

Title: Structural, anisotropic thermal diffusivity, and waveguide analyses in a few kinds of organosuperelastic and organoferroelastic molecular crystals

INTRODUCTION

Recently, various mechanical deformations such as elastic, plastic, superelastic, ferroelastic, and shape memory effect have been reported in organic crystals, otherwise known to exist in metals and polymers.¹ These mechanical behaviors with the advantages of low cost, easy processing, biocompatibility, and environmental friendliness make organic crystals prospective candidates for next-generation structural materials. Among various deformation behaviors, superelastic and ferroelastic exhibit intriguing diffusionless, precise, and reversible shape recovery in response to external shear stress crystals thereby keeping intact crystalline structure. Despite the similarity, superelastic (SE) and ferroelastic (FE) deformation differ in the manner of shape recovery. In SE, unloading the stress can cause the spontaneous release of strain, but applying shear stress in the opposite direction is necessary for the FE deformation to return to its initial shape. The underlying mechanism behind SE and FE deformation has been reported to be martensitic or twinning.¹ In martensitic transformations, the crystal structure of the daughter domain and mother domain are of different phases, whereas in mechanical twinning the daughter domain and mother domain have the same crystal phase with different orientations. Organic crystals with SE/FE deformation are potential candidates for smart sensors, soft robotics, thermomechanical actuators, optoelectronics, energy storage, and photonic circuits.² So far, superelasticity and ferroelasticity in organic crystals, their underlying mechanism, and comparable mechanical attributes to that of metal alloys and polymers have been extensively investigated and reported in organic crystals with various structural diversity.³

Understanding intermolecular interaction in an organic crystal is crucial for designing and controlling its mechanical deformation. The structure-property relationship of soft flexible organic crystals has been investigated by many research groups and utilized for designing functional organic crystals. Ghosh and Reddy reported that the isotropic packing with weak and dispersive interactions such as C–H $\cdots\pi$ in the caffeine cocrystals was responsible for its elastic bending.¹ In another study, plastically flexible organic crystals were achieved by introducing active slip planes in the crystal structure via incorporating various supramolecular weak interactions such as van der Waals, $\pi\cdots\pi$, and hydrogen bonding groups.⁴ Desiraju and Saha reported that through manipulation of strong (H-bonds) and weak (halogen–halogen) interactions in the mutually orthogonal directions, two-dimensional elastic and Plastic deformation can be obtained in organic crystals.⁵ However, the interactions manifesting the SE/FE deformation, design principles, and incorporation of multifunctional properties have not been investigated yet. Thus, in this study, the role of

intermolecular interactions and structural synthons responsible for superelastic and ferroelastic deformation in organic crystals was systematically investigated through the screening of various existing organic crystals and synthesizing organic crystals using the design principles of crystal engineering. Furthermore, the applicability of these crystals as thermomechanical actuators, optical waveguides, and thermal management devices was evaluated. The individual studies conducted in this thesis are described in the next section.

Part 1

Structural and Thermal Diffusivity Analysis of an Organoferroelastic Crystal Showing Scissor-Like Two-Directional Deformation Induced by Uniaxial Compression

Abstract – There is a rising demand for fully flexible wearable optoelectronics. The anisotropic interactions present in organic crystals constrain mechanical deformation to a specific direction, unlike the isotropic interactions found in metals and polymers, which allow for dimensionless flexibility. To address this, direction-independent deformation in organic crystals is actively investigated. In this study, the first example of a two-directional ferroelastic deformation in single crystals of *trans*-3-hexenedioic acid (THDA) by the application of uniaxial compression stress was demonstrated. The mechanical deformation, underlying mechanism, and thermal diffusivity were analyzed by force measurement techniques, single crystal X-ray diffraction (SXRD), and typical microscale temperature-wave analysis.

Result and discussion - Block-shaped crystals of THDA (Fig. 1a) were obtained by slow evaporation of it from a methanolic solvent. In mechanical deformation testing, upon application of compressive stress on (010) face of THDA single crystal, a two-directional ferroelastic deformation with a unique scissor-like deformation was observed (Fig. 1b). SXRD analyses of bent crystal of THDA revealed that the deformation is due to mechanical twinning. Along compressional direction, intermolecular sheets interacted via two evenly balanced and weak C–H···O interactions in a side-to-end manner, which was responsible for the two-directional deformation (Fig. 1c). Furthermore, the measured thermal diffusivities were found highly anisotropic and were 1.39 , 1.31 , and $4.68 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ along the *a*, *b*, and *c* axis, respectively (Fig. 1d). The molecules are strongly interacted by electrostatically dominated O–H···O hydrogen bonds with total aggregate interaction energy of $-69.1 \text{ kJ mol}^{-1}$ along the *c* axis, whereas dispersion dominated C–H···O interactions along the *a/b* axis with total aggregate interaction energy -12.8 and $-11.2 \text{ kJ mol}^{-1}$. The strong and weak interaction with its intermolecular distance could be correlated with the different thermal diffusivity values.

