*Supporting Information*

# Connectivity and Twist: Engineering High-Performance Green Phosphorescent OLEDs Using Unipolar Symmetric Bicarbazole Regioisomers

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## Experimental Section

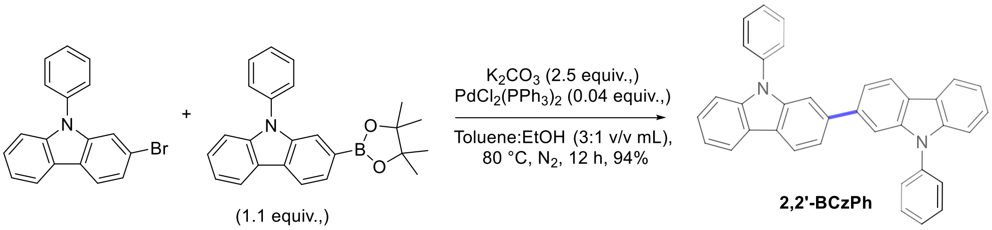
**1. General Aspects.** Unless otherwise stated, all the reagents were used as received from commercial sources. Dichloromethane (DCM) and chloroform were dried and distilled over $CaH_2$ as the dehydrating agent. Toluene is dried and distilled over a sodium/ketyl radical system. Methanol was distilled by using the magnesium cake as the drying agent. To perform the reaction, oven-dried glassware was used under a nitrogen atmosphere. The progress of the reactions was monitored by TLC (Thin Layer Chromatography) analysis using Merck silica gel (60 $F_{254}$) precoated plates (0.25 mm). The compounds were visualized to the naked eye under a UV lamp (366 or 254 nm) in a UV chamber or using phosphomolybdic acid (PMA) solution as a stain to detect the compound as a spot. The crude product thus obtained after the reaction was purified by silica gel (100-200 mesh) column chromatography. A combination of ethyl acetate and hexane was used as the mobile phase. Melting points of the compounds were measured by packing the compound in an open capillary on a melting point apparatus, and the values were corrected. To record the infrared spectra of the compounds, the JASCO FT/IR-4100 spectrometer instrument was used by preparing a dry KBr pellet, and IR signals are quoted in wavenumbers ($cm^{-1}$). $^{1}H$ (400 MHz) and $^{13}C$ (100 MHz) NMR spectra were recorded in ambient temperature using a Bruker Avance FT-NMR (400 MHz) spectrometer in deuterated chloroform ($CDCl_3$) with TMS as the internal reference. All the chemical shift values were reported in parts per million (ppm, $\delta$). All the reported $^{1}H$ NMR spectra were calibrated with the residual proton solvent peak ($CDCl_3$, $\delta = 7.26$ ppm) or tetramethylsilane ($\delta = 0.00$ ppm), and the $^{13}C$ spectra were referenced to $CDCl_3$, $\delta = 77.16$ ppm, respectively. The $^{1}H$ NMR multiplicities are abbreviated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublet; sept, septet, and the coupling constants ($J$) values were reported in Hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a Q-Tof Micro micro mass spectrometer. UV-visible absorption spectra of compounds in solution were recorded on an

AGILENT 8453 diode-array spectrophotometer, and films were recorded on a JASCO V-650 spectrophotometer using spectroscopic grade solvents, which are purchased commercially.

The starting materials, such as potassium carbonate, iodobenzene, Copper, sodium sulphate, $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ were purchased commercially and used without further purification, otherwise stated. All the other starting materials, 2-bromo-9-phenyl-9*H*-carbazole,[1, 2] 4-bromo-9-phenyl-9*H*-carbazole,[2, 3] 9-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole,[2] 9-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole[2] and 9*H*,9'*H*-1,1'-bicarbazole[4] were synthesized according to the literature-reported procedures, and characterized by $^1H$, $^{13}C$ NMR, and IR spectroscopy techniques, and the data were matched with the literature citations.

## 2. Experimental Procedure

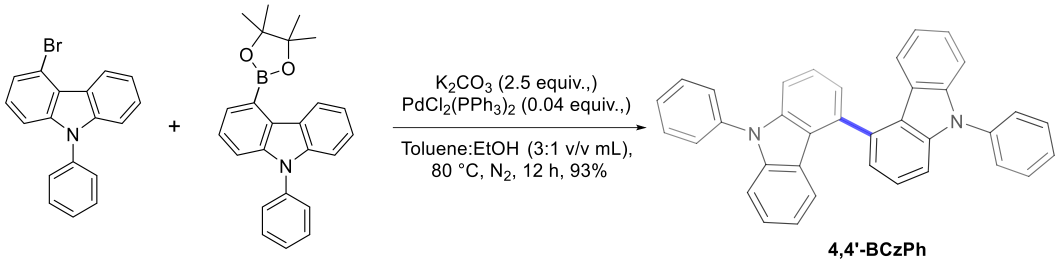
### ***Preparation of 9,9'-diphenyl-9H,9'H-2,2'-bicarbazole (2,2'-BCzPh)***



2-Bromo-9-phenyl-9*H*-carbazole[1, 2] (0.180 g, 0.48 mmol) and 9-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-carbazole[2] (0.130 g, 0.41 mmol) were dissolved in toluene (3 mL) and methanol (1 mL) mixture, and Suzuki coupled in the presence of potassium carbonate (0.140 g, 1.01 mmol) as base and $PdCl_2(PPh_3)_2$ (0.011 g, 0.02 mmol) as a catalyst at 80 °C. Time: 12 h. Yield: 0.222 g, 94%. White solid. $R_f = 0.40$ (19:1, Hexane/EtOAc). Mp: 234 – 236 °C. IR (neat, $cm^{-1}$): 3056, 2923, 2868, 2341, 1599, 1502, 1457, 1457, 1424, 1332, 1230, 812. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 8.16 (t, $J = 8.0$ Hz, 4H), 7.66-7.59 (m, 8H), 7.64 (s, 2H), 7.56

(d, $J$ = 8.0 Hz, 2H), 7.53-7.46 (m, 2H), 7.44-7.41 (m, 4H), 7.33-7.27 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 141.6 (× 2), 140.4, 137.8, 130.1, 127.6, 127.3, 126.0, 123.3, 122.6, 120.6, 120.5, 120.24, 120.19, 109.9, 108.8. HR ESI-MS: $[C_{36}H_{24}N_2]^+$ = $[M]^+$ calculated $m/z$ = 484.1939, found = 484.1933.

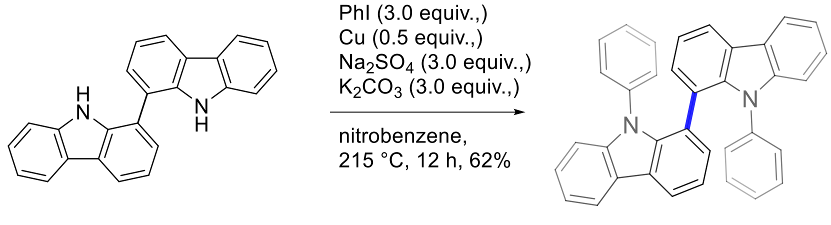
***Preparation of 9,9'-diphenyl-9H,9'H-4,4'-bicarbazole (4,4'-BCzPh)***



**4,4'-BCzPh**

4-Bromo-9-phenyl-9$H$-carbazole[2, 3] (0.180 g, 0.48 mmol) and 9-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9$H$-carbazole[2] (0.130 g, 0.41 mmol) were dissolved in toluene (3 mL) and methanol (1 mL) mixture and Suzuki coupled in presence of potassium carbonate (0.140 g, 1.01 mmol) as base and $PdCl_2(PPh_3)_2$ (0.011 g, 0.02 mmol) as a catalyst at 80 °C. Time: 12 h. Yield: 0.251 g, 93%. White solid. $R_f$ = 0.40 (19:1, Hexane/EtOAc). Mp: 202- 204 °C. IR (neat, $cm^{-1}$): 2923, 2860, 2357, 1592, 1501, 1455, 1326, 1208, 1077. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.73-7.63 (m, 8H), 7.60-7.50 (m, 6H), 7.45-7.40 (m, 2H), 7.36 (d, $J$ = 8.0 Hz, 2H), 7.25 (t, $J$ = 8.0 Hz, 2H), 7.01 (d, $J$ = 8.0 Hz, 2H), 6.84 (t, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): 141.6, 141.3, 137.9, 136.0, 130.1, 127.7, 127.6, 125.9, 125.7, 123.3, 122.5, 121.6, 119.8, 109.5, 109.1. HR ESI-MS: $[C_{36}H_{24}N_2]^+$ = $[M]^+$ calculated $m/z$ = 484.1939, found = 484.1927.

### *Preparation of 9,9'-diphenyl-9H,9'H-1,1'-bicarbazole (1,1'-BCzPh)*



**1,1'-BCzPh**

9*H*,9'*H*-1,1'-Bicarbazole[4] (0.300 g, 0.90 mmol), iodobenzene (0.552 g, 2.71 mmol), copper powder (0.029g, 0.452 mmol), sodium sulphate (0.385 g, 2.71 mmol) and potassium carbonate (0.374 g, 2.71 mmol) were dissolved in nitrobenzene (3 mL) and kept at reflux temperature. Time: 48 h. Yield: 62%. White solid. $R_f = 0.42$ (19:1, Hexane/EtOAc). Mp: 292 – 294 °C. IR (neat, cm$^{-1}$): 2921, 2859, 1585, 1487, 1457, 1408, 1219, 1165, 749. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.96 (d, $J$ = 7.6 Hz, 2H), 7.78 (d, $J$ = 7.6 Hz, 2H), 7.30 (t, $J$ = 7.2 Hz, 4H), 7.21 (t, $J$ = 7.2 Hz, 2H), 7.14 (d, $J$ = 7.6 Hz, 2H), 7.10 (d, $J$ = 8.4 Hz, 2H), 7.07-6.91 (m, 2H), 6.79-6.65 (m, 4H), 6.58-6.28 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): 142.0, 138.0, 136.6, 128.2, 127.0, 126.8, 126.2, 125.8, 124.3, 123.9, 123.4, 119.93, 119.90, 119.6, 119.3, 109.9. HR ESI-MS: $[C_{36}H_{24}N_2]^+ = [M]^+$ calculated *m/z* = 484.1939, found = 484.1927.

