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Maroua Louati, Sophie Barrau, Jean-François Tahon, Arnaud Brosseau, Marumi Takao, et al.. Is it possible to maintain photomechanical properties of crystalline diarylethenes after thermal amorphization?. *Journal of Molecular Structure*, 2022, *Journal of Molecular Structure*, 1261, pp.132857. 10.1016/j.molstruc.2022.132857 . hal-03799882

HAL Id: hal-03799882

<https://hal.science/hal-03799882>

Submitted on 6 Oct 2022

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Is it possible to maintain photomechanical properties of crystalline diarylethenes after thermal amorphization?

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ABSTRACT

The photomechanical properties of the photochromic 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (DTE) crystals, largely documented since the discovery by Irie *et al.* of its reversible photoswitching of crystallographic plane morphology, is renewed with a novel approach consisting on suppressing gradually dynamical effects through thermal amorphization. In the crystalline case, the reversibility of UV/Visible induced plastic deformations have been observed as expected. In addition, a number of large jumps for both cycles are reported for the first time for this molecule in contrast to being observed only during the first UV irradiation cycle for other DTEs. In the amorphous case, several striking results have been obtained: (i) the still present reversible photoinduced plastic deformations mimicking the crystalline case are interpreted in terms of apparent polyamorphism; (ii) the total vanishing of the jumps brings the evidence of the crucial role of the crystallinity for the propelling surface in contact with the substrate; (iii) the discovery of a never reported material jump during the first visible cycle. This last result is rationalized combining two features –a thermal one, a glass transition temperature very close to the room temperature ($T_g \approx 34^\circ\text{C}$) and –a photochemical one, an inefficient photoreversion allowing the other vibrational relaxation pathway to proceed inducing the required temperature rise to overpass the phase transition (Solid \rightarrow Liquid) responsible for the jump.

Keywords: dithienylethenes; thermal amorphization; crystals; photomechanical properties; plastic deformations; material jumping.

1. INTRODUCTION

The twenty-first century is resolutely turned towards the search for new, renewable and non-polluting energies. In this sense, transforming the (sun) light into mechanical forces is an old dream for a number of scientists which explains why molecular photoactuators represent an important subject nowadays illustrated by recent books^{1,2} and reviews.³⁻⁷ Among the various types of photo-thermal or photo-chemical photoactuators, dynamic molecular crystals⁸⁻¹² is a rising hot topic facing this apparent contradiction which considers molecules in dynamic crystals as frozen. In fact, regardless the external stimuli (heat, mechanical, light...), dynamic processes in molecular crystals have to be first classified as *deformation* in which crystal integrity is preserved (for example, bending, curling, coiling...) unlike the *disintegration* effect for which it is not (cracking, explosion...etc.). Then for the former, the deformation can be classified as either elastic or plastic,⁸ (soft materials terminology) distinguishing respectively the return or not of the starting shape material after stopping the external stimuli. As an evidence, a crystalline actuator would display more easily a plastic deformation compared to a polymeric one.^{1,10} Finally, among all possible plastic deformations of dynamic crystals, we will focus our attention on two representative modes, the photo-induced bending vs the photo-induced jumping knowing that the state-of-the-art is absolutely not at the same level for these two effects.

On the one hand, a great number of studies concerning photobending of crystal rationalization^{13,14} have identified key parameters such as the incident light power,^{15,16} the irradiation time,¹⁷ the illumination direction, the polarization angle,^{18,19} the crystal shape²⁰ or morphology.²¹ From a molecular point of view, photobending is explained in terms of modifications of crystalline parameters (via X-ray crystallographic analysis),²² co-crystallinity²³ or more recently on polymorphism.²⁴ In parallel, considerable efforts have been made so far to develop advanced mathematical models to predict the photoinduced bending.^{14,17} From a theoretical and mathematical approach, the explanations for the photoinduced bending effect rely on bimetallic models¹ which consider two different layers reactant/photoproduct along the irradiation direction inducing an internal strain and resulting in the crystal deformation.

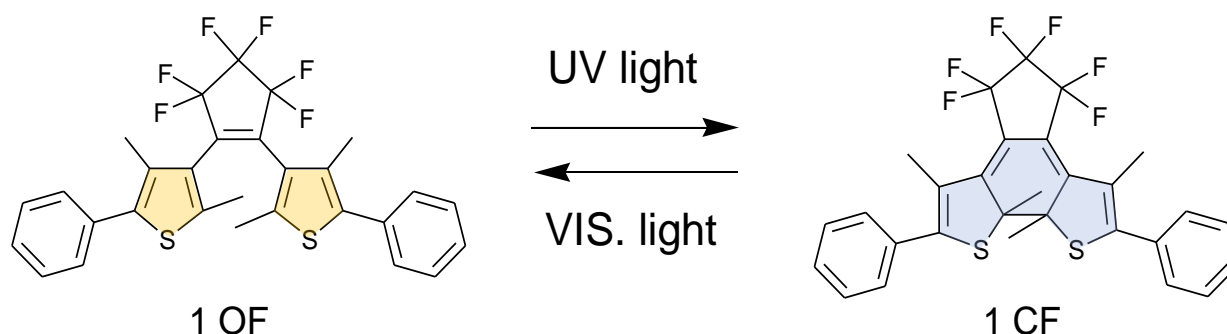
On the another hand, the photosalient effect or crystal jumping is less documented.²⁵ The first observation of jumping crystals^{26,27} were made on diarylethenes (DAEs), cobalt coordination compounds,²⁸ silver complexes²⁹ and the photoreactions involved are [2+2] cycloaddition,^{30,31} cis-trans isomerization¹² or photocyclization.^{32,33} From a general point of view, jumping motions are explained in terms of collective motion,³⁴ modification of crystallographic parameters,^{35,36} existence of different conformers with distinct photoswitching abilities³⁷ or phase transitions.^{35,38} Another important concept introduces the Grinfeld instabilities as periodic deformations of a surface

submitted to uniaxial stress particularly in the case of photoinduced jumping crystals. The latter is assimilated with strong absorption axis:²⁷ through an accumulation effect, the strain energy stored by the photo-induced molecular conformation changes is then released which gives the impulsion to propels the material at right direction with respect to the crystallographic plane presenting the Grinfeld instabilities.

