Electronic Supplementary Information

A Chiral Bipolar Host for Efficient Solution-processed Circularly Polarized Organic Light-emitting Diodes Via A Chirality Energy Transfer Process

Qiwei Dong[a,b], Binghong He[a], Wenjian Qiao[a,d], Weiguo Zhu[a]*, Pengfei Duan[c]*, Yafei Wang[a]*

[a]*Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Jiangsu Engineering Laboratory of Light-Electricity-Heat Energy-Converting Materials and Applications, School of Materials Science & Engineering, Changzhou University, Changzhou 213164, China.* Email: Y. Wang: qiji830404@hotmail.com

[b]*School of Materials Engineering, Changzhou Vocational Institute of Industry Technology, Changzhou 213164, China.*

[c]*CAS Center for Excellence in Nanoscience CAS Key Laboratory of Nano system and Hierarchical Fabrication National Center for Nanoscience and Technology (NCNST)Beijing 100190, P. R. China*. Email: P. Duan: duanpf@nanoctr.cn

[d]*ChinaZaozhuang Reinno Optoelectronic Information Co.,Ltd., China*.

1. General information

1.1 Materials

Unless other noted, all reagents used in the experiments were purchased from commercial sources without further purification. For column chromatography, silica gel with 200 ~ 300 mesh was used.

1.2 Measurements

To elucidate the structure of the compounds, ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker Dex-300/400/500 NMR instrument with CD_2Cl_2, $CDCl_3$, and DMSO as solvents. Mass spectra (MS) were recorded on a Bruker Auto flex MALDI-TOF instrument using dithranol as a matrix.

Thermogravimetric analysis (TGA) was conducted with a NETZSCH STA449 from 25°C to 800°C at a heating rate of 20°C/min under a N_2 atmosphere. UV-vis absorption spectra were acquired using a Shimadzu UV-1650PC spectrophotometer. Steady-state fluorescence/phosphorescence spectra (PL spectra) were measured with an Edinburgh FLS1000 fluorescence spectrophotometer. Circular Dichroism (CD) and Circularly Polarized Luminescence (CPL) spectra were recorded on JASCO J-1500 and JASCO CPL-200 spectrophotometers, respectively.

1.3 Devices fabrications

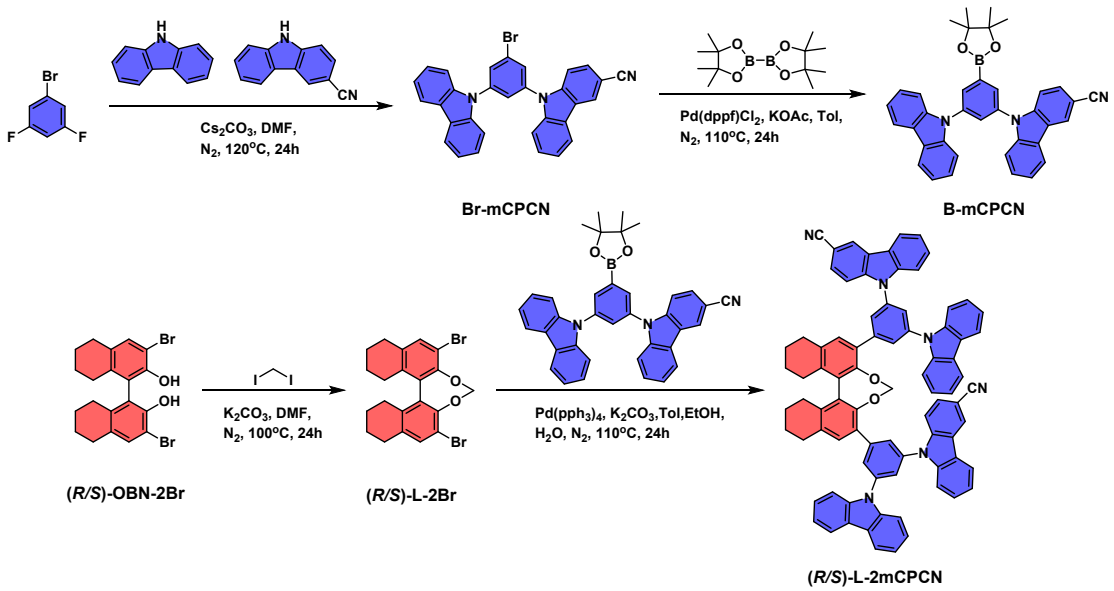
The substrates underwent a thorough cleaning process involving isopropyl alcohol, acetone, detergent, deionized water, and isopropyl alcohol in an ultrasonic bath, followed by overnight drying in the oven. Prior to this, the substrates were pre-treated with oxygen plasma to enhance the work function of the ITO film.

Subsequently, a 40 nm-thick layer of PEDOT: PSS was spin-coated onto the ITO substrates at 3200 rpm for 30 s and annealed at 150 ℃ for 15 min. The emissive layer was then spin-coated and annealed at either 60 ℃ or 110 ℃ for 30 min using a precursor solution containing various materials co-dissolved in chlorobenzene or toluene. Films of TmPyPB, LiF, and aluminum were prepared by thermal evaporation under a vacuum of 1 × 10-4 Pa. Each sample had an active area of 0.04 cm^2.

All the devices were encapsulated before characterization to prevent degradation and emission quenching caused by oxygen and water. The EL spectra and J–V–R curves were obtained with a

PHOTORESEARCH Spectra Scan PR735 photometer and a KEITHLEY 2400 Source Meter constant current source at room temperature. The EQE values were calculated by assuming a Lambertian distribution. The circularly polarized electroluminescence (CPEL) spectra were measured on a Jasco CPL-200 spectrophotometer with „Standard" sensitivity at 200 nm/min scan speed and respond time of 2.0 s employing "band" mode.

2. Synthesis routes and procedures for (*R/S*)-L-2mCPCN



Scheme S1 Synthetic route of **(*R*/*S*)-L-2mCPCN**

Preparation procedure for Compound Br-mCPCN

1-bromo-3,5-difluorobenzene (1.0 g, 5.18 mmol), carbazole (0.79 g, 4.71 mmol), 9H-carbazole-3-carbonitrile (0.91 g, 4.71 mmol), Cs_2CO_3 (3.07 g, 9.42 mmol) and 30 mL dry N, N-dimethylformamide are sequentially added in a 200 mL single-neck flask. The mixture was stirred reflux at 120 ℃ for 24 hours in nitrogen atmosphere. After cooling down to room temperature, the mixture was extracted with dichloromethane and washed with water and dried over $MgSO_4$. The solvent was removed by a rotatory evaporation and the crude product was purified by silica gel column chromatography (PE:DCM = 1:1) to give the **compound Br-mCPCN** as white solid (0.91 g, 38%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 8.15 (t, *J* = 6.8 Hz, 3H), 7.95 (s, 1H), 7.81 (s, 1H), 7.76 – 7.69 (m, 2H), 7.56 – 7.40 (m, 8H), 7.34 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.05, 141.07, 140.80, 140.12, 139.14, 129.66, 128.67, 127.89, 126.48, 125.48, 124.52, 123.97, 123.94, 123.89, 122.51, 110.41, 110.18, 109.45, 103.68.

