

Bent Ladder-type Hexaphenylene with Carbazole Core and Spiro Linkage as Stable and Efficient Blue Emitter

Zuoquan Jiang, Haiqing Yao, Zhongyin Liu, Chuluo Yang,* Cheng Zhong, Jingui Qin, Gui Yu, Yunqi Liu*

Department of Chemistry, Hubei Key Lab on Organic and Polymeric Optoelectronic Materials, Wuhan University, Wuhan 430072, P. R. China, and Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China

E-mail: clyang@whu.edu.cn; liuyq@mail.iccas.ac.cn

General Information ^1H -NMR and ^{13}C -NMR spectra were measured on a Varian Unity 300 MHz spectrometer using CDCl_3 as solvent and tetramethylsilane as an internal reference. Elemental analyses of carbon, hydrogen, and nitrogen were performed on Vario EL-III microanalyzer. MALDI-TOF mass spectrometric measurement was performed on Bruker Biflex III MALDI TOF instrument. EI-MS spectra were recorded on VJ-ZAB-3F-Mass spectrometer. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ from $30\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$ under argon. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of $15\text{ }^\circ\text{C min}^{-1}$ from $25\text{ }^\circ\text{C}$ to $700\text{ }^\circ\text{C}$. UV-Vis absorption spectra were recorded on Shimadzu UV-2550 spectrophotometer. PL spectra were recorded on Hitachi F-4500 fluorescence spectrophotometer. Cyclic voltammetry (CV) was carried out on a CHI voltammetric analyzer at room temperature in nitrogen-purged CH_2Cl_2 with tetrabutylammonium hexafluorophosphate (TBAPF_6) as the supporting electrolyte at scanning rate of 100 mV/s . A platinum disc and a silver were used as working electrode and quasi-referenced electrode, respectively. Ferrocene was used as internal reference for potential calibration. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram.

n-Butyllithium in hexane was purchased from Alfa Asia Chemical Co. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was purchased from Aldrich. The

intermediate 2,7-dibromo-*N*-(2-ethylhexyl)-3,6-bis(benzoyl)-carbazole and 4-(9,9'-spirobifluorenyl) pinacol boronate were prepared according to the literature. All reagents commercial available were used as received unless otherwise stated. The solvents (THF, diethyl ether, dichloromethane) were purified by conventional procedure and distilled under dry argon before using. All reactions were carried out using Schlenk techniques under an argon atmosphere.

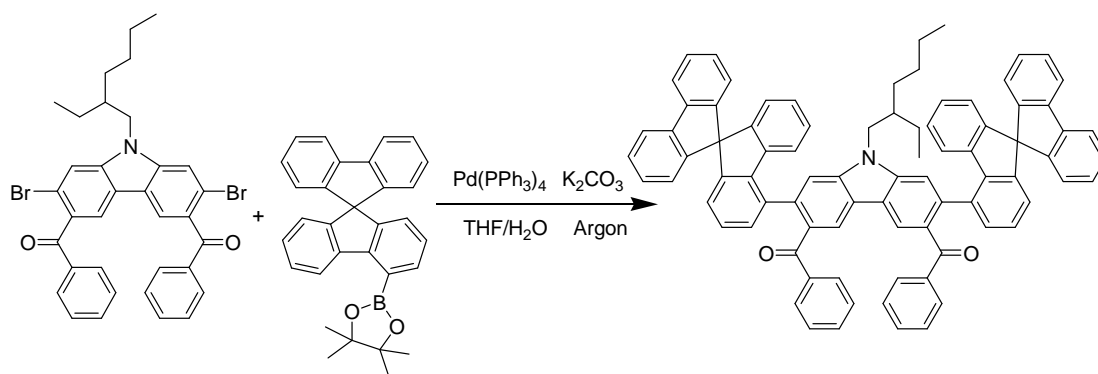
OLEDs Fabrication and Performance Measurements The ITO-coated glass substrates were etched, patterned, and washed with detergent, deionized water, acetone, and ethanol in turn. The multilayered devices ITO/BLHPC (40 nm)/TPBI (30 nm)/LiF (1 nm)/Al (100 nm) were fabricated, where BLHPC works as the hole-transporting and the emitting layer. TPBI is used as hole-blocking and electron-transporting layer. The organic layers were successively deposited onto the ITO/glass substrates at a pressure of 5×10^{-4} Pa. The thickness of the thin films was monitored by a quartz crystal oscillator placed near the substrates, and was calibrated *ex situ* by an Ambios Technology XP-2 surface profilometer. The active area of the OLED devices was 6 mm². The luminescence output and current-voltage characteristics were recorded with a Newport 2835-C multifunction optical meter and a Hewlette Packard 4140B semiconductor parameter analyzer. EL spectra and Commission Internationale de L'Eclairage (CIE) coordinates were measured with a Photo Research PR-650 spectrophotometer.

