< Supporting Information >

Enhanced Chiroptical Activity for Narrow Deep-Blue Emission in Axial Chiral Frameworks via Three-Dimensional Interlocking

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Table of Contents

1. General Informations

The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra of these chiral compounds were acquired at room temperature using a Bruker AV 500M/400M NMR spectrometer, with $CDCl_3$ or DMSO-d_6 as the solvent and tetramethylsilane as the internal standard. High-resolution mass spectrometry (HRMS) was performed using a Thermo Scientific LTQ Orbitrap XL mass spectrometer equipped with an electron spray ionization ion source. Thermogravimetric analysis (TGA) was undertaken using TGA-55 Instrument (TA Instruments, America) at a heating rate of 10 °C/min from 30 °C to 700 °C under nitrogen flushing. The thermal decomposition temperatures (T_d) were determined by the recorded temperature at 5% weight loss. Cyclic voltammetry (CV) measurements were carried out on a CHI600 electrochemical analyzer (Chenhua, China) at room temperature with a scan speed of 50 mV s^{-1}, using a conventional three-electrode system consisting of a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl standard electrode as the reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in anhydrous dichloromethane solution, and ferrocene was added as a calibrant in the whole measurement. The HOMO energy levels of the compounds were calculated according to the formula: E_{HOMO} (eV) = - [4.8 + ($E_{1/2(\mathrm{ox/red})}$ - $E_{1/2(\mathrm{Fc+/Fc})}$] (eV). The LUMO energy levels of the compounds were then deduced from the HOMO levels and the optical band gap. The UV-vis absorption spectra were obtained on a Shimadzu UV-2600 spectrophotometer (Shimadzu, Japan) at room temperature with a concentration of 1×10^{-5} M. Phosphorescence spectra were measured on a Hitachi F-7100 fluorescence spectrophotometer at 77 K. The transient photoluminescence (PL) decay curves were obtained by FluoTime 300 (PicoQuant GmbH) with a Picosecond Pulsed UV-LASTER (LASTER375) as the excitation source. The solid-state PL quantum efficiencies (Φ_{PL}s) were measured on a Hamamatsu UV-NIR absolute PL quantum yield spectrometer (C13534, Hamamatsu Photonics) equipped with an integrating sphere. The integrating sphere was purged with dry argon to maintain an inert atmosphere and all the samples were excited at 320 nm. The circular dichroism (CD) were measured on ChirascanTM circular dichroic spectropolarimeter. The circularly polarized luminescence (CPPL and CPEL) spectra were measured on Jasco CPL-300 spectrometer. The test mode adopts "Slit" mode with the Ex and Em Slit width 3000 μm and the digital integration time (D.I.T.) is 2.0s with multiple accumulations.

2. Theoretical Calculations

The geometrical and electronic properties of these chiral molecules at ground-states were computed by using DFT within the Gaussian 16 software package at the B3LYP/6-311g(d,p) level, which incorporates Grimme's dispersion correction.[1] Energy levels of excited states, including singlets and triplets, and the optimal geometrical configuration of the S_1 were determined through time-dependent DFT (TD-DFT) at the same level. The magnetic and electric dipole moments were outputted from optimized S_1 configuration at PBE0/def2-SVP level with Grimme's D3BJ empirical dispersion correction and incorporating the solvation model based on density (SMD, in toluene). NTO analysis was conducted using the Multiwfn 3.8 program.[2] Spin-orbit coupling constants between the S_1 and T_n (n = 1, 2, 3, 4, 5) states were computed by using PySOC, with parameter settings in accordance with their TD-DFT calculations. All computations were performed in the gas phase and visualized using GaussView 6.0 and VMD 1.9.3.[3]

3. Device Fabrication and Characterization

The ITO-coated glass substrates (sheet resistance: 15 Ω square-1) underwent consecutive ultrasonic cleaning with acetone/isopropanol, nitrogen gas drying, and a 20-minute UV-ozone treatment. Post-treatment, the substrates entered the deposition system. Organic layers, including HAT-CN, TAPC, TCTA, mCBP, DBFPO emitting layers (*R*-BNCz-Ph, *R*,*R*-BBNCz-Ph or *R*,*R*-BNCz-BN), ANT-BIZ, and a Liq layer, were thermally evaporated at 5×10^{-5} Pa with deposition rates of 0.2-3 Å/s. The cathode Al layer was deposited at 3 Å/s. Device measurements, including *J-V-L* properties, external quantum efficiency, and electroluminescence spectra, were conducted using a Keithley 2400 source meter and an absolute EQE measurement system (C9920-12, Hamamatsu Photonics, Japan). The device's emitting area is 0.09 cm^2.

4. Materials Synthesis and Characterization

All raw materials and anhydrous solvents were commercially available and used without further purification. The reactions were carried out under the protection of the high-purity argon atmosphere. All reactions were heated by metal sand bath (WATTCAS, LAB-500, https://www.wattcas.com).

***Synthesis of (R/S)-5H,5'H-6,6'-bibenzo[b]carbazole (R/S-BNCz)*:** (*S*/*R*)-[1,1'-binaphthalene]-2,2'-diamine (5.00g, 17.60mmol), 1-bromo-2-chlorobenzene (10.12 g, 52.8 mmol), $CsCO_3$ (17.20 g, 52.8 mmol), $Pd_2(dba)_3$ (0.05 g, 0.06 mmol), BINAP (1.06g, 1.70

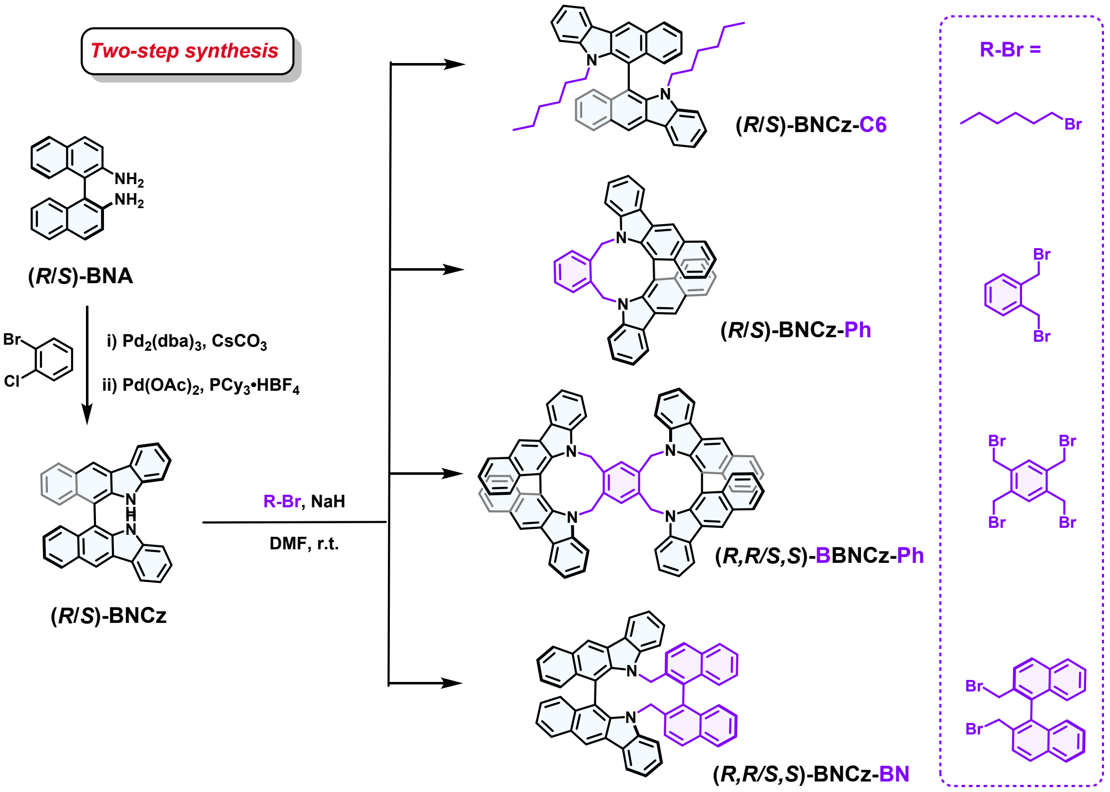
mmol) were dissolved in 50 mL dry toluene at room temperature. After blowing argon for 15 minutes, the reaction was stirred at 110 ºC for 24 h. Then $Pd(OAc)_2$ (0.19g, 0.85mmol), PCy_3HBF_4 (0.62 g, 1.69 mmol) were added, and the reaction was stirred at 150 ºC for another 24 h. After cooling to room temperature, toluene was removed by rotary evaporation. Subsequently, the resultant crude product underwent purification through the employment of silica gel column chromatography (eluent: petroleum ether/dichloromethane = 9:1 to 4:1, v/v), giving the title compound as white solid (4.95 g, yield 65%). ^1H NMR (400 MHz, DMSO-d_6) δ 10.32 (s, 2H), 8.94 (s, 2H), 8.37 (d, *J* = 7.7 Hz, 2H), 8.25 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.35 (m, 4H), 7.28 – 7.17 (m, 6H), 7.13 (d, *J* = 8.6 Hz, 2H). HRMS (ESI) m/z calcd for $C_{32}H_{21}N_2^+$ $[M+H]^+$ 433.1699, found 433.1698.