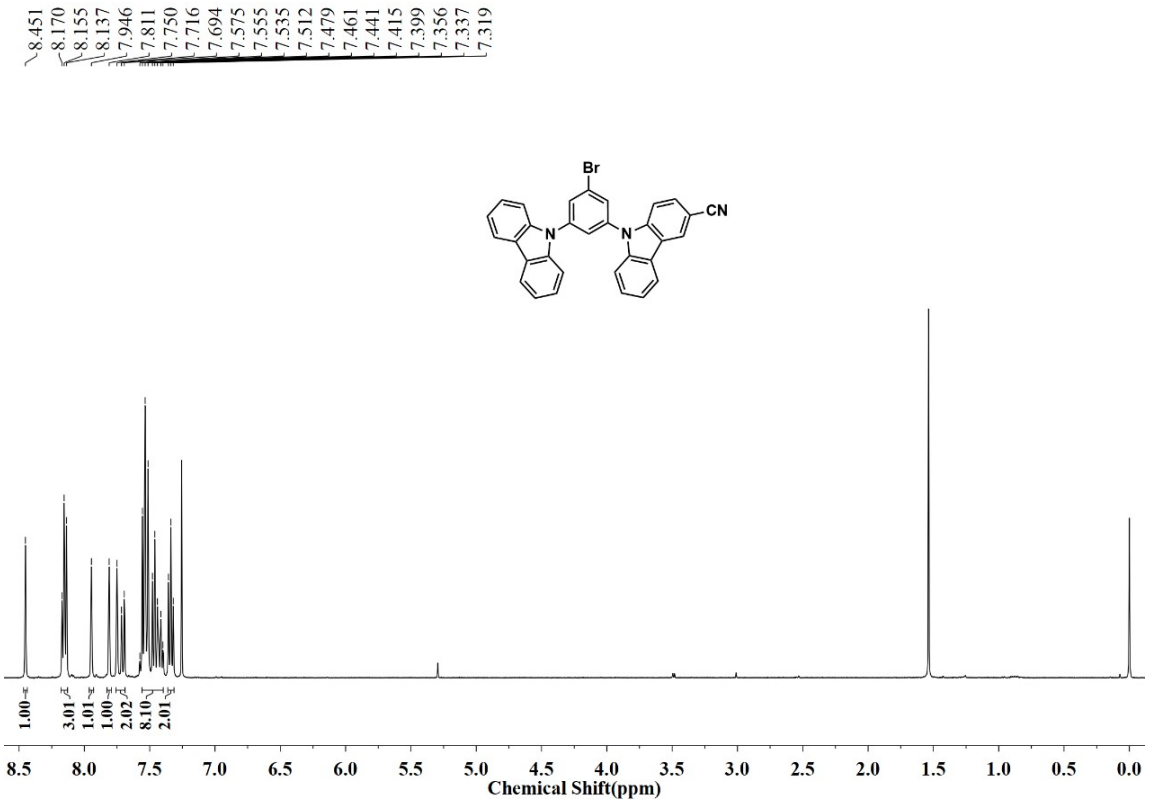


Fig. S1 ^{1}H NMR spectrum of **compound Br-mCPCN**

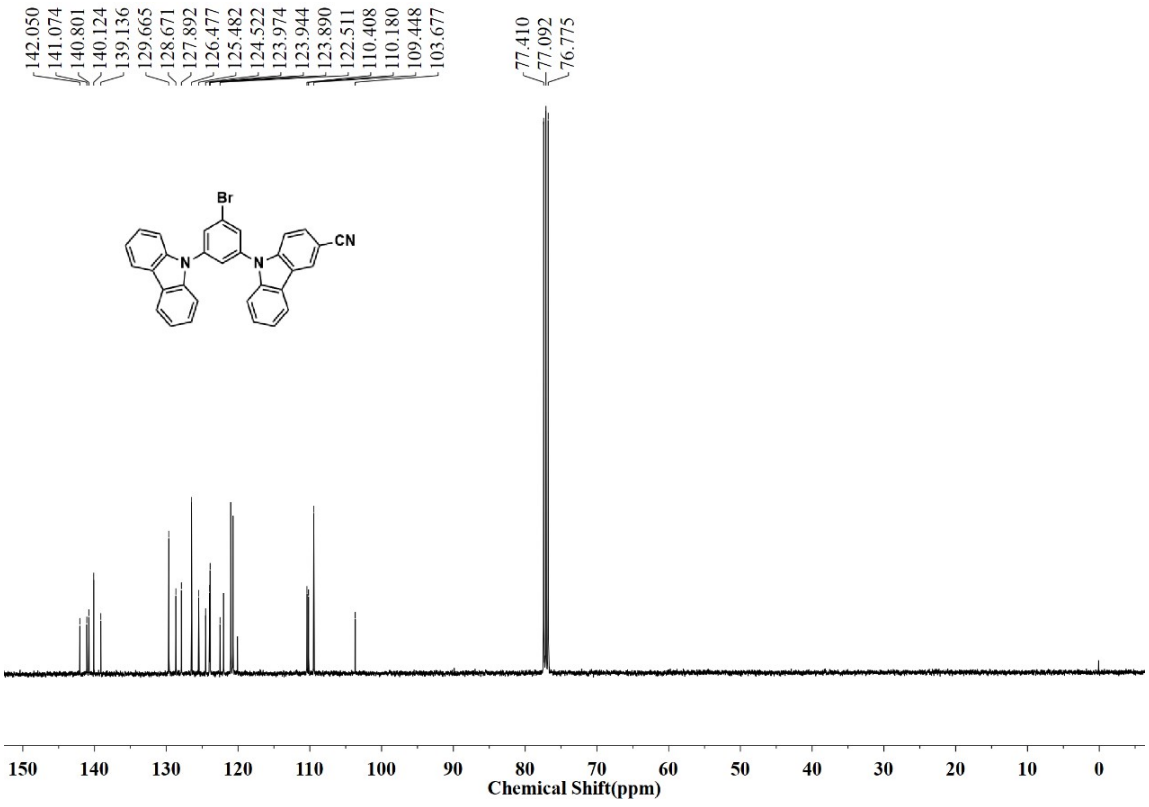


Fig. S2 ^{13}C NMR spectrum of **compound Br-mCPCN**

Preparation procedure for Compound B-mCPCN

Compound **Br-mCPCN** (0.52 g, 1 mmol), bis(pinacolato)diboron (0.29 g, 1.1 mmol), potassium acetate (0.37 g, 3.7 mmol), [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.03 g, 0.04 mmol) and 30 mL toluene are sequentially added in a 200 mL single-neck flask. The mixture was stirred reflux at 110 ℃ for 24 hours in nitrogen atmosphere. After cooling down to room temperature, the solvent was removed by a rotatory evaporation and then the mixture was extracted with dichloromethane and washed with water and dried over $MgSO_4$. The solvent was removed by a rotatory evaporation and the crude product was purified by silica gel column chromatography (PE:DCM = 1:1) to give the **compound B-mCPCN** as white solid (0.48 g, 88%).^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (s, 1H), 8.20 – 8.14 (m, 4H), 8.05 (s, 1H), 7.83 (s, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.46 (ddd, *J* = 29.7, 14.8, 7.2 Hz, 8H), 7.32 (t, *J* = 7.2 Hz, 2H), 1.37 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.44, 141.49, 140.58, 139.16, 137.54, 133.12, 132.02, 129.36, 128.20, 127.56, 126.13, 125.30, 123.58, 122.23, 121.45, 120.74, 120.46, 120.35, 120.29, 110.47, 110.28, 109.52, 102.92, 84.61, 24.90.

