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Communication

Solar-Powered Molecular Crystal Motor Based on an Anthracene–Thiazolidinedione Photoisomerization Reaction

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ABSTRACT: Assembling molecular machines into crystals provides a way to harness their power on large length scales, but the development of a crystal analogue to a molecular motor remains a challenge. The molecule (*Z*)-5-(anthracen-9-ylmethylene)-3-butylthiazolidine-2,4-dione (**C4-ATD**) has *E* and *Z* isomers with strongly overlapping absorption spectra. This spectroscopic property allows both $Z \rightarrow E$ and $E \rightarrow Z$ photoisomerization reactions to be driven by a single light source, and simulations indicate this property can provide a route to robust oscillatory motion. Reprecipitation in an aqueous surfactant enables the growth of single crystal microwires that exhibit continuous mechanical oscillations under a wide range of illumination conditions, including ambient solar irradiation. Molecular crystal motors provide a new approach for transforming continuous light into oscillatory mechanical motion.

In the simplest limit, a motor takes in a continuous source of energy and converts it into an uninterrupted mechanical rotation or oscillation. There is currently much interest in light-driven molecular motors that accomplish this transformation at the nanoscale because they could have broad applications in fields like medicine and engineering.[1−3] However, the directed motion of a molecular machine that operates in a condensed phase environment can be overwhelmed by Brownian forces that generate random diffusion.[4] One way to overcome this problem is to assemble multiple active molecules into an ordered array,[5,6] for example, a crystal[7] or liquid crystal elastomer,[8] whose collective motion can overcome Brownian forces.

The experimental challenge is how to coordinate molecular motions across a solid sample. Asymmetric heating provides one way to induce transient structural changes at specific locations that can be harnessed to generate oscillatory motion.[9−13] Photochemical reactions, like $E \rightarrow Z$ photoisomerizations in azobenzene-containing polymers and crystals, can generate a time-varying stress in the material that also gives rise to light-driven oscillatory motion[14−16] and translation.[17] In all cases, the observation of oscillatory motion requires the use of specific illumination conditions, with the angle of light incidence and polarization determined by the need for self-shadowing to modulate light absorption. If the motion relies on photothermal heating or a thermal back-reaction, it will also be sensitive to the heat conduction properties of the surrounding medium.[18] Ideally, a molecular motor assembly would not depend on thermal reactions and operate using a single light source. In practice, these requirements require that it be composed of molecules whose forward and reverse isomerizations are exclusively light-driven (P-type) and whose reactant and product absorption spectra have substantial overlap. Many standard photochromic molecules are designed to have widely separated reactant and product absorption spectra, like the diarylethenes.[19]

To confirm that a system with highly overlapped reactant and product absorption spectra is advantageous for generating robust oscillatory photomechanical motion, we analyzed a model in which $E \leftrightarrows Z$ photoisomerization reactions drive crystal twisting.[20] The effective rates of $Z \rightarrow E$ and $E \rightarrow Z$ photoisomerizations are given by the products $\sigma_Z I \phi_{ZE} \cos(\theta_Z)^2$ and $\sigma_E I \phi_{EZ} \cos(\theta_E)^2$, respectively, where σ_Z/σ_E are the absorption cross sections of the Z/E isomers, respectively; I is the light intensity; ϕ_{ZE} and ϕ_{EZ} are the quantum yields for the $Z \rightarrow E$ and $E \rightarrow Z$ photoisomerizations, respectively; and θ_Z/θ_E are the angles between the transition dipole moments (TDMs) of the isomers and the incoming light polarization vector. In solution the θ angles are randomly distributed, but in a crystal the TDMs are aligned and θ must be explicitly taken into account. Absorption of the incoming light can induce a photomechanical twisting that rotates the TDMs, causing the changing θ to modulate the light absorption.[20] This feedback loop can induce crystal rotation at a frequency Ω. One requirement to observe this rotation is that $\theta_E \neq \theta_Z$, i.e., the TDMs of the isomers had to have different orientations within the crystal frame. If we fix I and constrain the sum $\sigma_Z\phi_{ZE} + \sigma_E\phi_{ZE}$ = constant, the calculated data in Figure 1a show that Ω is maximized when $\frac{\sigma_E\phi_{E\rightarrow Z}}{\sigma_Z\phi_{Z\rightarrow E}} = 1$. This simple theory confirms

