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Crystal-to-Gel Transformation Stimulated by a Solid-State E→Z Photoisomerization

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Abstract

The molecule (*E*)-(5-(3-anthracen-9-yl-allylidene)-2,2-dimethyl-[1,3] dioxane-4,6-dione) (*E*-**AYAD**) undergoes an $E \rightarrow Z$ photoisomerization. In the solid-state, this photoisomerization can initiate a physical transformation of the crystal that is accompanied by a large volume expansion (~10 times), loss of crystallinity, and the growth of large pores. This physical change requires conversion of the ~10% conversion of the *E* to *Z* isomer and results in a gel-like solid with decreased stiffness that still retains its mechanical integrity. The induced porosity allows the expanding gel to engulf superparamagnetic nanoparticles in the surrounding liquid. The trapped superparamagnetic nanoparticles impart a magnetic susceptibility to the gel, allowing it to be moved by a magnetic field. The photoinduced phase transition, starting with a compact crystalline solid instead of a dilute solution, provides a new route for the *in situ* production of functional porous materials. (*Keywords: photochemistry, crystal, gel, isomerization, magnetism*)

The concept of molecular crystals as stiff and fragile objects has been upended by recent work demonstrating their ability to mechanically deform in response to external stimuli like heat, electrical, chemicals, or light.^[1] These mechanical motions reflect chemical changes inside the crystal that generate internal stress. In the case of light exposure, a photochemical reaction can create neighboring regions of reactant and product crystal phases, and the stress generated at the interface between these incommensurate phases powers a change in crystal shape.^[2] This "bimorph" mechanism underlies most photomechanical motions observed in crystals, like bending, twisting, jumping and peeling.^[3]

If the photochemical reaction does not induce a crystal-to-crystal phase change, a mechanical response can still be observed. For example, when exposed to a pulse of visible light crystalline nanowires composed of the photoreactive divinylanthracene molecule dimethyl-2(3anthracen-9-yl)allylidene)malonate (**DMAAM**) undergo a rapid coiling.^[4] This coiling is driven by $E \rightarrow Z$ or $Z \rightarrow E$ photoisomerization reactions and could be induced after 10-20% conversion of the starting isomer as long as a surfactant like sodium dodecyl sulfate (SDS) is present in solution. Without the surfactant present, the photoreaction proceeds much more slowly and no rapid shape change or amorphization can be observed.^[5] Subsequent characterization of this phenomenon suggested that the surfactant enables the molecules at the crystal surface to isomerize more easily, and the accompanying surface disruption then allows the surfactant to penetrate to the next layer and accelerate the transition to an amorphous mixture. A similar photoinduced amorphization process occurs in block-like microcrystals of DMAAM, in which the amorphous layers can be sequentially peeled off using short pulses of visible light.^[6] Unfortunately, in all these cases the amorphous **DMAAM** photoproduct phase dissolved in the aqueous surfactant solution within 2-3 hours, preventing its detailed characterization.

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In order to preserve the amorphous product phase, we hypothesized that lowering the conformational freedom of the ester groups by linking them together would reduce the molecular These considerations led us to synthesize the new divinylanthracene, (E)-5-(3solubility. anthracen-9-yl-allylidene)-2,2-dimethyl-[1,3]dioxane-4,6-dione), denoted (E)-AYAD, whose structure and photochemistry are shown in Scheme 1. This modification had the added benefit of shifting the absorption spectrum further into the visible region, from 450 nm to 480 nm. In solution, this molecule exhibits photophysical behavior similar to that of other divinylanthracene molecules (Supporting Information), in which the E and Z photoisomers can be interconverted using different wavelengths of light.^[5-7] In Figure 1a, we show the results of an experiment in chloroform where irradiation at 462 nm partially transforms the E isomer into the Z isomer, which can be partially converted back into the E isomer by illumination by 365 nm light. In the solid-state, the crystal packing of (E)-AYAD (Figure 1b) is similar to that of (E)-DMAAM, with the anthracene and divinyl moieties too far apart and misaligned to support intermolecular [2+2] or [4+4] photodimerization reactions.^[8] The crystal packing leaves the $E \leftrightarrow Z$ isomerization around the anthracene-adjacent double bond as the only viable chemical reaction pathway. Similar to DMAAM, irradiation of crystalline (E)-AYAD at 500 nm leads to rapid conversion of the E isomer into the Z isomer (Figure 1c). The main difference between the two derivatives is that the solubility of (*E*)-AYAD in alkane solvents is approximately $100 \times$ lower than that of **DMAAM**, as measured by the absorption of a saturated solution in hexanes (Supporting Information, Figure S10).

