# Supporting Information

# For

## Hierarchical Chiral MOFs with the Induced Chirality of AIE Ligands Exhibiting the Non-reciprocal CPL

Hong-Ru Fu,[a,c] Dan-Dan Ren,[a,b] Kun Zhang,[a,b] Shuang Wang,[a] Xu-Jing Yang,[a] Qing-Rong Ding,[c]* Ya-Pan Wu[b]*

[a]College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471934, P. R. China.

[b]College of Materials and Chemical Engineering, China Three Gorges University, Yichang 443002 China.

[c]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 350002, China.

*** Corresponding author E-mails:** *qrding@fjirsm.ac.cn, wyapan2008@163.com*

**Material Characterization**

All the chemicals were purchased commercially and used directly. UV-spectra analysis was carried out on Shimadzu UV-2600 spectrophotometer and Hitachi UH4150 spectrophotometer. Elemental analyses of C, H, and N were measured on a Perkin-Elmer 2400 elemental analyzer. Powder X-ray diffraction (PXRD) were performed on a Rigaku Dmax/2400 X-ray diffractometer operating at 40 kV and 100 mA, using Cu-Kα radiation (λ = 1.5406 Å). Thermogravimetric analysis (TGA) was carried out under nitrogen atmosphere on a Q600 SDY TGA-DTA-DSC thermal analyzer from room temperature to 700 °C with a heating rate of 5 °C/min. Quantum yields were tested on an Edinburgh Instruments FLS-980 spectrometer. Photoluminescence (PL) spectra were measured on a Hitachi F4500 luminescence spectrometer. CD spectra were recorded on a JASCO J-810. CPL spectra were measured on a JASCO CPL-300. The images of polarization are measured by upright fluorescence microscopy with 10 objective lens (Leica DM2500).

**Single-crystal X-ray crystallography**

Single crystal X-ray analysis of DCF-15/LCF-15 and DCF-16/LCF-16 were performed on a Rigaku SuperNova detector using Mo Kα radiation (λ = 0.71073 Å) at 100 K. The structure of Cd-CBCD was solved with direct methods and refined by the full matrix least-squares on $F^2$ with SHELXL and Olex2 software. Anisotropic displacement parameters were applied to all non-hydrogen atoms. The hydrogen atoms were included and generated geometrically. The free solvent molecules in Cd-CBCD were highly disordered, and no satisfactory disorder model could be achieved. Thus, the PLATON/SQUEEZE routine was used to remove their diffraction contributions. CCDC-2265022, 2265023, 2245208 and 2245209 contains the supplementary crystallographic data for this paper. A summary of crystallographic data and structure-refinement parameters is given in Table S1 and S2.

**The synthesis of DCF-15 and LCF-15**: $Cd(NO_3)_2·4H_2O$ (60 mg, 0.20 mmol), D-cam (20 mg, 0.10 mmol), TPPE (25 mg 0.04 mmol), DMF (6 ml), n-Butanol (2 ml) and $H_2O$ (0.5 ml) were mixed in a 20 ml glass vial by ultrasonic agitation for 10 min and kept at 100 °C for five days. Colorless crystals were obtained with a yield of 70% (based on TPPE). Anal. Calcd (%): C, 57.60; H, 6.28; N, 8.02. Found (%): C, 57.56; H, 6.31; N, 8.04. LCF-15 was prepared by the similar process, only using L-cam to replace D-cam. The yields of DCF-15/LCF-15 were calculated to be 78.3% and 78.9% based on the amounts of TPPE ligands.

**The synthesis of DCF-16 and LCF-16**: $Zn(NO_3)_2·6H_2O$ (56 mg, 0.20 mmol), D-cam (20 mg, 0.10 mmol), TPA (25 mg, 0.1 mmol), DMF (3 ml) and DMSO (1 ml) were mixed in a 20 ml glass vial by ultrasonic agitation for 10 min and kept at 100 °C for three days. Colorless crystals were obtained with a yield of 65% (based on TPA). Anal. Calcd (%): C, 57.60; H, 6.28; N, 8.02. Found (%): C, 57.56; H, 6.31; N, 8.04. LCF-16 was prepared by the similar process, only using L-cam to replace D-cam. The yields of DCF-16/LCF-16 were calculated to be 66.7% and 67.1% based on the amounts of TPA ligands.

**The CD and CPL measurements of DCF-15/LCF-15 and DCF-16/LCF-16**

CD spectra was measured on a JASCO J-1500 spectrophotometer. The samples were prepared by using the method for infrared measurement. A mixture of DCF-15/LCF-15 or DCF-16/LCF-16 and KBr (crystal/KBr 1:400, weight ratio, total weight of 100 mg) was finely ground and pressed into a transparent pellet with a diameter of 13 mm. The pellet was directly used for measurement

of CD. The wavelength and bandwidth of the monochromator were set to 280.0 and 1.0 nm, and the time-per-point of each sampling point was 0.5 s.

