

Electronic Supplementary Information (ESI) for

The equilibria and conversions between three excited states: the LE state and two charge transfer states, in twisted pyrene-substituted tridurylboranes

Ming-Guang Ren, Mao Mao and Qin-Hua Song*

Department of Chemistry, Joint Laboratory of Green Synthetic Chemistry, University of Science

and Technology of China, Hefei 230026, China

E-mail: qhsong@ustc.edu.cn

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I. Experimental details

General methods. All materials were obtained from commercial suppliers and used without further purification. Solvents of technical quality were dried and distilled prior to use. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV spectrometer (300 MHz for ^1H , 75 MHz for ^{13}C). 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. Fluorescence emission spectra in solution were measured on a Perkin-Elmer LS55 luminescence spectrometer. Mass spectra were obtained with a Micromass GCF-TOF mass spectrometer.

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_6) as electrolyte solution. The ferrocene- CH_2Cl_2 solution was used as a standard, shown in Figure S1.

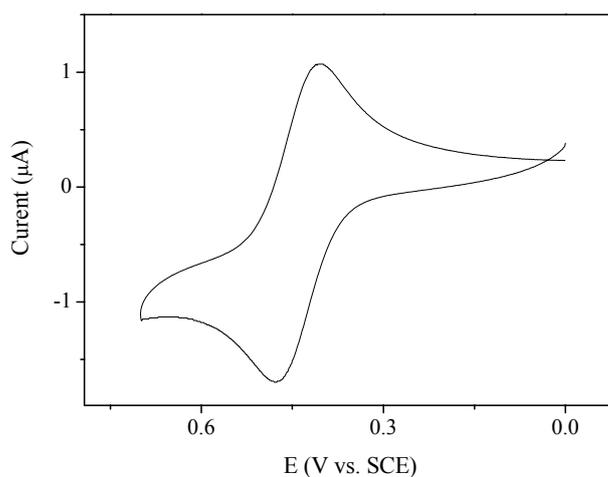


Figure S1. Cyclic voltammograms of ferrocene analyte at a scan rate 100 mVs^{-1} . The electrolyte was 0.1 M TBAPF_6 in anhydrous dichloromethane.

Measurements of fluorescence quantum yields. The fluorescence quantum yields (Φ_F) of **PB1–3** were determined in spectroscopic grade solvents. The optical density of the dilute solution of all compounds (the reference and **PB1–3**) was around 0.05 at the excitation wavelength, using quinine sulfate ($\Phi_r = 0.546$ in 0.1 N H_2SO_4)¹ as references at excitation wavelengths of 408 nm and 300 nm, respectively. The quantum yield is calculated using eq. S1.

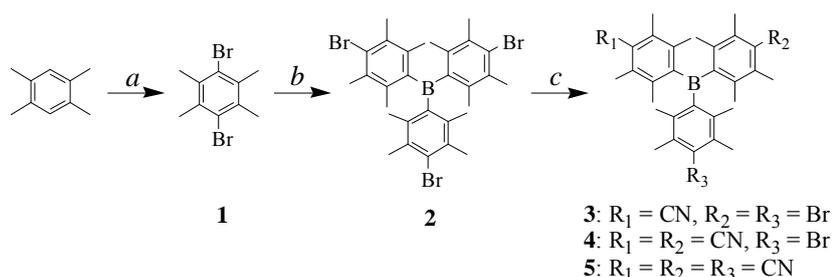
$$\Phi_F = \Phi_r (A_r F_s / A_s F_r) (\eta_s^2 / \eta_r^2) \quad (S1)$$

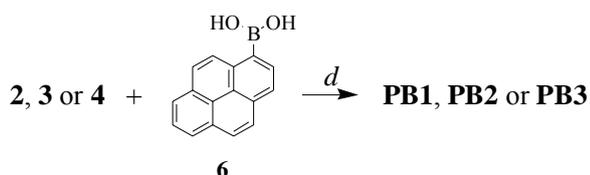
where, A_s and A_r are the absorbance of the sample and reference solutions, respectively at the same excitation wavelength, F_s and F_r are the corresponding relative integrated fluorescence intensities, the sample and reference, and η is the refractive index of the solvent.

Calculation methods. To understand electronic structures of tridurylborane **PB1–3**, 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 03.²

II. Synthesis procedures and characterization of new compounds

1³ and **2**³ were prepared according to the literature methods. The reactions of **2** with different amount of CuCN were carried out at 140°C in DMF solutions giving compounds **3**, **4** and **5**, respectively. The palladium-catalyzed Suzuki cross-coupling of compounds **2**, **3**, **4** with **5**, 2.1, 1.1 eq of the aryl substituted boronic acid (**6**)⁴ afforded the corresponding triarylboranes, **PB1**, **PB2** and **PB3**, respectively.





Scheme S1. Reagents and conditions: (a) Br₂, I₂, CH₂Cl₂; (b) *n*-BuLi, BF₃·Et₂O, Et₂O; (c) CuCN, DMF; (d) the boronic acid 6, and Pd(PPh₃)₄, toluene, EtOH, K₂CO₃, 120 °C.

4-(Bis(4-bromo-2,3,5,6-tetramethylphenyl)boryl)-2,3,5,6-tetramethylbenzonitrile (3).

Compound **2** (150 mg, 0.23 mM) and CuCN (23 mg, 0.25mM, 1.1 eq) was added to 10 ml flask, and 2 ml dry DMF as solvent, the mixture was kept at 140 °C for 5 h under nitrogen . The resulting solution was added with excess of CH₂Cl₂ and washed with H₂O, dried by MgSO₄, and purified using a silica gel column (CH₂Cl₂/petroleum ether = 1:3). The obtained product was a white solid, (85 mg, 62 %). R_f = 0.65 (CH₂Cl₂/petroleum ether = 1:1.5); m. p. 259–262 °C; ¹H NMR(300 MHz, CDCl₃, ppm): δ = 2.42 (s, 6 H), 2.37 (s, 12 H), 2.04 (s, 6 H) 1.96-1.97 (d, 12 H); ¹³C NMR(75 MHz, CDCl₃, ppm): δ = 152.7, 137.5, 137.4, 136.9, 136.6, 136.3, 134.4, 132.2, 118.4, 115.5, 22.6, 21.5, 21.0, 19.9, 19.8, 18.8, 18.7; IR (KBr, cm⁻¹) 2924, 2214, 1453, 1405, 1284, 1256, 1100, 853, 823.

4'-((4-Bromo-2,3,5,6-tetramethylphenyl)boranediyl) bis(2,3,5,6-tetramethyl benzonitrile) (4).

Compound **2** (150 mg 0.23 mM) and CuCN (43 mg, 0.48 mM, 2.1 eq) was added to 10 ml flask, and 2 ml dry DMF as solvent, the mixture was kept at 140 °C for 5h under nitrogen . The resulting solution was added with excess of CH₂Cl₂ and washed with H₂O, dried by MgSO₄, and purified using a silica gel column. The obtained product was a white solid, (72 mg, 58%). R_f = 0.5 (CH₂Cl₂/petroleum ether = 2:3); m. p. 268–272 °C; ¹H NMR (300 MHz, CDCl₃, ppm): δ = 2.41 (s, 12 H), 2.36 (s, 6 H), 1.98 (d, 12 H), 1.92 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 137.5, 137.4, 137.0, 136.6, 134.4, 132.2, 118.4, 115.5, 22.7, 21.5, 21.0, 19.9, 19.8, 18.8, 18.7; IR (KBr, cm⁻¹) 2922, 2214, 1452, 1403, 1287, 1259, 1094, 843,753, 684.

4,4',4''-Boranetriyltris(2,3,5,6-tetramethylbenzonitrile) (5).