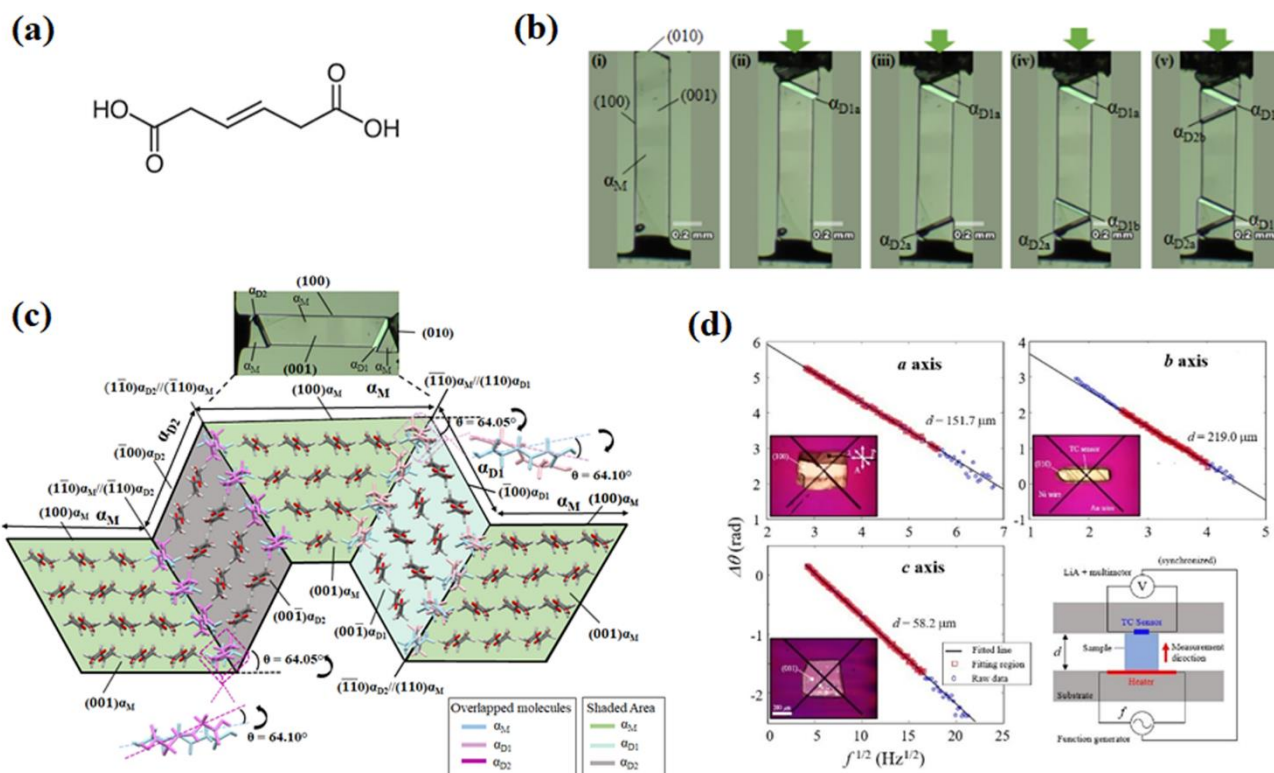


Figure 1. (a) Molecular structure of *trans*-3-hexanedioic acid, (b) Snapshots of deformed crystal upon application of compression test on the crystal face (010/010), (c) Estimated connecting manners of the parent (α_M) and daughter domains (α_{D1} and α_{D2}), and (d) Frequency dependence of the phase delay measured for along *a*, *b*, and *c* axis by microscale temperature-wave analysis method.

Conclusions – The influence of two crystallography graphically equivalent faces and arrangement of weak C–H···O interactions in a side-to-end manner in manifesting two-directional ferroelastic deformation was demonstrated. A correlation between the anisotropic thermal diffusivity and structural anisotropy was established, highlighting the application as a switchable thermal management device.

