

Facile Synthesis of Homochiral Compounds Integrating Circularly Polarized Luminescence and Two-Photon Excited Fluorescence

Wen-Ting Deng,^{+a} Hang Qu,^{+a} Zhe-Yu Huang,^a Lin Shi,^b Zhi-Yong Tang,^b Xiao-Yu Cao,^{*a} Jun Tao^{*ac}

^aState Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), Xiamen University, Xiamen 361005, P. R. China.

^bCAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, P. R. China.

^cKey Laboratory of Cluster Science of Ministry of Education, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, P. R. China.

+ These authors contribute equally to this work.

- 1. Instruments and Methods**
- 2. Syntheses**
- 3. Additional Tables and Figures**
- 4. Reference**

1. Instruments and Methods

(*R*)-2,2'-Bis-(methoxymethoxy)-6,6'-di(4-pyridyl)-1,1'-binaphthyl (abbr. *R-L*) and (*S*)-2,2'-Bis-(methoxymethoxy)-6,6'-di(4-pyridyl)-1,1'-binaphthyl (abbr. *S-L*) were synthesized according to references.^{1,2} Cadmium(II) nitrate and organic solvents were used without further purification.

IR spectra were recorded with KBr pellets on an AVATAR FT-IR 360 spectrophotometer (4000-500 cm⁻¹). Elemental analyses of C, H and N were performed on Vario EL III analyzer. High-resolution mass spectra (HRMS) were recorded on a Bruker En Apex Ultra 7.0T FT-MS mass spectrometer. Absorption spectra were recorded on Shimadzu UV2550 UV-vis spectrometer. ¹H- and ¹³C-NMR spectra were recorded on a Bruker AVIII-500 spectrometer (500 and 125 MHz, respectively) at 298 K. Deuterium reagents were DMSO-*d*₆ and CDCl₃. Chemical shifts were reported in ppm. Coupling constants (J values) were reported in Hertz. Internal quantum efficiency (IQE) was measured by FLS980 fluorescence spectrometer with a BaSO₄-base integrating sphere of Edinburgh instruments. In the QE measurement, the monochromatic light at 360nm was selected as the excitation source. The photoluminescence quantum efficiencies (PLQEs) were calculated by the equation: $\eta_{QE} = I_s / (E_R - E_S)$, in which I_s represents the luminescence emission spectrum of the sample, E_R is the spectrum of the excitation light from the empty integrated sphere (without the sample), and E_S is the excitation spectrum for exciting the sample.^{3,4} Fluorescence emission spectra were obtained by Hitachi F-7000 spectrometer. 5 mg crystal samples were placed in the sample pool and then sealed for testing. Circular polarization fluorescence (CPL) were carried out on JASCO CPL-200, and 5 mg crystalline samples were placed between two 1 cm² quartz chips and then sealed for testing. SHG experiments on *S-L*-Cd, *R-L*-Cd and KDP (particle size range of 72-100 μ m) were performed at 298 K by the Kurtz-Perry method³ with a Q-switched Nd:YAG laser at a wavelength of 1064 nm. The measured NLO coefficients were compared with that of KH₂PO₄ crystal ($\chi^{(2)}$ KDP = 0.39 pm/V). The circular dichroism (CD) spectra of

R-L and *S-L* in CHCl₃ solution were measured by using JASCO J-810, while solid-state samples (*R-L*-Cd and *S-L*-Cd) were prepared with compound/KBr ratio of 1:400. Two-photon images were taken in positive multi photon laser confocal system of Olympus FV1000MPE-B by 10x water mirror, using the LD405 fs semiconductor solid-state 800 nm laser, 5 mg crystalline samples were placed between two 1 cm² quartz chips and then sealed for testing.

Slow diffusion of diethyl ether into the solution (solvent: THF) gave colourless block crystals of compound *R/S-L*-Cd in two days.

Low-temperature X-ray diffraction data were collected on an Agilent SuperNova diffractometer with Cu-*K*α radiation ($\lambda = 1.54184 \text{ \AA}$) micro-focus X-ray sources. The raw data were collected and reduced by CrysAlisPro software. The *R/S-L*-Cd structures were solved by the SHELXT⁵ with Intrinsic Phasing and refined on F^2 by full-matrix least-squares methods with the SHELXL⁵ and OLEX2⁶ was used as GUI. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions using the riding model and refined isotropically. The instructions AFIX 23, AFIX 33 and AFIX 43 were used for the hydrogen atoms on the secondary -CH₂-, terminal-CH₃ groups and the aromatic C-H, respectively. A satisfactory disorder model for the solvent molecules (THF and Et₂O molecules) was not found, therefore the OLEX2 Solvent Mask routine (similar to PLATON/SQUEEZE) was used to mask out the disordered density.

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre and the deposition numbers are CCDC 1891270 and 1863298. The crystallographic data are listed in Tables S1. Selected bond distances and bond angles are listed in Table S2.

