Electronic Supplementary Information

Binaphthol-based Chiral Host Molecules for Efficient Solution-

processed Circularly Polarized OLEDs

Qiwei Dong^{a,b}, Chen Xiao^{a,c}, Binghong He^a, Xuefeng Yang^c, Songkun Zeng^a, Qihang Zhong^a, Pengfei Duan^c, Weiguo Zhu^a*, Yafei Wang^a*

^aJiangsu 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: W. Zhu: <u>zhuwg18@126.com</u>; Y. Wang: <u>qiji830404@hotmail.com</u>

^bSchool of Materials Engineering, Changzhou Vocational Institute of Industry Technology, Changzhou 213164, China.

^cCAS 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.

Contents

1	General information	S1
2	Synthetic procedures and characterized data	S2
3	Thermal properties	S19
4	Theoretical Calculations	S19
5	Ultraviolet Photoelectron Spectroscopy	S20
6	Electrochemical properties	S20
7	Photophysical properties	S21
8	Chiroptical properties	S22
9	CP-OLEDs performances	S22

1 General information

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

In order to determine the structure of the compound, ¹H NMR and ¹³C NMR spectra were acquired using a Bruker Dex-300/400/500 NMR instrument using CDCl₃ and DMSO as a solvent. Mass spectra (MS) were recorded on a Bruker Autoflex MALDI-TOF instrument using dithranol as a matrix.

Thermogravimetric analysis (TGA) was detected with a NETZSCH STA449 from 25°C to 800°C at a 20°C/min heating rate under N₂ atmosphere. UV-vis absorption spectra were recorded on a Shimadzu UV-1650PC. Steady-state fluorescence/phosphorescence spectra PL spectra were carried out by using Edinburgh FLS1000 fluorescence spectrophotometer. The UPS measurements were performed by PHI 5000 VersaProbe III with a base pressure of the analyzer chamber in the lower 10^{-8} Pa range.CD and CPL spectra were measured on JASCO J-1500 and JASCO CPL-200 spectrophotometers, respectively.

Solution-processed device: Poly (styrene sulfonate) (PEDOT: PSS) was purchased from Xi'an Polymer Light Technology Corp. Tris[2-(p-tolyl)pyridine]iridium(III) (Ir(mppy)₃), Bis(1-phenylisoquinoline)(acetylacetonato)iridium(III) (Ir(piq)₂(acac)),[bis(2-(diphenylphosphino) phenyl] ether oxide (DPEPO), (1,3,5-tri(m-pyrid-3-ylphenyl) benzene) (TmPyPB), and LiF were purchased from Lumtec. All commercially available reagents were used without further purification. In devices, PEDOT: PSS was used as hole injection material. Ir(mppy)₃ and Ir(piq)₂(acac) were chosen as emitter material and DPEPO was used as hole blocking materials. TmPyPB and LiF were used as electron transport and injection materials, respectively. ITO (Indium tin oxide) and Al (Aluminum) were used as anode and cathode materials, respectively.

The substrates were successively cleaned with isopropyl alcohol, acetone, detergent, deionized water, and isopropyl alcohol in an ultrasonic bath and then dried overnight in the oven. The substrates pre-treated by oxygen plasma to increase the work function of the ITO film. Then, 40 nm-thick PEDOT: PSS was spin-coated onto the ITO substrates at 3200 rpm for 30 s and annealed at 150 °C for 15 min. And then emissive layer was spin-coated and annealed at 60 °C or 110 °C for 30 min using a precursor containing different materials co-dissolved in chlorobenzene or toluene.

The films of DPEPO, TmPyPB, LiF and aluminum were prepared by thermal evaporation under a vacuum of 1×10^{-4} Pa. Each sample has an active area of 0.04 cm².

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 Synthetic procedures and characterized data



