Supporting Information

SYNTHESIS AND *IN VITRO* BIOLOGICAL EVALUATION OF A SECOND-GENERATION MULTIMODAL WATER-SOLUBLE PORPHYRIN-RAPTA CONJUGATE FOR THE DUAL-THERAPY OF CANCERS

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UV-VIS SPECTROSCOPY DATA

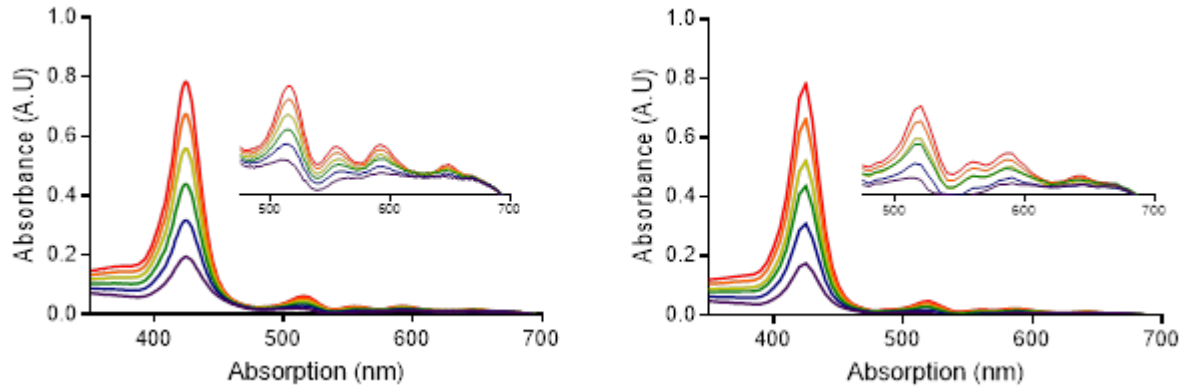

Figure S1. UV-Vis absorption spectra of aqueous solutions of **8** (left) and **9** (right).

FLUORESCENCE SPECTROSCOPY DATA

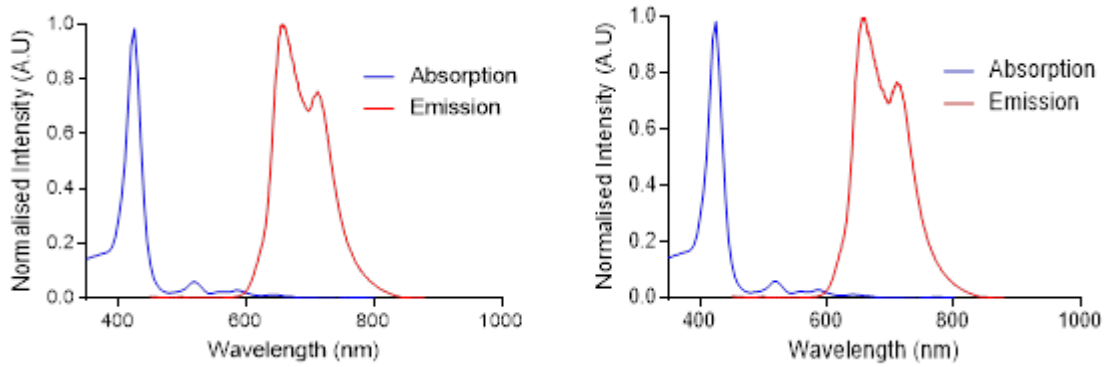

Figure S2. Normalized absorption and fluorescence emission spectra of aqueous solutions of **8** (left) and **9** (right).

RELATIVE SINGLET OXYGEN QUANTUM YIELD SPECTROSCOPY DATA

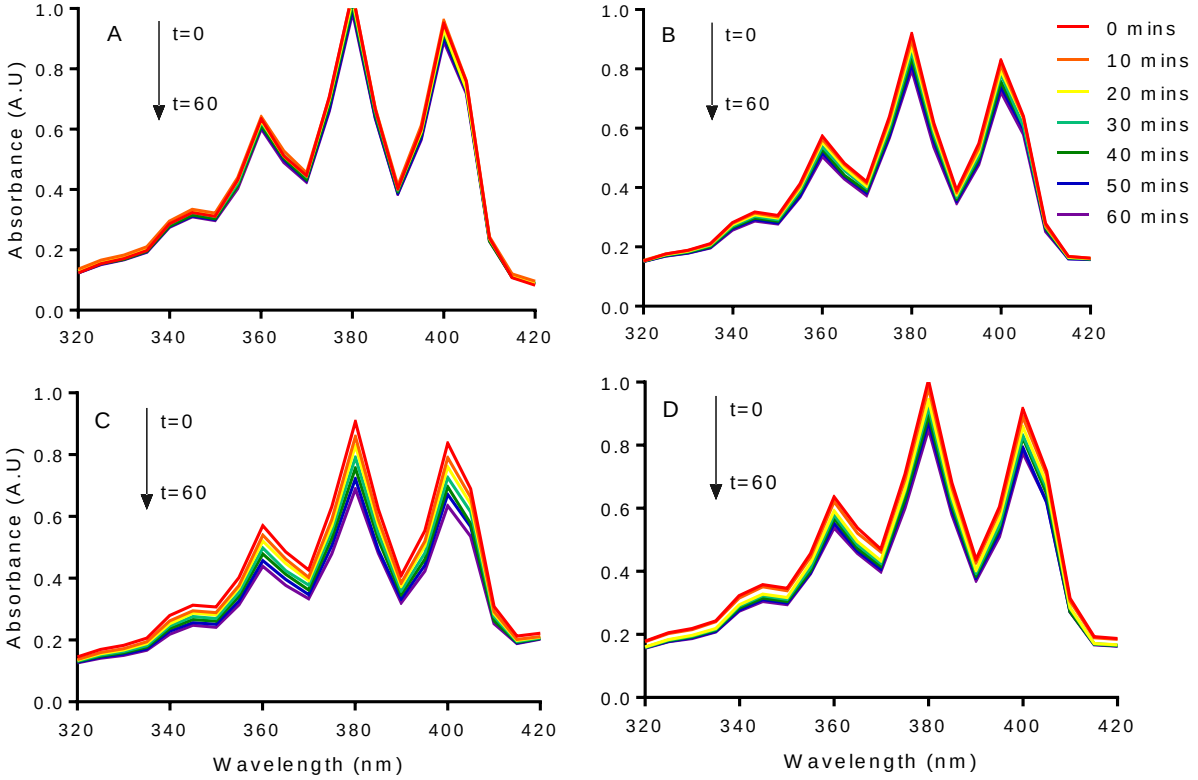

Figure S3. UV-Vis absorbance spectra of ABDA irradiated with red light (617-651 nm) with and without photosensitizer. Curves are averages of three independent experiments (n=3). A; ABDA only, B: ABDA irradiated in the presence of 3.7 μM of **8**, C: ABDA irradiated in the presence of 3.7 μM of **9**, D: ABDA irradiated in the presence of 3.7 μM of **TMePyP**.

^{31}P-NMR SPECTROSCOPY PHOTOSTABILITY DATA

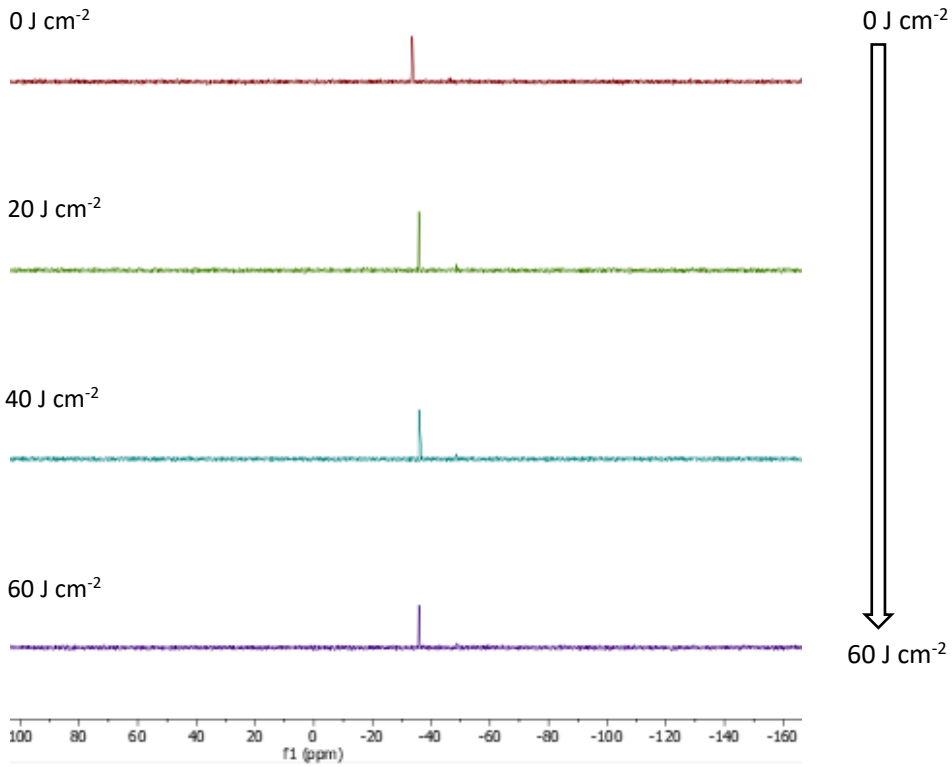

Figure S4. ^{31}P-NMR spectroscopy photostability data of compound **9** recorded after being irradiated with either 0, 20, 40 or 60 J cm^{-2} of white light demonstrating the photostability of the [Ru(η^6-arene)(C_2O_4)PTA] unit. Chemical shift (δ) measured in ppm.