### *Preparation of 9,9'-diphenyl-9H,9'H-3,3'-bicarbazole (3,3'-BCzPh)*

**3,3'-BCzPh** was synthesized following our previous report.[5, 6]

# 3. $^1$H and $^{13}$C NMR Scans

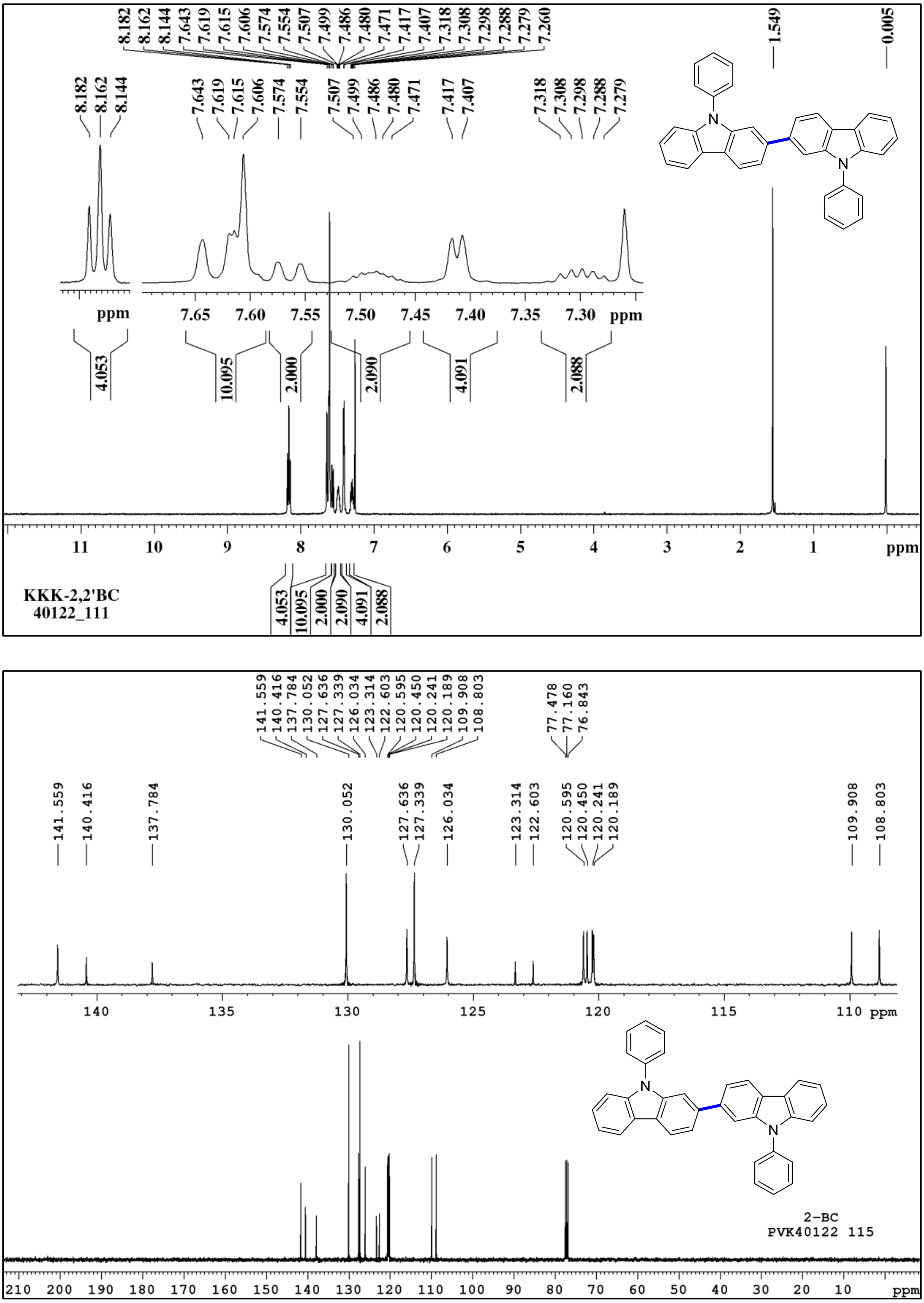


**Figure S1**. $^1$H and $^{13}$C NMR spectra of **2,2'-BCzPh** in $CDCl_3$.

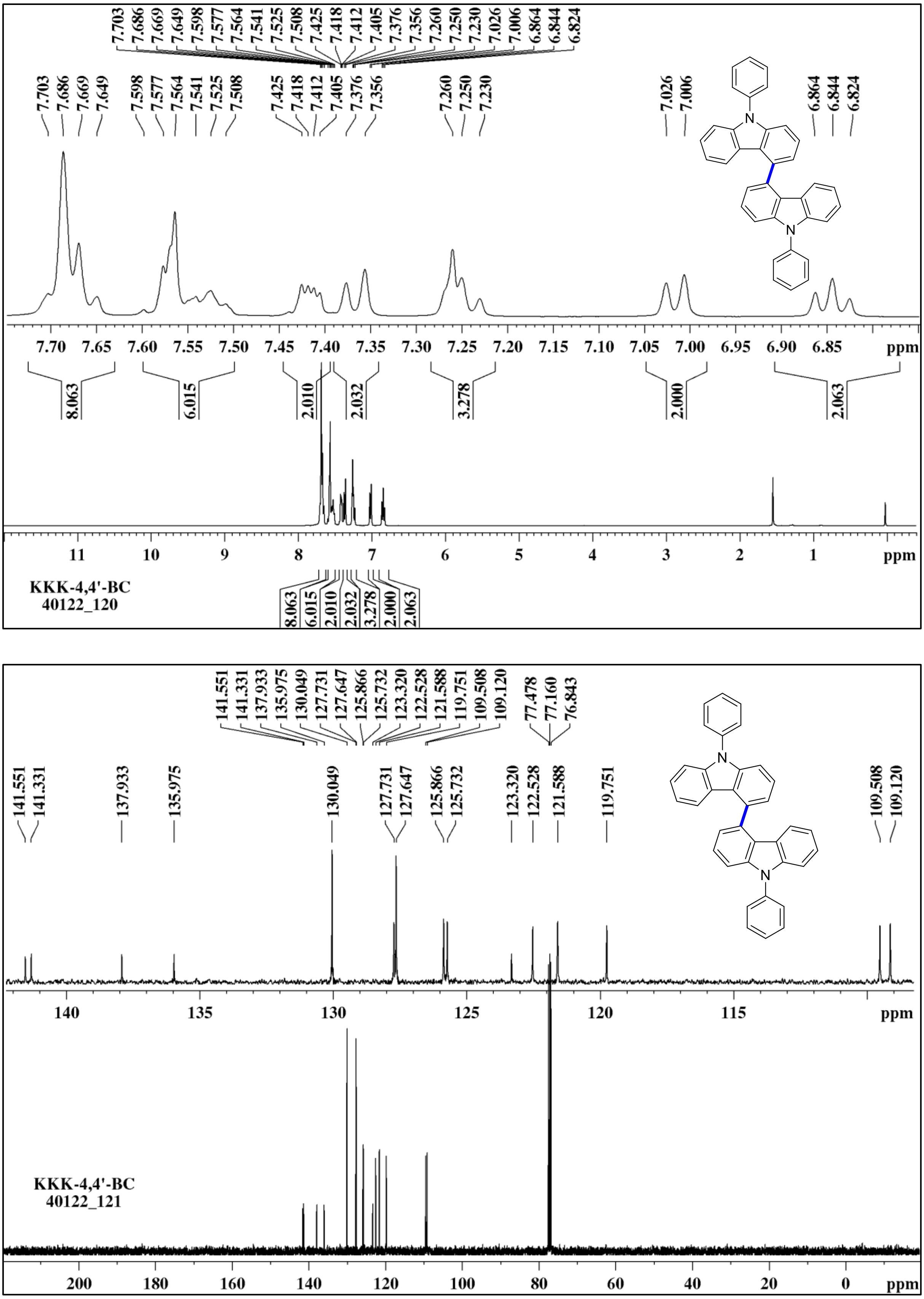
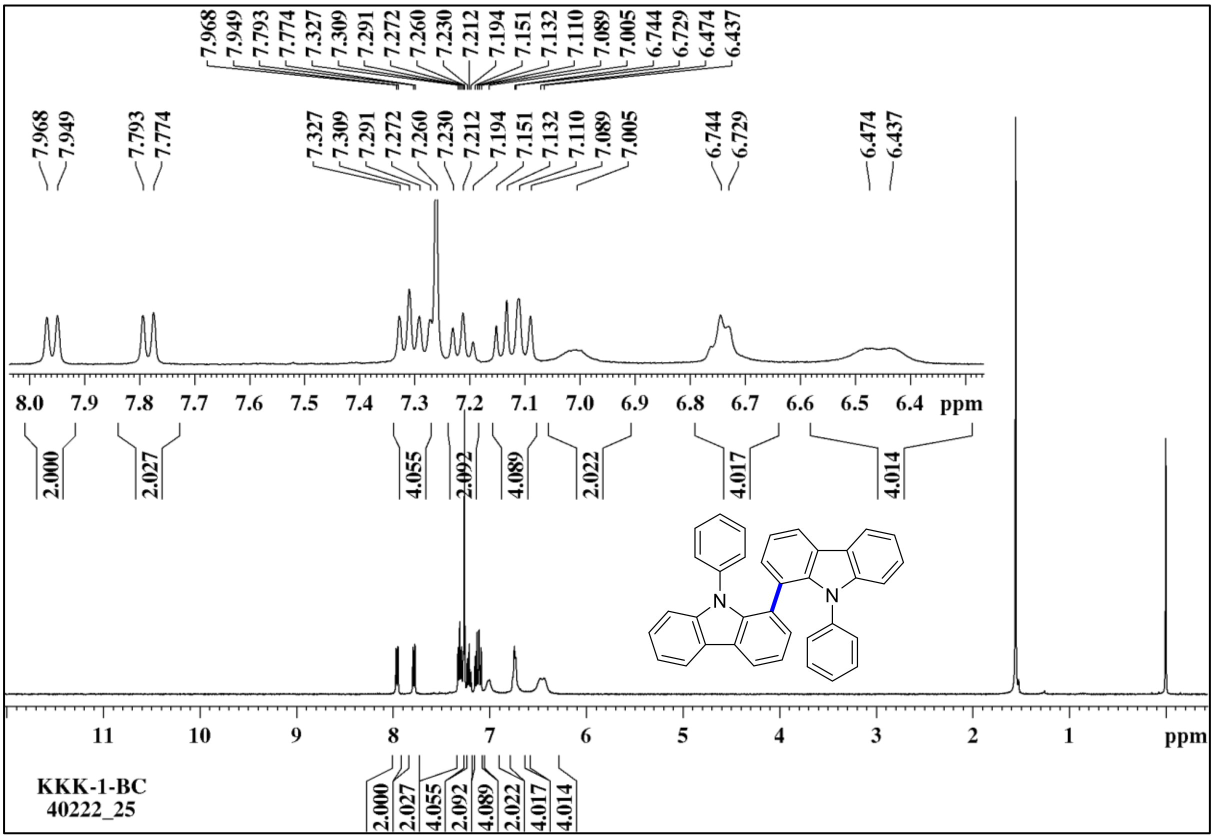


