Supporting Information

Dual facet of gold(III) in the reactions of gold(III) and porphyrins

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1. Experimental Section

1.1 General Experimental Information

Unless otherwise stated, all reactions were performed under an inert atmosphere of nitrogen in either standard Schlenk techniques or flame-dried flasks. UV-vis spectra were recorded on an Agilent 8453 UV-vis spectrometer equipped with an Agilent 89090A thermostat (±0.1 ℃). All NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrophotometer (300M for ^{1}H, and 282M for ^{19}F) or Bruker Avance 600 MHz spectrophotometer (600M for ^{1}H, and 564M for ^{19}F). All chemical shifts were reported in ppm and all coupling constants were in Hz. For ^{19}F NMR spectra，hexafluorobenzene in $CDCl_3$ was used as the internal reference at 0 ppm. Mass spectra were recorded on Bruker APEX IV FT-ICR Mass Spectrometer. GC/MS spectra we collected on Agilent 5975C/7890A. IR spectra were recorded on Nicolet Magna IR 750. X-ray Crystallography data was collected on a Rigaku Saturn 724 diffractometer at 173K.

1.2 Synthesis of Gold Porphyrins

General procedure: A mixture of $HAuCl_4 \cdot 4H_2O$ (30.9mg, 0.075mmol) and AgOTf (77.1mg, 0.3mmol) in 4mL THF wasadded to the solution of porphyrin (0.05mmol) and NaOAc (26.7mg, 0.325mmol) in CH_2Cl_2. The reaction mixture was stirred at room temperature for 1-2h. After the solvent was evaporated in vacuum, the residue was chromatographyed on silica column (using CH_2Cl_2 to remove free porphyrin and CH_2Cl_2/CH_3OH=50:1 to collect the product). After solvent evaporation, the solid was dissolved in 3mL acetone. 20mg LiCl dissolved in 5mL water was then added to the acetone solution and reddish-brown precipitation was obtained after acetone was removed. The resulted solid was filtrated and recrystallized from CH_2Cl_2/petroleum ether to afford corresponding product.

1.2.1 Gold(III) 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin

^{1}HNMR ($CDCl_3$, 300 MHz): δ 9.51 (s, 8H) ^{19}FNMR ($CDCl_3$, 282 MHz): δ 25.33-25.25 (m, 8F), 14.704 (t, 4F, J = 23.1 Hz), 3.06-2.88 (m, 8F); ESI-MS (M^+) m/z = 1169.0; HRMS-ESI (M^+): calc'd for $C_{44}H_8AuF_{20}N_4$: 1169.0095, found: 1169.0017.

1.2. 2 Gold(III) 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin

^{1}HNMR ($CDCl_3$, 300 MHz): 9.23(s, 8H, Por-H), 7.95(s, 12H, Ar-H); HRMS-ESI (M-Cl^+): calc'd

for $C_{44}H_{20}AuCl_8N_4$: 1084.8803, found: 1084.8766.

1.2.3 Gold(III) 5,10,15,20-tetrakis(phenyl)porphyrin (11b)

^{1}HNMR ($CDCl_3$, 300 MHz): δ 9.25 (s, 8H) 8.30(dd, 8H, *ortho*-Ar-H, J=7.5Hz, 1.5Hz), 7.83-7.86(m, 12H, Ar-H); HRMS-ESI (M-Cl^+): calc'd for $C_{44}H_{28}AuN_4$: 809.1974, found: 809.1968.

1.2.4 Gold(III) 5,10,15,20-tetrakis(3,5-ditertbutylphenyl)porphyrin

^{1}HNMR ($CDCl_3$, 300 MHz): δ 9.33 (s, 8H, Por-H), 8.09(d, 8H, *ortho*-Ar-H, J=1.5Hz), 7.91(t, 4H, *para*-Ar-H, J=1.5Hz), 1.53 (s, 72H, -$C(CH_3)_3$); HRMS-ESI (M-Cl^+): calc'd for $C_{76}H_{92}AuN_4$: 1257.6982, found: 1257.6952.

1.2.5 Gold(III) 5,10,15,20-tetrakis(2,6-dimethoxylphenyl)porphyrin

^{1}HNMR ($CDCl_3$, 300 MHz): 9.15 (s, 8H, Por-H), 7.85 (t, 4H, *para*-Ar-H, J=8.5Hz), 7.08 (d, 8H, *meta*-Ar-H, J=8.5Hz), 3.58 (s, 24H, -OCH_3); HRMS-ESI (M-Cl^+): calc'd for $C_{52}H_{44}AuN_4O_8$: 1049.2819, found: 1049.2826.

1.3 Synthesis of porpholactones

General Procedure: Porphyrins (for **3-8**) or silver porphyrins (for **9a-11**) (0.025 mmol), gold complex (0.05 mmol), AgOTf (0.1 mmol, 26.0 mg) and NaOAc (0.125 mmol, 10.5 mg) were added to a Schlenk tube, 2 mL acetic acid was added *via* syringe in succession. The resulting reaction mixture was refluxed for 12 h at 120ºC. The solvent was then removed under vacuum and the residue was then purified by flash column chromatography to give the products.

1.3.1 Synthesis and Characterization of [Au(Pic.)Cl_2]

[Au(Pic.)Cl_2] was synthesized according to the literature.[1] ^{1}H NMR (d^6-acetone, 300 MHz): δ 9.31(d, 1H, J = 6.0 Hz), 8.69 (t, 1H, J = 7.6 Hz), 8.26 (m, 1H), 8.20 (d, 1H, J = 7.6 Hz).

1.3.2 Synthesis and Characterization of [Au(bpy)Cl_2]Cl

[Au(bpy)Cl_2]Cl was synthesized according to the literature.[2] ^{1}H NMR (d^3-acetonitrile, 300 MHz): 8.45 (d, 2H, J = 6.9 Hz), 8.01-7.93 (m, 4H), 7.44 (dt, 2H, J_1 = 2.4 Hz, J_2 = 6.3 Hz).

1.3.3 Synthesis and Characterization of [Au(Salen)Cl]

[Au(Salen)Cl] was synthesized according to the literature.[3]

1.3.4 Synthesis and Characterization of [Au(Phen)Cl_2]Cl

[Au(Phen)Cl_2]Cl was synthesized according to the literature.[2]

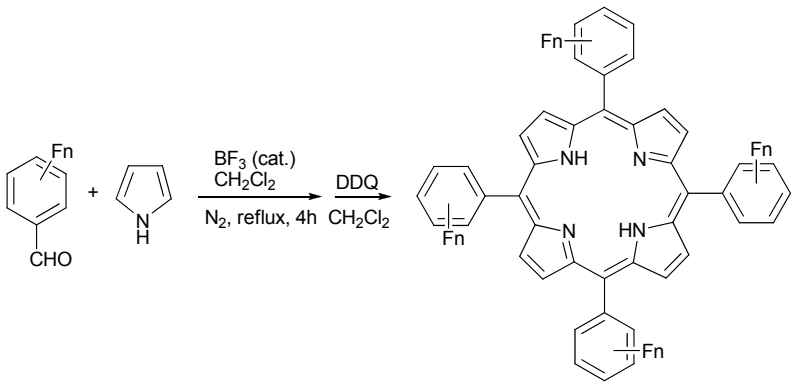
1.3.5 Synthesis and Characterization of [Au(DiPic)Cl]

Au(DiPic)Cl was synthesized according to the literature.[1]

1.3.6 Synthesis of Silver Porphyrins

General procedure: Porphyrins (0.1 mmol), AgOTf (0.2 mmol) and NaOAc (0.5 mmol) were dissolved in CH_2Cl_2/THF = 1:1(v/v), the mixture was refluxed for 12h, then the solvent was removed and the residue was purified by flash column chromatography to give the products (yields >80%).

1.3.7 Synthesis and Characterization of Prophyrins



All porphyrins were synthesized according to the literature.[5]

1.3.8 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.92 (s, 8H), -2.92 (s, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz): δ 25.45 (m, 8F), 10.62 (m, 4F), 0.505 (m, 8F); ESI-MS: *m/z* = 975.1 (MH^+).

1.3.9 5,10,15,20-Tetrakis(2,3,5,6-tetrafluorophenyl) porphyrin (4)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.93 (s, 8H), 7.65 (m, 4H), -2.78 (s, 2H); ^{19}F NMR ($CDCl_3$, 282

MHz): δ 25.11 (s, 8F), 24.39 (s, 8F); ESI-MS: *m/z* = 903.1 (MH^+).

1.3.10 5,10,15,20-Tetrakis(2,3,4,5-tetrafluorophenyl) porphyrin (5)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.86 (s, 8H), 7.79 (m, 4H), -2.99 (s, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz): δ 25.47 (m, 4F), 21.85 (m, 4F), 8.13 (m, 4F), 6.70 (m, 4F); ESI-MS: *m/z* = 903.1 (MH^+).

1.3.11 5,10,15,20-Tetrakis(2,4,6-trifluorophenyl) porphyrin (6)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.89 (s, 8H), 7.17 (t, 8H, J = 6.6 Hz), -2.84 (s, 2H);^{19}F NMR ($CDCl_3$, 282 MHz): δ 59.61, (t, 8F, J = 6.8 Hz), 55.77 (m, 4F); ESI-MS : *m/z* = 831.1 (MH^+).

1.3.11 5,10,15,20-Tetrakis(2,6-difluorophenyl) porphyrin (7)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.88 (s, 8H), 7.81 (m, 4H), 7.39 (q, 8H, J_1 = 6.6 Hz, J_2 = 1.8 Hz), -2.78 (s, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz): δ 53.49 (s, 8F); ESI-MS: *m/z* = 759.2 (MH^+).

1.3.12 5,10,15,20-Tetrakis(3,5-difluorophenyl) porphyrin (8)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.90 (s, 8H), 7.75 (s, 8H), 7.33 (s, 4H), -2.98 (s, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz): δ 50.5 (s, 8F); ESI-MS: *m/z* = 759.2 (MH^+).

1.3.13 5,10,15,20-Tetrakis(4-fluorophenyl) porphyrin (9)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.83 (s, 8H), 8.16 (dd, 8H, J_1= 5.4 Hz, J_2 = 2.4 Hz), 7.46 (m, 12H), -2.83 (s, 2H); ^{19}F NMR ($CDCl_3$, 564 MHz): δ 47.27 (s, 4F); ESI-MS: *m/z* = 687.2 (MH^+).

1.3.14 Gold(III) 5,10,15,20-tetrakis(2,3,5,6-tetrafluorophenyl)porphyrin (4b)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.49 (s, 8H,), 7.70-7.60 (m, 4H), ^{19}F NMR ($CDCl_3$, 282 MHz): δ 24.52-24.27 (m, 8F), 23.32-23.05(m, 8F). ESI-MS: *m/z* = 1097.1 (M^+).

1.3.15 Gold(III) 5,10,15,20-tetrakis(2,3,4,5-tetrafluorophenyl)porphyrin (5b)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.51 (s, 8H), 7.90-7.70 (m, 4H), ^{19}F NMR ($CDCl_3$, 282 MHz): δ 25.23-25.20 (m, 4F), 21.54-21.40-23.05(m, 4F), 7.70 (m, 4F), 6.30-5.80 (m, 4F). ESI-MS: *m/z* = 1097.1 (M^+).