BRIGHTFIELD AND FLUORESCENCE MICROSCOPY

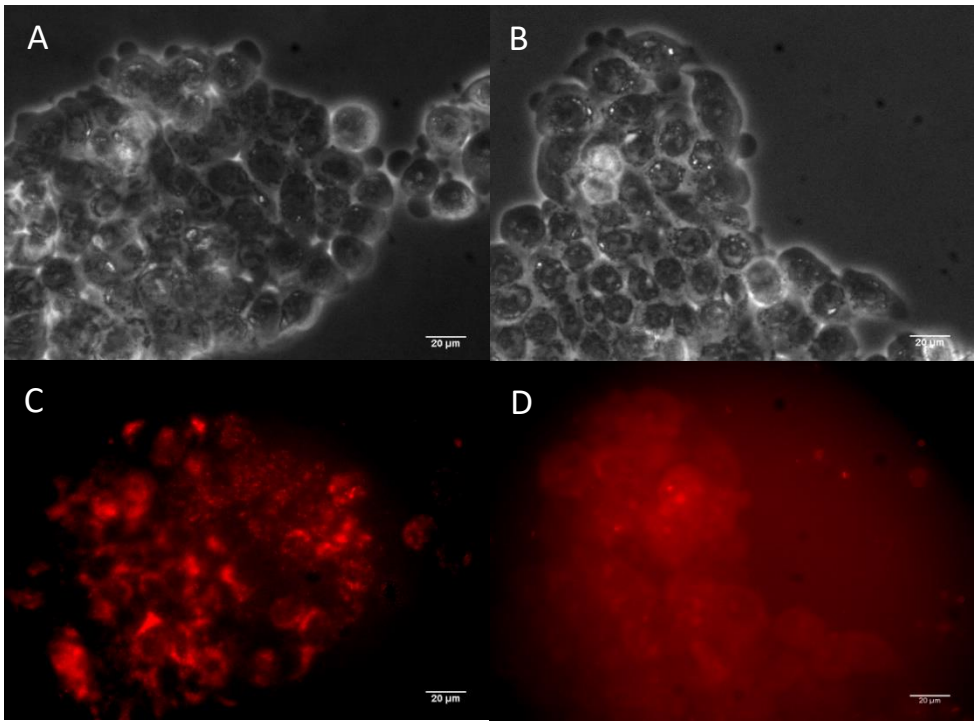

Figure S5. Brightfield micrographs of HT-29 cells incubated for 24-hours with 10 µM concentrations of **8** (A) and **9** (B). Fluorescence micrographs of HT-29 cells incubated for 24-hours with 10 µM concentrations of **8** (C) and **9** (D).

SYNTHETIC PROTOCOLS
RAPTA Compounds
Complex **1** was synthesised as previously described:

(1) Murray, B. S.; Menin, L.; Scopelliti, R.; Dyson, P. J. Conformational control of anticancer activity: the application of arene-linked dinuclear ruthenium(II) organometallics. *Chem. Sci.*, **2014**, *5*, 2536-2545.

Complex 2: TBTU (160 mg, 0.498 mmol) and **1** (178 mg, 0.349 mmol) were suspended in DMSO (4 mL) then DIPEA (364 µL, 2.09 mmol) was added and the mixture was left to stir for 5 min. Methylamine hydrochloride (24 mg, 0.355 mmol) was then added and the reaction mixture was left to stir. After 2 hr the yellow solution that had formed was added to a silica gel column (4 cm x 20 cm loaded in acetone) with acetone (20 mL) in excess in the solvent reservoir. The solvent was eluted to allow the yellow suspension to settle onto the silica gel. The column was then eluted with acetone (200 mL to remove DMSO) then MeOH (300 mL) followed by MeOH/H_2O (500 ml, 9:1). The product eluted as a yellow solution – this was filtered then dried at 65 °C under reduced pressure. The residue was dissolved in MeOH (30 mL) with heating, allowed to cool and left to vapour diffuse (48 hr) with diethyl ether to yield a precipitate. The solvent was decanted and the precipitated solid washed with diethyl ether then dissolved in H_2O (5 mL) and lyophilized to leave the product as an orange solid (51 mg, 0.096 mmol, 28 % (yield based on partially hydrated complex)). ^{1}H NMR (400 MHz, D_2O, 25ºC): δ=5.94 (d, J = 6.5 Hz, 2H; Ar-H), 5.90 (d, J = 6.0 Hz, 2H; Ar-H), 4.56 (s, 6H; PTA), 4.15 (s, 6H; PTA), 2.66 (s, 3H; -NHCH_3), 2.58 (s, 4H; CH_2-CH_2), 2.05 (s, 3H; Ar-CH_3); ^{31}P{^{1}H} NMR (162 MHz, D_2O, 25ºC): δ =-32.8 (s, PTA); ^{13}C{^{1}H} NMR (100 MHz, D_2O, 25ºC): δ=174.5, 166.1, 98.8, 96.6, 88.4 (d, J = 3.0 Hz), 87.7 (d, J = 3.5 Hz), 70.7 (d, J = 6.5 Hz), 48.5 (d, J = 15.5 Hz), 35.5, 28.2, 25.8, 17.3; HRMS (ESI$^+$) m/z [M+H]$^+$ calcd for $C_{19}H_{28}N_4O_5RuP$: 525.0853, found 525.0840; elemental analysis calcd for $C_{19}H_{27}N_4O_5PRu•0.5H_2O$: C 42.86, H 5.30, N 10.52, found: C 42.56, H 5.16, N 10.30.

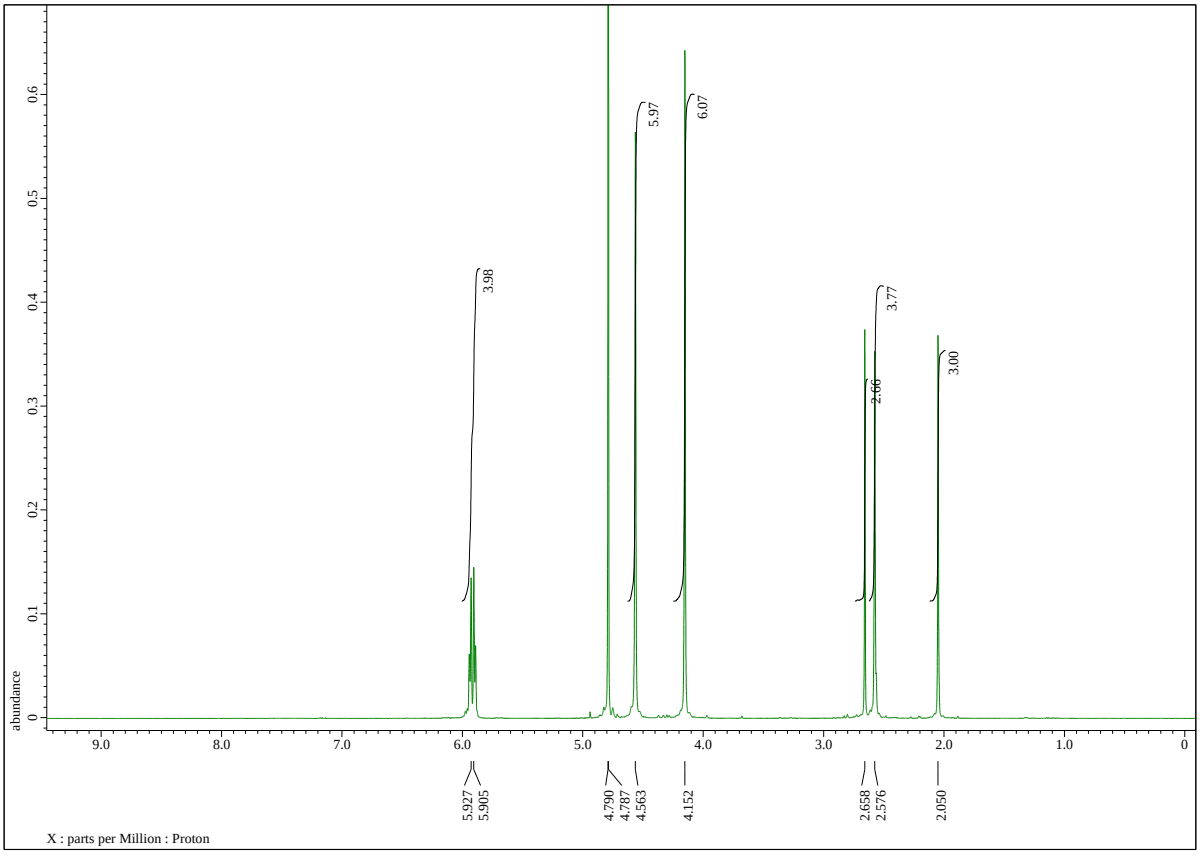

Figure S6. ^{1}H NMR spectrum of **2**. D_2O was used as NMR solvent.

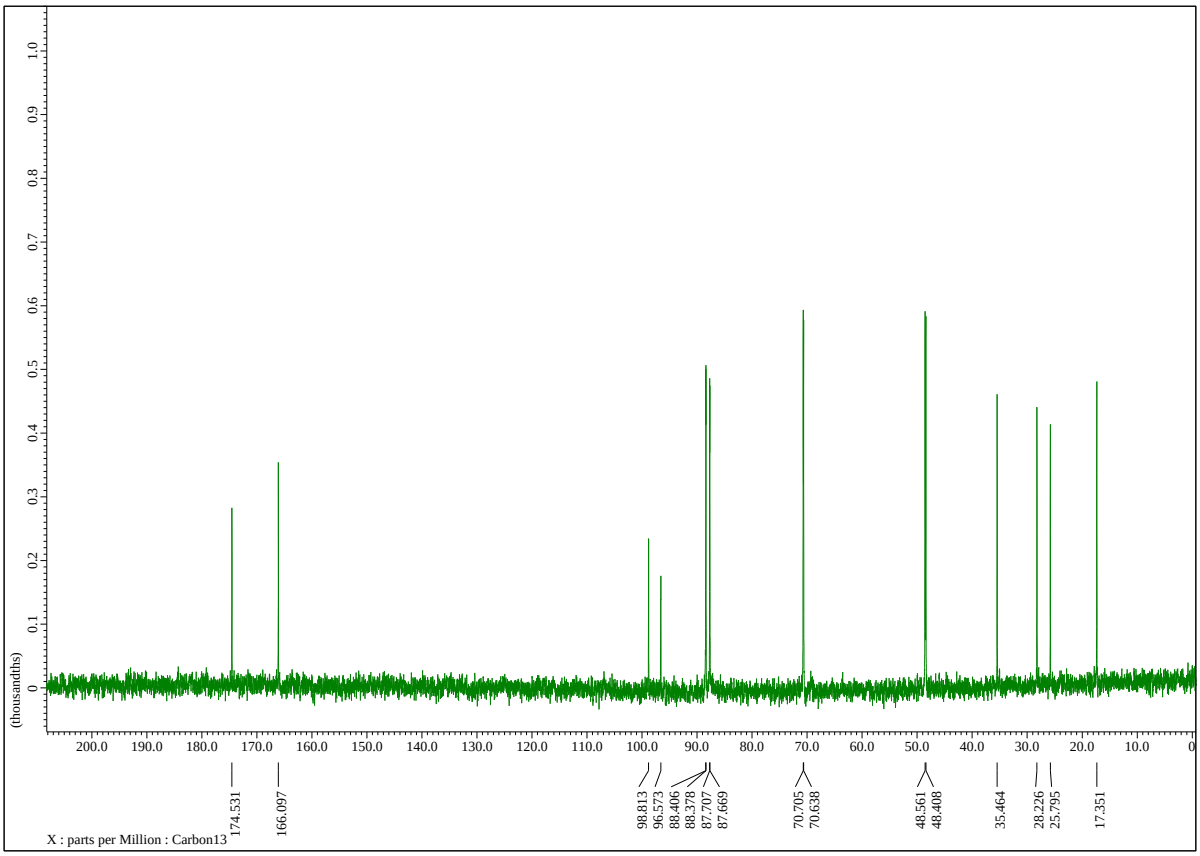

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **2**. D_2O was used as NMR solvent.

