

Photoinduced Curling of Organic Molecular Crystal Nanowires**

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Materials that transform light into mechanical motion are interesting from both fundamental and technological perspectives. Photomechanical materials usually consist of photoreactive molecules assembled in an ordered matrix, for example a liquid crystal polymer.^[1,2] The use of molecular crystals as photomechanical materials is challenging, since strain between reacted and unreacted crystal phases often leads to fracture and crystal disintegration.^[3] While there are examples of macroscopic crystals that can support light-induced shape changes,^[4–8] a more general approach is to shrink at least one of the structure's dimensions to the nanometer scale so that interfacial strain can be dissipated at the surface, preventing fracture.^[9–11] Such small-scale photomechanical structures could be useful in fields like cell biology, but generating complex motions remains a challenge. In most photomechanical actuators, directional motion, for example, bending, is induced by illumination of one side of the crystal, creating a bimorph structure consisting of a layer of reacted molecules adjacent to a layer of unreacted molecules.^[12] The interfacial strain between the two phases drives directional motion like bending. But illuminating only one side of a nanostructure becomes impractical once the size of the structure falls below the diffraction limit of the excitation light.

One goal of our research has been to develop molecular crystal nanostructures where the directional response is “built in” by the crystal shape and molecular packing. Previously, we showed that microribbons composed of 9-anthracene carboxylic acid could reversibly twist under uniform illumination, providing an example of how complex motion could be initiated by nondirectional light.^[13] This motion was driven by the [4+4] photodimerization of the anthracene rings, resulting in a temporary two-phase (monomer and dimer) system whose interaction provided strain energy to twist the crystal. Photomechanical materials based on dimerization reactions are not ideal since this bimolecular reaction requires two molecules to be in close proximity, placing severe constraints on the crystal structure of potential materials.^[14] We have recently begun synthesizing anthracene-9-(1,3-butadiene) derivatives with the goal of developing photomechanical materials powered by a unimolecular $E \rightarrow Z$ reaction that can be initiated by visible light ($\lambda > 430$ nm). An added requirement is that nanostructures composed of this molecule should be able to execute complex motions under uniform illumination conditions. We have recently synthesized a novel anthracene-9-(1,3-butadiene) derivative, dimethyl-2(3-(anthracen-9-yl)allylidene)malonate (DMAAM). Here, we study its solid-state structure and reactivity and show that a pulse of visible light can induce a curling motion in crystalline nanowires. Considerable effort has been devoted to making static coiled nanowires,^[15–17] usually by changing extrinsic factors like the nanowire's surface chemistry or solvent environment. The coiling observed in this study is qualitatively different, since it relies on intrinsic chemical changes taking place inside the wire itself, namely the $E \leftrightarrow Z$ photoisomerization. This motion occurs under uniform illumination conditions and illustrates how a molecular crystal nanostructure can undergo a nontrivial and possibly useful geometry change after photoexcitation.

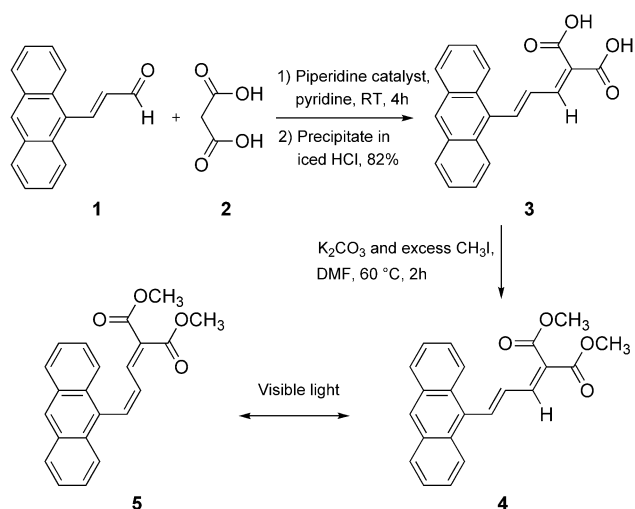
The synthesis of (*E*)- and (*Z*)-DMAAM isomers is outlined in Scheme 1 and described in detail in the Supporting Information. Both molecules are stable at room temperature in the dark and can be crystallized from various organic solvents. The *E* and *Z* isomers have overlapping absorption spectra in the solid state, as shown in Figure 1, that are very similar to those in dilute solution, suggesting that strong intermolecular interactions are absent in both crystals. The detailed crystal structures for both molecules are given in the Supporting Information and are discussed below.