As a matter of fact, one of the common points to better understand the behavior of bending and jumping crystals relies on the exact knowledge of the crystalline parameters and the intermolecular forces between each molecule within the unit cell through X-ray analysis. In this sense, in the framework of actual photoactuators (excluding thermoactuators activated by light with ambient temperature reachable T_g), amorphization of the crystalline sample is therefore expected to decrease, modify or even suppress any photomechanical effect. The interplay between crystalline and amorphous nature of a sample has moderately been explored in the literature. This has been demonstrated recently on 4-hydroxy-2-(2-pyridinylmethylene)-hydrazide for which irreversible UV isomerization results in amorphization of the crystal and a subsequent diminution for the deformations.³⁹ In the same line, concerning grass-like photoresponsive microcrystals of DAE, it has been demonstrated that the Young modulus is reduced (friction forces raised) by amorphization of the outer layer of the fibrils through UV-induced photocyclization.⁴⁰

Recently, several papers have been published to provide a better understanding on the implication of crystallinity/amorphicity toward photomechanical efficiencies using a well-known member of the DAE family, the 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene noticed DTE in the following (see Scheme 1). Indeed, this molecule has been used in 2001 by Irie *et al.* to demonstrate the reversible surface morphological changes of a macrocrystal consisting on UV-induced 1 nm height steps or valleys depending on the crystallographic plane under irradiation. Those morphological changes due to regularly packed DTE in the open form (OF) transforming into closed form (CF) were totally reversible upon photoreversion using visible light.⁴¹ Uchida *et al.* have demonstrated for DTE that an increase of temperature above T_g to reach the softened state was a key parameter to observe and control microcrystalline aggregations (instead of the steps and valleys described by Irie *et al.* at ambient temperature).^{42,43} More recently, highly crystalline DTE nanowires have been investigated showing reversible and high amplitude bending/flattening movements. The good performance of such photoresponsive nanoactuators relies on their nanometric sizes and their abilities to maintain their crystallinity during the forward and reverse reactions. Recently, Bardeen *et al.* have investigated the mechanical properties of DTE for different morphologies -macro-crystals, nanowire single crystals and amorphous films- by means of AFM nanoindentation measurements.²¹ Unlike macrocrystal and amorphous films, successive

photoswitching irradiation cycles of nanocrystals induced a drastic decrease of the Young's modulus explained in term of amorphization of the nanostructure.



Scheme 1 - Molecular structure of open- (OF) and closed- (CF) forms isomers of DTE (1) used in this work.

In this article, we decided to investigate the photomechanical actuation of DTE in the crystalline state and in the amorphous state, obtained through thermal treatment consisting on cooling from the melt. We expected to reduce or modify the photo-actuation properties of the material to better highlight the importance of the crystallinity. Instead, comparing micrometric crystals of DTE after recrystallization with amorphous DTE obtained after thermal treatment, unexpected common points and differences were found. Furthermore, a visible-induced jumping effect was also reported. A qualitative attempt to rationalize such new effects is proposed and the potentiality of these new approaches is considered for future experiments.

2. EXPERIMENTAL SECTION

Sample preparations. DTE molecule (white powder) was purchased from Tokyo Chemical Industry Co. Ltd. Two different processes were applied to obtain recrystallized and amorphous DTE denoted in the following as respectively DTE-crys and DTE-am. First, a recrystallization was required to obtain crystals with pronounced photomechanical responses compared to the pristine powder. DTE powder (OF) was then dissolved in an equivolume blend of *n*-hexane and acetone at room temperature. Then, a subsequent slow evaporation was initiated during several days (sample kept in the dark) at ambient temperature resulting in large and small block-like crystals. The procedure used to obtain DTE-am from the commercial product is a heating/cooling thermal treatment at conventional rate (10°C/min): a heating up to 150°C (to reach the melting state; see later); an isotherm of 2 min and then a cooling down to room temperature.

Structural studies. The amorphous or crystalline character of the resulting materials were evidenced by both differential scanning calorimetry (DSC) and Wide-Angle X-ray Scattering (WAXS). Thermal characterization was achieved on a DSC-Q20 Perkin-Elmer instrument

calibrated according to standard procedures using a high purity indium sample. For the analyses, samples were placed into aluminum pans. Samples were heated and cooled under nitrogen atmosphere between -70°C and 150°C at a rate of $10^{\circ}\text{C}/\text{min}$. WAXS experiments were performed at room temperature on a Xeuss 2.0 (Xenocs) equipment operating under vacuum with a GeniX3D microsource ($\lambda=1.54 \text{ \AA}$) at 0.6 mA and 50 kV and a 2D Pilatus 3R 200 K detector. The sample-to-detector distance was 120 mm. The samples were refilled into glass capillaries. The background of the glass capillary was subtracted for each sample measurement.

Photomechanical effects observations. A wide-field inverted microscope (Nikon, Eclipse Ti-U) with *in-situ* UV-visible irradiation was developed in order to probe the photomechanical response of materials in the solid state at the microscopic scale. The set-up configuration was dedicated to collect the transmission light through a solid sample and record the images upon UV-visible light exposure. The samples were deposited on a glass substrate. The photoinduced mechanical effects were investigated upon irradiation from the lower side with visible light (LED, Lumencor, Spectra X, $\lambda=550 \text{ nm}$, $12 \text{ mW}/\text{cm}^2$) and from the upper side of the microscope with UV light from (Xe/He lamp, Lightningcure LC3, Hamamatsu, equipped with Semrock interferential filters, $\lambda=313 \text{ nm}$, $44 \text{ }\mu\text{W}/\text{cm}^2$). The transmission optical images were recorded by means of an Electron Multiplying Charge Coupled Device camera (EMCCD, Andor iXon Ultra 897) within an exposure time of 1 s during a total time-period of 10 min (600 pictures per acquisition). The images were then analyzed using the ImageJ software.

3. RESULTS AND DISCUSSION

3.1 Crystalline vs amorphous DTE

Thermal features. Thermal properties of crystalline DTE revealed by thermal analysis were first investigated using DSC experiments. Figure 1a shows the thermograms of two consecutive heating runs (1st and 2nd) and then a later heating run (3rd) after four weeks of white (100% OF) and blue crystals (almost 100% CF isomers) of the photochromic molecules, respectively.