1.3.16 Gold(III) 5,10,15,20-tetrakis(2,4,6-trifluorophenyl)porphyrin (6b)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.48 (s, 8H), 7.18 (t, 4H, J = 4.8 Hz), ^{19}F NMR ($CDCl_3$, 282 MHz):

δ 56.67 (t, 4F, *J* = 3.6 Hz), 55.24(s, 8F). ESI-MS: *m/z* = 1025.1 (M^+).

1.3.17 Gold(III) 5,10,15,20-tetrakis(2,6-difluorophenyl)porphyrin (7b)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.50 (s, 8H), 7.55-7.52 (m, 4H), 7.23 (m, 8H) ^{19}F NMR ($CDCl_3$, 282 MHz): δ 83.33 (m, 8F). ESI-MS: *m/z* = 953.1 (M^+).

1.3.18 Gold(III) 5,10,15,20-tetrakis(3,5-difluorophenyl)porphyrin (8b)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.46 (s, 8H), 7.80-7.0 (d, 4H, *J* = 5.7 Hz), 7.34-7.29 (m, 8H), ^{19}F NMR ($CDCl_3$, 282 MHz): δ 50.03 (s, 8F). ESI-MS: *m/z* = 953.1 (M^+).

1.3.19 Gold(III) 5,10,15,20-tetrakis(4-fluorophenyl)porphyrin (9b)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.25 (s, 8H), 8.24-8.20 (m, 8H), 7.74-7.69 (m, 8H). ^{19}F NMR ($CDCl_3$, 282 MHz): δ 50.08 (m, 4F). ESI-MS: *m/z* = 881.0 (M^+).

1.3.20 Gold(III) 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin (10b)

^{1}HNMR ($CDCl_3$, 300 MHz): *δ*=9.23 (s, 8H, Por-H), 8.20 (d, 8H, Ar-H, *J*=8.1Hz), 7.84 (d, 8H, Ar-H, *J*=8.1Hz); (d_6-acetone, 300MHz): *δ*=9.46 (s, 8H, Por-H), 8.35 (d, 8H, Ar-H, *J*=8.1Hz), 7.97 (d, 8H, Ar-H, *J*=8.1Hz); HRMS-ESI (M-Cl^+): calc'd for $C_{44}H_{24}AuCl_4N_4$: 947.0391, found: 947.0372.

1.4 Mechanistic Studies

Porphyrin *$H_2F_{20}TPP$* (0.025 mmol), gold complex (0.05 mmol), AgOTf (0.1 mmol, 26.0 mg) and NaOAc (0.125 mmol, 10.5 mg) were added to a Schlenk tube, 2 mL acetic acid was added *via* syringe in succession. The resulting reaction mixture was refluxed for 12 h at 120ºC. The solvent was then removed under vacuum and the residue was then purified by flash column chromatography to give the products.

1.4.1 Spectra Data for β-Acetylated $H_2F_{20}TPP$

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.98-8.84 (m, 7H), 2.25 (s, 3H), -3.02 (s, 1H). ^{19}FNMR: δ 25.79-25.69 (m, 4F), 24.36-24.01 (m, 4F), 13.43-13.23 (m, 2F), 12.56-12.77 (m, 2F), 2.80-2.60 (m, 4F), 2.05-1.88 (m, 4F). IR (cm^{-1}): 1774.3 (C=O); ESI-MS (MH^+) *m/z* = 1011.0; HRESI-MS (MH^+): calc'd for $C_{42}H_7F_{20}N_4O_4$: 1011.0143, found: 1011.0148.

1.5 Spectra for β-Monochloroporphyrins

1.5.1 β-Monochloro tetra(pentafluorophenyl)porphyrins (β-Cl-F_{20}TPP) (2)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.00 (d, 4H, J = 5.1 Hz), 8.83 (s, 2H), 8.78 (s, 1H), -3.014 (s, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz): δ 25.39-25.15(m, 6F), 25.61 (dd, 2F, J_1 = 7.8 Hz, J_2 = 24.3 Hz), 11.09-10.77 (m, 3F), 10.18 (t, 1F, J = 22.8 Hz), 0.85-0.50 (m, 6F), -0.24 - -0.42 (m, 2F); HRMS-ESI (MH^+): calc'd for $C_{44}H_{10}ClF_{20}N_4$: 1009.0269, found:1009.0269.

2. Spectra data for porpholactones

2.1 Tetra(pentafluorophenyl)porpholactone (3)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.92 (d, 1H, J = 5.4 Hz), 8.89 (d, 1H, J = 4.8 Hz), 8.86 (d, 1H, J = 3.6 Hz), 8.82 (d, 1H, J = 4.2 Hz), 8.65 (dd, 2H, J_1 = 4.8 Hz, J_2 = 42.0 Hz), -1.80 (s, 1H), -2.10 (s, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz): δ 25.12-24.93 (m, 4F), 24.73 (dd, 2F, J_1 = 7.2 Hz , J_2 = 16.8 Hz), 11.33 (quad, 3F, J = 22.5 Hz)， 10.60 (t, 1F, J = 22.2 Hz), 1.14-0.87 (m, 6F), 0.46-0.29 (m, 2F); ESI-MS (MH^+) *m/z* =993.0; HRESI-MS (MH^+): calc'd for $C_{43}H_9F_{20}N_4O_2$: 993.0405, found 993.0402; IR (cm^{-1}): 1774 (C=O), 1793 (C=O); UV-vis (CH_2Cl_2), λ_{max} (logε) : 409 (5.18), 510 (3.95), 545 (3.81), 589 (3.60), 642 (4.03).

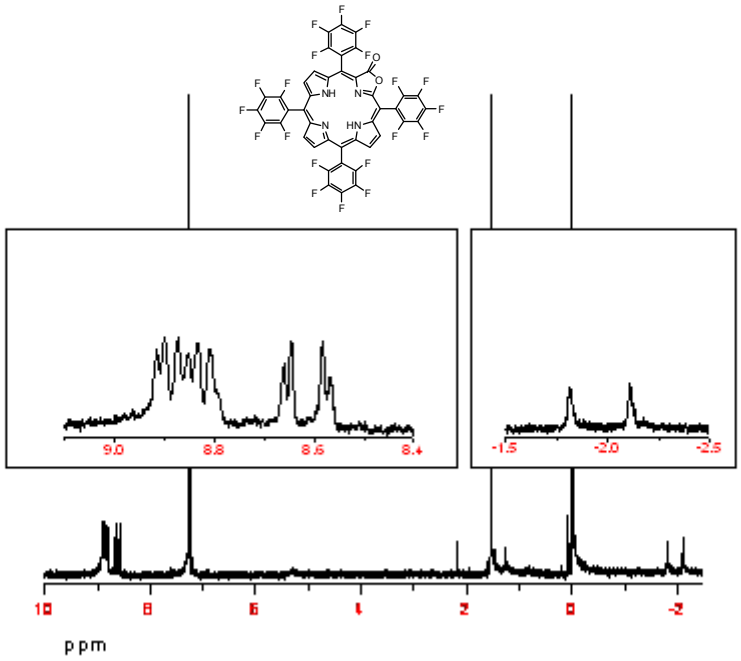


Figure S1. ^{1}H NMR spectrum of **3** ($CDCl_3$)

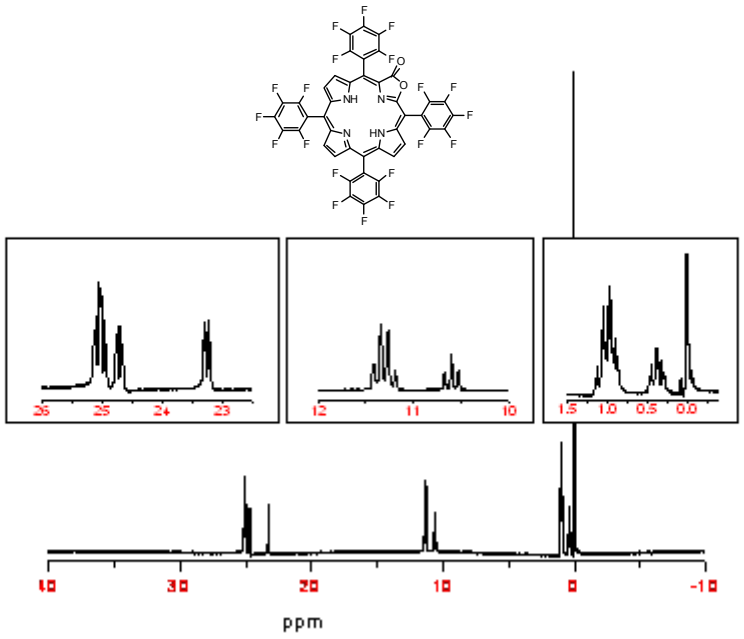


Figure S2. ^{19}F NMR spectrum of **3** ($CDCl_3$)

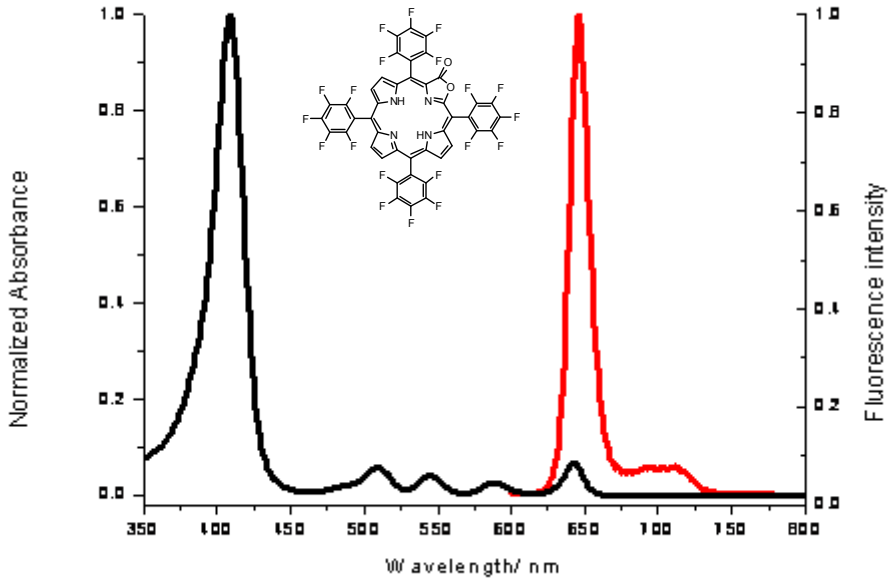


Figure S3. UV-vis (Black trace) and fluorescence (Red trace) spectra of **3** (CH_2Cl_2)

