

SUPPORTING INFORMATION

Bis-naphthobipyrrolylmethene derived BODIPY complex: An intense near-infrared fluorescent dye

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Instrumentation and reagents:

NMR spectra were recorded on a Bruker Avance-400 MHz FT NMR spectrometer using tetramethylsilane (TMS, $\delta = 0$) as an internal standard at room temperature. Spectroscopic grade solvents were used for all absorbance, fluorescence and quantum yield measurement. Mass spectral determinations were carried out by Bruker Maxis HRMS by ESI techniques. UV-Visible spectra were recorded on a Perkin Elmer Lambda 35 UV-Visible spectrometer. Fluorescence was recorded on HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer. Crystallographic data for compounds **8** and **9** were collected on BRUKER SMART-APEX CCD diffractometer. Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation was used to collect X-ray reflections on the single crystal. Data reduction was performed using Bruker SAINT^{S1} software. Intensities for absorption were corrected using SADABS^{S2} and refined using SHELXL-97^{S3} with anisotropic displacement parameters for non-H atoms. Hydrogen atoms on N were experimentally located in difference electron density maps. All C-H atoms were fixed geometrically using HFIX command in SHELX-TL. A check of the final CIF file using PLATON^{S4} did not show any missed symmetry. The CCDC numbers of compounds **8** and **9** are 946926 and 946927.

Fluorescence lifetime measurements were carried out using a time correlated single-photon counting (TCSPC) spectrometer (Horiba Jobin Yvon IBH). Nano LED source (λ_{exc} 639 nm) was used as the excitation source and an MCP photomultiplier (Hamamatsu R3809U-50) as the detector. The pulse repetition rate of the laser source was 1MHz. The width of the instrument response function, which was limited by the fwhm of the exciting pulse, was around 100 ps. The

lamp profile was recorded by placing a scatterer (dilute solution of Ludox in water) in place of the sample. The time resolved emission decay profiles were collected at steady state emission maxima. Decay curves were analyzed by nonlinear least-squares iteration procedure using IBH DAS6 (Version 2.2) decay analysis software. The quality of the fit was assessed by inspection of the χ^2 values and the distribution of the residuals.

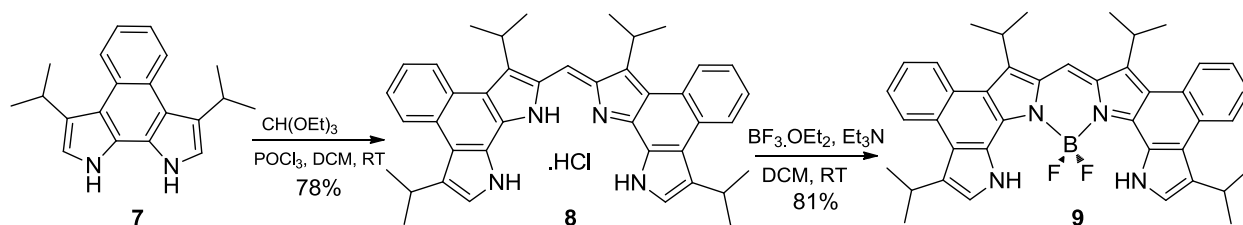
^{S1} SAINT, version 6.45 /8/6/03, Bruker AXS, **2003**.

^{S2} Sheldrick, G. M.; *SADABS*, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, **1997**.

^{S3} Sheldrick, G. M.; *SHELXS-97* and *SHELXL-97*, Programs for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany, **1997**.

^{S4} (a) Spek, A. L.; *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **2002**; (b) Spek, A. L.; *J. Appl. Cryst.* **2003**, *36*, 7-13.

Reaction Scheme:



Synthetic Procedure:

Synthesis of 8: Di-isopropyl-naphthobipyrrole **7** (200 mg, 0.69 mmol) was placed in a 50 mL round bottom flask fitted with nitrogen inlet and stirring bar. Dissolved in 20 mL dichloromethane. To this solution triethylorthoformate (0.116 mL, 0.69 mmol) was added, followed by addition of freshly distilled POCl₃ (0.032 mL, 0.34 mmol). The reaction mixture was stirred for overnight at room temperature. After completion of the reaction, reaction mixture was washed with water; organic layer was evaporated under reduced pressure. The dark green solid thus obtained was purified over a silica column using CH₂Cl₂ as eluent. Yield 78% (170 mg).

^1H NMR (400 MHz, CDCl_3): δ = 1.46 (d, J = 6.8 Hz, 12H, $-\text{CH}_3$ alkyl); 1.79 (d, J = 7.2 Hz, 12H, $-\text{CH}_3$ alkyl); 3.66 (m, 2H, $-\text{CH}$ alkyl); 4.35 (m, 2H, $-\text{CH}$ alkyl); 7.34 (s, 2H, α -CH pyrrole); 7.50 (m, 4H, CH naphthalene); 8.16 (s, 1H, CH meso); 8.38 (m, 4H, CH naphthalene); 11.70 (s, 2H, NH); 12.60 (s, 2H, NH); ^{13}C NMR (100 MHz, CDCl_3): δ = 23.54, 23.95, 26.70, 27.50, 119.15, 120.65, 121.92, 124.66, 124.80, 125.15, 125.74, 125.91, 126.07, 126.13, 129.30, 129.53, 129.71, 137.88, 149.22; HR-MS (ESI): m/z calcd for $\text{C}_{32}\text{H}_{86}\text{ClN}_8$: 1217.6664; found 1217.6664 [$2\text{M}-\text{Cl}$] $^+$.

Synthesis of 9: To a solution of **8** (600 mg, 0.96 mmol) dissolved in DICHLOROMETHANE (120 mL) was added triethylamine (4 mL, 28.7 mmol), stirred for 10 minutes. $\text{BF}_3\cdot\text{OEt}_2$ (5.4 mL, 43.2 mmol) was then added slowly. The reaction mixture was stirred for overnight at room temperature. After completion of the reaction, diluted with DICHLOROMETHANE (50 mL) washed with 1N HCl. Organic layer was dried over anhydrous Na_2SO_4 , evaporated to dryness. Purified over a silica column using CHCl_3 as eluent. Yield 496 mg (81%).

^1H NMR (400 MHz, CDCl_3): δ = 1.47 (d, J = 6.8 Hz, 12H, $-\text{CH}_3$ alkyl); 1.72 (d, J = 7.2 Hz, 12H, $-\text{CH}_3$ alkyl); 3.68 (m, 2H, $-\text{CH}$ alkyl); 4.24 (m, 2H, $-\text{CH}$ alkyl); 7.30 (s, 2H, α -CH pyrrole); 7.47 (m, 4H, CH naphthalene); 8.12 (s, 1H, CH meso); 8.37 (m, 4H, CH naphthalene); 9.99 (brs, 2H, NH); ^{13}C NMR (100 MHz, CDCl_3): δ = 23.72, 24.49, 26.83, 27.94, 122.15, 123.20, 124.54, 124.74, 125.02, 125.51, 125.70, 125.77, 127.00, 129.30, 129.64, 135.33, 139.62, 146.66; HR-MS (ESI): m/z calcd for $\text{C}_{41}\text{H}_{42}\text{BF}_2\text{N}_4$: 639.3471; found 639.3470 [$\text{M}+\text{H}$] $^+$; ^{11}B NMR (128 MHz, CDCl_3): δ = -6.58 (brs, 1B); ^{19}F NMR (376.4 MHz): δ = -138.64 (brs, 2F).

