Supporting Information

Chiral mesostructured In_2O_3 films twisted with different crystal orientations

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Experimental Procedures

Materials

InCl₃·4H₂O, CO(NH₂)₂, Na₃C₆H₅O₇·2H₂O and Mal were purchased from Aladdin. All reagents were used as received without further purification.

Substrate pretreatment

FTO was utilized as the substrate (with dimensions of $50 \times 10 \times 1.1$ mm, coating thickness = 500 nm, sheet resistance $\leq 15 \Omega$), which was sequentially rinsed with acetone, ethanol and deionized water each for 10 min in an ultrasonic bath for depositing CMIFs-300. The washed FTO was further subjected to hydrophilic treatment for preparing CMIFs-104.

Preparation of CMIFs

CMIFs-300 can be synthesized over a wide range of molar compositions of L/D-Mal : $Na_3C_6H_5O_7 \cdot 2H_2O$: $InCl_3 \cdot 4H_2O$: $CO(NH_2)_2$: $H_2O = x$: 1.5 :1 : 5.83 : 277.78, where *x* can range from 1.17 to 1.92. In a typical synthesis, 8.64 mmol L-Mal and 9 mmol $Na_3C_6H_5O_7 \cdot 2H_2O$ were dissolved in 30 mL deionized water while stirring. After then, 6 mmol $InCl_3 \cdot 4H_2O$ and 35 mmol $CO(NH_2)_2$ were added to the mixture to obtain a homogeneous solution. The above solution was allowed to react under room temperature with stirring for 30 min. Afterwards, the precursor and FTO glass were transferred into Teflon-line autoclave (50 mL) and heat at 180 °C for 24 h. After reaction, the substrate was rinsed using deionized water and absolute ethanol several times to remove any residuals and then dried at 80 °C for 12 h. All organic compounds in the film was wiped off through calcination at 450 °C for 9 h, and CMIFs-300 were obtained finally.

With the same route, CMIFs-104 can be synthesized with a typical molar composition of L/D-Mal : $InCl_3 \cdot 4H_2O$: $CO(NH_2)_2$: $H_2O = 4.0 : 1.0 : 6.0 : 2.0$.

Characterization

SEM images were observed using a JEOL JSM-7900 in GBSH mode, with an accelerating voltage of 15 kV and a working distance of 4 mm. TEM images were obtained through a JEOL JEM-F200 TEM microscope operating at 200 kV, with images recorded by a Gatan OneView IS camera. The thin section with a thickness of 50-60 nm was prepared using Leica EM UC7 Ultramicrotome equipped with a diamond knife, by blending In₂O₃ powder scraped off from the CMIFs-300 with epoxy resin and then solidifying it. XRD patterns were obtained using Rigaku Miniflex 600 powder diffractometer equipped with Cu K α radiation ($\lambda = 1.5418$ Å, 40 kV, 15 mA) with a sweep speed of 0.2° min-1 and the scanning range of 10-80°. Solid-state nuclear magnetic resonance (NMR) spectra were examined using a 600 M AVANCE NEO solid-state NMR spectrometer furnished with a ZrO₂ rotor, with a resonance frequency of 150 and 600 MHz, a spinning speed of VR = 15 kHz, a 0.49 s excitation pulse, a 4 s relaxation delay, and 900 scans. CD and MCD spectra were taken on a JASCO J-1500 spectropolarimeter fitted with MCD apparatus, and the data were obtained with a scanning rate of 10° min-1 in the range of 350-800 nm without and with applying the magnetic field not exceeding ± 1.5 T at room temperature. Magnetic properties were measured using a Magnetic Property Measurement System (MPMS, Quantum Design) with 9 Tesla magnets.

DFT calculations and MD simulations

All first-principles calculations were conducted through the VASP program,¹ in which the Kohn–Sham equations were settled via the Perdew, Burke, and Ernzerhof exchange–correlation functional ² under the condition of projector-augmentedwave (PAW) pseudopotentials.³ An amendment to the PBE wave function was made (PBE + U) through considering a repulsive onsite Coulomb interaction, U.⁴ The orbital dependence of the Coulomb and exchange interactions has been considered in this scheme, utilizing the Hubbard parameter with a value of 7 eV for the In.⁵ The cutoff-energy of plane-wave functional was set as 520 eV and the Brillouin zones were sampled through Monkhorst–Pack special k-point grids ⁶ in order to ensure geometrical and energetic convergence for In₂O₃ structure and Mal absorption in the paper. MD simulations with a classical force field were utilized to model In₂O₃ nanoplate with particular