Synthesis of 5,5'-dihexyl-5H,5'H-6,6'-bibenzo[b]carbazole (R/S)-BNCz-C6 : Intermediate *R*/*S*-BNCz (1.00 g, 2.31 mmol), NaH (0.17 g, 6.93 mmol) were dissolved in 60 mL dry DMF at room temperature. The mixture was stirred at room temperature under argon for 30 minutes, followed by the addition of 1-bromohexane (0.76g, 4.62mmol). The reaction mixture was then stirred at room temperature for 12 h. After the reaction finish, the mixture was poured into water, the crude product was collected by filtration and washed with water. The crude product was further purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 5:1, v/v), giving the **(*R/S*)-BNCz-C6** as a white solid (0.844 g, yield 61%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 2H), 8.33 (dd, *J* = 7.8, 1.2 Hz, 2H), 8.16 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.53 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 2H), 7.48 (ddd, *J* = 8.0, 6.5, 1.2 Hz, 2H), 7.38 - 7.25 (m, 4H), 7.19 – 7.15 (m, 4H), 3.31 (td, *J* = 6.8, 6.4, 3.1 Hz, 4H), 1.01 - 0.82 (m, 2H), 0.77 – 0.61 (m, 6H), 0.59 (dq, *J* = 10.7, 5.4 Hz, 6H), 0.41 – 0.34 (m, 4H), 0.20 – 0.11 (m, 4H). HRMS (ESI) m/z calcd for $C_{44}H_{45}N_2^+$ $[M+H]^+$ 601.3577, found 601.3572.

Synthesis of (R/S)-BNCz-Ph : Intermediate *R*/*S*-BNCz (1g, 2.31mmol), NaH (0.17 g, 6.93 mmol) were dissolved in 60 mL dry DMF at room temperature. The mixture was stirred at room temperature under argon for 30 minutes, followed by the addition of 1,2-bis(bromomethyl)benzene(0.61 g, 2.31 mmol). The reaction mixture was then stirred at room temperature for 12 h. After the reaction finish, the mixture was poured into water, the crude product was collected by filtration and washed with water. The crude product was further purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 5:1, v/v), giving the **(*R/S*)-BNCz-Ph** as a white solid (0.912 g, yield 74%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 2H), 8.20 (d, *J* = 7.7 Hz, 2H), 8.05 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.32 (m, 2H), 7.32 – 7.24 (m, 6H), 7.19 (s, 2H), 7.06 – 6.96 (m, 4H), 6.74 (d, *J* = 8.7 Hz, 2H), 6.13 (d, *J* = 16.0 Hz, 2H), 4.59 (d, *J* = 16.0 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.33, 139.67, 136.34, 133.81, 133.30, 128.76, 128.44, 127.48, 127.17, 125.61, 125.55, 125.41, 123.53, 123.10, 120.65, 119.73, 119.22, 112.21, 110.59, 53.44, 48.41. HRMS (ESI) m/z calcd for $C_{40}H_{27}N_2^+$ $[M+H]^+$ 535.2169, found 535.2171.

***Synthesis of (R,R/S,S)-BBNCz-Ph*:** Intermediate *R*/*S*-BNCz (1 g, 2.31 mmol), NaH (0.17 g, 6.93 mmol) were dissolved in 60 mL dry DMF at room temperature. The mixture was stirred at room temperature under argon for 30 minutes, followed by the addition of 1,2,4,5-Tetrakis(bromomethyl)benzene (1.04 g, 2.31 mmol). The reaction mixture was then stirred at room temperature for 12 h. After the reaction finish, the mixture was poured into water, the crude product was collected by filtration and washed with water. The crude product was further purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 4:1, v/v), giving the **(*R,R/S,S*)-BBNCz-Ph** as a white solid (0.983 g, yield 43%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.70 (s, 4H), 8.23 (d, *J* = 7.7 Hz, 4H), 8.11 (d, *J* = 8.2 Hz, 4H), 7.39 – 7.32 (m, 14H), 7.21 (t, *J* = 7.1 Hz, 4H), 7.05 (t, *J* = 8.4 Hz, 4H), 6.68 (d, *J* = 8.7 Hz, 4H), 6.09 (d, *J* = 15.7 Hz, 4H), 4.65 (d, *J* = 15.7 Hz, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.24, 139.36, 138.11, 135.96, 133.86, 128.83, 128.38, 127.37, 125.60, 125.58, 125.19, 123.56, 123.15, 120.83, 119.82, 119.20, 112.24, 110.25, 47.48. HRMS (ESI) m/z calcd for $C_{74}H_{47}N_4^+$ $[M+H]^+$ 991.3795, found 991.3794.

***Synthesis of (R,R/S,S)-BNCz-BN*:** Intermediate *R*/*S*-BNCz (1 g, 2.31 mmol), NaH (0.17 g, 6.93 mmol) were dissolved in 60 mL dry DMF at room temperature. The mixture was stirred at room temperature under argon for 30 minutes, followed by the addition of *R/S*-2,2′-Bis(bromomethyl)-1,1′-binaphthalene (1.02 g, 2.31 mmol). The reaction mixture was then stirred at room temperature for 12 h. After the reaction finish, the mixture was poured into water, the crude product was collected by filtration and washed with water. The crude product was further purified by column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 5:1, v/v), giving the **(*R,R/S,S*)-BNCz-BN** as a white solid (0.89 g, yield 54%).^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.51 (s, 2H), 8.20 (d, *J* = 6.5 Hz, 2H), 7.79 (d, *J* = 9.6 Hz, 2H), 7.47 – 7.41 (m, 2H), 7.29 (s, 2H), 7.25 – 7.17 (m, 4H), 7.15 (dd, *J* = 8.6, 0.8 Hz, 2H), 7.08 – 7.02 (m, 2H), 6.88 – 6.81 (m, 4H), 6.75 – 6.69 (m, 2H), 6.54 (d, *J* = 8.5 Hz, 2H), 6.30 (d, *J* = 8.1 Hz, 2H), 6.11 (d, *J* = 8.6 Hz, 2H), 5.09 (d, *J* = 16 Hz, 2H), 4.78 (d, *J* = 16 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.15, 139.91, 133.92, 133.48, 133.30, 131.44, 130.41, 128.44, 127.94, 127.48, 126.90, 126.72, 126.45, 125.87, 125.71, 125.46, 125.38, 124.71, 123.32, 122.80, 121.78, 119.31, 118.63, 118.42, 112.52, 108.93, 48.63. HRMS (ESI) m/z calcd for $C_{54}H_{35}N_2^+$ $[M+H]^+$ 711.2795, found 711.2792.



Scheme S1. Synthesis routes of the four pairs chiral emitters.

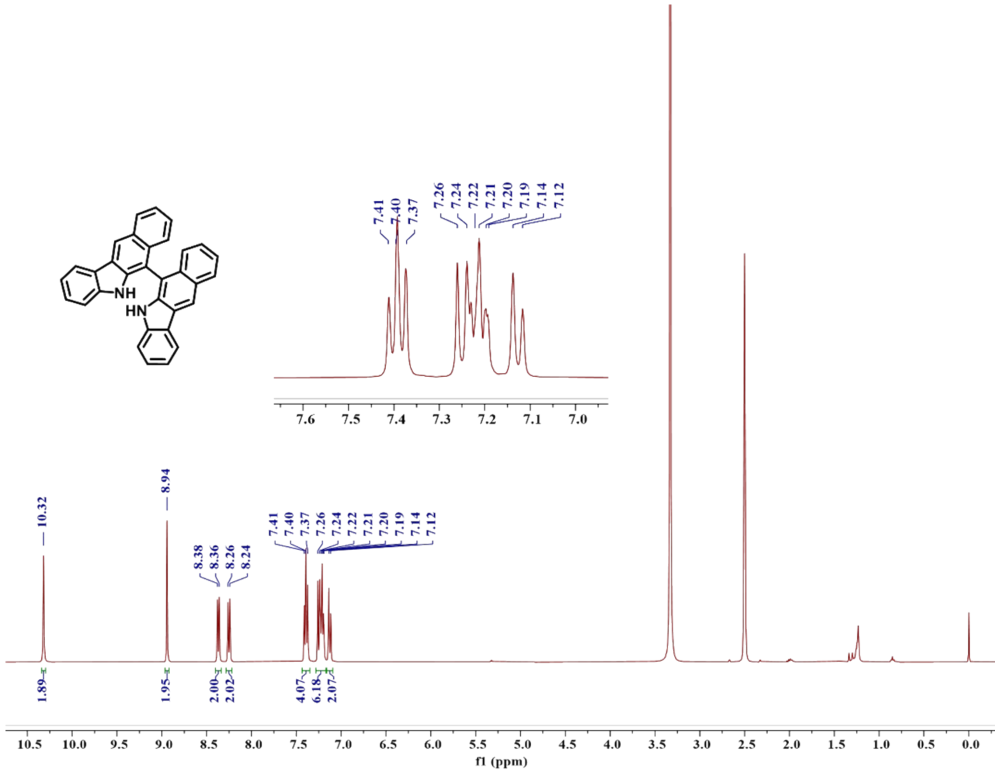


Figure S1. ^{1}H NMR spectrum of BNCz in DMSO-d_6 (400 MHz, 25 ºC).

