Supporting Information for

Phenanthro[9,10-d]imidazole-quinoline Boron Difluoride Dyes with Solid-State Red Fluorescence

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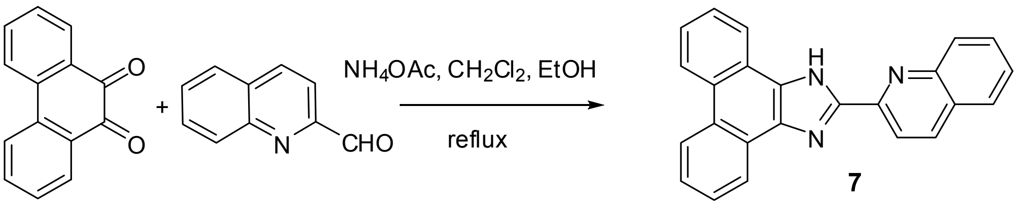
Materials and instruments

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Solvents used were purified and dried by standard methods prior to use. Twice-distilled water was used throughout all experiments. Melting points were determined with a Beijing taike XT-4 microscopy and were uncorrected. ESI-MS analyses were performed using a Waters Micromass ZQ-4000 spectrometer. High resolution mass spectrometric (HRMS) analyses were measured on a Finnigan MAT 95 XP spectrometer. Electronic absorption spectra were obtained on a LabTech UV Power spectrometer; Photoluminescent spectra were recorded with a HITACHI F4600 fluorescence spectrophotometer. Fluorescence spectrophotometer with the excitation and emission slit widths were at 5.0 nm. Absolute quantum yields were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system. Fluorescence lifetimes were determined on a lifetime and steady state spectrometer (FL3-P-TCSPC) using the time-correlated picosecond single photon counting (TCSPC) system. X-Ray single-crystal diffraction data were collected on a Bruker SMART 1000 CCD areadetector diffractometer. Fluorescence miscroscopy was performed with a Nikon eclipase TE300 inverted fluorescence microscopy. ^{1}H spectra were measured on an INOVA-400 spectrometer using TMS as an internal standard. TLC analyses were performed on silica gel plates and column chromatography was conducted over silica gel (mesh 200-300), both of which were obtained from the Qingdao Ocean Chemicals.

DFT calculations

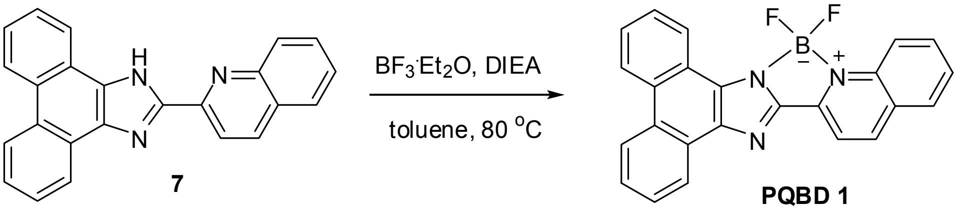
Density functional theory (DFT) and TD-DFT calculations were carried out with the Gassian 09 program package. [1] All the calculations were performed on systems in the gas phase using the Becke's three-parameter hybrid functional with the LYP correlation functional (B3LYP), 6-311G(d) basis set.

Scheme S1. Synthesis of 2-(quinolin-2-yl)-1H-phenanthro[9,10-d]imidazole （**7**）



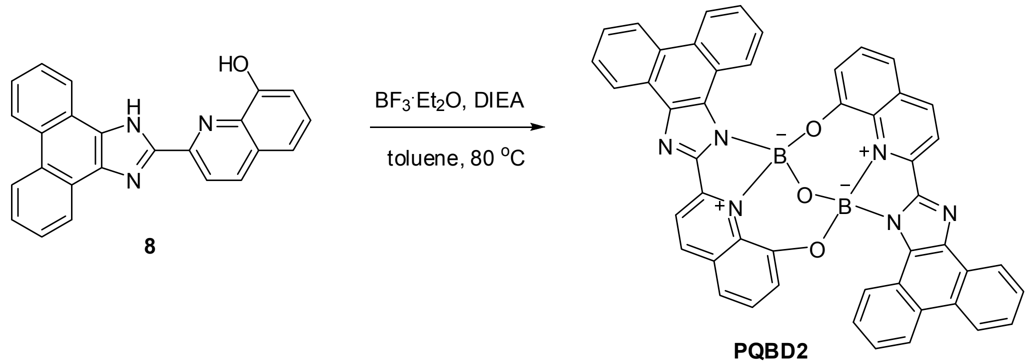
A mixture of phenanthrene-9, 10-dione (104 mg, 0.5 mmol), ammonium acetate (780 mg, 5 mmol), glacial acetic acid (10 mL), and quinoline-2-carbaldehyde (94.2 mg, 0.6 mmol) was heated to reflux. After reaction for 2 h, the reaction mixture was cooled, filtered, washed with ethanol, and dried to afford compound **7** (light yellow solid, 155.3 mg, 0.45 mmol, 90 %). mp 175-178 °C. ^{1}H NMR (400 MHz, d6-DMSO), δ =14.15(s, 1H), 8.98(s, 1H), 8.89-8.88(d, *J* = 6.8 Hz, 2H), 8.68(s, 1H), 8.63-8.61(d, *J* = 8.8 Hz, 1H), 8.59-8.57(d, *J* = 8.4 Hz, 1H), 8.29-8.27 (d, *J* = 8.4 Hz, 1H), 8.10-8.08(d, *J* = 8.0 Hz, 1H), 7.91-7.87(t, *J* = 7.4 Hz, 1H), 7.78-7.75(t, *J* = 7.0 Hz, 2H),7.70-7.69(d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, d6-DMSO):149.2, 149.1, 147.6, 137.6, 130.7, 128.9, 128.5, 128.1, 127.2, 127.2, 126.1, 124.2, 119.6.

Scheme S2. Synthesis of compound **PQBD 1**.



A stirred solution of compound **7** (345.0 mg, 1.0 mmol) in toluene (40 mL) was added N,N-Diisopropylethylamine (DIEA) (0. 8 mL), and then heated at 80°C. After 30 minutes, $BF_3 \cdot Et_2O$ (0.8 mL) was added, and the color of the solution immediately changed from yellow to red. The reaction mixture was further stirred for 1 h at 80°C. After toluene was removed under reduced pressure, the solid was collected and purified by silica-gel column chromatography (dichloromethane : petroleum ether, 1:1, v/v) to give compound **PQBD 1** as a nacarat solid powder (255.5 mg, 0.65 mmol, 65%). mp 284-286 °C. ^{1}H NMR (400 MHz, d6-DMSO), δ =9.24-9.22 (d, *J* = 8.8 Hz, 1H), 8.96-8.94(d, *J* = 8.4 Hz, 1H), 8.91-8.89 (d, *J* = 8.0 Hz, 1H), 8.63-8.61(d, *J* = 7.6 Hz, 1H), 8.56-8.53(d, *J* = 8.4 Hz, 1H), 8.46-8.41(t, *J* = 9.0 Hz, 2H), 8.39-8.36(d, *J* = 8.4 Hz, 1H), 8.26-8.22(t, *J* = 8.0 Hz, 1H), 7.95-7.92(t, *J* = 7.4 Hz, 1H), 7.87-7.84(t, *J* =7.0 Hz, 1H), 7.80-7.76(t, *J* = 7.0 Hz, 1H), 7.74-7.70(t, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, d6-DMSO):216.9, 215.5, 163.8, 148.1, 146.6, 143.1, 139.2, 135.5, 131.3, 130.4, 129.4, 128.9, 128.5, 128.0, 127.3, 126.6, 124.8, 124.4, 123.1, 122.5, 120.3, 116.1. EI-MS: m/z = 393.1, calc. for $C_{24}H_{14}BF_2N_3$ = 393.2; HRMS (EI): m/z calcd for [$C_{24}H_{14}BF_2N_3$]: 393.1243, Found: 393.1240.

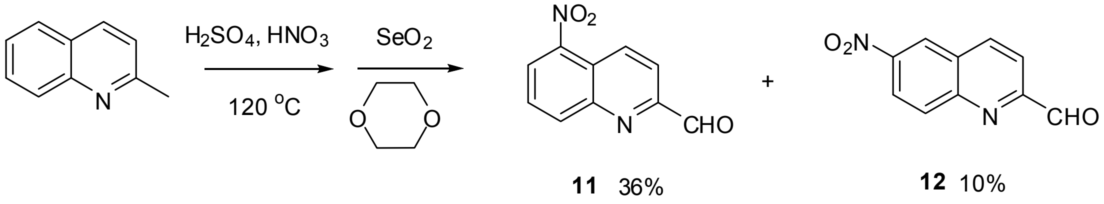
Scheme S3. Synthesis of compound **PQBD 2**.



Compound **8** was synthesized according to a reported method.[2] Compound **8** (361.0 mg, 1.0 mmol) and DIEA (0. 8 mL) were added to toluene (40 mL), and then heated at 80°C. After 30 minutes, $BF_3\cdot Et_2O$ (0.8 mL) was added, and the color of the solution immediately changed from yellow to orange. The reaction mixture was further stirred for 1.5 h at 80 °C. After toluene was removed under reduced pressure, the solid was collected and purified by silica-gel column chromatography using dichloromethane as eluent to afford compound **PQBD 2** as a orange solid powder (122.7 mg, 0.30 mmol, 30%). mp >300 °C. ^{1}H NMR (400 MHz, d-TFA), δ =9.39-9.37(d, *J* = 8.4 Hz, 2H), 8.85-8.82(d, *J* = 8.8 Hz, 2H), 8.76-8.74(d, *J* = 7.6 Hz, 2H), 8.68-8.66(d, *J* = 8.4 Hz, 2H), 8.45-8.43(t, *J* = 4.6 Hz, 2H), 8.02-8.00(t, *J* = 8.0 Hz, 2H), 7.88-7.86(t, *J* = 3.6 Hz, 4H), 7.77-7.75 (d, *J* = 8.0 Hz, 2H), 7.66-7.62(t, *J* = 8.0 Hz, 2H), 7.52-7.49(t, *J* =7.8 Hz, 2H), 7.40-7.39(d, *J* = 7.6 Hz, 2H), 6.62-6.58(t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, d-TFA):147.7, 142.4, 137.7, 133.2, 131.6, 131.4, 130.0, 129.6, 128.9, 128.1, 126.5, 126.0, 123.4, 123.3, 122.8, 121.2, 120.9, 119.1. EI-MS: m/z = 756.2, calc. for $C_{48}H_{28}B_2N_3O_3$ = 756.2; HRMS (EI):

m/z calcd for [$C_{48}H_{28}B_2N_3O_3$]: 756.2252, Found: 756.2256.