CPL spectra for all samples were recorded on a JASCO CPL-300 spectrophotometer in the solid state with scanning speed. The basic mode is used. Ex slit width, Em slit width, and accumulations of 100 nm $min^{-1}$, 2000 um, 2000 um, and 2, respectively. The excitation wavelength was 360 nm and the DV values were about 0.5 V for DCF-15/LCF-15. As for DCF-16/LCF-16, expect that the excitation wavelength was 280 nm, the others are similar to that of DCF-15/LCF-15.

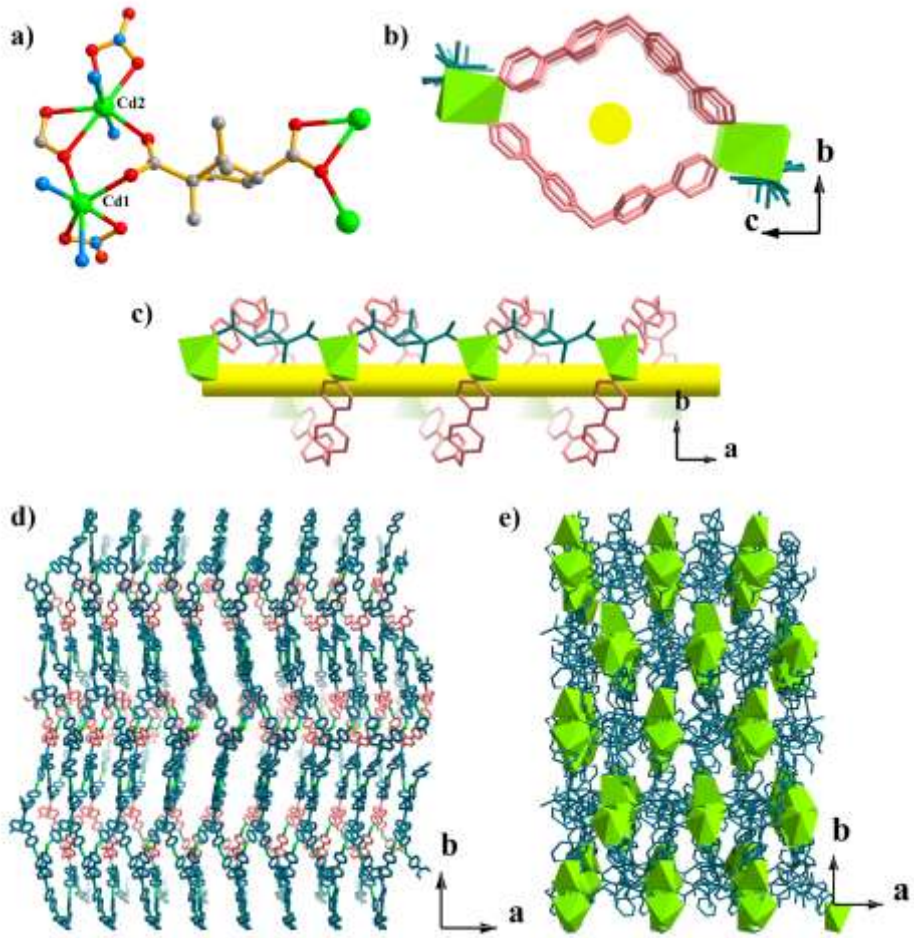


**Figure S1.** (a) The coordination model of D-cam; (b) the left-handed (*M*) helical chain assembled from $Cd^{2+}$ ions and TPPE in DCF-15 in the direction of a axis; (c) the left-handed (*M*) helical chain assembled from $Cd^{2+}$ ions and TPPE in DCF-15 in the direction of b axis; (d) the left-handed (*M*) helical chain assembled from $Cd^{2+}$ ions and TPPE in DCF-15 in the direction of c axis; (e) the 3D structure of DCF-15 in the direction of c axis.