chiral defects according to DFT calculations mentioned above. The chiral ligands were removed from the models demonstrated by our experiments. The MD simulations were carried out by Open Babel toolbox,⁷ the universal force field (UFF) was utilized to handle bonding and nonbonding interactions ⁸ of the model. The Coulombic force was calculated based on atoms with a cut-off distance of 1.55 nm. NVT ensemble was manipulated by the Nosé method ⁹ under the ambient temperature of 298 K. The total production time was set up to 10 ns followed by 1 ns pre-equilibrium with a time step of 1 fs.

Supplementary Figures



Figure S1. XRD patterns (a), Transmitted CD and UV-Vis spectra (b), and SEM images (c) of L-CMIFs-104 synthesized with synthetic molar composition of x L-Mal: 15 $InCl_{3}$ ·4H₂O: 90 CO(NH₂)₂: 1666.67 H₂O, where x=40, 60, 80, 90, respectively.



Figure S2. XRD patterns (a), transmitted CD and UV-Vis spectra (b), and SEM images (c) of L-CMIFs-300 synthesized with synthetic molar composition of 9.00 $Na_3C_6H_5O_7\cdot 2H_2O$: x L-Mal: 6.00 $InCl_3\cdot 4H_2O$: 35.00 $CO(NH_2)_2$: 1666.67 H_2O , where x=7.02, 8.64, 10.0, 11.5, respectively.



Figure S3. The fabrication strategies for CMIFs-300 (a_{1-4}) and CMIFs-104 (b_{1-4}). (a_1) The FTO substrate was sequentially rinsed with acetone, ethanol and deionized water to remove surface impurities, and then subjected to hydrophilic treatment for better nucleating of InOOH crystals. (a_2) InOOH seeds grew on the FTO substrate in a homogeneous solution composed of Na₃C₆H₅O₇·2H₂O, Mal, InCl₃·4H₂O, CO(NH₂)₂ and deionized water, in which Na₃C₆H₅O₇·2H₂O and Mal combined with InOOH by chemical bond. (a_3) Formation of chiral mesostructured InOOH films utilizing Mal and Na₃C₆H₅O₇·2H₂O as symmetry-breaking agent and structure-directing agent respectively by a hydrothermal method. (a_4) Chiral mesostructured In₂O₃ films with the

(300) exposed plane and the [110] helical axis were obtained by a calcination post-treatment process in air atmosphere. (b₁) The FTO substrate was sequentially rinsed with acetone, ethanol and deionized water to remove surface impurities. (b₂) InOOH seeds grew on the FTO substrate in a homogeneous solution composed of Mal, $InCl_3 \cdot 4H_2O$, $CO(NH_2)_2$ and deionized water, in which Mal combined with InOOH by chemical bond. (b₃) Formation of chiral mesostructured InOOH films utilizing Mal as both symmetry-breaking agent and structure-directing agent by a hydrothermal method. (b₄) Chiral mesostructured In_2O_3 films with the (104) exposed plane and the helical axis close to [211] direction were obtained by a calcination post-treatment process in air atmosphere.



Figure S4. Solid-state NMR spectra of L-CMIF-300. (a) solid-state ¹³C CP/MAS NMR (600 MHz) spectrum, (b) solid-state ¹³C NMR (600 MHz) spectrum.



Figure S5. The relationship among different crystal planes in the In₂O₃.

As is shown in the picture, the (0006) and (03Error!6) planes are vertical to (10Error!0), resulting in their disappeared diffraction peaks in the XRD patterns of CMIFs-30Error!0. Besides, the (11Error!6), (10Error!4) and (21Error!4) planes are also almostly perpendicular to the (10Error!0) plane, leading to their much weaker reflections in the XRD patterns of CMIFs-30Error!0 that cannot be observed as well.



Figure S6. Crystallography structure of antipodal CMIFs-104 deposited on FTO substrates.¹⁰ (a) XRD patterns (λ =1.5418 Å) of antipodal CMIFs-104. (b-c) Crystal structure of In₂O₃ and growth direction of nanoflake of CMIFs-104 along the substrate. Reproduced with permission from ref [10], copyright 2024 Springer.



Figure S7. Illustration of chirality transfer from chiral organic molecule to mesostructured In_2O_3 .