Scheme S4. Synthesis of compounds **11** and **12**.

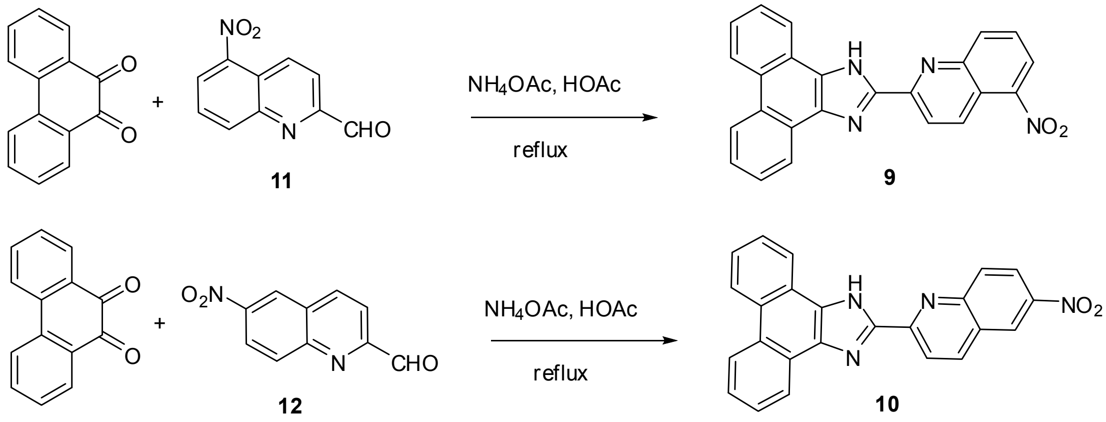


11 36%

12 10%

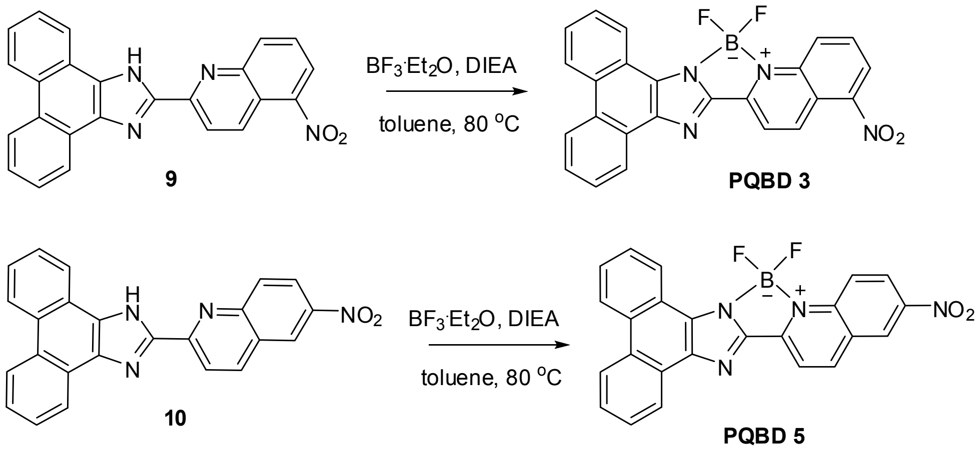
A solution of H_2SO_4 (5 mL) and HNO_3 (5 mL) was slowly dropped to 2-methylquinoline (1 mL) at 0 °C. After stiring for 20 min at room temperature, the solution was heated at 60 °C for 4 h. After cooling to room temperature, the reaction mixture was neutralized with NaOH to pH= 3-4, filtered, washed with water and brine, dried in vacuo. The crude product (500 mg, 2.7 mmol) and SeO_2 (354 mg, 3.2 mmol) were dissolved in 1,4-dioxane (50 mL), and the mixture was refluxed under nitrogen atmosphere for 3 h. After 1,4-dioxane was removed under reduced pressure, the solid was collected and purified by silica-gel column chromatography using dichloromethane/ petroleum ether (1:6, v/v) or dichloromethane/ petroleum ether (1:4, v/v) as the eluent to give compound **12** as a white solid powder (54.5 mg, 0.27 mmol, 10%) or compound **11** as a white solid powder (196.3 mg, 0.97 mmol, 36%), respectively. Compound **11:** ^{1}H NMR (400 MHz, $CDCl_3$), δ =10.25(s, 1H), 9.20-9.18 (d, *J* = 9.2 Hz, 1H), 8.60-8.58(d, *J* = 8.8 Hz, 1H), 8.54-8.51(dd, *J* = 1.2 Hz and 6.4, 1H), 8.26-8.23(d, *J* = 8.8 Hz, 1H), 7.96-7.92(t, *J* = 8.0 Hz, 1H); Compound **12:** ^{1}H NMR (400 MHz, $CDCl_3$), δ =10.26(s, 1H), 8.884-8.878 (d, *J* = 2.4 Hz, 1H), 8.60-8.57(dd, *J* = 2.4 Hz and 7.2, 1H), 8.56-8.54(d, *J* = 8.4 Hz, 1H), 8.44-8.41(d, *J* = 9.6 Hz, 1H), 8.20-8.17(d, *J* = 8.4 Hz, 1H).

Scheme S5. Synthesis of compounds **9** and **10**.



A mixture of phenanthrene-9, 10-dione (104 mg, 0.5 mmol), ammonium acetate (780 mg, 5 mmol), glacial acetic acid, and 5-nitroquinoline-2-carbaldehyde (121.2 mg, 0.6 mmol) or 6-nitroquinoline-2-carbaldehyde (121.2 mg, 0.6 mmol) was heated to reflux. After reaction for 1 h, the mixture was cooled, filtered, washed with ethanol, and the solid was collected and purified by silica-gel column chromatography using dichloromethane/ ethyl acetate (20:1, v/v) mixture as the eluent to give compound **9** or **10** as an orange yellow solid powder (146 mg, 0.38 mmol, 75%), mp 230-233 °C for **9**, 198-200 °C for **10**. Compound **9**: ^{1}H NMR (400 MHz, d6-DMSO), δ =14.28(s, 1H), 9.05-9.03(d, *J* = 9.2 Hz, 1H), 8.94-8.86 (m, 3H), 8.83-8.81 (d, *J* = 9.2 Hz, 1H), 8.68-8.66 (d, *J* = 8.0 Hz, 1H), 8.62-8.60 (d, *J* = 8.8 Hz, 1H), 8.50-8.48(d, *J* = 8.0 Hz, 1H), 8.08-8.04(t, *J* = 8.0 Hz, 1H), 7.79-7.75(t, *J* = 7.6 Hz, 2H), 7.72-7.69(t, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, d6-DMSO):151.8, 149.9, 147.6, 145.6, 135.4, 132.5, 131.3, 128.8, 128.5, 128.2, 127.1, 125.8, 124.5, 123.7, 122.6, 122.1, 120.1; ESI-MS(negative mode): m/z = 389.2 [M-H], calc. for $C_{24}H_{14}N_{4}O_{2}$ = 390.4; Compound **10**: ^{1}H NMR (400 MHz, d6-DMSO), δ =14.32(s, 1H), 9.17-9.16(d, *J* = 6.8 Hz, 1H), 8.91-8.89(d, *J* = 8.4 Hz, 3H), 8.77-8.74(d, *J* = 8.8 Hz, 1H), 8.67(s, 1H), 8.58-8.56(d, *J* = 9.6 Hz, 1H), 8.42-8.40(d, *J* = 9.6 Hz, 1H), 8.32-8.30(d, *J* = 8.8 Hz, 1H), 7.79-7.75(t, *J* = 7.4 Hz, 2H), 7.72-7.68 (t, *J* = 7.2 Hz, 2H).

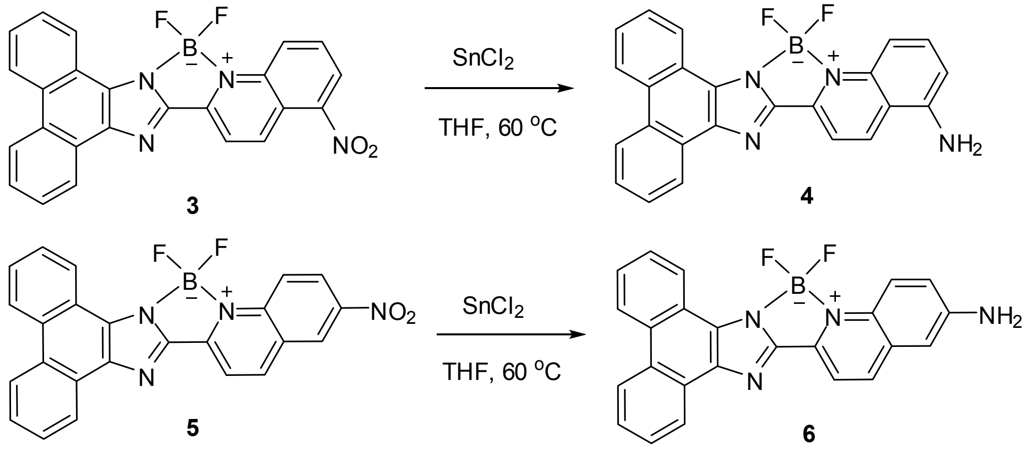
Scheme S6. Synthesis of compounds **PQBD 3** and **PQBD 5**.



