Solvent Switchable Dual Emission from a Bichromophoric Ruthenium-BODIPY complex.

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Electronic Supporting Information

Experimental

Materials

All materials were purchased from Sigma Ireland, and used without further purification unless otherwise noted.

General procedures.

Anhydrous $MgSO_4$ was used to dry all organic extracts. All volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by colour and TLC using commercial glass backed thin layer chromatography (TLC) plates (Kieselgel 60 F254). The plates were observed under UV light at 254 and 365 nm. Flash column chromatography was used throughout for all separations using silica gel (LC60A35-70 μM). High performance liquid chromatography (HPLC) was performed using a Varian LC 940 series with a Hichrom C18 250 x 4.6 mm column fitted with a photodiode array detector (150-900 nm), a 50 μl injection loop, auto sampler and auto collector. Dual detection wavelength was set for 280 nm. The mobile phase was of HPLC grade quality, filtered and purged with nitrogen prior to use. Mobile phase A consisted of deionised water (with 0.1% v/v trifluoroacetic acid (TFA)) and mobile phase B contained acetonitrile (with 0.1% v/v TFA). The mobile phase gradient was initially set for 5%:95% (solvent A:solvent B) and ended up as a 50%:50% (solvent A:solvent B) mixture over the 45 min run time. Samples were also filtered (0.8 μm pore size) prior to injection. UV-vis spectra were obtained on a Jasco V-670 spectrophotometer. Fluorescence spectra were collected on a a Varian Cary eclipse fluorescence spectrometer. The emission lifetimes were collected on a Fluotime 100 spectrometer with a 450 nm laser pulsed from a PDC 800-B. NMR spectra were recorded either at 400 and 100 MHz, respectively or at 600 and 150 MHz, respectively from a Bruker instrument. Deuteriated solvents were used for homonuclear lock, and the signals are referenced to the deuteriated solvent peaks. HR-MS analysis was carried out in Chemistry and Chemical Biology Laboratory, University College Dublin.

Synthesis;

4-(1,10-phenanthrolin-6-yl) benzaldehyde (3) To 5-bromo-1,10-phenanthroline **(1)** (400 mg, 1.5 mmol) was added 4-formylphenyl boronic acid (300 mg, 2.0 mmol), $Pd(dppf)_2\ Cl_2 \cdot$ DCM (120 mg, 0.4 mmol) in Dioxane (4 ml) and stirred. Following this K_2CO_3 (424 mg, 3.0 mmol) in H_2O (1 ml) was added and the reaction mixture heated to reflux for 6 h (TLC). The reaction mixture was then cooled

and diluted to 25 ml with DCM and dried over $MgSO_4$ and concentrated to dryness. The residue was then dissolved in DCM and purified on silica gel using DCM:MeOH (9:1). The product was then triturated from hot $CHCl_3$ with cold pentane to yield **(3)** (382 mg, 72 %) as an off white solid, R_f 0.3 (DCM:MeOH 9.5:0.5); δ_H(400 MHz; $CDCl_3$) 10.17 (s, 1H, C*H*O), 9.26 (t, *J* = 1.7 Hz, 1H, Ar-*H*), 9.24 (t, *J* = 1.6 Hz, 1H, Ar-*H*), 8.30 (dd, *J* = 1.7 & 8.1 Hz, 1H, Ar-*H*), 8.23 (dd, *J* = 1.5 & 8.4 Hz, 1H, Ar-*H*), 8.09 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.79 (s, 1H, Ar-*H*), 7.74 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.70 (dd, *J* = 4.4 & 8.0 Hz, 1H, Ar-*H*), 7.63 (dd, *J* = 4.3 & 8.3 Hz, 1H, Ar-*H*); ^{13}C NMR ($CDCl_3$) δ 191.7, 150.8, 150.4, 146.5, 146.0, 145.2, 137.5, 136.1, 135.9, 134.0, 130.7, 130.0, 127.8, 127.3, 126.9, 123.6, 123.0 PPM; HR MS (TOF MS ES$^+$): *m/z* = 285.1034 Calcd for ($C_{19}H_{12}N_2O$ + H^+) = 285.1028.

Ethyl (2,2'-bipyridin-4-yl) benzoate (4) To 4-bromo-2,2'-bipyridine **(2)** (250 mg, 1.1 mmol) was added 4-ethoxycarbonylphenyl boronic acid (236 mg,1.2 mmol), $Pd(dppf)_2$ Cl_2· DCM (86 mg, 0.1 mmol) in Dioxane (3.5 ml) and stirred. Following this K_2CO_3 (292 mg, 2.1 mmol) in H_2O (0.5 ml) was added and the reaction mixture heated to reflux for 4 h (TLC). The reaction mixture was then cooled and diluted to 25 ml with DCM and dried over $MgSO_4$ and concentrated to dryness. The residue was then dissolved in DCM and purified on silica gel using DCM:MeOH (9:1). The product was then triturated from hot $CHCl_3$ with cold pentane to yield **(4)** (234 mg, 70 %) as an off white solid; δ_H(600 MHz; $CDCl_3$) 8.68 (d, *J* = 5.0 Hz, 1H, Ar-*H*), 8.64 (dd, *J* = 1.0 & 3.8 Hz, 1H, Ar-*H*), 8.62 (d, *J* = 1.2 Hz, 1H, Ar-*H*), 8.39 (d, *J* = 7.9 Hz, 1H, Ar-*H*), 8.10 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.78 (td, *J* = 1.8 & 7.6 Hz, 1H, Ar-*H*), 7.76 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.49 (dd, *J* = 1.8 & 5.0 Hz, 1H, Ar-*H*), 7.28 (dddd, *J* = 1.1, 2.7 & 4.9 Hz, 1H, Ar-*H*), 4.35 (q, *J* = 7.0 Hz, 2H, C$H_2$$CH_3$), 1.36 (t, *J* = 7.0 Hz, 3H, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 166.2, 156.9, 155.9, 149.8, 149.2, 148.3, 142.6, 137.0, 130.9, 130.3, 127.2, 123.9, 121.7, 121.3, 119.1, 61.2, 14.4 ppm. HR MS (TOF MS ES$^+$): *m/z* = 305.1282 Calcd for ($C_{19}H_{17}N_2O_2$ + H^+) = 305.1290.

(2,2'-bipyridin-4-yl) benzoic acid (6) To compound **(4)** (200 mg, 0.6 mmol) was added DCM (6 ml) and stirred. Following this a solution of crushed NaOH (100 mg, 2.5 mmol) in MeOH (0.73 ml) was added and the solution stirred until full consumption of starting material (TLC). The solvent was then removed *in vacuo* to yield a gel like residue which was dissolved in H_2O (12.5 ml) and neutralised with 1M HCL and filtered. The product was then washed with H_2O and resudiual water was sublimed to yield **(6)** (90%) as a peach colored solid; δ_H(400 MHz; DMSO-d_6) 13.19 (bs, 1H, COO*H*), 8.77 (d, *J* = 5.0 Hz, 1H, Ar-*H*), 8.73 (d, *J* = 4.0 Hz, 1H, Ar-*H*), 8.70 (d, *J* = 1.0 Hz, 1H, Ar-*H*), 8.45 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 8.09 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 7.99 (m, 3H, Ar-*H*), 7.82 (dd, *J* = 1.7 & 5.1 Hz, 1H, Ar-*H*), 7.50 (m, 1H, Ar-*H*); ^{13}C NMR (DMSO-d_6) δ 166.8, 153.1, 152.1, 149.3, 148.7, 147.9, 140.6, 139.8, 131.8, 130.6,

127.5, 125.5, 122.7, 122.1, 119.1 ppm; HR MS (TOF MS ES$^+$): *m/z* = 277.0983 Calcd for ($C_{17}H_{12}N_2O_2$ + H^+) = 277.0977.

1,3,5,7-tetramethyl-5-phenanthroline-4,4'-difluoroboradiazaindacene (5) 5-phenanthroline benzaldehyde **(3)** (300 mg, 1.1 mmol) was added to N_2 purged DCM (60 ml) with 2,4-dimethylpyrrole (230 mg, 2.4 mmol) with TFA (cat). The reaction mixture was stirred at r.t for 5 h (TLC). Added to this was *P*-chloroanil (270 mg) in DCM (20 ml) and stirred for 30 min followed by the addition of Et_3N and $BF_3.OEt_2$ (2.76 ml) and the reaction mixture stirred overnight. The crude reaction mixture was washed with H_2O (2 x 50 ml) and concentrated to a residue which was purified on silica gel by flash chromatography (DCM:MeOH 95/5) trituration of the isolated fraction from hot $CHCl_3$ with cold pentane yielded a bright red solid (160 mg, 28%). δ_H(600 MHz; $CDCl_3$) 9.18 (m, 2H, Ar-*H*), 8.23 (dd, *J* = 1.6 & 8.0 Hz, 1H, Ar-*H*), 8.15 (dd, *J* = 1.5 & 8.4 Hz, 1H, Ar-*H*), 7.76 (s, 1H, Ar-*H*), 7.63 (dd, *J* = 4.2 & 8.0 Hz, 1H, Ar-*H*), 7.62 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.56 (dd, *J* = 4.3 & 8.3 Hz, 1H, Ar-*H*), 7.43 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 5.98 (s, 2H, pyr-*H*), 2.52 (s, 6H, C*H*$_3$), 1.50 (s, 6H, C*H*$_3$); ^{13}C NMR ($CDCl_3$) δ 155.8, 150.6, 150.3, 146.5, 145.9, 142.8, 140.9, 139.7, 137.9, 136.0, 134.9, 134.0, 131.4, 130.7, 128.5, 128.0, 127.6, 126.9, 123.6, 123.0, 121.5, 14.7, 14.6 ppm; ^{19}F NMR $CDCl_3$ δ -146.13 (d), -146.32 (d); HR MS (TOF MS ES$^+$): *m/z* = 503.2239 Calcd for ($C_{31}H_{25}BN_4F_2$ + H^+) = 503.2219.

1,3,5,7-tetramethyl-2,6-dibromo-5-phenanthroline-4,4'-difluoroboradiazaindacene (7) (30 mg, 0.06 mmol) of **(5)** was added to anhydrous DCM (20 ml) with stirring. Added to this via a pressure equalizing dropping funnel was Br_2 (10 µL, 0.18 mmol) in DCM (2.5 ml) over 30 min. The solution was stirred for an additional 2 h (TLC). The solvent was then removed *in vacuo* and the crude product crystallised from DCM:MeOH (90/10) with pentane. This resulted in a dark red solid (28 mg, 70%). δ_H(600 MHz; DMSO-d_6) 9.44 (dd, *J* = 1.4 & 4.7 Hz, 1H, Ar-*H*), 9.41 (dd, *J* = 1.4 & 5.0 Hz, 1H, Ar-*H*), 9.26 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 8.74 (dd, *J* = 1.0 & 8.4 Hz, 1H, Ar-*H*), 8.55 (s, 1H, Ar-*H*), 8.36 (dd, *J* = 4.9 & 8.2 Hz, 1H, Ar-*H*), 8.29 (dd, *J* = 4.7 & 8.5 Hz, 1H, Ar-*H*), 7.92 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 7.79 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 2.60 (s, 6H, C*H*$_3$), 1.59 (s, 6H, C*H*$_3$); ^{13}C NMR (DMSO-d_6) δ 153.4, 148.2, 147.2, 142.9, 142.1, 140.0, 138.8, 138.4, 138.2, 138.0, 136.9, 133.8, 131.0, 129.8, 129.0, 128.6, 128.3, 127.4, 126.3, 126.1, 111.4, 13.7, 13.5 ppm; ^{19}F NMR DMSO-d_6 δ -143.3 (d), -143.4 (d); HR MS (TOF MS ES$^+$): *m/z* = 661.0385 Calcd for ($C_{31}H_{24}BN_4F_2{}^{79}Br^{81}Br$) = 661.0408.