DFT Calculations The geometrical and electronic properties of BLHPC were performed with the Gaussian 03 program package (M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J.

Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian, Inc.*, Wallingford CT, **2004**.). The calculation was optimized by means of the B3LYP (Becke three parameters hybrid functional with Lee-Yang-Perdew correlation functionals) with the 6-31G(d) atomic basis set.³² Molecular orbitals were visualized using Gaussview.

Synthesis

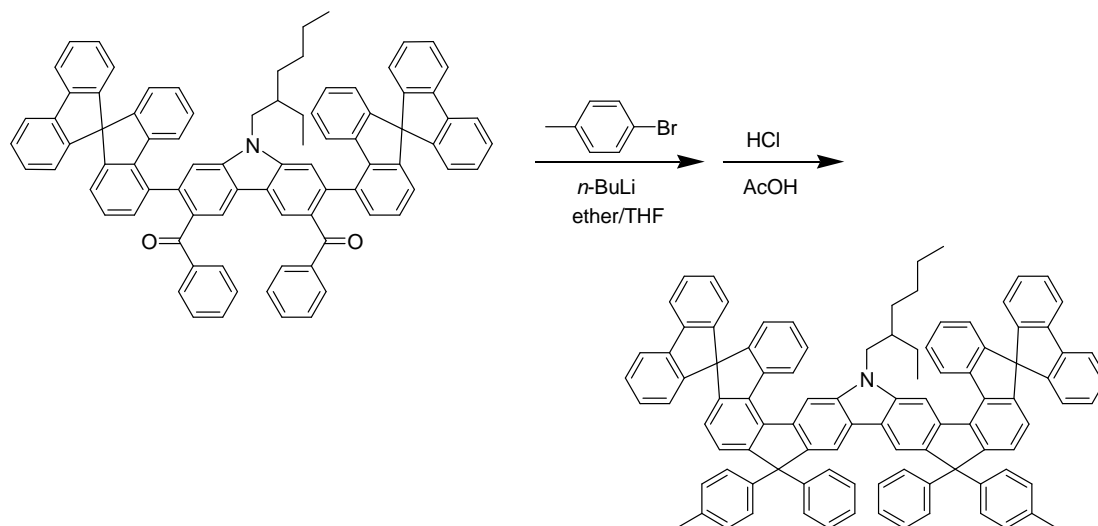
3,6-dibenzoyl-2,7-di(9,9'-spirofluorenyl-4-yl) -*N*-(2-ethylhexyl)carbazole (**1**)



A mixture of 3,6-dibenzoyl-2,7-dibromo-*N*-(2-ethylhexyl)carbazole (0.65 g, 1.00 mmol), 4-(9,9-spirobifluorenyl) pinacol boronate (1.00 g, 2.26 mmol), Pd(PPh₃)₄ (0.10 g, 4% mmol) and potassium carbonate (2.8 g, 20 mmol) in 30 ml of THF and 10 ml of distilled water in a 100 ml round bottom was refluxed for 2 days under argon. The mixture was extracted with chloroform. The combined organic extracts were dried over anhydrous Na₂SO₄ and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using EtOAc/petroleum = 1/4 as eluent to afford the product as a pale yellow powder (0.77 g, yield: 69%). ¹H NMR (300 MHz, CDCl₃, δ): 8.62 (s, 2H), 7.86-7.784 (m, 6H), 7.74 (d, *J* = 7.8 Hz, 4H), 7.41-7.31 (m, 10H), 7.20-6.95 (m, 16H), 6.87 (d, *J* = 8.1 Hz, 2H), 6.68 (t, *J* = 6.3 Hz, 2H), 6.58 (d, *J* = 8.1 Hz, 2H), 6.37 (d, *J* = 8.1 Hz, 2H), 4.36 (d, *J* = 7.2 Hz, 2H), 1.57-1.14 (m, 9H), 0.93-0.67 (m, 6H); ¹³C NMR (75 MHz, CDCl₃, δ): 149.31, 149.24, 149.20, 148.67, 142.88, 142.09, 141.55, 139.14, 139.06, 138.97, 136.28, 132.26, 132.07, 130.73, 129.87, 127.97, 127.85, 127.75, 127.31, 127.22, 127.07, 124.24, 124.09, 123.34, 122.88, 122.16, 122.09, 122.00, 120.20, 119.99, 111.86, 65.65, 48.06, 39.81, 30.96, 28.84, 24.84, 22.91, 14.03, 11.17. Anal. Calcd. for C₈₄H₆₁NO₂ (%): C,