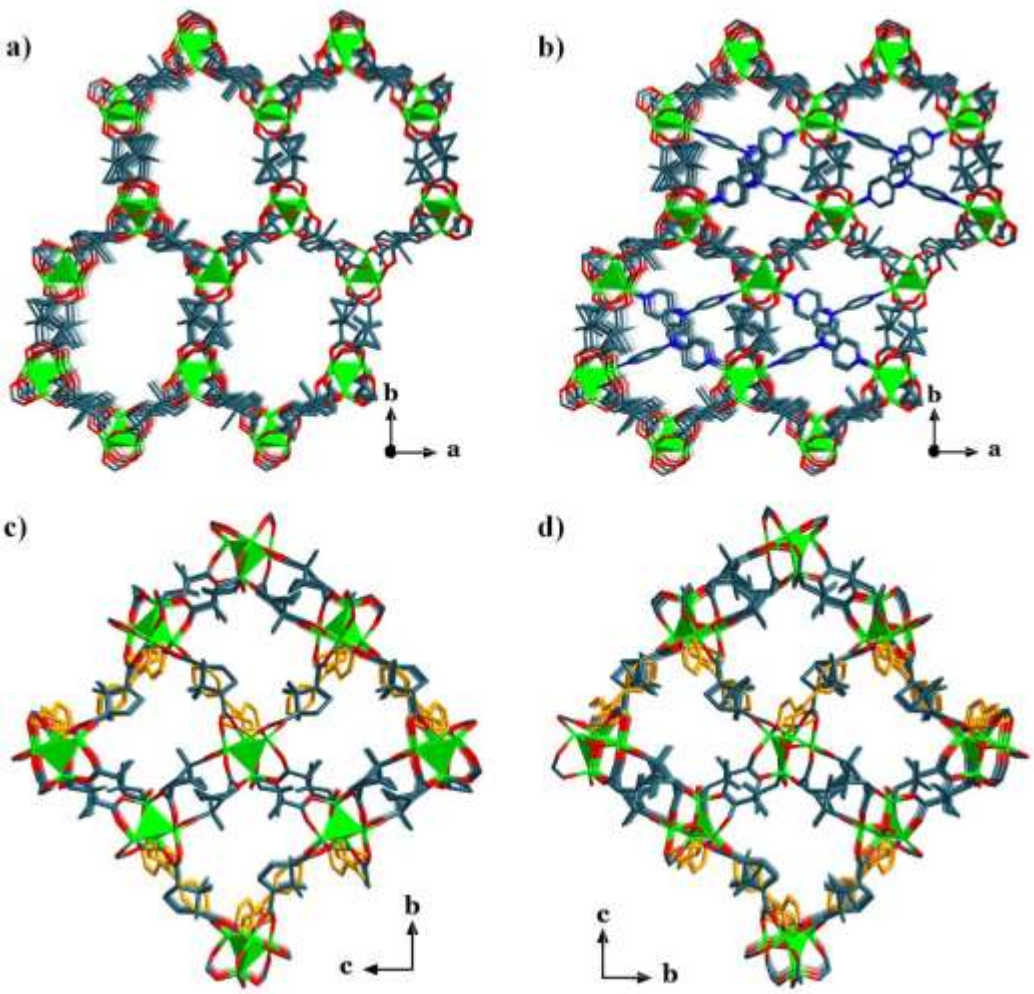


**Figure S2.** (a) The framework assembled of D-cam and $Zn^{2+}$ ions in DCF-16 in the direction of c axis; (b) the final framework of DCF-16 in the direction of c axis; (c) the final framework of DCF-16 in the direction of a axis; (d) the final framework of LCF-16 in the direction of a axis.

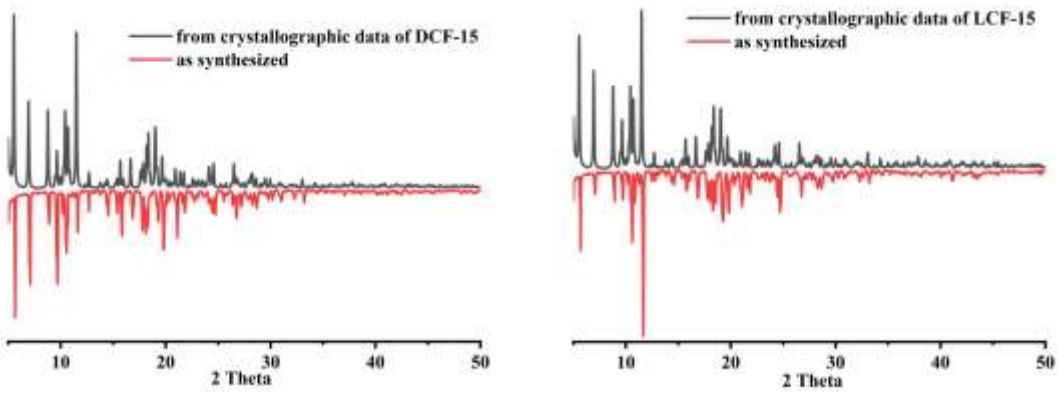


**Figure S3.** PXRD patterns of as-synthesized DCF-15 and LCF-15. All simulated patterns are calculated from the corresponding single-crystal structures. Test conditions：working voltage and current is 40 kV and 40 mA, respectively.

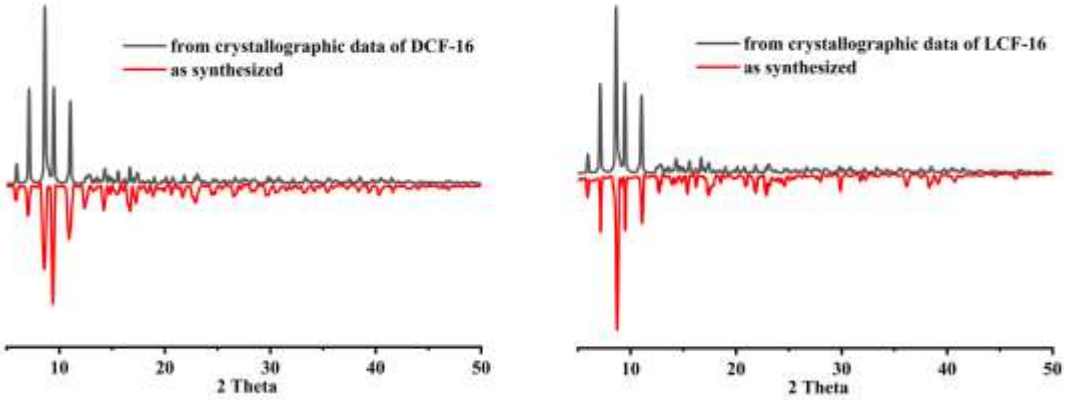


**Figure S4.** PXRD patterns of as-synthesized DCF-16 and LCF-16. All simulated patterns are calculated from the corresponding single-crystal structures. Test conditions：working voltage and current is 40 kV and 40 mA, respectively.