Figure S1: ^1H NMR Spectrum of compound 8 in CDCl_3 .

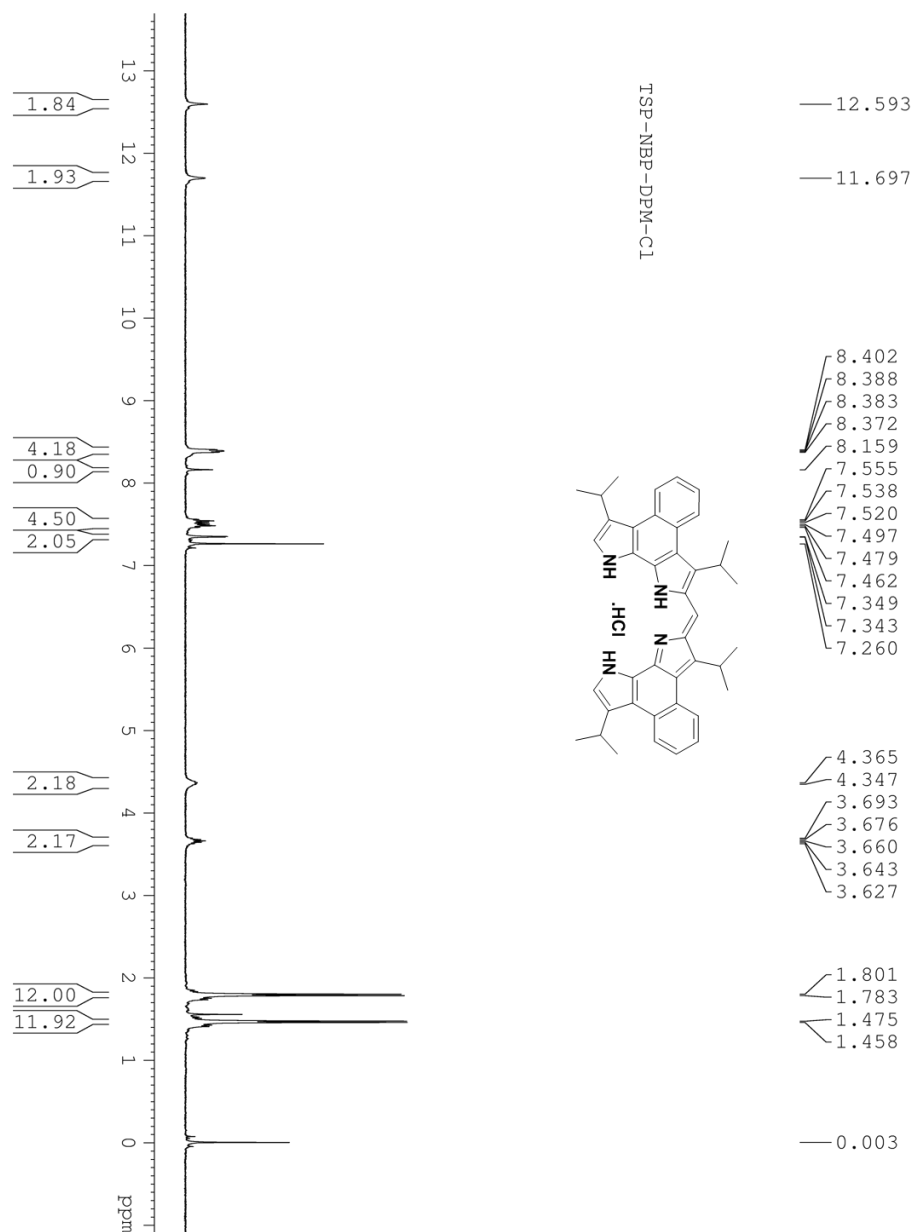


Figure S2: ^1H NMR Spectrum of compound 8 (D_2O exchange) in CDCl_3 .

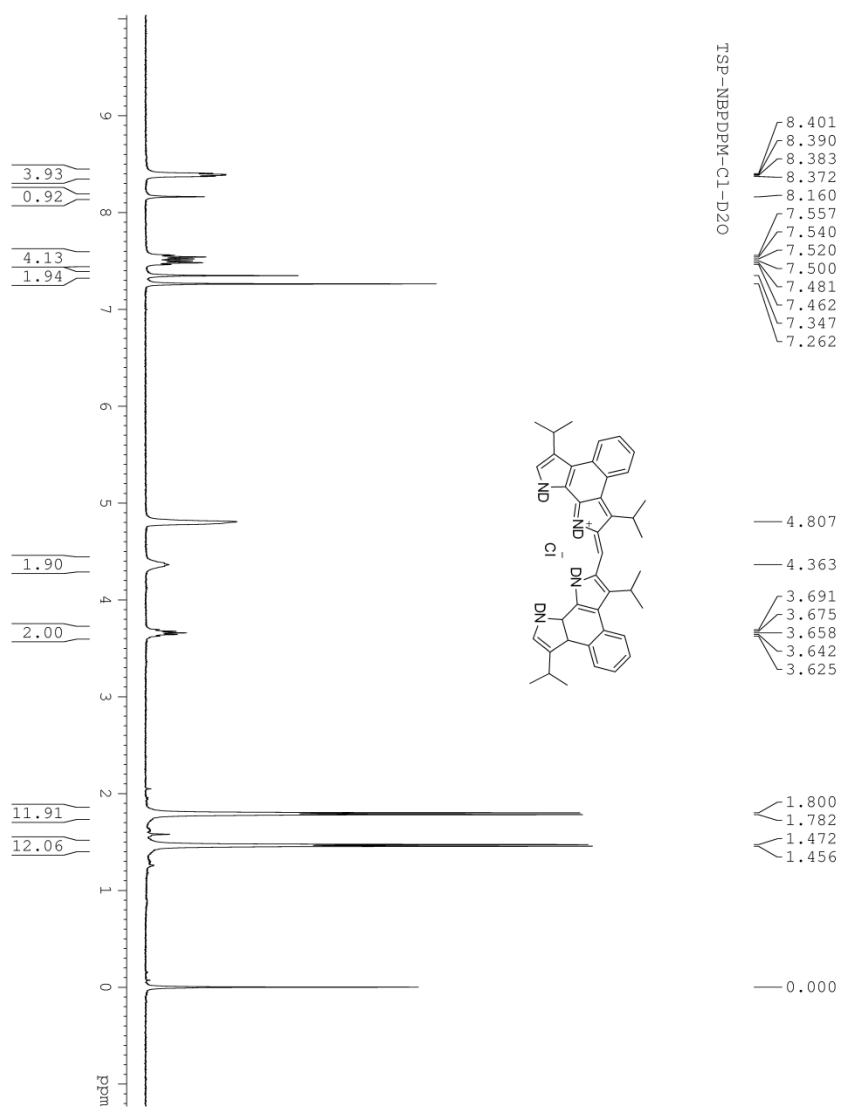


Figure S3: ^{13}C NMR Spectrum of compound 8 in CDCl_3 .

