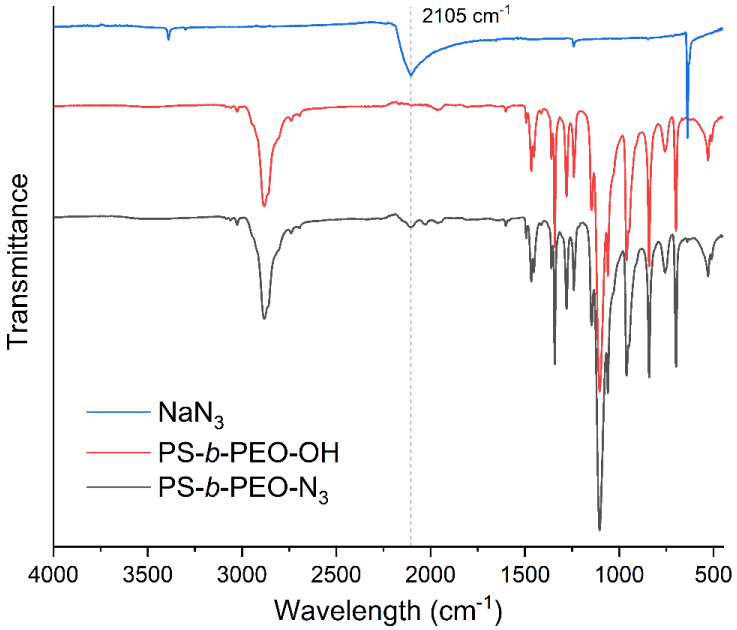
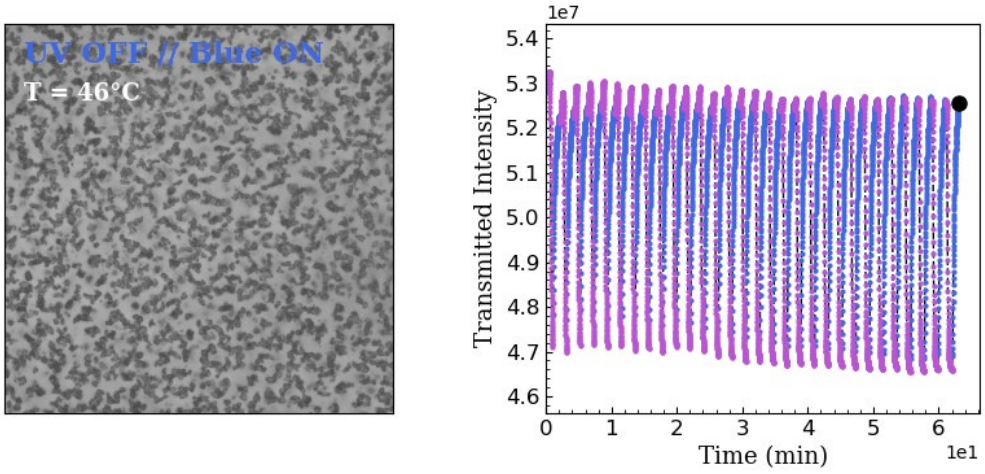
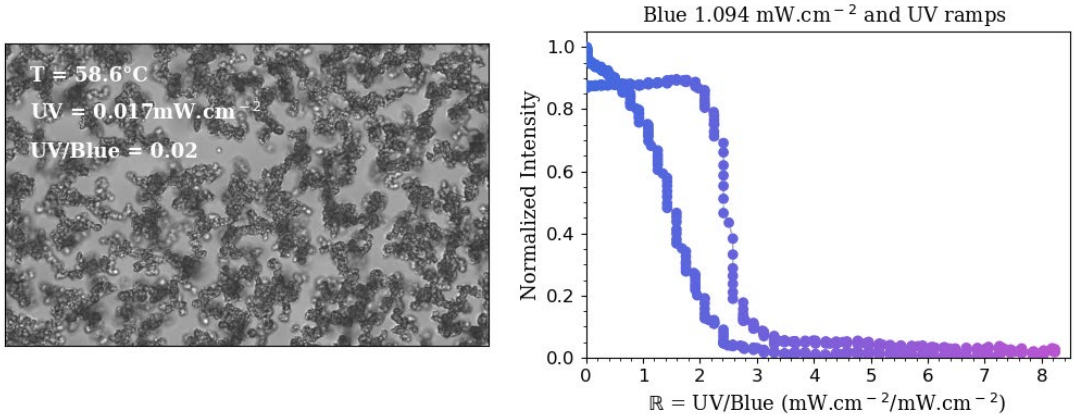


Figure S7: Infrared (IR) spectroscopy analysis of PS-PEO-N_3. IR spectra of (top, blue) NaN_3, (middle, red) PS-*b*-PEO and (bottom, black) PS-PEO-N_3. The signal highlighted with the dotted vertical line at approximately 2100 cm^{-1} is diagnostic for the introduced azide moiety. The IR spectrum of NaN_3 was included as reference. The low signal intensity of the azide can be rationalized by the fact that the relatively long polymer chains carry only one $–N_3$ group.