Part 2

Thermo-mechanical reversibility in a shape memory organic salt

Abstract – In this study, a supramolecular organic salt comprised of Dodecafluorosuberlic acid (DFSA) and 1,2-bis(4-pyridyl) ethane (BPE) was synthesized. The DFSA was selected to introduce weak dispersive interactions involving fluorine in the crystal structure. The synthesized crystals demonstrated a two-directional superelastic deformation coupled with the shape memory effect in response to stress and heat. The dual responsive deformation behavior of the crystal was exhaustively analyzed by force measurement technique and mechanistic elucidation by temperature-controlled SXRD and ^{13}C solid-state NMR.

Result and discussion- The organic salt crystals were obtained by dissolving an equimolar amount of the DFSA and BPE in hot methanol (Fig. 2a). The temperature-dependent stress-strain curves indicated that the crystals demonstrated a two-directional stress-induced phase transformation in both increasing and decreasing temperature conditions, unlike general shape memory alloys which exhibit one-directional stress-induced phase transition (Fig. 2b). The temperature-controlled single-crystal XRD analyses revealed the changes in unit cell parameters caused by the different crystal packing accompanied by the conformational changes of acid and bipyridine moieties, indicating the transformation from α to martensitic β form (Fig. 2c). The different conformation changes were facilitated by conformational, and rotational modifications of the flexible phenyl and long-chain acidic carbons. The variable temperature ^{13}C solid-state NMR spectra showed the phase transition from α to β form was facilitated by the conformation conversion of the bipyridine rings (Fig. 2d).

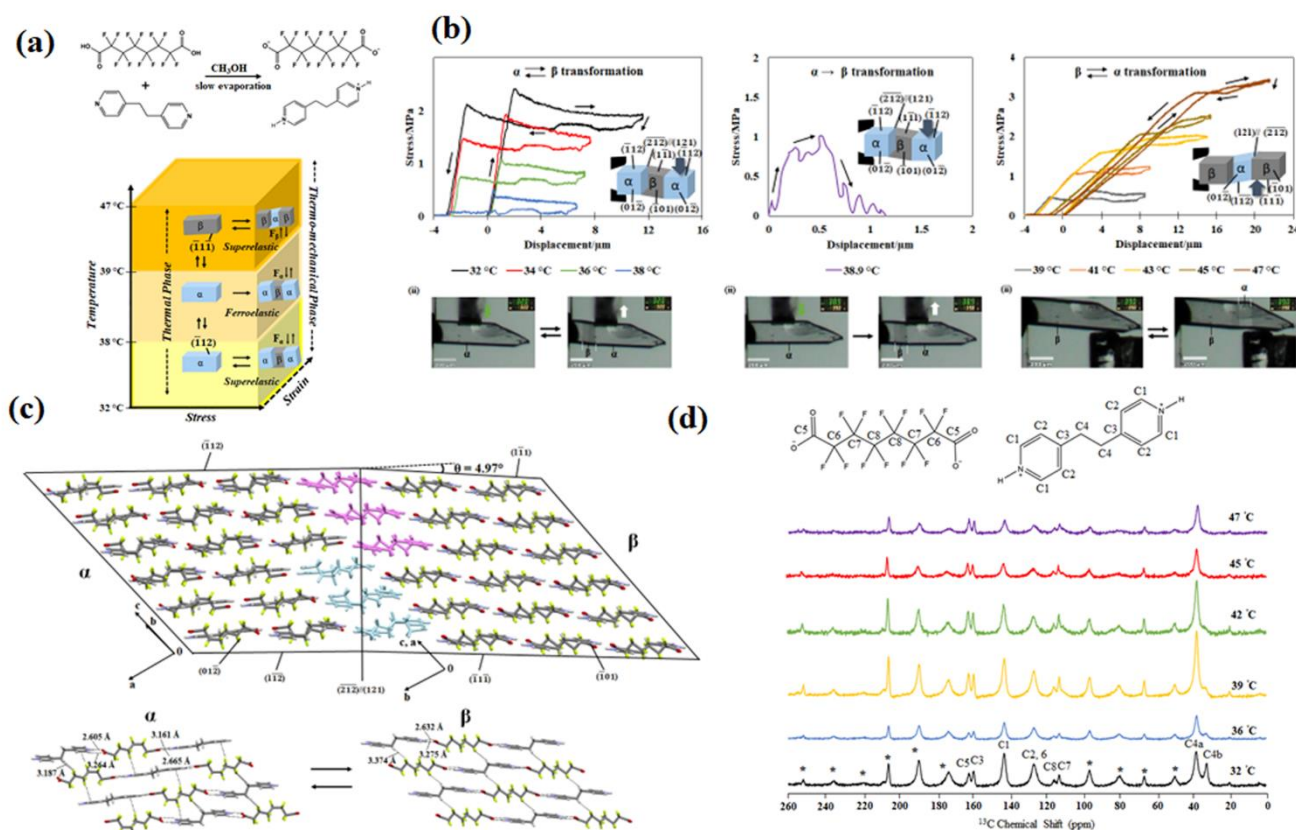


Figure 2. (a) Molecular structures and synthesis of organic salt and phase diagram for indicating the relationships between thermal and thermo-mechanical transition, (b) Stress–displacement curves of two-directional stress-induced transition, (c) Estimated connecting manners of an α domain and β domain, and (d) ^{13}C CP/MAS NMR spectrum of crystal measured at 7 kHz from 32 °C to 47 °C. Asterisks denote the spinning sidebands.

