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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Communication

Highly Twisted Azobenzene Ligand Causes Crystals to Continuously Roll in Sunlight

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Cite This: *J. Am. Chem. Soc.* 2022, 144, 16773−16777

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ABSTRACT: Direct conversion of solar energy to mechanical work promises higher efficiency than multistep processes, adding a key tool to the arsenal of energy solutions necessary for our global future. The ideal photomechanical material would convert sunlight into mechanical motion rapidly, without attrition, and proportionally to the stimulus. We describe crystals of a tetrahedral isocyanoazobenzene−copper complex that roll continuously when irradiated with broad spectrum white light, including sunlight. The rolling results from bending and straightening of the crystal due to blue light-driven isomerization of a highly twisted azobenzene ligand. These findings introduce geometrically constrained crystal packing as a strategy for manipulating the electronic properties of chromophores. Furthermore, the continuous, solar-driven motion of the crystals demonstrates direct conversion of solar energy to continuous physical motion using easily accessed molecular systems.

Photoactive materials that harness nanoscale molecular transformations to generate macroscopic motion have promising applications in microfluidics, information storage, flexible electronics, and as artificial muscles.[1−7] Chromophores that respond to visible light are especially desirable as they avoid the use of harmful ultraviolet (UV) light and can be used in devices powered by solar energy.[8,9]

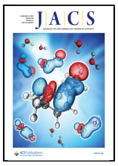
Because of their rapid, reversible *cis*−*trans* isomerization and facile synthesis,[10,11] azobenzenes represent an ideal class of photoactive compounds whose properties have been exploited for applications in biology[12−14] and materials science.[15−19] While azobenzene crystals have been shown to photomechanically bend,[20,21] curl,[22] crack,[23] and slowly crawl[24] under UV light, azobenzene systems that respond to visible light in the solid state are rare.[20,25−28] Rarer still are examples of azobenzene systems exhibiting continuous motion induced by visible light[29−33] or sunlight.[27,34,35]

In this work we present the first example of solar-powered continuous motion in azobenzene single crystals. While strategies to allow visible light control over azobenzene isomerization typically rely on extensive substitution on the azobenzene rings,[36−39] this work demonstrates that molecular conformations imposed by crystal packing can produce visible light responsive azobenzene crystals. We show that a tetrahedral Cu(I)−isocyanoazobenzene complex packs in the solid state with one highly twisted azobenzene ligand, resulting in crystals that continuously roll under white light stimulus (Figure 1a−c, Movie S1), including sunlight (Movie S2). This discovery represents a new avenue for the design of visible light responsive materials from simple commercial starting materials.

Combining tetrakis(acetonitrile)copper(I) hexafluorophosphate ($[Cu(MeCN)_4][PF_6]$) with 4-isocyanoazobenzene (CNAB) in acetonitrile at room temperature yields $[Cu(CNAB)_4][PF_6]$ (**1**) as an orange powder (Figure 1a). Diffusing hexanes vapor into a solution of **1** in tetrahydrofuran (THF) produces rodlike crystals, henceforth **1T**, with a variety of dimensions. These crystals are responsive to broad spectrum white light and blue light. Under white or blue light and a thin coating of oil, thick crystals crack, thin crystals bend (Movie S4 and Movie S5), and intermediate size crystals (height:length 0.02−0.04, height:width 0.61−0.94) roll. With oil as a lubricant, the crystals roll continuously and even move across the slide, while without oil they bend or jump (Movie S6). The rolling speed is linearly dependent on the light irradiance (Figures 1d and S5), and the crystals roll faster in a hemispherical cavity (>60 rolls/min; Movie S7). The crystals also roll upon exposure to bright, unfocused sunlight (Movie S2) and without apparent mechanical fatigue. We continuously illuminated one crystal under white light for 5 days (500000 full rotations) and observed no damage or change in rolling rate (Movie S7).

