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Single Crystals Popping Under UV Light: A Photosalient Effect Triggered by a [2+2] Cycloaddition Reaction**

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Abstract: *The extremely rare examples of dynamic single crystals where excitation by light or heat induces macroscopic motility present not only a visually appealing demonstration of the utility of molecular materials for conversion of energy to work, but they also provide a unique opportunity to explore the mechanistic link between collective molecular processes and their consequences at a macroscopic level. Here, we report the first example of a photosalient effect (photoinduced leaping) observed with crystals of three coordination complexes which is induced by a [2+2] photocycloaddition reaction. Unlike a plethora of other dimerization reactions, when exposed to even weak UV light, single crystals of these materials burst violently, whereby they are propelled to travel several millimeters. The results point to a multistep mechanism where the strain energy that has been accumulated during the dimerization triggers a rapid structure transformation which ultimately results in crystal disintegration.*

Popping of popcorn is a mechanistically unique phenomenon.[1] As the hard shell of corn kernels breaks at high temperature, the thermal energy is converted into mechanical energy whereupon the kernels are self-actuated. The underlying theory invoked to explain this process calls upon the abrupt increase in temperature which causes strong thermal expansion of sugar/starch in the interior of the kernels and of the cellulose of the cover peel, resulting from rapid accumulation of very high strain. The pressure of the superheated water in the interior of the sealed kernel increases up to ca. 9.2 atm (931 kPa) and adds up to the strain on the cellulose cover. Around 450 K, the strain induced by thermal expansion exceeds the elastic threshold of the cover and the pericarp bursts out, whereby the endosperm turns out as a soft and less dense, spongy foam. If the kernel is heated slowly, the fierce popping is not observed as the strain created during the slow heating is dissipated before it reaches the threshold. Despite the burgeoning research on mechanical effects in crystals,[2] a synthetic mimic of such a unique ballistic event of efficient self-actuation has not yet been designed.

Herein we report the first instance of an extremely rare phenomenon, photosalient effect,[2a,n] where a mechanical response that visually (and to some extent, mechanistically) resembles the popping of popcorn kernels on a hot surface occurs in single crystals in response to a solid state [2+2] cycloaddition reaction.[3] The photosalient effect is a sudden and rapid actuation of crystals when they are excited with UV light whereby the crystals are propelled to distances many times their own size.[2a] While studying the photoreactivity of the coordination metal complexes $[Zn_2(benzoate)_4(L)_2]$ (**1**–**3**) [L = 2F-4spy (2′-fluoro-4-styrylpyridine) in **1**, 3F-4spy (3′-fluoro-4-styrylpyridine) in **2** and 4spy (4-styrylpyridine) in **3**] we serendipitously noted that when crystals of these materials are exposed to even weak UV light, they pop violently (Movie SV1 and SV2 in the Supporting Information, SI). Although several instances of such actuating behavior of crystals induced by heat[4] and light[2l,n] are known, to the best of our knowledge, crystal motility driven by a [2+2] cycloaddition reaction has not been reported yet. In an attempt to establish a mechanistic link between the macroscopic manifestation of the photosalient effect and its origin at a molecular level, we attempted to capture the kinematic details of this extremely rare phenomenon using a high-speed camera. We also utilized a variety of analytical methods, including single crystal/powder X-ray diffraction (XRD) and microscopy, with kinematic (motion) analysis of the crystal locomotion.

Light yellow block-shaped single crystals of **1**–**3** were obtained by slow evaporation of methanol solution of $Zn(NO_3)_2$, sodium benzoate and the respective pyridyl ligand. Single-crystal XRD (SXRD) data showed that **1**–**3** are isomorphous and isostructural (Table S1 in SI). Due to the similarities, only the structure of **1** is described here in detail along with the differences in packing with respect to the other two compounds. **1** crystallizes in the monoclinic space group *C*2/*c*. A crystallographic inversion center is present at the middle of the paddle-wheel structure (Figure 1a) where half of the formula unit of **1** is located in the asymmetric unit. The pyridyl and phenyl rings in the 2F-4spy ligand are twisted by 6°. The 2F-4spy ligands are packed in a head-to-tail fashion along the $[1\bar{1}0]$ axis (Figure 1b). The fluorophenyl and pyridyl rings from the adjacent molecules are aligned parallel and separated at 3.69 Å, indicating strong $\pi\cdots\pi$ interactions. As a consequence, the centroids of the $C{=}C$ bonds are at