Conclusions – The shape memory effect of the crystal was facilitated by thermal superelastic-ferroelastic interconversion. In the crystal packings, the conformational changes of the bipyridine

moiety facilitate the martensitic phase transformation, where forward stress for superelastic deformation increased with the presence of halogen interactions ($C-H\cdots F$ and $C-F\cdots\pi$), highlighting the importance of weak dispersive interaction.

Part 3

A role of intermolecular interaction modulating thermal diffusivity in organosuperelastic and organoferroelastic cocrystals

Abstract- In this study, the mechanical deformation in two cocrystals of 1,4-diiidotetrafluorobenzene with 1,2-bis(4-pyridyl)ethane (**1**) and pyrene (**2**) was investigated (Fig. 3a). The parent compound and cofomers were chosen to introduce distinct weak interactions such as halogen bond, $C-H\cdots F$, and $\pi\cdots\pi$ interactions in the crystal structure and check their influence in varying the deformation behavior.

Result and discussion- The two cocrystals **1** and **2** exhibited different mechanical deformations, superelasticity, and ferroelasticity, respectively (Fig. 3b). The single crystal of cocrystal **1** crystallized in a triclinic crystal system with space group $P\bar{1}$ formed via $C-I\cdots N$ halogen bond, $C-H\cdots F$ weak hydrogen bond, and the $\pi\cdots\pi$ stacking interactions, whereas the single crystals of **2** in a monoclinic crystal system with space group $P2_1/c$ formed via intermolecular interactions, halogen bonding ($C-I\cdots I-C$, $C-I\cdots\pi$), weak hydrogen bonding $C-H\cdots F$ and $\pi\cdots\pi$ stacking. Mechanical twinning manifested both superelastic and ferroelastic deformations, however, in each complex, the deformation produced a different bending angle and dissipated energy (Fig. 3c, d). From the energy framework analysis, it was found that $C-I\cdots N$ halogen interaction in cocrystal **1** is a strong, electrostatically dominant interaction with energy of -21.1 kJ/mol that holds the structure together with weak $C-H\cdots F$ interactions. In contrast, weak electrostatic $C-I/C-I$ interactions were found to be accompanied by the presence of the dispersion-dominated $C-H\cdots F$ and $\pi\cdots\pi$ interactions, which have a -8.6 kJ/mol energy along the ac plane in cocrystal **2**. These significant distinct interactions such as $C-I\cdots N$, $C-I$, and $C-H\cdots F$ in cocrystal **1**, lead to superelastic transformation rather than ferroelastic deformation (Fig. 4b). Furthermore, anisotropic thermal diffusivity tests were conducted. The superelastic cocrystal exhibited higher thermal diffusivity than the ferroelastic cocrystal, due to the symmetrical and relatively robust intermolecular interactions (Fig. 4a, b).

