

Electronic Supplementary Information (ESI) for

# Fluorescent pyrene-centered starburst oligocarbazoles with excellent thermal and electrochemical stabilities

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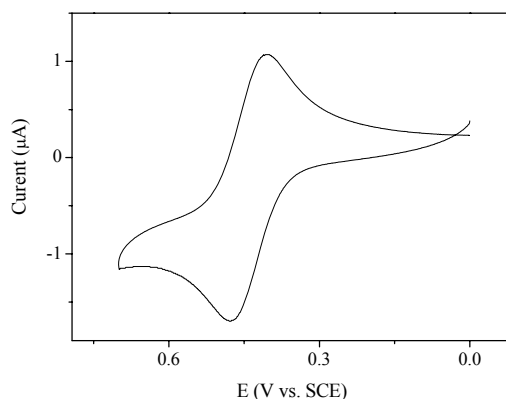
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## I. General Methods.

All materials were obtained from commercial suppliers and used without further purification. Solvents of technical quality were distilled prior to use.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV spectrometer (300 MHz for  $^1\text{H}$ , 75 MHz for  $^{13}\text{C}$ ). Elemental analyses performed at the Analytic Center of University of Science and Technology of China. FT-IR spectra were carried out on a Bruker Vector22 Infrared Spectrometer, on samples prepared as KBr pellets. UV-vis absorption spectra were recorded at room temperature with a Shimadzu UV-2401PC UV-vis spectrometer on dichloromethane by use cell path lengths of 1cm. Fluorescence emission spectra in solution were measured on a Perkin-Elmer LS55 luminescence spectrometer and fluorescence emission spectra in film were measured on JY Fluorolog-3-Tou luminescence spectrometer. Mass spectra were obtained with a Micromass GCF-TOF and MALDI-TOF mass spectrometer. Matrix assisted laser (337 nm) desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained in positive mode with no matrix on a AB Sciex Q-star instrument and in all cases showed the molecular ion peaks  $\text{M}^+$  with patterns that are in good agreement with simulated data.



**Figure S1.** Cyclic voltammograms of ferrocene analyte at a scan rate  $100 \text{ mVs}^{-1}$ . The electrolyte was 0.1 M TBAPF<sub>6</sub> in anhydrous dichloromethane.

Thermogravimetric analysis (TGA) was carried out using a TGA Q5000IR instrument (heating rate of  $10^\circ\text{C min}^{-1}$ ). Differential scanning calorimetry (DSC) was carried out under nitrogen on a VP-DSC instrument (scanning rate of  $10^\circ\text{C min}^{-1}$ ). Electrochemical measurements were carried out in dichloromethane at room temperature with a CHI620D multipurpose equipment interfaced to PC.

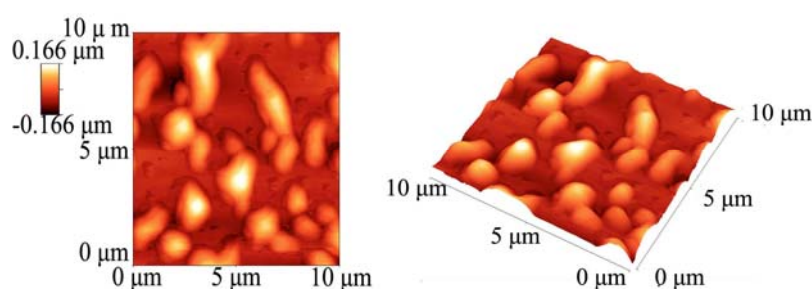
The working electrode was a glassy carbon electrode. The counterelectrode was a Pt wire, and the reference electrode was a SCE and (0.1M) tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as electrolyte solution. The ferrocene-CH<sub>2</sub>Cl<sub>2</sub> solution was used as a standard, shown in Figure S1.

**Measurements of fluorescence quantum yields.** The fluorescence quantum yields ( $\Phi_F$ ) of compounds 1–3 were determined in spectroscopic grade solvents. The optical density of the dilute solution of all compounds (the reference and compounds 1–3) was around 0.05 at the excitation wavelength, using fluorescein ( $\Phi_r = 0.90$  in 0.1N NaOH)<sup>1</sup> solution and quinine sulfate ( $\Phi_r = 0.546$  in 0.1N H<sub>2</sub>SO<sub>4</sub>)<sup>2</sup> as references at excitation wavelengths of 408 nm and 300 nm, respectively. The quantum yield is calculated using equation 1.

$$\Phi_F = \Phi_r (A_r F_s / A_s F_r) (\eta_s^2 / \eta_r^2) \quad (1)$$

where,  $A_s$  and  $A_r$  are the absorbance of the sample and reference solutions, respectively at the same excitation wavelength,  $F_s$  and  $F_r$  are the corresponding relative integrated fluorescence intensities, the sample and reference, and  $\eta$  is the refractive index of the solvent.

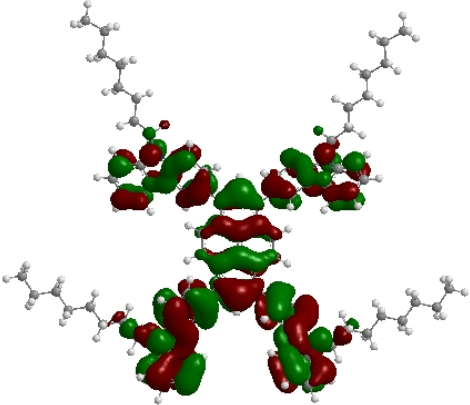
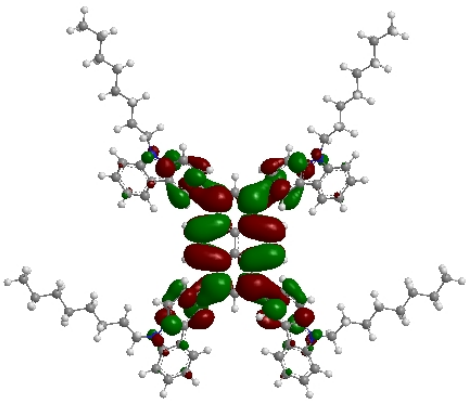
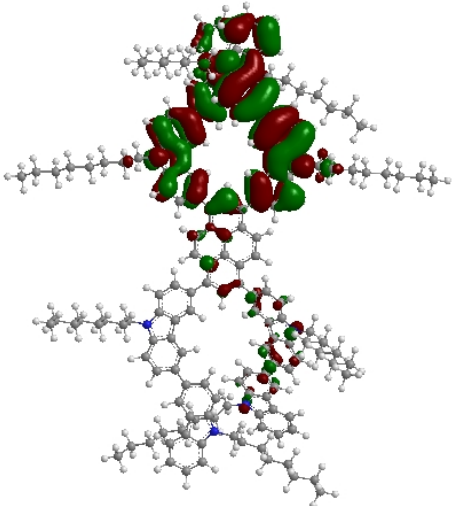
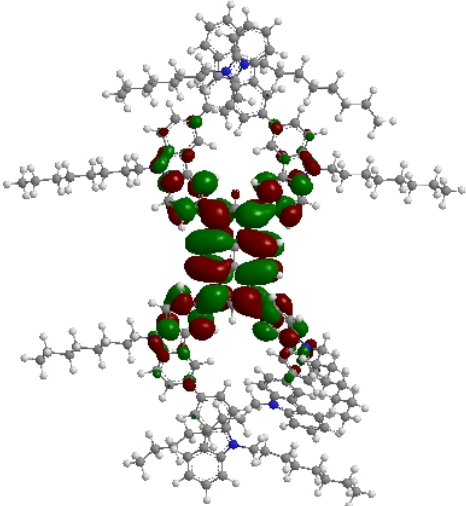
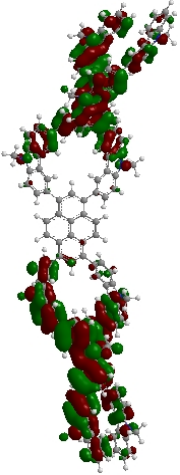
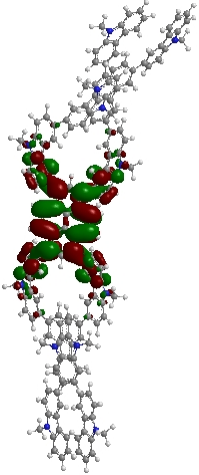
**Film preparation and film morphology.** The films are prepared by spin-coating THF solutions of dendrimers (2 wt %) on SiO<sub>2</sub>/Si substrate at a spin speed of 2000 rpm. Although dendrimers have hyperbranched structures, they exhibit good film-forming ability, their film morphology is detected by atomic force microscopy (AFM) at a tapping model, and the image of 3 are displayed in Figure S2, a essentially smooth and amorphous film can be obtained from the dendrimer solution by simple spin-coating method. The thickness of the film is about 200 nm.



**Figure S2.** AFM images of a thin-film prepared by spin-coating 5 wt% THF solution of 3 on glass

substrate at a spin speed of 2000 rpm.

**Table S1.** Frontier molecular orbital plots of optimized structures of compounds **1–3**.

Compounds	HOMO	LUMO
1		
2		
3		

**Calculation methods and results.** To understand electronic structures of starburst molecules **1–3**, the ground-state geometry of the molecules were first optimized at AM1 level and then their frontier

molecular orbitals were calculated at the B3LYP/6-31G level of theory with Gaussian 03.<sup>3</sup> In order to simplify the calculation, the octyl groups of compound **3** was replaced with methyl groups in the calculation. The calculation results were listed in Table S1.

**Solvent Effects.** To investigate solvent effects, the absorption and fluorescence spectra of **1–3** in various solvents were measured, and their maximum absorption peaks and fluorescence emission peaks were listed in Table S2. Overall, these spectra are insensitive to solvent, only a small red shift with solvent polarity. In the absorption spectra, the red shift in the visible region should be ascribed to the  $\pi$ - $\pi^*$  transition of the pyrene core. The red shift in the fluorescence spectra increases with the number of generation, for example, the peaks are 461, 468 and 471 nm for dendrimers **1**, **2** and **3** in DMF respectively. Although the conjugation system of **3** is the smallest, it gives the biggest red shift. This should derive from their oxidation potentials that decrease with the number of generation. With the electron-donating ability of the carbazole-based arm enhances, an intramolecular charge-transfer process occurs from the carbazole arm to the pyrene core, leading to a solvatochromic shift.

