Direct observation of reversible single-crystal-to-single-crystal *E*⇄*Z* photoisomerization of an azo molecule

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Abstract

Single-crystal-to-single-crystal (SCSC) photoisomerization is direct structural transformation of crystalline photoswitches in the solid state, preserving the long-range order in the crystal lattice. Azo molecules, as one of the most widely used photoswitches, has not yet achieved SCSC isomerization. The relatively large free volume required for isomerization poses significant challenge for its SCSC transformation. Here we demonstrated for the first time that an azobispyrazole underwent high-quality reversible *E*⇄*Z* SCSC isomerization by light irradiations. We found that the similarity in crystal lattice parameters between *E* and *Z* crystals and the efficient photoisomerization ability of azo molecules are key factors facilitating the single crystal to single crystal photoisomerization of azo molecules. Our work opens an avenue for the single crystal photochemistry of azo molecules and offers new opportunities for developing light-controlled single-crystal materials and devices.

Introduction

There is a growing consensus that efficient photoswitching under crystalline state could facilitate better communication between photoswitches and their environment, which shows great promise for applications to advanced porous materials, optoelectronic devices, photo energy storage and smart actuators, etc.[1-5]. Despite extensive research on molecular photoswitches[6], there are relatively few reports of their molecular crystals that can exhibit efficient photoisomerization[7]. Azo molecules are the most prevailing photoswitches; they undergo large conformational changes upon $E\rightleftarrows Z$ isomerization, making them one of the most powerful photoactive tools for light-controlled systems[8-12]. However, unlike the efficient switching of azo molecules solution and amorphous states, crystalline-state switching proves challenging due to close molecular packing and the shortage of free space for conformational change between planar *E* isomer and non-planar *Z* isomer[13]. Indeed, the photoisomerization of azo molecules in crystals is generally limited to the near-surface region.

Some creative strategies have been employed to increase the free volume for isomerization, such as increasing bulkiness of substituents[14], forming a three-dimensional tetramer[15], and incorporating switches as auxiliary ligands in transition metal complexes[16]. However, these azo molecules undergo isomerization in a crystal-to-amorphous or amorphous-to-amorphous manner, and crystal-to-crystal azobenzene isomerization remains a great challenge. Interestingly, Barrett et al. reported the single crystal of the *Z* isomer of a perhalogenated azobenzene was irreversibly transformed into a polycrystalline state of *E* isomer under light irradiation[17]. They also developed solid-state supramolecular strategy to form halogen bonded *Z*-azo cocrystal that underwent complete and irreversible photoisomerization in single-crystal-to-polycrystal fashion[18]. Recently, our group demonstrated that reversible $E\rightleftarrows Z$ isomerizations of azobispyrazoles occured in crystalline phase, namely the single crystal-to-polycrystal transition during $E\rightarrow Z$ photoisomerization and polycrystal-to-polycrystal transition during backward $Z\rightarrow E$ photoisomerization[19]. Nevertheless, single-crystal-to-single-crystal (SCSC) photoisomerization, the most fascinating conversion in the crystal chemistry of azo molecules, has not been realized so far. This is associated with the great challenge to keep the single crystallinity after the dynamic isomerization process.

Surprisingly, the single crystals of ethyl-substituted azobispyrazole **1** were observed to can undergo *E*⇄*Z* SCSC transformation by 365 nm and 500 nm light irradiations, as unambiguously evidenced by single-crystal X-ray diffraction (SCXRD) analyses (Figure 1). We believe that such single crystal photochemistry of azo molecules offers new opportunities for developing light-controlled crystal materials and devices.

