Supporting Information

Multi-gram Synthesis of a Water Soluble Porphyrazine and derived seco-Porphyrazine Labeling Agents

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Copies of $^1$H and $^{13}$C NMR spectra
**General Experimental Procedures.** All reactions were carried out in under N₂ using solvents and reagents as commercially supplied, unless otherwise stated. Column chromatography was carried out on silica gel, particle size 40-63 µm, using flash techniques (eluants are given in parenthesis). Analytical thin layer chromatography was performed on pre-coated silica gel plates with visualization under UV light or by staining using KMnO₄ spray reagent. IR spectra were recorded as thin films and quoted in cm⁻¹. ¹H NMR spectra, recorded at 400 or 500 MHz and referenced to the residual solvent peaks at 7.26 ppm (CDCl₃), 7.19 (d₅-pyridine) or 2.50 (d₆-DMSO) are quoted in ppm to 2 decimal places with coupling constants (J) to the nearest 0.1 Hz. ¹³C NMR spectra, recorded at 100 MHz or 125 MHz and referenced to solvent at 77.0 ppm (CDCl₃) or 149.9 (d₅-pyridine) or 39.4 (DM d₆-DMSO), are quoted in ppm to 1 decimal place.
2-Amino-3-((4-methoxycarbonyl)phenylmethylene)amino-2-butenedinitrile (3). Nitrile 2 (4.0 g, 37 mmol), methyl 4-formylbenzoate (6.0 g, 37 mmol) and EtOH (160 mL) were heated to reflux for 18 h. The resultant yellow precipitate was filtered and washed with EtOH (2 x 40 mL) to provide imine 3 (7.54 g, 81 %) as a yellow solid, which was insoluble in most organic solvents and used without further purification: mp 284-286 °C; IR (Nujol) 3441, 3295, 2237, 2207, 1721, 1606, 1292, 1111 cm\(^{-1}\); \(^1\)H NMR (300 MHz, \(d_6\)-DMSO) \(\delta\) 3.88 (s, 3H), 8.01 (d, 2H, \(J = 8.0\) Hz), 8.17 (d, 2H, \(J = 8.0\) Hz), 8.31 (s, 1H); \(^{13}\)C NMR (75 MHz, \(d_6\)-DMSO) \(\delta\) 52.8, 102.7, 114.1, 114.7, 128.5, 129.5, 129.8, 131.9, 140.1, 153.9, 166.3; MS (CI) \(m/z\) 255 [M + H]\(^+\); HRMS (CI) calcd. for C\(_{13}\)H\(_{11}\)N\(_4\)O\(_2\): [M + H]\(^+\), 255.0882, found: [M + H]\(^+\), 255.0894.

2-Amino-3-((4-methoxycarbonyl)phenylmethyl)amino-2-butenedinitrile (4). NaBH\(_4\) (5.00 g, 132 mmol) was added in 3 portions to imine 4 (9.00 g, 35 mmol) in THF (170 mL) and MeOH (120 mL). The slurry was stirred for 4 h, during which time the solids dissolved. The solution was added to ice and H\(_2\)O (600 mL), giving a yellow solid, which was filtered off, dried under N\(_2\), and dried by azeotrope with PhMe (2 x 70 mL) to leave dinitrile 4 (8.38 g, 92%) as a pale yellow solid, which was used without further purification: IR (Nujol) 3404, 3338, 3242, 2209, 1702, 1292 cm\(^{-1}\); \(^1\)H NMR (400 MHz, \(d_6\)-DMSO) \(\delta\) 3.85 (s, 3H), 4.32 (br s, 2H), 5.75 (br s, 3H), 7.44 (d, 2H, \(J = 8.2\) Hz), 7.96 (d, 2H, \(J = 8.2\) Hz); \(^{13}\)C NMR (100 MHz, \(d_6\)-DMSO) \(\delta\) 48.4, 52.0, 107.0, 108.9, 115.6, 116.5, 127.4, 128.5, 129.3, 145.0, 166.0; MS (CI) \(m/z\) 274 [M + NH\(_4\)]\(^+\); HRMS (CI) calcd. for C\(_{13}\)H\(_{16}\)N\(_5\)O\(_2\): [M + NH\(_4\)]\(^+\), 274.1304, found: [M + NH\(_4\)]\(^+\), 274.1310.

