

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

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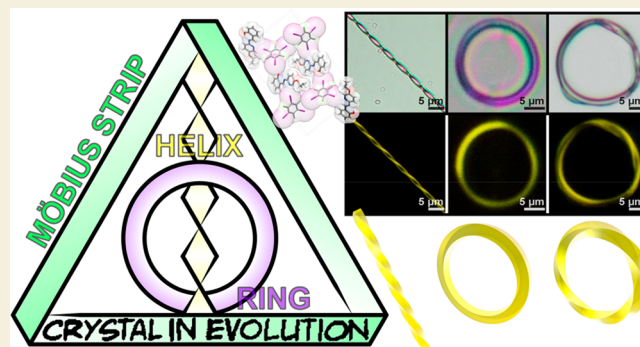


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**ABSTRACT:** Luminescent Möbius strip microstructures have been created for the first time based on flexible organic single crystals via a template-free solution self-assembly. We herein demonstrated a rationally designed morphological evolution toward Möbius strips from rings and helices. Our findings lay the foundation for the future construction of complex matters with predetermined morphologies and functions from crystal systems.

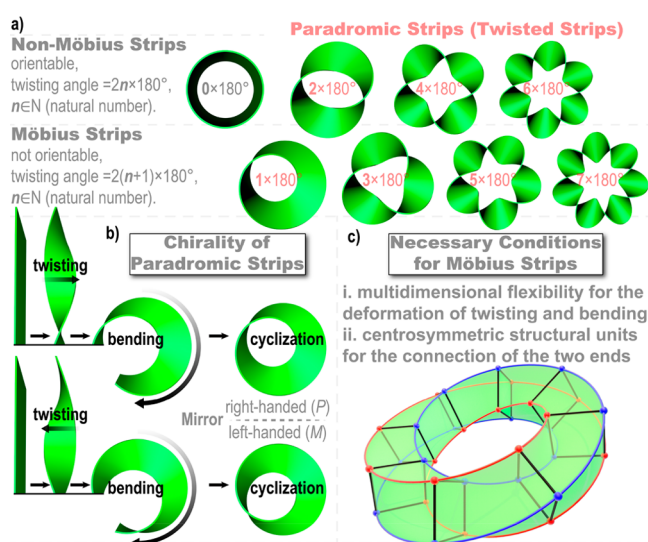


**KEYWORDS:** Möbius strip, crystal engineering, photoluminescence, microstructure, morphological evolution

Möbius strip, the best known unorientable strip (Figure 1a),<sup>1</sup> had been discovered and conceived in 1858 first by German mathematician Johann Benedict Listing and named after August Ferdinand Möbius, who completed a similar conceptualization months later.<sup>2,3</sup> It would be fair to say that the Möbius strip is one of the few icons that originates from

mathematics but has been widely absorbed as high-level thought by various sciences, arts, and cultures<sup>4–8</sup> and even could serve as a general technical tool for productivity improvement.<sup>9,10</sup> In recent decades, chemists have also been inspired to create new materials with unique Möbius topologies, especially at the molecular level,<sup>11–19</sup> because not only do the  $\sigma$  bonds with an axisymmetric electron cloud distribution endow the molecular skeleton with excellent flexibility for possible bending and twisting<sup>20–25</sup> but also the synthesis skills have been well-developed to manipulate the creating and breaking of covalent bonds at will.<sup>26,27</sup> However, for higher-order complex materials of dynamic supramolecular systems,<sup>28</sup> a template-free bottom-up creation toward such elegant and complicated Möbius strip structures could be easily achieved by nature<sup>8,29</sup> but are presently almost unthinkable and untouchable for humans,<sup>27,30–35</sup> because of the lack of proven methodologies in manipulating pluralistic intermolecular forces accurately toward a complex morphological evolution.

We have been obsessed with creating complex architectures via a close-to-nature self-evolution approach based on crystal systems<sup>36,37</sup> and target a challenging Möbius strip in this contribution. To do that, first of all, we need to decompose the



**Figure 1.** Schematic representation for the Möbius strips and related strips. (a) Scope and definition of Möbius strips, non-Möbius strips, and paradiromic strips. (b) Chirality of paradiromic strips. (c) Necessary conditions for Möbius strips.