Compound **2** (150 mg 0.23 mM) and CuCN (103 mg, 5 eq) was added to 10 ml flask, and 2 ml dry DMF as solvent, the mixture was kept at 140 °C for 5 h under nitrogen . The resulting solution was added with excess of CH₂Cl₂ and washed with H₂O, dried by MgSO₄, and purified using a silica gel column. The obtained product was a white solid, (90 mg, 81%). R_f = 0.2 (CH₂Cl₂/petroleum ether = 2:3) ; m. p. 270–275 °C; ¹H NMR (300 MHz, CDCl₃, ppm): δ = 2.41 (s, 18 H), 1.94 (s, 18 H); ¹³C

NMR (75 MHz, CDCl₃, ppm) δ = 151.9, 137.7, 137.5, 136.5, 19.9, 18.8; IR (KBr, cm⁻¹) 2924, 2214, 1620, 1453, 1405, 1381, 1284, 1256, 1100, 1080, 854, 823; MS (GCF -TOF): *m/z* calculated for C₃₃H₃₆BN₃ [M]⁺ 485.3002; found: 485.2878.

Tris(2,3,5,6-tetramethyl-4-(pyren-1-yl)phenyl)borane (PB1).

Compound **2** (150 mg, 0.232 mmol), **6** (257 mg, 1.04 mmol, 4.5 eq), and Pd(PPh₃)₄ (30 mg, 0.025 mmol) were added into a 25 mL flask. Degassed toluene (2 mL), EtOH (1 mL) and degassed aqueous K₂CO₃ solution (2 mL, 2 M) was then added into the flask. The solution was kept at 120°C and stirred vigorously under nitrogen for 50 h. The resulting brownish solution was extracted with excess CH₂Cl₂, dried by MgSO₄, and purified using a silica gel column (CH₂Cl₂/petroleum ether = 1:8). The obtained product was a white solid (124 mg, 53 % yield). R_f = 0.2 (CH₂Cl₂/petroleum ether = 1:5); m. p. 254–258 °C; ¹H NMR (300 MHz, CDCl₃, ppm): δ = 8.29 (d, *J* = 7.8 Hz, 3 H), 8.09–8.22 (m, 12 H), 8.00 (t, 6 H), 7.87 (d, *J* = 7.8 Hz, 3 H), 7.67 (m, 3 H) 2.36 (s, 18 H), 1.82–1.86 (d, 18 H); ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 149.5, 141.3, 141.2, 138.9, 136.1, 136.0, 135.9, 132.6, 132.5, 131.5, 131.2, 130.2, 129.1, 127.5, 127.4, 127.0, 125.9, 125.3, 125.0, 124.9, 124.8, 20.6, 20.3, 20.2, 17.9, 17.8; IR (KBr, cm⁻¹) 2920, 1639, 1601, 1453, 1394, 1290, 1261, 961, 859, 843, 756; MS (GCF -TOF): *m/z* calculated for C₇₈H₆₃B [M]⁺ 1011.5023; found: 1011.5100.

4-(Bis(2,3,5,6-tetramethyl-4-(pyren-1-yl)phenyl)boryl)-2,3,5,6-tetramethylbenzotrile (PB2)

Compound **3** (80 mg, 0.135 mM) and **6** (100 mg, 0.406mM, 3 eq) and Pd(PPh₃)₄ (20 mg, 0.017 mmol) were added into a 10 mL flask. Degassed toluene (2 mL), EtOH (1 mL) and degassed aqueous K₂CO₃ solution (1 mL, 2 M) was then added into the flask. The solution was kept at 120 °C and stirred vigorously under nitrogen for 50 h. The resulting brownish solution was extracted with excess CH₂Cl₂, dried by MgSO₄, and purified using a silica gel column. (CH₂Cl₂/petroleum ether = 1:3-1:2). The obtained product was a white solid (65.4 mg, 58 %), R_f = 0.6 (CH₂Cl₂/petroleum ether = 1:1.5); m. p. 250–255 °C; ¹H NMR (300 MHz, CDCl₃, ppm): δ = 8.12–8.34 (m, 10 H), 7.94–8.02 (m, 4 H), 7.83 (d, *J* = 7.8 Hz, 2 H), 7.58 (d, *J* = 7.5, 2 H), 2.42 (s, 6 H), 2.39 (s, 12 H), 2.02 (s, 6 H), 1.95 (s, 12 H); ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 151.8, 141.3, 141.2, 138.8, 136.1, 136.0, 135.9, 132.6, 132.5, 131.5, 131.2, 130.2, 129.1, 127.5, 126.9, 125.9, 125.3, 125.0, 124.9, 124.8, 21.5, 20.6, 19.9, 18.9, 18.1; IR (KBr, cm⁻¹) 2924, 2214, 1453, 1405, 1381, 1284, 1256, 1100, 1080, 853, 823; MS (GCF -TOF): *m/z* calculated for C₆₃H₅₄BN [M]⁺ 835.4349; found: 835.9178.

4,4'-((2,3,5,6-Tetramethyl-4-(pyren-1-yl)phenyl)boranediyl)bis(2,3,5,6-tetramethylbenzotrile) (PB3).

Compound **4** (100 mg, 0.185 mmol) and **6** (91 mg, 0.37mM, 2 eq) and Pd(PPh₃)₄ (20 mg, 0.017 mmol) were added into a 10 mL flask. Degassed toluene (2 mL), EtOH (1mL) and degassed aqueous K₂CO₃ solution (1 mL, 2 M) was then added into the flask. The solution was kept at 120 °C and stirred vigorously under nitrogen for 50 h, The resulting brownish solution was extracted with excess CH₂Cl₂, dried by MgSO₄, and purified using a silica gel column. (CH₂Cl₂/petroleum ether = 1:3-1:2). The obtained product was a white solid (75.8 mg, 62 %). R_f = 0.48 (CH₂Cl₂/petroleum ether = 2:3) ; m. p. 258–262 °C; ¹H NMR (300 MHz, CDCl₃, ppm): δ = 8.12 - 8.27 (m, 5 H), 7.97-8.04 (m, 2 H), 7.77 (d, *J* = 7.5 Hz, 1 H), 7.50 (d, *J* = 9.0 Hz, 1 H), 2.44 (s, 12 H), 2.06 (s, 6 H), 1.97 (s, 12 H), 1.91(s, 6 H); ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 153.2, 142.7, 137.9, 137.3, 136.8, 136.3, 136.1, 135.9, 134.1, 133.9, 133.3, 131.4, 131.1, 130.3, 128.8, 127.6, 127.5, 127.2, 127.1, 126.0, 125.2, 124.9, 124.8, 118.6, 115.3, 29.7, 20.3, 20.2, 20.1, 19.9, 19.3, 18.9, 18.7, 17.7; IR (KBr, cm⁻¹) 2922, 2214, 1452, 1403, 1287, 1259, 1094, 843, 753, 684; MS (GCF -TOF): *m/z* calculated for C₄₈H₄₅BN₂ [M]⁺ 660.3676; found: 660.3748.

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III. Solvent effects

Solvatochromic effects from solvent polarity.

The dipole moment (μ_e) of the fluorescent state can be estimated from the slope (m_f) of the plot (Figure S2) of the energies of the fluorescence maxima (ν_f) against the solvent parameter Δf in terms of eq. S2, S3 and S4 and listed in Table S1.

$$\nu_f = -\frac{2\mu_e(\mu_e - \mu_g)}{4\pi\epsilon_0 hca^3} \Delta f + C \quad (\text{S2})$$

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{0.5(n^2 - 1)}{2n^2 + 1} \quad (\text{S3})$$

$$a = \left(\frac{3M}{4N\pi d}\right)^{\frac{1}{3}} \quad (\text{S4})$$

where μ_g is the ground-state dipole moment, a is the solvent cavity (Onsager) radius, which was derived from Avogadro's number (N), molecular weight (M), and density ($d = 1$), and ϵ , ϵ_0 , and n are the solvent dielectric constant, vacuum permittivity, and solvent refractive index, respectively.

