Crystal Engineering

Deutsche Ausgabe: DOI: 10.1002/ange.201509319
Internationale Ausgabe: DOI: 10.1002/anie.201509319

Elastic Organic Crystals of a Fluorescent π-Conjugated Molecule

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Abstract: *An elastic organic crystal of a π-conjugated molecule has been fabricated. A large fluorescent single crystal of 1,4-bis[2-(4-methylthienyl)]-2,3,5,6-tetrafluorobenzene (over 1 cm long) exhibited a fibril lamella morphology based on slip-stacked molecular wires, and it was found to be a remarkably elastic crystalline material. The straight crystal was capable of bending more than 180° under applied stress and then quickly reverted to its original shape upon relaxation. In addition, the fluorescence quantum yield of the crystal was about twice that of the compound in THF solution. Mechanical bending–relaxation resulted in reversible change of the morphology and fluorescence. This research offers a more general approach to flexible crystals as a promising new family of organic semiconducting materials.*

Organic single crystals of π-conjugated molecules are often likened to assembled “Jenga”: weak intermolecular interactions, a densely packed structure, and anisotropic ordering.[1] Charge carriers or excitons can move through the ordered π system. In general, however, single crystals of an organic compound are mechanically weak and susceptible to breakage under applied stress. Crystalline nanomaterials formed from a few layers of an orientated molecular assembly occasionally show flexibility (soft) to overcome stress breakage,[2–4] but single organic crystals of macroscopic dimension are generally less flexible (hard). Bendable organic crystals occasionally show irreversible (plastic) deformation under applied stress. A mechanism, in which bending causes slipping between the crystal planes and disrupts the ordered structure, has recently been proposed for plastically (irreversibly) bendable organic crystals.[5–9] Thus, almost all crystals lack mechanical toughness at large scales. Macroscopic organic single crystals sometimes bring out hidden properties of the molecule. Actuation of photochromic molecular crystals is a very important example where light-induced molecular transformation of the crystals causes macroscopic reversible motion.[10–12] Similar to these properties, reversible mechanical properties (such as elasticity and self-healing) are an important topic in organic materials. Elastic bending of organic single crystals is a rare phenomenon, and it has only been shown in a few recent reports.[13–16] A needle cocrystal formed from caffeine and 4-chloro-3-nitrobenzoic acid in methanol showed elastic bending ability under applied stress.[13,14] Methanol in the cocrystal contributed to the elastic flexibility, which was lost upon desorption of methanol. Some pure organic crystals (such as terephthalamide, 2,6-dichlorobenzylidine-4-fluoro-3-nitroaniline) also show elastic bending with high repetition and energy storage.[15,16] The terephthalamide crystal was elastically bent by crystal-to-crystal transformation,[16] but the mechanisms for the other crystals are not clear.[13–15] Moreover, these single crystals are not large (on the millimeter length scale).[13–16] Thus, the fabrication of novel macroscopic crystalline materials composed of an elastic π system with macroscopic orientation and high purity is a challenging topic.

Self-assembly is a critical process in all living organisms, and is becoming increasing important in chemistry and material science.[17,18] Organic single crystals are the purest self-assembled structures of organic molecules, but crystal growth defects (such as stacking faults, grain boundaries, and impurities) make the formation of macroscopic single crystals very difficult. However, the bottom-up strategy for forming large single crystals is very important for the development of elastic organic single crystals of π-conjugated molecules. Crystal growth of organic compounds toward pure single crystals with macroscopic dimensions (on the centimeter length scale) and specific character depends on their molecular design. Herein we report a macroscopic elastic π-conjugated molecular crystal. The single crystal shows elastic bending mechanics and mechanofluorochromics based on the deformation of the π system by macroscopic mechanical motion.

1,4-Bis[2-(4-methylthienyl)]-2,3,5,6-tetrafluorobenzene (**1**) was synthesized in high yield by the palladium(0)-catalyzed Stille cross-coupling reaction of 1,4-dibromo-2,3,5,6-tetrafluorobenzene with 2-tri(*n*-butyl)tin-4-methylthiophene (Figure 1 A). Large pale-yellow crystals (thickness: 30–400 μm, width: 700–4000 μm, length: 10–60 mm) were obtained from a biphasic methanol–dichloromethane solution containing **1** (Figure S1 in the Supporting Information). The crystal structure of **1** contains S···F (2.719 Å) and F···H (2.218 Å) intramolecular contacts that are significantly shorter than the sums of their van der Waals radii ($d_{SF} = r_S + r_F = 3.27$ Å, $d_{FH} = r_F + r_H = 2.67$ Å) (Figure 1 B). These contacts result in highly planar molecules with a maximum torsion angle of 1.27° between the tetrafluorophenylene and thiophene units. The molecules form a slip-stacked assembly. The center-to-center separation between the thiophene–tetrafluorobenzene–thiophene planes is 2.347 Å (Figure 1 B). The fibril lamella[19] morphology originates from the slip-stacked molecular wires at the (010) and (001) faces (Figure 1 C) through the self-assembly of planar tetrafluorophenylene–thiophene molecules.