2. Syntheses

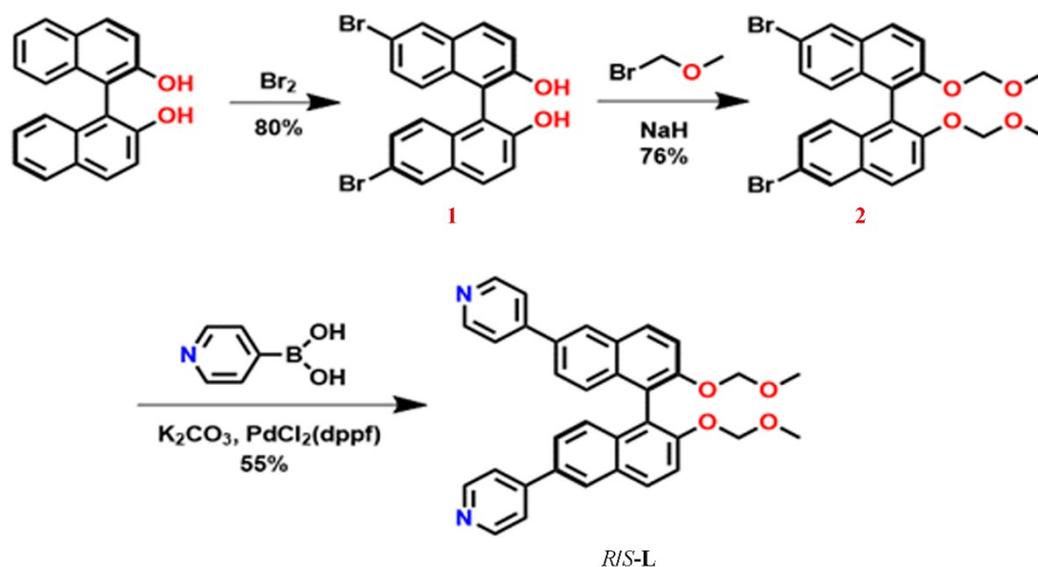


Figure S1. Synthetic procedure for *R*- and *S*-L¹.

Synthesis of 1: *R*- or *S*-BN (2.8 g, 10 mmol) was added into chloroform (60 mL) and stirred until dissolved. The mixture was cooled to 0 °C and bromine (1.7 mL) in chloroform (10 mL) was added slowly into the solution. After 24 hours, the reaction was quenched with saturated sodium thiosulfate aqueous solution (50 mL). The organic layer was washed with saturated sodium chloride solution and deionized water, and dried over anhydrous sodium sulfate. After evaporation of solvents, the solid was recrystallized from methanol to give *R*- or *S*-**1** as a white powder (3.5 g, yield 80%). ¹H NMR (500 MHz, CDCl₃): δ 8.05 (d, *J* = 1.8 Hz, 2H), 7.90 (d, *J* = 9.0 Hz, 2H), 7.40 (d, *J* = 9.0 Hz, 2H), 7.37 (dd, *J* = 9.0, 2.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 152.98, 130.87, 130.71, 130.45, 125.87, 118.98, 118.02, 110.63. HRMS (*m/z*): [M+Na]⁺ calcd for [C₂₀H₁₂O₂Br₂Na]⁺ 466.9081, found 466.9085.

Synthesis of 2: NaH (0.5 g, 12.5 mmol) was added into dry THF (100 mL) in a 250 mL round bottom flask at 0 °C under nitrogen atmosphere. To the mixture with stirring a solution of **1** (2.4 g, 5.6 mmol) in THF (25 mL) was dropwise added. The mixture was

then stirred at 0°C for 1 h, and allowed to warm up to room temperature for 15 min. The mixture was re-cooled to 0°C, and bromomethyl methyl ether (1.61 g, 13 mmol) was dropwise added. The reaction mixture was warmed to room temperature and stirred for 4.5 h. Saturated aqueous NH₄Cl (25 mL) solution was added to the flask, and the mixture was extracted with CH₂Cl₂ (3×50 mL). The organic layers were combined, washed with brine and dried over Na₂SO₄. Further purification by silica gel column chromatography (ethyl acetate/petroleum = 1:10, v/v) produced white powder of **2** (2.2 g, 76% yield). ¹H NMR (500 MHz, CDCl₃): δ 8.03 (s, 2H), 7.88–7.84 (m, 2H), 7.59 (dd, J = 9.1, 2.2 Hz, 2H), 7.29 (d, J = 9.0 Hz, 2H), 6.98 (dd, J = 9.0, 2.5 Hz, 2H), 5.10–5.06 (m, 2H), 4.98 (q, J = 2.1 Hz, 2H), 3.18–3.14 (m, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 152.98, 132.39, 131.89, 130.86, 130.69, 130.59, 130.45, 129.88, 129.72, 128.71, 127.13, 125.88, 120.71, 118.99, 118.05, 118.01, 110.67, 99.98, 95.02, 55.93. HRMS (*m/z*): [M+Na]⁺ calcd for [C₂₄H₂₀O₄Br₂Na]⁺ 554.9606, found 554.9612.

Synthesis of L: Pyridin-4-ylboronic acid (4.91 g, 40 mmol), K₂CO₃ (5.51 g, 40 mmol), and PdCl₂(dppf) (100 mg, 0.137 mmol) were added to a THF/H₂O (100 mL, 5:1, v/v) solution containing **2** (4.2 g, 8 mmol). The reaction mixture was heated to reflux for 72 h and filtered after cooling to room temperature. After the filtrate was concentrated, water (30 mL) was added, and the mixture was extracted with ethyl acetate (3×50 mL). The combined organic phase was washed with water (3×50 mL) and brine (50 mL), dried over anhydrous Na₂SO₄, and then evaporated to afford pure brown solid, which was further purified by silica gel column chromatography (ethyl acetate/petroleum/trimethylamine = 6:3:1, v/v/v) to give **L** (2.31 g, 55% yield).

R-L: ¹H NMR (500 MHz, DMSO): δ 8.65 (d, J = 4.6 Hz, 4H), 8.48 (s, 2H), 8.21 (d, J = 9.1 Hz, 2H), 7.80 (d, J = 4.5 Hz, 4H), 7.72 (d, J = 9.1 Hz, 4H), 7.11 (d, J = 8.9 Hz, 2H), 5.16 (dd, J = 23.9, 6.9 Hz, 4H), 3.10 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 153.53, 150.29, 148.10, 134.09, 133.58, 130.22, 129.85, 126.52, 126.43, 125.02, 121.59, 120.72, 117.87, 95.08, 55.96. HRMS (*m/z*): [M+Na]⁺ calcd for [C₃₄H₂₈N₂O₄Na]⁺ 551.1947, found 551.1952. Elemental Calc. for C₃₄H₂₈N₂O₄

(%): C, 77.25; H, 5.34; N, 5.30. Found: C, 77.27; H, 5.52; N, 5.33.

