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

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ABSTRACT

Self-assembly of colloidal particles enables the formation of complex superstructures, yet precise control over assembled structures remains challenging and assembly pathways primarily rely on temperature, a global trigger. Here, we introduce a strategy to dynamically modulate DNA-mediated colloidal interactions using azobenzene-functionalized DNA strands (azoDNA) grafted on colloidal particles, programming the interaction landscapes in space and time. Photo-isomerization of the azobenzene moiety allows reversible and continuous tuning of the stability of DNA duplexes, enabling light-controlled regulation of interparticle binding under isothermal conditions. By varying illumination conditions, the effective melting temperature of the colloids can be adjusted over a wide range, allowing reversible assembly, spatially patterned aggregation, and dynamic reconfiguration of colloidal structures at the scale of a few particles. Beyond reversible switching, we show that the slow thermal relaxation of azobenzene provides a new route to relaxation-mediated colloidal crystallization, in which the gradual recovery of DNA stickiness promotes ordered crystal growth. These results demonstrate how light can be used to program both the strength and the temporal evolution of DNA-mediated interactions, offering a versatile platform for spatiotemporally controlled self-assembly and adaptive colloidal materials.

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INTRODUCTION

Self-assembly of colloidal particles is a versatile bottom-up approach that enables the creation of a wide variety of superstructures with tailored properties at both the micron and nanometer scale. The assembly process is autonomous, meaning that the final equilibrium assembly is programmed into the individual building blocks. Both particle shape and interactions between particles play pivotal roles in the assembly process. For successful assembly, the inter-particle potential must precisely balance attractive and repulsive forces. Achieving this balance prevents kinetically arrested states, allowing the targeted superstructure to form.

A powerful strategy to engineer the interparticle potential is to functionalize colloidal surfaces with supramolecular motifs capable of programmable and reversible interactions. These motifs interact with each other via well-defined, short-ranged intermolecular interactions. When these motifs are immobilized onto the colloidal surface, the attractive forces they generate at the molecular level are effectively translated to the colloidal scale.

Among the many systems explored, colloidal particles functionalized with well-designed deoxyribonucleic acid (DNA) fragments have emerged as one of the most powerful platforms for programmable colloidal assembly, enabling the fabrication of ordered crystals(1–8) and finite-sized assemblies.(9–12) The assembly of these particles is driven by the hybridization of the

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terminal single-stranded DNA fragments (sticky-ends) into duplexes between complementary coatings. The high specificity of the molecular recognition of two DNA strands of given sequences opens the way for the rational design of DNA coatings to dictate the binding strength between two given colloids. DNA-based colloidal systems are then highly tunable and sticky-ends formed of 4 to 12 bases are sufficient to encode a broad range of orthogonal interactions. In addition, DNA-functionalized particles show a temperature-responsive assembly behavior. This responsiveness originates from the non-covalent hydrogen bonds that drive DNA hybridization. Only at sufficiently low temperatures are the DNA duplexes stable and do DNA-mediated attractions dominate the inter-colloidal potentials. Once heated above a critical melting temperature (T_m) hybridization is no longer favorable, leading to effective steric repulsion and hence disassembly. The thermo-sensitive behavior has been frequently leveraged to obtain dynamic, reconfigurable, and/or reversible colloidal assemblies.(13)

While DNA hybridization enables highly specific binding, most DNA-mediated colloidal systems rely on interaction strengths that are fixed by sequence design and can only be modulated globally through temperature. There are several limitations that limit the degree of control over the assembly. First of all, the melting transition separating the assembled and disassembled state is typically sharp. Over only a narrow temperature range, the attractive and repulsive interactions are balanced appropriately such that the particles can access their equilibrium configuration, i.e. a small temperature window in which the particles can diffuse while bound.(14, 15) This implies that in order to prevent defects in the assembly and the formation of undesired fractal structures, the control of temperature is key.(16) This is especially critical for micron to submicron scale

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particles that can easily fall into kinetically trapped configurations. Secondly, temperature acts as a global control parameter, preventing local or spatiotemporal control over colloidal interactions and assembly pathways.

Here, we address these challenges and expand the DNA-colloid toolbox by decorating micron-sized colloidal particles with self-complementary azobenzene-functionalized DNA strands (azoDNA). This approach allows the interaction landscape between particles to be programmed in both space and time using light, control of their (dis)assembly not only with temperature but also using light as an orthogonal trigger (Figure 1). The azobenzene moiety is a well-known molecular photo-switch that can reversibly transition between a flat *trans* and kinked *cis* conformation upon irradiation with blue (λ = 455 nm) and UV light (λ = 365 nm), respectively. The relaxation of the *cis* azobenzene back to the *trans* ground state can also follow a thermal process with slower dynamics.(17) Once incorporated into the phosphate backbone of a DNA sequence, the azobenzene group modulates the formation of the DNA duplex by its conformational state, as was previously shown for DNA strands in solution.(18–20) At the molecular level, the flat *trans* azobenzene can intercalate into the DNA duplex, establishing π-π interactions with the strands, leading to a stabilization of the duplex. On the other hand, the *cis* isomer effectively disturbs the stability of the duplex due to steric hindrance. Nakasone et al.(21) recently reported that an isothermal *trans*-to-*cis* isomerization of the azobenzene moiety dramatically increases the dissociation rate of the DNA duplex and thereby makes de-hybridization photo-sensitive. The

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number of azobenzenes introduced, their location in the sequence, and the surrounding bases were proven to affect the photo-switching behavior of such azoDNA strands in solution.(22, 23)

Once grafted to the surface of nanoparticles, the light responsiveness of the azoDNA can be harnessed to modulate the interaction between 10 to 30 nm gold nanoparticles to create responsive clusters(24) and patterned nano-crystals.(25) These pioneering studies established proof-of-concept, focusing in particular on the opportunity to use the azobenzene as a light-guided molecular switch to turn interparticle interactions ON and OFF. Here we explore in more detail the effects of introducing an azobenzene into the sticky-end of a model micron-sized DNA-coated particle (DCP). We show that light-triggered isothermal switching between a melted and an aggregated state can be accessed over a wide temperature range. We then demonstrate that azoDNA, once grafted to the surface of a microparticle, is more than an ON/OFF switch and allows fine tuning of the melting temperature of a batch of azoDCP by exposing the samples to mixed illumination conditions of blue and UV light. We effectively modulate the coverage of DNA sticky ends capable of forming stable duplexes by varying the power ratio of UV to blue light. By applying dynamic and on-demand light patterns to the sample, we also demonstrate spatiotemporally resolved control of the interaction between particles, approaching control at the single-particle level. We further use this strategy to correct defects in assembled structures. Finally, by exploiting the slow thermal relaxation of the *cis* azobenzene back to the *trans* state, we demonstrate a relaxation-driven assembly pathway in which particle stickiness gradually recovers over time, enabling the formation of large, well-ordered colloidal crystals. The time scale for stickiness recovery by thermal relaxation is in the order of minutes to hours, while the photo-

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induced isomerization of the azobenzene allows recovering attractive particles in seconds. This approach establishes light as a powerful handle to program locally both the strength and the temporal evolution of DNA-mediated colloidal interactions, providing new strategies for directing assembly pathways in reconfigurable colloidal materials.