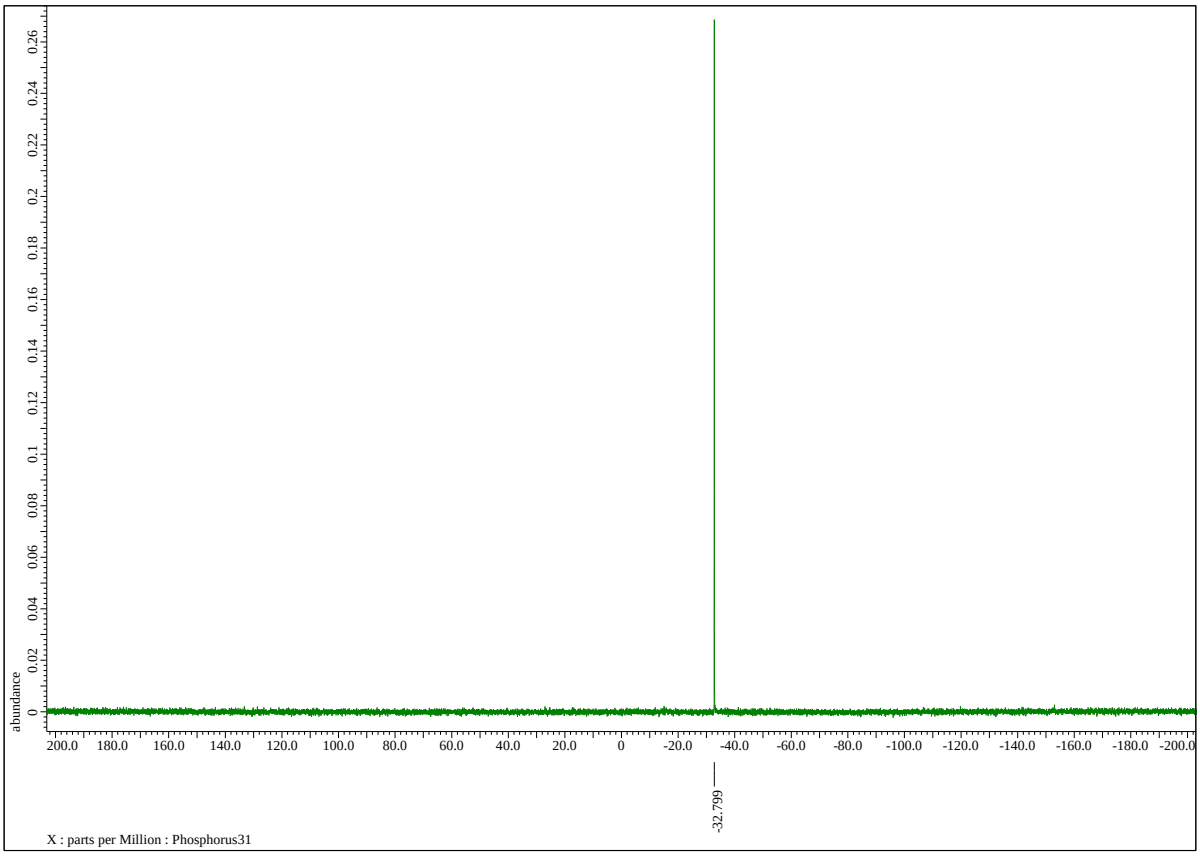

Figure S8. $^{31}P\{^{1}H\}$ NMR spectrum of **2**. D_2O was used as NMR solvent.

Porphyrin Compounds

Compounds **3-5** were all synthesised as described according to the methods of Yap *et al*.[2] All structural determination data matched with previously published works unless stated otherwise.

(2) Yap, Y. Y.; Price, T. W.; Savoie, H.; Boyle R. W.; Stasiuk, G. J. Selective radiolabelling with ^{68}Ga under mild conditions: a route towards a porphyrin PET/PDT theranostic agent. *Chem. Commun.*, **2018**, *54*, 7952–7954.

5-[4-(2-(2-(2-Boc-aminoethoxy)ethoxy)ethaneaminocarbonyl)phenyl]-10,15,20-tris-(4-pyridyl)porphyrin (3):[2] Under an inert atmosphere, to a solution of 5-[4-carboxyphenyl]-10,15,20-tri-(4-pyridyl)porphyrin (500 mg, 755.5 mmol) in DMF (20 mL) was added tert-butyl (2-(2-(2-aminoethoxy)ethoxy)ethyl)carbamate (280 mg, 1.133 mmol) and TBTU (600 mg, 1.133 mmol) and DIPEA (2 mL). The reaction was stirred at 80 ºC overnight. Bulk solvent was removed under reduced pressure. The crude was taken in DCM and washed with copious amounts of water. The organic layer was separated and dried with anhydrous $MgSO_4$. The semi-crude was dissolved in a minimum of DCM and eluted onto a silica chromatography column. The product eluted in DCM/MeOH (93:7) as the first major red band. The fractions were collected and bulk solvent removed under reduced pressure. The solids were dissolved in a minimum of MeOH and precipitated over Et_2O to yield a deep purple crystalline powder (556 mg, 623.0 mmol, 82% yield). R_F: 0.50 (silica, 9:1, DCM/MeOH); ^{1}H NMR (400 MHz, $CDCl_3$, 25ºC, TMS): δ=9.05 (dd, J=4.4 Hz, 10H; o-Py-H, overlapping 4H; β-H), 8.85 (d, 4H; o-Ar-H, m-Ar-H), 8.16 (dd, J=4.4 Hz, 10H; o-Py-H, overlapping 4H; β-H), 3.73 (m, 12H; CH_2-CH_2), 1.24 (s, 9H; NHBoc), -2.92 (s, 2H, N-H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25ºC, TMS): δ=156.08 (C=O), 150.95 (NHBoc), 147.90, 142.90, 134.70, 134.42, 129.66, 128.45, 126.88, 126.70, 125.72, 124.49, 124.45, 118.93, 118.54, 117.45, 110.30, 70.62, 70.37, 55.12, 45.31, 43.21, 40.41, 28.46; HRMS (MALDI) m/z $M^{+\cdot}$ calcd for $C_{53}H_{49}N_9O_5$: 891.3868 found: 891.3851; UV-Vis (DCM): λ_{max} 418 (24742), 516 (3936), 550 (,383), 590 (1678), 651 nm (58 mol^{-1}dm^{3}cm^{-1}).

5-[4-(2-(2-(2-Boc-aminoethoxy)ethoxy)ethaneaminocarbonyl)phenyl]-10,15,20-tris-(N-methyl-4-pyridinium)porphyrin triiodide (4):[2] Under an inert atmosphere, **3** (200 mg, 0.224 mmol) was dissolved in DMF (80 mL) and the flask fitted with a triethylamine trap bubbler. Methyl iodide (3 mL) was added dropwise and the reaction stirred at 40 ºC overnight. Excess diethyl ether (200 mL) as added to the flask and the precipitate filtered off under gravity through a plug of cotton wool. The crude precipitate was dissolved in methanol and precipitated from diethyl ether (100 mL). The product was filtered under reduced pressure to give a burgundy solid which was washed copiously with diethyl ether. The powder was dissolved in a minimum of methanol and precipitated over diethyl ether to give lustrous purple crystals (250 mg, 0.190 mmol, 84% yield). R_F: 0.37 (silica, 8:1:1, acetonitrile/water/$KNO_{3(aq)}$); Rt: 9.75 mins (C-18 silica); ^{1}H NMR (400 MHz, DMSO-d6, 25ºC): δ=9.44 (d, 6H; m-Py-H), 9.14 (m, 8H; β-H), 8.97 (d, 6H; o-Py-H), 8.31 (d, 2H; m-Ar-H), 7.91 (d, 2H; o-Ar-H), 6.90 (s, 1H; NHBoc), 4.60 (m, 9H; Py-CH_3), 3.14 (m, 4H; CH_2-CH_2), 1.32 (s, 9H; NHBoc), -3.08 (s, 2H; NH); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d6, 25ºC): δ=173.99 (C=O), 168.68 (CO-O), 166.68, 164.01, 163.56, 144.64, 137.15, 136.18, 135.39, 130.84, 128.65, 126.95, 125.54, 92.21, 91.49, 80.14, 79.72, 30.29, 23.84; HRMS (ESI+) m/z [M-3I]$^{3+}$ calcd for $C_{56}H_{58}N_9O_5$: 312.1507 found: 312.1515. UV-Vis (MeOH): λ_{max} 426 (91,213), 519 (6601), 560 (2390), 595 (2202), 650 nm (497 mol^{-1}dm^{3}cm^{-1}).

5-[4-(2-(2-(2-Aminoethoxy)ethoxy)ethaneaminocarbonyl)phenyl]-10,15,20-tris-(N-methyl-4-pyridinium)porphyrin triiodide (5):[2] **4** (200 mg, 0.152 mmol) was dissolved in DCM/TFA (10 mL, 1:1) and stirred for 3 h. Bulk solvent was removed under reduced pressure and the product precipitated from a minimum of methanol over diethyl ether to yield a deep purple crystalline powder (182 mg, 0.127 mmol, 81%). R_F: 0.16 (silica, 8:1:1, acetonitrile/water/$KNO_{3(aq)}$); Rt: 11.0 mins (C-18 silica); ^{1}H NMR (400 MHz, DMSO-d6, 25ºC): δ=9.44 (d, 6H; m-Py-H), 8.99 (d, 6H; o-Py-H, overlapping 8H; β-H), 8.31 (dd, 4H; o-Ar-H, m-Ar-H), 7.87 (d, 3H; NH_3), 4.69 (s, 9H; Py-CH_3), 3.63 (m, 10H; CH_2-CH_2), 3.00 (t, 2H; CH_2-CH_2), -3.06 (s, 2H, NH); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d6, 25ºC): δ=166.68 (C=O), 158.44, 158.14, 157.05, 144.74, 143.61, 134.74, 132.66, 126.61, 126.43, 122.38, 119.40, 116.42, 115.92, 115.28, 70.30, 70.04, 69.55, 67.29, 48.40, 39.18; HRMS (ESI+) m/z [M-3I]$^-$ calcd for $C_{51}H_{50}N_9O_3$: 278.8007 found: 278.8001; UV-Vis (MeOH): λ_{max} 426 (192171), 518 (14154), 555 (6800), 595 (5137), 650 nm (2328 mol^{-1}dm^{3}cm^{-1}).