The common mechanism by which photoresponsive azobenzene crystals bend or crack is well-understood:[21,40,41] *trans*-to-*cis* isomerization of azobenzene molecules occurs at the exposed surface, with the degree of isomerization decreasing with distance from the surface and giving rise to strain from the difference between the lattice of the *cis* molecules and that of the *trans*. This strain causes the crystals to crack or bend toward or away from the light source.[21,40,41] Limited light penetration into the crystal means that as little as 1% of the azobenzene molecules are isomerized.[21]

Received: August 18, 2022
Published: September 9, 2022



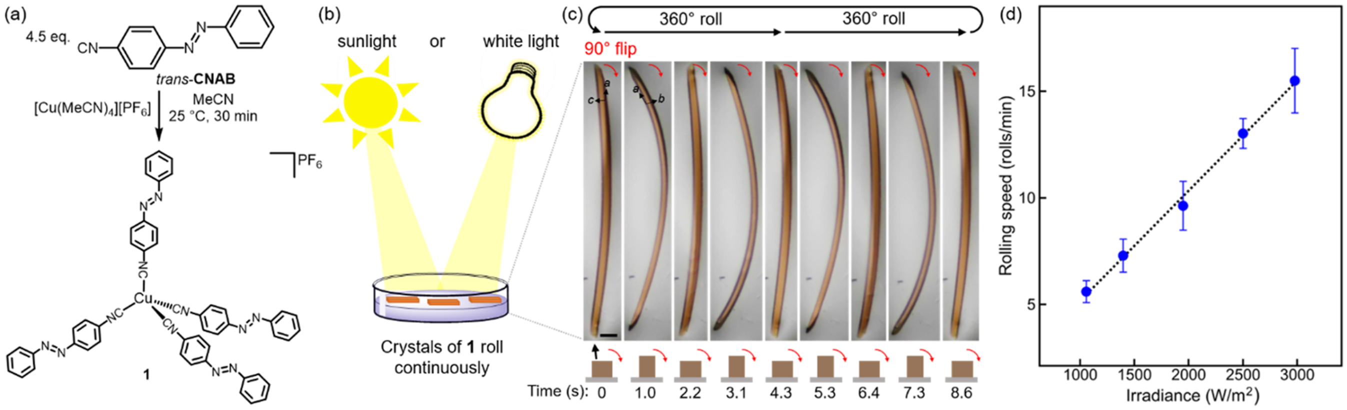


Figure 1. (a) Synthesis of **1**. (b) Illustration of crystal rolling. (c) Images of a **1T** crystal rolling taken from Movie S1; the scale bar is 20 μm. (d) Average rate of rolling on a flat surface vs white light irradiance (measured at 532 nm) for five crystals from one batch of **1T**. The error bars represent the standard deviations and the dashed line is the linear fit (slope = 5.2×10^{-3}).

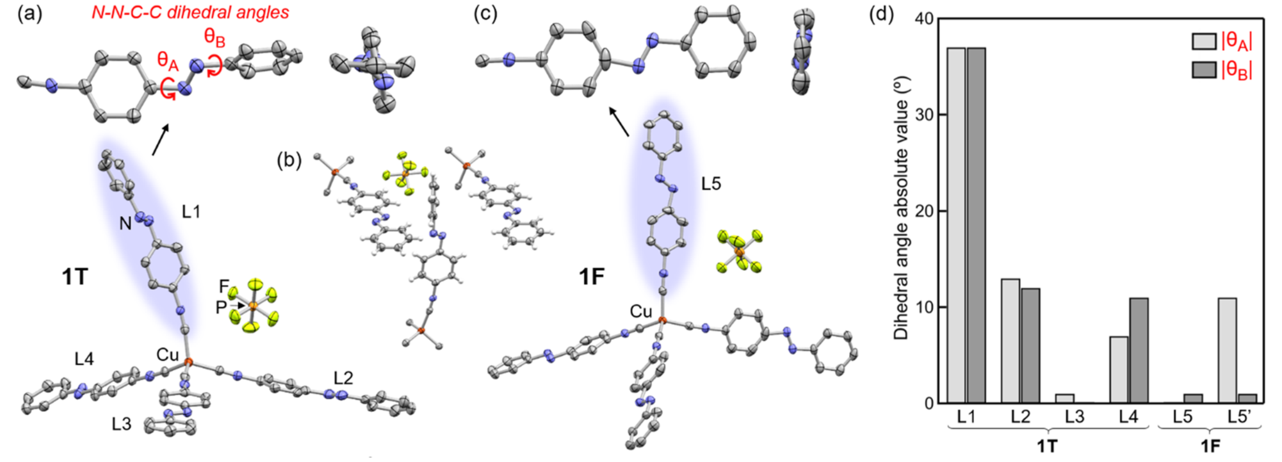


Figure 2. (a) Molecular structure of **1T** highlighting twisted CNAB L1, as determined by SCXRD. (b) Congested packing of **1T** surrounding L1. (c) Molecular structure of **1F**. H atoms are omitted in (a, c) for clarity. (d) Absolute value of the N═N−C−C dihedral angles in **1T** (L1–L4) and the two crystallographically disordered CNAB units in **1F** (L5 and L5′).

