Design and synthesis of charged porphyrin dimers for polyoxometallate recognition.

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General methods:

Dichloromethane used for reactions or column chromatography was distilled from calcium hydride. Tetrahydrofuran and toluene were distilled over sodium/benzophenone ketyl under argon. All other commercially available reagents and solvents were used without further purification. Bases (K_3PO_4, K_2CO_3, Cs_2CO_3 and Na_2CO_3) were oven-dried at 100 °C. Analytical thin layer chromatography (TLC) was carried out on silica gel 60 F_{254} (Merck) and column chromatography was performed with silica gel or alumina from Merck (alumina oxide 60 standardized or silica gel 60, 0.04-0.063 µm). Nuclear magnetic resonance spectra were recorded on Bruker Avance spectrometers at 300, 400, 500 or 600 MHz. The chemical shifts are given in parts-per-million (ppm) on the delta scale. The solvent peak was used as reference value: for ^{1}H NMR: $CDCl_3$ = 7.26 ppm, DMSO-d_6 = 2.50 ppm, for ^{13}C NMR: $CDCl_3$ = 77.23 ppm, DMSO-d_6 = 39.52 ppm. The data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptuplet, m= multiplet), coupling constant (J/ Hz) and the integration. Mass spectra were obtained by ESI-TOF or MALDI-TOF (337 nm nitrogen laser for desorption, dithranol used as matrix) experiments. High resolution mass spectra (HRMS) data were recorded on a microTOF spectrometer equipped with orthogonal electrospray interface (ESI). The ions (*m/z*) were analyzed on a Bruker Daltonics microTOF for ESI and a Bruker Autoflex II TOF-TOF for MALDI. The parent ions, $[M+H]^+$, $[M+K]^+$, $[M+Na]^+$ or $[M^{n+}]$ are given. UV-visible spectra were recorded on a Cary 5000 UV/vis/NIR double-beam spectrometer in dichloromethane or chloroform. Molar extinction coefficients were determined for samples with analyte concentrations ranging from 5.10^{-6} to 5.10^{-5} mol.L^{-1}. X-Ray data analysis and solving of the structures were performed by Dr. Lydia Karmazin and Dr. Corinne Bally (Service de Radiocristallographie, Fédération de chimie LeBel, Strasbourg) using a Brucker APEX II DUO Kappa-CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å).

Binding studies were carried out with spectroscopic grade DMF (Carlo Erba, 99.9% for spectroscopy). To prevent any photochemical degradation, all solutions were protected from daylight exposure. All stock solutions were prepared using an Mettler Toledo XA105 Dual Range (0.01/0.1 mg - 41/120 g) to weigh samples, and complete dissolution in DMF was achieved using an ultrasonic bath. The concentrations of stock solutions of the receptors and substrates were calculated by the quantitative dissolution of solid samples in DMF.

Luminescence titrations were carried out on solutions of dimers and monomers with absorbances lower than 0.1. The titrations of 2 mL of dimer or monomer with $[Mo_6O_{19}][(Bu_4N)_2]$ ([Dimers] = 6.43 x 10^{-6} M and [Monomers] = 4.39 x 10^{-6} M) were carried out in a 1 cm Hellma quartz optical cell by the addition of known microvolumes of solutions of $[Mo_6O_{19}][(Bu_4N)_2]$ with an Eppendorf Research plus. The excitation wavelengths were set at 517 or 559 nm. The luminescence spectra were recorded from 550 to 800 nm on a Perkin-Elmer LS-50B instrument maintained at 25 °C. The slit widths were set between 15 and 20 nm for the emission. Luminescence titrations were conducted under precise and identical experimental conditions.

The spectrophotometric titration of **9** with $[Mo_6O_{19}][(Bu_4N)_2]$ ([**9**] = 1.76 x 10^{-2} M) was carried out in a 1 cm Hellma quartz optical cell by the addition of known microvolumes of solutions of $[Mo_6O_{19}][(Bu_4N)_2]$ with an Eppendorf Research plus. Special care was taken to ensure that complete equilibration was attained. The corresponding UV-vis spectra were recorded from 300 to 800 nm on a Cary 300 (Varian) spectrophotometer maintained at 25 °C.

The spectrophotometric data were analyzed with Specfit[1] program that adjusts the absorptivities and the stability constants of the species formed at equilibrium. Specfit uses factor analysis to reduce the absorbance matrix and to extract the eigenvalues prior to the multiwavelength fit of the reduced data set according to the Marquardt algorithm.[2,3]

Porphyrin 3

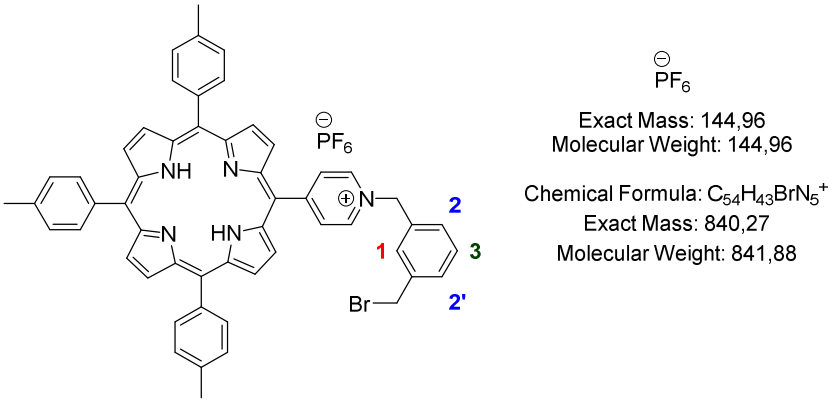
Prepared following the **GP1** and using α,α'-dibromo-m-xylene(160 mg, 1.60 mmol, 20 eq) and porphyrin **1** (50 mg, 0.08 mmol, 1 eq). The crude product was purified by silica gel column chromatography (CH_2CL_2 and gradually ending with CH_2CL_2/Acetone 9/1). The compound **3** (73 mg, 0.071 mmol, 87%) was obtained as a purple solid.

^{1}H NMR (500 MHz, Acetone-d_6): δ 9.73 (d, *J* = 6.6 Hz, 2H, H-*ortho*-py$^+$), 9.16 (d, *J* = 6.6 Hz, 2H, H-*meta*-py$^+$), 9.03 – 8.84 (m, 8H, H-β-pyrrolic), 8.23-8.06 (m, 6H, H-tolyl), 7.93 (s, 1H, H**1**), 7.81 (dt, *J* = 7.0, 2.0 Hz, 1H, H**3**), 7.68 (d, *J* = 7.7 Hz, 6H, H-tolyl), 7.65 – 7.59 (m, 2H, H**2** and H**2'**), 6.43 (s, 2H, Py$^+$-CH_2-Ar), 4.81 (d, *J* = 5.5 Hz, 2H, Ar-CH_2-Br), 2.72 (s, 9H, -CH_3), -2.72 (s, 2H, free base).
^{13}C NMR (126 MHz, Acetone-d_6) δ 161.1, 145.4, 144.3, 139.2, 139.1, 139.0, 135.4, 134.8, 134.4, 130.6, 129.2, 129.1, 128.7, 128.7, 128.7, 123.7, 123.7, 122.5, 122.5, 113.1, 64.3, 27.6, 21.7.
^{31}P NMR (203 MHz, Acetone-d_6) δ -144.0 (hept, *J* = 711.7 Hz).
^{19}F NMR (471 MHz, Acetone-d_6) δ -72.6 (d, *J* = 711.7 Hz).

UV-Vis (DMF)**:** λ (ε) = 419 (223000), 516 (12700), 552 (7700), 591 (5700), 647 nm (4100 $M^{-1}.cm^{-1}$).

ESI-TOF: *m/z* = 840.27 Calcd for $C_{54}H_{43}N_5Br$ ([M^+]): 840.27.

TLC (silica) R_f: 0.25 (CH_2CL_2/Acetone 9/1).



NMR ^{1}H:

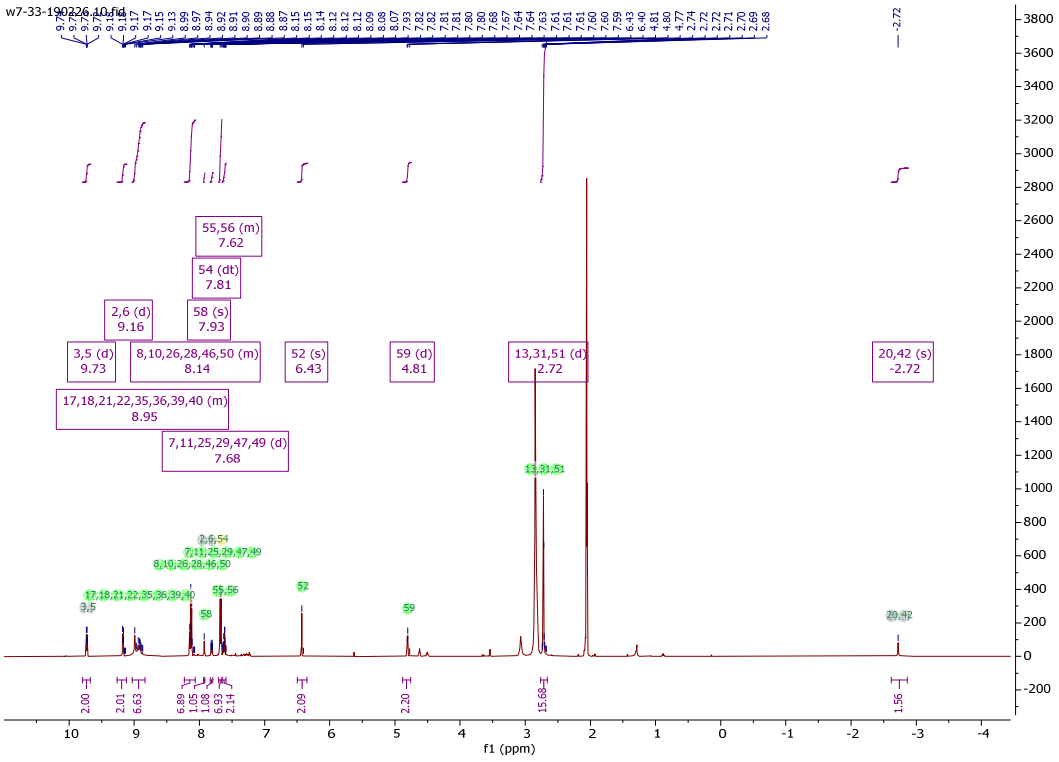


Fig. S1: ^{1}H NMR Spectrum of **3** in DMSO-d6

NMR ^{13}C:

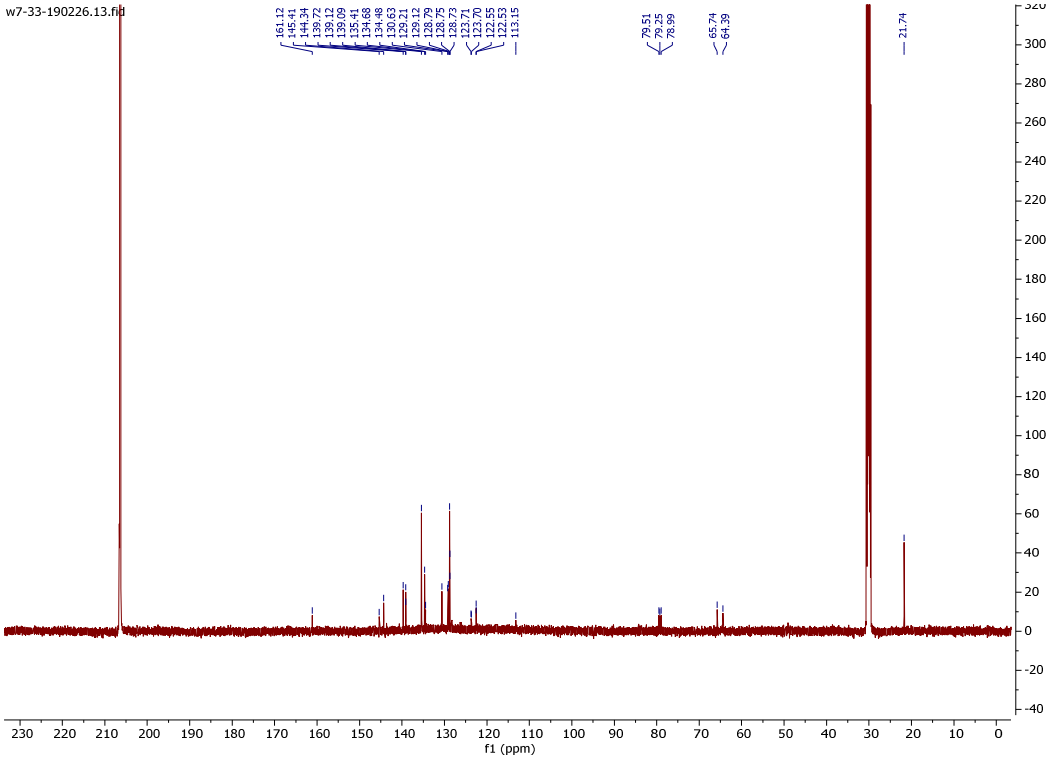


Fig. S2: ^{13}C NMR Spectrum of **3** in DMSO-d6

NMR ^{31}P:

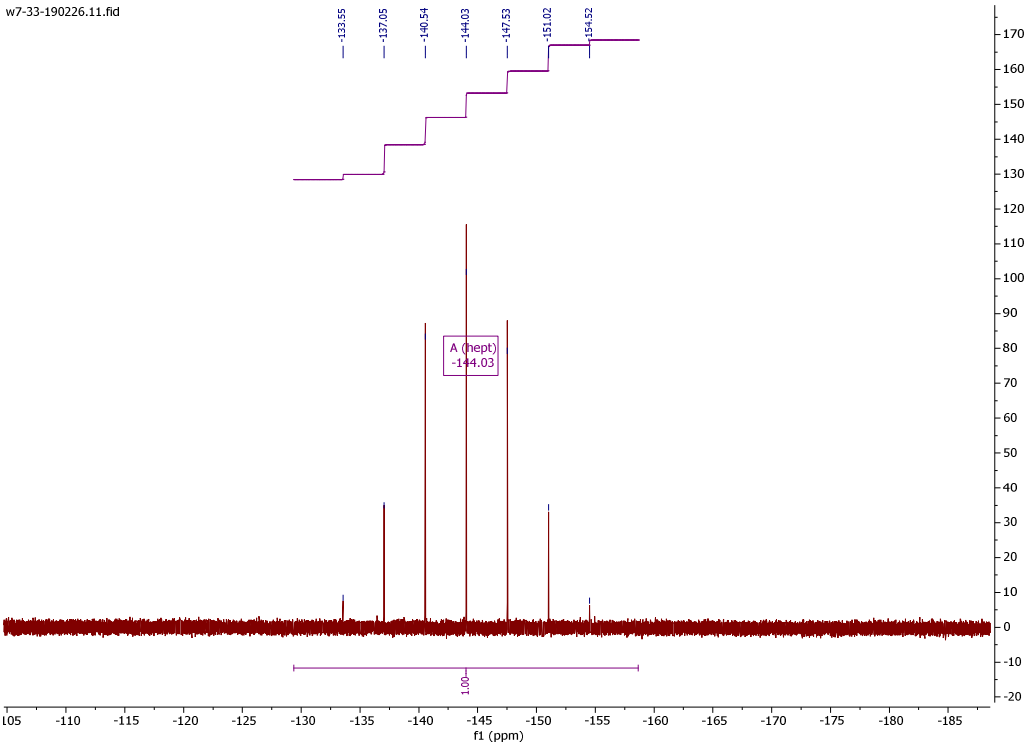


*Fig. S3: ^{31}P NMR Spectrum of **3** in DMSO-d6*

NMR ^{19}F:

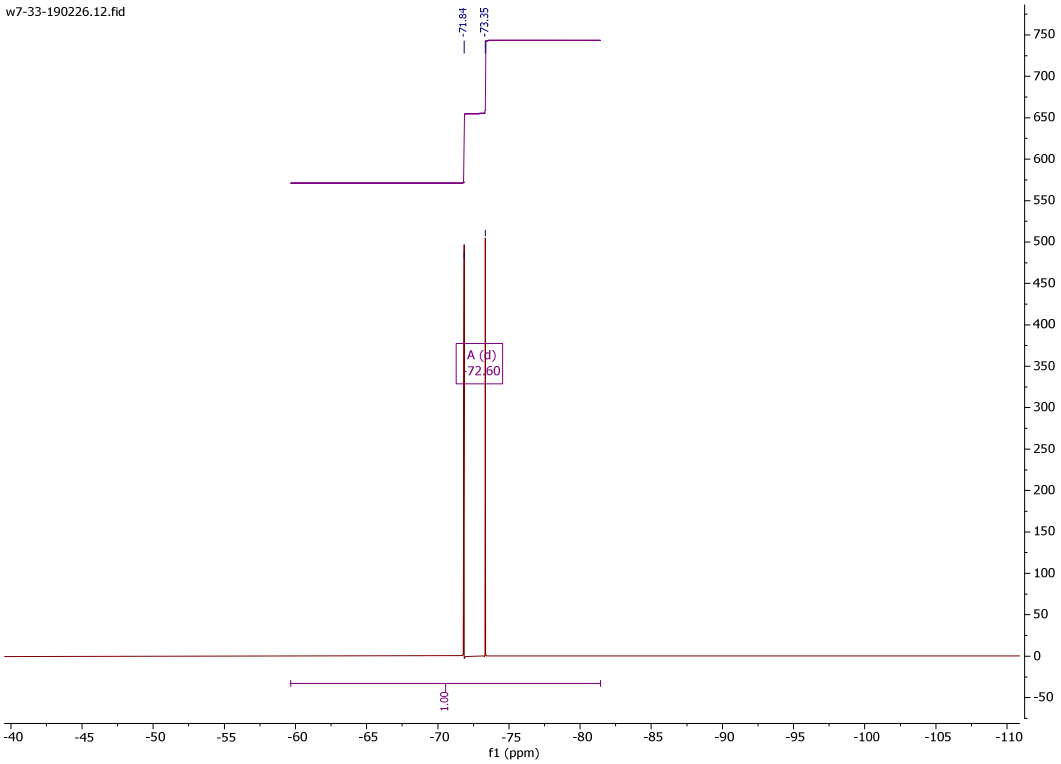
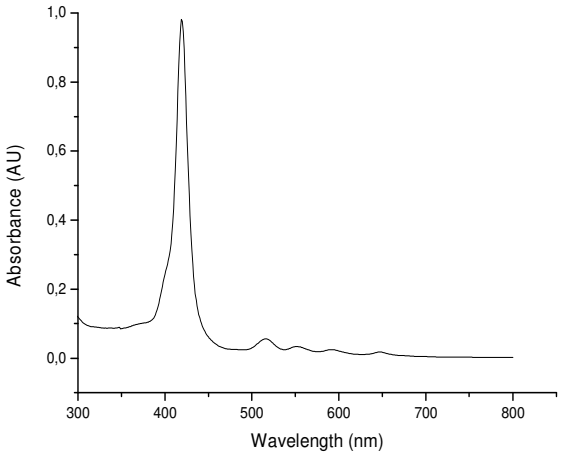


Fig. S4: ^{19}F NMR Spectrum of **3** in DMSO-d6



UV-Visible :

Fig. S5: UV-visible Spectrum of **3** in DMF (C= 4.39 x 10^{-6} M)

Porphyrin 4

Prepared following the **GP1** and using α,α'-dibromo-m-xylene (160 mg, 1.60 mmol, 20 eq) and porphyrin **1** (50 mg, 0.08 mmol, 1 eq). The crude product was purified by silica gel column chromatography (CH_2CL_2 and gradually ending with CH_2CL_2/Acetone 9/1). The compound **4** (76 mg, 0.073 mmol, 91%) was obtained as a purple solid.

^{1}H NMR (400 MHz, Acetone-d_6): δ 9.72 (d, *J* = 6.8 Hz, 2H, H-*ortho*-py$^+$), 9.16 (d, *J* = 6.8 Hz, 2H, H-*meta*-py$^+$), 9.03 – 8.95 (m, 4H, H-β-pyrrolic), 8.91 (q, *J* = 4.9 Hz, 4H, H-β-pyrrolic), 8.17 – 8.06 (m, 6H, H-tolyl), 7.94 (d, *J* = 8.0 Hz, 2H, H**1**), 7.75 (d, *J* = 8.0 Hz, 2H, H**2**), 7.69 – 7.59 (m, 6H, H-tolyl), 6.43 (s, 2H, Py$^+$-**CH_2**-Ar), 4.78 (s, 2H, Ar-**CH_2**-Br), 2.70 (s, 6H, -CH_3), 2.69 (s, 3H, -CH_3), -2.73 (s, 2H, free base).