2-Dimethylamino-3-((4-methoxycarbonyl)phenylmethyl)amino-2-butenedinitrile (5). Dinitrile 4 (6.50 g, 25.4 mmol) in THF (90 mL) were added to NaH (4.79 g, 208 mmol, 60 % suspension in mineral oil) in THF (210 mL) at -30 °C. The mixture as allowed to warm to -10 °C when Me\(_2\)SO\(_4\) (16 g, 127 mmol) was added over 30 min. The mixture was subsequently
stirred at room temperature for 18 h. Rotary evaporation and chromatography
(hexanes:EtOAc 7:3) gave dinitrile 5 (7.175 g, 95%) as a yellow solid: $R_f$ 0.42, 0.51
(hexanes:EtOAc 13:7); IR (film) 2183, 1722, 1596, 1436, 1384, 1281, 1108 cm$^{-1}$; $^1$H NMR
(300 MHz, CDCl$_3$) δ 2.71 (s, 3H), 2.83 (s, 6H), 3.94 (s, 3H), 4.17 (s, 2H), 7.35 (d, 2H,
$J = 8.0$ Hz), 8.05 (d, 2H, $J = 8.0$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 41.1, 42.2, 52.2, 58.3,
113.5, 114.0, 114.9, 121.6, 128.6, 129.8, 130.0, 141.6, 166.7; MS (CI) m/z 316 [M + NH$_4$]$^+$;
HRMS (CI) calcd. for C$_{16}$H$_{22}$N$_5$O$_2$: [M + NH$_4$]$^+$, 316.1773, found: [M + NH$_4$]$^+$, 316.1777.

(9-Hydroxy-1,4,7-trioxanonyl)-phenylacetonitrile (8). Chloride 7 (221 g, 1.31 mol) was
added to 4-hydroxybenzyl cyanide 6 (100.0 g, 654 mmol) and K$_2$CO$_3$ (181 g, 1.31 mol) in
MeCN (1.3 L), the mixture was heated to reflux for 60 h and cooled to room temperature. It
was filtered and the solid was washed with Et$_2$O. The combined organic layers were washed
with H$_2$O (2X), dried (MgSO$_4$), filtered and rotary evaporated to provide nitrile 8 as a yellow
oil, which was used without further purification: $R_f$ 0.13 (hexanes:EtOAc 2:8); $^1$H NMR (400
MHz, CDCl$_3$) δ 2.64 (br s, 1H), 3.58 - 3.60 (m, 2H), 3.66 - 3.71 (m, 8H), 3.84 (t, 2H, $J = 4.8$
Hz), 4.11 (t, 2H, $J = 4.8$ Hz), 6.89 (d, 2H, $J = 8.8$ Hz), 7.20 (d, 2H, $J = 8.7$ Hz); $^{13}$C NMR
(100 MHz, CDCl$_3$) δ 22.7, 61.6, 67.4, 70.2, 70.7, 72.3, 115.1, 118.1, 122.0, 129.0, 158.4; MS
(CI) m/z 283 [M + NH$_4$]$^+$; HRMS (CI) calcd. for C$_{14}$H$_{23}$N$_2$O$_4$: [M + NH$_4$]$^+$, 283.1658; found:

(9-(2-Tetrahydropyranxyloxy)-1,4,7-trioxanonyl)-phenylacetonitrile (9). 3,4-Dihydropyran
(275 g, 3.27 mol), nitrile 8 and p-TsOH (150 mg, 0.8 mmol) in CH$_2$Cl$_2$ (1.0 L) were stirred at
0 °C for 30 min and at room temperature for 18 h under N$_2$. The solution was washed with
saturated aqueous NaHCO$_3$ solution and brine (2X) and the organic phase was dried (MgSO$_4$),
filtered, rotary evaporated and chromatographed (hexanes:Et$_2$O 3:7) to give nitrile 9 (202.6 g,
89% for two steps) as a yellow oil: $R_f$ 0.58 (hexane:EtOAc 1:4); $^1$H NMR (400 MHz, CDCl$_3$) δ 1.47 - 1.84 (m, 6H), 3.46 - 3.49 (m, 1H), 3.56 - 3.62 (m, 1H), 3.66 - 3.73 (m, 8H), 3.82 - 3.87 (m, 4H), 4.10 (t, 2H, $J = 4.9$ Hz), 4.61 (t, 1H, $J = 3.6$ Hz), 6.89 (d, 2H, $J = 8.6$ Hz), 7.20 (d, 2H, $J = 8.6$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 19.7, 23.0, 25.6, 30.8, 62.4, 66.9, 67.8, 69.9, 70.6, 70.8, 72.7, 99.2, 115.4, 118.4, 122.2, 129.3, 158.8; MS (CI) m/z 367 [M + NH$_4$]$^+$; HRMS (CI) calcd. for C$_{19}$H$_{31}$N$_2$O$_5$: [M + NH$_4$]$^+$, 367.2233, found: [M + NH$_4$]$^+$, 367.2240.