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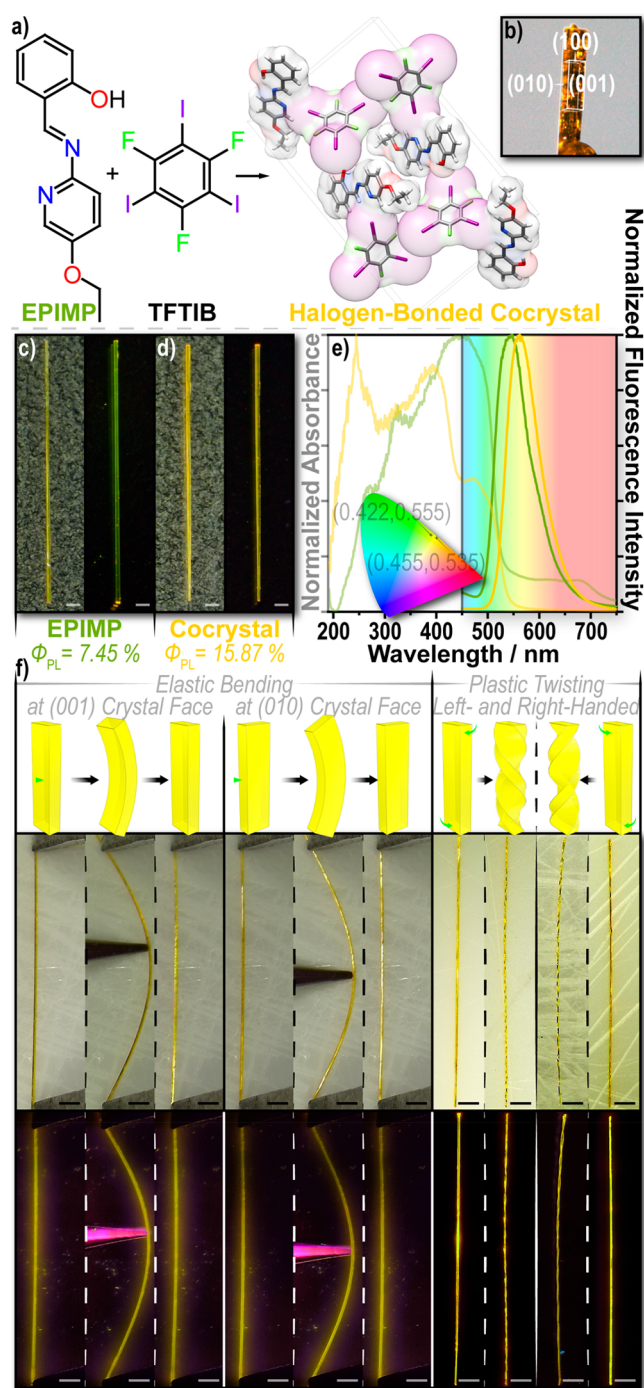
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Möbius strip into several mechanical processes, which are twisting, bending, and cyclization (Figure 1b). Accordingly, it would be a plausible choice to take flexible organic single crystals as a model system: 1) The self-bending of organic single crystals has been achieved in our previous study through solution crystallization, even with a controllable length/width/curvature.<sup>37</sup> We believe that a similar process could also lead to a self-bending of other flexible organic single crystals. 2) Organic compounds might crystallize into twisted morphologies spontaneously when grown from a melt, with or without additives.<sup>38–43</sup> Likewise, one recent example indicated that it is also possible for crystals to twist when crystallizing from supersaturated solutions.<sup>44</sup> Although all of the current self-twisting organic crystals were discovered accidentally from experimental findings, not constructed through a thoughtful design, we consider that mechanically reconfigurable crystals with macroscopically twistable natures may have the tendency of self-twisting during solution growth.<sup>45,46</sup> 3) The cyclization might be easily realized by drawing support from soft or hard templates;<sup>47–51</sup> however, we still wish to take a chance on a template-free approach and count on probability. Also depending on probability is the number of the twists in one strip. All twisted strips are paradiromic strips. Only those with an odd number of twists are Möbius strips (Figure 1a). We do not know yet whether the chirality of Möbius strips is able to be controlled (Figure 2b). A proper combination of all three mechanical processes above will lead us to Möbius strips.