2.1 Synthetic procedures

Scheme S1 Synthetic route of (R/S)-BN-mCP and (R/S)-BN-2mCP

Preparation procedure for (R)-BN-Et

Acetone (8 mL) was added to a 25 mL two-neck flask charged with (*R*)-[1,1'-binaphthalene]-2,2'diol (500 mg, 1.75 mmol), Bromoethane (158.54 mg, 1.46 mmol) and K₂CO₃ (1608.76 mg, 11.64 mmol) in nitrogen atmosphere. The mixture was stirred at 70 °C for 24 hours. After cooling down to room temperature, the acetone was removed by a rotatory evaporation and then the mixture was diluted with dichloromethane and washed with water and dried over MgSO₄. The solvent was removed by a rotatory evaporation and the crude product was purified by silica gel column chromatography (PE: DCM = 3:2) to give the product (*R*)-BN-Et as white sticky substance (366 mg, 80%).¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 9.1 Hz, 1H), 7.91 – 7.82 (m, 3H), 7.44 (d, *J* = 9.1 Hz, 1H), 7.38 – 7.16 (m, 6H), 7.05 (d, *J* = 8.4 Hz, 1H), 4.98 (s, 1H), 4.13 – 4.01 (m, 2H), 1.10 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 155.33, 151.33, 134.19, 133.89, 130.88, 129.73, 129.57, 129.16, 128.18, 128.13, 127.24, 126.33, 125.13, 125.03, 124.25, 123.20, 117.59, 116.45, 115.63, 115.32, 65.25, 14.92. (**Fig. S1, S2**).

Preparation procedure for (R)-BN-2Br

Dry N, N-Dimethylformamide (20 mL) was added to a 50 mL two-neck flask charged with (*R*)-BN-Et (1.2 g, 3.82 mmol), 1,3-dibromo-5-fluorobenzene (1.16 g, 4.58 mmol) and CS₂CO₃ (1.49 g, 4.58 mmol) in nitrogen atmosphere. The mixture was stirred at 120 °C for 24 hours. After cooling down to room temperature, the mixture was diluted with dichloromethane and washed with water and dried over MgSO₄. The solvent was removed by a rotatory evaporation and the crude product was purified by silica gel column chromatography (PE) to give the product (*R*)-BN-2Br as white solid (1.46 g, 69%).¹H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.77 (m, 4H), 7.41 (ddd, *J* = 8.1, 5.4, 2.6 Hz, 1H), 7.31 – 7.12 (m, 8H), 6.80 (d, *J* = 1.5 Hz, 2H), 3.96 (q, *J* = 7.0 Hz, 2H), 1.06 (t, *J* = 7.0 Hz, 3H).¹³C NMR (126 MHz, Chloroform-*d*) δ 159.52, 154.18, 150.90, 134.34, 133.90, 131.35, 130.06, 130.00, 128.94, 128.16, 128.06, 127.61, 126.70, 126.65, 126.26, 125.45, 125.37, 125.10, 123.63, 122.62, 120.64, 119.94, 117.72, 114.19, 64.46, 15.08. (Fig. S3, S4).

Preparation procedure for (R)-BN-mCP

Dry toluene (10 mL) was added to a 50 mL two-neck flask charged with (*R*)-BN-2Br (366 mg, 0.66 mmol), 9H-carbazole (329.42 mg, 1.97 mmol), Pd₂(dba)₃ (48.12 mg, 0.05 mmol), 'Bu₃PHBF₄ (30.49 mg, 0.11 mmol) and 'BuONa (252.44 mg, 2.63 mmol) in nitrogen atmosphere. The mixture was stirred at 120 °C for 24 hours. After cooling down to room temperature, the toluene was removed by a rotatory evaporation and then the mixture was diluted with dichloromethane and washed with water and dried over MgSO₄. The solvent was removed by a rotatory evaporation and the rude product was purified by silica gel column chromatography (PE: DCM = 8:1) to give the product (*R*)-BN-mCP as white solid (365 mg, 77%). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 (dd, *J* = 18.1, 8.3 Hz, 5H), 7.96 – 7.88 (m, 3H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.41 – 7.32 (m, 6H), 7.29 – 7.26 (m, 8H), 7.24 – 7.15 (m, 6H), 7.02 (d, *J* = 1.7 Hz, 2H), 3.71 – 3.49 (m, 2H), 0.48 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 154.13, 140.16, 139.28, 134.18, 133.59, 131.24, 129.96, 129.91, 128.91, 128.02, 127.86, 126.69, 126.44, 125.99, 125.19, 125.16, 124.98, 123.60,

123.44, 120.82, 120.27, 120.20, 117.96, 114.32, 109.84, 64.28, 14.25. TOF-MS (ESI) m/z calcd for C₅₂H₃₆N₂O₂ [M]⁺: 720.28; found:720.54. (**Fig. S5, S6, S15**).