**Figure S2**. $^{1}$H and $^{13}$C NMR spectra of **4,4’-BCzPh** in $CDCl_3$.



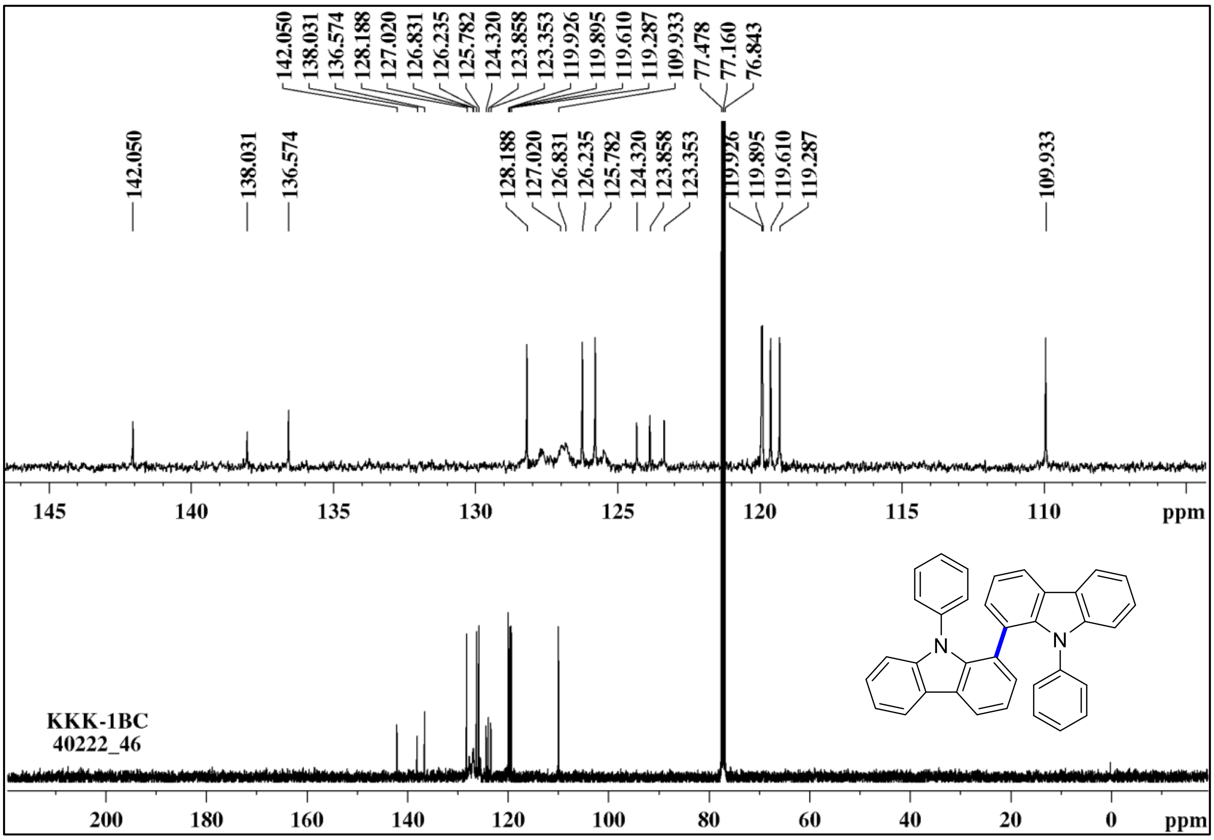


**Figure S3**. $^1$H and $^{13}$C NMR spectra of **1,1'-BCzPh** in $CDCl_3$.

## 4. X-ray Crystal Structure Characterization Details

The single crystals of **1,1'-BCzPh**, **2,2'-BCzPh,** and **4,4'-BCzPh** suitable for X-ray determination were grown by slow evaporation of their solution (1:1 v/v, mL) in Chloroform and toluene or MeOH. The transparent crystal was chosen and mounted along its longest dimension. The X-ray intensity data for **1,1'-BCzPh** was collected on Bruker AXS (Kappa Apex 2) CCD diffractometer equipped with a graphite monochromated MoKα (λ = 0.7107 Å) radiation source at 297 K. The multi-scan absorption correction was applied to the dataset using the program SADABS. The structures were solved by direct method and were refined on $F^2$ by a full-matrix least-squares technique using SHELXL-2014. The details of structure and refinement are provided in Tables S1, S2, and S3.

**Table S1.** Crystal data and structure refinement for compound **1,1'-BCzPh**.

| | | |
|---|---|---|
| Identification code | **1,1'-BCzPh, CCDC 2361782** | |
| Empirical formula | $C_{36}H_{24}N_2$ | |
| Formula weight | 484.57 g/mol | |
| Temperature | 297(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 10.4412(10) Å | α = 111.360(3) ° |
| | b = 11.5134(12) Å | β = 106.462(4) ° |
| | c = 12.4565(13) Å | γ = 102.652(4) ° |
| Volume | 1247.3(2) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.290 $g/cm^3$ | |
| Absorption coefficient | 0.075 $mm^{-1}$ | |
| F(000) | 508 | |
| Crystal size | 0.230 x 0.170 x 0.070 mm | |
| Theta range for data collection | 3.373 to 25.999°. | |
| Index ranges | -12<=h<=12, -14<=k<=14, -15<=l<=15 | |
| Reflections collected | 56058 | |
| Independent reflections | 4887 [R(int) = 0.1042] | |
| Completeness to theta = 25.999° | 99.8 % | |
| Absorption correction | Semi-empirical from equivalents | |

| | |
|---|---|
| Max. and min. transmission | 0.745 and 0.497 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 4887 / 0 / 343 |
| Goodness-of-fit on $F^2$ | 1.111 |
| Final R indices [I>2sigma(I)] | $R_1 = 0.0568$, $wR_2 = 0.1335$ |
| R indices (all data) | $R_1 = 0.0908$, $wR_2 = 0.1549$ |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.229 and -0.187 e. Å$^{-3}$ |

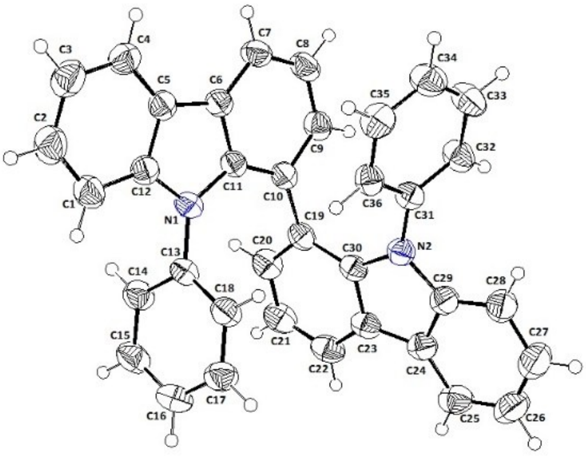


**Figure S4.** The ORTEP diagram of **1,1'-BCzPh** drawn at a 40% probability level.

**Table S2.** Crystal data and structure refinement for compound **2,2'-BCzPh**.

| | | |
|---|---|---|
| Identification code | **2,2'-BCzPh, CCDC 2361784** | |
| Empirical formula | $C_{36}H_{24}N_2$ | |
| Formula weight | 484.57 g/mol | |
| Temperature | 297(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 16.6717(7) Å | α = 90 ° |
| | b = 7.6442(4) Å | β = 106.796(2) ° |
| | c = 20.2120(8) Å | γ = 90 ° |
| Volume | 2465.96(19) Å$^3$ | |
| Z | 4 | |
| Density (calculated) | 1.305 g/cm$^3$ | |

| | |
|---|---|
| Absorption coefficient | 0.076 mm$^{-1}$ |
| F(000) | 1016 |
| Crystal size | 0.250 x 0.220 x 0.180 mm |
| Theta range for data collection | 2.105 to 24.999°. |
| Index ranges | -19<=h<=19, -9<=k<=7, -24<=l<=23 |
| Reflections collected | 15979 |
| Independent reflections | 4325 [R(int) = 0.0271] |
| Completeness to theta = 24.999° | 100 % |
| Absorption correction | none |
| Max. and min. transmission | 0.745 and 0.497 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 4325 / 0 / 344 |
| Goodness-of-fit on $F^2$ | 1.032 |
| Final R indices [I>2sigma(I)] | $R_1 = 0.0385$, $wR_2 = 0.0909$ |
| R indices (all data) | $R_1 = 0.0589$, $wR_2 = 0.1027$ |
| Extinction coefficient | 0.0044(6) |
| Largest diff. peak and hole | 0.174 and -0.126 e. Å$^{-3}$ |