S-L: ^1H NMR (500 MHz, CDCl_3): δ 8.65 (d, $J = 5.6$ Hz, 4H), 8.18 (s, 2H), 8.06 (d, $J = 9.1$ Hz, 2H), 7.67 (d, $J = 9.1$ Hz, 2H), 7.58 (d, $J = 5.7$ Hz, 2H), 7.51 (d, $J = 8.8$ Hz, 4H), 7.28 (d, $J = 8.8$ Hz, 2H), 5.08 (dd, $J = 43.6, 6.9$ Hz, 4H), 3.20 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 153.53, 150.29, 148.10, 134.09, 133.58, 130.22, 129.85, 126.52, 126.43, 125.02, 121.59, 120.72, 117.87, 95.08, 55.96. HRMS (m/z): $[\text{M}+\text{Na}]^+$ calcd for $[\text{C}_{34}\text{H}_{28}\text{N}_2\text{O}_4\text{Na}]^+$ 551.1947, found 551.1942. Elemental Calc. for $\text{C}_{34}\text{H}_{28}\text{N}_2\text{O}_4$ (%): C, 77.25; H, 5.34; N, 5.30. Found: C, 77.29; H, 5.63; N, 5.34.

Syntheses of $[\text{Cd}(\text{NO}_3)_2(\text{R-L})_2]\cdot\text{THF}$ (*R-L*-Cd) and $[\text{Cd}(\text{NO}_3)_2(\text{S-L})_2]\cdot\text{THF}$ (*S-L*-Cd)

A mixture of $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (0.0308 g, 0.1 mmol) and *R-L* (0.0265 g, 0.05 mmol) in tetrahydrofuran (10 mL) was stirred for 20 minutes, then the formed precipitate was filtered off. Slow diffusion of diethyl ether into the solution gave colorless block crystals of compound *R-L*-Cd in two days. Compound *S-L*-Cd was synthesized by the same method except the use of *S-L*. Yield: ~72% based on cadmium(II) nitrate. Compound *R-L*-Cd: Elemental Calc. for $\text{C}_{72}\text{H}_{64}\text{CdN}_6\text{O}_{15}$ (%): C, 63.32; H, 4.72; N, 6.15. Found: C, 63.25; H, 4.25; N, 6.22.

3. Additional Tables and Figures

Table S1. Crystal data and structural refinements for compounds *R-L*-Cd and *S-L*-Cd

Compound	<i>R-L</i> -Cd	<i>S-L</i> -Cd
Empirical formula	$\text{C}_{72}\text{H}_{64}\text{CdN}_6\text{O}_{15}$	$\text{C}_{72}\text{H}_{64}\text{CdN}_6\text{O}_{15}$
Formula mass	1365.69	1365.69
Temperature (K)	100.01(10)	100.01(10)
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> 1	<i>P</i> 1
<i>a</i> (Å)	10.1560(3)	10.1547(5)
<i>b</i> (Å)	12.1202(3)	12.0754(5)

c (Å)	15.9290(4)	15.9307(6)
α (deg)	110.664(2)	110.603(4)
β (deg)	90.320(2)	90.185(4)
γ (deg)	93.114(2)	92.969(4)
V (Å ³)	1831.25(9)	1825.58(14)
Z	1	1
D_c (g·m ⁻³)	1.238	1.242
F (000)	706.0	706.0
Crystal size (mm)	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 9, -18 ≤ l ≤ 19	-12 ≤ h ≤ 10, -12 ≤ k ≤ 14, -18 ≤ l ≤ 19
θ min, max (deg)	7.81, 143.102	7.834, 143.392
Goodness-of-fit on F^2	1.030	1.042
Final R indice [$I > 2\sigma(I)$]	$R1 = 0.0436$, $wR2 = 0.1147$	$R1 = 0.0487$, $wR2 = 0.1237$
R indices (all data)	$R1 = 0.0439$, $wR2 = 0.1153$	$R1 = 0.0493$, $wR2 = 0.1240$
Largest diff. peak and hole / e·Å ⁻³	1.03 and -1.01	1.31 and -0.90
Flack parameter	0.050(5)	0.035(6)
CCDC	1891270	1863298

Table S2. Selected bond distances (Å) and angles (°) for compounds R -L-Cd and S -L-Cd

Compound R -L-Cd			
Cd1-N1	2.315(6)	Cd1-N2	2.319 (6)
Cd1-N3A	2.375(5)	Cd1-N4B	2.399(5)
Cd1-O1	2.346(5)	Cd1-O2	2.466(5)
Cd1-O3	2.619(6)	N1-Cd1-N2	175.2(2)
N1-Cd1-N3A	86.9(2)	N1-Cd1-N4B	92.0(2)
N2-Cd1-N3A	97.7(2)	N2-Cd1-N4B	84.1(2)
N3A-Cd1-N4B	160.88(17)	N1-Cd1-O1	89.8 (2)

N1-Cd1-O2	95.3(2)	N1-Cd1-O3	86.8(2)
N2-Cd1-O1	92.1(2)	N2-Cd1-O2	84.49(19)
N2-Cd1-O3	89.4(2)	N3A-Cd1-O2	76.05(19)
N3A-Cd1-O3	124.64 (19)	N4B-Cd1-O2	123.03(19)
N4B-Cd1-O3	74.30 (19)	O1-Cd1-O2	158.67(15)
O1-Cd1-O3	151.27(17)	O1-Cd1-N3A	83.58(19)
O1-Cd1-N4B	77.32(19)	O2-Cd1-O3	49.97(17)