For a proof of concept, we devised a flexible halogen-bonded cocrystal (Figure 2a,b, CCDC 2071222) composed of a newly designed Schiff base, (*E*)-2-(((5-ethoxypyridin-2-yl)imino)-methyl)phenol (EPIMP, CCDC 2071219), and 1,3,5-trifluoro-2,4,6-triiodobenzene (TFTIB) for the following reasons: 1) A Schiff base is presently the only type of compound whose crystals have been systematically studied on the link between the molecular skeleton and macroscopic mechanical flexibility (mainly elastic bending).<sup>52,53</sup> The additional introduction of the ethoxy group in EPIMP will further increase the flexibility of the molecules, thus promoting the flexibility of the crystals.<sup>54</sup> Besides, aromatic Schiff bases exhibit optical functions (Figure 2c,d);<sup>55</sup> thus, luminescent architectures are predictable. 2) The planar molecule TFTIB with uncommon  $C_{3h}$  symmetry serves as a halogen-bond donor, linking to the pyridine ring of the Schiff base which is a halogen-bond acceptor, propitious to generate spatially misfit interactions (Figure S16), raising the feasibility of twisting morphologies.<sup>44</sup> 3) It should be noted that TFTIB is often used for static quenching of luminescence in  $\pi$ - $\pi$  stacking along with other chromophores;<sup>56–58</sup> however, in our case, due to the significant size differences, there is no  $\pi$ - $\pi$  stacking between EPIMP and TFTIB, only halogen bonding, which is beneficial for the presence of luminescence.<sup>59,60</sup> The halogen-bonded cocrystal EPIMP-TFTIB emits bright yellow luminescence with an absolute quantum yield ( $\Phi_{PL}$ ) of 15.87% (Figure 2c-e), higher than twice that of the green-light-emitting single-component EPIMP crystal ( $\Phi_{PL} = 7.45\%$ ).

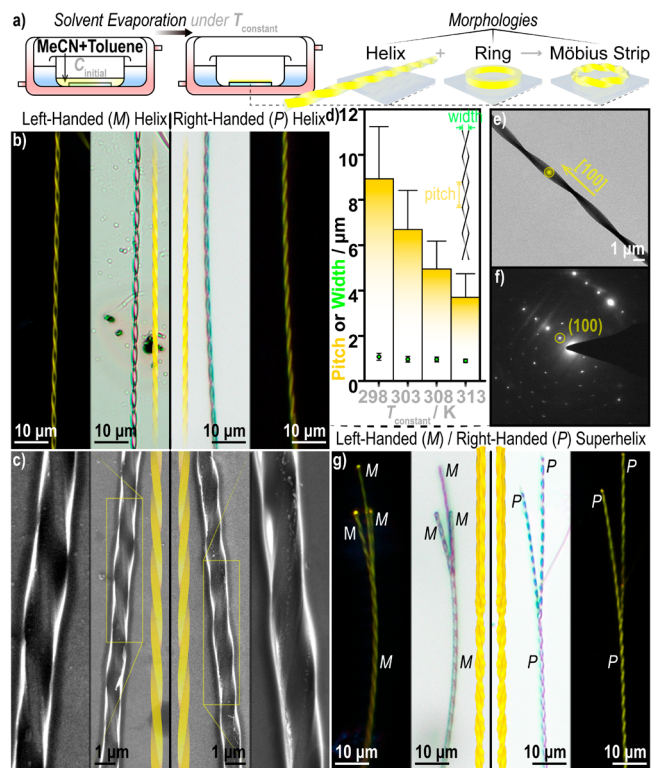
Macroscopically, the cocrystals show multidimensional flexibility (Figure 1c), including elastic bending when applying force at both the (001) and (010) crystal faces and plastic twisting into left- and right-handed helices when applying torsion forces at the two ends (Figure 2f, Movie S1, and Figures S12–S15).<sup>61</sup> Additionally, the cocrystal possesses a centrosymmetric structure with the space group  $P2_1/c$  (Figure 2a), satisfying one necessary condition for constructing Möbius



**Figure 2.** Multidimensional flexibility of the halogen-bonded cocrystal EPIMP-TFTIB. (a, b) Formation of the cocrystal (a) and corresponding crystal face identification (b) by X-ray crystallography. (c–e) Photoluminescence of the single-component EPIMP crystal and the cocrystal, including the microphotographs (c and d, respectively) of both under bright (left) and dark field (right), absorbance and fluorescence spectra of both (e), and the corresponding CIE 1931 chromaticity diagram (e, inset) with a CIE coordinate of (0.422, 0.555) for the EPIMP crystal and a CIE coordinate of (0.455, 0.535) for the cocrystal. (f) Flexibility of the cocrystal, including elastic bending and recovering at (001) and (010) crystal faces (left) and plastic twisting into left- and right-handed helices (right). Schematic models (top) and the corresponding microphotographs under bright (middle) and dark (bottom) fields. Conditions: bright field, standard white light source; dark field, 365 nm UV light source; scale bar, 1 mm.

strips, that the two ends of the crystals are capable of connecting together structurally after twisting an odd multiple of  $180^\circ$  (Figure 1c).