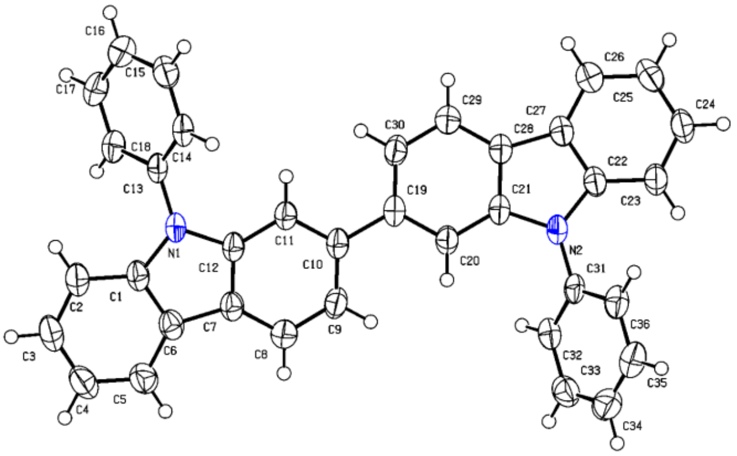


**Figure S5.** The ORTEP diagram of **2,2'-BCzPh** drawn at a 50% probability level.

**Table S3.** Crystal data and structure refinement for compound **4,4'-BCzPh**.

| | |
|---|---|
| Identification code | **4,4'-BCzPh, CCDC 2361783** |
| Empirical formula | $C_{36}H_{24}N_2$ |
| Formula weight | 484.57 g/mol |
| Temperature | 297(2) K |

| | | |
|---|---|---|
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P b c a | |
| Unit cell dimensions | a = 7.2607(2) Å | α = 90 ° |
| | b = 23.5218(10) Å | β = 90 ° |
| | c = 29.6886(11) Å | γ = 90 ° |
| Volume | 5070.4(3) Å$^3$ | |
| Z | 8 | |
| Density (calculated) | 1.270 g/cm$^3$ | |
| Absorption coefficient | 0.074 mm$^{-1}$ | |
| F(000) | 2032 | |
| Crystal size | 0.200 x 0.150 x 0.100 mm | |
| Theta range for data collection | 3.241 to 25.997°. | |
| Index ranges | -8<=h<=8, -29<=k<=29, -36<=l<=36 | |
| Reflections collected | 61601 | |
| Independent reflections | 4961 [R(int) = 0.0431] | |
| Completeness to theta = 25.997° | 99.7 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7459 and 0.6656 | |
| Refinement method | Full-matrix least-squares on F$^2$ | |
| Data / restraints / parameters | 4961 / 0 / 343 | |
| Goodness-of-fit on F$^2$ | 1.202 | |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.0693, w$R_2$ = 0.1654 | |
| R indices (all data) | $R_1$ = 0.0835, w$R_2$ = 0.1739 | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.221 and -0.257 e. Å$^{-3}$ | |

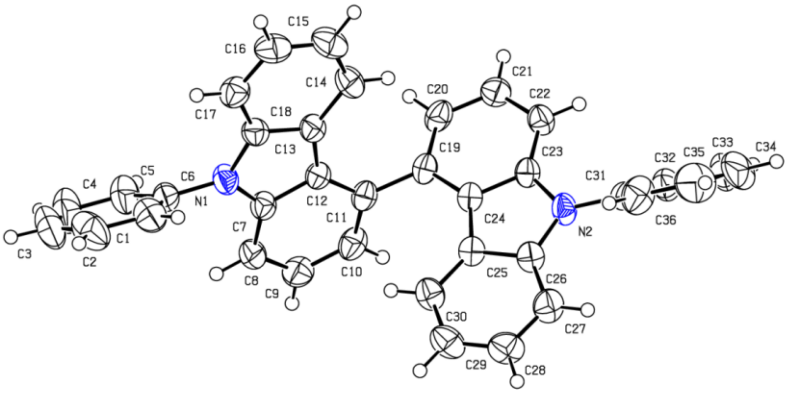


**Figure S6.** The ORTEP diagram of **4,4’-BCzPh** drawn at a 50% probability level.

## 5. Electrochemical Measurements

Electrochemical experiments were done in a single-compartment glass cell at room temperature (25 ± 1 °C). Voltammograms reported with the positive potential pointing as the positive X-coordinates and increasing anodic currents pointing as the positive Y-coordinates. The voltammetric measurement was conducted using the electrochemical workstation (CH Instruments 660A) with the conventional three-electrode system. It consists of glassy carbon (area = 0.07 cm$^2$) as a working electrode, which was polished with 0.05 μm alumina on Buehler felt pads and was ultrasonicated for 1 minute to remove the alumina residue. Platinum wire is used as the counter electrode. All the potentials were taken using an Ag/AgCl, KCl (saturated) reference electrode. All the experiments were conducted in dichloromethane using the tetrabutylammonium hexafluorophosphate (TBAPF$_6$, 0.1 M) as the non-aqueous supporting electrolyte under a nitrogen gas atmosphere. The concentrations of the **BCzPh**s were typically ca. 1 mM and the scan rate was 50-100 mV/sec. The cyclic voltammogram was calibrated using ferrocene as the standard for each experiment and corrected appropriately. The HOMO energy values were calculated using the following equation from the onset of the first oxidation potential derived from differential pulse voltammogram (DPV). The HOMO energy level for the ferrocene/ferrocenium (Fc/Fc$^+$) standard is 4.8 eV with respect to the zero-vacuum level.

$$E_{\mathrm{HOMO}}\ (\mathrm{eV}) = -(E_{\mathrm{OX}}{}^{\mathrm{onset}} - \mathrm{E}_{\mathrm{Fc/Fc+}}{}^{\mathrm{onset}}) - 4.80\ \mathrm{eV}$$

LUMO energy values were derived by adding the HOMO ($E_{\mathrm{HOMO}}$) energy values with the energy gap ($E_{\mathrm{g}}$) obtained from the onset of the UV-visible absorption spectra.

$$E_{\mathrm{LUMO}} = E_{\mathrm{HOMO}} + E_{\mathrm{g}}$$

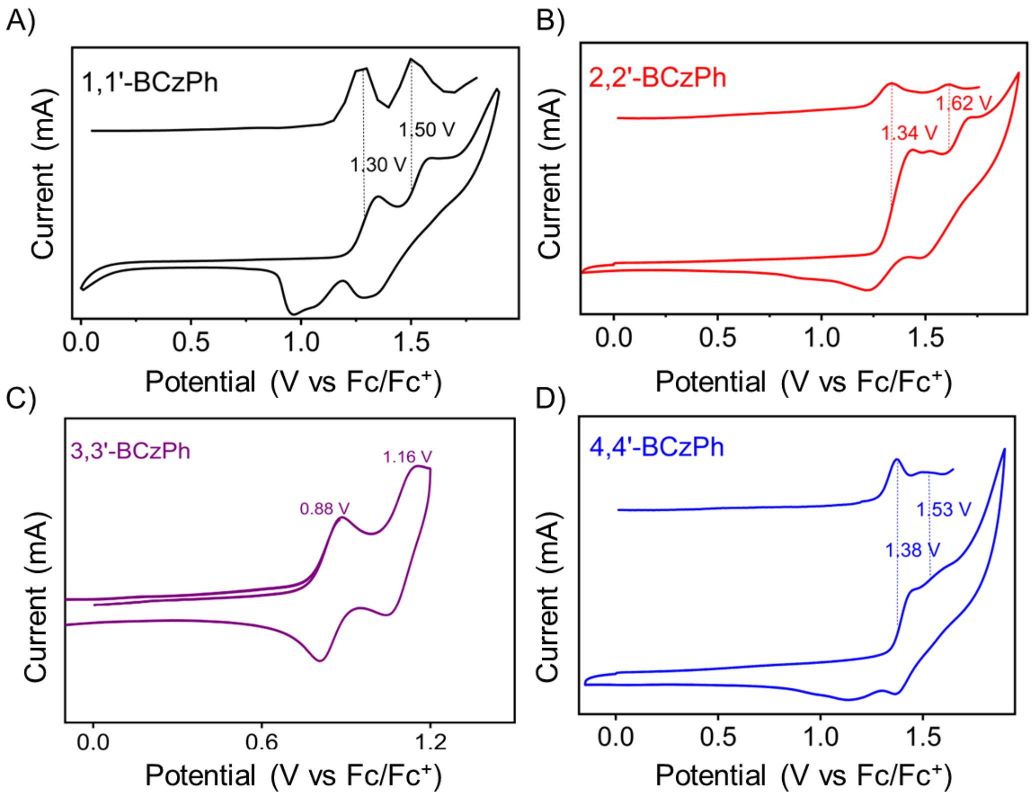


**Figure S7.** Cyclic voltammograms along with DPV scans of isomeric **BCzPh**s (A-D) in dichloromethane (ca. $10^{-5}$ M).

**Table S4.** Electrochemical properties of **BCzPh**s.

| HTM | $E_{\text{ox1}}$ (V) | $E_{\text{ox2}}$ (V) | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) |
|---|---|---|---|---|
| **1,1’-BCzPh** | +1.30 | +1.50 | -5.56 | -2.22 |
| **2,2’-BCzPh** | +1.34 | +1.62 | -5.60 | -2.32 |
| **3,3’-BCzPh** | +0.88 | +1.16 | -5.45 | -2.18 |
| **4,4’-BCzPh** | +1.38 | +1.53 | -5.64 | -2.32 |

## 6. Thermal Analyses

Thermogravimetric analyses (TGA) were performed on a TGA Q500 V20.10 Build 36 instrument under a nitrogen gas atmosphere at a 20 °C/min heating rate. Differential Scanning

Calorimetry (DSC) studies were performed on a DSC Q200 MDSC instrument under a nitrogen gas atmosphere at a 10 °C/min heating rate.