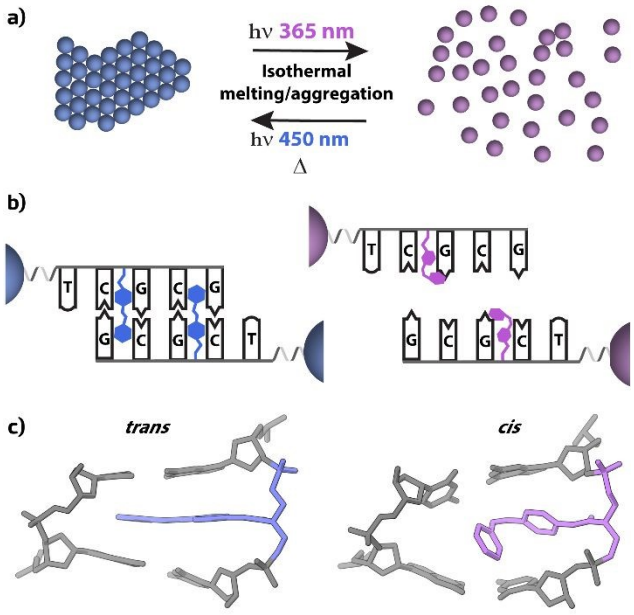

Figure 1. a) Schematic representation of the light-responsive (dis)assembly of micron-sized colloidal particles with self-complementary azobenzene-functionalized DNA strands (azoDCP). b-c) Graphical depiction b) and molecular scale representation c) of DNA duplex formation and disruption based on the conformational state of the azobenzene fragment incorporated on the DNA backbone. The *trans* conformation (left, blue) promotes hybridization via intercalation, while the *cis* conformation (right, purple) interferes with formation of hydrogen bonds between the complementary DNA strands due to steric hindrance.

RESULTS AND DISCUSSION

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Creating light responsive DNA-coated colloids from light irresponsive particles

The surface functionalization of colloidal particles with DNA sequences is performed by following the procedure previously reported by Oh et al.(26) Briefly, polystyrene (PS) particles (diameter 0.82 μm or 1.00 μm) were functionalized with a (polystyrene-*b*-polyethylene oxide)-azide block-copolymer (PS-*b*-PEO-N_3) via a swelling/deswelling method. This procedure results in particles with surface-tethered PEO chains bound to the particles via physical entrapments of the hydrophobic PS block. The terminal azide groups enable copper-free click coupling of DBCO-terminated DNA strands to the particle surface. The grafted short oligonucleotides consist of a short coding segment, here referred to as sticky-end, that will program the interactions between particles and a short polyT segment typically formed of 6 to 12 bases playing the role of a spacer. The DNA sticky-ends used in this work are composed of a short self-complementary sequence formed of four bases (CGCG). The introduction of an azobenzene moiety inserted as a pendent group in the DNA backbone in between the first C and G bases (azoDNA, C/azobenzene/GCG, Figure 1b) confers the photo-responsivity to the duplex formation. Colloidal particles decorated with non-photosensitive sticky-ends (CGCG) are referred to as no-azoDCP while their photosensitive counterparts (C/azobenzene/GCG) are referred to as azoDCP.

To assess whether the azobenzene photo-switch affects the duplex formation between self-complementary DNA strands on the surface of colloidal particles akin to its influence on hybridization in solution, the assembly and disassembly of azoDCP suspended in a PBS buffer ([NaCl] = 150 mM, pH = 7.4) was monitored by optical microscopy as a function of temperature and illumination history. The aggregation state of the sample was determined by measuring so-

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called melting curves (Figure 2a). These curves display, as a function of temperature, the normalized intensity of the transmitted light through the sample observed in bright-field microscopy. This measure is a proxy for the aggregation state of the system. In the fully dissociated state, the free particles are homogeneously dispersed in the field of view, blocking a significant part of the illumination light. Conversely, in the clustered state, the particles are locally concentrated into aggregates, creating highly transmitting areas devoid of any colloids. Therefore, low and high transmissions correspond to the disassembled and assembled state, respectively. Importantly, the absolute value of the transmitted intensity is not the relevant parameter here, as it can vary between experiments due to small differences in particle density, microscope alignment, and illumination intensity. Instead, the aggregation behavior is captured by the evolution of the transmitted intensity with temperature, in particular in the sharp transition between the high-transmission (aggregated) and low-transmission (dispersed) states. The temperature at which this transition occurs is defined as the melting temperature (T_m) of the system (Supporting Figure S1). To prevent an undesired impact of the observation of the particles, we used red light (~640 nm) to illuminate the samples in bright field microscopy, far from the absorption bands of both the *cis* and *trans* isomers of the azobenzene moiety.

The azoDCP reversibly assemble and disassemble upon cooling and heating just like the no-azoDCP. However, there is a clear difference in their T_m even for native samples (i.e. relaxed in the dark to the *trans* state) before any photo-switching. Compared to the no-azoDCP ($T_{m\,no\text{-}azo}$ = 56.1 ˚C), the T_m of azoDCP increases by approximately 14 ˚C up to 69.8 ˚C ($T_{m\,azo\text{-}dark}$, Figure 2a, black curve). In the dark-state, the azobenzenes prefer to reside in their thermodynamically favorable

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trans conformation. For a molecular azoDNA system, the fraction of azobenzenes in the *trans* conformation was found to be > 90%.(27) Attractive π-π interactions between these relatively flat isomers and the hydrophobic core of the DNA duplexes, increases the stability of the DNA duplex.(18, 19) Hence, higher temperatures are required to break the DNA mediated colloidal interaction.

In contrast, the non-planar *cis* conformation of the azobenzene, which is typically generated upon exposure to UV light (λ_{max} = 365 nm), destabilizes the DNA duplexes due to steric hindrance. This destabilizing effect renders the sticky-ends inactive, effectively decreasing the grafting density of active DNA strands, resulting in a drop of the T_m of the system. As a consequence, while maintaining a suspension of azoDCP at a temperature (T_{sample}) between $T_{m\text{-}cis}$ of the $T_{m\text{-}trans}$, isothermal photo-regulated DNA (de)hybridization and hence reversible (dis)assembly of azoDCP is possible.

