

Electronic Supplementary Information (ESI)

Highly Twisted Biphenyl-Linked Carbazole-Benzimidazole Hybrid Bipolar Host Materials for Efficient PhOLEDs

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1. Experimental Details

General Procedures. All reactions were performed under argon atmosphere and solvents were distilled from appropriate drying agents prior to use. All commercial available chemical reagents were used without further purification unless otherwise stated. ¹H and ¹³C NMR spectra of compounds were collected on a Varian 400 MHz spectrometer at room temperature. Mass spectra were obtained on a JEOL SX-102A instrument operating in fast atom bombardment (FAB) mode. Elemental analysis was carried out with an elemental Vario EL-III instrument for NCSH analysis.

Physical Measurements. Steady state photophysical characteristics of compounds were both collected in solutions and solid films, where solutions were probed at room temperature by using 5×10^{-6} M dichloromethane (CH₂Cl₂) solutions while neat films were prepared by vacuum (2×10^{-6} torr) deposition on a quartz plate and probed at respective temperatures for solid-state optical measurements. Absorption spectra were recorded using a U2800A spectrophotometer (Hitachi). Fluorescence spectra were recorded at 300 K using a Hitachi F-4500 spectrophotometer upon exciting at the absorption maxima. Phosphorescent spectra in neat film were obtained using a luminescence spectrometer (HORIBA FluroMax-4P) at 10K. Photoluminescent quantum efficiency (Φ_{PL}) was measured under nitrogen

flow using an integrating sphere with luminescence spectrometer (HORIBA FluroMax-4P) as the optical detector. Transient PL decays were measured under excitation by a pulsed nitrogen laser ($\lambda = 337$ nm, 10 Hz, 700 ps pulses) combined with a photomultiplier tube (R928, Hamamatsu) and a synchronous oscilloscope (500 MHz resolution). The experimental HOMO energy levels were determined by atmospheric ultraviolet photoelectron spectroscopy (Rikken Keiki AC-2); the LUMO energy levels were estimated by the equation of $LUMO = HOMO + E_g$ (where E_g is the optical band gap determined from the absorption threshold). Thermogravimetric analysis (TGA) was performed under nitrogen using a TA instrument Dynamic Q500 thermogravimetric analyzer. The sample was heated from 50 °C to 800 °C with a heating rate of 10 °C /min under nitrogen atmosphere. Differential scanning calorimeter (DSC) studies were carried out on a PerkinElmer Jade DSC at a heating rate of 10 °C /min under nitrogen flushing.

X-ray Structural Analysis. The chosen crystal was mounted on a glass fiber. Data collection of **PhczCBI** was carried out on a BRUKER SMART APEX CCD diffractometer with Mo radiation ($\lambda = 0.71073$ Å) at 150(2) K. **PhczNBI** was transferred to a NONIUS Kappa CCD diffractometer with Mo radiation ($\lambda = 0.71073$ Å) at 150(2). After data collection, the frames were integrated and absorption corrections were applied. Using SHELXTL¹ program on PC computer made the structure analysis. The structure was solved using the SHELXS-97² program and refined using SHELXL-97³ program by full-matrix least squares on F^2 values. All of non-hydrogen atoms are refined anisotropically. Hydrogen atoms attached to the carbons were fixed at calculated positions and refined using a riding mode. Drawings were produced using Diamond 3.0 software. CCDC 1007528 (**PhczNBI**) and 1007529 (**PhczCBI**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Cyclic Voltammetry. The oxidation potentials were determined in CH_2Cl_2 solutions (1.0 mM) containing 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte at a scan rate of 300 mV s⁻¹ using CHI619B potentiostat. The reduction potentials were determined in DMF solutions (1.0 mM) containing 0.1 M tetra-n-butylammonium perchlorate (TBAP). A glassy carbon electrode and platinum wire were used as the working and counter electrodes, respectively. All potentials were recorded versus Ag/AgCl (sat'd) as a reference electrode and calibrated with the ferrocenium/ferrocene redox couple.

Time-of-flight (TOF) mobility measurements. Carrier-transport properties were studied by the time-of-flight (TOF) transient photocurrent technique in the structure: ITO glass/ organic film /Ag (200 nm), which were then placed inside a cryostat and kept under vacuum. The thickness of organic film was monitored in situ with a quartz sensor and calibrated by a thin film thickness measurement (K-MAC ST2000). A pulsed nitrogen laser (337 nm) was used as the excitation light source through the transparent electrode (ITO) inducing photogeneration of a thin sheet of excess carriers. Under an applied dc bias, the transient photocurrent was swept across the bulk of the organic film toward the collection electrode (Ag), and then recorded with a digital storage oscilloscope. Depending on the polarity of the applied bias, selected carriers (holes or electrons) are swept across the sample with a transit time of t_T . With the applied bias V and the sample thickness D , the applied electric field $E = V/D$, and the carrier mobility is then given by $\mu = D/(t_T E) = D^2/(Vt_T)$, in which the carrier transit time, t_T , can be extracted from the intersection of two asymptotes to the tail and plateau sections in the double-logarithmic plots.

OLED device fabrications. All chemicals were purified through vacuum sublimation prior to use. The OLEDs were fabricated through vacuum deposition of the materials at 10^{-6} Torr onto the ITO-coated glass substrates having a sheet resistance of $15 \Omega \text{ sq}^{-1}$. The ITO surface was cleaned ultrasonically; i.e. with acetone, methanol, and deionized water in sequence and finally with UV-ozone. The deposition rate of each organic material was ca. $1\text{--}2 \text{ \AA s}^{-1}$. Subsequently, Liq was deposited at 0.1 \AA s^{-1} and then capped with Al (ca. 5 \AA s^{-1}) through shadow masking without breaking the vacuum. The $J\text{--}V\text{--}L$ characteristics of the devices were measured simultaneously in a glove-box using a Keithley 6430 source meter and a Keithley 6487 picoammeter equipped with a calibration Si-photodiode. EL spectra were measured using a photodiode array (Ocean Optics USB2000).