Ru(bpy-Ar-COOH)$_2$Cl$_2$ (8) $RuCl_3.3H_2O$ (151 mg, 0.56 mmol), was added to degassed DMF under a steady stream of N_2 and heated with stirring to 100 °C. Compound **(6)** (151 mg, 0.56 mmol) was added and the reaction mixture was allowed to stir for 10 min. The temperature was then raised to 140 °C and LiCl (5 equiv) was added and stirred for another 10 min. The remaining **(6)** (151 mg, 0.56 mmol) was added and reaction allowed to proceed for 7 h. The DMF was then removed and

acetone:H_2O (1/3) was added to induce precipitation and the mixture was filtered and washed with acetone to yield a purple solid (130 mg, 32%). ^{1}H NMR pattern shows a broad signal pattern integrating for 22 Ar-*H*. Fac and Mer isomers reamined unresolved as seperated isomers not needed.

Ru(bpy-Ar-COOH)$_2$-phen-Ar-BODIPY-Br$_2$ (9) Compound **(7)** (100 mg, 0.14 mmol) was added to a solution of EtOH:H_2O 3/1 (20 ml) and heated to reflux. Compound **(8)** (91 mg, 0.14 mmol) was then added and the solution left at reflux for 12 h. The reaction mixture was then concentrated to half volume and a saturated $LiClO_4$ solution was added resulting in a red precipitate which was filtered and purified on silica gel $CHCl_3$:MeOH:CH_3COOH 76/20/4 to yield a red solid (65 mg, 33%). δ_H(600 MHz; DMSO-d_6) 9.28 (m, 4H, Ar-*H*), 8.90 (D, *J* = 8.34 Hz, 1H, Ar-*H*), 8.56 (m, 2H, Ar-*H*), 8.28 (m, 5H, Ar-*H*), 8.09 (m, 9H, Ar-*H*), 7.96 (m, 7H, Ar-*H*), 7.74 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 7.66 (m, 3H, Ar-*H*), 7.42 (m, 1H, Ar-*H*), 2.56 (s, 6H, C*H*$_3$), 1.53 (s, 6H, C*H*$_3$); ^{13}C NMR (DMSO-d_6) δ 166.7, 157.5, 157.4, 157.3, 156.8, 156.6, 153.4, 152.5, 152.4, 151.8, 151.7, 147.2, 147.0, 146.6, 146.5, 142.2, 140.4, 139.2, 139.0, 138.8, 138.0, 137.0, 134.9, 134.3, 134.1, 133.8, 132.2, 131.2, 130.0, 129.8, 128.6, 128.4, 128.1, 128.0, 127.9, 127.8, 127.6, 127.5, 126.8, 124.9, 124.8, 121.8, 121.7, 111.4, 13.6, 13.5 ppm; ^{19}F NMR DMSO-d_6 δ -143.2 (d), -143.4 (d); HR MS (TOF MS ES$^+$): *m/z* = 657.0539 Calcd for ($C_{65}H_{47}BBr_2N_8O_4F_2Ru$ + 2H$^+$ -2ClO_4 / 2) = 657.0674, *m/z* = 656.0592 calcd for ($C_{65}H_{47}BBr_2N_8O_4F_2Ru$ / 2) = 656.0596. Elemental Analysis: calculated (%) for $C_{65}H_{47}N_8O_{16}BBr_2F_2NaCl_3Ru$ – C; 47.75, H; 2.90, N; 6.85. Found (%) C; 47.74, H; 2.88, N; 6.81.

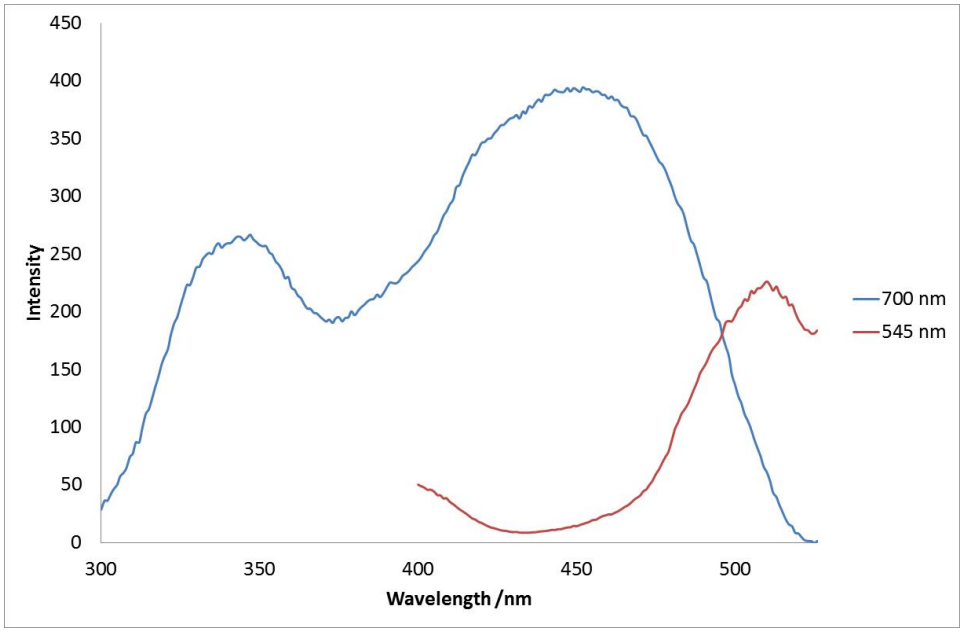
Real-time confocal luminescent imaging

CHO cells were seeded at 2.5 x 10^5 cells in 2 mL media on 35 mm glass-bottom culture dishes. Cells were grown for 24 h at 37 °C at 5 % CO_2. The growth media was removed and 15 uM of the Ruthenium-BODIPY complex in phenol red-free media was added and left to incubate for 24 h at 37 °C at 5 % CO_2 in the dark. The dye/media solution was removed and cells were washed with PBS supplemented with 1.1 mM $MgCl_2$ and 0.9 mM $CaCl_2$. Cells were imaged using a Zeiss LSM 510 Meta confocal microscope using a 63x oil immersion objective lens. A 458 nm argon ion laser was used to excite the complex. The BODIPY emission was collected using a band-pass 505-550 nm filter. The ruthenium emission was collected using a long pass 560 nm filter. The exciation/λ scan was carried out using the 458 nm argon ion laser and emission was collected between 497 and 754 nm with a step size of 10 nm.

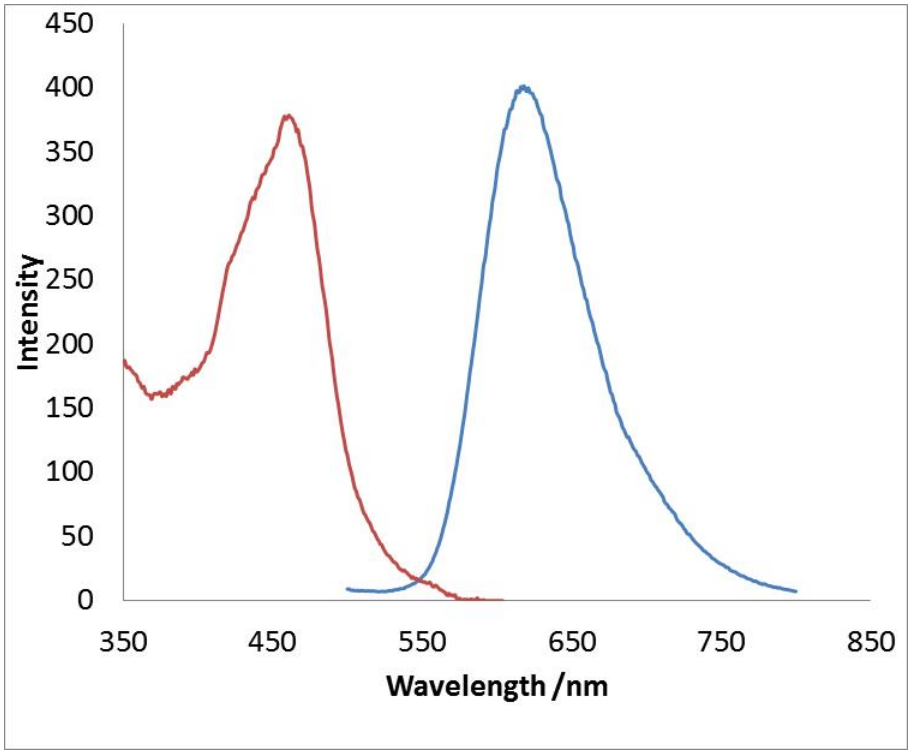
Cell Viability Assay

CHO cells were seeded in a 96-well plate in 100 µL of media at 1 x 10^4 cells per well for 24 h at 37ºC with 5% CO_2. Ruthenium-BODIPY was added to give final concentrations of 150, 100, 50, 15, 1, 0.1 µM. Cells were incubated for 24 h at 37ºC at 5% CO_2 in the dark. 10 µL of Resazurin (Alamar Blue) reagent was added to each well, and incubated for a further 7 h in the dark at 37ºC. The resazurin was converted to resorufin in viable cells and its absorbance was measured at 570 nm, with background measured at 600 nm using a Tecan 96-well plate reader.

Excitation Spectra

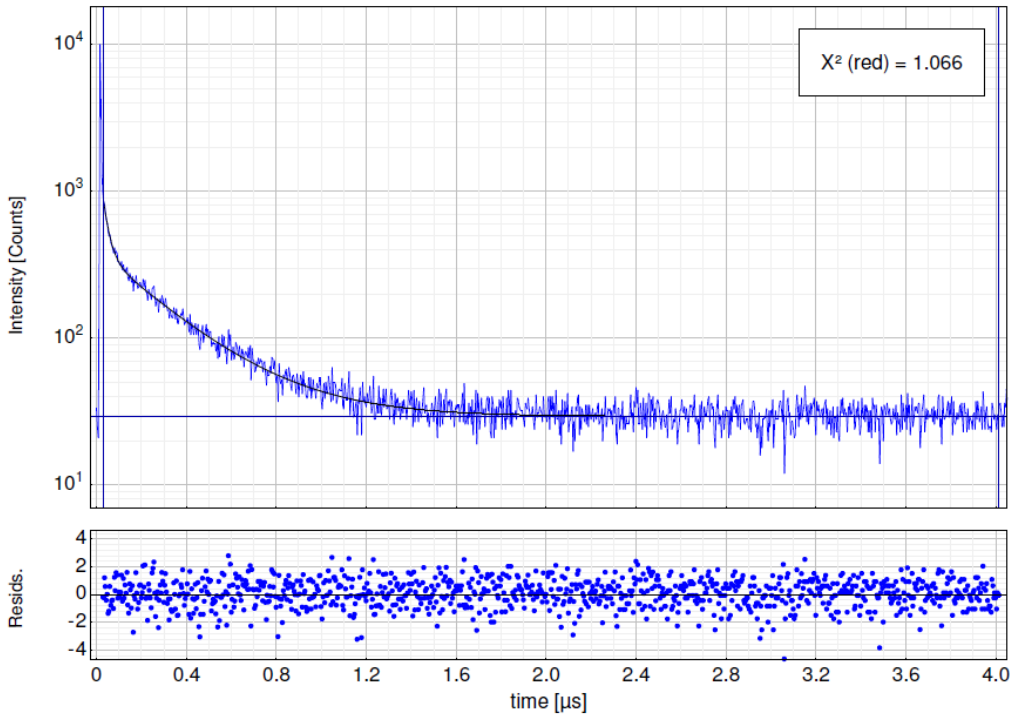


S1. Excitation spectra for the dyad (9) 50 µmol in methanol, monitoring for emission centred at 700 nm ad 545 nm.



