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 °C). All NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrophotometer (300M for 1H, and 282M for 19F) or Bruker Avance 600 MHz spectrophotometer (600M for 1H, and 564M for 19F). All chemical shifts were reported in ppm and all coupling constants were in Hz. For 19F NMR spectra, hexafluorobenzene in CDCl3 was used as the internal reference at 0 ppm. Mass spectra were recorded on Bruker APEX IV FT-ICR Mass Spectrometer. GC/MS spectra were 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 HAuCl4·4H2O (30.9mg, 0.075mmol) and AgOTf (77.1mg, 0.3mmol) in 4mL THF was added to the solution of porphyrin (0.05mmol) and NaOAc (26.7mg, 0.325mmol) in CH2Cl2. The reaction mixture was stirred at room temperature for 1-2h. After the solvent was evaporated in vacuum, the residue was chromatographed on silica column (using CH2Cl2 to remove free porphyrin and CH2Cl2/CH3OH=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 CH2Cl2/petroleum ether to afford corresponding product.

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

1HNMR (CDCl3, 300 MHz): δ 9.51 (s, 8H) 19FNMR (CDCl3, 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 C44H8AuF20N4: 1169.0095, found: 1169.0017.

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

1HNMR (CDCl3, 300 MHz): δ 9.23 (s, 8H, Por-H), 7.95 (s, 12H, Ar-H); HRMS-ESI (M-Cl+): calc’d

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

¹HNMR (CDCl₃, 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 C₄₄H₂₈AuN₄: 809.1974, found: 809.1968.

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

¹HNMR (CDCl₃, 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(CH₃)₃); HRMS-ESI (M-Cl⁺): calc’d for C₇₆H₉₂AuN₄: 1257.6982, found: 1257.6952.

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

¹HNMR (CDCl₃, 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, -OCH₃); HRMS-ESI (M-Cl⁺): calc’d for C₅₂H₄₄AuN₄O₈: 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.)Cl₂]

[Au(Pic.)Cl₂] was synthesized according to the literature.¹ ¹H NMR (d₆-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)Cl₂]Cl

[Au(bpy)Cl₂]Cl was synthesized according to the literature.² ¹H NMR (d₃-acetonitrile, 300 MHz): 8.45 (d, 2H, J = 6.9 Hz), 8.01-7.93 (m, 4H), 7.44 (dt, 2H, J₁ = 2.4 Hz, J₂ = 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)Cl₂]Cl

[Au(Phen)Cl₂]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 CH₂Cl₂/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

¹H NMR (CDCl₃, 300 MHz): δ 8.92 (s, 8H), -2.92 (s, 2H); ¹⁹F NMR (CDCl₃, 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)

¹H NMR (CDCl₃, 300 MHz): δ 8.93 (s, 8H), 7.65 (m, 4H), -2.78 (s, 2H); ¹⁹F NMR (CDCl₃, 282
1.3.10 5,10,15,20-Tetrakis(2,3,4,5-tetrafluorophenyl) porphyrin (5)

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.86 (s, 8H), 7.79 (m, 4H), -2.99 (s, 2H); $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ 25.47 (m, 2F), 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): $\delta$ 8.89 (s, 8H), 7.17 (t, 8H, $J = 6.6$ Hz), -2.84 (s, 2H); $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ 59.61 (m, 4F), 55.77 (m, 4F); ESI-MS: $m/z = 831.1$ (MH$^+$).

1.3.12 5,10,15,20-Tetrakis(2,6-difluorophenyl) porphyrin (7)

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.89 (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): $\delta$ 50.5 (m, 8F); ESI-MS: $m/z = 759.2$ (MH$^+$).

1.3.13 5,10,15,20-Tetrakis(3,5-difluorophenyl) porphyrin (8)

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 9.89 (s, 8H), 7.75 (s, 8H), 7.33 (s, 4H), -2.98 (s, 2H); $^{19}$F NMR (CDCl$_3$, 564 MHz): $\delta$ 32.5 (m, 8F); 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): $\delta$ 9.49 (s, 8H), 7.70-7.60 (m, 4H), $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ 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): $\delta$ 9.51 (s, 8H), 7.90-7.70 (m, 4H), $^{19}$F NMR (CDCl$_3$, 282 MHz): $\delta$ 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): $\delta$ 9.48 (s, 8H), 7.18 (s, 8H), $^{19}$F NMR (CDCl$_3$, 282 MHz):
\[ \delta 56.67 \text{ (t, 4F, } J = 3.6 \text{ Hz), 55.24 (s, 8F). ESI-MS: } m/z = 1025.1 \text{ (M}^+\text{).} \]