2. Syntheses and Characterizations

Synthesis of 3-(2'-bromobiphenyl-2-yl)-9-phenyl-9H-carbazole (3). A double-necked flask charged with 2-bromo-2'-iodobiphenyl **1** (15.2g, 42.3 mmol), 9-phenyl-3-(4, 4, 5, 5 - tetramethyl-1,3,2-dioxaborolan-2-yl)-9H carbazole **2** (14.9g, 40.3 mmol), $\text{Pd}(\text{PPh}_3)_4$ (1.86g, 1.61 mmol), $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (44.5g, 141 mmol) was vacuumed and refilled with argon. The flask was then injected with degassed 1,4-dioxane (120mL) and degassed water (30 mL) and refluxed for 48 h. The mixture was cooled to room temperature and 10% aq. HCl was added till the solution was neutralized, and then was extracted with ethyl acetate (100 mL \times 2). The combined

organic layers was washed with brine and dried over MgSO₄. The solution was concentrated to obtain the residue which was purified on a silica column gel using CH₂Cl₂/hexane (1:10) as eluent to give a white solid **3**. (12.6g, 67%) ¹H NMR (CDCl₃, 400 MHz): δ [ppm] 8.00 (d, *J* = 7.6 Hz, 1H), 7.96 (s, 1H), 7.49-7.61 (m, 7H), 7.43 (t, *J* = 8 Hz, 2H), 7.35-7.38 (m, 3H), 7.25-7.27 (m, 1H), 7.18-7.22 (m, 2H), 7.10-7.17 (m, 2H), 7.00-7.05 (m, 1H). ¹³C NMR (CDCl₃, 100 MHz): δ [ppm] 142.21, 141.11, 140.55, 139.38, 139.18, 137.17, 132.58, 132.08, 131.82, 130.40, 130.14, 129.37, 127.94, 127.75, 127.34, 126.93, 126.57, 126.41, 126.04, 125.46, 123.60, 123.08, 122.65, 120.84, 119.81, 119.57, 109.54, 108.70. MS (m/z, FAB⁺): 473.1 (83), 475.1 (90) [M⁺]. HRMS (m/z, FAB⁺) Calcd. for C₃₀H₂₀⁷⁹BrN: 473.0779. Found: 473.0782. Calcd. for C₃₀H₂₀⁸¹BrN: 475.0759. Found: 475.0773.

Synthesis of 3-(2-bromophenyl)-9-phenyl-9H-carbazole (6). **6** was prepared according to the similar procedure as **3** but using 1-bromo-2-iodobenzene instead of 2-bromo-2'-iodobiphenyl **1** as the starting material. (Yield: 83%) ¹H NMR (Acetone-d₆, 400 MHz): δ [ppm] 8.23-8.28 (m, 2H), 7.65-7.76 (m, 5H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.40-7.52 (m, 6H), 7.28-7.33 (m, 2H). ¹³C NMR (DMSO-d₆, 100 MHz): δ [ppm] 142.22, 140.30, 139.22, 136.47, 132.66, 132.40, 131.65, 129.97, 128.73, 127.64, 127.56, 127.32, 126.49, 126.25, 122.49, 122.30, 122.21, 121.01, 120.53, 119.99, 109.52, 108.91. MS (m/z, FAB⁺): 397.1 (93), 399.1 (100) [M⁺]. HRMS (m/z, FAB⁺) Calcd. for C₂₄H₁₆⁷⁹BrN: 397.0466. Found: 397.0474. Calcd. for C₂₄H₁₆⁸¹BrN: 399.0446. Found: 399.0434.

Synthesis of 9-phenyl-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole (7). To a solution of 3-(2-bromophenyl)-9-phenyl-9H-carbazole **6** (7.0 g, 17.6 mmol) in THF (60 mL) at -78 °C was slowly added n-butyllithium (16.5 mL, 1.6 M in hexane, 26.4 mmol). The mixture was stirred at -78 °C for 1 h. 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (7.2 mL, 35.2 mmol) was added to the solution in a portion, and the resulting mixture was warmed to room temperature and stirred for 8 h. The mixture was quenched with water and extracted with diethyl ether. The combined organic layers were washed with brine and dried over MgSO₄. The solvent was concentrated under reduced pressure, and the afforded crude was then rinsed with hexane, giving a white solid as product **7**. (7.12 g, 91 %) ¹H NMR (Acetone-d₆, 400 MHz): δ [ppm] 8.26 (d, *J* = 8 Hz, 1H), 8.20 (s, 1H), 7.65-7.75 (m, 5H), 7.41-7.57 (m, 7H), 7.27-7.38 (m, 2H), 1.18(s, 12H). ¹³C NMR (Acetone-d₆, 100 MHz): δ [ppm] 148.69, 141.87, 140.76, 138.33, 136.15, 135.37, 130.80, 129.99, 128.29, 128.20, 127.55, 126.78, 126.37, 124.26, 123.81, 121.64, 121.11, 120.80, 110.46, 109.85, 84.22, 25.08. MS (m/z, FAB⁺): 445.3 (100) [M⁺].

HRMS (m/z, FAB⁺) Calcd. for C₃₀H₂₈BNO₂: 445.2213. Found: 445.2211.

Synthesis of 9-phenyl-3-(4''-(2-phenyl-1*H*-benzo[*d*]imidazol-1-yl)-[1,1':2',1''-terphenyl]-2-yl)-9*H*-carbazole (PhczNBI). A mixture of 3-(2'-bromobiphenyl-2-yl)-9-phenyl-9*H*-carbazole **3** (1.01 g, 2.11 mmol), 4-(2-phenyl-1*H*-benzo[*d*]imidazol-1-yl)phenylboronic acid **5** (0.66 g, 2.11 mmol), Pd(PPh₃)₄ (0.13 g, 0.11 mmol) and K₂CO₃ (1.17 g, 8.43 mmol) was stirred in degassed xylene (20 mL) and degassed water (5 mL) solution under argon atmosphere. After tri(*tert*-butyl)phosphine (4.2 mL, 0.05 M in toluene, 0.21 mmol) was added into the solution, the mixture was refluxed for 48 h. The reaction mixture was cooled to room temperature and extracted with CH₂Cl₂ (50 mL × 2). The organic layer was washed with brine and dried over MgSO₄. The solvent was removed by rotary evaporation, and the crude was purified on a silica gel column chromatography using hexane/ethyl acetate (5:1) as eluent to provide white solid **PhczNBI** (0.87 g, 62%). ¹H NMR (CD₂Cl₂, 400 MHz): δ [ppm] 7.82 (d, *J* = 7.6 Hz, 1H), 7.56-7.62 (m, 7H), 7.49-7.54 (m, 3H), 7.33-7.47 (m, 13H), 7.22-7.31 (m, 2H), 7.09-7.14 (m, 2H), 7.04 (d, *J* = 8.8 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 8.8 Hz, 2H). ¹³C NMR (CD₂Cl₂, 100 MHz): δ [ppm] 152.12, 143.03, 141.47, 141.38, 140.92, 140.55, 139.94, 139.78, 139.34, 137.49, 137.43, 134.95, 132.71, 131.81, 131.52, 130.60, 130.33, 130.17, 129.86, 129.76, 129.47, 129.36, 128.29, 127.85, 127.79, 127.68, 127.50, 127.36, 126.78, 126.75, 126.18, 125.82, 123.35, 123.22, 122.78, 121.37, 119.95, 119.96, 119.67, 110.60, 109.83, 108.87. MS (m/z, FAB⁺): 664.2 (4) [(M + H)⁺]. HRMS (m/z, FAB⁺) Calcd. for C₄₉H₃₃N₃: 663.2674. Found: 663.2682. Anal. Calcd for C₄₉H₃₃N₃: C, 88.66; H, 5.01; N, 6.33. Found: C, 88.85; H, 5.20; N, 6.30.