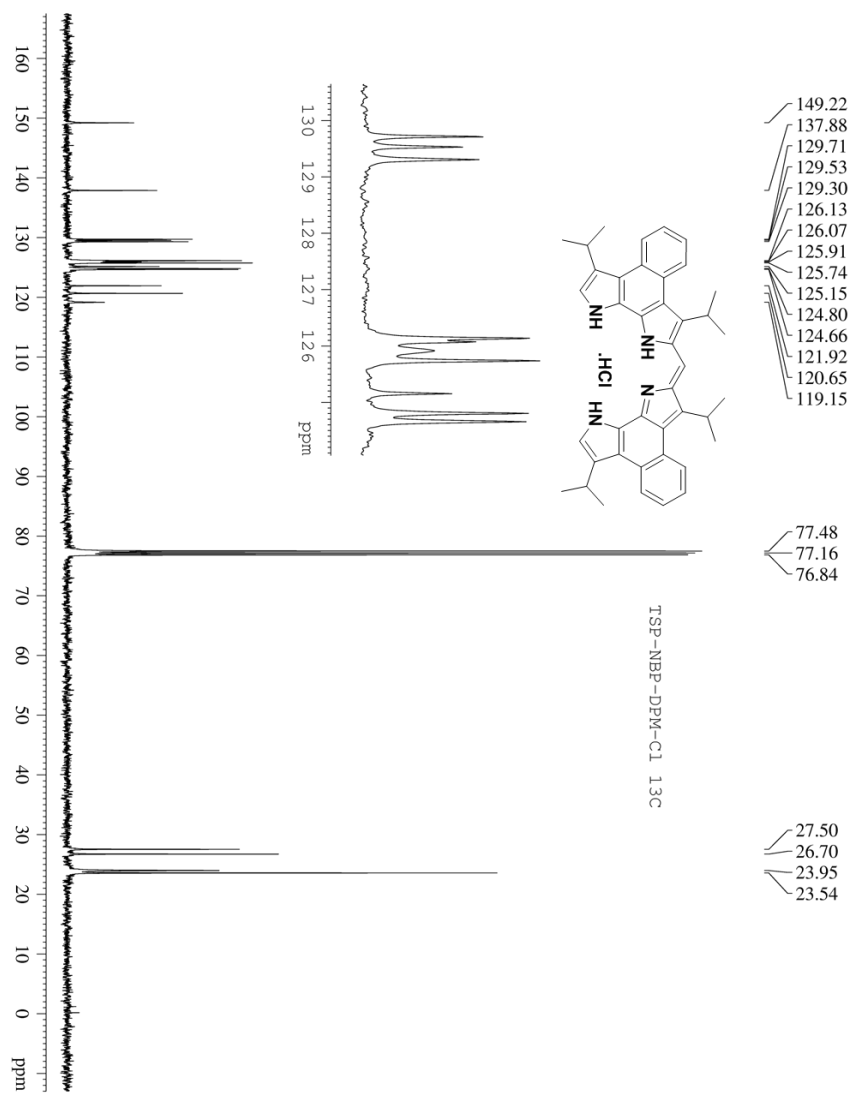


Figure S4: ^1H NMR Spectrum of compound 9 in CDCl_3 .

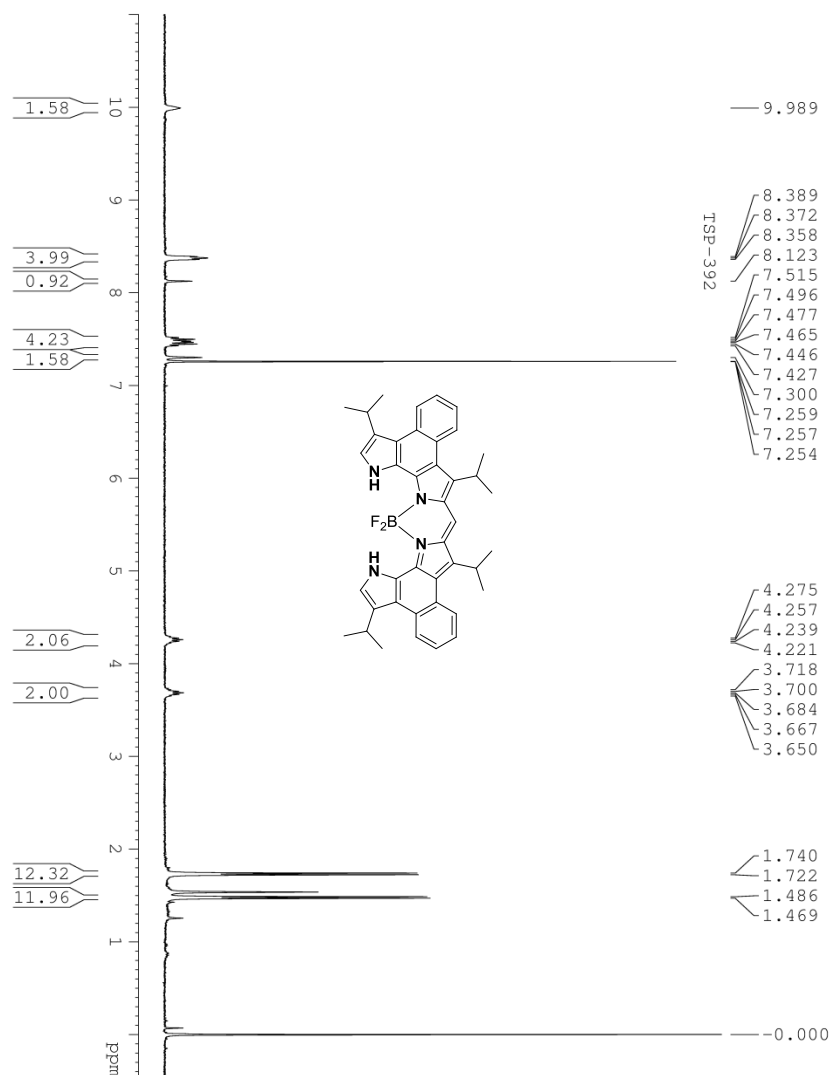


Figure S5: ^1H NMR Spectrum compound 9 (D_2O exchange) in CDCl_3 .