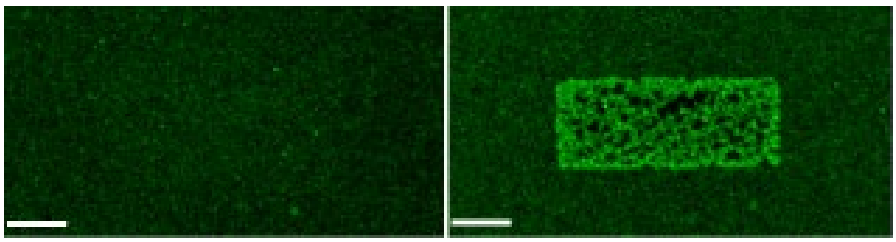
3. Supporting movies



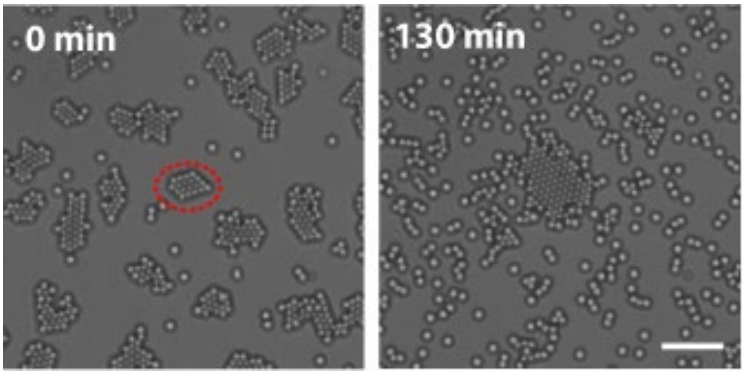
Supporting Movie SM1: Light switch and colloids. Isothermal light induced disassembly and assembly of 0.82 µm polystyrene particles decorate with azo-DNA, suspended in a PBS buffer, [NaCl] = 150 mM. While kept at 46 °C, azoDCP are sequentially cyclically exposed to UV (1.17 mW·cm^{-2}) and blue light (1.16 mW·cm^{-2}), one change per minute (Light illumination setup: see Section 1.8b). AzoDCP reversibly disassemble under UV and reassemble under blue light. Field of view 225 µm × 225 µm.



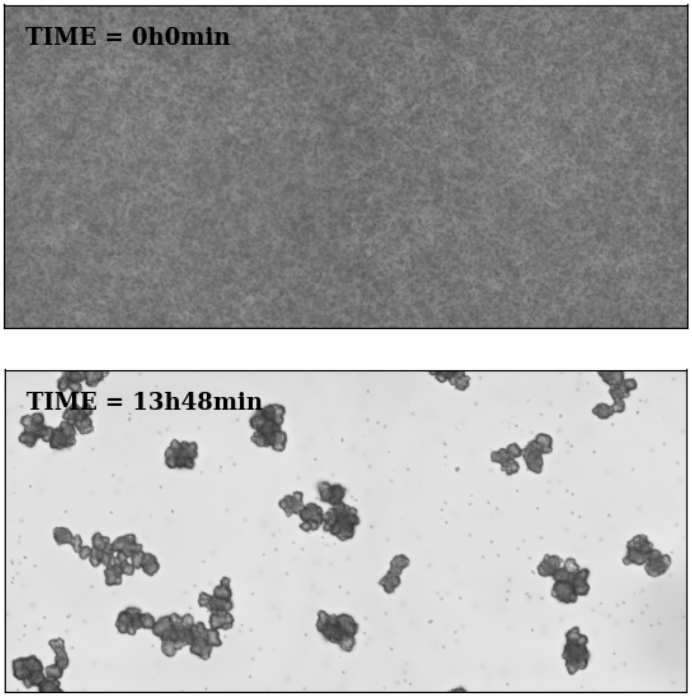
Supporting Movie SM2: Cyclic melting under light. Isothermal light induced cyclic melting and aggregation of 0.82 µm azoDCP, suspended in a PBS buffer, [NaCl] = 150 mM, maintained at 58.5 °C. Equivalent to a melting curve obtained thanks to a change of temperature, the control of the interaction is here piloted by the irradiation conditions. The sample is irradiated with a mixture of UV and blue light in the ration ℝ between 0 and 8.2 (Light illumination setup: see Section 1.8b). The blue intensity is kept constant at 1.1 mW·cm^{-2} while the UV intensity is cycled from 0 to 9 mW·cm^{-2}. Field of view: 240 µm × 150 µm.