A self-deformation of both the bending and twisting of the cocrystals through a bottom-up solution crystallization is what we pursue.<sup>37</sup> For that, we screened a variety of solvents and got some elementary results. An unsaturated solution of 1:1 EPIMP and TFTIB (molar ratio, with a concentration of  $C_{\text{initial}}$  for both) was placed in a glass container with a cover and maintained at a constant temperature  $T_{\text{constant}}$  (Figure 3a). One



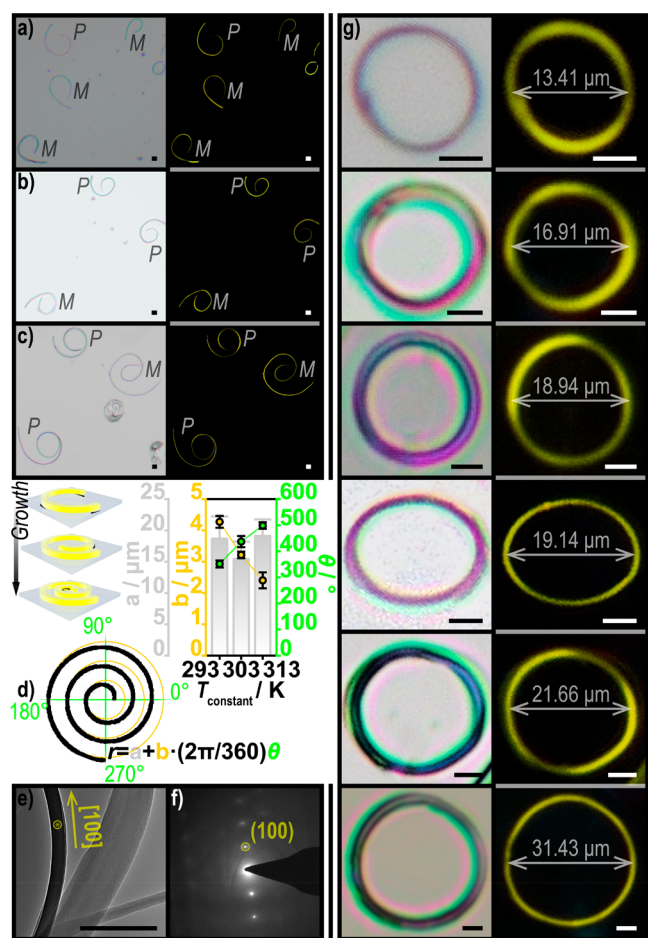
**Figure 3.** Helices. (a) Schematic representation for the preparation of the helices, rings, and Möbius strips. (b) Microphotographs and schematic representations of the helices in left-handed (*M*) and right-handed (*P*) helices under bright and dark fields. (c) Scanning electron microscope images with partial enlargements and schematic representations of the helices in left-handed (*M*) and right-handed (*P*) helices. (d) Statistical pitch and width of the helices changing along with the variation of  $T_{\text{constant}}$ , with error bars added. (e, f) Transmission electron microscope images (e) and corresponding selected area electron diffraction patterns (f) of one helix. (g) Microphotographs and schematic representations of the superhelices in left-handed (*M*) and right-handed (*P*) modes under bright and dark fields. Conditions: bright field, standard white light source; dark field, 365 nm UV light source.

slide glass was preplaced at the bottom of the container for further crystal growth through slow solvent evaporation. The self-twisting crystals were found in polar organic solvents (methanol, ethanol, acetonitrile, and acetone). The self-bending crystals were found in a benzene series (benzene, toluene, *m*-xylene, *p*-xylene, and isopropylbenzene). When a concentrated solution was diluted with a large amount of water,<sup>48</sup> straight crystals emerged on the slide glass. Further experiments on the twisting and bending were carried out in acetonitrile (MeCN) and toluene systems.<sup>37</sup>