5-[4-(2-(2-(2-Aminoethoxy)ethoxy)ethaneaminocarbonyl)phenyl]-10,15,20-tris-(4-pyridyl)porphyrin (6): To a solution of 5-[4-(2-(2-(2-boc-aminoethoxy)ethoxy)ethaneaminocarbonyl)phenyl]-10,15,20-tris-(4- pyridyl)porphyrin (200 mg, 0.220 mmol) in DCM (10 mL) was added TFA (5 mL). The mixture was stirred for 3 hrs at room temperature. Bulk solvent was removed under reduced pressure and the crude dissolved in a minimum of methanol and precipitated over diethyl ether to give a deep purple solid which was used without further purification (187 mg, 0.207 mmol, 94% yield). R_F: 0.37 (silica, 8:2, DCM/MeOH); ^{1}H NMR (400 MHz, DMSO-d6, 25ºC): δ=9.04 (d, 6H; m-Py-H), 8.87 (s, 8H; β-H), 8.28 (m, 4H; m-Ar-H, o-Ar-H overlapping 6H; o-Py-H), 7.79 (brs, 2H; NH_2) 3.60 (m, 5H; CH_2-CH_2 overlapping residual NMR solvent), 3.04 (m 6H; CH_2-CH_2), -3.07 (s, 2H; N-H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d6, 25ºC): δ=169.01(C=O), 149.34, 148.88, 143.11, 134.68, 134.59, 129.69, 126.44, 118.18, 117.93, 70.24, 70.13, 69.52, 30.94, 29.73; HRMS (ASAP) m/z [M+H]$^+$ calcd for $C_{48}H_{42}N_9O_3$: 792.3411 found: 792.3403. UV-Vis (MeOH): λ_{max} 405 (112570), 504 (9147), 536 (3166), 582 (2858), 647 nm (1071 mol^{-1}dm^{3}cm^{-1})

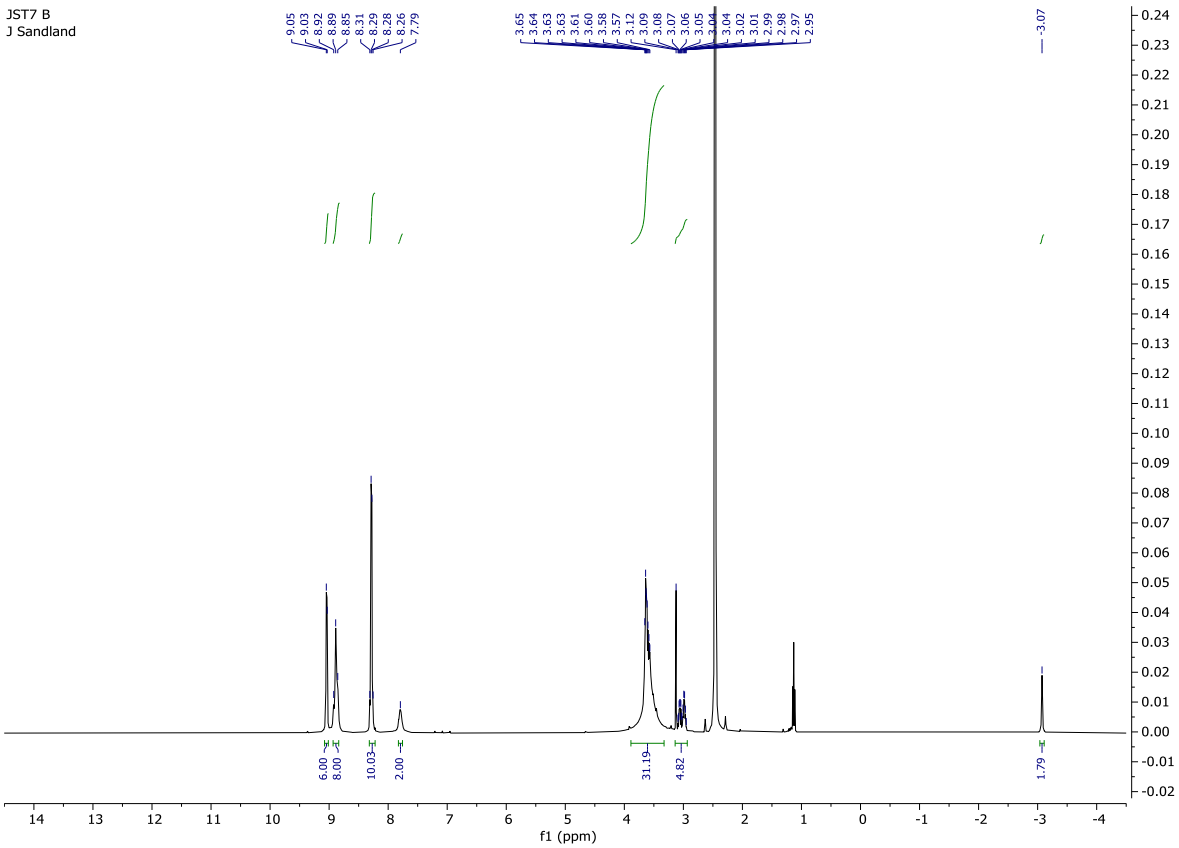

Figure S9. ^{1}H NMR spectrum of **6**. DMSO-d6 was used as NMR solvent.

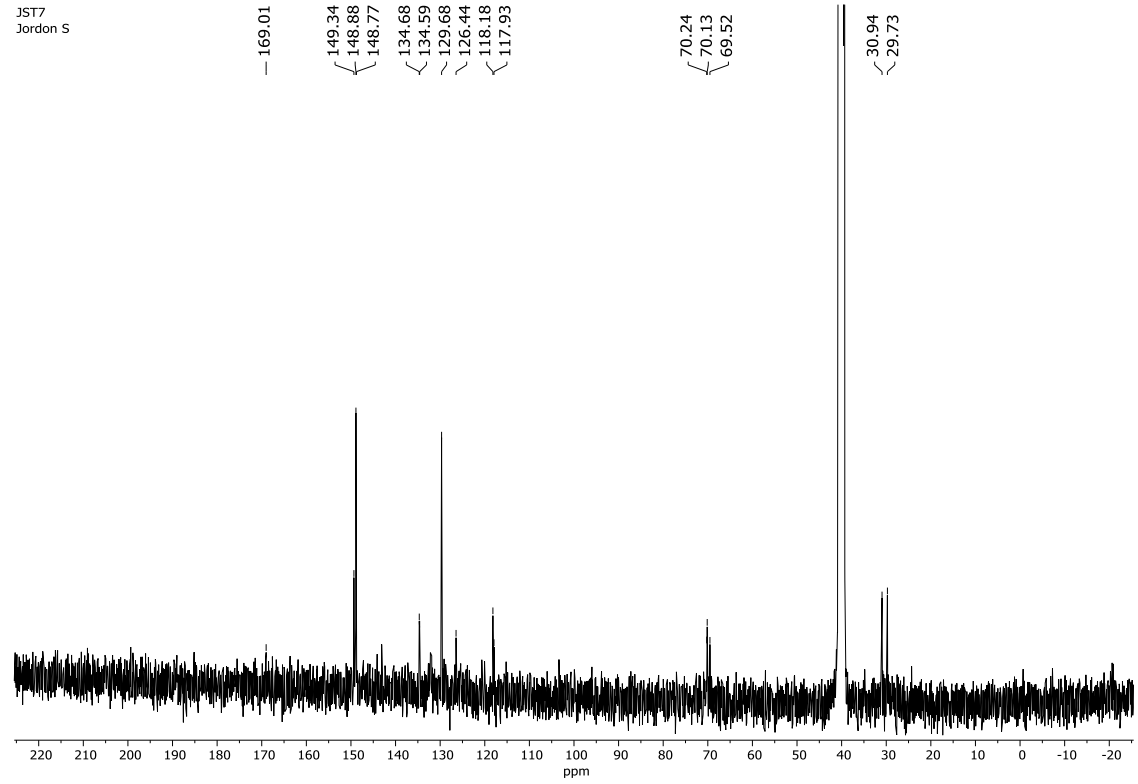

Figure S10. ^{13}C{^{1}H} NMR spectrum of **6**. DMSO-d6 was used as NMR solvent.

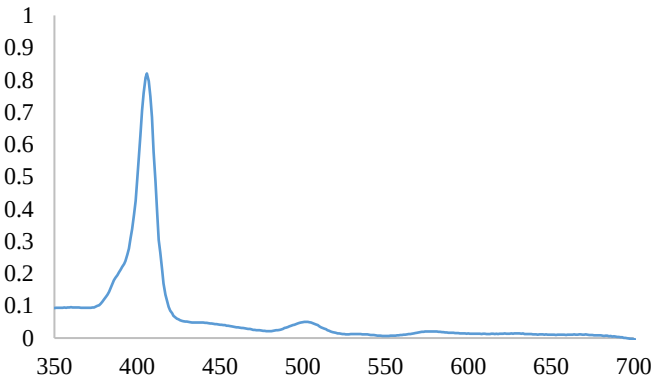

Figure S11. UV-Vis spectrum of **6** in MeOH.

5-[4-(2-(2-(2-Acetimideethoxy)ethoxy)ethaneaminocarbonyl)phenyl]-10,15,20-tris-(4-pyridyl)porphyrin (7): To a solution of **6** (100 mg, 0.111 mmol) in DMF (10 mL) was added DIPEA (5 mL, 3.71 g, 28.7 mmol). Acetic anhydride (2 mL, 2.16 g, 21.16 mmol) was added dropwise and the reaction stirred overnight at room temperature. A second aliquot of acetic anhydride (2 mL, 2.16 g, 21.16 mmol) and DIPEA (5 mL, 3.71 g, 28.7 mmol) was added and the mixture heated to 70 ºC for 4 hr with stirring. Bulk solvent was removed under reduced pressure. The crude was taken in DCM and washed with copious amounts of water. The organic layer was separated and dried with anhydrous $MgSO_4$. The semi-crude was dissolved in a minimum of DCM and eluted onto a silica chromatography column. The product eluted in DCM/MeOH (93:7) as the first major red band. The fractions were collected and bulk solvent removed under reduced pressure. The solids were dissolved in a minimum of DCM and precipitated over hexane to yield a deep purple crystalline powder (67 mg, 0.080 mmol, 72% yield). R_F: 0.87 (silica, 95:5, DCM/MeOH); ^{1}H NMR (400 MHz, DMSO-d6, 25ºC): δ=9.01 (d, J=4.9 Hz, 6H; o-Py-H), 8.86 (d, J=6.2 Hz, 8H; β-H), 8.28 (m, 4H; o-,m-Ar-H), 8.34 (d, 6H, o-Py-H), 7.92 (s, 1H; N-H), 3.59 (m, 10H; CH_2-CH_2), 3.41 (t, J=5.9 Hz, 2H; CH_2-CH_2), 1.73 (s, 3H; CONH-CH_3), -3.08 (s, 2H; N-H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d6, 25ºC): δ=169.79 (C=O), 149.35, 148.91, 134.71, 129.69, 126.45, 117.96, 70.18, 69.75, 69.52, 23.11 (CONH-CH_3); HRMS (ESI+) m/z $[M+Na]^+$ calcd for $C_{50}H_{43}N_9O_4{}^{23}Na$: 856.3336 found: 856.3334; UV-Vis (DCM): λ_{max} 425 (126890), 518 (9172), 561 (3322), 595 (3310), 650 nm (1482 $mol^{-1}dm^3cm^{-1}$).