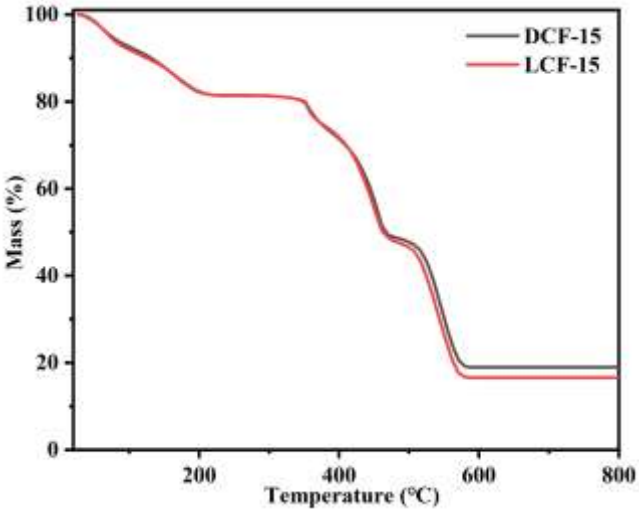


**Figure S5.** TG curves of DCF-15 and LCF-15 under air conditions.

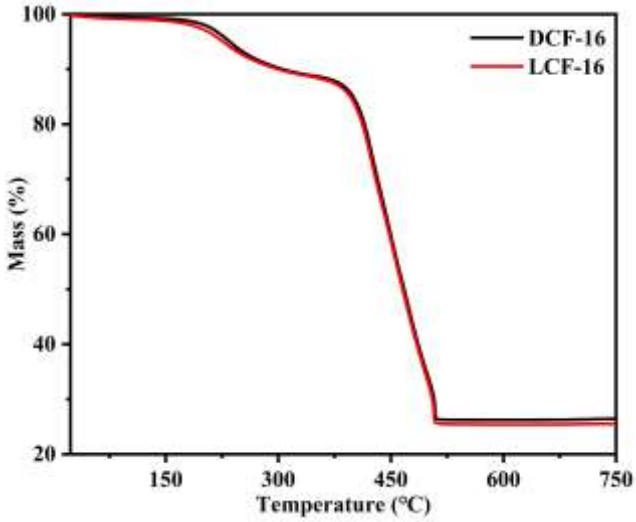


**Figure S6.** TG curves of DCF-16 and LCF-16 under air conditions.

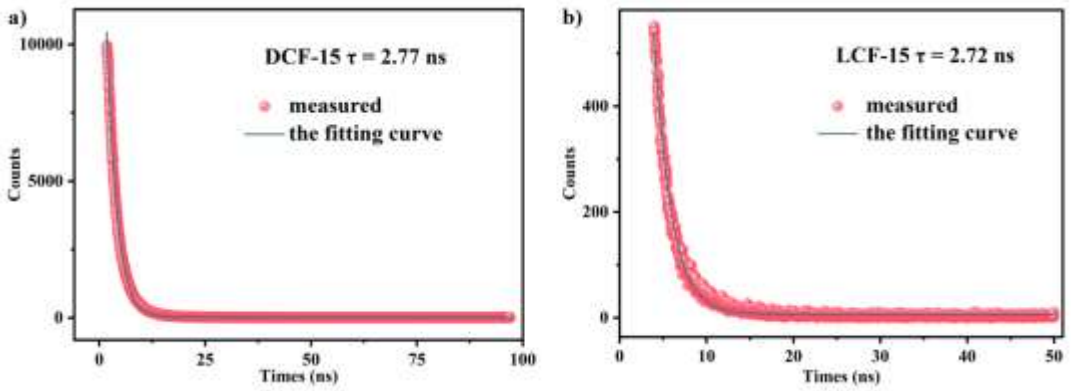


**Figure S7.** The fluorescent lifetimes of DCF-15 and LCF-15 at room conditions.

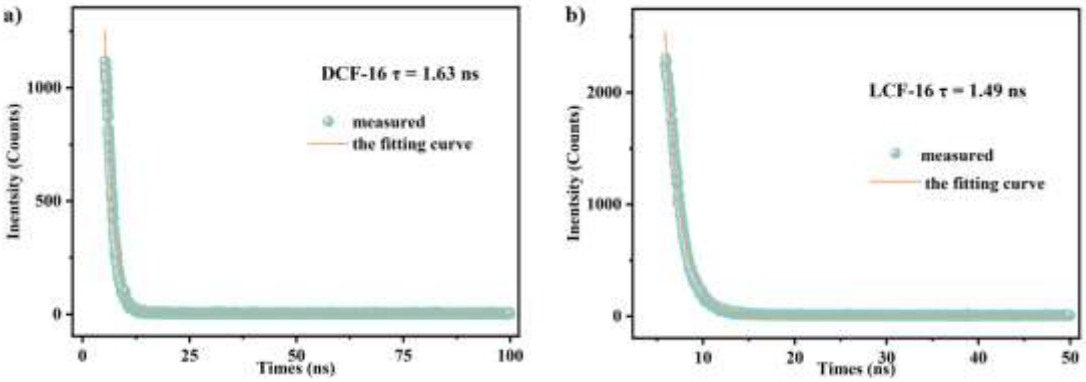


**Figure S8.** The fluorescent lifetimes of DCF-16 and LCF-16 at room conditions.

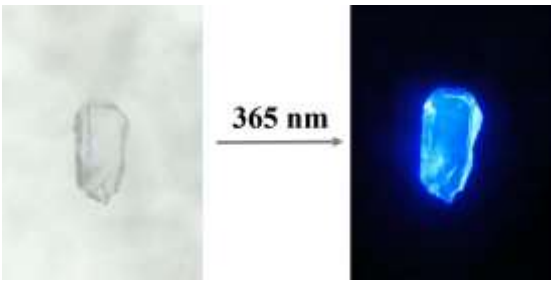