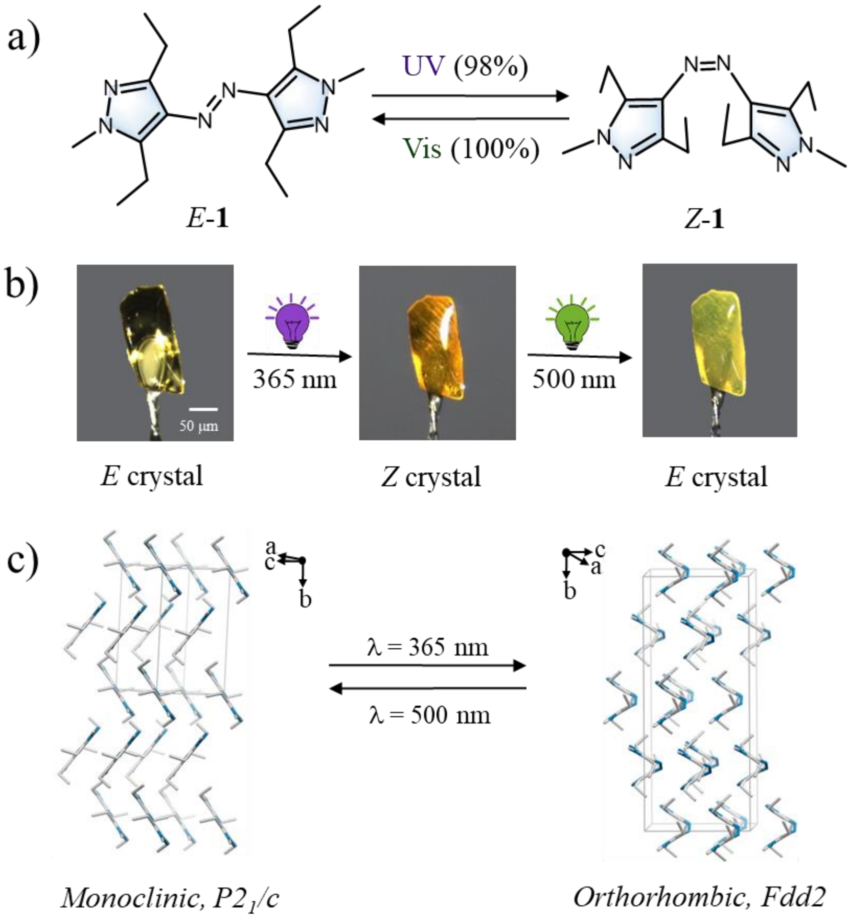

Figure 1. a) Chemical structure of *E*-**1** (left) and *Z*-**1** (right) and near-quantitative bidirectional photoconversions under 365 nm and 500 nm irradiations in MeCN solutions. b) The reversible single-crystal-to-single-crystal photoisomerization of **1**: Single crystal of **1** before irradiation, after irradiation (rt, 365 nm, 5 min) and followed by irradiation (rt, 500 nm, 1 min). c) Molecular packing of single crystals of *E*-**1** and *Z*-**1**.

Results and Discussion

Photoisomerization in solution and solid state

Compound **1** was readily synthesised by diazo coupling with 2,4-pentadione and subsequent cyclization.[10,20] It exhibited excellent photoswitching propertities in acetonitrile solutions, which can achieve (near-)quantitative isomerization in both directions by 365 nm and 500 nm light irradiations, respectively, and long *Z*-isomer thermal half-lives of 19.6 days. Moreover, the powder of compound **1** was observed to undergo fast and reversible photochromism, which was confirmed to proceed via a crystal-to-crystal transformation as evidenced by powder X-ray diffraction (PXRD) analysis. Compared to the pristine photoswitch core (molecule **2**)[20], the bulky ethyl substitutions at ortho positions not only preserved the excellent photoswitching properties of the core but also imparted a looser molecular packing to the crystal (with a density of 1.176 g/cm^3 for **1** and 1.298 g/cm^3 for **2**), which was advantageous for isomerization in the crystalline state.

Table 1. Crystallographic data associated with photoinduced reversible single-crystal-to-single-crystal transformation of **1**.

species	cryst. syst.	space group	Unit cell dimensions							Z	d (g/cm^3)	R1
			a (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)	V (g/cm^3)			
E-**1**[a]	Monoclinic	$P2_1/c$	8.0647	12.7458(5)	8.3170(3)	90.00	92.43	90.00	855.28	2	1.176	0.039
Z-**1**[b]	Orthorhombic	Fdd2	11.9244(10)	25.945(2)	10.7987(9)	90.00	90.00	90.00	3340.9(5)	8	1.203	0.058
E-**1'**[c]	Monoclinic	$P2_1/c$	8.1138(12)	12.7641(19)	8.2765(13)	90.00	92.409(9)	90.00	856.4(2)	2	1.173	0.21

[a] grown in 2:1 (v/v) n-hexane/ dichloromethane solutions in the dark. [c] The single crystal was irradiated with 365 nm light for 15 min. [c] The single crystal was irradiated with 500 nm light for 1 min.