^{13}C NMR (126 MHz, Acetone -d_6): δ -72.5 (d, *J* = 707.7 Hz)

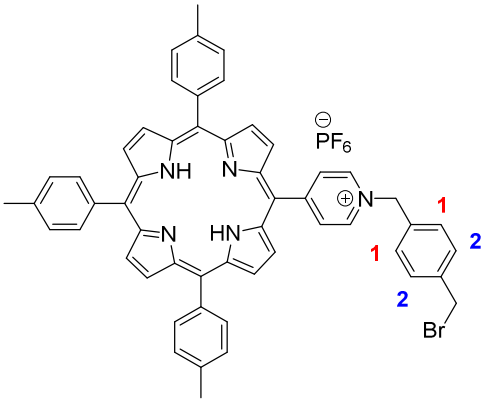
^{31}P NMR (121 MHz, Acetone -d_6): δ -144.2 (hept, *J* = 707.7 Hz)

^{19}F NMR (282 MHz, Acetone -d_6): δ 160.9, 144.2, 141.2, 139.5, 138.8, 135.2, 134.5, 134.5, 131.3, 131.0, 128.5, 128.5, 123.4, 122.3, 113.0, 65.0, 33.4, 27.5, 21.5.

UV-Vis (DMF)**:** λ (ε) = 421 (314000), 518 (19000), 556 (11800), 592 (7300), 649 nm (6600 $M^{-1}.cm^{-1}$).

HRMS, ESI-TOF: *m/z* = 840.2685 Calcd for $C_{54}H_{43}BrN_5^+$ ([M^+]): 840.2696.

TLC R_f: 0.24 (CH_2CL_2/Acetone 9/1).



PF6

Exact Mass: 144,96
Molecular Weight: 144,96

Chemical Formula: $C_{54}H_{43}BrN_5^+$
Exact Mass: 840,27
Molecular Weight: 841,88

NMR ^{1}H:

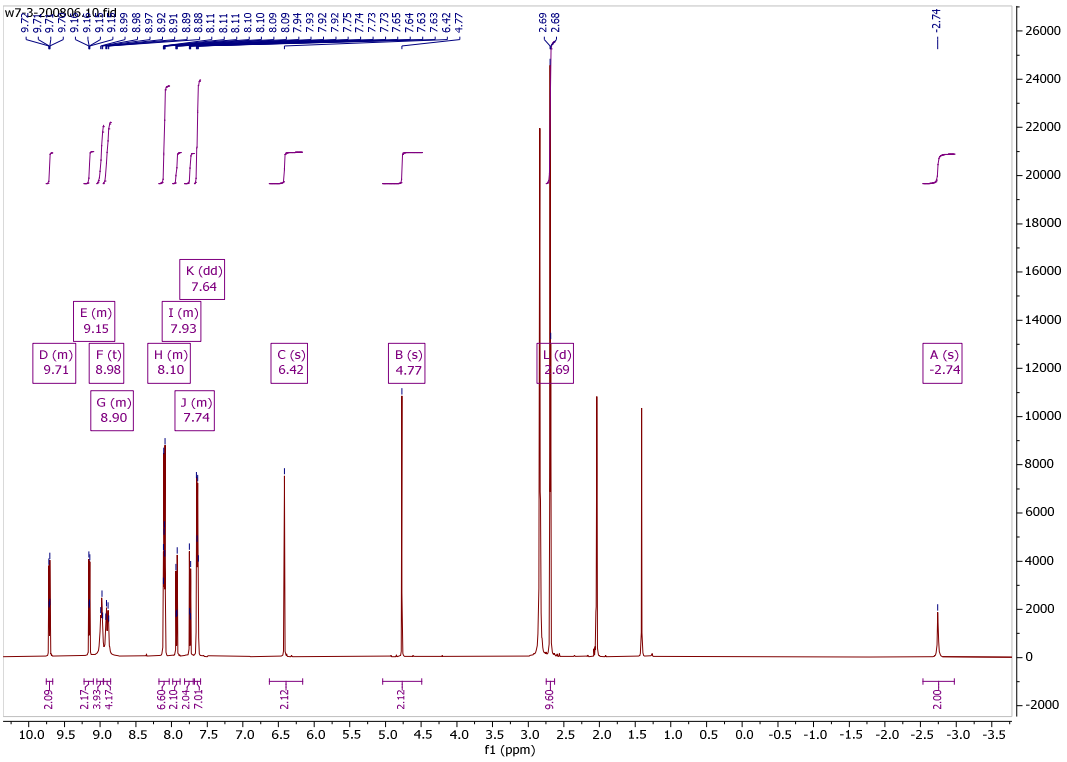


*Fig. S6: ^{1}H NMR Spectrum of **4** in DMSO-d6*

NMR ^{13}C:

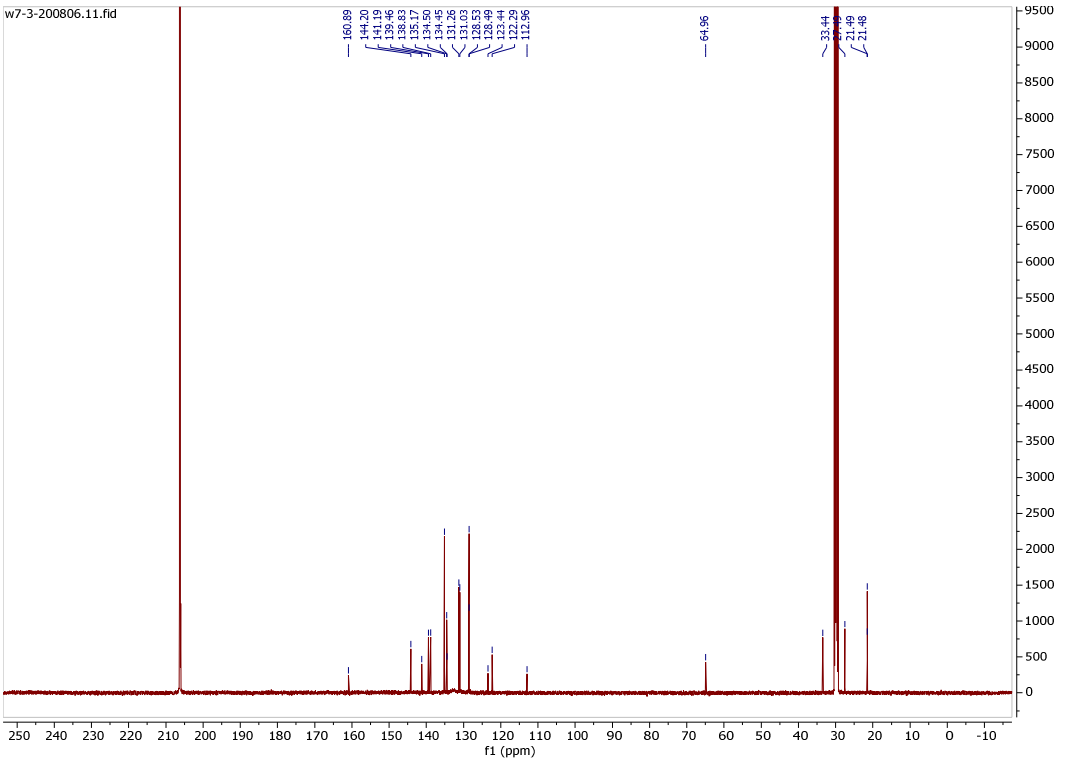


Fig. S7: ^{13}C NMR Spectrum of **4** in DMSO-d6

NMR ^{31}P:

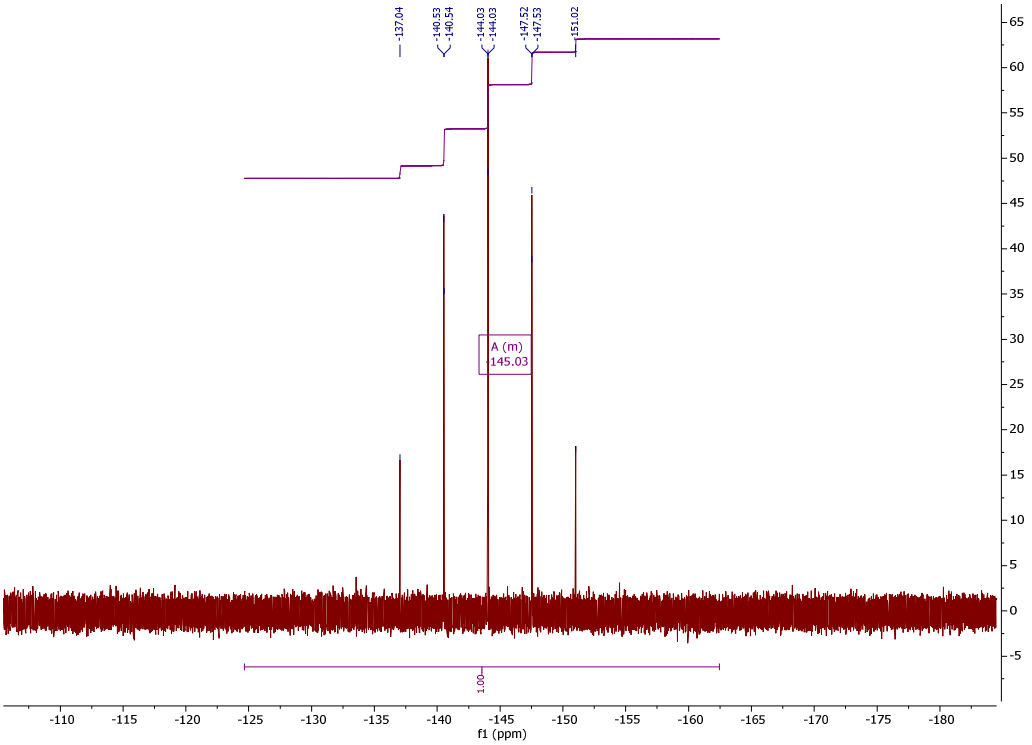


Fig. S8: ^{31}P NMR Spectrum of **4** in DMSO-d6

NMR ^{19}F:

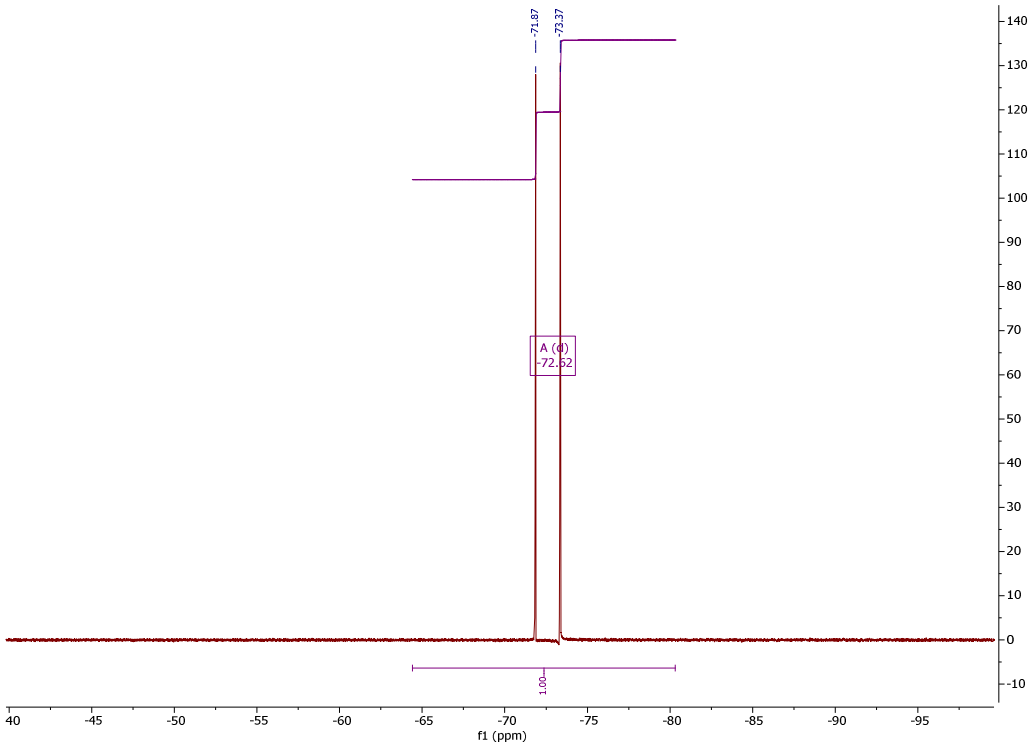


*Fig. S9: ^{19}F NMR Spectrum of **4** in DMSO-d6*

UV-Visible:

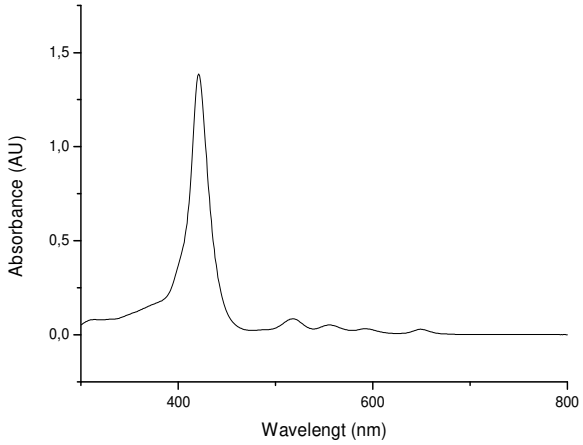


*Fig. S10: UV-visible Spectrum of **4** in DMF (C= 4.39 x 10^{-6} M)*

Porphyrin 5

Prepared following the **GP1** and using α,α'-dibromo-m-xylene (160 mg, 1.60 mmol, 20 eq) and porphyrin **2** (50 mg, 0.08 mmol, 1 eq). The crude product was purified by silica gel column chromatography (CH_2CL_2 and gradually ending with CH_2CL_2/Acetone 9/1). The compound **5** (68 mg, 0.065 mmol, 79%) was obtained as a purple solid.

^{1}H NMR (400 MHz, Acetone-d_6): δ 10.21 (m, 1H, H-py$^+$-**b**), 9.79 (dt, *J* = 6.2, 1.5 Hz, 1H, H-py$^+$-**a**), 9.60 (dt, *J* = 8.0, 1.5 Hz, 1H, H-py$^+$-**d**), 9.04-8.88 (m, 8H, H-β-pyrrolic), 8.81 (dd, *J* = 8.1, 6.2 Hz, 1H, H-py$^+$-**c**), 8.18-8.07 (m, 2H, H-tolyl), 7.97 (br s, 1H, H**1**) 7.83 (dd, *J* = 7.6, 1.6 Hz, 1H, H**2'**), 7.70 – 7.61 (m, 7H, H-tolyl and H**2**), 7.58-7.55 (m, 1H, H**3**), 6.45 (s, 2H, Py$^+$-**CH_2**-Ar), 4.68 (s, 2H, Ar-**CH_2**-Br), 2.71 (s, 3H, -CH_3), 2.70 (s, 6H, -CH_3), -2.78 (s, 2H, free base).

^{13}C NMR (126 MHz, Acetone-d_6): δ 150.1, 148.1, 145.2, 144.0, 140.8, 139.5, 139.5, 138.8, 135.2, 131.5, 130.9, 130.9, 130.2, 128.5, 128.5, 128.3, 123.1, 122.1, 110.6, 65.7, 33.5, 21.5.

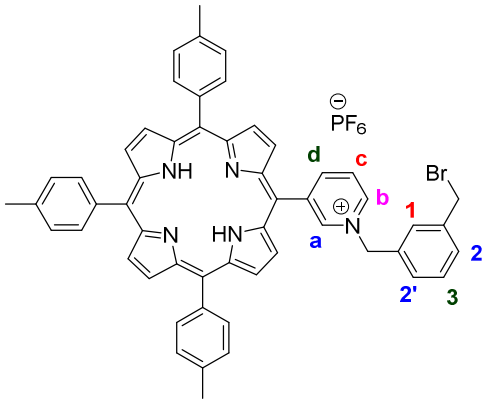
^{31}P NMR (121 MHz, Acetone-d_6): δ -144.3 (hept, *J* = 707.5 Hz)

^{19}F NMR (282 MHz, Acetone-d_6): δ -72.60 (d, *J* = 707.5 Hz)

UV-Vis (DMF)**:** λ (ε) = 422 (312000), 517 (18000), 552 (8900), 591 (6400), 649 nm (5700 $M^{-1}.cm^{-1}$).

HRMS, ESI-TOF: *m/z* = 840.2658 Calcd for $C_{54}H_{43}BrN_5^+$ ([M^+]) : 840.2696.

TLC R_f : 0.19 (CH_2CL_2/Acetone 9/1).



PF6

Exact Mass: 144,96
Molecular Weight: 144,96

Chemical Formula: $C_{54}H_{43}BrN_5^+$
Exact Mass: 840,27
Molecular Weight: 841,88

MN ^{1}H :

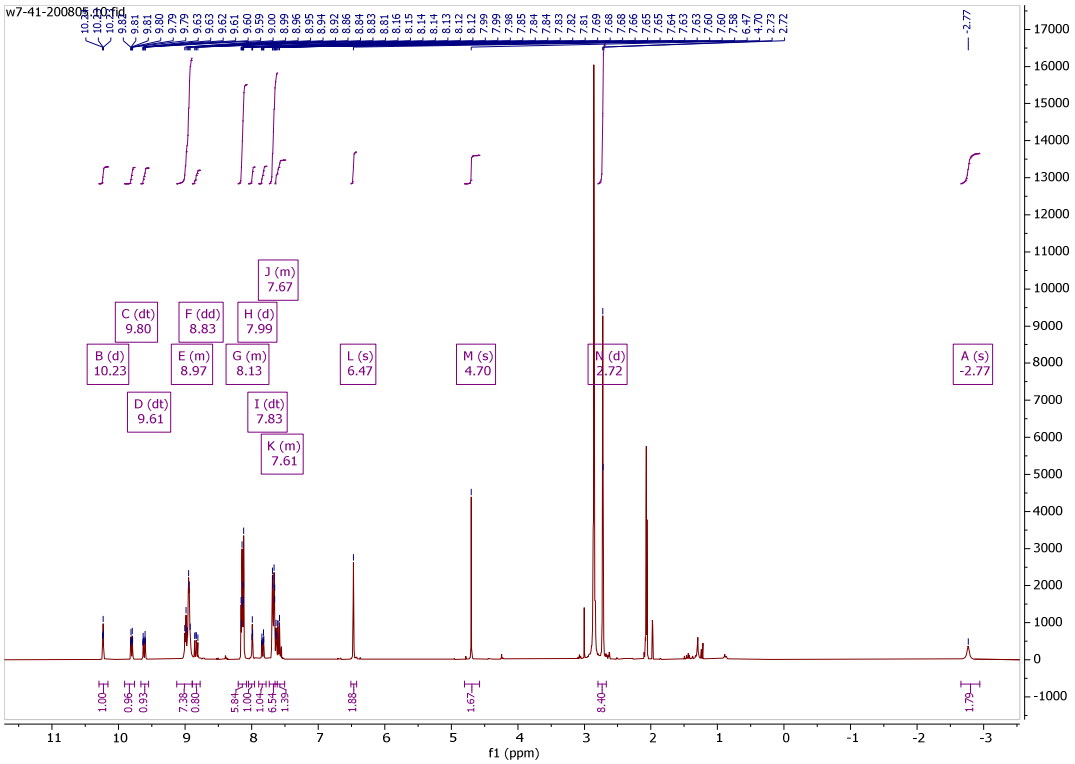


*Fig. S11: ^{1}H NMR Spectrum of **5** in DMSO-d6*

NMR ^{13}C:

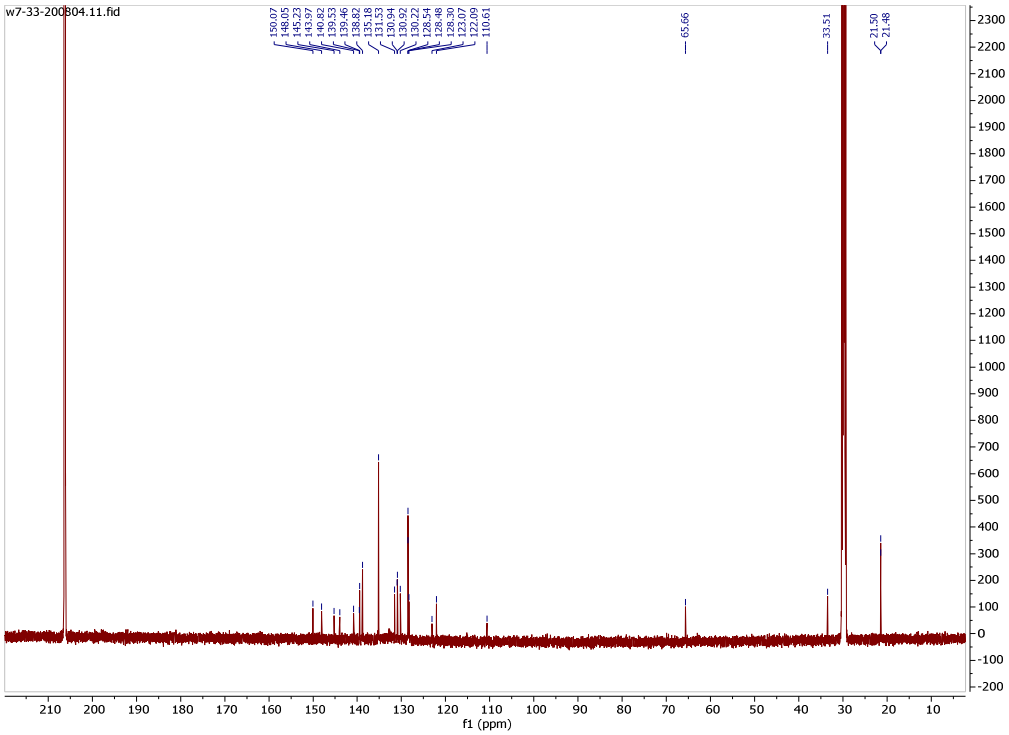


*Fig. S12: ^{13}C NMR Spectrum of **5** in DMSO-d6*

NMR ^{31}P:

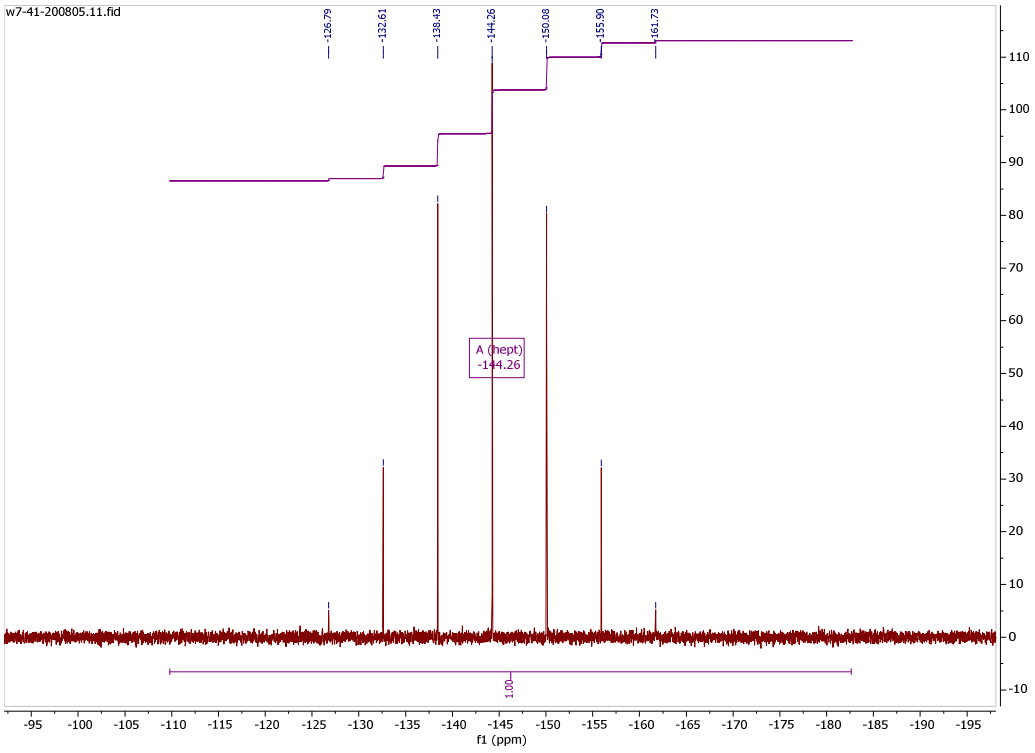


*Fig. S13: ^{31}P NMR Spectrum of **5** in DMSO-d6*

NMR ^{19}F:

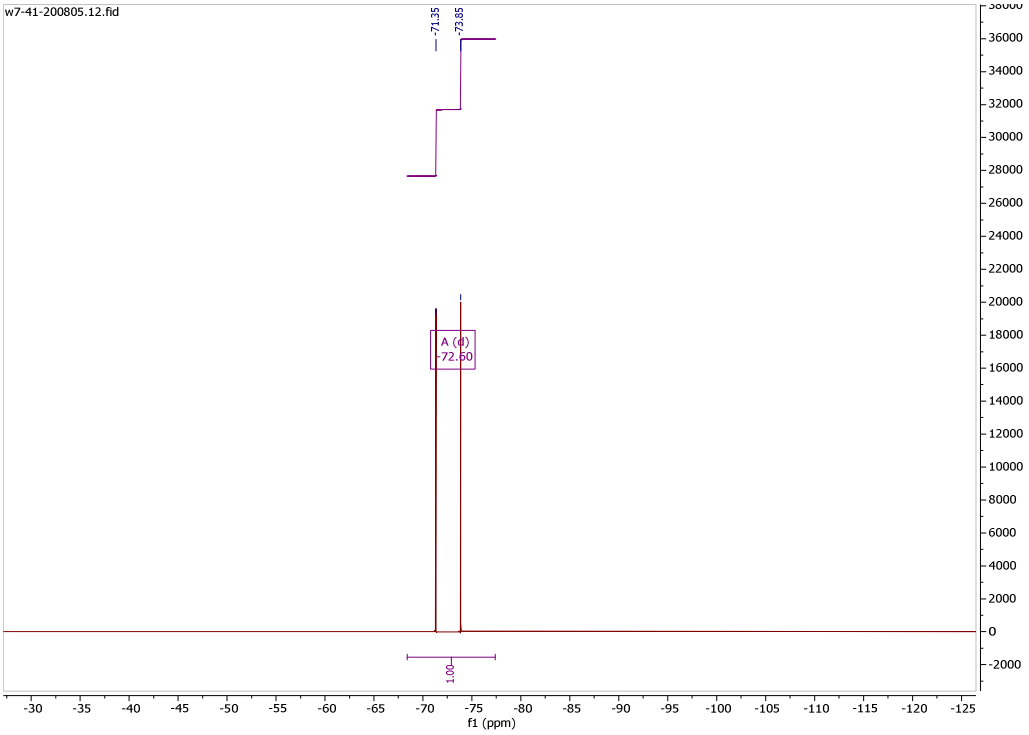


*Fig. S14: ^{19}F NMR Spectrum of **5** in DMSO-d6*

UV-Visible:

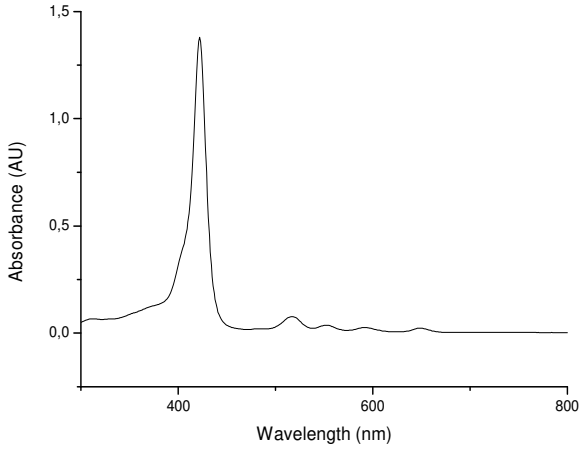


*Fig. S15: UV-visible Spectrum of **5** in DMF (C= 4.39 x 10^{-6} M)*

Porphyrin 6

^{1}H NMR (400 MHz, Acetone-*d*$_6$): δ 10.19 (s, 1H, H-py$^+$-**a**), 9.79 (d, *J* = 6.2 Hz, 1H, H-py$^+$-**b**), 9.59 (d, *J* = 7.9 Hz, 1H, H-py$^+$-**d**), 9.10-8.87 (m, 8H, H-β-pyrrolic), 8.80 (dd, *J* = 7.9, 6.2 Hz, 1H, H-py$^+$-**c**), 8.21 – 8.06 (m, 6H, H-tolyl), 7.86 (d, *J* = 8.1 Hz, 2H, H**1**), 7.74 – 7.58 (m, 8H, H-tolyl and H**2**), 6.44 (s, 2H, Py$^+$-**CH$_2$**-Ar), 4.69 (s, 2H, Ar-**CH$_2$**-Br), 2.71 (s, 6H, -CH_3), 2.71 (s, 3H, -CH_3), -2.78 (s, 2H, free base).

^{13}C NMR (126 MHz, Acetone-*d*$_6$): δ 50.1, 148.2, 145.2, 139.5, 138.8, 135.2, 134.7, 131.2, 130.8, 128.5, 128.5, 128.3, 123.1, 122.1, 65.6, 33.3, 21.5.

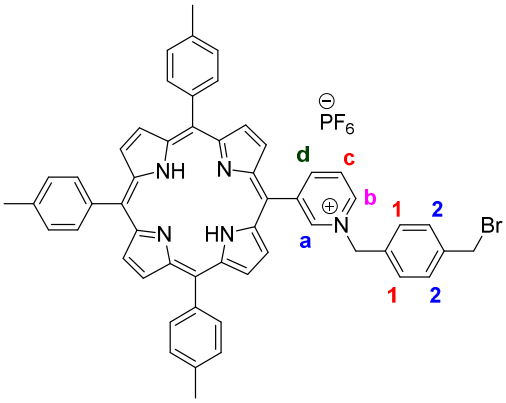
^{31}P NMR (121 MHz, Acetone -*d*$_6$): δ -141.3 (hept, *J* = 707.5 Hz)

^{19}F NMR (282 MHz, Acetone -*d*$_6$): δ -72.6 (d, *J* = 707.5 Hz)

UV-Vis (DMF)**:** λ (ε) = 422 (314000), 517 (17500), 552 (8500), 591 (6000), 649 nm (5200 $M^{-1}.cm^{-1}$).

HRMS, ESI-TOF: *m/z* = 840.2644 Calcd for $C_{54}H_{43}BrN_5^+$ ([M^+]): 840.2696.

TLC R_f: 0.23 (CH_2CL_2/Acetone 9/1).



PF6

Exact Mass: 144,96
Molecular Weight: 144,96

Chemical Formula: $C_{54}H_{43}BrN_5^+$
Exact Mass: 840,27
Molecular Weight: 841,88

NMR ^{1}H:

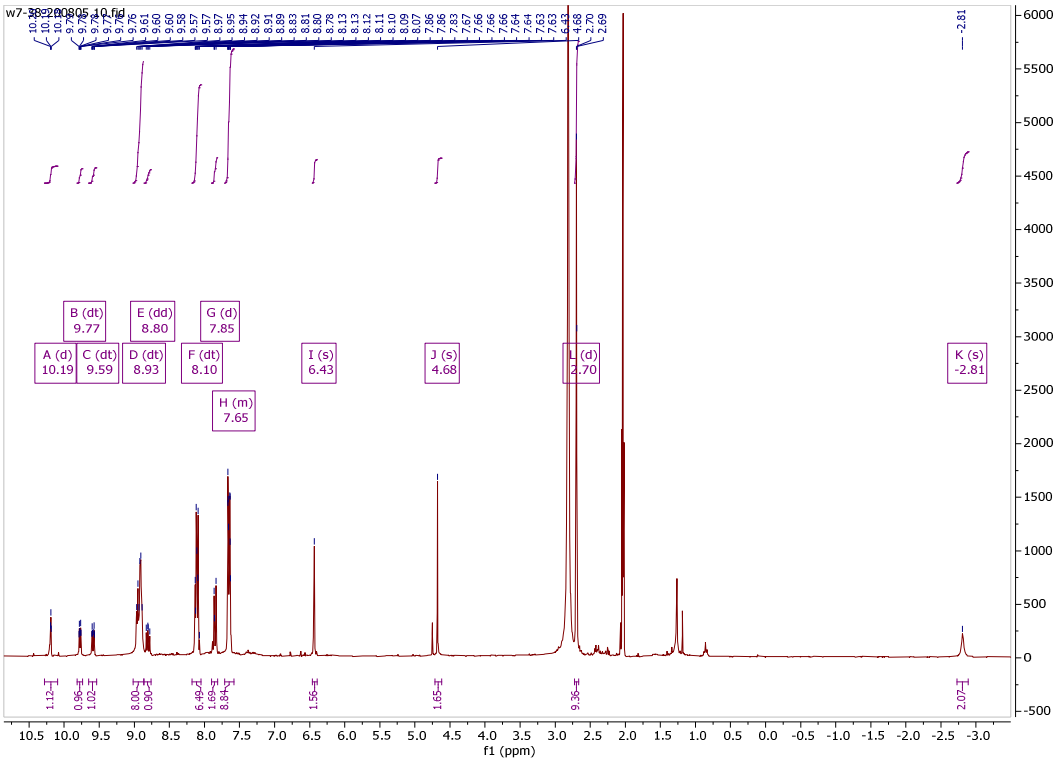


*Fig. S16: ^{1}H NMR Spectrum of **6** in DMSO-d6*

NMR ^{13}C:

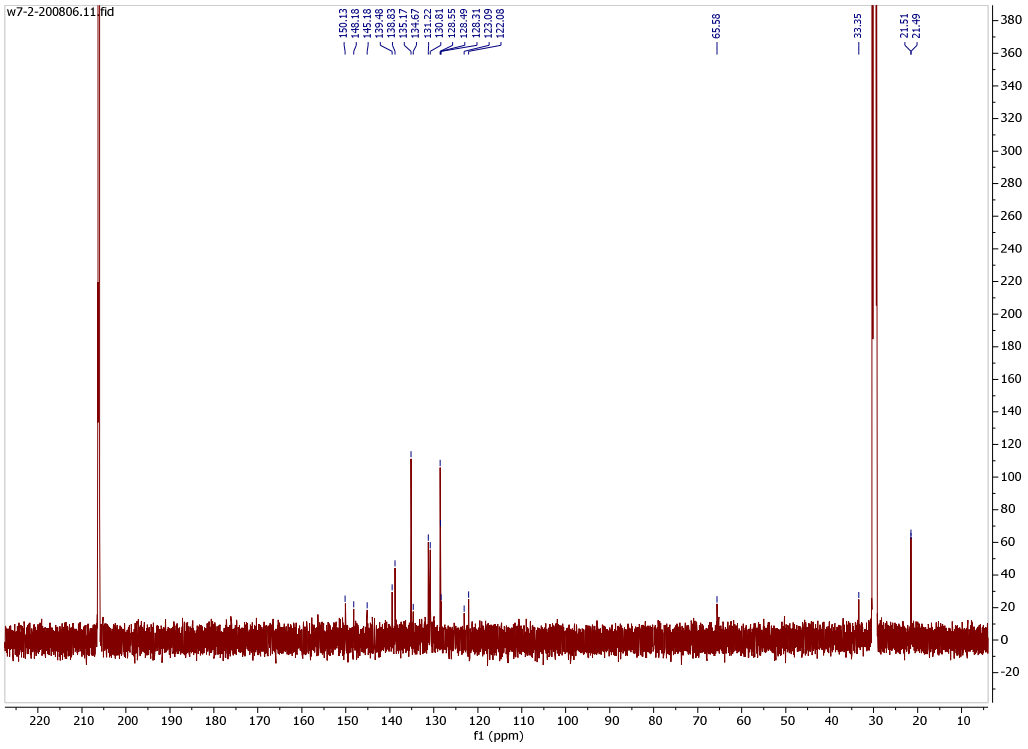


*Fig. S17: ^{13}C NMR Spectrum of **6** in DMSO-d6*

NMR ^{31}P:

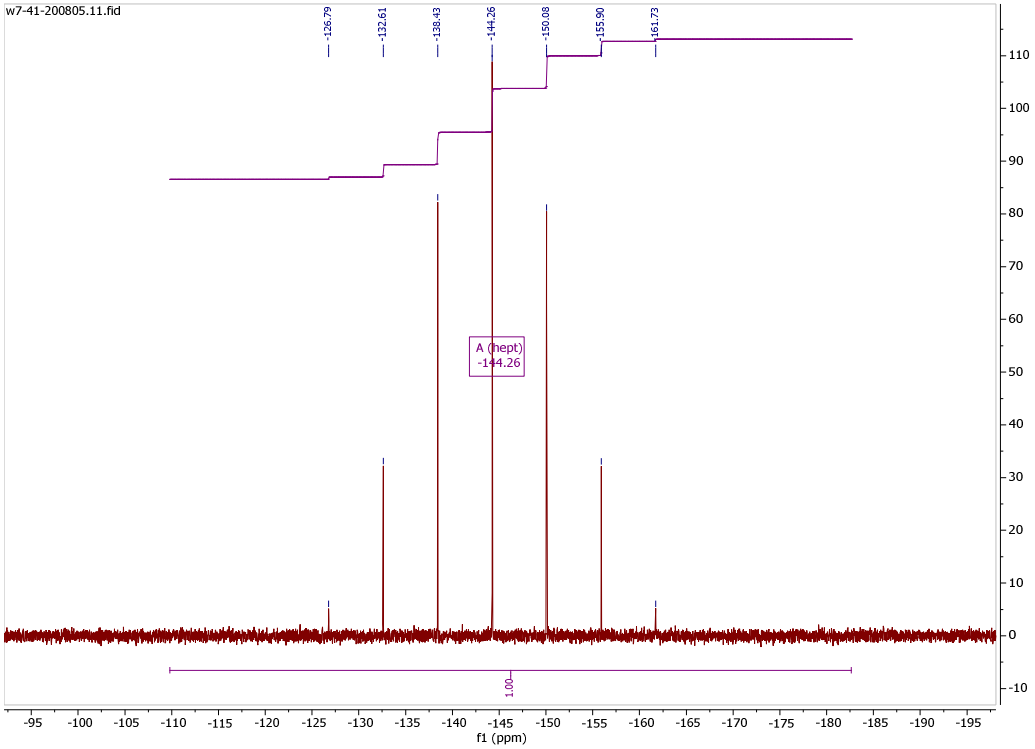


*Fig. S18: ^{31}P NMR Spectrum of **6** in DMSO-d6*

NMR ^{19}F:

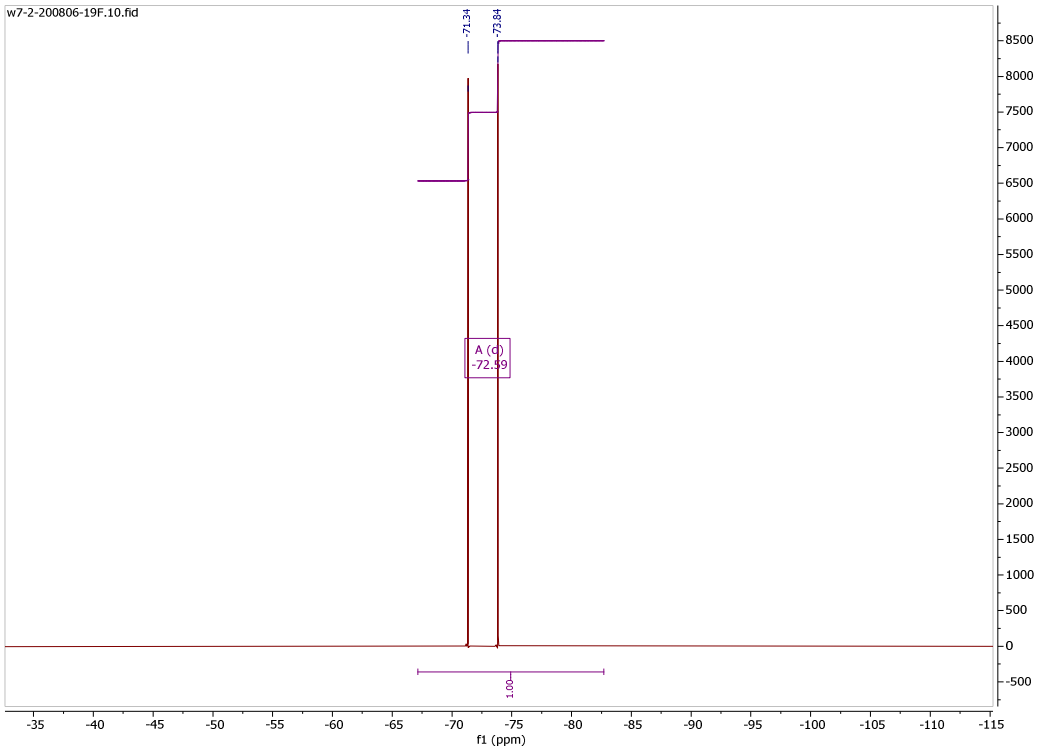


*Fig. S 19: ^{19}F NMR Spectrum of **6** in DMSO-d6*

UV-Visible:

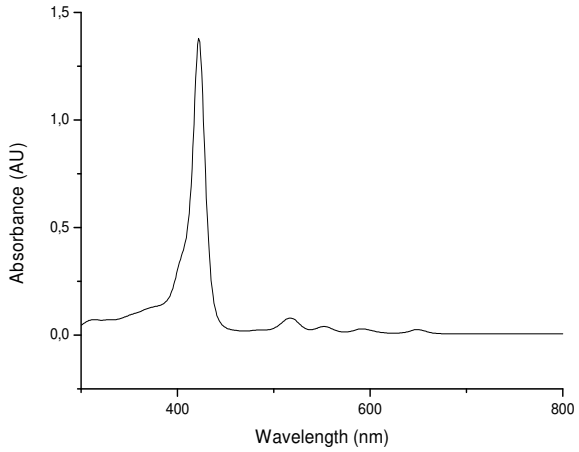


*Fig. S20: UV-visible Spectrum of **6** in DMF (C= 4.39 x 10^{-6} M)*

General procedure for the dimeric products (GP2):

Bis-porphyrin 7

Prepared following the **GP2** and using the single porphyrin **3** (61 mg, 0.062 mmol, 1 eq) (Method A) or α,α'-dibromo-m-xylene (18 mg, 0.062 mmol, 1 eq) (Method B) and porphyrin **1** (204 mg, 0.31 mmol, 5 eq). The crude product was purified by silica gel column chromatography ($_{CH2CL2}$ and gradually ending with a solution of KPF_6 (27 mM) in acetone. The bis-porphyrin **7** (80 mg, 0.047 mmol, 75%) or (49 mg, 0.029 mmol, 46%) was obtained as a purple solid.