Synthesis of 9-phenyl-3-(4''-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)-[1,1':2',1''-terphenyl]-2-yl)-9*H*-carbazole (PhczCBI). **PhczCBI** was prepared according to the similar procedure as **PhczNBI** but using 4-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)phenylboronic acid **4** instead of **5** as the starting material. (Yield: 62%) ¹H NMR (CD₂Cl₂, 400 MHz): δ [ppm] 7.85 (d, *J* = 8.4 Hz, 1H), 7.60-7.64 (m, 3H), 7.51-7.55 (m, 3H), 7.46-7.50 (m, 3H), 7.39-7.45 (m, 5H), 7.31-7.38 (m, 4H), 7.25-7.30 (m, 3H), 7.14-7.19 (m, 3H), 7.04-7.08 (m, 3H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.91-6.94 (m, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.42 (d, *J* = 8.4 Hz, 2H). ¹³C NMR (CD₂Cl₂, 100 MHz): δ [ppm] 152.43, 143.54, 142.44, 141.77, 141.32, 140.93, 140.47, 140.23, 139.64, 138.05, 137.98, 137.55, 133.24, 132.19, 132.00, 130.66, 130.23, 130.12, 129.84, 129.31, 128.83, 128.71, 128.07, 128.00, 127.95, 127.85, 127.79, 127.69, 127.19, 126.02, 123.85, 123.43, 123.36, 123.07, 121.61, 120.45, 120.03, 119.91, 110.75, 110.00, 108.97. MS (m/z, FAB⁺): 664.2 (100) [(M + H)⁺]. HRMS (m/z, FAB⁺) Calcd.

for C₄₉H₃₃N₃: 663.2674. Found: 663.2680. Anal. Calcd for C₄₉H₃₃N₃: C, 88.66; H, 5.01; N, 6.33. Found: C, 88.43; H, 5.29; N, 6.30.

Synthesis of 9-phenyl-3-(2'-(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)-[1,1'-biphenyl]-2-yl)-9*H*-carbazole (PhczDCBI). PhczDCBI was prepared according to the similar procedure as PhczNBI but using **7** and 2-(2-bromophenyl)-1-phenyl-1*H*-benzo[*d*]imidazole **8** instead of **5** and **3**, respectively, as the starting material. (Yield: 73%) ¹H NMR (CD₂Cl₂, 400 MHz): δ [ppm] 7.73 (d, *J* = 8 Hz, 1H), 7.46-7.65 (m, 7H), 7.40-7.43 (m, 2H), 7.27-7.38 (m, 5H), 7.13-7.24 (m, 8H), 7.06-7.10 (m, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 8 Hz, 1H), 6.64-6.66 (m, 2H), 6.53 (d, *J* = 8.4 Hz, 1H). ¹³C NMR (CD₂Cl₂, 100 MHz): δ [ppm] 152.66, 143.59, 141.83, 141.64, 141.29, 139.97, 139.10, 137.99, 136.68, 136.34, 133.14, 132.57, 132.30, 131.29, 130.99, 130.55, 130.20, 129.54, 128.02, 127.88, 127.78, 127.67, 127.16, 126.74, 126.14, 123.73, 123.42, 123.13, 122.73, 121.31, 121.24, 120.65, 120.11, 110.55, 110.07, 109.21. MS (m/z, FAB⁺): 588.2 (100) [(M + H)⁺]. HRMS (m/z, FAB⁺) Calcd. for C₄₃H₂₉N₃: 587.2361. Found: 587.2359. Anal. Calcd for C₄₃H₂₉N₃: C, 87.88; H, 4.97; N, 7.15. Found: C, 87.65; H, 4.77; N, 7.20.

3. Supplementary Table

Table S1. Crystal data for **PhczNBI** and **PhczCBI**.

	PhczNBI	PhczCBI
Empirical formula	C ₄₉ H ₃₃ N ₃	C ₄₉ H ₃₃ N ₃
Formula weight	663.27	663.27
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
<i>a</i> (Å)	11.8108(2)	10.7471(7)
<i>b</i> (Å)	11.8531(2)	13.3671(9)
<i>c</i> (Å)	14.4264(2)	13.5963(8)
α (deg)	86.6414(10)	79.376(2)
β (deg)	72.8960(9)	88.390(2)
γ (deg)	66.2337(9)	70.557(2)
Cell volume (Å) ³	1762.45(5)	1809.1(2)
<i>Z</i>	2	2
Density (calc) Mg/m ³	1.251	1.297
<i>F</i> (000)	696	738
Temperature (K)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073
Reflections collected	22321	18225
Independent reflns (<i>R</i> _{int})	8049 (0.0362)	8267 (0.0406)
<i>R</i> (<i>F</i>), <i>wR</i> 2 [<i>I</i> >2 σ (<i>I</i>)]	0.0468, 0.1137	0.0684,0.1319
<i>R</i> (<i>F</i>), <i>wR</i> 2 (all data)	0.0821, 0.1300	0.0973,0.1458
CCDC number	CCDC 1007528	CCDC 1007529

Table S2. The average absolute photoluminescence quantum yield (Φ_{PL}) of **PhczNBI**, **PhczCBI**, **PhczDCBI** and mCP:10 wt% FIrpic under excitation by a xenon lamp ($\lambda_{\text{ex}} = 290\text{-}330\text{ nm}$) at room temperature.

	PhczNBI	PhczCBI	PhczDCBI	mCP
Avg. PLQY (Φ_{PL}, %) ^a	71	39	73	95

^a Obtained from the average of three times of repeated measurements.

