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Chemical reaction method for growing photomechanical organic microcrystals[†]

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(*E*)-3-(Anthracen-9-yl)acrylic acid (9-AYAA) exhibits a strong photomechanical response in bulk crystals but is challenging to grow in microcrystalline form. High quality microcrystals of this molecule could not be grown using techniques like sublimation, reprecipitation, and the floating drop method. If the *tert*butyl ester of 9-AYAA is used as a starting material, however, high quality, size-uniform microwires could be grown *via* acid catalyzed hydrolysis. 9-AYAA microwires with uniform length and thickness were produced after a suspension of (*E*)-*tert*-butyl 3-(anthracen-9-yl)acrylate ester microparticles was tumble-mixed in a mixture of phosphoric acid and sodium dodecyl sulfate at 35 °C. The dependence of the results on temperature, surfactant and precursor concentration, and mixing mode was investigated. This chemical reaction-growth method was extended to grow microplates of 9-anthraldehyde using the corresponding acylal as the starting material. Under 475 nm irradiation, the 9-AYAA microwires undergo a photoinduced coiling-uncoiling transition, while the 9-anthraldehyde microplates undergo a folding-unfolding transition.

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Introduction

In the past decade there has been increased interest in molecular crystals that can deform or actuate when exposed to UV or visible light.¹⁻³ In the majority of cases, this deformation is driven by a crystal-to-crystal photochemical reaction where the simultaneous presence of two different crystal phases (reactant and product) leads to internal strain that drives bending⁴⁻⁹, twisting^{10,11} or jumping.¹² The nature of the deformation depends not only on the chemical reaction and crystal packing, but also on the overall shape of the crystal itself.^{10,13,14} To make molecular crystal actuators with welldefined properties, it is vital to control their shape and dimensions. Photoreactive molecular crystals with large dimensions tend to either shatter or disintegrate when irradiated due to buildup of internal stress between the photoproduct and reactant phases.¹⁵ This problem can often be solved by shrinking the crystal to micron dimensions.^{16–18} A separate

Kingdom of Saudi Arabia. E-mail: rabihalkaysi@gmail.com, kaysir@ksau-hs.edu ^b Department of Chemistry University of California, Riverside 501 Big Springs Road, Riverside, CA 92521, USA. E-mail: christopher.bardeen@uc.edu ^c Materials Science Research Institute, National Nanotechnology Center, King Abdulaziz City for Science and Technology (KACST), Riyadh 11442, Kinedom of Saudi Arabia problem is that large molecular crystals can prevent the photoreaction from going to completion because photoproduct absorption on the surface blocks incident radiation from reaching the rest of the reactant inside the crystal.¹⁹ The practical application of photoreactive molecules requires the capability to grow them as well-defined micron-sized crystals.

In recent years we have developed a general method for fabricating highly crystalline and uniformly shaped molecular crystal nanorods by using solvent annealing inside anodic aluminum oxide (AAO) templates.²⁰ Unfortunately, the limited pore sizes and lengths of these AAO templates limits the types of crystal shapes that can be formed. This template method requires the liberation of the annealed wires by polishing and dissolution of the AAO in an acid or base. Surface templating methods have been used to grow arrays of organic crystals, but size and shape control remain challenging.²¹⁻²³ It is also likely that the ability of surfacebound crystals to respond to light will be diminished. Freefloating microcrystals can be grown without the use of templates, but at the expense of size and shape control. There are reports in which aqueous self-assembly can yield crystals with uniform or variable shapes,²⁴⁻²⁹ but these cases tend to be molecule-specific and have not involved photochemically reactive species. We have grown molecular crystal microribbons and micro-needles of various 9-anthracene carboxylic acid derivatives,^{10,30,31} 4-chloro-cinnamic acid¹³ and 9-methylanthracene¹⁴ using the floating drop method, in which evaporation of a good solvent leaves ribbon or needleshaped crystals on the surface of ultrapure water.³² But this

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method often yields a wide range of sizes and the crystals can aggregate as well. For many molecules, it is difficult or impossible to grow well-defined microcrystals using either method.