**Figure S9.** The photographs LCF-16 from fluorescence microscope.

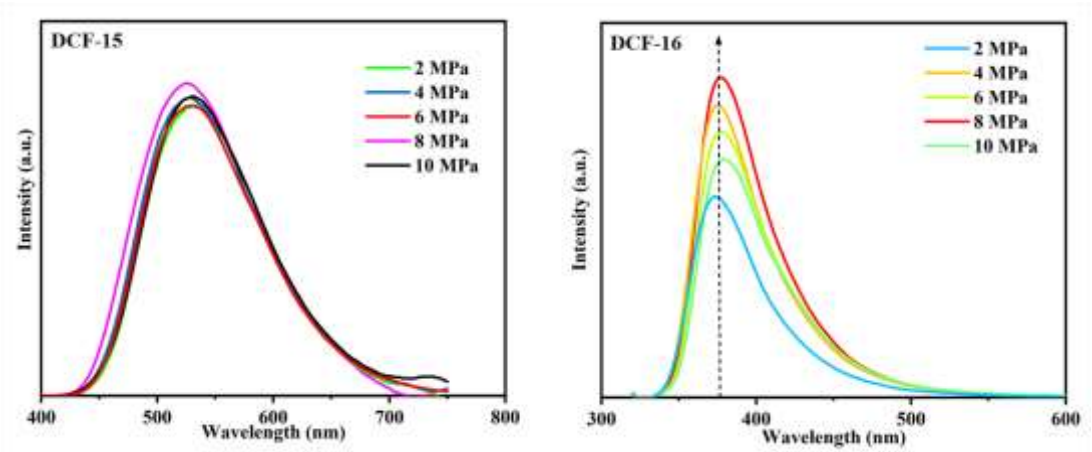


**Figure S10.** The emission behaviors of DCF-15 and DCF-16 under different pressure from 2 to 10 MPa. Using a similar method for the infrared measurement, the samples were prepared by adopting the KBr pellet.

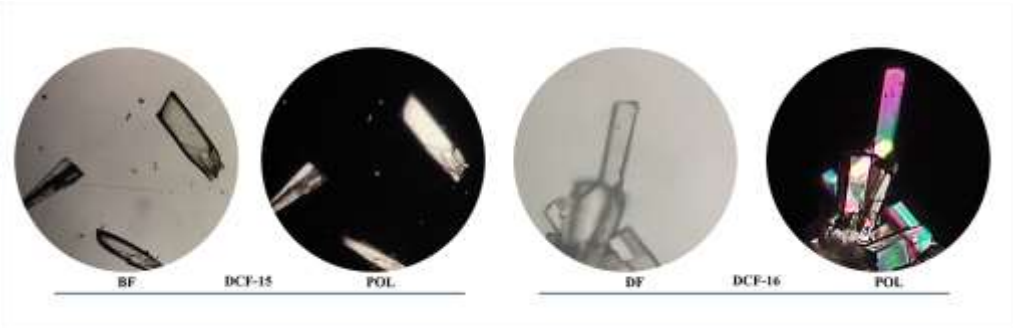


**Figure S11.** The photographs of DCF-15 and DCF-16 were obtained by upright fluorescence microscopy with 10 objective lens (Leica DM2500) under BF (bright field) and POL (polarization) mode, respectively.