4. Supplementary Figures

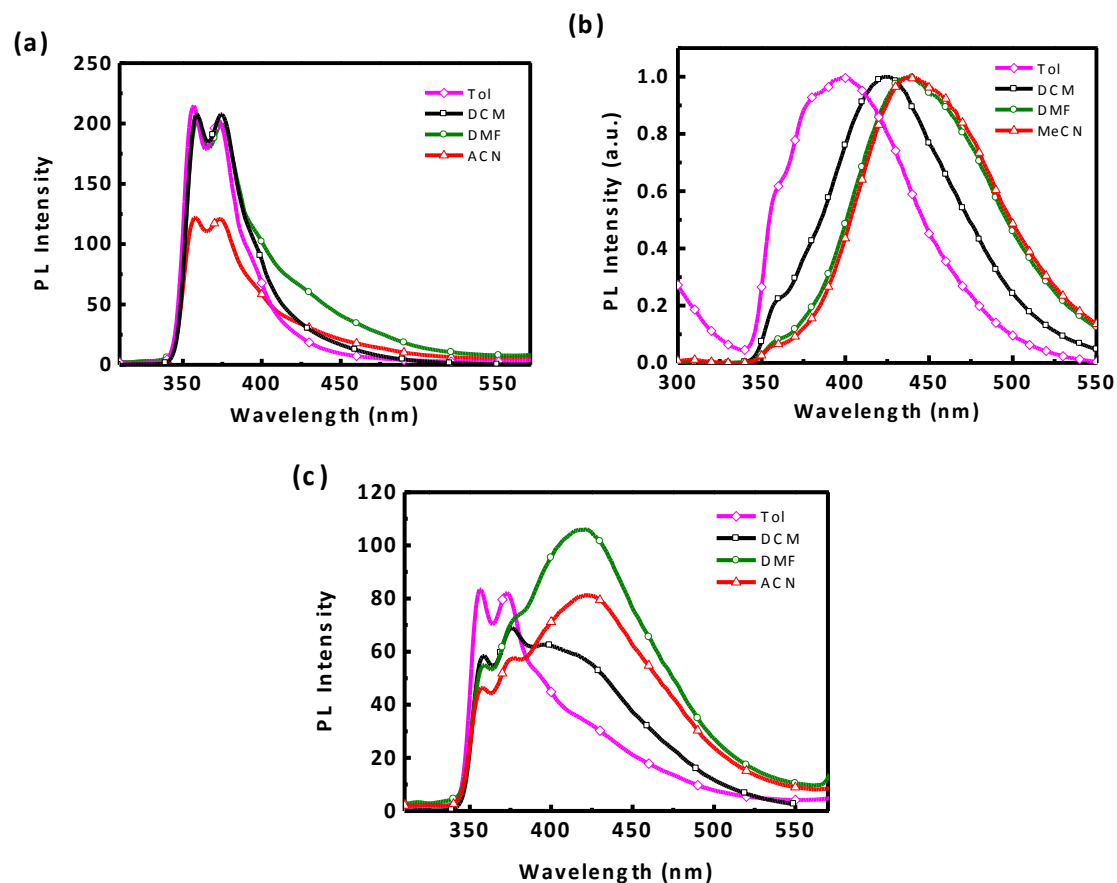


Fig. S1 The solvatochromic emission spectra of (a) **PhczNBI**, (b) **PhczCBI**, and (c) **PhczDCBI** in various solvents, where Tol (\diamond), DCM (\square), ACN (Δ) and DMF (\circ) represents toluene, dichloromethane, acetonitrile and *N,N*-dimethylformamide solution, respectively.