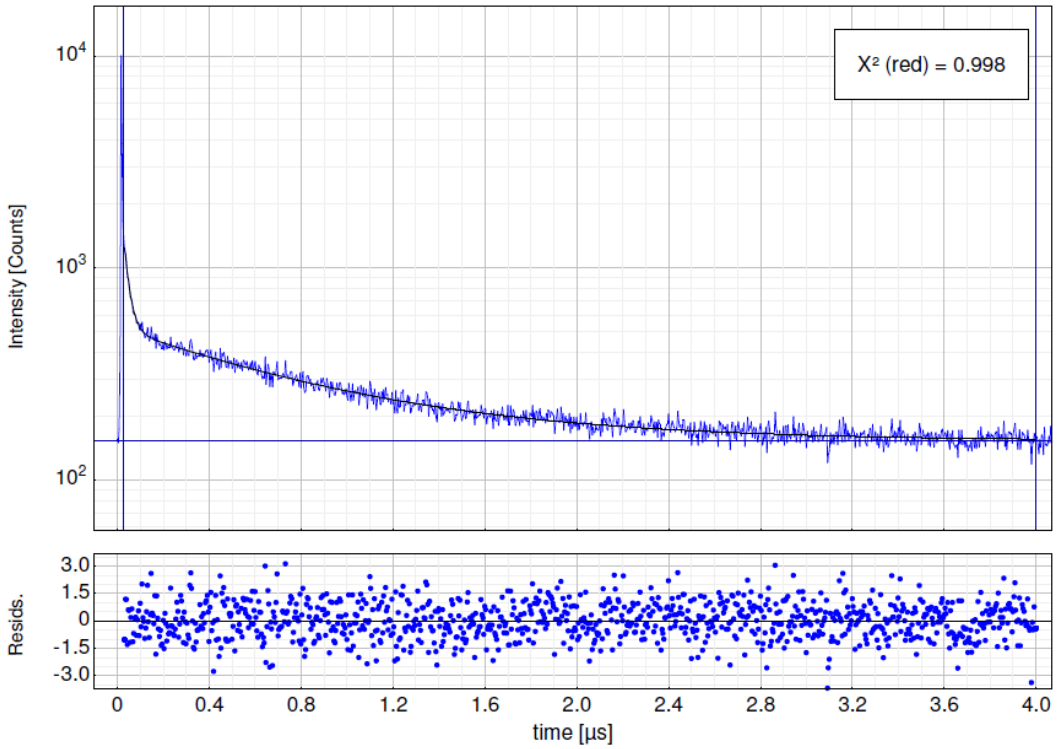
S2. Excitation spectrum (red) and emission spectrum (blue) for dyad (9) 50 µmol in aqueous PBS, excitation was collected for emission at 630 nm.

Emission Lifetime Data;



$$I(t) = \sum_{i=1}^{n} A_i \, e^{-\frac{t}{\tau_i}}$$

Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	335.0	-12.7	+12.7	Fitting
τ_1 [µs]	0.3063	-0.0107	+0.0107	Fitting
A_2 [Cnts]	487.4	-70.2	+70.2	Fitting
τ_2 [µs]	0.02471	-0.00443	+0.00443	Fitting
Bkgr. Dec [Cnts]	29.29	-1.01	+1.01	Fitting

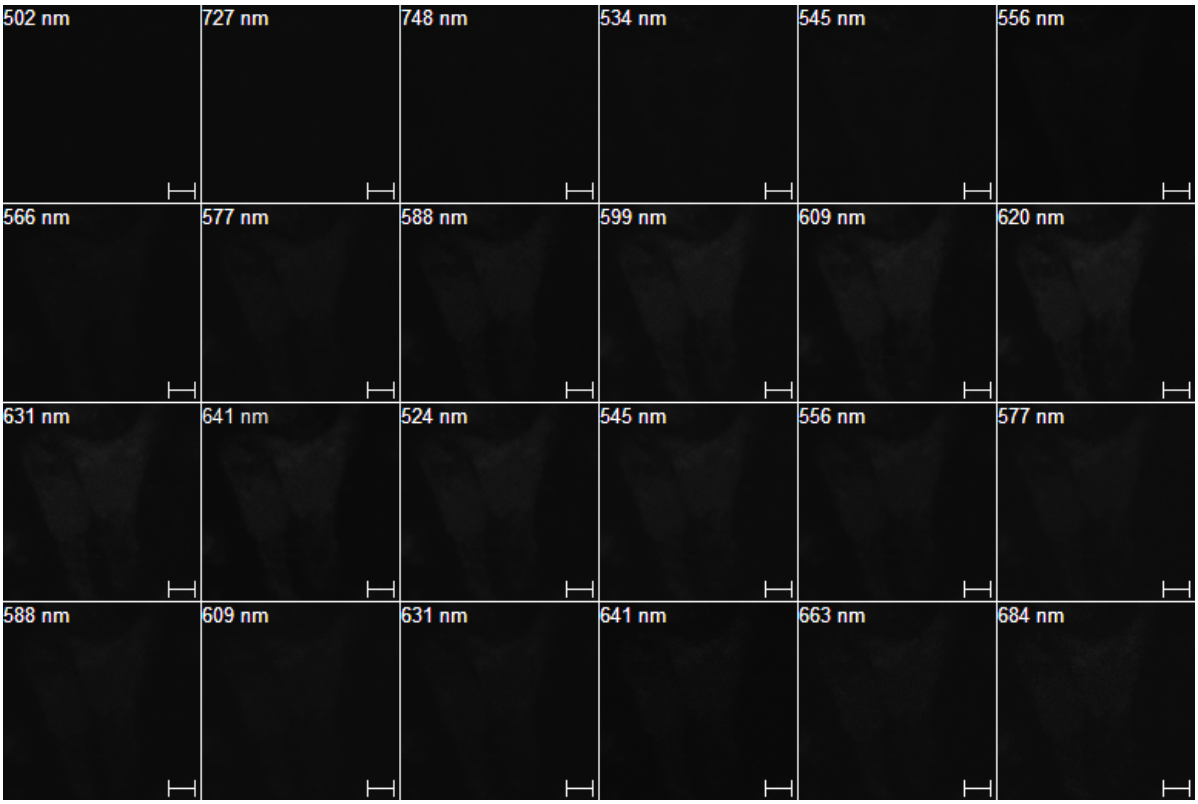


$$I(t) = \sum_{i=1}^{n} A_i \, e^{-\frac{t}{\tau_i}}$$

Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	355.04	-9.57	+9.57	Fitting
τ_1 [µs]	0.8250	-0.0252	+0.0252	Fitting
A_2 [Cnts]	730.5	-83.7	+83.7	Fitting
τ_2 [µs]	0.02366	-0.00345	+0.00345	Fitting
Bkgr. Dec [Cnts]	153.18	-2.26	+2.26	Fitting

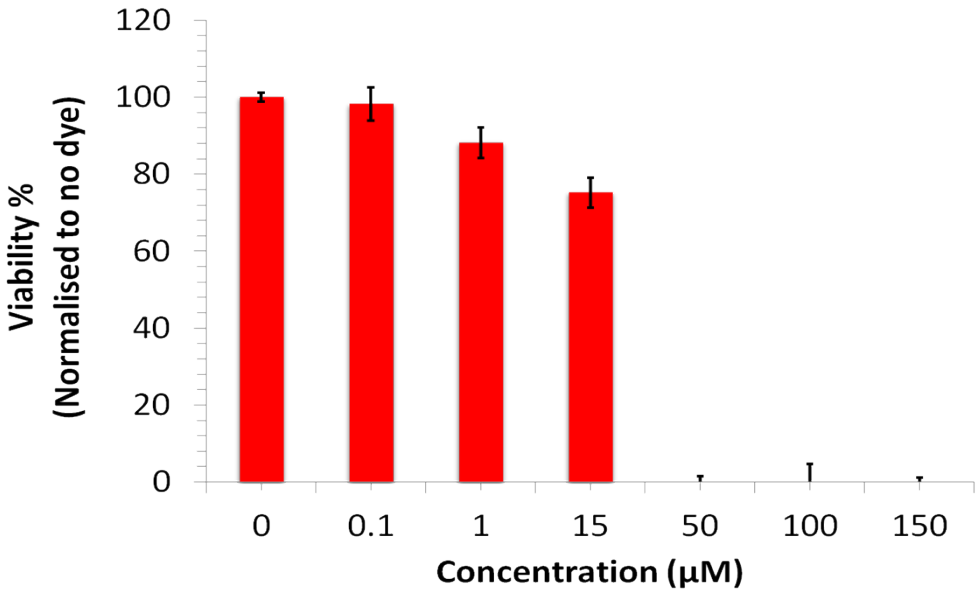
S3. Time correlated Single Photon counting trace for Dyad (9) 3 x10^{-6} M in (a) aerated methanol (b) de-aerated methanol (following 30 minutes bubbling with N_2 gas)

Excitation/λ scan

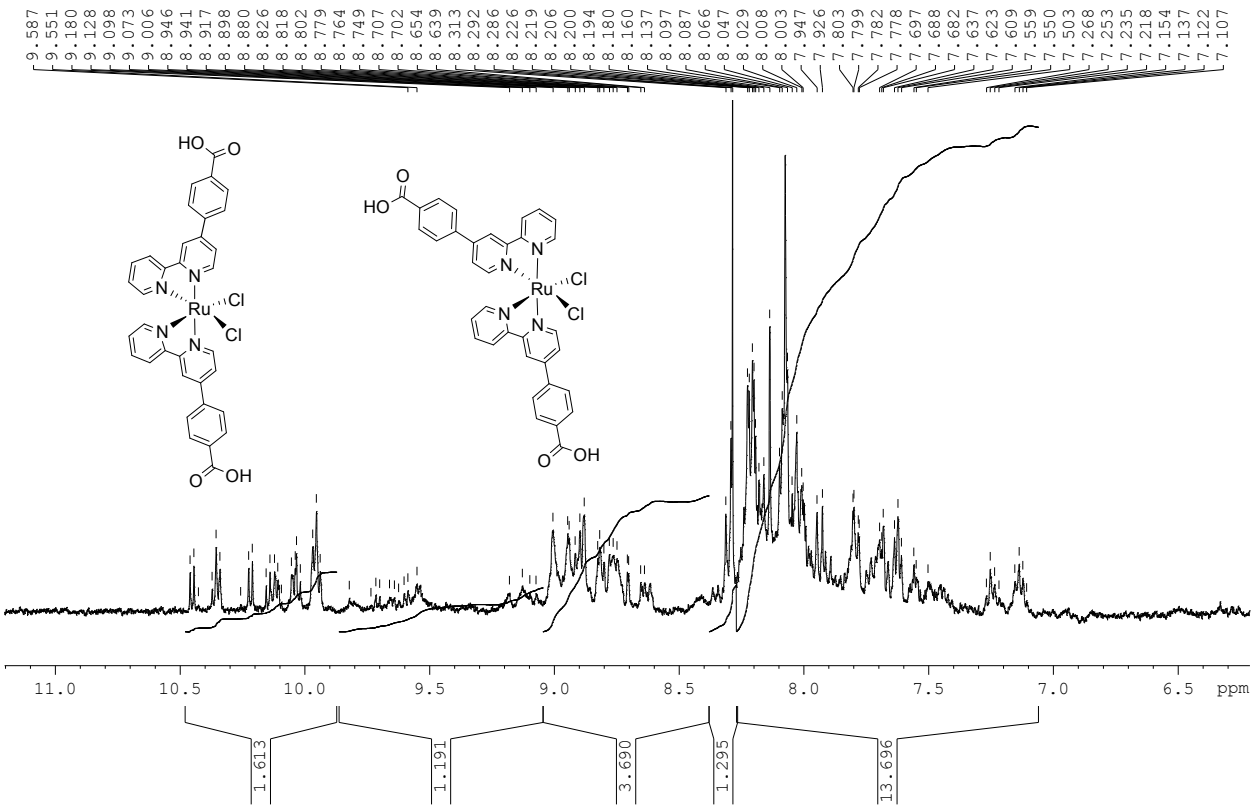


S4. Excitation scan of Ruthenium-BODIPY complex in CHO cells (15 μM) demonstrating no BODIPY emission at 529-550 nm when excited with a 458 nm argon laser. Scale bar = 10 μM