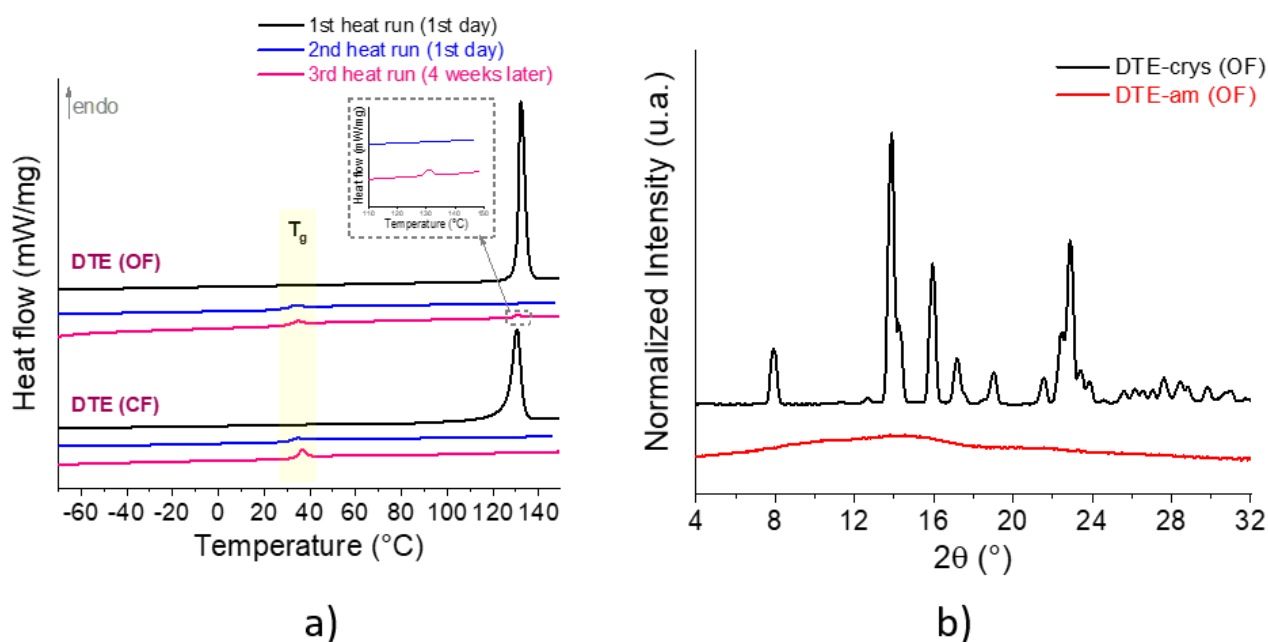


Figure 1 : a) DSC curves of DTE-crys as a function of temperature before (white OF crystals) and after UV illumination (blue CF crystals); b) WAXS integrated profiles at room temperature of DTE in its OF isomers for the crystalline (after recrystallization) and amorphous states (after thermal treatment).

In the first heating run (black line, Figure 1a), endotherms appear at 132°C ($\Delta H_{m(OF)}$ of 63.8 J/g) and 131°C ($\Delta H_{m(CF)}$ of 53.7 J/g) attributed to the melting of DTE crystals. In the second heating run (blue line, Figure 1a), i.e. after the sample cooling from the melt at conventional cooling rate, none of the isomers showed any melting peak meaning that the crystallization does not occur during cooling. Furthermore, only endothermic steps associated to the glass transition (T_g) were noticed at about 34°C (OF) and 36°C (CF). Thus, the lack of crystallization together with the presence of T_g mean that the DTE cooled from the molten state remains amorphous. Recovery of the crystallinity at ambient temperature is slower than expected. In fact, a small endothermic peak (non-quantifiable) at 131.6°C characteristic of the melt of DTE-OF crystals starts to appear from the fourth week as demonstrated in Figure 1a (pink line). We have assessed quantitatively the recrystallization (area integration) which was found to be 1.5 % after 1 month. It is worth to be precise that with photomechanical observations being performed few days after thermal treatment, one can consider the sample as fully amorphous without any crystalline residue.

Structural characterization. To analyze the structure of DTE-crys and DTE-am, samples were characterized by WAXS as displayed in Figure 1b). The integrated intensity profile at room temperature exhibits several sharp diffraction peaks related to the crystalline structure of DTE-crys (OF) at room temperature. The profile is compared to the WAXS data calculated for a monoclinic

arrangement from single crystal X-ray data.^{13,41,43} Based on those previous studies, several diffraction peaks at $2\theta = 7.8^\circ$, 13.6° , 14.1° and 23.5° are associated to the (200), (20-2), (002) and (600) Miller planes respectively. Few peaks are ascribed to CF contaminations when compared with those of pure OF/CF diffractograms (probably induced by ambient light). At first glance, except for some CF contamination, DTE-crys stands in a pure monoclinic system. Reversely, no diffraction peak was observed concerning the DTE-am (OF) sample at room temperature. Instead, an overlaid broad amorphous halo appears with a maximum at $\sim 14^\circ$, which represents a clear evidence that all the 3D crystalline arrangement, keystone of any photomechanical effects reported so far, is totally blurred out upon thermal treatment.

Photomechanical effects reported. We will now investigate photomechanical effects comparing DTE-crys and DTE-am upon similar UV/vis irradiation conditions. After recrystallization or thermal treatment, either DTE-crys or DTE-am were deposited directly on a glass microscopy slide of the wide-field microscope setup revealing a high variety of object shapes with micrometric sizes. Successive illumination sequences of 600 s duration alternating between UV and Visible light cycles (with a 10 s OFF sequence in between) were recorded. The resulting videos for DTE-crys (4 illumination sequences) and DTE-am (4 illumination sequences) are shown in the supporting information (Video S1-Cycle1/Cycle2 and Video S2-Cycle1/Cycle2). The three snapshots at the beginning (before illumination), after first UV irradiation cycle ($t=600$ s) and after first visible irradiation cycle ($t=1200$ s) are displayed in Figure 2 where the regions of interest (ROI) related to different types of photomechanical effects are highlighted following a color code: deformations (orange), rocking (green), sudden jumps inward the field of view (blue) or outward (red). For the jumping effects, selected snapshots (Figure 3) and temporal histograms (Figure 4) are distinguished within jump-in (ROI #1 and #9 in Figure 2) and jump-out (ROI #2 and #13 in Figure 2) motions. It is worth noting that successive jumps are sometimes apparent (e.g. ROI #3). Note that for both crystalline and amorphous samples all jumps are reported during the first irradiation cycle. At the opposite, tens of objects are quasi-static under UV/Vis light irradiations but instead display either some irreversible rocking (green ROI #4/10 in Figure 2 and Figure S4 for more details) or breathing effect, i.e. reversible contraction/expansion effect (orange ROI #5/7, #6/8, #11/14 in Figure 2). The distinction between irreversible rocking and reversible breathing is somewhat tedious because it can be difficult to assess the full three-dimensional geometrical changes of the micro-objects since the inverted optical microscope provides only a two-dimensional visualization of the sample. For that reason, as shown in Figure 5, we will focus our attention on the easily recognizable breathing effects noticed for both DTE-crys (ROI #5/7) and DTE-am (ROI #11/14).