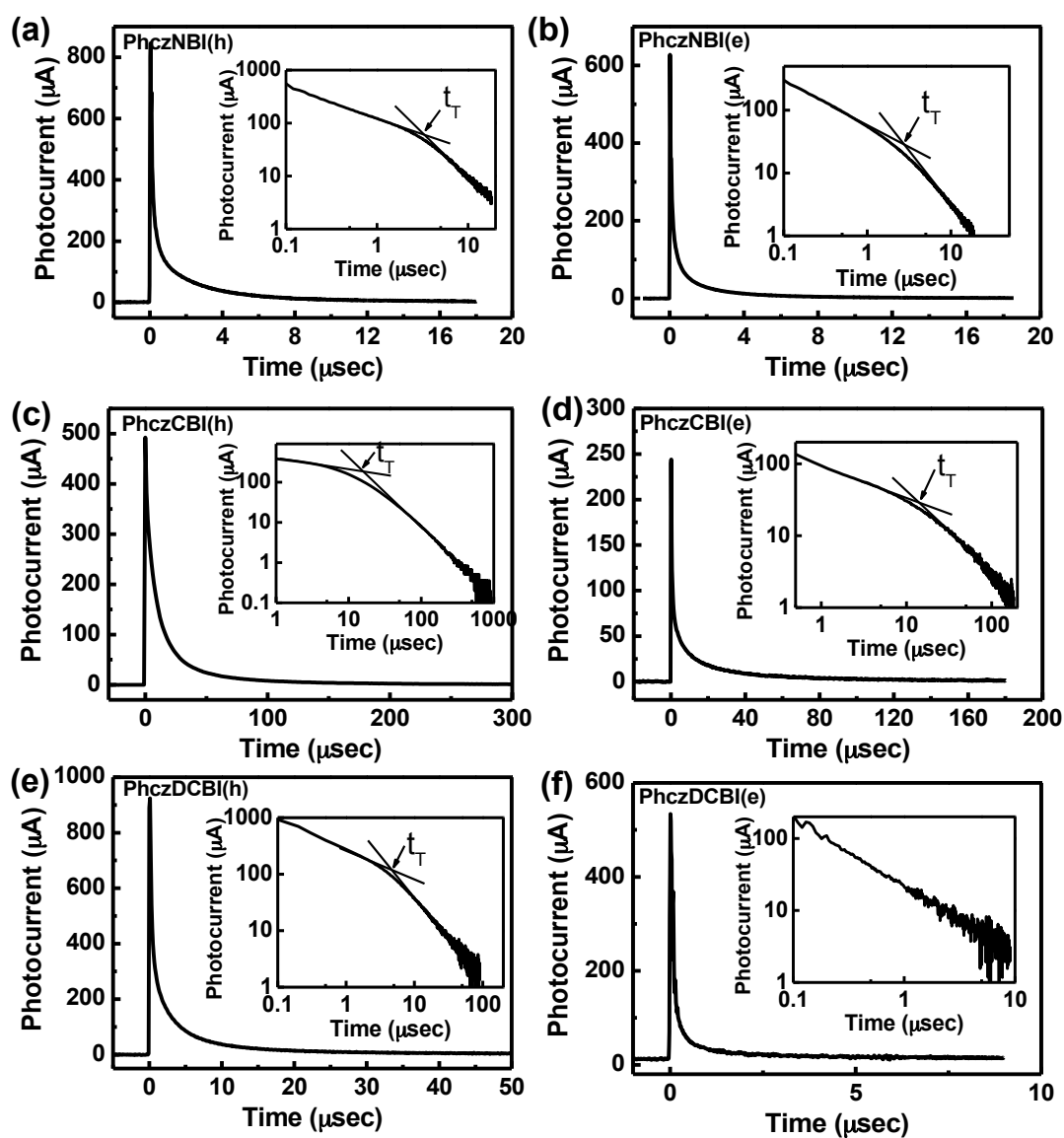


Fig. S2 Typical transient photocurrent signals for **PhczNBI** (1.36 μm thick) at $E = 6.6 \times 10^5$ V/cm, **PhczCBI** (1.33 μm thick) at $E = 6.8 \times 10^5$ V/cm and **PhczDCBI** (1.54 μm thick) at $E = 9.8 \times 10^5$ V/cm: (a)(c)(e) holes; (b)(d)(f) electrons. Insets are the double logarithmic plots of (a)-(f)

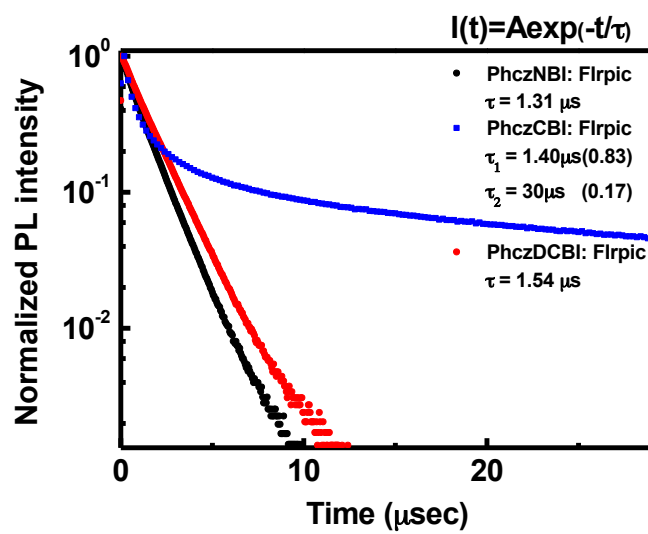


Fig. S3 Transient PL decay of **PhczNBI**, **PhczCBI** and **PhczDCBI** :10 wt% Flrpic under excitation by a nitrogen laser ($\lambda=337$ nm, 10 Hz, 700 ps pulses) at room temperature.

Fig. S5 ^{13}C NMR spectrum of **3** (100 MHz, CDCl_3 , 25 $^\circ\text{C}$).

STANDARD 1H OBSERVE
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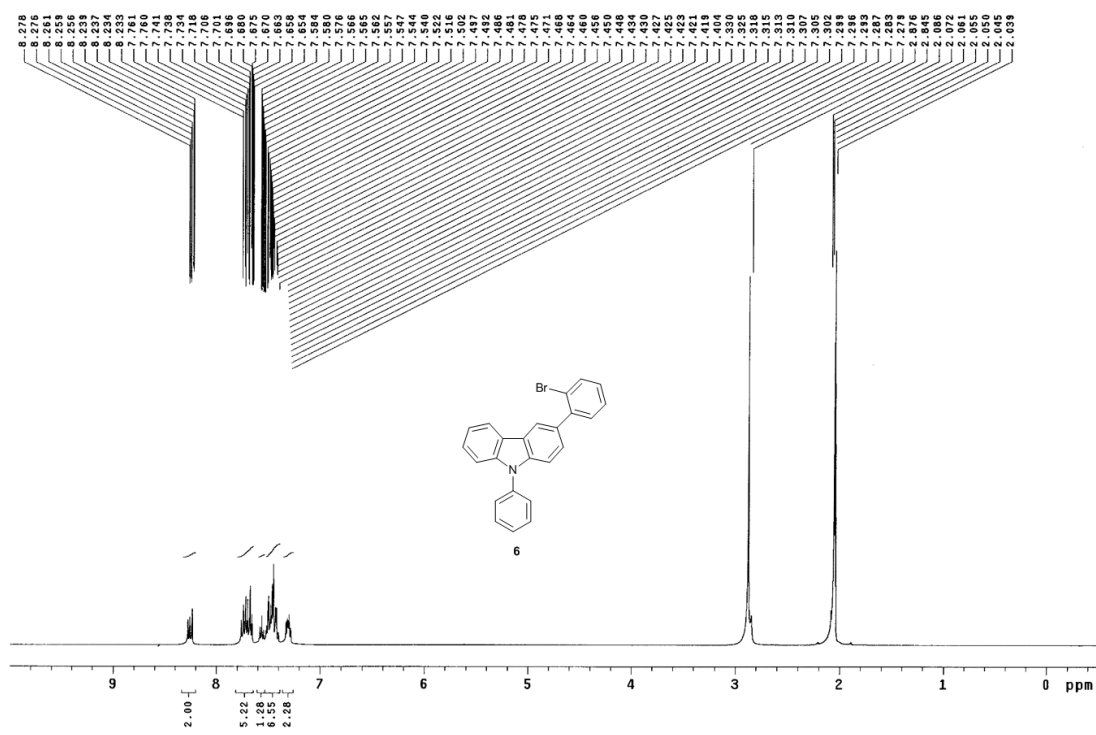


Fig. S6 ^1H NMR spectrum of **6** (400 MHz, Acetone- d_6 , 25 °C).