Two types of nanowires, composed of either pure (*E*)- or pure (*Z*)-DMAAM, were made using solvent-annealed crystallization inside the channels of commercially available anodic aluminum oxide (AAO) templates.^[18] After dissolution of the AAO template in phosphoric acid, the 200 nm

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Scheme 1. Synthesis of (*E*)-dimethyl 2-(3-(anthracen-9-yl)allylidene)-malonate (DMAAM) (**4**), and photoisomerization to (*Z*)-DMAAM (**5**).

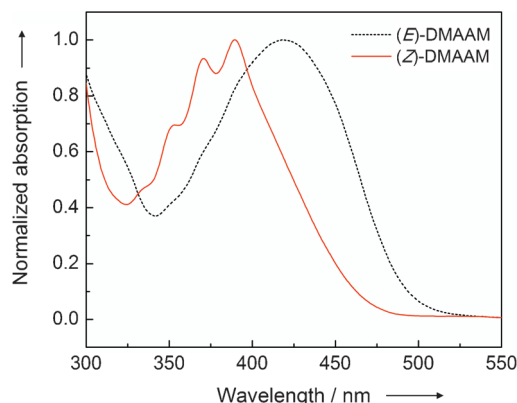


Figure 1. Absorption spectra of thin solid films of (*E*)-DMAAM (dotted black line), and (*Z*)-DMAAM (solid red line).

diameter nanowires were imaged using SEM. Figure 2a shows a side view of the (*E*)-DMAAM nanowires, while Figure 2b shows a cross-sectional view of the (*Z*)-DMAAM nanowires. The highly crystalline nature of the nanowires can be seen from the TEM images of a single wire and its accompanying electron diffraction pattern shown in Figure 2c and d. The arrangement of the diffraction spots provides information as to the orientation of the unit cell relative to the wire axis. In order to confirm that this crystal orientation is a general feature of the nanowires, we measured powder X-ray diffraction (PXRD) patterns for bulk nanowire samples. Figure 2e shows a calculated PXRD pattern for a true powder of randomly oriented crystallites. Figure 2f shows the experimental PXRD pattern for (*E*)-DMAAM powder, which corresponds well to the predicted pattern in terms of peak intensities and positions. This data confirms that the single-crystal structure is useful for assigning peaks from an experimental powder pattern. In Figure 2g we show the PXRD pattern for (*E*)-DMAAM nanowires aligned inside their AAO template and pointed upward relative to the