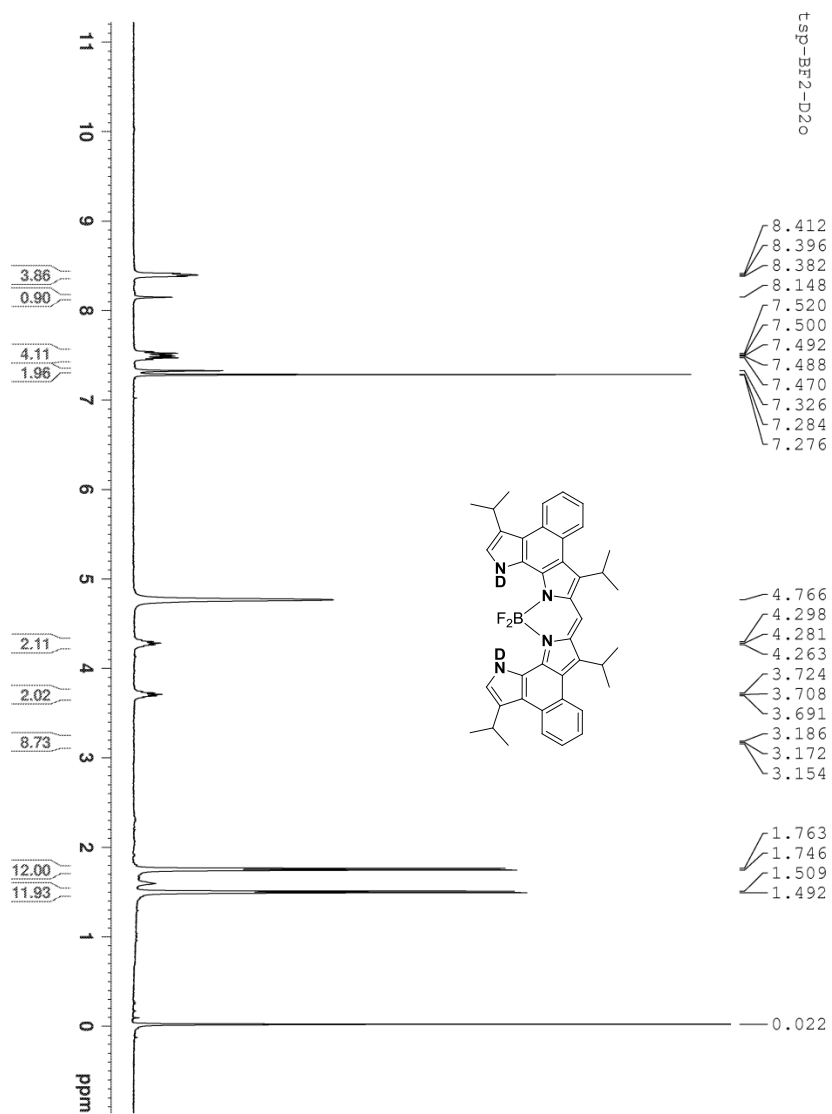


Figure S6: ^{13}C NMR Spectrum of compound 9 in CDCl_3 .

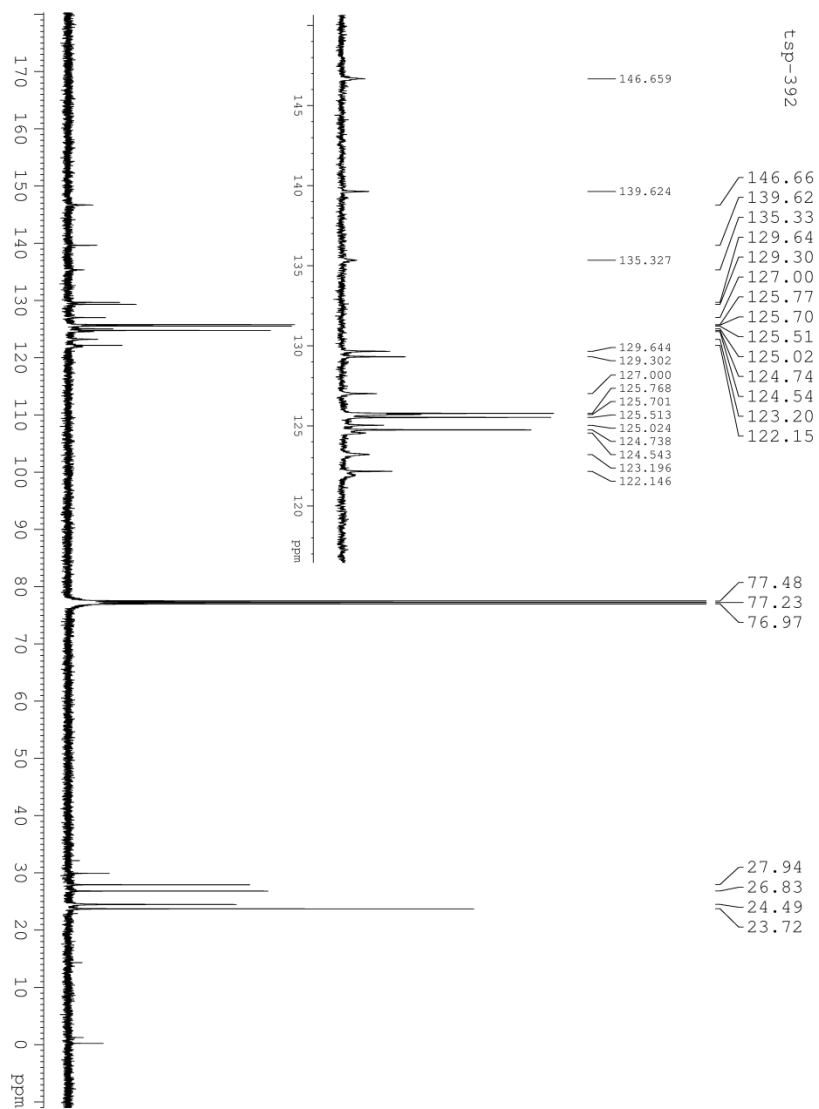


Figure S7: ^{11}B NMR Spectrum of compound 9 in CDCl_3 .