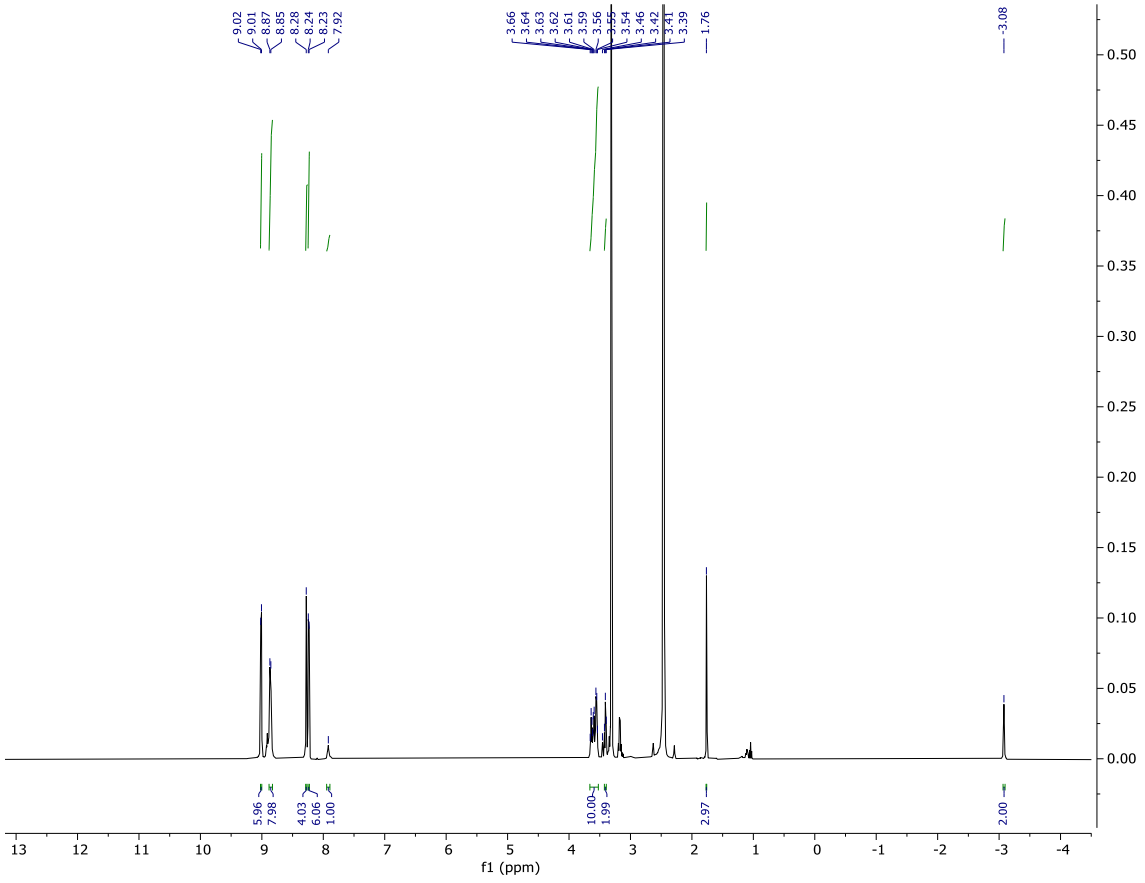

Figure S12. ^{1}H NMR spectrum of **7**. DMSO-d6 was used as NMR solvent.

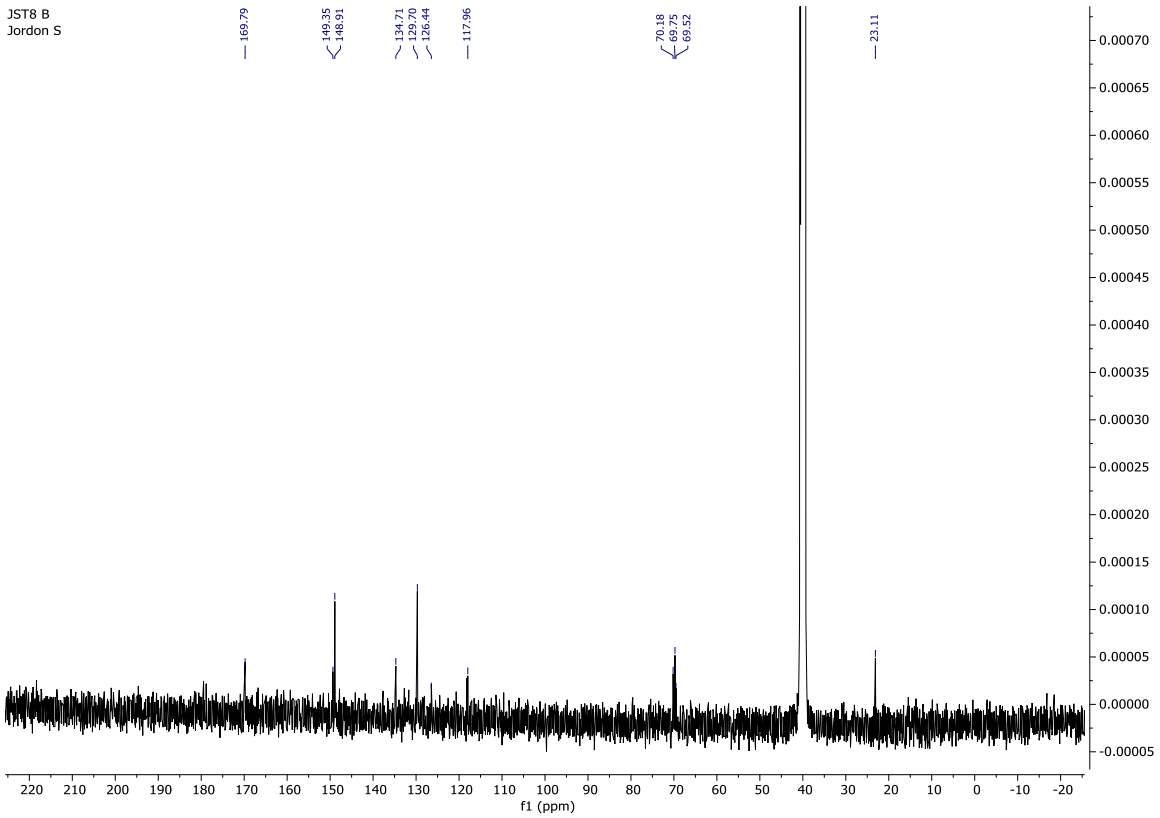

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of **7**. DMSO-d6 was used as NMR solvent.

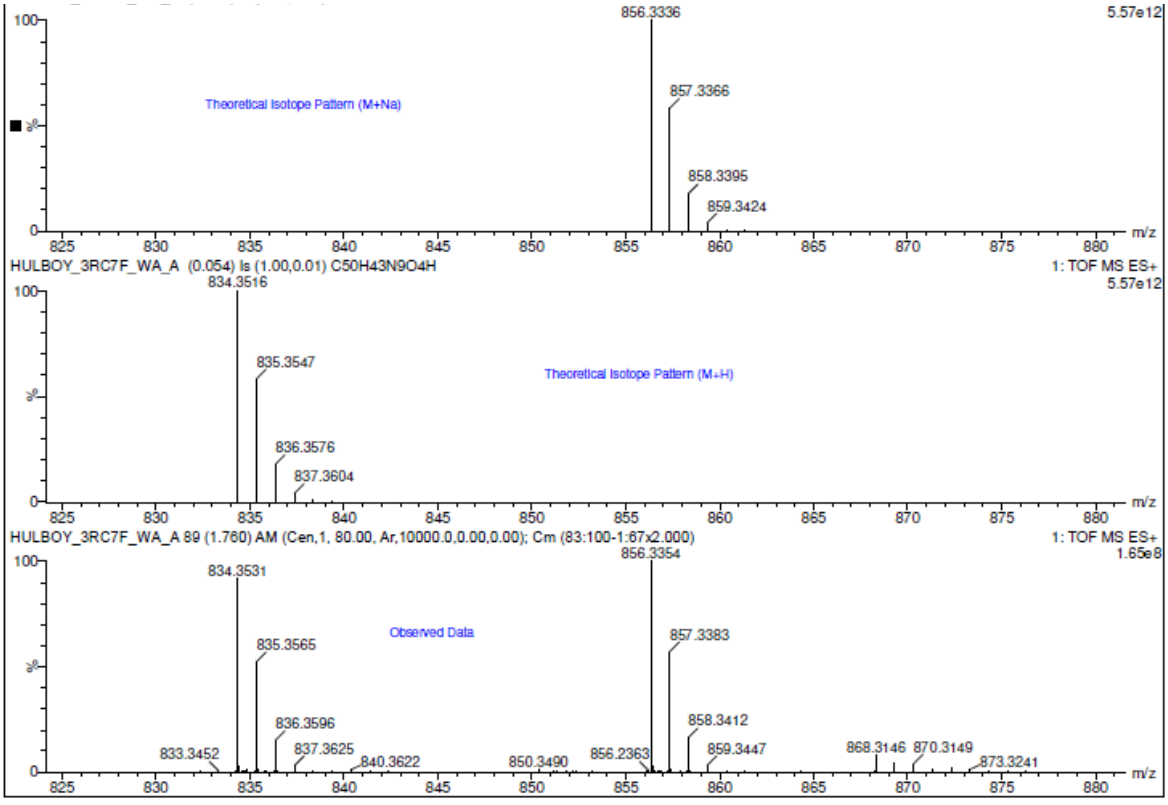

Figure S14. ESI+ HRMS of **7.**

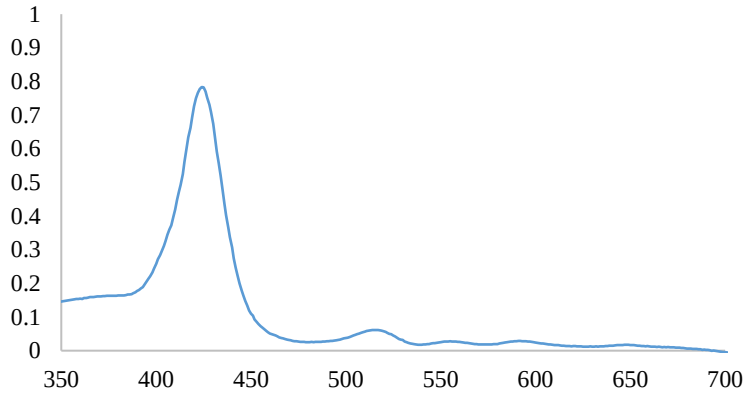

Figure S15. UV-Vis spectrum of **7** obtained in DMSO.