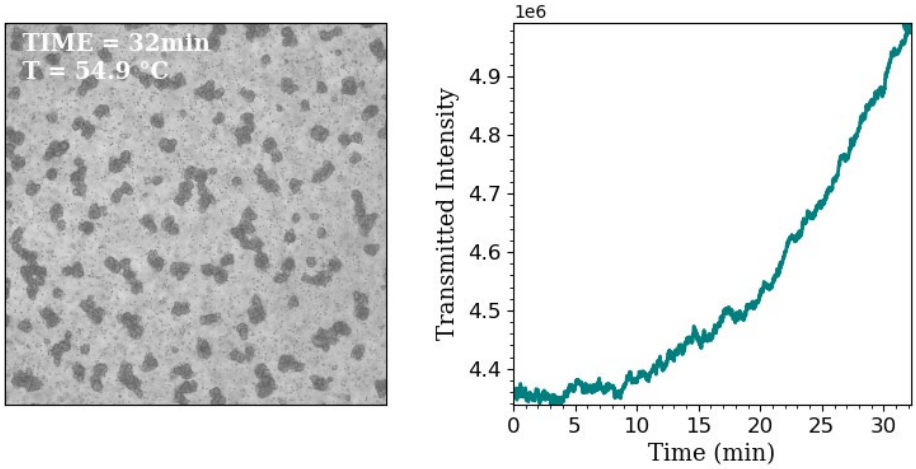
Supporting Movie SM3: Patterned writing and erasing cycles. Linked to Figure 4 (Light illumination setup: see Section 1.8d). Reversible, spatially confined clustering of azoDCP at T_{sample} = 47.5 °C (below $T_{m\ azo\text{-}blue}$ and above $T_{m\ azo\text{-}UV}$) followed by confocal microscopy. The writing/erasing starts by exposing UV light to the complete field of view, yielding a suspension of well-dispersed particles. Delivery of a rectangular blue light pattern (5.3 $mW \cdot cm^{-2}$) on the sample while keeping the rest exposed to UV (1.1 $mW \cdot cm^{-2}$) resulted in a localized assembly (see Figure 4 for schematic representations of the applied illumination patterns). Reapplying UV exposure on the complete field of view, erases the written rectangle. This cycle was repeated five times. Field of view: 650 µm × 410 µm.



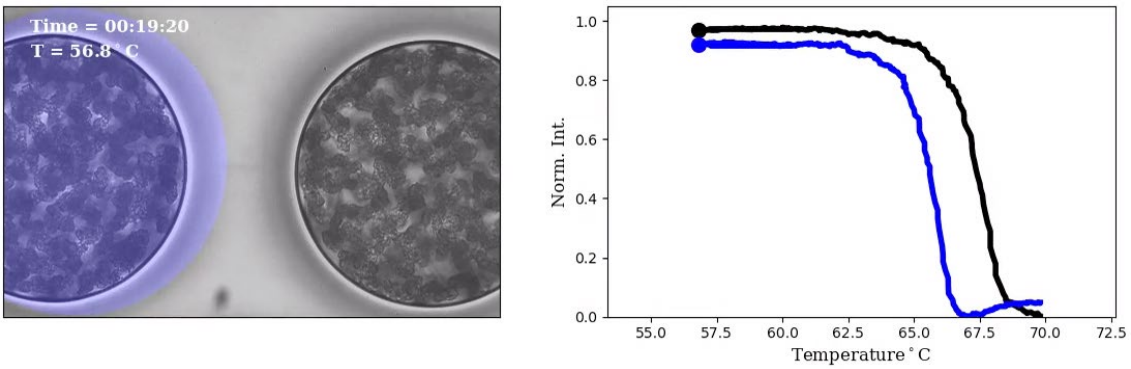
Supporting Movie SM4: Selective melting and growth of 2D colloidal crystals. Linked to Figure 5 (Light illumination setup: see Section 1.8d). Transmission optical microscopy movie showing the manipulation of the 2D crystallization of azoDCP by local exposure to blue (5 $mW \cdot cm^{-2}$, blue highlighted areas throughout the movie) and UV light (2.4 $mW \cdot cm^{-2}$, purple highlighted areas throughout the movie). Crystallization was confined in 2D by addition of 3 wt% F127 in a PBS buffer ([NaCl] = 51.4 mM). The movie starts with a large collection of crystallites assembled during a quench below the melting temperature (T_{sample} = 49 ºC < T_m). Subsequently, the temperature was increase to 52 ºC and kept constant throughout the duration of the movie. Local UV illumination increases the fraction of single azoDCP available for growing a selected crystallite. To enable growth, the surroundings of the selected crystallites are illuminated with blue light. The exact position and shape of illuminated areas are dynamically adjusted to follow the shape of the growing crystallite and selectively melt unwanted, newly forming crystallites throughout the duration of the movie. Field of view: 130 µm × 100 µm.