Controlling the rate of crystal growth is vital to obtain a uniform sample of micron-sized crystals with useful properties. Often this control is achieved by varying monomer concentration and growth conditions (temperature, growth medium, rate of solvent evaporation). In this paper we describe a new approach based on the chemical reaction of a precursor molecule, followed by a controlled reprecipitation of the photoreactive product molecule. Acid catalyzed hydrolysis of randomly shaped reactant crystals with acid sensitive functional groups, like tert-butyl esters or acylals, combined with gentle agitation in a surfactant solution, can yield significant control over crystal size and shape for molecules with COOH or CHO functionalities. In the current paper, we apply this chemical reaction-growth sequence to make photomechanically active microcrystals of two anthracene derivatives, (E)-3-(anthracen-9-yl)acrylic acid (9-AYAA) and 9-anthraldehyde (9-AA). New crystal shapes lead to qualitatively new types of photomechanical responses for both microwires of 9-AYAA and microplates of 9-AA. Our results demonstrate that efforts to grow novel crystal shapes can be rewarded by the observation of novel photomechanical behaviors.

Results and discussion

In the following, we will focus on growing crystals of (E)-tertbutyl 3-(anthracen-9-yl)acrylate to form (E)-3-(anthracen-9yl)acrylic acid (9-AYAA) (Scheme 1a) under acidic conditions. Crystals of the *tert*-butyl ester are photostable and have no photomechanical response. On the other hand, 9-AYAA molecular crystals are photomechanically responsive when excited with UV (365 nm) or visible light (475 nm).³³

Previously, we grew large (millimeter dimension) crystals of 9-AYAA by solvent evaporation and sublimation and determined its crystal structure.³³ We found that these crystals could bend after prolonged UV or visible light illumination. Attempts to grow smaller crystals that might show more dramatic photomechanical behavior were unsuccessful. Reprecipitation of a 9-AYAA-THF solution into an aqueous solution of phosphoric acid/sodium dodecyl sulfate (SDS) yielded both randomly shaped microcrystals and micro-tubes. Using the floating drop method over pure water or a phosphoric acid-SDS solution yielded branched or randomly shaped crystals with no apparent control over size and morphology. Sublimation of 9-AYAA also yielded a broad distribution of macro crystal sizes and variable shapes. Representative SEM and optical microscope images of these results are shown in Fig. 1.

It appeared that **9-AYAA** crystallized rapidly and without a preferred growth axis under standard conditions. In order to grow more regularly shaped crystals, we wanted to slow down the nucleation and growth processes. We decided to use an *in situ* chemical reaction to gradually release the molecule of interest into the solution. Since **9-AYAA** is a carboxylic acid, we chose a *tert*-butyl ester as our precursor molecule. Acid sensitive functional groups such as *tert*-butyl esters or acylals can be cleaved at low pH to yield the corresponding



Scheme 1 a) Acid catalyzed hydrolysis of a *tert*-butyl ester leads to the formation of a carboxylic acid (9-AYAA) and 2-methylpropene gas. b) Acid catalyzed hydrolysis of an acylal yields an aldehyde and water-soluble acetic acid.



Fig. 1 a) SEM image of reprecipitated 9-AYAA in 3.6 M $H_3PO_4/0.1\%$ SDS at room temperature without mixing. b) Optical microscope image of 9-AYAA crystals prepared by the floating drop method. c) Optical microscope image of 9-AYAA prepared by sublimation. Panels b) and c) are with the same scale, scale bar = 100 μ m.

carboxylic acid³⁴ or aldehyde³⁵ respectively (Scheme 1a and b). For high yield product formation, the reactant has to be in a homogenous phase with the aqueous acid. Since the organic molecule precursors in this paper are not water soluble, we used the amphiphilic SDS as a pseudo phase transfer catalyst to enable the hydrolysis.

When a suspension of randomly shaped tert-butyl-9-AYAA ester microcrystals in a 3.6 M H₃PO₄/0.1% SDS was tumblemixed at 35 °C, the tert-butyl ester was slowly hydrolyzed to generate microwires of 9-AYAA. The microwires had strikingly uniform lengths and thicknesses as shown in Fig. 2. The length of the microwires grew steadily over a period of several days until all the reactant was consumed. A plot of microwire length versus time (Fig. 3) shows that the growth was initially fast then gradually tapered off to reach a final length with a narrow distribution. Optical microscopy images showed that the microwire width remained constant throughout the growth process, with an average width of 990 nm and an average standard deviation of 12%. During the growth process, microwire growth could be halted by simply cooling the sample to <0 °C or washing away the acid-SDS solution. To optimize the growth of the 9-AYAA microcrystals, we examined the effects of several different parameters, as described below.