**Table S2.** Absorption peaks and fluorescence emission peaks of **1–3** measured in various solvents.

Compds	Solvent	$\lambda_{\text{max}}^{\text{abs}}$	$\lambda_{\text{F}}$
<b>1</b>	Toluene	403	451
	THF	405	452
	Ethyl estate	403	451
	CH <sub>2</sub> Cl <sub>2</sub>	406	454
	Acetone	408	456
	DMF	412	461
<b>2</b>	Toluene	405	455
	THF	408	456
	Ethyl estate	407	456
	CH <sub>2</sub> Cl <sub>2</sub>	409	461
	acetone	411	461
<b>3</b>	DMF	415	468
	Toluene	395	455
	THF	398	456
	Ethyl estate	397	455
	CH <sub>2</sub> Cl <sub>2</sub>	400	460
	acetone	400	461
	DMF	405	471

## References

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- 2 J. N. Demas and J. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.
- 3 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, 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 03, Revision B.01, Gaussian, Inc., Pittsburgh PA, 2003.

## II. Characterization Data of New Compounds

**9-octyl-9H-carbazol-3-ylboronic acid (6).** *n*-BuLi (1.6 M in hexanes, 3 mL, 4.8 mmol) was added dropwise to a solution of 3-bromo-9-octyl-9H-carbazole (1.43 g, 4 mmol, 1.2 eq) in anhyd THF (20 mL) at  $-78^{\circ}\text{C}$ . The mixture was stirred at this temperature for 1 h, then  $\text{B}(\text{OCH}_3)_3$  (1.26 ml, 12 mmol, 3 eq) was added and the mixture was stirred for 16 h while allowing the temperature to rise to  $20^{\circ}\text{C}$ . HCl (24 mL, 2 M) was added, the organic layer separated, the aqueous layer extracted with  $\text{CH}_2\text{Cl}_2$  ( $20 \times 3$  ml), the combined organic layer dried over  $\text{MgSO}_4$ , and evaporated to dryness. Chromatography on silica gel eluting with  $\text{CH}_2\text{Cl}_2$  and ether afforded **6** as a colorless solid (617 mg, yield 47.8%).  $^1\text{H}$  NMR (300 MHz, DMSO):  $\delta$  = 8.59 (s, 1 H), 8.09 (d, 1 H,  $J$  = 7.5 Hz), 7.90 (d, 1 H,  $J$  = 8.1 Hz), 7.52–7.60 (m, 2 H), 7.44 (t, 1 H,  $J$  = 7.2 Hz), 7.20 (t, 1 H,  $J$  = 7.5 Hz, Ar-*H*), 4.37 (t, 2 H,  $J$  = 6.9 Hz, N- $\text{CH}_2$ ), 1.76 (dd, 2 H, N- $\text{CH}_2$ - $\text{CH}_2$ ), 1.17–1.26 (m, 10 H), 0.81 (t, 3 H,  $J$  = 7.2 Hz,  $\text{CH}_2$ - $\text{CH}_3$ ); IR (KBr):  $\nu(\text{tilde})$  ( $\text{cm}^{-1}$ ) = 3448, 2923, 2852, 1625, 1595, 1467, 1430, 1348, 1251, 1142, 809, 771, 749, 710; TOFMS (EI) calcd for ( $\text{M}^+$ )  $\text{C}_{20}\text{H}_{26}\text{BNO}_2$ : 323.2370, found 323.3375.

**6'-bromo-9,9'-dioctyl-3,3'-bi(9H-carbazole) (12).** **6** (323 mg, 1 mmol), **8** (1.09 g, 2.5 mmol, 2.5 eq) and  $\text{Pd}(\text{PPh}_3)_4$  (35 mg, 0.03 mmol, 3 %) were added into a 50 mL flask. Degassed toluene (25 mL) and degassed aqueous  $\text{K}_2\text{CO}_3$  solution (10 mL, 2 M) was then added into the flask. The solution was kept at  $90^{\circ}\text{C}$  and stirred vigorously under nitrogen for 25 h. The resulting solution was extracted with excess  $\text{CH}_2\text{Cl}_2$ , dried by  $\text{MgSO}_4$ , and purified using a silica gel column ( $\text{CH}_2\text{Cl}_2$ : Petroleum ether = 1:30) and **9** as colorless liquid was obtained (401 mg, yield 63.2 %).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.40 (s, 1 H), 8.38 (s, 1 H), 8.34 (s, 1 H), 8.18 (d, 1 H,  $J$  = 7.5 Hz), 7.78–7.86 (q, 2 H), 7.41–7.56 (m, 5 H), 7.22–7.30 (m, 2 H), 4.23 (t, 4 H,  $J$  = 7.2 Hz, N- $\text{CH}_2$ ), 1.80 (dd, 4 H, N- $\text{CH}_2$ - $\text{CH}_2$ ), 1.23–1.38 (m, 20 H), 0.86 (m, 6 H,  $\text{CH}_2$ - $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 140.0, 139.5, 133.9, 133.5, 129.3, 126.1, 125.6, 122.2, 118.9, 110.9, 109.2, 81.2, 43.3, 31.8, 29.4, 29.2, 29.0, 27.3, 22.6, 14.1.; IR (KBr):  $\nu(\text{tilde})$  ( $\text{cm}^{-1}$ ) = 3212, 2928, 2854, 1527, 1597, 1473, 1451, 1344, 1151, 1133, 877, 796, 745, 719; TOFMS (EI) ( $\text{M}^+$ )  $\text{C}_{40}\text{H}_{47}\text{BrN}_2$ : 635.7187, found 635.7190.

**6'-boronic acid-9,9'-dioctyl-3,3'-bi(9H-carbazole) (13).** *n*-BuLi (2.8 M in hexanes, 1.5 mL, 4.2 mmol) was added dropwise to a solution of **9** (1.4 g, 2.2 mmol, 1.6 eq) in anhyd THF (15 mL) at  $-78^{\circ}\text{C}$ . The mixture was stirred at this temperature for 1.5 h, then  $\text{B}(\text{OCH}_3)_3$  (0.7 mL, 7 mmol, 3 eq) was added and the mixture was stirred for 16 h while allowing the temperature to rise to  $20^{\circ}\text{C}$ . HCl (10 mL, 2 M) was added, the organic layer separated, the aqueous layer extracted with  $\text{CH}_2\text{Cl}_2$ , the organic layer dried over  $\text{MgSO}_4$ , and evaporated to dryness and purified using a silica gel column (EtOAc : Petroleum ether = 1:5) and **10** was obtained as a white solid (444 mg, yield 34 %).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.42 (s, 1 H), 8.33 (s, 1 H), 8.21 (d, 1 H,  $J = 7.8$  Hz), 7.83 (d, 2 H  $J = 7.2$  Hz), 7.63 (s, 1 H), 7.40–7.53 (m, 4 H), 7.21–7.27 (m, 2 H), 7.06 (dd, 1 H,  $J = 8.7$  Hz  $J = 2.4$  Hz), 4.33 (m, 4 H, N- $\text{CH}_2$ ), 1.92 (m, 4 H, N- $\text{CH}_2$ - $\text{CH}_2$ ), 1.23–1.40 (m, 20 H), 0.89 (m, 6 H,  $\text{CH}_2$ - $\text{CH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 140.1, 139.6, 133.9, 133.5, 129.4, 126.1, 125.6, 122.3, 119.0, 110.9, 109.2, 81.3, 43.4, 31.9, 29.5, 29.3, 29.1, 27.4, 22.7, 14.2.; IR (KBr):  $\nu(\text{tilde})$  ( $\text{cm}^{-1}$ ) = 3214, 2925, 2852, 1527, 1597, 1474, 1451, 1342, 1151, 1132, 877, 796, 745, 719 ; TOFMS (EI) ( $\text{M}^+$ )  $\text{C}_{40}\text{H}_{49}\text{BN}_2\text{O}_2$ : 600.6403, found 600.6400.

**6'-bromo-9,9'-dioctyl-6-(9-octyl-9H-carbazol-3-yl)-3,3'-bi(9H-carbazole) (14).** **6** (209 mg, 0.65 mmol), **13** (784 mg, 0.97 mmol, 1.5 eq) and  $\text{Pd}(\text{PPh}_3)_4$  (30 mg, 0.03 mmol) were added into a 50 mL flask. Degassed toluene (15 mL) and degassed aqueous  $\text{K}_2\text{CO}_3$  solution (5 mL, 2 M) was then added into the flask. The solution was kept at  $90^{\circ}\text{C}$  and stirred vigorously under nitrogen for 48 h. The resulting solution was extracted with excess  $\text{CH}_2\text{Cl}_2$ , dried by  $\text{MgSO}_4$ , and purified using a silica gel column ( $\text{CH}_2\text{Cl}_2$ : Petroleum ether = 1:20) and **14** as white solid was obtained (310 mg, yield 49.8 %).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.53 (s, 2 H), 8.53 (s, 1 H), 8.47 (s, 1 H), 8.41 (s, 1 H), 8.23 (d, 1 H,  $J = 7.5$  Hz), 7.83–7.90 (m, 4 H), 7.72 (s, 1 H), 7.47–7.55 (m, 7 H), 7.23 (m, 1 H), 4.32–4.40 (m, 6 H, N- $\text{CH}_2$ ), 1.92–1.99 (m, 6 H, N- $\text{CH}_2$ - $\text{CH}_2$ ), 1.28 (m, 30 H), 0.90 (m, 9 H,  $\text{CH}_2$ - $\text{CH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 140.9, 139.9, 139.6, 133.9, 133.4, 128.3, 126.3, 125.7, 125.6, 124.9, 123.8, 123.7, 123.5, 123.3, 122.5, 120.5, 119.0, 118.8, 111.6, 110.3, 109.2, 108.9, 108.8, 43.3, 31.9, 29.5, 29.4, 29.3, 29.0, 27.4, 27.3, 22.7, 14.1; IR (KBr):  $\nu(\text{tilde})$  ( $\text{cm}^{-1}$ ) = 2925, 1600, 1472, 1347, 1270, 1227, 1206, 1150, 1054, 874, 797, 745, 727 ; TOFMS (EI) calcd for ( $\text{M}^+$ )  $\text{C}_{60}\text{H}_{70}\text{BrN}_3$ : 913.1220, found 913.1225.