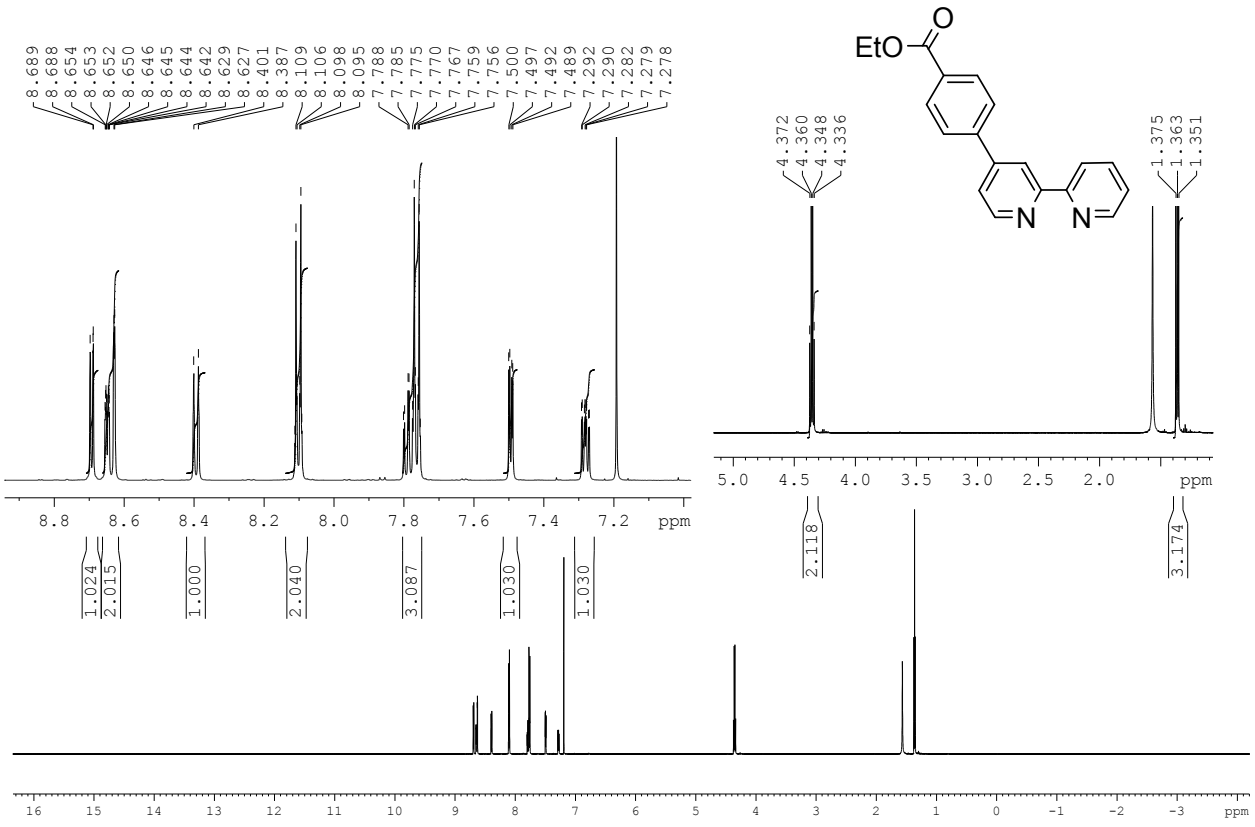
Cell Viability Studies



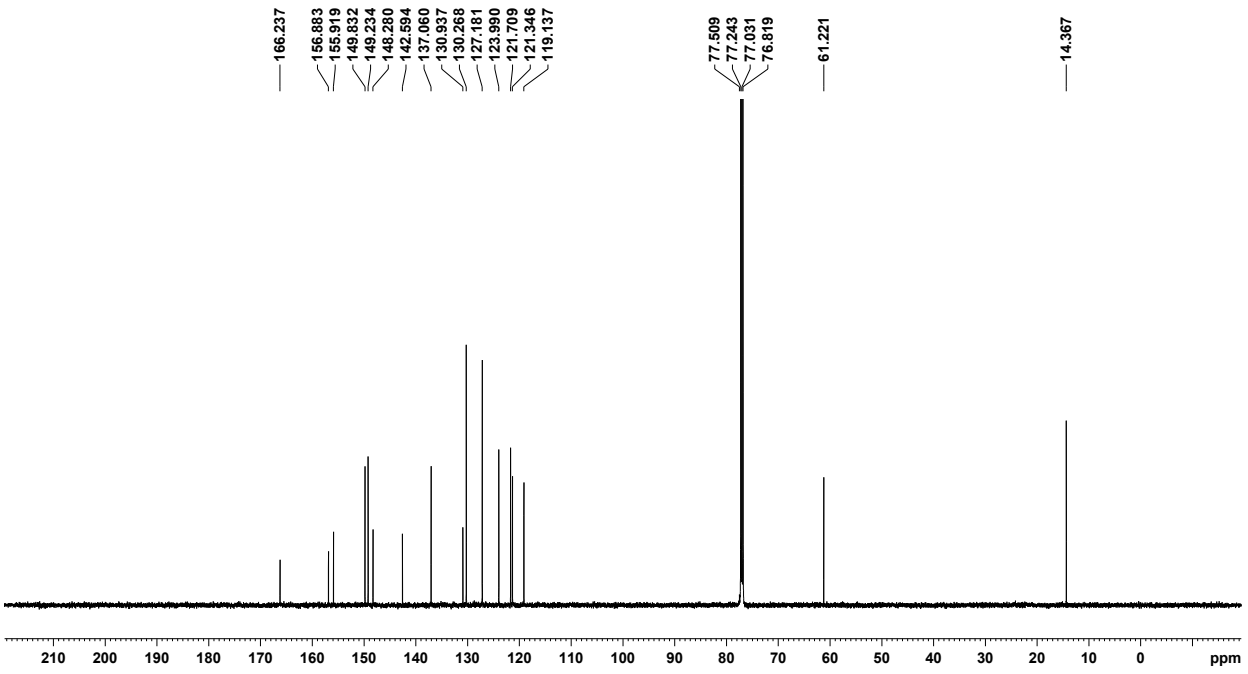
S5. Viability studies for the ruthenium-BODIPY dyad; carried out in CHO cells in the dark using the Resazurin (Alamar blue) reagent. (n=3)



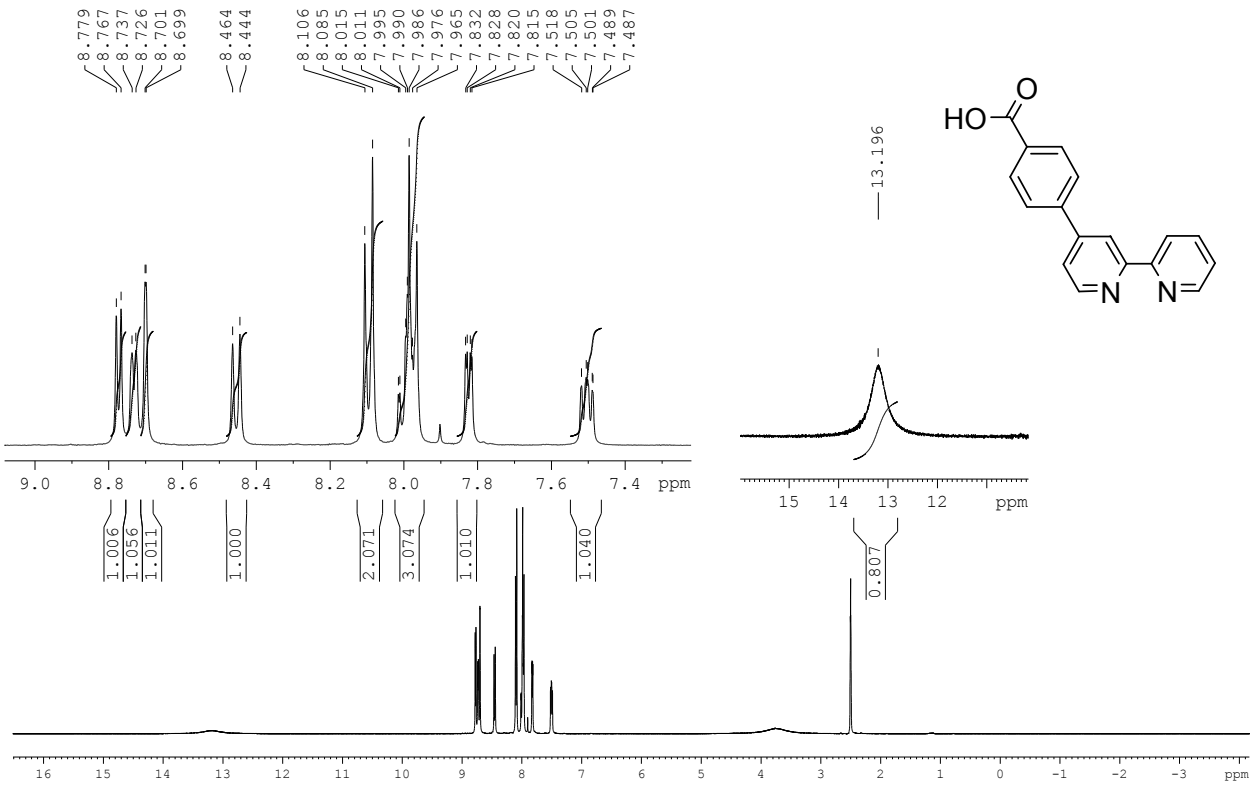
S6. ^{1}H NMR of (8) in DMSO-d_6 reveal a mixture of fac and mer isomers which did not separate on HPLC.



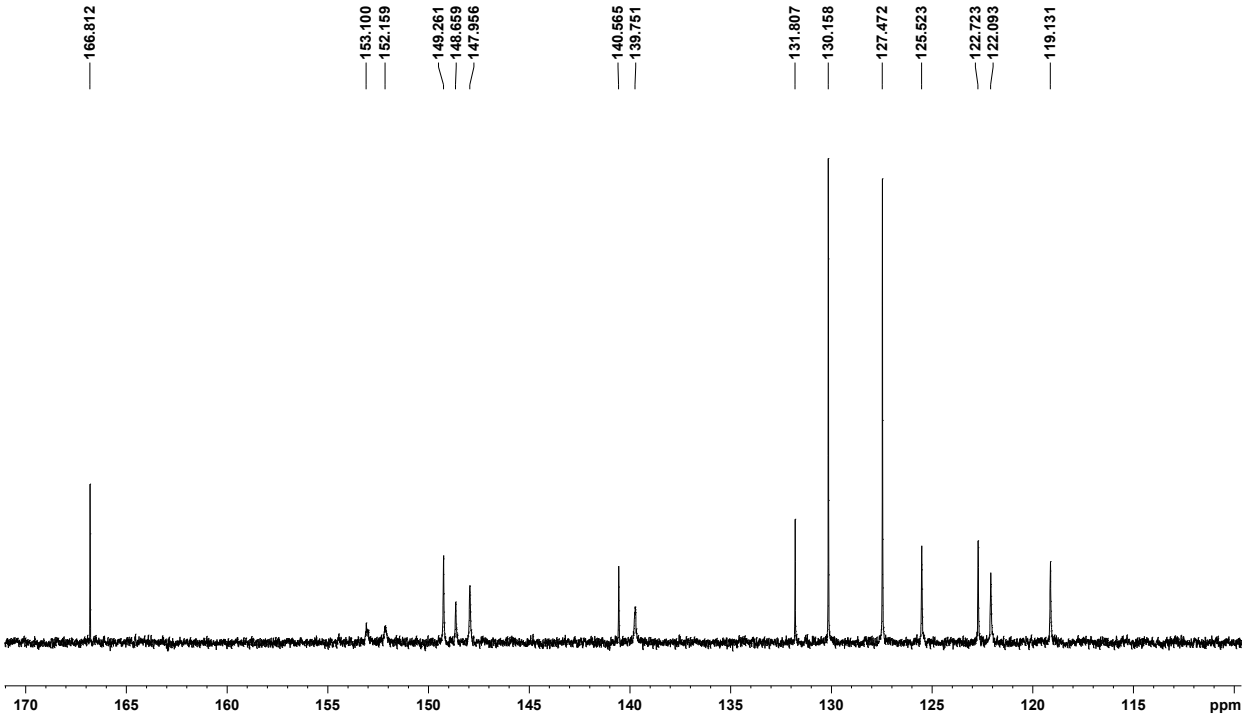
S7. ^{1}H NMR spectra of (4) in $CDCl_3$.