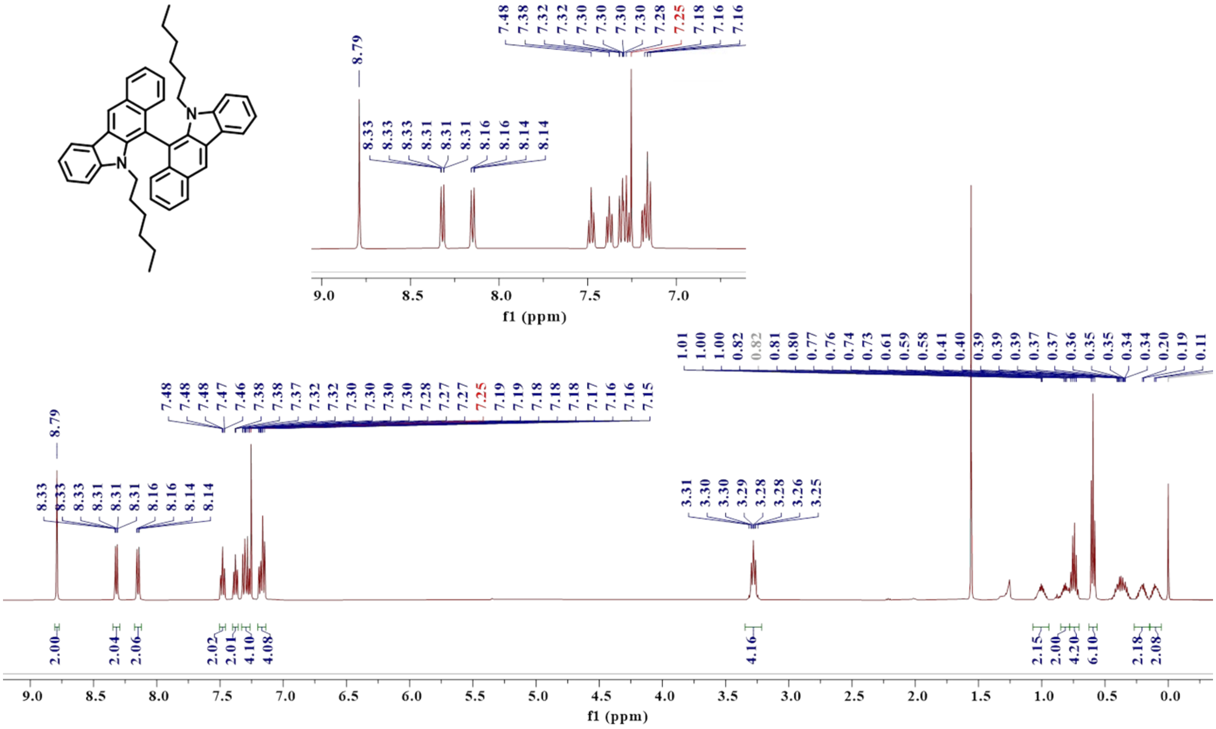


Figure S2. ^{1}H NMR spectrum of BNCz-C6 in Chloroform-*d* (500 MHz, 25 ºC).

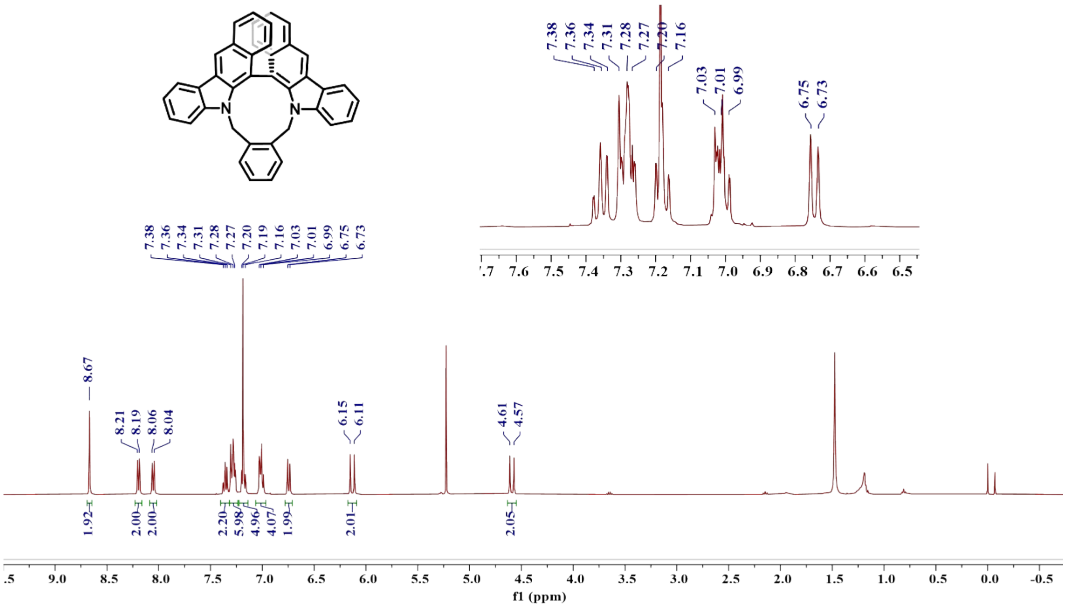


Figure S3. ^{1}H NMR spectrum of BNCz-Ph in Chloroform-*d* (400 MHz, 25 ºC).

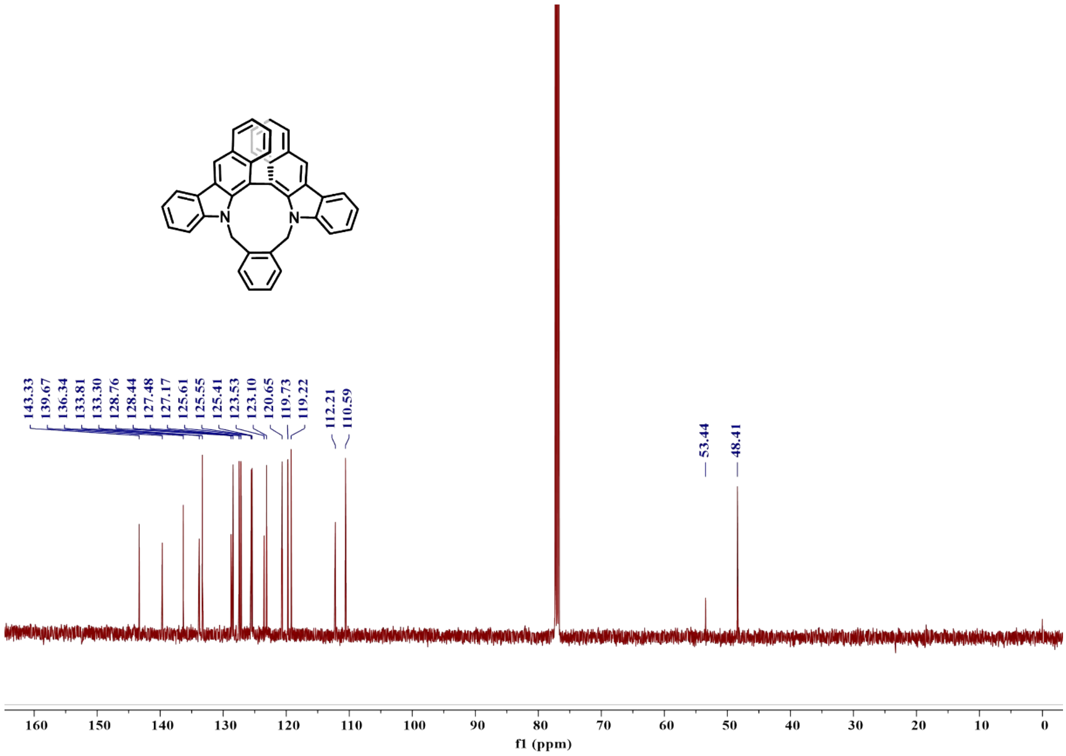


Figure S4. ^{13}C NMR spectrum of BNCz-Ph in Chloroform-*d* (126 MHz, 25 ºC).

