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Article

Twinning-Based Organosuperelasticity and Chirality in a Single Crystal of an Achiral Donor−Acceptor Type Schiff Base Induced by Charge-Transfer Interactions

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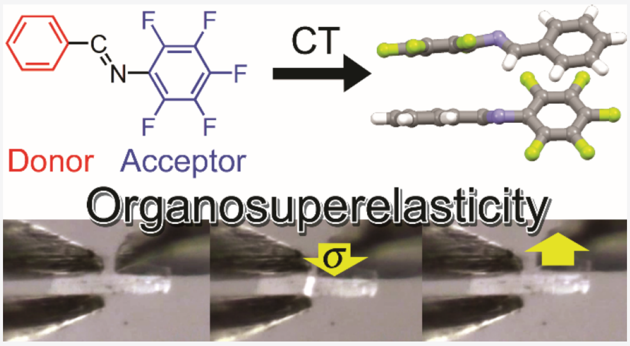
ABSTRACT: A charge-transfer (CT) interaction stabilizes molecular assemblies and can form a useful supramolecular synthon in crystal engineering. Herein we demonstrate preparation of a chiral single crystal showing twinning-based organosuperelasticity by forming a CT complex of an achiral donor−acceptor type Schiff base: *N*-(2,3,4,5,6-pentafluorophenyl)-1-phenylmethanimine. Pseudo-180° symmetry of a single-component CT complex originating from an antiparallel molecular assembly is the key to mechanical twinning. The chiral crystallization induced by CT interactions is also noteworthy because of the potential development of materials showing CT-based functions coupled with chirality.



■ INTRODUCTION

In mechanical twinning, atoms and/or molecules change their orientation by keeping their relative position relationship along with macroscopic crystal deformation.[1−5] The directions of anisotropic properties of single crystals, e.g. polarity[6−9] and magnetism,[10] are changed via mechanical twinning. Unique mechanical behaviors by mechanical twinning, e.g. ferroelasticity[8,11−23] and superelasticity (or elastic twinning or pseudoelasticity)[14,19,22,24−33]—diffusionless plastic deformation characterized by spontaneous strain and spontaneous shape recoverability, respectively—are also noteworthy. These characteristics make mechanical twinning fascinating in materials science, and reliable design guidelines are required for practical applications. Not only inorganic crystals[1−5,34] but also organic crystals show mechanical twinning[35−38] despite the general conception of the brittleness. From the viewpoint of symmetry, mechanical twinning in atomic crystals strongly correlates with packing symmetry,[39−41] while the structural symmetry of (super)molecules is also a critical factor in molecular crystals. For example, (super)molecules having (pseudo-)180° rotation symmetry can achieve 180° rotation symmetry of twinned domains only by small molecular movements such as orientation and conformation changes, referred to as pseudo-180° rotation, instead of true 180° molecular rotation in the crystalline state.[19,20,32] A charge-transfer (CT) interaction is a useful approach for construction of a supermolecule with such symmetry as described below.

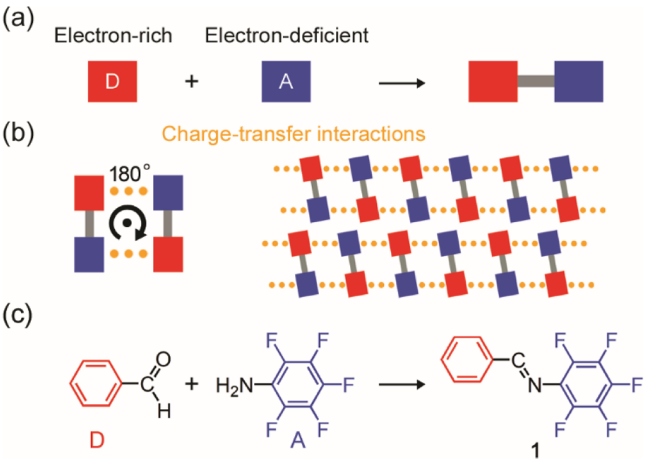


Figure 1. Schematic representation of (a) a molecule having an electron donor and acceptor moiety and (b) the representative molecular arrangement of a single-component CT complex. An electron-rich (donor, **D**) and electron-deficient groups (acceptor, **A**) are shown in red and blue, respectively. (c) Structural formula of **1**.