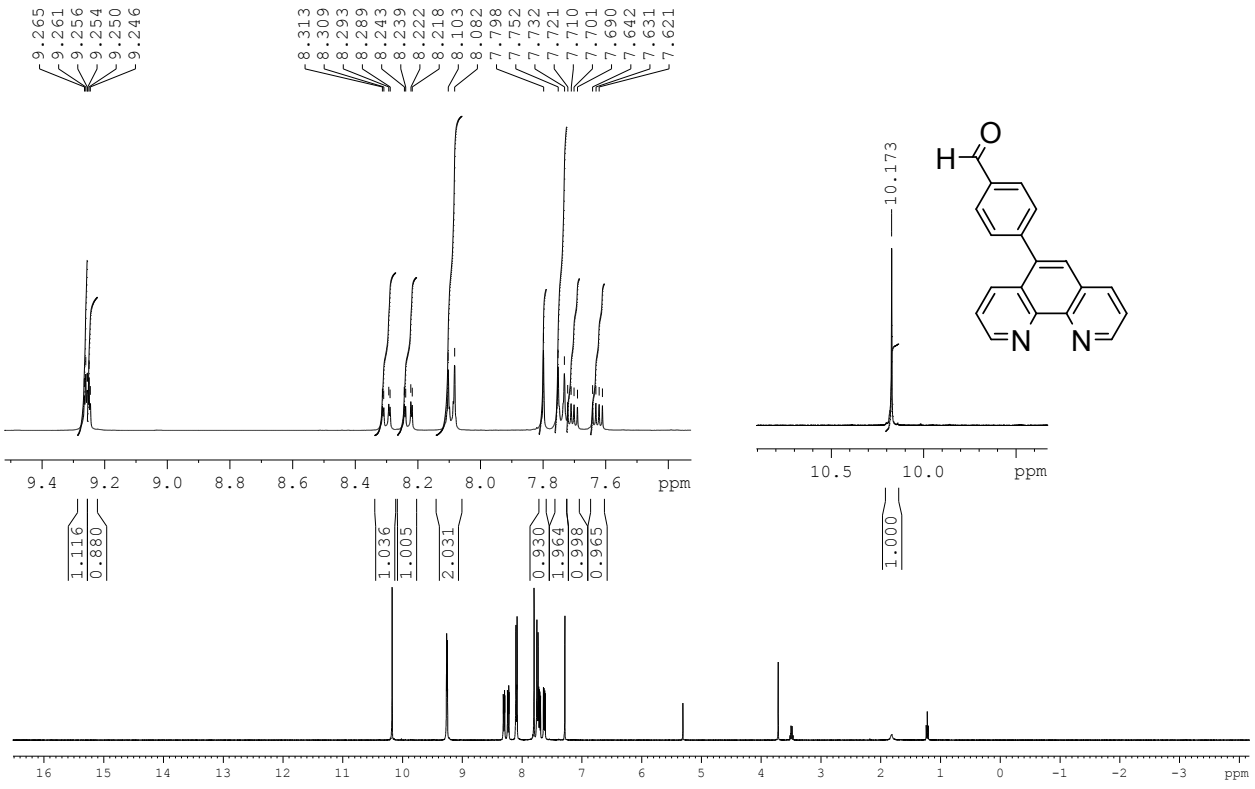
S8. ^{13}C NMR spectra of (4) in $CDCl_3$.



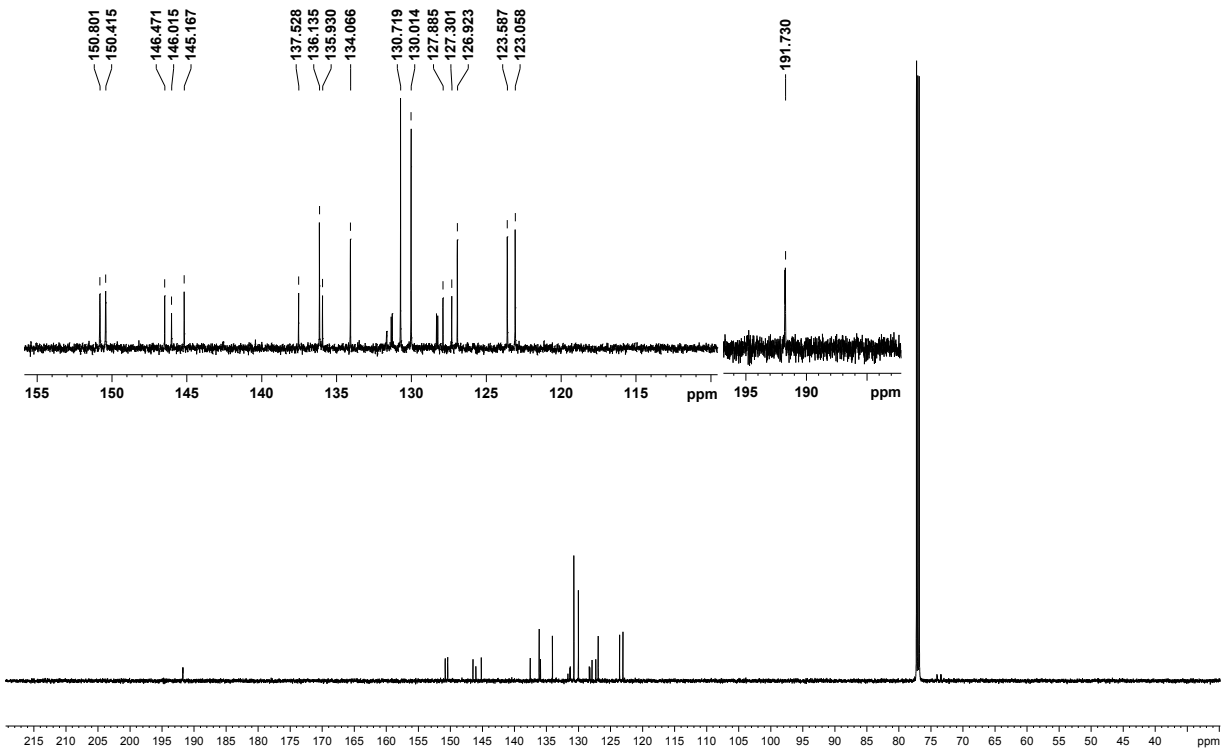
S9. ^{1}H NMR spectra of (5) in DMSO-d_6.



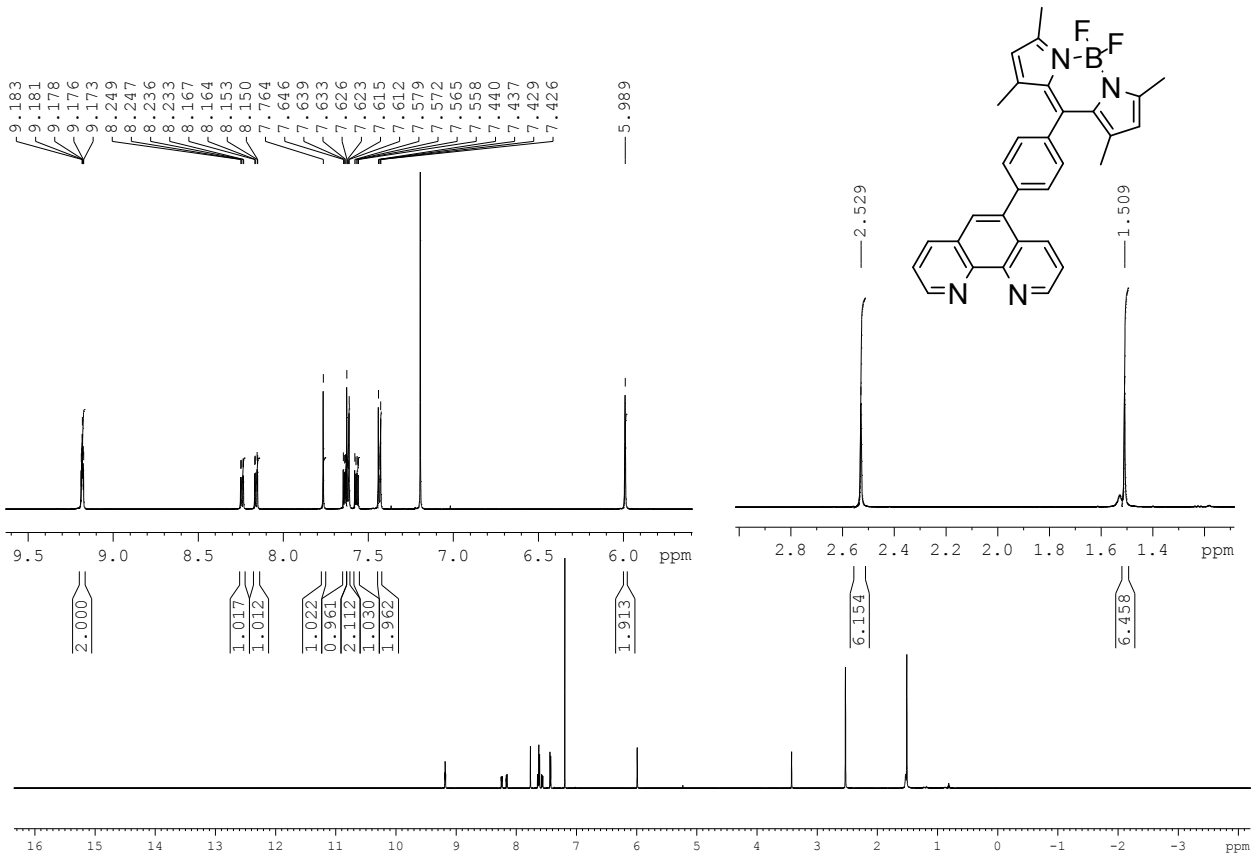
S10. ^{13}C NMR spectra of (5) in DMSO-d_6.