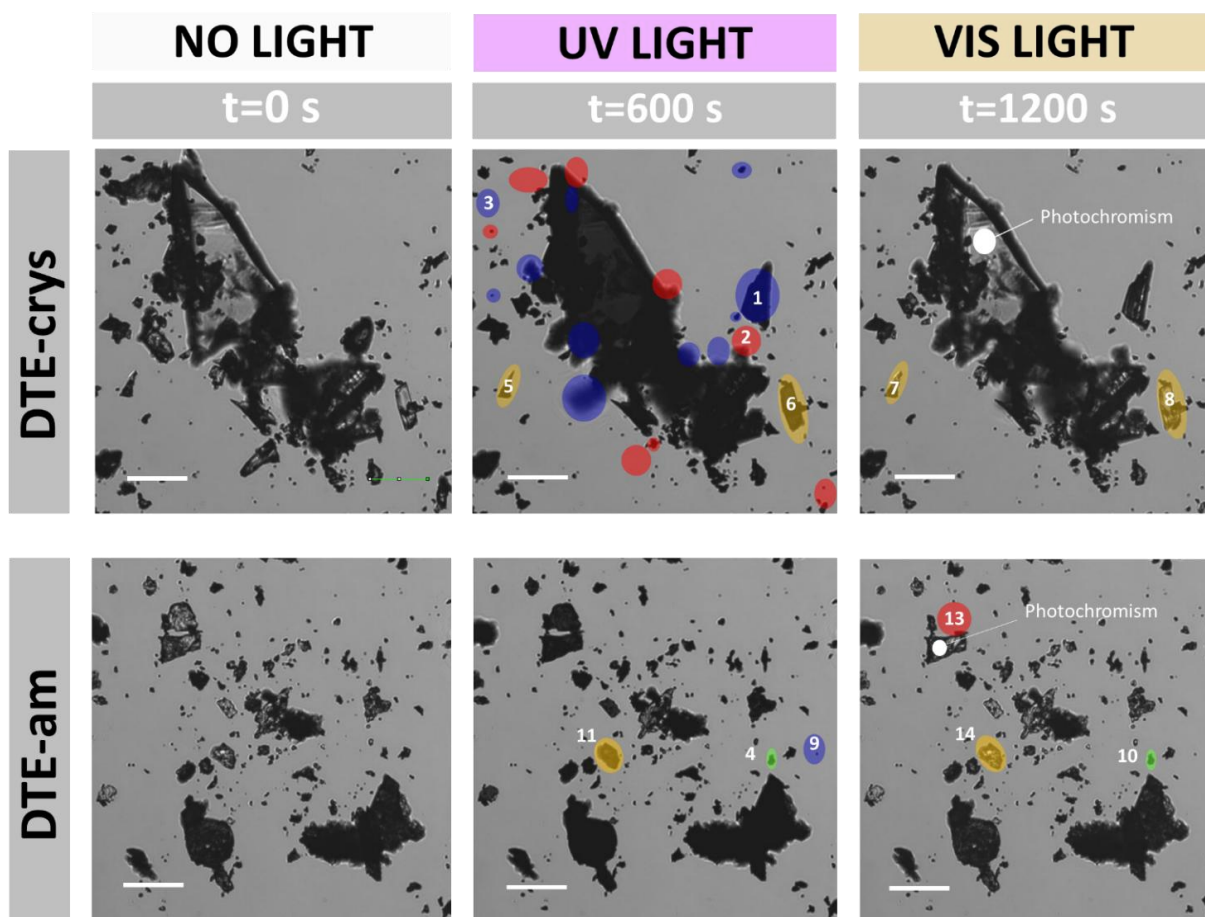


Figure 2: Wide-field microscopy snapshots of DTE-crys vs DTE-am before (left), after UV irradiation (middle) and after visible irradiation (right). Regions of interest (ROI) are highlighted according to the distinct photomechanical effect classification: jump in (blue), jump out (red), rocking (green) and breathing deformations (orange). The numbers from 1 to 14 indicate the ROI illustrated by a zoom (see Figure 3, Figure 5 or supporting information). The ROI “photochromism” refers to Figure 4. Scale bar = 50 μm .

3.2 Photomechanical crystalline DTE

At first instance, considering the crystalline case by paying attention to the Video S1 and Figure 2, two classes of photo-responsive movements were identified: plastic deformations and jumps.

Photochromic transformation. Before proceeding to further descriptions, it is worth noticing that the largest crystal with triangle shape displays a change of color when the irradiation is switched between UV and visible. Focusing on the central region of this large immobile crystal (see ROI “photochromism”), we have taken benefit of pixel intensity changes to assess the photo-cyclization and photo-cycloreversion kinetics as illustrated in Figure 4. By fitting the intensity profile, we found a bi-exponential behavior during the photo-cyclization (coloration) step with $\tau_1=18$ s and $\tau_2=274$ s. For the photo-cycloreversion (fading) kinetic, it was clearly a mono-exponential with a characteristic time of $\tau_3=5$ s. Contrasting with the mono-exponential behavior observed in solution,

the bi-exponential discoloration kinetics of nanocrystalline spiropyrans have been reported recently by Garcia-Garibay *et al.*, who explained it in terms of crystal packing influence on the merocyanine conformations.⁴⁴ Indeed, unlike solution, in the solid state, the merocyanine species cannot fully unfolded giving rise to pseudo Z and E conformers. Those two different populations influence the kinetic response. By analogy, to rationalize our bi-exponential curve displayed in Figure 4, it seems reasonable to consider a possible influence of the surrounding cavity on the pathway between antiparallel and pseudo-parallel conformers but rather in the excited state (no such influence expected in the ground state⁴⁵ according to Irie *et al.*). Note that this hypothesis is consistent with the simple mono-exponential photoreversion curve because the conformational-blocked CF species may not be influenced by its crystalline (or amorphous) immediate surrounding. As an evidence, further investigation has to be undertaken in the future to definitively confirm this hypothesis. Keeping in mind the qualitative relevance of those photoswitching characteristic times, it will be instructive to compare them with the temporal occurrences of jumping.