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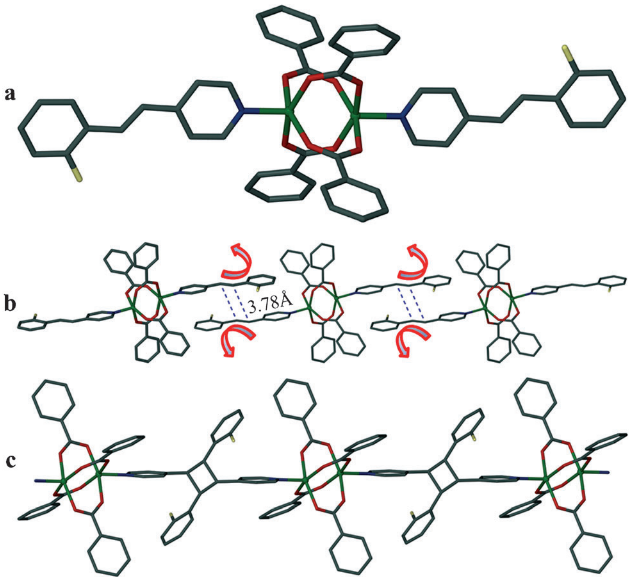

Figure 1. Crystal structure of metal complex **1** and 1D CP **4a**. a) Coordination geometry in the structure of the monomer, **1**. b) Relative disposition of the olefin groups in **1**. c) Structure of 1D CP **4** recrystallized from a sample of photoreacted **1**.

a distance of 3.78 Å. Similarly, the pairs of C=C bond in **2** and **3** are also suitably juxtaposed for [2+2] cycloaddition reactions.[3,5]

It is clear from the packing that the olefin pairs in **1**–**3** are preoriented to undergo quantitative photochemical reaction[5] and the resultant product is expected to be a 1D coordination polymer (CP) in which the [Zn_2(benzoate)$_4$] paddle-wheels are connected by photodimerized cyclobutane ligands (Figure 1c). The course of photoreactivity with time was followed under UV light by integrating the disappearing signals due to the protons of the pyridyl group in 2F-4spy at 8.57 ppm and of the evolving signal from the same proton in *rctt*-2F-ppcb (*rctt*-2F-ppcb = *rctt*-1,3-bis(4-pyridyl)-2,4-bis(2′-fluoro-phenyl)cyclobutane) ligand at 8.37 ppm as well as the tertiary proton of the cyclobutane ring at 4.75 ppm in the ^{1}H NMR spectra, after dissolving the irradiated powdered sample in [D$_6$]DMSO solution at specific intervals of time (Figure S3–S5 in SI). All compounds **1**–**3** showed quantitative photoconversion of their C=C bonds to cyclobutane ring in a single step within 60 min of UV exposure (Figure S6). After the photopolymerization of **1**–**3**, the respective 1D CPs (hereafter, **4**, **5** and **6**, respectively) maintained the crystallinity, as confirmed with powder X-ray diffraction (PXRD) patterns (Figure S13–S15 in SI). Crystal structure determination of a recrystallized sample of the final photoproduct of **1** provided further evidence of the 1D CP, [Zn_2(benzoate)$_4$(*rctt*-2F-ppcb)] (**4a**; Figure 1c). The photoproduct **4a** crystallized in space group $P\bar{1}$, and expectedly, contained the robust centrosymmetric binuclear paddle-wheel unit connecting the cyclobutane spacer ligand *rctt*-2F-ppcb.