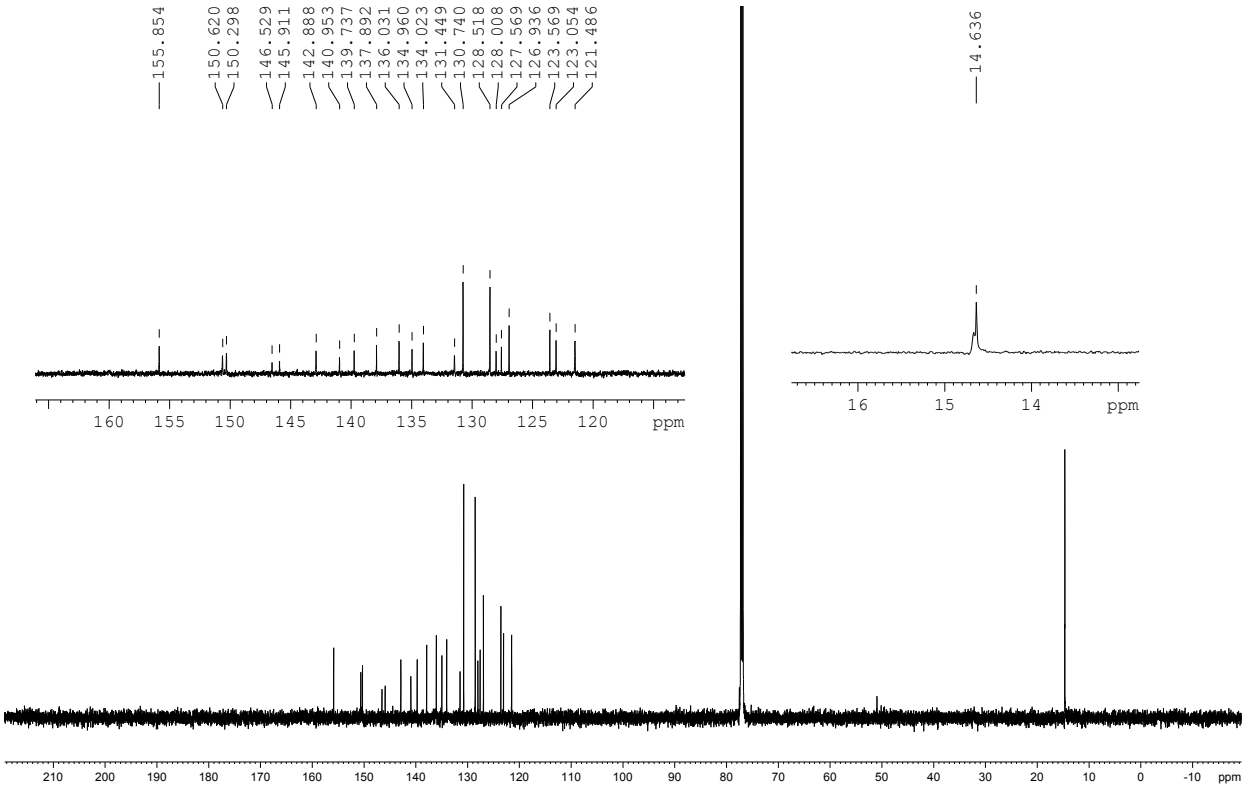
S11. ^{1}H NMR spectra of (3) in $CDCl_3$, inset aromatic region and C<u>H</u>O.



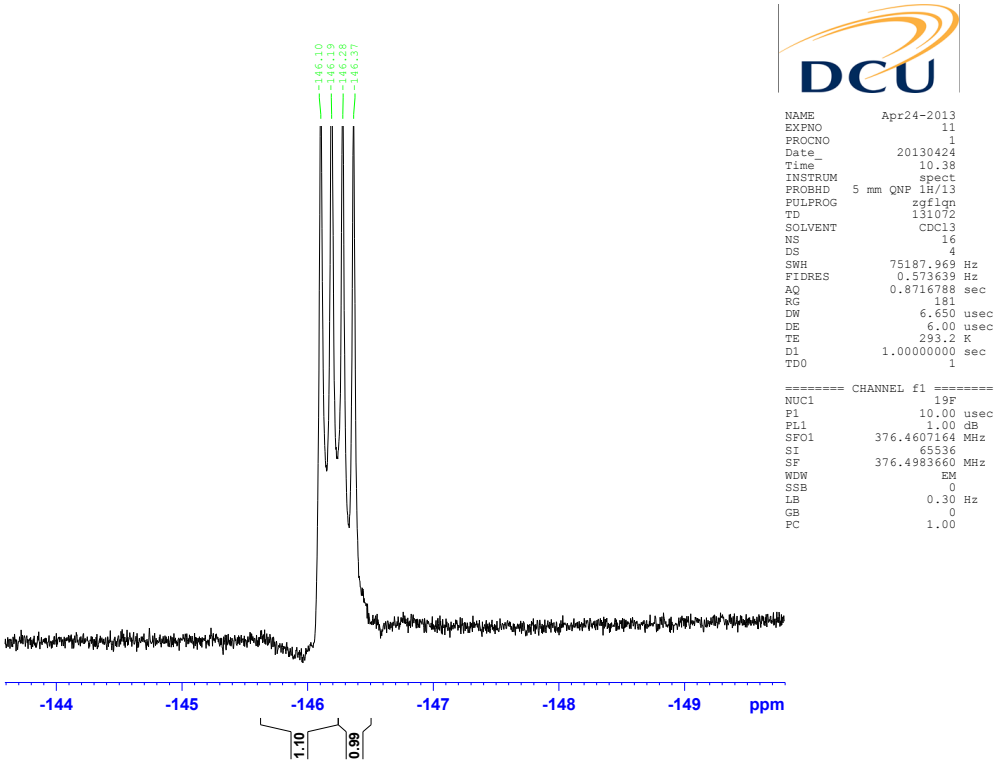
S12. ^{13}C NMR spectra of (3) in $CDCl_3$, inset aromatic region and C<u>H</u>O.



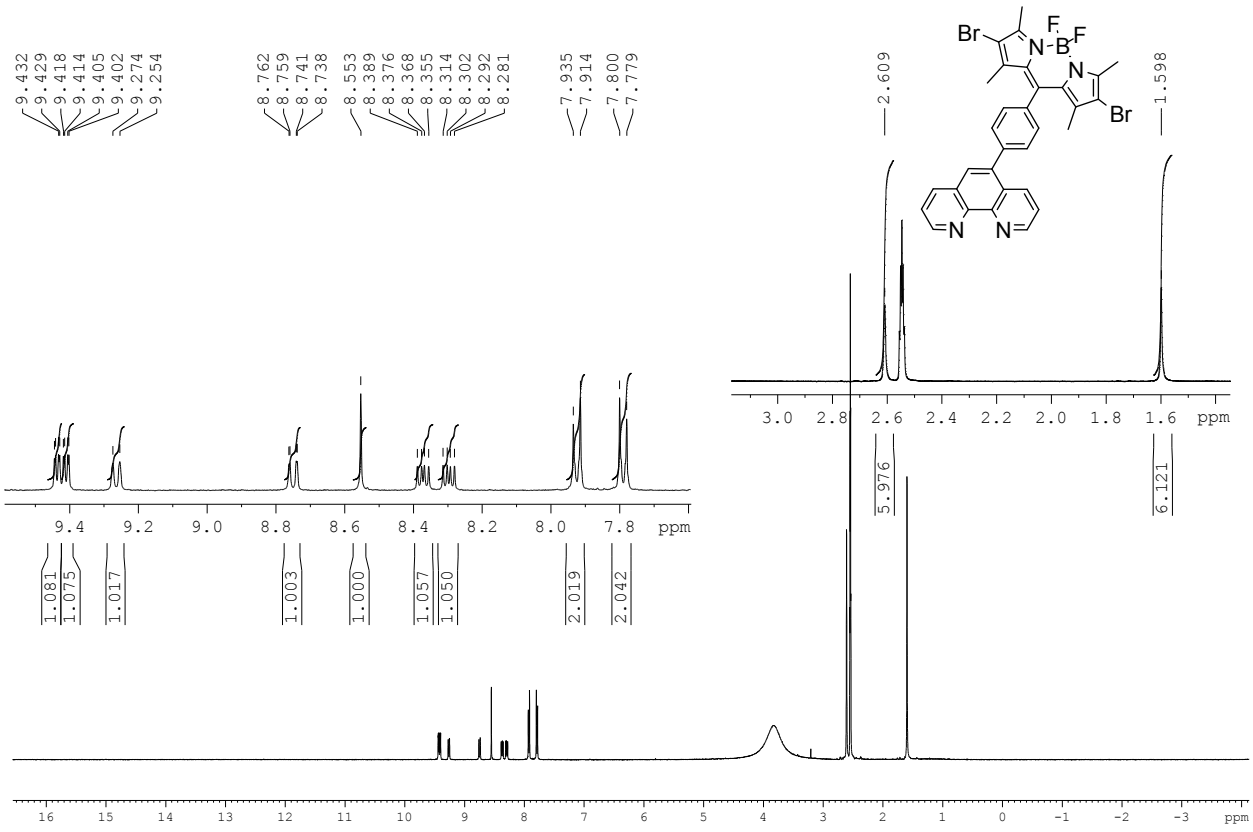
S13. ^{1}H NMR spectra of (5) in $CDCl_3$, inset aromatic region and C<u>H</u>$_3$.



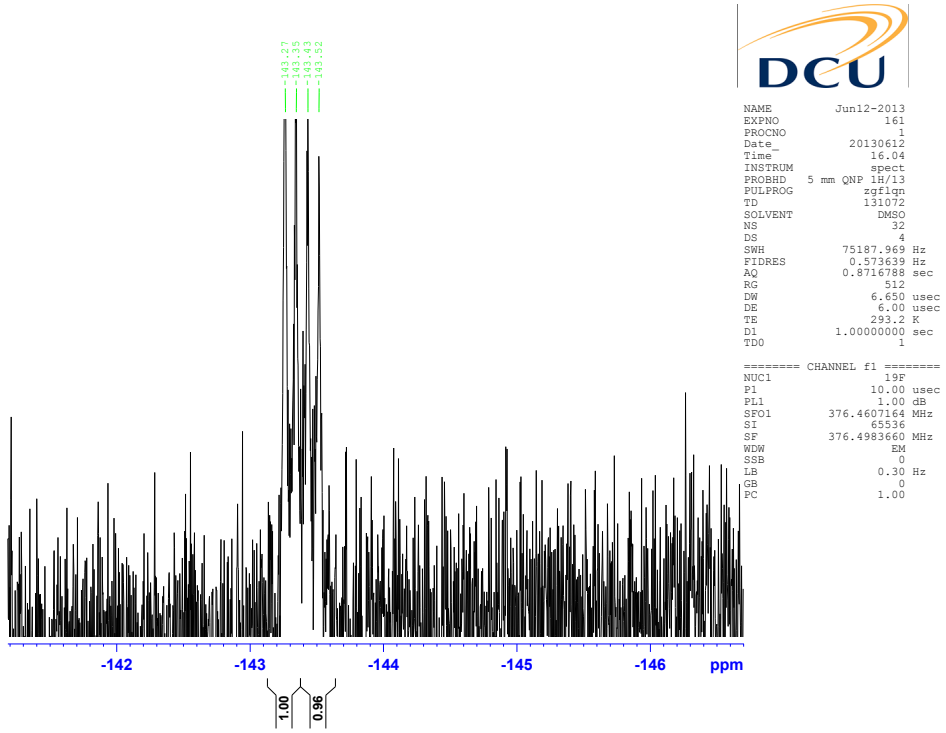
S14. ^{1}H NMR spectra of (5) in $CDCl_3$, inset aromatic region and $C\underline{H}_3$.