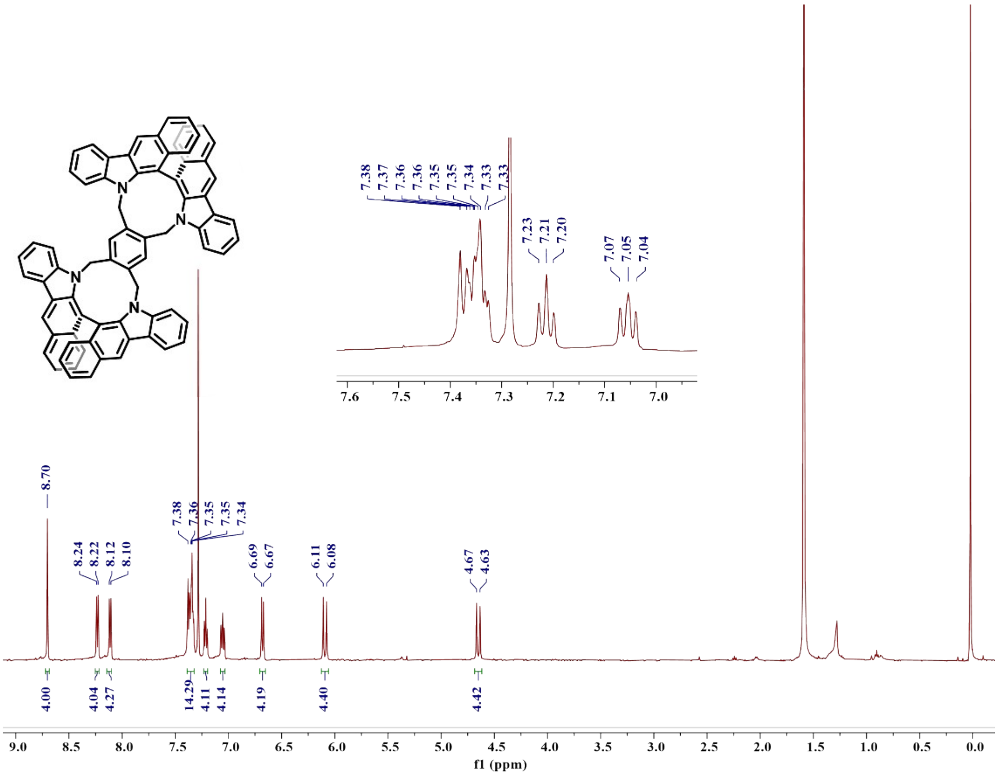


Figure S5. ^{1}H NMR spectrum of BBNCz-Ph in Chloroform-*d* (500 MHz, 25 ºC).

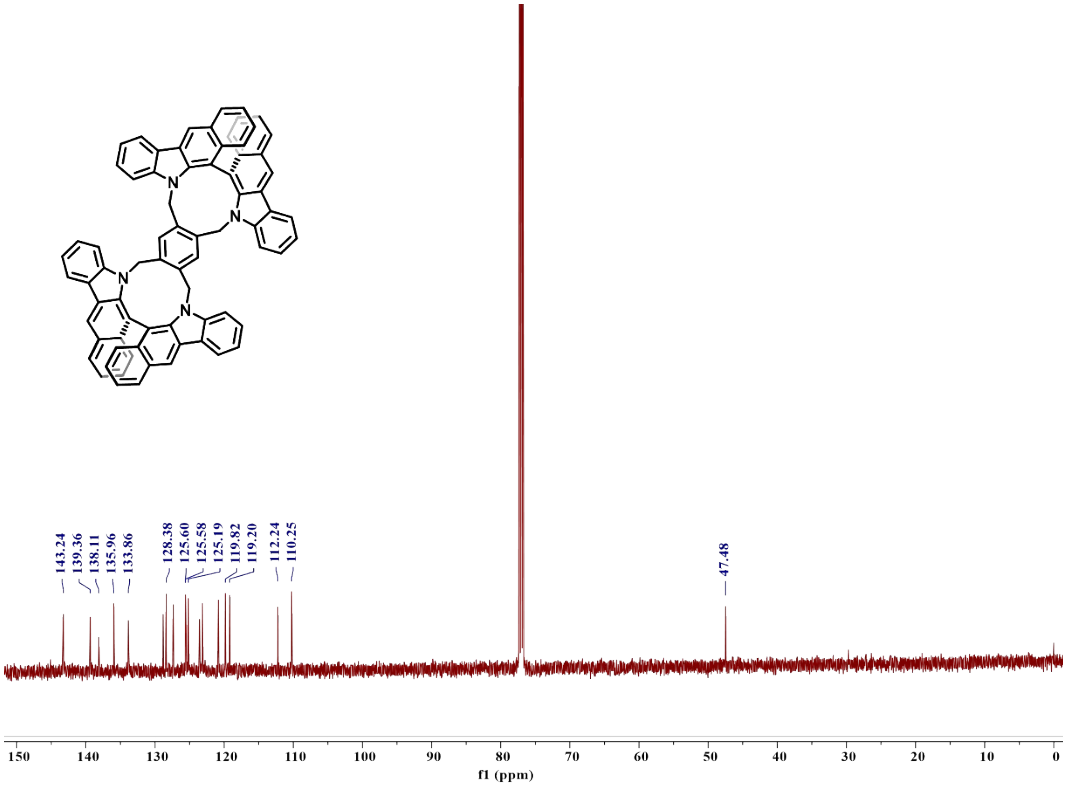


Figure S6. ^{13}C NMR spectrum of BBNCz-Ph in Chloroform-*d* (126 MHz, 25 ºC).

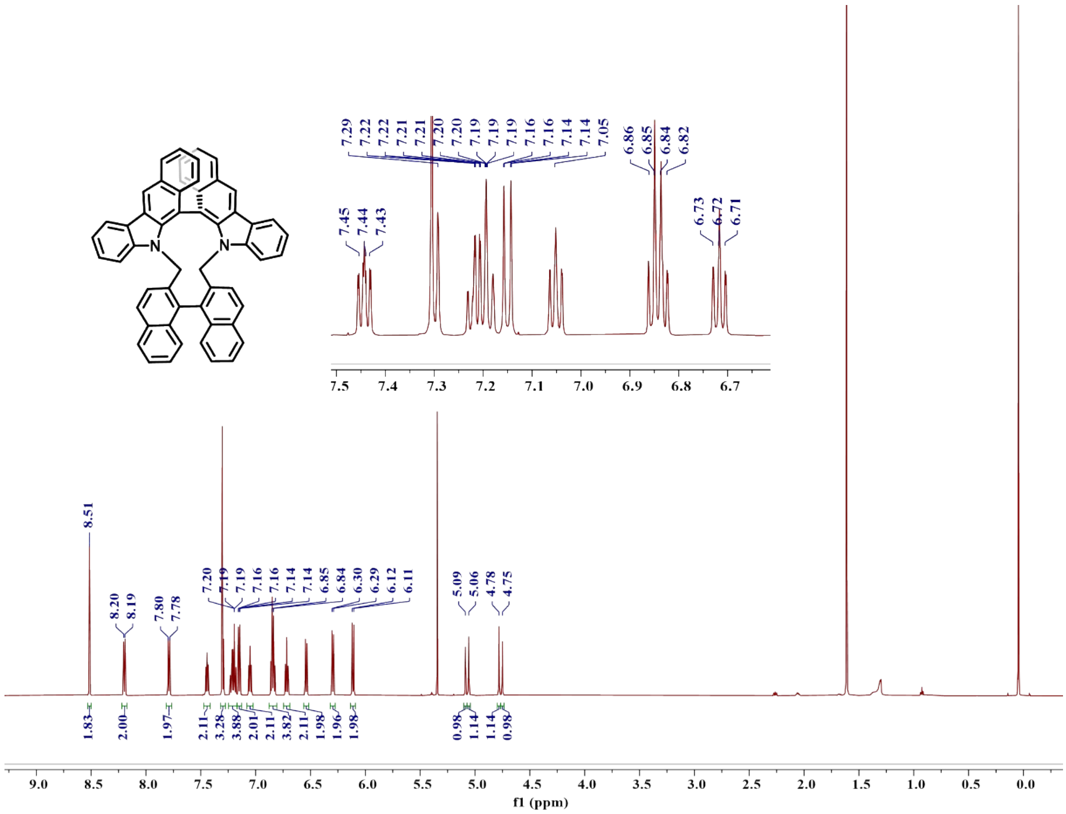


Figure S7. ^{1}H NMR spectrum of BNCz-BN in Chloroform-*d* (600 MHz, 25 ºC).