**9,9'-dioctyl-6-(9-octyl-9H-carbazol-3-yl)-3,3'-bi(9'H-carbazol)-6'-yl boronic acid (15).** *n*-BuLi (2.84 M in hexanes, 0.6 mL, 1.6 mmol, 1.6 eq) was added dropwise to a solution of **14** (910 mg, 1.0 mmol) in anhyd THF (8 mL) at  $-78^{\circ}\text{C}$ . The mixture was stirred at this temperature for 1.5 h, then  $\text{B}(\text{OCH}_3)_3$  (0.3 mL, 4.2 mmol, 4 eq) was added and the mixture was stirred for 16 h while allowing the temperature to rise to room temperature. HCl (5 mL, 2 M) was added, the organic layer separated, the aqueous layer extracted with  $\text{CH}_2\text{Cl}_2$ , the organic layer dried over  $\text{MgSO}_4$ , and evaporated to dryness. Purified using a silica gel column (Ethyl acetate : Petroleum ether = 1:6), and **15** as white solid was obtained (158 mg, yield 18 %).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.50 (s, 4 H), 8.30 (s, 1 H), 8.19 (d, 1 H,  $J$  = 7.5 Hz), 7.81–7.86 (m, 4 H), 7.45–7.56 (m, 8 H), 7.24–7.29 (m, 1 H), 4.30 (m, 6 H, N- $\text{CH}_2$ ), 1.87–1.96 (m, 6 H, N- $\text{CH}_2$ - $\text{CH}_2$ ), 1.26 (m, 30 H), 0.87 (m, 9 H,  $\text{CH}_2$ - $\text{CH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ): 141.0, 140.0, 139.8, 134.0, 133.5, 128.4, 126.4, 125.8, 125.7, 125.0, 123.9, 123.8, 123.6, 123.4, 122.6, 120.6, 119.1, 118.9, 111.7, 110.4, 109.3, 109.0, 108.9, 43.4, 32.0, 29.6, 29.5, 29.4, 29.2, 27.5, 27.4, 22.8, 14.3; IR (KBr):  $\nu(\text{tilde})$  ( $\text{cm}^{-1}$ ) = 2928, 1602, 1474, 1348, 1270, 1227, 1205, 1151, 1054, 874, 797, 745, 727; TOFMS (EI) calcd for ( $\text{M}^+$ )  $\text{C}_{60}\text{H}_{72}\text{BN}_3\text{O}_2$ : 878.0437, found 878.0435.

**1,3,6,8-tetrakis(9-octyl-9H-carbazol-3-yl)pyrene (1).** **16** (207.2 mg, 0.4 mmol), **6** (775.7 mg, 2.4 mmol, 6 eq), and  $\text{Pd}(\text{PPh}_3)_4$  (50 mg, 0.043 mmol) were added into a 50 mL flask. Degassed toluene (30 mL) and degassed aqueous  $\text{K}_2\text{CO}_3$  solution (25 mL, 2 M) was then added into the flask. The solution was kept at  $90^{\circ}\text{C}$  and stirred vigorously under nitrogen for 50 h. The resulting brownish solution was extracted with excess  $\text{CH}_2\text{Cl}_2$ , dried by  $\text{MgSO}_4$ , and purified using a silica gel column ( $\text{CH}_2\text{Cl}_2$ : Petroleum ether = 1:6). The obtained product was a yellow solid (350 mg, 66.7 % yield).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.45 (s, 4 H), 8.33 (s, 4 H, pyrene-*H*), 8.29 (s, 2 H, pyrene-*H*), 8.13 (d, 4 H,  $J$  = 7.8 Hz), 7.85 (d, 4 H,  $J$  = 8.4 Hz), 7.20–7.58 (m, 16 H), 4.37 (t, 8 H,  $J$  = 6.9 Hz, N- $\text{CH}_2$ ), 1.94 (dd, 8 H,  $J$  = 7.2 Hz, N- $\text{CH}_2$ - $\text{CH}_2$ ), 1.25–1.45 (m, 40 H), 0.85 (t, 12 H,  $J$  = 6.9 Hz,  $\text{CH}_2$ - $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 140.9, 139.8, 137.9, 132.1, 130.8, 128.7, 128.4, 126.5, 125.5, 123.1, 123.0, 122.5, 120.6, 118.9, 108.8, 108.5, 43.3, 31.8, 29.4, 29.2, 27.4, 22.6, 14.1; IR (KBr):  $\nu(\text{tilde})$  ( $\text{cm}^{-1}$ ) = 2923, 1730, 1599, 1489, 1465, 1347, 1330, 1262, 1150, 805, 746, 730; MS (MALDI-TOF):  $m/z$  Calcd. for [ $\text{M}$ ] $^+$

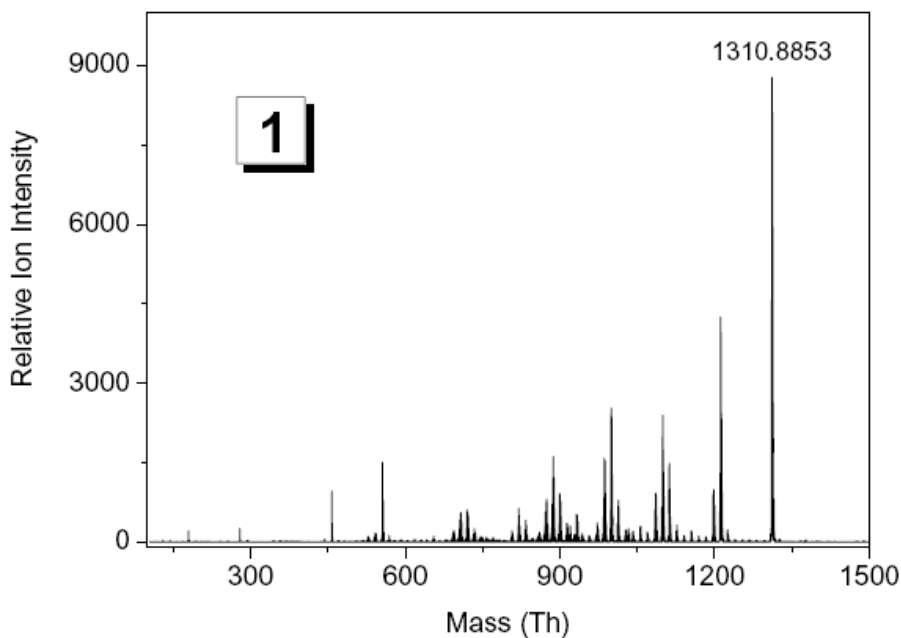
1310.8640; found:1310.8853; Elemental analysis calcd (%) for C<sub>96</sub>H<sub>102</sub>N<sub>4</sub>: C 87.89, H 7.84, N 4.27; found C 88.03, H 7.72, N 4.25.

**1,3,6,8-tetrakis(9,9'-dioctyl-9H,9'H-[3,3'-bicarbazol]-6-yl)pyrene (2).** **16** (56 mg, 0.11 mmol), **10** (388 mg, 0.65 mmol, 5 eq), and Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 0.07 mmol) were added into a 25 mL flask. Degassed toluene (5 mL) and degassed aqueous K<sub>2</sub>CO<sub>3</sub> solution (2 mL, 2 M) was then added into the flask. The solution was kept at 90 °C and stirred vigorously under nitrogen for 50 h. The resulting brownish solution was extracted with excess CH<sub>2</sub>Cl<sub>2</sub>, dried by MgSO<sub>4</sub>, and purified using a silica gel column (CH<sub>2</sub>Cl<sub>2</sub>: Petroleum ether = 1:5). The obtained product was a yellow solid (242 mg, yield 92.5 %) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.57 (s, 4 H), 8.45 (d, 4 H, *J* = 1.2 Hz), 8.40 (s, 4 H, pyrene-*H*), 8.39 (d, 4 H, *J* = 1.5 Hz), 8.38 (s, 2 H, pyrene-*H*), 8.12 (d, 4 H, *J* = 7.8 Hz), 7.79–7.90 (m, 12 H), 7.59 (d, 4 H, *J* = 8.4 Hz), 7.52 (d, 4 H, *J* = 8.4 Hz), 7.35–7.43 (m, 12 H), 7.16 (t, 4 H, *J* = 6.9 Hz), 4.40 (t, 8 H, *J* = 6.9 Hz, N-CH<sub>2</sub>), 4.25 (t, 8 H, *J* = 6.9 Hz, N-CH<sub>2</sub>), 1.98 (t, 8 H, *J* = 7.2 Hz, N-CH<sub>2</sub>-CH<sub>2</sub>), 1.85 (t, 8 H, *J* = 7.2 Hz, N-CH<sub>2</sub>-CH<sub>2</sub>), 1.22–1.47 (m, 80 H), 0.85 (m, 24 H, CH<sub>2</sub>-CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 139.8, 139.2, 139.0, 138.4, 136.9, 132.4, 132.2, 131.1, 129.7, 127.8, 127.4, 125.5, 124.4, 122.6, 122.3, 122.0, 121.5, 119.4, 118.0, 117.8, 117.6, 107.9, 107.8, 107.6, 107.4, 42.4, 42.1, 30.7, 28.3, 28.1, 27.9, 26.4, 26.3, 21.5, 13.0; IR (KBr): ν(tilde) (cm<sup>-1</sup>) = 2923, 1600, 1474, 1346, 1260, 1225, 876, 796, 743, 726, ; MS (MALDI-TOF): *m/z*. Calcd. for [M]<sup>+</sup> 2419.8764; found: 2419.9221; Elemental analysis calcd (%) for C<sub>176</sub>H<sub>194</sub>N<sub>8</sub>: C 87.30, H 8.08, N 4.63; found C 87.36, H 8.00, N 4.54.