90.37; H, 5.51; N, 1.25. Found: C, 90.75; H, 6.00; N, 0.80. MALDI-TOF-MS: m/z 1116.7 [M^+].

BLHPC.



4-Bromotoluene (0.2 g, 1.1 mmol) in ether (6 ml) were treated with *n*-BuLi (0.5 ml, 2.4 M in hexane, 1.2 mmol) at -10 °C for 30 min, then quenched with a solution of **1** (0.31 g, 0.28 mmol) in THF (10 ml). After stirring at -10 °C for 1 hour, the mixture was allowed to warm to room temperature. The solution was quenched with water and extracted twice with CH₂Cl₂. The combined organic extracts were dried over anhydrous Na₂SO₄ and concentrated by rotary evaporation. The crude product was dissolved in boiling acetic acid (4 ml) and added concentrated HCl(aq) (0.5 ml). The reaction was allowed to reflux for 2 hours, then quenched with water (40 ml). The precipitate was purified by column chromatography on silica gel using CH₂Cl₂/petroleum = 1/3 to afford the product as a yellow powder (0.29 g, yield: 82%). ¹H NMR (300 MHz, CDCl₃, δ): 8.76 (d, *J* = 7.2 Hz, 2H), 8.61 (s, 2H), 7.92 (s, 2H), 7.80 (d, *J* = 7.2 Hz, 4H), 4.43 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 7.5 Hz, 4H), 7.25 (d, *J* = 6.6 Hz, 4H) 7.19-7.05 (m, 18H), 6.98 (d, *J* = 8.1 Hz, 4H), 6.79 (t, *J* = 8.1 Hz, 6H), 6.52 (d, *J* = 8.1 Hz, 2H), 4.46 (d, *J* = 5.7 Hz, 2H), 2.21 (s, 6H), 1.89-0.78 (m, 15H); ¹³C NMR (75 MHz, CDCl₃, δ): 152.69, 149.51, 149.34, 148.34, 147.44, 144.28, 143.46, 142.03, 141.86, 141.22, 138.24, 136.30, 129.20, 128.65, 128.43, 128.16, 127.96, 126.65, 124.06, 123.47, 120.16, 117.96, 117.66, 115.70, 100.30, 66.03, 64.45, 48.04, 39.01, 30.58, 28.68, 24.78, 23.28, 21.25, 14.28, 11.24. Anal. Calcd. for C₉₈H₇₃N(%):C, 93.07; H, 5.82; N, 1.11. Found: C, 92.75; H, 6.16; N, 0.82. MALDI-TOF-MS: m/z 1263.7 (M^+).

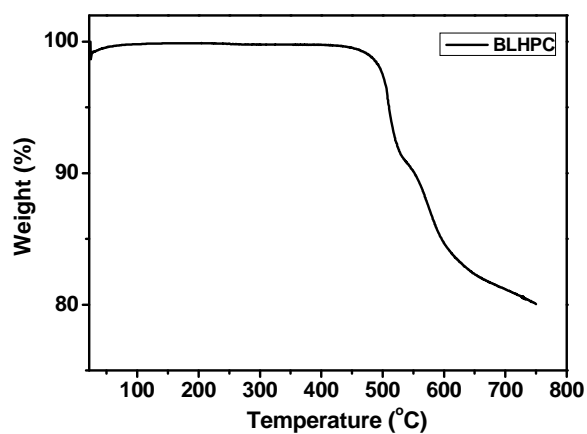


Figure S1. TGA thermogram of **BLHPC**.