Plastic deformations. First, as expected, a great number of plastic deformations induced by both UV and visible irradiations were observed. We classified these deformations as plastic because when UV or visible illumination was turned OFF, as seen on Video S1 for 600-610 s and 1200-1210 s intervals respectively, the crystals maintained their shapes until a new irradiation was triggered. These mechanical effects involve crystals of different shapes and sizes (Figure 2), and their photomechanical responses induce some breathing effects as seen in ROI #5/#7 or bending motions of the material within ROI #6/#8 (Figure S3 for more details) which are directly related with the photoconversion process. As a matter of fact, such results are similar to either the 7% volume contraction/expansion of the monocrystal lattice of 1,2-bis(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclopentene under UV/visible light reported several years ago^{41,46,47} or the bending/flattening DTEs needle shaped nanocrystal reported recently.^{13,14} The crystal identified in ROI #5/#7 was magnified for two cycles of equal duration (10 min) in Figure 3. When this curved triangular crystal was illuminated under UV light, two small lateral shrinking deformations were observed concomitant with an increase of the median long axis. Then, the initial shape was recovered under visible irradiation (note that when the light was turned OFF, the crystal remained immobile). By analogy with the structurally related 1,2-bis(2,5-dimethyl-3-thienyl-perfluorocyclopentene)⁴⁵, this effect corroborates the individual molecular effects of the photochromic reaction: during the photocyclization, the long axis of the molecule shrinks, the short axis of the molecule extends and the overall thickness of the molecule decreases. These microscopic molecular changes result in macroscopic photomechanical motions, the direction of the latter being

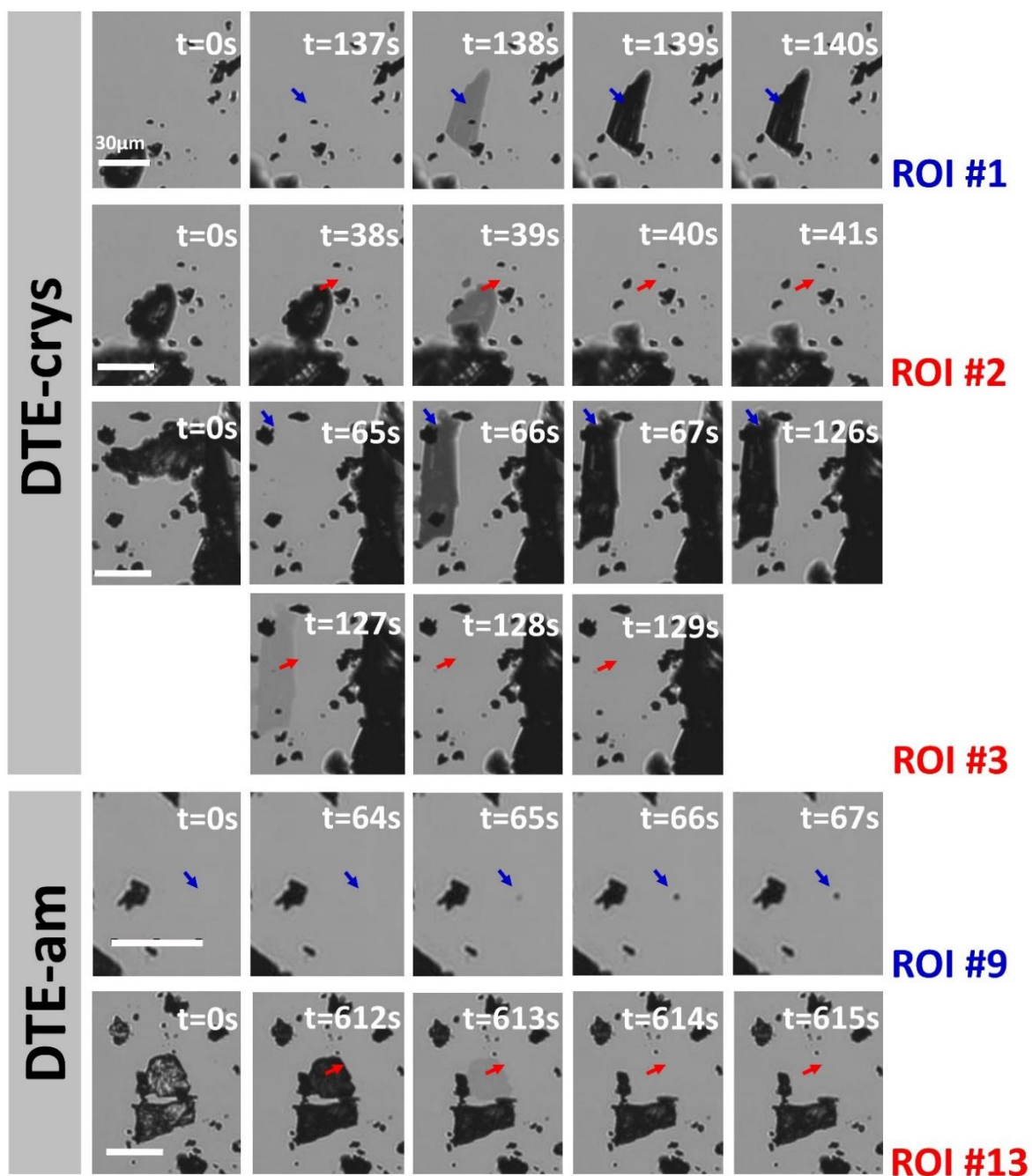


Figure 3: (upper panels) DTE-crys: snapshots displaying jump in moves (ROI #1), jump out moves (ROI #2), and combination of jumps in and out (ROI #3) during the first UV irradiation cycle; (lower panels) DTE-am: snapshots displaying jump in moves (ROI #9) and jump out moves (ROI #13) during the first UV irradiation cycle. Scale bar = 30 μm .

the results of the molecular packing orientation. Disrupting the molecular packing was the main purpose of our amorphization approach, as described in the next part (3.3).