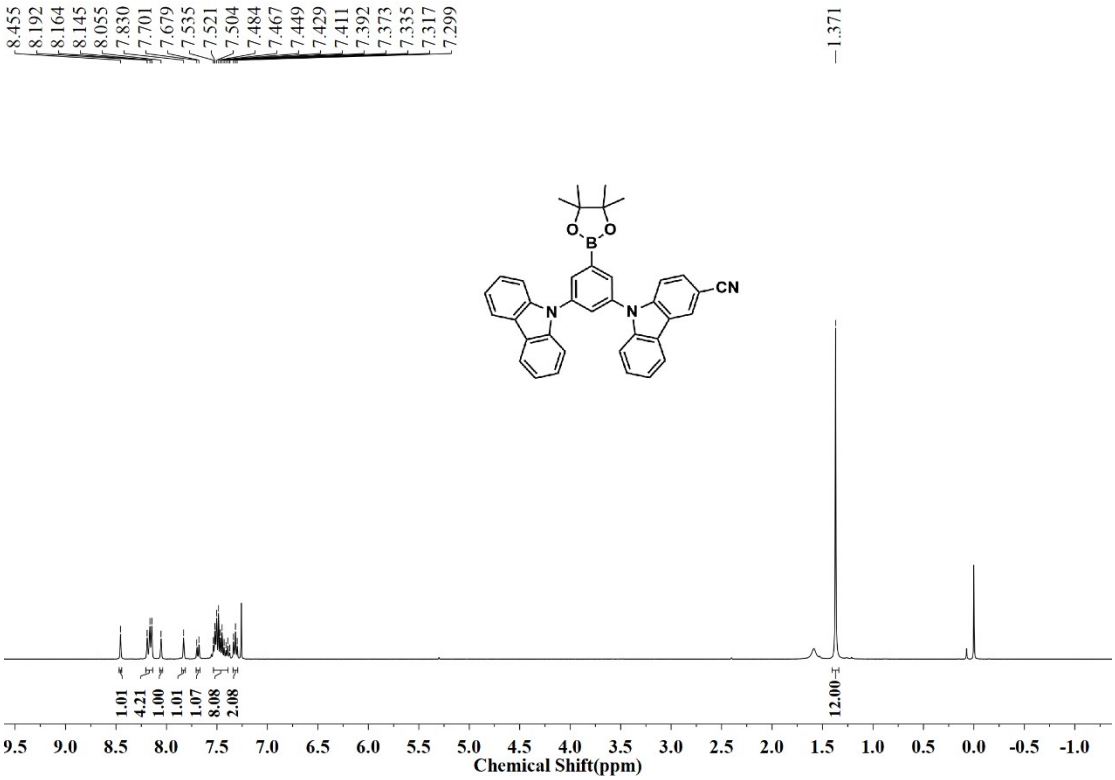


Fig. S3 ^{1}H NMR spectrum of **compound B-mCPCN**

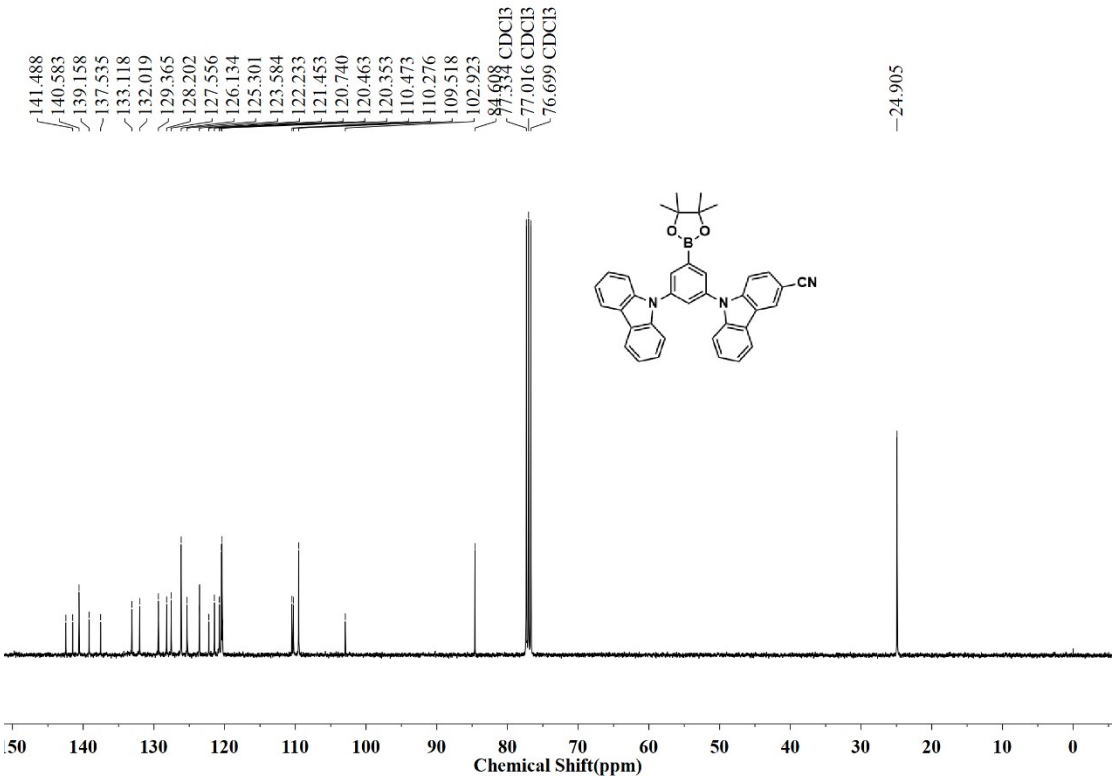


Fig. S4 ^{13}C NMR spectrum of **compound B-mCPCN**

Preparation procedure for Compound (R/S)-L-2Br

Compounds (*R/S*)-3,3'-dibromo-5,5',6,6',7,7',8,8'-octahydrobinaphthol (5.0 g, 11.05 mmol), diiodomethane (5.92 g, 22.10 mmol), potassium carbonate (6.11 g, 44.20 mmol), and 50 mL anhydrous N, N-dimethylformamide were sequentially added in a 200 mL single-neck flask. The reaction system was subjected to three nitrogen purges, followed by reflux at 100 ℃ for 24 hours. After cooling, water was added, and the mixture was extracted with dichloromethane (3×60 mL) and washed with water (3×100 mL). The organic phase was dried over anhydrous magnesium sulfate, filtered, and the filtrate was concentrated to remove the solvent. The solvent was removed by a rotatory evaporation and the crude product was purified by silica gel column chromatography (PE: DCM = 6:1) to give the white solid. **compound (*R*)-L-2Br** (3.21 g, 63%); **compound (*S*)-L-2Br** (3.33 g, 65%).**(*R*)-L-2Br:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (s, 2H), 5.36 (s, 2H), 2.80 (q, *J* = 6.0 Hz, 4H), 2.61 (ddd, *J* = 15.9, 9.3, 4.6 Hz, 2H), 2.26 (dt, *J* = 16.5, 5.4 Hz, 2H), 1.84 – 1.74 (m, 6H), 1.55 – 1.41 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.69, 137.19, 136.58, 132.60, 132.16, 112.42, 99.95, 28.89, 27.62, 22.35, 22.12.**(*S*)-L-2Br:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (s, 2H), 5.36 (s, 2H), 2.80 (q, *J* = 6.0 Hz, 4H), 2.61 (ddd, *J* = 15.9, 9.3, 4.6 Hz, 2H), 2.26 (dt, *J* = 16.4, 5.4 Hz, 2H), 1.91 – 1.68 (m, 6H), 1.52 (ddd, *J* = 12.2, 9.3, 4.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.69, 137.19, 136.58, 132.60, 132.16, 112.42, 99.95, 28.89, 27.62, 22.35, 22.12.