1T crystals bend and crack by the mechanism described above. When crushed **1T** crystals are dissolved and examined by ^{1}H NMR, all the CNAB units are *trans*. After 15 s of exposure to 456 nm blue light, dissolution of the crushed crystals results in a ^{1}H NMR with 2.5% of the CNAB units isomerized to the *cis* isomer (Figure S20). This *cis* percentage decreases as the crystals thermally relax back to the all-*trans* state in the dark (Figure S20). **1T** crystals bend away from the light source, indicating that the *cis* lattice is expanded relative to that of the *trans*, because isomerization leads to expansion of the light-exposed face relative to the dark face of the crystal.[42]

As the light used to roll the crystals also provides heat, we examined the rolling behavior at various temperatures to further demonstrate that the rolling is due to isomerization rather than a photothermal process. A **1T** crystal under white light rolls at 15, 5, and −5 °C, while a **1T** crystal that rolls at 25 °C stops rolling at 40 and 60 °C (Movie S8). Higher temperatures prevent rolling, likely by allowing rapid isomerization back to the more thermally stable *trans* isomer.

To explain why blue light triggers this isomerization, we turn to the crystal structure of **1T**. Single-crystal X-ray diffraction (SCXRD) reveals that **1T** features a highly twisted azobenzene (Figure 2a,b). The twist of the phenyl rings with respect to the N═N bond is described by the N═N−C−C dihedral angles, θ_A and θ_B (Figure 2d) In **1T**, two azobenzenes are twisted out of planarity, one with $\theta_A = -13°$ and $\theta_B = -12°$ and another with $\theta_A = \theta_B = 37°$. In contrast to **1T**, crystals of an undistorted polymorph of **1** (**1F**, Figure 2c) formed by slow cooling of a saturated solution of **1** in 1:1 hexanes:THF do not respond to blue or white light (Figure S15), suggesting that the photomechanical response of **1T** crystals arises from the severely twisted azobenzene. To evaluate this hypothesis, we examine the electronic transitions of the two polymorphs in detail.

The *trans* and *cis* isomers of azobenzene feature overlapping bands in the UV ($\pi \rightarrow \pi^*$) and the visible ($n \rightarrow \pi^*$), as do CNAB and **1** in solution (Figure 3a,b). Typically, UV light drives *trans*-to-*cis* isomerization and visible light drives back to the *cis* isomer, as the *trans* has the higher extinction coefficient in the UV while that of the *cis* is higher in the visible.[10,43] Shifting the *trans* $n \rightarrow \pi^*$ band away from the *cis* peak allows for visible light isomerization in both directions.[38] Since 1985, theory has predicted that in the absence of *ortho* substitution twisting the phenyl rings will blue-shift the *trans* $n \rightarrow \pi^*$ peak due to loss of conjugation,[44] but experimental validation of this prediction has not yet been realized.

The diffuse reflectance electronic absorption spectra of **1T** and **1F** show that the $n \rightarrow \pi^*$ transition of **1T** is blue-shifted