^{1}H NMR (500 MHz, DMSO-*d*$_6$,): δ 9.62 (d, *J* = 6.0 Hz, 4H, H-*ortho*-py$^+$), 9.12 (d, *J* = 6.0 Hz, 4H, H-*meta*-py$^+$), 8.83 (d, *J* = 4.5 Hz, 4H, H-β-pyrrolic), 8.74 (d, J = 4.5 Hz, 4H, H-*β*-pyrrolic), 8.38 (d, J = 4.7 Hz, 4H, H-*β*-pyrrolic), 8.35 (d, *J* = 4.7 Hz, 4H, H-*β*-pyrrolic), 8.24 (s, 1H, H**1**), 8.12-8.02 (m, 6H, H-*ortho*-tolyl and H**2**), 7.89 (d, *J* = 7.7 Hz, 1H, H**3**), 7.65 (d, *J* = 7.4 Hz, 4H, H-*meta*-tolyl), 7.01 (d, *J* = 7.3 Hz, 8H, H-*ortho*-tolyl), 6.69 (d, *J* = 7.3 Hz, 8H, H-*meta*-tolyl), 6.33 (s, 4H, -CH_2-), 2.69 (s, 6H, -CH_3), 2.24 (s, 12H, -CH_3), -3.06 (s, 4H, free base).

^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 158.5, 143.4, 138.1, 137.6, 137.3, 136.7, 135.5, 134.2, 133.4, 132.8, 131.0, 130.4, 129.7, 127.7, 126.9, 121.7, 120.3, 112.4, 63.1, 21.1, 20.6.

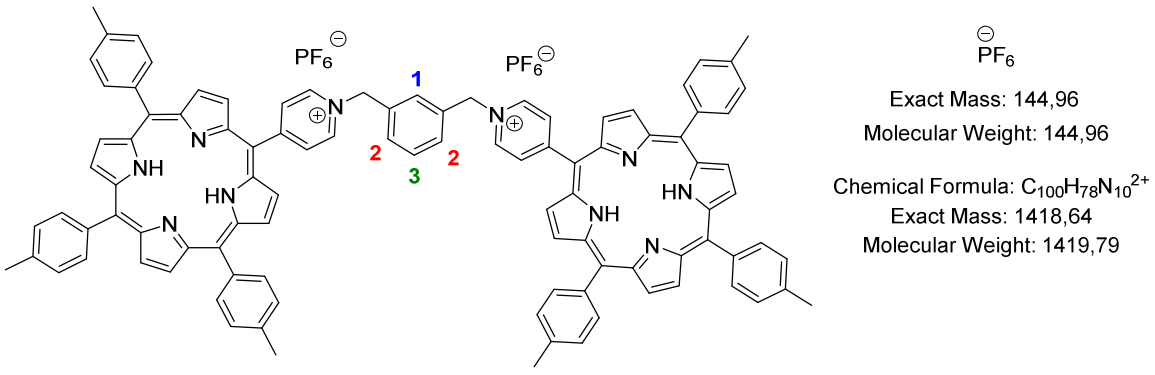
^{31}P NMR (121 MHz, DMSO-*d*$_6$): δ -144.2 (hept, *J* = 711.3 Hz).

^{19}F NMR (282 MHz, DMSO-*d*$_6$): δ -70.1 (d, *J* = 711.3 Hz).

UV-Vis (DMF)**:** λ (ε) = 419 (198000), 516 (11300), 552 (6300), 591 (4500), 648 nm (3700 $M^{-1}.cm^{-1}$).

ESI-TOF: *m/z* = 709.83 Calcd for $C_{100}H_{78}N_{10}^{2+}$ ([M^{2+}]): 709.32.

TLC R_f: 0.26 (solution of KPF_6 (27 mM) in Acetone).



NMR ^{1}H:

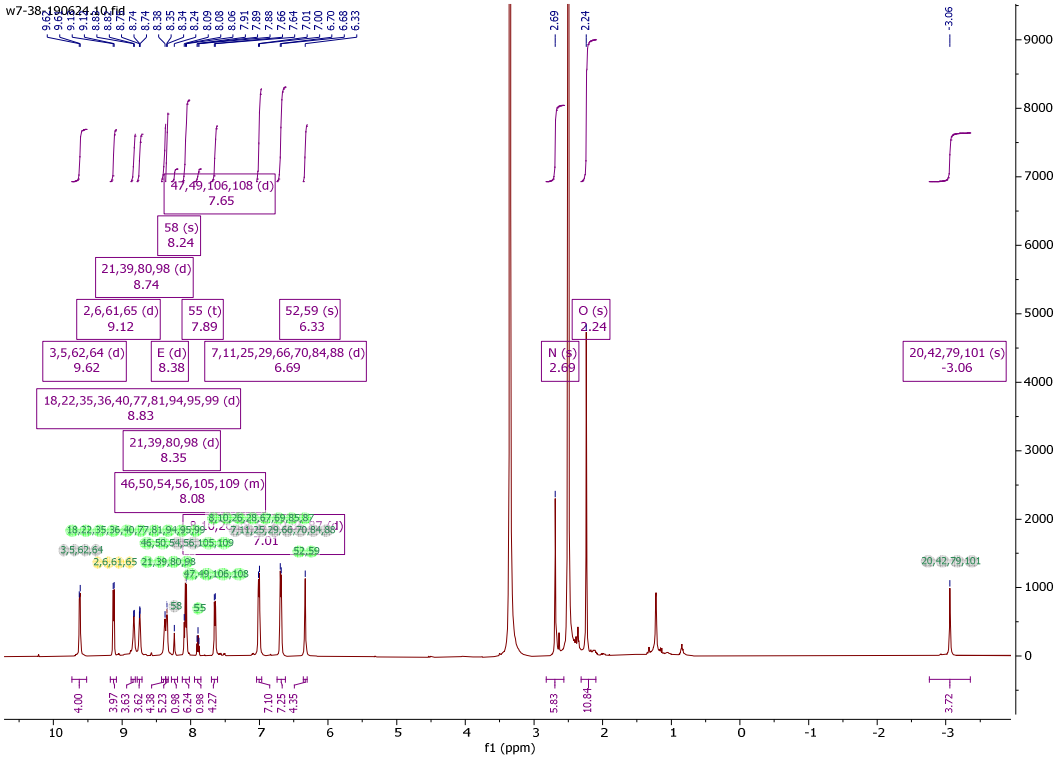


*Fig. S21: ^{1}H NMR Spectrum of **7** in DMSO-d6*

NMR ^{13}C:

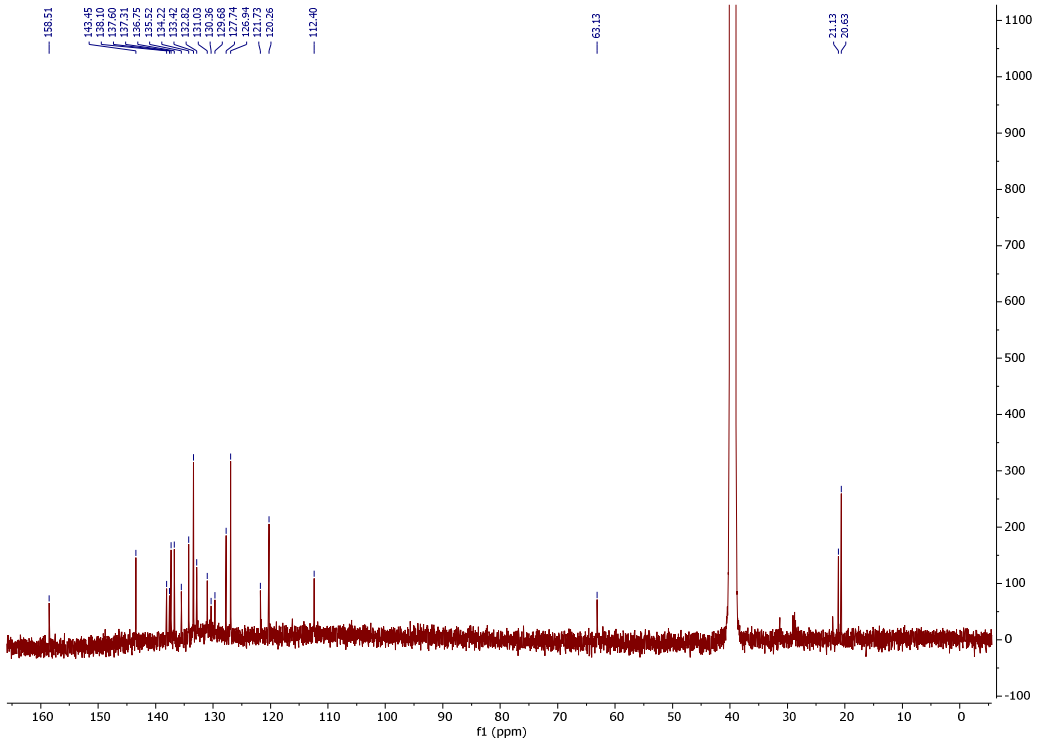


*Fig. S 22: ^{13}C NMR Spectrum of **7** in DMSO-d6*

NMR ^{31}P:

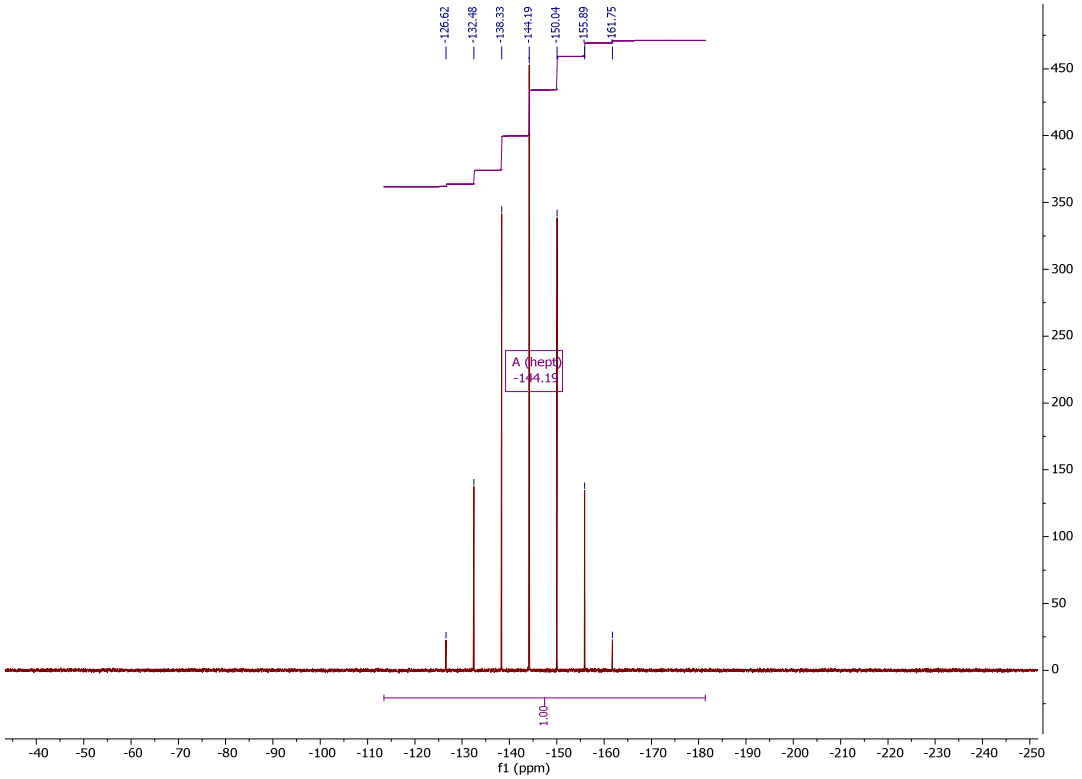


*Fig. S23: ^{31}P NMR Spectrum of **7** in DMSO-d6*

NMR ^{19}F:

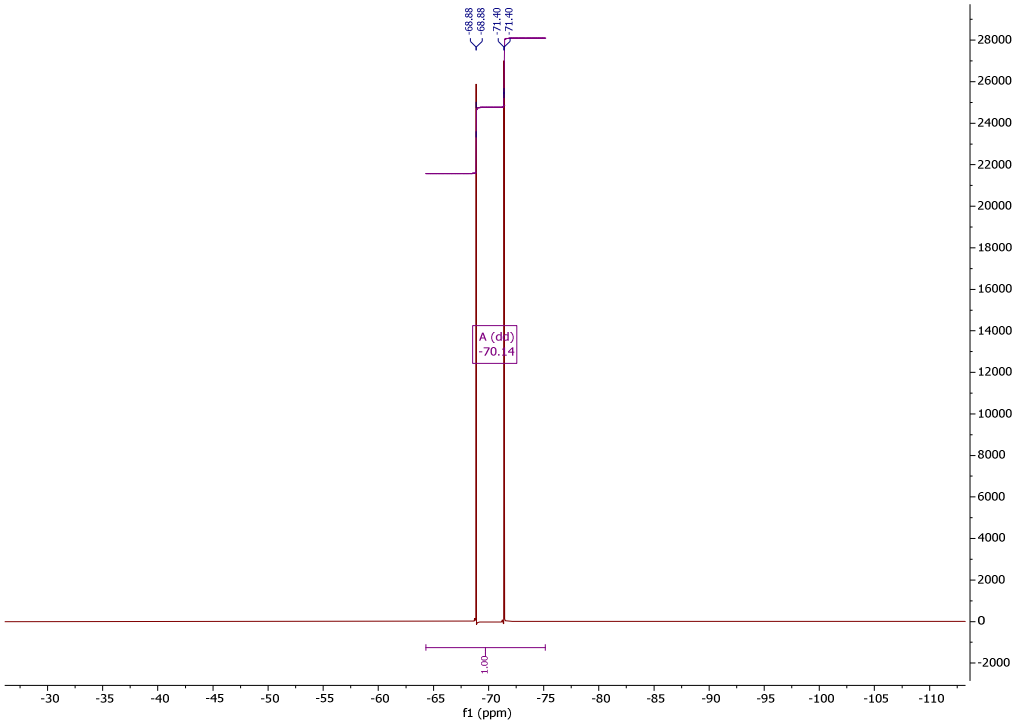


*Fig. S24: ^{19}F NMR Spectrum of **7** in DMSO-d6*

UV-Visible:

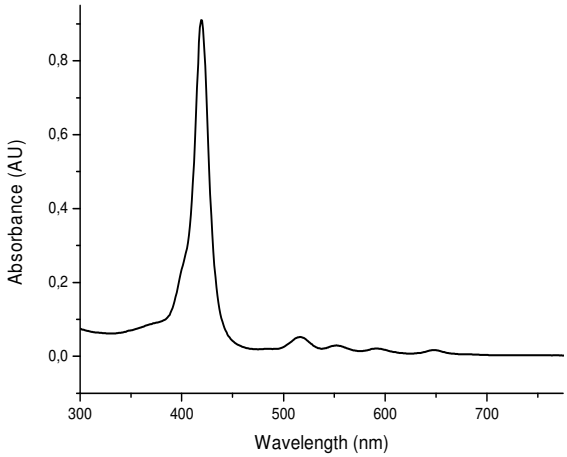


*Fig. S25: UV-visible Spectrum of **7** in DMF (C= 6.43 x 10^{-6} M)*

Bis-porphyrin 8

Prepared following the **GP2** and using single porphyrin **4** (61 mg, 0.062 mmol, 1 eq) (Method A) or α,α'-dibromo-p-xylene (18 mg, 0.062 mmol, 1 eq) (Method B) and porphyrin **1** (204 mg, 0.31 mmol, 5 eq). The crude product was purified by silica gel column chromatography ($_{CH2CL2}$ and gradually ending with a solution of KPF_6 (27 mM in acetone). Compound **8** (72 mg, 0.042 mmol, 68%) or (40 mg, 0.024 mmol, 38%) was obtained as a purple solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.66 (d, *J* = 6.2 Hz, 4H, H-*ortho*-py^{+}), 9.12 (d, *J* = 6.2 Hz, 4H, H-*meta*-py^{+}), 9.06 – 8.99 (m, 4H, H-β-pyrrolic), 8.97 – 8.92 (m, 4H, H-β-pyrrolic), 8.90 – 8.81 (m, 8H, H-β-pyrrolic), 8.11 (s, 4H, H-aryl), 8.10 – 8.04 (m, 12H, H-*ortho*-tolyl), 7.65 (d, *J* = 7.8 Hz, 8H, H-*meta*-tolyl), 7.61 (d, *J* = 7.8 Hz, 4H, H-*meta*-tolyl), 6.28 (s, 4H, -CH_2-), 2.68 (s, 6H, -CH_3), 2.64 (s, 12H, -CH_3), -2.89 (s, 4H, free base).

^{13}C NMR (126 MHz, DMSO-d_6): δ 158.8, 143.8, 138.5, 138.2, 138.2, 138.1, 138.0, 136.5, 135.9, 134.6, 133.7, 130.8, 128.2, 122.5, 121.4, 113.1, 111.1, 69.0, 30.1, 21.6, 21.5.

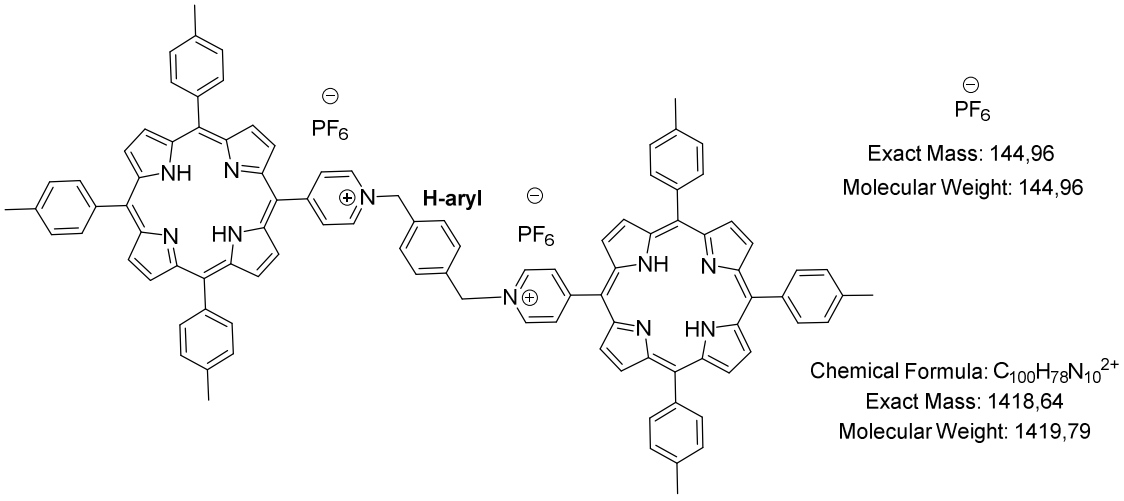
^{31}P NMR (121 MHz, DMSO-d_6): δ -141.27 (hept, *J* = 711.3 Hz)

^{19}F NMR (282 MHz, DMSO-d_6): δ -70.14 (d, *J* = 711.3 Hz)

UV-Vis (DMF)**:** λ (ε) = 422 (354000), 518 (37600), 556 (29200), 592 (22400), 650 nm (19300 $M^{-1}.cm^{-1}$).