The macroscopic morphology of each face was determined by optical microscopy. Two faces of the crystal (thickness: 58 μm, width: 875 μm, length: 42 mm) were observed. One face is very smooth with no characteristic

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201509319.

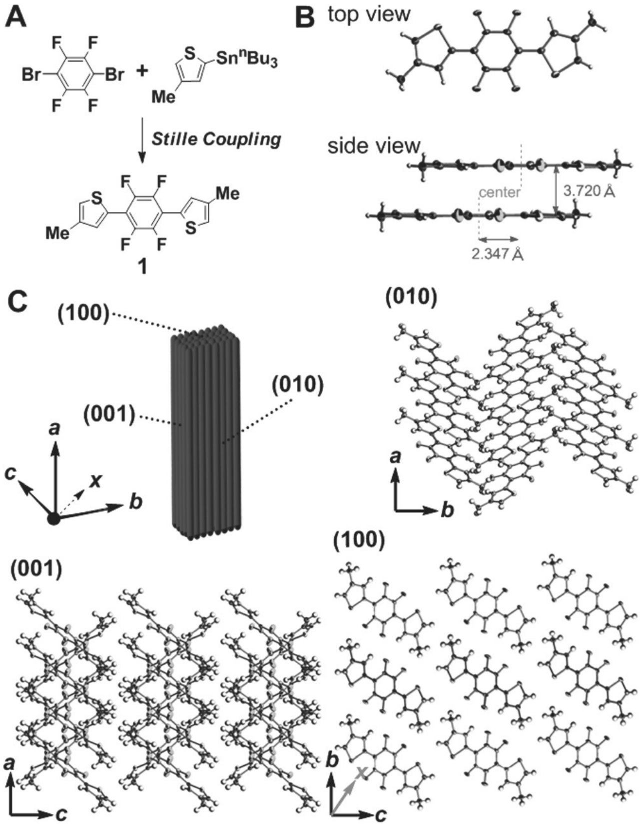

Figure 1. (A) Synthesis of **1** by Stille cross-coupling. (B) Top and side views of the molecular structure of **1** in the single crystal. (C) Morphology and crystal structure of the single crystal. Compound **1** shows an enhanced slip-stacked π–π overlap and lamellar structure consisting of slip-stacked molecular wires along the *a* direction.

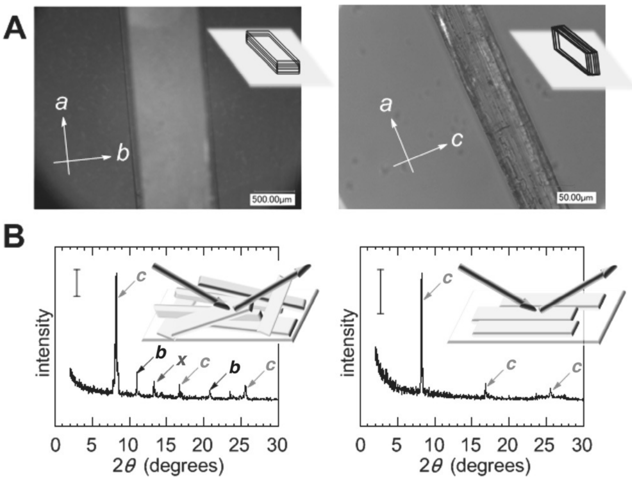

Figure 2. A) Optical microscope images of the smooth (left) and lamellar faces (right) of the crystal. B) XRD patterns of the crystal on a platinum substrate. Bar = 400 counts per second (cps).

surface morphology (Figure 2 A, left). The other face appears smooth, but the lamellar morphology is observed along the *a* axis (Figure 2 A, right). Because of the differences in the densities of the packed structures and the directions of molecule **1** in the fibril lamella of the slip-stacked molecular wires, the refraction of light by the two faces is very different. To link the morphology and the structure of each face of the crystal, X-ray diffraction (XRD) analysis of the crystal was performed. When the crystal was randomly set, many diffraction peaks are observed (Figure 2 B, left). Patterns derived from one lamella structure are observed when the smooth crystal face was set to be parallel to the substrate (Figure 2 B, right). According to the Bragg equation, the length was calculated as 10.7 Å, which corresponds to one lamella layer along the *c* axis. Thus, the face shown in Figure 2 A (left) is the (010) face. The other patterns were calculated to have lengths of 8.05 and 6.66 Å, which are the lamella layers in the *b* and *x* directions (Figure 2 B, right). Thus, the macroscopic lamella face corresponds to the (001) face.