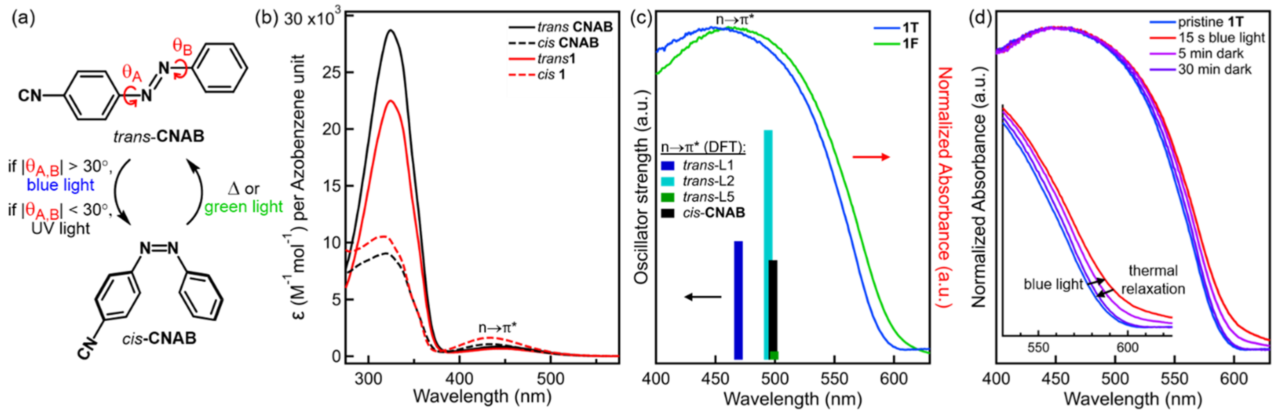


Figure 3. (a) CNAB isomerization. (b) Electronic absorption spectra of *trans*- and *cis*-CNAB and **1** in MeCN as molar absorptivity (ε) per CNAB unit. (c) Normalized diffuse reflectance solid state electronic absorption spectra of **1T** and **1F** with DFT-calculated energies and relative oscillator strengths of n−π* transitions of *cis*- and *trans*-CNAB for N═N−C−C dihedral angles relevant to the structures of **1T** and **1F**. (d) Normalized diffuse reflectance solid-state electronic absorption spectra of **1T** before and after exposure to 456 nm light with irradiance 329 W/m^2 and upon thermal relaxation back to the *trans* in the dark.

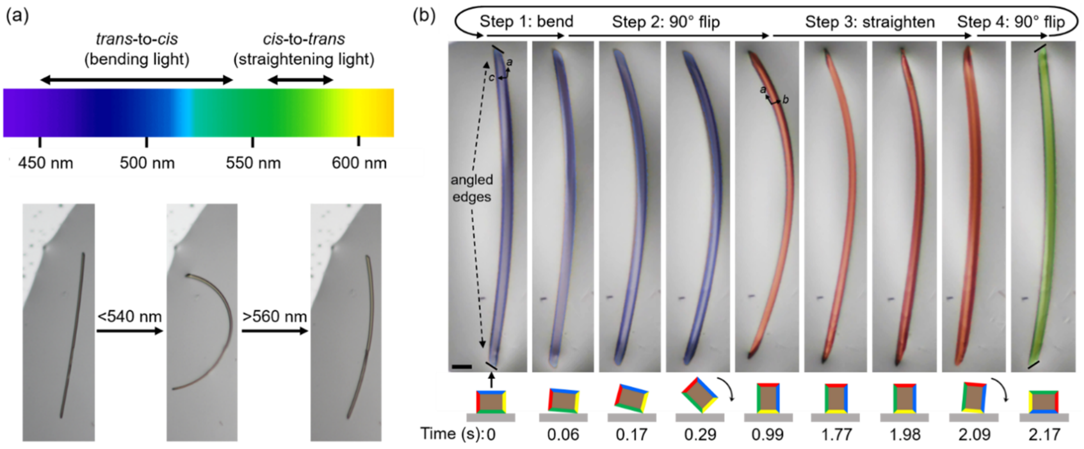


Figure 4. (a) Wavelength ranges of **1T** bending and straightening. (b) Stepwise breakdown of **1T** crystal rolling 180° under white light taken from Movie S1; the scale bar is 20 μm. The images in (b) are false colored to specify which face of the crystal is up.

compared to that of **1F** (Figure 3c). Because the spectrum of **1T** includes contributions from all four azobenzene units, the blue-shift of the most twisted azobenzene is likely even larger than what is observed in the aggregate. The shift is consistent with the theoretical results of Bunce and Zerner[44] and our calculations on *trans*-CNAB (Figure 3c).

Unlike in *ortho*-substituted azobenzenes where green light drives *trans*-to-*cis* isomerization due to red-shifting of the *trans* n → π* peak, here crystal packing allows blue light to drive the same process via a twist-induced blue-shift of the *trans* n → π* peak. We can further prove this by observing the change in the n → π* peak of **1T** after irradiation with 456 nm blue light of irradiance 329 W/m^2—the n → π* peak is red-shifted by the partial *trans*-to-*cis* isomerization in the solid state, reverting to the original signal gradually over 60 min in the dark, consistent with thermal relaxation back to the *trans* (Figure 3d). This conclusively demonstrates that the *trans* n → π* transition in **1T** is higher energy than that of the *cis*. By contrast, **1F** crystals show no change in absorbance after irradiation with blue light (Figure S11), consistent with the assignment of the blue-light responsive nature of **1T** to its highly twisted CNAB arm. This finding both accounts for the photomechanical response of **1T** crystals to blue and white light and establishes shape-constrained crystal packing as a powerful design strategy for the manipulation of chromophores.