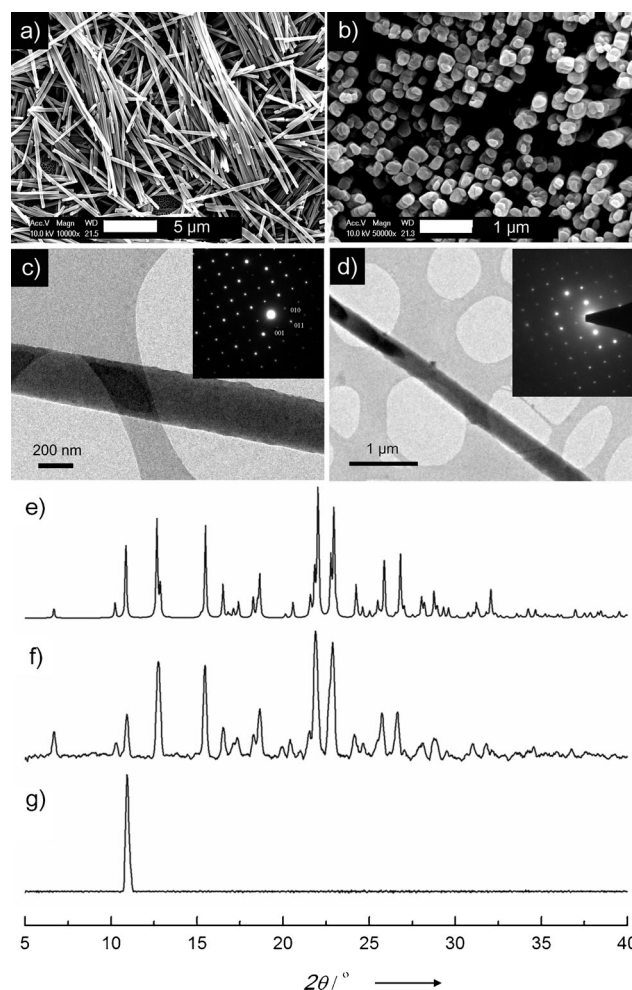


Figure 2. a) SEM micrograph of (*E*)-DMAAM nanowires in horizontal view. b) SEM micrograph of (*Z*)-DMAAM nanowires in vertical view. c) TEM micrograph of an (*E*)-DMAAM nanowire and its electron diffraction pattern (inset). d) TEM micrograph of a (*Z*)-DMAAM nanowire and its electron diffraction pattern (inset). e) Calculated PXRD pattern of (*E*)-DMAAM. f) Experimental PXRD pattern of (*E*)-DMAAM. g) PXRD pattern of aligned (*E*)-DMAAM nanowires inside AAO pores.

PXRD substrate. Only one peak, corresponding to the (011) Miller plane, exhibits appreciable intensity. This plane must be oriented parallel to the substrate and therefore perpendicular to the long axis of the nanowires. (PXRD data for (*Z*)-DMAAM are given in Supporting Information.) Analysis of both the TEM diffraction pattern of single nanowires and PXRD patterns for multiple wires oriented in an AAO template are consistent with crystalline nanowires where the (011) Miller plane is oriented perpendicular to the wire axis for both *E* and *Z* isomers.

Highly anisotropic deformations are observed when the nanowires are irradiated with visible light. In our experiments, the light was supplied by a filtered microscope lamp with an intensity of 100–200 mW cm^{−2}. In Figure 3, we show a sequence of images where a single 200 nm diameter (*E*)-DMAAM nanowire is irradiated using a 1 s pulse of light with $\lambda > 450$ nm, which overlaps with the low-energy edge of its absorption spectrum. When exposed to light, the wire

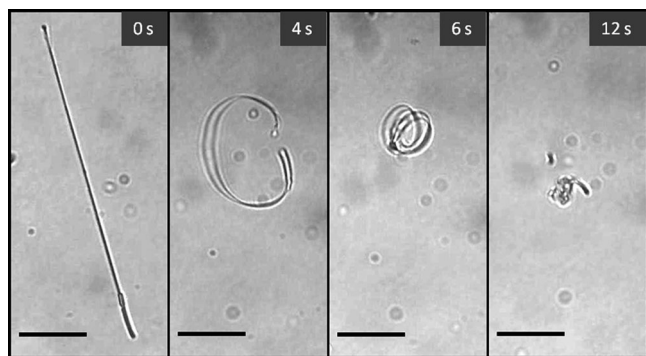


Figure 3. Snapshots showing coiling of an (*E*)-DMAAM nanowire after 1 s of light exposure at time 0 s. Scale bars: 10 μm .

immediately begins to curl. This curling continues for several seconds even after the light is turned off, until the wire has collapsed into a tightly coiled ball. Images and videos of similar photoinduced curling of other nanowires can be found in the Supporting Information. 150 and 80 nm diameter wires showed the same curling behavior as the larger diameter nanowires (Supporting Information). Exposing (*Z*)-DMAAM nanowires to the same illumination conditions also resulted in curling, as shown in Figure 4. All experiments