Anal. calcd. for C$_{19}$H$_{31}$N$_2$O$_5$: C, 65.31; H, 7.79; N, 4.01. Found: C, 65.40; H, 7.75; N, 4.11.

(Z,E)-2,3-Di-(9-(2-tetrahydropyranoyloxy)-1,4,7-trioxanonyl)-phenyl)-2-butenedinitrile (10). 30% Aqueous NaOH (1.0 L) and Bu$_4$NCl (512 mg) were added sequentially with stirring to nitrile 10 (160 g, 459 mmol) in CCl$_4$ (84 g, 552 mmol) at room temperature. After 12 h, CH$_2$Cl$_2$ was added to the yellow solution and the mixture was extracted with CH$_2$Cl$_2$ (3X). The combined organic layers were washed with brine, dried (MgSO$_4$), rotary evaporated and chromatographed on Et$_3$N-deactivated silica gel (Et$_2$O) to give the mixture of dinitriles E-10 and Z-10 (148.8 g, 213.8 mmol) as a viscous yellow oil. Z-10 isomer: $R_f$ 0.28 (EtOAc); IR (film) 2215, 1602, 1509, 1451, 1422, 1352, 1300, 1257, 1181, 1123, 1074, 1034, 834 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.55 - 1.88 (m, 12H), 3.52 (m, 2H), 3.63 (m, 2H), 3.72 (m, 12H), 3.89 (m, 8H), 4.16 (m, 4H), 4.65 (m, 2H), 6.85 (d, 4H, $J = 9$ Hz), 7.29 (d, 4H, $J = 9$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 19.5, 25.4, 30.6, 62.3, 66.7, 67.7, 69.5, 70.6, 70.7, 70.9, 99.0, 115.2, 117.4, 123.3, 130.4, 131.0, 160.8; MS (FAB) m/z 694 [M$^+$]; HRMS (FAB) calcd. for C$_{38}$H$_{50}$N$_2$O$_{10}$: [M$^+$], 694.3465, found: [M$^+$], 694.3461. E-10 isomer: $R_f$ 0.33 (EtOAc); IR (film) 2218, 1603, 1512, 1453, 1351, 1300, 1254, 125, 1182, 1125, 1075, 1034, 835 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.54 - 1.89 (m, 12H), 3.53 (m, 2H), 3.64 (m, 2H), 3.74 (m, 12H), 3.91 (m, 8H), 4.23 (m, 4H), 4.66 (m, 2H), 7.05 (d, 4H, $J = 9$ Hz), 7.80 (d, 4H, $J = 9$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 19.5, 25.4, 30.6, 62.3, 66.7, 67.8, 69.5, 70.6, 70.7, 71.0, 99.0,
115.2, 117.3, 122.7, 124.7, 130.4, 161.3; MS (FAB) \textit{m/z} 694 [M$^+$]; HRMS (FAB) calcd. for C$_{38}$H$_{50}$N$_2$O$_{10}$: [M$^+$], 694.3465, found: [M$^+$], 694.3463.