Figure 2a shows that experimentally illumination strongly modulates the interaction strength between azoDCP. Exposing a dark-state azoDCP system to UV light (λ_{max} = 365 nm, 3 mW·cm^{-2}) led to a pronounced decrease in T_m (ΔT_m = 32 ˚C, $T_{m\ azo\text{-}UV}$ = 38.3 ˚C). This effect is fully reversible: when the sample is kept in the dark, *cis* isomers slowly relax thermally back to the *trans* state, restoring the higher melting temperature. Blue light illumination (λ_{max} = 455 nm, 10 mW·cm^{-2}) also displaces the population of photo-switches back to a *trans* rich conformation, recovering their duplex-stabilizing ability, resulting in a $T_{m\ azo\text{-}blue}$ of 68.1 ˚C. Consequently, we have a substantial

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temperature window of nearly 30 ˚C in which (dis)assembly of azoDCP can be photo-regulated. Notably, the experimentally observed shifts in melting temperature are substantially larger than those typically reported for analogous free azoDNA oligonucleotides in solution. This amplification arises from the multivalent and cooperative nature of the colloidal interactions, whereby each colloid–colloid contact is mediated by multiple azoDNA duplexes whose collective response magnifies relatively modest changes in the stability of the individual duplexes. As anticipated, this temperature window is absent for colloidal particles decorated with non-azobenzene DNA where the T_m proved to be independent of the illumination history (Supporting Figure S2).

To illustrate this photo-controlled assembly, an azoDCP dispersion in PBS buffer was equilibrated at 46 ˚C (Figure 2b) and exposed to UV and blue light consecutively (1.17 $mW \cdot cm^{-2}$ and 1.16 $mW \cdot cm^{-2}$ respectively). A reversible switch between a fully aggregated and a dispersed state was attained (Figure 2c). Because the sample was kept at a temperature far below $T_{m\ azo\text{-}blue}$, aggregates that lack any structural order were formed under blue light illumination, *i.e.*, upon turning ON the attractive interactions. Cluster (dis)assembly was highly reversible upon repetitive exposure to UV and blue light. Up to 30 consecutive cycles were performed without significant changes in the responsiveness of the system, indicating the absence of significant light-induced DNA degradation (see Supporting Movie SM1). Additionally, Supporting Figure S2 shows that exposing no-azoDNA to UV does not induce any damage on the DNA. At the start of each UV exposure to trigger disassembly of the aggregates, a minor increase in the intensity of transmitted light was measured rather than an immediate decrease (Figure 2b). We attribute this to a

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densification or enhanced local ordering of the clusters as the inter-particle attraction weakens. Similar rolling rearrangements have been reported in conventional DNA-coated colloids and are required to form crystalline assemblies.(14, 15) Continued exposure weakens the inter-particle bonds further, eventually leading to cluster disintegration as signified by the decrease in transmitted light. The subsequent exposure to blue light leads to a rapid aggregation of the particles. Under these conditions, the recovery of the sticky state occurred on the time scale of seconds (Figure 2b). Considering that for a micron-sized colloid, the time to diffuse over its own distance via Brownian motion is on the order of seconds, the system is likely limited by particle diffusion rather than azobenzene isomerization back to the *trans* state. On the contrary, the slight delay observed between the start of the exposure to UV and the disassembly of the aggregates can be attributed to the fact that once intercalated into a duplex, the isomerization of a *trans* azobenzene to its *cis* form is sterically hindered and less efficient than previously reported for molecularly dissolved azoDNA.(27, 28, 21)

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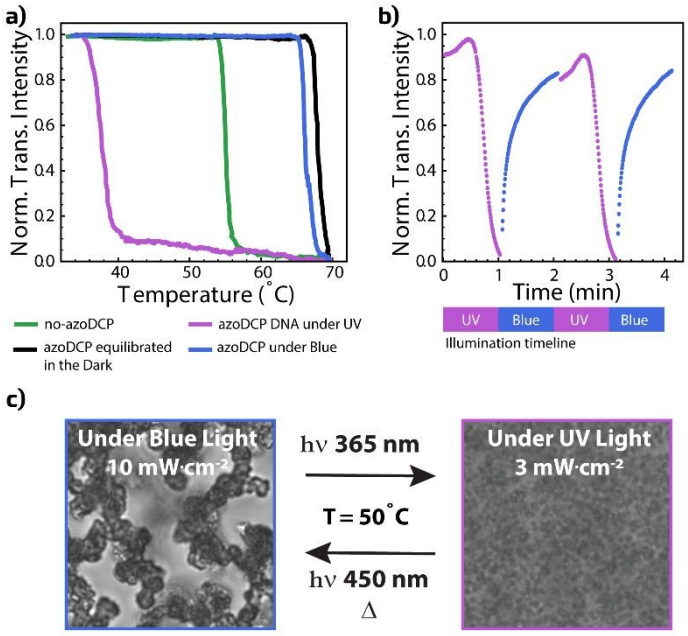

Figure 2. a) Melting curves for 0.82 μm PS particles decorated with self-complementary GCGC (green, no-azoDCP) and G/azobenzene/CGC sticky-ends in order to measure their melting temperature T_m under various light illumination conditions. The particles grafted with the azoDNA (azoDCP) were measured in the dark equilibrated state (reported in black, $T_{m\ azo\text{-}dark}$ = 69.8 ˚C), upon exposure to blue (λ = 455 nm, 10 mW·cm^{-2} reported in blue, $T_{m\ azo\text{-}blue}$ = 68.1 ˚C) and UV (λ = 365 nm, 3 mW·cm^{-2} reported in purple, $T_{m\ azo\text{-}UV}$ = 38.3 ˚C). The no-azoDCP $T_{m\ non\text{-}azo}$ was measured at 56.1 ˚C, and proved independent of the illumination conditions (Supporting Figure S2). b) Normalized transmitted intensity versus time during two light-mediated isothermal (dis)assembly cycles at 46 ˚C, measured by optical microscopy. UV exposure (1.17 mW·cm^{-2}) caused disassembly of the particles and a decrease of the transmitted intensity (purple). A subsequent blue light illumination (1.16 mW·cm^{-2}) triggered aggregation of the particles, signified by an increased light transmission through the sample (see Supporting Movie SM1). c) Representative light microscopy images during blue and UV light illumination, field of view 50x50 μm². Illumination conditions described in the Materials and Methods section 1.8b for all panels.