Photoisomerization in single crystals

The crystal of *E*-**1** were grown by slow evaporation of 2:1 (v/v) n-hexane/ dichloromethane solutions in the dark. Through SCXRD, it was surprising and gratifying to observe that, upon exposure to 365 nm light at room temperature, a bulk single crystal of *E*-**1** (0.300 mm x 0.180 mm x 0.120 mm) was transformed into the single crystal of *Z*-**1** (0.300 mm x 0.180 mm x 0.120 mm) within 15 minutes, accompanied by a noticeable change in color from yellow to orange (Figure1b). In comparison to the *E*-**1** crystal, the space group of *Z*-**1** crystal transformed from the centrosymmetric $P2_1/c$ to the non-centrosymmetric Fdd2. The high-quality SCXRD result of *Z*-**1** indicated that the sample maintained its single-crystallinity very well during *E*→*Z* photoisomerization.

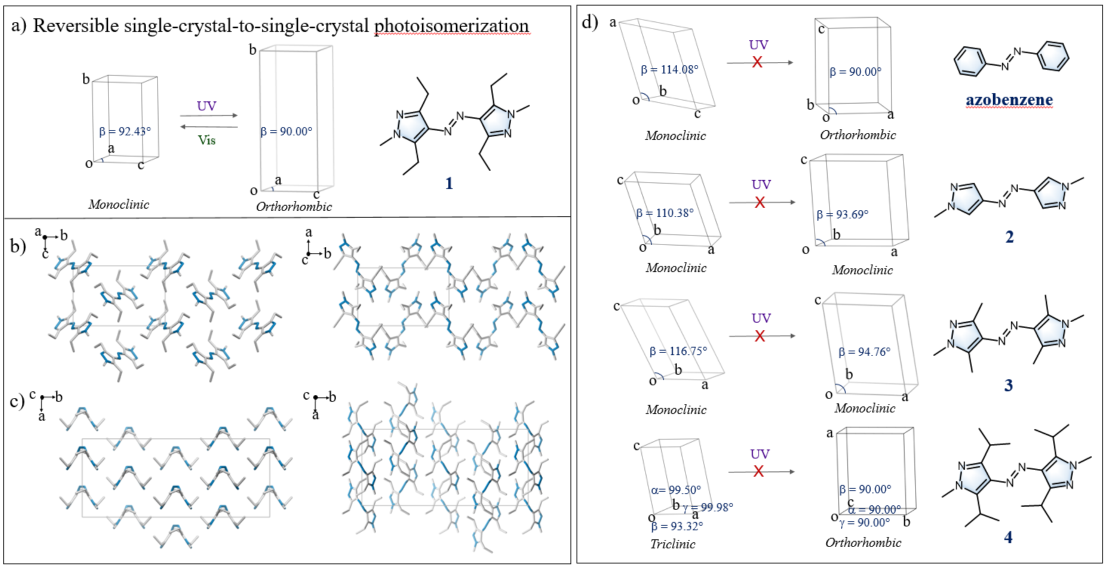

Figure 2. a) The crystal lattice shapes and X-ray structures of *E*-**1** and *Z*-**1**. b) Crystalline packing of *E*-**1** as viewed from **a**, the (100) face, **b**, the (010) face. c) Crystalline packing of *Z*-**1** as viewed from **a**, the (100) face, **b**, the (010) face. d) Differences in cell shape between the E crystal and Z crystal. No single-crystal-to-single-crystal structural transformation has been observed in compounds **1**–**4** and azobenzene.