As with **DMAAM**, (*E*)-**AYAD** microcrystals do not undergo any discernible shape change when exposed to light in pure water, as shown in Figures 2a-d. Polarized light microscopy images indicate a gradual loss of crystalline order after 30 min of irradiation at 532 nm with an intensity of 430 mW cm⁻² (Supporting Information, Movie S1 and Figure S11). When the same experiment

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is done on microcrystals in the presence of a surfactant (0.025 M SDS), the crystal rapidly expands into a gelatinous mass (Figures 2e-h). This expansion is accompanied by a loss of the sharp edges and the optical birefringence (Supporting Information, Figure S12). Videos of this expansion are provided in the Supporting Information (Movies S2 and S3). The light-induced morphology changes are not due to simple melting. First, the melting point of (E)-AYAD is $231-234^{\circ}C$, so a temperature increase of this magnitude would vaporize the surrounding water. In the absence of light, the crystal suspension can be heated to around 100°C without any change in shape (Supporting Information, Figure S13). This temperature is much higher than that caused by the microscope lamp illumination. Second, there is a clear boundary that expands outward, albeit in random directions as the shape distorts, with no indication of liquification that would lead to the formation of hydrophobic droplets or tendrils. There is also no sign of fragmentation or the detachment of smaller particles during the shape change. Third, when the light is removed, the expansion stops immediately, maintaining its shape without collapsing into a spherical droplet to minimize surface area. Simple heating would lead to shrinkage after removal of the light as the object cools. Lastly, the total volume occupied by the gelatinous product phase is roughly $10\times$ greater than that of the original crystal. Melting without solvent incorporation would not be expected to generate such a large volume change, as the solid and melt densities are typically within 10% of each other.

Instead of melting, the morphology changes in Figures 2e-h are consistent with a crystalto-gel transition, in which the solid becomes porous and incorporates the solvent into its interior. Scanning electron microscopy (SEM) images of crystals before and after illumination confirm that the smooth surfaces of the unreacted crystal transform into an irregular sponge-like surface with pores on the order of 100 nm in diameter (Figures 3a-d). The SEM images are taken after drying and sputter-coating, and we were concerned that this processing might affect the appearance of the product phase. To confirm the porous nature of the reacted crystal surface, we used atomic force microscopy (AFM) to image the expanded solid in air. Figures 3e and 3f show AFM images of the surface before and after irradiation. They confirm that the smooth surface of the unreacted crystal gives way to a corrugated surface with deep indentations whose depth was greater than 300 nm. The expanded solid is moderately stable in air, retaining its overall shape even after drying. Incorporation of water into the porous solid is consistent with the observed loss of adhesion of many crystals to the glass surface during irradiation. In many cases, a previously stationary crystal would detach from the microscope slide and start drifting through the solution after the light was turned on as it expanded (Supporting Information, Figure S14).

The AFM measurements also provide a preliminary way to characterize the mechanical properties of the expanded solid. Measurements on gelated crystals in air show that the surface stiffness decreases from 9.0 N/m to 3.6 N/m after reaction, consistent with a softening due to loss of crystallinity and solvent incorporation. The stiffness is proportional to the Young's modulus, although it also depends on sample thickness and tip area (Supporting Information). The same tip was used for both measurements, and assuming no change in thickness, the stiffness decrease implies a decrease of 60% in the Youngs modulus. This probably underestimates the actual decrease due to 1) the loss of water in the air-exposed sample and 2) the likelihood that the expanded gel is thinner than the original crystal. Despite this softening, the expanded solid does retain some degree of mechanical coherence. After expansion, the gel-like produce maintains its shape as it drifts and rotates in solution (Supporting Information, Figure S15 and Movie S3) and can interact with rigid surfaces like an alumina filter or glass sidewall without deforming or breaking apart.

NMR analysis of the reacted crystal indicated that only ~12% of the (*E*) isomer was converted to the (*Z*) form even after prolonged illumination (Supporting Information, Figure S16). The overlap of the (*E*) and (*Z*) charge-transfer bands in the absorption spectra in Figure 1 likely leads to a photostationary state that limits conversion to the (*Z*) isomer. The loss of crystallinity can be initiated by the presence of a relatively small amount of photoproduct, as observed previously for **DMAAM** nanowires and microblocks.^[4-6] Furthermore, (*E*)-**AYAD** only acts as a gelator when starting from the crystal form. Attempts to generate a solution-to-gel (sol-gel) transition starting with dilute (*E*)-**AYAD**/SDS solutions were unsuccessful. (*E*)-**AYAD** is not sufficiently soluble for us to observe any sign of gel formation by changing temperature, irradiation or by slow solvent evaporation. It appears that the only route to the gel is by starting with undissolved (*E*)-**AYAD**, i.e. the crystal, and inducing gelation using photochemical disruption.