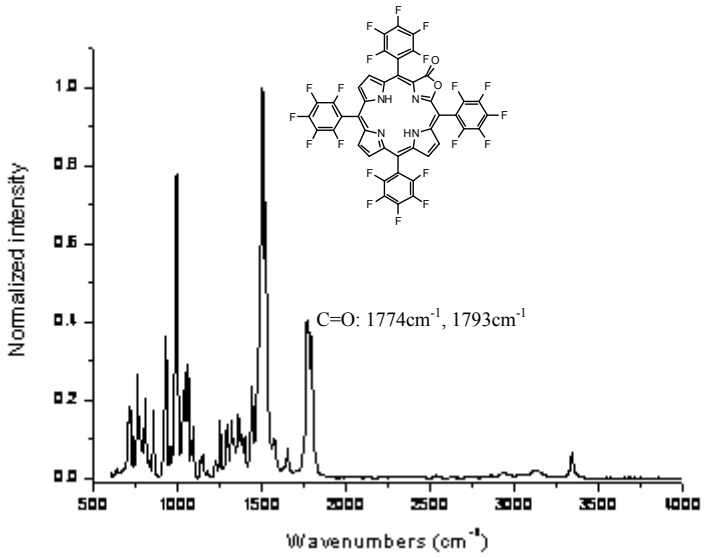


Figure S4. FT-IR of **3**

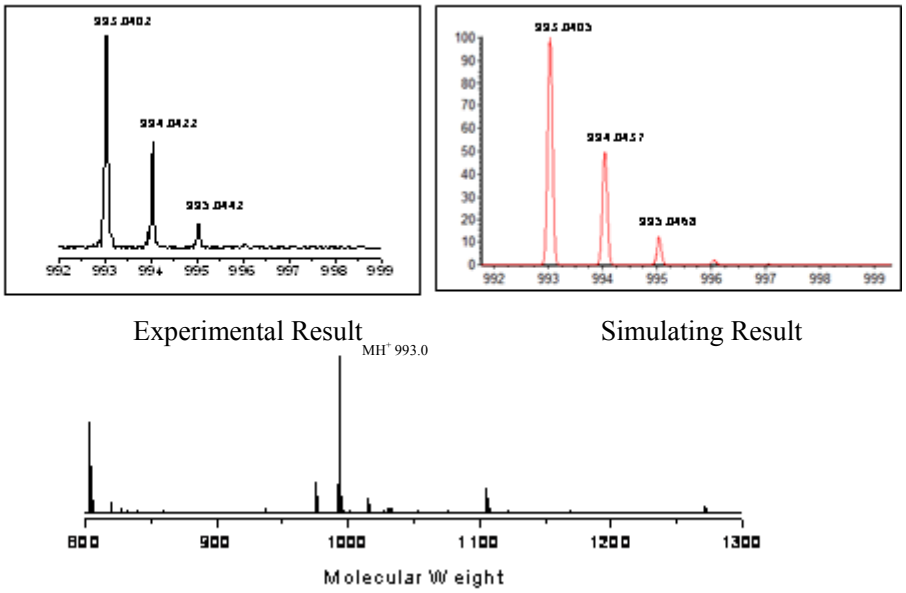


Figure S5. MS of **3**

2.2 Tetra(2,3,5,6-tetrafluorophenyl)porpholactone (4a)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.90 (s, 1H, J = 4.8 Hz), 8.86 (s, 1H, J = 4.2 Hz), 8.83 (s, 1H, J = 4.2 Hz), 8.79 (s, 1H, J = 3.0 Hz), 8.66 (dd, 2H, J_1 = 4.8 Hz, J_2 = 42.0 Hz), 7.65-7.53 (m, 4H), -1.76 (s, 1H), -2.06 (s, 1H); ^{19}F NMR ($CDCl_3$, 564 MHz): δ 24.46 (broad), 24.11 (broad), 23.83 (broad), 23.21 (broad), 22.76 (broad); ESI-MS (MH^+) *m/z* = 921.1; HRESI-MS (MH^+): calc'd for $C_{43}H_{13}F_{16}N_4O_2$: 921.0872, found: 921.0767; IR (cm^{-1}): 1768 (C=O), 1795 (C=O); UV-vis (CH_2Cl_2), λ_{max} (logε) : 413 (5.25), 510 (3.96), 544 (3.33), 588 (3.52), 642 (3.68).

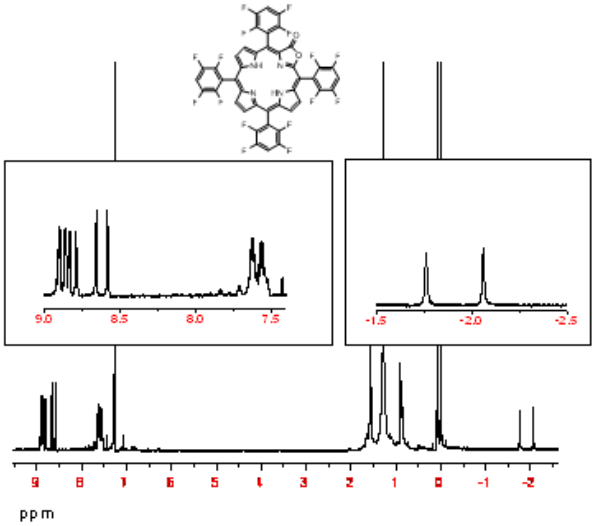


Figure S6. ^{1}H NMR spectrum of **4a** ($CDCl_3$)

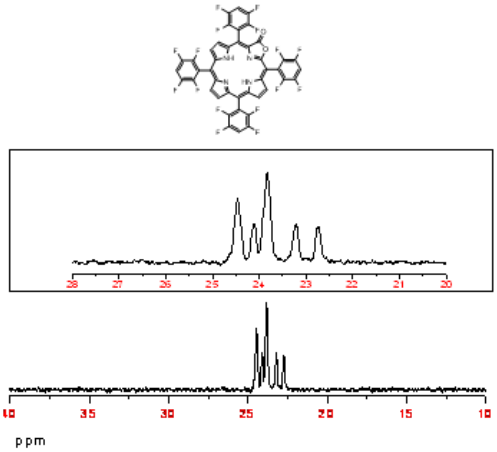


Figure S7. **^{19}F NMR spectrum of** 4a **($CDCl_3$)**

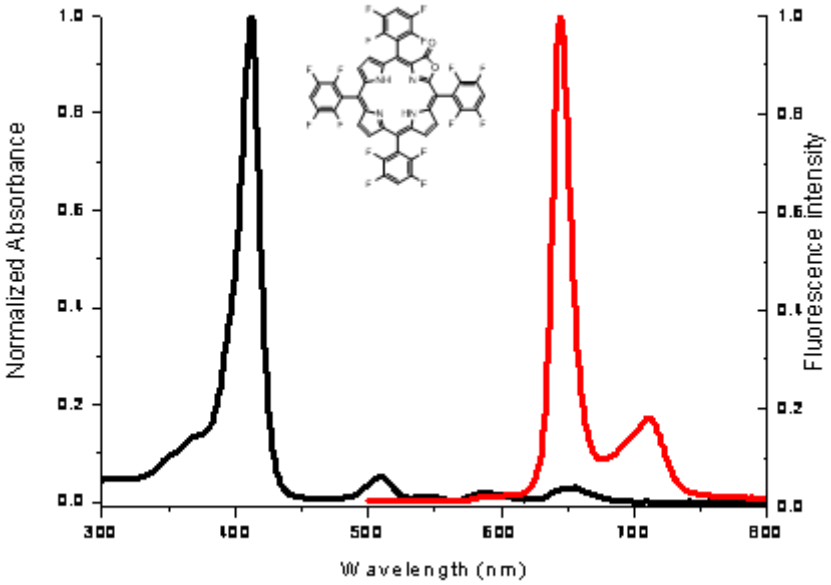


Figure S8. UV-vis (Black trace) and fluorescence (Red trace) spectra of **4a** (CH_2Cl_2)

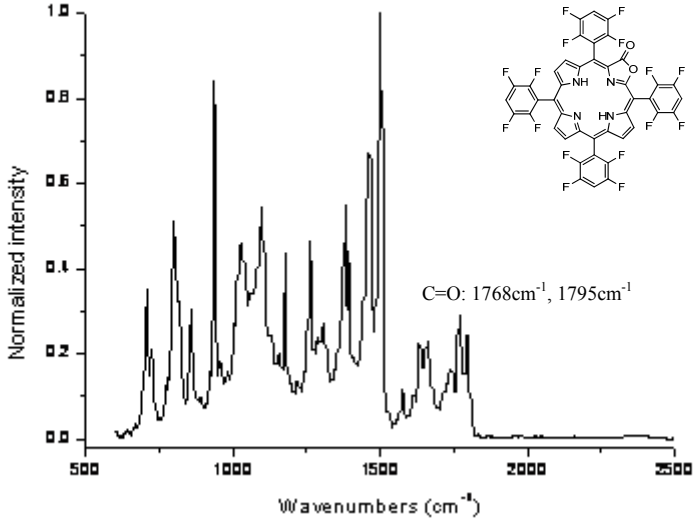


Figure S9. FT-IR of **4a**

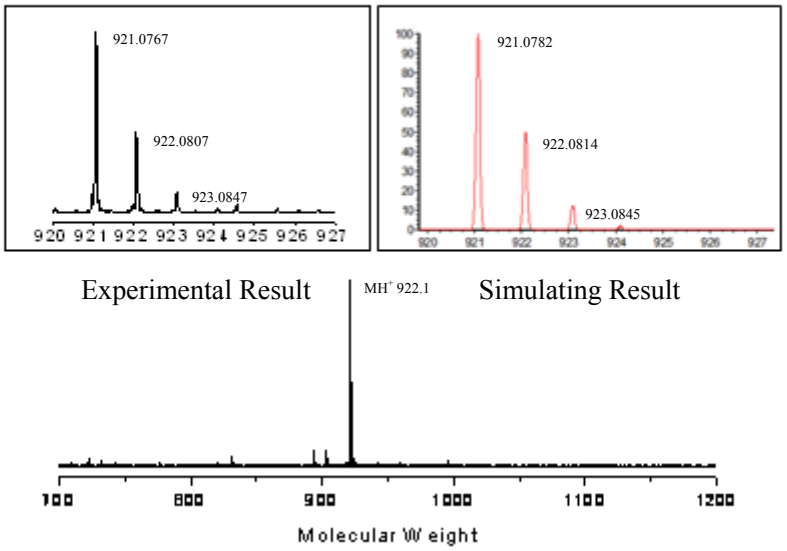


Figure S10. MS of **4a**

2.3 Tetra(2,3,4,5-tetrafluorophenyl)porpholactone (5a).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.87 (s, 1H, J = 4.8 Hz,), 8.84 (s, 1H, J = 4.2 Hz), 8.80 (s, 1H, J = 4.2 Hz), 8.74 (s, 1H, J = 4.2 Hz), 8.62 (dd, 2H, J_1 = 4.8 Hz, J_2 = 39.0 Hz), 7.65-7.48 (broad, 4H,), -1.86 (s, 1H), -2.18 (s,1H); ^{19}F NMR ($CDCl_3$, 282 MHz): δ 25.25 (broad), 22.33 (broad), 8.92(m), 8.32 (t), 7.40 (m), 6.73 (m); ESI-MS (MH^+) m/z = 921.1; HRESI-MS (MH^+): calc'd for $C_{43}H_{13}F_{16}N_4O_2$: 921.0782, found: 921.0770; IR (cm^{-1}): 1790 (C=O); UV-vis (CH_2Cl_2), λ_{max} (logε) : 413 (5.24), 510 (3.98), 547 (3.47), 586 (3.54), 642 (3.42).