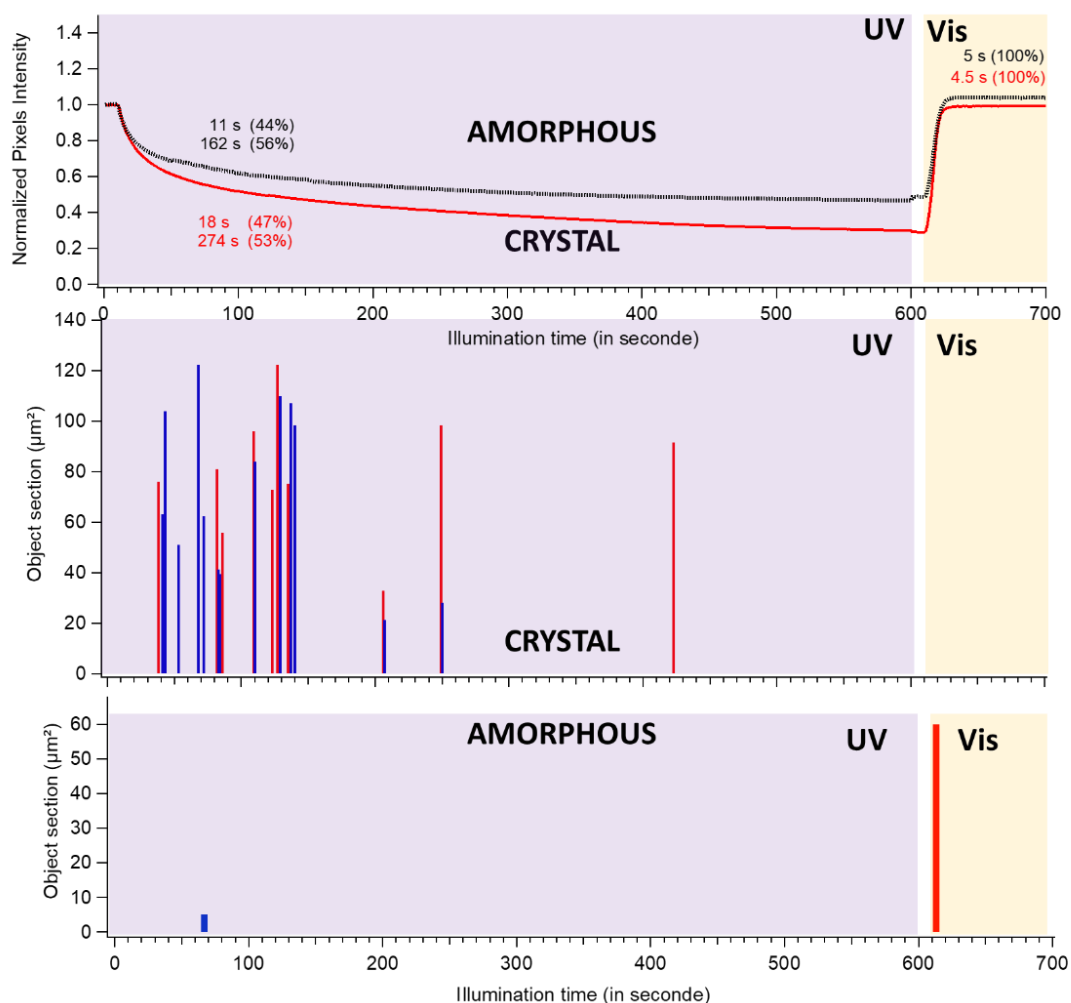


Figure 4: (Upper panel) Intensity variation as a function of time for the ROI marked as ‘photochromism’ in Figure 1 for DTE-crys (red) and DTE-am (black). The characteristic times (with respective normalized pre-exponential factors) are deduced from bi- or mono-exponential fitting; (Lower panels) histogram events for the jumping events inward (blue) and outward (red) the microscope field of view, together with the cross-section sizes of the jumping materials, for both DTE-crys and DTE-am

Material jumping. Apart from the plastic deformations that rely on the photoswitching processes, several sudden crystal jumps were identified during the first UV irradiation cycle while no such jumps occur during the following visible cycle. Note that, even if crystal jumping or “photosalient effect” have been reported in the past for other dithienylethenes,^{48,49} this is the first time that such light-induced jumps are reported for this particular DTE compound.

As a matter of fact, crystals may jump inside or outside the microscope field of view. For the experimental acquisition described here, eight jumps inward the field of view (“jumps in”) were counted during the first UV sequence with moderate density power $P_{uv}=44 \mu\text{W}\cdot\text{cm}^{-2}$ (red ROIs in Figure 2), a specific example being displayed by snapshots in Figure 3 (ROI #1). For the first UV illumination cycle, jumps outward the field of view (“jumps out”) were observed as well, twelve

occurrences in total (blue ROIs in Figure 2) with a representative example (ROI #2) displayed in Figure 3. The overall jumping events (in and out) are gathered in Figure 4. The temporal graph plotted as a function of time and indicating the cross-section sizes of the jumping objects, brings evidences about: (i) a latent period of time $t_{\text{lat}}=38$ s where no jump occurs, an average $\bar{t}_{\text{jump}} \approx 130$ s (jump in/out included), and the last jump occurring at $t_{\text{end}}= 423$ s; (ii) a non-Gaussian distribution with no evident correlation related to the objects section; (iii) an absence of effect under visible light despite a high density power in comparison with UV ($P_{\text{vis}}=12$ mW.cm⁻²). These three observations lead to the following analysis. First, the origin of the latent period has been explained by Naumov *et al.* as the lower limit of time for the system to accumulate sufficient stress in the material to induce the apparent photomechanical effects.²⁸ It has been found that this latent period is correlated with the volume of the crystal and the section normal to the irradiation axis²⁸ but unfortunately we were not able to assess precisely such quantities. It is worth noticing that the large majority of the observed jumps occurs between 38 s and 130 s while the characteristic times for the photochromic conversion characteristic times are $\tau_1=18$ and $\tau_2=274$ s (*vide supra*). The latent period t_{lat} being thus much higher compared to τ_1 , it nicely confirms the cumulative effect theory proposed by Naumov during photocyclizations: a large number of photoconverted molecules are necessary, layer by layer, taking into account the light penetration inside the material, in order to produce enough mechanical stress and release the accumulated energy to induce a sudden macroscopic jump. To the best of our knowledge, the quantitative correlation between photocyclization characteristic times τ_1 and τ_2 and the dynamic times either t_{lat} or \bar{t}_{jump} was not documented in the literature. Finally, it is important to highlight a surprising event of successive jumps detected on a single crystal within two steps (ROI #3 in Figure 2 and Figure 3): after 65 s of UV irradiation a rectangular crystal jumped inward the optical detection field of the microscope; it stayed immobile during 60 s and suddenly it jumped again outward the microscope field of view. It is striking to observe the similarity of the two periods duration and it can be rationalized reminding the ability of certain crystallographic planes to display photoinduced morphological steps/valleys⁴¹ or Grinfeld surface instability compared to insensitive ones. Indeed, let us consider a crystal standing on a propelling crystallographic plane receiving light for a given duration inducing a jump. If this crystal lands on a parallel crystallographic plane (with similar Miller indices), it may jump a second time after an irradiation period similar to the first one. In brief, this double jump is another proof for the specificity regarding the photomechanical abilities of certain crystallographic planes compared to inactive ones. By the way, the competition between dynamics vs inactive crystallographic planes may explain the lack of jumps for the second and third illumination cycles because the propelling

crystallographic planes have been fully promoted during the first cycle through either mono-jump (crystal landing to an inactive plane) or double jumps (crystal landing to dynamic plane jumping again).