Compound **9** (390.0 mg, 1.0 mmol) or compound **10** (390.0 mg, 1.0 mmol), and DIEA (0. 8 mL) were added to toluene (40 mL), and then heated at 80 °C. After 30 minutes, $BF_3 \cdot Et_2O$ (0.8 mL) was added, and the color of the solution immediately changed from yellow to red. The reaction mixture was further stirred for 30 min at 80 °C. After toluene was removed under reduced pressure, the solid was collected and purified by silica-gel column chromatography using petroleum ether/ dichloromethane/ ethyl acetate (20:10:1, v/v) mixture as eluent to afford compound **PQBD 3** (262 mg, 0.60 mmol, 60%) or compound **PQBD 5** (87.6 mg, 0.20 mmol, 20%) as a red solid powder. mp 293-295 °C for **PQBD 3**, 297-300 °C for **PQBD 5**. Compound **PQBD 3**: ^{1}H NMR (400 MHz, d6-DMSO), δ =9.51-9.48(d, *J* = 9.2 Hz, 1H), 8.96-8.94(d, *J* = 8.4 Hz, 1H), 8.91-8.89(d, *J* = 8.0 Hz, 1H), 8.73-8.71(d, *J* = 9.6 Hz, 1H), 8.67-8.65(d, *J* = 7.2 Hz, 1H), 8.63-8.61(d, *J* = 7.6 Hz, 1H), 8.44-8.42(d, *J* = 7.6 Hz, 1H), 8.40-8.36 (t, *J* = 7.8 Hz, 1H), 7.88-7.84(t, *J* = 7.6 Hz, 1H), 7.81-7.77(t, *J* =7.6 Hz, 2H), 7.75-7.71(d, *J* = 7.6 Hz, 1H); EI-MS: m/z = 483.2, calc. for $C_{24}H_{13}BF_2N_4O_2$ = 438.2; HRMS (EI): m/z calcd for [$C_{24}H_{13}BF_2N_4O_2$]: 438.1094, Found: 438.1102. Compound **PQBD 5**: ^{1}H NMR (400 MHz, d6-DMSO), δ =9.45(s, 2H), 8.96-8.94(d, *J* = 8.4 Hz, 1H), 8.91-8.89(d, *J* = 8.4 Hz, 2H), 8.71-8.69(d, *J* = 8.8 Hz, 1H), 8.63-8.62(d, *J* = 7.6 Hz, 1H), 8.50-8.48(d, *J* = 9.2 Hz, 1H), 8.45-8.43(d, *J* = 7.6 Hz, 1H), 7.88-7.84 (t, *J* = 7.6 Hz, 1H), 7.81-7.78(t, *J* = 7.4 Hz, 2H), 7.75-7.35(t, *J* =7.6 Hz, 1H); EI-MS: m/z = 483.2, calc. for $C_{24}H_{13}BF_2N_4O_2$ = 438.2;

HRMS (EI): m/z calcd for [$C_{24}H_{14}BF_2N_4O_2$]: 438.1094, Found: 438.1106.

Scheme S7. Synthesis of compounds **PQBD 4** and **PQBD 6**.



Compound **PQBD 3** (438.0 mg, 1.0 mmol) or compound **PQBD 5** (438.0 mg, 1.0 mmol), and $SnCl_2 \cdot 2H_2O$ (4.5 g, 20 mmol) were added to THF (30 mL), and then heated at 60°C. After 2-3 h, THF was removed under reduced pressure, and the solid was collected and purified by silica-gel column chromatography using dichloromethane/ ethyl acetate (20:1, v/v) mixture as eluent to afford compound **PQBD 4** (346 mg, 0.85 mmol, 85%) or compound **PQBD 6** (326 mg, 0.80 mmol, 80%) as a brown solid powder. mp 265-267 ^{o}C for **PQBD 4**, 276-249 ^{o}C for **PQBD 6**. Compound **PQBD 4**: ^{1}H NMR (400 MHz, d6-DMSO), δ =9.35-9.33(d, *J* = 8.8 Hz, 1H), 8.94-8.92(d, *J* = 8.4 Hz, 1H), 8.90-8.88(d, *J* = 8.4 Hz, 1H), 8.62-8.60(d, *J* = 7.6 Hz, 1H), 8.46-8.44(d, *J* = 8.0 Hz, 1H), 8.31-8.29(d, *J* = 8.8 Hz, 1H), 7.87-7.85(t, *J* = 8.0 Hz, 2H), 7.79-7.76 (q, *J* = 7.6 Hz, 2H), 7.74-7.68(t, *J* = 7.6 Hz, 1H), 7.45-7.43(d, *J* =8.4 Hz, 1H), 6.94-6.92(d, *J* = 8.0 Hz, 1H), 6.90(s, 2H); ^{13}C NMR (100 MHz, d6-DMSO):149.3, 148.3, 145.9, 143.0, 140.4, 136.9, 131.0, 129.3, 128.4, 128.0, 127.4, 127.2, 126.4, 124.7, 124.3, 123.1, 122.9, 122.5, 118.2,120.0, 109.4, 105.8. EI-MS: m/z = 408.0, calc. for $C_{24}H_{14}BF_2N_4O_2$ = 408.2; HRMS (EI): m/z calcd for [$C_{24}H_{15}BF_2N_4$]: 408.1352, Found: 408.1354. Compound **PQBD 6**: ^{1}H NMR (400 MHz, d6-DMSO), δ =8.94-8.92(d, *J* = 8.4 Hz, 1H), 8.89-8.87(d, *J* = 8.0 Hz, 1H), 8.77-8.75(d, *J* = 8.8 Hz, 1H), 8.60-8.58(d, *J* = 7.6 Hz, 1H), 8.42-8.40(d, *J* = 8.0 Hz, 1H), 8.26-8.24(d, *J* = 8.8 Hz, 1H), 8.14-8.12(d, *J* = 8.8 Hz, 1H), 7.84-7.81 (t, *J* = 7.6 Hz, 1H), 7.78-7.74(t, *J* = 8.0 Hz, 2H), 7.72-7.67(dd, *J* =8.0 Hz, 1H), 7.62-7.60(d, *J* = 9.2 Hz, 1H), 7.14(s, 1H), 6.44(s, 2H); ^{13}C NMR (100 MHz, d6-DMSO):150.0, 149.6, 143.3, 142.4, 140.4, 132.6, 131.6, 130.6, 130.0, 128.1, 127.8, 127.4, 126.9, 126.1, 126.0, 124.6, 124.2, 122.8, 122.4, 121.4, 115.5, 105.6. EI-MS: m/z = 408.2, calc. for $C_{24}H_{14}BF_2N_4O_2$ = 408.2; HRMS (EI): m/z calcd for [$C_{24}H_{15}BF_2N_4$]: 408.1352, Found: 408.1364.

References:

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
2. Eseola, A. O.; Zhang, M.; Xiang, J. F.; Zuo, W. W.; Li, Y.; Woods, J. A. O.; Sun, W. H.; *Inorg. Chim. Acta*, **2010**, *363*, 1970.

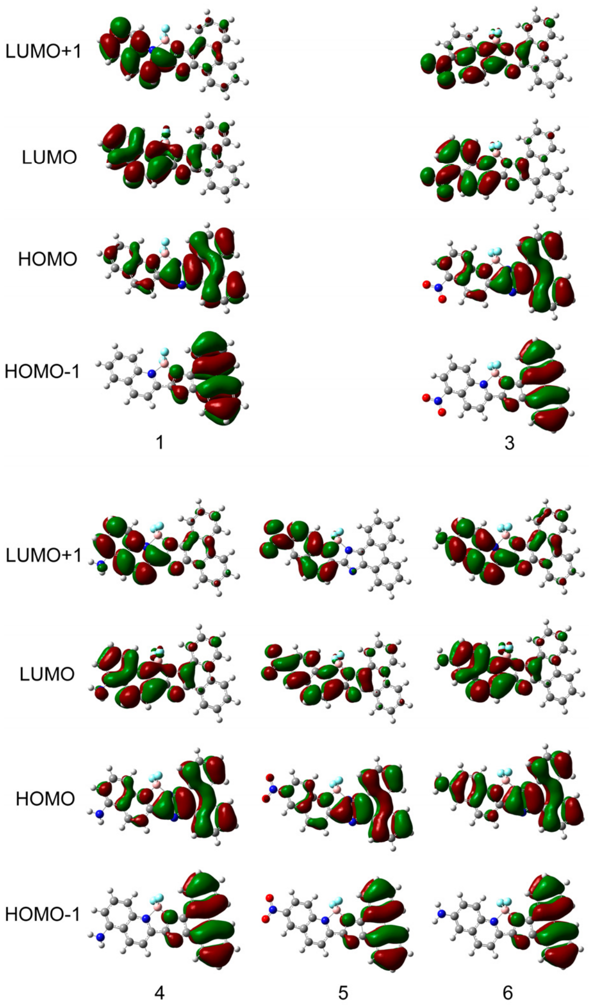


Figure S1. DFT optimized structures and molecular orbital plots (HOMO, HOMO -1, LUMO and LUMO+1) of compounds **PQBD 1**, **3**, **4**, **5**, and **6**. Notably, **PQBD 2** is too big for the calculation to be accomplished within a reasonable amount of time. For clarity, **PQBD 1**, **3**, **4**, **5**, and **6** are simplified as **1**, **3**, **4**, **5**, and **6** in the figure.

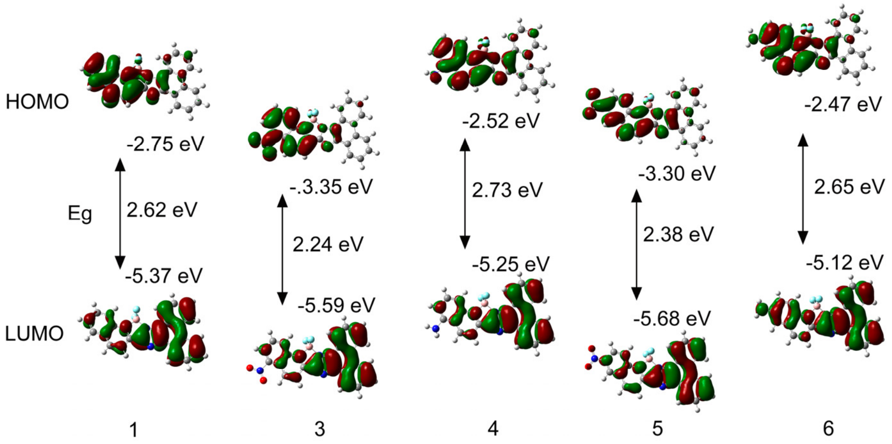


Figure S2. Calculated molecular orbitals and energy levels of compounds **PQBD 1**, **3**, **4**, **5**, and **6**.

Table S1: Photophysical data for the new dyes **PQBD 1-6** in dichloromethane.

Compound	λ_{max}[a] (nm)	lgε_{max}	λ_{em}[b] (nm)	SS[c] (nm)	Φ_F[d]	τ (ns)	k_f[e] ($10^8 s^{-1}$)	k_{nr}[e] ($10^8 s^{-1}$)
PQBD 1	476	4.56	585	109	0.90	4.89	1.84	0.20
PQBD 2	472	4.65	568	100	0.89	3.65	2.44	0.30
PQBD 3	518	4.08	633	115	0.03	2.67	0.11	3.63
PQBD 4	468	4.34	580	112	0.10	2.19	0.46	4.10
PQBD 5	530	4.39	631	101	0.39	2.18	1.79	2.80
PQBD 6	482	4.16	577	95	0.81	2.96	2.74	0.64

[a]: λ_{max} =Absorption maximum;[b] λ_{em} =emission maximum; [c] SS= Stokes shift; [d] Φ_F = fluorescence quantum yield (rhodamine 6G was used as a reference dye, Φ_F = 0.95 in water); [e] $k_f=\Phi_F \times \tau$; $k_{nr} = (1 - \Phi_F)/\tau$.