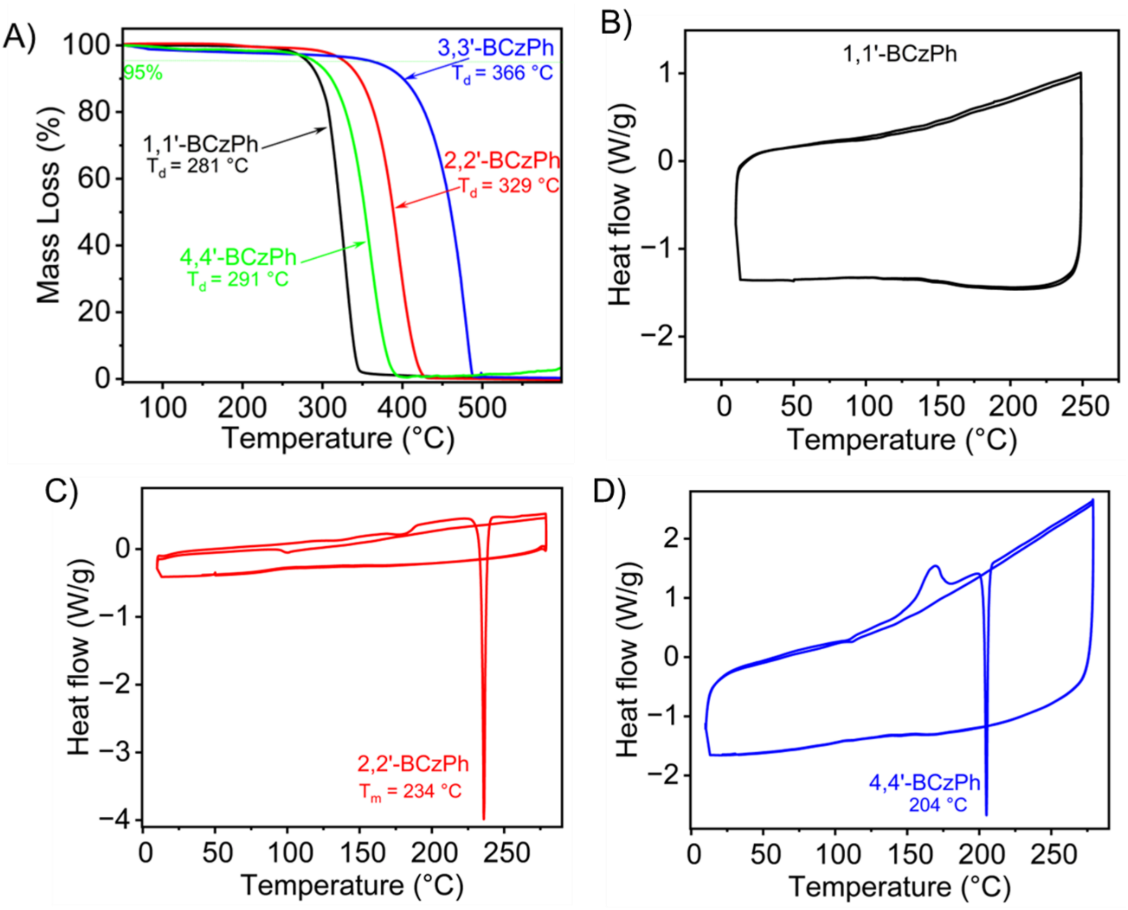


**Figure S8.** Thermogravimetry curves (A) and differential scanning calorimetry thermograms (B-D, 2 heating-cooling cycles) of regioisomeric **1,1'-/2,2'-/4,4'-BCzPh**s, respectively.

## 7. Photophysical Characterization Details

### Preparation of the films and solutions for UV-visible absorbance and fluorescence

Optical absorption and photoluminescence measurements of compounds in solution were recorded by directly dissolving the compounds in the dichloromethane solution (2 mg/mL). The solution state UV visible absorption and emission spectra were recorded using the 1 cm pathlength quartz cuvette and the concentration of the solution was ca. 1.0 × $10^{-5}$ M. The emission spectra of these compounds were recorded in chloroform dilute (ca. 1.0 × $10^{-6}$ M) solutions on Horiba Fluoromax-4. For measuring the relative fluorescence quantum yields of compounds (**1,1'-BCzPh**, **2,2'-BCzPh**, **4,4'-BCzPh**), the DCM (spectral grade, nitrogen bubbled) solutions were made in such a way that their absorbance at ca. λ = 325 nm was between 0.05 and 0.1. The sample was excited at λ = 325 nm, and their emission spectrum was recorded in the right-angle mode (335-640 nm). The quantum yields for the (**1,1'-BCzPh**, **2,2'-BCzPh**, **4,4'-BCzPh**) derivatives were calculated using the following relationship:

$$\varphi_u = \varphi_s \left({}^{A_s}/_{A_u}\right)^* \left({}^{I_u}/_{I_s}\right)^* \left({}^{\eta_s}/_{\eta_u}\right)^2$$

Where the subscripts "s" and "u" refer to standard and unknown samples, $A_u$ and $A_s$ to absorbances of the sample and the standard at the excitation wavelength, $I_u$ and $I_s$ to the integrated emission area intensities of the sample and the standard, and $\eta_u$ and $\eta_s$ to the refractive indexes of the corresponding solutions. For quantum yield determination, Diphenylanthracene was chosen as the reference, and the reported quantum yield in cyclohexane is 0.90 ± 0.04.[7] The PLQE values reported here correspond to the average value of three independent determinations.

From the onset wavelength ($\lambda_{onset}$) of the absorption spectra, the energy gap ($E_g$) of the (**1,1'-BCzPh**, **2,2'-BCzPh**, **4,4'-BCzPh**) derivatives was determined by using the formula,

$$E_g = \frac{1240}{\lambda_{onset}}$$

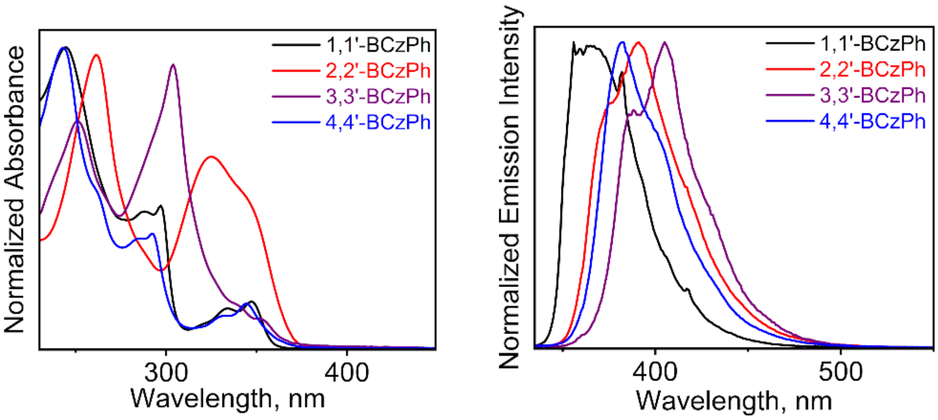


**Figure S9.** Normalized UV-vis absorption (left) and emission (right) spectra of isomeric **BCzPhs** in dichloromethane (ca. $10^{-5}$ M).

**Table S5.** A comparison of optical, electrochemical and thermal properties of **BCzPh**s with **BCz**s of unipolar structure.

| HTM | Wavelength (nm) | | | | $E_g$ (eV) | $E_{HOMO}$ (eV) | $E_{LUMO}$ (eV) |
|---|---|---|---|---|---|---|---|
| | $\lambda_{onset}$ | $\lambda_{abs}$ | $\lambda_{em}$ | QY | | | |
| **1,1'-BCzPh** | 366 | 332, 347 | 363 | 60% | 3.39 | -5.56 | -2.22 |
| **2,2'-BCzPh** | 378 | 325, 349 | 390 | 76% | 3.28 | -5.60 | -2.32 |
| **3,3'-BCzPh** | 379 | 310, 361 | 406 | 21% | 3.27 | -5.45 | -2.18 |
| **4,4'-BCzPh** | 373 | 330, 344 | 382 | 59% | 3.32 | -5.64 | -2.32 |
| **CBP**[8] | 363 | 293, 328 | 379 | - | 3.42 | -5.69 | -2.27 |
| ***m*CP**[9] | 347 | 326, 340 | 348 | - | 3.50 | -5.90 | -2.40 |

## 8. DFT Calculated FMOs[10]

The optimization of molecules is carried out by utilizing theoretical methods and employing Density Functional Theory (DFT) calculations. The software involved in optimizing the electronic ground state geometry of molecules in the gas phase without any symmetric considerations is Gaussian 16 and B3LYP functional in a 6-31G(d) basis set.[10]