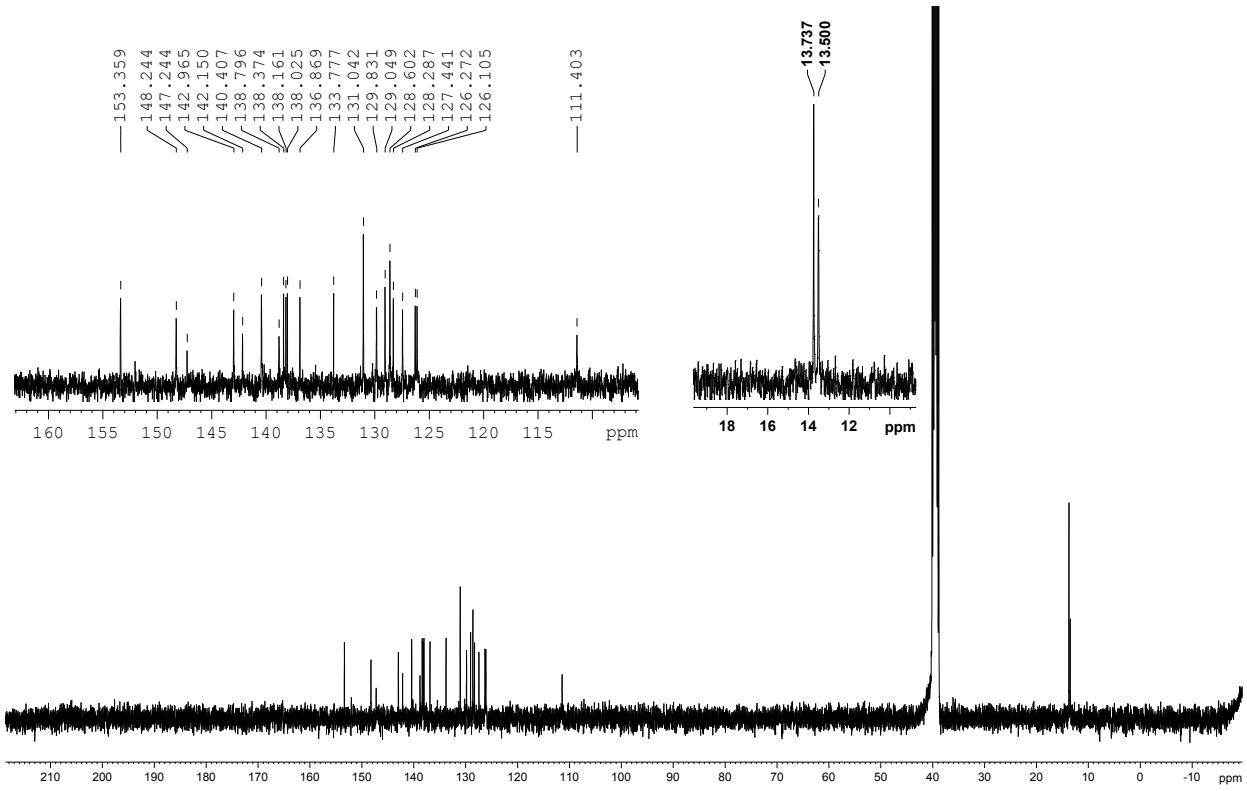
S15. ^{19}F NMR spectra of (5) in $CDCl_3$.



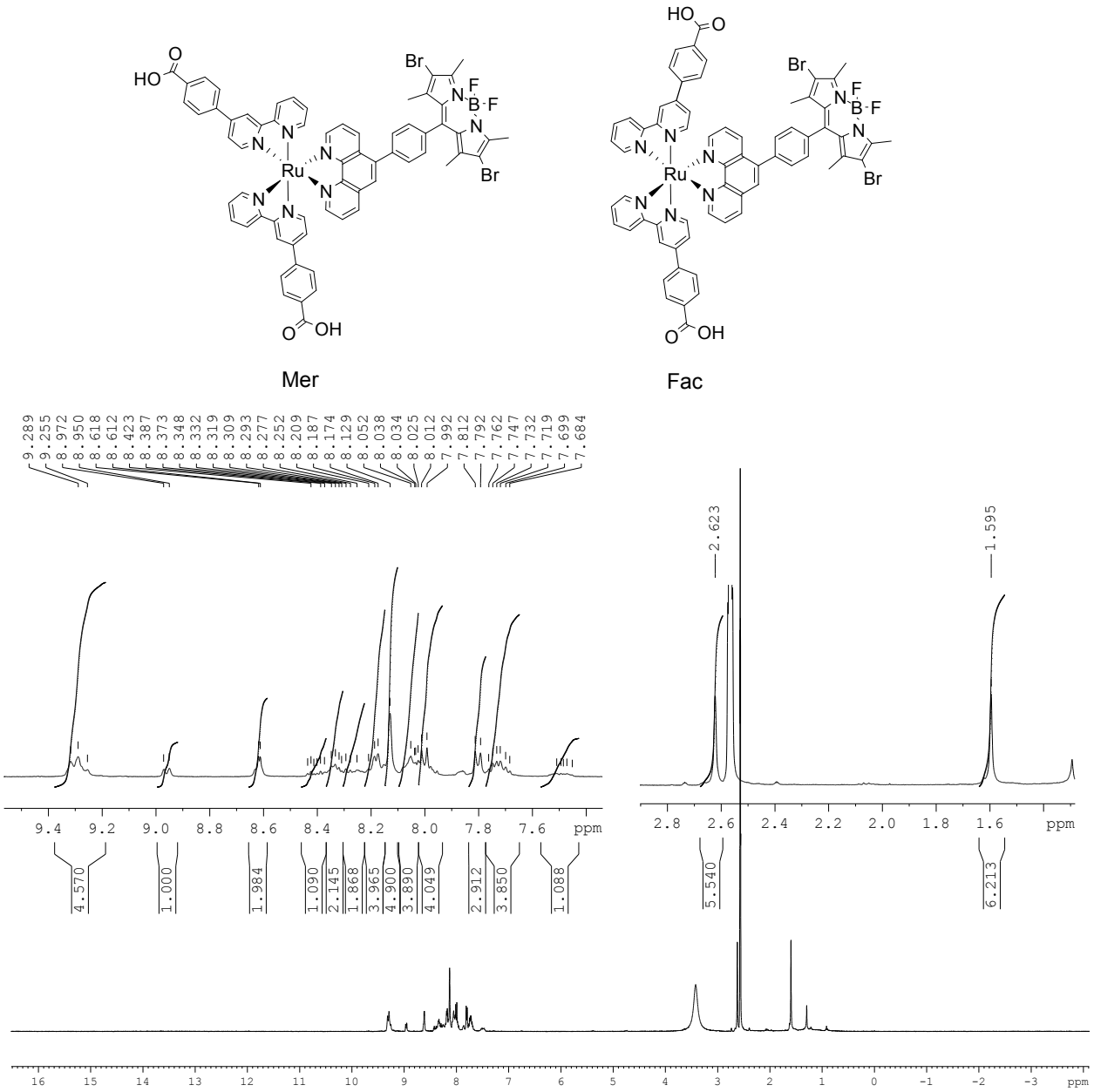
S16. ^{1}H NMR spectra of (7) in DMSO-d_6, inset aromatic region and C$\underline{H}_3$.



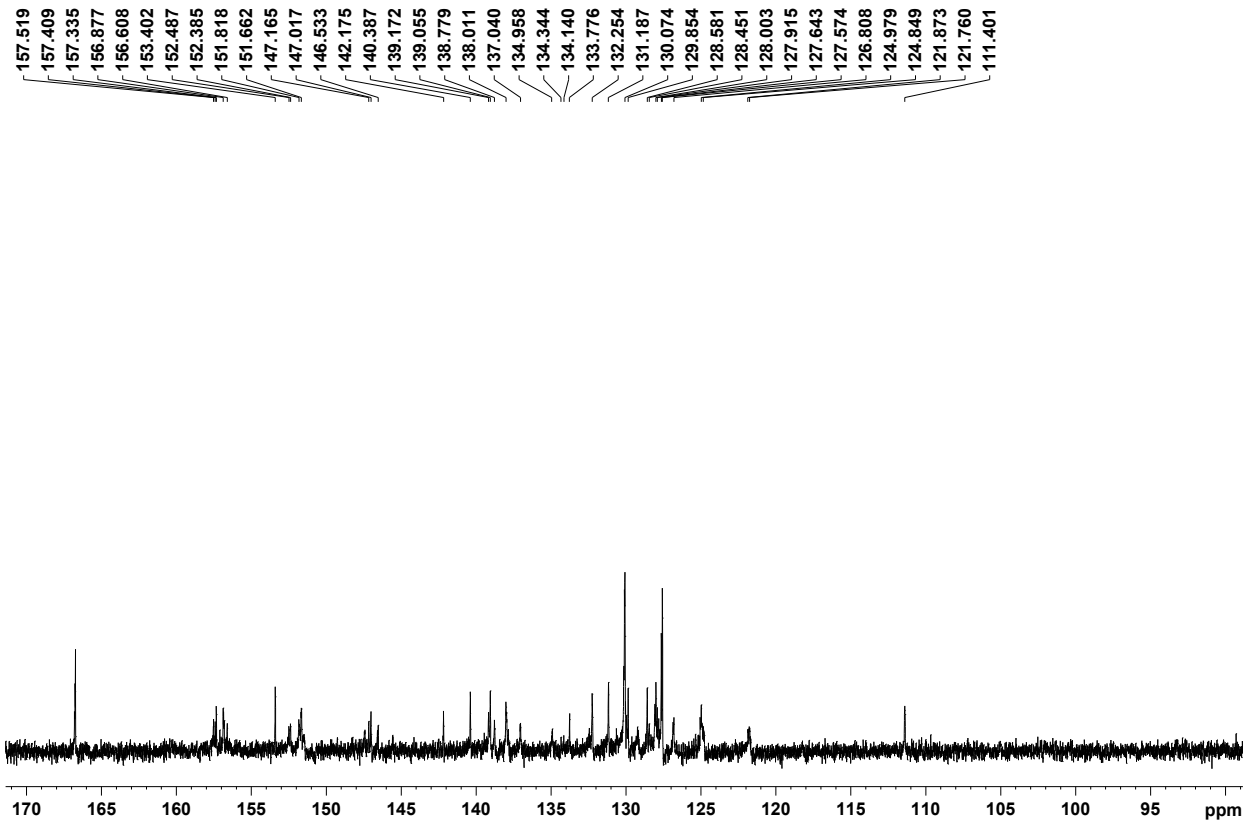
S17. ^{19}F NMR spectra of (7) in DMSO-d_6.



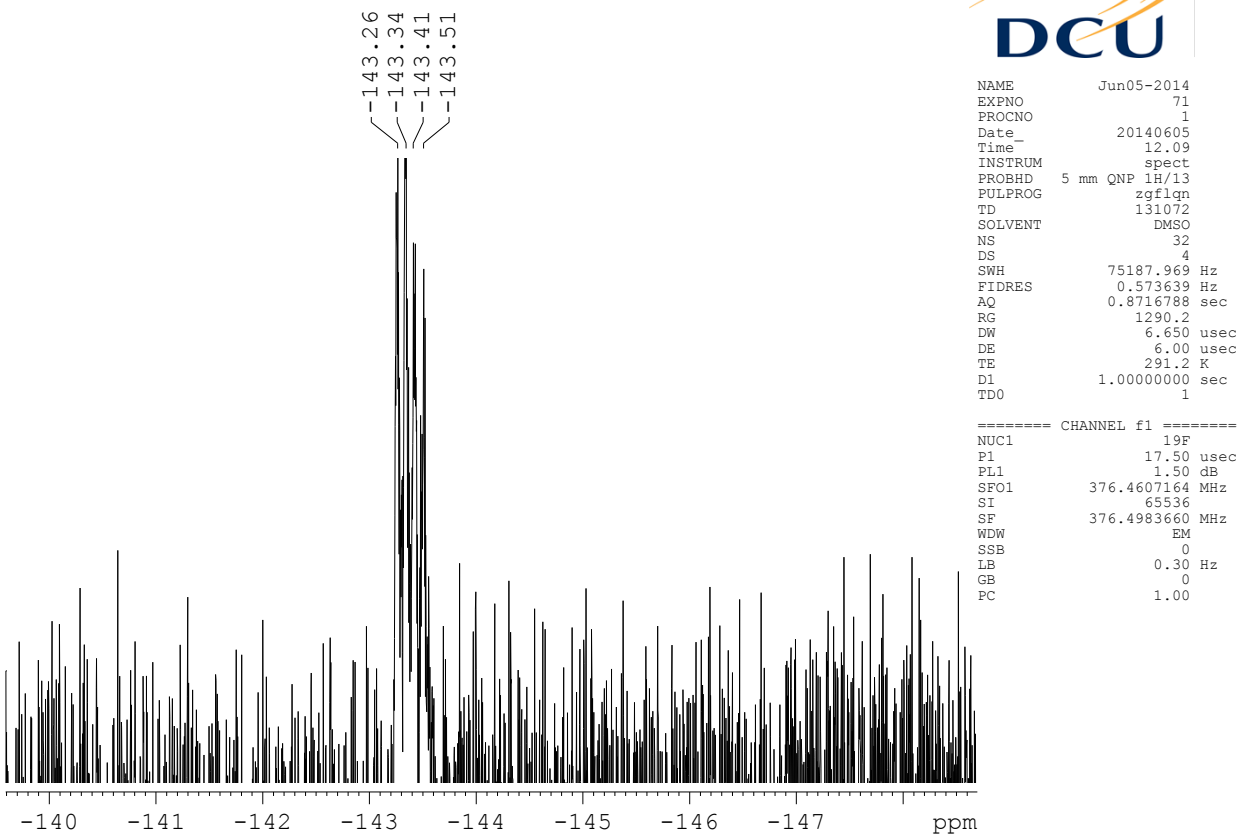
S17. ^{13}C NMR spectra of (7) in DMSO-d_6, inset aromatic region and C<u>H</u>$_3$.