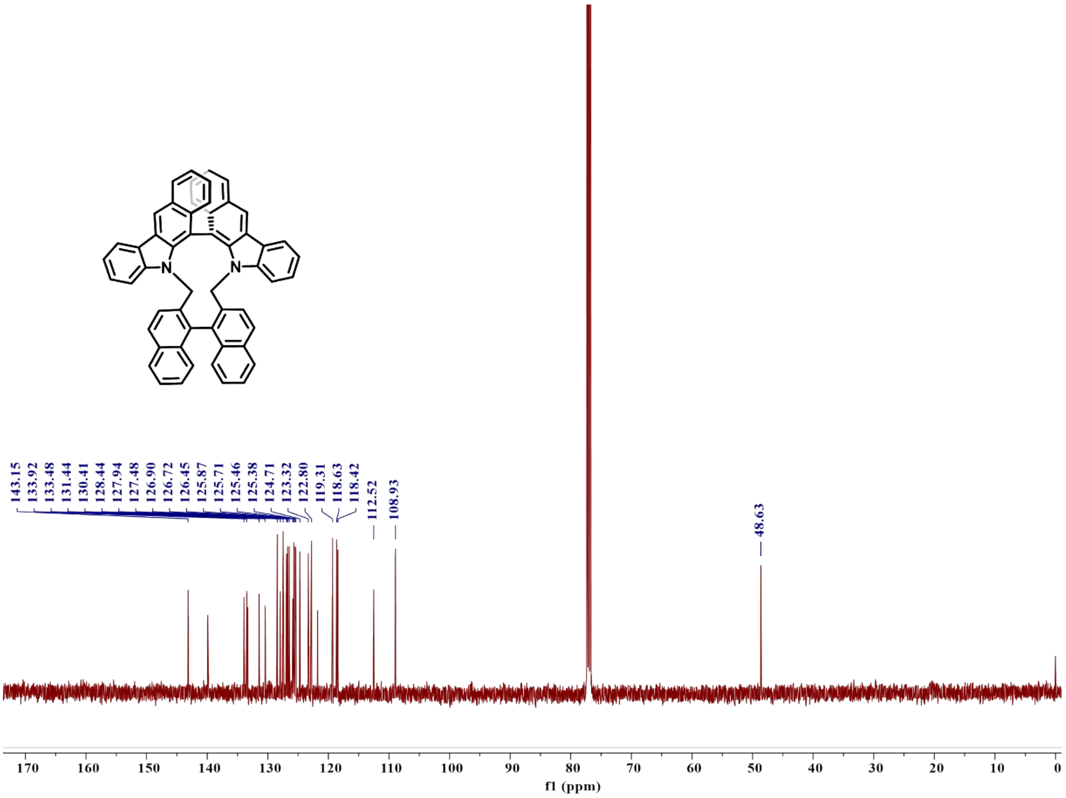


Figure S8. ^{13}C NMR spectrum of BNCz-BN in Chloroform-*d* (126 MHz, 25 ºC).

5. Single Crystal measurements

The single crystals of **(*R/S*)-BNCz-Ph**, **(*R,R/S,S*)-BBNCz-Ph** and **(*R,R/S,S*)-BNCz-BN** were prepared from a methanol/dichloromethane mixed solution by slowly evaporating method. X-ray single crystals data were collected on a Bruker D8 Venture diffractometer using GaKα radiation (for BNCz-BN, λ = 1.34139) and CuKα radiation (for BNCz-Ph, λ = 1.54178) sources. The selected crystal were kept at 170.00 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization.

Compound name: (*R*)-BNCz-Ph; CCDC number: 2372805.

Compound name: (*S*)-BNCz-Ph; CCDC number: 2372807.

Compound name: (*R,R*)-BBNCz-Ph; CCDC number: 2372808.

Compound name: (*R,R*)-BNCz-BN; CCDC number: 2372806.

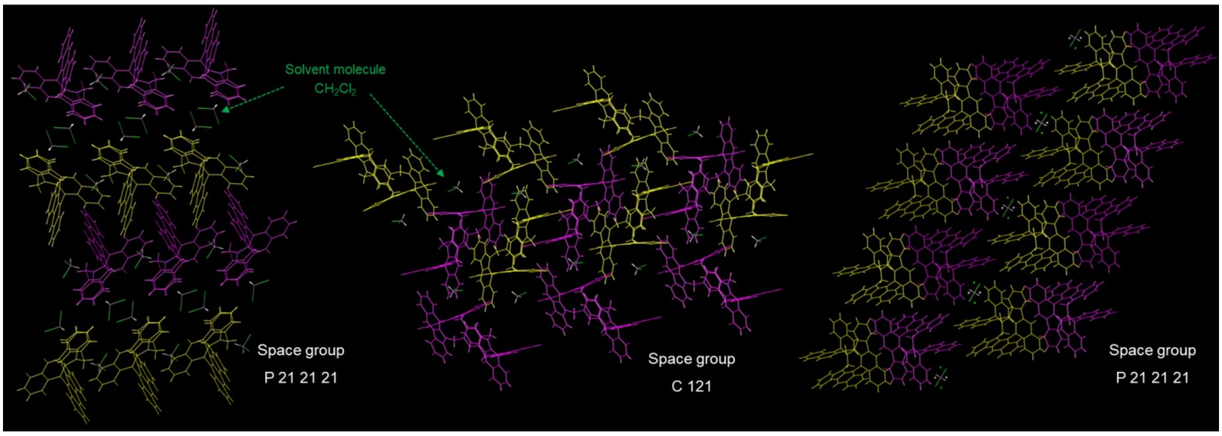


Figure S9. The packing models in single crystals of *R*-BNCz-Ph, *R,R*-BBNCz-Ph, and *R,R*-BNCz-BN, distinguished with two different colors.

6. Thermal stability and electrochemical property

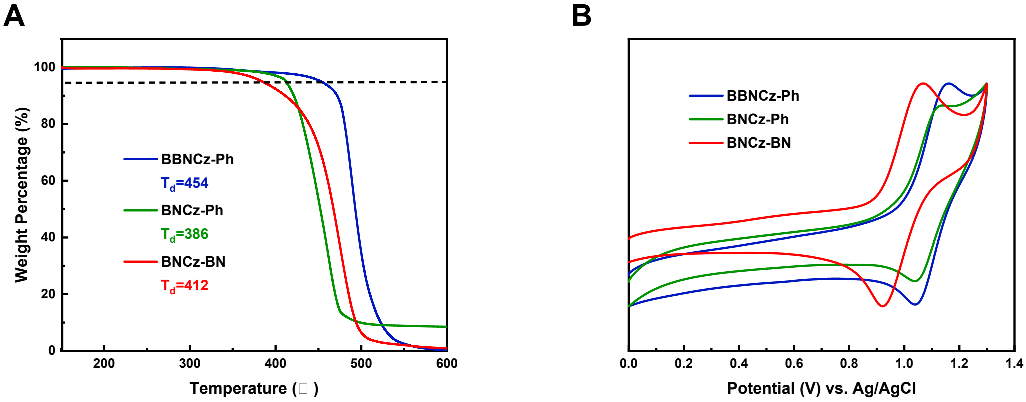


Figure S10. (A) Thermal gravimetric analysis (TGA) curves at a heating rate of 10 °C min^{-1}, (B) the oxidation curves obtained from the cyclic voltammetry (CV) measurement for the emitters.

7. Photophysical properties

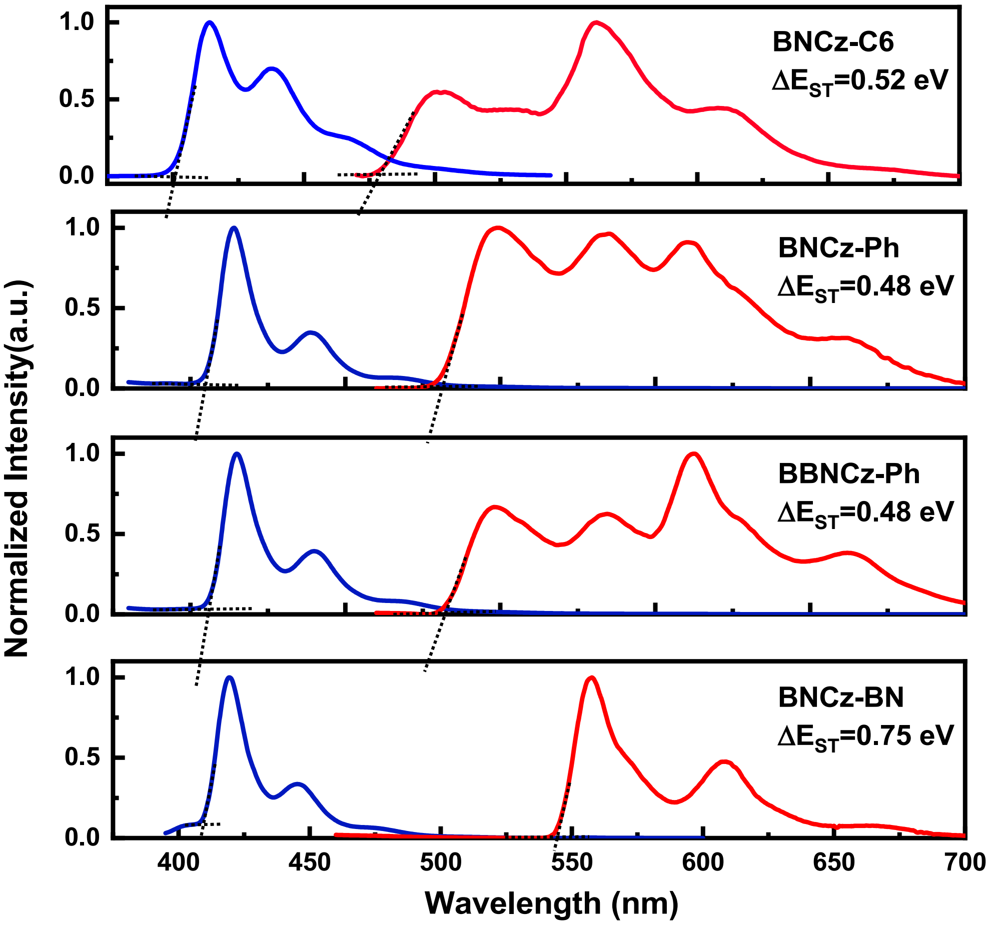


Figure S11. Normalized fluorescence (blue line) and phosphorescence (red line) spectra of BNCz-C6, BNCz-Ph, BBNCz-Ph and BNCz-BN at 77 K (in toluene solutions, 1 × 10^{-5} M).