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

\[ ^1\text{H NMR (CDCl}_3, 300 \text{ MHz): } \delta 9.50 \text{ (s, 8H), 7.55-7.52 (m, 4H), 7.23 (m, 8H) } ^{19}\text{F NMR (CDCl}_3, 282 \text{ MHz): } \delta 83.33 \text{ (m, 8F). ESI-MS: } m/z = 953.1 \text{ (M}^+\text{).} \]

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

\[ ^1\text{H NMR (CDCl}_3, 300 \text{ MHz): } \delta 9.46 \text{ (s, 8H), 7.80-7.0 (d, 4H, } J = 5.7 \text{ Hz), 7.34-7.29 (m, 8H), } ^{19}\text{F NMR (CDCl}_3, 282 \text{ MHz): } \delta 50.03 \text{ (s, 8F). ESI-MS: } m/z = 953.1 \text{ (M}^+\text{).} \]

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

\[ ^1\text{H NMR (CDCl}_3, 300 \text{ MHz): } \delta 9.25 \text{ (s, 8H), 8.24-8.20 (m, 8H), 7.74-7.69 (m, 8H). } ^{19}\text{F NMR (CDCl}_3, 282 \text{ MHz): } \delta 50.08 \text{ (m, 4F). ESI-MS: } m/z = 881.0 \text{ (M}^+\text{).} \]

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

\[ ^1\text{HNMR (CDCl}_3, 300 \text{ MHz): } \delta = 9.23 \text{ (s, 8H, Por-H), 8.20 (d, 8H, Ar-H, } J=8.1\text{Hz), 7.84 (d, 8H, Ar-H, } J=8.1\text{Hz); (d}_6\text{-acetone, 300MHz): } \delta = 9.46 \text{ (s, 8H, Por-H), 8.35 (d, 8H, Ar-H, } J=8.1\text{Hz), 7.97 (d, 8H, Ar-H, } J=8.1\text{Hz); HRMS-ESI (M-Cl+): calc'd for C}_{44}\text{H}_{24}\text{AuCl}_{4}\text{N}_4: 947.0391, \text{ found: 947.0372.} \]

1.4 Mechanistic Studies

Porphyridin \( H_{2}F_{20}TPP \) (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 120°C. 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 \( \beta \)-Acetylated \( H_{2}F_{20}TPP \)

\[ ^1\text{H NMR (CDCl}_3, 300 \text{ MHz): } \delta 8.98-8.84 \text{ (m, 7H), 2.25 (s, 3H), -3.02 (s, 1H). } ^{19}\text{FNMR: } \delta 25.79-25.69 \text{ (m, 4F), 24.36-24.01 (m, 4F), 13.43-13.23 (m, 2F), 12.56-12.77 (m, 2F), 2.80-2.60 (m, 4F), 2.05-1.88 (m, 4F). IR (cm}^{-1}\text{): } 1774.3 \text{ (C=O); ESI-MS (MH}^+\text{) } m/z = 1011.0; \text{ HRESI-MS (MH}^+\text{): calc'd for C}_{42}\text{H}_{7}\text{F}_{20}\text{N}_{4}: 1011.0143, \text{ found: 1011.0148.} \]
1.5 Spectra for β-Monochloroporphyrins

1.5.1 β-Monochloro tetra(pentafluorophenyl)porphyrins (β-Cl-F20TPP) (2)

$^1$H NMR (CDCl₃, 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 (CDCl₃, 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 C₄₄H₁₀ClF₂₀N₄: 1009.0269, found: 1009.0269.

2. Spectra data for porpholactones

2.1 Tetra(pentafluorophenyl)porpholactone (3)

$^1$H NMR (CDCl₃, 300 MHz): δ 8.92 (d, 1H, $J = 5.4$ Hz), 8.89 (d, 1H, $J = 4.8$ Hz), 8.86 (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 (CDCl₃, 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 C₄₃H₁₉F₂₀N₄O₂: 993.0405, found 993.0402;
IR (cm⁻¹): 1774 (C=O), 1793 (C=O); UV-vis (CH₂Cl₂), $\lambda_{max}$ (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$_2$Cl$_2$)

![UV-vis and fluorescence spectra of 3](image)