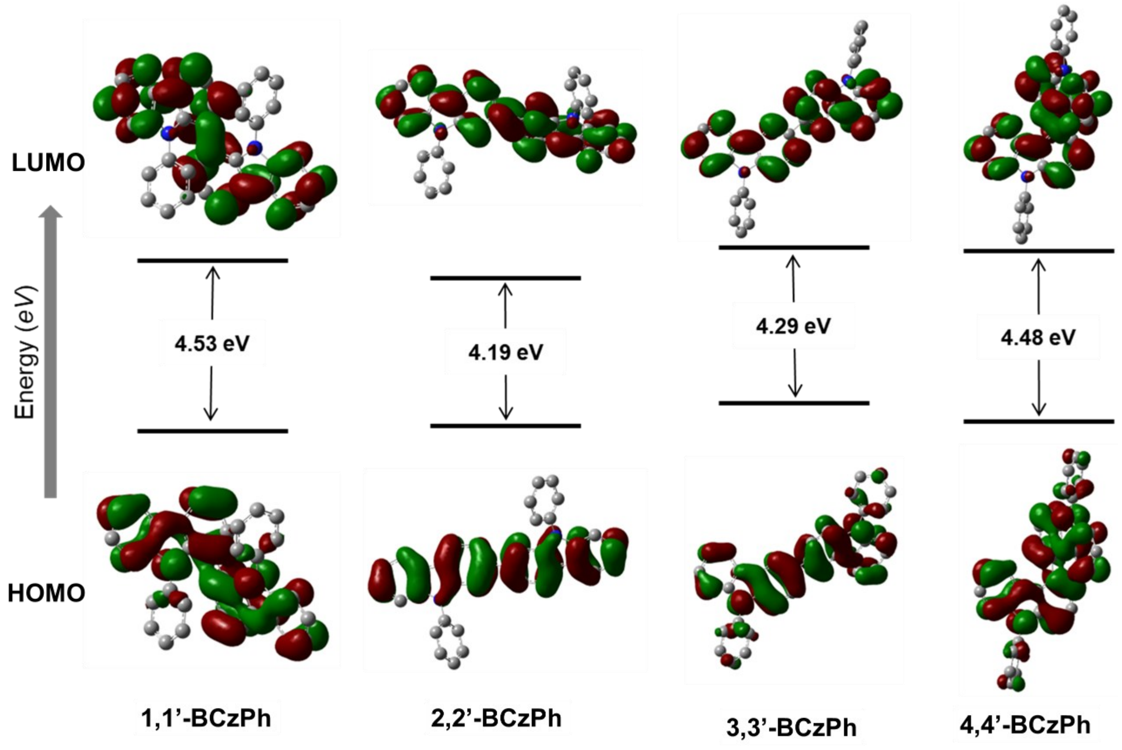


**Figure S10.** Frontier molecular orbital (HOMO: bottom row; LUMO: top row) pictures of regioisomeric **BCzPh**s and the calculated $E_g$.

**Table S6.** DFT derived HOMO, LUMO energies, and HOMO-LUMO energy gap of regioisomeric **BCzPh**s, in eV.

| HTM | $E_{\mathrm{HOMO}}$ (eV) | $E_{\mathrm{LUMO}}$ (eV) | ($\Delta E_{\mathrm{HOMO-LUMO}}$) (eV) |
|---|---|---|---|
| **1,1’-BCzPh** | -5.27 | -0.74 | 4.53 |
| **2,2’-BCzPh** | -5.26 | -1.07 | 4.19 |
| **3,3’-BCzPh** | -4.97 | -0.68 | 4.29 |
| **4,4’-BCzPh** | -5.20 | -0.72 | 4.48 |

**Table S7.** Cartesian coordinates of molecule **1,1’-BCzPh** in the ground state.

| | | | |
|---|---|---|---|
| C | -4.43009700 | -1.03534900 | 1.30648700 |
| H | -4.15146400 | -1.99787300 | 1.72242200 |
| C | -5.66800700 | -0.46112800 | 1.58570900 |

| | | | |
|---|---|---|---|
| H | -6.36316800 | -0.99149500 | 2.23109800 |
| C | -6.03422300 | 0.78790100 | 1.05321500 |
| H | -7.00781300 | 1.20762500 | 1.29013800 |
| C | -5.15988400 | 1.48873000 | 0.22825100 |
| H | -5.44248700 | 2.45563200 | -0.18037100 |
| C | -3.90953700 | 0.93187700 | -0.06779300 |
| C | -2.78248500 | 1.37075400 | -0.85868300 |
| C | -2.56971700 | 2.52421600 | -1.61836500 |
| H | -3.34063700 | 3.28775300 | -1.68205000 |
| C | -1.36347800 | 2.67185000 | -2.29107200 |
| H | -1.17640100 | 3.55614400 | -2.89336900 |
| C | -0.38152100 | 1.67709900 | -2.19954700 |
| H | 0.55415900 | 1.80284100 | -2.73669800 |
| C | -0.54608000 | 0.51034200 | -1.44147800 |
| C | -1.77901300 | 0.36324000 | -0.77036300 |
| C | -3.55931600 | -0.32699800 | 0.47240700 |
| C | -1.68231200 | -1.93399800 | 0.36971800 |
| C | -2.22097200 | -3.09594300 | -0.19467400 |
| H | -3.04679400 | -3.01143000 | -0.89488000 |
| C | -1.69416400 | -4.34300500 | 0.14032000 |
| H | -2.11562800 | -5.24150800 | -0.30219800 |
| C | -0.62461900 | -4.43497400 | 1.03297300 |
| H | -0.20967700 | -5.40609800 | 1.28831300 |
| C | -0.09116700 | -3.27583900 | 1.59901500 |
| H | 0.73920300 | -3.34056300 | 2.29633900 |
| C | -0.62591000 | -2.02805200 | 1.27925000 |
| H | -0.22604500 | -1.12603400 | 1.73001300 |
| C | 0.54616000 | -0.51044100 | -1.44138000 |
| C | 0.38162800 | -1.67727900 | -2.19933800 |

| | | | |
|---|---|---|---|
| H | -0.55404400 | -1.80307100 | -2.73649100 |
| C | 1.36360200 | -2.67201700 | -2.29079200 |
| H | 1.17652900 | -3.55637000 | -2.89300400 |
| C | 2.56985300 | -2.52427900 | -1.61812700 |
| H | 3.34081500 | -3.28777600 | -1.68177000 |
| C | 2.78257700 | -1.37075000 | -0.85854000 |
| C | 3.90967300 | -0.93175500 | -0.06777700 |
| C | 5.16001500 | -1.48860300 | 0.22830400 |
| H | 5.44260200 | -2.45553700 | -0.18025100 |
| C | 6.03436400 | -0.78772000 | 1.05321100 |
| H | 7.00795600 | -1.20742800 | 1.29015500 |
| C | 5.66814700 | 0.46134200 | 1.58562700 |
| H | 6.36330700 | 0.99175400 | 2.23098200 |
| C | 4.43023100 | 1.03553900 | 1.30638400 |
| H | 4.15160500 | 1.99808700 | 1.72227100 |
| C | 3.55944600 | 0.32714500 | 0.47234000 |
| C | 1.77907900 | -0.36326500 | -0.77025600 |
| C | 1.68227000 | 1.93398800 | 0.36971300 |
| C | 2.22114200 | 3.09606900 | -0.19420300 |
| H | 3.04726600 | 3.01174400 | -0.89407600 |
| C | 1.69415100 | 4.34304900 | 0.14081500 |
| H | 2.11579600 | 5.24164600 | -0.30133900 |
| C | 0.62419500 | 4.43481800 | 1.03299400 |
| H | 0.20911000 | 5.40587900 | 1.28833800 |
| C | 0.09051500 | 3.27554700 | 1.59854700 |
| H | -0.74018200 | 3.34009300 | 2.29549600 |
| C | 0.62544500 | 2.02784500 | 1.27878100 |
| H | 0.22539700 | 1.12572700 | 1.72917500 |
| N | -2.26852500 | -0.66749800 | 0.05370000 |

| | | | |
|---|---|---|---|
| N | 2.26861700 | 0.66757300 | 0.05368700 |

**Table S8.** Cartesian coordinates of molecule **2,2’-BCzPh** in the ground state.

| | | | |
|---|---|---|---|
| C | 5.22068300 | -0.89130400 | -0.13629300 |
| C | 6.60404000 | -0.90455100 | 0.06133700 |
| H | 7.13216600 | -0.02128400 | 0.40502700 |
| C | 7.28596400 | -2.09022000 | -0.20507400 |
| H | 8.36205600 | -2.12507400 | -0.05767700 |
| C | 6.61292300 | -3.23641000 | -0.66223100 |
| H | 7.17408800 | -4.14552100 | -0.85883600 |
| C | 5.23688700 | -3.21357200 | -0.86960800 |
| H | 4.71900000 | -4.09762700 | -1.23253900 |
| C | 4.52716000 | -2.03486800 | -0.61048800 |
| C | 3.13509400 | -1.65988000 | -0.72883800 |
| C | 1.97380900 | -2.33722200 | -1.11783000 |
| H | 2.02334400 | -3.37366100 | -1.44162300 |
| C | 0.75496600 | -1.67159700 | -1.09488900 |
| H | -0.14042300 | -2.18702000 | -1.42829800 |
| C | 0.65408300 | -0.32223500 | -0.67878000 |
| C | 1.81277100 | 0.36557700 | -0.28982700 |
| H | 1.74914400 | 1.38777200 | 0.06689000 |
| C | 3.03614300 | -0.30351500 | -0.32880800 |
| C | 4.62090400 | 1.46537000 | 0.49065400 |
| C | 4.28909000 | 2.58053900 | -0.28920700 |
| H | 3.80787900 | 2.43356200 | -1.25113100 |
| C | 4.58970700 | 3.86352100 | 0.16754300 |
| H | 4.32748900 | 4.72396500 | -0.44198400 |
| C | 5.23859000 | 4.04265700 | 1.39083000 |

| | | | |
|---|---|---|---|
| H | 5.47802800 | 5.04296300 | 1.74033000 |
| C | 5.57776700 | 2.92981200 | 2.16287400 |
| H | 6.07721600 | 3.06084000 | 3.11892600 |
| C | 5.26283400 | 1.64444600 | 1.72261700 |
| H | 5.50071500 | 0.77702700 | 2.33042800 |
| C | -0.66548900 | 0.35923300 | -0.64925300 |
| C | -1.81397300 | -0.34358900 | -0.25693700 |
| H | -1.74264500 | -1.38191700 | 0.04733400 |
| C | -3.03722100 | 0.32615200 | -0.23563900 |
| C | -5.23150300 | 0.87952600 | -0.05413100 |
| C | -6.60742200 | 0.88734200 | 0.19037700 |
| H | -7.12042900 | 0.00134400 | 0.54957500 |
| C | -7.29967300 | 2.07531200 | -0.03597600 |
| H | -8.37058400 | 2.10539600 | 0.14611100 |
| C | -6.64246800 | 3.23194700 | -0.48993800 |
| H | -7.21199600 | 4.14150500 | -0.65841200 |
| C | -5.26985700 | 3.22188900 | -0.71966100 |
| H | -4.76123900 | 4.11958100 | -1.06163400 |
| C | -4.54971000 | 2.04154300 | -0.49965300 |
| C | -3.15196100 | 1.68741400 | -0.61439700 |
| C | -2.00059800 | 2.38065600 | -1.00474400 |
| H | -2.06211900 | 3.42219000 | -1.30958700 |
| C | -0.77809300 | 1.72154900 | -1.01689400 |
| H | 0.10991700 | 2.25139700 | -1.34740400 |
| C | -4.60459700 | -1.47942700 | 0.53687700 |
| C | -3.95487700 | -2.01851900 | 1.65453100 |
| H | -3.23598200 | -1.41254500 | 2.19704900 |
| C | -4.24377900 | -3.31912800 | 2.06706100 |
| H | -3.73368200 | -3.73149900 | 2.93326700 |

|  |  |  |  |
|---|---|---|---|
| C | -5.19336000 | -4.08130700 | 1.38373700 |
| H | -5.42165700 | -5.09128600 | 1.71229500 |
| C | -5.84793800 | -3.53917000 | 0.27592800 |
| H | -6.58389200 | -4.12780800 | -0.26496300 |
| C | -5.55014300 | -2.24669500 | -0.15537600 |
| H | -6.03687000 | -1.82922600 | -1.03132700 |
| N | 4.30790800 | 0.15652900 | 0.03342500 |
| N | -4.30562600 | -0.15806200 | 0.10640700 |