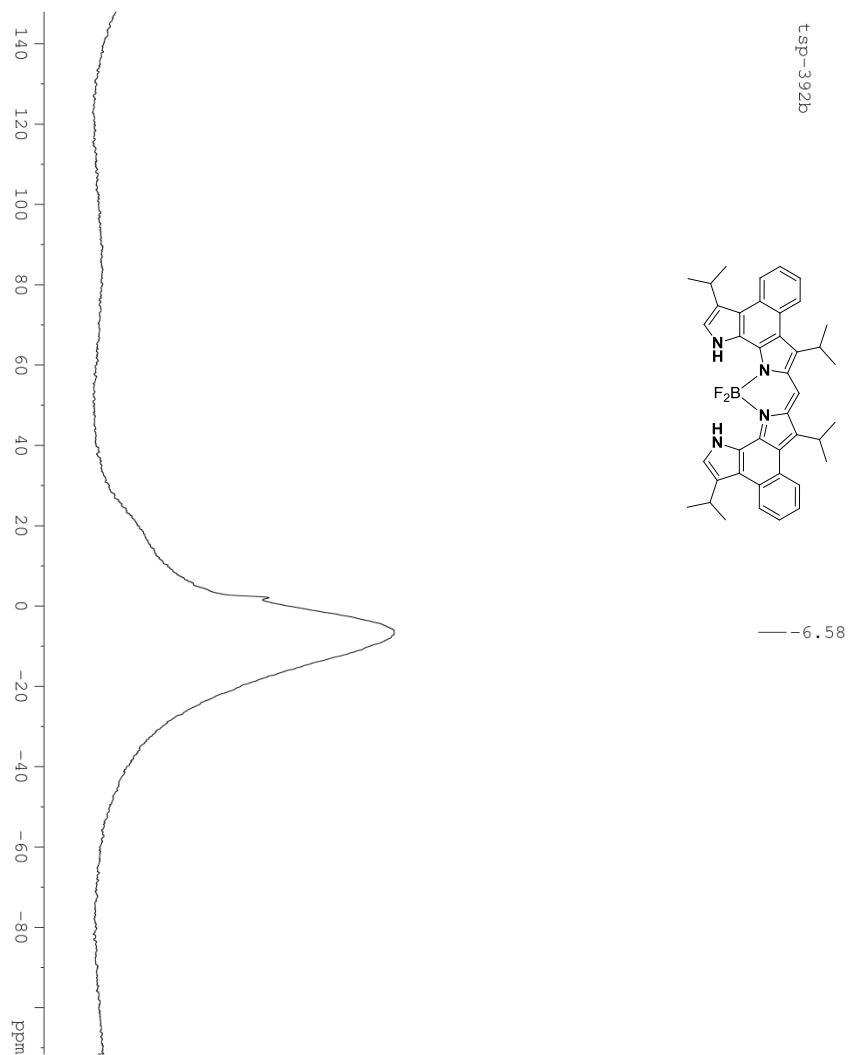


Figure S8: ^{19}F NMR Spectrum of compound 9 in CDCl_3 .

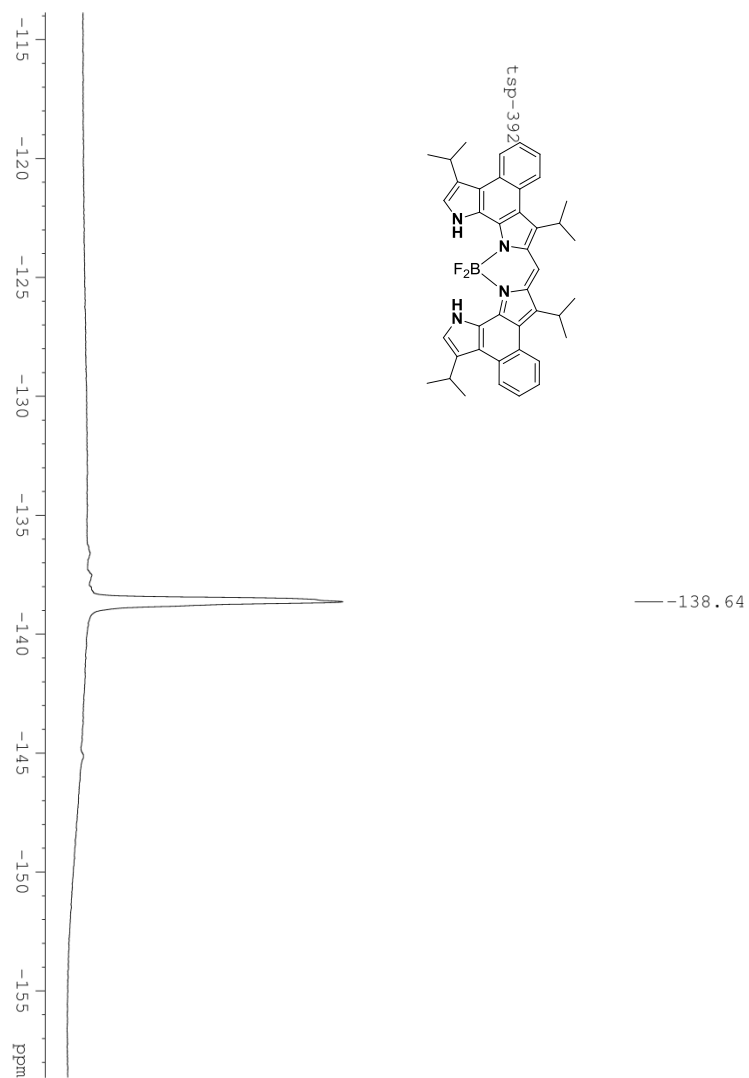


Figure S9: UV-vis spectra of compound 9 in different solvent.

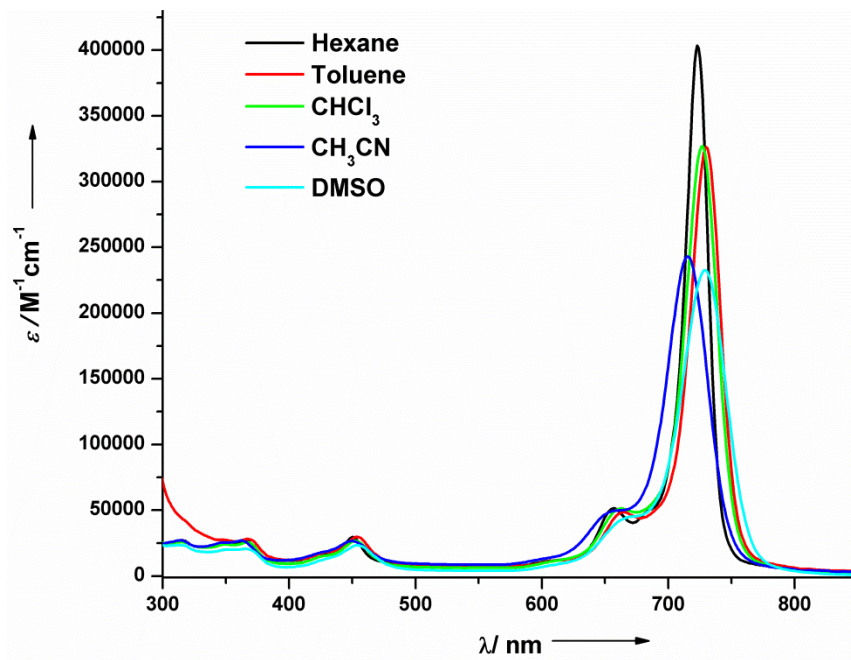


Figure S10: Normalized emission spectra of compound 9 in different solvent.