The value of μ_g was calculated at the B3LYP-31G level with Gaussian 03.

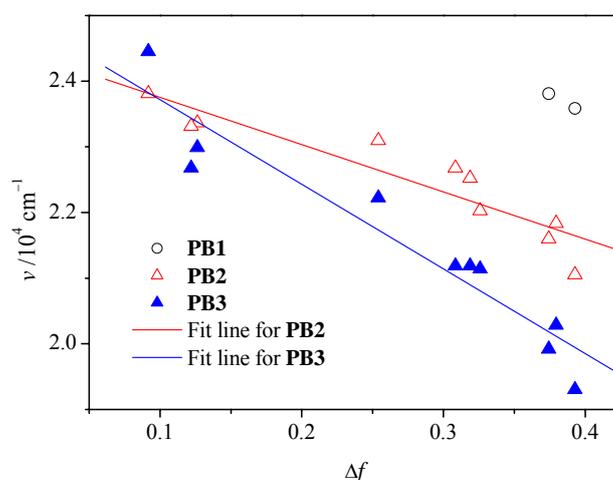


Figure S2. Solvent polarity (Δf) dependence of the fluorescence maxima of **PB1–3**.

Table S1. Maxima of absorption (λ_{abs}) and fluorescence (λ_f , $\nu_{\text{max}}^{\text{em}}$), Stokes shifts ($\Delta\nu_{\text{st}}$) and fluorescence quantum yields (Φ_{F}) of tridurylboranes in ten solvents.

Comp.	Solvent	λ_{abs} /nm	λ_f /nm	$\nu_{\text{max}}^{\text{em}}$ /cm ⁻¹	$\Delta\nu_{\text{st}}$ /cm ⁻¹	Φ_{F}
PB1	Hexane	344	396	25253	3817	0.044
	toluene	344	397	25189	3881	0.127
	dioxane	344	398	25126	3944	0.147
	chloroform	344	396	25253	3817	0.159
	THF	345	397	25189	3796	0.184
	CH ₂ Cl ₂	345	397	25189	3796	0.192
	DCE	345	397	25189	3796	0.204
	ethanol	345	396	25253	3733	0.140
	acetone	345	420	23810	5176	0.118
	CH ₃ CN	344	424	23585	5485	0.112
PB2	Hexane	343	420	23810	5345	0.061
	toluene	343	428	23364	5790	0.178
	dioxane	344	429	23310	5760	0.186
	chloroform	343	433	23095	6060	0.199
	THF	343	441	22676	6479	0.214
	CH ₂ Cl ₂	343	444	22523	6632	0.202
	DCE	343	454	22026	7128	0.180
	ethanol	344	458	21834	7236	0.151
	acetone	345	463	21598	7387	0.120
	CH ₃ CN	343	475	21053	8102	0.083
PB3	Hexane	342	409	24450	4790	0.193
	toluene	343	435	22988	6166	0.203
	dioxane	344	441	22676	6394	0.262
	chloroform	343	450	22222	6932	0.368
	THF	343	472	21186	7968	0.292
	CH ₂ Cl ₂	345	472	21186	7799	0.255
	DCE	343	473	21142	8013	0.239
	ethanol	344	493	20284	8786	0.089
	acetone	343	502	19920	9234	0.059
	CH ₃ CN	343	518	19305	9849	0.043

Isoemissive point for PB1 in methanol-glycerol binary solvents.

The transformation from the LE state to the ICT state of **PB1** occurs when the ratio of methanol-glycerol binary mixtures is changed from 60:40 to 40:60, and this process is shown in Figure S3.

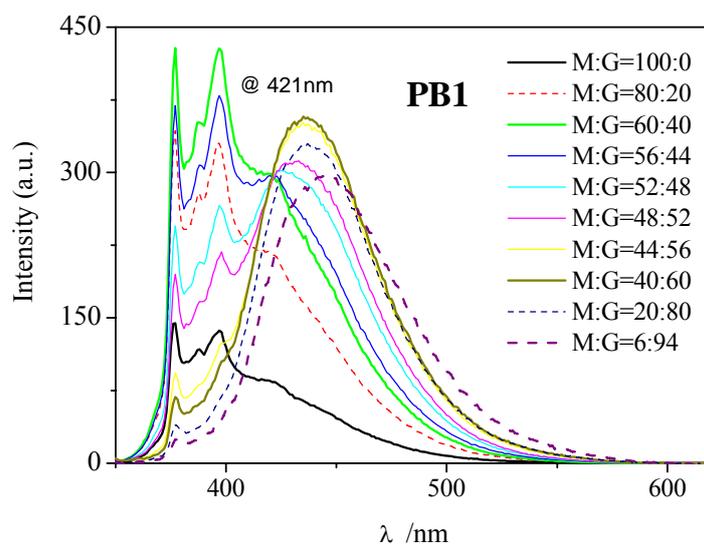
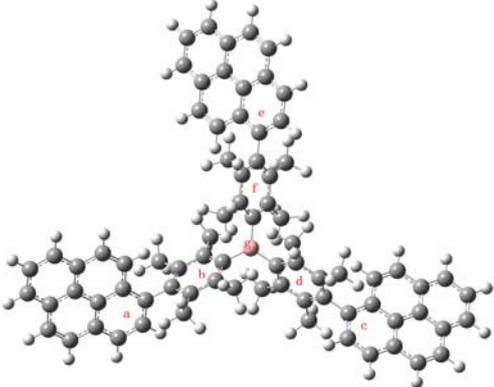
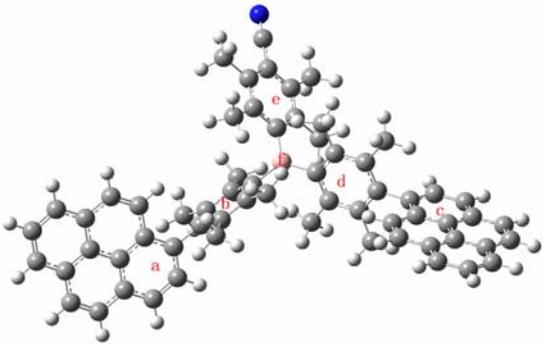
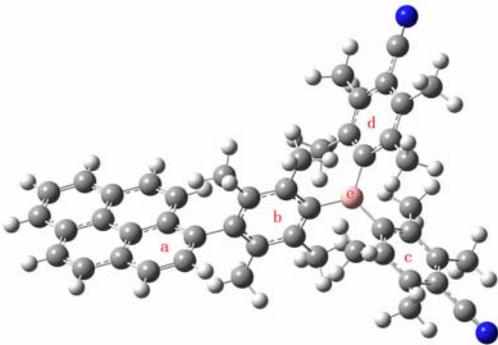
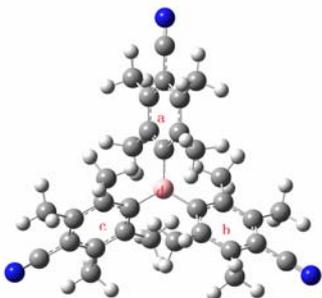


Figure S3. Fluorescence spectra of **PB1** in methanol-glycerol binary mixtures (v/v from 100:0 to 6:94) at room temperature.

Table S2. Relative dihedral angles in tridurylboranes of **PB1–3** and **5** (isovalue = 0.04 a.u.).

Compd.	Structures	Dihedral angle between two planes		
		Boron plane ^a and duryl	Duryl and pyrene	Boron plane ^a and pyrene
PB1		bg: 55.884 dg: 55.952 fg: 56.120	ab: 88.533 cd: 87.210 ef: 88.000	ag: 32.649 dg: 31.258 eg: 31.880
PB2		bf: 50.723 df: 52.728 ef: 52.506	ab: 84.709 cd: 84.695	af: 44.568 cd: 44.577
PB3		be: 50.114 ce: 52.111 de: 52.148	ab: 84.565	ab: 45.321
5		ad: 55.731 bd: 55.741 cd: 55.741		

^a The central boron to form three B-C bonds is completely trigonal planar.