In the switching experiment described above we found that $T_{m\ azo\text{-}blue}$ was consistently lower (~2 ˚C) compared to the dark-state system. This implies that under blue light illumination the fraction of *cis*-azobenzene is greater than in the dark state. Non-UV light induced photo-switching

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of azobenzene moieties to *cis* has been reported before, but could only be achieved efficiently by introduction of chemical substituents on the aromatic rings.(29–32) We hypothesize that blue light can force a fraction of the azobenzene fragments into their *cis* conformation. Given that the DNA-mediated interaction between two complementary particles involves on the order of a hundred strands, even a small fraction of isomerization towards the *cis* conformation can lead to a measurable weakening of the interparticle attraction. This behavior opens then windows of temperature in which the particles attractive interaction can be recovered through two complementary mechanisms by reverting *cis* conformers back to their *trans* state: fast blue illumination and slow thermal relaxation. On the one hand, UV exposure can induce a large decrease in T_m and is reversible upon exposure to blue light with a fast response time with a characteristic time scale of seconds. On the other hand, blue light illumination, opens a small actuation temperature window of approximately two degrees with a slow recovery of the sticky state with a characteristic time scale of minutes to hours, which is strongly temperature-dependent and relies only on the thermal relaxation of the *cis*-azobenzene in the dark. This latter relaxation pathway is not suitable for fast actuation, though it can be exploited for systems that require slow processes like the crystallization of colloidal particles. This aspect will be discussed in more detail later on.

Continuous tuning of azoDCP interactions with mixed illumination

The photo-isomerization of the azobenzene moieties can be used to reversibly (dis)assemble azoDCP and leveraged to precisely tune the T_m of the system post-synthesis and externally, *i.e.*,

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without any changes to the sample itself. This is because the azoDCP T_m is dependent on previously described characteristics, e.g., DNA grafting density and salt concentration with the addition of the light condition history. This additional adjustable knob exists thanks to the simultaneous illumination of the sample with blue and UV light that enables control over the steady-state *cis/trans* composition of the azobenzene moieties, schematized in Figure 3a. To achieve intermediate interaction strengths, we illuminate the suspension simultaneously with UV light (365 nm) and blue light (455 nm). UV illumination drives the azobenzene groups toward the *cis* state, weakening DNA hybridization, while blue light promotes the *trans* state, strengthening particle binding. The balance between these two processes determines the steady-state fraction of *trans* and *cis* azobenzenes, and therefore the effective DNA binding strength. Figure 3b shows that the melting temperature of the colloidal assemblies can be continuously tuned by varying the relative intensities of UV and blue illuminations. As the UV intensity increases relative to the blue light, intensity ratio R of UV over blue light from 0 to 6.5, the melting temperature gradually decreases from 68.1 ˚C and 53 ˚C, reflecting the progressive weakening of DNA-mediated attractions. We previously showed that this temperature window can be opened even more as the melting temperature under pure UV (3 $mW \cdot cm^{-2}$, $R = \infty$) was measured at 38 ˚C. Upon increasing the relative intensity of UV light, the effective T_m of the particles decreases as the fraction of destabilizing *cis* isomers increases with respect to stabilizing *trans* isomers. The fraction of DNA strands that actively participate in colloid-colloid bond formation, i.e., 'active' DNA, was estimated as a function of R and reported in Figure 3c. To this end, a set of calibration particles was prepared by varying the ratio of sticky (azoDNA) and non-sticky (polyT) DNA sequences

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(see Supporting Figure S3 for details). Diluting the active DNA strands results in a drop of the T_m as fewer duplexes can be formed at the contact point between the colloids. Under the assumption that the fully relaxed dark state is composed of only *trans* isomers, mapping $T_m[R]$ to this calibration curve allows assessing the fraction of *trans* isomers for a given illumination condition. It shows that exclusively blue light illumination (1.1 $mW \cdot cm^{-2}$) already modifies the ground photo-stationary state, increasing the *cis* population. Blue light illumination places the system in a configuration where already an estimated 20% of the sticky-ends are rendered inactive (azo in the *cis* state). Additional UV illumination progressively increases the fraction of *cis* azobenzene up to 50% when $R = 6.5$. Reducing the *trans* fraction from approximately 100% (dark conditions) to 80% (under blue illumination) leads to a modest 2 ˚C drop in T_m, whereas further decreasing it from 80% to 50% causes a more significant drop of about 10 ˚C. The resulting decrease of T_m is non-linear: T_m decreases more rapidly with increasing cis-fraction for *cis*-rich brushes than for *trans*-rich brushes (Supporting Figure S3). The first 20% *cis* weakens the interactions less than the next 30% *cis*. T_m is relatively independent on coverage at sufficiently high coverage and becomes much more coverage dependent at lower coverages of active DNA.

The azoDCP photosensitivity can now be exploited to determine isothermal light-induced melting curves (Figure 3d and Supporting Movie SM2) from which we can extract a melting light composition $R_m[T]$ at a given temperature T. To this end, azoDCP suspended in PBS buffer at a fixed temperature (T_{sample} = 58.5 ˚C) below $T_{m\text{-azo blue}}$ were exposed to a mixture of UV and blue light of slowly linearly evolving composition R, from 0 to 8.2 in 30 min and down to 0,

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symmetrically. At first, exposed to blue light ($R = 0$), particles were fully aggregated, the amount of *trans* isomers in their sticky ends was high enough to maintain a strong adhesion between the particles. When R reached 2.5, the population of *trans* isomers was too low and the binding energy between azoDCP not sufficient to maintain the aggregated state. The particles then rapidly dissociated to form a melt. Decreasing R back to 0 resulted in the aggregation of the particles below $R \sim 2.1$. The hysteresis is attributed to the influence of the azobenzene environment on the photo-conversion of *trans* to *cis* azobenzene as reported by Samai et al.(27) Within a duplex, the *trans*-to-*cis* conversion is less efficient due to hindrance by the local environment, so that particle dissociation triggered by *trans*-to-*cis* conversion of azobenzenes requires a higher R than particle association induced by *cis*-to-*trans* switching.

These results demonstrate the possibilities of light as additional trigger to tailor the interactions between DNA functionalized colloids in a similar fashion as temperature does. In addition to isothermal switching between assembled and disassembled states over a broad temperature range (>30 ˚C), the T_m of a single batch of azoDNA particle can be set on-demand by exposing the particles simultaneously to UV and blue light.

