Supporting Information for:

Luminescent Möbius Strip of a Flexible Halogen-Bonded Cocrystal Evolved from Ring and Helix

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Author Contributions:

Y.C. and B.J. contributed equally to this work. Y.C. conceptualized the project, directed the study, determined the experimental methods, wrote the manuscript, and drew all the figures. Y.C., B.J. and Z.C. prepared the samples, performed most of the experiments and characterization. Y.C. and B.J. analyzed and discussed the results, and organized the supporting information together. J.G. acquired funding for the whole study. All authors commented on the manuscript.

Supplement Files Involve:

- A PDF File (Supplementary text with experimental information, figures and tables)
- Movies
  - Movie about the flexibility of one single crystal of the halogen-bonded cocrystal (Movie_S1.mp4)
  - Movie about the elastic bending of one plastic twisted halogen-bonded cocrystal (Movie_S2.mp4)
- Crystallographic Data
  - Single crystal structure of single-component crystal EPIMP, CCDC 2071219 (Cif_S1.cif)
  - Single crystal structure of halogen-bonded cocrystal EPIMP-TFTIB, CCDC 2071222 (Cif_S2.cif)

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All reagents were commercially available and used as received without further purification. 5-ethoxypyridin-2-amine (98%) was purchased from Shanghai Bide Pharmatech Ltd.. Salicylaldehyde (99.5%), 1,3,5-trifluoro-2,4,6-triiodobenzene (TFTIB, 98%), dichloromethane (99.5%) and hexane (99.5%) were purchased from Meryer (Shanghai) Chemical Technology Co., Ltd.. Ethanol (water content<0.15%) was purchased from Tianjin Kangkede Technology Company. M-xylene (99%) and p-xylene (99%) were purchased from Aladdin. Isopropanol (99.5%), benzene (99.5%) and toluene (99.5%) were purchased from Tianjin Damao Chemical Reagent Factory. Acetonitrile (MeCN, 99.5%), acetone (99.5%) and methanol (99.5%) were purchased from Tianjin Kemiou Chemical Reagent Company. All water used in our experiments is distilled water.

The X-ray powder diffraction data were collected using a Rigaku D/max 2500. The X-ray single crystal diffraction data was collected on Rigaku FRX rotating anode single-crystal X-ray diffractometer. The absorption spectra of the crystals were measured on UV-2700 spectrophotometer (Shimadzu Instruments). The luminescence spectra, lifetime and absolute quantum yield of the crystals were measured using a FLS 1000 (Edinburgh Instruments) configured with an integrated sphere. Three different scanning electron microscopes (SEM), including FEI Apreo S LoVac, FEI Nanosem 430 and Hitachi TM 4000 PLUS tabletop microscope, were used to characterize the morphology of the crystals. The transmission electron microscope (TEM) images and corresponding selected area electron diffraction (SAED) patterns were collected by FEI TecnaiG2 F20S-Twin. In the process of product characterization, the proton nuclear magnetic resonance (1H-NMR) spectroscopy was collected on Bruker Avance III (600MHz). The high-resolution mass spectrum (HRMS) was collected on Thermo Scientific Q Exactive. Two optical microscopes were used. The stereoscopic microscope (Nikon SMZ745T) was used to record micrographs of the centimeter-scale crystals. The polarizing optical microscope (Nikon ECLIPSECi-E) with a reflection model was used to observe and record the micrometer-scale crystals. A 365 nm monochromatic ultraviolet light point light source from an HTLD-4 II UVLED (Shenzhen Zhijun Optoelectronic Technology Corporation, Φ=10 mm, DC 12-32 V) was used when taking the photos of luminescent crystals in dark field. In the process of materials preparation, the constant temperature was kept by a temperature control system (JULABO, CF41). The drying process was carried out in the vacuum drying oven (Taisite, DZ-2BC II).
1. Synthesis of (E)-2-(((5-ethoxypyridin-2-yl)imino)methyl)phenol (EPIMP): 5-ethoxypyridin-2-amine (3.00 g, 21.7 mmol) and salicylaldehyde (3.98 g, 32.6 mmol) were added into 20 mL ethanol in a 50 mL reaction bottle and the resulting mixture was refluxed with stirring for 4 h. After cooling to room temperature, the solid product was obtained by filtering, and further recrystallizing in ethanol to afford 4.45 g (18.4 mmol, yield: 84.79%) product as yellow powders. \[^1\text{H}-\text{NMR}\] (600 MHz, CD\(_2\)Cl\(_2\), ppm, Figure S2): \(\delta = 13.36\) (s, 1H, -OH), 9.30 (s, 1H, -CH=N-), 8.08 (dd, 1H, \(J=2.2, 1.4\) Hz, ArH), 7.42 (dd, 1H, \(J=7.6, 1.7\) Hz, ArH), 7.30 (ddd, 1H, \(J=8.3, 7.2, 1.7\) Hz, ArH), 7.24-7.18 (m, 2H, ArH), 6.92-6.84 (m, 2H, ArH), 4.03 (q, 2H, \(J=7.0\) Hz, -OCH\(_2\)H), 1.36 (t, 3H, \(J=7.0\) Hz, -CH\(_3\)). \[^{HRMS}\] (ESI, Figure S3): Calcd for C\(_{14}\)H\(_{14}\)N\(_2\)O\(_2\) [M]: 242.11, found: 243.11 (M+H\(^+\)).