To determine the crystal structure of the photoproduct directly, a crystal of **1** was irradiated using very weak UV light from a single UV LED source ($\lambda = 375$ nm) for 15 min, which minimized the crystal deterioration. Diffraction data were collected on the irradiated crystal at room temperature. The main structure remained identical, however, new electron density peaks evolved in the difference Fourier map, indicating formation of a cyclobutane ring.[6] The disorder was modeled successfully in the refinement by inclusion of the 1D CP, **4**, which refined to 21.2(4) % (Figure S2 in SI). It clearly indicated that the photochemical reaction in **1** is incomplete and that the photoproduct **4** co-exists with the reactant **1** (78.8(4) %) in the single crystal. This result corroborated the conclusion based on the ^{1}H NMR spectra that the photodimer is the only product whose evolution triggers the popping, and that there are no other chemical intermediates, as observed previously.[7] Attempts to increase the exposure time to obtain single crystals containing higher yield of **4** remained fruitless, because the crystals quickly disintegrated (Figure S10d in SI) and the remaining debris was not suitable for diffraction experiments.

Since the crystals of **1** and **2** have long block morphology with well-defined faces, we analyzed the orientation of the reactant and product molecules in the respective crystals in an attempt to correlate these to the photomechanical motion of single crystals. The crystal packing of **1** is made up of alternating 1D chains which are slightly skewed relative to each other (Figure 2a). The 1D chains interact through π⋯π interactions to form sheets (Figure 2b) that run parallel to the (102) and $(\bar{1}02)$ planes which are at angles of nearly 108° and 72° to the crystal faces $(\bar{1}10)$ and (110), respectively. The reaction centers are at the olefin bonds of the 2F-4spy ligands in the sheets (Figure 2a). Dimerization between the ligands of neighboring chains that are related by $(^1/_2-x, {}^1/_2-y, 1-z)$ and run parallel to the $(102/\bar{1}02)$ plane draws the double bonds and the respective ligands closer to each other to form a cyclobutane ring.

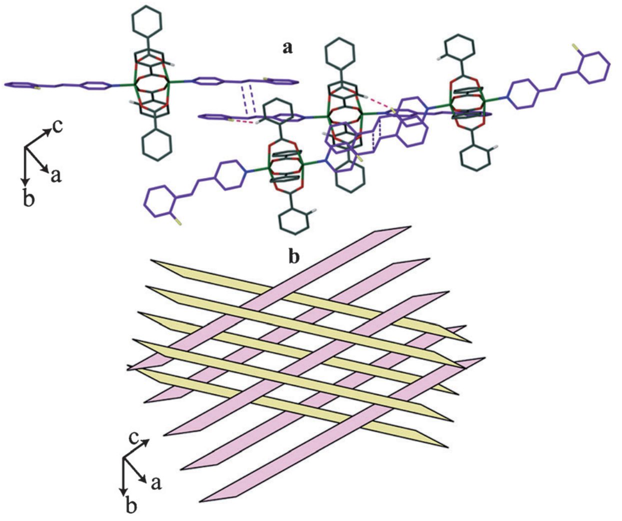

Figure 2. a) View of the crystal structure showing the nearly orthogonal 2F-4spy ligands (in purple). b) Schematic representation of the relative orientation of the adjacent 1D chains within the lattice.

In contrast to **1** and **2**, large single crystalline blocks of **3** with random and ill-defined morphology were obtained from methanol, which exhibited significantly weaker popping under UV light; i.e., the crystals showed very slow molecular motions such as jumping to very small distances and in few cases they did not show any molecular motions. However, from ethanol we obtained thin rod-like crystals (Figure S11 in SI) with morphology similar to **1** and **2**. These crystals were actuated faster and to longer distances compared to the blocks, similar to **1** and **2**. The face indices of this habit were identical to those of **1** and **2**. We conclude that indeed, the rate of actuation/mechanical motion of single crystals is morphology-dependent.