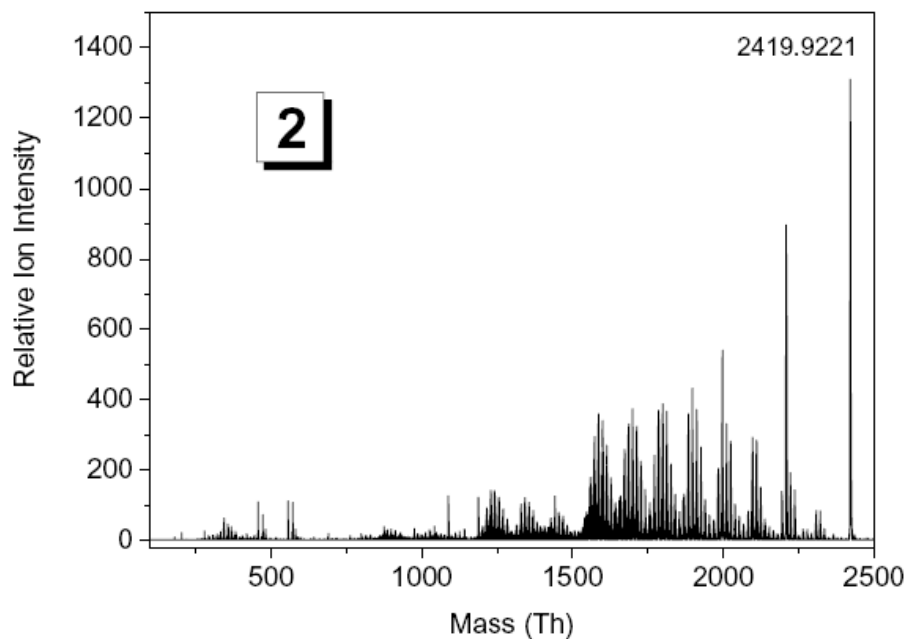
**1,3,6,8-tetrakis(9,9',9''-trioctyl-9H,9'H,9''H-[3,3':6',3''-tercarbazol]-6-yl)pyrene (3).** **16** (18.6 mg, 0.0359 mmol), **15** (158 mg, 0.179 mmol, 6 eq), and Pd(PPh<sub>3</sub>)<sub>4</sub> (20 mg, 0.04 mmol) were added into a 25 mL flask. Degassed toluene (5 mL) and degassed aqueous K<sub>2</sub>CO<sub>3</sub> solution (2 mL, 2 M) was then added into the flask. The solution was kept at 90 °C and stirred vigorously under nitrogen for 50 h. The resulting brownish solution was extracted with excess CH<sub>2</sub>Cl<sub>2</sub>, dried by MgSO<sub>4</sub>, and purified using a silica gel column (CH<sub>2</sub>Cl<sub>2</sub>: Petroleum ether = 1:3). The obtained product was a yellow solid (102 mg, yield 81 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.58 (s, 3 H), 8.44–8.54 (m, 13 H), 8.40 (s, 2 H, pyrene-*H*), 8.37 (s, 4 H, pyrene-*H*), 8.11–8.17 (m, 5 H), 7.77–7.87 (m, 21 H), 7.32–7.59 (m, 30 H), 7.17 (t, 4 H),

4.21–4.01 (m, 24 H, N-CH<sub>2</sub>), 1.81–1.93 (m, 24 H, N-CH<sub>2</sub>-CH<sub>2</sub>), 1.25 (d, 148 H), 0.83 (s, 42 H, CH<sub>2</sub>-CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):140.9, 140.3, 134.0, 133.5, 137.9, 133.3, 132.2, 128.7, 128.5, 125.6, 123.7, 123.4, 123.1, 122.6, 120.5, 119.0, 118.9, 118.7, 109.0, 108.9, 108.7, 108.6, 43.2, 31.8, 29.7, 29.4, 29.2, 29.0, 27.3, 22.6, 14.0 ; IR (KBr):  $\nu(\text{tilde})$  (cm<sup>-1</sup>) =2925, 2853, 1602, 1475, 1347, 1261, 1227, 1025, 875, 797, 745, 727; MS (MALDI-TOF): *m/z* Calcd. for [M]<sup>+</sup> 3530.3303; found: 3530.8186; Elemental analysis calcd (%) for C<sub>256</sub>H<sub>286</sub>N<sub>8</sub>: C 87.08, H 8.16, N 4.76; found C 87.13, H 8.23, N 4.65.

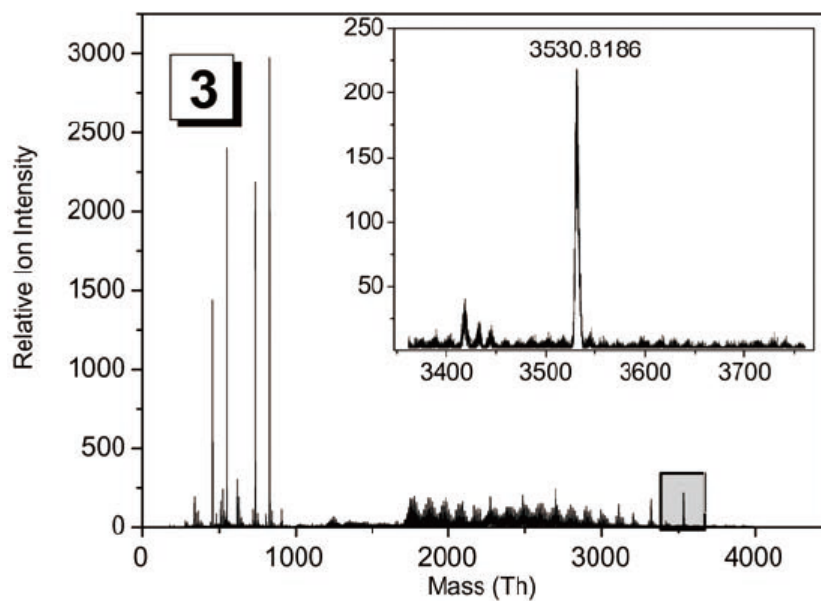
### III. MALDI-TOF mass spectrum of **1**, **2** and **3**



**Figure S3.** Mass spectrum of compound **1**



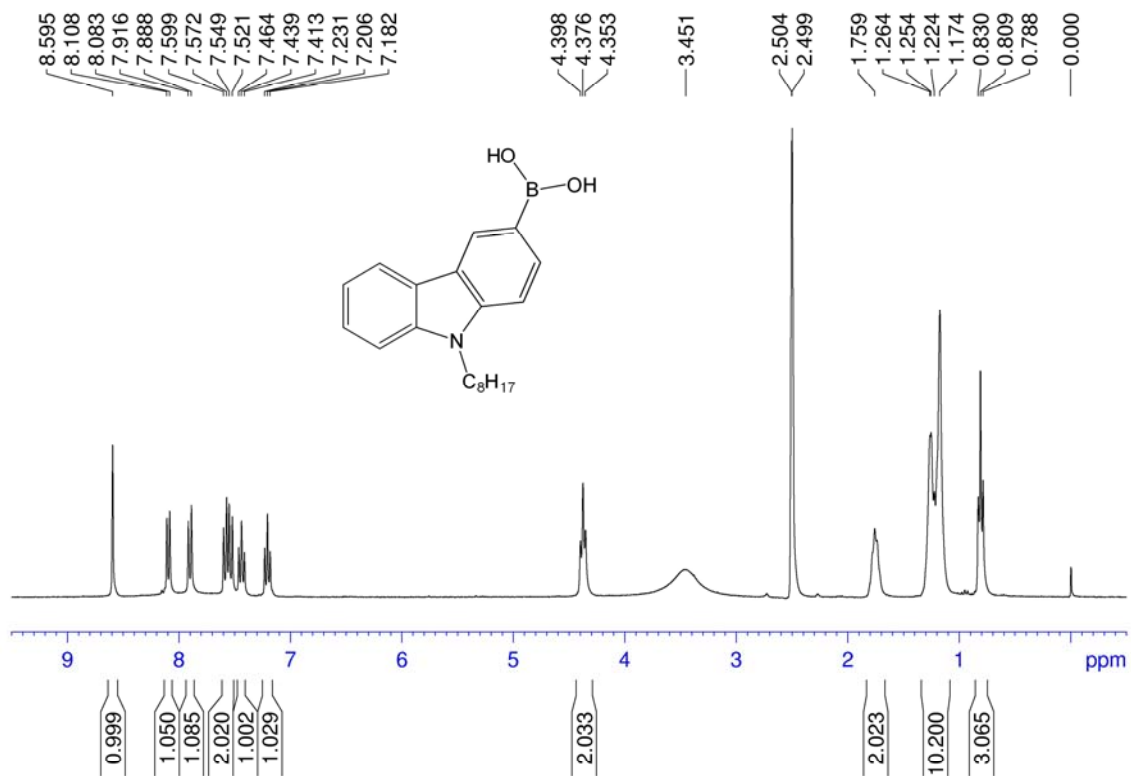
**Figure S4.** Mass spectrum of compound 2



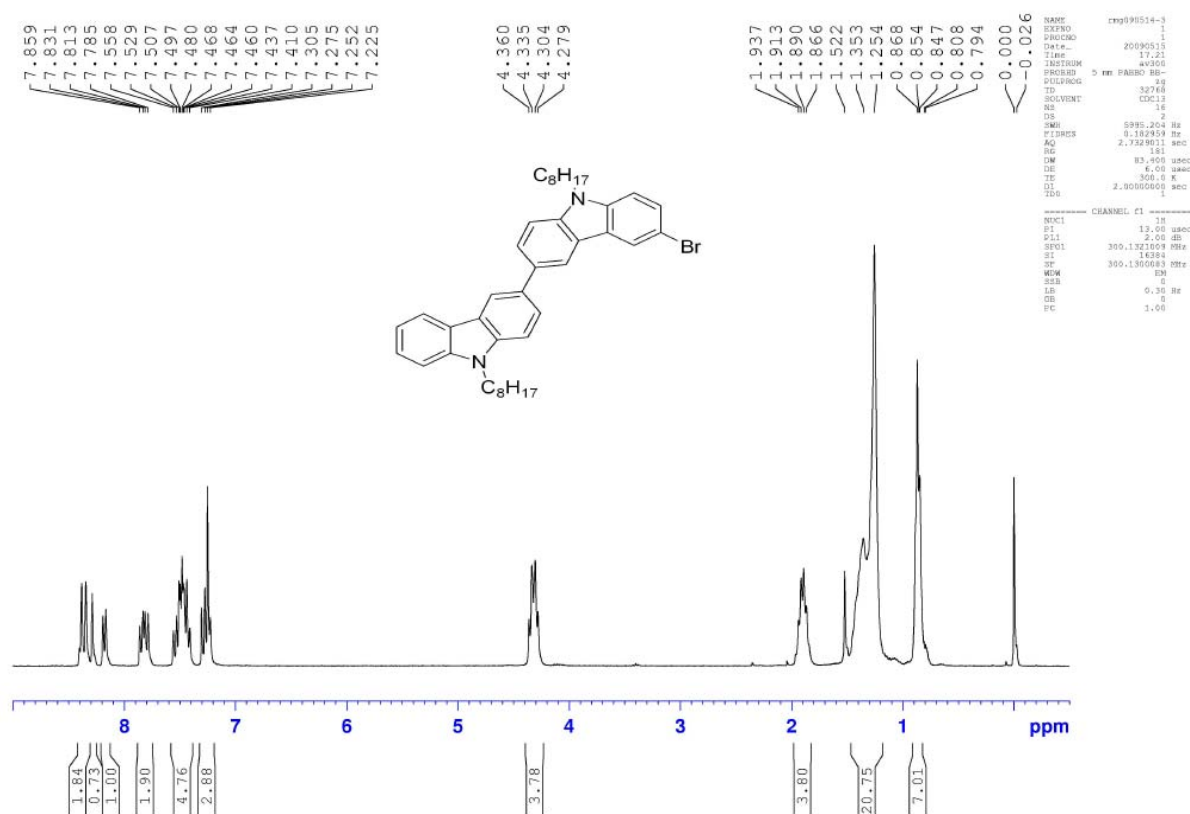
**Figure S5.** Mass spectrum of compound 3