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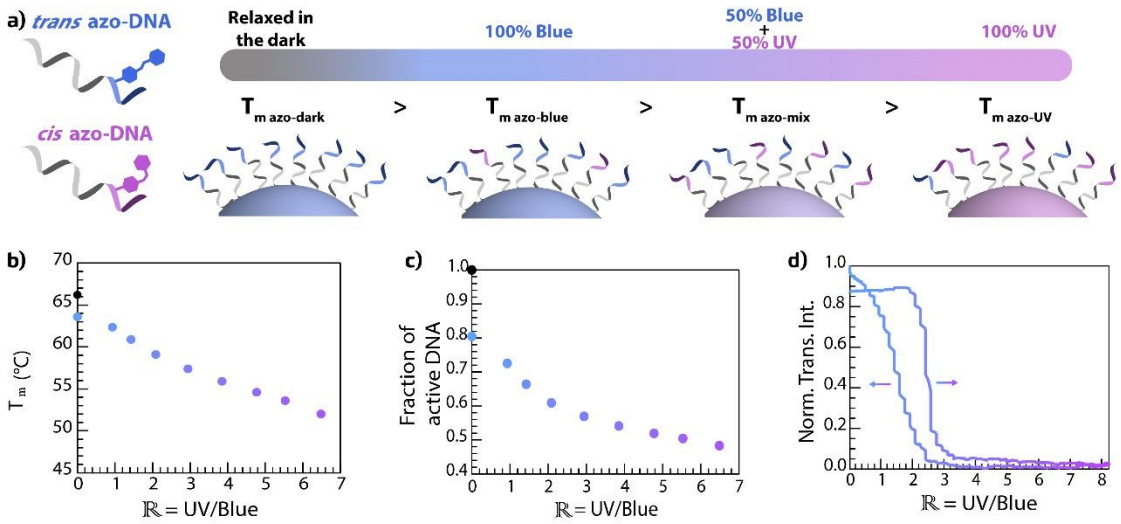

Figure 3. a) Schematic representation of tuning the azoDCP's T_m by simultaneous UV and blue light illumination. The relative intensity of UV and blue light R determines the fractions of azoDNA carrying *cis* (in purple) and *trans* (in blue) isomers of the azobenzene photo-switches. b) Influence of exposure to UV (0 to 7.15 mW·cm^{-2}) and blue light (1.1 mW·cm^{-2}) on the melting temperature (T_m). Increasing the UV intensity results in a decrease in T_m. The black dot corresponds to the $T_{m\ azo\text{-}dark}$ c) Fraction of active DNA strands available at the surface of a colloid to establish bonds with a partner particle as a function of the illumination conditions R (ratio of the intensity of UV and blue light). The black dot corresponds to azoDCP fully relaxed in the dark. The fraction of active DNA strands was determined by comparing the T_m of panel b) to a set of control experiments in which colloids were functionalized with mixtures containing various ratios of sticky and non-sticky DNA (see Supporting Figure S3). d) Isothermal Light induced melting curve of azoDCP kept at a constant temperature of 58.5 ˚C. The blue light intensity was kept constant at 1.1 mW·cm^{-2} while the UV intensity was linearly increased from 0 to 9 mW·cm^{-2} (R = 0 to 8.2) in 30 min then symmetrically brought down to 0 (see Supporting Movie SM2). Illumination conditions described in the Materials and Methods section 1.8b for panels b to d.

Light-induced spatiotemporal (dis)assembly of azoDCP

The unique feature of using light as a trigger is that it can be delivered precisely in space and time, surpassing traditional global triggers like temperature. To achieve spatiotemporal control over colloidal (dis)assembly, we examined an azoDCP dispersion at a fixed temperature, T_{sample} =

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47.5 ˚C (in PBS buffer with 69 mM of NaCl, $T_{m\ azo\text{-}UV} \approx 22$ ˚C $< T_{sample} < T_{m\ azo\text{-}blue} \approx 55$ ˚C) subjected to patterned UV (1.1 mW·cm^{-2}) and blue light (5.3 mW·cm^{2}) with the use of a digital mirror device (DMD, see Materials and Methods section 1.8d and Supporting Figure S4 for more information on the experimental setup). Initially, T_{sample} was set well below the system's $T_{m\ azo\text{-}dark}$ or $T_{m\ azo\text{-}blue}$. Under these conditions, the particles are strongly mutually attractive, leading to the formation of disordered clusters. These clusters were disassembled by illuminating the complete field of view with UV light ($T_{sample} > T_{m\ azo\text{-}UV} \approx 22$ ˚C, Figure 4a). Next, a blue light pattern was projected on the sample to write a rectangular shape (190 x 75 μm). Driven by the azobenzene isomerization, the T_m of the system in this defined area increases above T_{sample} ($T_{sample} < T_{m\ azo\text{-}blue} \approx 55$ ˚C, causing locally the formation of an aggregate of particles. Due to the higher local density of fluorescent particles, the aggregated area appears as a bright feature when observed by fluorescence microscopy.

Erasing the written feature was easily achieved by exposing the full field of view to UV light. In accordance to the time scales observed for global redispersion after UV exposure (Figure 2b), these finite-sized features fully disappeared over the course of seconds to minutes. The writing/erasing cycle was repeated five times to showcase the reversibility of the system (see Supporting Movie SM3).

These experiments demonstrate that interactions can be dynamically written, erased, and reconfigured at the micrometer scale. This spatiotemporal control is not limited to simple shapes, arbitrary patterns can be projected by the DMD, offering programmable assembly with spatial

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resolution approaching single particles. The assemblies can be erased locally by using a patterned UV illumination in a similar fashion.

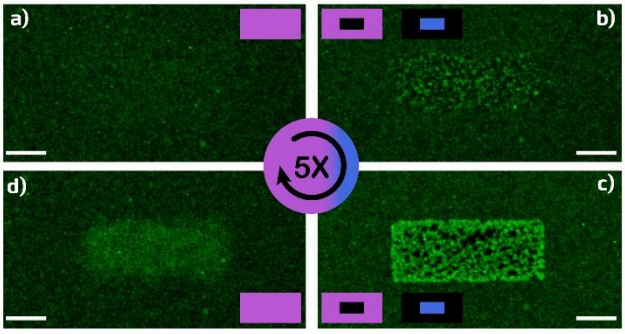

Figure 4. Demonstration of using UV and spatially-patterned blue light triggers generated with a digital mirror device (DMD) to write and erase arbitrarily shaped clusters comprising azoDNA-functionalized particles. The particles are maintained at T_{sample} = 47.5 ˚C, below $T_{m\ azo\text{-}blue}$ and above $T_{m\ azo\text{-}UV}$. Confocal microscopy images of (a-c) a sample exposed to a UV pattern and (b-d) exposed to rapid alternating patterns of a rectangular blue light (5.3 mW·cm^{-2}) and the complementary pattern in UV (1.1 mW·cm^{-2}). The respective patterns are reported as insets for each conditions. The writing/erasing starts by exposing UV light to the complete field of view, yielding a suspension of well-dispersed particles (a). Delivery of a rectangular blue light pattern on the sample while keeping the rest exposed to UV resulted in a localized progressive assembly (b and c, after 4 min of illumination). Reapplying UV exposure on the complete field of view, erases the written rectangle (d, after 4 min of UV illumination). The particles are then left in the dark for 2 min in order to allow their spatial redistribution by diffusion. This cycle was repeated five times. (see Supporting Movie SM3) For all panels: Scale bar = 50 µm. Illumination conditions described in the Materials and Methods section 1.8d for all panels.