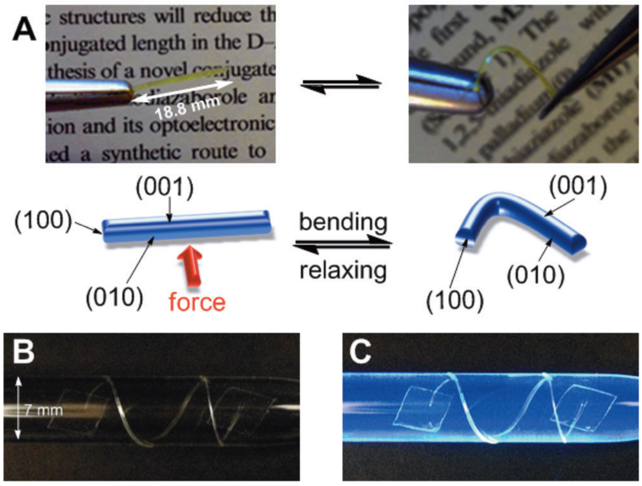

Figure 3. A) Images and illustrations showing bent and relaxed crystals. When bent from the (001) plane, the pale-yellow crystal of **1** quickly regained its original shape upon relaxation. B) Crystal wound around a Pasteur pipette. The original crystal is shown in Figure S1 B. C) Fluorescence of the wound crystal.

Figure 3 A shows the relaxed and bent shapes of the large single crystal. Surprisingly, when bent from the (001) plane, the crystal quickly regained its original straight shape upon relaxation without breaking or cracking, therefore demonstrating its elastic flexibility. Thus, it was possible to wind the crystal around a Pasteur pipette (Figure 3 B), and fix the rolled crystal with Scotch tape. The elastic π-conjugated crystal showed fluorescence under UV irradiation at 365 nm (Figure 3 C). Previous reports did not address these properties in densely packed π-conjugated molecules,[20,21] which may result from potential quenching caused by aggregation between slip-stacked molecules.[22] The excitation and fluorescence spectra of **1** in THF and in the crystal are shown in Figure S3. The excitation spectrum of **1** in THF showed a maximum at 365 nm, similar to its absorption spectrum. In comparison, the crystal showed a sharp excitation band peaked at 427 nm. The fluorescence peak (λ_{max}) showed a remarkable red-shift from 406 nm in THF to 503 nm in the crystal. The quantum yields (Φ) of the solution and the crystals were measured based on an absolute method using an integrating sphere equipped with a multichannel spectrometer. Compound **1** also exhibited a lower quantum yield in THF ($\Phi = 0.145$) than in the crystal ($\Phi = 0.252$), which is consistent with aggregation-induced enhanced emission.[22] These phenomena arise from the planar structure of **1** and the restriction of intramolecular rotation in the aggregated state.

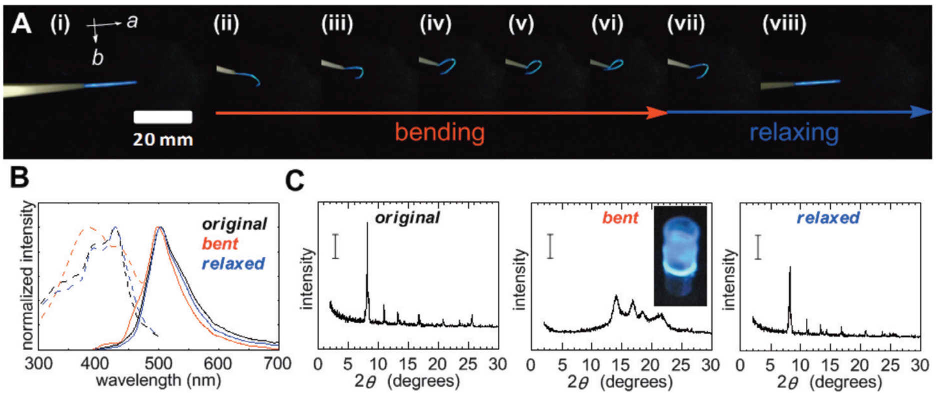

Figure 4. A) Fluorescence images of the elastic bending–relaxation cycle of the crystal under UV irradiation at 365 nm. B) Normalized excitation spectra (dotted line) and fluorescence spectra (solid line) of **1** in the original crystal (black), bent crystal (red), and relaxed crystal (blue). C) XRD patterns of the original, bent, and relaxed crystals of **1**. Bar = 400 cps. The inserted graphic is a bent crystal on a straw under UV irradiation.