Compound *S*-L-Cd

Cd1-N1	2.310(7)	Cd1-N2	2.341(7)
Cd1-N5A	2.385(5)	Cd1-N6B	2.402(5)
Cd1-O1	2.350(6)	Cd1-O2	2.627(7)
Cd1-O3	2.458(6)	N1-Cd1-N2	176.6(3)
N1-Cd1-N5A	92.7(2)	N1-Cd1-N6B	85.5(2)
N2-Cd1-N5A	84.8(2)	N2-Cd1-N6B	97.5(2)
N5-Cd1-N6	160.66(17)	N2-Cd1-O1	91.7(2)
N2-Cd1-O2	89.3(2)	N2-Cd1-O3	84.3(2)
N1-Cd1-O2	87.9(2)	N1-Cd1-O1	90.0(2)
N1-Cd1-O3	95.2(2)	N5A-Cd1-O2	74.9(2)
N5A-Cd1-O3	123.7(2)	N6B-Cd1-O2	124.2(2)
N6B-Cd1-O3	75.7(2)	O1-Cd1-O2	151.99(18)
O1-Cd1-O3	157.92(17)	O2-Cd1-O3	49.92(18)
O1-Cd1-N5A	77.4(2)	O1-Cd1-N6B	83.4(2)

Symmetry codes: A) $1+x, 1+y, 1+z$; B) $-1+x, -1+y, -1+z$

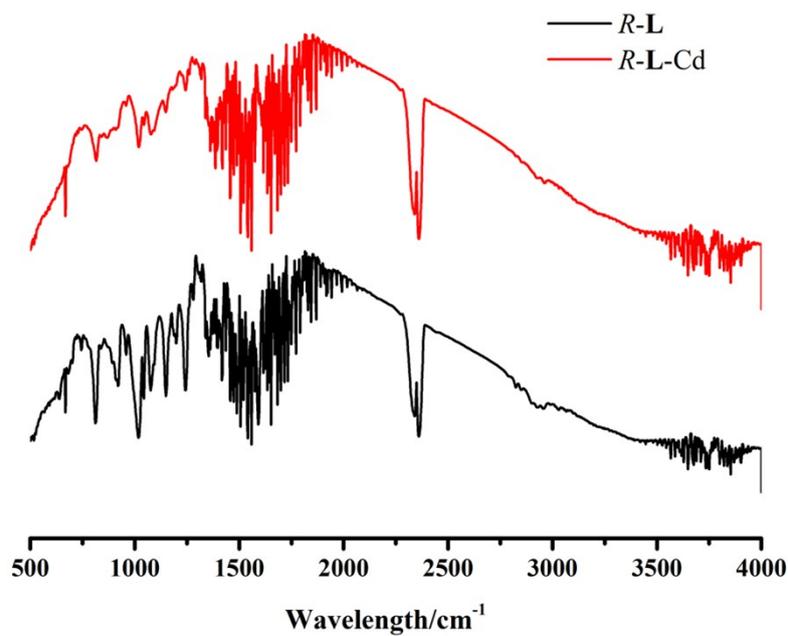


Figure S2. IR spectra of *R-L* and *R-L-Cd*.

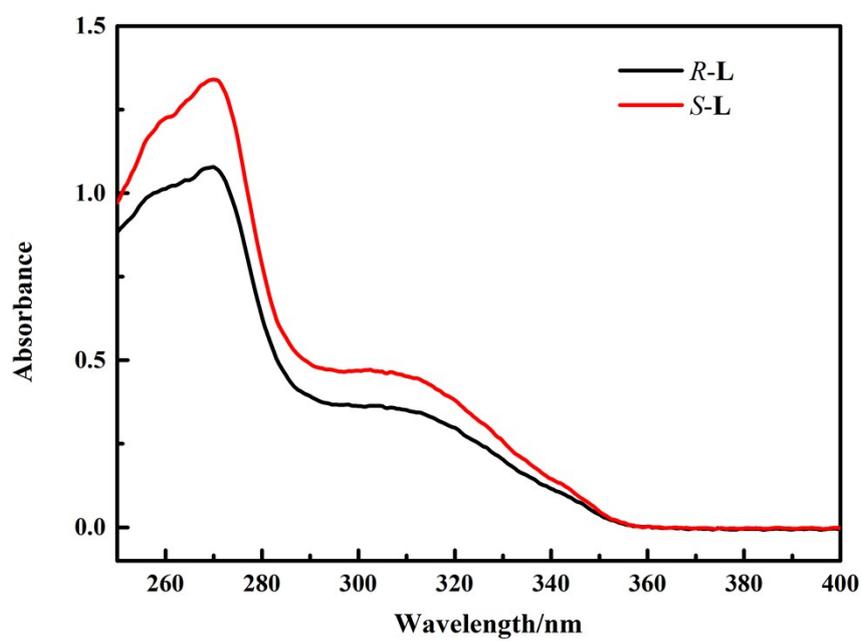


Figure S3. UV-visible spectra of *R-L* and *S-L* in CHCl₃ solution.