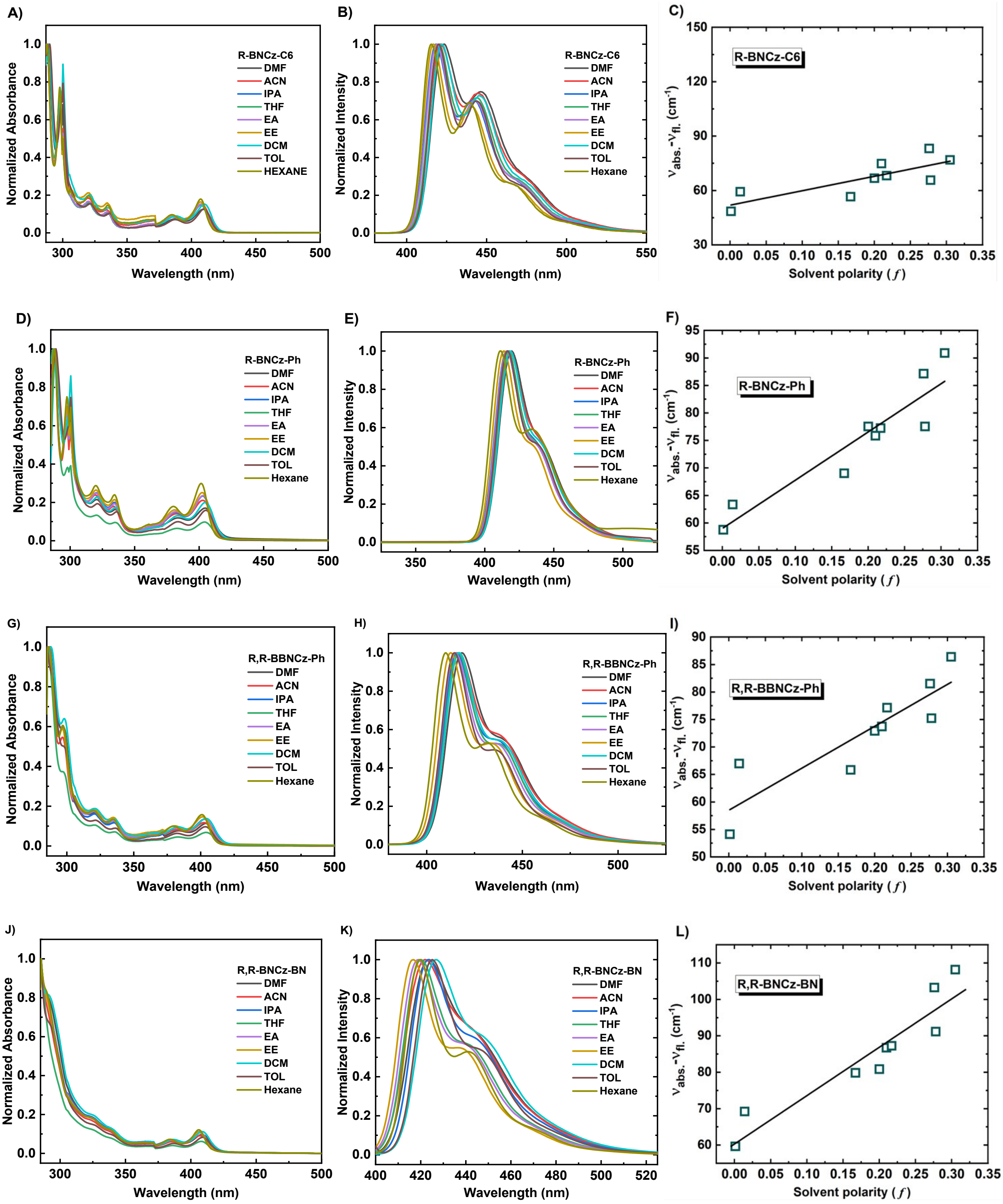


Figure S12. Solvent polarity-dependent absorption and fluorescence spectra, as well as linear correlation of orientational polarization of solvent media *versus* Stokes shift ($\nu_{abs.}-\nu_{fl.}$) for these chiral emitters. A), B), and C) for BNCz-C6, D), E), and F) for BNCz-Ph, G), H), and I) for BBNCz-Ph and J), K), and L) for BNCz-BN, respectively.

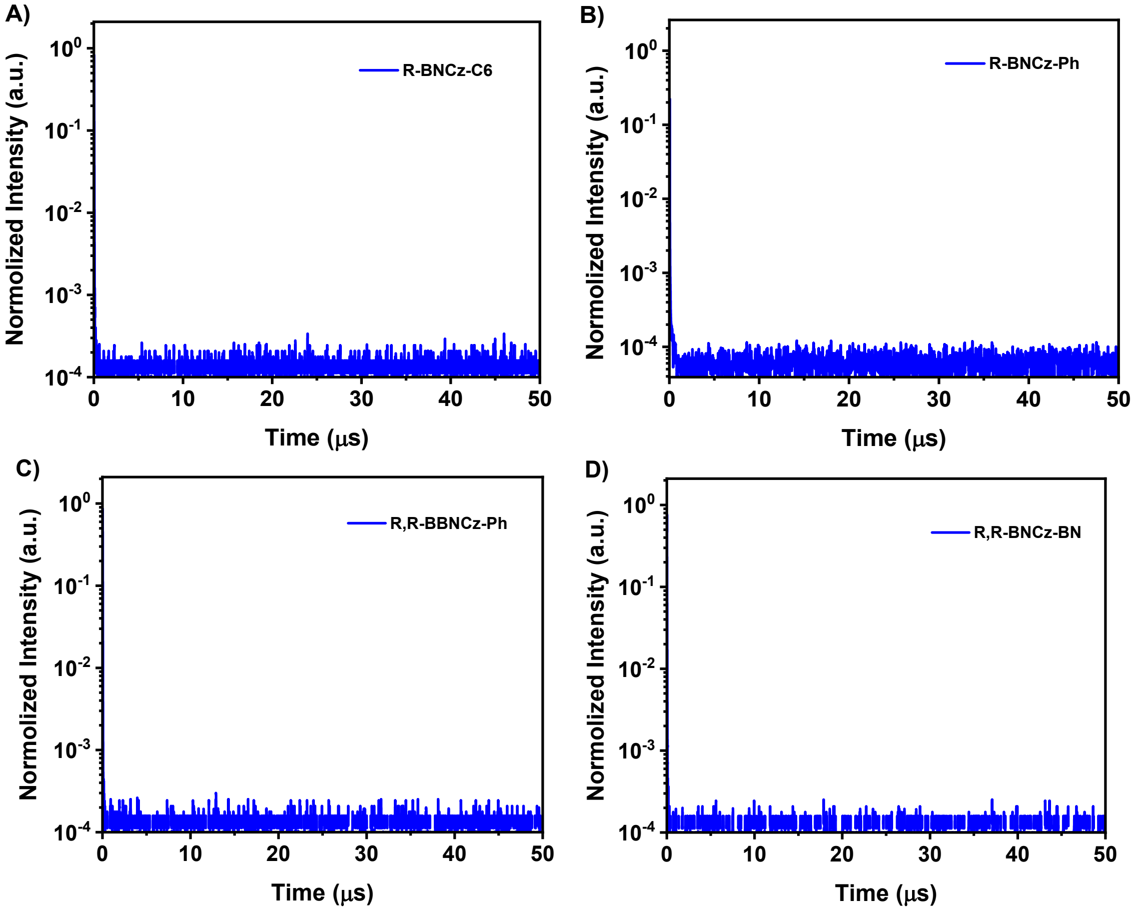


Figure S13. Transient photoluminescence spectra at microsecond scale of these chiral emitters (doped in *m*CBP:DBFPO, 1:1 matrix).