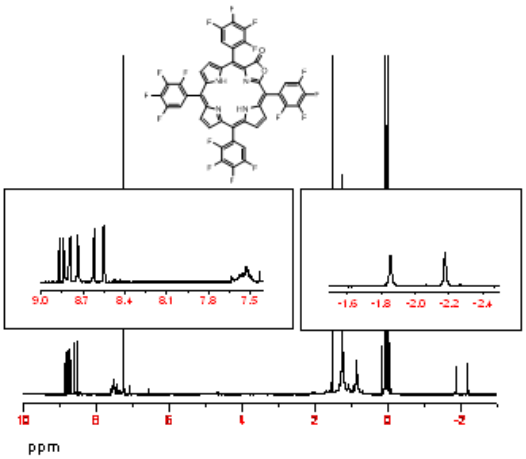


Figure S11. ^{1}H NMR spectrum of **5a** ($CDCl_3$)

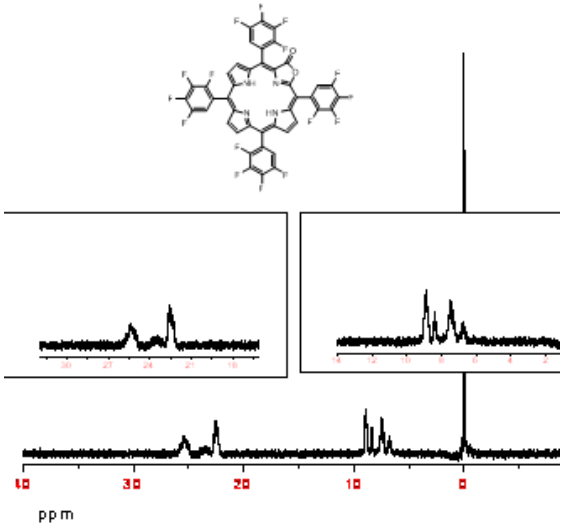


Figure S12. ^{19}F NMR spectrum of 5a ($CDCl_3$)

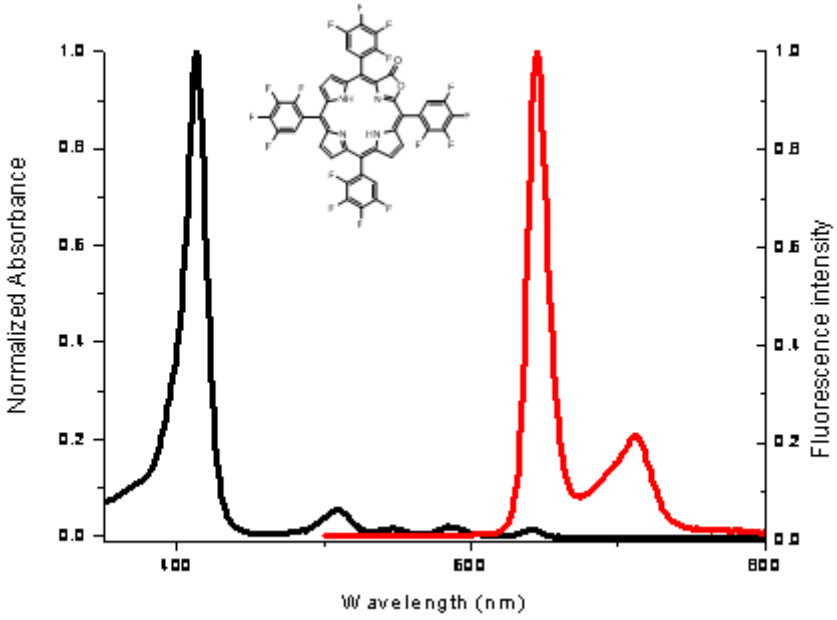


Figure S13. UV-vis (Black trace) and fluorescence (Red trace) spectra of **5a** (CH_2Cl_2)

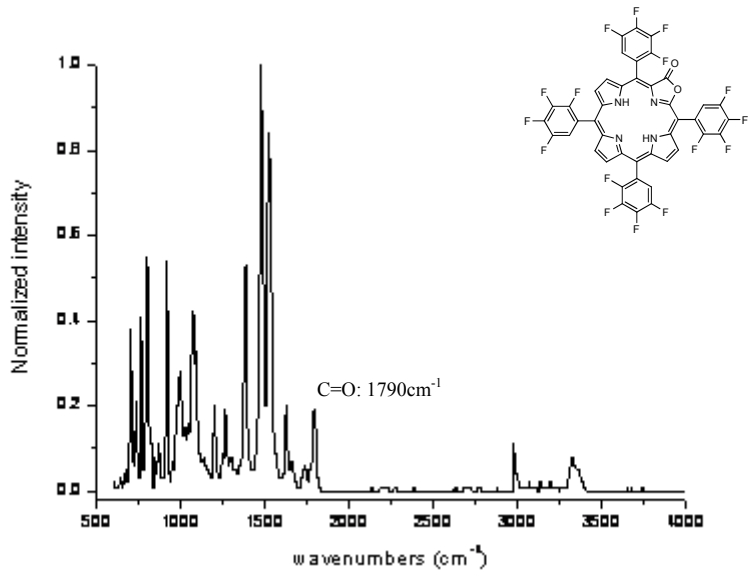


Figure S14. FT-IR of **5a**

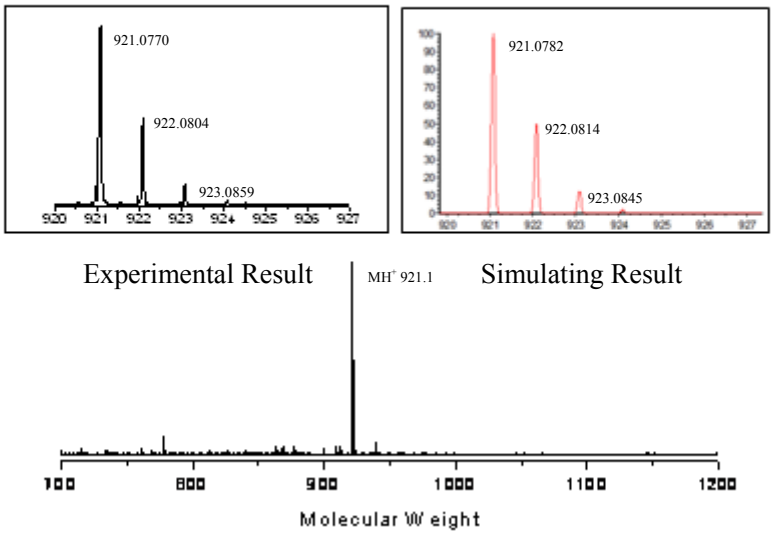


Figure S15. MS of **5a**

2.4 Tetra(2,4,6-trifluorophenyl)porpholactone (6a)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.90 (s, 1H, J = 4.8 Hz), 8.87 (s, 1H, J = 4.2 Hz), 8.83 (s, 1H, J = 4.2 Hz), 8.79 (s, 1H, J = 4.2 Hz), 8.64 (dd, 2H, J_1 = 4.8 Hz, J_2 = 42.0 Hz), 7.79 (m, 8H), -1.84 (s, 1H), -2.10 (s, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz): δ 48.24-47.80 (m, 8F), 47.51 (m, 1H), 47.20 (t, 2H, J = 7.05Hz), 45.75 (t, 2H, J = 7.05Hz); ESI-MS(MH^+) m/z = 849.1; HRESI-MS (MH^+): calc'd for $C_{43}H_{17}F_{12}N_4O_2$: 849.1159, found:849.1163; IR (cm^{-1}): 1790 (C=O); UV-vis (CH_2Cl_2), λ_{max} (logε) : 412 (5.02), 511 (3.73), 547 (3.44), 587(3.36), 642 (3.50).

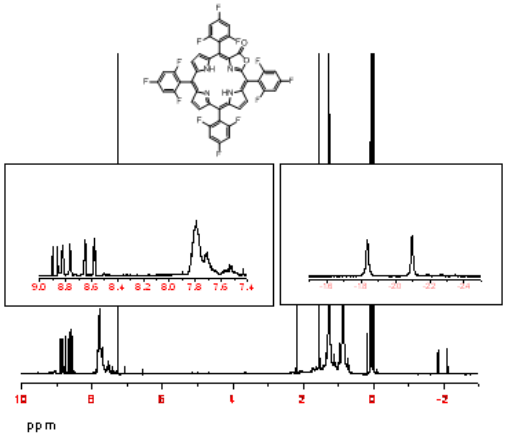


Figure S16. ^{1}H NMR spectrum of **6a** ($CDCl_3$)

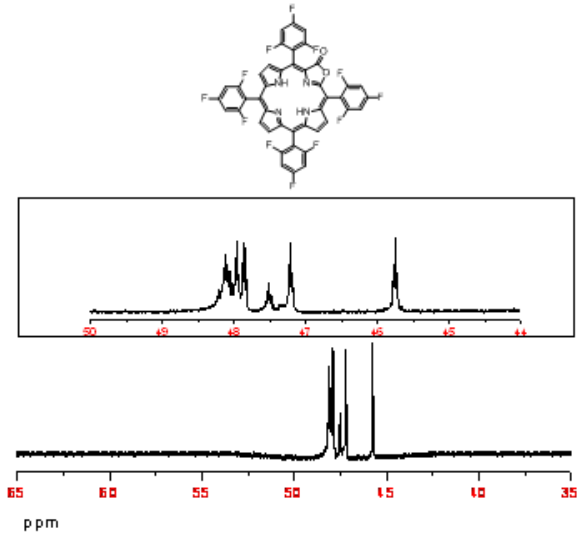


Figure S17. ^{19}F NMR spectrum of **6a** ($CDCl_3$)

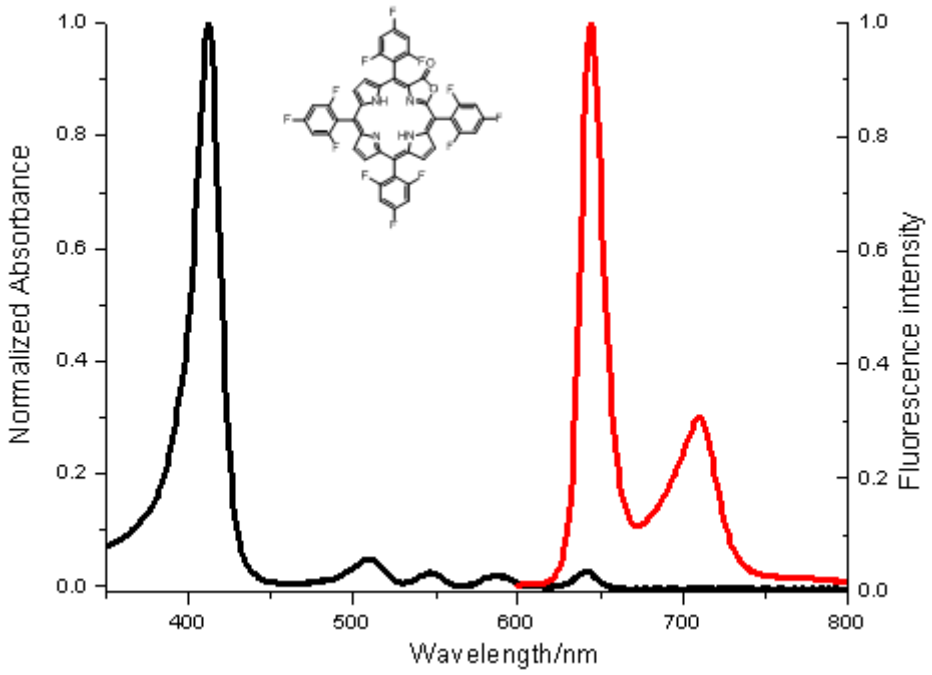


Figure S18. UV-vis (Black trace) and fluorescence (Red trace) spectra of **6a** (CH_2Cl_2)