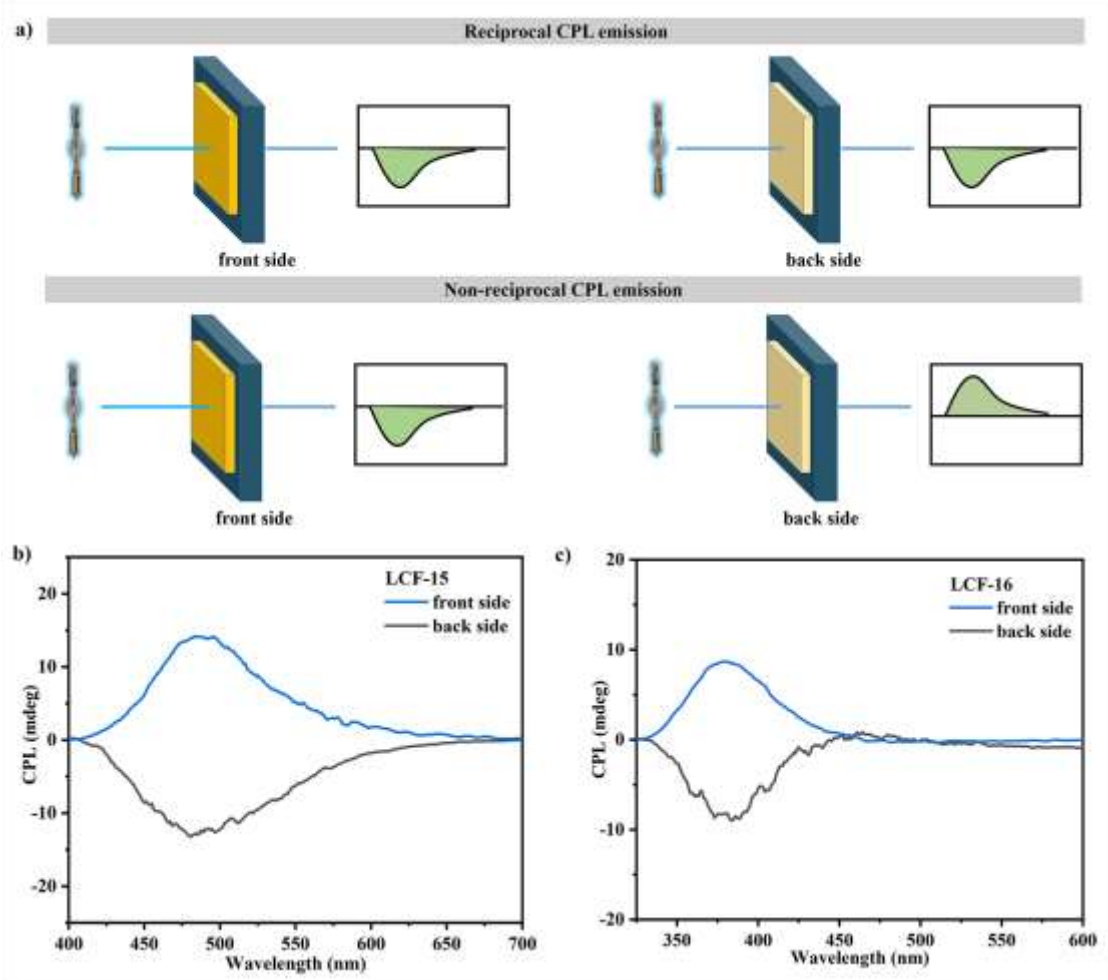


**Figure S12.** (a) Evaluation of reciprocal or non-reciprocal component of CP emission. (b,c) Non-reciprocal CPL of LCF-15 and LCF-16: CPL spectra for the front (blue line) and the back side (red line) of thin film sample.

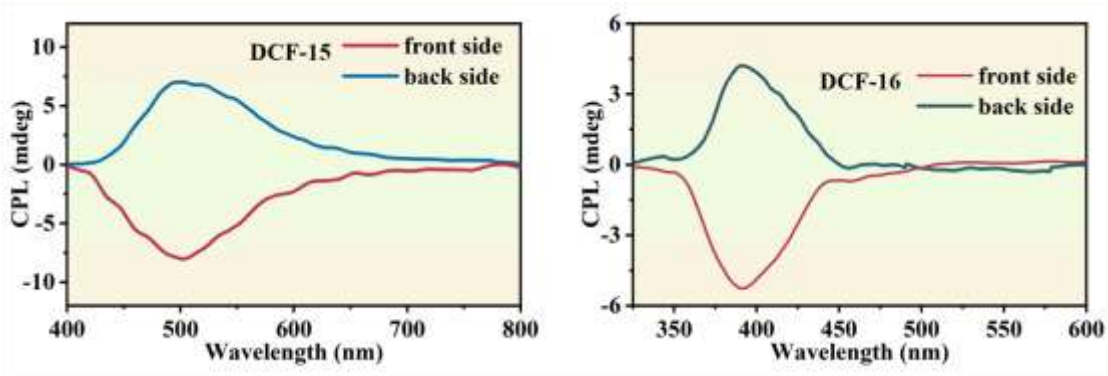


**Figure S13.** Non-reciprocal CPL of DCF-15 and DCF-16: CPL spectra for the front (blue line) and the back side (red line) of thin film sample.