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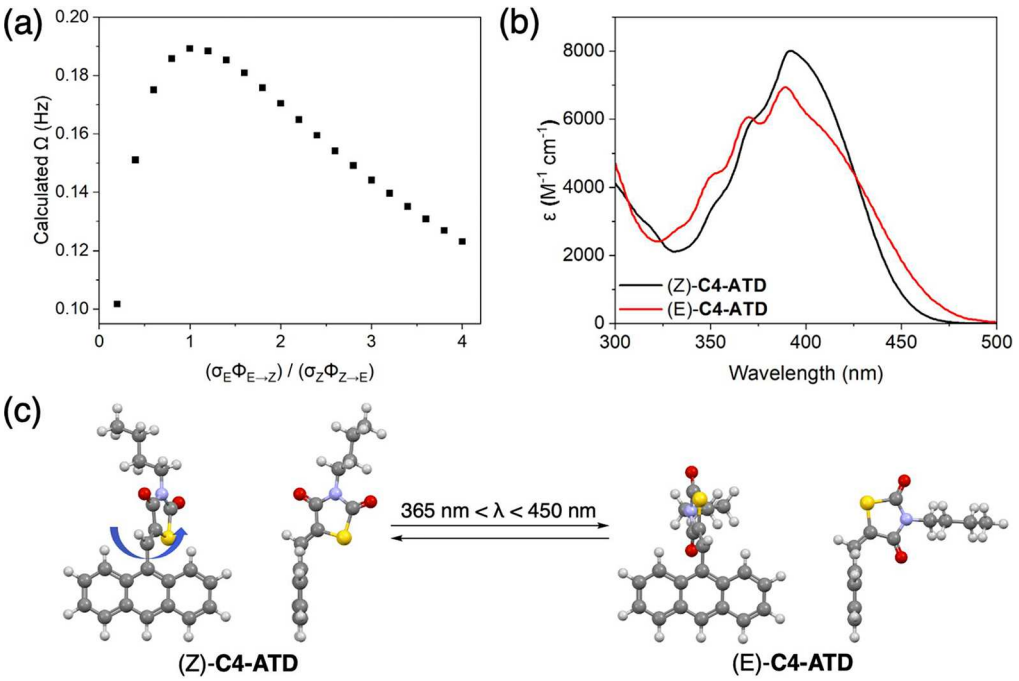

Figure 1. (a) Calculated dependence of crystal twist frequency (Ω) on the absorption cross section (σ) and photoisomerization quantum yield (ϕ) of the *E* and *Z* isomers, showing that the oscillation frequency is maximized when $\frac{\sigma_E\phi_{E\to Z}}{\sigma_Z\phi_{Z\to E}} = 1$. (b) Steady-state UV/vis absorption spectra of (*Z*)-**C4-ATD** and its *E* photoisomer in DMF. (c) Ground-state DFT optimized structures of both **C4-ATD** isomers viewed perpendicular (left) and parallel (right) to the anthracene ring; gray (carbon), white (hydrogen), yellow (sulfur), red (oxygen), blue (nitrogen).

that balancing the forward and backward reaction rates can provide a strategy to enhance oscillatory motion.

To meet these requirements, we synthesized the molecule (*Z*)-5-(anthracen-9-ylmethylene)-3-butylthiazolidine-2,4-dione (**C4-ATD**). A two-step synthesis of this compound with high yield begins with the Knoevenagel condensation of 9-anthraldehyde with thiazolidine-2,4-dione, followed by N-alkylation using 1-bromobutane and potassium carbonate. Details of the synthesis and characterization are given in the Supporting Information. Thiazolidine-2,4-dione, a heterocyclic small molecule employed in treating type 2 diabetes mellitus,[21] was chosen due to the presence of an N−H group, allowing for straightforward modification through alkylation. The similar conjugation in the *Z* and *E* isomers of **C4-ATD** causes them to have very similar absorption spectra in solution, both in terms peak wavelength and in terms of absorption coefficient, as shown in Figure 1b.