#### IV. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of New Compounds

**Figure S6.**  $^1\text{H}$  NMR spectrum of **6** in DMSO.



**Figure S7.**  $^1\text{H}$  NMR spectrum of **9** in  $\text{CDCl}_3$ .



**Figure S8.**  $^{13}\text{C}$  NMR spectrum of **9** in  $\text{CDCl}_3$ .

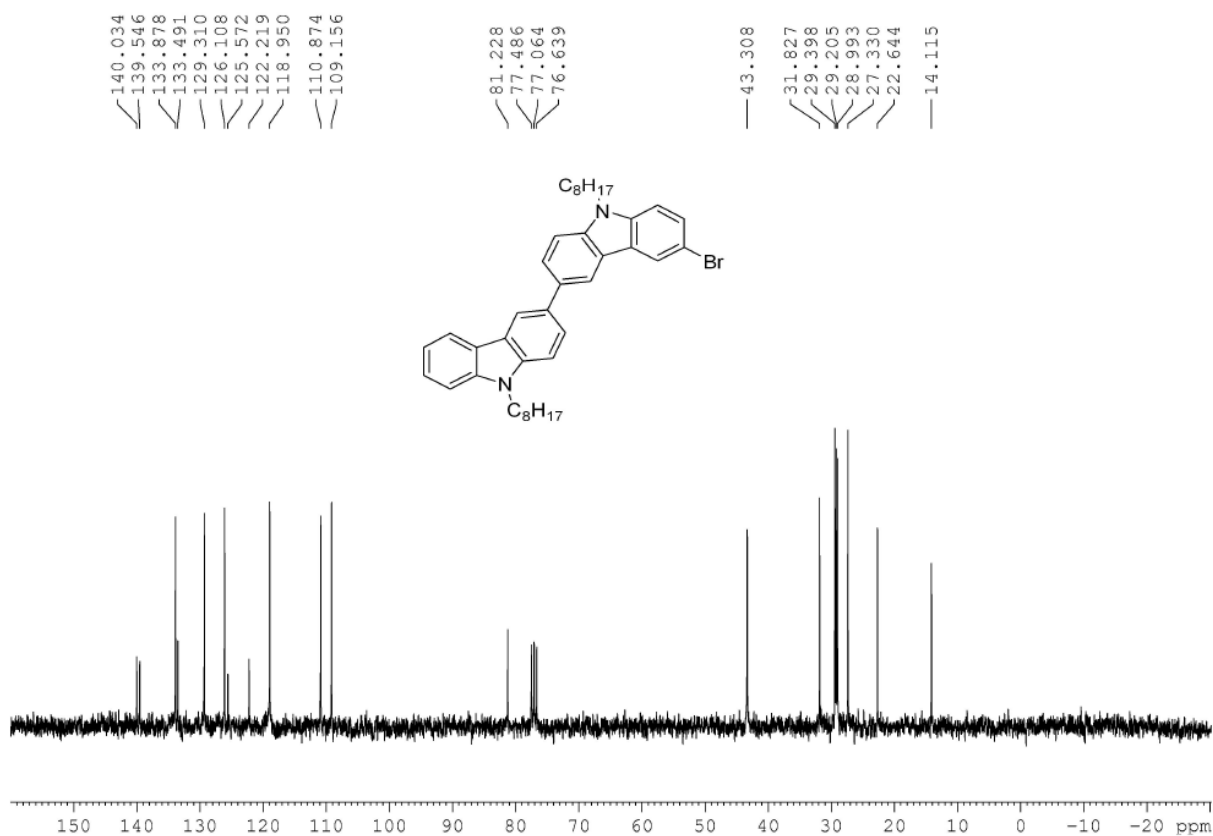


Figure S9.  $^1\text{H}$  NMR spectrum of **10** in  $\text{CDCl}_3$

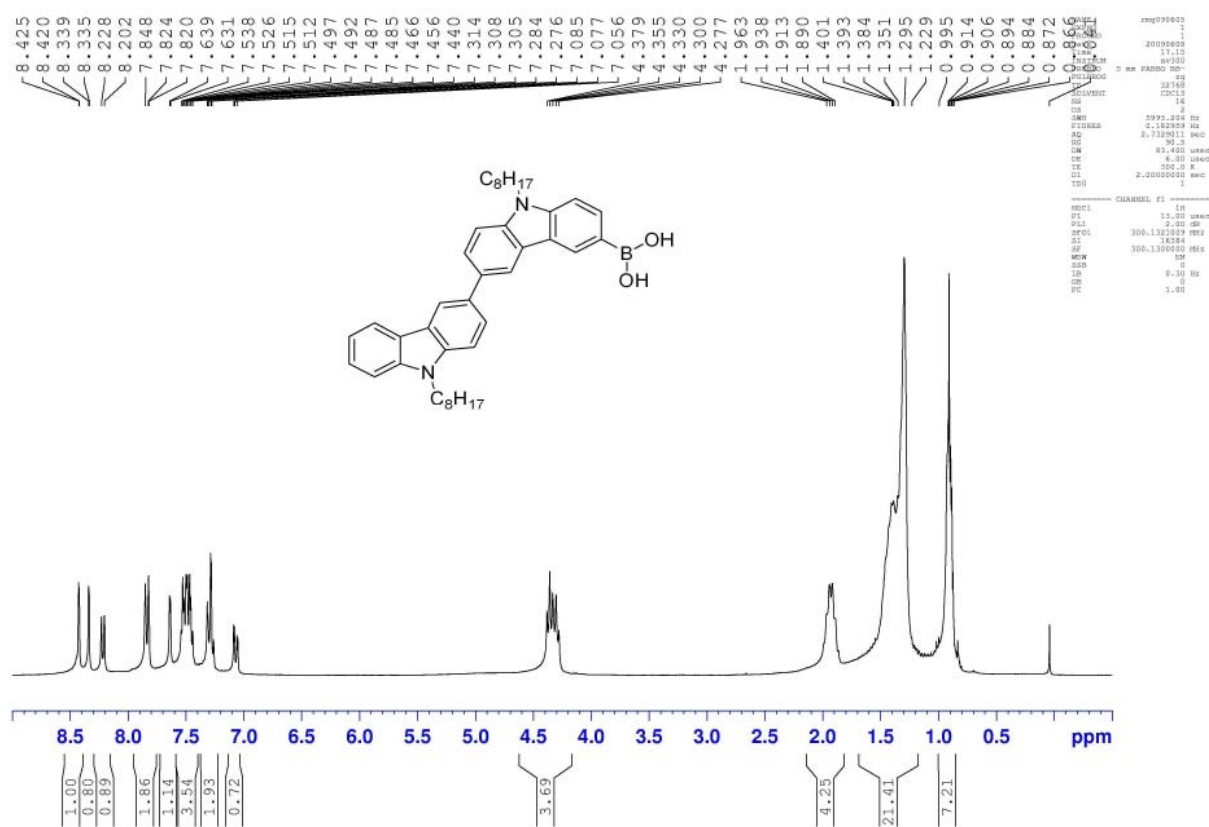
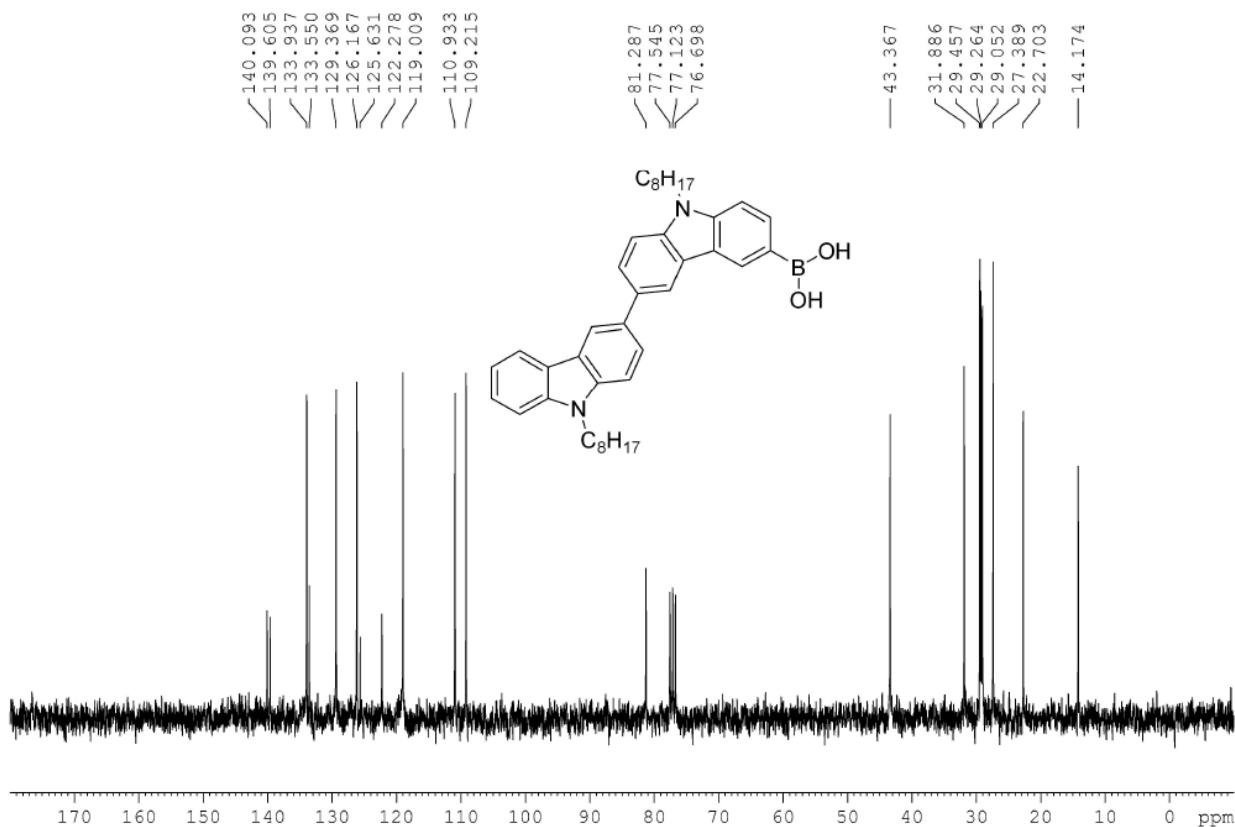
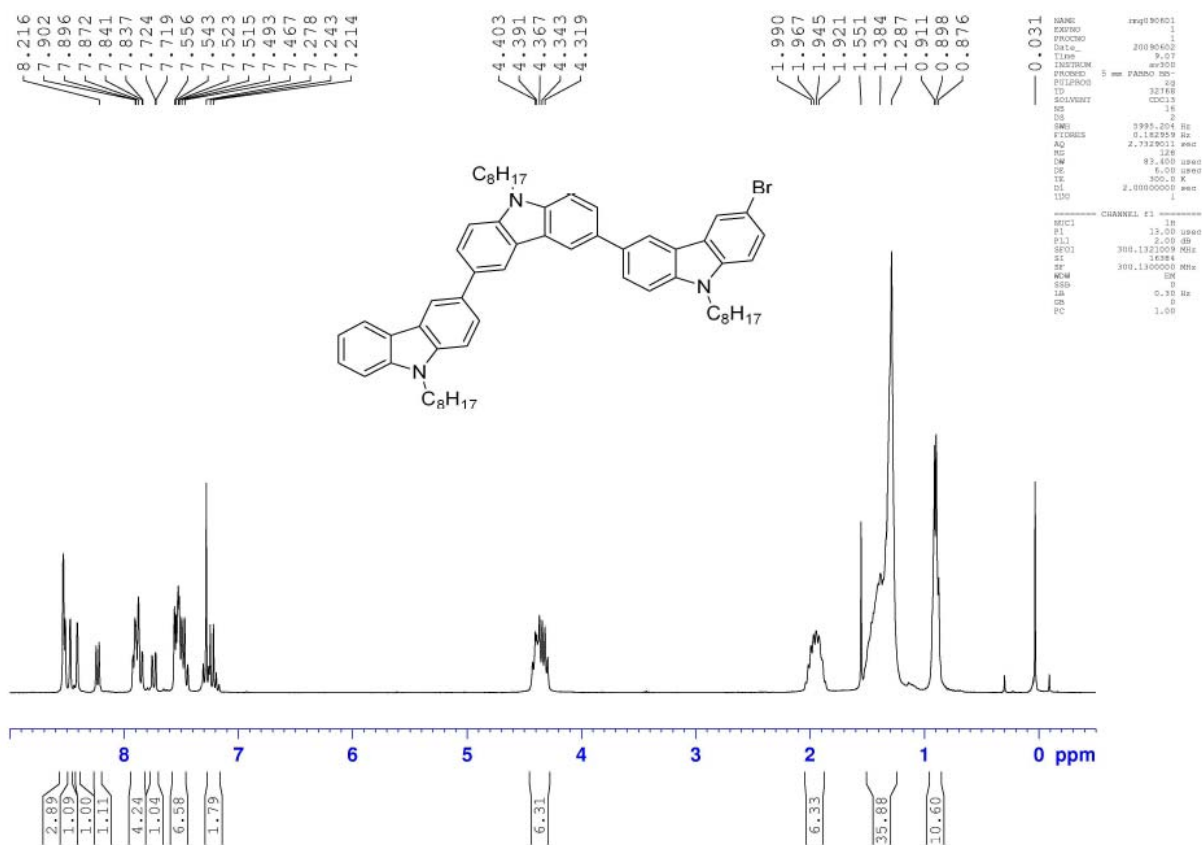