1) Temperature

The rate of microwire growth and maximum length depends on temperature. Higher temperatures lead to faster nanowire growth at the expense of uniformity and final length, as illustrated in Fig. 3. Starting with the same initial conditions, growth at 45 °C yielded nanowires that were on average 35% shorter than microwires grown at 30 °C. But it took only 30 hours for these wires to reach their maximum length, as compared to several days at 30 °C. The microwires grown at higher temperatures were on average wider than those grown at lower temperatures, with many incidents of fused crystals with a star-shaped morphology. We found the optimum temperature to be around 35 °C with 0.1% SDS, which provided a good compromise between crystal quality and growth time.

2) Surfactant and H₃PO₄ concentration

When the *tert*-butyl ester precursor was stirred at 35 °C in 3.6 molar aqueous phosphoric acid (pH ~1) or dilute HCl, there was no observed cleavage of the acid sensitive functional group. Even after several days of mixing at high temperatures no product crystals were observed. This was expected since the reactant has negligible solubility in the acid solution. After adding SDS to make a 0.1% (w/v) solution in H₃PO₄, the acid catalyzed hydrolysis occurs over a period of several days at room temperature or several hours at 45 °C. The concentration of SDS plays a crucial role in the uniformity of the obtained microwires. In general for SDS concentrations >0.6% we obtained randomly shaped and fused crystals of



Fig. 2 a) Optical microscope image of 9-AYAA microwires, scale bar = 500 μ m. b) SEM image of 9-AYAA microwires. In both images the microwires were grown with 3.6 M H₃PO₄/0.1% SDS at 35 °C with gentle rotation-mixing. Inset: Zoomed image of a 9-AYAA microwire tip.



Fig. 3 Plot of the length *versus* time of **9-AYAA** microwires grown at various temperatures. The error bars reflect standard deviation in length.

9-AYAA (ESI,† Fig. S1). Thus the optimum SDS concentration was between 0.1% and 0.3% to generate microwires with the most uniform dimensions. When the concentration of SDS dropped to 0.05%, microwire formation slowed down dramatically and we again observed a high proportion of nonuniform crystals. The use of a cationic surfactant, centrimonium bromide (CTAB), did not yield well-defined crystals. We found the optimum concentration of phosphoric acid was between 1 and 3.5 M to give uniform microwires. For higher concentrations (>7.5 M) the crystals precipitated out as a tangled mass of very long microwires with variable thicknesses, rather than as separated microwires (ESI,† Fig. S2). When a dilute HCl/0.1% SDS solution with similar pH was used instead of phosphoric acid, randomly shaped clusters of 9-AYAA crystals were liberated. It may be that the presence of undissociated phosphoric acid helps slow the reaction-growth process by increasing the viscosity of the solution. It is possible that a more extensive investigation of different surfactants and acids could improve on our results, but that is beyond the scope of this paper.

3) Mixing

We noticed that mixing the sample was required for the formation of uniform micro-structures. When we allowed a sample to sit at 35 °C undisturbed for several days, we obtained microcrystals and microwires with a much broader distribution of lengths and widths (ESI,† Fig. S3). The mode of mixing also affected the uniformity of the crystals. Stirring the mixture with a magnetic stirrer resulted in much shorter microwires with variable lengths. We suspect that the microwires tend to break when struck by the magnetic stirring rod. The best mode of mixing utilized a 90° tumble rotator mixer set at speeds ranging from 8 to 24 rpm. Higher rotation speeds caused the microwires to stick to the edge to the vial and the formation of undesirable SDS foam.

4) Precursor concentration

The initial amount of the ester precursor affected the uniformity and length of the microwires. The optimum ester concentration was 0.1 mg mL⁻¹ yielding uniform microwires with a narrow size distribution and a final length of 200 micrometers on average. Increasing the initial ester concentration resulted in poorer uniformity with no increase in length. In order to grow longer 9-AYAA microwires, we had to add a fresh *tert*-butyl ester suspension in SDS/H₃PO₄ (0.1 mg mL⁻¹) to a suspension of previously grown microwires. This sequential addition led to microwires whose average length doubled to ~400 microns (ESI,† Fig. S4). Adding additional aliquots of precursor solution resulted in even longer microwires, although these tended to snap or become entangled with each other.