Figure S1. The synthetic procedure of EPIMP.

Figure S2. \[^1\text{H}-\text{NMR}\] spectrum of EPIMP in CD\(_2\)Cl\(_2\).
2. **Preparation of the centimeter-scale EPIMP single crystals:** EPIMP (48.5 mg, 0.2 mmol) was dissolved well in 10 mL ethanol at room temperature. After solvent evaporation for 1-2 days, yellow needle-like centimeter-scale EPIMP crystals were obtained.

3. **Preparation of the centimeter-scale EPIMP-TFTIB halogen-bonded cocrystals:** EPIMP (97 mg, 0.4 mmol) and TFTIB (204 mg, 0.4 mmol) were dissolved well in 2 mL dichloromethane at the bottom of a test tube. Then we carefully layered 6 mL hexane on the top of the above-mentioned dichloromethane solution. The test tube was sealed. After solvent diffusion for 3-5 days, the yellow needle-like centimeter-scale EPIMP-TFTIB halogen-bonded cocrystals was obtained and further determined by powder X-ray diffraction characterization.

4. **Preparation of the micrometer-scale EPIMP-TFTIB halogen-bonded cocrystals:** The temperature of the whole experiment was precisely controlled by temperature control system (JULABO, CF41). The detailed preparation procedure of different microstructures is as follows.

4.1 **Preparation of the helixes:** EPIMP (5 mg, 0.021 mmol) and TFTIB (10.5 mg, 0.021 mmol) were dissolved well in 10 mL MeCN in a glass bottle with cover and ultrasound at 298 K for 5 min to form a solution with a concentration $C_{initial}$ (2.1 mmol·L⁻¹). The culture dish with cleaned glass slides (area: 2 cm×2 cm) inside was covered and placed in the water bath at a $T_{constant}$ of 298 K for 1 h. Then, 5 mL solution was transferred to the prepared culture dishes with a $T_{constant}$ of 298 K and kept the solvent evaporating slowly. After completely evaporation, the products appeared on the substrates and were dried in the drying oven at 313 K for 3 h.
**Notes:** 1) The helix crystals are observed in a wide \( C_{\text{initial}} \) range from 1 mmol·L\(^{-1}\) to 8.2 mmol·L\(^{-1}\). 2) The superhelix crystals could appear in all the above concentrations. With the increase in \( C_{\text{initial}} \), there is a growing trend towards superhelix, and the number of the strands of helixes in the superhelix expands, too.

### 4.2 Preparation of the helixes with controllable pitch

The process was similar to that mentioned in 4.1 section, but with a variable \( T_{\text{constant}} \) of 298 K, 303 K, 308 K, 313 K. The temperature of each experiment was precisely controlled by temperature control system (JULABO, CF41).

**Notes:** The pitch value of each helix in the statistical data was an average value, calculated by dividing the total length by the number of twists.