The observation of a photoinduced crystal-to-gel transition is remarkable for two reasons. First, it is a unique type of physical transformation. Photoisomerization has been used to induce swelling in an already formed gel^[9] and to induce gel-liquid transitions in solution.^[10] Both cases involve a transition between two disordered phases with the solvent already incorporated. The photoinduced gelation of (*E*)-**AYAD** begins with a dense, ordered single crystal. We hypothesize that the surfactant facilitates the molecular rearrangements needed for photoisomerization, perhaps analogous to the acid-induced melting recently observed in acetaldehyde phenylhydrazone crystals.^[11] This surface photoisomerization then opens up fissures in the crystal, in effect increasing the surface area, both water and surfactant can then penetrate into the interior and cause further reaction and amorphization. The idea that gelation begins at the surface is supported by time-resolved imaging of the crystal, which shows the morphology changes starting at the outside edges of the crystal and migrating inward (Figure 2f). Figure 4 shows a cartoon of this process, in

which porosity develops through a combination of amorphization and solvent penetration. This picture of gelation based on networks of molecular aggregates (either crystalline or non-crystalline) is consistent with current pictures of how low molecular weight gels are formed.^[12]

The interaction of a crystalline solid with a solvent is generally assumed to have only two dissolution or incorporation of the solvent through specific host-guest possible outcomes: interactions. The (E)-AYAD crystal-to-gel transformation appears to involve "solvation" that lies between these two extremes, since the solvent disrupts the crystal integrity and facilitates the growth of disorder but cannot overcome the lipophilic interaction between AYAD molecules to fully dissolve them. It is possible that this "partial solvation" may be due to a time averaging of reactant and product solubilities. (Z)-AYAD has a slightly higher solubility in alkane solvents (×3) and surfactant aqueous ($\times 2$) solution than (E)-AYAD (Supporting Information, Figure S17 and S18). Coupled with the overlapping absorption spectra of both isomers at the irradiation wavelength, the differing solubilities could lead to a dynamic photoequilibrium between the soluble Z isomer and the less soluble E isomer, accompanied rapid dissolution/deposition at the surface of the crystal. A similar light-driven dynamic equilibrium between E and Z isomers has been invoked to explain photoinduced pattern formation in polymers that contain azobenzene chromophores.^[13]

The second remarkable feature of this crystal-to-gel transition is its large volume change. Large reversible expansions of crystalline solids induced by hydration have been observed.^[14] In these cases, the volume change is induced by the addition of a separate chemical species that drives the system to a new equilibrium structure. The (*E*)-**AYAD** crystal is not porous and does not support any type of host-guest interaction that could attract H_2O or surfactant guest molecules in the absence of photoisomerization. The large volume change occurs only under highly nonequilibrium conditions, made possible by the light-driven isomerization reactions that facilitate penetration of the solvent into the crystal. Typical minimum gelation concentrations are on the order of $1\%^{[15]}$, which would suggest that even large expansions (up to $100\times$) may be possible using this strategy.

Finally, we briefly touch on possible applications of this photoinduced gelation. The physical expansion of the gel can be used to generate work or to disrupt it surroundings. For example, if the crystal was enclosed inside a membrane, the light-induced expansion could be used to burst the membrane. A second application is to take advantage of the expanding gel to entrap objects from the surrounding medium and acquire their properties. From the images in Figure 3 and the Supporting Information (Figure S19), gelation opens up channels with diameters on the order of 50-150 nm. One could imagine a light-activated sponge that soaks up nanoparticles in a hard-to-access environment. We first tried to use the gel to entrap fluorescent microparticles from the surrounding solution, but the absorption of the solid-state (E)-AYAD extends out to 700 nm and either quenched or absorbed the nanoparticle emission, leaving only surface adsorbed particles visible. We then performed an experiment using superparamagnetic colloidal nanocrystal clusters (CNCs) with an average diameter of 70 nm.^[16] Before irradiation, intact crystals can be imaged using transmission electron microscopy (TEM), as shown in Figure 5a. Some CNCs rest outside the (E)-AYAD microcrystals, suggesting CNCs cannot be entrapped by the (E)-AYAD crystals without light exposure. After irradiation, aggregated CNCs were visible, encased in an organic layer, as shown in Figure 5b. Clear interfacial boundaries can be seen between magnetic CNCs and (E)-AYAD samples, indicating the CNCs are incorporated into the AYAD gel after light irradiation.^[17] Their incorporation into the gel is consistent with the relatively large pores (≥ 70 nm diameter) resulting from the light-induced gelation.