We proposed a possible chirality transfer mechanism on the basis of the resulting structure. Figure a exhibits that the primary chirality of individual nanoflake originating from right-handed crystal lattice distortions could be induced by the chiral arrangement of L-Mal assembly. The carboxyl groups were well chemically bonded with the In^{3+} and O^{2-} firstly. After adding $CO(NH_2)_2$, the In^{3+} and O^{2-} were precipitated to form InOOH. During the hydrothermal reaction, the right-handed alignment of Mal molecules would result in the asymmetric displacement of In and O atoms and the generation of primary chiral nanoflake consequently. As shown in Fig. b, the secondary chiral nanoplate was induced by the left-handed stacking of nanoflakes, which was a more stable structure due to the maximized interaction and minimized structural conflict in this stacking arrangement. Therefore, the right-handed lattice distortions of the nanoflake was derived from the helical arrangement of the L-Mal, which further generated the secondary nanoplate in a left-handed stacking manner.



Figure S8. Morphology of D-CMIF-300 deposited on the FTO substrate. (a) Top-view and sideview SEM images at varying magnifications. (b) Schematic drawing of D-CMIF-300. (c) Schematic drawing of hierarchical chirality and primary [110] twisted axis of D-CMIF-300. The synthetic molar composition was 1.50 Na₃C₆H₅O₇·2H₂O : 1.44 D-Mal : 1.00 InCl₃·4H₂O : 5.83 CO(NH₂)₂ : 277.83 H₂O.



Figure S9. Morphology of L-CMIF-104 deposited on the FTO substrate. (a_1-a_2) Top-view SEM images at varying magnifications of L-CMIF-104. (b_1) Schematic drawing of L-CMIF-104. (b_2) Schematic drawing of hierarchical chirality and primary [104] twisted axis of L-CMIF-104.¹⁰ Reproduced with permission from ref [10], copyright 2024 Springer.



Figure S10. Primary and secondary chirality of L-CMIF-104. (a-b) Side-view TEM images and the corresponding FDs of the nanoflake. (c-e) Front-view TEM images, FD and the structural model of the nanoflake.¹⁰ Reproduced with permission from ref [10], copyright 2024 Springer.





As is well-known, the stabilization energy of the crystal surface is calculated as follows: $E_{stabalization}=E_{surface}+E_{absorption}-E_{bulk}-E_{molecule}$. As shown in Fig. S9a, within the CMIFs-104 synthesis system utlizing Mal as both the structure directing agent and the symmetry-breaking agent, the adsorption energy of the Mal molecule on the (100) and (0001) crystal planes of InOOH is -4.21 eV and -4.37 eV respectively, so the Mal molecule could be combined with (0001) crystal plane more stably. As shown in Fig. S9b, within the CMIFs-300 synthesis system employing the Mal as the symmetry breaking agent and the Na₃C₆H₅O₇·2H₂O as the structure directing agent, the adsorption energy of the Mal molecule on the (100) and (0001) crystal planes of InOOH is-4.92 eV and -4.35 eV respectively, so the Mal and Na₃C₆H₅O₇·2H₂O could be combined with (100) crystal plane more stably. In summary, in the hydrothermal synthesis system without and with Na₃C₆H₅O₇·2H₂O, Mal preferentially bound to the (0001) and (100) crystal planes of InOOH, resulting in the formation of CMIFs-104 with twisted axis close to [211] and CMIFs-300 with [110] helical axis respectively.





The values of adsorption energy indicate the calculated relative stability concerning the corresponding adsorption orientations. This result suggests a preferred adsorption pattern of L-Mal on the (100) crystal surface of InOOH as is shown in Fig. S10a₆.



Figure S13. DFT calculations of possible chemical bonding orientations of L-Mal on the (0001) crystalline surface of InOOH monolayer.

The values of adsorption energy indicate the calculated relative stability concerning the corresponding adsorption orientations. This result suggests a preferred adsorption pattern of L-Mal on the (0001) crystal surface of InOOH as is shown in Fig. S11a₆.

104	configuratio n								
	energy	-0.53 eV	-0.78 eV	-1.72 eV	-1.65 eV	-1.81 eV	-2.02 eV	-1.39 eV	-1.57 eV
300	configuratio n								
	energy	-1.04 eV	-1.72 eV	-0.70 eV	-1.29 eV	-1.43 eV	-2.19 eV	-2.03 eV	-1.67 eV

Table S1. The relative energy of each related configuration between Mal and InOOH in L-CMIF-300 and L-CMIF-104 respectively.