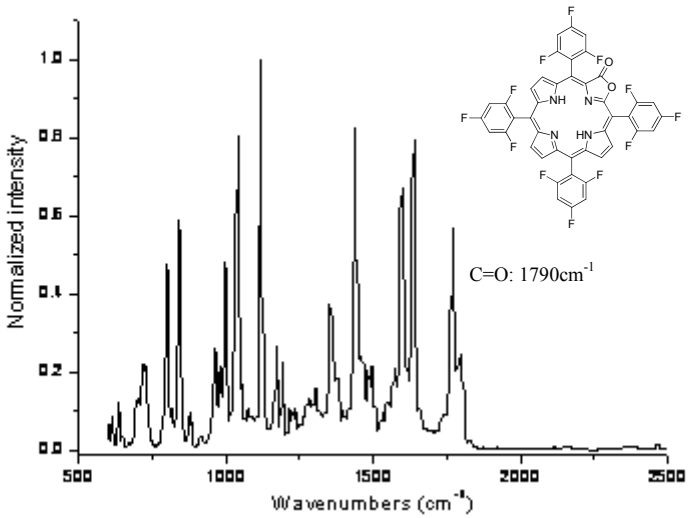


Figure S19. FT-IR of **6a**

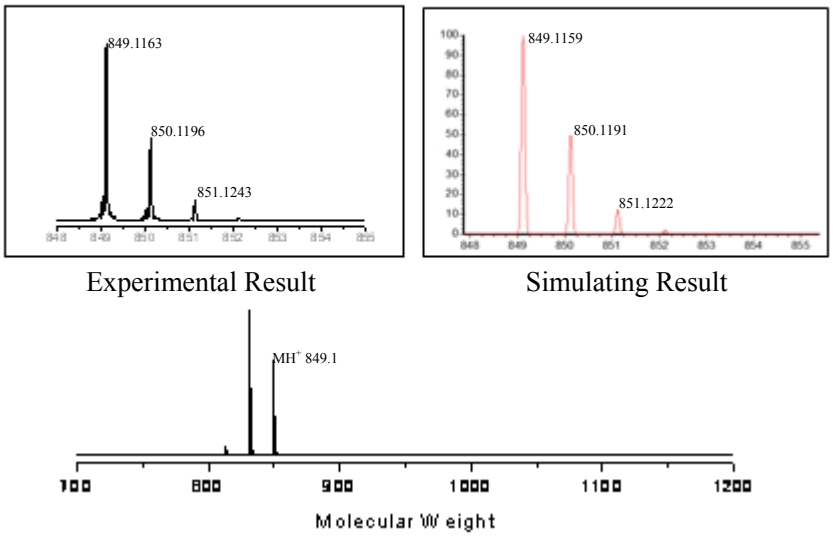


Figure S20. MS of **6a**

2.5 Tetra(2,6-difluorophenyl)porpholactone (7a)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.85-8.70 (m, 4H), 8.66 (d, 1H, J = 4.8Hz), 8.64 (d, 1H, J = 4.8Hz), 8.56 (d, 1H, J = 4.5Hz), 7.73-7.77 (m, 4H), 7.40-7.33 (m, 8H), -1.69 (s, 1H), -2.02 (s, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz): δ 40.47-39.82 (m, 6F), 39.24 (m, 1F), 37.94 (m, 1F); ESI-MS (MH^+) *m/z* = 777.2; HRESI-MS (MH^+): calc'd for $C_{43}H_{21}F_8N_4O_2$: 777.1536, found: 777.1544; IR (cm^{-1}): 1780 (C=O); UV-vis (CH_2Cl_2), λ_{max} (logε) : 412 (4.97), 512 (3.72), 548 (3.58), 588(3.48), 641 (3.56).

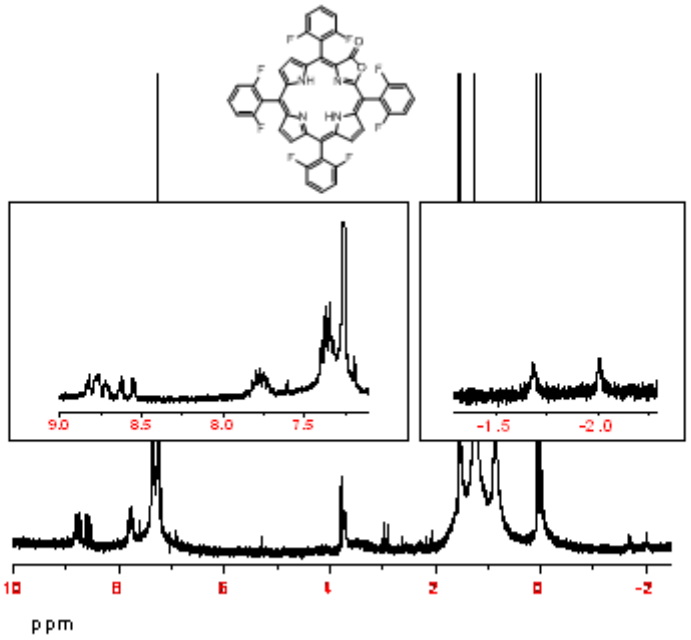


Figure S21. ^{1}H NMR spectrum of **7a** ($CDCl_3$)

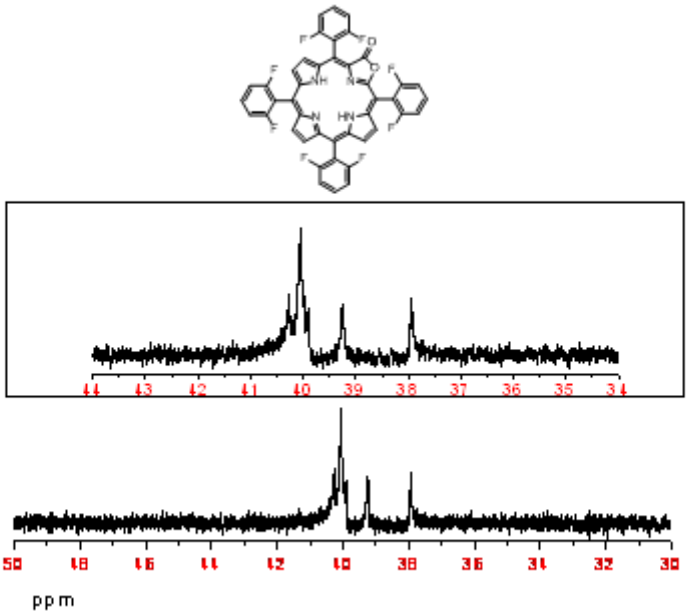


Figure S22. ^{19}F NMR spectrum of **7a** ($CDCl_3$)

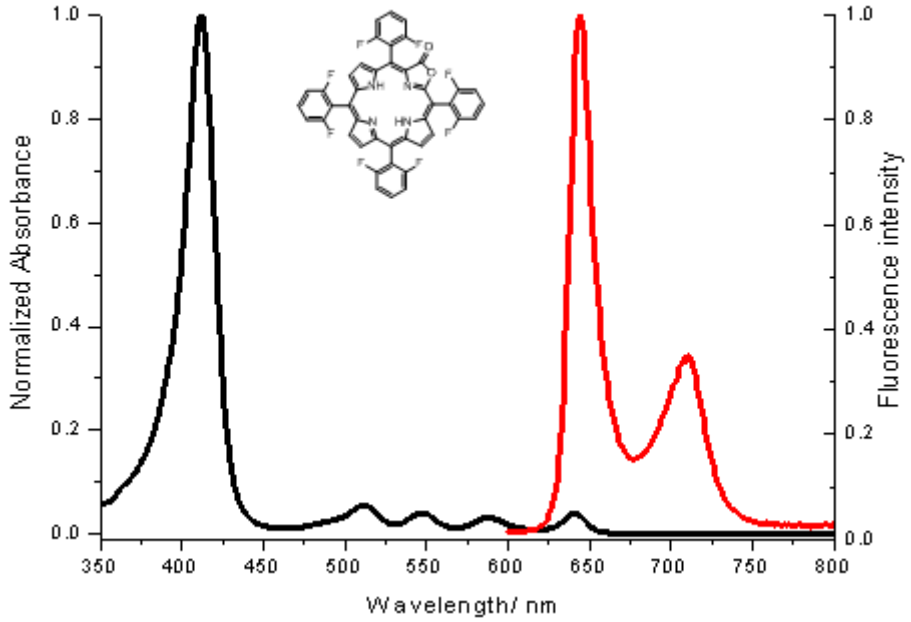


Figure S23. UV-vis (Black trace) and fluorescence (Red trace) spectra of **7a** (CH_2Cl_2)