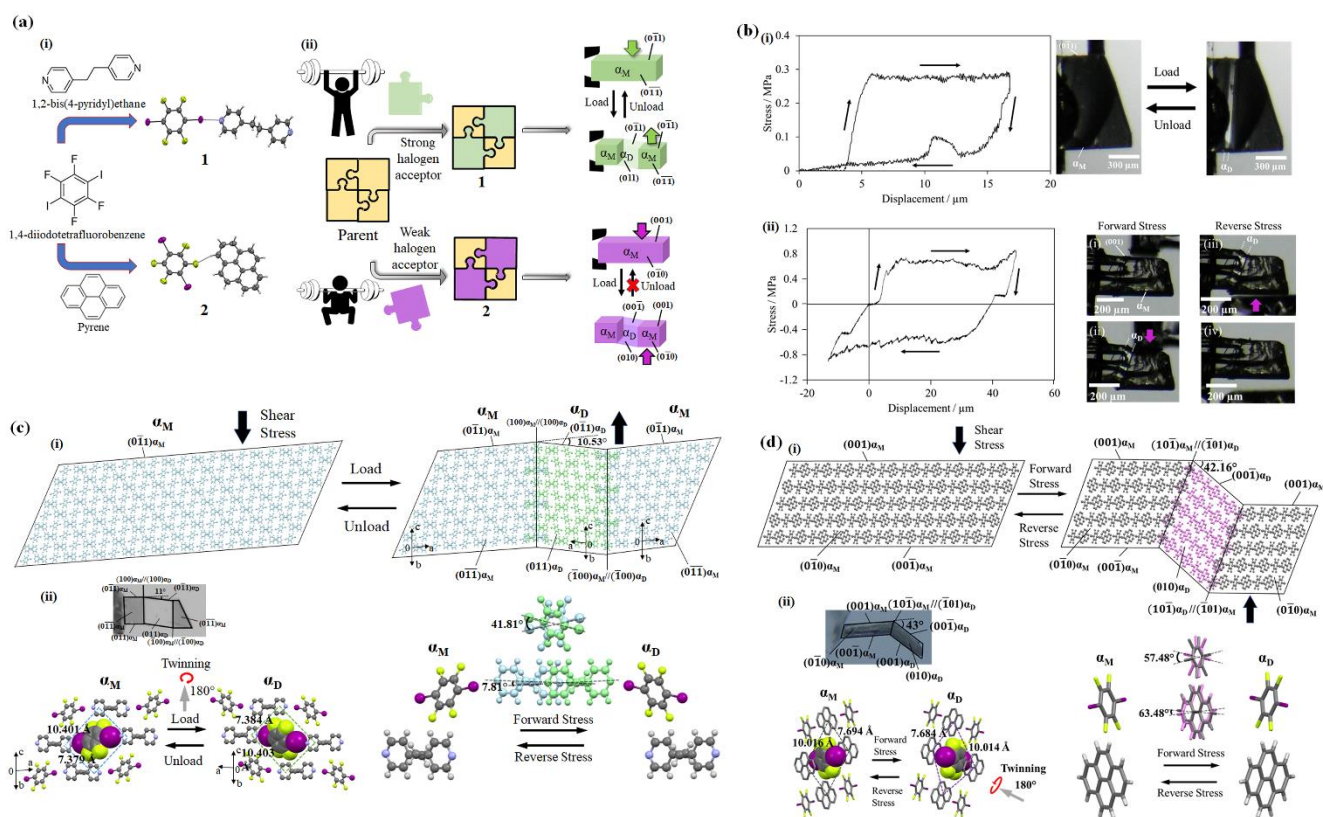


Figure 3. (a) Molecular structures and formation of cocrystals **1** and **2** with illustration of the difference in the mechanical deformation of interest, (b) Stress-strain test with its snapshots of (i) cocrystals **1** and (ii) **2**, (c-d) Estimated connecting manners of the α_M domain and α_D domain of cocrystal **1** and **2** with molecular movements, respectively.