The apparent cause for the popping and disintegration of these single crystals was due to the strain generated during the photochemical reaction in the crystal as a result of structural transformation. To perform kinematic (motion) analysis, well-shaped crystals of **1**–**3** were selected and excited with a medium-pressure Hg-lamp. The rapid motion of the crystals was captured with an optical microscope coupled to a high-speed camera operating at time-resolution of up to $5\times10^3\ \mathrm{s}^{-1}$. About 20 crystals of each compound were examined (the statistical analysis has been shown in Table S4, SI). The high-speed recordings of the samples exposed to UV light showed that the crystals exploded and jumped in different directions from their original position (see Movies SV1–SV8 in the SI). The crystals exhibited predominantly three kinematic effects illustrated by the snapshots in Figure 3: a) very long crystals predominantly underwent rolling or flipping, b) medium-size crystals hopped with separation of a small piece off the crystal that propelled the remaining part into a spinning or linear motion, and c) small-size crystals showed splitting into several pieces with explosion. Thus, not only does the popping depend on the morphology of the single crystal, but it also depends on its size.[2j,k] These factors could alter not only the rate of actuation, but also the type of mechanical motion such as popping, hopping, leaping, sliding, and rolling.[2j,4b] This sample-dependent behavior can be explained by the strain created along different axes in an anisotropic structure.[8]

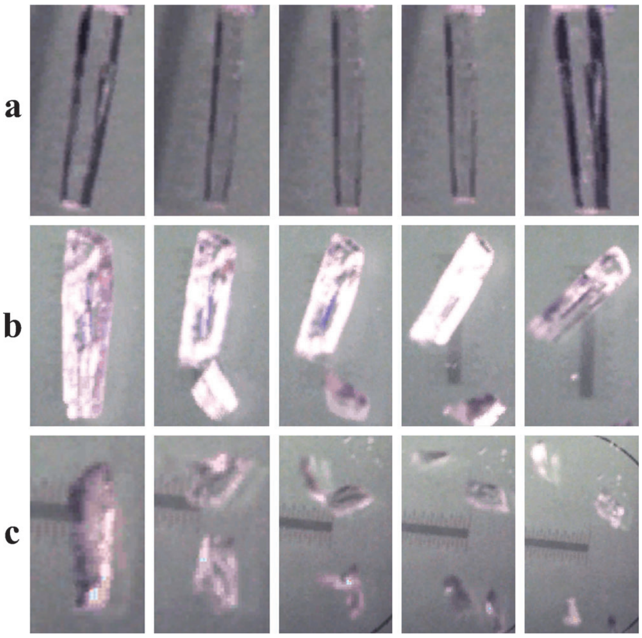

Figure 3. Various kinematic effects observed with crystals of **1** and **2**. a) Rolling or flipping, b) separation of a small fraction off the crystal which propels the remaining portion of the crystal, c) explosion or splitting of a crystal.

Inspection of crystals that have been restrained from motion by immersion in thin layer of oil showed development of visible parallel cracks in their interior (Figure 4a and b).