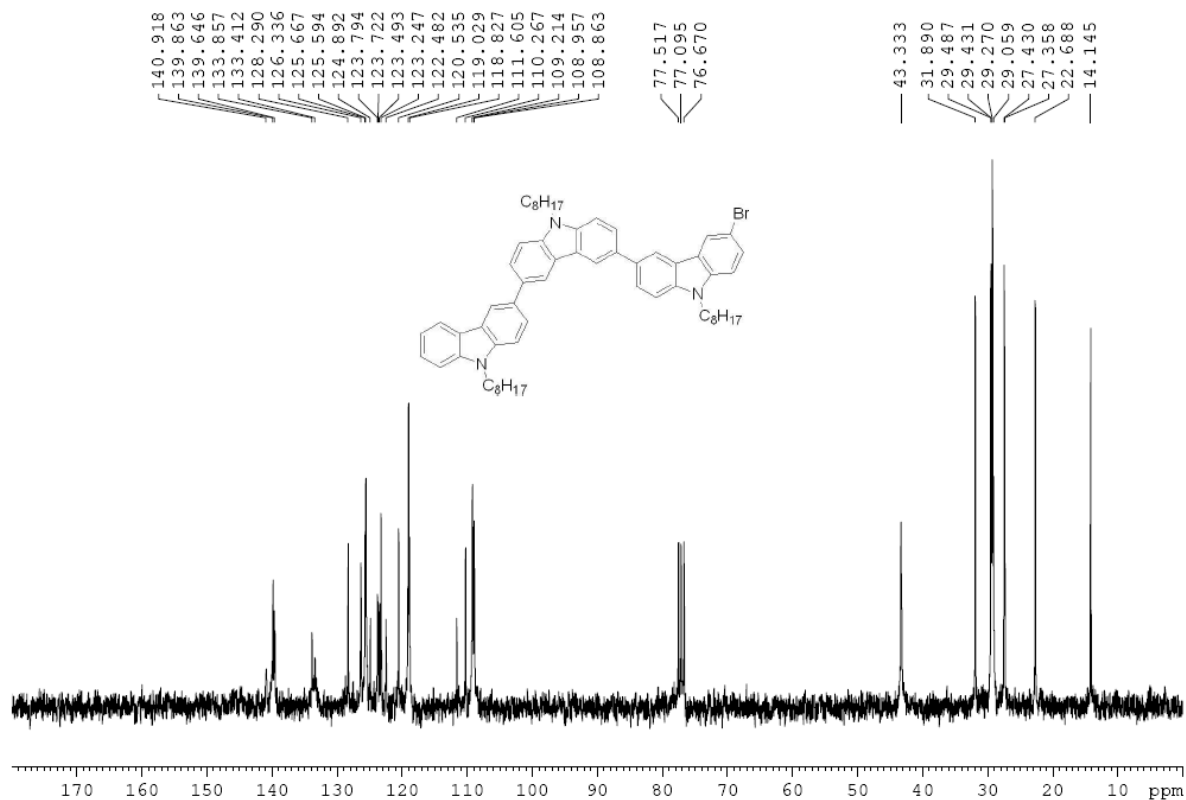
Figure S10.  $^{13}\text{C}$  NMR spectrum of **10** in  $\text{CDCl}_3$ .