IV. Photographs of the solutions of **PB1–PB3** on illumination with UV light

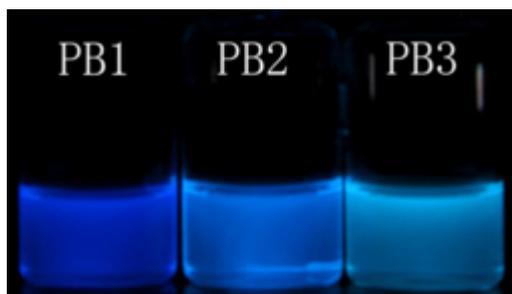


Figure S4. Photograph of **PB1–3** in THF on irradiation with UV light at room temperature.

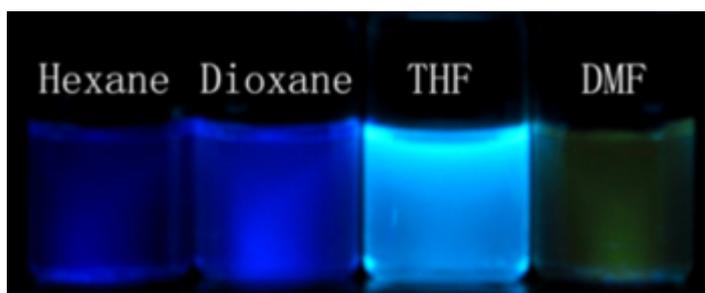


Figure S5. Photograph of **PB3** in four solvents on irradiation with UV light at room temperature.



Figure S6. Photographs of **PB1** (left), **PB2** (middle) and **PB3** (right) in two or three ethanol-glycerol binary solvents (v/v) on irradiation with UV light at room temperature.

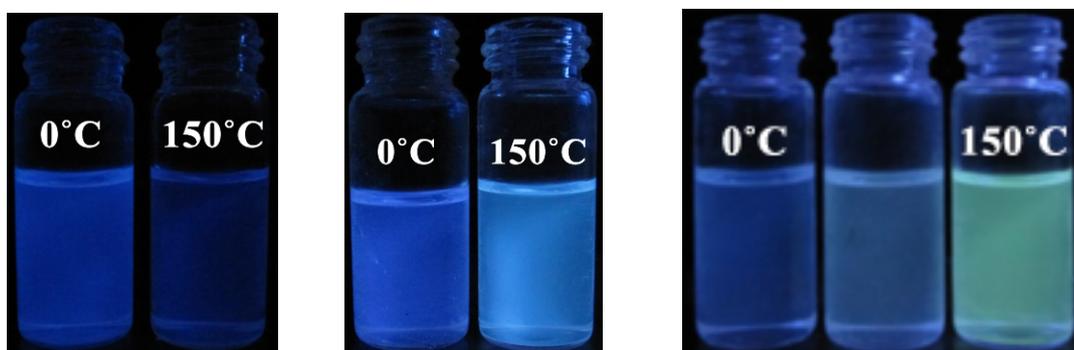
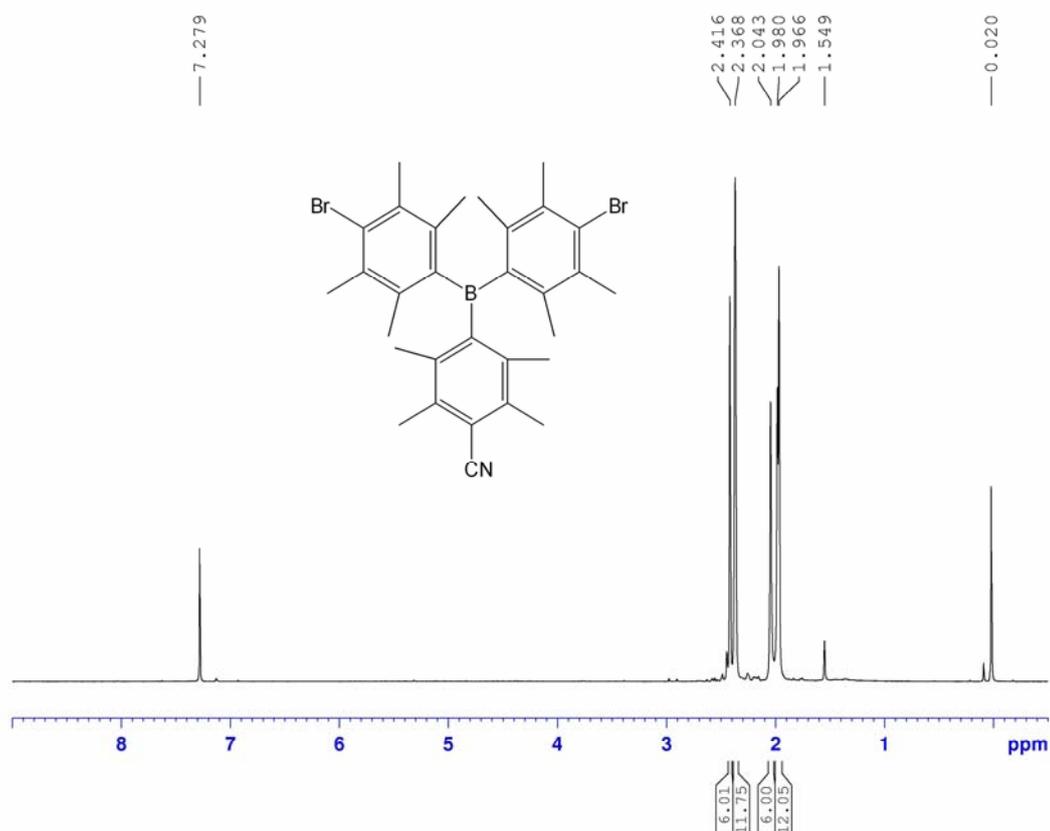


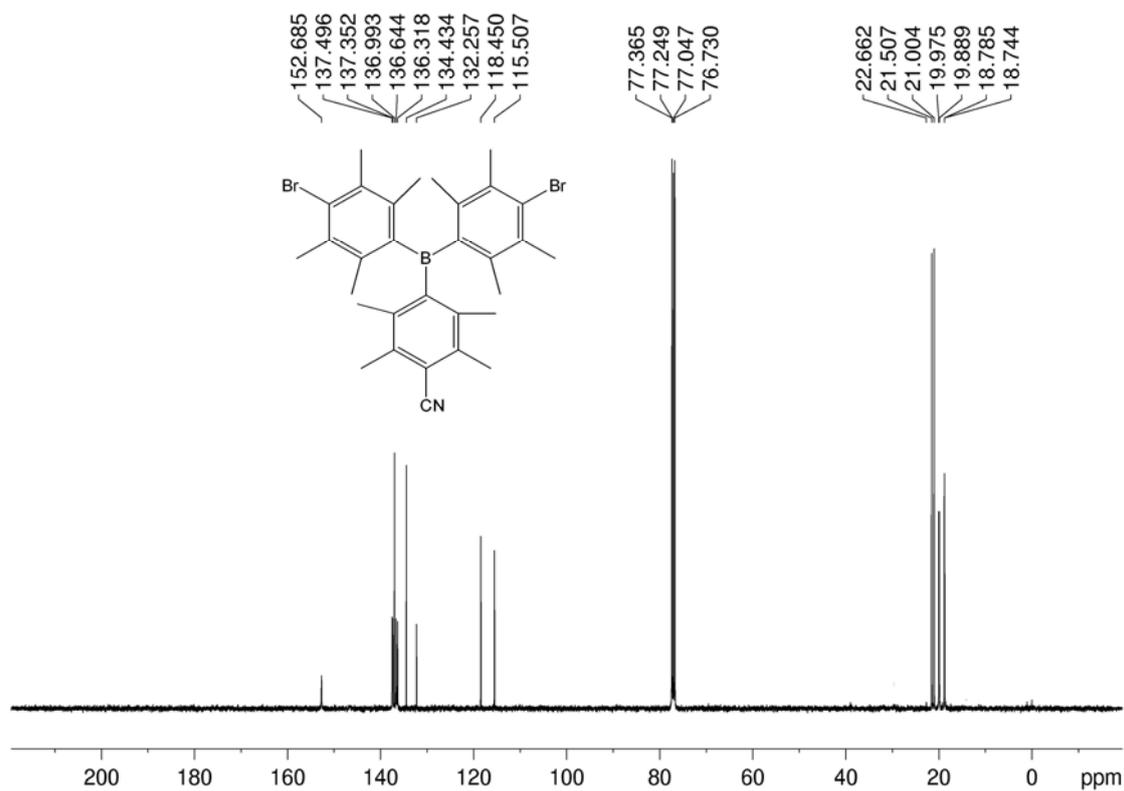
Figure S7. Photograph of **PB1** (left), **PB2**(middel) and **PB3** (right) in the ethanol-glycerol (v/v, 6:94) binary solvent on irradiation with UV light at two or three temperatures.