Figure S14. (a₁) The achiral arrangement of In and O atoms on the (100) crystal plane of InOOH monolayer; (a₂) Asymmetric deformation formed on the (100) crystal plane of InOOH monolayer resulted from the displacement of In and O atoms after L-Mal absorption.



Figure S15. (a_1) The achiral arrangement of In and O atoms on the (0001) crystal plane of InOOH monolayer; (a_2) Asymmetric deformation formed on the (0001) crystal plane of InOOH monolayer resulted from the displacement of In and O atoms after L-Mal absorption.



Figure S16. The side-view and the front-view primary chirality of individual nanoflake in lefthanded chiral mesostructured InOOH film owning [10Error!0] helical axis with twist lengths of 8×2×1 and 12×2×1 respectively.



Figure S17. The side-view and the front-view primary chirality of individual nanoflake in lefthanded chiral mesostructured InOOH film owning [0001] helical axis with twist lengths of 8×3×1 and 12×3×1 respectively.



Figure S18. Transmitted UV-Vis and CD spectra of L-CMIF-30Error!O measured at different angles by rotating the sample with the direction of incident light as the axis.

The coincident CD spectra at different angles demonstrate that the artifact of LD can be negligible.



Figure S19. CD detection mechanism. Schematic diagram of measuring CD spectra of (a) the CMIFs-300 and (b) the CMIFs-300 saturated with water (isotropic liquid) in the transmission mode. Red and blue arrows represent R-CP and L-CP, respectively. I is the incident light ($I_L=I_R$), A is the absorbed light, T is the transmitted light, S is the scattered light, D is the detected light.

Based on the characteristic mechanism demonstrated in the Fig. S17a, with identical incident Land R-CP light ($I_L=I_R$), part of circularly polarized beams were selectively absorbed by CMIF-300 and then electron transition from valence band to conduction band of In_2O_3 was excited; Part were scattered containing normal non-selective diffuse reflection and selectively circularly polarized Bragg resonance-induced reflection ($\lambda=Pn_{average} \sin \alpha$, where λ is the wavelength, *P* is the pitch length, $n_{average}$ is the effective refractive index of the medium and environment, and α is the angle between the incident light and the surface of the chiral film); And the remaining part traversed the CMIF-300 and FTO substrate and entered into the detector, the detected light was equal to the transmitted one (D=T). Consequently, the transmitted CD spectra of L--CMIF-300 and D-CMIF-300 exhibit both electron transition absorption-based and scatteringbased signals [CD=(A_L-A_R)+(S_L-S_R)]. As shown in Fig. S17b, the transmitted CD of L-CMIF-300 was further detected by infiltrating it with water (isotropic liquid) in order to extract out the absorption-based part because the scattering-based OA would be weakened after saturating with water originated from the disappearance of optical chiral interface with decreasing difference between two media's optical refractive indices from In_2O_3 (*n*=3.48) and air (*n*=1.00) to In_2O_3 and water (*n*=1.33).



Figure S20. Morphology and structure of Rac-IF-300. (a) XRD patterns of Rac-IF-300 and FTO substrate. (b) Transmitted UV-Vis and CD spectra of Rac-IF-300. (c) SEM images of different magnifications of Rac-IF-300. The Rac-IF-300 was synthesized in the same way as the CMIFs-300 except substituting L/D-Mal for the racemic one. The synthetic molar composition was 1.50 Na₃C₆H₅O₇·2H₂O : 0.72 L-Mal : 0.72 D-Mal : 1.00 InCl₃.4H₂O : 5.83 CO(NH₂)₂ : 277.83 H₂O.



Figure S21. Morphology and structure of A-IF-300. (a) XRD patterns of A-IF-300 and FTO substrate. (b) Transmitted UV-Vis and CD spectra of A-IF-300. (c) SEM images of different magnifications of A-IF-300. The achiral In_2O_3 film was synthesized in the same way as the CMIF-300 without adding the Mal. The synthetic molar composition was 1.50 Na₃C₆H₅O₇·2H₂O : 1.00 InCl₃·4H₂O : 5.83 CO(NH₂)₂ : 277.83 H₂O. SEM.



Figure S22. XRD patterns, OAs and morphologies of L-CMIFs-300 during a man-made peening process from 0 min to 8 min. (a) XRD patterns of L-CMIFs-300. (b) Transmitted UV-Vis and CD spectra of L-CMIFs-300. (c) SEM images of L-CMIFs-300.