### 4.3 Preparation of the self-bending crystals

EPIMP (10 mg, 0.041 mmol) and TFTIB (21 mg, 0.041 mmol) were dissolved well in 10 mL toluene in a glass bottle with cover and ultrasound at 298 K for 5 min to form a solution with a concentration \( C_{\text{initial}} \) (4.1 mmol·L\(^{-1}\)). The culture dish with cleaned glass slides (area: 2 cm×2 cm) inside was covered and placed in the water bath at a \( T_{\text{constant}} \) of 293 K for 1 h. Then, 5 mL solution was transferred to the prepared culture dishes with a \( T_{\text{constant}} \) of 293 K and kept the solvent evaporating slowly. After completely evaporation, the products appeared on the substrates and were dried in the drying oven at 313 K for 3 h.

**Notes:** 1) The self-bending crystals could be prepared in a wide \( C_{\text{initial}} \) range from 0.21 mmol·L\(^{-1}\) to 4.1 mmol·L\(^{-1}\). 2) The rings could be found randomly when we observed the glass slides of self-bending crystals.

### 4.4 Preparation of the spiral lines

EPIMP (0.5 mg, 0.0021 mmol) and TFTIB (1.05 mg, 0.0021 mmol) were dissolved well in 10 mL toluene in a glass bottle with cover and ultrasound at 298 K for 5 min to form a solution with a concentration \( C_{\text{initial}} \) (0.21 mmol·L\(^{-1}\)). The culture dish with cleaned glass slides (area: 2 cm×2 cm) inside was covered and placed in the water bath at a \( T_{\text{constant}} \) of 293 K for 1 h. Then, 5 mL solution was transferred to the prepared culture dishes with a \( T_{\text{constant}} \) of 293 K and kept the solvent evaporating slowly. After completely evaporation, the products appeared on the substrates and were dried in the drying oven at 313 K for 3 h.

### 4.5 Preparation of the spiral lines with controllable \( b \) and \( \theta \)

The process was similar to that mentioned in 4.4 section, but with a variable \( T_{\text{constant}} \) of 293 K, 303 K, 313 K. The temperature of each experiment was precisely controlled by temperature control system (JULABO, CF41).

The fitting of the abstract curves of the spiral-like crystals could be achieved by the modified Archimedes spiral equation in polar coordinates systems,

\[
r = a + b \cdot \frac{2\pi \theta}{360}
\]

(Equation S1)

where \( a \) and \( b \) are constants that \( a \) affects the origin of the coordinate and \( b \) determines the distance between two adjacent rounds, \( r \) is the radial distance and \( \theta \) is the polar angle (Figure S4).
Notes: 1) The growth direction of spiral-like crystals is from outside to inside according to our experimental phenomena. 2) For spiral-like crystals, we wanted to adopt an appropriate mathematical model to describe and perform statistical analysis. Three models, including the Archimedes spiral equation, hyperbolic spiral equation and logarithmic spiral equation, are used to fit the spiral-like crystals, showing that the Archimedes spiral equation has the best goodness of fit. 3) We converted the unit of parameter \( \theta \) from mathematically used radians to degrees and directly reflected it in the formula for a more straightforward expression. 4) There will be subjective influence on the numerical value of a because the polar coordinates systems were drawn artificially.

4.6 Preparation of the Möbius strips: EPIMP (10 mg, 0.041 mmol) and TFTIB (21 mg, 0.041 mmol) were dissolved well in 10 mL mixed solvent (toluene/MeCN=1:1, volume ratio) in a glass bottle with cover and ultrasound at 298 K for 5 min to form a solution with a \( C_{\text{initial}} \) of 4.1 mmol·L\(^{-1}\). The culture dish with cleaned glass slides (area: 2 cm×2 cm) inside was covered and placed in the water bath at a \( T_{\text{constant}} \) of 313 K for 1 h. Then, 5 mL solution was transferred to the prepared culture dishes with a \( T_{\text{constant}} \) of 313 K and kept the solvent evaporating slowly. After completely evaporation, the products appeared on the substrates and were dried in the drying oven at 313 K for 3 h.