HR-ESI-TOF: *m/z* = 709.8236 Calcd for $C_{100}H_{78}N_{10}^{2+}$ ([M^{2+}]): 709.8216.

TLC R_f: 0.31 (solution of KPF_6 (5 mM) in Acetone).



NMR ^{1}H:

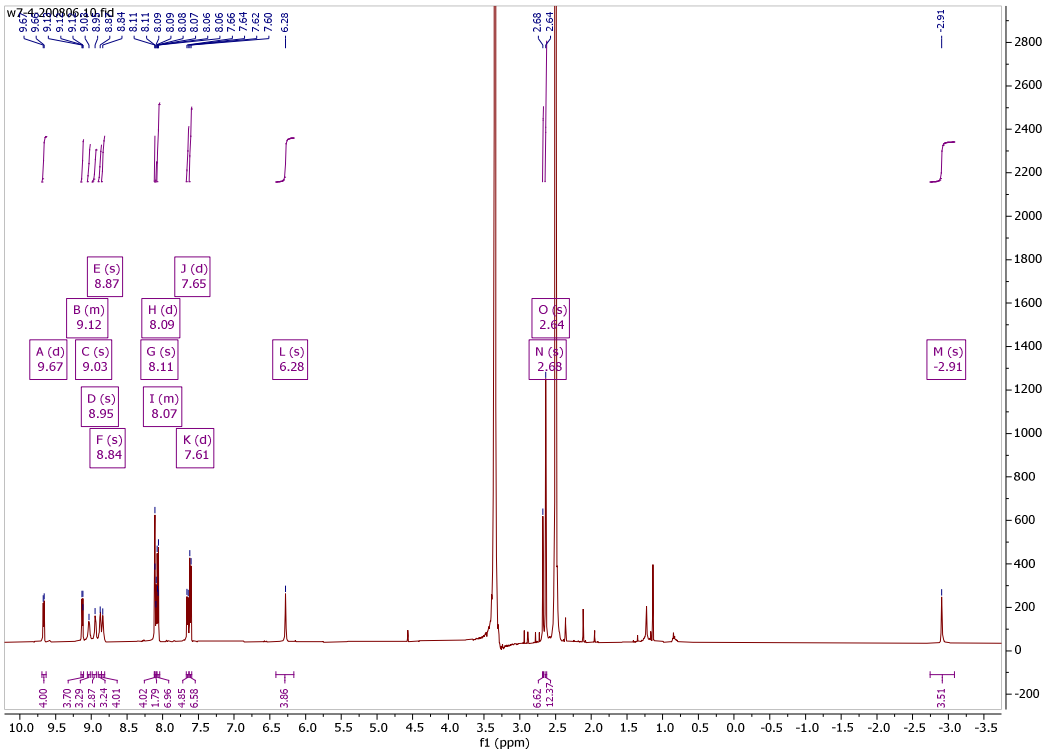


*Fig. S26: ^{1}H NMR Spectrum of **8** in DMSO-d6*

NMR ^{13}C:

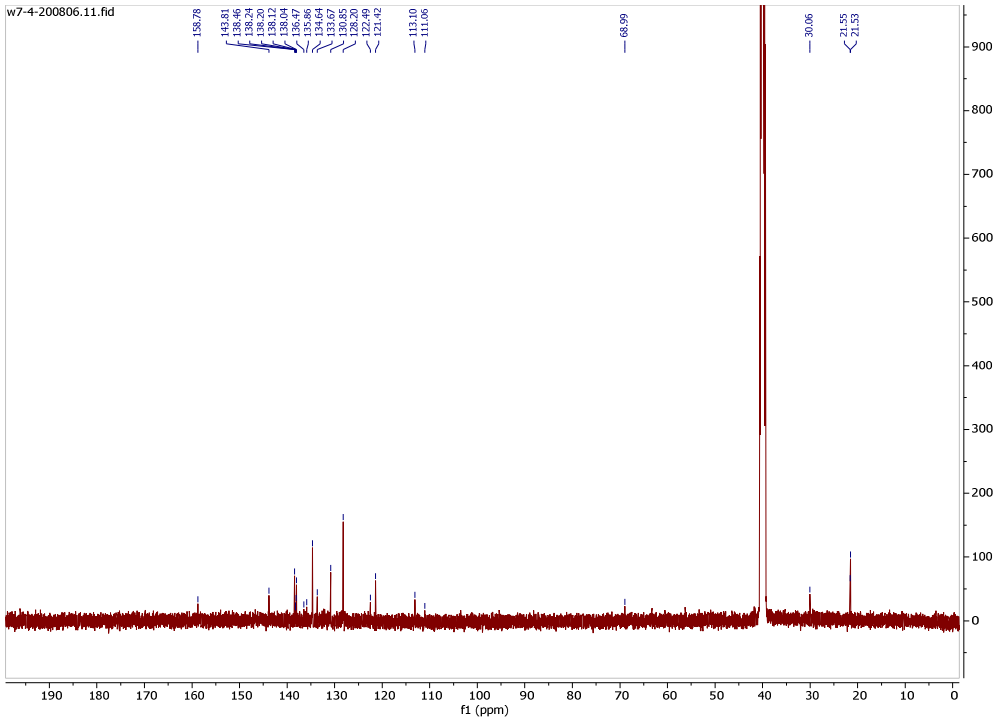


*Fig. S27: ^{13}C NMR Spectrum of **8** in DMSO-d6*

NMR ^{31}P:

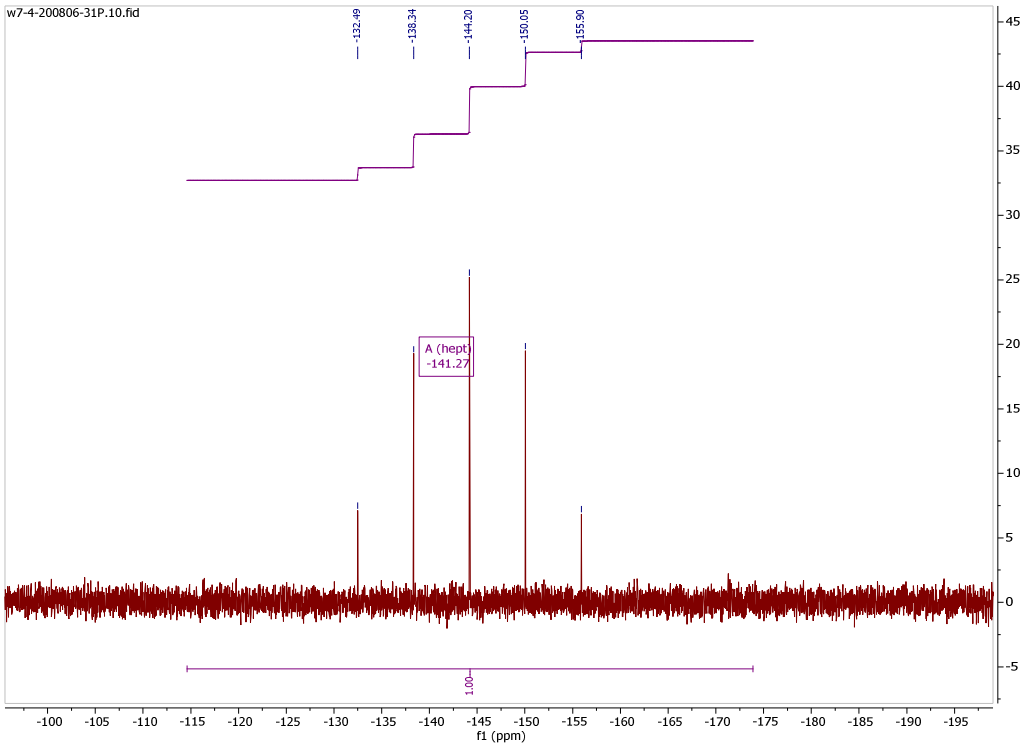


*Fig. S 28: ^{31}P NMR Spectrum of **8** in DMSO-d6*

NMR ^{19}F:

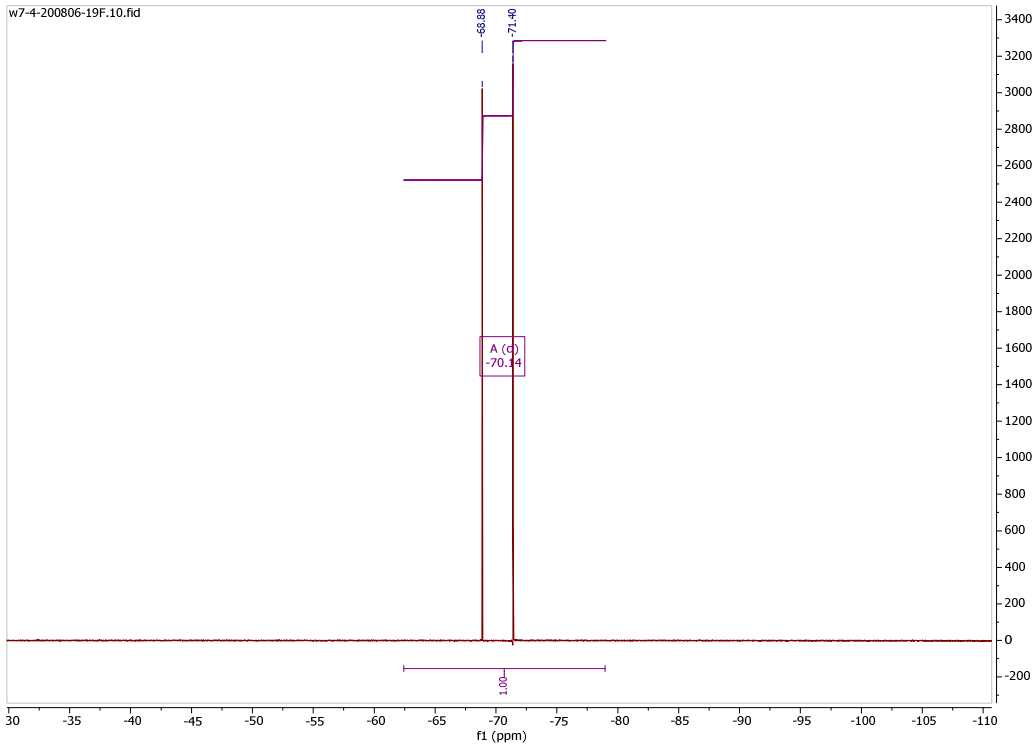


*Fig. S29: ^{19}F NMR Spectrum of **8** in DMSO-d6*

UV-Visible:

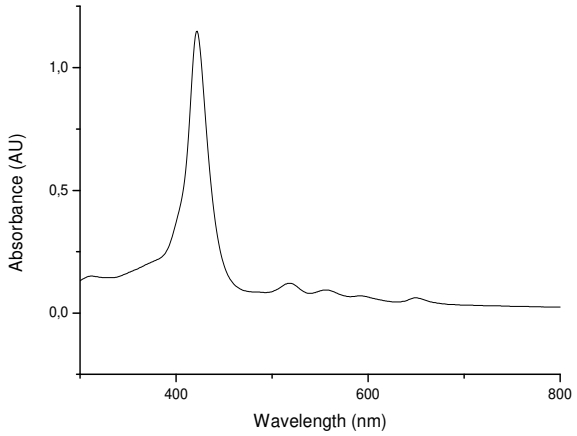


*Fig. S30: UV-visible Spectrum of **8** in DMF (C= 6.43 x 10^{-6} M)*

Bisporphyrin 9

Prepared following the **GP2** and using single porphyrin **5** (61 mg, 0.062 mmol, 1 eq) (Method A) or α,α'-dibromo-m-xylene (18 mg, 0.062 mmol, 1 eq) (Method B) and porphyrin **2** (204 mg, 0.31 mmol, 5 eq). The crude product was purified by silica gel column chromatography ($_{CH2CL2}$ and gradually ending with a solution of KPF_6 (27 mM in acetone). Compound **9** (67 mg, 0.039 mmol, 63%) or (51 mg, 0.030 mmol, 48%) was obtained as a purple solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 10.19 (s, 2H, H-py$^+$-**a**), 9.62 (d, *J* = 6.5 Hz, 2H, H-py$^+$-**b**), 9.38 (d, *J* = 7.9 Hz, 2H, 2H, H-py$^+$-**d**), 8.89 – 8.79 (m, 8H, H-β-pyrrolic), 8.75 – 8.65 (m, 8H, H-β-pyrrolic), 8.54 (dd, *J* = 7.9, 6.5 Hz, 2H, H-py$^+$-**c**), 8.13 – 8.05 (m, 4H, H-tolyl-**2**), 8.01 (s, 1H, H**1**), 7.86 (d, *J* = 7.7 Hz, 2H, H**2**), 7.80 (d, *J* = 7.3 Hz, 4H, H-tolyl-**3**), 7.71 (t, *J* = 7.7 Hz, 1H, H**3**), 7.69 – 7.59 (m, 8H, H-tolyl-**3** and H-tolyl-**1**), 7.40 (d, *J* = 7.3 Hz, 4H, H-tolyl-**4**), 7.22 (d, *J* = 7.8 Hz, 4H, H-tolyl-**4**), 6.21 (s, 4H, -CH_2-), 2.68 (s, 6H, -CH_3), 2.49 (s, 12H, -CH_3), -3.01 (s, 4H, free base)

^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 1148.9, 147.0, 144.4, 141.6, 138.1, 137.8, 137.7, 137.6, 137.4, 135.4, 134.2, 134.0, 133.9, 133.8, 130.5, 130.2, 130.2, 130.2, 129.3, 127.8, 127.7, 127.6, 127.6, 127.4, 127.0, 121.7, 120.6, 110.2, 104.9, 55.9, 32.2, 29.6, 21.1, 20.9.

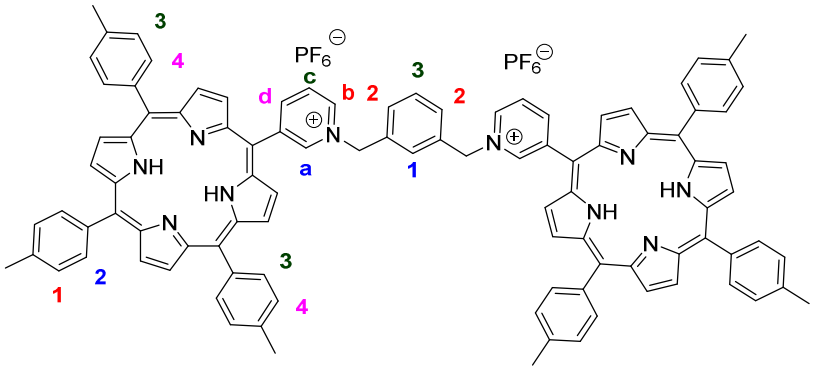
^{31}P NMR (121 MHz, DMSO-*d*$_6$): δ -144.19 (hept, *J* = 711.3 Hz).

^{19}F NMR (282 MHz, DMSO-*d*$_6$): δ -70.13 (d, *J* = 711.3 Hz).

UV-Vis (DMF)**:** λ (ε) = 422 (154000), 516 (9800), 552 (4700), 590 (3600), 647 nm (2500 $M^{-1}.cm^{-1}$).

HR-ESI-TOF: *m/z* = 709.8220 Calcd for $C_{100}H_{78}N_{10}^{2+}$ ([M^{2+}]): 709.8216.

TLC R_f: 0.21 (solution of KPF_6 (5 mM) in Acetone).



NMR ^{1}H:

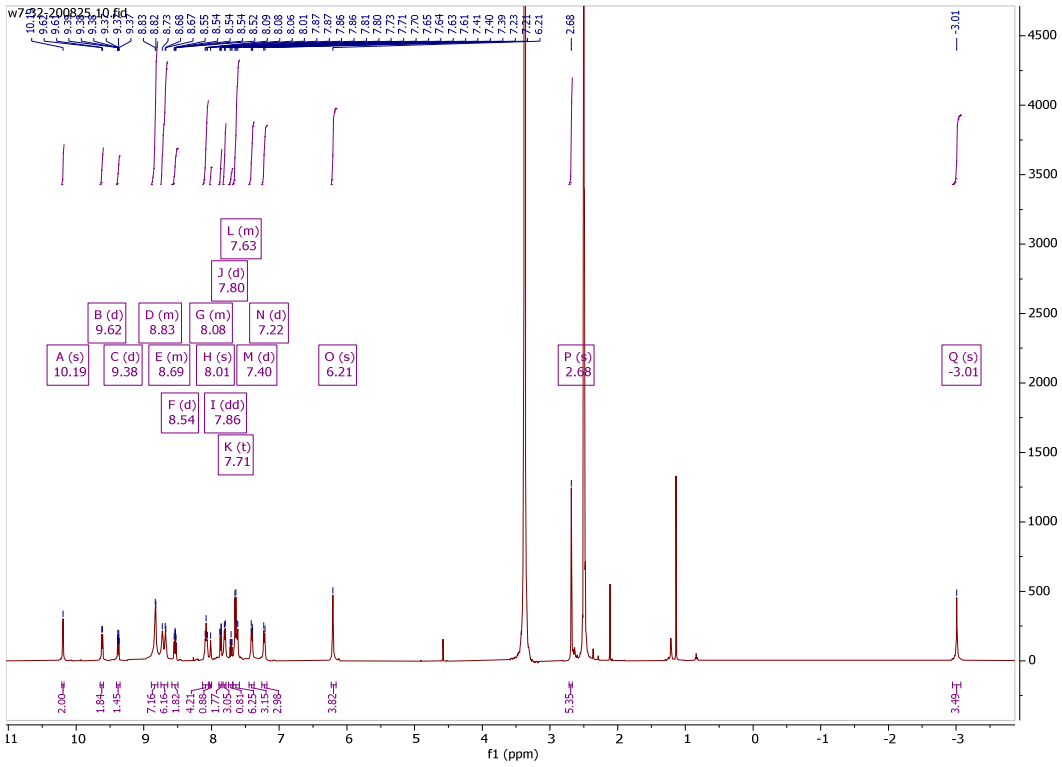


*Fig. S31: ^{1}H NMR Spectrum of **9** in DMSO-d6*

NMR ^{13}C:

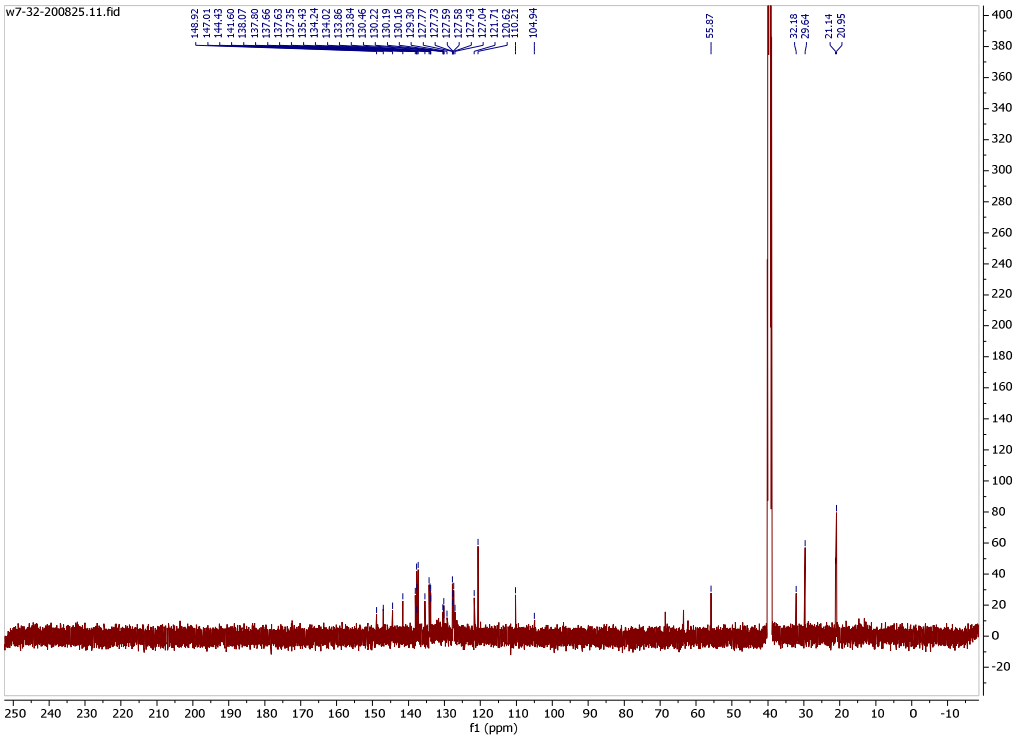


*Fig. S 32: ^{13}C NMR Spectrum of **9** in DMSO-d6*

NMR ^{31}P:

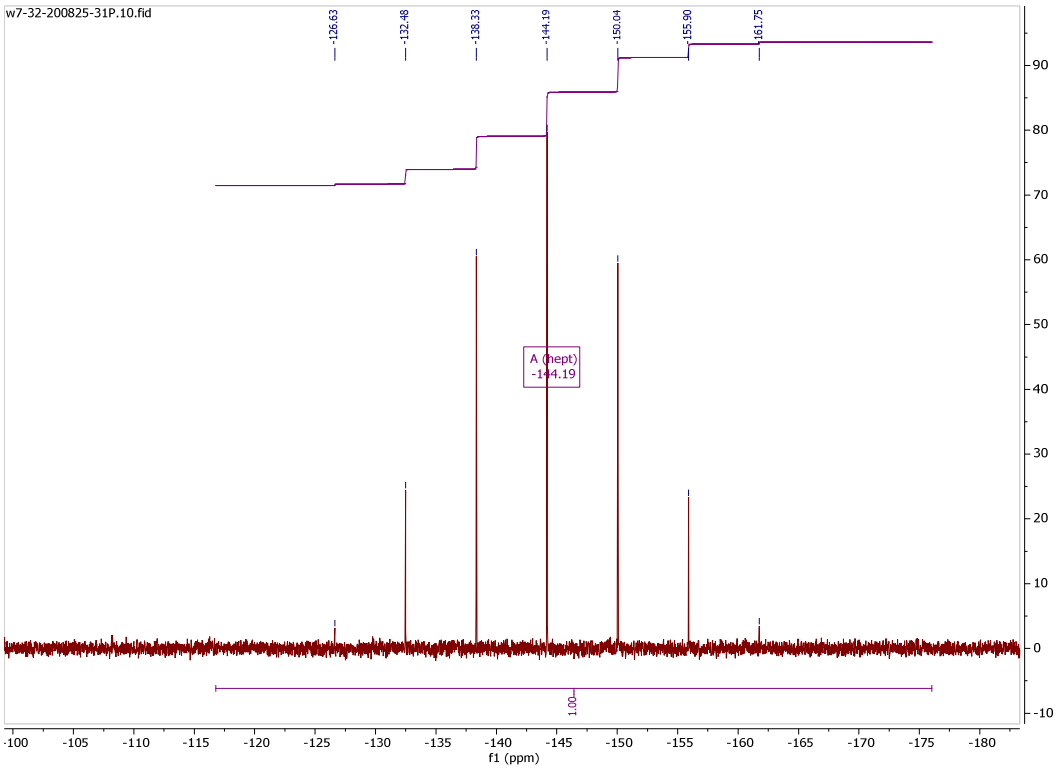


*Fig. S33: ^{31}P NMR Spectrum of **9** in DMSO-d6*

NMR ^{19}F:

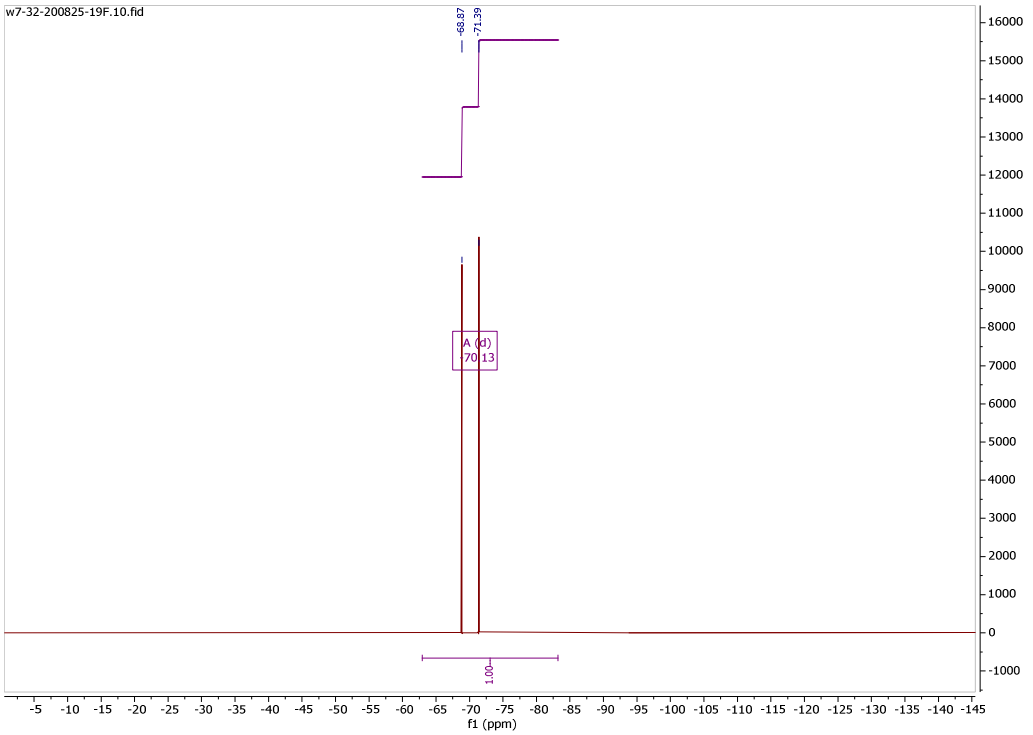


*Fig. S34: ^{19}P NMR Spectrum of **9** in DMSO-d6*

UV-Visible:

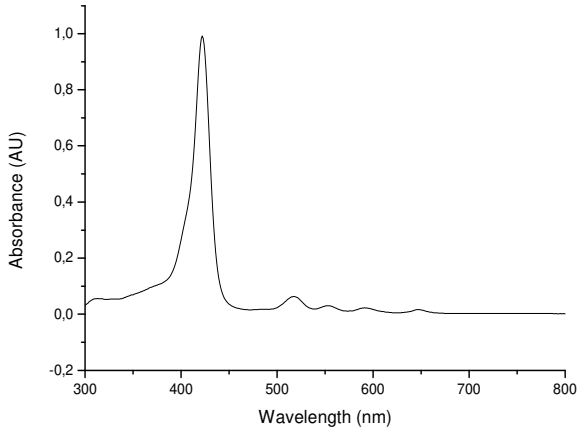


*Fig. S35: UV-visible Spectrum of **9** in DMF (C= 6.43 x 10^{-6} M)*

Bisporphyrin 10

Prepared following the **GP2** and using single porphyrin **6** (61 mg, 0.062 mmol, 1 eq) (Method A) or α,α'-dibromo-p-xylene (18 mg, 0.062 mmol, 1 eq) (Method B) and porphyrin **2** (204 mg, 0.31 mmol, 5 eq). The crude product was purified by silica gel column chromatography ($_{CH2CL2}$ and gradually ending with a solution of KPF_6 (27 mM in acetone). The compound **10** (76 mg, 0.044 mmol, 71%) or (34 mg, 0.020 mmol, 32%) was obtained as a purple solid.

^{1}H NMR (500 MHz, DMSO-*d*$_6$): δ 10.26 (s, 2H, H-py$^+$-**a**), 9.71 (d, *J* = 6.3 Hz, 2H, H-py$^+$-**b**), 9.39 (d, *J* = 7.9 Hz, 2H, H-py$^+$-**d**), 8.88 – 8.82 (m, 8H, H-β-pyrrolic), 8.77 – 8.69 (m, 8H, H-β-pyrrolic), 8.64 (dd, *J* = 7.9, 6.3 Hz, 2H, H-py$^+$-**c**), 8.15 – 8.04 (m, 4H, H-tolyl-**2**), 7.91 (s, 4H, H-aryl), 7.83 (d, *J* = 7.7 Hz, 4H, H-tolyl-**3**), 7.70 – 7.58 (m, 8H, H-tolyl-**3** and H-tolyl-**1**), 7.34 (d, *J* = 7.7 Hz, 4H, H-tolyl-**4**), 7.15 (d, *J* = 7.7 Hz, 4H, H-tolyl-**4**), 6.17 (s, 4H, -CH_2-), 2.68 (s, 6H, -CH_3), 2.41 (s, 12H, -CH_3), -2.97 (s, 4H, free base).

^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 162.3, 148.7, 147.0, 144.4, 141.6, 138.1, 137.8, 137.6, 137.3, 135.7, 134.2, 134.0, 133.8, 133.8, 129.8, 127.7, 127.5, 127.4, 127.2, 121.7, 120.7, 110.3, 63.3, 55.8, 35.8, 30.8, 21.1, 20.8.

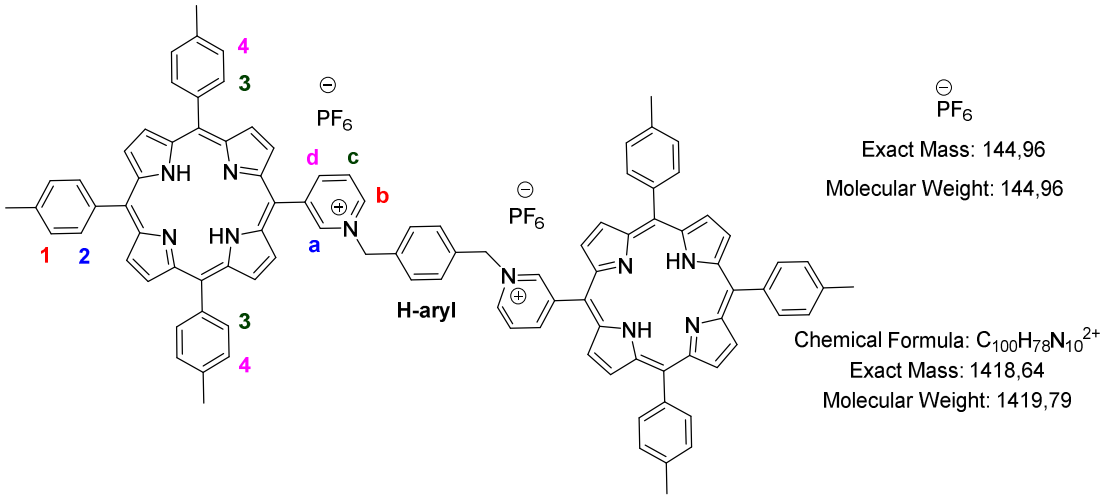
^{19}F NMR (282 MHz, DMSO-d6): δ -144.2 (hept, J = 711.3 Hz).

^{31}P NMR (121 MHz, DMSO-d6): δ -70.1 (d, J = 711.3 Hz).

UV-Vis (DMF)**:** λ (ε) = 420 (101000), 516 (8500), 552 (5900), 590 (4800), 649 nm (4200 $M^{-1}.cm^{-1}$).

HR-ESI-TOF: *m/z* = 709.3229 Calcd for $C_{100}H_{78}N_{10}^{2+}$ ([M^{2+}]): 709.3200.

TLC R_f: 0.28 (solution of KPF_6 (5 mM) in acetone).



NMR ^{1}H:

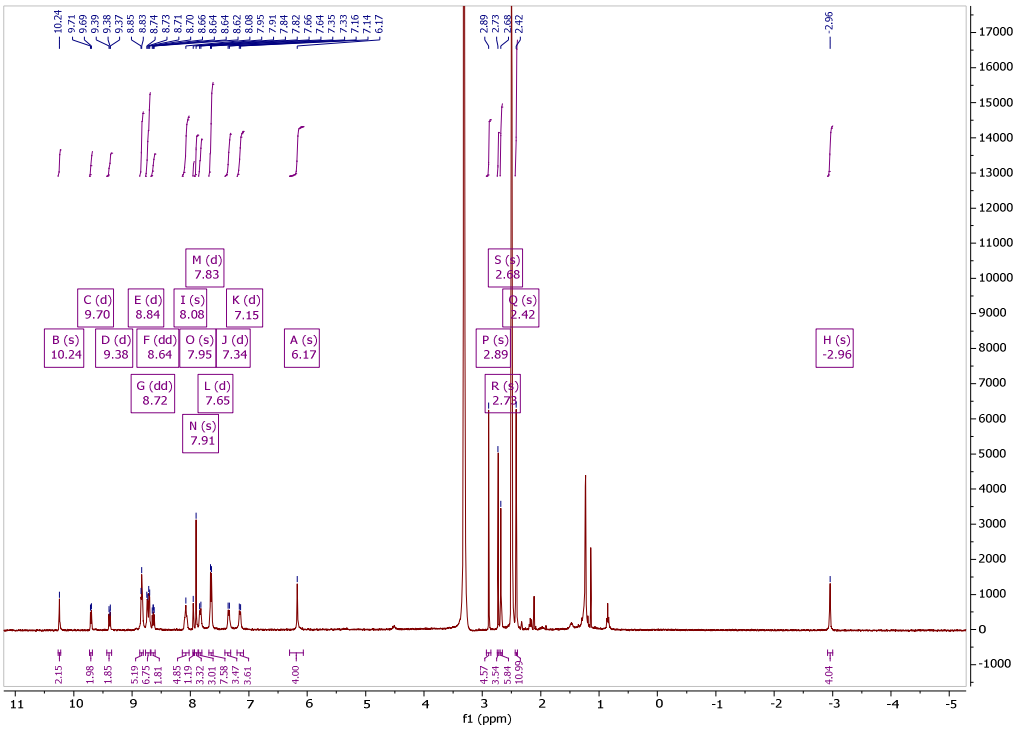


*Fig. S36: ^{1}H NMR Spectrum of **10** in DMSO-d6*

NMR ^{13}C:

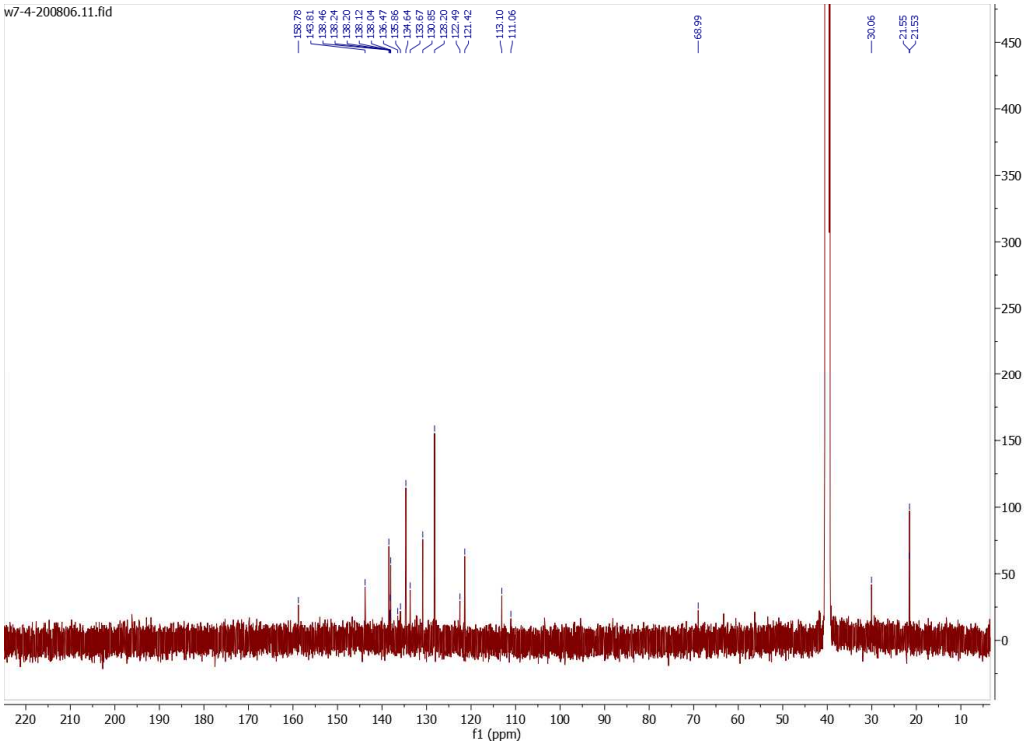


*Fig. S37: ^{13}C NMR Spectrum of **10** in DMSO-d6*

NMR ^{31}P:

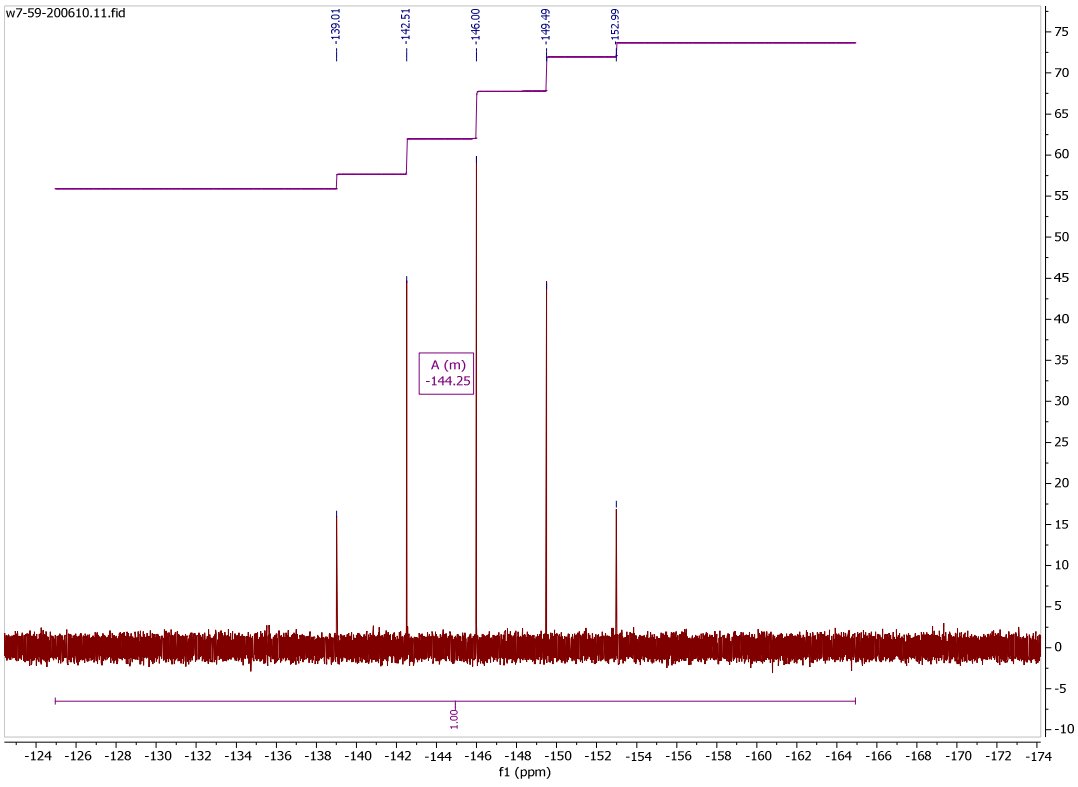


*Fig. S38: ^{31}P NMR Spectrum of **10** in DMSO-d6*

NMR ^{19}F:

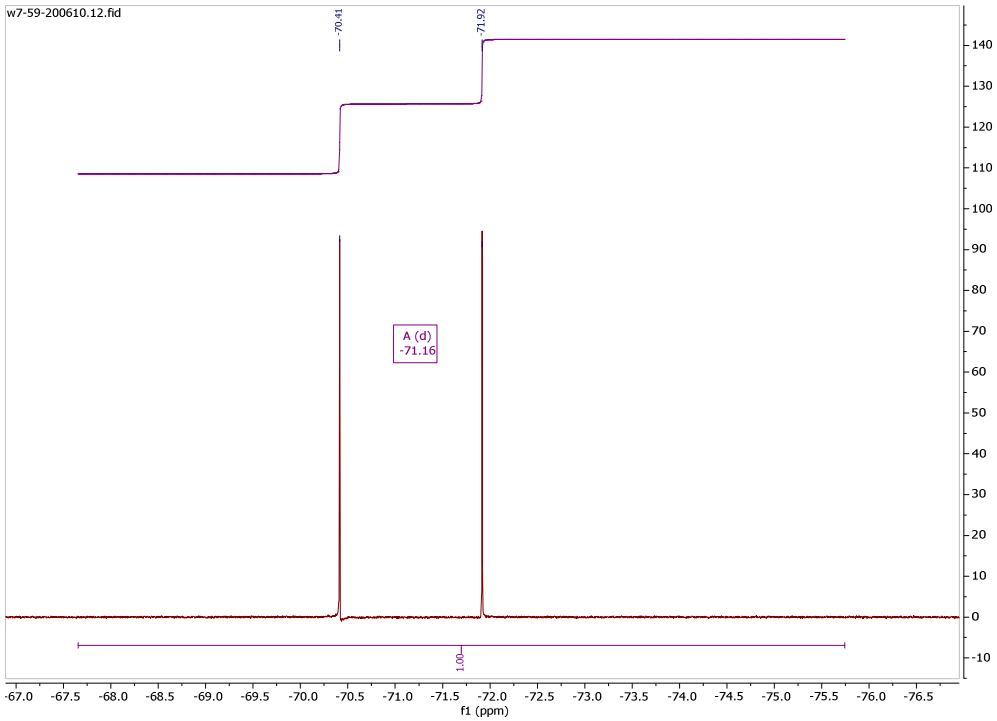


*Fig. S39: ^{19}P NMR Spectrum of **10** in DMSO-d6*

UV-Visible:

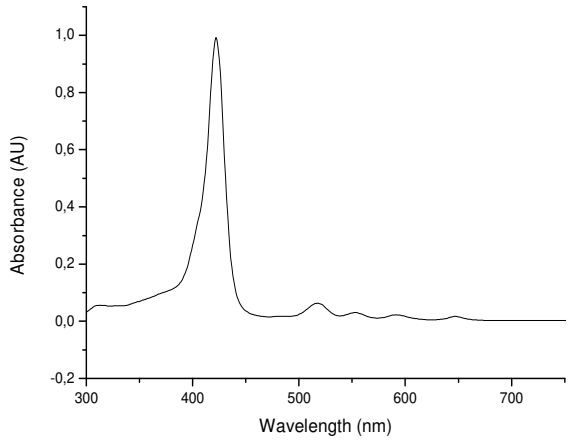


*Fig. S40: UV-visible Spectrum of **10** in DMF (C= 6.43 x 10^{-6} M)*

Supporting Data

3 + $[Mo_6O_{19}][(Bu_4N)_2]$

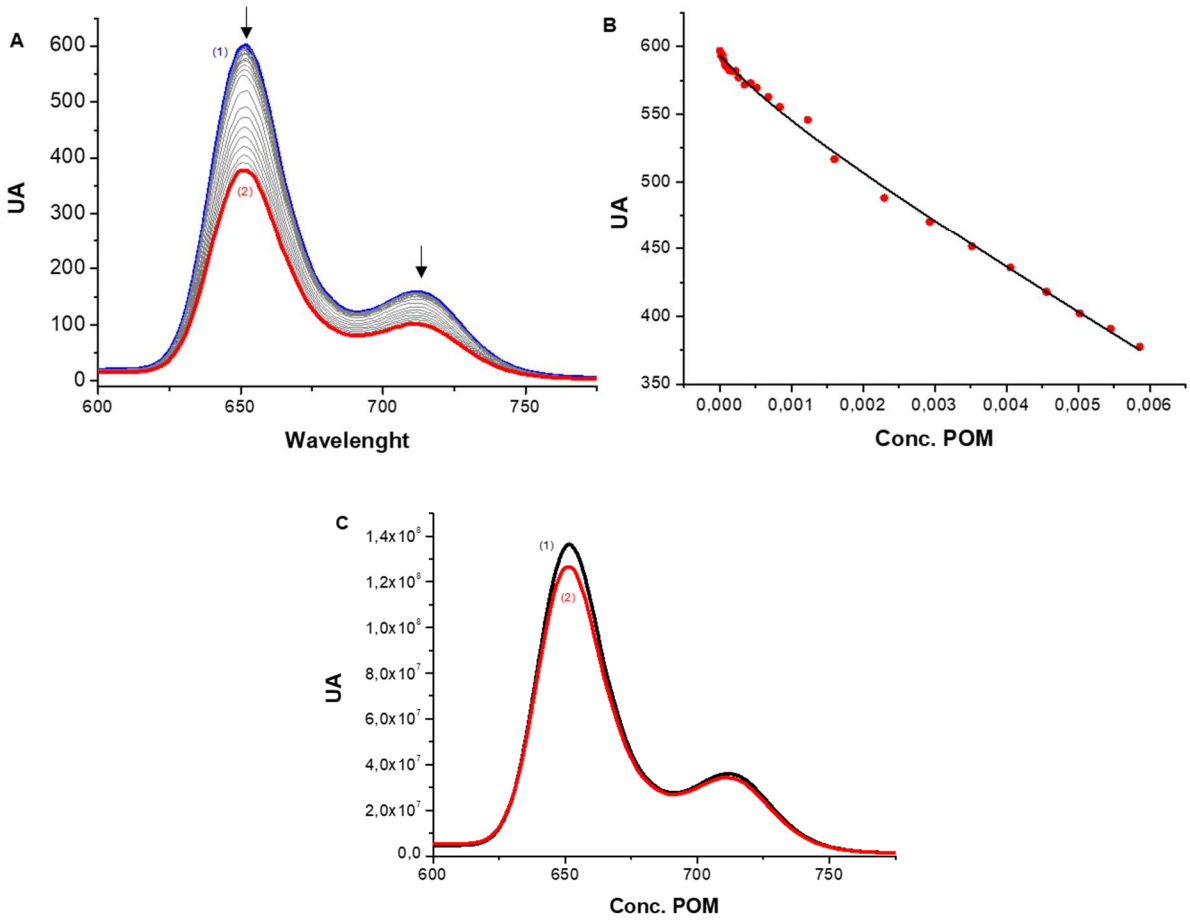
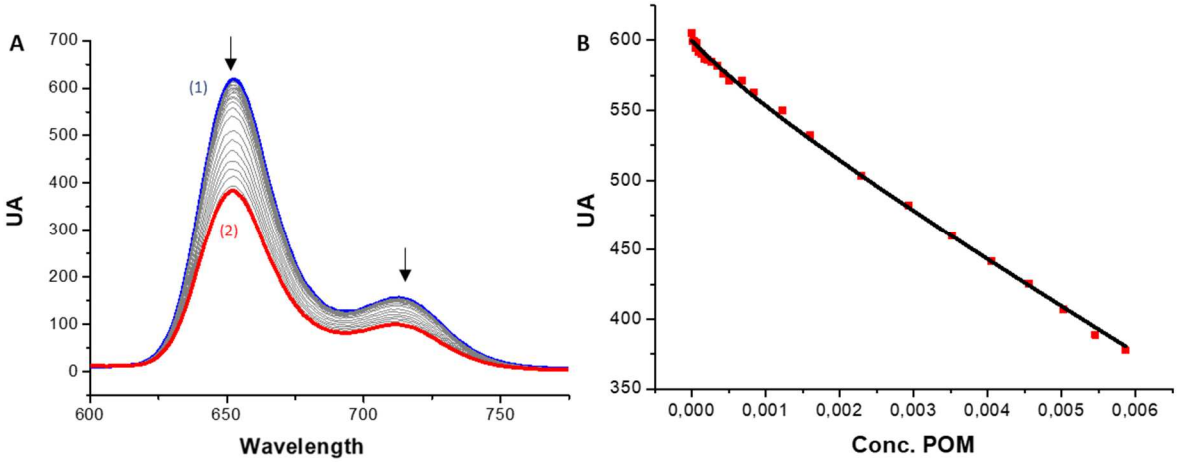


*Fig. S41:A) Luminescence spectrophotometric titration of **3** with $[Mo_6O_{19}][(n\text{-}Bu)_4N]_2$. Solvent DMF, T = 25,0 °C, λex = 518 nm, emission slit width 20 nm, (1) [**3**] = 4.39 x 10^{-6} M; (2) [POM] / [**3**] = 2000B) Variation of the emission intensity at 650 nm versus the concentration of $[Mo_6O_{19}][(n\text{-}Bu)_4N]_2$ C) Relative recalculated fluorescence spectra of **3** (a) and **3**-POM (b)*

7 + $[Mo_6O_{19}][(Bu_4N)_2]$



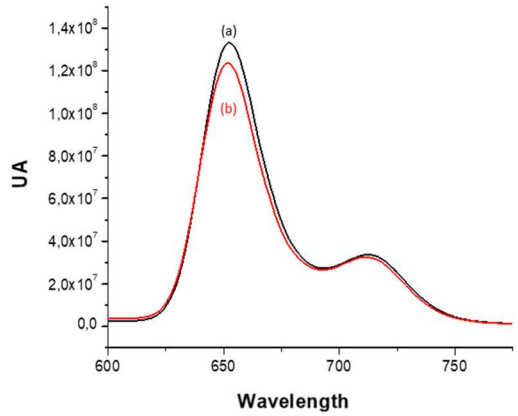


*Fig. S42: A) Luminescence spectrophotometric titration of **7** with $[Mo_6O_{19}][(n\text{-}Bu)_4N]_2$. Solvent DMF, T = 25,0 °C, λex = 518 nm, emission slit width 20 nm, (1) [**7**] = 6.43 x 10^{-6} M; (2) [POM] / [**7**] = 1700 B) Variation of the emission intensity at 650 nm versus the concentration of $[Mo_6O_{19}][(n\text{-}Bu)_4N]_2$ C) Relative recalculated fluorescence spectra of **7** (a) and **7**-POM (b)*

4 + $[Mo_6O_{19}][(Bu_4N)_2]$

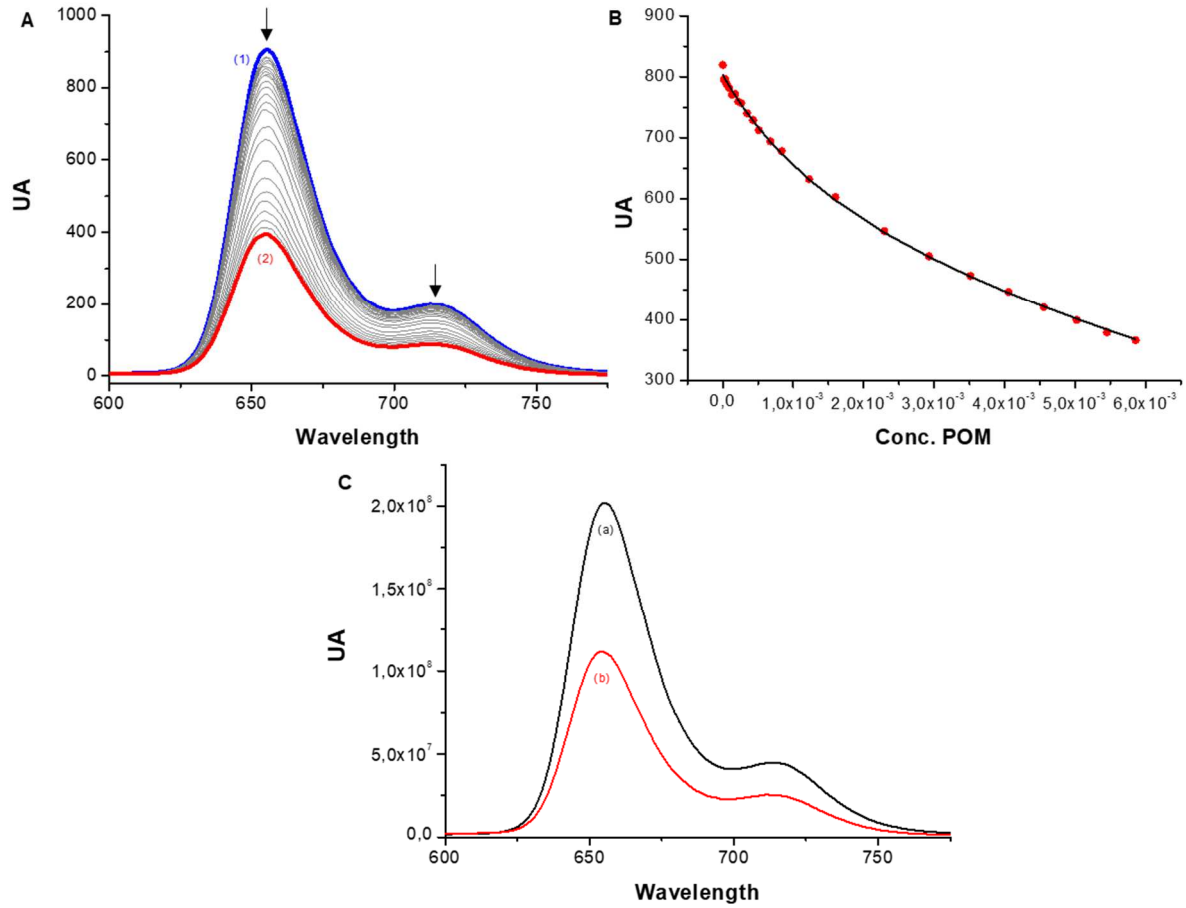


*Fig. S43: A) Luminescence spectrophotometric titration of **4** with $[Mo_6O_{19}][(n\text{-}Bu)_4N]_2$. Solvent DMF, T = 25,0 °C, λex = 518 nm, emission slit width 20 nm, (1) [**4**] = 4.39 x 10^{-6} M; (2) [POM] / [**4**] = 2000 B) Variation of the emission intensity at 650 nm versus the concentration of $[Mo_6O_{19}][(n\text{-}Bu)_4N]_2$ C) Relative recalculated fluorescence spectra of **4** (a) and **4**-POM (b)*

8 + $[Mo_6O_{19}][(Bu_4N)_2]$

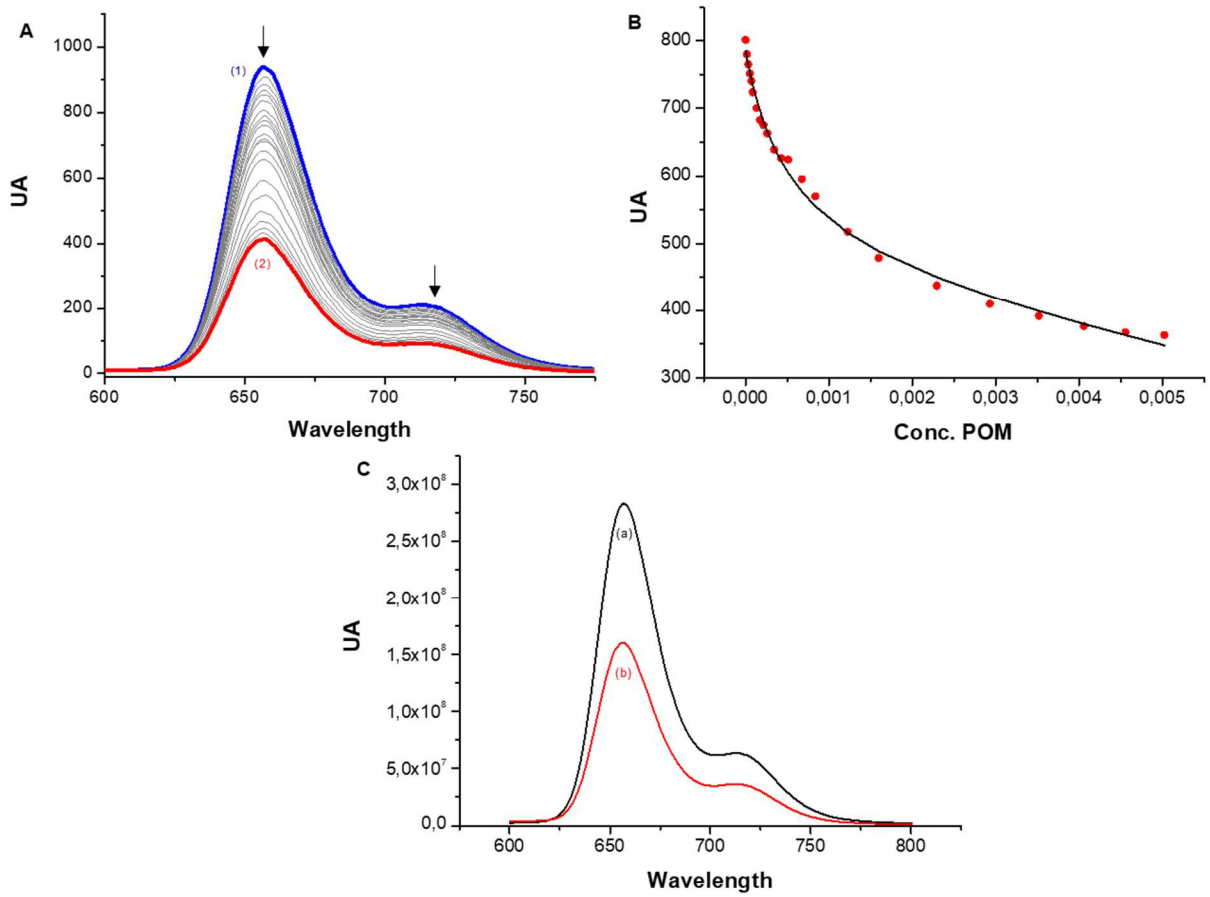
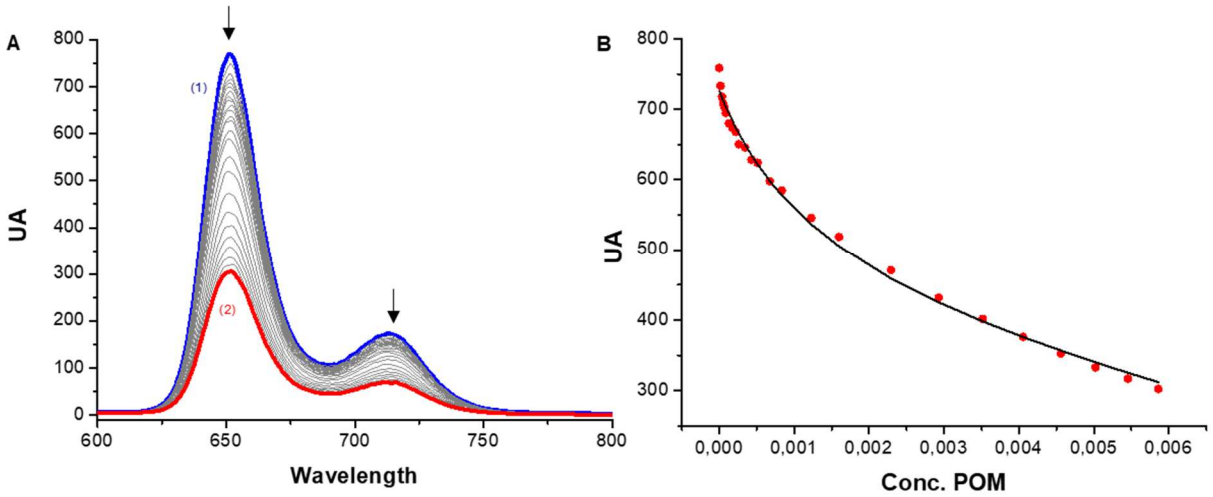


*Fig. S44: A) Luminescence spectrophotometric titration of **8** with $[Mo_6O_{19}][(n\text{-}Bu)_4N]_2$. Solvent DMF, T = 25,0 °C, λex = 518 nm, emission slit width 20 nm, (1) [**8**] = 6.43 x 10^{-6} M; (2) [POM] / [**8**] = 1700 B) Variation of the emission intensity at 650 nm versus the concentration of $[Mo_6O_{19}][(n\text{-}Bu)_4N]_2$ C) Relative recalculated fluorescence spectra of **8** (a) and **8**-POM (b)*

5 + $[Mo_6O_{19}][(Bu_4N)_2]$



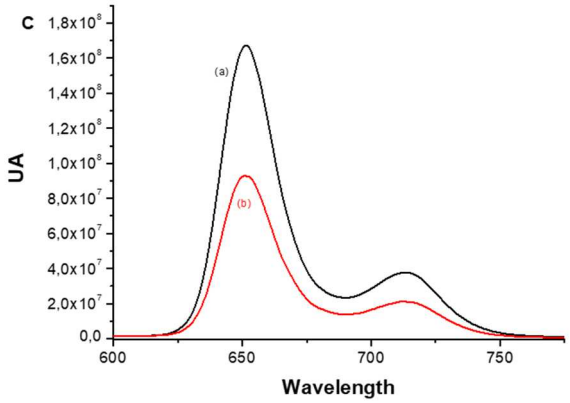


*Fig. S45: A) Luminescence spectrophotometric titration of **5** with $[Mo_6O_{19}][(n\text{-}Bu)_4N]_2$. Solvent DMF, T = 25,0 °C, λex = 518 nm, emission slit width 20 nm, (1) [**5**] = 4.39 x 10^{-6} M; (2) [POM] / [**5**] = 2000 B) Variation of the emission intensity at 650 nm versus the concentration of $[Mo_6O_{19}][(n\text{-}Bu)_4N]_2$ C) Relative recalculated fluorescence spectra of **5** (a) and **5**-POM (b)*