3.3 Photomechanical amorphous DTE

As already discussed, we expected the suppression of the reversible photomechanical activity of our DTE material after thermal amorphization. Surprisingly, the photomechanical effects were not suppressed, they were observed to be comparable to the crystalline case as one can see on Video S2, Figure 2 and Figure 3. Indeed, certain common points, such as breathing objects, and drastic differences, like the lack of jumps, were noticed, as we will review carefully in the following. However, even if it seems obvious that photoswitching ability is an individual process taking place at the molecular scale, inspection of the photochromic performances under amorphization is still a prerequisite. As previously done for the crystalline case, we qualitatively assessed the photo-(dis)coloration kinetics by tracking the intensity time-profiles at the center of an immobile amorphous object (indicated in Figure 2) and the result is gathered together in Figure 4 (together with the crystalline case, for sake of comparison). Once again, the photocyclization kinetic curve is well fitted by a bi-exponential function with both characteristic times, $\tau_1=11$ s and $\tau_2=162$ s, well shorter than the crystalline case (18 and 274 s respectively). Even if the precise rationalization of such a shortening of τ_1/τ_2 seems out of reach, the finding of these two characteristic times confirms the influence of the condensed phase on the photocyclization process⁴⁴ whatever its degree of (dis)order. In the same vein, the photo-cycloreversion is mono-exponential and the characteristic time of 4.5 s is quite similar to crystalline case (5 s), which strengthens the hypothesis of a cycloreversion reaction relatively insensitive to the microenvironment of the DTE molecules. Note that we already found this distinction between photo-cyclization and photo-cycloreversion within the study of constrained supramolecular DTEs by time-resolved spectroscopy.⁵⁰ In summary, amorphization seems to accelerate the photo-cyclization process (more free volume around each individual molecule) while no effect is found for the reversion process.

Plastic deformations. As the crystalline case (DTE-crys), tens of plastic deformations induced reversibly by both UV and visible irradiation were observed for DTE-am (at least the two first cycles) as evidenced in Figure 5 (lower panel), corresponding to an amorphous piece with the shape of “baseball glove” (26×15 μm). In the continuity of its crystalline counterpart DTE-crys, one clearly observes a contraction of the DTE-am materials (less than 10%) of the CF compared to the OF in such a way that the “baseball glove” opens (visible) or closes (UV) itself under irradiation.

Such light-induced deformation for amorphous DTEs (we excluded the possibility of such big residual crystalline pieces as explained above) is an unexpected fact, suggesting that crystallographic periodicity is not the unique key parameter to promote -at the macroscopic scale- the photoinduced effect happening at molecular level. This last statement has to be counterbalanced if one considers possible relationships between crystalline and amorphous state more and more investigated this last decade. For example, investigating various polymorphic and amorphous TiO₂ samples, Elliot *et al.* have brought evidence for a similar Ti-O bond strength.⁵¹ In the same line, concerning the glacial phase of Triphenyl Phosphite (TPP), Targus *et al.* have introduced the concept of “apparent polyamorphism” for which the apparently amorphous solid phase was revealed to be a ‘poor’ crystal made of separated nanocrystallites which is distinct from the stable crystalline phase, but whose stability is nevertheless governed by collective effects. In such a “poorly crystallized” material, the small number of unit cells contained in the crystallites, the polydispersity of the crystallites, the rotational disorder could all combine to explain the absence of narrow Bragg peaks, thus resulting in a structure that at first glance looks amorphous.⁵² Clearly, the combination of the amorphous signature by WAXS (Figure 1) together with the similarity of the photomechanical plastic deformations for the crystalline case points toward either (i) some maintained short-range order between DTE molecules during the thermal amorphization process, (ii) or some polyamorphism with domains made of nanocrystallites clusters. If our last hypothesis was valid, DTE-am would represent an excellent candidate to study and clarify the blurred relationship between crystalline and amorphous phases, and their related properties.

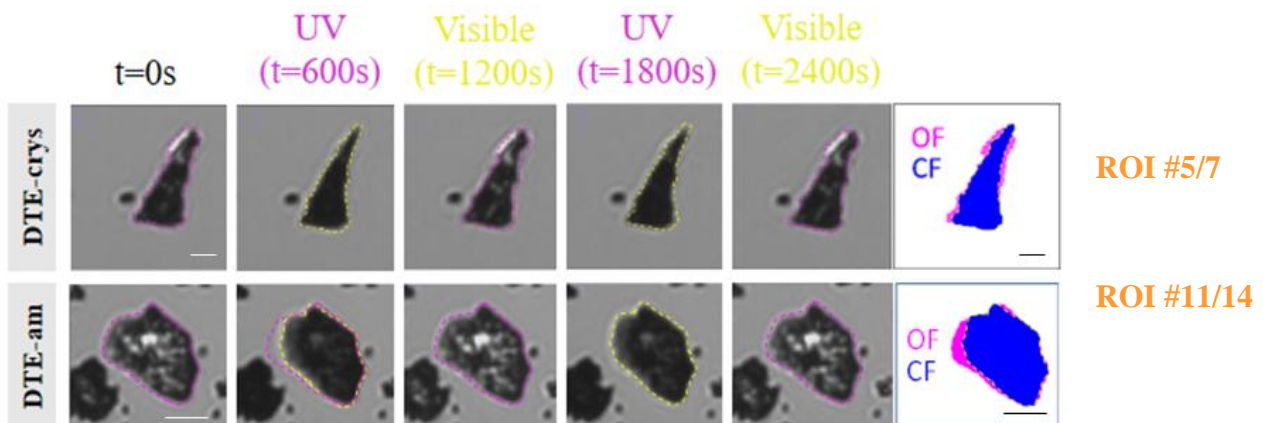


Figure 5: Snapshots of DTE-crys (ROI #5/7) and DTE-am (ROI #11/14) after successive UV and visible irradiation cycles of 600s duration. Scale bar = 10 μ m.