The photochemistry of **C4-ATD** is similar to that of the hemi-indigos previously reported by Wolf and co-workers[22] and involves the $Z \rightarrow E$ photoisomerization about the olefin bond that connects the anthracene and the thiazolidinedione headgroup (Figure 1c). ^{1}H NMR (Figure S5) and HPLC analysis (Figure S8) confirmed the nature of this photochemical transformation in both solution and the solid state. The *E* isomer is kinetically stable in both solution and the solid state, with no thermal isomerization back to the *Z* form in solution even after a day at room temperature or at 50 °C (Figure S9). Density functional theory calculations indicated that this stability arises from a large barrier (~200 kJ/mol) along the torsion coordinate of the isomerization (Figure S20). When excited at 405 nm, a photostationary state was attained consisting of 51% *Z* and 49% *E* isomers (Table S1), which shows that at this wavelength **C4-ATD** comes close to fulfilling the ideal criterion $\frac{\sigma_E\phi_{E\to Z}}{\sigma_Z\phi_{Z\to E}} = 1$. Finally, we used time-dependent density functional theory to calculate that the TDM rotates from 28° with respect to the anthracene 9−10 carbon axis in the *Z* isomer to −9° in the *E* isomer (Figure S21). This rotation of the TDM is similar in magnitude to that which gave rise to dual wavelength powered oscillatory motion in previous work.[20]

The synthesis of a photochromic molecule with favorable spectroscopic properties is the first step to create a molecular crystal motor. During self-assembly, this molecule must also (a) adopt a packing geometry that enables the photoisomerization and (b) grow into a crystal shape that allows macroscopic motion to be observed. Fulfilling condition (a) required adjusting the crystallization conditions to grow a polymorph that supports the photoisomerization reaction. Polymorph **A** (Figure 2a) was obtained under standard crystal growth methods like slow solvent evaporation. This polymorph did not exhibit solid-state photoreactivity (Figures S6 and S7) or photomechanical motion. We attribute the lack of reactivity to **A**'s packing that causes the anthracene rings to restrict the rotation of the thiazolidinedione rings necessary for photoisomerization. However, reprecipitation into an aqueous surfactant solution resulted in the growth of a different polymorph **B** (Figure 2b) that supported photoisomerization. Polymorph **B** has the thiazolidinedione rings lined up to form a corridor of flexible moieties that can easily rotate upon light exposure. The crystal packing in polymorph **B** also spaces the anthracene 5.2 Å apart, beyond the threshold for [4 + 4] photodimerization.[23] The stacked packing motif of polymorph **B** also helps fulfill condition (b) since it provides a preferred growth direction that facilitates formation of quasi-one-dimensional crystals in the shape of wires or ribbons. The SEM images in Figures 2c and 2d show both morphologies,

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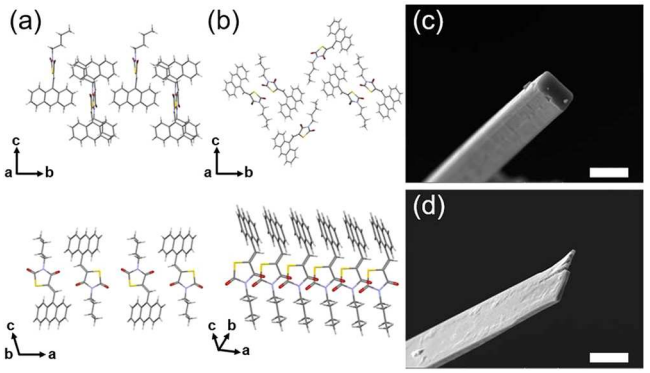

Figure 2. Molecular crystal packings of (a) polymorph **A** and (b) polymorph **B** for **C4-ATD** viewed down the *a*-axis and along the stacking plane. Cross-sectional SEM images of polymorph **B** crystals in the form of a (c) wire and (d) ribbon. Scale bars: (c) 5 μm and (d) 20 μm.

which can be obtained selectively by modifying the growth conditions (Supporting Information). These morphologies possess a low second moment of inertia that facilitates deformations like bending and twisting.[24,25] The absorption spectrum collected from a thin film of the **B**-form microcrystals showed considerable broadening but only about a 10 nm red-shift of the main absorption peak, suggesting that the electronic states of the molecule in the crystal are similar to those of the molecule in solution (Figure S16). Powder X-ray diffraction patterns of the crystals obtained under specific growth conditions confirmed that they were predominantly either **A** or **B** forms (Figure S19).