To further isolate the effects of specific wavelengths of light on the rolling process itself, we irradiated **1T** crystals using bandpass filters. The bending and straightening of a thin crystal signify surface isomerization to *cis* and *trans*, respectively.[23] Light from 450 to 530 nm bends crystals, light from 530 to 560 nm produces no response, and light from 560 to 580 nm straightens crystals (Figures 4a and S1). Thus, we can also demonstrate from the behavior of single crystals that blue light isomerizes azobenzenes at the surface of **1T** from *trans* to *cis*, while green light reverses the process, consistent with both spectroscopic data and calculations.

Finally, we can parse the motion of a **1T** crystal into four stages: (1) starting with the widest part of the crystal, the *ac* face, facing up, the crystal bends away from the light, (2) it tips onto its thinner side such that the *ab* face is now face up, (3) it straightens, and (4) it is unstable on its thin edge and falls over such that the top face is now the opposite *ac* face to that which was originally face up (Figure 4b). The continued rolling is the iteration of this process. We attribute the tipping in step 2 to the slanted crystal ends—a feature that also contributes to the rolling mechanism of azobenzene crystals that roll briefly when heated through a thermal phase transition.[45] The stepwise

https://doi.org/10.1021/jacs.2c08815
J. Am. Chem. Soc. 2022, 144, 16773−16777

rolling mechanism of the **1T** crystals is also similar to the thermally induced rolling mechanism of liquid crystalline elastomer rods prepared by the Cai group.[46]

While the bending process is clearly attributable to blue light, straightening (step 3) could be due to *cis*-to-*trans* isomerization of the bent face by green light, *trans*-to-*cis* isomerization of the newly exposed opposite face by blue light, or both. We irradiated a crystal by using only 450−550 nm light, excluding light that drives the *cis*-to-*trans* isomerization. Though the crystal still rolled, step 3 was markedly slower (∼11 s) compared to the same crystal under broad spectrum white light (∼1.5 s) (Movie S9 and Movie S1). While blue light alone is sufficient to roll the crystals, the fast rolling under white light is actively facilitated by the presence of green light and thus by both *trans*-to-*cis* and *cis*-to-*trans* isomerization.

Our data present a complete picture of how and why **1T** crystals roll under blue light, white light, and sunlight and demonstrate that crystal packing alone can dramatically change the electronic absorption and physical response of an azobenzene chromophore. Given these results, the electronic manipulation of well-known chromophores by crystal packing using novel geometric templates promises to be a rich and productive area of study. Lastly, the crystals described above exhibit complex and continuous motion and are easily prepared in two steps from commercial starting materials, making them excellent candidates for solar-driven micro-actuators.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c08815.

Experimental methods, computational methods, crystallographic tables (PDF)

Movie S1 (MP4)

Movie S2 (MP4)

Movie S3 (MP4)

Movie S4 (MP4)

Movie S5 (MP4)

Movie S6 (MP4)

Movie S7 (MP4)

Movie S8 (MP4)

Movie S9 (MP4)

Movie S10 (MP4)

Accession Codes

CCDC 2104171−2104172 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via 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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Author Contributions

[#]A.K.B. and I.B.S. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded by the National Science Foundation CAREER Award DMR-1751949 and CBET-2017198. X.R. acknowledges support from the Columbia MRSEC on Precision-Assembled Quantum Materials (PAQM) (DMR-2011738). A.K.B. is supported by an Arnold O. Beckman Postdoctoral Fellowship in Chemical Sciences. I.B.S. was partially supported by the NSF CHE-2023568 CCI Phase I: Center for Chemistry with Electric Fields (CHEF). We thank P. Bartholomew, C. Cuomo, A. Mayfield, and E. Meirzadeh for helpful discussions, the Shared Materials Characterization Laboratory at Columbia University and M. Rajeswaran for assistance with X-ray crystallography, C. Nuckolls and the Nuckolls lab for the use of their microscope, and A. Paoletta, L. Venkataraman, M. Spencer, Y. J. Bae, and X. Zhu for the loan of filters and lenses. The authors acknowledge the use of facilities and instrumentation supported by NSF through the Columbia University, Materials Research Science and Engineering Center DMR-2011738.

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