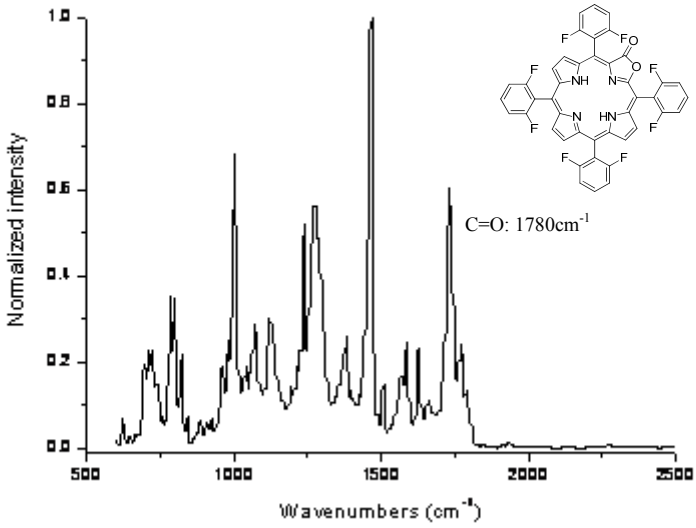


Figure S24. FT-IR of **7a**

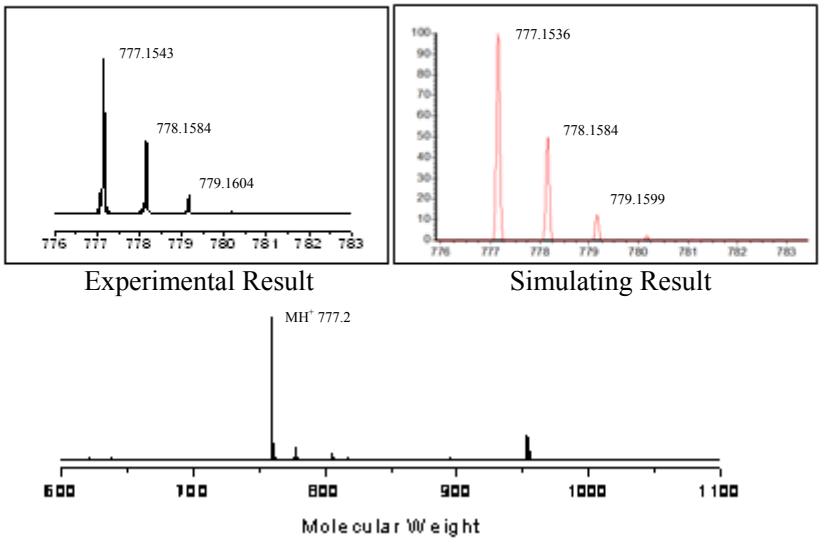


Figure S25. MS of **7a**

2.6 Tetra(3,5-difluorophenyl)porpholactone (8a)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.87 (dd, 2H, J_1 = 4.8 Hz, J_2 = 11.4 Hz), 8.77 (d, 1H, J = 4.8 Hz), 8.66 (d, 1H, J = 4.8Hz), 8.63 (d, 1H, J = 4.8Hz), 8.56 (d, 1H, J = 4.8Hz), 7.76-7.62(m, 8H), 7.54-7.48 (m, 4H), -1.85 (s, 1H), -2.20 (s, 1H); ^{19}F NMR ($CDCl_3$, 564 MHz): δ 51.69 (s, 2F), 51.32 (s, 2F), 51.18 (s, 2F), 50.61 (s, 2F); ESI-MS (MH^+) *m/z* = 777.2; HRESI-MS (MH^+): calc'd for $C_{43}H_{21}F_8N_4O_2$: 777.1536, found: 777.1529; IR (cm^{-1}): 1780 (C=O); UV-vis (CH_2Cl_2), λ_{max} (logε) : 415 (4.84), 514 (3.48), 552 (3.20), 567 (3.09), 641 (2.95).

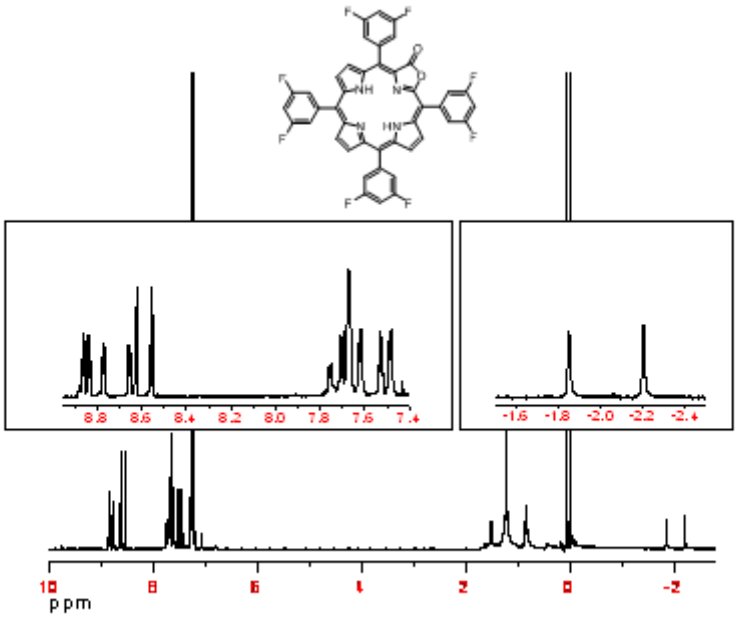


Figure S26. ^{1}H NMR spectrum of **8a** ($CDCl_3$)

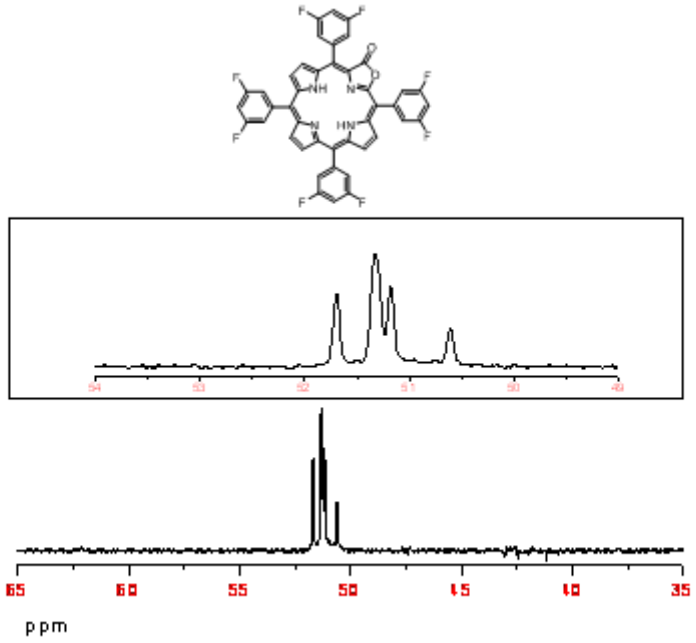


Figure S27. ^{19}F NMR spectrum of **8a** ($CDCl_3$)

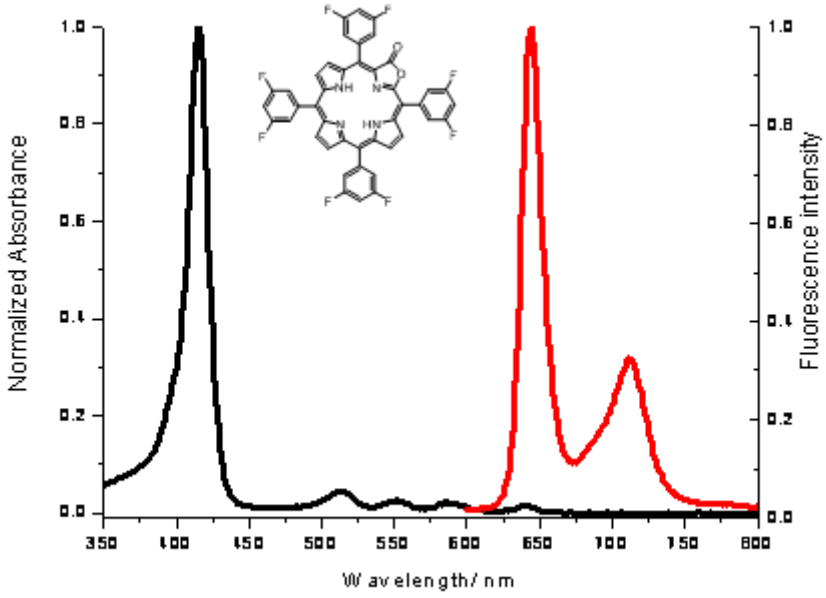


Figure S28. UV-vis (Black trace) and fluorescence (Red trace) spectra of **8a** (CH_2Cl_2)

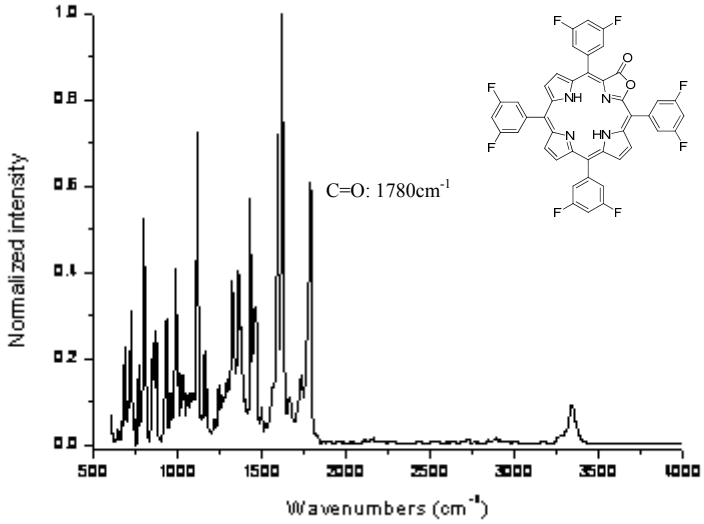


Figure S29. FT-IR of **8a**

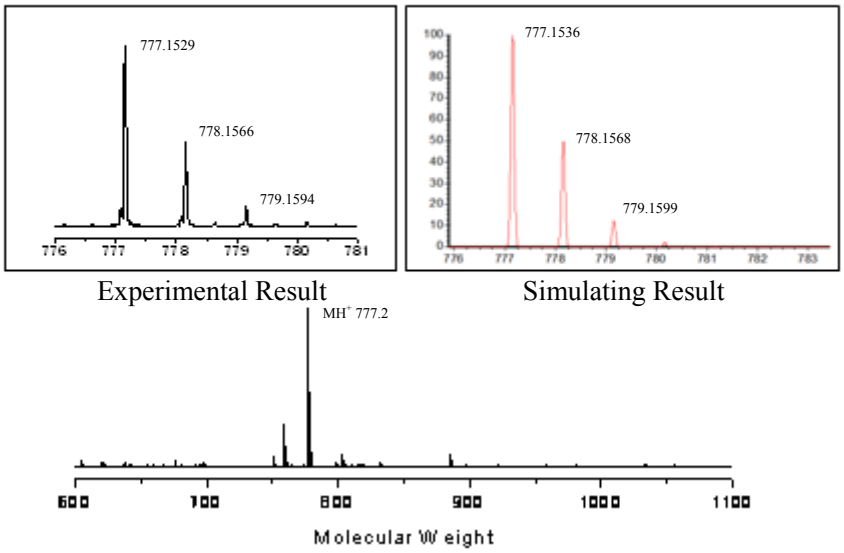


Figure S30. MS of **8a**

2.7 Tetra(4-fluorophenyl)porpholatcone (9a)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.85-8.80 (m, 4H), 8.68 (dd, 2H, J_1 = 2.4 Hz, J_2 = 5.1 Hz), 8.57-8.50 (m, 4H), 8.01-7.98 (m, 8H), 7.85-7.80 (m, 4H), -1.76 (s, 1H), -2.07 (s, 1H); ^{19}F NMR ($CDCl_3$, 564 MHz): δ 11.31 (q, 3F, J = 40.0Hz), 10.60 (t, 1F, J = 40.7Hz); ESI-MS (MH^+) *m/z* 705.2; HRESI-MS (MH^+): calc'd for $C_{43}H_{25}F_4N_4O_2$: 705.1913, found: 705.1908; IR (cm^{-1}): 1790 (C=O); UV-vis (CH_2Cl_2), λ_{max} (logε) : 418 (4.41), 516 (2.80), 548 (2.79), 588 (2.37), 644 (1.89).