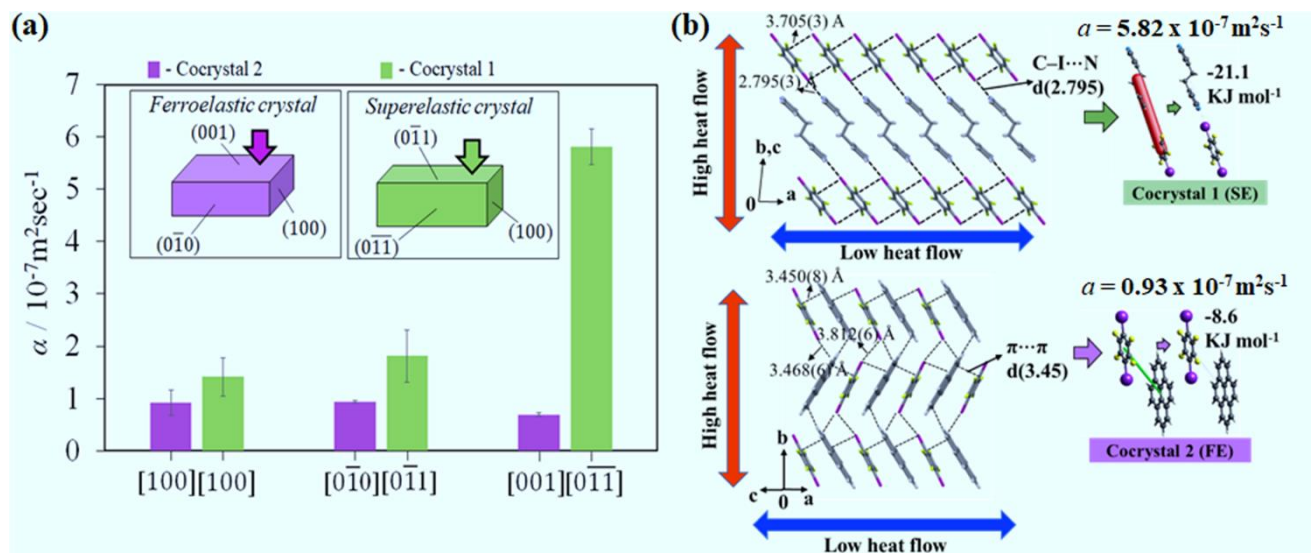


Figure 4. (a) The obtained thermal diffusivity values of cocrystals **1** (light green colored) and **2** (purple colored) and (b) Crystal packing with the 3D topology of energy frameworks of cocrystal **1** (i) and **2**.

Conclusions - The difference in the deformation behavior was due to the distinct combination of strong halogen bonds such as C–I···N, C–I···I–C and weak interactions such as C–H···F and $\pi\cdots\pi$ interactions in the crystal structure of each cocrystal, highlighting the interplay of strong and weak inter-molecular interactions in the organosuperelastic and organoferroelastic deformation behavior. Additionally, higher thermal diffusivity was found along symmetrical and robust intermolecular interacting superelastic crystals. This relationship will help in designing crystals for desired thermal management purposes.

Part 4

A reversible and spatially controllable optical waveguiding through stair-case like deformed ferroelastic organic crystals

Abstract – Based on the insights from the above studies, three isostructural Schiff bases comprising of 6-bromo-2-hydroxy-3-methoxybenzaldehyde with the following respective anilines (4-fluoroaniline, 4-chloroaniline, and 4-bromoaniline) were synthesized (Fig. 5a). In the design, two halogen atoms were placed in an orthogonal direction in the structure to obtain a bi-directional ferroelastic deformation. The crystals exhibited versatile two-directional ferroelastic deformation and photoluminescent properties. These properties were then utilized to construct robust photonic waveguides such as reversible Z-shaped photonic structures, closed-loop networks, and staircase-like hybrid waveguides.

Result and discussion- The ferroelastic nature of the three isomorphous crystals **1-X (F, Cl, and Br)** were confirmed by the hysteresis loop in the respective stress-displacement curve (Fig. 5d-f). Single crystal X-ray diffraction, Xpac, and unit cell similarity index revealed that all crystals are isomorphous to each other. All crystals exhibited photoluminescence under UV light. The deformation was due to mechanical twinning (Fig. 5g-h). The reversible and diffusionless nature of ferroelastic deformation enabled the construction of optical waveguides with sharp bends and minimum optical loss (Fig. 6a, b). Furthermore, the bi-directional nature of ferroelastic crystals was utilized to make reconfigurable sharply bent photonic waveguides and closed-loop geometries which showed enhanced signal control and intensity (Fig. 6c). Furthermore, integrating three chemically distinct ferroelastic crystals resulted in a novel staircase-like hybrid photonic waveguide, proving efficient light-squeezing capability (Fig. 6d).