^{13}C OBSERVE
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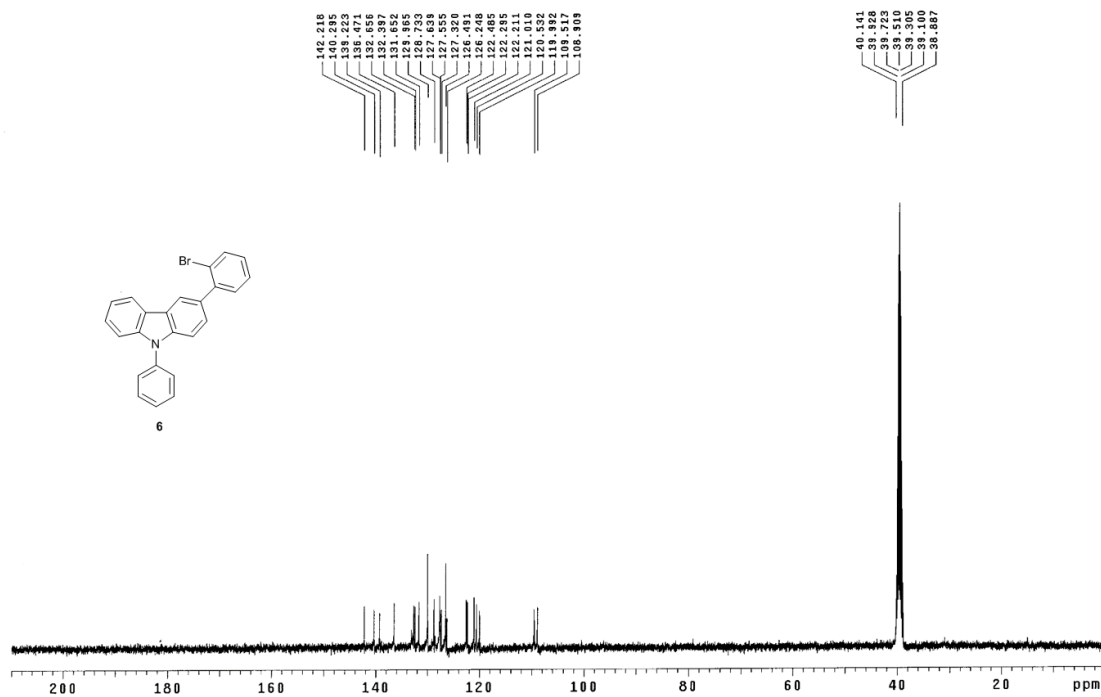


Fig. S7 ^{13}C NMR spectrum of **6** (100 MHz, Acetone- d_6 , 25 $^\circ\text{C}$).

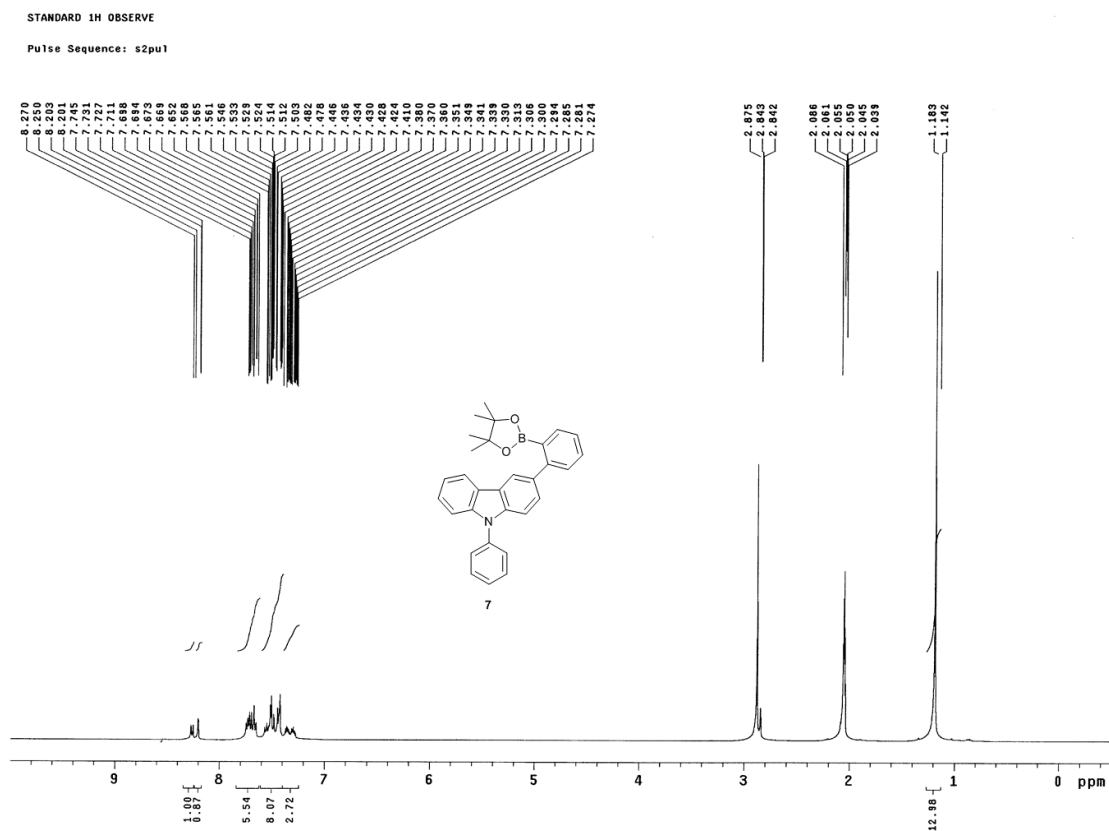


Fig. S8 ^1H NMR spectrum of **7** (400 MHz, Acetone- d_6 , 25 $^\circ\text{C}$).