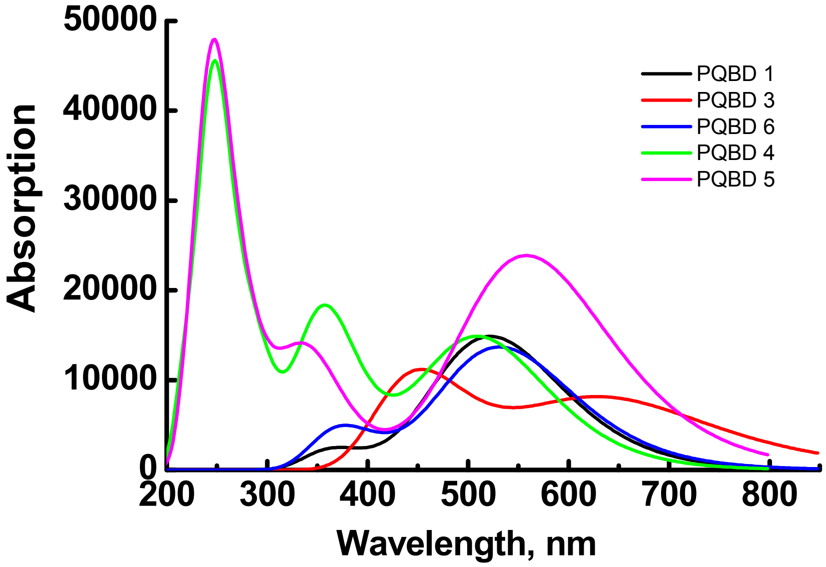


Figure S3. Theoretical absorption spectrum of compounds **PQBD 1**, **3**, **4**, **5**, and **6** calculated by TD-DFT.

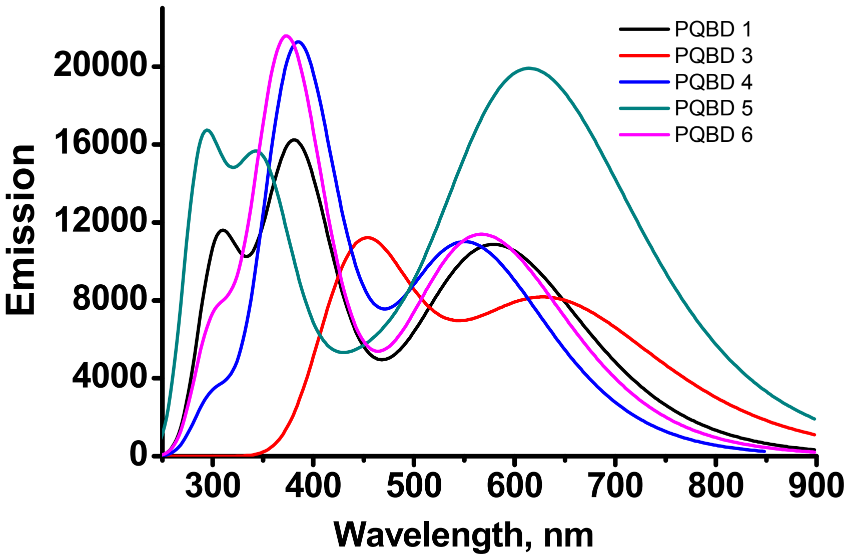


Figure S4. Theoretical emission spectrum of compounds **PQBD 1**, **3**, **4**, **5**, and **6** calculated by TD-DFT.

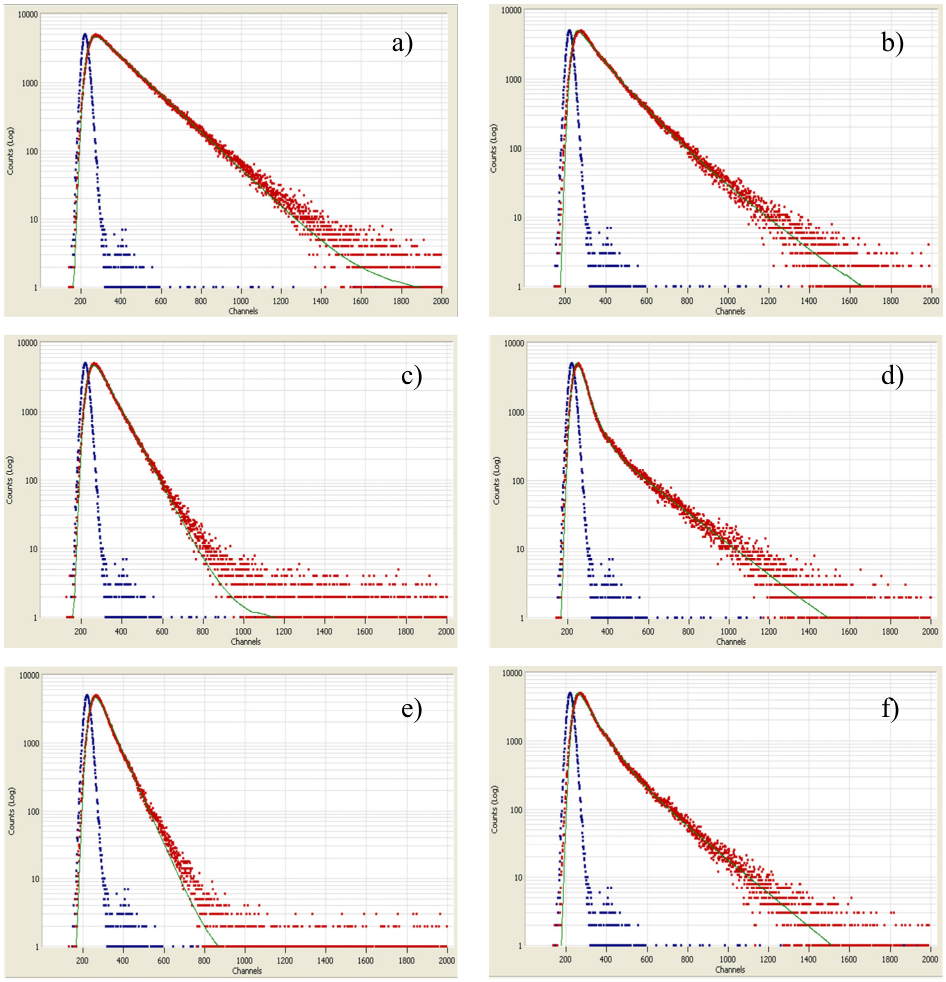


Figure S5. Lifetime decay profiles of **PQBD 1** (a), **PQBD 2** (b), **PQBD 3** (c), **PQBD 4** (d), **PQBD 5** (e), and **PQBD 6** (f) in dichloromethane.

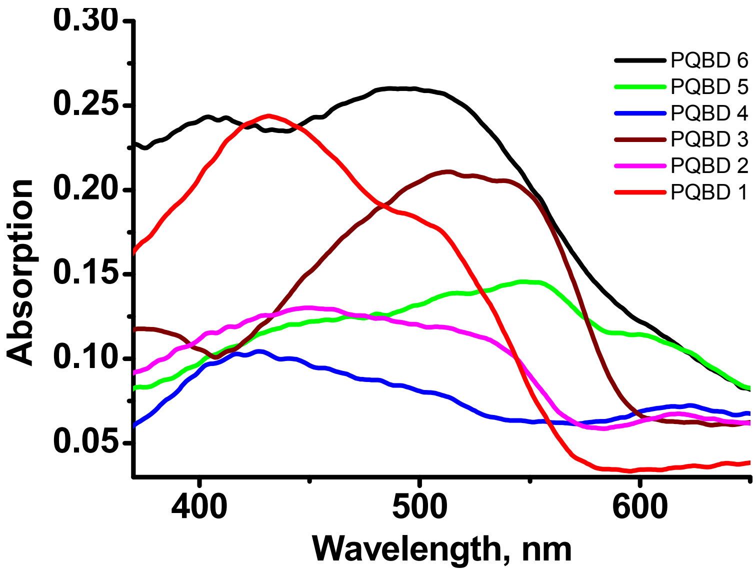


Figure S6. Normalized absorption of **PQBD 1**–**6** in the solid state.

Table S2. Photophysical data of **PQBD 1-6** in the solid state.

Compound	λ_{max} (nm)	λ_{em} (nm)	SS (nm)	Φ_{solid}	CIE_x	CIE_y
PQBD 1	431, 500	622	160	0.184	0.63	0.36
PQBD 2	449, 515	610	133	0.182	0.57	0.42
PQBD 3	513, 540	640	125	0.018	0.64	0.36
PQBD 4	427, 504	642	187	0.032	0.61	0.39
PQBD 5	514, 547	658	120	0.035	0.64	0.35
PQBD 6	404, 486	586	146	0.051	0.54	0.45

SS = Stokes shift; Φ_F = fluorescence quantum yield (measured by using an integrating sphere with an error of ±3%);

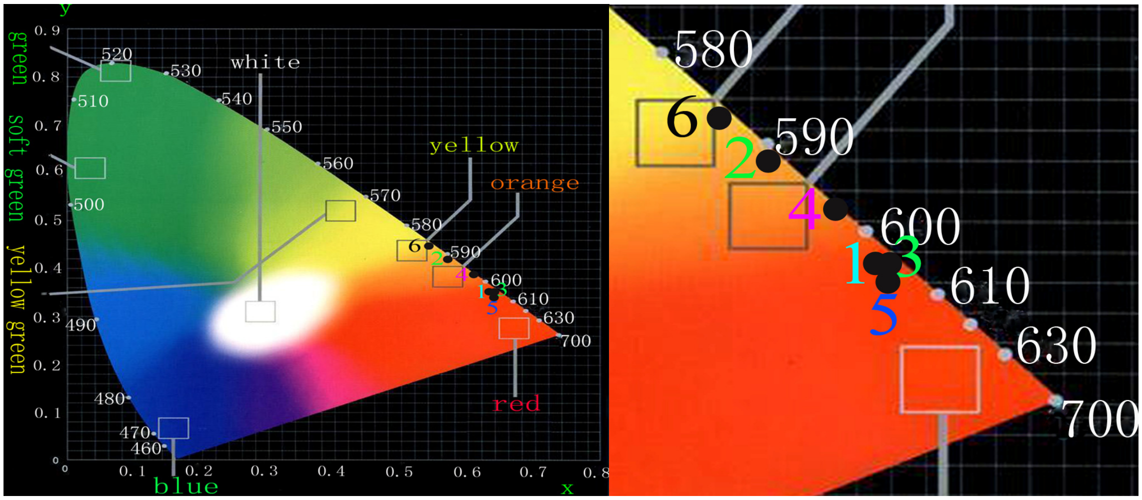


Figure S7. Left: Emission colors of dyes **PQBD 1-6** in the solid state, **PQBD 1**: (0.63, 0.36), **PQBD 2**: (0.57, 0.42), **PQBD 3**: (0.64, 0.36), **PQBD 4**: (0.61, 0.39), **PQBD 5**: (0.64, 0.35), **PQBD 6**: (0.54, 0.45) in a CIE 1931 chromaticity diagram. Right: The magnification of the left graph in the red area. For clarity, **PQBD 1**, **3**, **4**, **5**, and **6** are simplified as **1**, **3**, **4**, **5**, and **6** in the figure.