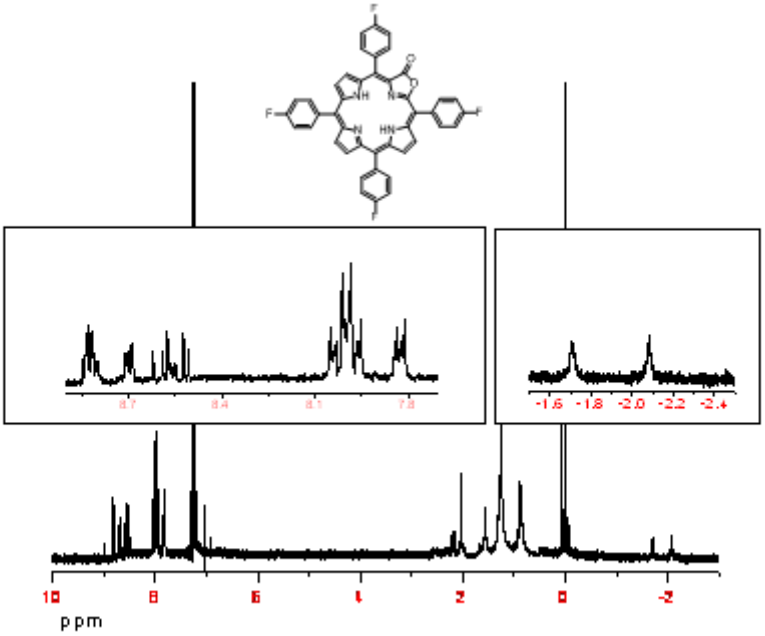


Figure S31. ^{1}H NMR spectrum of **9a** ($CDCl_3$)

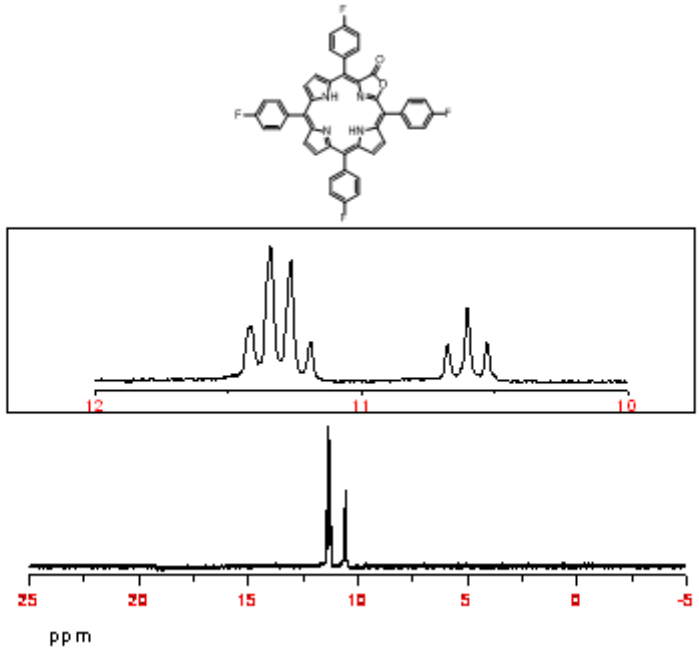


Figure S32. ^{19}F NMR spectrum of **9a** ($CDCl_3$)

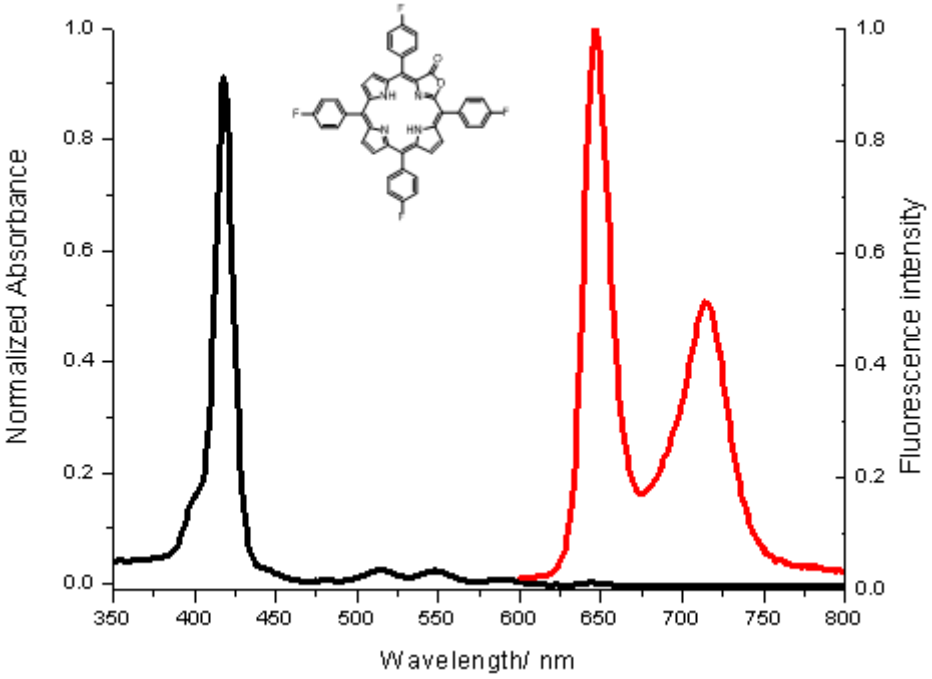


Figure S33. UV-vis (Black trace) and fluorescence (Red trace) spectra of **9a** (CH_2Cl_2)

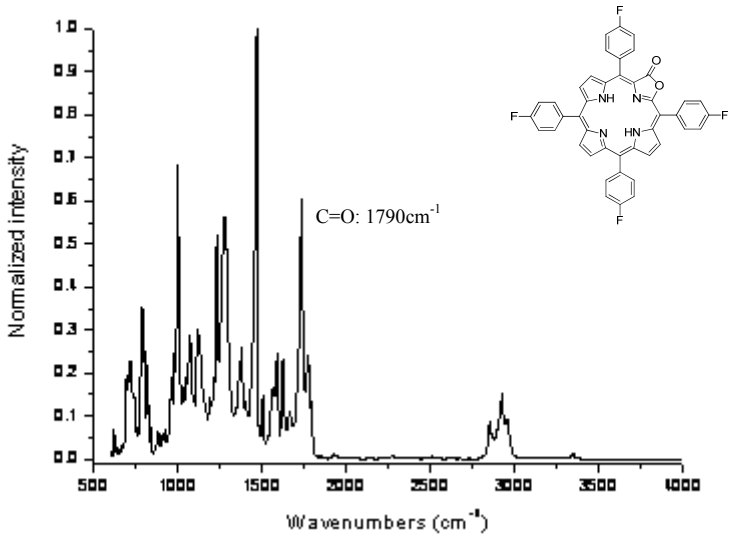


Figure S34. FT-IR of **9a**

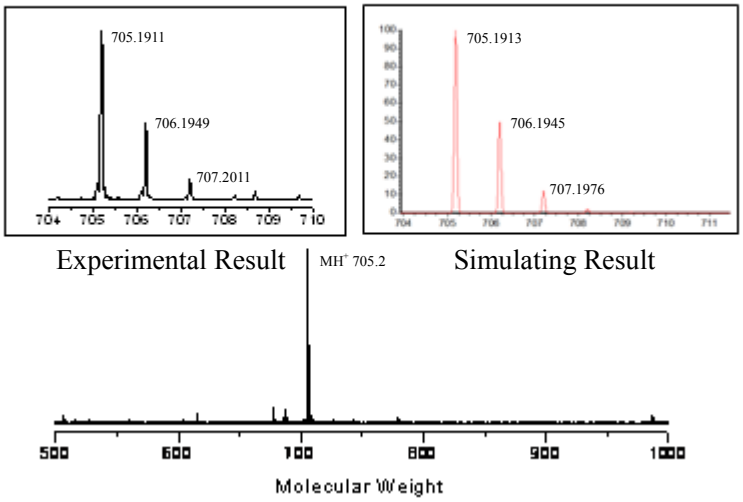


Figure S35. MS of **9a**

2.8 Tetra(4-chlorophenyl)porpholatcone (10a)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.94 (s, 1H), 8.82-8.64 (m, 2H), 8.60-8.50 (m, 2H), 8.07-8.00 (t, 6H, *J* = 8.1 Hz), 7.90 (s, 1H), 7.87 (s, 1H), 7.78-7.69 (m, 9H), -1.75 (s, 1H), -2.11 (s, 1H); ESI-MS (MH^+) *m/z* = 769.1; HRESI-MS (MH^+): calc'd for $C_{43}H_{25}Cl_4N_4O_2$: 769.0731, found: 769.0735; IR (cm^{-1}): 1790 (C=O); UV-vis (CH_2Cl_2), λ_{max} (logε) : 419 (5.23), 519 (3.83), 557 (3.75), 589 (3.46), 641 (3.00).

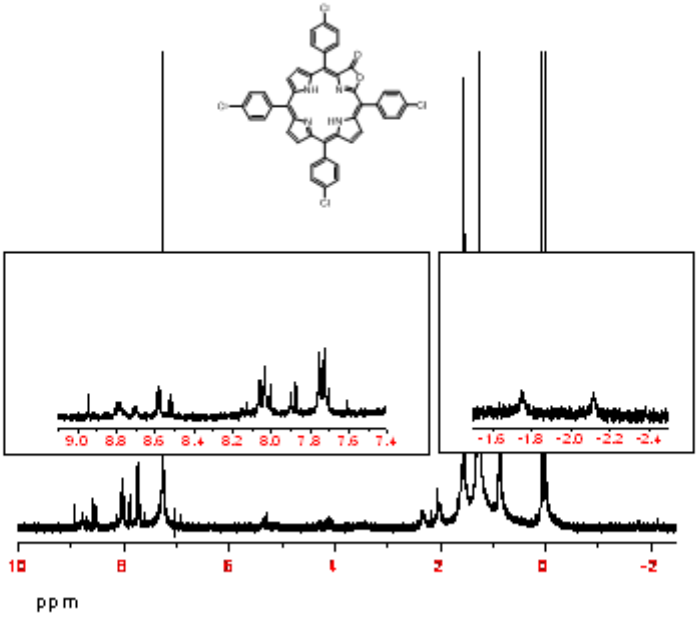


Figure S36. ^{1}H NMR spectrum of **10a** ($CDCl_3$)