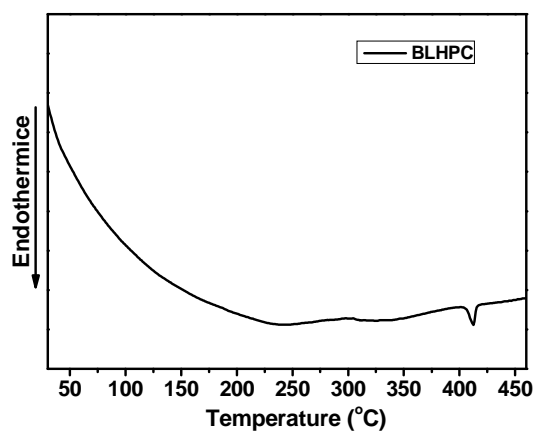


Figure S2. DSC thermogram of **BLHPC**.

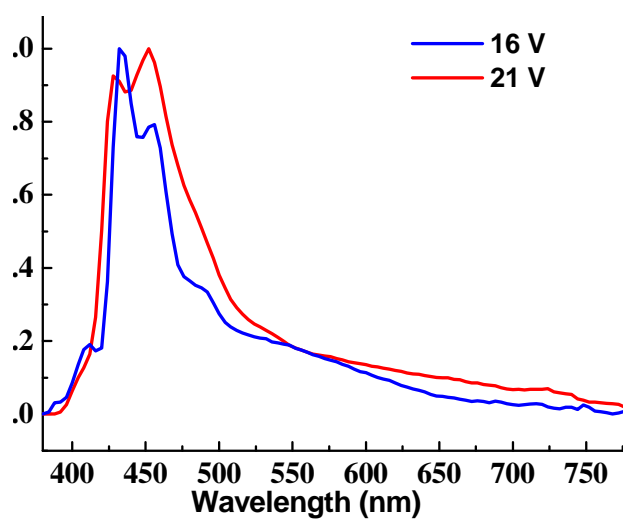
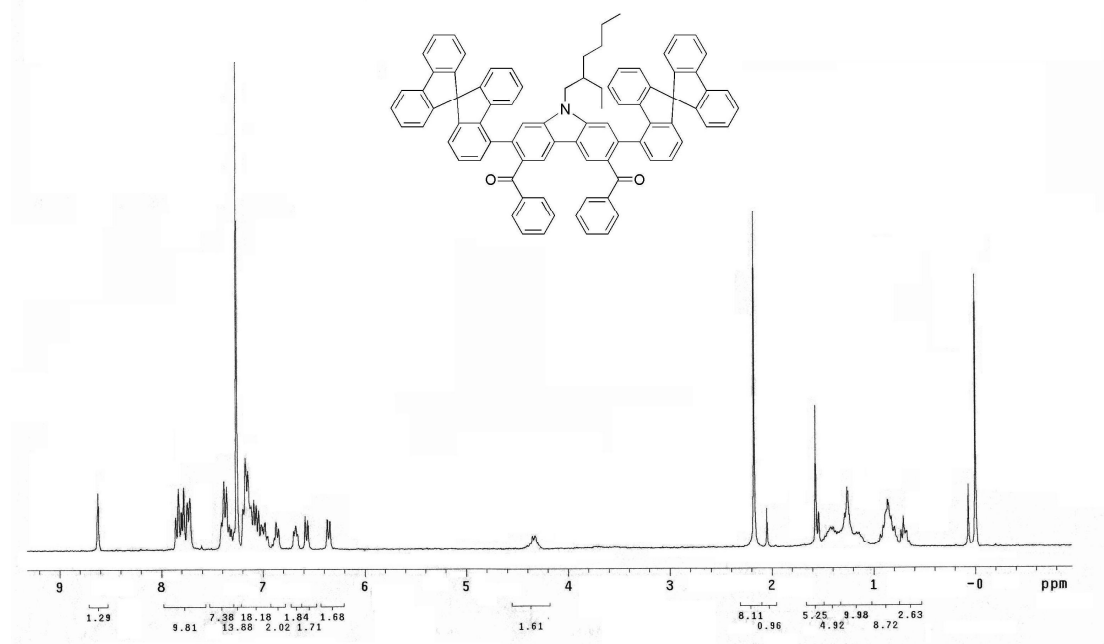
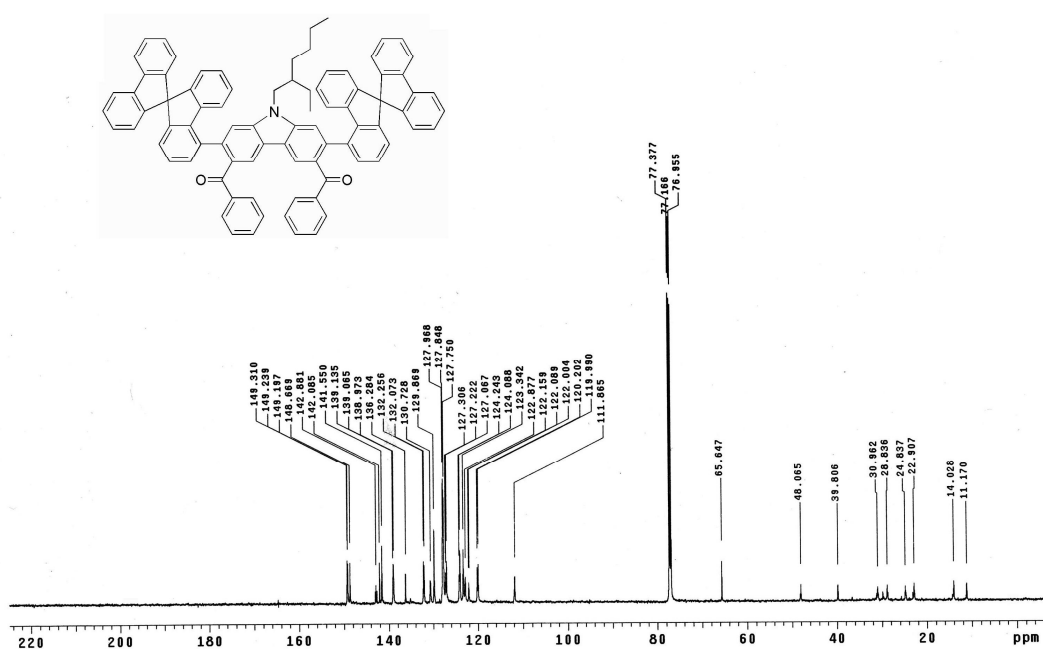