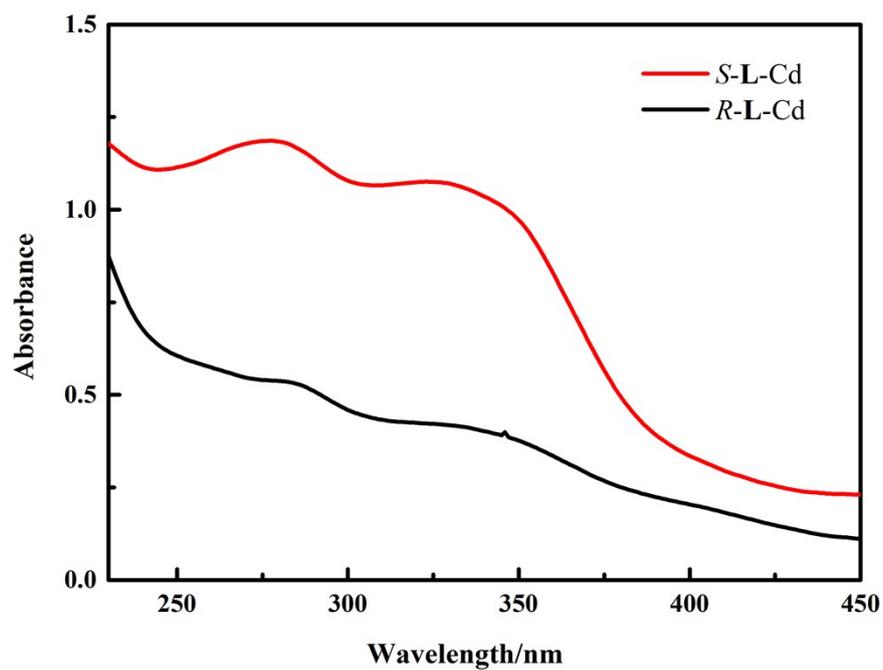


Figure S4. UV-visible spectra of *R-L-Cd* and *S-L-Cd* with solid pellets.

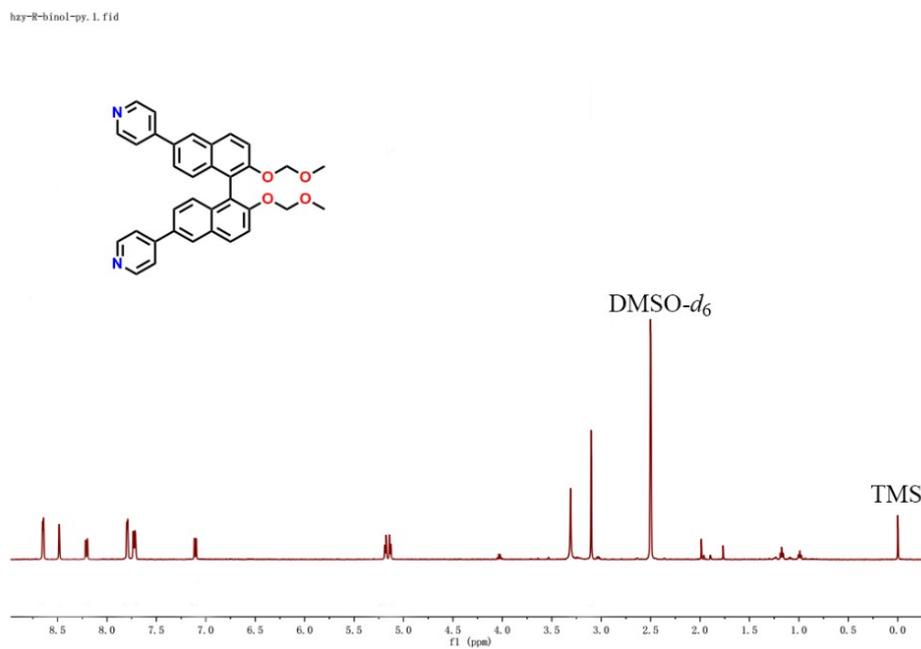


Figure S5. Initial ¹H-NMR spectrum of *R-L* (500 MHz).

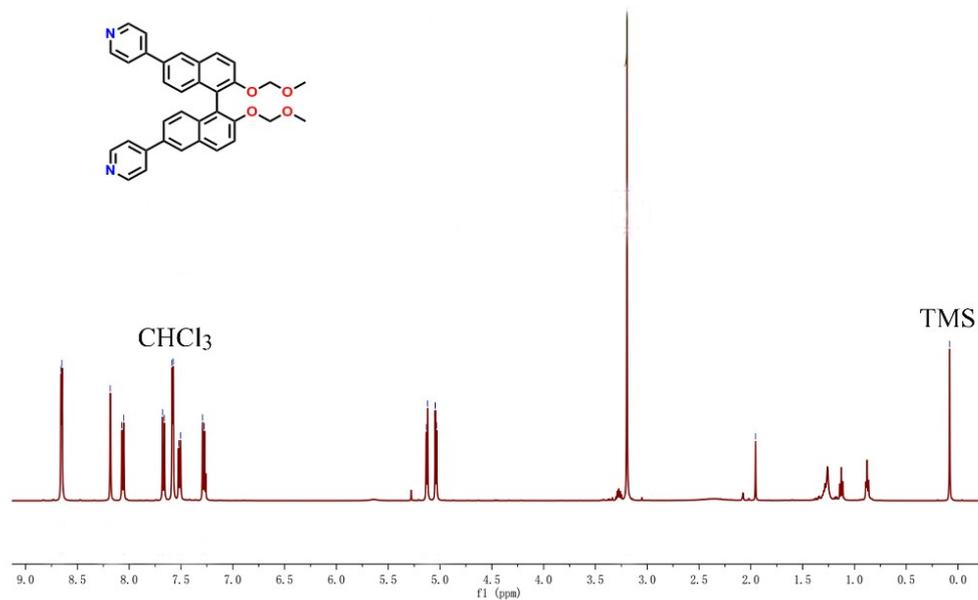


Figure S6. Initial ¹H-NMR spectrum of *S-L* (500 MHz).