We tested the ability of **B**-form crystals to support oscillatory motion by using 365 and 405 nm lamp sources as well as a broadband solar simulator. When exposed to these light sources, **C4-ATD** crystal wires and ribbons underwent an undulating motion that reflects a variable twist period along the length of the crystals. Note that twisting with a long spatial period often appears as a bend. Examples of motions induced by 365 nm and solar simulated radiation are shown in Figure 3. To observe motions with periods on the order of 1 s, light intensities on the order of 100 mW/cm^2 were required, but slower oscillations could be induced even under ambient solar light intensities (Movie S6). The light-induced twisting oscillations could generate a center-of-mass translation, as

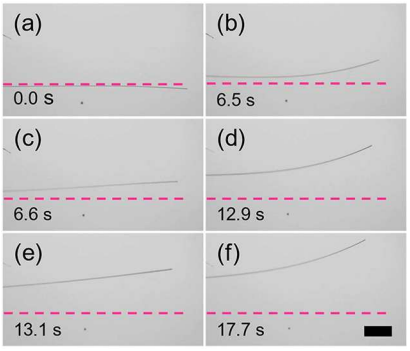

Figure 4. Sequential microscopy images showing center-of-mass translation and oscillatory bending of a **C4-ATD** wire under 405 nm illumination (127 mW/cm^2). The pink dashed line marks the crystal position at t = 0.0 s. Scale bar: 250 μm.

can be seen from the motion of the ribbon in Figure 4 relative to a stationary object in the center of the frame. The oscillatory motion could be maintained for at least 1 h under all illumination conditions with no signs of slowing down or photochemical damage. If the light was removed, the motion immediately ceased. The wire maintained its deformed shape until the light was turned on again without any sign of thermal relaxation. The aqueous environment enabled the suspended crystals to freely move and sustain the light-induced motion. Continuous motion was not observed for dry wires lying on a glass surface, probably due to surface adhesion that was stronger than the photomechanical forces. Crystallization of polymorph **B** from aqueous surfactant sometimes resulted in multibranched crystals. When exposed to 365 nm light, the crystalline legs could propel the entire structure, suggesting that these microwires could support collective motions when organized into larger structures (Movie S8).

The frequency of oscillation depended on the incident light intensity, as shown in Figure 5a. Under 405 nm, the frequency increased linearly after a threshold value of ~0.5 mW/cm^2 is reached. At higher intensities, the slope decreased, showing the saturation behavior observed previously.[20] In photothermal systems, the oscillation frequency is usually fixed by the mechanical properties of the object and is not tunable by light intensity.[9,26] The **C4-ATD** crystal oscillations were also less sensitive to light polarization than the previously studied (*Z*)-2-(3-(anthracen-9-yl)allylidene)malononitrile crystals.[20] For

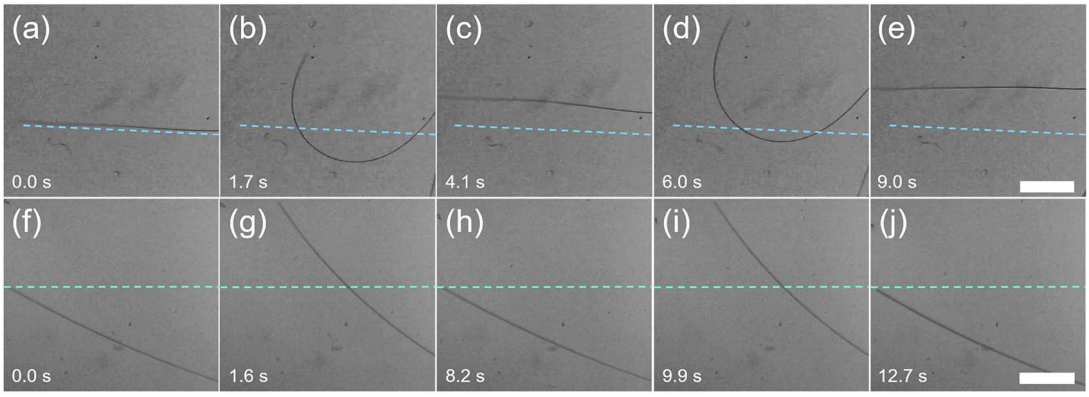

Figure 3. Sequential microscopy images showing oscillatory bending of a **C4-ATD** wire under (a–e) 365 nm illumination (50 mW/cm^2) and (f–j) simulated solar sunlight (780 mW/cm^2). The blue dashed line is based on the initial crystal position at t = 0.0 s. The green dashed line acts as a reference point for the tip of the crystal at t = 0.0 s. Scale bars: (a–e) 50 μm and (f–j) 200 μm.