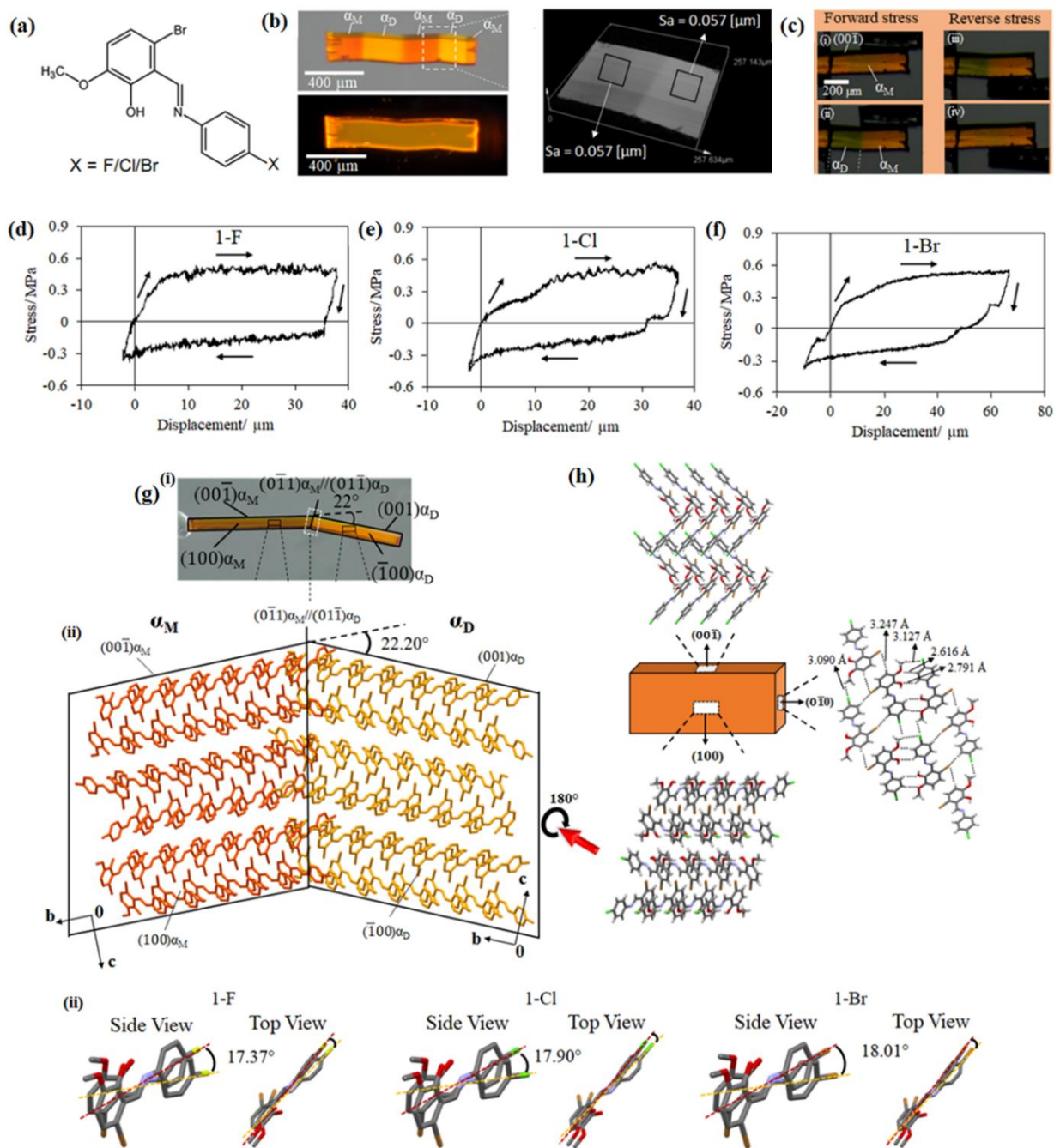


Figure 5. (a) Molecular structures of **1-X** (**F**, **Cl**, and **Br**). (b) Ferroelastically deformed crystal of **1-Cl** under polarized white light, and UV light, respectively with surface roughness of mother and daughter domain of ferroelastically deformed crystal of **1-Cl**, (d-f) Stress-displacement curves of a single crystal of **1-F**, **1-Cl**, and **1-Br**, respectively. (g-h) Estimated connecting manners of an α_M domain and α_D domain of **1-Cl** with molecular movements.