5-[4-(2-(2-(2-Acetimideethoxy)ethoxy)ethaneaminocarbonyl)phenyl]-10,15,20-tris-(N-methyl-4-pyridinium)porphyrin trichloride (8): 7 (50 mg, 0.060 mmol) was dissolved in DMF (80 mL) and the flask fitted with a triethylamine trap bubbler. Methyl iodide (1 mL) was added dropwise and the reaction stirred at 40 ^{o}C overnight. Excess diethyl ether (100 mL) as added to the flask and the precipitate filtered off under gravity through a plug of cotton wool. The crude precipitate was dissolved in methanol and precipitated from diethyl ether (100 mL). The product was filtered under reduced pressure to give a burgundy solid which was washed copiously with diethyl ether to yield the product as a deep purple crystalline solid as the triiodide salt. The product was dissolved in water (5 mL) and excess ammonium hexafluorophosphate added, the precipitate was collected via filtration under reduced pressure, the solids were dissolved in acetone (5 mL) and excess tetrabutylammonium chloride added, the precipitate was collected via filtration under reduced pressure and the solids dried until reaching constant mass to yield a deep purple powder (56 mg, 0.056 mmol, 94% yield). R_F: 0.34 (silica, 8:1:1, acetonitrile/water/$KNO_{3(aq)}$); Rt: 10.10 mins (C-18 silica); ^{1}H NMR (400 MHz, DMSO-d6, 25^{o}C): δ=9.45 (d, J=6.5 Hz, 6H; m-Py-H), 9.15 (s, 4H; o-Py-H), 9.04 (s, 2H; o-Py-H), 8.98 (d, J=6.5 Hz, 8H; β-H), 8.31 (d, J=5.7 Hz, 4H; o-,m-Ar-H), 7.93 (s, 1H; N-H), 4.68 (s, 9H; Py-CH_3), 3.60 (m, 8H; CH_2-CH_2), 3.42 (t, 2H; CH_2-CH_2), 3.18 (m, 2H, CH_2-CH_2), 1.77 (s, 3H; CONH-CH_3), -3.08 (s, 2H; N-H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d6, 25^{o}C): δ=169.84 (C=O), 166.63 (C=O), 157.16, 144.73, 142.96, 134.74, 132.65, 126.61, 122.40, 115.93, 114.9, 70.15, 69.73, 69.56, 48.42 (Py-$\underline{C}H_3$), 34.91, 23.14 (NHCO-CH_3); HRMS (ESI+) m/z $[M\text{-}3Cl]^{3+}$ calcd for $C_{53}H_{52}N_9O_4$: 292.8042 found: 292.8047; UV-Vis (H_2O): λ_{max} 423 (125893), 521 (8913), 562 (4677), 588 (4365), 645 nm (1479 $mol^{-1}dm^3cm^{-1}$); Fluorescence: (H_2O): λ_{ex} 425 nm, λ_{em} 658, 714 nm.

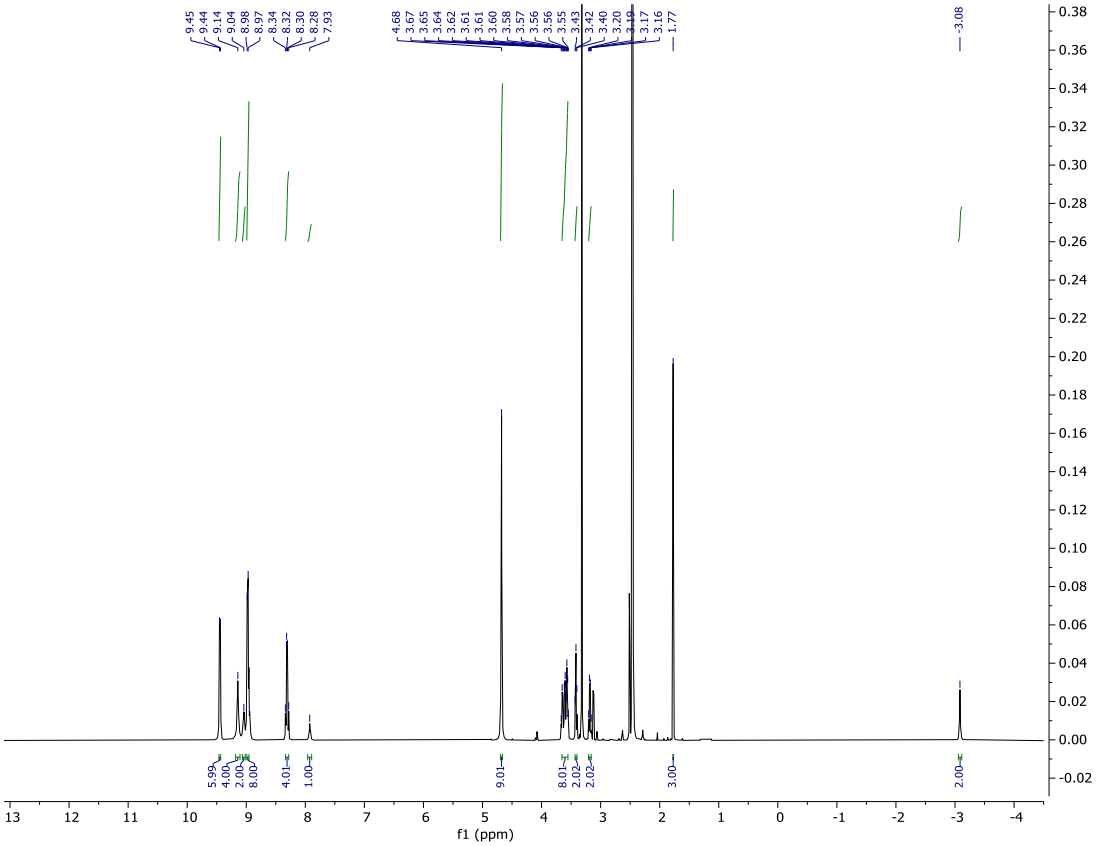

Figure S16. ^{1}H NMR spectrum of **8**. Deuterated DMSO-d6 was used as NMR solvent.

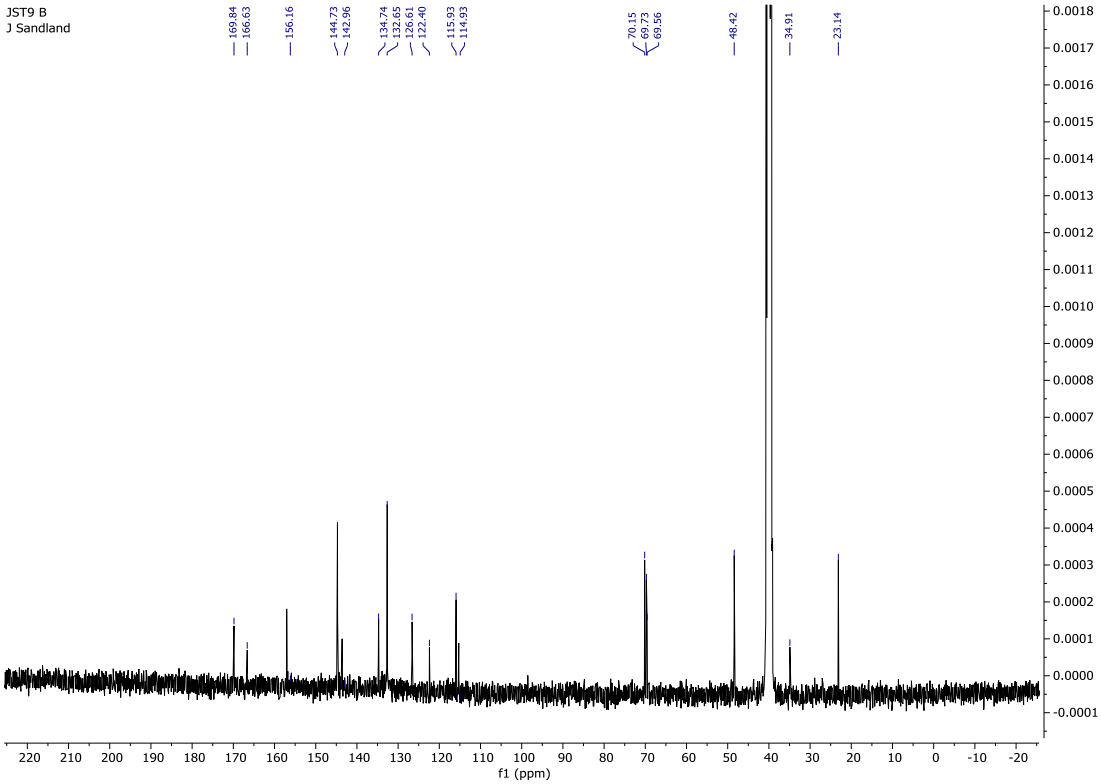

Figure S17. ^{13}C{^{1}H} NMR spectrum of **8**. Deuterated DMSO-d6 was used as NMR solvent.