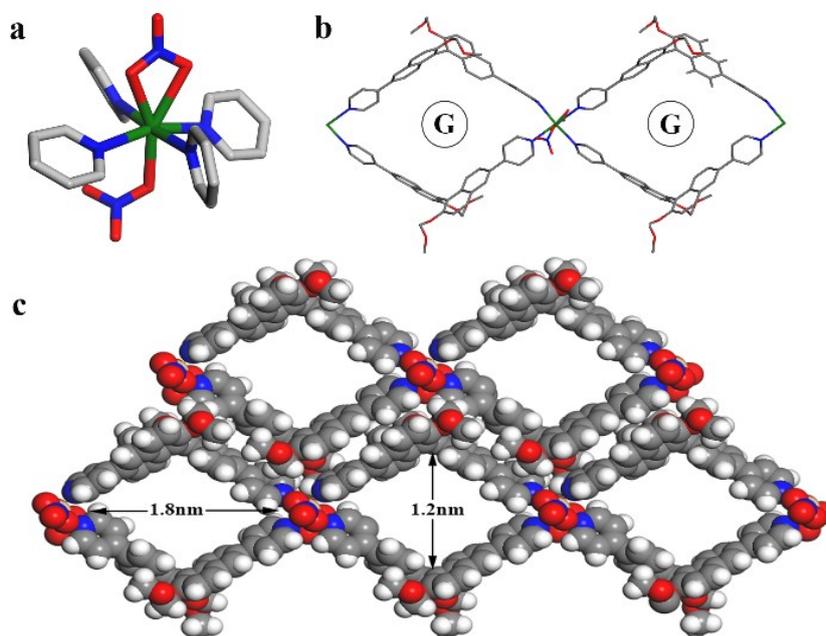


Figure S7. The coordination environment around Cd(II) ion in *R-L-Cd* and *S-L-Cd*.

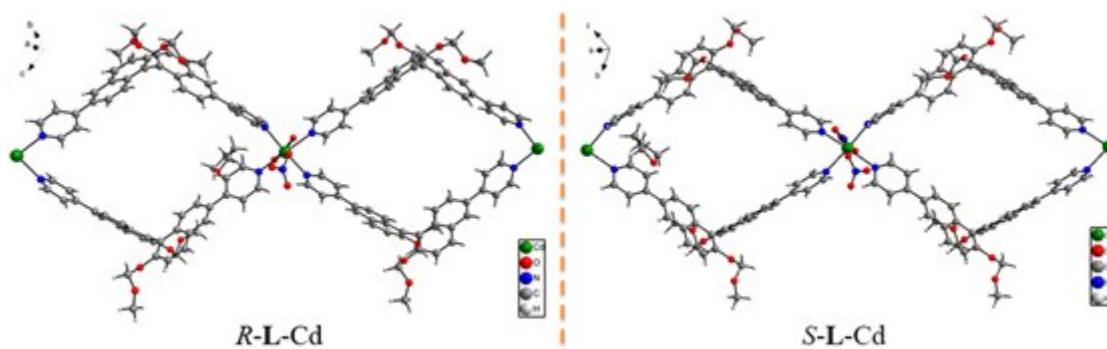


Figure S8. The crystal structures of *R*-L-Cd (left) and its enantiomer *S*-L-Cd (right).

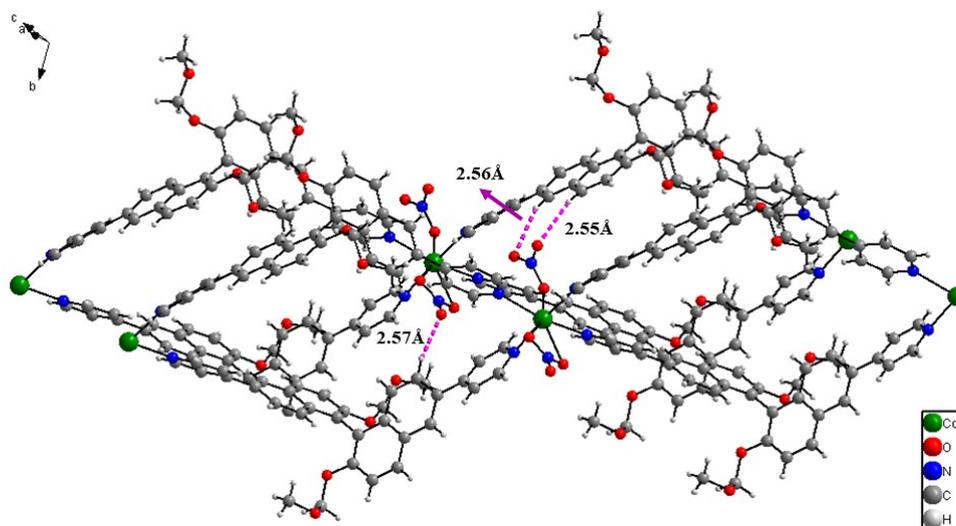


Figure S9. The hydrogen bonds in (*R/S*)-L-Cd.