9 + $[Mo_6O_{19}][(Bu_4N)_2]$

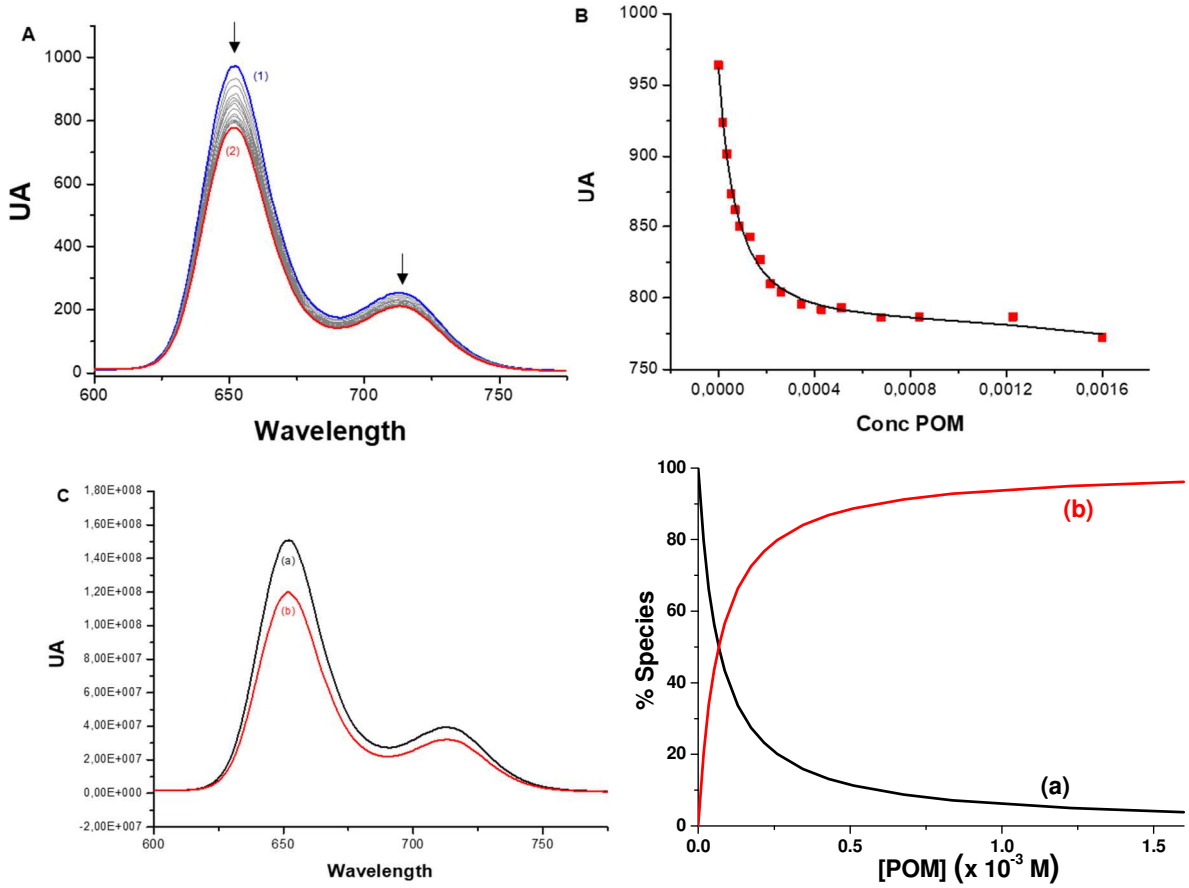


*Fig. S46: A) Luminescence spectrophotometric titration of **9** with $[Mo_6O_{19}][(n\text{-}Bu)_4N]_2$. Solvent DMF, T = 25,0 °C, λex = 517 nm, emission slit width 20 nm, (1) [**9**] = 6.43 x 10^{-6} M; (2) [POM] / [**9**] = 340 B) Variation of the emission intensity at 650 nm versus the concentration of $[Mo_6O_{19}][(n\text{-}Bu)_4N]_2$ C) Relative recalculated fluorescence spectra of **9** (a) and **9**-POM (b). D) Distribution diagrams of the species formed between **9** and POM, namely **9** (a) and **9**-POM (b).*

6 + $[Mo_6O_{19}][(Bu_4N)_2]$

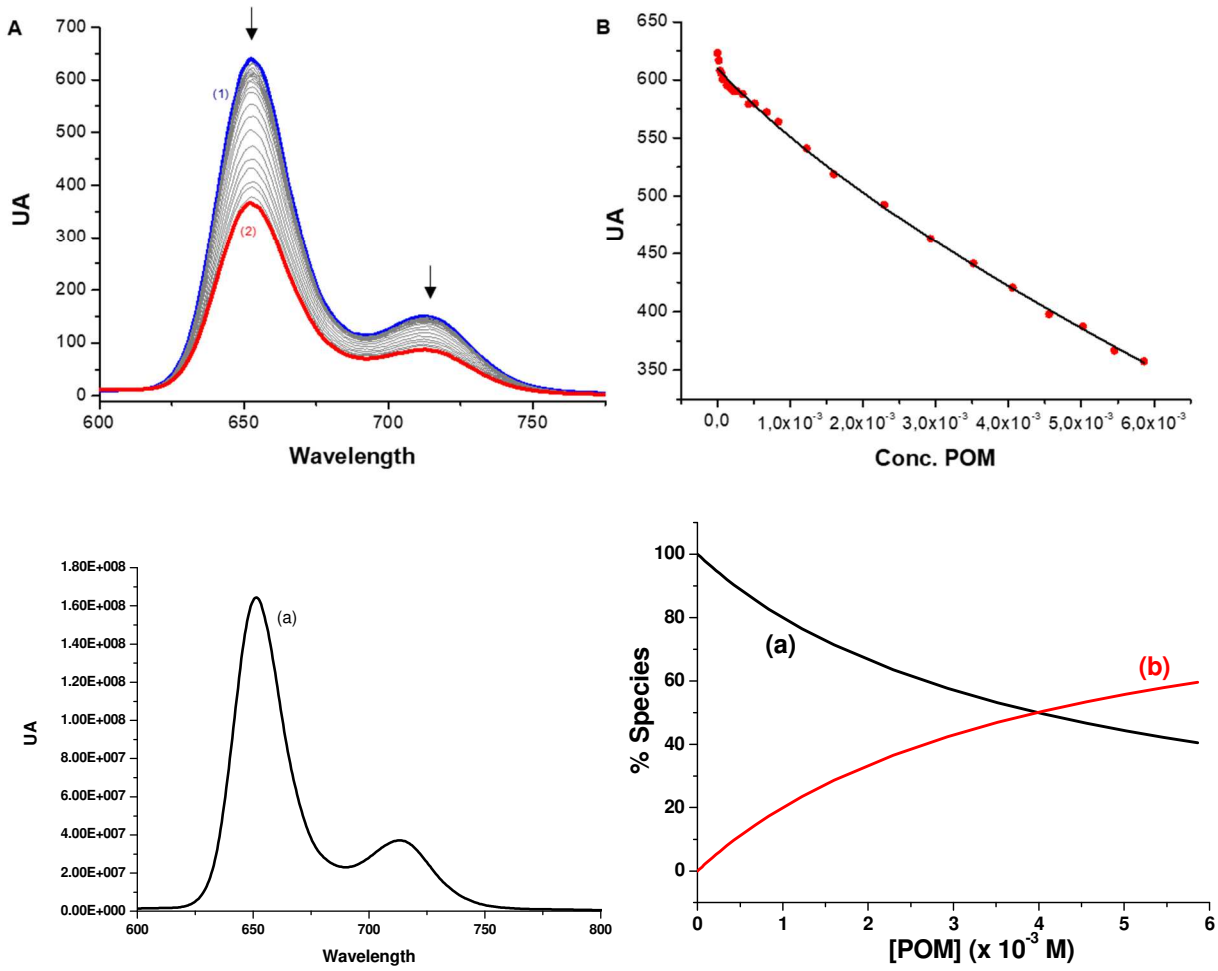


*Fig. S47: A) Luminescence spectrophotometric titration of **6** with $[Mo_6O_{19}][(n\text{-}Bu)_4N]_2$. Solvent DMF, T = 25,0 °C, λex = 518 nm, emission slit width 20 nm, (1) [**6**] = 4.39 x 10^{-6} M; (2) [POM] / [**6**] = 2000 B) Variation of the emission intensity at 650 nm versus the concentration of $[Mo_6O_{19}][(n\text{-}Bu)_4N]_2$ C) Relative recalculated fluorescence spectra of **6** (a), **6**-POM being not an emitting species(b). D) Distribution diagrams of the species formed between **6** and POM, namely **6** (a) and **6**-POM (b).*

10 + $[Mo_6O_{19}][(Bu_4N)_2]$

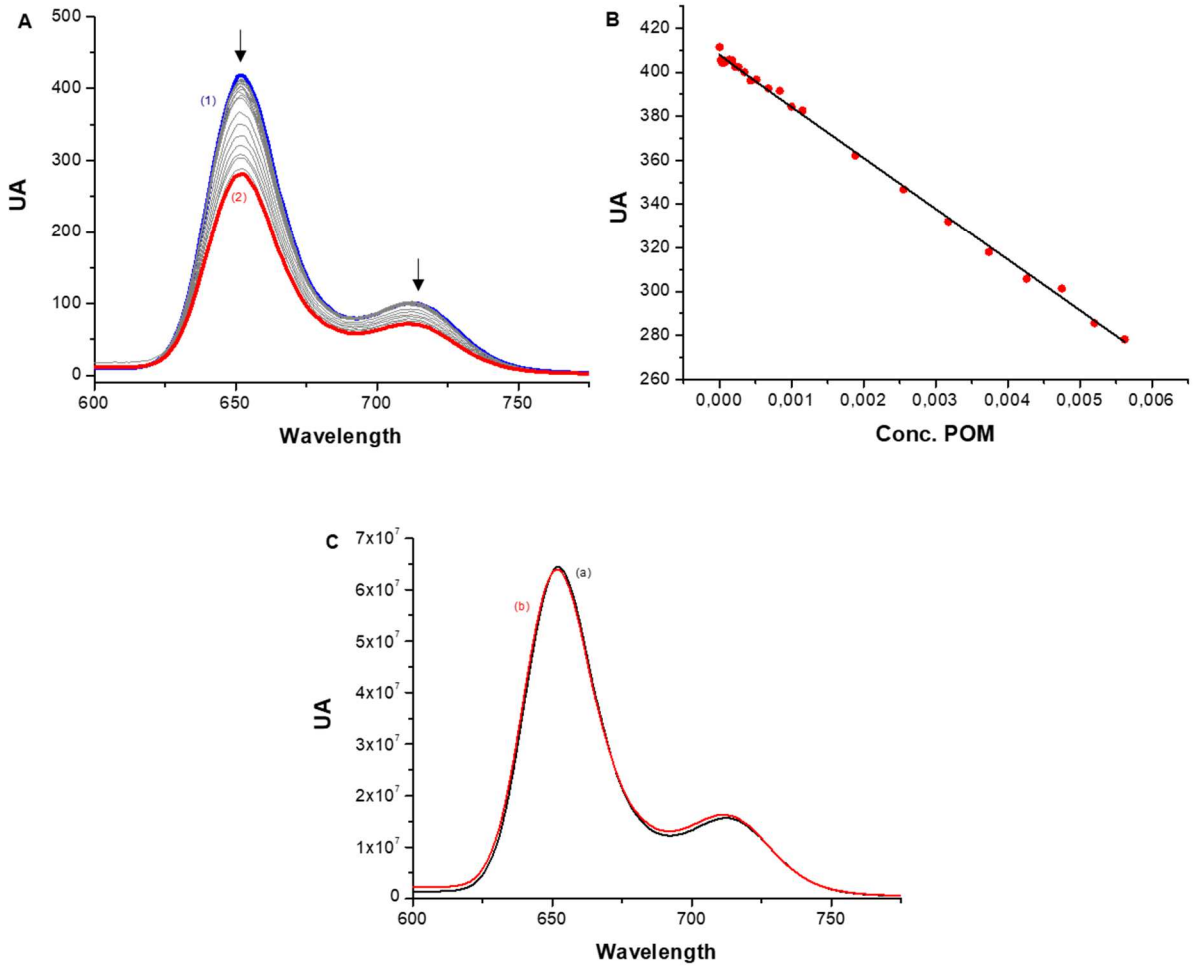


*Fig. S48: A) Luminescence spectrophotometric titration of **10** with $[Mo_6O_{19}][(n\text{-}Bu)_4N]_2$. Solvent DMF, T = 25,0 °C, λex = 518 nm, emission slit width 20 nm, (1) [**10**] = 6.43 x 10^{-6} M; (2) [POM] / [**10**] = 1700 B) Variation of the emission intensity at 650 nm versus the concentration of $[Mo_6O_{19}][(n\text{-}Bu)_4N]_2$ C) Relative recalculated fluorescence spectra of **10** (a) and **10**-POM (b)*

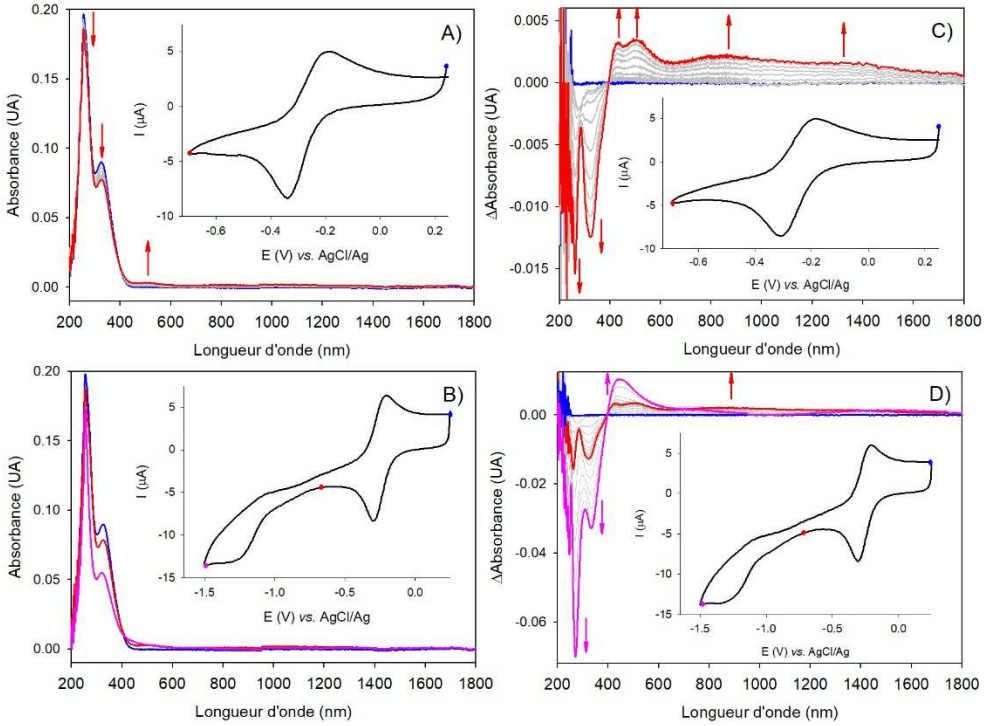


Fig. S49: Spectroelectrochemistry of $[Mo_6O_{19}]$ $[(n\text{-}Bu)_4N]_2$. A) and C) first reduction, B) and D) second reduction. DMF + 0.1 M $TBAPF_6$. Optically transparent thin film spectroelectrochemical cell (OTTLE, optical path: 0.2 mm) equipped with an Au mini-grid (working electrode) and CaF_2 type optical windows. Pseudo-reference: AgCl / Ag. c = 5 $mV.s^{-1}$. For C) and D), the baseline (blank) was recorded in the presence of $[Mo_6O_{19}]$ $[(n\text{-}Bu)_4N]_2$

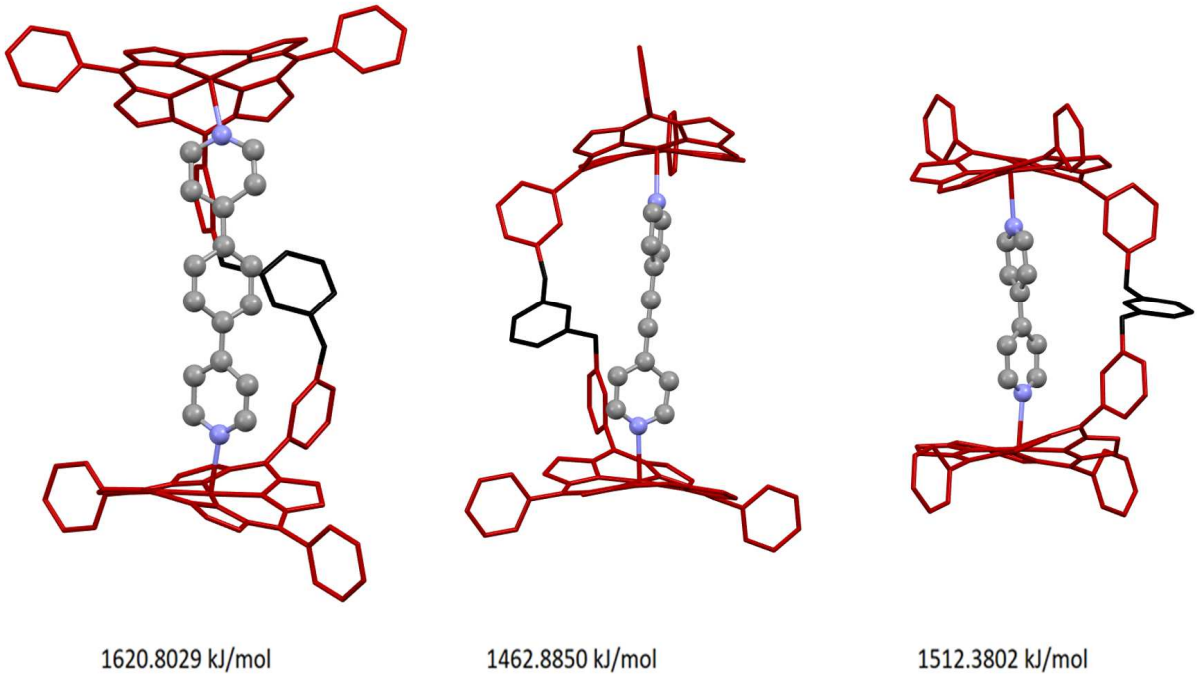


Fig. S50: MM2 calculated structures of bipy coordination complexes of ***9Zn₂*** *with 4-(p-phenyl-4-pyridyl)-pyridine, 4,4'-dipyridylacetylene and 4,4'-bipyridine. Color code: Burgundy = porphyrins, black = spacer, CPK = guest.*

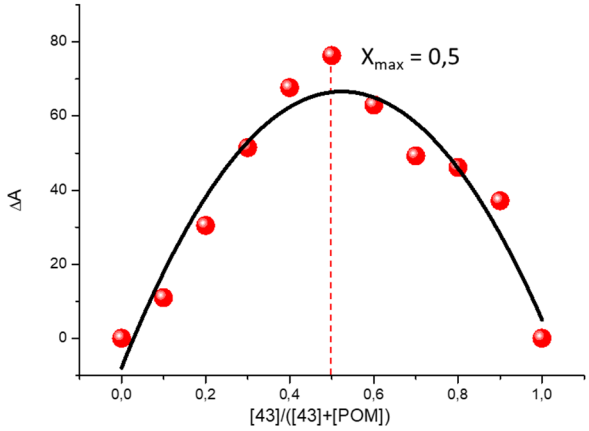


Fig. S51: Fluorescence quenching Titration of ***9*** *with $[Mo_6O_{19}][(Bu_4N)_2]$. Solvent DMF, T = 25.0 °C, λ_{ex} = 647 nm, emission and excitation slits of 9 and 9 nm. $\Delta A/\Delta A_{max}$ at 714 nm; $([\mathbf{9}]_{tot} + [POM_{tot}]) = 2.5\ 10^{-4}$ M*

References

[1] H. Gampp, M. Maeder, C. J. Meyer, A. D. Zuberbühler, *Talanta* **1985**, *32*, 95–101.
[2] D. W. Marquardt, *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431–441.
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