Subsequently, the *Z*-crystal underwent a rapid transformation into the *E*-**1**' crystal upon exposure to 500 nm light within 1 minute and the color of the crystal reverted to opaque yellow. The rapid *Z*→*E* SCSC isomerization rate was probably attributed to the larger free volume of the *Z* isomer which facilated molecular motion.The obtained R value for *E*-**1**' (0.21) was higher than that for *Z*-**1** (0.058), indicating a significant decrease in the crystal quality during such a rapid *Z*→*E* SCSC photoisomerization (Table 1). The resulting structures were identical to those of *E*-**1** and *Z*-**1** single crystals grown from solution, unambiguously confirming the reversible single-crystal-to-single-crystal transformation in **1**. The shape of the crystal did not undergo significant changes during the *E*⇄*Z* transformation and the crystal reamins intact without cracking or distortion after five cycles of reversible photoisomeization by alternate irradiations with ultraviolet and visible light. Such SCSC photoisomerization of **1** could be well repeated with different samples.

Typically, the transformation from single crystal to single crystal involves relatively small changes in both the initial and final lattices, in order to maintain the integrity of the single-crystalline phase[21]. Single crystal of **1** undergo *E*→*Z* transition occurring at room temperature, involving changes in the unit-cell parameters from monoclinic, $P2_1/c$ (a = 8.0647Å, b = 12.7458(5) Å, c = 8.3170(3) Å, α= 90°, β = 92.43°, γ = 90°) to orthorhombic, Fdd2 (a = 11.9244(10) Å, b = 25.945(2) Å, c = 10.7987(9) Å, α, β, γ = 90°). Their unit cells between *E*-**1** and *Z*-**1** slightly differed by Δa = 3.86 Å, Δc = 2.48 Å, Δβ= 2.43°, while Δb = 13.20 Å (Figure 2 and Table1). The two-fold elongation of the unit cell along the long-axis of the crystal (*b*-axis) was attributed to a change in the periodicity of molecular packing accompained by a pronounced structural transformation (Figure 1c). Actually, since the crystal is formed by the periodically ordered aggregate of unit cells in three-dimensional space, very similar unit-cell shapes made the overall stacking arrangement of the crystal undergo only minimal changes upon isomerization, which was favorable for keeping the single-crystalline state[22]. By comparision, molecules undergoing substantial alterations in unit-cell shape before and after isomerization posed challenges in observing single-crystal-to-single-crystal transformations (Figure 2d). As examplified by the pristine azobispyrazole core (molecule **2**), the unit-cell shape exhibited significant difference between the *Z* crystal and the *E* crystal (Δβ= 16.69°) and no succeseful SCSC isomerization results were obtained (Figure 2d). As an another example, the single crystal of isopropyl-substituted azobispyrazole (molecule **4**) collapsed upon 365 nm irradiation, with distinct unit-cell alterations from the *E* crystal to the *Z* crystal (Δa = 15.10 Å, Δb = 8.68 Å, Δc = 1.56 Å, Δα = 9.50°, Δβ = 3.32°, and Δγ = 9.98°) (Figure 2d).

We have explored the SCSC conversion process based on SCXRD analysis and confirmed that the SCSC transition follows an order→disoder→order process. During the transformation process, there are not only conformational change of azo molecules but also the sliding and shifting of molecular layers. The sliding and shifting plays important roles in relieving the internal stress during conformational change in the crystalline state. The molecular motion continues until a stable new single-crystal phase was obtained. A more detailed description of the SCSC conversion process will be reported latter.

Conclusion

We have demonstrated for the first time that the single crystal of an azo molecule can undergo a reversible, single-crystal-to-single-crystal isomerization, characterized by SC-XRD analyses. The resulting structures obtained by SCSC transformation were identical with those grown in solutions of pure isomers. During such SCSC transformations, $E \rightarrow Z$ occurrs in very similar cystal lattices, which is important for preserving the integrity of the single-crystalline phase. Moreover, molcular motions such as sliding and shifting of molecular layers in the crystal help to relieve the internal stress brought by conformational change. Such single-crystal photochemistry of azo molecules offers new opportunities for developing light-controlled single-crystal materials and devices.

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