Preparation procedure for (S)-BN-mCP

The synthesis method and procedure are the same as (*R*)-BN-mCP. ¹H NMR (400 MHz, Chloroform-d) δ 8.06 (dd, J = 18.1, 8.3 Hz, 5H), 7.96 – 7.88 (m, 3H), 7.61 (d, J = 8.9 Hz, 1H), 7.41 – 7.32 (m, 6H), 7.29 – 7.26 (m, 8H), 7.24 – 7.15 (m, 6H), 7.02 (d, J = 1.7 Hz, 2H), 3.71 – 3.49 (m, 2H), 0.48 (t, J = 7.0 Hz, 3H). ¹³C NMR (126 MHz, Chloroform-d) δ 154.13, 140.16, 139.28, 134.18, 133.59, 131.24, 129.96, 129.91, 128.91, 128.02, 127.86, 126.69, 126.44, 125.99, 125.19, 125.16, 124.98, 123.60, 123.44, 120.82, 120.27, 120.20, 117.96, 114.32, 109.84, 64.28, 14.25. TOF-MS (ESI) m/z calcd for C₅₂H₃₆N₂O₂ [M]⁺: 720.28; found:720.21. (**Fig. S7, S8, S16**).

Preparation procedure for (R)-BN-4Br

Dry N, N-Dimethylformamide (30 mL) was added to a 100 mL two-neck flask charged with(*R*)-[1,1'-binaphthalene]-2,2'-diol (1.02 g, 3.56 mmol), 1,3-dibromo-5-fluorobenzene (2 g, 7.88 mmol) and CS₂CO₃ (2.78 g, 7.88 mmol) in nitrogen atmosphere. The mixture was stirred at 120 °C for 24 hours. After cooling down to room temperature, the mixture was diluted with dichloromethane and washed with water and dried over MgSO₄. The solvent was removed by a rotatory evaporation and the crude product was purified by silica gel column chromatography (PE) to give the product (*R*)-**BN-4Br** as white solid (1.68 g, 63%).¹H NMR (500 MHz, DMSO-*d*₆) δ 8.15 (d, *J* = 9.0 Hz, 2H), 8.07 (d, *J* = 7.9 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.48 – 7.31 (m, 6H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 1.5 Hz, 4H).¹³C NMR (126 MHz, DMSO-*d*₆) δ 158.24, 150.02, 133.27, 130.96, 130.67, 128.45, 127.73, 127.30, 125.64, 125.11, 122.84, 121.87, 119.64, 119.34. (**Fig. S9, S10**).

Preparation procedure for (R)-BN-2mCP

Dry toluene (25 mL) was added to a 50 mL two-neck flask charged with (*R*)-BN-4Br (900 mg, 1.19 mmol), 9H-carbazole (897.91 mg, 5.37 mmol), Pd₂(dba)₃ (87.46 mg, 0.09 mmol), 'Bu₃PHBF₄ (55.43 mg, 0.19 mmol) and 'BuONa (458.79 mg, 4.77 mmol) in nitrogen atmosphere. The mixture was stirred at 120 °C for 24 hours. After cooling down to room temperature, the toluene was removed by a rotatory evaporation and then the mixture was diluted with dichloromethane and washed with water and dried over MgSO₄. The solvent was removed by a rotatory evaporation and the crude product was purified by silica gel column chromatography (PE: DCM = 7:1) to give the product (*R*)-BN-2mCP as white solid (559 mg, 43%).¹H NMR (400 MHz, DMSO-*d*₆) δ 8.24 (dd, *J*

= 9.0, 5.0 Hz, 2H), 8.02 (dd, *J* = 13.5, 8.2 Hz, 10H), 7.76 (d, *J* = 8.9 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.26 (t, *J* = 7.6 Hz, 8H), 7.15 (dt, *J* = 24.8, 7.0 Hz, 22H), 6.91 – 6.85 (m, 4H).¹³C NMR (126 MHz, DMSO-*d*₆) δ 159.62, 151.73, 139.99, 139.62, 133.73, 131.15, 128.83, 127.53, 126.57, 125.89, 125.56, 123.28, 122.66, 121.00, 120.78, 120.68, 119.14, 115.14, 109.89. TOF-MS (ESI) m/z calcd for C₈₀H₅₀N₄O₂ [M]⁺: 1098.39; found:1098.45. (**Fig. S11, S12, S17**).