Material Jumping. Unlike plastic deformations, two drastic differences were noticed for the jumping processes of the amorphous sample (DTE-am) compared to the crystalline sample (DTE-

crys). First, as seen in Figure 2 and Video S2, the jumping behavior previously highlighted for crystals under first UV cycle was totally absent for the amorphous materials, except for one small object which jumped inward the field of view (Figure 3, ROI #9, $t=65$ s). We could rationalize the behavior of small jumping objects (radius of 2.5 μm) in terms of the polymorphism hypothesis proposed above i.e. given that the amorphous sample of DTE is composed of a large number of nanocrystallites their cumulative effects results in relatively small jumps. The lack of jumping events clearly highlights the prime importance of the pure crystallinity for the propelling face in contact with the substrate to accumulate and release enough energy for the jump. As already discussed, the photoactive crystalline planes of DTE have been explained in terms of regularly packed DTE molecules in the OF.⁴¹ Reducing (or suppressing) this regularity (periodicity of the unit cell) by thermal amorphization totally cancels this dynamic effect.

Reversely, although the jumps were not observed for DTE-crys under visible irradiation, the amorphous analogs DTE-am displayed a large-amplitude jump outward the field of view (ROI #13; in Figure 1 and Figure 3) immediately after switching on the visible light. Note that this jumping object (ROI #13) under visible illumination is considerably bigger ($28 \times 20 \mu\text{m}$) compared to the one identified under UV light ($3 \times 2.5 \mu\text{m}$). To the best of our knowledge, this is the first time that a diarylethene material was reported to be jumping under visible light. Excluding any rationalization related with the cycloreversion process (it would be observed for the crystalline case otherwise), this novel mechanism is clearly specific of the amorphous state. As an evidence, inspection of reachable room temperature region T_g ranging within $[25-40^\circ\text{C}]$ suggests the possibility of a thermosalient effect, as an alternative mechanism to a photosalient effect. In the past, the thermosalient effect has been reported in the literature due to large anisotropic thermal expansion coefficients,⁵³ promoted by hydrogen-bonded lattice solvent release^{54,55} or explained in terms of phase transition between polymorphs.⁵⁶⁻⁵⁹ None of these types of mechanisms can adequately account for the jumps of amorphous DTE in the CF. However, the extensive work of Uchida *et al.* dealing with topological studies on microcrystalline/amorphous states is helpful. This group has published scanning probe microscopy images on a single crystal of DTE derivatives in the CF below and beyond the T_g , bringing clear evidence that the well-known step/valley formation⁶⁰ reported by Irie *et al.* is strongly impacted by an elevation of temperature as small as 5°C (see Figure 1 of ref⁴³). In our case, even if we did not expect subsequent temperature rise (irradiation source without residual NIR component) through light absorption, the combination of the high intensity regime (12 mW/cm^2) together with major vibrational deactivation pathways, more efficient than the photoreversion process itself (low quantum yield for the photo-cycloreversion process and fluorescence of DTE⁶¹) are probably responsible for the moderate rise of temperature

inducing the jump. Knowing that the room temperature degree was 23°C, this very small temperature increase, to reach the amorphous softened state, may change drastically the glass-material interactions resulting in the propulsion of the material through kinetic energy. Note that the lack of such jump, by thermosalient effect, just during the first moments of UV irradiation may be due to a lack of temperature increase because of (i) lower UV intensity regime (44 $\mu\text{W}/\text{cm}^2$) and (ii) the photocyclization process, which is so efficient that it does not allow a sufficient heating by alternate vibrational deactivation processes. We believe that attempting to correlate the photoswitching quantum yields with photomechanical activity would represent a promising work track for future investigations.

4. Conclusion

With the final aim to gain better understanding of photomechanical effects for crystalline DTE, we have investigated the consequence of thermal amorphization. After a thermal treatment (cooling from the melt at conventional cooling rate), crystalline DTE was turned into completely amorphous material with T_g close to ambient temperature. In the crystalline case (DTE-crys), two main photomechanical effects have been observed: (i) reversible UV-visible deformations analogous of bending/flattening of needle shaped nanowire²⁰ reported in the past, well rationalized by the contraction/expansion of the crystallographic lattices between OF and CF, and (ii) long-range jumps or successive-jumps occurring only under UV illumination, explained in term of photoinduced steps/valleys formation of certain crystallographic planes⁴¹ or Grinfeld surface instability^{26,27}. For the amorphous sample (DTE-am), the reversible deformation trend is surprisingly maintained which strengthened the importance of the OF/CF gradient along the thickness of the photochromic material rather than the crystallographic periodicity. Alternatively, this continuity between the crystalline and the amorphous samples was rationalized in terms of apparent polyamorphism, a concept invoked in the past to explain the glassy state of TPP. Reversely, the UV-induced jumps disappear except for very isolated events (section of few μm^2) suggesting the possible existence for a size or an irradiance threshold. Furthermore, due to easily reachable T_g temperature, a jump induced by the visible light has been highlighted, probably due to thermosalient effect, the rise of temperature being due to the predominance of vibrational relaxation of the excited DTE in the CF over the photoinduced ring-opening reaction.

In the future, controlling the shape of the amorphous material through appropriate micrometric size molds would allow quantitative studies to decipher the size and irradiation power impact on the photomechanical effects, and better rationalize the different routes chosen by the system towards plastic deformations and/or jumping. To investigate more deeply the possible local molecular alignment (apparent polyamorphism hypothesis), we plan to implement open and crossed Nicols

polarizers into our microscope to track birefringence effects on both crystalline and amorphous objects. In parallel, partial amorphization of selected crystallographic planes through laser-induced temperature rise would be instructive as well. Such additional experiments are now under investigation in our laboratories.

Acknowledgments

The authors are grateful to University of Lille for granting a PhD fellowship to Maroua Louati. The Chevreul Institute is thanked for its help in the development of this work through the ARCHI_CM project supported by the “Ministère de l’Enseignement Supérieur de la Recherche et de l’Innovation”, the region “Hauts-de-France”, the ERDF program of the European Union and the “Métropole Européenne de Lille”.

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