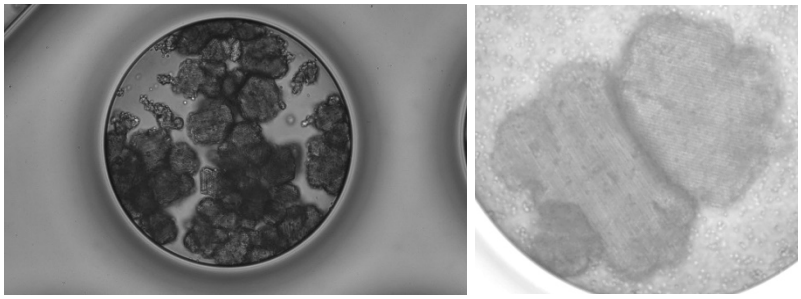
Supporting Movie SM5: Relaxation close to $T_{m\ azo\text{-}dark}$. Temporal evolution of a suspension of 0.82 µm polystyrene azoDCP, in PBS buffer, [NaCl] = 150 mM, kept at a constant temperature of 62 °C, after they have been exposed to $\mathbb{R}$ = 2 (Blue = 14 mW·cm^{-2} and UV = 28 mW·cm^{-2}) for 30 min then observed in the dark (Light illumination setup: see Section 1.8b). The slow thermal relaxation of the azobenzene progressively induce a recovery of the attractive interaction between particles. Under these conditions, the particles can crystalize and form well-ordered colloidal crystals. Field of view: 333 µm × 157 µm.



Supporting Movie SM6: Relaxation far from $T_{m\ azo\text{-}dark}$. Temporal evolution of a suspension of 0.82 µm polystyrene azoDCP, in PBS buffer, [NaCl] = 150 mM, kept at a constant temperature of 55 °C, after they have been exposed to $\mathbb{R}$ = 8 (Blue = 4.07 mW·cm^{-2} and UV = 32.26 mW·cm^{-2}) for 30 min then observed in the dark Light illumination setup: see Section 1.8b). The slow thermal relaxation of the azobenzene progressively induce a recovery of the attractive interaction between particles. Under these conditions, the particles do not crystalize but form random aggregates. Field of view: 225 µm × 225 µm.



Supporting Movie SM7: Melting in the dark vs under blue. Two SU8 wells filled with a suspension of 0.82 µm polystyrene azoDCP, in PBS buffer, [NaCl] = 150 mM, kept at 56.8 °C. A light pattern, disk of blue light, is projected on the sample through the microscope objective (Light illumination setup: see Section 1.8c) in order to only expose the left well with blue light (0.55 mW·cm^{-2}) while the right well is kept in the dark. Temperature cycles (linear ramps at 0.8 °C.min^{-1}) are then applied to the whole sample. The normalized transmitted intensity through each well reveal a clear temperature gap in the order of 2 °C between $T_{\text{m azo-dark}}$ and $T_{\text{m azo-blue}}$ and illustrates our ability to control locally the Tm of colloidal particles without the need to change the buffer conditions of the DNA coating. Field of view: 240 µm × 150 µm.



Supporting Movie SM8: Selective melting and growth of colloidal crystals using only blue light and thermal relaxation of the azobenzene. Prior to the recording, a suspension of azoDCP is confined into a SU8 well (diameter 130 µm, height ~ 50 µm) and annealed in the vicinity of $T_{\text{m azo-dark}}$. The polycrystalline sample is then kept at 66.6 °C (1.5 °C below $T_{\text{m azo-dark}}$) and exposed to a blue light pattern (progressive increase up to 0.55 mW·cm^{-2} for 24 min) in order to dissociate most of the crystals, keeping only a couple of them (Light illumination setup: see Section 1.8c). Then the sample is left in the dark. The thermal relaxation of the azo progressively induces the recovery of the attractive character of the particles. The evolution of the strength of the interaction is slow enough so that the particles can crystallize. The initial crystallites grow while additional nucleation sites are visible. A subsequent series of patterned light illumination (0.55 mW·cm^{-2} for 5 min at 87 min, 3 min at 135 min and 2 min at 159 min) followed by thermal relaxation steps leads to very large well-ordered crystals that would have required a very long time to grow with a classical thermal annealing. Field of view: 240 µm × 150 µm.