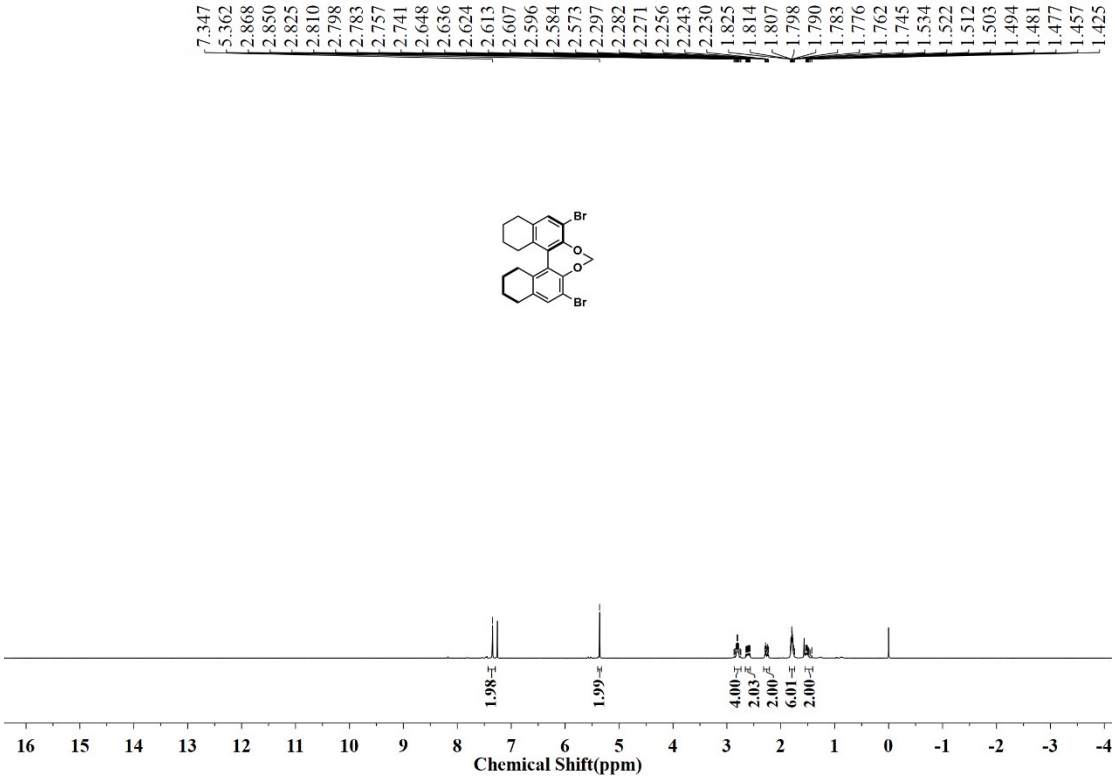


Fig. S5 ^{1}H NMR spectrum of **compound (*R*)-L-2Br**

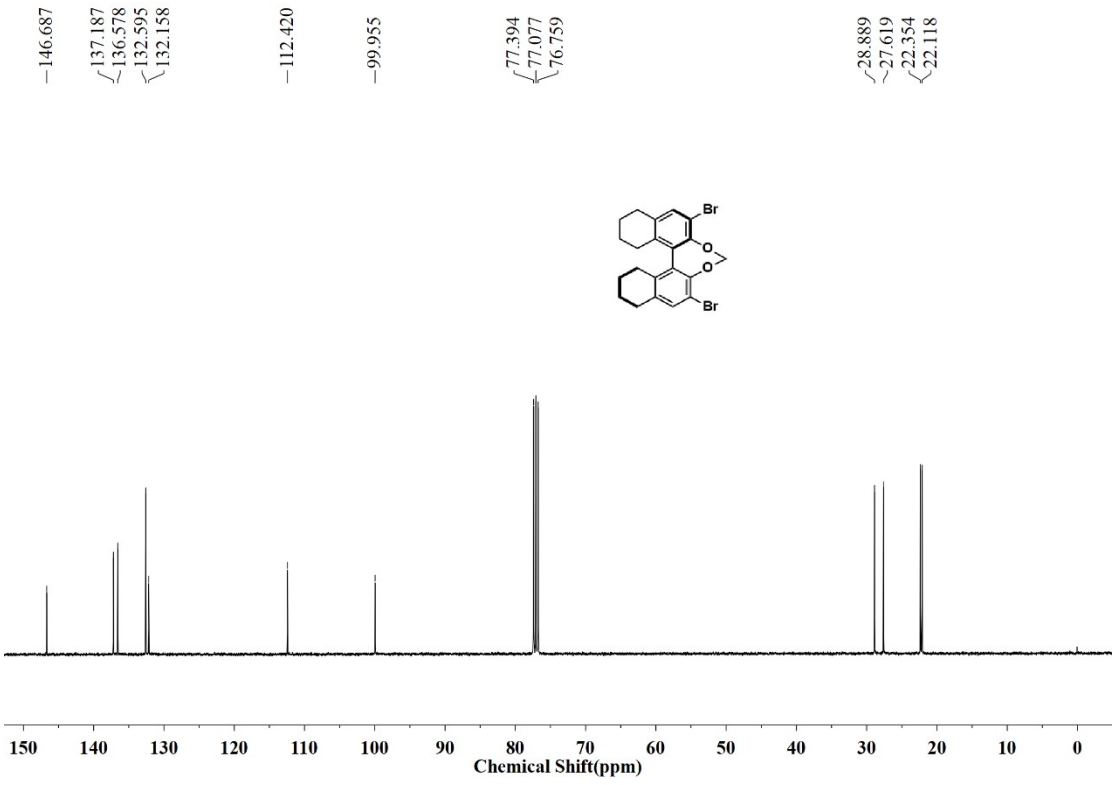


Fig. S6 ^{13}C NMR spectrum of **compound (*R*)-L-2Br**

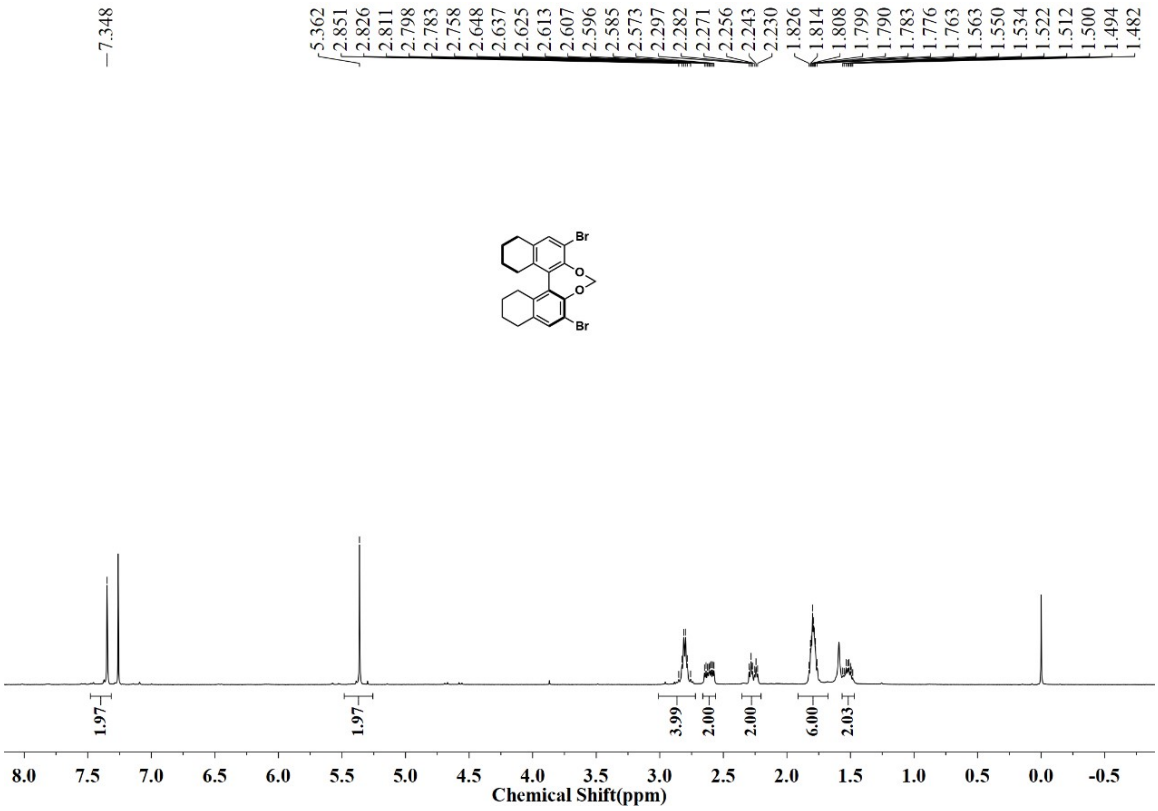


Fig. S7 ^{1}H NMR spectrum of **compound (*S*)-L-2Br**

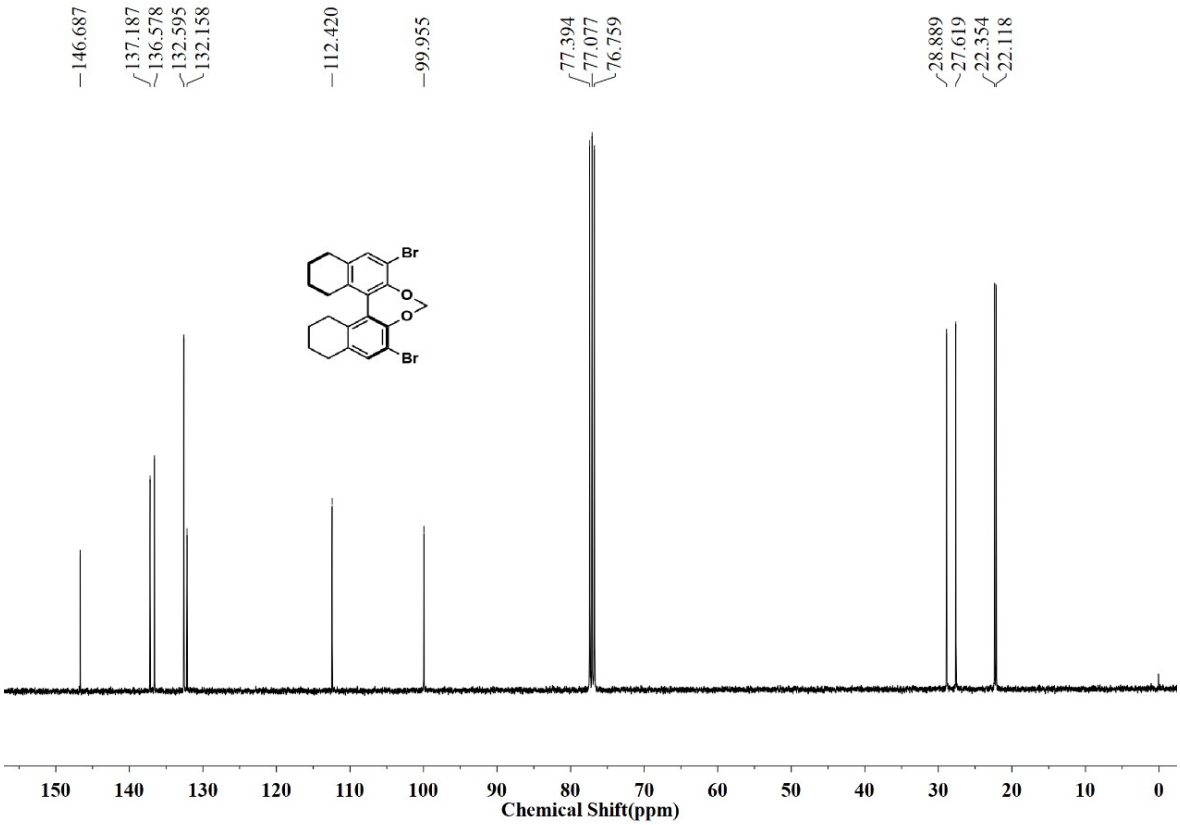


Fig. S8 ^{13}C NMR spectrum of **compound (*S*)-L-2Br**

Preparation procedure for Compound (R/S)-L-2mCPCN

In a 100 mL single-neck flask, the following compounds were sequentially added: **(*R/S*)-L-2Br** (0.33 g, 0.71 mmol), **B-mCPN** (0.87 g, 1.56 mmol), tetrakis(triphenylphosphine)palladium (0.04 g, 0.04 mmol), K_2CO_3 (0.69 g, 4.97 mmol), along with 20 mL of toluene, 2.5 mL of ethanol, and 2.5 mL of distilled water. The reaction system underwent three nitrogen purges, followed by reflux at 110 ℃ for 24 hours. After cooling, the solvent was removed using a rotary evaporator, and water was added. The mixture was then extracted with dichloromethane (3×50 mL) and subjected to water washes (3×80 mL). The organic phase was dried over anhydrous magnesium sulfate, filtered, and the filtrate was collected. The solvent was removed by a rotatory evaporation and the crude product was purified by silica gel column chromatography (PE: DCM = 2:3) to give the white solid. **compound (*R*)-L-2mCPCN** (0.48 g, 58%); **compound (*S*)-L-2mCPCN** (0.50 g, 60%). **(*R*)-L-2mCPCN:** ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 1.4 Hz, 2H), 8.19 (dt, *J* = 7.8, 1.5 Hz, 6H), 8.04 (t, *J* = 1.7 Hz, 2H), 7.92 (t, *J* = 1.8 Hz, 2H), 7.78 (t, *J* = 1.9 Hz, 2H), 7.69 (dd, *J* = 8.6, 1.6 Hz, 2H), 7.64 – 7.57 (m, 8H), 7.55 – 7.33 (m, 14H), 5.32 (s, 2H), 3.01 – 2.78 (m, 6H), 2.49 (dt, *J* = 16.9, 5.8 Hz, 2H), 1.89 (dtt, *J* = 8.4, 6.2, 4.0 Hz, 6H), 1.73 – 1.63 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.65, 142.20, 141.26, 141.22, 140.33, 139.28, 138.62, 137.67, 135.71, 131.95, 130.12, 129.39, 128.91, 127.60, 127.43, 126.53, 126.19, 125.38, 123.73, 123.68, 123.29, 122.37, 121.62, 120.86, 120.58, 120.54, 120.18, 110.48, 110.27, 109.51, 103.13, 29.18, 27.85, 22.51, 22.27. TOF-MS (ESI) *m/z* calcd for $C_{83}H_{56}N_6O_2$ $[M]^+$:1168.45; found: 1168.513. **(*S*)-L-2mCPCN:**^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.49 (d, *J* = 1.4 Hz, 2H), 8.19 (dt, *J* = 7.8, 1.5 Hz, 6H), 8.04 (t, *J* = 1.7 Hz, 2H), 7.92 (t, *J* = 1.8 Hz, 2H), 7.78 (t, *J* = 1.9 Hz, 2H), 7.69 (dd, *J* = 8.6, 1.6 Hz, 2H), 7.64 – 7.57 (m, 8H), 7.55 – 7.33 (m, 14H), 5.32 (s, 2H), 3.01 – 2.78 (m, 6H), 2.49 (dt, *J* = 16.9, 5.8 Hz, 2H), 1.89 (dtt, *J* = 8.4, 6.2, 4.0 Hz, 6H), 1.73 – 1.63 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.65, 142.20, 141.26, 141.22, 140.33, 139.28, 138.62, 137.67, 135.71, 131.95, 130.12, 129.39, 128.91, 127.60, 127.43, 126.53, 126.19, 125.38, 123.73, 123.68, 123.29, 122.37, 121.62, 120.86, 120.58, 120.54, 120.18, 110.48, 110.27, 109.51, 103.13, 29.18, 27.85, 22.51, 22.27. TOF-MS (ESI) *m/z* calcd for $C_{83}H_{56}N_6O_2$ $[M]^+$:1168.45; found: 1168.492.