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The precise spatiotemporal control over the interparticle interactions between azoDCP that allows to generate predesigned patterns on demand, may also be exploited to dissolve defects and delete off-target polymorphs that emerge during colloidal crystallization. To this end, undesired crystal nuclei could be selectively targeted for disintegration as well as particles at the periphery of a growing crystal, which have not properly assembled. Since these do not occupy a lattice position, their inclusion would introduce defects in the crystal lattice.

To investigate these opportunities, we set out to grow colloidal crystals of azoDCP. We first target 2D crystals to achieve optimal image quality for the direct observation of the crystalline order. The crystallization process was strictly confined into two dimensions by adding 3 wt% of F127 to a PBS buffer ([NaCl] = 51.4 mM) to generate a depletion interaction between the particles and the substrate (see Materials and Methods section). This concentration of surfactant is enough to keep the particles close to the substrate while preventing the depletion-induced self-assembly of the colloidal particles when the DNA interaction is turned off. First, the sample was equilibrated for 1h at 49 ˚C, a temperature below $T_{m\ azo\text{-}blue}$, resulting in the formation of small 2D crystallites (Figure 5a), similar to those observed for no-azoDCP. The temperature was increased to 52 ˚C, just below the melting temperature of the crystals. A crystallite was selected for further growth, while surrounding clusters were selectively disintegrated by localized UV light exposure (Figure 5a and b). As a result, the reservoir of free particles available for growth could be replenished. However, these UV-illuminated particles are not mutually attractive as $T_{sample} > T_{m\ azo\text{-}UV}$. Because thermal relaxation converts only a small fraction of the *cis* conformers back to their *trans* counterparts on the time scale of the experiment, blue light illumination is required for fast photo-

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conversion to render the particles attractive again. To confine the attachment of the newly formed singlet particles to the selected crystallite, a blue light pattern was projected to the surrounding area, effectively bringing T_m of the particles close to T_{sample}. The size and shape of this pattern was dynamically adjusted to follow the shape of the growing crystallite. Consequently, only the selected crystal grows, while additional nucleation sites in the surrounding area are suppressed.

In addition to the removal of undesired crystallites, UV light was also used to modulate the shape of the growing crystal by removing a defect-rich fragment (Figure 5e). The selective particle detachment induced by local illumination exclusively affects the selected areas, demonstrating the fine spatial control over the interaction between azoDCP.

After the complete illumination sequence (see Supporting Movie SM4), the selected crystal grew significantly (Figure 5a versus f), showcasing the potential of light-guided local manipulation of colloidal assembly processes. This approach allows selective growth of target crystals while suppressing nucleation elsewhere, highlighting how light can direct assembly pathways at the single-particle level.

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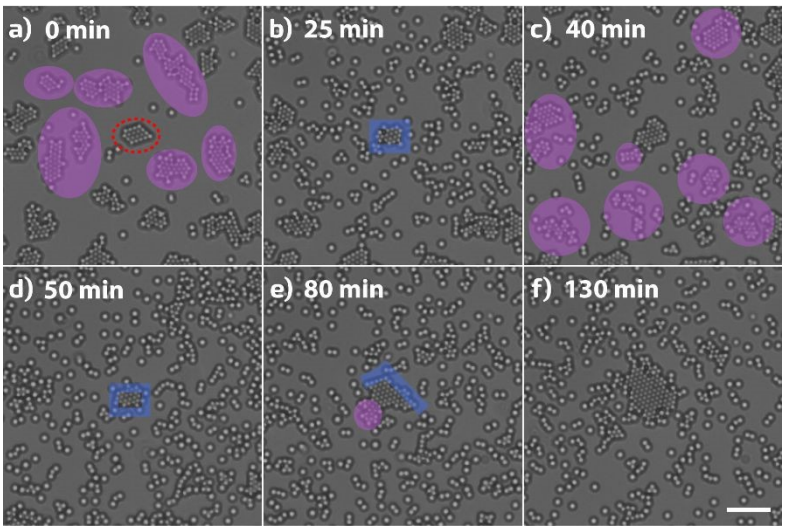

Figure 5. Manipulation of the 2D crystallization of azoDCP by local exposure to blue (5 mW·cm^{-2}) and UV light (2.4 mW·cm^{-2}). Transmission optical microscopy images of a) crystallites assembled during a quench below the melting temperature (T_m). The crystallite highlighted by the red dashed line was selected for further growth. The surrounding crystallites were illuminated with UV light (purple shaded areas) resulting in b) their selective disassembly. Exposing the sample area surrounding the selected crystal to blue light resulted in c) crystal growth. The selective melting and growth steps (a-b) were repeated (c-d) to further increase the crystal size. The size and shape of the crystal could be controlled by site-selective illumination e) with UV light followed by local illumination with blue light resulting in the final crystal f). Scale bar = 10 μm. Illumination conditions described in the Materials and Methods section 1.8d for all panels.

Defect annealing was also achieved for patchy azoDCP. Janus particles(33) comprising a PS and poly(3-(trimethoxysilyl)propyl methacrylate) (PTPM) lobe (respectively red and green on Figure 6, Supporting Figure S5 and Movie SM5) were site-selectively modified with the same azoDNA sequence as used for their spherical counterparts. The azoDNA sequences were present on the PS patches, while the PTPM lobes were left unfunctionalized. Dictated by their non-isotropic DNA-mediated attraction confined to the PS part of the particles, these building blocks assembled into pseudo-1D colloidal fibers at temperatures close to their T_m as previously reported for similar

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building blocks.(33) Preferential formation of PS-PS patch-patch inter-particle bonds and morphologies of the fibers were visualized by confocal microscopy. Similarly to the crystallization of spherical particles, the assembly of these Janus particles is prone to defects, for example, branching points. Figure 6 shows that undesired branches could be selectively removed by locally exposing the defect to UV light (1.8 mW·cm^{-2}). This illumination causes the detachment of a small cluster from the fiber (Figure 6b) and its final complete disassembly into singlet particles (Figure 6c).