Table S3. Crystal data structure refinement for **PQBD 1-2**.

	single crystals	
	PQBD 1	**PQBD 2**
Empirical formula	$C_{24}H_{14}BF_2N_3$	$C_{48}H_{26}B_2N_6O_6$
Formula weight	393.19	756.37
Temperature/K	293.0	293.0
Crystal system	monoclinic	triclinic
Space group	*P*2(1)/c	*P-1*
a/Å	12.5133	13.009
b/Å	8.5931	14.636
c/Å	17.3356	22.764
α/°	90	78.187
β/°	107.854	75.189
γ/°	90	79.830
V/Å^3	1774.3	4066
Z	4	4
ρ_{calc} mg/m^3	1.472	1.236
m/mm^{-1}	0.102	0.078
F(000)	808	1560
Crystal size/mm^3	0.212×0.156×0.123	0.154×0.132×0.045
2Θrange for data collection	1.71 to 25.99°	1.58 to 25.05
Index ranges	$-15 \le h \le 15$, $-10 \le k \le 10$, $-21 \le l \le 20$	$-14 \le h \le 15$, $-16 \le k \le 17$, $0 \le l \le 27$
Reflections collected	10435	14370
Independent reflections	3488[R(int)= 0.0391]	14370[R(int)= 0.0000]
Data/restraints/parameters	3488/0/271	14370/0/1063
Goodness-of-fit on F^2	1.012	0.756
Final R indexes [I>2σ (I)]	$R_1 = 0.0423$, $wR_2 = 0.1019$	$R_1 = 0.0923$, $wR_2 = 0.1931$
Final R indexes [all data]	$R_1 = 0.0655$, $wR_2 = 0.1132$	$R_1 = 0.2637$, $wR_2 = 0.2354$
Largest diff. peak/hole/ e Å^{-3}	0.174/-0.197	0.331/-0.271

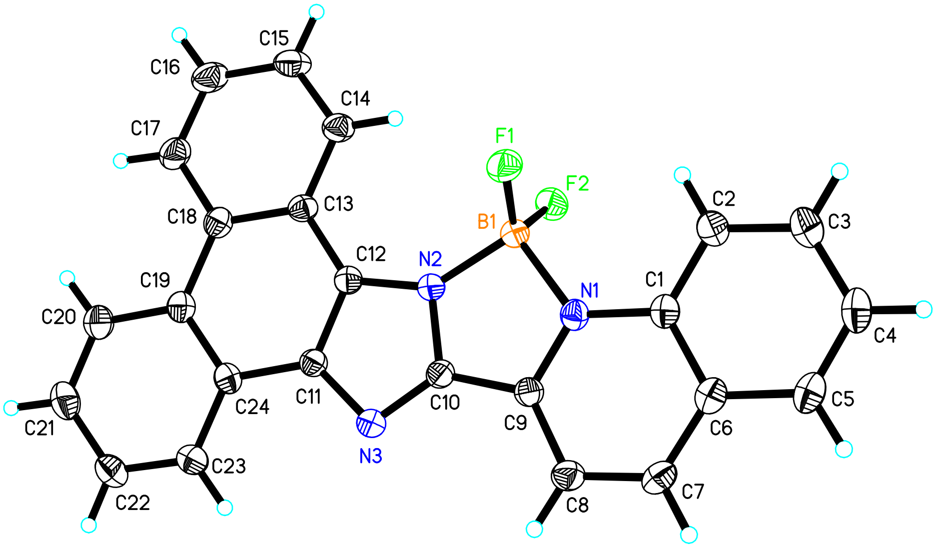


Figure S8. X-ray crystal structure of **PQBD 1** with 50% probability.

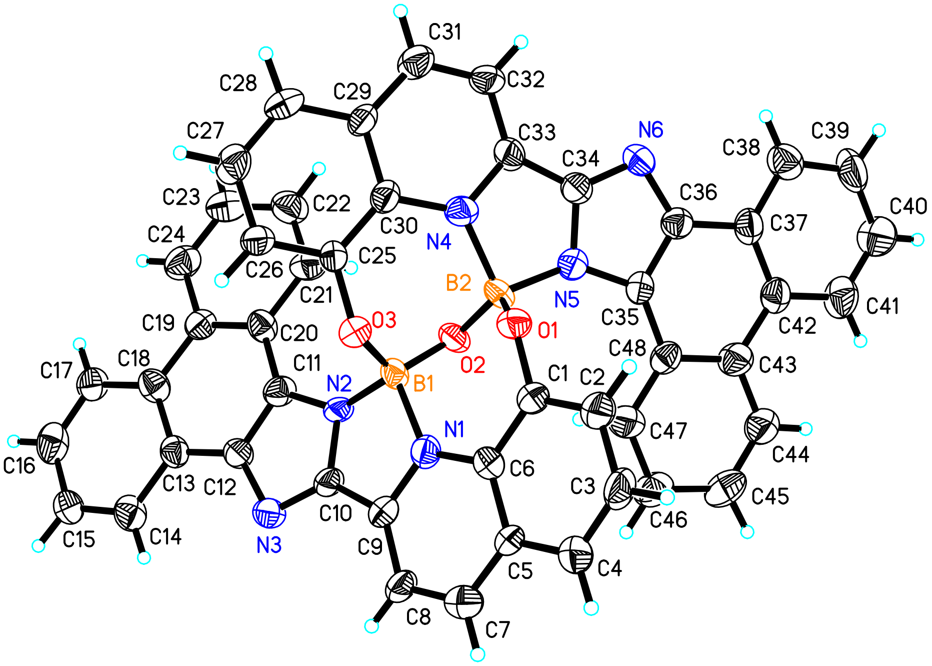


Figure S9. X-ray crystal structure of **PQBD 2** with 50% probability.

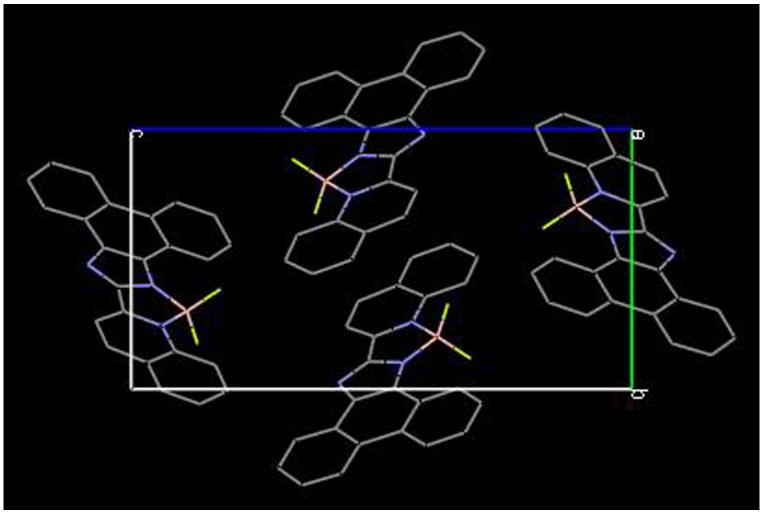


Figure S10. A part of a crystal-packing pattern of **PQBD 1** along the a axis. Hydrogen atoms have been omitted for clarity.