Notes: 1) Most prepared samples are bent helixes. A few Möbius and non-Möbius paradromic strips have been noticed. 2) There is a chance to find Möbius strips in a wide \( T_{\text{initial}} \) range from 293 K to 313 K.
4.7 **Sample preparation for SEM characterization:** The sample preparation method was similar to that of the helix and bent crystals above-mentioned in 4.1 and 4.3 section, but used cleaned Si/SiO$_2$ wafers (Hefei Kejing Material Technology Company, p-doped, SiO$_2$ 300 nm thick, 10 nF·cm$^{-2}$, area 2 cm×2 cm) instead of glass slides. And then Si/SiO$_2$ wafers with the prepared samples were placed on the sample stage using conductive tape and coated with gold for enhancing conductivity. SEM analysis was carried out with FEI Nanosem 430 with an operating voltage of 15 kV and FEI Apreo S LoVac with an operating voltage of 2-5 kV at room temperature. Si/SiO$_2$ wafers were separately ultrasound in the acetone, ethanol, isopropanol, and water for 15 min and blown with nitrogen, and dried in the drying oven at 343 K for 3 h before use.

*Notes:* The as-prepared products on the glass slides could be observed directly in the low vacuum mode of the tabletop Microscope Hitachi TM 4000 PLUS with an operating voltage of 10 kV at room temperature.

4.8 **Sample preparation for TEM characterization:** A drop of MeCN solution of EPIMP and TFTIB for the helixes, or toluene solution for the bent crystals was carefully dropped on a duplex carbon film (Beijing Zhongxingbairui Technology Company, 200+200 mesh) several times and then it was dried in the drying oven at 313 K. Some products appeared on the duplex carbon film.

*Notes:* It is not easy to acquire SAED patterns of micrometer-scale organic crystals because they are easily damaged by high-energy electron beam bombardment. We tried our best to adopt a variety of sample preparation methods and test conditions to do that. Some issues are will need attentions, as follows: 1) Because the prepared helixes are so easy to drift after being bombarded by an electron beam, a duplex carbon film is used to fix the prepared products to avoid movement as much as possible. 2) Using low-voltage TEM with an operating voltage less than 80 kV to prevent damage to the sample as much as possible. 3) The SAED patterns were collected firstly and then the morphologies because of the instability of organic under the radiation of the high-energy electron beam. Although all the above issues have been carefully noticed, the rate of success of obtaining the SAED patterns of the micrometer-scale crystals is still very low.

4.9 **Sample preparation for powder X-ray diffraction characterization:** The sample preparation method was similar to that of the helix and bent crystals above-mentioned in 4.1 and 4.3 section, but used cleaned tailor-made powder X-ray diffraction sample stages (size: 35 mm×50 mm×2 mm, without groove) instead of glass slides. And then tailor-made powder X-ray diffraction sample stages with the as-prepared samples were directly used for data collection.

4.10 **Three-point bending test of centimeter-scale EPIMP-TFTIB halogen-bonded cocrystals:** The flexibility of the crystals, including elastic bending and plastic twisting, was characterized by tweezers and man hands and recorded by the stereoscopic microscope equipped with a LED white light source and a 365 nm monochromatic ultraviolet light point light source from an HTLD-4 II UVLED (Shenzhen Zhijun Optoelectronic Technology Corporation, $\Phi$=10 mm, DC 12-32 V), as shown in Figure S5.
Figure S5. Photographs of the experimental observation system for record the mechanical behavior of EPIMP-TFTIB halogen-bonded cocrystals under the bright field (LED white light on, top) and the dark field (365nm UV light on, LED white light off, bottom).

Notes: 1) Because the UV light source is unable to be embedded in the stereoscopic microscope, the microphotographs under the dark field were captured by an external excitation of 365 nm UV light, and thus inevitably resulted in incomplete black background. 2) Newly prepared samples are better for the mechanical characterizations of bending and twisting. 3) As widely known, thinner crystals are easy to bent when an external force is applied, and slender crystals are easy to twist.
**Crystal Morphology Calculation**

The simulated morphology with Miller index of the EPIMP-TFTIB halogen-bonded cocrystal was calculated using BFDH model in Mercury based on the single crystal structure (CCDC 2071222).

**Figure S6.** Morphology simulation with crystal planes marked.
**Fluorescence Lifetime Measurement**

**Figure S7.** Luminescence lifetime measurement of EPIMP single crystals (at 557 nm, 2.06 ns), calculated from two lifetimes which are 1.96 ns with 95.5% donation and 4.26 ns with 4.5% donation) under an excitation wavelength of 387 nm.

