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Strong Photomechanical Effects in Photochromic Organic Microcrystals

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Photomechanical effects are observed in single crystals of a thiazole-based diarylethene. Crystalline state photochromism has been characterized by absorption microspectroscopy. Clear single crystals turn colored under ultra-violet irradiation. When the energy absorbed by crystals reaches about ten microjoules, they jump. When we prevent crystals from jumping, parallel, equidistant cracks appear due to elastic energy dissipation. These phenomena are associated with a phototransformation ratio of only a few percent.

Keywords: microcrystals; photochromism; photomechanics

INTRODUCTION

The large molecular structural changes caused by the photochromic reaction in crystals induce local stresses in the rigid crystalline lattice. Different macroscopic consequences of these local stresses have already been reported. Reversible nanometric surface morphology changes of diarylethene single crystals have been characterized [1].

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In this paper, we report on strong mechanical effects caused by the photochromic reaction of single crystals of a new thiazole-based diarylethene [2]. Under UV irradiation, colorless single crystals turn colored because of the formation of the closed-ring isomer. After a few seconds of irradiation, we observe jumps as long as 500 μm for micrometric crystals. When we prevent crystals from jumping, thin, parallel, regularly spaced cracks appear on crystals surfaces.

These two phenomena are associated with a phototransformation ratio of only a few percent. They are associated to the relaxation of the stress accumulated in crystals during the photoreaction. Their characteristics are typical of the elastic interaction.

EXPERIMENTAL, RESULTS AND DISCUSSION

Materials and General Procedures

Synthesis of the molecule studied here is described elsewhere [2]. The colorless single crystals of (1,2-Bis[5′-methyl-2′-(2″-pyridyl)thiazolyl] perfluorocyclopentene) (**1a**) turn red upon irradiation with 365 nm light. The color change results from the formation of the closed-ring isomer (**1b**) (Fig. 1). A broad absorption band appears in the visible region with a maximum at 550 nm (Fig. 2). The typical size of crystals studied is about several tens of micrometers.

Experiments have been done using a Zeiss Axiovert 200 microscope. Crystals are irradiated with a mercury lamp filtered at 365 nm (4 mW/cm^2 on sample). They are probed with an unpolarized halogen lamp of sufficiently low energy to avoid the back reaction.

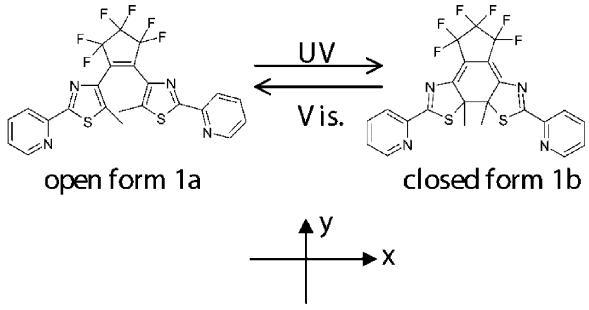

FIGURE 1 Photochromism of diarylethene.

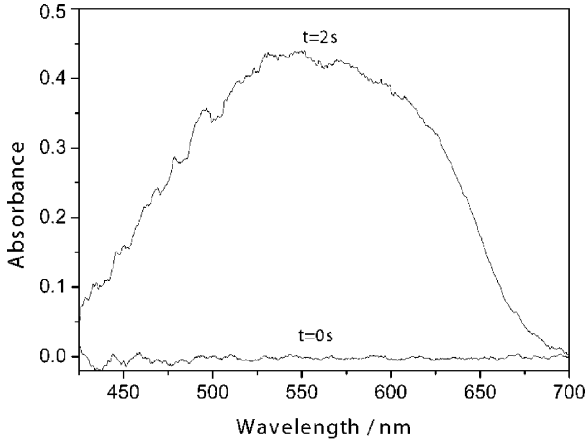

FIGURE 2 Absorption spectra of a diarylethene single crystal after 2 s of irradiation.