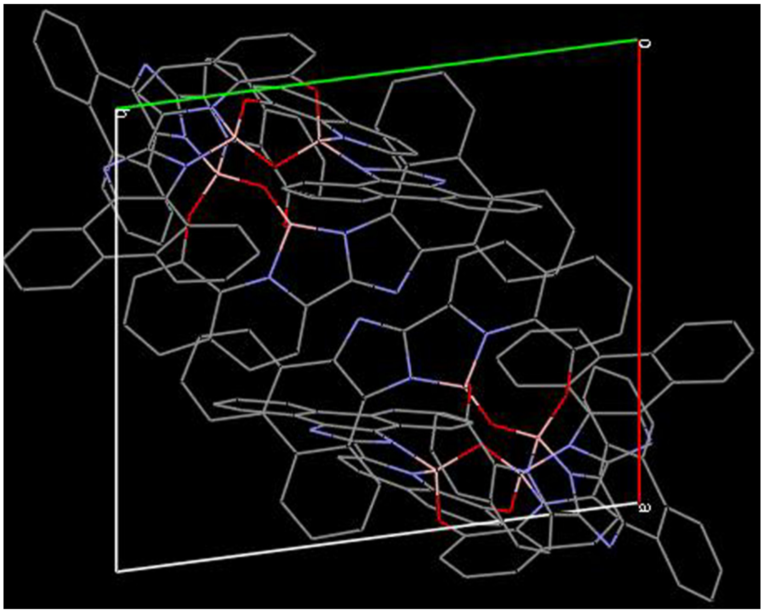
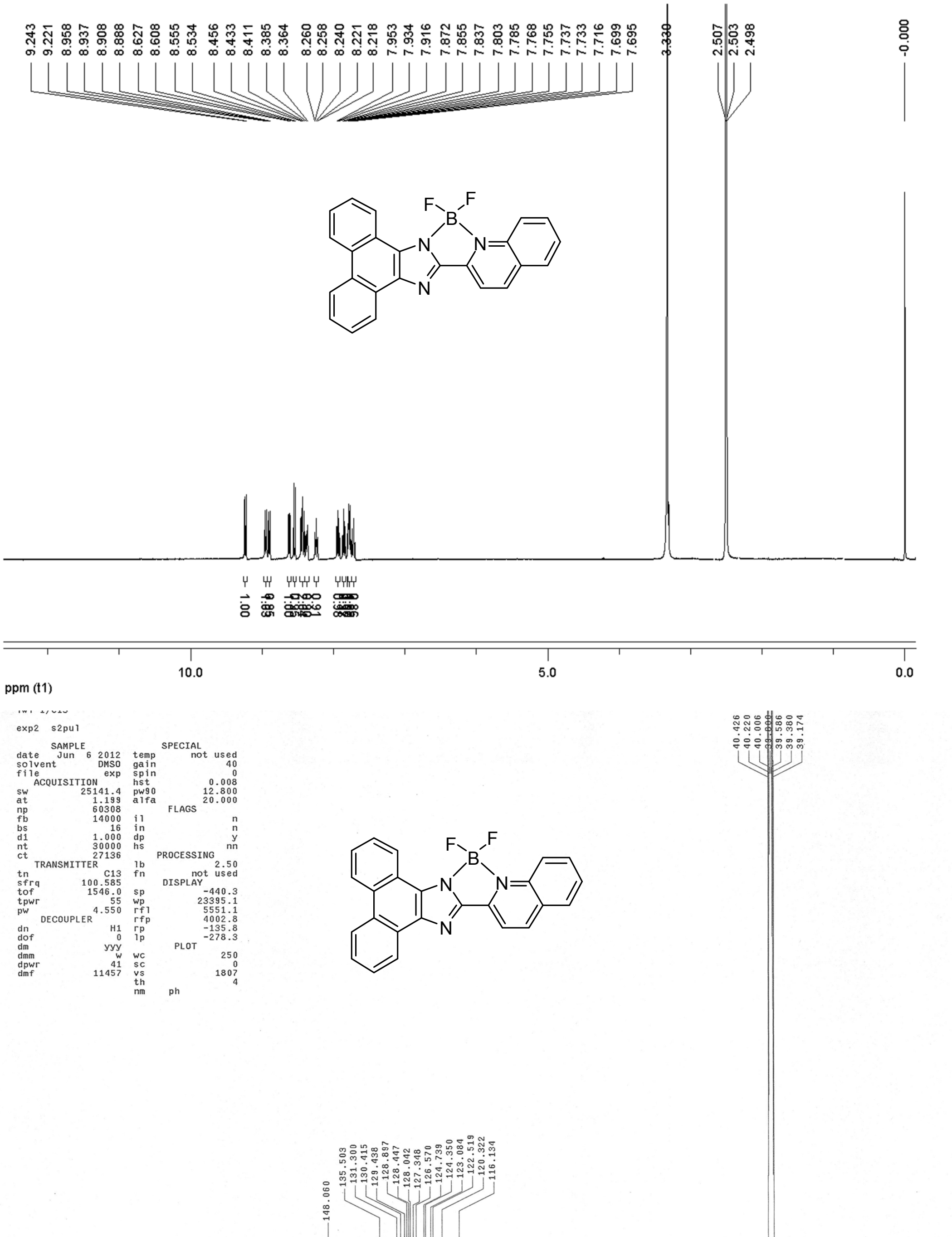


Figure S11. A part of a crystal-packing pattern of **PQBD 2** along the c axis. Hydrogen atoms have been omitted for clarity.



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bs               16  in                 n
d1            1.000  dp                 y
nt            30000  hs                nn
ct            27136        PROCESSING
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pw            4.550  rfl           5551.1
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Figure S12. ^{1}H and ^{13}C NMR spectra of **PQBD 1** in *d6*-DMSO.

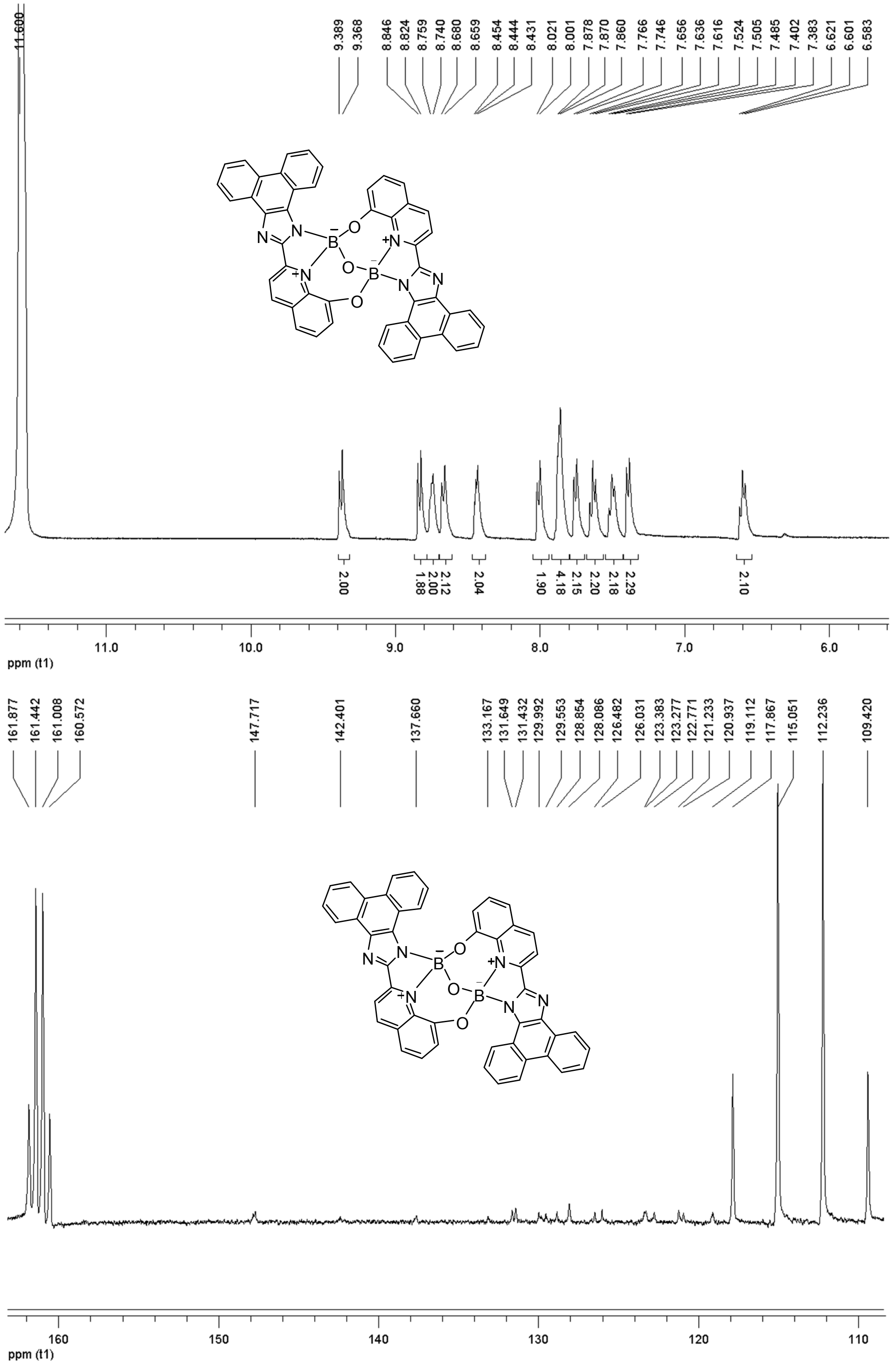


Figure S13. ^{1}H and ^{13}C NMR spectra of **PQBD 2** in *d*-TFA.