The trapped CNCs allow the expanded gel to be manipulated by an external magnetic field. The microcrystals without light irradiation barely move under external magnetic field even after a collision with a huge aggregate of magnetic CNCs, as shown in Figure 5c and Movie S4. On the other hand, an exposed gel with entrapped CNCs could be pulled over a distance of 180 μ m or more by a magnet with a field strength on the order of 100 Gauss with an average speed of about 1.4 μ m s⁻¹, as shown in Figure 5d and Movie S5.

In conclusion, we have shown that the newly synthesized molecule (*E*)-**AYAD** can undergo a photoinduced crystal-to-gel transition in aqueous surfactant solutions. The gelation is accompanied by a large volume expansion (>10×) that enables it to engulf surrounding nanoparticles. We hypothesize that the gelation is driven by the synergistic action of molecular photoisomerization that disrupts the local crystal packing, followed by solvent penetration that facilitates further photoisomerization reaction deeper inside the crystal, eventually leading to a porous, amorphous gel. We have demonstrated how this crystal-to-gel transformation can enable new types of photo-controlled processes like spatially selective nanoparticle trapping or environmental disruption. The discovery of a new route to expanded porous solids, based on photoismerization in a compact crystal starting material, opens up new opportunities for the application of low-molecular weight gels as dynamic materials.

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Graphic abstract



The molecule (*E*)-(5-(3-anthracen-9-yl-allylidene)-2,2-dimethyl-[1,3] dioxane-4,6-dione) ((*E*)-**AYAD**) undergoes an $E \rightarrow Z$ photoisomerization in the crystal state that drives a dramatic physical transformation characterized by a large volume expansion, loss of crystallinity, and high porosity. This photoinduced crystal-to-gel transition can be used to entrap superparamagnetic nanoparticles in the surrounding liquid.



Scheme 1. Reaction scheme of (*E*)-AYAD that undergoes *E* and *Z* photoisomerization respectively.

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Figure 1. (a) UV-Vis absorption spectra of (*E*)-**AYAD** in solution (chloroform as solvent, concentration = 6.9×10^{-5} M, intensity of 462 nm light is 15 mW/cm² and the intensity of 365 nm light is about 2.85 mW/cm²). (b) Crystal structure of (*E*)-**AYAD** viewed along *a* axis. (c) UV-Vis absorption spectra of solid-state polycrystalline thin film of (*E*)-**AYAD** under light irradiation (532 nm light at 50 mW/cm²)

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Figure 2. (a)-(d) Optical microscope images of (*E*)-**AYAD** microcrystals in pure water under light irradiation for about 30 min (532 nm, 430 mWcm⁻²). (e)-(h) Optical microscope images of (*E*)-**AYAD** microcrystals suspended in aqueous surfactant solution under light irradiation with the same time scale of (a)-(d). The red rectangle indicates the original crystal. Scale bar: 50 μ m



Figure 3. Scanning electron microscopy (SEM) images of (*E*)-**AYAD** microcrystals before (a) and after light irradiation (b)-(d), showing various phases of gelation. The images in (b)-(d) are of different crystals. Scale bar: 5 μ m. Atomic force ficroscopy (AFM) images of surface of (*E*)-**AYAD** microcrystals before (e) and after (f) light irradiation.



Figure 4. Schematic illustration of the changes of (*E*)-**AYAD** microcrystals under light irradiation in aqueous surfactant solution.



Figure 5. (a) Transmission electron microscopy (TEM) image of (*E*)-**AYAD** microcrystals with magnetic CNCs before light irradiation. (b) TEM image of (*E*)-**AYAD** incorporated with CNCs after light irradiation. Black scale bar: 200 nm (c) (*E*)-**AYAD** crystal without UV light irradiation. As an external magnetic field is applied (purple arrow), the superparamagnetic CNCs aggregate and migrate along the direction of the field, but the (*E*)-**AYAD** crystal is barely affected. The drift of position is due to the collision between the crystal and a big aggregate of CNCs. (d) (*E*)-**AYAD** crystal after UV light irradiation and becomes a gel. When the magnetic field is applied, the CNCs go inside the body of (*E*)-**AYAD** and the gel can move in the direction of the magnetic field. The yellow dash line indicates the position of **AYAD** gel. White scale bar: 50 µm.

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