To demonstrate that the chemical reaction-crystal growth method could be extended to acyclal derivatives (Scheme 1b), we used similar conditions to generate microcrystals of 9-anthraldehyde (9-AA). The crystal structures of both this molecule and its photodimer have been determined previously.^{36,37} When 0.1 mg mL⁻¹ of the acylal was added to 3.6 M H₃PO₄/0.1% SDS and tumble mixed at 35 °C, 9-AA grew as rectangular microplates with rounded edges, with dimensions of about 100 µm by 150 µm (Fig. 4). The dimensions of these rectangular crystals were uniform to within ~10%, and the microplates were the only morphology seen in the sample. Note that we did not do a systematic investigation of the growth parameters as we did for 9-AYAA. We were able to extend this method to include other 9-AA derivatives. For example starting with the propylal derivative of 9-AA,³⁸ the reaction-growth yielded similarly shaped microplates but with slightly different morphology.

The success of the chemical reaction method for crystal growth deserves some comment. The production of uniform crystals suggests that the initial nucleation events are followed



Fig. 4 Optical microscope image of microplates of 9-AA. Scale bar = $250 \mu m$.

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by a slower growth phase, corresponding to a two-step process that starts in the labile region of an Ostwald-Miers diagram and then moves into the metastable region.³⁹ It is possible that the nucleation rate of crystals is limited by the fact that crystallizing molecules are only produced in the presence of SDS, which solubilizes them until they can be added to an already formed crystal. In this scenario, the chemical reaction serves as a way to control both the concentration of the crystallizing molecules, and also their local environment. Simply adding molecules to a surfactant solution cannot afford this level of controlled release over the course of hours.

The dynamics of the 9-AYAA and 9-AA microcrystals under illumination were investigated to demonstrate that the reaction-crystal growth technique can produce photomechanically responsive structures. When a 9-AYAA microwire was illuminated with 475 nm light, the wire started to bend, eventually forming a circular loop. A unique feature of these microwires was their ability to form a closed loop when partially photoreacted, then open back up as the photoreaction goes to completion. A typical coiling-uncoiling sequence for a 9-AYAA microwire is shown in Fig. 5. By halting the reaction at specific times (Fig. 3) we can obtain microwires with predetermined lengths that affects how many times the wire can coil upon illumination, with longer wires forming more coils (ESI,† Videos 1-3). When crystalline microplates of 9-AA were illuminated with visible light (475 nm) on their dominant face (corresponding to the (002) Miller plane, ESI⁺ Fig. S7), they folded and then unfolded exclusively along the long crystal axis, as shown in Fig. 6 (ESI,† Video 4). In both crystal types, the photodeformation is maximized at an intermediate point in the photoreaction, after which the fully reacted crystals return to close to their original shapes. These observations are consistent with our previous results showing that 9-methylanthracene microribbons and microneedles also maximize their bend or twist when roughly equal amounts of reactant and product are present in the crystal, then return to their original shape as they become predominantly the product phase.¹⁴

The structural changes that underlie the photomechanical deformations appear to be different for 9-AYAA and 9-AA. Although it is well-positioned to undergo a [4 + 4] photodimerization in its crystal form,³³ 9-AYAA appears to preferentially undergo a trans-cis photoisomerization. Analysis of the solid-state reaction by high-pressure liquid chromatography shows that a complicated mixture of products is formed, possibly including oligomers produced by sequential asymmetric [2 + 4] dimerization reactions enabled by the trans-cis isomerization (ESI,† Fig. S5). ¹H-NMR of the product revealed the presence of overlapping multiplets in the aromatic region, also suggesting the presence of multiple photoproducts (ESI,† Fig. S6). This complicated photoproduct mixture drives a crystal-to-amorphous transition, as inferred from the loss of structure in the powder X-ray diffraction (PXRD) pattern (Fig. 7). The coiling of the microwire is reminiscent of the photoinduced coiling of nanowires composed of an anthracene-9-(1,3-butadiene) derivative, dimethyl-2(3-(anthracen-9-yl)allylidene)malonate, which also involved a crystal-to-amorphous transition.⁴⁰ The difference here is that



Fig. 5 Optical microcopy images of 9-AYAA microwire (~60 μ m long) coiling and uncoiling when exposed to 475 nm light: a) before light exposure; b) during light exposure; c) after light exposure. Scale bar = 30 μ m for panels a), b) and c).



Fig. 6 Optical Microscopy images of **9-AA** microplate folding and unfolding when exposed to 475 nm light: a) before light exposure; b) during light exposure; c) after light exposure. Scale bar = 50 μ m for panels a), b) and c).