**Figure S11.**  $^1\text{H}$  NMR spectrum of **14** in  $\text{CDCl}_3$

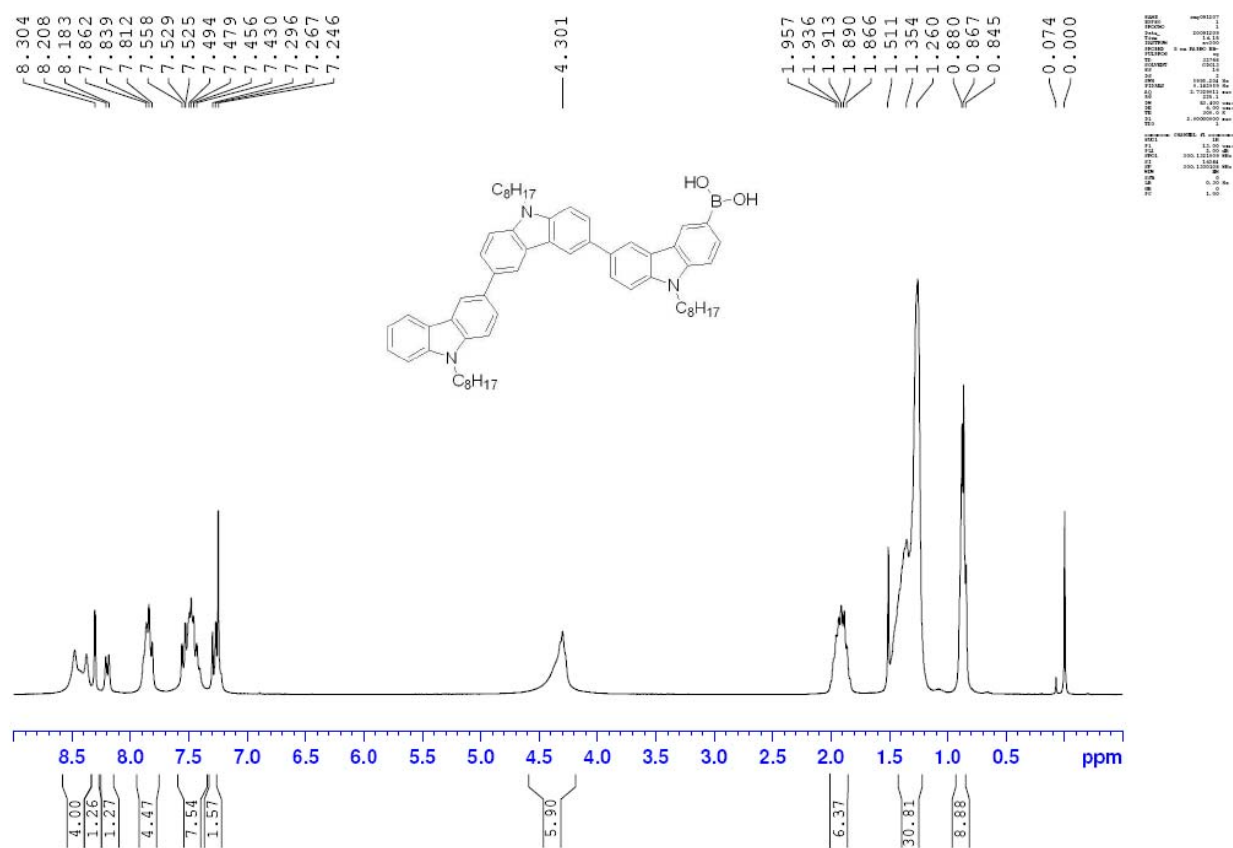


**Figure S12.**  $^{13}\text{C}$  NMR spectrum of **14** in  $\text{CDCl}_3$





**Figure S13.**  $^1\text{H}$  NMR spectrum of **15** in  $\text{CDCl}_3$



**Figure S14.**  $^{13}\text{C}$  NMR spectrum of **15** in  $\text{CDCl}_3$

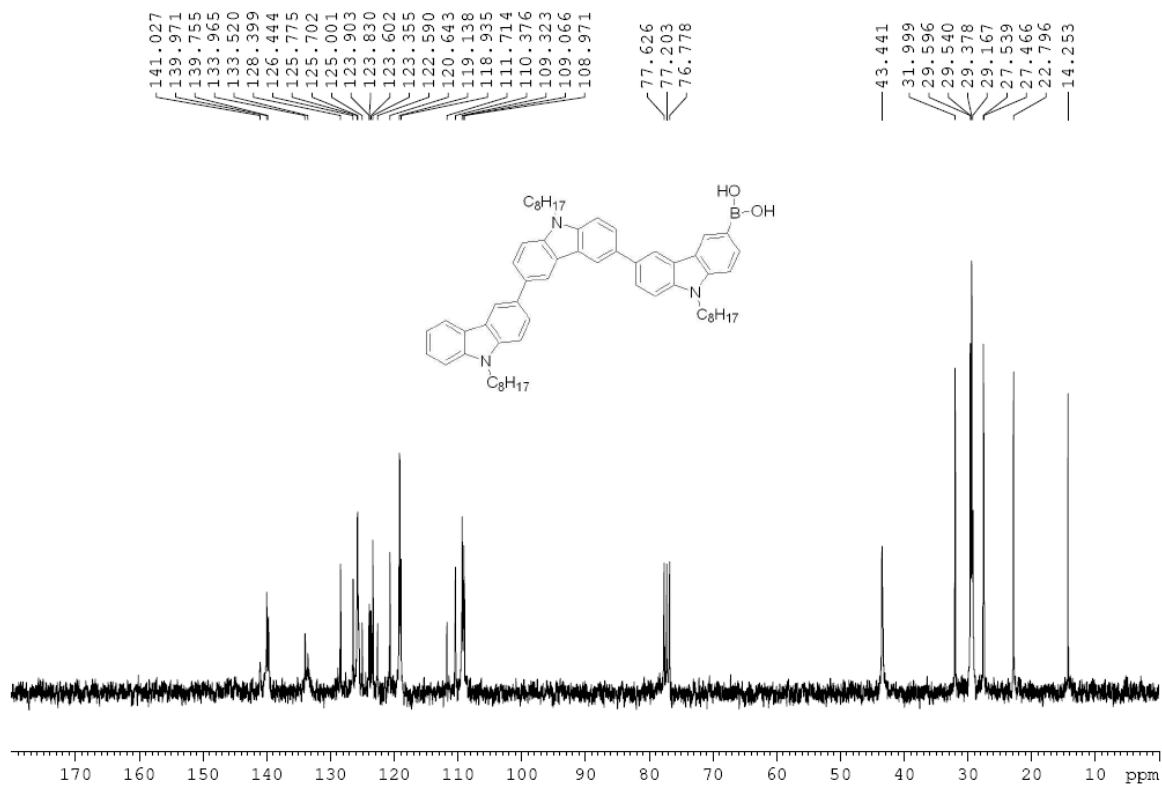


Figure S15.  $^1\text{H}$  NMR spectrum of **1** in  $\text{CDCl}_3$

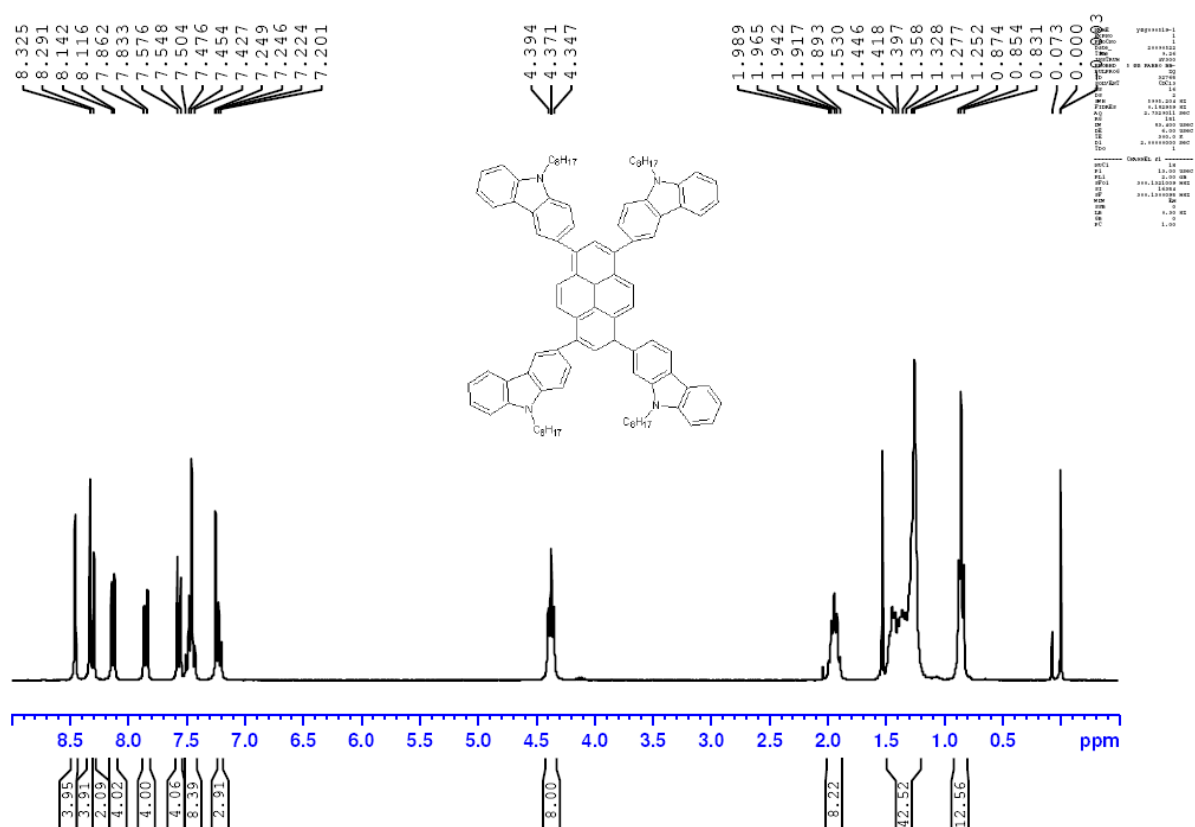
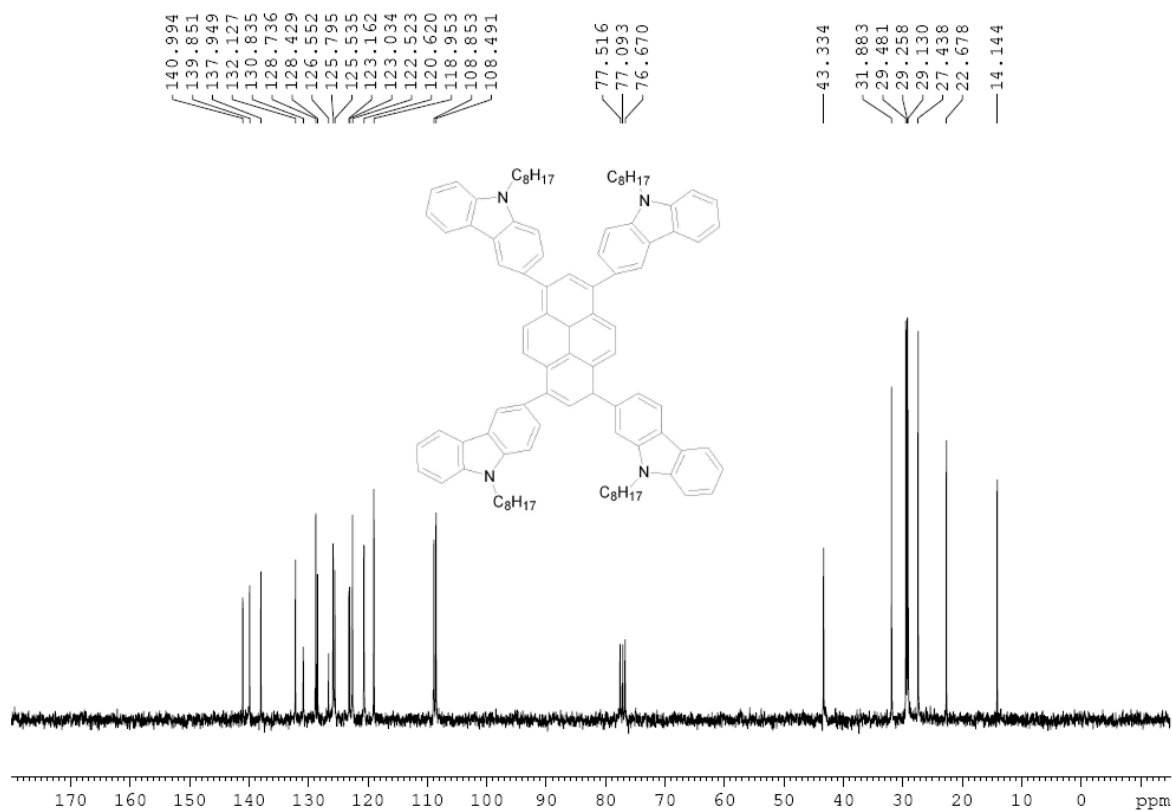
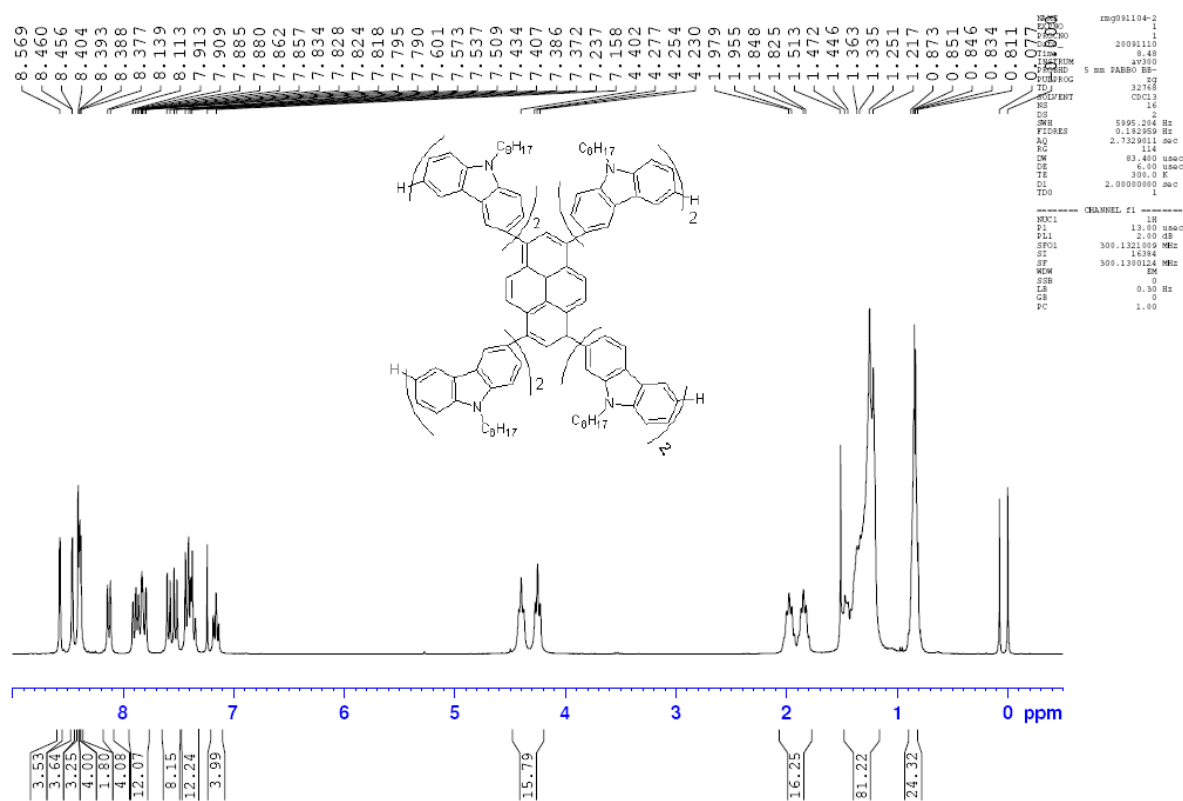