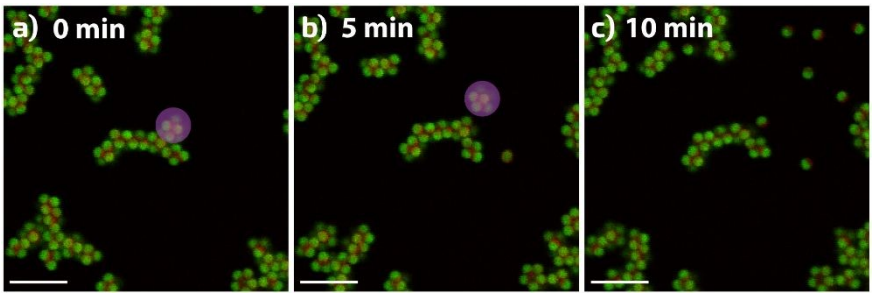

Figure 6. Manipulation of azoDNA-functionalized patchy particles by local exposure to UV light (1.8 mW·cm^{-2}). The patchy particles comprise two parts: a polystyrene part (PS) azoDNA (represented in red) functionalized at its surface by an azoDNA brush and a poly(3-(trimethoxysilyl)propyl methacrylate) part (PTPM) (represented in green). The mutually attractive DNA guided interactions between the PS surfaces at temperatures close to T_m drive assembly into pseudo-1D colloidal fibers. Assembly defects, such as branch points (a), can selectively be removed by local UV exposure, resulting in the detachment of the undesired branch (b) and its disintegration into single particles (c). Scale bars = 10 μm. Illumination conditions described in the Materials and Methods section 1.8d for all panels.

Relaxation-driven crystallization via thermal cis to trans isomerization Beyond fast light-induced switching, we exploit the slow thermal relaxation of *cis*-azobenzene to drive a new assembly pathway. Up to this point, we relied on the use of a combination of UV and blue light, simultaneous or alternating illumination, to control the isomerization state of the azobenzene

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moieties grafted to the backbone of DNA sticky ends and mostly neglected and did not yet exploit the ability of the *cis* azobenzene to relax thermally to the *trans* conformation. This process has been proven to be relatively slow compared to the photo-induced isomerization.(17, 20) Figure 7a (Supporting Movie SM6) shows a sample of azoDCP kept at 62 ˚C exposed to a mixed illumination at $R = 2$ (UV = 28 mW·cm^{-2} and blue = 14 mW·cm^{-2}), then kept in the dark for 12 h. The suspension is initially well-dispersed. According to the calibration curve (Figure 3b) under this light condition, the programmed melting temperature is indeed near 59 ˚C. Illumination allows us to generate enough inactive DNA strands at the particle surface to lower the azoDCP melting temperature to a value below the temperature of the sample ($T_{m\,azoR=2} < 62$ ˚C). While maintaining a fixed temperature for an extended period of time, the particles progressively aggregate and even crystallize. We attribute this phenomenon to the thermal relaxation of the azobenzene moieties. The distribution between the *cis* and *trans* conformations progressively relaxes towards the ground state which is *trans* rich. At the particle level, the number of inactive DNA strands (bearing a *cis* isomer) decreases and the corresponding melting temperature goes up until reaching the temperature of the sample. At that point, the particles start to aggregate. AzoDCP with a melting temperature around 62 ˚C have approximately 90% of their DNA coating in the sticky state and a small evolution of this composition does not have a strong impact on their melting temperature as revealed by the calibration curve (Supporting Figure S3). This means that, while the final 10% of inactive strands relax, the ability for the particles to roll on each other is conserved allowing the particles to crystallize.

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On the other hand, when a similar experiment is performed at 55 ˚C (sample prepared at R = 8, UV = 33 mW·cm^{-2} and blue = 8 mW·cm^{-2}, Supporting Movie SM7), only random aggregates are observed. This is due to the aforementioned non-linear dependence of T_m on the fraction of *cis* conformers (Figure S3). For particles decorated with a *cis*-rich brush, T_m is strongly affected by a small fraction of *cis* conformers relaxing to the *trans* state. Under these conditions, the time spent under 'rolling conditions' is too short to be conducive for colloidal crystallization, the particles totally recover their aggregated state in less than 30 min.

Earlier on, we showed that, on top of the ON/OFF switch based on UV and blue light illuminations, two states differing in their *cis*/*trans* occupancy can be generated without UV light exposure; namely by blue light illumination of the dark state. For a sample exposed to blue light, the recovery of the fully sticky state can only rely on slow thermal relaxation in the dark. We then reported a small shift of the melting temperature for azoDCP between a fully relaxed dark state and a sample exposed to blue light (Figure 2a). This temperature shift, on the order of 2 ˚C, reveals that a fraction of the *trans* isomers are converted to *cis* isomers by exposure to blue light. Supporting Movie SM8 shows directly how this subtle shift of T_m can be locally programmed into a colloidal suspension of azoDCP. Two populations of azoDCP were spatially confined in neighboring SU8 wells (Supporting Figure S6 and Materials and Methods section 1.11). One of these wells was kept in the dark while a blue disk was patterned on the second one (0.55 mW·cm^{-2}; illumination conditions reported in the Materials and Methods section 1.8c). Running subsequent temperature cycles to the full sample clearly revealed the high control of the local melting temperature thanks to light irradiation. This relaxation-driven assembly represents a new pathway

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distinct from conventional thermal annealing, allowing temporal programming of colloidal crystallization using molecular kinetics.