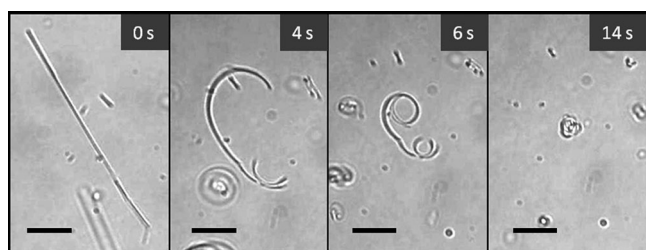


Figure 4. Snapshots showing coiling of a (*Z*)-DMAAM nanowire after a 1 s pulse of light exposure at time 0 s. Scale bars: 10 μm .

were done in an aqueous suspension, and typically the yield of curled nanowires was > 80%. If the sample was allowed to dry, or if the nanowires adsorbed to a glass surface, the photoinduced curling was reduced or not observed at all. The possible role of heating was assessed using a heated microscope stage. (*E*)-DMAAM nanowires in an aqueous suspension showed no sign of curling when heated up to 85°C, a temperature well above what could be induced by the illumination lamp.

We hypothesized that $E \leftrightarrow Z$ molecular level photoisomerization events drive the curling motion. This class of 9-substituted-anthracene-1,3-butadiene derivatives is known to undergo a $E \rightarrow Z$ photoisomerization in solution,^[19] and we confirmed that the *E* form could photoisomerize into the *Z* form in dilute solution. Somewhat surprisingly, the $E \rightarrow Z$ photoisomerization is also the dominant photochemical pathway in the solid-state. Figure 5 shows a view of the crystal structures of both isomers. (*E*)-DMAAM crystallizes in a head-to-tail herringbone pair motif commonly seen for

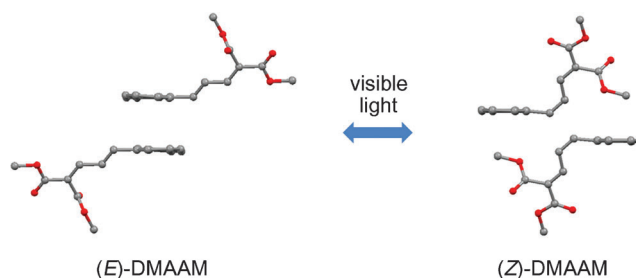


Figure 5. Crystal packing change between (*E*)-DMAAM and (*Z*)-DMAAM isomers.

anthracenes substituted at the 9-position. Given the cofacial arrangement of the anthracene rings, with an intermolecular distance of 3.7 Å, one might expect that the [4+4] photodimerization would be facile in this crystal. But when powders were exposed to light at wavelengths 365 nm and higher, no evidence for this reaction was seen. The crystals retained a yellow color, and ¹H NMR spectrum of the dissolved (*E*)-DMAAM after photoreaction confirmed that up to 90% of the *E* isomer could be converted to the *Z* isomer after a period of hours, but no trace of the [4+4] photodimer could be detected. Absorption spectra of suspended nanowires during irradiation showed only conversion between *E* and *Z* forms (Supporting Information). A possible explanation for the lack of [4+4] dimerization is suggested by the structure of the *Z* crystal. It can be seen that isomerization of the dimethoxy side chains alters their packing. The resulting side chain rearrangement ends up pulling the anthracenes apart, preventing the anthracene rings from undergoing a subsequent [4+4] dimerization. This conformational change of the side chains is also expected to disrupt the monomer packing. But because a transition between the two crystal structures would require very large molecular rearrangements, a photo-induced single-crystal-to-single-crystal transformation between *E* and *Z* forms must be considered unlikely. This $E \rightarrow Z$ photoisomerization probably proceeds through a hula-twist or bicycle pedal mechanism, similar to other solid-state $E \rightarrow Z$ photoisomerizations.^[20–22]