It should be noted that all the crystals self-twist into left-handed (*M*) and right-handed (*P*) helices when crystallizing from single MeCN solvent (Figure 3b,c and Figure S21), and their rates are almost equal. We have tried to add some chiral additives (*D*-/*L*-limonene, *D*-/*L*-tartaric acid, *D*-/*L*-malic acid) to regulate the chirality of the helices, but no positive effects were achieved.<sup>62</sup> The helices were determined by X-ray crystallographic methods as the cocrystals (Figure S9). It is worth noting that the EPIMP itself cannot crystallize into helices under identical operating conditions. As the  $T_{\text{constant}}$  value rises, the width barely changes while the pitch of the helices becomes shorter (Figure 3d), which is consistent with conventional cognition.<sup>44</sup> What is really encouraging is that the helix still maintains the ordered structure of a single crystal (Figure 3e,f). Unexpectedly, we found that helices with the same chirality could further assemble into a chiral superhelix whose chirality is consistent with the helices (Figure 3g). With the increase in  $C_{\text{initial}}$ , there is a growing trend toward superhelices, and the number of the strands of helices in the superhelix expands as well (Figure S20). To the best of our knowledge, this is the only case so far of a higher-order helix, i.e., superhelix, composed of crystals.

The cocrystals crystallize into bent morphologies in a single toluene solvent (Figure 3a and Figure S10). We tried to control the curvature of the bent crystals but found that it changes at different regions of one crystal and thus cannot be fitted by an arc.<sup>37</sup> Further attempts were carried out until spiral-like morphologies appeared regularly at extremely dilute  $C_{\text{initial}}$  values (Figure 4a–d). The left-handed (*M*) and right-handed (*P*) spiral lines are nearly equal in number. Interestingly, the spiral-like crystals were observed to grow in a bent shape with an outside-in direction, which is the opposite of the inside-out direction when we draw spiral lines mathematically (Figure 4d). We fitted each spiral line in polar coordinate systems with a modified Archimedes spiral,  $r = a + b(2\pi/360)\theta$ , 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. We drew polar coordinates artificially; thus, there will be a subjective influence on the numerical value of  $a$ . Still, regularity has been discovered in  $b$  and  $\theta$  that, as the  $T_{\text{constant}}$  rises, the distance between two adjacent rounds ( $2\pi b$ ) decreases while the number of rounds of the spiral line ( $\theta$ ) increases (Figure 4a–d). It is good to perceive a few sparse rings coming into view when observing the slide glasses (Figure S24). We considered them as single-crystal rings, as the bent crystal still maintains the ordered structure of a single crystal based on the selected area electron diffraction pattern (Figure 4e,f). It is better to state here that the rings are rare in number (less than one-tenth of all bent crystals) and random in location (Figure 4g), mainly because the formation of the rings here is a template-free process, embodied as uncontrollable cyclization (Figures S22 and S23).<sup>48,63</sup>

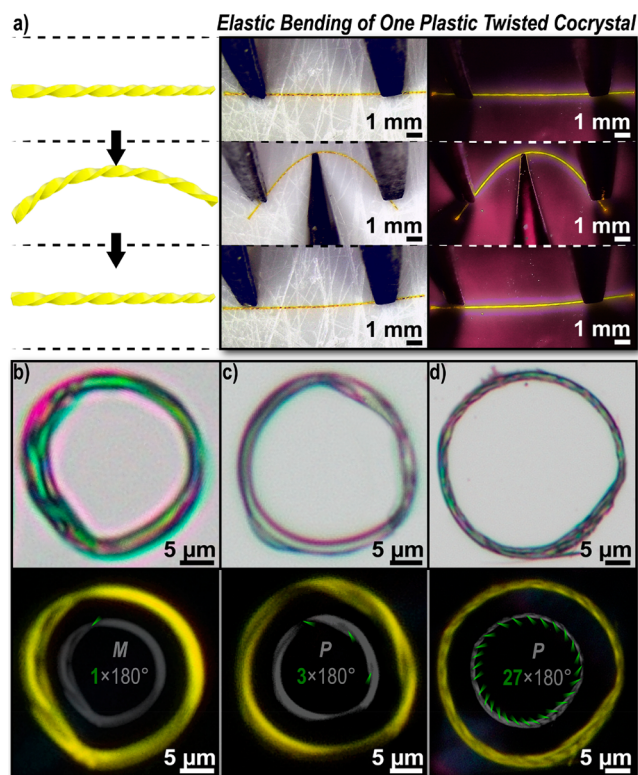
Further bending of the twisted crystals is seldom carried out by researchers,<sup>64</sup> whereas such multidimensional flexibility is one of the vital structural foundations for Möbius strips (Figure 5a, Movie S2, and Figure S17). To make Möbius strips, we integrated the formation conditions of the helices and rings, using a mixed solvent of MeCN and toluene (1:1 volume ratio, Figure 3a). Most of what we obtained were bent helices as we might have guessed, but a few Möbius and non-Möbius paradromic strips were noticed at a very low probability (less than one-tenth of all crystals; Figure 5b–d