**Figure S8.** Luminescence lifetime measurement of EPIMP-TFTIB halogen-bonded cocrystal (at 562 nm, 2.53 ns), calculated from two lifetimes which are 2.37 ns with 94% donation and 5.04 ns with 6% donation) under an excitation wavelength of 392 nm.
X-Ray Diffraction Patterns

Figure S9. Simulated crystallographic diffraction pattern of EPIMP-TFTIB halogen-bonded cocrystal (simulated from single crystal structure, CCDC 2071222) and X-ray diffraction pattern of the prepared micrometer-scale EPIMP-TFTIB halogen-bonded cocrystal with helix morphology.

Figure S10. Simulated crystallographic diffraction pattern of EPIMP-TFTIB halogen-bonded cocrystal (simulated from single crystal structure, CCDC 2071222) and X-ray diffraction pattern of the prepared micrometer-scale EPIMP-TFTIB halogen-bonded cocrystal with bent morphology.

Notes: The X-Ray diffraction results confirm that the micrometer-scale helixes and bent crystals are all cocrystals.
X-Ray Single Crystal Diffraction Characterization

The sample were tested on a ROD, Synergy Custom system, HyPix diffractometer. The crystal was kept at 113 K during data collection. Using Olex2,[1] the structure was solved with the SHELXT[2] structure solution program using Intrinsic Phasing and refined with the SHELXL[3] refinement package using Least Squares minimisation. The 3-dimensional measured reciprocal space was reconstructed and visualized by Ewald3D embedded in CrysAlispro.[4] The two single crystal structure data are shared by us, could be downloaded from the Cambridge structural database, and summarized in Table S1. All the CIFs were available in the supporting files.

Figure S11. Face indexing of a EPIMP single crystal (left) and EPIMP-TFTIB halogen-bonded cocrystal (right).
Table S1. Crystal structure information of EPIMP single crystal and EPIMP-TFTIB halogen-bonded cocrystal. These two structures are newly reported by us, available from Cambridge Crystallographic Data Centre.

|                    | EPIMP       | EPIMP-TFTIB |
|--------------------|-------------|-------------|
| CCDC               | 2071219     | 2071222     |
| Formula            | C\textsubscript{14}H\textsubscript{14}N\textsubscript{2}O\textsubscript{2} | C\textsubscript{6}F\textsubscript{3}I\textsubscript{3}, C\textsubscript{14}H\textsubscript{14}N\textsubscript{2}O\textsubscript{2} |
| Space Group        | \textit{Pna}2\textsubscript{1} | \textit{P2\textsubscript{1}/c} |
| Crystal System     | orthorhombic | monoclinic  |
| a (Å)              | 23.0457(13) | 4.5631(2)   |
| b (Å)              | 10.7404(5)  | 27.7298(7)  |
| c (Å)              | 4.8775(3)   | 17.7063(6)  |
| α (deg)            | 90          | 90          |
| β (deg)            | 90          | 91.254(3)   |
| γ (deg)            | 90          | 90          |
| V (Å\textsuperscript{3}) | 1207.28(12) | 2239.91(14) |
| Z                  | 4           | 4           |
| R-factor           | 5.28        | 3.57        |
| wR\textsubscript{2} | 12.53       | 8.09        |
| Temperature (K)    | 113         | 113         |
Origin of Mechanical Properties

All crystals display some degree of mechanical elastic behavior when subjected to applied force and could be explained by a universal model developed by Jack K. Clegg. Nevertheless, we still analyzed the origin of mechanical properties from the perspective of molecular structure and intermolecular interaction in details, because this part has been included in most of the related studies.

1. **Crystal structure of EPIMP-TFTIB halogen-bonded cocrystal and interaction analysis:** The EPIMP molecules are relatively planar attributed to the intramolecular N-H···O hydrogen bond between the -OH and CH=N groups and stack parallelly through π-π interactions along the [100] direction, which is the longest dimension (growth direction) of the cocrystal, determined by the face indexing of single crystal (Figure S11). The TFTIB molecules are also planar and stack parallelly through π-π interactions along the [100] direction (Figure S12). There are edge-to-face T-shape π-π interactions, intermolecular C-I···N and C-I···O halogen bonds between the planar molecules TFTIB and EPIMP in the {100} plane group.