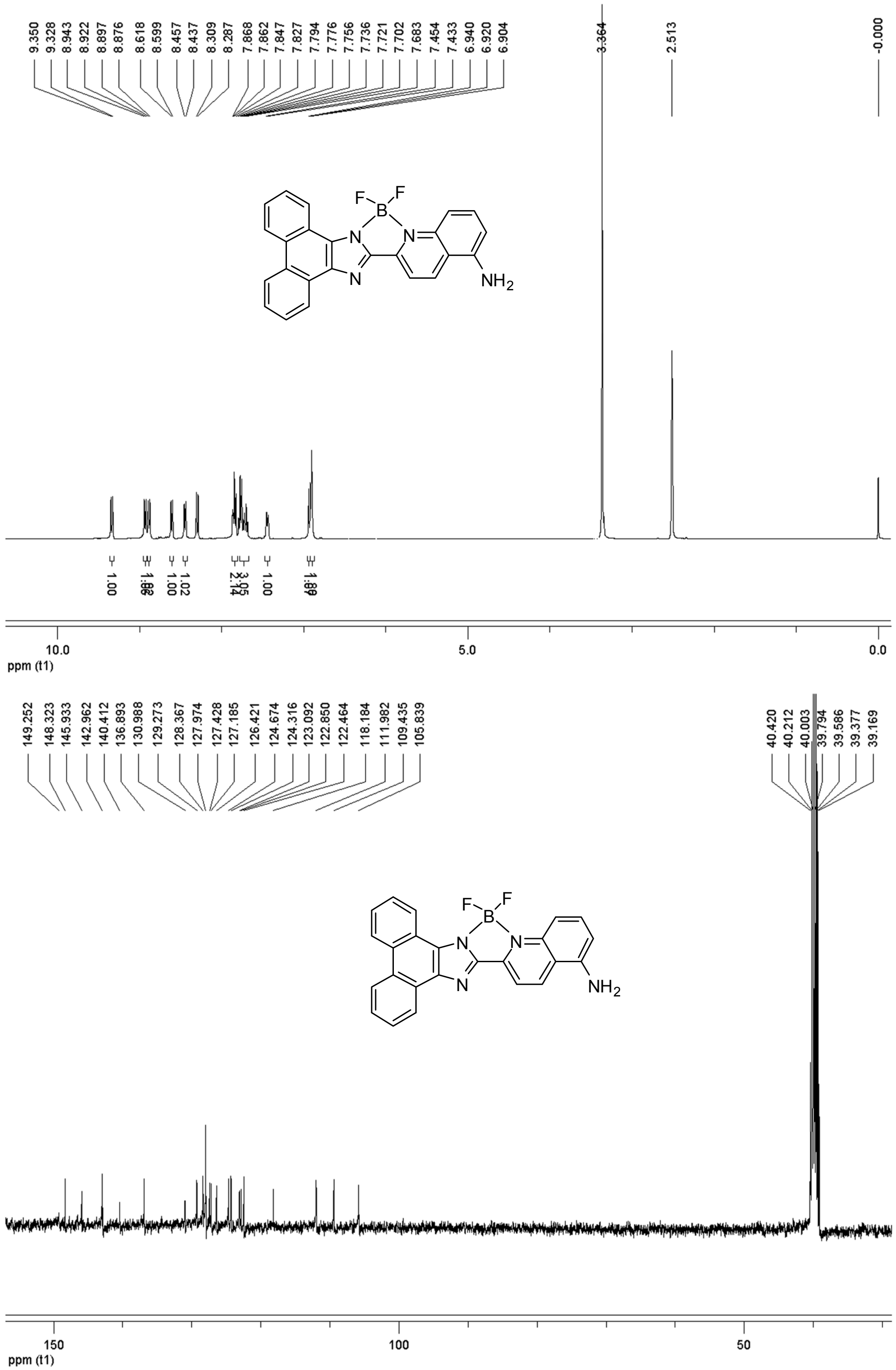
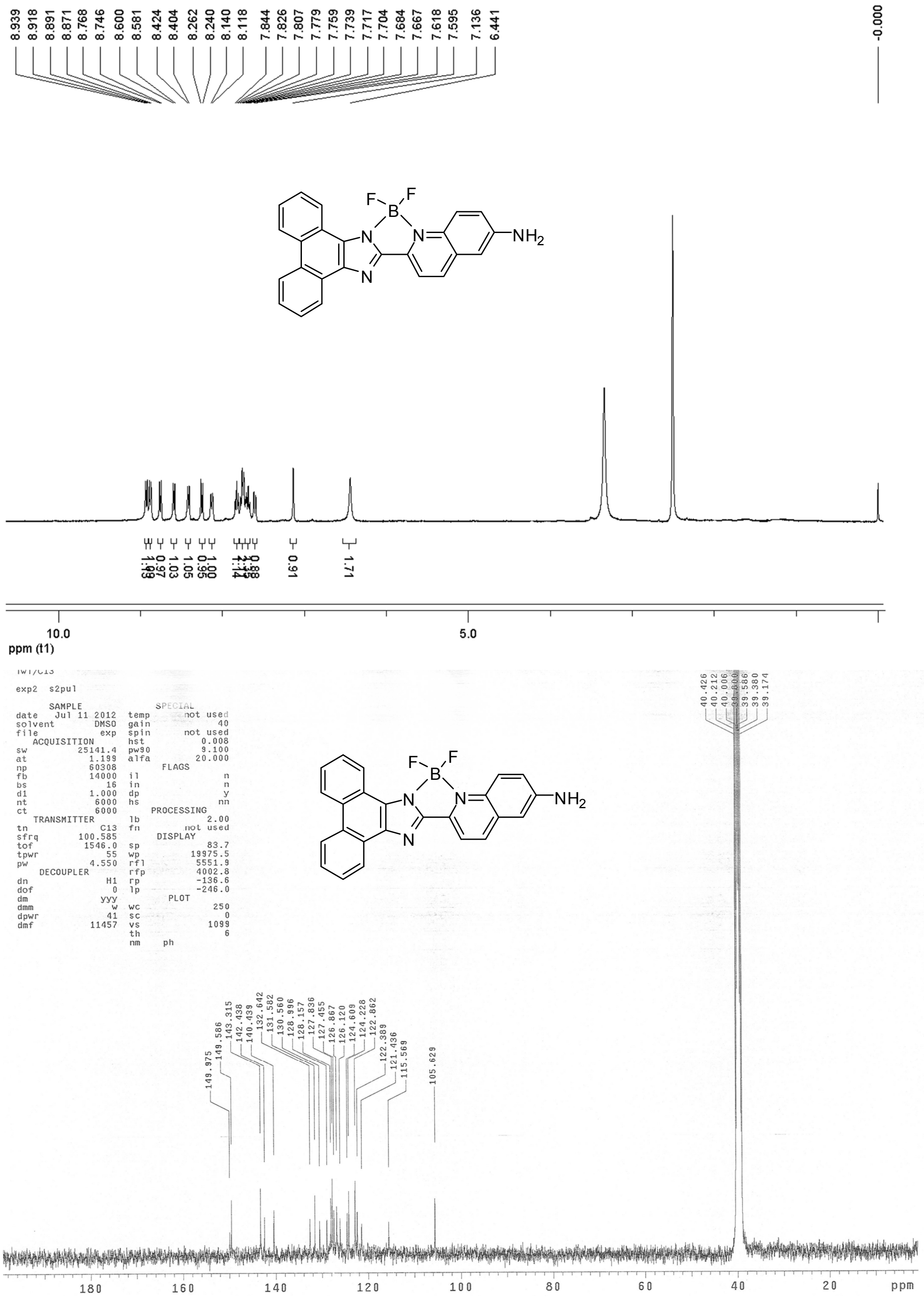


Figure S14. ^{1}H and ^{13}C NMR spectra of **PQBD 4** in *d6*-DMSO



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at            1.199  alfa          20.000
np            60308           FLAGS
fb            14000  il                 n
bs               16  in                 n
d1            1.000  dp                 y
nt             6000  hs                nn
ct             6000        PROCESSING
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tn              C13  fn          not used
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pw            4.550  rfl           5551.9
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dpwr             41  sc                 0
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                     nm    ph
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Figure S15. ^1H and ^{13}C NMR spectra of **PQBD 6** in *d6*-DMSO