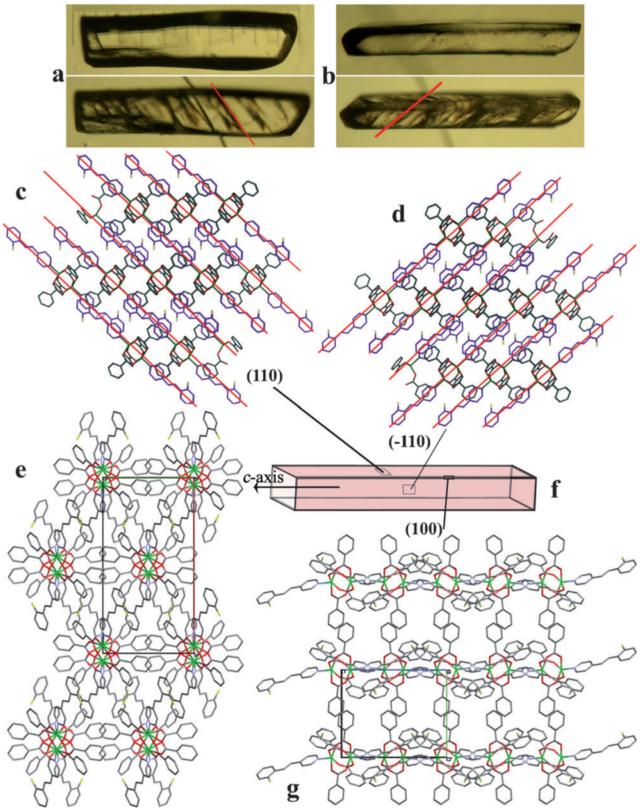

Figure 4. Structure–property correlations of the photosalient effect in **1**. a,b) Crystals of **1** whose motility has been restrained by cryo-oil (the crystal faces (110) and $(\bar{1}10)$ are shown here before and after UV irradiation, respectively. c–g) Projection of the molecular packing of **1** viewed along different faces of the crystal. Red lines in diagrams (c) and (d) show the direction of cracking of the crystal. The hydrogen atoms were omitted for clarity.

The relationship between the external morphology and the internal packing of molecules is shown in Figure 4c–g. The distance between the cracks depends on the irradiation time. Irradiation with LED light for 20 min generated cracks 20–40 μm distant from each other, with an average separation of 27 μm (Figure S10 in SI).

The anisotropy in the distortion of the unit cell as a result of photochemical reaction could provide a hint to the mechanisms of disintegration and the subsequent locomotion. Crystals of **1** were subjected to UV light of low power density by exposure to light from a 375 nm LED for 25–30 min. The unit cell determined at 200 K before and after UV irradiation showed significant changes in the cell parameters ($\Delta a = 0.362(48)$, $\Delta b = 0.038(24)$, $\Delta c = 0.187(32)$ Å, $\Delta\beta = 2.12(2)°$, $\Delta V = 75.5(26)$ Å^3; Table S2, SI). After UV irradiation, the unit cell of **1** crystals expanded by +1.44% along the *a*-axis, and +1.20% along the *c*-axis (200 K). The change (+0.31%) was negligible along the *b*-axis. The strain accumulated over a long range resulted in generation of cracks in the [111] direction and nearly orthogonal to *c*-axis, i.e., the longest dimension of the crystal (Figure 4a,b and Figure S10 in SI). From the distance between the cracks, we calculated that about 4.9×10^4 parallel layers react before a sufficient stress has been accumulated for the crack to appear. This macroscopic separation occurs at very high rate, estimated to less than 1.2 m s^{-1} from the high-speed recordings, providing sufficient kinetic energy for the pieces to fly apart.

A comparison of the crystal data of the partially polymerized sample $(\mathbf{1})_{0.212}(\mathbf{4})_{0.788}$ with that of **1** implies that even after ca. 21% polymerization there is a significant increase in the volume of the crystals that pop out (in air) or crack (in oil). The density and the unit volume for the 1D CP **4**, calculated from the partially polymerized product from LED experiments of **1** are 1.371 g cm^{-3} and 4910.4 Å^3. This calculated density matched fairly well the density, measured by the flotation method, of the powder obtained after quantitative conversion of **1** into **4** (1.394(3) g cm^{-3}). Since **4a** is a recrystallized product, the molecules packed better (in $P\bar{1}$) relative to either $(\mathbf{1})_{0.212}(\mathbf{4})_{0.788}$ or **4**, affording a more tightly packed structure with density of 1.501 g cm^{-3}. These results show that there is an increase of volume by 11% (corresponding to 486.3 Å^3) during the photodimerization. The two phases (**1** and **4**) can coexist in a single crystal with ca. 21% of **4**. Beyond this ratio, the phase-heterometry[9] creates stress due to the increase of unit cell volume and the release of stress causes the ballistic motion of the crystals.