Figure S3. EL spectrum of **BLHPC**.

^1H NMR spectrum of **1**

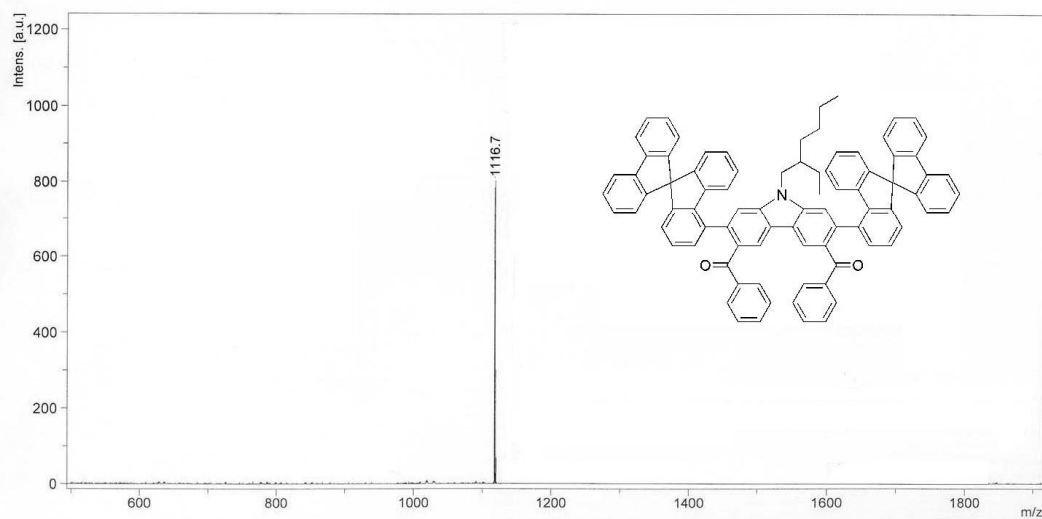


^{13}C NMR spectrum of **1**

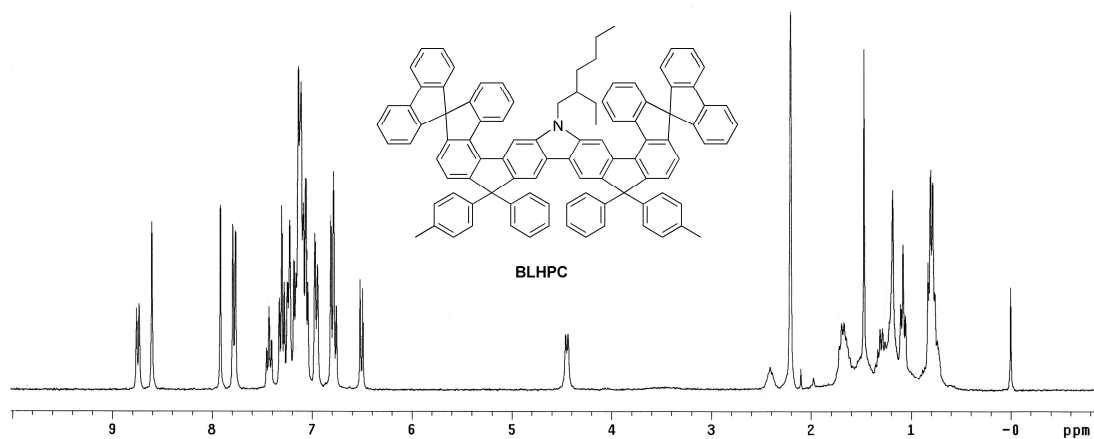


MS spectrum of **1**