To clearly observe the macroscopic elastic bending motion, we investigated the mechanical performance of the crystal under UV irradiation at 365 nm (Figure 4A and Video S1). The straight crystal (i) bent under applied stress (ii)–(vi) and relaxed upon stress reduction (vii and viii) to recover its original shape. The crystal bending angle exceeded 180° (vi). Reversible bending-relaxation of the crystal can be cycled many times (Video S2). The new π system of the crystal offers elastic mechanical motion with no structural defects. The elasticity parameters of the crystal were estimated using a previous concept.[23] A bent crystal sample was prepared by fixing a crystal on a straw with Scotch tape at the edges. The strain (ε_n) was estimated using the relation[23]

$$\varepsilon_n = d/2r \tag{1}$$

where d corresponds to the length of the (001) plane ($d = 128\ \mu m$) and r is the radius ($r = 1.5$ mm). Thus, $\varepsilon_n = 4.27\,\%$. The large motion with high repetition and energy storage is because of a change of the densely packed structure. The macroscopic elastic behavior is based on structural slippage[13,14] or crystal-to-crystal transformation[16] of the crystalline structure.

We were interested in the structural behavior of the original, bent, and relaxed crystals. Both fluorescence spectra and X-ray diffraction (XRD) patterns were measured: 1) the original crystal on the straw substrate, 2) the bent crystal on the straw, and 3) the relaxed crystal on the straw. It is noteworthy that the crystal showed a slightly different fluorescence band when it was mechanically bent (Figure 4A). The bent crystal showed a characteristic band at around 450 nm. The quantum yield of the original crystal on the straw substrate was 0.092. Because the observed fluorescence and excitation bands of the crystal were similar to that of the crystalline powder state of **1** (Figure S4), this is probably because of a structure gap between the π systems caused by macroscopic mechanical motion. This crystal also showed a blue-shifted excitation band at 383 nm. When the bent crystal relaxed upon force removal, the spectrum exhibited a red-shifted band, which was identical to the original spectrum. These results suggest that the lamellar sheets formed by compound **1** in the slip-stacked structure may adopt a partially distorted orientation under tension and compression. The mechanofluorochromism[24–26] of the single crystal was induced by mechanical bending–relaxation. The XRD patterns of the crystal of **1** showed sharp peaks in the original shape but broad peaks in the bent shape (Figure 4C). Upon relaxation, the XRD pattern showed sharp diffraction peaks that matched the original pattern. Thus, the elastic behavior is not based on a single crystal-to-crystal transformation.

The alternating π-conjugated structure having the tetrafluorophenylene and thiophene cores affords a rigid π-plane derived from S⋅⋅⋅F and F⋅⋅⋅H interactions. No free-rotation between the π units and the slip-stacked packing between the π planes would realize fabrication of very large single crystal having fibril lamella morphology. The blue-shifted spectra of the bent crystal (Figure 4B) indicate that slipping of the π planes causes inhibition of the efficient energy transfer between the molecules. The molecular plane would be capable of sliding to longer and shorter slipping (center-to-center separation) lengths, within a short length range, upon applied stress, and then back to the original length upon relaxation (Figure S5A). Expansion and contraction of the slip-stacked molecular wires occur on one side and the opposite side of the fibril lamella crystal, respectively (Figure S5B). Interlock of the jagged slip-stacked molecular wires may prevent the sliding between the wires of the fibril lamella (Figure S5C).

In conclusion, we fabricated a large single crystal composed of slip-stacked molecular wires of the planar π-conjugated molecule 1,4-bis[2-(4-methylthienyl)]-2,3,5,6-tetrafluorobenzene. Unlike most organic crystals, the straight crystal bent under applied stress and quickly reverted to its original shape upon relaxation. The crystal was capable of bending more than 180°. The fluorescence quantum yield of molecule **1** in the crystal was approximately twice the value in THF solution, which is evidence of aggregation-induced enhanced emission. The single crystal showed a unique mechanofluorochromic ability caused by mechanical bending-relaxation motion. This work opens up the field of soft mater and crystal chemistry. Further studies, including processability of the single-crystal **1** into fibers and details of photochemistry, are in progress.

Acknowledgements

This work was supported by a Grant-in-aid for Young Scientists (B) 15K17872 and Scientific Research (C) 26410141, and the Cooperative Research Program of the Network Joint Research Center for Materials and Devices. We would like to thank Prof. Takanori Fukushima and Dr. Fumitaka Ishiwari at the Tokyo Institute of Technology (Titech) for equipment access and support for the absolute luminescent quantum yield measurements, Dr. Shinsuke Inagi at Titech for ^{19}F NMR measurements, and Prof. Yoshinobu Yokomori and Dr. Natsumi Kamiya at the National Defense Academy (NDA) for X-ray crystal structure analysis, digital microscopy, XRD measurements, and valuable advice.

Keywords: crystal engineering · elasticity · fluorescence · organic crystals · π-conjugated molecules

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 2701–2704
Angew. Chem. **2016**, *128*, 2751–2754

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Received: October 6, 2015
Revised: November 16, 2015