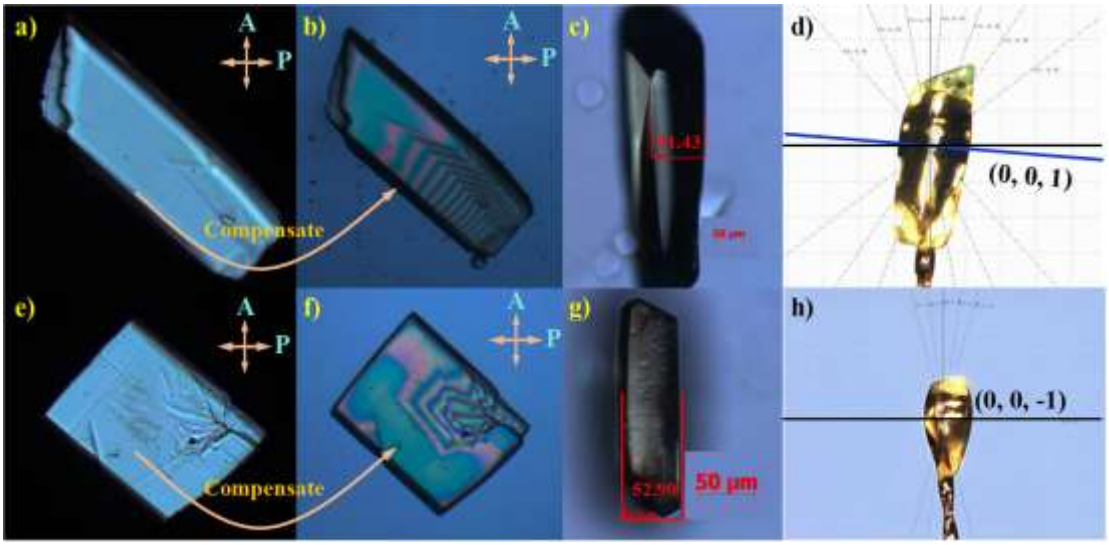


**Figure S14.** The optical properties under a polarizing microscopic, the thickness and the crystallization direction of DCF-15 and LCF-15. (a–d) DCF-15, (e-h) LCF-15.

The birefringence of DCF-15 and LCF-15 were investigated. As shown in Figure S14, in DCF-1 with a (001) crystal plane at a thickness of about 91.43 μm, an optical path difference of 11350.96 nm was obtained, indicating a birefringence of 0.124. Similarly, the (00-1) crystal plane of LCF-15 with the thickness of about 52.90 μm has a birefringence of 0.122.

The optical path difference and thickness were measured on a polarizing microscope (ZEISS Axio Scope. A1) equipped with a compensator.[1] The crystal face indices were ascertained using the single crystal orientation method on the above single crystal diffractometer.[2]

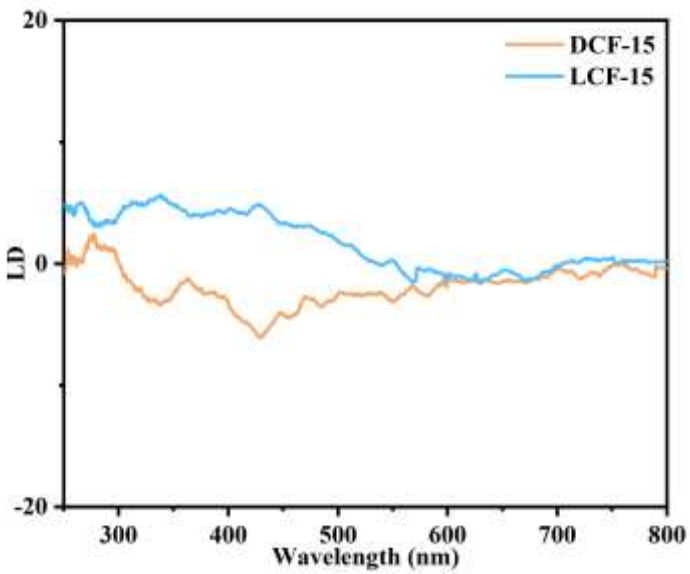


**Figure S15.** LD spectra of DCF-15/LCF-15.

**Table S1.** The crystallographic parameters of DCF-15 and LCF-15

| Identification code | DCF-15 | LCF-15 |
|---|---|---|
| Number of CCDC | 2245209 | 2245208 |
| Empirical formula | $C_{55}H_{42}N_6O_{10}Cd_2$ | $C_{56}H_{46}N_6O_{10}Cd_2$ |
| Formula weight | 1171.74 | 1187.79 |
| Temperature/K | 293 | 293 |
| Crystal system | orthorhombic | orthorhombic |
| Space group | $P2_12_12_1$ | $P2_12_12_1$ |
| a / Å | 9.6554(2) | 9.6443(3) |
| b / Å | 17.7129(4) | 17.6700(6) |
| c / Å | 36.6589(6) | 36.6530(10) |
| $\alpha$ / ° | 90 | 90 |
| $\beta$ / ° | 90 | 90 |
| $\gamma$ / ° | 90 | 90 |
| Volume/ Å$^3$ | 6269.6(2) | 6246.2(3) |
| Z | 4 | 4 |
| $\rho$calcg/cm$^3$ | 1.241 | 1.263 |
| $\mu$ / mm$^{-1}$ | 0.731 | 0.735 |
| F(000) | 2360 | 2400 |
| Crystal size/ mm$^3$ | 0.10 × 0.20 × 0.30 | 0.16 × 0.16 × 0.20 |
| Radiation | MoK$\alpha$ ($\lambda$ = 0.71073) | MoK$\alpha$ ($\lambda$ = 0.71073) |
| 2θ range for data collection/° | 6.668 to 58.928 | 6.646 to 58.504 |
| Index ranges | -8 ≤ h ≤ 13, -21 ≤ k ≤ 22, -48 ≤ l ≤ 32 | -13 ≤ h ≤ 10, -17 ≤ k ≤ 23, -24 ≤ l ≤ 49 |
| Reflections collected | 22080 | 20715 |
| Independent reflections | 12971 [$R_{int}$ = 0.0411, $R_{sigma}$ = 0.0781] | 13045 [$R_{int}$ = 0.0385, $R_{sigma}$ = 0.0852] |
| Goodness-of-fit on F$^2$ | 1.041 | 1.096 |
| Flcak | -0.04(2) | -0.050(17) |
| $R_1$ [I>2σ (I)] | $R_1$ = 0.0728, $wR_2$ = 0.2034 | $R_1$ = 0.0725, $wR_2$ = 0.2030 |
| $wR_2$ (all data) | $R_1$ = 0.0913, $wR_2$ = 0.2291 | $R_1$ = 0.0912, $wR_2$ = 0.2237 |