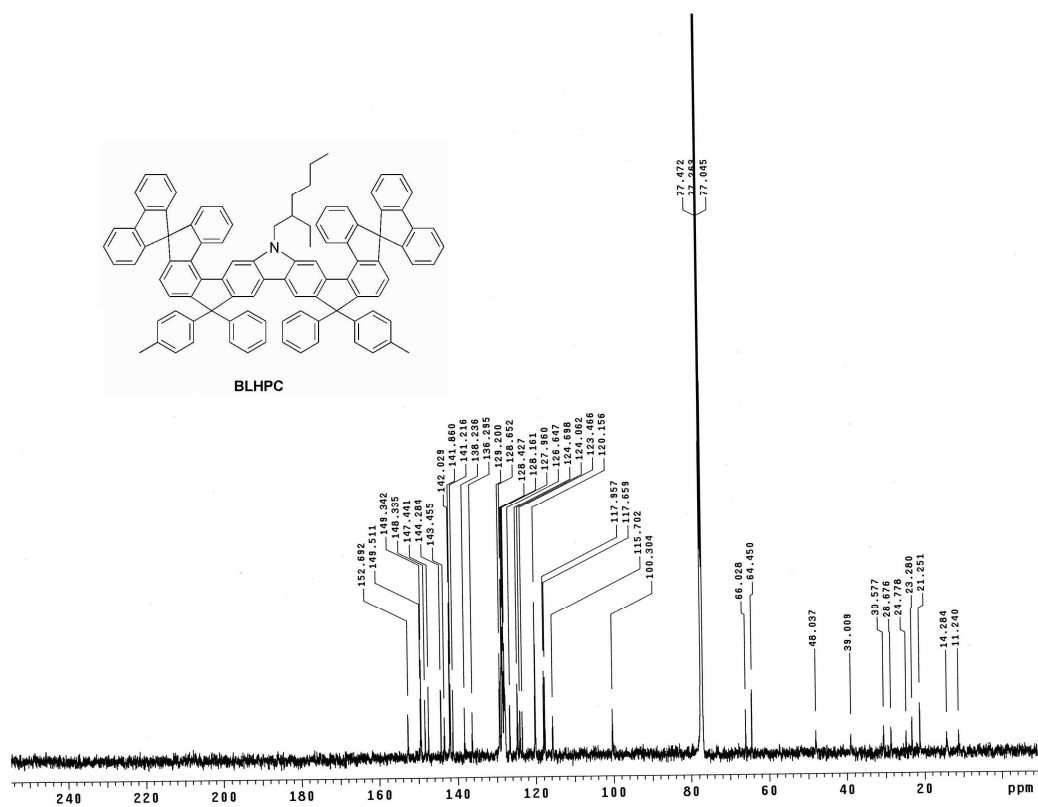
MALDI-TOF, CCA, J10, 2008, 12, 04



^1H NMR spectrum of BLHPC



^{13}C NMR spectrum of BLHPC



MS spectrum of BLHPC

MALDI-TOF,DHB,JZQ3,2008,5,27