Preparation procedure for (S)-BN-2mCP

The synthesis method and procedure are the same as (*R*)-BN-2mCP. ¹H NMR (400 MHz, DMSO- d_6) δ 8.26 (d, J = 8.8 Hz, 2H), 8.09 – 7.98 (m, 10H), 7.77 (d, J = 8.9 Hz, 2H), 7.44 (s, 2H), 7.26 (t, J = 7.6 Hz, 8H), 7.15 (dt, J = 25.7, 8.2 Hz, 22H), 6.89 (s, 4H). ¹³C NMR (126 MHz, DMSO- d_6) δ 159.62, 151.73, 139.99, 139.62, 133.73, 131.15, 128.83, 127.53, 126.57, 125.89, 125.56, 123.28, 122.66, 121.00, 120.78, 120.68, 119.14, 115.14, 109.89. TOF-MS (ESI) m/z calcd for C₈₀H₅₀N₄O₂ [M]⁺: 1098.39; found:1098.25. (**Fig. S13, S14, S18**).

2.2 Characterization data





Fig. S1 ¹H NMR spectrum of (*R*)-BN-Et in CDCl₃.

































Fig. S15 Mass spectrum of (*R*)-BN-mCP.



Fig. S16 Mass spectrum of (S)-BN-mCP.



Fig. S17 Mass spectrum of (*R*)-BN-2mCP.



Fig. S18 Mass spectrum of (S)-BN-2mCP.



报告用户:	System
报告方法:	LC 报告
报告方法I	D: 3045 30451
页码: 1 (共	计 1)

项目名称: CZCS_OLED_Defaults 打印日期: 2022/12/15 13:07:57 PRC

Fig. S19 HPLC of (*R*)-BN-mCP.



报告用户: System 报告方法: LC 报告 报告方法 ID: 3045 30451 页码: 1 (共计 1) 项目名称: CZCS_OLED_Defaults 打印日期: 2022/12/15 13:08:54 PRC

Fig. S20 HPLC of (S)-BN-mCP.



报告用户: System
报告方法: LC 报告
报告方法 ID: 3035 30357
页码: 1 (共计 1)

项目名称: CZCS_OLED_Defaults 打印日期: 2022/12/15 13:05:23 PRC

Fig. S21 HPLC of (*R*)-BN-2mCP.



	(分钟)	。 (微伏)	面积 (微伏*秒)	% 面积
1	2.197	259	1253	0.0199
2	2.322	161	938	0.0149
3	2.626	210	1349	0.0214
4	2.927	278	1824	0.0289
5	3.242	1091323	6298378	99.9149

报告用户: System 报告方法: LC 报告 报告方法 ID: 3045 30451 页码: 1 (共计 1) 项目名称: CZCS_OLED_Defaults 打印日期: 2022/12/15 13:06:52 PRC

Fig. S22 HPLC of (S)-BN-2mCP.

3 Thermal properties



Fig. S23 (a) TGA curves of the hosts in N_2 with the heating rate of 20°C min⁻¹; (b) DSC traces of the hosts recorded at a heating rate of 10°C min⁻¹.



Fig. S24 HOMO and LUMO orbital distributions, calculated band gaps and S_1 and T_1 energy levels for compounds based on DFT at the B3LYP functional and 6-31G(d) basis set.

4 Theoretical Calculations



5 Ultraviolet Photoelectron Spectroscopy

Fig. S25 Ultraviolet photeletron spectra UPS spectra of (a) (R)-BN-mCP, (b) (R)-BN-2mCP.



6 Electrochemical properties

Fig. S26 CV curves of the (R)-BN-mCP and (R)-BN-2mCP in CH₃CN solution

The redox property of the (*R*)-BN-mCP and (*R*)-BN-2mCP was investigated by cyclic voltammetry (CV) measurement in acetonitrile solution. As shown in **Figure S26**, only irreversible oxidation (E_{ox}) waves were detected for the hosts in the range of 0~1.5 V. According to the oxidation onset, the E_{ox} are evaluated to be 1.22 for (*R*)-BN-mCP and 1.29 for (*R*)-BN-2mCP relative to ferreocenium/ferrocenc (Fc/Fc⁺, $E_{Fc/Fc^+} = 0.48$ V). According to the emperical formulae of E_{HOMO}

= $-(E_{\text{ox}} - E_{\text{Fc/Fc+}} + 4.8)$ eV and $E_{\text{LUMO}} = -(E_{\text{HOMO}} + \text{Eg})$ eV, the HOMO/LUMO energy level of (*R*)-BN-mCP and (*R*)-BN-2mCP are calculated to be -5.54/-1.89 and -5.61/-1.85 eV.



7 Photophysical properties

Fig. S27 (a) UV-vis spectra and PL spectra (λ_{ex} =300 nm) in doped PMMA film (10%) at room temperature;(b) fluorescence lifetime in doped PMMA film (10%) at room temperature.