**Table S9.** Cartesian coordinates of molecule **4,4'-BCzPh** in the ground state.

|  |  |  |  |
|---|---|---|---|
| C | 5.76705200 | -0.36604200 | -1.50036900 |
| H | 5.08274700 | -0.31795500 | -2.34169800 |
| C | 7.10899900 | -0.69409100 | -1.69203500 |
| H | 7.47356200 | -0.89228500 | -2.69627700 |
| C | 7.97570800 | -0.78472600 | -0.60101800 |
| H | 9.01869000 | -1.04796400 | -0.75289200 |
| C | 7.49542200 | -0.53516800 | 0.68607800 |
| H | 8.16472300 | -0.59764400 | 1.53979300 |
| C | 6.15939100 | -0.18718400 | 0.88413900 |
| H | 5.78587000 | 0.03258800 | 1.87946900 |
| C | 5.28837500 | -0.10655200 | -0.20980500 |
| C | 3.02149400 | -0.44270700 | 0.81175500 |
| C | 3.23205500 | -1.59323300 | 1.57520600 |
| H | 4.20006000 | -2.08216300 | 1.60223900 |
| C | 2.15063300 | -2.09419200 | 2.29462600 |
| H | 2.28188100 | -2.98614500 | 2.90128500 |
| C | 0.89520800 | -1.46946800 | 2.25288900 |
| H | 0.07129700 | -1.87963700 | 2.82964700 |

|  |  |  |  |
|---|---|---|---|
| C | 0.67353400 | -0.32395900 | 1.48124200 |
| C | 1.75463800 | 0.19750800 | 0.74283400 |
| C | 1.90334000 | 1.31493900 | -0.17387200 |
| C | 1.03673500 | 2.30843100 | -0.65196400 |
| H | 0.00189800 | 2.33329800 | -0.32940700 |
| C | 1.52281100 | 3.26469900 | -1.53868500 |
| H | 0.85661300 | 4.03629600 | -1.91425400 |
| C | 2.86603800 | 3.24767700 | -1.95014200 |
| H | 3.22735100 | 4.00983100 | -2.63550700 |
| C | 3.74863800 | 2.27170600 | -1.49448800 |
| H | 4.78722200 | 2.26497600 | -1.80842300 |
| C | 3.25190400 | 1.30500400 | -0.61590000 |
| C | -0.67350500 | 0.32389200 | 1.48120300 |
| C | -0.89512500 | 1.46944000 | 2.25283600 |
| H | -0.07119100 | 1.87957200 | 2.82958300 |
| C | -2.15050400 | 2.09424100 | 2.29453300 |
| H | -2.28171800 | 2.98621800 | 2.90116600 |
| C | -3.23195000 | 1.59332500 | 1.57510400 |
| H | -4.19991700 | 2.08232700 | 1.60209400 |
| C | -3.02144800 | 0.44277100 | 0.81168900 |
| C | -1.75462400 | -0.19752200 | 0.74281200 |
| C | -1.90337100 | -1.31496500 | -0.17387500 |
| C | -3.25192200 | -1.30497300 | -0.61592400 |
| C | -3.74869500 | -2.27171400 | -1.49445100 |
| H | -4.78727100 | -2.26494500 | -1.80840700 |
| C | -2.86614600 | -3.24777500 | -1.95000400 |
| H | -3.22748800 | -4.00996500 | -2.63531200 |
| C | -1.52292100 | -3.26484200 | -1.53853300 |
| H | -0.85677200 | -4.03651500 | -1.91403200 |

| | | | |
|---|---|---|---|
| C | -1.03680800 | -2.30853900 | -0.65187300 |
| H | -0.00197300 | -2.33341000 | -0.32930100 |
| C | -5.28835600 | 0.10662400 | -0.20982300 |
| C | -6.15930200 | 0.18739300 | 0.88419200 |
| H | -5.78568100 | -0.03224000 | 1.87951400 |
| C | -7.49533800 | 0.53532300 | 0.68618500 |
| H | -8.16458900 | 0.59791500 | 1.53992900 |
| C | -7.97573300 | 0.78471900 | -0.60092200 |
| H | -9.01873600 | 1.04791100 | -0.75272800 |
| C | -7.10911600 | 0.69394100 | -1.69197800 |
| H | -7.47373700 | 0.89198900 | -2.69622900 |
| C | -5.76713500 | 0.36593500 | -1.50036700 |
| H | -5.08291300 | 0.31776000 | -2.34175500 |
| N | 3.92359800 | 0.23744200 | -0.01112400 |
| N | -3.92356900 | -0.23734500 | -0.01120300 |

## 9. Film Morphology

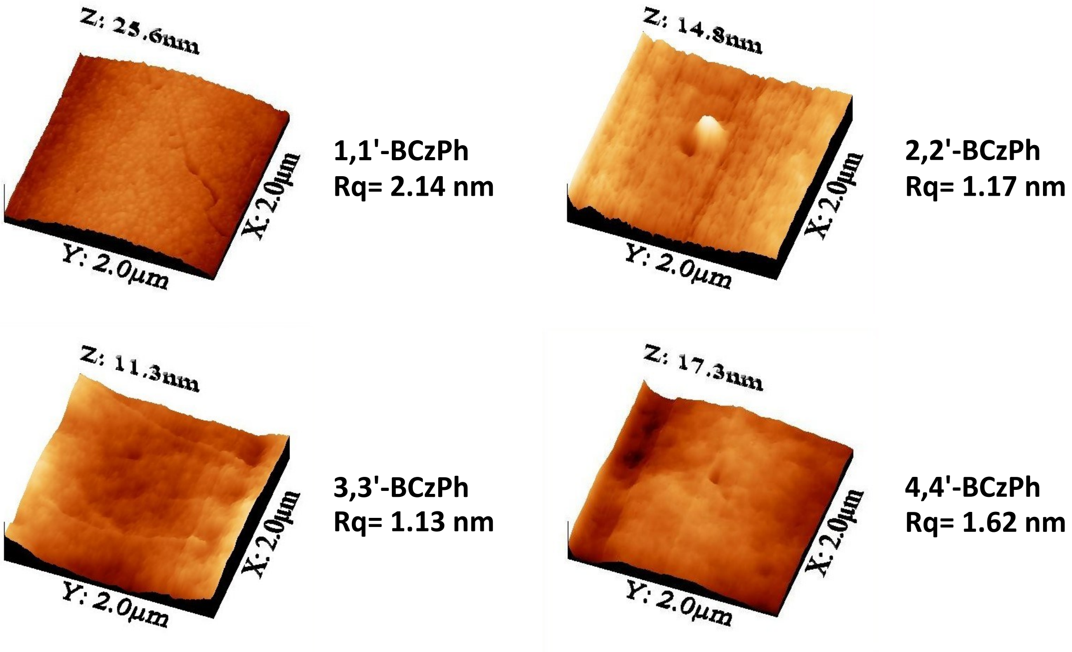


**Figure S11.** AFM images of **BCzPh**-based compounds on the glass substrate.

## 10. Calculation formula for carrier mobility

The *J–V* curves of the hole-only and electron-only devices revealed the detected current densities for this series of compounds. Since the target compounds possess similar HOMO/LUMO levels, this result was mainly related to the charge transport conditions. The hole mobilities were estimated according to the SCLC theory ($J = 9\varepsilon\varepsilon_0\mu E^2/8L$), assuming that the evaporated organic solid films have inherently disordered morphology. This theory states that the charge mobility dependence on the electric field ascribed to organic semiconductors ($\mu = \mu_0 \exp(\beta E^{1/2})$), resulting in the expression

$$J = \left[\frac{9\varepsilon\varepsilon_0}{8L}\mu_0 \exp\left(\beta E^{1/2}\right)\right] E^2 ;$$

where ε is the relative dielectric constant, with an approximate value of 3 for the studied materials, $\varepsilon_0$ is the vacuum permittivity, $E$ is the electric field, $L$ is the thickness of the organic film, $\mu_0$ is the mobility at zero field and $\beta$ is the Poole–Frenkel factor. The linearization of this equation enabled the determination of $\mu_0$ and $\beta$ for the adequate high bias range. The corresponding description has been added to Supporting Information.