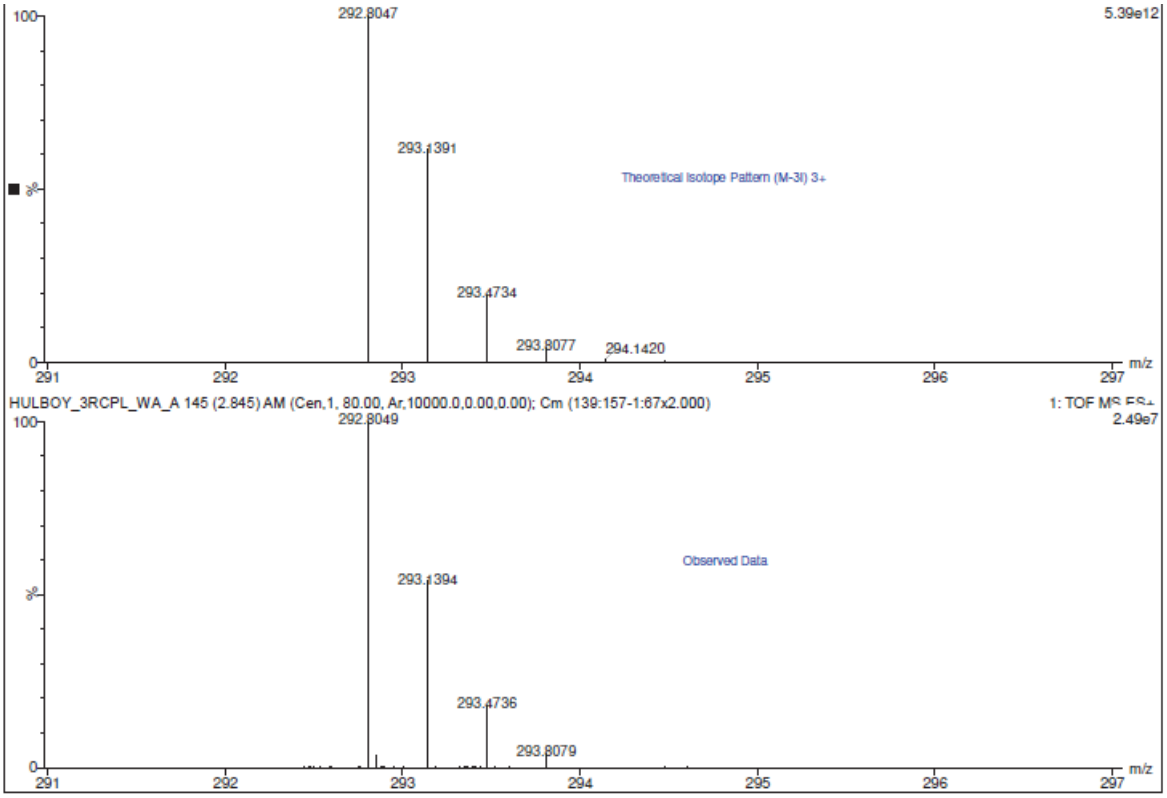

Figure S18. ESI+ HRMS of **8.**

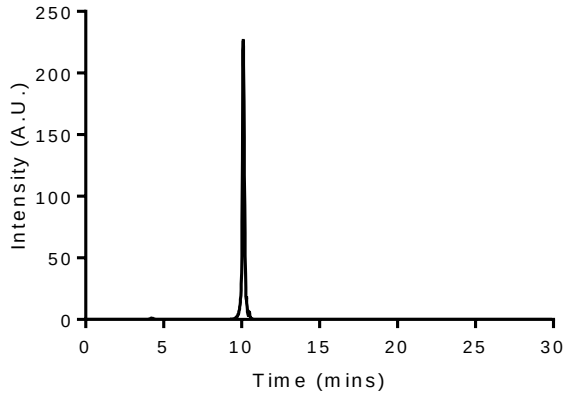

Figure S19. Analytical HPLC of **8**.

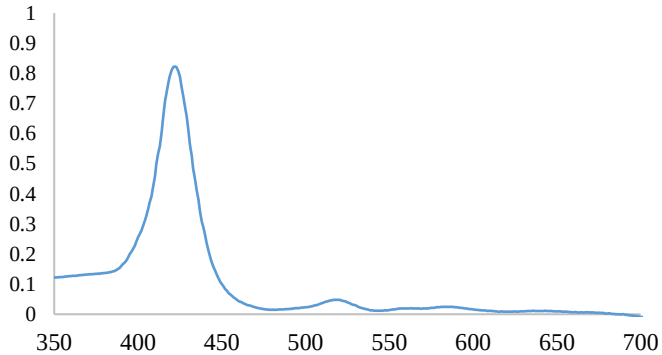

Figure S20. UV-Vis spectrum of **8** obtained in water.

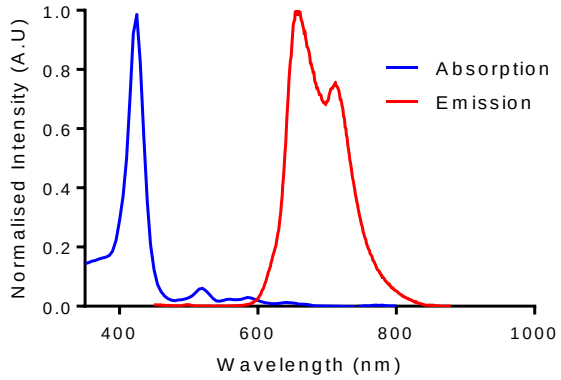

Figure S21. Fluorescence absorpbtion-emission spectrum of **8** obtained in water.

Conjugate (9): 5 (49 mg, 0.096 mmol) and TBTU (31 mg, 0.097 mmol) were suspended in DMSO (1 ml) followed by the addition of DIPEA (49 µL, 0.286 mmol). The mixture was stirred for 5 min followed by the addition of **1** (40 mg, 0.032 mmol) (a 3:1 ratio of **5** and **1** was utilised to push amide formation with **1** to completion as a 1:1 ratio was found to result in quantities of unreacted **1**). The dark coloured mixture was stirred for 3 h whilst protected from light then diluted with acetone (12 mL) and left to stand for 13 h at 4°C, the precipitate was collected by centrifugation. The collected solid residue was suspended in acetone (10 mL) and the solids collected by centrifugation. The combined solids were dried under reduced pressure then dissolved in H_2O (0.5 mL) followed by the addition of a solution of NH_4PF_6 (31 mg, 0.190 mmol) in H_2O (0.5 mL) to yield a precipitate that was collected by centrifugation. The solids were taken in H_2O (3 mL) then collected by centrifugation. The collected solid was dried under reduced pressure then dissolved in acetone (2.5 mL) followed by the addition of a solution of tetrabutylammonium chloride (93 mg, 0.335 mmol) in acetone (0.5 mL). The precipitate was collected by centrifugation then the collected solid dispersed in acetone (1 mL) and collected by centrifugation. The solid was suspended in acetone:H_2O (9:1, 10 mL) and the insoluble material collected by centrifugation. The collected solid was then dissolved in H_2O (1 mL) followed by the addition of acetone (9 mL), the mixture was vigorously shaken then allowed to stand for 30 min, followed by centrifugation to collect the solid. This process was repeated followed by washing of the collected solid in acetone (3 x 10 mL) and collection by centrifugation. The solid was dissolved in H_2O (1 mL) then lyophilized to yield a purple solid (8 mg, 5.51 µmol, 17% yield). R_F: 0.32 (silica, 8:1:1, acetonitrile/water/$KNO_{3(aq)}$); ^{1}H-NMR (400 MHz, DMSO-d6, 25°C): δ=9.44 (m, 6H; m-Py-H), 9.07 (m, 6H; o-Py-H), 8.96 (m, 8H; β-H, overlapping 2H, N<u>H</u>-CO), 8.30 (m, 4H; o-,m-Ar), 5.76-5.87 (m, 4H; Ru-Ar), 4.68 (s, 9H; Py-CH_3), 4.32 (s, 6H; PTA), 3.95 (s, 6H; PTA), 3.56 (m, 12H; CH_2-CH_2), 1.84 (s, 3H; Ar-CH_3) (-CH_2CH_2-Ar- signal not observed as this is obscured by residual solvent signal); ^{31}P-NMR (162 MHz, D_2O, 25°C): δ=-33.76 (s, PTA). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d6, 25°C): δ=173.02 (<u>C</u>=O), 169.80 (<u>C</u>=O), 164.44, 157.15, 143.86, 132.86, 125.38, 121.63, 114.85, 114.60, 86.72, 85.11, 70.06, 69.42, 68.55, 48.38, 47.93, 47.79, 39.66, 38.90, 34.36, 26.75; HRMS (ESI+) m/z $[M]^{3+}$ calcd for $C_{69}H_{72}N_{12}O_8PRu$: 443.1458 found: 443.1446; UV-Vis (H_2O): λ_{max} 426 (131825), 525 (7943), 565 (4571), 595 (3388), 650 nm (1047 $mol^{-1}dm^3cm^{-1}$). ; Fluorescence: (H_2O): λ_{ex} 426 nm, λ_{em} 656, 710 nm.

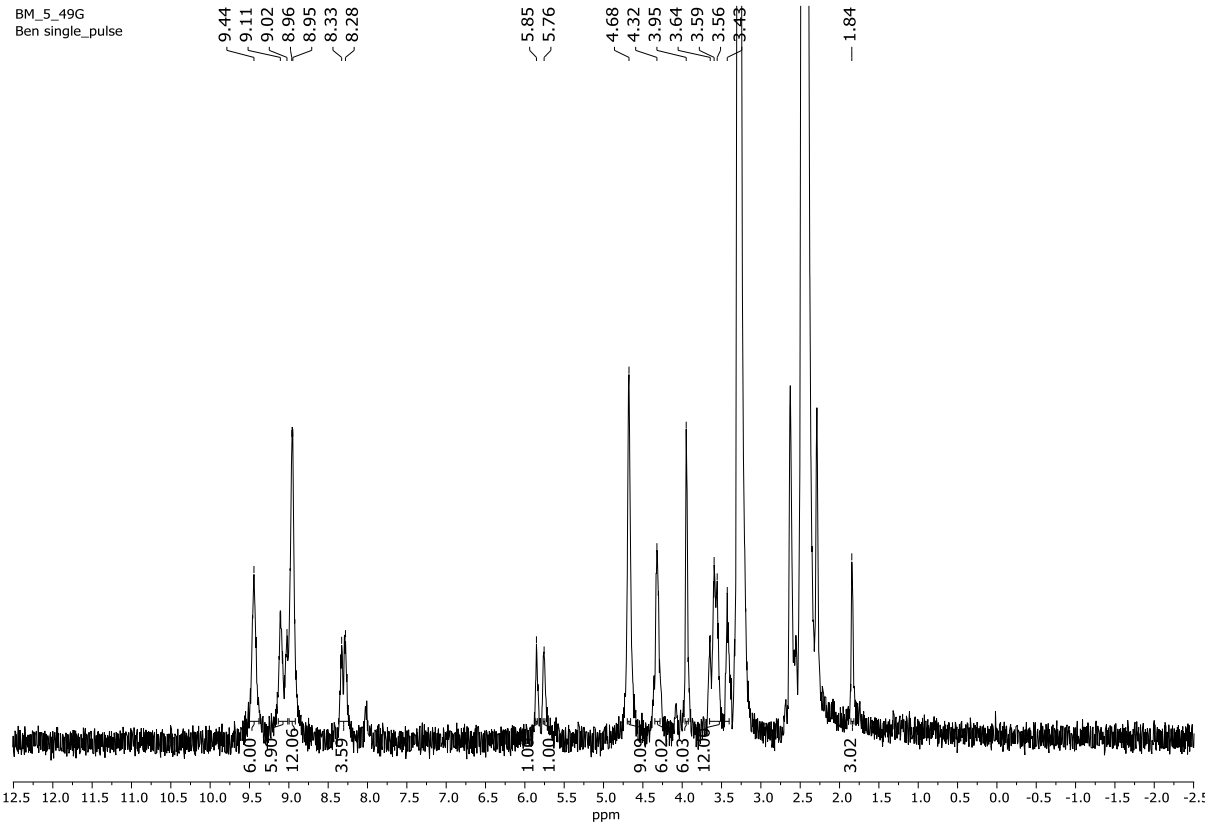

Figure S22. ^{1}H NMR spectrum of **9**. DMSO-d6 was used as NMR solvent.