A CT interaction is an interaction between an electron-rich donor and electron-deficient acceptor (Figure 1a),[42] leading to formation of stable molecular assemblies[43,44] and functional

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materials.[45−49] Predictable assembly manners with specific molecular distance are applicable to chemical reactions[50,51] and crystal engineering.[52] Especially, a molecule having both donor and acceptor moieties tends to form antiparallel stacking (Figure 1b). A resulting single-component CT complex has (pseudo-)180° rotation symmetry, which is preferable in mechanical twinning.

Herein we demonstrate superelasticity in a chiral single crystal of an achiral donor−acceptor Schiff base, *N*-(2,3,4,5,6-pentafluorophenyl)-1-phenylmethanimine (**1**) (Figure 1c),[53,54] belonging to the Sohncke space group *P*1. The mechanism of superelasticity was investigated by force measurements and X-ray crystallographic studies.

EXPERIMENTAL SECTION

Preparation of a Single Crystal of Compound 1. Pentafluoroaniline and benzaldehyde were purchased from Tokyo Chemical Industry Co., Ltd. and used as received. Their condensation reaction in ethanol followed by evaporation of the solution afforded a powdered sample of **1**. Single crystals of **1** were prepared by recrystallization of the powder from chloroform or toluene by a slow evaporation method.

Force Measurements. Shear tests were carried out on a universal testing machine. A crystal fixed on a glass base was sheared by a glass jig attached to a load cell, and deformation behaviors were observed under a polarization microscope coupled with a digital camera.

Single-Crystal X-ray Structure Analysis. Single-crystal X-ray diffraction measurements of single and mechanically twinned crystals of **1** were performed at 303 K (30 °C) on a Bruker Smart APEX diffractometer equipped with a CMOS detector (Bruker Photon III C14) with a nitrogen-flow temperature controller using a rotating anode X-ray source (Mo Kα radiation (λ = 0.71073 Å)). Multiscan absorption corrections were applied using the SADABS program.[55] The structure was solved by intrinsic phasing methods (SHELXT)[56] and refined by full-matrix least-squares calculations on F^2 (SHELXL).[57] Non-hydrogen atoms were refined anisotropically; hydrogen atoms were fixed at calculated positions by a riding model approximation. Crystal face indexing was performed using SMART in a SHELXL Ver. 6.12 program package. Miller plane interplanar angles were measured using Mercury CSD 4.3.1.[58]

RESULTS AND DISCUSSION

Mechanical Characterization. Compound **1** is a kind of imine (or Schiff base) that has been known to be a thermo- and/or photochromic material[59,60] and a mechanically responsive material,[61,62] especially that synthesized from salicylaldehyde derivatives.[63−67] A powdered sample of **1** (melting point T_m = 125−126 °C)[68] was prepared by mixing pentafluoroaniline and benzaldehyde in a 1:1 molar ratio in ethanol at 60 °C and evaporating the solution. Platelet or columnar single crystals of **1** were afforded by slow evaporation of the toluene solution.

Superelasticity was confirmed in a crystal of **1** by shearing it under an optical microscope equipped with polarizing plates at room temperature (Figure 2a and Movie S1). Upon application of force, a **1** single crystal bent ca. 23° by converting its mother (α_M) domain into a daughter (α_D) domain. The deformed crystal reverted to its original shape upon removal of the stress by reconversion of the α_D domain into the α_M domain, indicating superelasticity. A stress-displacement curve of the deformation was recorded by force measurement for quantitative characterization of the superelasticity (Figure 2b−d). A crystal of **1** fixed on a base was sheared by a glass jig at the speed of 3 μm s^{-1} under polarized white (PW) light. A sudden drop of shear stress from σ = 1.40 MPa to 0.32 MPa was observed when an α_D domain was generated from an α_M domain. The α_D domain grew as the shear stress was increased. Spontaneous reverse deformation of the crystal, or contraction of the α_D domain, was observed upon unloading the stress. The crystal reverted to its initial shape and a typical superelastic hysteresis loop can be drawn (solid line in Figure 2b). The stress for forward (σ_f)/reverse (σ_r) deformation, energy storage density (E_s), energy storage efficiency (η), and superelastic index (χ) are 0.28 MPa/0.19 MPa, 72 kJ m^{-3}, 0.69, and 0.31, respectively, according to the stress-displacement curve. The deformation stress is relatively large among the reported organosuperelastic materials by mechanical twinning (Table S1).[19,28,30−33]