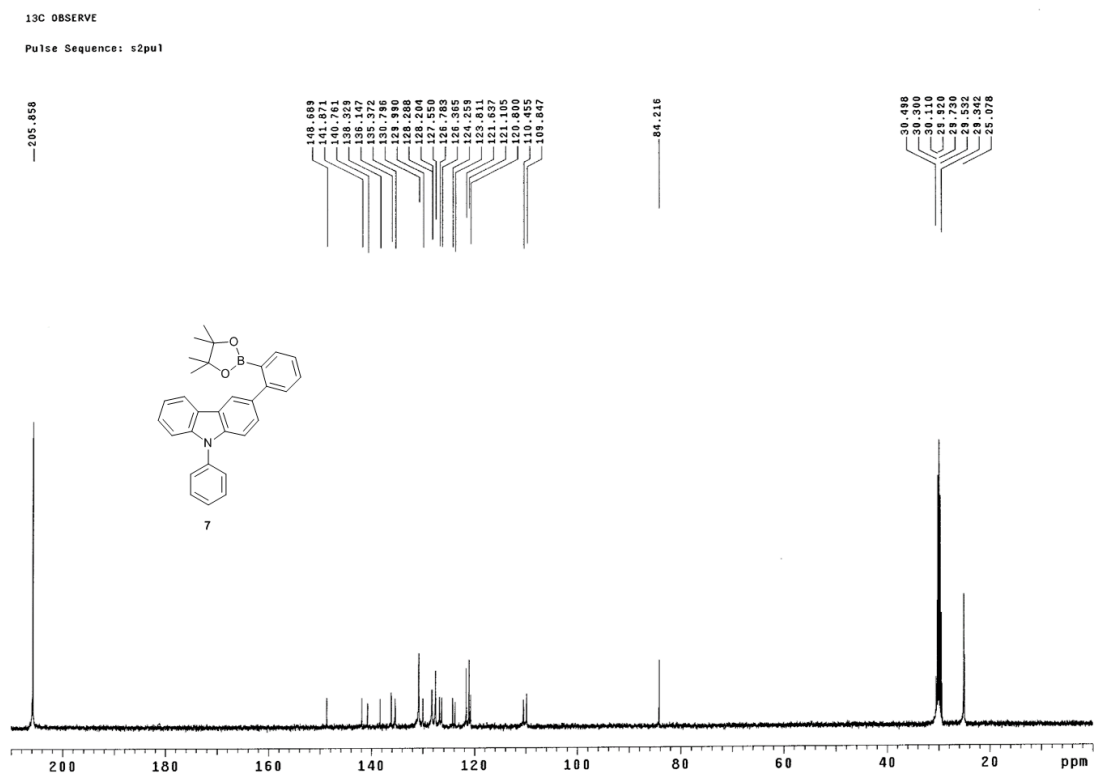


Fig. S9 ^{13}C NMR spectrum of **7** (100 MHz, Acetone- d_6 , 25 $^\circ\text{C}$).

STANDARD 1H OBSERVE

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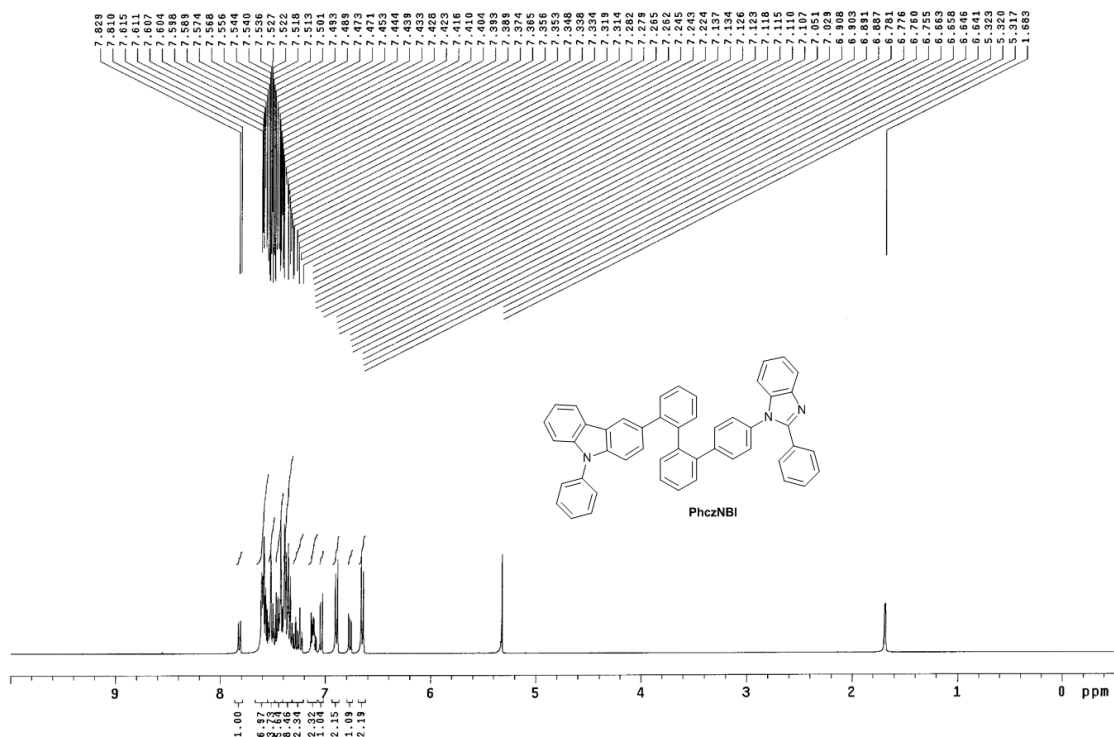


Fig. S10 ¹H NMR spectrum of PhczNBI (400 MHz, CD₂Cl₂, 25 °C).

¹³C OBSERVE

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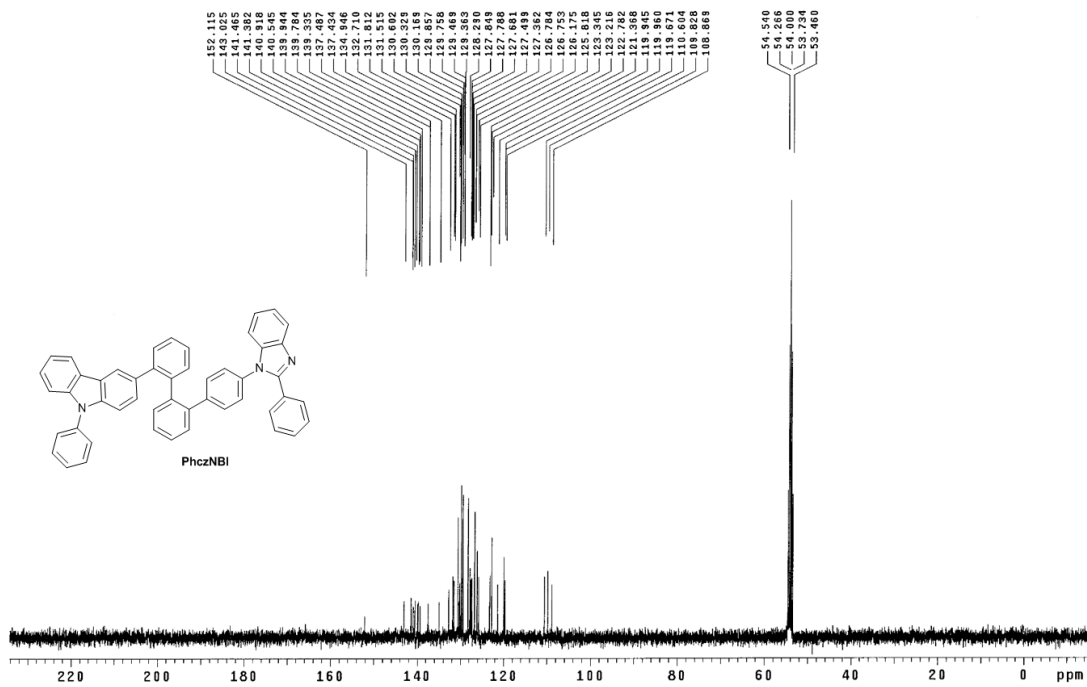


Fig. S11 ¹³C NMR spectrum of PhczNBI (100 MHz, CD₂Cl₂, 25 °C).