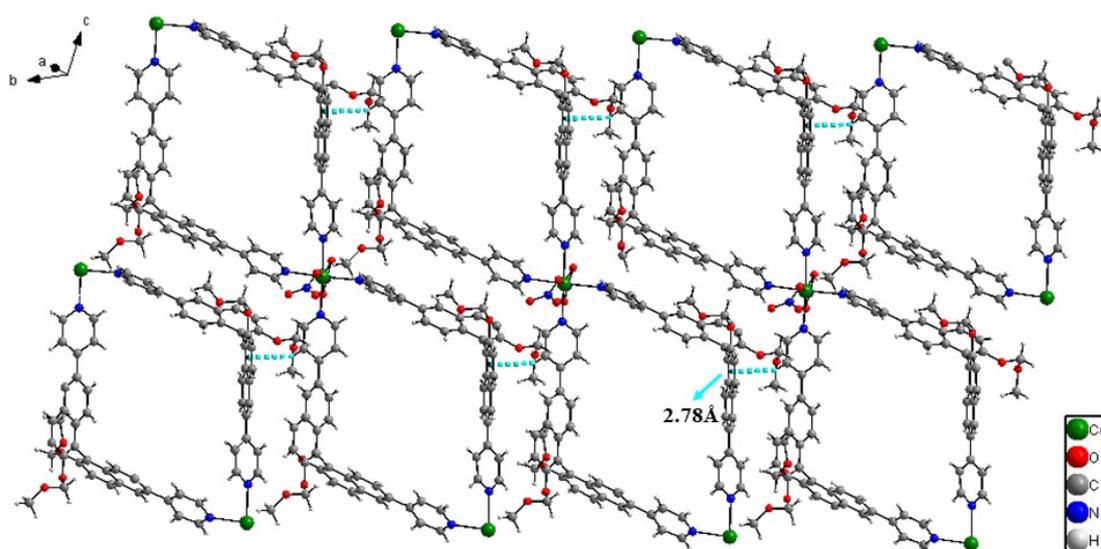


Figure S10. The C-H... π interactions in (*R/S*)-L-Cd.

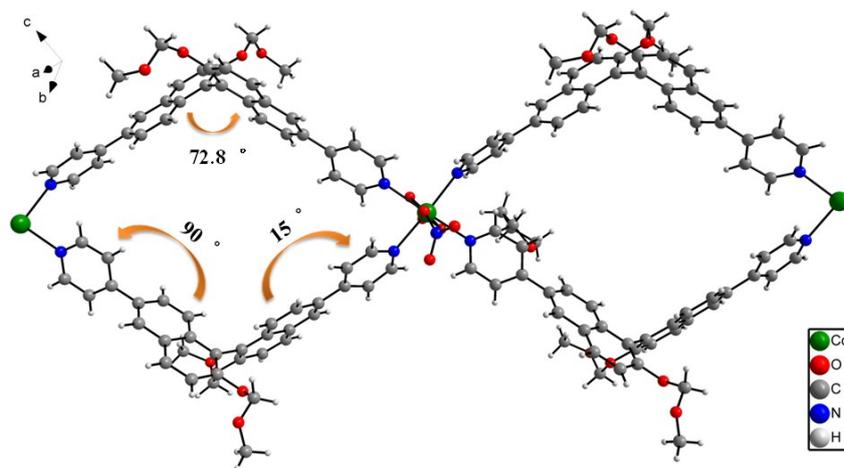


Figure S11. The torsion angles between naphthalene rings and torsion angles between pyridine and naphthalene rings.

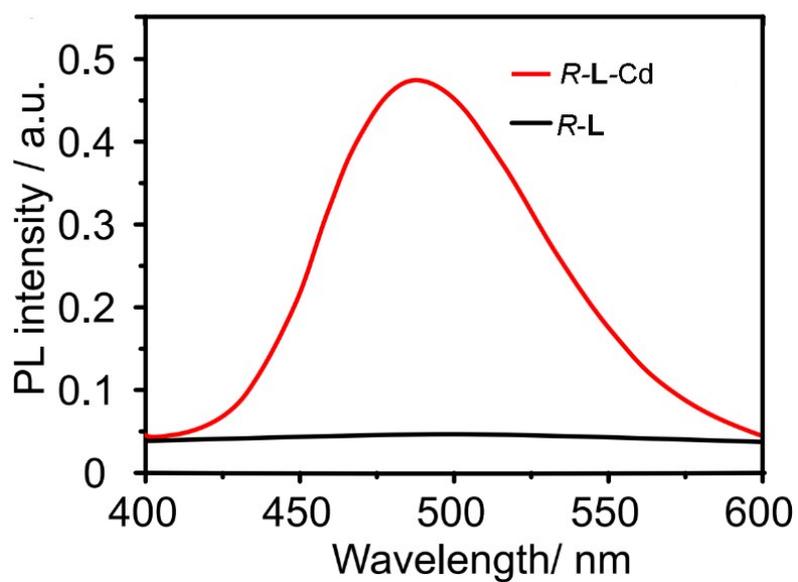


Figure S12. Single-photon excited fluorescent spectra of *R-L* (black) and *R-L-Cd* (red), excited at 360 nm

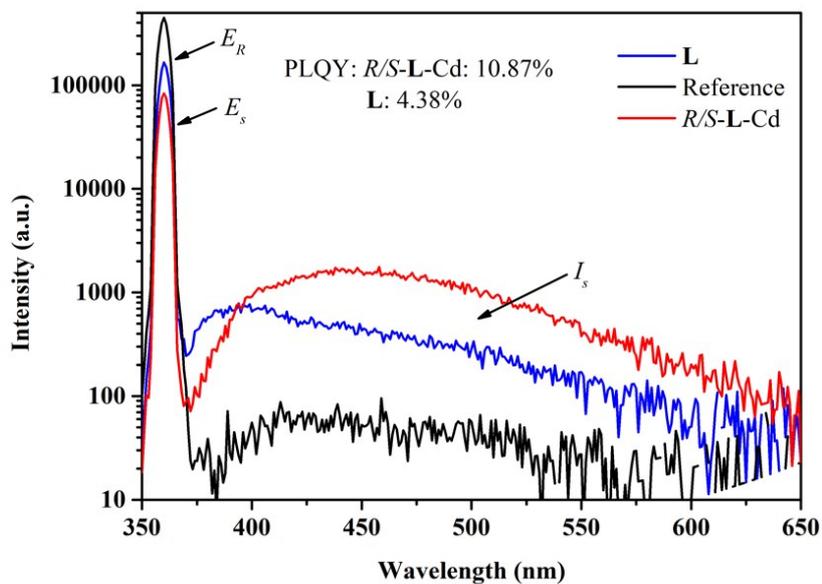


Figure S13. Excitation lines of reference and emission spectra of **L** and **R/S-L-Cd** by an integrating sphere. The PLQYs were calculated by the equation: $\eta_{QE} = I_s / (E_R - E_S)$.