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = \{\Sigma[_w(|F_o|2 - |F_c|^2)^2]/\Sigma[_w(|F_o|4)]\}^{1/2}$, $w$ = 1/[\s^2^(Fo^2^)+(0.1391P)^2^+0.3555P] where P = (Fo^2^+2Fc^2^)/3 for DCF-15.
$W$ = 1/[\s^2^(Fo^2^)+(0.1212P)^2^+0.7181P] where P = (Fo^2^+2Fc^2^)/3 for LCF-15.

**Table S2. The crystallographic parameters of DCF-16 and LCF-16**

| Identification code | DCF-16 | LCF-16 |
|---|---|---|
| Number of CCDC | 2265022 | 2265023 |
| Empirical formula | $C_{45}H_{39}N_4O_{13}Zn_4$ | $C_{45}H_{43}N_4O_{13}Zn_4$ |
| Formula weight | 1105.36 | 1100.24 |
| Temperature/K | 293 | 293 |
| Crystal system | orthorhombic | orthorhombic |
| Space group | $P2_12_12_1$ | $P2_12_12_1$ |
| a / Å | 13.6565(3) | 13.6827(4) |
| b / Å | 14.1762(4) | 14.1989(7) |
| c / Å | 29.6834(9) | 29.7700(14) |
| $\alpha$ / ° | 90 | 90 |
| $\beta$ / ° | 90 | 90 |
| $\gamma$ / ° | 90 | 90 |
| Volume/ $Å^3$ | 5746.6(3) | 5783.7(4) |
| Z | 4 | 4 |
| $\rho$calcg/$cm^3$ | 1.263 | 1.264 |
| $\mu$ / $mm^{-1}$ | 1.704 | 1.693 |
| F(000) | 2305 | 2224 |
| Crystal size/ $mm^3$ | 0.12 × 0.13 × 0.17 | 0.12 × 0.13 × 0.19 |
| Radiation | MoK$\alpha$ ($\lambda$ = 0.71073) | MoK$\alpha$ ($\lambda$ = 0.71073) |
| 2θ range for data collection/° | 6.62 to 58.498 | 6.752 to 58.380 |
| Index ranges | $-11 \leq h \leq 18$, $-38 \leq k \leq 19$, $-19 \leq l \leq 12$ | $-11 \leq h \leq 18$, $-19 \leq k \leq 12$, $-38 \leq l \leq 40$ |
| Reflections collected | 19296 | 22617 |
| Independent reflections | 10496 [$R_{int}$ = 0.0296, $R_{sigma}$ = 0.0546] | 12140 [$R_{int}$ = 0.0344, $R_{sigma}$ = 0.0637] |
| Goodness-of-fit on $F^2$ | 1.027 | 1.032 |
| Flcak | 0.017(7) | 0.017(8) |
| $R_1$ [I>2σ (I)] | $R_1$ = 0.0532, $wR_2$ = 0.1473 | $R_1$ = 0.0527, $wR_2$ = 0.1325 |
| $wR_2$ (all data) | $R_1$ = 0.0662, $wR_2$ = 0.1565 | $R_1$ = 0.0663, $wR_2$ = 0.1413 |

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = \{\Sigma[_w(|F_o|2 - |F_c|^2)^2]/\Sigma[_w(|F_o|4)]\}^{1/2}$, $w$ = 1/[\s^2^(Fo^2^)+(0.0982P)^2^+1.9486P] where P=(Fo^2^+2Fc^2^)/3 for DCF-16.
$w$ = 1/[\s^2^(Fo^2^)+(0.0766P)^2^+2.2395P] where P=(Fo^2^+2Fc^2^)/3 for LCF-16.

## REFERENCES


1. H. Sha, R. Su, Z. Xiong, Z. Wang, P. Shan, C. He, X. Yang, X. Long, Adv. Optical Mater. 2021, 9, 2100080.
2. X. Xu, F. Wang, W. Xu, H. Lu, L. Lv, H. Sha, X. Jiang, S. Wu, S. Wang, Adv. Sci. 2023, 10, 2206833.