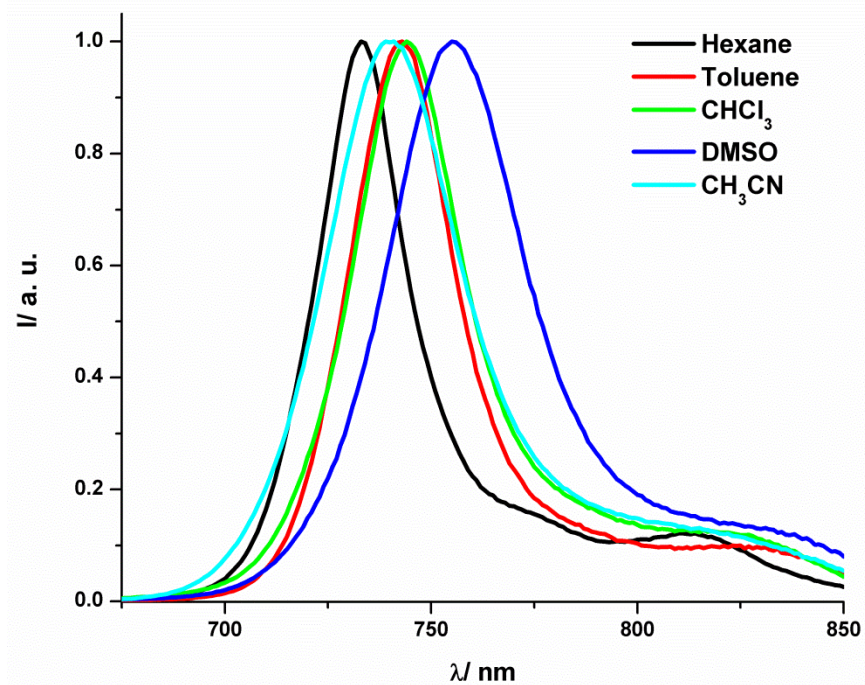


Figure S11: POV-Ray picture of packing pattern in crystal structure of compound 8.

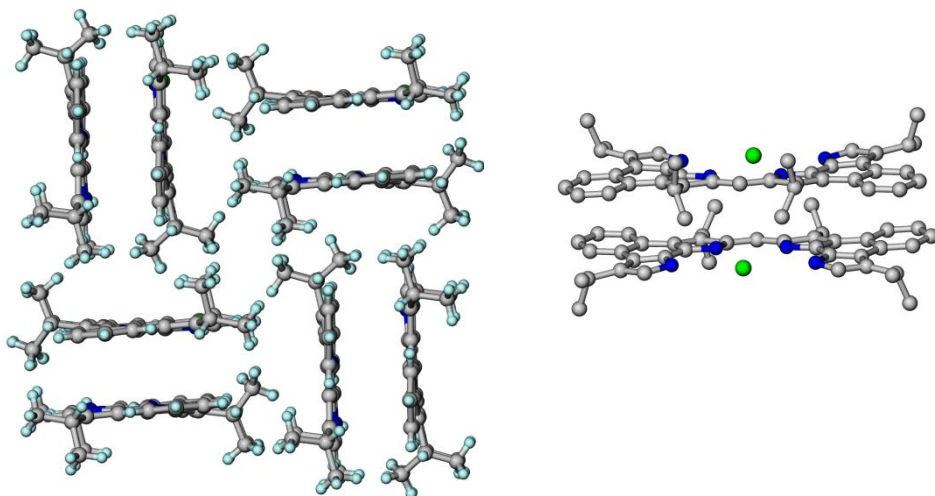


Figure S12: POV-Ray picture of packing pattern in crystal structure of compound 9.

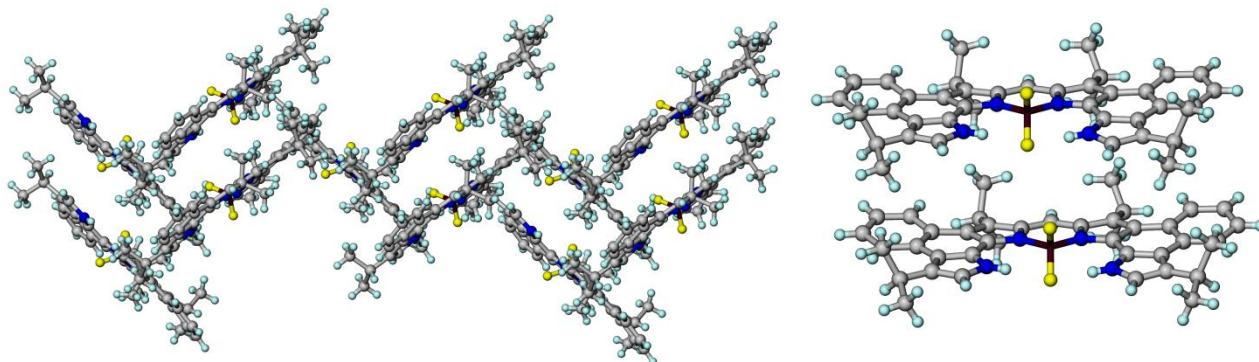


Figure S13 Excitation Spectra of 9 in hexane (emission at 790 nm).

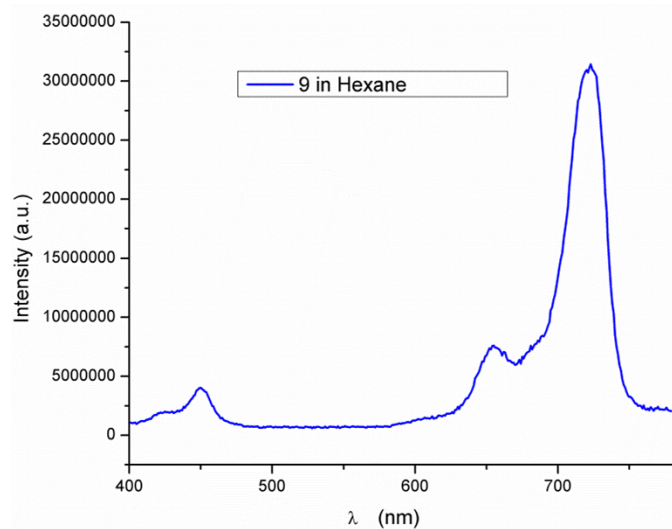


Figure S14 Excitation Spectra of 9 in toluene (emission at 790 nm).