Fig. 7 Powder X-ray diffraction patterns of *trans*-**9**-**AYAA** microcrystals a) before irradiation, showing well-resolved peaks; b) after irradiation, showing loss of structure indicative of amorphous product.

the 9-AYAA wires partially uncoil, rather than undergoing a complete collapse in their amorphous product phase. 9-AA, on the other hand, is known to undergo a [4 + 4] photodimerization in the solid-state.41,42 The reaction of the cofacial 9-AA molecules leads to a crystal-to-crystal transition, and we have confirmed that the photoproduct PXRD pattern has the peaks predicted from the structure of the dimer crystal (ESI,† Fig. 7).³⁷ Thus the physical basis of the photoinduced motion is different for the two molecules. Both start as crystalline solids, but the 9-AYAA coiling is driven predominantly by a unimolecular isomerization that leads to a crystal-to-amorphous transition, while the 9-AA folding is driven by [4 + 4] photodimerization of the 9-AA molecules leading to a crystal-to-crystal transition. We note that more detailed mechanistic information about the photomechanical response could be obtained by determining the relation between specific crystal axes and the coiling or folding. But measuring the absolute orientations of individual microcrystals before and after irradiation is somewhat complicated and beyond the scope of the current paper. The main point is that these types of solid-state photoreactions can lead to interesting shape changes, provided the crystal has the appropriate shape.

Conclusion

As mentioned above, we think that the size and shape control achieved using the chemical reaction-crystal growth method originates in the slow release of product molecules generated by an *in situ* hydrolysis reaction. This growth strategy is sensitive to precursor and surfactant concentrations, temperature, and agitation speed. It is likely that the ideal set of conditions will depend on the molecule to be crystallized. While the acid hydrolysis method is only suited to growing crystals of carboxylic acids and aldehydes, we think that the general concept may be applicable to the crystallization of other types of molecules as long as a suitable precursor reaction can be found. The use of an *in situ* chemical reaction to control crystal growth provides a new approach to the preparation of

microcrystals with controlled shapes and/or sizes. The motivation for growing such crystals is that they can exhibit useful types of photomechanical shape changes, like the coiling and folding motions demonstrated in this work.

Experimental

Synthesis of precursor molecules

All starting materials used were purchased from TCI America and used without further purification. Synthesis of the *tert*-butyl esters and acylals was accomplished following procedures previously established in the literature^{33,43} respectively.

9-AYAA microcrystal growth

A 3.6 molar solution of H_3PO_4 in distilled water was prepare by diluting the appropriate volume of 15 M phosphoric acid (85% in water) then adding enough SDS to make a 0.1% (w/v) solution in the phosphoric acid. To the acid solution, a measured quantity of the *tert*-butyl ester to make a 0.1 mg ml⁻¹ concentration was added directly and briefly sonicated for 2 minutes to disperse the crystals. In a typical experiment we added 1 mg ester to 10 ml of 3.6 M $H_3PO_4/0.1\%$ SDS in a 50 ml glass vial with a PTFE lined screw cap. In general the mole ratio of SDS to reactant was 10:1. The vial was tightly capped and mounted on a tumble rotator (Labquake tube rotator from Thermo Scientific) set at 8 rpm. The rotator was placed inside an oven set at 35 °C. The reaction was allowed to mix for a couple of days depending on the desired length of the microwires.

9-AA microcrystal growth

Microplates of 9-anthraldehyde were grown using similar conditions to 9-AYAA. 0.1 mg mL⁻¹ of the acylal precursor was added to 3.6 M $H_3PO_4/0.1\%$ SDS and tumble mixed at 35 °C. Characterization of the microplates using an SEM was unsuccessful because the 9-AA sublimed under the high vacuum conditions of the SEM.

Characterization

The crystallinity of the microcrystals was confirmed by observing them using a cross polarized filter in a microscope. All of the microcrysals exhibited a uniform birefringence, indicating that they were composed of a single crystal domain. **9-AYAA** microwire length measurements were performed by placing a 20 microliter sample of the microwire suspension to a microscope glass slide and measuring the length of approximately 100 microwires. Several samples were collected and averaged. SEM measurements were performed using JEOL JSM-6510LV scanning electron microscope. Samples were sputter coated with Pt prior to scanning. Powder X-ray diffraction data were collected on a PANalytical Empyrean X-ray powder diffractometer (CuK radiation, $\lambda = 1.540598$ Å, 45 KV/40 mA power) at 296 K.

Photomechanical studies were performed using Nikon Eclipse 80 fluorescence microscope equipped with a 2 MP digital camera. The samples were illuminated with 475 nm light, passing through a band pass filter, from a 100 W medium pressure Hg lamp.

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