Com poun ds	^a λ _{abs} /nm	^a λ _{em} /nm	^b λ _{abs} /nm	^b λ _{em} /nm	^c S ₁ /eV	^{<i>c</i>} <i>T</i> ₁ /eV	^{<i>d,e</i>} E _Н омо /eV	^{<i>d,e</i>} E _{LU} мо /eV	<i>^fT</i> _d ∕°C	<i>¤Tg</i> ∕°C	Eg ^{opt} /eV
(<i>R</i>)- BN- mCP	293,3 26,33 9	364	233,2 93,32 6,339	365	3.72	2.61	-5.55 ^d -5.54 ^e	-1.90 ^d -1.89 ^e	359	107	3.65
(<i>R</i>)- BN- 2mC P	282,2 93,32 6,339	345,3 60	233,2 93,32 6,339	348,3 61	3.76	2.67	-5.91 ^d -5.61 ^e	-2.15 ^d -1.85 ^e	524	177	3.76
mCP	282,2 93,32 6,339	345,3 60	240,2 93,32 6,339	348,3 61	3.72	3.16	-5.90	-2.40			

Table S1 Photophysical data of the three compounds.

a: Measured in 10⁻⁵M toluene at room temperature (λ_{ex} =300 nm); b: 10 wt% in PMMA 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 UPS; e: collected from CV measurement f: in N₂ with the heating rate of 20 °C min⁻¹. g: in N₂ with the heating rate of 10 °C min⁻¹.

8 Chiroptical properties



Fig. S28 (a) CPL spectra of the Ir(mppy)₃ doped in (R/S)-BN-mCP host; (b) g_{PL} spectra of the Ir(mppy)₃ doped in (R/S)-BN-mCP host; (c) CPL spectra of the Ir(mppy)₃ doped in (R/S)-BN-2mCP host; (d) g_{PL} spectra of the Ir(mppy)₃ doped in (R/S)-BN-2mCP host.

9 CP-OLEDs performances



Fig. S29 UV-vis spectra (guest) and PL spectra (host) (λ_{ex} =300 nm) measured in toluene solution (10⁻⁵ M).



Fig. S30 Devices structures of (a) Green OLEDs, (b) two emitters OLEDs and (c) the molecular

structures in the devices.



Fig. S31 The mobility of chiral hosts of (*R*)-BN-mCP and (*R*)-BN-2mCP.



Fig. S32 EL properties of the green CP-OLEDs devices: a) CE-luminance curves; b) current densityvoltage-luminance curves



Fig. S33 EL properties of based on (*R/S*)-BN-2mCP: Ir(mppy)₃:Ir(piq)₂(acac) : a) CE-luminance curves; b) EQE-luminance curves; c) current density-voltage-luminance curves; d) normalized EL spectra (Inset: emission pictures of the devices).

Device		V _{ON}	L _{max}	CE _{max}	EQE _{max}	CIE	Peak	$g_{ m EL}$
EML : host: Ir	V	cd m ⁻²	cd A ⁻¹	%	(x, y)	nm	×10 ⁻³	
(R)-BN-mCP	80:20	2.8	5022	44.37	12.7	(0.30,0.62)	518	□1.7
(<i>S</i>) -BN-mCP	80:20	2.8	7230	43.85	12.4	(0.30,0.62)	518	□1.3
(R)-BN-2mCP	80:20	2.8	15070	61.03	17.1	(0.30,0.63)	518	□1.3
(S) -BN-2mCP 80:20		2.8	15000	46.45	13.0	(0.30,0.62)	518	□2.1

Table S2 EL data for the green CP-OLEDs devices

Table S3 EL data for the CP-OLEDs devices

Device host: Ir(mppy)3:Ir(piq)2(acac)		V _{ON} V	L _{max} cd m ⁻²	<i>CE</i> _{max} cd A ⁻¹	EQE _{max} %	<i>CIE</i> (x, y)	<i>g</i> el ×10 ^{−3}
(D) DN	84.5:15: 0.5	3.2	11260	33.93	11.9	(0.32,0.60)	
(K)-BN-	84:15: 1.0	3.2	7849	20.96	11.6	(0.43,0.52)	
ZIIICP	83.5:15: 1.5	3.2	10060	18.56	12.1	(0.45,0.50)	□1.1
	84.5:15: 0.5	3.2	12040	35.57	11.6	(0.31,0.61)	
(3) -BN-	84:15: 1.0	3.2	6577	23.18	12.0	(0.40,0.54)	
2mCP	83.5:15: 1.5	3.2	10740	17.66	11.4	(0.43,0.51)	