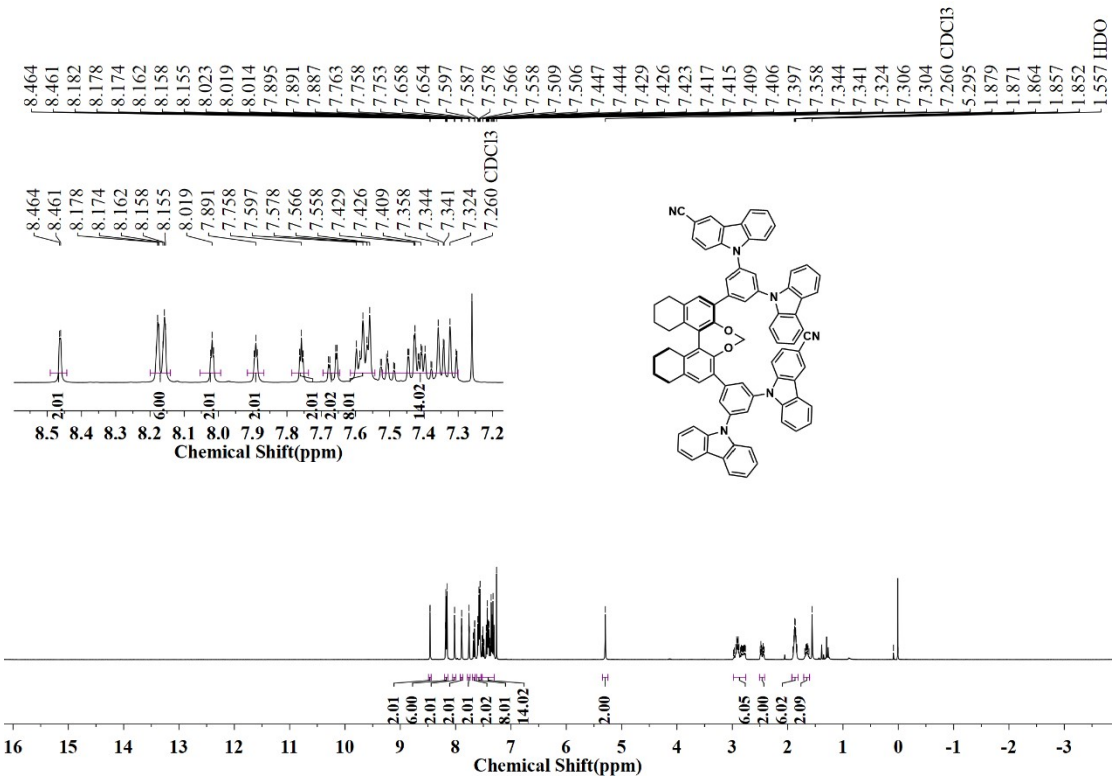


Fig. S9 [1]H NMR spectrum of **compound (*R*)-L-2mCPCN**

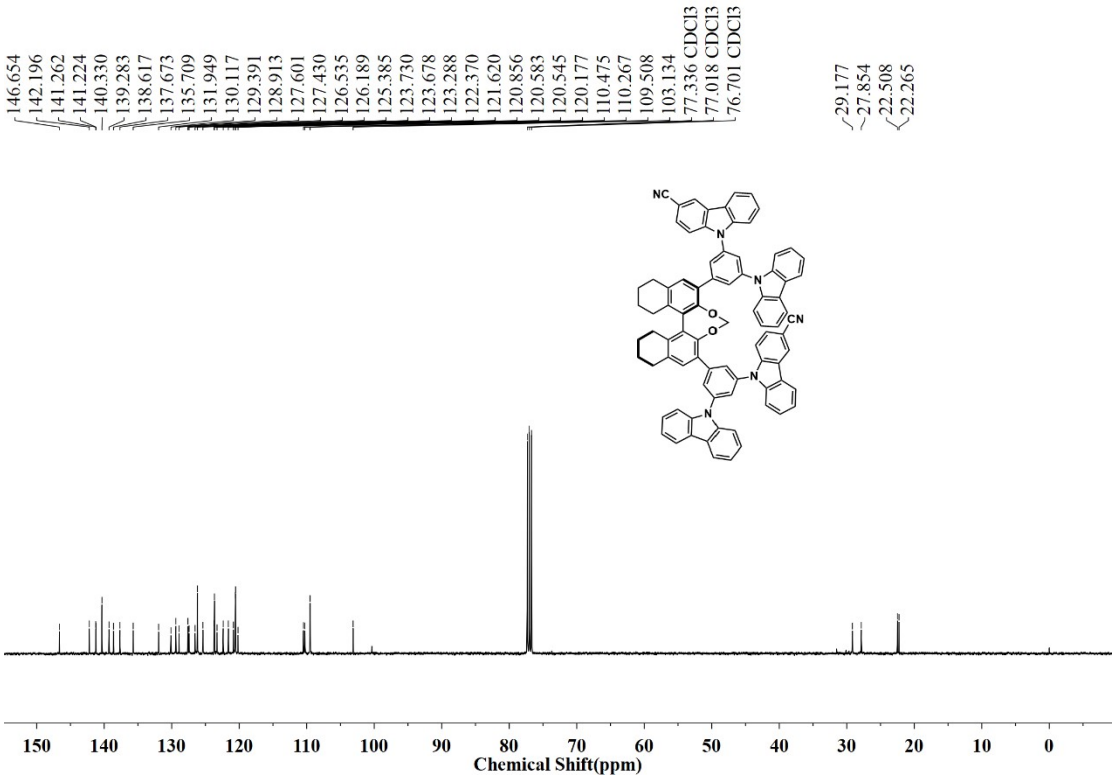


Fig. S10 [13]C NMR spectrum of **compound (*R*)-L-2mCPCN**

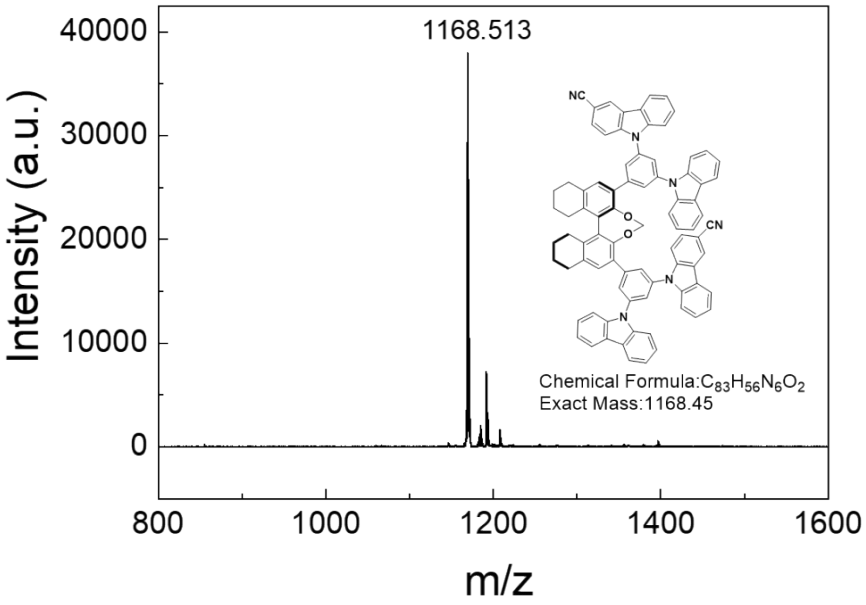


Fig. S11 Mass spectrum of **compound (*R*)-L-2mCPCN**

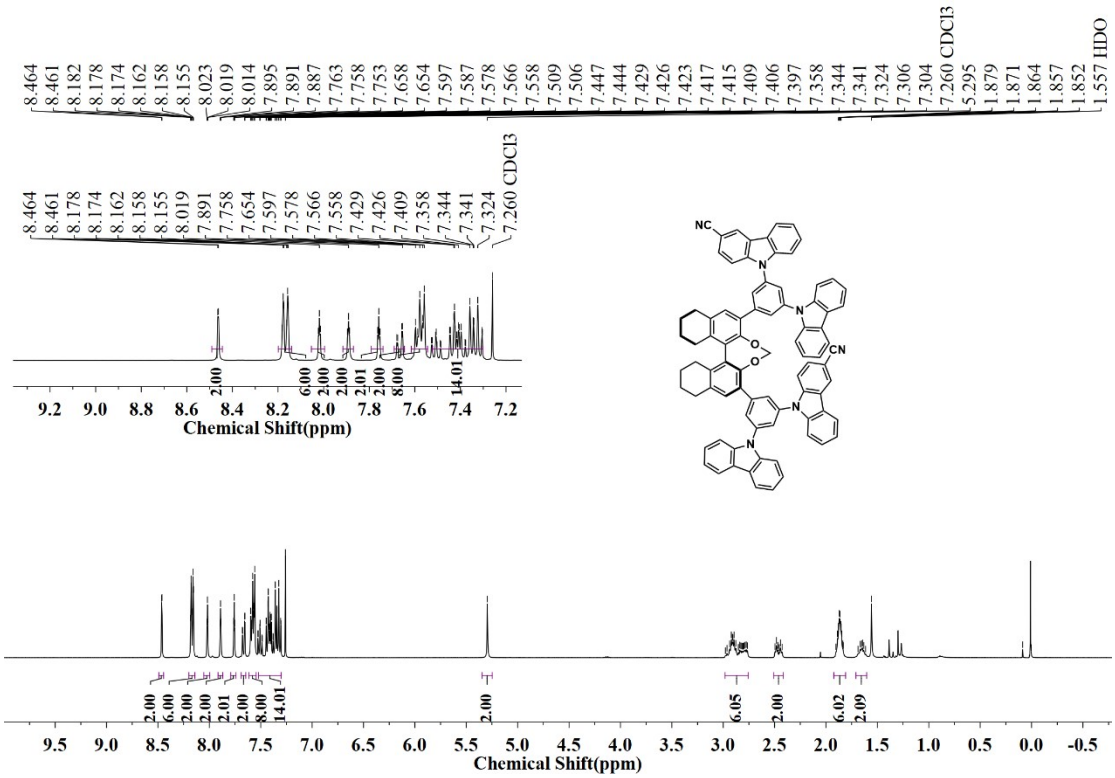


Fig. S12 ^{1}H NMR spectrum of **compound (*S*)-L-2mCPCN**

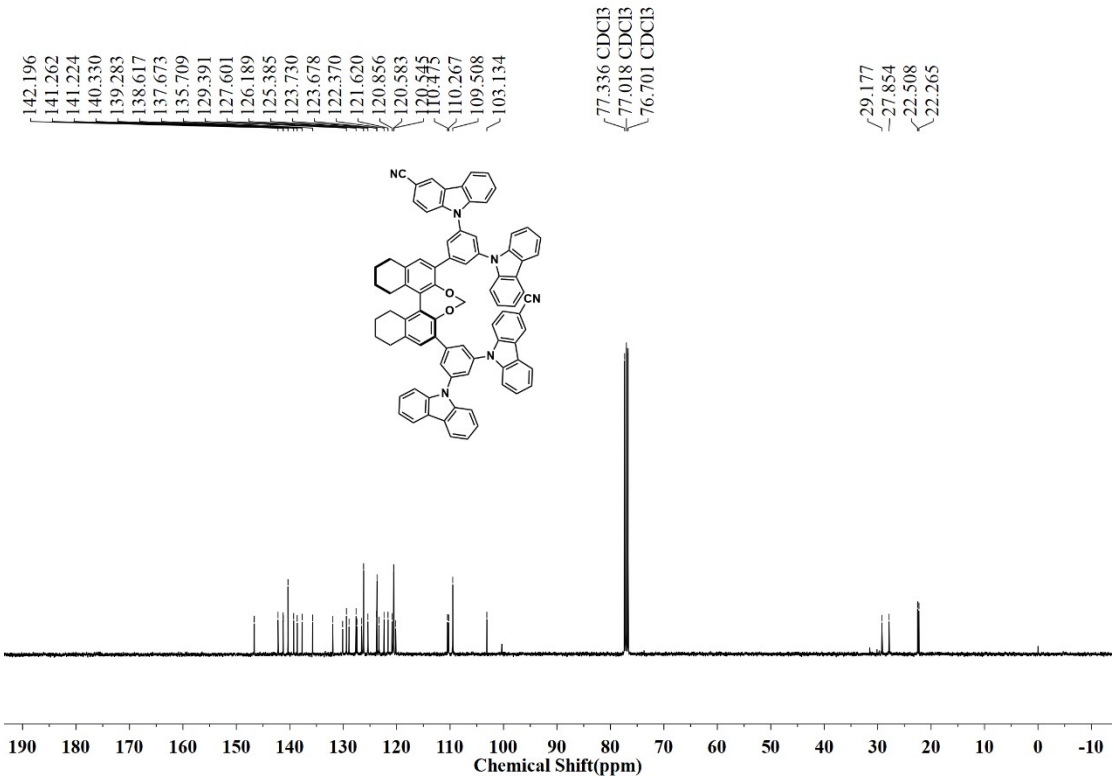


Fig. S13 ^{13}C NMR spectrum of **compound (*S*)-L-2mCPCN**

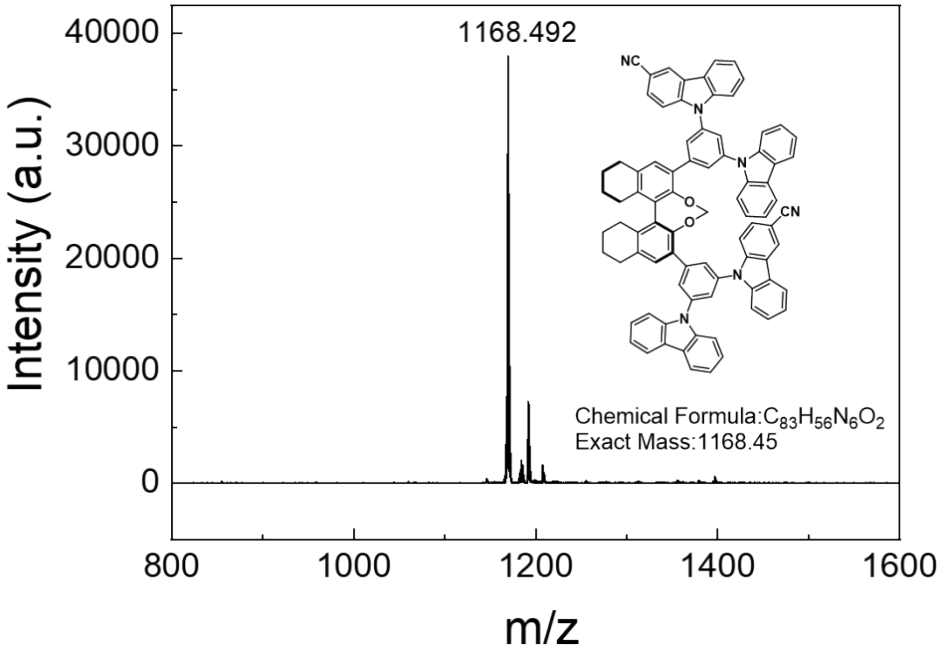


Fig. S14 Mass spectrum of **compound (*S*)-L-2mCPCN**

3. Supplementary data

Table S1 Photophysical data of the three compounds.

Compounds	$^{a,b}\lambda_{abs}$ /nm	$^{a,b}\lambda_{em}$ /nm	$^{c}S_1$ /eV	$^{c}T_1$ /eV	$^{d}E_{HOMO}$ /eV	$^{d}E_{LUMO}$ /eV	$^{e}T_d$ /°C	^{f}Tm /°C	E_g^{opt} /eV
(*R*)-L-2mCPCN	326,339[a] 326,339[b]	348,364[a] 350,366[b]	3.67	3.05	-5.64	-2.11	461[f]	228[h]	3.53[h]
mCPCN	326,339[a] 326,339[a]	348,364[a] 349,365[b]	3.71	3.15	-5.80[g]	-2.24[g]	313[g]	222[g]	3.56[g]

a: measured in 10^{-5} M toluene at room temperature (λ_{ex}=300 nm); b: measured in doped PMMA film (10%) at room temperature (λ_{ex}=300 nm); c:calculated for the onsets of the low-temperature (77 K) fluorescence and phosphorescence (λ_{ex}=300 nm); d: collected from CV measurement; e: in N_2 with the heating rate of 20℃ min^{-1}. f: in N_2 with the heating rate of 10℃ min^{-1}.g: derived from the initial literature introducing mCPCN. (*J. Mater. Chem*., 2012, 22, 16114). h: calculated for the onsets of the UV-vis absorption spectra.