Fig. S13 ^{13}C NMR spectrum of **PhczCBI** (100 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$).

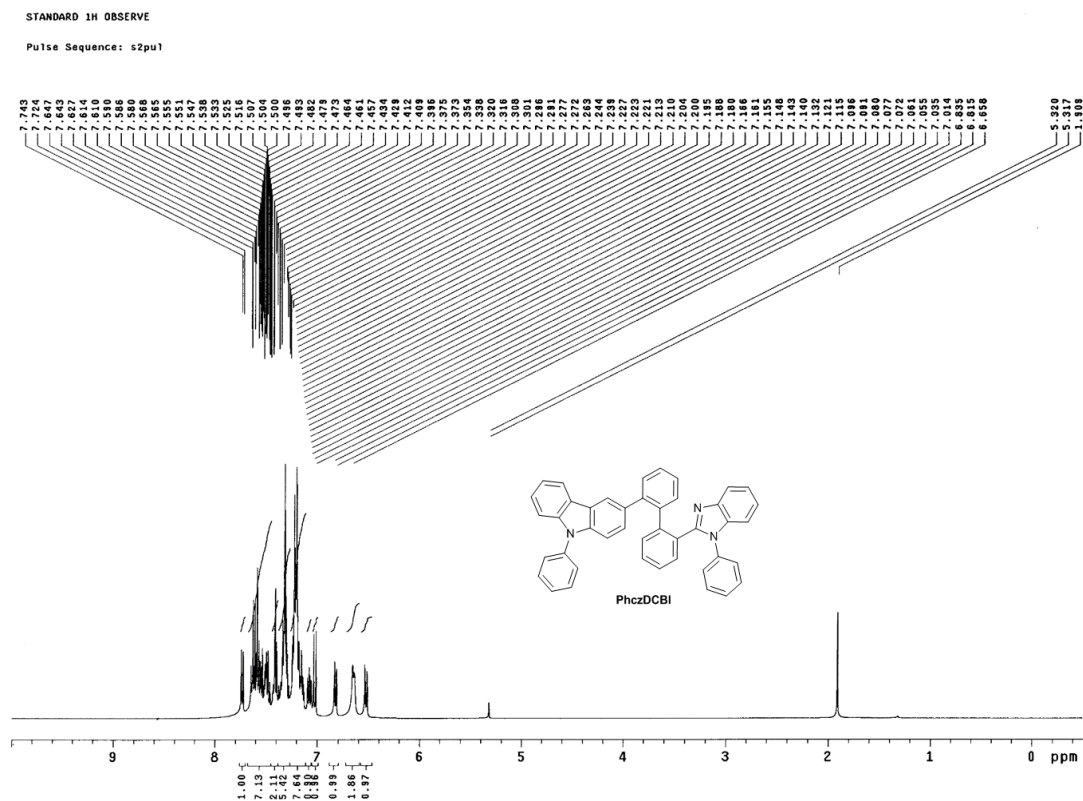


Fig. S14 ^1H NMR spectrum of **PhczDCBI** (400 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$).

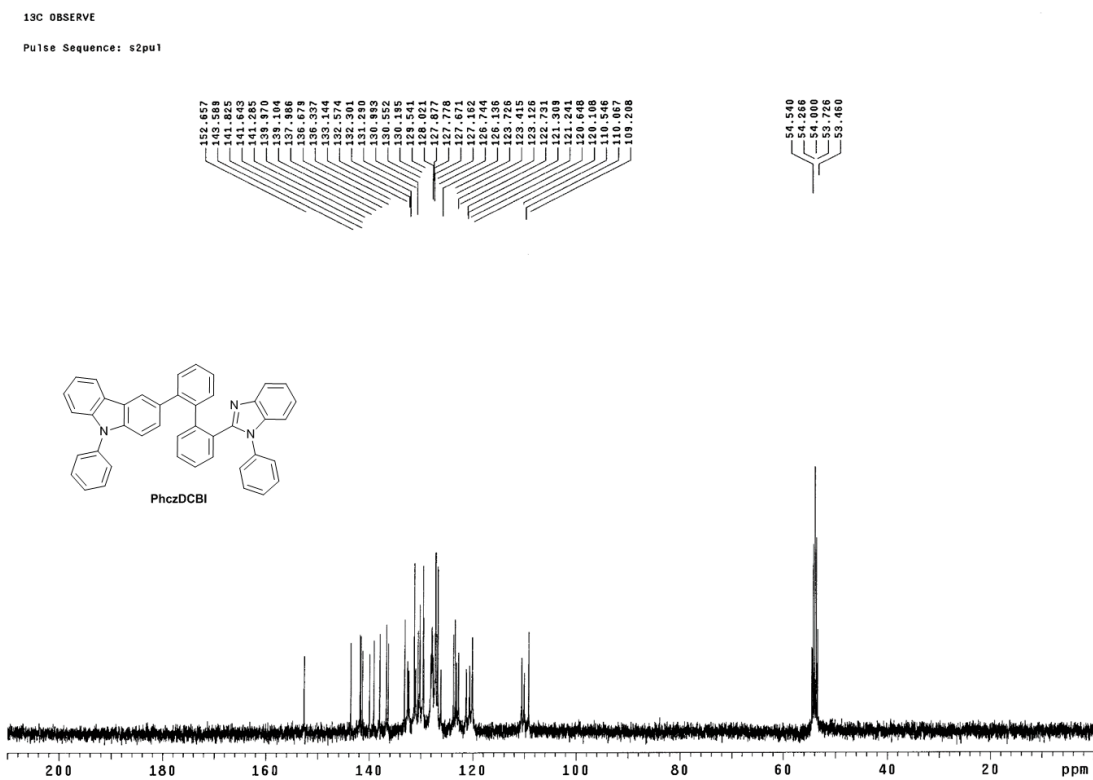


Fig. S15 ^{13}C NMR spectrum of **PhczDCBI** (100 MHz, CD_2Cl_2 , 25 °C).

References

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- ² SHELXS-97, Sheldrick, G. M., *Acta. Cryst.*, 1990, **A46**, 467-473.
- ³ SHELXL-97, Sheldrick, G. M., University of Göttingen, Germany, 1997.