8. Chiroptical properties

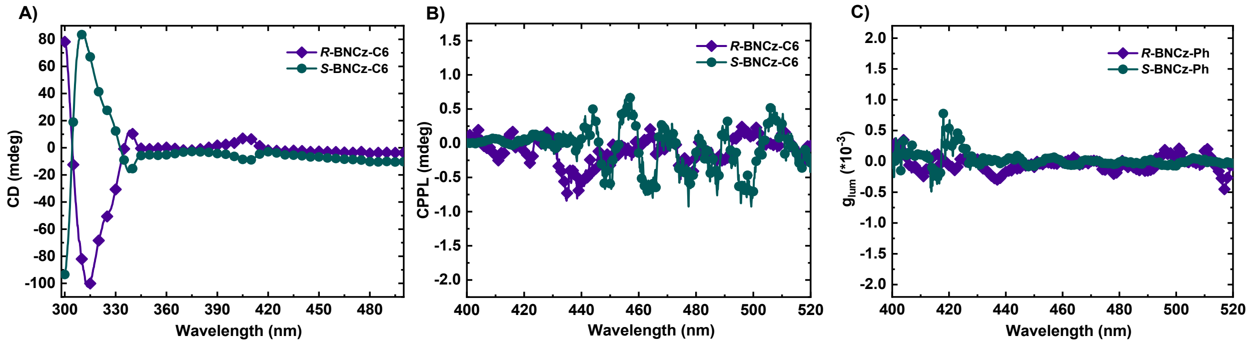


Figure S14. A) CD and B) CPPL spectra of the R/S-BNCz-C6 in dilute toluene (1×10^{-5} M), and C) the corresponding g_{lum} values.

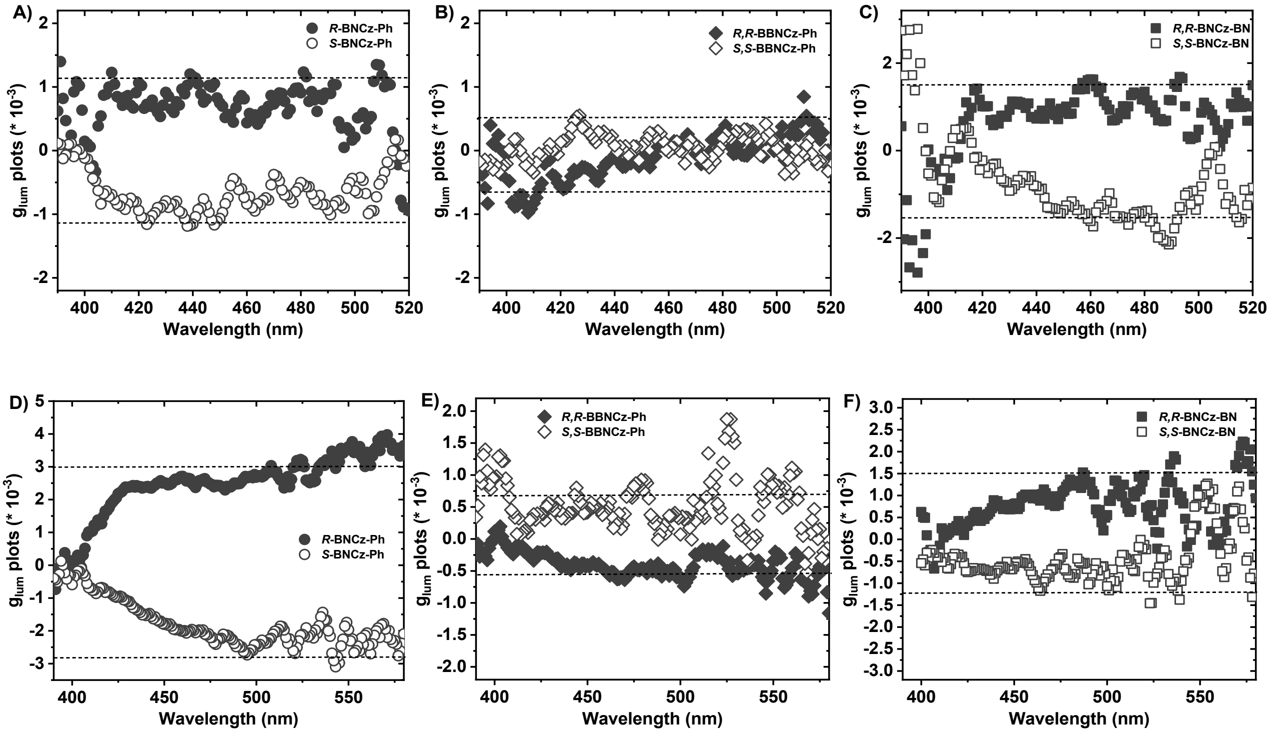


Figure S15. The fitting g_{lum} values of A/B) (*R*/*S*)-BNCz-Ph, C/D) (*R,R*/*S,S*)-BBNCz-Ph, and E/F) (*R,R*/*S,S*)-BNCz-BN in 1×10^{-5} M toluene (the upper layer) and in doped thin films (20 wt.% doped in mCBP:DBFPO matrix, the under layer).

9. Theoretical calculations

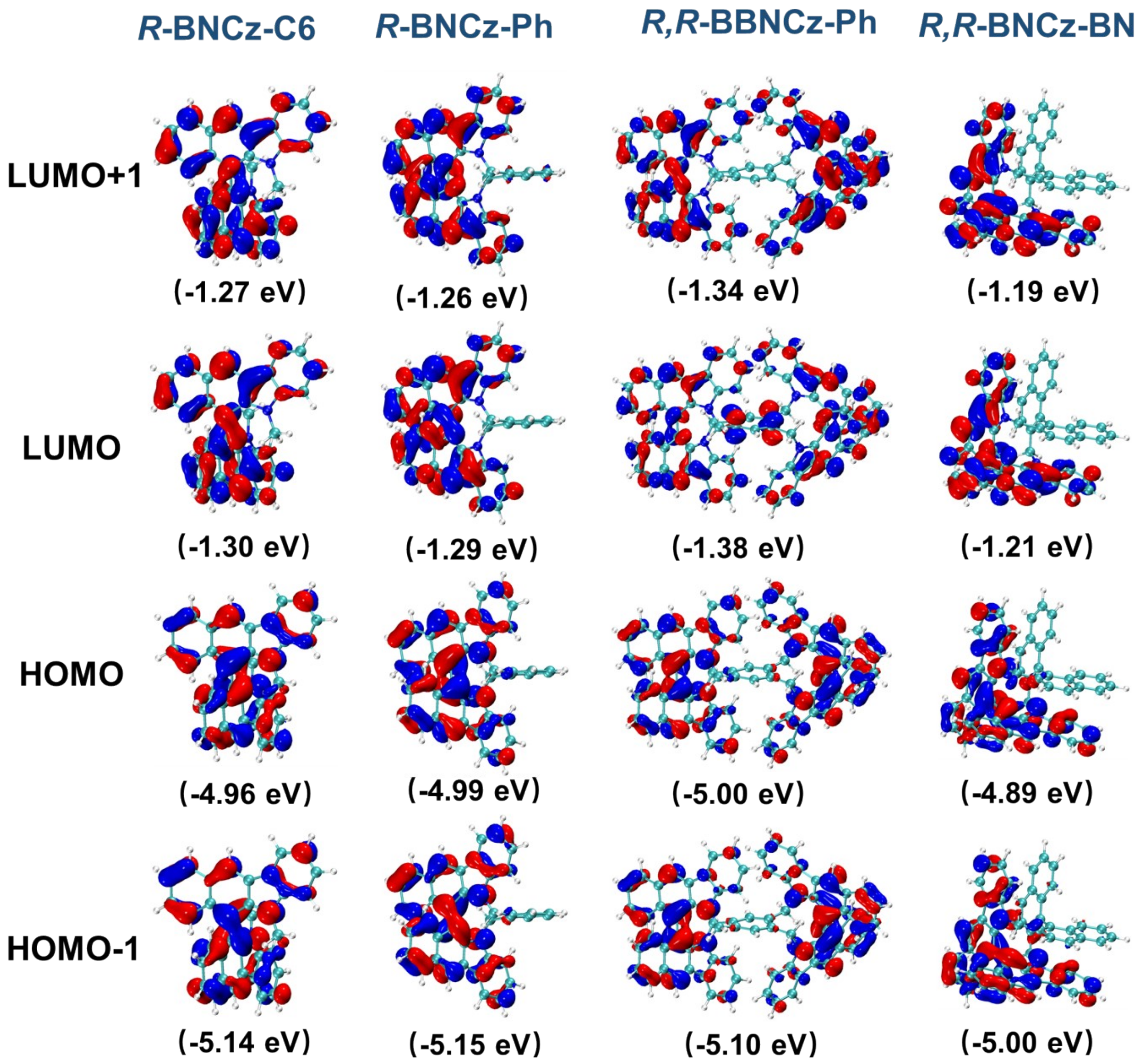


Figure S16. The LUMO+1, LUMO, HOMO, HOMO-1 energy levels and orbital distribution maps of these chiral molecular models.