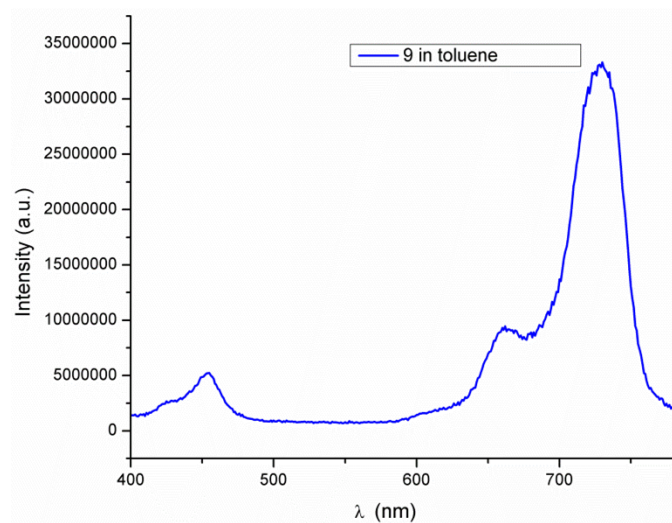


Figure S15 Excitation Spectra of 9 in CHCl_3 (emission at 790 nm).

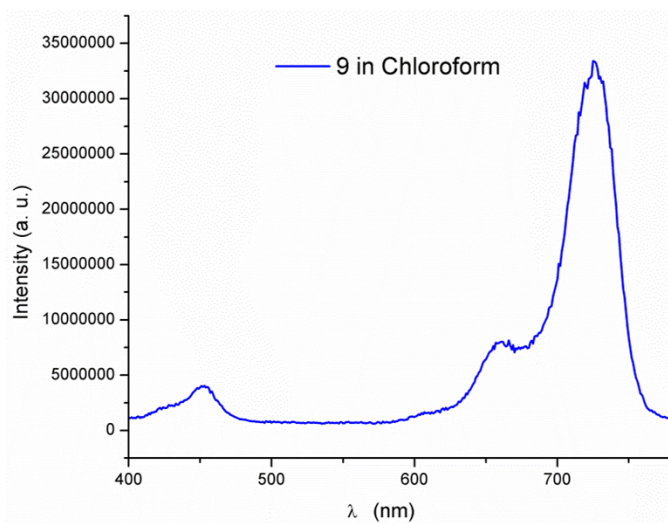


Figure S16 Excitation Spectra of 9 in acetonitrile (emission at 790 nm).

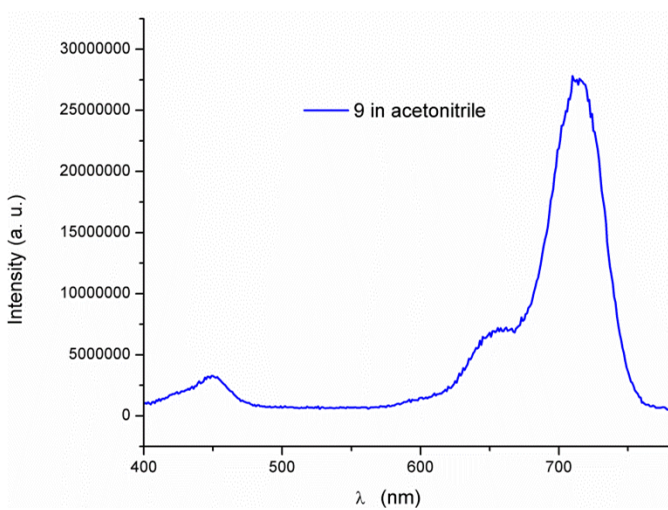


Figure S17 Excitation Spectra of 9 in DMSO (emission at 790 nm).

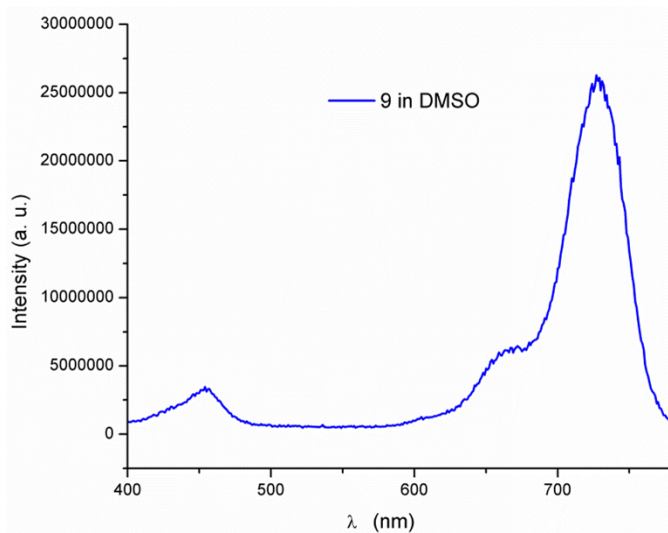


Figure S18 Fluorescence decay profile of 9 in different solvent.

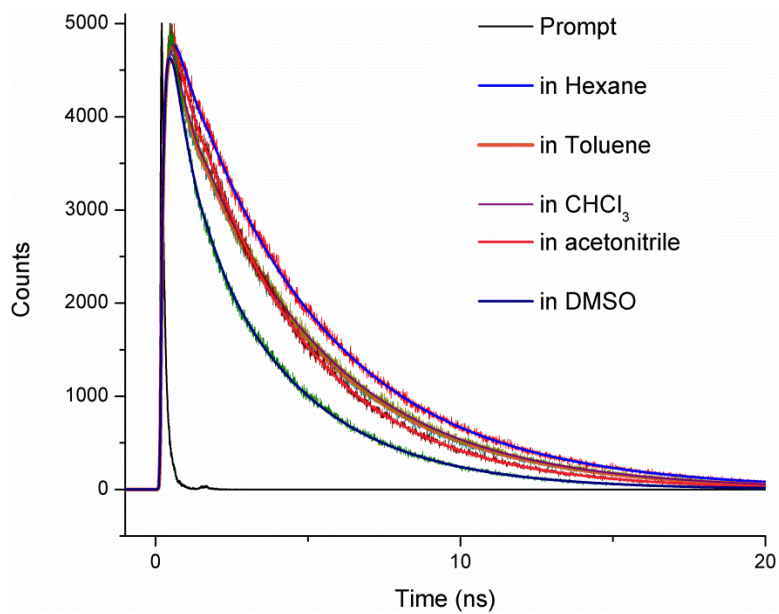


Figure S19 Fluorescence decay profile of 9 in hexane.

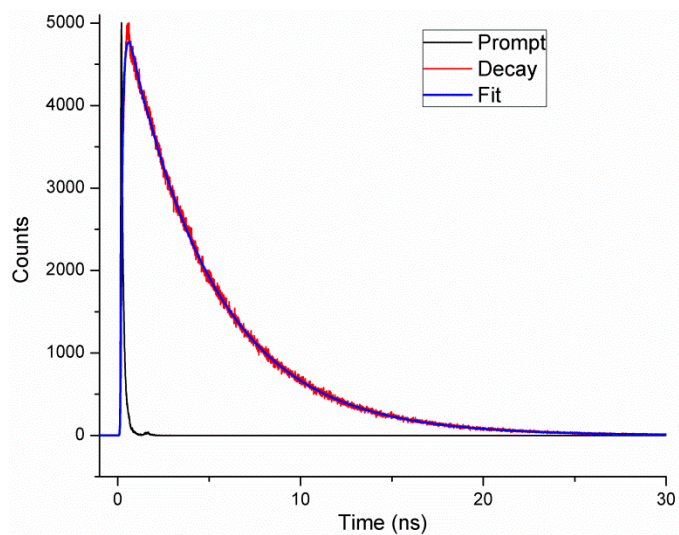


Figure S20 Fluorescence decay profile of 9 in toluene.