The 300 diffraction in XRD patterns of L-CMIFs-300 declined remarkably with increasing peening time. Besides, the intensity of transmitted CD peaks decreased significantly with the prolongation of destruction time, and a weak signal related to primary chirality induced absorption-based OA centered approximately at 382 nm was maintained finally, which indicate that multiple OAs originate from the co-effect of mesostructured chiral structures and the primary atomic lattice distortion in the CMIFs-300 is indestructible. Moreover, in SEM images of

L-CMIFs-300, the mesostructured chirality disappeared gradually with increasing destruction time, and primary twisted crystal lattices remained finally.



Figure S23. Multiple OAs of CMIFs-104. Transmitted UV/Vis and CD spectra ofantipodal CMIFs-104 before (solid lines) and after (dashed lines) saturation with water.¹⁰ Reproduced with permission from ref [10], copyright 2024 Springer.



Figure S24. Peak-differentiation-imitating analysis of transmitted CD and UV-Vis spectra of L-CMIF-300 and L-CMIF-300 saturated with water. (a₁-a₂) Schematic diagram for summarizing the multiple OAs of L-CMIF-300 and L-CMIF-300 infiltrated with water: (A1) positive absorptionbased OA came from the primary right-handed distorted nanoflake; and (A2) negative absorption-based OA resulted from secondary left-handed alignment of nanoflakes; (S1) negative scattering-based OA originated from the primary right-handed twisted nanoflake; and (S2) positive scattering-based OA arised from secondary left-handed stacking of nanoflakes. The obtained CD signals were the superposition of above OA signals. (b₁-b₂) Schematic diagram for summarizing the UV-Vis absorptions of L-CMIF-300 and L-CMIF-300 infiltrated with water: (A) electron transition-based absorption of L-CMIF-300, (S) scattering-based absorption of L-CMIF-300, and (F) the absorption of FTO substrate. The obtained absorptions were the superposition of above absorptions.

Handedness	Absorption-based CD signal	Scattering-based CD signal		
Right-handedness (primary)	382 nm (O 2 <i>p</i> →ln 5 <i>s</i>)	435 nm		
Left-handedness (secondary)		 425 nm		

Table S2. Illustration of chiralities and OAs in each level of chiral structure in L-CMIF-300.



Figure S25. MCD experimental set-up.¹⁰ Reproduced with permission from ref [10].



Figure S26. The simplified mechanism of MCD.¹⁰ Reproduced with permission from ref [10].



Figure S27. MCD spectra of CMIFs-104 after saturating with water under parallel (solid lines) and antiparallel (dashed lines) magnetic fields.¹⁰ Reproduced with permission from ref [10], copyright 2024 Springer.



Figure S28. Transmitted CD and UV-Vis spectra of antipodal CMIFs-300 under various external magnetic fields. Transmitted CD and UV-Vis spectra of antipodal CMIFs-300 under positive (a) and negative (b) external magnetic fields.



Figure S29. MCD spectra of antipodal CMIFs-300 with external magnetic field of ±1.5 T at 100 K, 150 K and 200 K respectively.

With the decrease of temperature, there was no significant change in the MCD spectra of both L-CMIF-300 and D-CMIF-300, which indicates that the C term of MCD in the diamagnetic In_2O_3 with nondegenerate ground state is zero.



Figure S30. MCD spectra of antipodal CMIFs-300 under various external magnetic fields ranging from ± 0.5 T to ± 1.5 T at ambient temperature of 293 K.



Figure S31. Peak-differentiation-imitating analysis of multilevel MCD signals of L-CMIF-300 and L-CMIF-300 saturated with water. (A) Absorption-based MCD signal contributed by the transition of spin-polarized electron, (S1) negative scattering-based MCD signal resulted from the primary right-handed distorted nanoflake and (S2) positive scattering-based MCD signal arised from secondary left-handed alignment of nanoflakes. The obtained MCD spectra were the superposition of above signals.



Figure S32. MCD spectra of A-IF-300 with external magnetic fields ranging from ± 0.5 T to ± 1.5 T at ambient temperature of 293 K.



Figure S33. (a) MCD spectra of CMIFs-300 after a man-made peening process about 8 min under antiparallel magnetic fileds of 1.5 T. (b) MCD spectra of FTO under antiparallel magnetic fileds of 1.5 T.

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