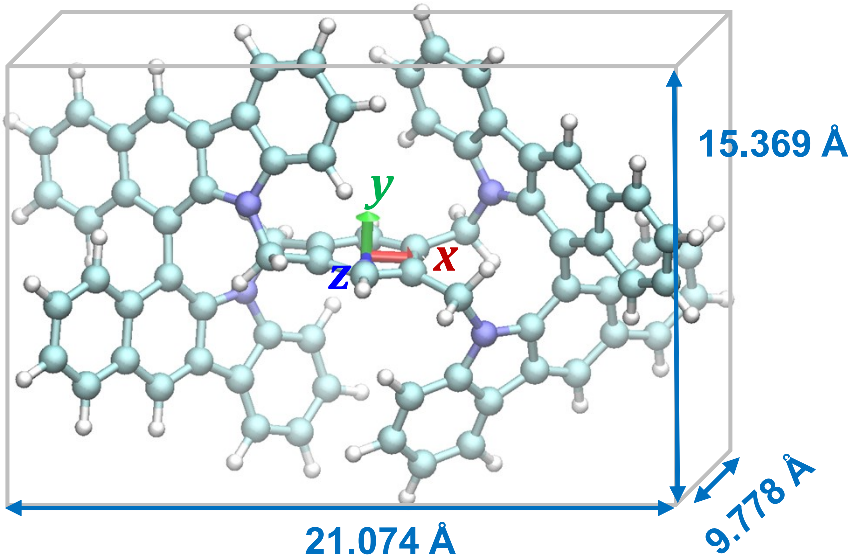


Figure S17. The spatial three-dimensional dimension of *R*,*R*-BBNCz-Ph with optimized S_1 configuration.

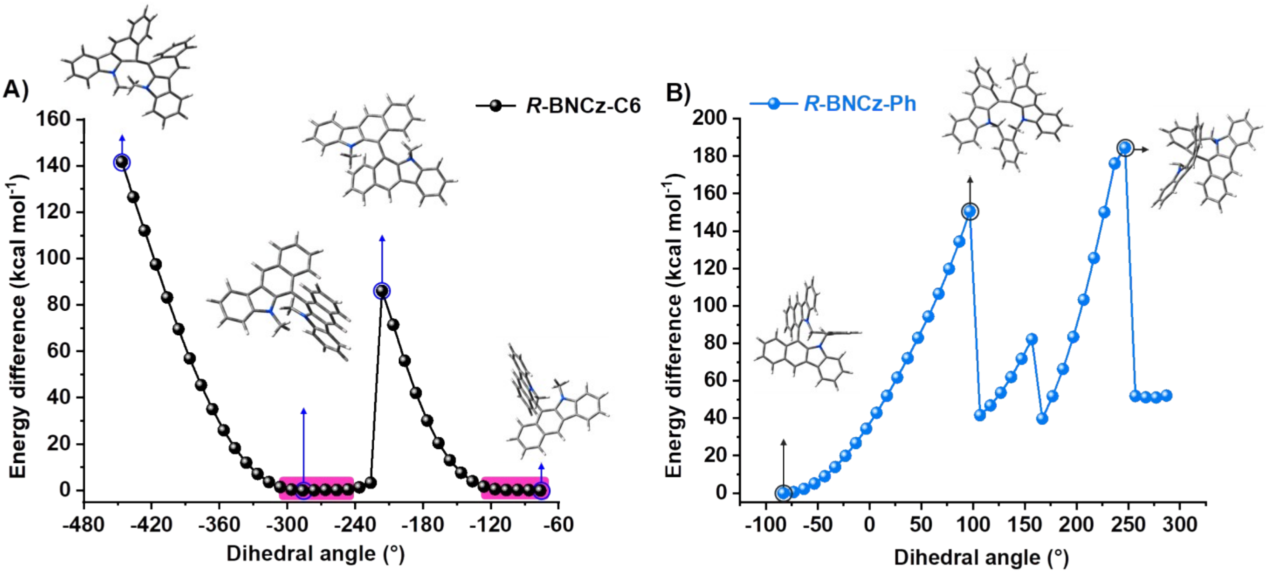
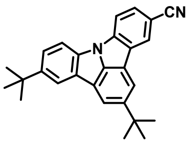
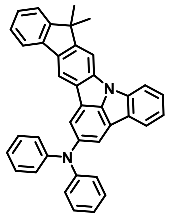
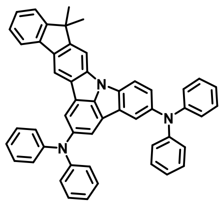
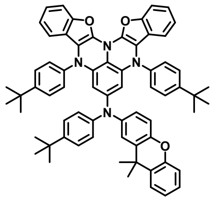
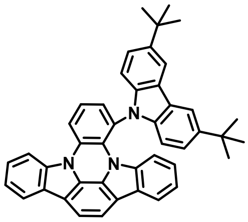
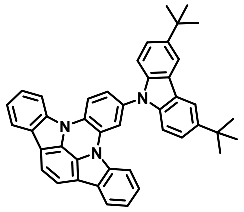
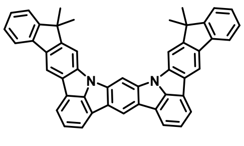
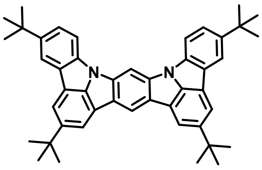
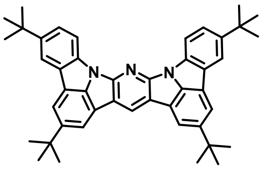
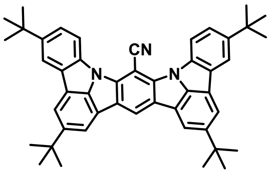
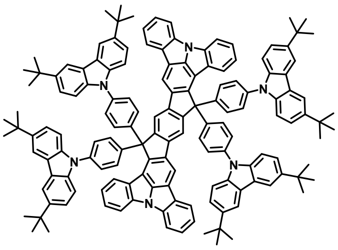
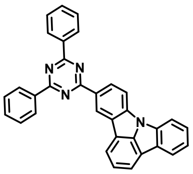
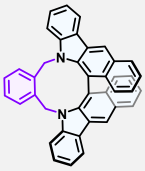
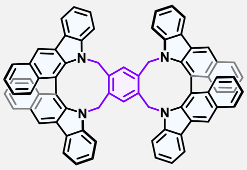
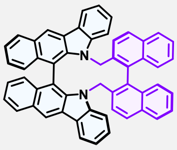


Figure S18. Flexible scanning of dihedral angle along with the chiral axis for A) R-BNCz-C6 and B) R-BNCz-Ph with step size (10°).

10. Electroluminescent performance

Table S1. Comparison of the narrow-band blue fluorescence emitter-based OLEDs.

Name	Chemical structure	FWHM [nm]	ELpeak [nm]	$\eta_{\mathrm{c,max}}$/ $\eta_{\mathrm{p,max}}$/ $\eta_{\mathrm{EQE,max}}$	CIE [x, y]	Ref.
BuICzCN		**42.9**	**414**	**0.38/0.25/1.16**	**0.166, 0.044**	4
IDCz-DPA		**41**	**456**	**4.4/--/5.3**	**0.14, 0.09**	5
IDCz-2DPA		**35**	**466**	**6.4/--/5.6**	**0.13, 0.15**	5
OBN-2		**23**	**455**	**6.0/ 6.4/ 5.7**	**0.139, 0.121**	6
OCzN		**41**	**418**	**3.5/2.5/6.9**	**0.18, 0.08**	7
MCzN		**51**	**432**	**4.7/4.1/6.1**	**0.16, 0.09**	7
m-FLDID		**27**	**411**	**--/--/5.2**	**0.163, 0.027**	8

tDIDCz		**14**	**401**	**--/--/3.3**	**0.164, 0.018**	9
Nm-ICz		**42**	**412**	**--/--/3.0**	**0.164, 0.025**	9a
CNm-ICz		**42**	**427**	**--/--/3.7**	**0.161, 0.027**	9a
4*t*Cz- DICz		**22**	**424**	**1.02/0.71/3.97**	**0.17, 0.03**	10
ICZ-TAZ		**46**	**406**	**0.76/0.63/4.02**	**0.162, 0.037**	11
BNCz-Ph		**25**	**452**	**1.07/0.94/4.23**	**0.157, 0.024**	**This work**
BBNCz-Ph		**30**	**455**	**2.69/2.64/5.35**	**0.166, 0.049**	**This work**
BNCz-BN		**33**	**455**	**1.38/1.21/4.00**	**0.158, 0.036**	**This work**

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