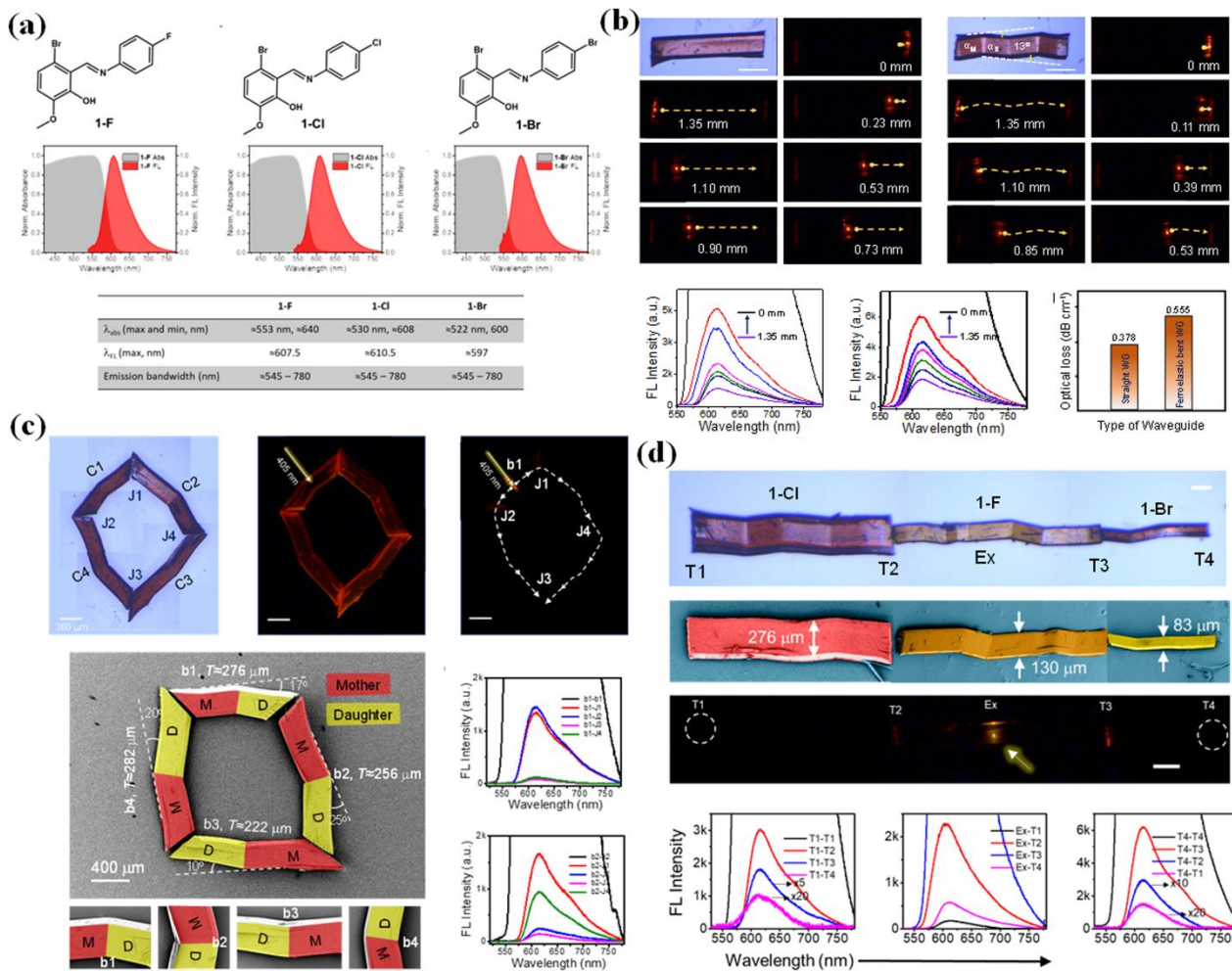


Figure 6. (a) Molecular structures of **1-X** with solid-state optical characteristics, (b) Optical waveguiding characteristics of straight and ferroelastic bent 1-Cl crystal waveguide (WG), (c) Photonic aspects of the fabricated closed-loop structure from bent 1-Cl crystal WGs, and (d) light squeezing in a hybrid photonic circuit test.

Conclusions- In this study, the criteria of intermolecular interaction leading to bi-directional deformation was proved. Furthermore, the potentiality of bidirectional ferroelastic organic crystals as flexible optical waveguides was demonstrated for the first time.

Overall conclusion and future implications of this study

The research works in this thesis investigated the structural role such as intermolecular interactions and their arrangement behind superelastic and ferroelastic deformation in organic crystals and the potentiality of these crystals as optical waveguides and thermal management devices. For the investigation, the crystal engineering design approach was utilized to introduce specific weak intermolecular interactions such as C-H \cdots π , C-H \cdots F, C-H \cdots O, $\pi\cdots\pi$, halogen-halogen in the preparation of multicomponent solids such as cocrystals, salts, and single component solids i.e., three

isomorphous Schiff bases. A correlation was established between the influence of these weak interactions and strong H-bonds in the crystal structure with resulting deformation behaviors such as shape memory effect, superelasticity, or ferroelasticity. Specifically, comparatively strong, and directional interactions such as C–I \cdots N, C–I, and C–H \cdots F resulted in superelastic deformation. In contrast, dispersion-dominated weak interactions such as C–H \cdots F and $\pi\cdots\pi$ interactions resulted in ferroelastic deformation. Furthermore, these weak intermolecular interactions also contributed to enhancing the material attributes such as forward/coercive stress, and elastic modulus of crystals with superelastic/ferroelastic properties. The presence of weak interactions C–H \cdots O in the orthogonal plane leading to unprecedented scissor like two-directional ferroelastic deformation was also established. Based on these insight, the isomorphous Schiff bases were designed such that two halogen atoms were placed in an orthogonal direction in the structure resulting in versatile bi-directional ferroelastic cocrystals. In addition, the photoluminescent and optical waveguiding properties were introduced by electron density via $\pi\cdots\pi$ interaction. Thus, the established structure-property relationship will aid in the designing of superelastic and ferroelastic crystals with desirable and controllable mechanical properties. The stimuli-responsive behavior, anisotropic thermal diffusivity analysis of these crystals, and flexible optical waveguide construction indicate the practical utility of these crystals as next-generation thermomechanical actuators, thermal management devices, and optical waveguides.

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