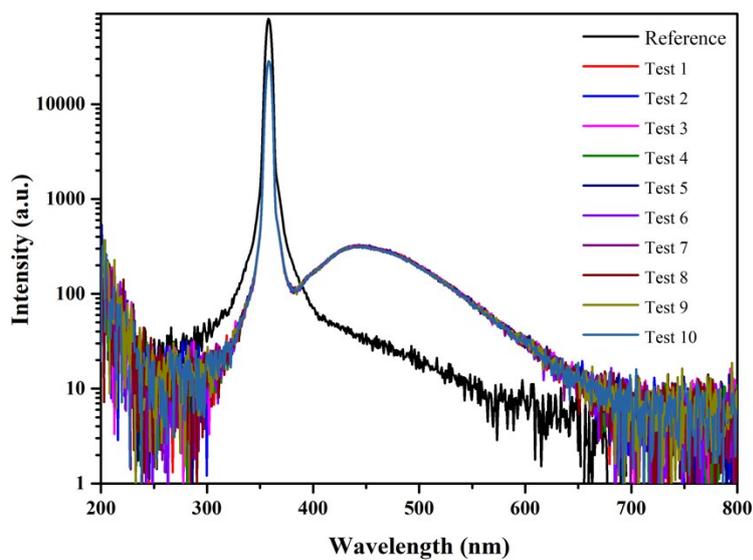


Figure S14. Excitation lines of reference and emission spectra of **R/S-L-Cd** by an integrating sphere measured for 10 times. The PLQYs were calculated by the equation: $\eta_{QE} = I_s / (E_R - E_S)$.

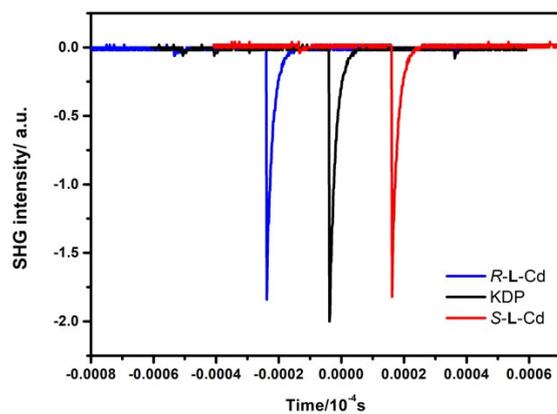


Figure S15. The SHG signals of *S-L-Cd* (Red), *R-L-Cd* (blue) and KDP (black) by using 1064 nm irradiation.

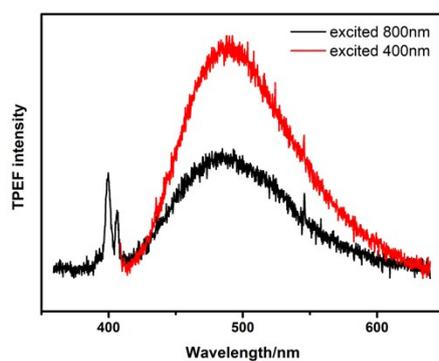


Figure S16. Single-photon and two-photon excited fluorescent spectra of homochiral *S-L-Cd*, excited at 800 nm and 400 nm, respectively.

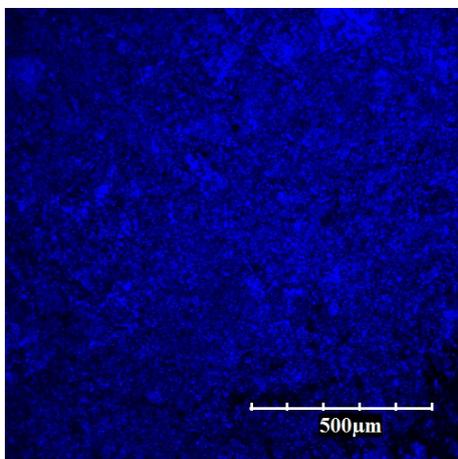


Figure S17. TPEF image of homochiral *S-L-Cd* with 10x water mirror.

4. References

- (1) J. Bunzen, T. Bruhn, G. Bringmann, A. Lützen, Synthesis and Helicate Formation of a New Family of BINOL-Based Bis(bipyridine) Ligands. *J. Am. Chem. Soc.* **2009**, *131*, 3621.
- (2) Q. W. Zhang, D. F. Li, X. Li, P. B. White, M. Jasmin, X. Ma, H. Ågren, R. J. M. Nolte, H. Tian, Multicolor Photoluminescence Including White-Light Emission by a Single Host-Guest Complex. *J. Am. Chem. Soc.* **2016**, *138*, 13541.
- (3) W. W. Chen, Y. W. Zhuang, L. Wang, Y. Lv, J. B. Liu, T. L. Zhou, R. J. Xie, Color-Tunable and High-Efficiency Dye-Encapsulated Metal–Organic Framework Composites Used for Smart White-Light-Emitting Diodes. *ACS Appl. Mater. Interfaces.* **2018**, *10*, 18910.
- (4) J. B. Liu, Y. X. Zhuang, L. Wang, T. L. Zhou, N. Hirosaki, R. J. Xie, Achieving Multicolor Long-Lived Luminescence in Dye Encapsulated Metal–Organic Frameworks and Its Application to Anticounterfeiting Stamps. *ACS Appl. Mater. Interfaces.* **2018**, *10*, 1802.
- (5) G. M. Sheldrick, *Acta Crystallogr. Sect. C*, **2015**, *71*, 3-8.
- (6) O. V. Dolomanov, L. J. Bourhis, R. J. K. Gildea, H. J. Puschmann, *Appl. Crystallogr.* **2009**, *42*, 339-341.