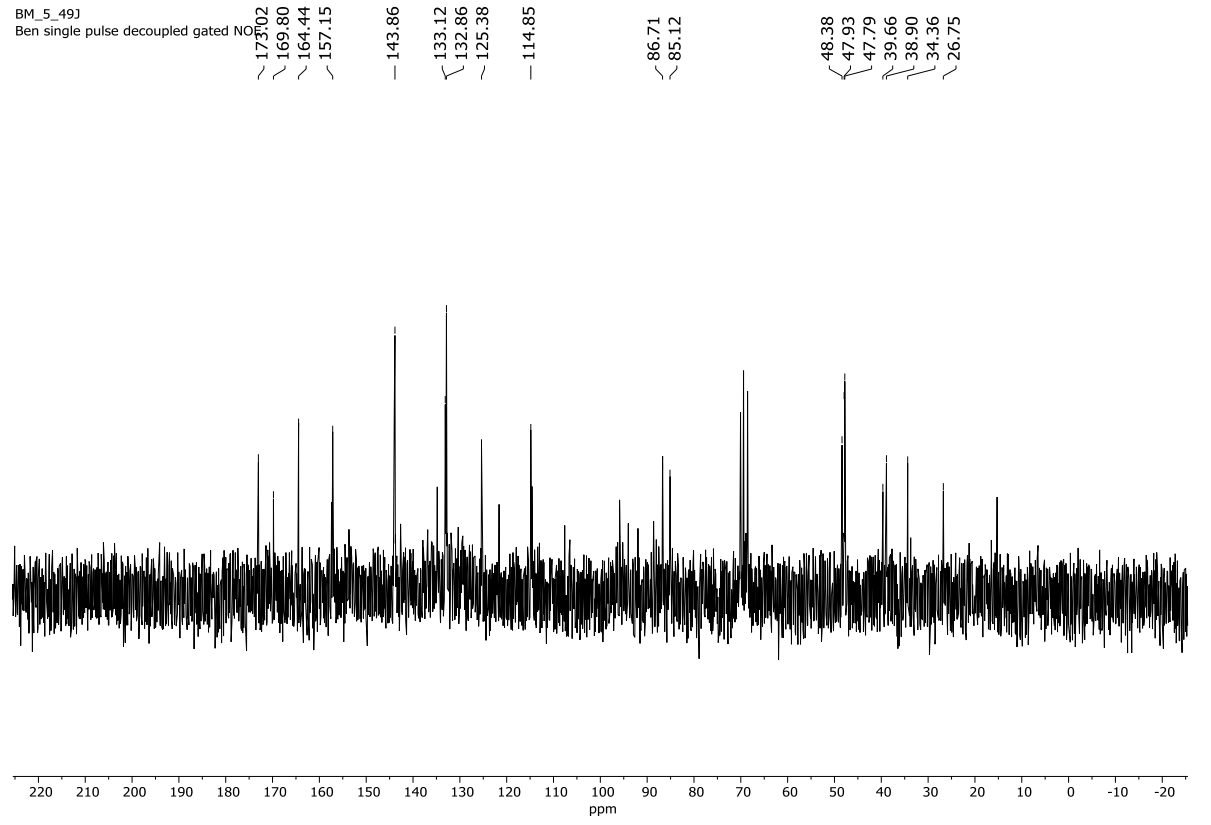

Figure S23. Solvent supressed ^{13}C{^{1}H} NMR spectrum of **9**. DMSO-d6 was used as NMR solvent.

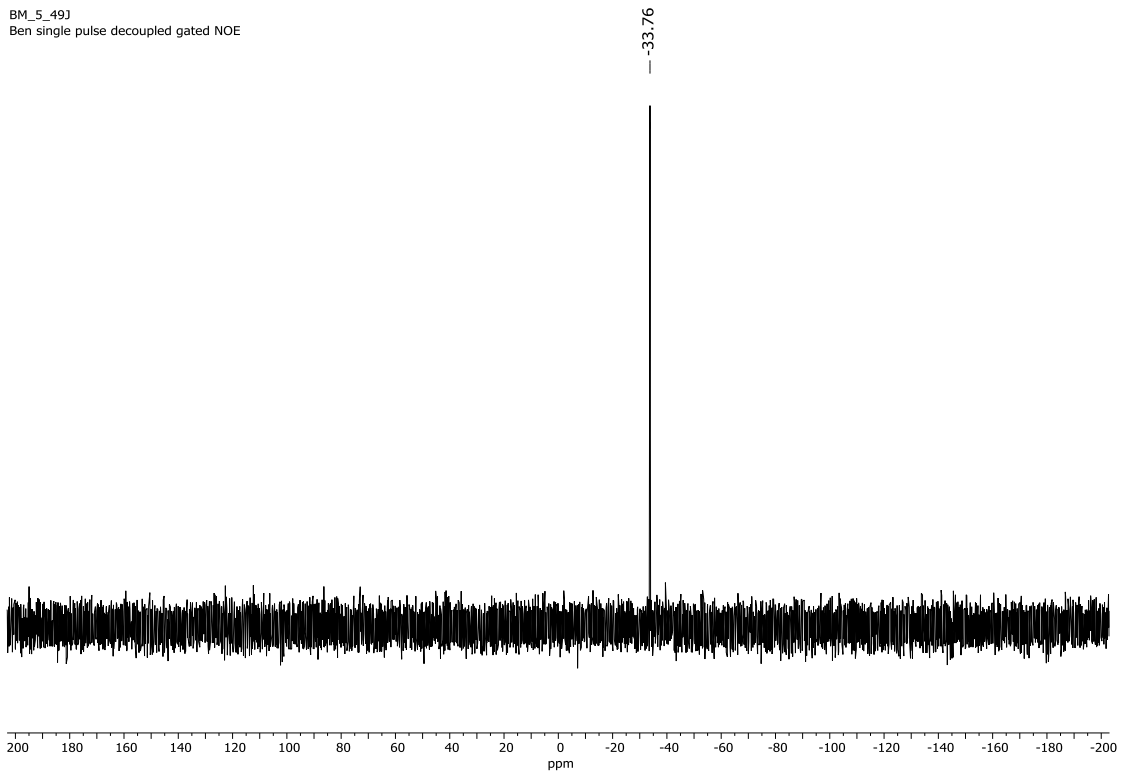

Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum of **9**. DMSO-d6 was used as NMR solvent.

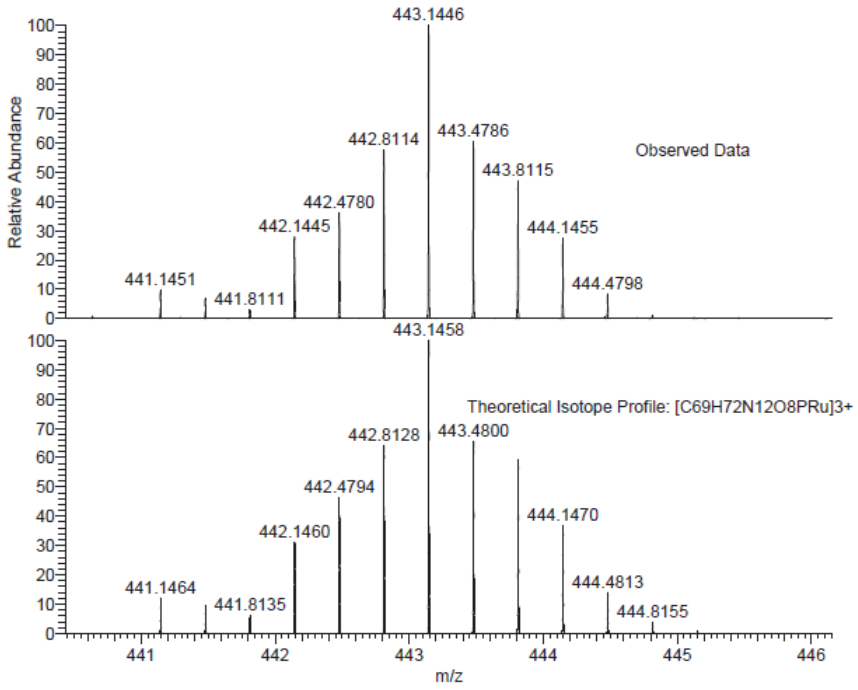

Figure S25. ESI+ HRMS of **9**.

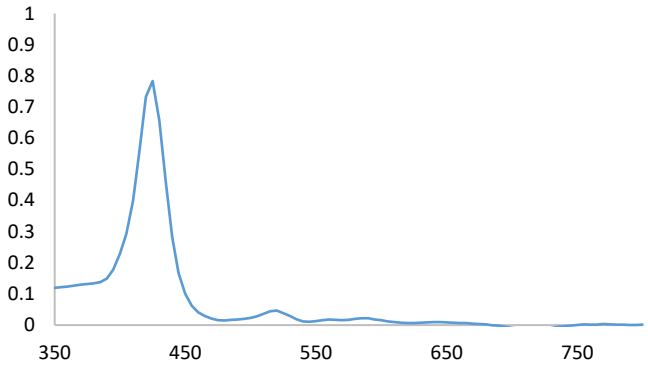

Figure S26. UV-Vis spectrum of **9** obtained in water.

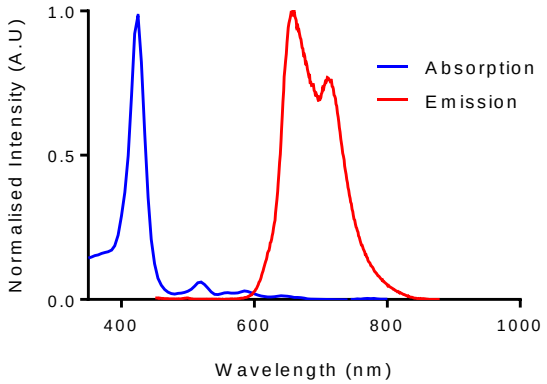

Figure S27. Fluorescence absorpbtion-emission spectrum of **9** obtained in water.