Even though it is unimolecular, the $E \rightarrow Z$ photoreaction does not proceed to 100% completion. ¹H NMR spectra of light-exposed (*E*)-DMAAM nanowires show that only 40–80% of the molecules are converted to (*Z*)-DMAAM after a 1 s pulse of light (Supporting Information). Even at 20% conversion, significant curling could be observed. After prolonged light exposure at $\lambda > 450$ nm, we could only attain 90% conversion to (*Z*)-DMAAM. Several factors may explain why this photochemical reaction does not proceed to 100% completion. One explanation is that even though our $\lambda > 450$ nm photoexcitation light is tuned to the long-wavelength edge of the (*E*)-DMAAM absorption spectrum, it still has some overlap with the (*Z*)-DMAAM absorption and can induce both $E \rightarrow Z$ and $Z \rightarrow E$ isomerization reactions. Thus, we would expect to attain a photostationary state where the relative amounts of *E* and *Z* isomers depends on the ratio of their quantum yields and absorption coefficients at the lamp wavelengths. A second factor is the

crystal environment, itself, where defects or high product densities may inhibit further photoisomerization. Assessing the relative importance of these two factors requires a full investigation of DMAAM solid-state photophysics, which is beyond the scope of this paper.

It is interesting that curling occurs in both the *E* and *Z* nanowires, despite the fact that they have very different starting crystal structures. From the previous discussion, we can conclude that the curling motion originates from the generation of a mixture of *E* and *Z* isomers in an initially single-component, crystalline wire. Previously, crystal twisting has been explained by invoking a heterometry mechanism,^[13,23] where the simultaneous presence of two different phases in a single crystal leads to internal strain that deforms the overall crystal shape. Clearly, the curling observed here requires the presence of both reactant and product species, consistent with the heterometry mechanism. But although we can identify the crystalline reactant as one phase, the exact nature of the second phase is unclear. Unlike our previous experiments on photodimer systems,^[24,25] we could find no peaks corresponding to a photoproduct crystal phase in PXRD experiments performed during irradiation. We directly imaged the sample after photoreaction using TEM in an attempt to identify *E* and *Z* domains within the curled nanowires. Unfortunately, the work-up involved drying and washing the nanowires on a TEM grid, and this process appears to decompose the nanowires. Examination of the photoreacted sample revealed only fragments of amorphous organic material. The lack of crystallinity in the nanowire fragments is consistent with the PXRD data showing that no new crystal phase is formed.

Taken together, these observations suggest that the curling is driven by the generation of an amorphous product phase, rather than by a crystal-to-crystal phase transition. We think that photoreaction of either the pure *E* or *Z* crystal results in an amorphous phase that interacts with the remaining crystalline reactant phase. Recent results on the photoreaction of triazoline crystals support the idea that large structural changes, of the type illustrated in Figure 5, can lead to the formation of mixed crystal-amorphous phases.^[26] The induction time for completing the coil could reflect the time required for the amorphous product and crystalline reactant phases to rearrange themselves within the nanowire. A similar delayed mechanical response has been observed in the photoreaction of dinitroanthracene crystals.^[27] The fact that this curling transition occurs starting from either crystalline (*E*)- or (*Z*)-DMAAM suggests that it could be a general phenomenon where a partial crystal → amorphous transition can be induced photochemically. If this interpretation is correct, then the nanowire curling may be analogous to the curling of a hair fiber when exposed to a high temperature. In that case, partial melting of the keratin protein matrix allows the hair to curl in one direction. In the present case, the loss of crystallinity occurs at low temperature due to a photochemical reaction, rather than thermal melting.

In conclusion, we have synthesized a new anthracene derivative, DMAAM, whose solid-state photochemistry involves only the *E* → *Z* photoisomerization, despite a crystal packing geometry that should permit the [4+4] dimerization

as well. When single-crystal nanowires of this molecule are grown, this photoisomerization reaction drives a dramatic change in the crystal shape, where straight nanowires rapidly curl and collapse into tightly coiled bundles. This photo-induced motion is observed for nanowires composed of either (*E*)- or (*Z*)-DMAAM and may involve interactions between crystalline reactant and amorphous product phases. This heterometry mechanism, arising from a solid-state unimolecular photochemical reaction, could provide a way to design novel photoresponsive structures that rapidly change their extent in response to visible light.

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