## 11. Fabrication and Characterization of PhOLEDs

Indium tin oxide (ITO)-coated glass and commercial organic materials were purchased from Lumtec and Shine Materials Technology. Organic materials were subjected to temperature-gradient sublimation in a high vacuum before use. The ITO substrate was washed in sequence with deionized water and acetone, followed by treatment with plasma for 5 minutes. The bottom-emitting OLEDs were fabricated using ITO as the anode, followed by the deposition of multiple organic layers, topped by a metal cathode layer. The organic and metal layers were deposited by thermal evaporation in a vacuum chamber with a base pressure of $< 10^{-6}$ Torr. Device fabrication was completed in a single cycle without breaking the vacuum. The deposition rates of organic materials and aluminium were respectively kept at around 0.1 and 0.5 nm $s^{-1}$. The active area was defined by the shadow mask ($2 \times 2$ $mm^2$). Current density-voltage-luminance characterization was done using two Keysight B2901A current source-measure units equipped with a calibrated Si-photodiode. The electroluminescent spectra of the devices were recorded using an Ocean Optics spectrometer (Ocean Optics 2000).

## 12. Correlation Diagram

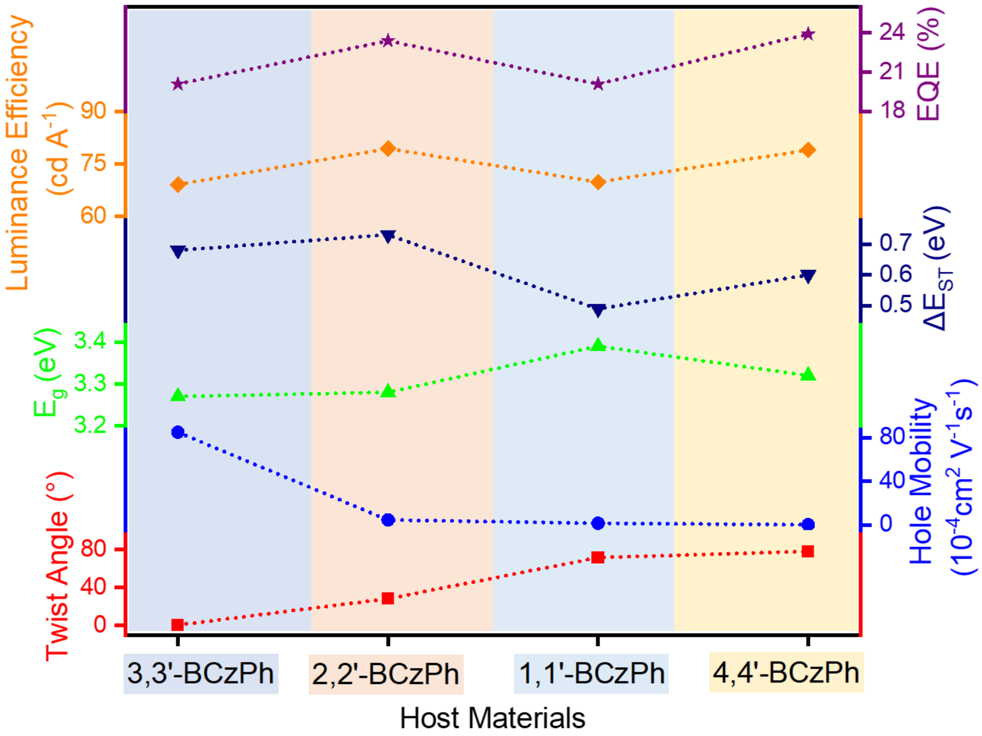


**Figure S12.** The correlation diagram of twist angle with hole mobility, $E_g$, $\Delta E_{ST}$ and device performance characteristics, such as luminance and external quantum efficiencies of all the four **BCzPh** isomers.

**13. Table S10.** Comparison of the device performance of unipolar **BCzPh**s reported herein with other analogous **BCz** derivatives (bipolar/unipolar) known in the literature using dopant emitters Ir(ppy)$_3$ or FIrpic.

| **Hosts** | **T$_1$ (eV)** | **Device Configuration** | **V$_{on}$ (V)** | **Max CE (cd A$^{-1}$ )** | **Max PE (lm W$^{-1}$)** | **Max EQE (%)** | **Luminance (cd/m$^2$)** | **Color / CIE (x, y)** | **Ref.** |
|---|---|---|---|---|---|---|---|---|---|
| CBP bipolar | 2.55 | ITO/PEDOT:PSS (40 nm)/NPB (40 nm)/CBP:6 wt% Ir(ppy)$_3$ (30 nm)/TPBI (30 nm)/LiF (1 nm)/Al (100 nm) | 4.0 | 59.58 | 30.29 | 17.10 | 60033 | 0.30, 0.62 | 8 |
| 3,3’-BCzPh | 2.87 | ITO (130 nm)/TAPC (40 nm)/FIrpic 11 wt% - BCz (10 nm)/B3PyPB (50 nm)/LiF (1 nm)/Al (100 nm) | 3.6 | 36.6 | 32.3 | 16.4 | -- | Blue | 11 |
| *m*CP | 3.00 | ITO (130 nm)/TAPC (40 nm)/FIrpic 11 wt% - BCz (10 nm)/B3PyPB (50 nm)/LiF (1 nm)/Al (100 nm) | 4.4 | 30.1 | 21.5 | 13.8 | -- | Blue | 11, 12 |
| DOBCz | 2.70 | ITO/HAT-CN (10 nm)/TAPC (40 nm)/ 10 wt % [Ir(ppy)$_2$(acac)] - DOBCz (20 nm)/TmPyPB (50 nm)/Liq (2 nm)/Al (120 nm) | 4.56 | 61.8 | 41.7 | 16.8 | -- | 0.32, 0.63 | 13 |
| DSBCz | 2.65 | ITO/HAT-CN (10 nm)/TAPC (40 nm)/ 10 wt % [Ir(ppy)$_2$(acac)] - DSBCz (20 nm)/TmPyPB (50 nm)/Liq (2 nm)/Al (120 nm) | 4.63 | 51.5 | 34. 5 | 14.6 | -- | 0.33, 0.63 | 13 |
| BCz1 | -- | ITO/m-MTDATA (20 nm)/TAPC (20 nm)/EML(30 nm)/BCz1 (30 nm)/TmPyPB (30 nm)/Al (100 nm) | 3.3 | 13.4 | 10.5 | 5.8 | 3295 | 0.31, 0.51 | 14 |
| *o*-CBP | 3.00 | ITO/NPB (40 nm)/*o*-CBP:FIrpic (30 nm)/BCP (15 nm)/AlQ (30 nm)/LiF (1 nm)/Al (150 nm) | 5.7 | 10.98 | 2.37 | -- | 8794 | 0.19, 0.46 | 15 |
| *o*-CDBP | 2.73 | ITO/NPB (40 nm)/*o*-CDBP:FIrpic (30 nm)/BCP (15 nm)/AlQ (30 nm)/LiF (1 nm)/Al (150 nm) | 8.7 | 8.82 | 2.68 | -- | 13624 | 0.19, 0.43 | |
| 1,1’-BCzPh | 2.78 | (ITO) (120 nm)/TAPC (30 nm)/**BCzPh** – 8 wt.% Ir(ppy)$_3$ (25 nm)/B3PyMPM (50 nm)/LiF (1.5 nm)/Al (150 nm) | 2.2 | 70.5 | 91.9 | 20.1 | 96953 | 0.34, 0.60 | ***This Work*** |
| 2,2’-BCzPh | 2.54 | | | 81.0 | 108.6 | 23.4 | 92593 | 0.36, 0.60 | |
| 3,3’-BCzPh | 2.87 | | | 69.6 | 82.1 | 20.1 | 203494 | 0.35, 0.60 | |
| 4,4’-BCzPh | 2.73 | | | 83.1 | 108.8 | 23.9 | 80158 | 0.34, 0.61 | |

## 14. References

1. C.-L. Ho, L.-C. Chi, W.-Y. Hung, W.-J. Chen, Y.-C. Lin, H. Wu, E. Mondal, G.-J. Zhou, K.-T. Wong and W.-Y. Wong, *J. Mater. Chem.*, 2012, **22**, 215-224.
2. S. Kang, H. Jung, H. Lee, S. Lee, M. Jung, J. Lee, Y. Chul Kim and J. Park, *Dyes Pigm.*, 2018, **156**, 369-378.
3. M. Kim and J. Y. Lee, *Org. Electron.*, 2013, **14**, 67-73.
4. P. Pandit, T. Nakamura and S. Higashibayashi, *Chem. Lett.*, 2015, **44**, 1336-1338.
5. S. Maddala, C.-L. Chung, S.-Y. Wang, K. Kollimalayan, H.-L. Hsu, P. Venkatakrishnan, C.-P. Chen and Y. J. Chang, *Chem. Mater.*, 2020, **32**, 127-138.
6. S. Mallick, S. Maddala, K. Kollimalayan and P. Venkatakrishnan, *J. Org. Chem.*, 2019, **84**, 73-93.
7. S. Hamai and F. Hirayama, *J. Phys. Chem. B*, 1983, **87**, 83-89.
8. T. Zhang, Y. Liang, J. Cheng and J. Li, *J. Mater. Chem. C*, 2013, **1**, 757-764.
9. H. Mu, Y. Jiang and H. Xie, *Org. Electron.*, 2019, **66**, 195-205.
10. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Journal*, 2016.
11. H. Sasabe, N. Toyota, H. Nakanishi, T. Ishizaka, Y.-J. Pu and J. Kido, *Adv. Mater.*, 2012, **24**, 3212-3217.
12. X. W. Lou, L. A. Archer and Z. Yang, *Adv. Mater.*, 2008, **20**, 3987-4019.
13. X.-Y. Liu, Y.-L. Zhang, X. Fei, L.-S. Liao and J. Fan, *Chem. Eur. J.*, 2019, **25**, 4501-4508.
14. M.-H. Tsai , Y.-H. Hong , C.-H. Chang , H.-C. Su , C.-C. Wu , A. Matoliukstyte , J. Simokaitiene , S. Grigalevicius , J. V. Grazulevicius and C.-P. Hsu, *Adv. Mater.*, 2007, **19** , 862.
15. S. Tokito, T. Iijima , Y. Suzuri , H. Kita , T. Tsuzuki and F. Sato, *Appl. Phys. Lett.*, 2003, **83**, 569.

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