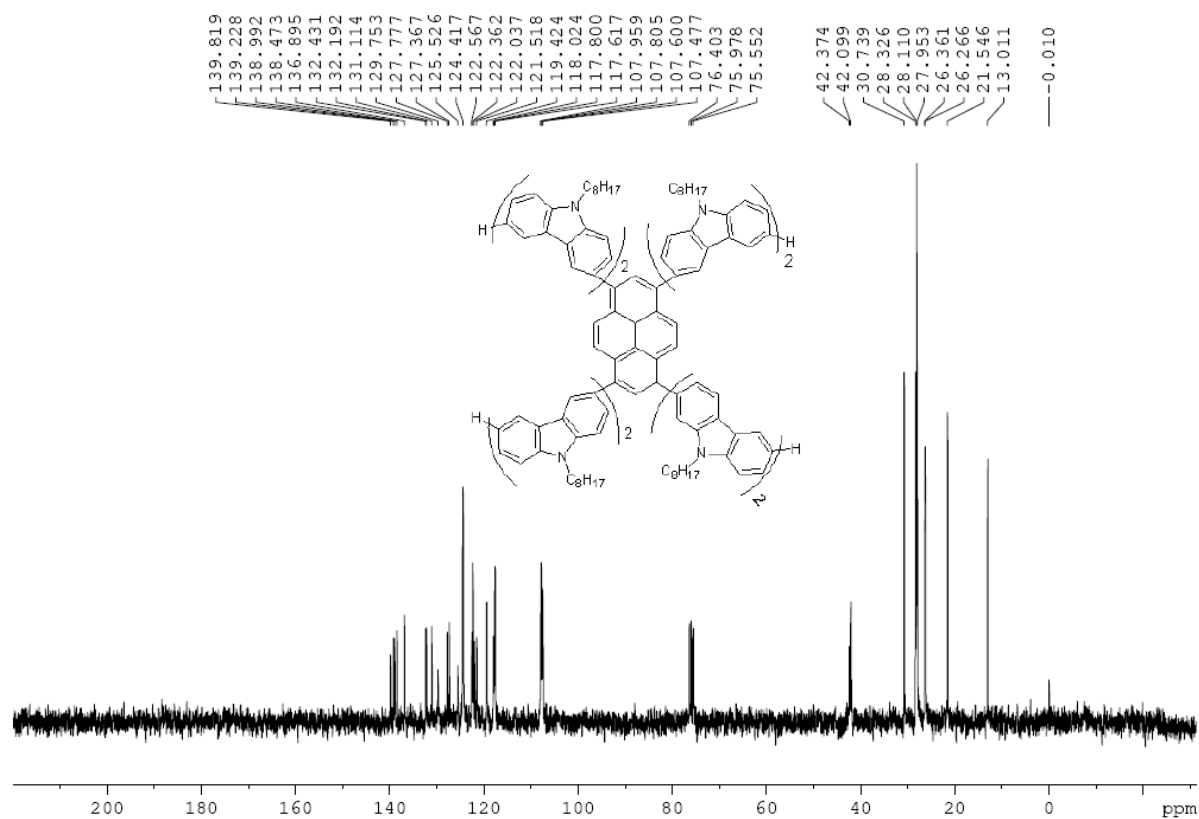
Figure S16.  $^{13}\text{C}$  NMR spectrum of **1** in  $\text{CDCl}_3$



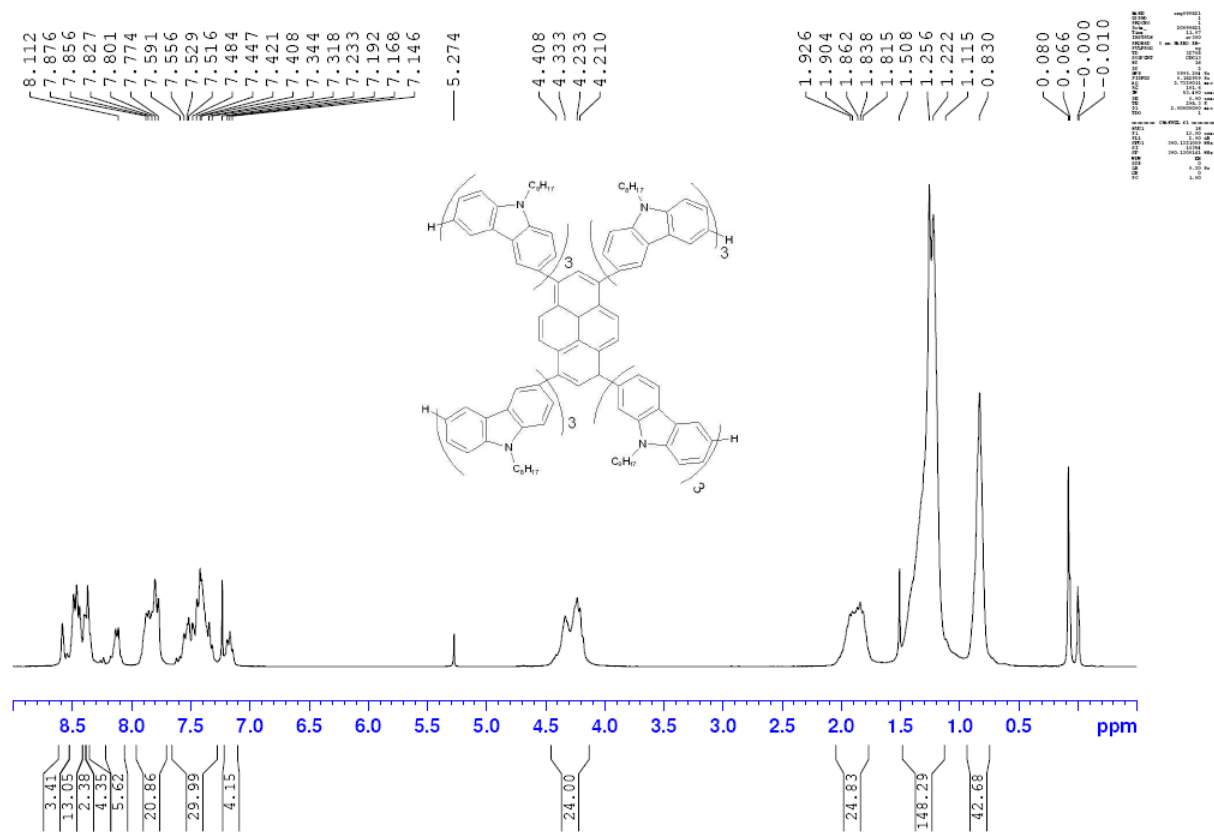
**Figure S17.**  $^1\text{H}$  NMR spectrum of **2** in  $\text{CDCl}_3$



**Figure S18.**  $^{13}\text{C}$  NMR spectrum of **2** in  $\text{CDCl}_3$



**Figure S19.**  $^1\text{H}$  NMR spectrum of **3** in  $\text{CDCl}_3$



**Figure S20.**  $^{13}\text{C}$  NMR spectrum of **3** in  $\text{CDCl}_3$