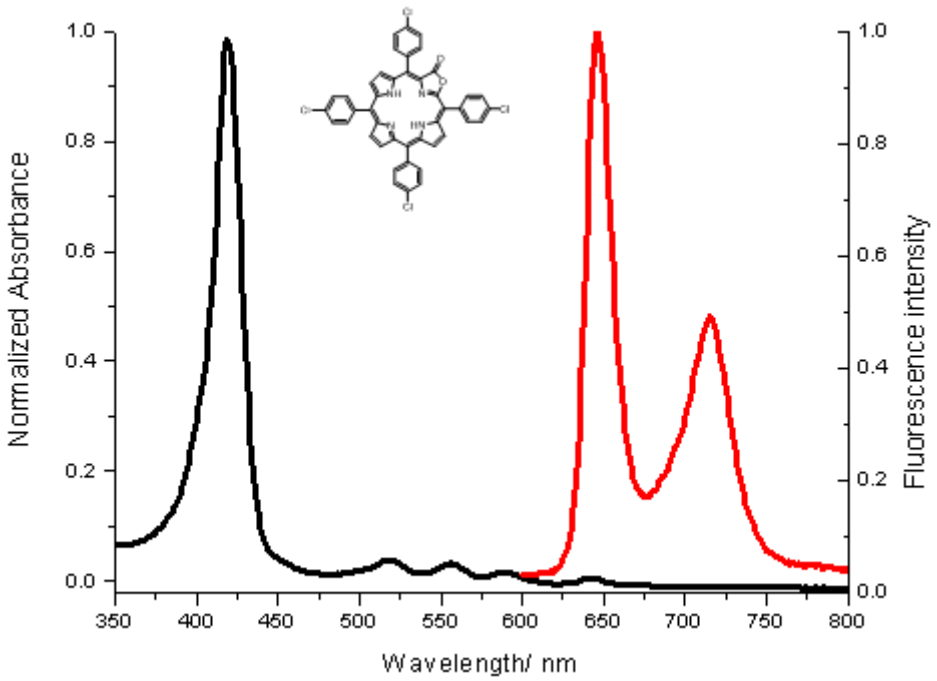


Figure S37. UV-vis (Black trace) and fluorescence (Red trace) spectra of **10a** (CH_2Cl_2)

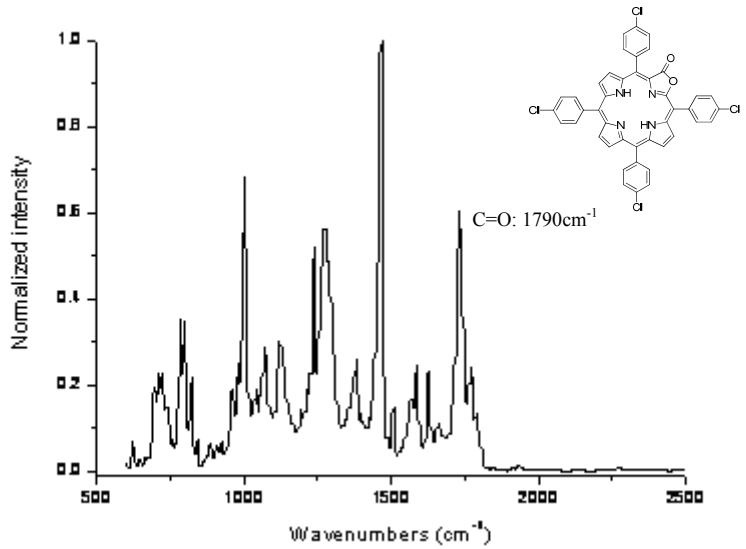


Figure S38. FT-IR of **10a**

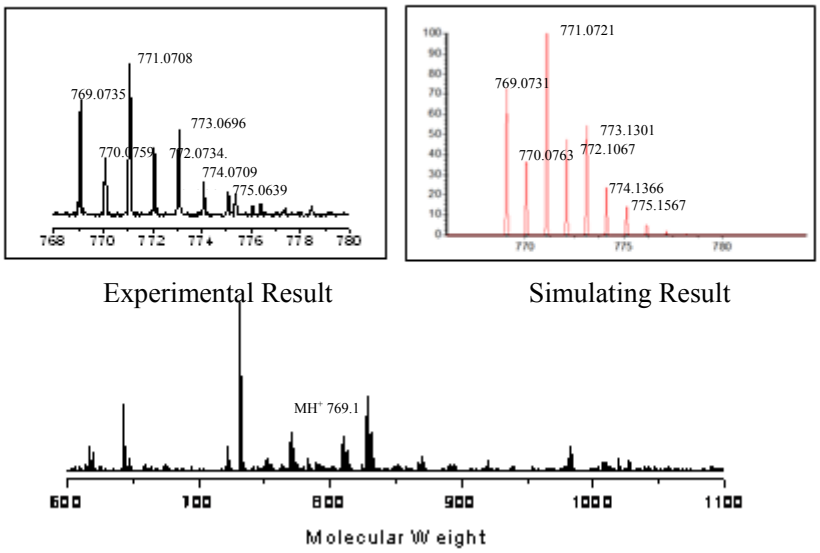


Figure S39. MS of **10a**

2.9 Tetraphenyl porpholactone (11a)

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.81-8.75 (m, 4H), 8.70 (dd, 2H, J_1 = 2.1 Hz, J_2 = 5.1 Hz), 8.60-8.56 (m, 4H), 8.53 (d, 2H, J = 4.5Hz), 8.14-8.08 (m, 10H), 7.98-7.95 (m, 4H), -1.71 (s, 1H), -2.08 (s, 1H); ESI-MS (MH^+) *m/z* 633.2, ($M+Na^+$) *m/z* = 655.2; HRESI-MS (MH^+): calc'd for $C_{43}H_{29}N_4O_2$: 633.2290, found: 633.1711; HRESI-MS ($M+Na^+$): calc'd for $C_{43}H_{28}N_4O_2Na$: 655.2110, found: 655.2102; IR (cm^{-1}): 1780 (C=O); UV-vis (CH_2Cl_2), λ_{max} (logε) : 418 (5.43), 521 (3.98), 554 (4.07), 589 (3.76), 641 (3.43).

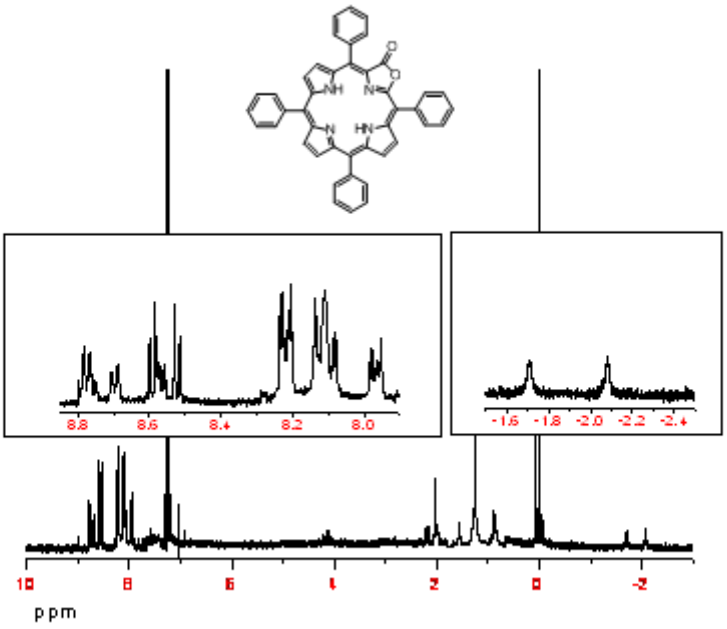


Figure S40. ^{1}H NMR spectrum of **11a** ($CDCl_3$)

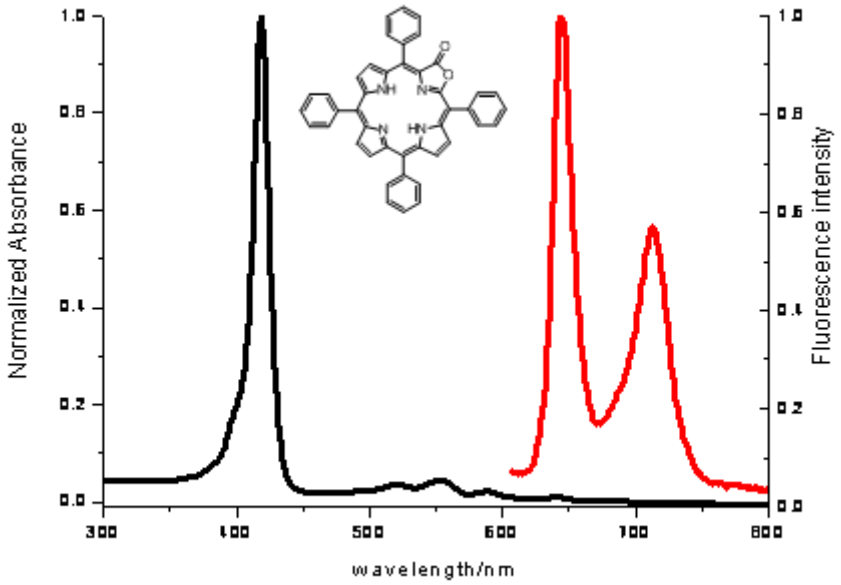


Figure S41. UV-vis (Black trace) and fluorescence (Red trace) spectra of **11a** (CH_2Cl_2)

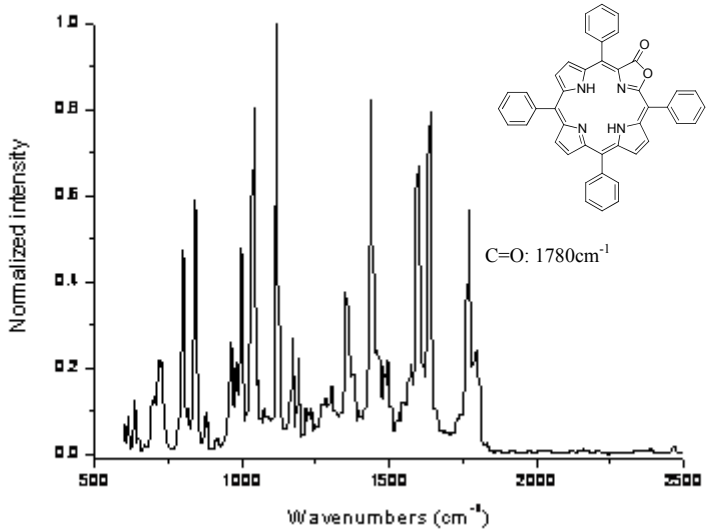


Figure S42. FT-IR of **11a**

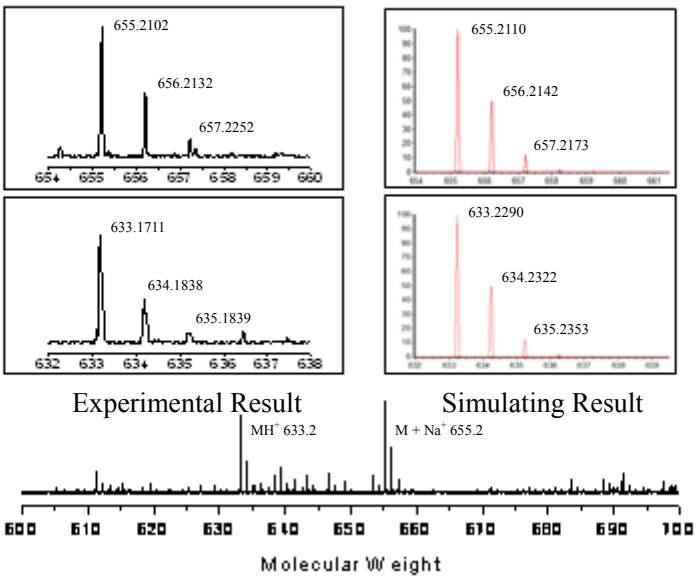


Figure S43. MS of **11a**

3. References

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