C=O: 1774 cm$^{-1}$, 1793 cm$^{-1}$

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

![FT-IR spectra of 3](image)
Figure S5. MS of 3
2.2 Tetra(2,3,5,6-tetrafluorophenyl)porpholactone (4a)

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 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): $\delta$ 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$_4$O$_2$: 921.0872, found: 921.0767; IR (cm$^{-1}$): 1768 (C=O), 1795 (C=O); UV-vis (CH$_2$Cl$_2$), $\lambda_{max}$ (log$\varepsilon$): 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$_2$Cl$_2$)

Figure S9. FT-IR of 4a

C=O: 1768 cm$^{-1}$, 1795 cm$^{-1}$
Figure S10. MS of 4a
2.3 Tetra(2,3,4,5-tetrafluorophenyl)porpholactone (5a).

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 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): $\delta$ 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$_4$O$_2$: 921.0782, found: 921.0770; IR (cm$^{-1}$): 1790 (C=O); UV-vis (CH$_2$Cl$_2$), $\lambda_{max}$ (log$\varepsilon$): 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$_2$Cl$_2$)

**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): $\delta$ 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): $\delta$ 48.24-47.80 (m, 8F), 47.51 (m, 1H), 47.20 (t, 2H, $J$ = 7.05 Hz), 45.75 (t, 2H, $J$ = 7.05 Hz); ESI-MS(MH\(^+\)) $m/z$ = 849.1; HRESI-MS (MH\(^+\)): calc’d for C\(_{43}\)H\(_{17}\)F\(_{12}\)N\(_4\)O\(_2\): 849.1159, found:849.1163; IR (cm\(^{-1}\)): 1790 (C=O); UV-vis (CH\(_2\)Cl\(_2\)), $\lambda$\(_{\text{max}}\) (log$\varepsilon$) : 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$_2$Cl$_2$)

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): $\delta$ 8.85-8.70 (m, 4H), 8.66 (d, 1H, $J = 4.8$Hz), 8.64 (d, 1H, $J = 4.8$Hz), 8.56 (d, 1H, $J = 4.5$Hz), 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): $\delta$ 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$_8$N$_4$O$_2$: 777.1536, found: 777.1544; IR (cm$^{-1}$): 1780 (C=O); UV-vis (CH$_2$Cl$_2$), $\lambda_{\text{max}}$ (log $\varepsilon$) : 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$_2$Cl$_2$)
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): $\delta$ 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, $J = 4.8$Hz), 8.63 (d, 1H, $J = 4.8$Hz), 8.56 (d, 1H, $J = 4.8$Hz), 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): $\delta$ 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$_8$N$_4$O$_2$: 777.1536, found: 777.1529; IR (cm$^{-1}$): 1780 (C=O); UV-vis (CH$_2$Cl$_2$), $\lambda_{\text{max}}$ (log$\varepsilon$): 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$_2$Cl$_2$)
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): $\delta$ 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): $\delta$ 11.31 (q, 3F, $J = 40.0$Hz), 10.60 (t, 1F, $J = 40.7$Hz); ESI-MS (MH$^+$) $m/z$ 705.2; HRESI-MS (MH$^+$): calc’d for C$_{43}$H$_{25}$F$_4$N$_4$O$_2$: 705.1913, found: 705.1908; IR (cm$^{-1}$): 1790 (C=O); UV-vis (CH$_2$Cl$_2$), $\lambda_{\text{max}}$ (log $\varepsilon$) : 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$_2$Cl$_2$)
Figure S34. FT-IR of \textit{9a}

C–O: 1790 cm$^{-1}$

Figure S35. MS of \textit{9a}

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

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 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$_4$N$_4$O$_2$: 769.0731, found: 769.0735; IR (cm$^{-1}$): 1790 (C=O); UV-vis (CH$_2$Cl$_2$), $\lambda_{\text{max}}$ (log$\varepsilon$) : 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 (CH₂Cl₂)

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, \(J = 4.5\)Hz), 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\(_4\)O\(_2\): 633.2290, found: 633.1711; HRESI-MS (M+Na\(^+\)): calc'd for C\(_{43}\)H\(_{28}\)N\(_4\)O\(_2\)Na: 655.2110, found: 655.2102; IR (cm\(^{-1}\)): 1780 (C=O); UV-vis (CH\(_2\)Cl\(_2\)), \(\lambda_{\text{max}}\) (log\(\varepsilon\)) : 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 (CH₂Cl₂)

Figure S42. FT-IR of 11a
3. References


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**Figure S43.** MS of 11a