Characterization of the Jumps

In order to characterize jumps, we record absorption at 550 nm (absorption maximum) every 300 ms during the irradiation. An example is given Figure 3. The optical density increases first strongly with irradiation during the first seconds. As the colored form absorbs

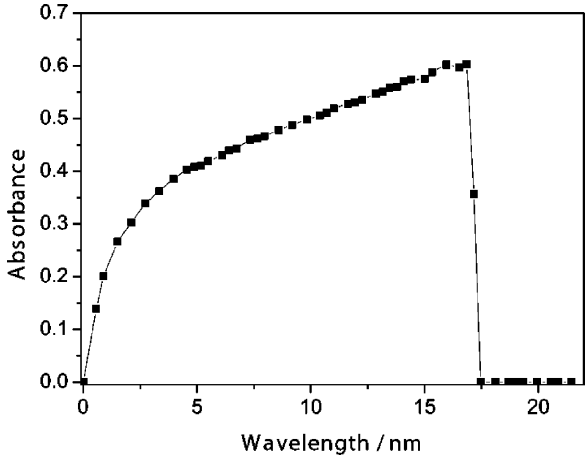

FIGURE 3 Time evolution of the absorbance at 550 nm for a single crystal irradiated with 365 nm light.

also UV light, the sample tends to a photo-stationary state and the growth ratio decreases after 5 s of irradiation. After 17 s of irradiation, the optical density decreases abruptly, which corresponds to the crystal jump.

We measure on these curves the irradiation time and the optical density reached by crystals when they jump. These results, for about 20 crystals, show that the absorbed energy is in the microjoule range and that jumps occur for a phototransformation ratio of about 1%. The kinetic energy necessary for a typical crystal jump is about 10^{-13} J. Thus, the absorbed energy is 7 order of magnitude larger than the kinetic energy needed for a jump.

The low value of the transformation ratio excludes the hypothesis of a phase transition. An elastic model shows that the strain energy accumulated during the photoreaction is enough to produce the jump kinetic energy [3].

Characterization of Cracks

When we prevent crystals from jumping, we observe the apparition of thin, parallel, equidistant cracks (Fig. 4). The optical density value when the first cracks appear corresponds to a phototransformation ratio of about 1%. The study of the variation of absorbance with polarization shows that fractures are parallel to the x-axis of the molecule as shown in Figure 1 [4–6]. Other studies show that the cell volume tends to decrease with the cyclization of the molecule [4–7]. This induces local stresses in the crystal lattice, which relaxes in the cracks formation [8]. The periodicity of these cracks could be associated with a Grinfeld instability [9–11].

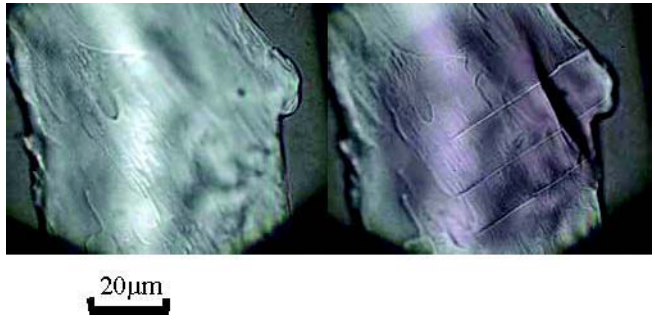

FIGURE 4 A single crystal before (left) and after (right) irradiation. Three cracks appear on the colored crystal.

CONCLUSION

UV photoexcitation of diarylethene single-crystals leads to conformation changes of photochromic molecules. When a few percent of phototransformation is reached, the elastic energy relaxes in two different ways of stress relaxation: crystals jumps and cracks formation.

REFERENCES

[1] Irie, M., Kobatake, S., & Horichi, M. (2001). *Science*, *291*, 1769.
[2] Giraud, M. et al., submitted to *New J. Chem.*
[3] Colombier, I. et al., submitted to *Phys. Rev. Lett.*
[4] Kobatake, S., Yamada, T., Uchida, K., Kato, N., & Irie, M. (1999). *J. Am. Chem. Soc.*, *121*, 2380.
[5] Kobatake, S., Yamada, M., Yamada, T., & Irie, M. (1999). *J. Am. Chem. Soc.*, *121*, 8450.
[6] Irie, M., Lifka, T., Kobatake, S., & Kato, N. (2000). *J. Am. Chem. Soc.*, *122*, 4871.
[7] Yamada, T., Kobatake, S., & Irie, M. (2000). *Bull. Chem. Soc. Jpn.*, *73*, 2179.
[8] Berréhar, J., Lapersonne-Meyer, C., Schott, M., & Villain, J. (1989). *J. Phys. France*, *50*, 923.
[9] Berréhar, J., Caroli, C., Lapersonne-Meyer, C., & Schott, M. (1992). *Phys. Rev. B*, *46*(20), 13487.
[10] Grinfeld, M. A. (1986). *Dok. Akad. Nauk SSSR*, *290*, 1358.
[11] Srolovitz, D. J. (1989). *Acta Metall.*, *37*, 621.