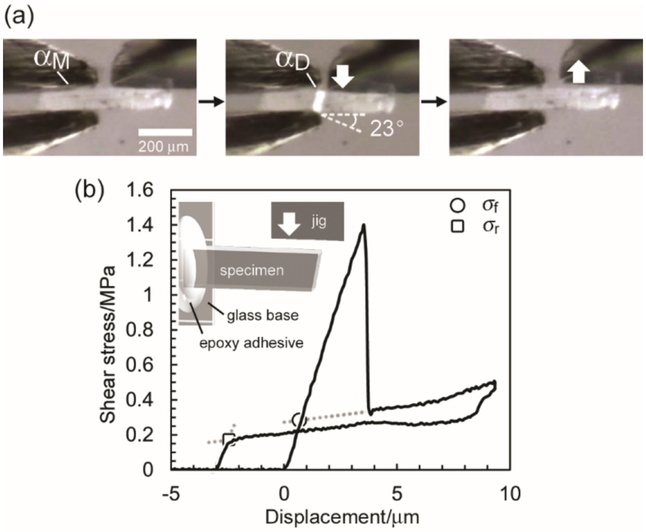

Figure 2. (a) Superelastic behavior of a single crystal of **1** induced by tweezers (Movie S1). (b) Stress-displacement curve of a single crystal of **1** (height 159 μm, thickness 195 μm) recorded at room temperature under polarized white (PW) light with a schematic representation of the experimental setup.

Crystallographic Studies. Crystallographic studies on a single and deformed crystal of **1** revealed a possible mechanism of the superelasticity (Figure 3). The structure of a crystal of **1** belongs to the Sohncke space group *P*1 even though molecule **1** is achiral, suggesting chiral crystallization, which is an important phenomenon from both fundamental[69−74] and practical viewpoints.[75−78] There are two crystallographically independent molecules, Z1 and Z2, and in both of them the pentafluorophenyl group twists ca. 47° due to steric repulsion between its fluorine atom at the *ortho* position and a hydrogen atom at the C═N moiety in the crystal structure (Figure 3a(i,ii)). The Z1 and Z2 molecules are assembled along the *b* axis by intermolecular CT interactions between their phenyl (donor) and pentafluorophenyl (acceptor) groups (Figure 3a(iii,iv)). Interestingly, crystal structures of **1** and a cocrystal of **1** and *N*-phenyl-2,3,4,5,6-pentafluorobenzenemethanimine are isomorphous and belong to the space group *P*1,[79] meaning that the crystal structure is dominated by the CT interaction. Namely, an effective formation of single-component CT complexes, which induces (supra)molecular distortion, can be one of the possible factors inducing chiral crystallization. In the deformed crystal of **1**, an α_D domain was generated from an α_M domain. The two domains are related by 180° rotation about the axis perpendicular to the interface $(010)\alpha_M \| (0\bar{1}0)\alpha_D$ (or $(010)\alpha_D \| (0\bar{1}0)\alpha_M$), by interconversion of Z1 and Z2