![Figure S12.](image)

**Figure S12.** The crystal structure of EPIMP-TFTIB halogen-bonded cocrystal with the distances of π-π interactions marked. The blue planes are the TFTIB planes and the red planes are the EPIMP planes. The distance of π-π interactions between TFTIB molecules is 3.629 Å and the distance of π-π interactions between EPIMP molecules is 3.255 Å.
About the two-dimensional elastic bending of the cocystal, the $\pi$-stacking columns along the [100] direction keep the crystals retaining intact macrostructures when the external force is applied on the (010) or (001) plane, and recovering to straight when the external force is withdrawn from the crystals. Structurally, the distance between the molecules was expanded along the outer arc and was compressed along the inner arc, accompanied by the nonparallel rotating of molecules.$^6$ In general, the $\pi-\pi$ interaction will maintain the stability of the structure.

About plastic twisting of the cocystal, when applying torsion force at the two ends of cocystal, shear stress will cause the movement of molecules (Figure S15). However, the $\pi-\pi$ interactions along the [100] direction will keep the crystal structure from collapsing, and the halogen-bond interaction is easy to break and reform, which may be jointly responsible for plastic twisting.

Figure S13. The crystal structure of EPIMP-TFTIB halogen-bonded cocystal viewed along the [100] (top), [001] (left) and [010] (right) directions as determined by face indexing.
Figure S14. The molecular chains of EPIMP-TFTIB halogen-bonded cocrystal labeled in the same color viewed along the [100] (top), [010] (middle) and [001] (bottom) directions. The blue line marks the halogen bonds between EPIMP and TFTIB as well as the intramolecular hydrogen bonds of EPIMP.
Figure S15. Schematic representation of plastic twisting of adjacent layers sequentially misoriented along with the [100] directions. The rotation angle is exaggerated and all the hydrogen atoms are omitted for clarity.

2. Dihedral angle of the plane of EPIMP and the plane of TFTIB:

Figure S16. The relative position between the plane of EPIMP and the plane of TFTIB viewed along the [100] (left), [010] (middle) and [001] (right) directions.
Figure S17. The elastic bending and recovering of a plastic twisted cocrystal under bright field (standard white light source, top) and dark field (365 nm UV light source, bottom).
Figure S18. Microphotographs of the helixes at $T_{\text{constant}}=293$ K under bright field (standard white light source, left) and dark field (365 nm UV light source, right). Scale bar, 5 μm.

Figure S19. Microphotographs of the helixes at $T_{\text{constant}}=313$ K under bright field (standard white light source, left) and dark field (365 nm UV light source, right). Scale bar, 10 μm.
Figure S20. The helixes and superhelixes. a-f) Microphotographs of the helixes in left-handed (M) and right-handed (P) under bright field (standard white light source) and dark field (365 nm UV light source). g-k) Microphotographs of the superhelixes in left-handed (M) and right-handed (P) under bright field (standard white light source) and dark field (365 nm UV light source). Scale bar, 1 μm.

Notes: We observed that a superhelix consists of 16 helixes under a C\text{initial} of 6 mmol·L\text{−1} (Figure S20k).
Figure S21. Scanning electron microscope images of the helixes (a-f) in left-handed (M) and right-handed (P), the superhelixes (g-h) in right-handed (P) and the overall images of helixes (i-j). Scale bar, 1 μm.
Figure S22. Microphotographs of the sample prepared at toluene solvent without temperature control under bright field (standard white light source, left) and dark field (365 nm UV light source, right). Scale bar, 10 μm.
Figure S23. Microphotographs of the rings or nearly rings under bright field (standard white light source) and dark field (365 nm UV light source). Scale bar, 1 μm.
Figure S24. Scanning electron microscope images of the rings or nearly rings. Scale bar, 1 μm.
**Figure S25.** Microphotographs of the sample prepared at a mixed solvent of toluene and MeCN with both helix and ring morphology under bright field (standard white light source, left) and dark field (365 nm UV light source, right). Left: toluene/MeCN=2:1, volume ratio. Right: toluene/MeCN=1:2, volume ratio. Scale bar, 10 μm.