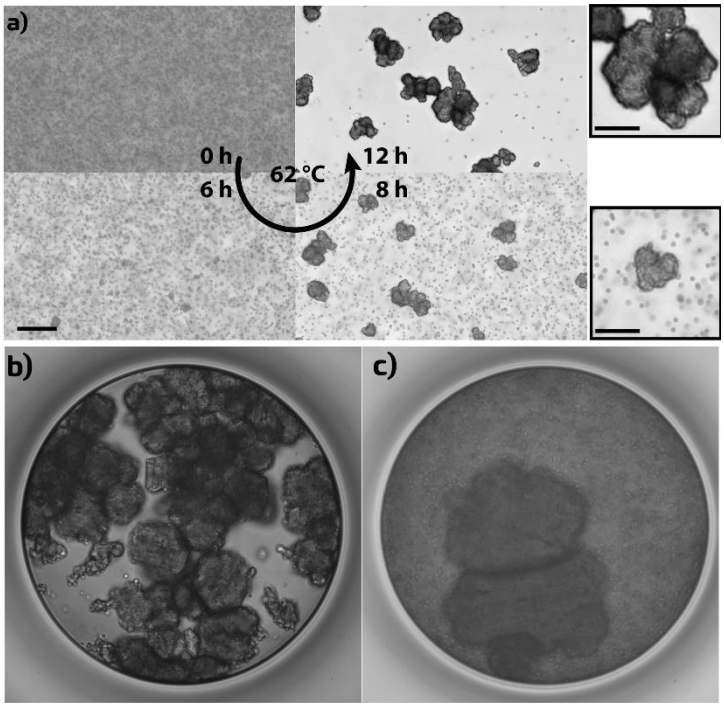

Figure 7. a) Thermal relaxation induced crystallization at 62 ˚C of a batch of 0.82 µm azoDCP, prepared at R = 2 (UV = 28 mW·cm^{-2} and blue = 14 mW·cm^{-2}) then kept in the dark. Particles start to show attractive interactions after 6 h of relaxation, forming small crystallites. These small crystals then progressively grow until the suspension is fully crystallized. Scale bars 20 µm, insets scale bars 10 µm b) Polycrystalline sample of 0.82 µm azoDCP, confined in an SU8 well, prepared by classic thermal annealing and maintained at 66.6 ˚C (1.5 ˚C below $T_{m\ azo\text{-}dark}$). c) Same well, after the selective melting of undesired crystallites by exposure to patterned blue light (0.55 mW·cm^{-2}) and subsequent growth of the surviving crystals by thermal relaxation of the azobenzene in the dark (multiple cycles). Diameter of the well: 130 µm. Illumination conditions described in the Materials and Methods section 1.8b for panel A and section 1.8c for *panels b and c.*

We then exploited this ability as a fine eraser to precisely select particles and aggregates to melt while keeping crystallites of interest in a near vicinity with the final goal of going from a myriad

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of small colloidal crystals to a well-ordered configuration. To explore this idea, we started from a set of azoDCP confined in a SU8 well, relaxed in the dark, and performed a first thermal annealing following a classical slow cooling close to $T_{m\ azo\text{-}dark}$. Under these annealing conditions, the particles assembled into a large number of crystallites (Figure 7b and Supporting Movie SM8), of various sizes and orientations as a result of the large number of nucleation events in this confined space. Reducing the cooling rate would decrease the nucleation density and thus promote the growth of larger crystals.(34) However, since nucleation events occur randomly in space, polycrystals cannot be avoided and with this particle size, the largest crystals formed are in the order of 20 - 40µm. By applying a designed low intensity blue pattern (0.55 $mW{\cdot}cm^{-2}$), only a few crystallites were kept in the middle of a suspension of singlet particles. A following thermal relaxation step without any light irradiation resulted in the growth of the remaining crystals with some nucleation and growth of undesired crystallites. Repeating this step twice resulted in very large crystals that would have been very difficult or impossible to grow by direct thermal annealing (Figure 7c). The ability of the freshly generated free singlet particles to relax back to their sticky state while being able to crystallize is the key feature that allows this fine control.

CONCLUSIONS

We demonstrate that incorporating azobenzene into DNA sticky ends provides dynamic, light-tunable control over colloidal interactions. This enables isothermal, reversible switching, spatiotemporal patterning, defect correction, and relaxation-driven crystallization. We demontrate

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the versatility offered by the introduction of an azobenzene moiety into the sticky ends decorating a set of DNA-coated colloidal particles (azoDCP). Maintained in the dark or upon illumination with blue light, the azobenzenes remain predominantly in their flat *trans* conformation, whereas exposure to UV light triggers their isomerization towards a population richer in their bent *cis* state. Depending on its conformation, this molecular light switch either stabilizes the DNA duplexes formed between complementary particles by intercalation or destabilizes them mainly by steric hindrance that prevents robust hydrogen bonding between the single-stranded sticky ends. This light-dependent (de)stabilization was shown to have a pronounced effect on the melting temperature (T_m) of the particles. As a result, azoDCP can be reversibly (dis)assembled under isothermal conditions by switching between blue and UV light irradiation. Furthermore, the effective T_m could be precisely tuned by simultaneous illumination with blue and UV light at controlled relative intensities. The ability to use light to control T_m of azoDCP opens up a wide range of possibilities. In particular, it allows to leverage the robustness of guiding colloidal assembly via DNA moieties in a spatiotemporal fashion. The assembly behavior of azoDCP can be dynamically controlled with spatial resolution ranging from a few hundred microns to micron length scales using local patterns of UV and blue light. This novel feature was demonstrated by repetitively writing and erasing clusters into arbitrary shapes, controlling 2D crystallization of isotropic spheres, and manipulating pseudo-1D self-assembled fibers consisting of patchy particles site-specifically modified with the azoDNA sequences. In addition, based on the thermal relaxation of the azobenzene, we report for the first time the relaxation-induced self-assembly pathway of azoDCP exposed to blue light and allowed to relax to its *trans*-rich stable state. This slow process

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combined with patterned light is a powerful tool to locally form random fractal aggregates or a crystalline phase in a melt on demand. Instead of a macroscopic knob such as temperature, these light sensitive particles can be locally annealed in order to erase and correct defects in already assembled structures.

Ultimately, these results provide a promising light-based strategy for manipulating colloidal assemblies on demand and with high spatial resolution. We believe that this level of control will be instrumental in the ongoing effort to create well-defined colloidal assemblies with tailored structures and properties, possibly in combination with other light induced modulation of DNA interactions.(35–38) We also envision using this novel interaction between colloidal building blocks to carve directly into colloidal crystals, for example to create 3D optical crystalline guides, or to access on demand reconfigurable matter.

SUPPORING INFORMATION

Materials and Methods describing all experimental details; representation of T_m determination (Figure S1); control of the effect of UV on the sample (Figure S2); calibration curve of T_m *vs.* sticky DNA coverage (Figure S3); Scheme of the DMD setup (1.8.d.) (Figure S4); SEM and confocal images of patchy particles (Figure S5); SEM of SU8 Patterns used to confine the particles (Figure S6); IR spectroscopy analysis of PS-PEO-N_3 (FigureS7); Movie cyclic light switch (Supporting Movie SM1); Cyclic melting under light (Supporting Movie SM2); Patterned writing and erasing cycles (Supporting Movie SM3); Selective melting and growth of 2D

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colloidal crystals (Supporting Movie SM4); Relaxation close to Tm azo-dark (Supporting Movie SM5); Relaxation far from Tm azo-dark (Supporting Movie SM6); Melting in the dark vs under blue (Supporting Movie SM7); Selective melting and growth of colloidal crystals using only blue light and thermal relaxation of the azobenzene (Supporting Movie SM8)

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Data availability statement:

The data supporting this article have been included as part of the ESI† or are available from the corresponding authors upon reasonable request.