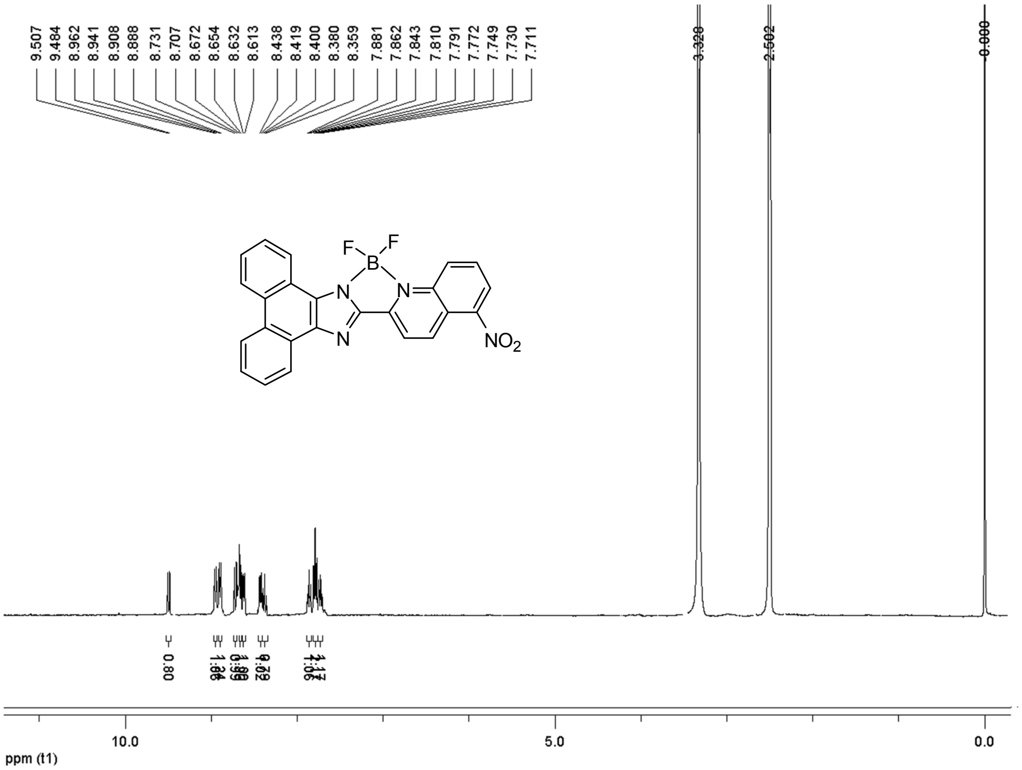

Figure S16. ^{1}H NMR spectra of **PQBD 3** in *d6*-DMSO

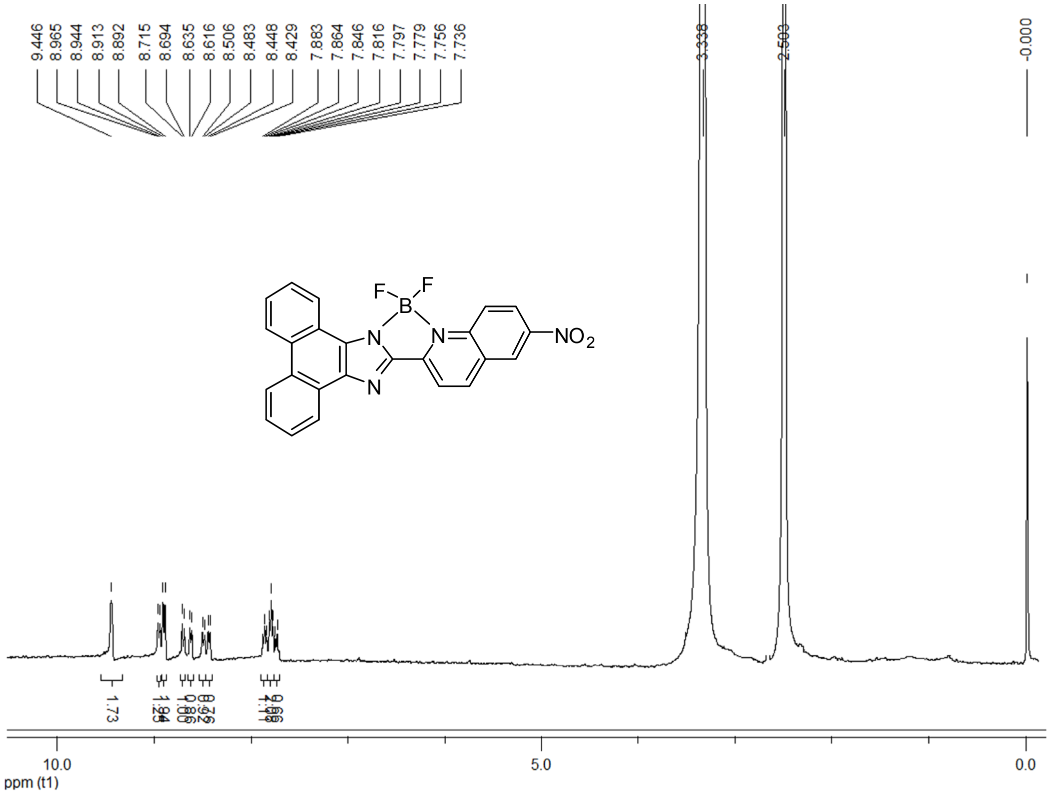

Figure S17. ^{1}H NMR spectra of **PQBD 5** in *d6*-DMSO

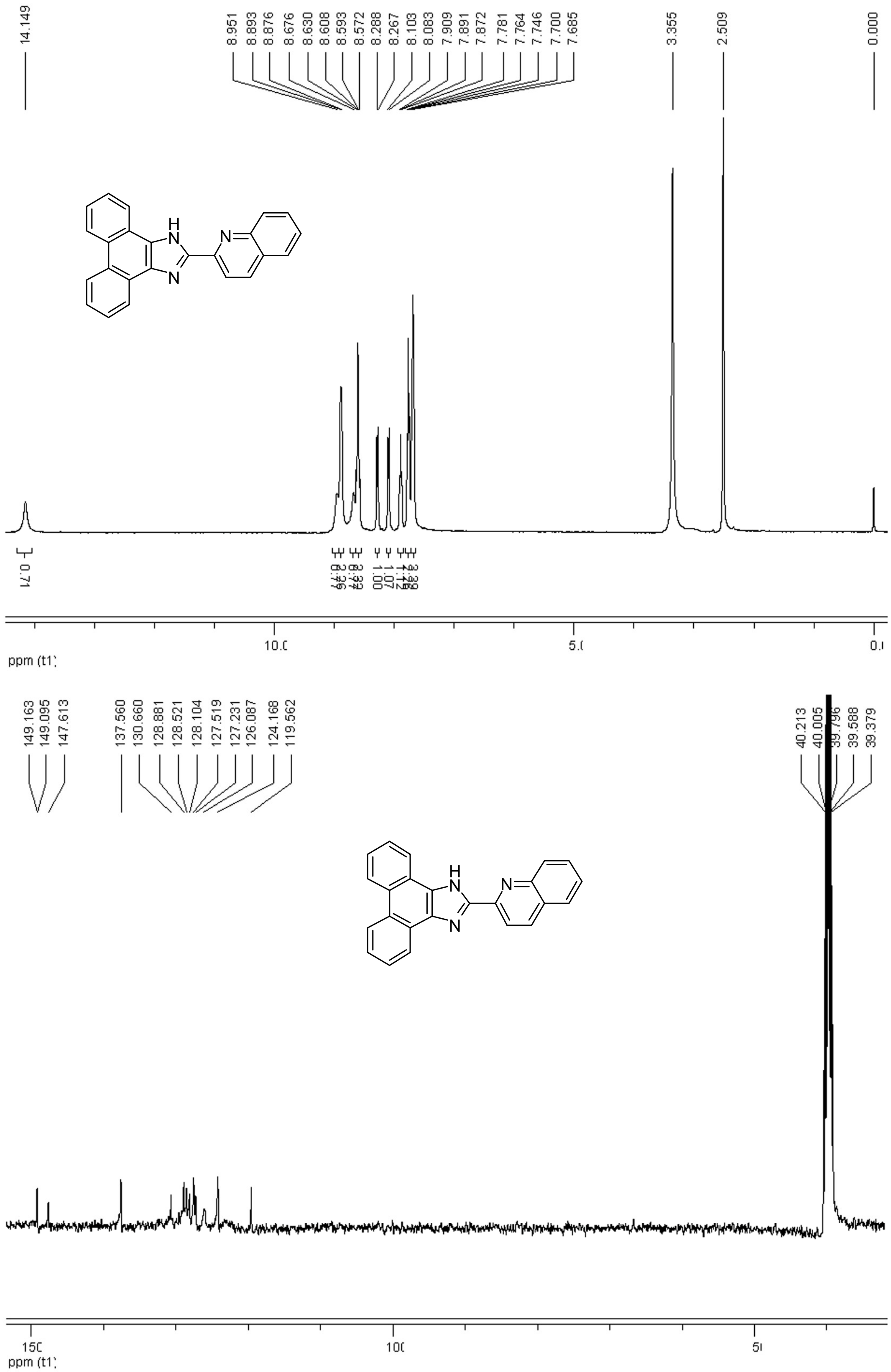

Figure S18. ^{1}H and ^{13}C NMR spectra of compound **7** in *d6*-DMSO

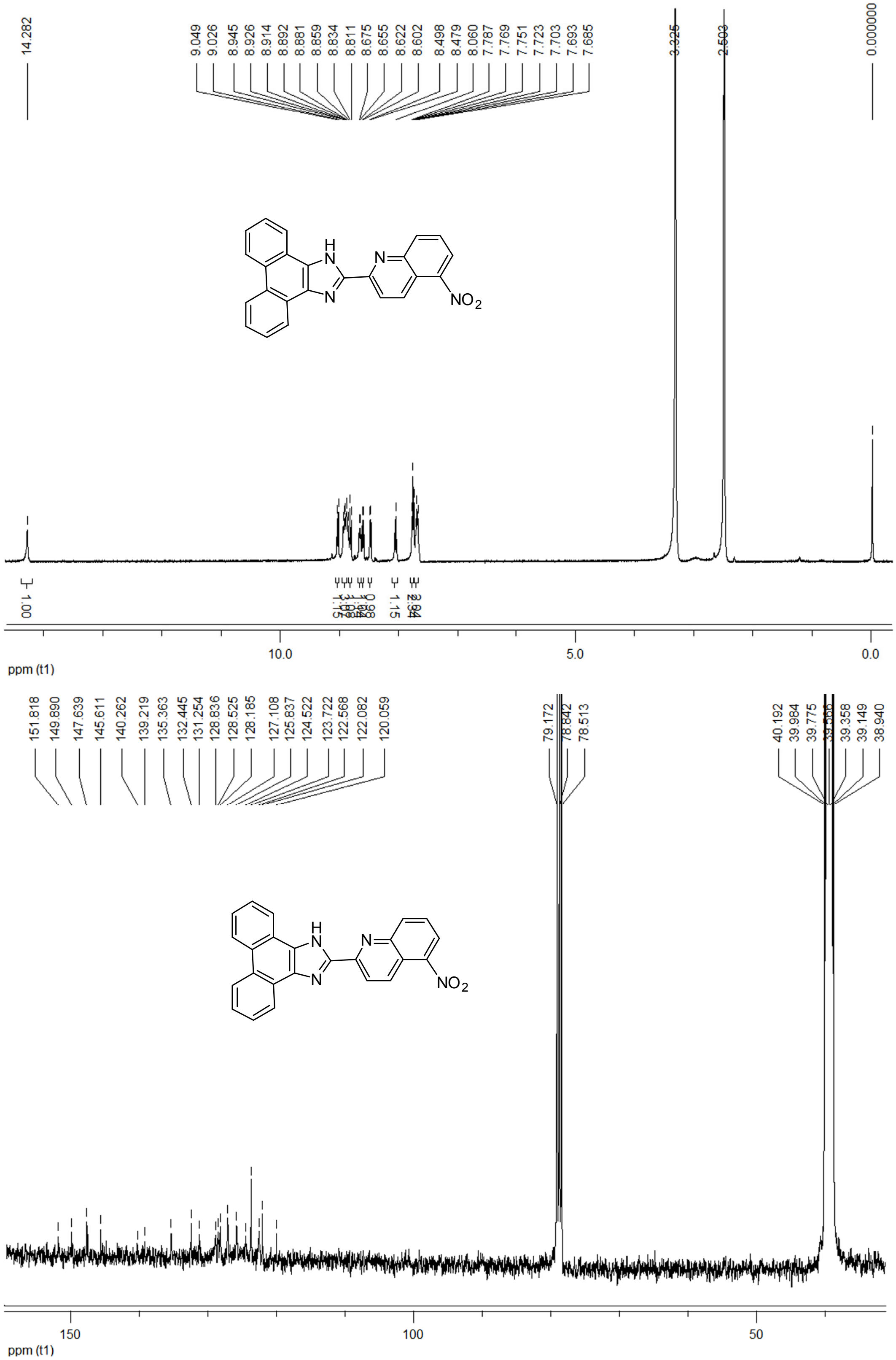

Figure S19. ^{1}H and ^{13}C NMR spectra of compound **9** in *d6*-DMSO

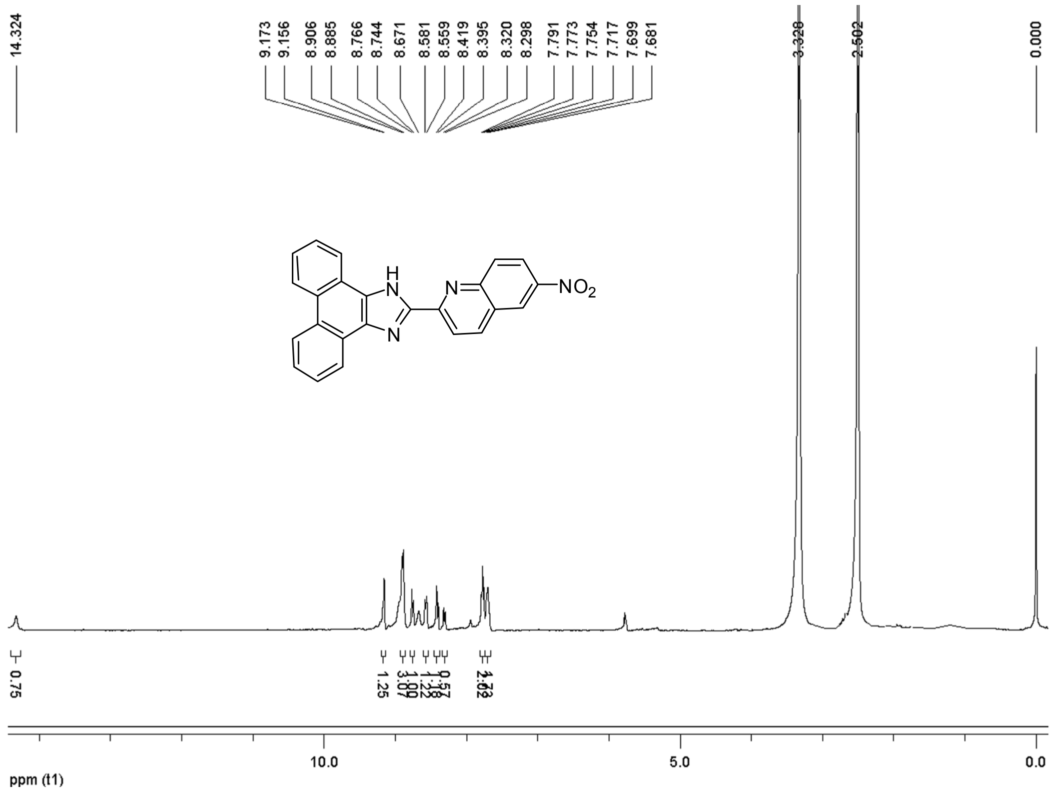

Figure S20. ^{1}H NMR spectra of compound **10** in *d6*-DMSO