V. ^1H and ^{13}C NMR spectra of new compounds

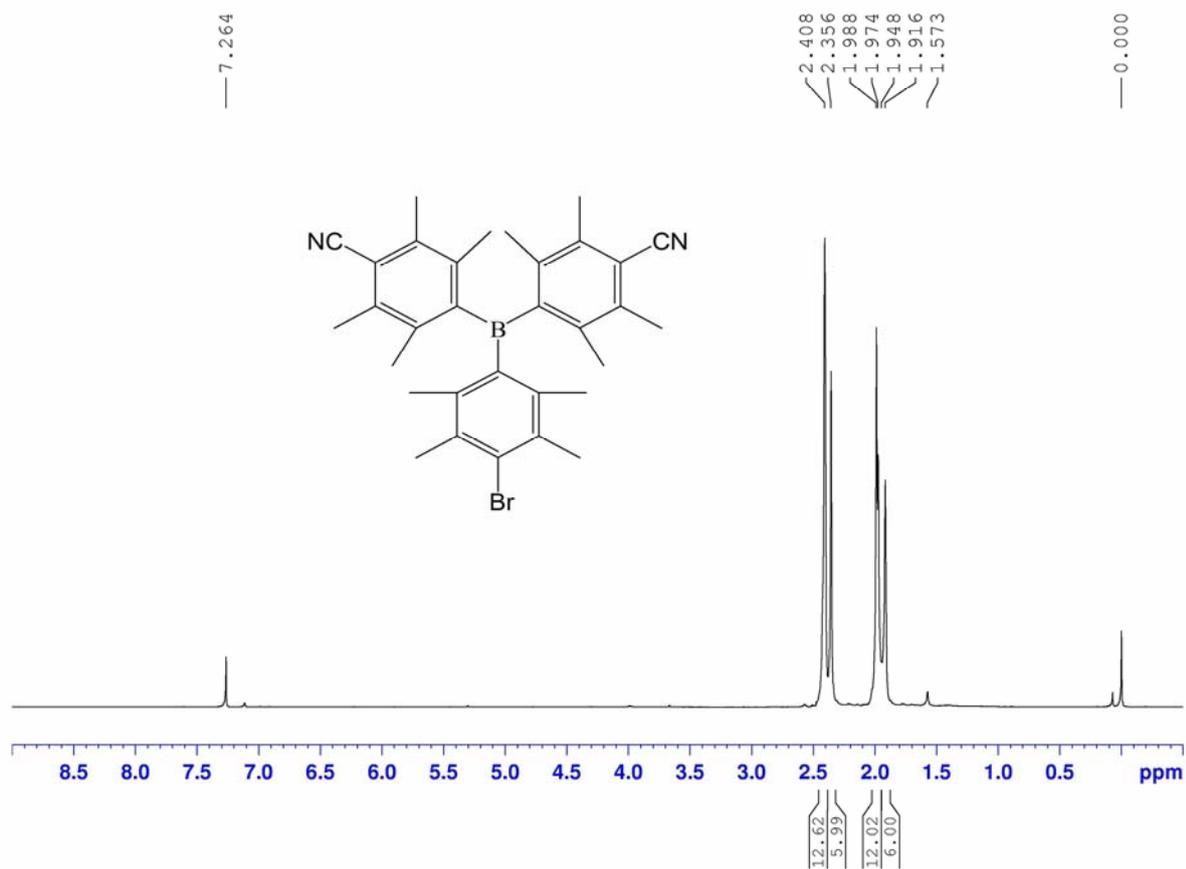
^1H NMR spectrum of compound **3**



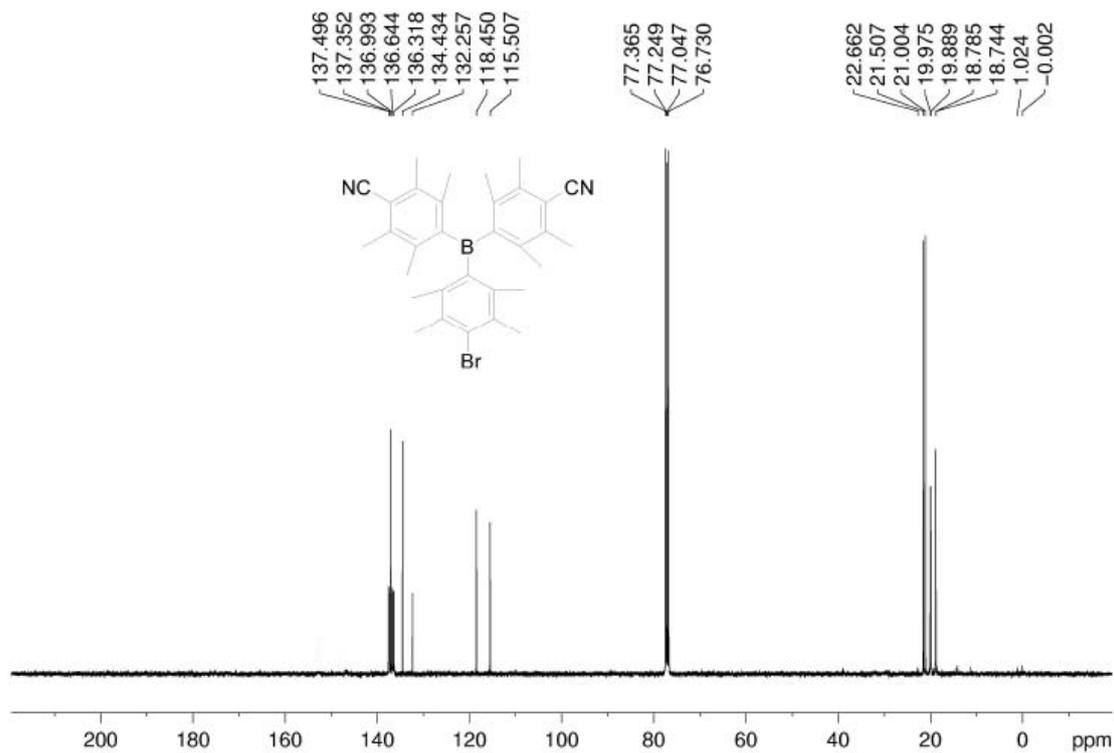
^{13}C NMR spectrum of compound **3**