**Figure S26.** Microphotographs of the Möbius strip prepared at mixed solvent (toluene/MeCN=1:1, volume ratio), $T_{\text{constant}}=313$ K under bright field (standard white light source, left) and dark field (365 nm UV light source, right). Inset: partial enlargements of the Möbius strip. Scale bar, 5 μm.
Figure S27. Microphotographs of the Möbius strips, non-Möbius paradromic strips or nearly paradromic strips under bright field (standard white light source) and dark field (365 nm UV light source). Scale bar, 1 μm.
**Energy Framework**

Energy frameworks were performed to visualize intermolecular interactions in the flexible crystal of EPIMP-TFTIB halogen-bonded cocrystal in a more quantitative way. CrystalExplorer 17 was employed to calculate based on Gaussian HF/3-21G molecular wavefunctions. The tube size in the energy frameworks is 200, and the cut-off energy value is -5 kJ·mol⁻¹.

![Energy framework diagram](image)

**Figure S28.** Energy framework of EPIMP-TFTIB halogen-bonded cocrystal viewed along different axis.
Figure S29. Molecular structure pairs and the interaction energies (kJ/mol) obtained from energy frameworks calculation for EPIMP-TFTIB halogen-bonded cocrystal. Scale factors are in the bottom right table.
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**Additional Issues**

Additional issues are some points not mentioned in the manuscript while discussed with the reviewers.

1. **The circular dichroism spectroscopy of left-handed and right-handed helixes.**

   In theory, the circular dichroism (CD) spectroscopy of left-handed helixes and right-handed helixes should exhibit the opposite signal. We have tried to use CD spectroscopy to confirm left-handed helixes and right-handed helixes and their circularly polarized luminescence during the research. But in practice, we cannot acquire left-handed and right-handed helixes samples that meet the dose required for the test. In addition, we have tried to add some chiral additives, including \( D/L \)-limonene, \( D/L \)-tartaric acid and \( D/L \)-malic acid, to regulate the chirality of the helixes, but no positive effects have been achieved. Consequently, we think this system cannot be regulated chirality through chiral additives to achieve circularly polarized luminescence, which will be further explored and found in other systems.

2. **The relationship between crystal diameter and its flexibility.**

   For centimeter-scale crystals, the flexibility is related to crystal size and thinner crystals are easy to bent, and slender crystals are easy to twist. For micrometer-scale crystals, their width did not show noticeable changes in our system and did not affect their flexibility according to our experimental results. Also, the superhelix crystal displayed a similar twisting capability to each helix crystal that formed them even though their diameters were different.

3. **The general comments of one reviewer on this work.**

   This research article reports an original contribution on Möbius strip microstructures. While at the molecular level, challenging Möbius-type molecules has been synthesized and characterized with outstanding properties in the last decade, higher-order Möbius supramolecular systems are lacking. The authors took up this challenge and carefully designed a rational and complex protocol starting from flexible organic single crystals to make Möbius strips.

   The manuscript is convincing from a methodological point of view combining state-of-the-art experimental techniques to characterize the topology and luminescent properties of the newly created Möbius strips. A main drawback of the new structures concerns the uncontrollable chirality, hindering future applications. It might be desirable if the authors could propose a possible way to control the helical chirality of the Möbius strip microstructures. At the molecular level, it has been shown that solvents, metals, pH, substituents, and even external forces are good stimuli to control the \( \pi \)-conjugation topology (i.e. Möbius vs Hückel) in porphyrinoid macrocycles (Chem. Rev. 2017, 117, 4, 2584; Chem. Rev. 2017, 117, 4, 2257).

   An interesting aspect is that the cocrystals show multidimensional flexibility at the macroscopic level, including elastic bending when applying force at both the (001) and (010) crystal faces, and plastic...
twisting into left- and right-handed helixes when applying torsion forces at the two ends. This fact remembers a recent work at the microscopic level in which mechanical force were proven to induce mechanochemically triggered topology changes in porphyrinoid macrocycles (Chem. Eur. J. 2021, 27, 3397). This multidimensional flexibility of the Möbius strips is an intriguing property to be exploited in future applications. In the current manuscript, it is missing to mention some possible future applications of such novel architectures. Note that the Möbius-type molecules has opened new horizons in different domains including useful building blocks for single-molecule electronic devices.