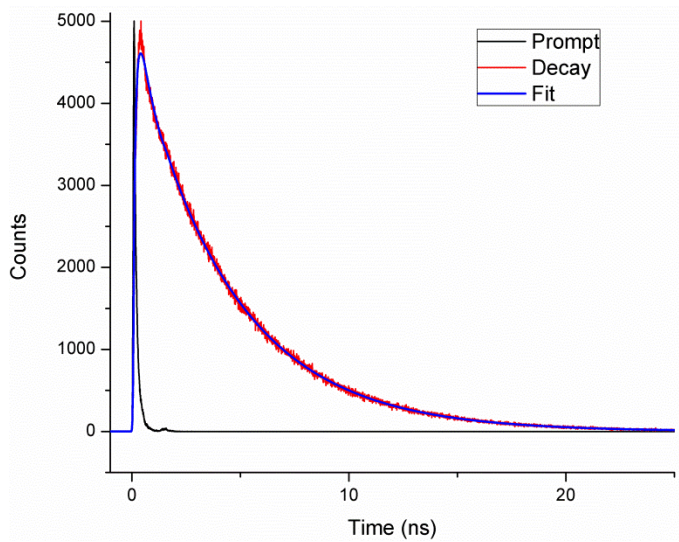


Figure S21 Fluorescence decay profile of 9 in chloroform.

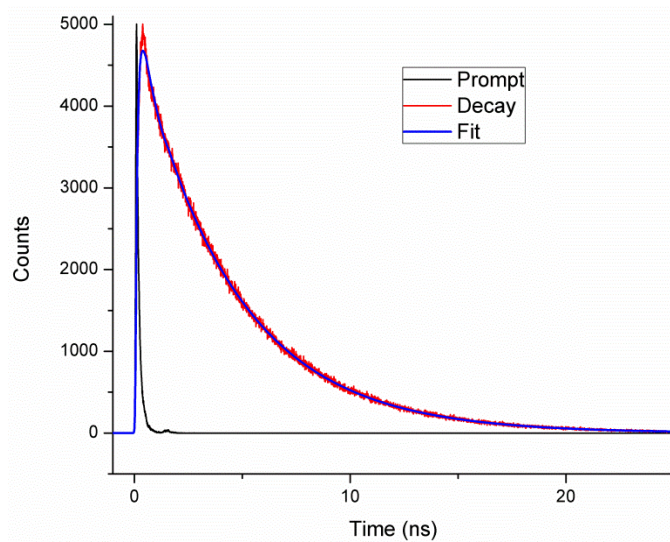


Figure S22 Fluorescence decay profile of 9 in acetonitrile.

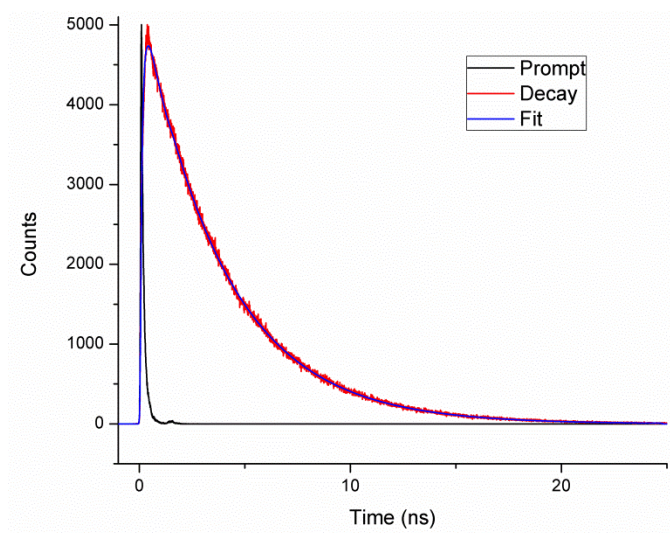


Figure S23 Fluorescence decay profile of 9 in DMSO.

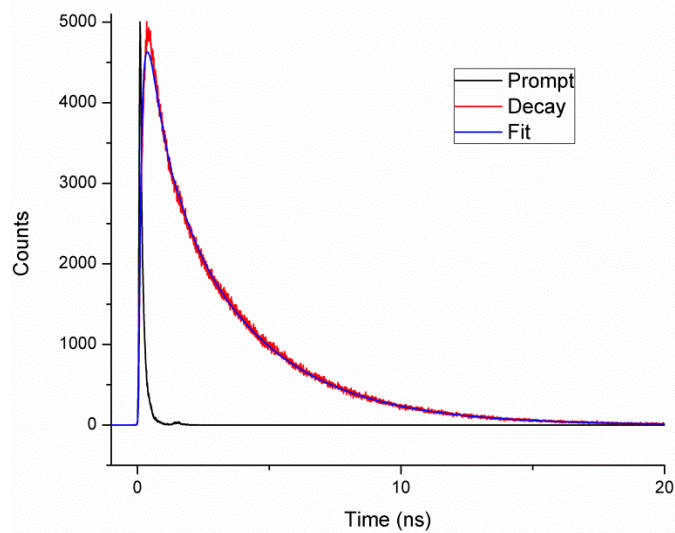


Figure S24 UV-Vis spectrum of 9 in acetonitrile at different concentration.

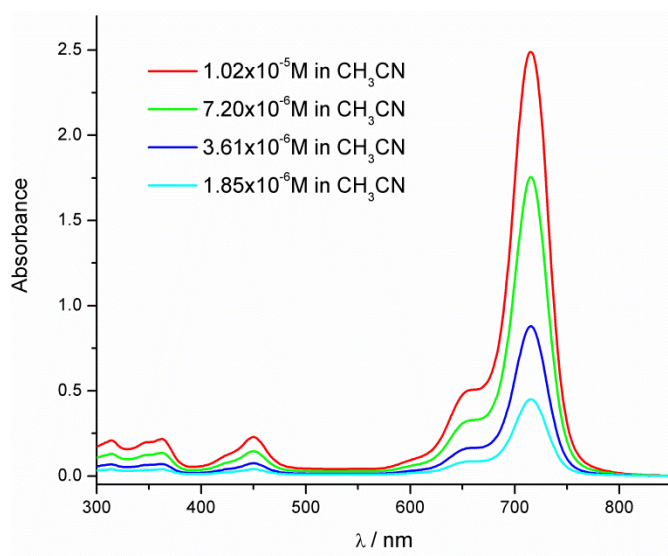


Figure S25 Plot of absorbance vs. concentration at 715 nm (absorption maxima) of 9 in acetonitrile.