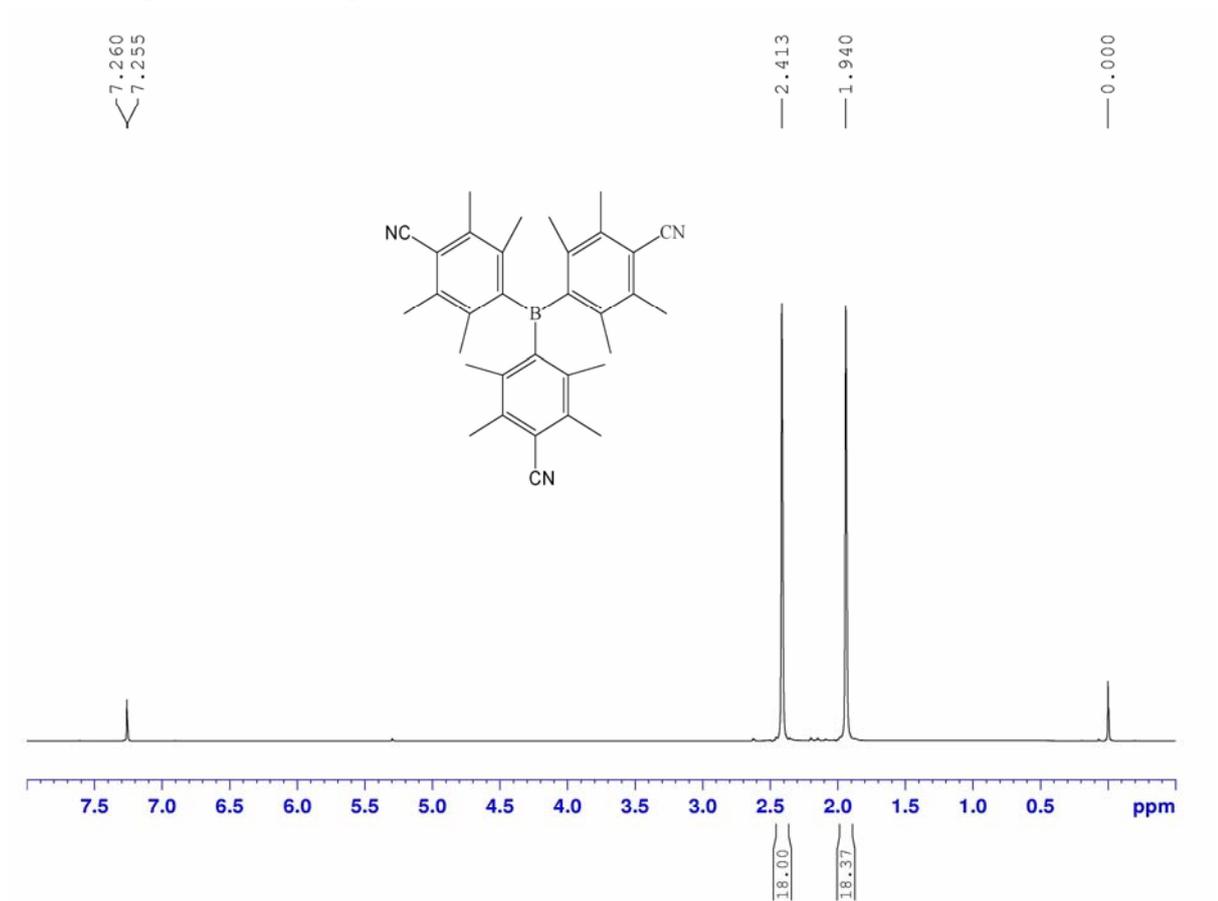
¹H NMR spectrum of compound **4**



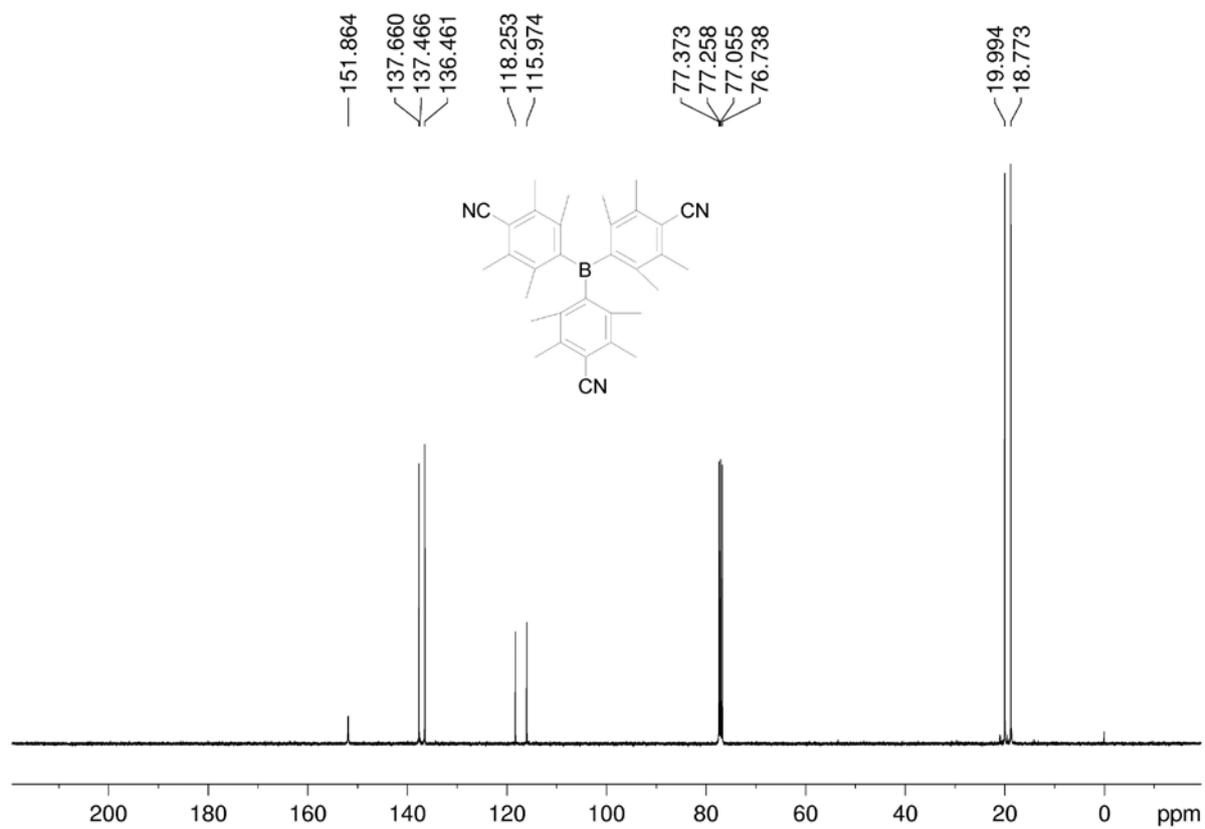
¹³C NMR spectrum of compound **4**



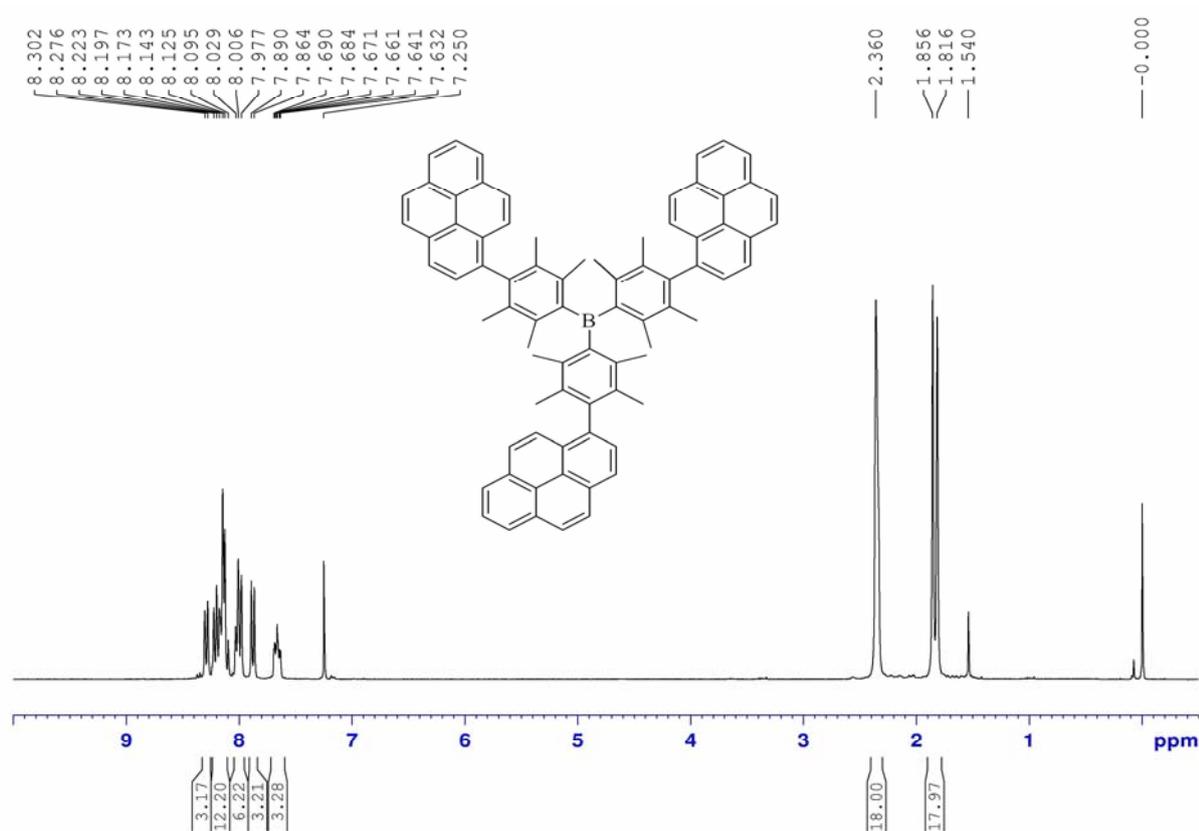
¹H NMR spectrum of compound **5**