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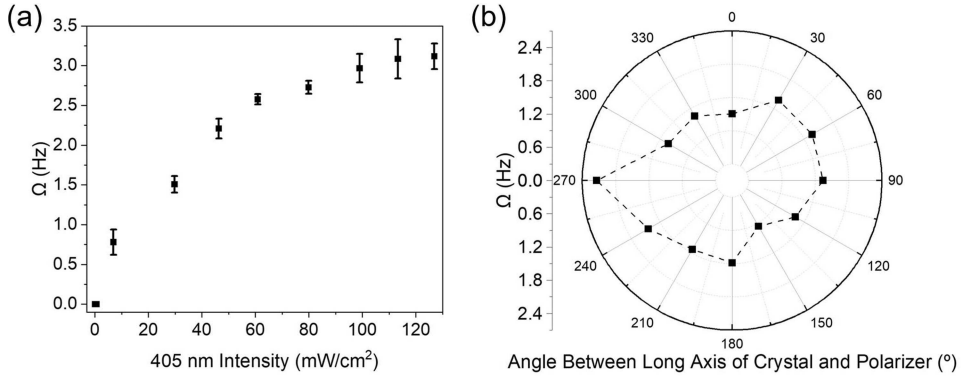

Figure 5. (a) Dependence of oscillation frequency Ω of a **C4-ATD** wire on the 405 nm illumination intensity. (b) Dependence of Ω on the angle of the 405 nm light polarization with respect to the long axis of a **C4-ATD** wire.

C4-ATD the dependence of the oscillation frequency on the 405 nm polarization direction relative to the crystal long axis was close to isotropic (Figure 5b), with some variability between different crystals (Figure S14). This contrasts with the $\cos^2$ dependence characteristic of a single dipole-allowed transition. This lack of directionality results from the fact that the 405 nm light simultaneously excites two different isomers with different TDM orientations, effectively scrambling the polarization dependence in the same way that different overlapping transitions lower the fluorescence anisotropy from a single molecule.[27]

The physical mechanism underlying the twisting can be attributed to isomerization reactions that take place primarily near the surface due to the high optical density of the crystals. The presence of a layer of *E* isomers adjacent to *Z* isomers leads to an anisotropic stress or torque that can drive twisting through a bimorph mechanism.[28,29] This mechanism is supported by HPLC analysis of *Z* isomer crystals exposed to 365 nm light for an extended period (>5 min) that showed a conversion from *Z* to *E* of only ∼4%, much less than the ∼50% conversion observed for **C4-ATD** in solution. The value of 4% is at the lower end due to experimental challenges of obtaining a uniformly irradiated sample of crystals. Note that the solid never reaches a true photostationary state because the surface regions oscillate back and forth between *Z* and *E* populations as it rotates within the light path.

In conclusion, we report the synthesis and characterization of a new molecule, **C4-ATD**, whose $Z \rightarrow E$ photoisomerization induces large geometry changes but only slight changes in its absorption profile. By assembling this molecule into the correct crystal polymorph and shape, it exhibits robust photomechanical oscillations under a variety of conditions, including ambient solar irradiation. Preliminary experiments on crystals composed of other molecules containing the **ATD** motif suggest that it may provide a general route to molecular crystal motors.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c05566.

Experimental procedures, synthesis of small molecules, NMR, HPLC, crystallographic data, UV/vis, and TD-DFT calculations (PDF)

Oscillatory bending of **C4-ATD** wire under 365 nm light (Movie S1); oscillatory bending of **C4-ATD** wire under simulated sunlight (Movie S2); bending and translation of **C4-ATD** wire under 405 nm light (Movie S3); pair of **C4-ATD** wires exhibiting translational motion under 405 nm light (Movie S4); **C4-ATD** crystals under 405 nm illumination walking across slide (Movie S5); demonstration of a **C4-ATD** wire flexing under simulated sunlight (1 sun intensity) (Movie S6); a **C4-ATD** crystal undergoing flagella-like oscillation under 405 nm light (Movie S7); display of multibranched **C4-ATD** crystals undergoing spider-like crawling under 365 nm light (Movie S8) (ZIP)

Accession Codes

CCDC 2349712−2349713 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2, 1EZ, UK; fax: + 44 1223 336033.

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Notes

The authors declare no competing financial interest.

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