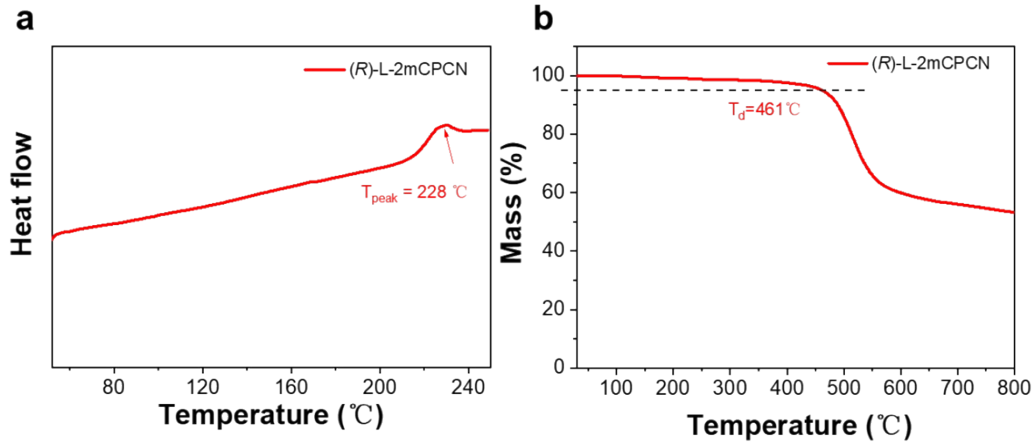


Fig. S15 (a) DSC traces of the hosts recorded at a heating rate of 10°C min^{-1};(b) TGA curves of the hosts in N_2 with the heating rate of 20°C min^{-1}.

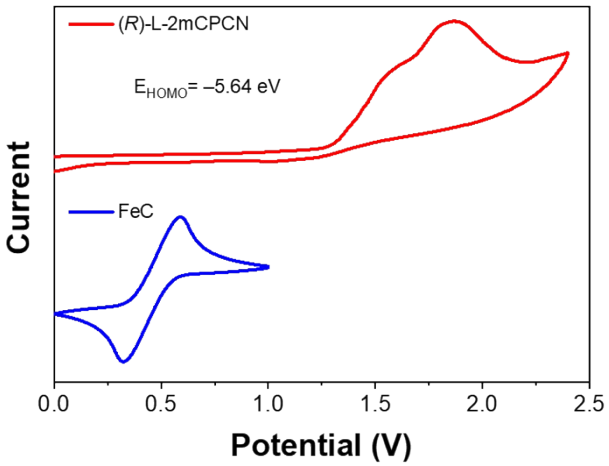


Fig. S16 CV curves of the (*R*)-L-2mCPCN in CH_3CN solution. The redox property of the (*R*)-L-2mCPCN was investigated by cyclic voltammetry (CV) measurement in acetonitrile solution. Only irreversible oxidation (E_{ox}) waves were detected for the hosts in the range of 0~2.5 V. According to the oxidation onset, the E_{ox} are evaluated to be 1.32 eV for (*R*)-L-2mCPCN relative to ferrocenium/ferrocene (Fc/Fc^+, $E_{Fc/Fc+}$ = 0.48 eV). According to the empirical formulae of $E_{HOMO} = -(E_{ox} - E_{Fc/Fc+} + 4.8)$ eV and $E_{LUMO} = -(E_{HOMO} + Eg)$ eV, the HOMO energy level of (*R*)-L-2mCPCN is calculated to be –5.64 eV.

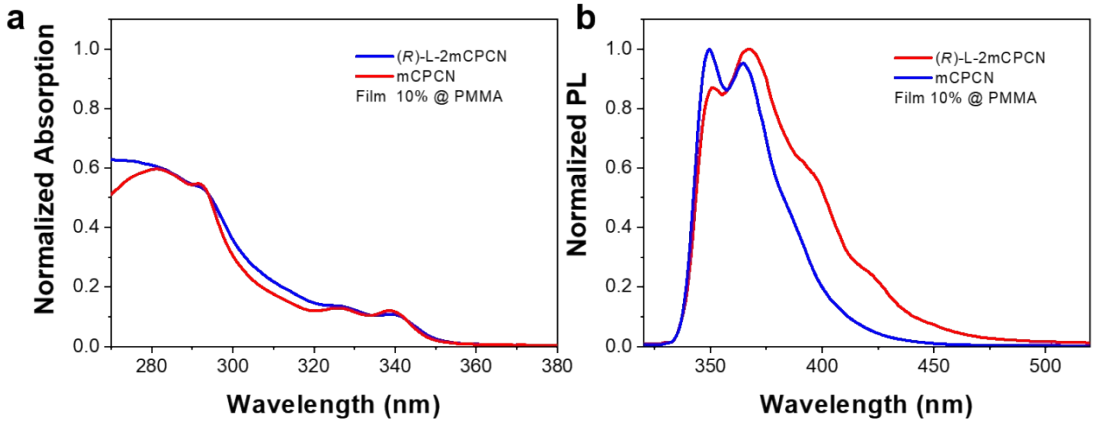


Fig. S17 (a) UV-vis spectra of compounds (*R*)-L-2mCPCN and mCPCN in doped PMMA film (10%). (**b)** PL spectra of compounds (*R*)-L-2mCPCN and mCPCN in doped PMMA film. The excitation is 300 nm Xe lamp.

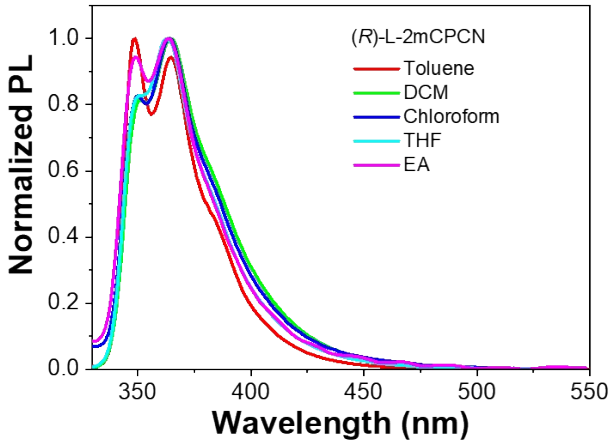


Fig. S18 PL spectra of (*R*)-L-2mCPCN in different kinds of solvents (10^{-5} M). The excitation is 300 nm Xe lamp.

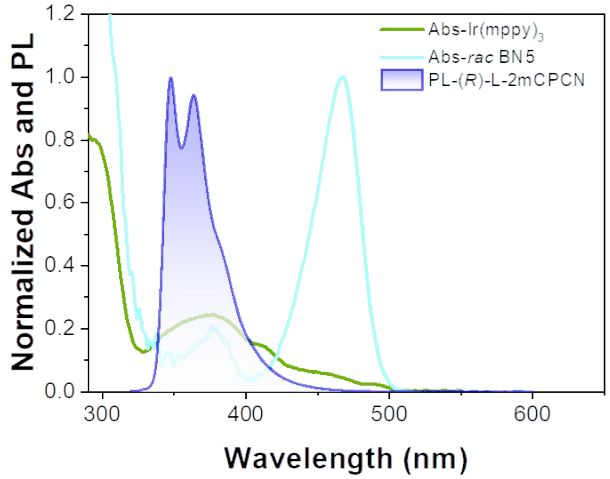


Fig. S19. UV-vis spectra (guest) and PL spectra (host) (λ_{ex}=300 nm) measured in toluene solution (10^{-5} M)

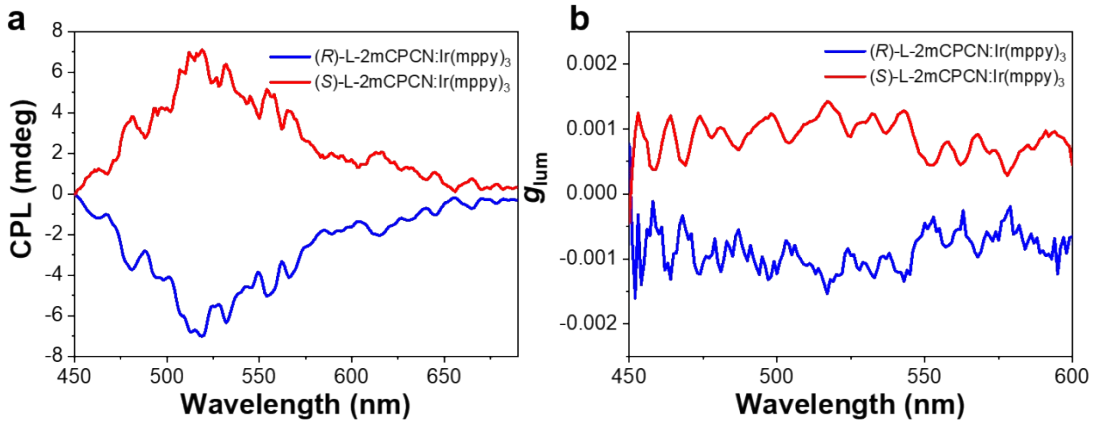


Fig. S20 (a) CPL spectra of the Ir(mppy)$_3$ doped in (*R/S*)-L-2mCPCN host; **(b)** g_{PL} spectra of the Ir(mppy)$_3$ doped in (*R/S*)-L-2mCPCN host.