To monitor the reaction course, the evolution of the photoproduct phase was followed in situ, by time-resolved PXRD experiments (Figure 5, S12 in SI). The kinetics of the reaction was modeled by applying the JMAK model,[10] which has been successfully applied previously to a number of [4+4] dimerizations.[11] The model relies on the equation $\ln(-\ln(1-x)) = n\ln(t) + n\ln(k)$ that is represented graphically as Sharp–Hancock plot and yields a straight line with a slope that equals to n and has intercept $n\ln(k)$, where t is the collapsed time, $x(t)$ is the evolved fraction of the product, k [s^{-1}] is the reaction rate constant and n is the Avrami exponent. Although in the original theory, n can have values of minimum 1, recently More et al. obtained a fractional value in the case of 9-anthracenecarboxylic acid dimerization, successfully describing the reaction kinetics by including a negative autocatalytic step, an indication of autoinhibition.[11b] Accordingly, we conclude that the reaction starts homogeneously but it is autoinhibited, which corresponds to the popping and increased mosaicity of the crystals. On the other hand, the formation of 1D CPs **4–6** from the Zn^{II} complexes, **1–3** follow simple first-order kinetics with rate constants 1.068×10^{-3} s^{-1}, 0.8917×10^{-3} s^{-1}, and 0.9817×10^{-3} s^{-1} respectively (Figure S7–S9 in SI).

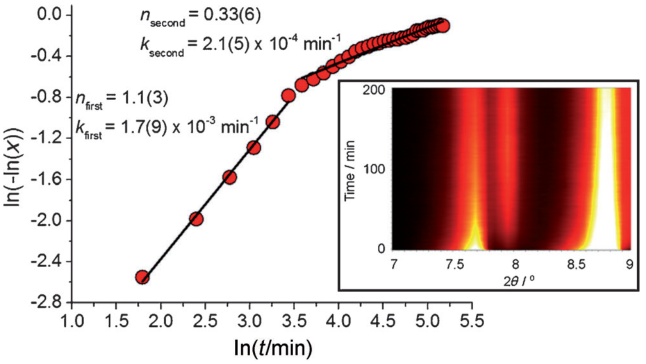

Figure 5. Sharp–Hancock plot of **1** showing two different kinetic regimes. Inset: Two-dimensional projection of the observed X-ray intensity, plotted as a function of diffraction angle and time.

The collective results support the hypothesis that a phase-heterometry in the course of the polymerization in these Zn^{II} complexes causes very high strain in the crystal, accompanied by sudden expansion of the unit cell volume. The fast photoreaction and the short time available for release of the generated stress during formation of the new phase result in accumulation of strain to a threshold value, beyond which it is released by one of several ballistic events. In a far analogy, this behavior resembles the popping of rapidly heated popcorn kernels.

In summary, here we report for the first time, an unprecedented photoactuation of single crystals due to a solid state [2+2] cycloaddition reaction. The photosalient effect of these materials is attributed to the strain created by sudden expansion during the [2+2] cycloaddition reaction, which is very similar to the popping of corn kernels on a hot plate as a result of a rapid expansion of inside starch part compared to outer shell. The three isotypical coordination complexes undergo similar photoreaction and exhibit similar photoactuating phenomenon leading to the formation of 1D CPs. This result sets the path for systematic studies into the effects of chemical modification on the photosalient effect. The dependence of the mechanical effect on crystal morphology is attributed to the alignment of reactive C=C bonds relative to the specific crystallographic axes in the generation of strain during the photochemical reaction. The elongation of the crystals in the [001] direction was found to enhance the popping relative to the other habits. The time profile of the reaction monitored by in situ time-resolved PXRD and solution ^{1}H NMR spectroscopy showed that due to the phase heterometry, after the formation particular amount of photo product, the strain created in the crystal caused the mechanical motion of single crystals. Having demonstrated that solid-state [2+2] photo cycloaddition reactions can be utilized for conversion of light into mechanical motion, this study opens the door for further studies into materials for alternative energy conversion. In retrospect, the impressive motility of these materials due to the photosalient effect suggests that careful control over the crystal shape and size could be a viable approach to the design of photoactuating systems with improved photomechanical properties.

CCDC 979137 (**1**), 979138 (**3**), 979139 (**2**), 979140 ($(\mathbf{1})_{0.212}(\mathbf{4})_{0.788}$), 979141 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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