S18. ^{1}H NMR spectra of dyad (9) in DMSO-d_6, the complex is prepared and purified as a mixture of unresolved fac and mer isomers.



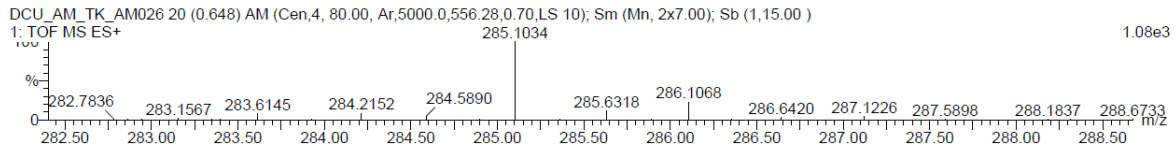
S19. ^{13}C NMR spectra of dyad (9) in DMSO-d_6.



S20. ^{19}F NMR spectra of dyad (9) in DMSO-d_6.

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 1000.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
11 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

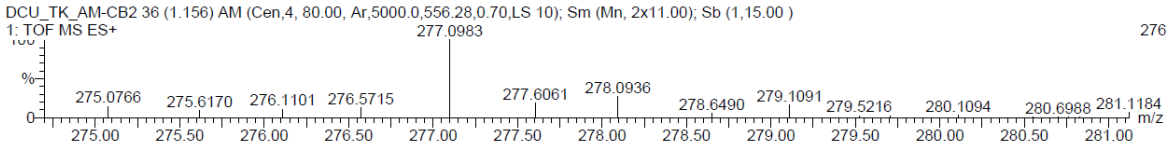


Minimum:				-1.5		
Maximum:		200.0	20.0	1000.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
285.1034	285.1028	0.6	2.1	14.5	1	C19 H13 N2 O

S21. HRMS of (3).

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 1000.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

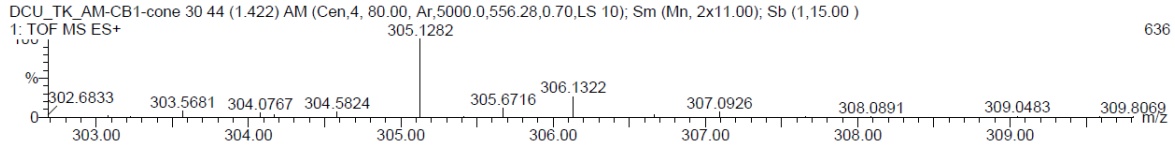


Minimum:				-1.5		
Maximum:		200.0	50.0	1000.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
277.0983	277.0977	0.6	2.2	12.5	1	C17 H13 N2 O2

S22. HRMS of (6).

Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 1000.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
1 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

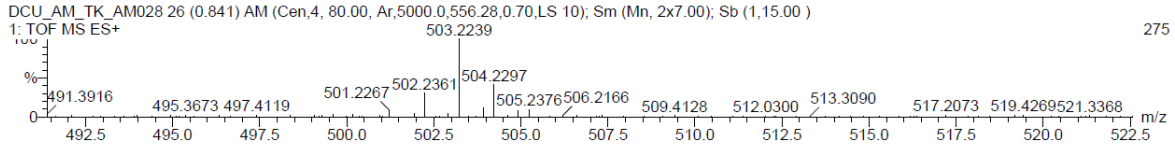


Minimum:				-1.5		
Maximum:		200.0	100.0	1000.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
305.1282	305.1290	-0.8	-2.6	12.5	1	C19 H17 N2 O2

S23. HRMS of (4).

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 1000.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
4 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

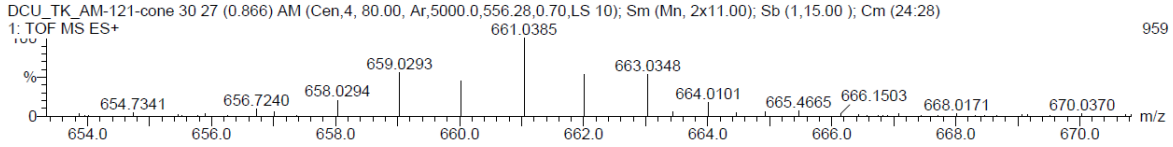


Minimum:				-1.5		
Maximum:		200.0	20.0	1000.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
503.2239	503.2219	2.0	4.1	20.5	1	C31 H26 B N4 F2

S24. HRMS of (5).

Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 1000.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

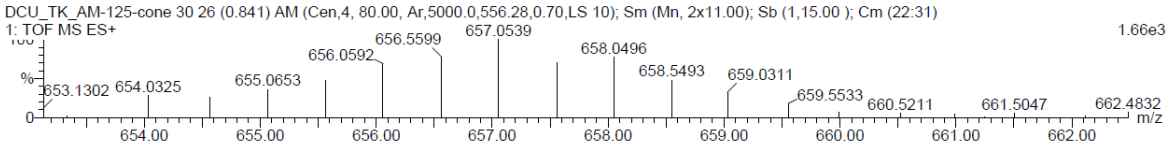


Minimum:				-1.5		
Maximum:		200.0	100.0	1000.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
661.0385	661.0408	-2.3	-3.5	20.5	1	C31 H24 B N4 F2 79Br 81Br

S25. HRMS of (7).

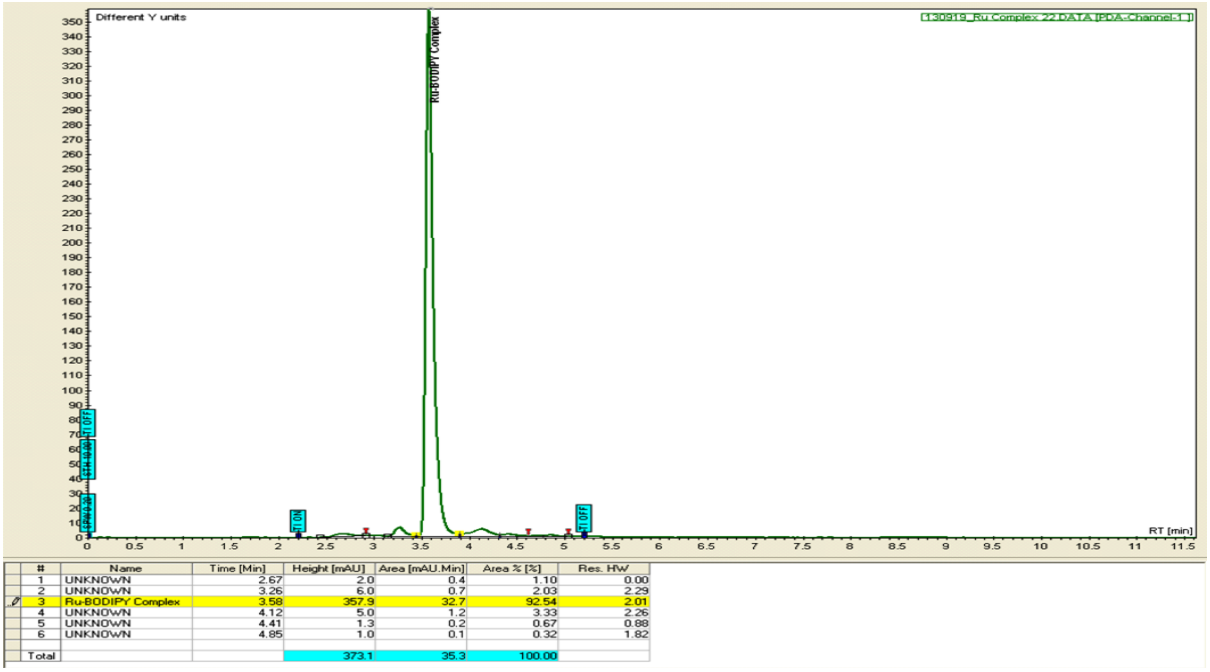
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 0 results within limits (all results (up to 1000) for each mass)



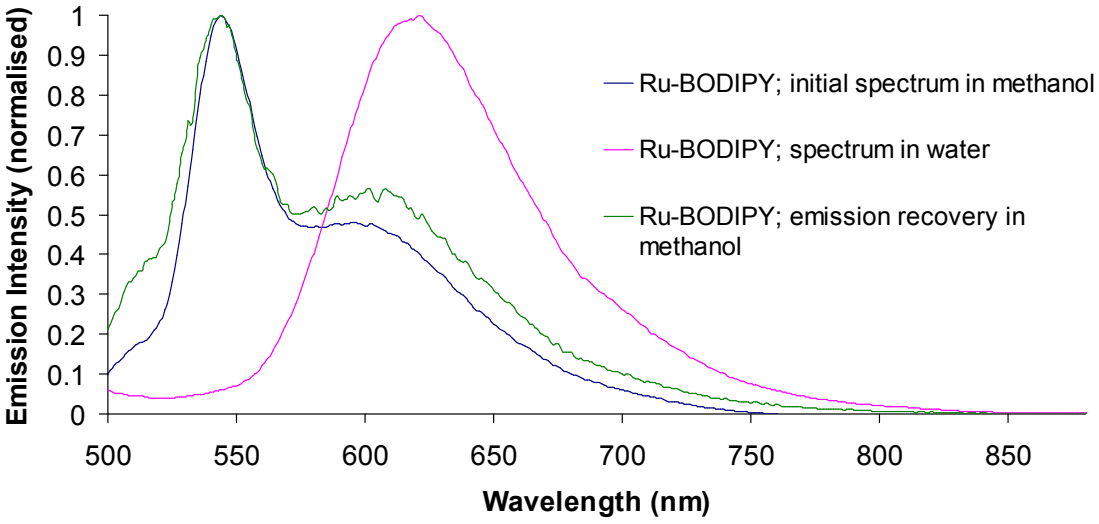
Minimum:				-1.5		
Maximum:		200.0	10.0	1000.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
656.0592	---					

S26. HRMS of dyad (9).



#	Name	Time [Min]	Height [mAU]	Area [mAU.Min]	Area % [%]	Res. HW
1	UNKNOWN	2.67	2.0	0.4	1.10	0.00
2	UNKNOWN	3.26	6.0	0.7	2.03	2.29
3	Ru-BODIPY Complex	3.58	357.9	32.7	92.54	2.01
4	UNKNOWN	4.12	5.0	1.2	3.33	2.26
5	UNKNOWN	4.41	1.3	0.2	0.67	0.88
6	UNKNOWN	4.85	1.0	0.1	0.32	1.82
Total			373.1	35.3	100.00	

S27. HPLC trace of dyad (9).



S28. Normalised emission intensity (excited wavelength of 460 nm) of Ru-BODIPY dyad highlighting the luminescent emission recovery upon changing solvent from methanol to water, and back again.

The intensity of the recovered spectrum is lower than the first methanol and water spectra because it is collected by remixing approximately 100 µL of the aqueous solution back into pure methanol.