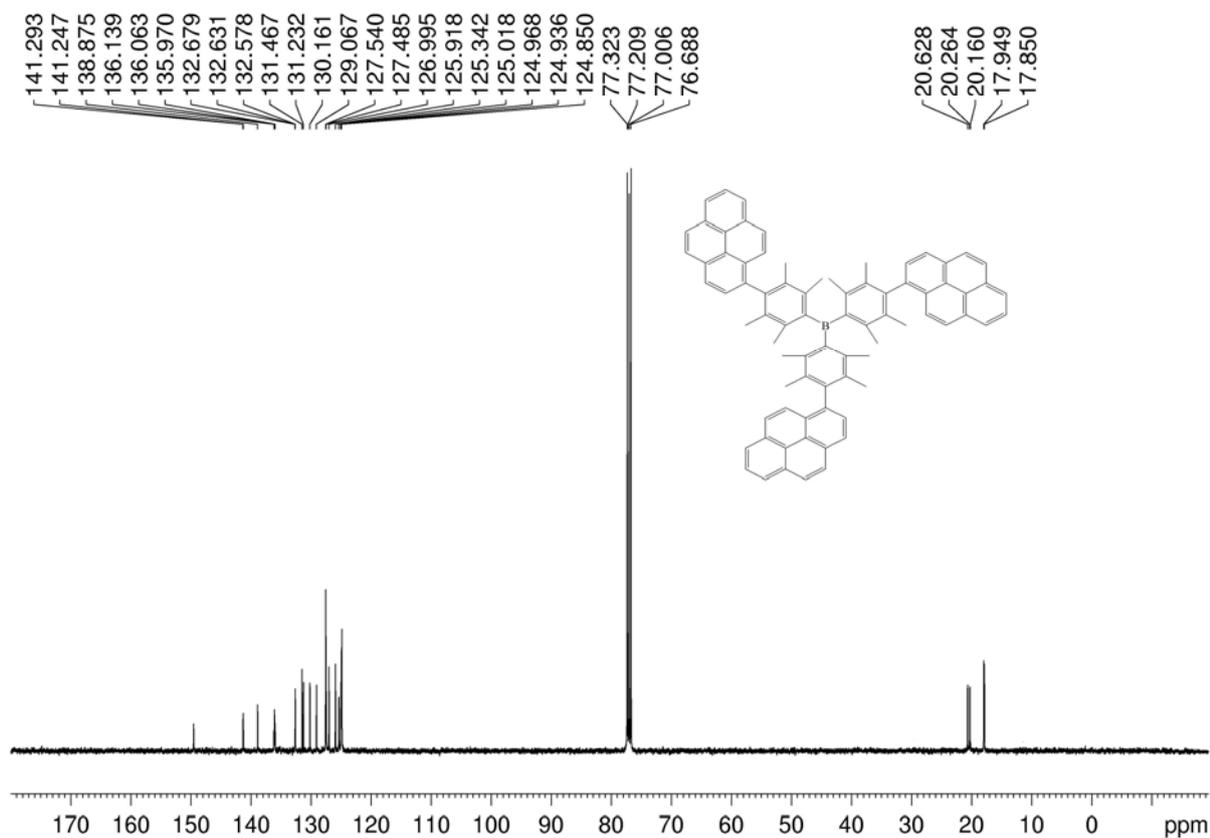
¹³C NMR spectrum of compound **5**



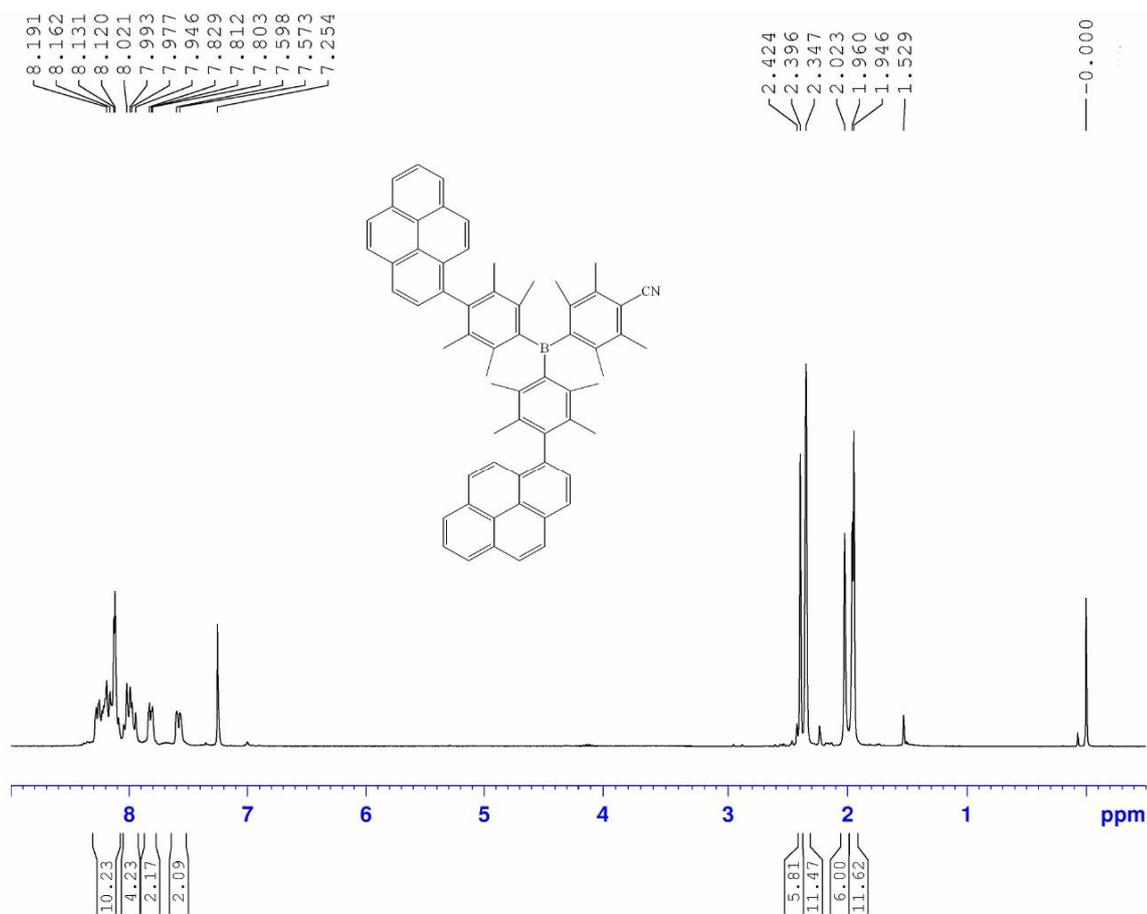
^1H NMR spectrum of compound **PB1**



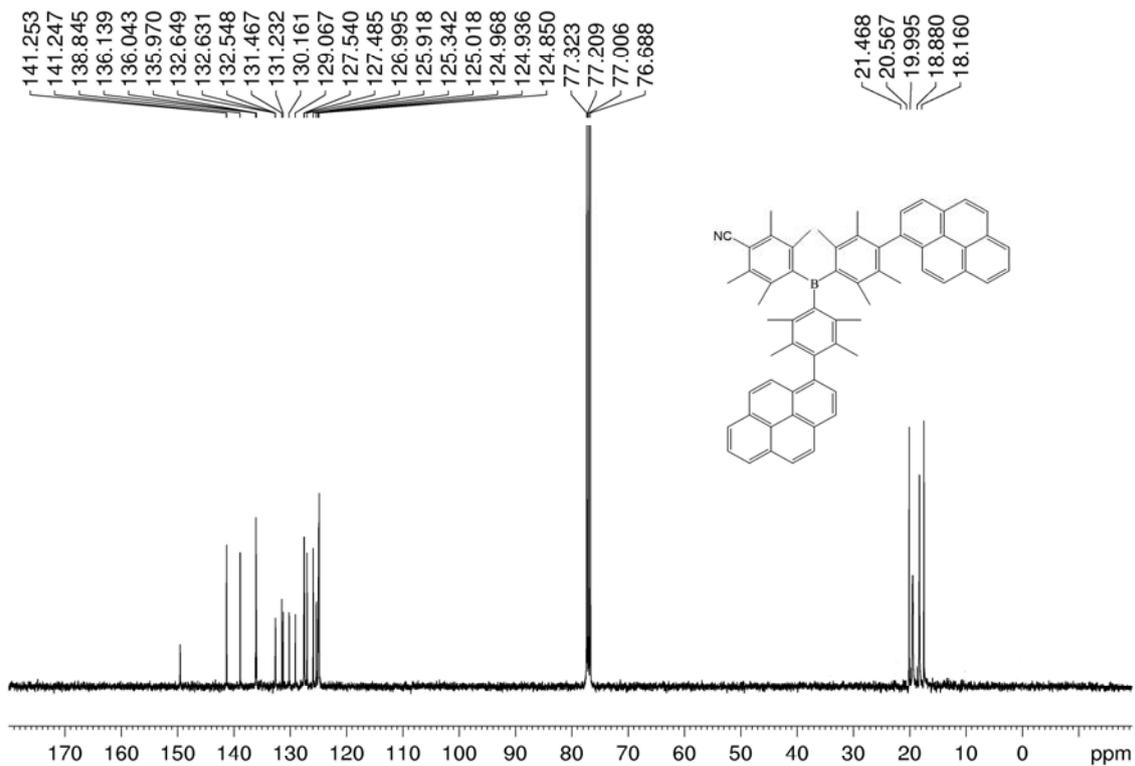