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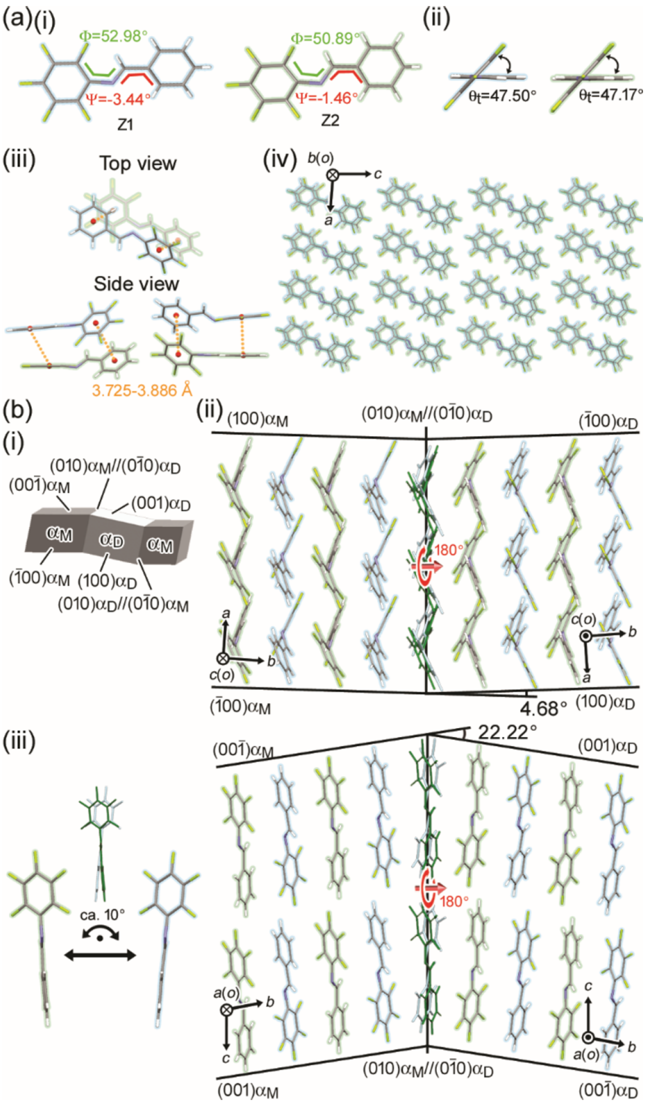

Figure 3. (a) (i) Torsion and (ii) twist angles in crystallographically independent molecules Z1 and Z2, (iii) a CT complex of Z1 and Z2 showing the distances between centroids of phenyl (donor) and pentafluorophenyl (acceptor) groups, and (iv) a packing diagram viewed along the *b* axis in a single crystal of **1**. (b) (i) Schematic representation of a mechanically twinned crystal of **1** with face indices, (ii) molecular correspondence at the interface of α_M and α_D domains, and (iii) molecular movement during the deformation estimated on the basis of X-ray diffraction measurements.

molecules via molecular conformation and orientation changes of ca. 2° and ca. 10°, respectively (Figure 3a(i),b). As a result, a crystal of **1** bends 22.22° along the *c* axis which is in good agreement with the bending angle of 23° measured under an optical microscope (Figure 2a). The relatively large deformation stress in superelasticity is most likely due to the relatively large bending angle and structural transition of the robust CT complex.

■ CONCLUSION

In conclusion, we reported superelasticity and chirality in a Schiff base crystal by exploiting CT interactions. X-ray crystallographic studies of the crystal revealed that the formation of a single-component CT complex led to twinning-based superelasticity and chiral crystallization by induction of pseudo-180° rotation symmetry and (supra)-molecular strain, respectively. The existence of crystallographically independent molecules is another factor for the ability of mechanical twinning by reducing molecular movement in twinning in the crystalline state.[18,19,32] Our results demonstrate the potential applicability of a CT interaction as a tool for supramolecular synthesis in crystal engineering to introduce mechanical properties, superelasticity in the present study, and chirality in addition to electrical and magnetic functions.[45−49]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.0c01350.

Detailed information about experimental procedures, mechanical characterization, and crystallographic studies (PDF)

Superelastic behavior of a crystal of **1** induced by tweezers at room temperature observed by an optical microscope equipped with polarizing plates (MOV)

Accession Codes

CCDC 1974112−1974114 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

T.S. designed the material, analyzed the experimental data, and prepared the manuscript. T.S. and S.S. carried out experiments. S.T. designed the project and edited the manuscript.

Notes

The authors declare no competing financial interest.

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