**Figure 4.** Spiral lines and rings. (a–d) Microphotographs under bright (left) and dark (right) fields of the spiral lines with a variable  $T_{\text{constant}} = 293$  K (a), 303 K (b), and 313 K (c) and corresponding statistics of the parameters ( $a$ ,  $b$  and  $\theta$ ) for drawing a spiral line (d), with error bars added. Inset of (d): schematic representations for the growth process of the spiral lines (top left) and the mathematical expression for the spiral line (bottom left). (e, f) Transmission electron microscope image (e) and corresponding selected area electron diffraction pattern (f) of one self-bending crystal. (g) Microphotographs of several rings with different diameters under bright (left) and dark fields (right). Conditions: bright field, standard white light source; dark field, 365 nm UV light source; scale bar, 5  $\mu\text{m}$ .

and Figures S26 and S27). Even so, we call it a success that this work presents the first Möbius strip in molecular crystal systems. Although a crystallographic identification of the Möbius strips cannot be completed because of the very small amount of samples, it is reasonable to believe them to be single-crystal Möbius strips because both the helices and rings are single crystals.

It is important to note that the successful creation of Möbius strips is a small-probability event, though a very rational design has been carefully proposed and carried out by us. There have been too many unsuccessful cases to show (Figure S27). First, because of the template-free process, the cyclization for both the rings and Möbius strips is not guaranteed. Second, the flexibility of the crystals is an elusive factor, making it unable to control when the flexibility is good and hard for self-deformation when poor. Otherwise, the problem of the uncontrollable chirality should be of concern, which limits



**Figure 5.** Möbius strips. (a) Schematic representation and corresponding microphotographs of the elastic bending and recovering of a plastic twisted cocystal under bright and dark fields. (b–d) Microphotographs of the self-deformed Möbius strips under bright and dark fields: left-handed ( $M$ ) with a twisting angle of  $1 \times 180^\circ$  (b), right-handed ( $P$ ) with a twisting angle of  $3 \times 180^\circ$  (c), and right-handed ( $P$ ) with a twisting angle of  $27 \times 180^\circ$  (d). Conditions: bright field, standard white light source; dark field, 365 nm UV light source.

the possibility for future multifunctional applications. Basically, our Möbius strip is a major breakthrough and is sure to become a classic. As in the well-known dictum by Richard Phillips Feynman, “What I cannot create, I do not understand”,<sup>65,66</sup> a successful design is the most powerful tool to enrich our cognitive systems. In addition to the creation, we are the first to introduce functionality (photoluminescence) into Möbius strip microstructures. This contribution will guide the future creation of single-crystal systems with versatile microstructures and functions.<sup>58,67,68</sup>

## ■ ASSOCIATED CONTENT

### Data Availability Statement

All data supporting the findings of this study are presented in the paper and/or the Supporting Information. The associated raw data are available from the corresponding author upon reasonable request.

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacsau.2c00469>.

Chemicals and instruments, detailed experimental procedures, crystal morphology calculations, fluorescence lifetime measurements, X-ray diffraction patterns, X-ray single crystal diffraction characterization, origin of

mechanical properties, additional graphs, and energy framework (PDF)

Movie of the flexibility of a single crystal of the halogen-bonded cocrystal (MP4)

Movie of the elastic bending of a twisted halogen-bonded cocrystal (MP4)

Single-crystal structure of the single-component crystal EPIMP, CCDC 2071219 (CIF)

Single-crystal structure of the halogen-bonded cocrystal EPIMP-TFTIB, CCDC 2071222 (CIF)

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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. CRediT: **Yifu Chen** conceptualization, software, supervision, visualization, writing-original draft, writing-review & editing; **Bo Jing** data curation, formal analysis, investigation, methodology, writing-review & editing; **Zewei Chang** investigation, methodology; **Junbo Gong** funding acquisition.

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## Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

CCDC, Cambridge Crystallographic Data Centre; EPIMP, (E)-2-(((5-ethoxypyridin-2-yl)imino)methyl)phenol; MeCN, acetonitrile; TFTIB, 1,3,5-trifluoro-2,4,6-triiodobenzene; UV, ultraviolet rays

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