^{13}C NMR spectrum of compound **PB1**



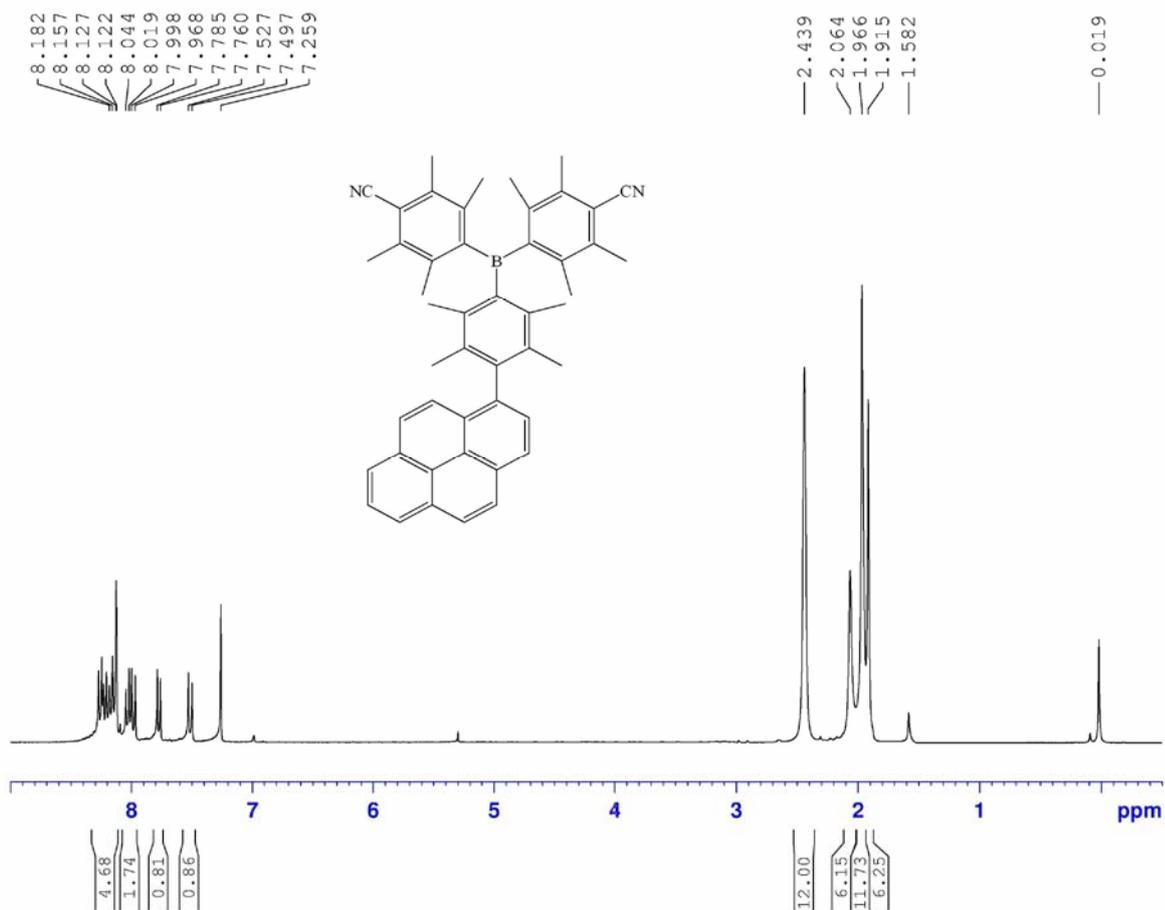
¹H NMR spectrum of compound **PB2**



¹³C NMR spectrum of compound **PB2**



¹H NMR spectrum of compound **PB3**



¹³C NMR spectrum of compound **PB3**