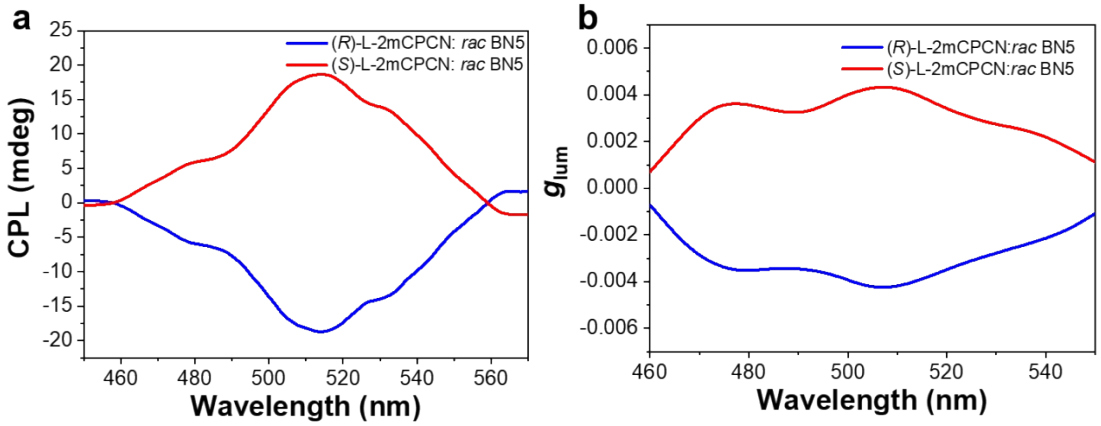


Fig. S21 (a) CPL spectra of the *rac* BN5 doped in (*R/S*)-L-2mCPCN host; **(b)** g_{PL} spectra of spectra of the *rac* BN5 doped in (*R/S*)-L-2mCPCN host.

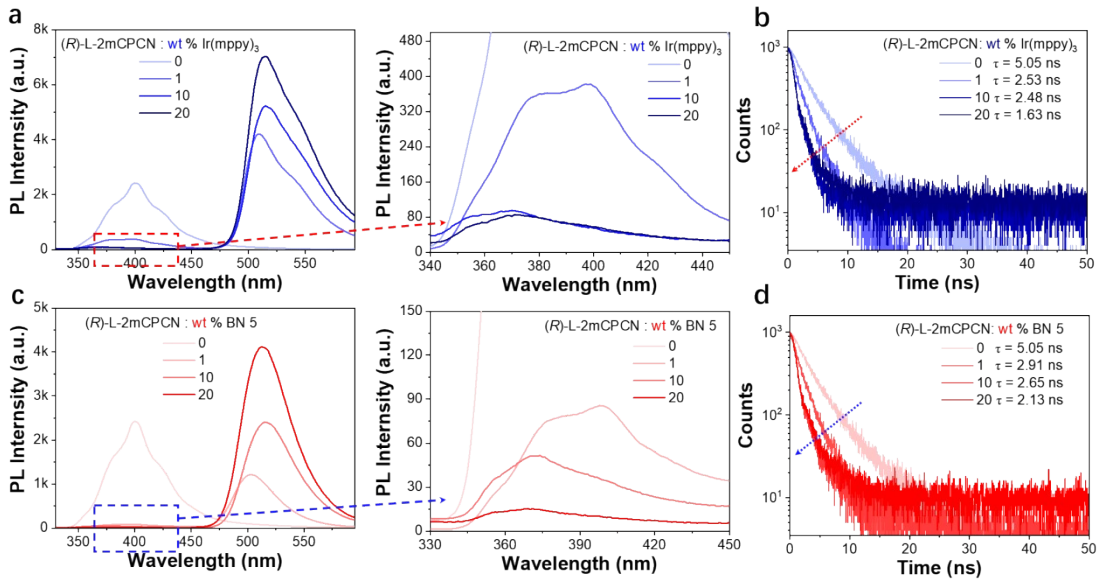


Fig. S22. (a)(c) PL spectra of (*R*)-L-2mCPCN in doped film with different weight ratio of achiral dopant ($Ir(mppy)_3$ or *rac* BN5). The excitation is 300 nm Xe lamp. **(b)(d)** Time-resolved emission of the (*R*)-L-2mCPCN in doped film with different weight ratio of achiral dopant ($Ir(mppy)_3$ or *rac* BN5). The excitation is 277 nm. The doped films were prepared by spin-coating with 1700 r/min (drop 20 uL). the concentration is 10 mg/mL at toluene solution.

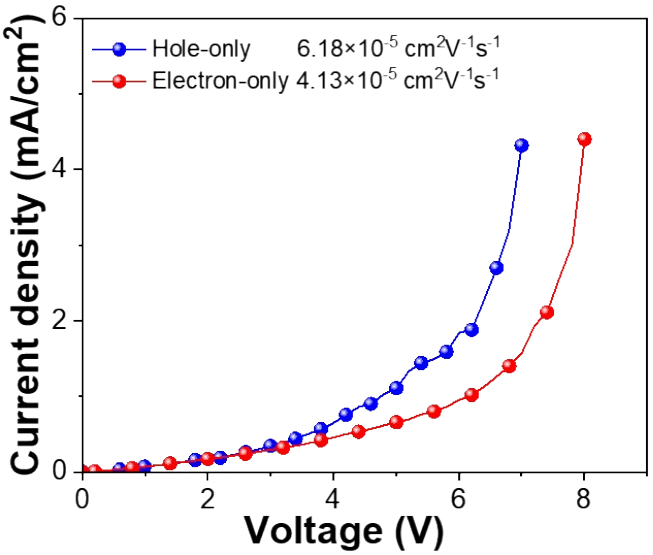


Fig. S23 The mobility of chiral bipolar host of **(*R*)-L-2mCPCN**

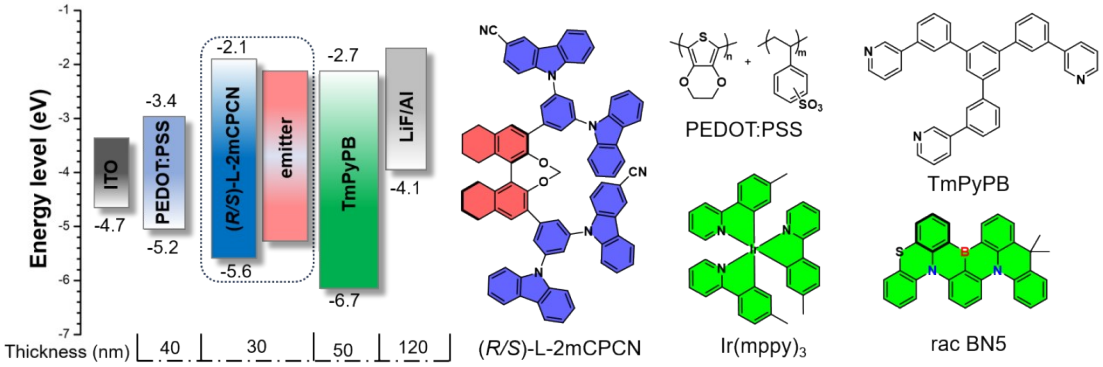


Fig. S24 Energy-level diagrams of devices and molecular structures of materials utilized in device fabrication

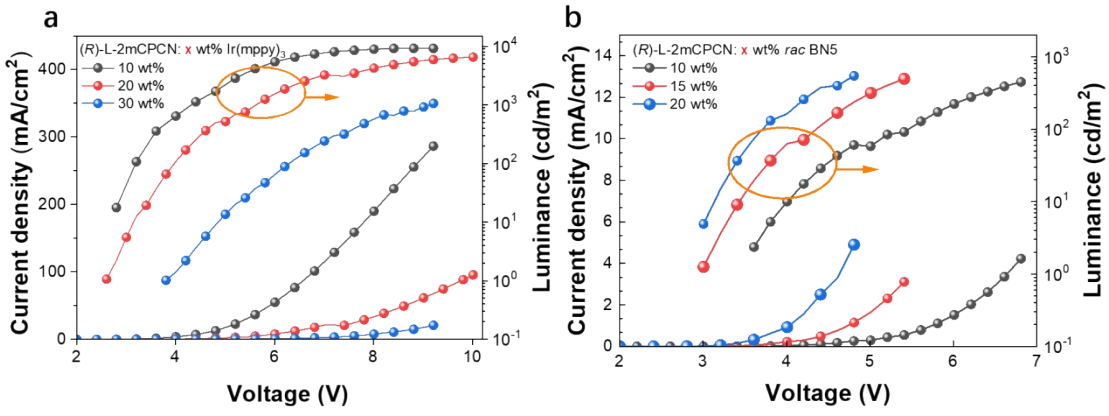


Fig. S25 Current density-voltage-luminance curves

Table S2 EL data for the devices base on (*R*)-L-2mCPCN: x wt% $Ir(mppy)_3$

Device: EML (*R*)-L-2mCPCN: x wt%$Ir(mppy)_3$	**V_{ON} V**	**L_{max} cd m^{-2}**	**CE_{max} cd A^{-1}**	**EQE_{max} %**	**Peak nm**	**FWHM**	**CIE (x, y)**
10 wt%	2.8	9193	31.4	8.8	520	69.1	(0.30,0.61)
20 wt%	2.6	6513	38.8	10.7	522	72.4	(0.31,0.61)
30 wt%	3.8	1059	8.9	2.5	516	64.1	(0.29,0.62)

Table S3 EL data for the devices base on (*R*)-L-2mCPCN: x wt% *rac* BN5

Device: EML (*R*)-L-2mCPCN: wt% *rac* BN5	**V_{ON} V**	**L_{max} cd m^{-2}**	**CE_{max} cd A^{-1}**	**EQE_{max} %**	**Peak nm**	**FWHM**	**CIE (x, y)**
10 wt%	3.6	449	29.4	8.5	522	56.8	(0.24,0.64)
15 wt%	3.0	496	31.7	9.0	524	58.3	(0.26,0.64)
20 wt%	3.0	545	25.4	7.2	522	57.9	(0.26,0.63)