[2,3,7,8,12,13,17,18-Octakis-(9-(2-tetrahydropyranoxy)-1,4,7-trioxanonyl)-phenyl-porphyrazinato]magnesium(II) (12). Freshly cut Na (10 mg, 0.43 mmol) was added to (E,Z)-dinitrile 10 (500 mg, 0.7 mmol) in \textit{n}-BuOH at 75 °C. After 5 min, NH$_3$ was bubbled through the solution for 3 h and the mixture was cooled to room temperature. Mg turnings (86 mg, 3.6 mmol) and I$_2$ (ca. 1 crystal) in 1-BuOH (10 mL) were heated to reflux for 6 h and cooled to room temperature. Both solutions were combined and heated to reflux for 20 h. The mixture was filtered (celite) and the solids washed with CH$_2$Cl$_2$. The combined filtrate and extracts were rotary evaporated and chromatographed (MeOH:CHCl$_3$:Et$_2$O 1:9:9) to give porphyrazine 12 (152 mg, 31%) as a blue-green solid: \textit{R}$_f$ 0.59 (MeOH:CHCl$_3$:Et$_2$O 9.5:45.3:45.3); IR (film) 1606, 1514, 1496, 1454, 1287, 1248, 1179, 1123, 1073, 1035, 984, 842 cm$^{-1}$; UV-vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\varepsilon$) 343 (4.10), 387 (4.42), 599 (3.91) nm; $^1$H NMR (500 MHz, d$_5$-pyridine) $\delta$ 1.45 - 1.91 (m, 48H), 3.56 - 4.85 (m, 120H), 7.53 (d, 16H, $J = 8.0$ Hz), 8.75 (d, 16H, $J = 8.0$ Hz); $^{13}$C NMR (125 MHz, d$_5$-pyridine) $\delta$ 19.8, 25.9, 25.4, 31.0, 62.2, 67.1, 68.1, 70.1, 71.0, 71.2, 99.1, 115.0, 128.1, 141.4, 158.6, 159.3; MS (MALDI) \textit{m/z} 2803 [M$^+$]; HRMS (MALDI) calcd. for C$_{152}$H$_{200}$MgN$_8$O$_{40}$: [M$^+$], 2803.5490, found: [M$^+$], 2803.3434.

[2-Dimethylamino-3-(4-(hydroxycarbonyl)phenylmethyl)amino-7,8,12,13,17,18-hexakis-(9-(2-tetrahydropyranoxy)-1,4,7-trioxanonyl)-phenyl-porphyrazinato]magnesium(II) (15). (Method 1). Freshly cut Na (360 mg, 15.65 mmol) was added to a mixture of the (E,Z)-dinitrile 10 (112 g, 161 mmol) and dinitrile 5 (6.8 g, 23.0 mmol) in \textit{1}-BuOH (1500 mL). After 5 min, NH$_3$ was bubbled through the mixture, which was stirred and heated to 100 °C for 12 h and subsequently cooled to room temperature. Separately, with mechanical stirring, Mg turnings (11.04 g, 460 mmol) and 1-BuOH (1000 mL) were heated at reflux for 20 h and
cooled to room temperature. The two solutions were combined, heated to reflux for 48 h, cooled and filtered through celite. After rotary evaporation, the residue was dissolved in 1-PrOH (3.5 L) and aqueous NaOH (1M; 1000 mL) was added followed by MeOH (120 mL) and the mixture was stirred at room temperature for 36 h. The mixture was washed with saturated aqueous NH$_4$Cl (3X) and the combined aqueous phases back-extracted with EtOAc. The combined organic layers were rotary evaporated and the residue was dissolved in CH$_2$Cl$_2$ and washed with brine. The organic layer was directly chromatographed (CH$_2$Cl$_2$:Et$_2$O 1:1; MeOH:CH$_2$Cl$_2$:Et$_2$O 1:9:9; MeOH:CH$_2$Cl$_2$:Et$_2$O 1:3:3) to give porphyrazine 15 (18.42 g, 33%) as a blue oil. (Method 2) The Pz 14 (650 mg, 0.265 mmol) was dissolved in 1-PrOH (110 mL) and MeOH (3.5 mL) followed by aqueous NaOH (1M, 27 mL) were added. The mixture was stirred at room temperature for 60 h and subsequently washed with saturated aqueous NH$_4$Cl. The combined organic layers were dried (MgSO$_4$), filtered and evaporated. The residue was purified on an Amberlyst A26 column (previously washed by 15% aqueous NaOH followed by MeOH). All the impurities were first eluted with MeOH and the porphyrazine 15 was eluted with aqueous NaOH (15%; 50 mL) in MeOH (100 mL). The eluate was evaporated, saturated aqueous NH$_4$Cl added and the mixture extracted with CH$_2$Cl$_2$ (3X). The combined organic layers were dried (MgSO$_4$), filtered and evaporated to yield porphyrazine 15 (460 mg, 72%) as a blue oil: IR (film) 3332, 1606, 1581, 1454, 1288, 1247, 1178, 1122, 1074 cm$^{-1}$; UV-vis (CH$_2$Cl$_2$) $\lambda_{max}$ (log $\epsilon$) 337 (4.64), 673 (4.39) nm; $^1$H NMR (400 MHz, d$_5$-pyridine) $\delta$ 1.30 - 1.90 (m, 36H), 3.40 - 4.10 (m, 87H), 4.38 - 4.45 (m, 8H), 4.74 (t, 6H, $J$= 3.6 Hz), 7.41 (2d, 12H, $J$= 8.4 and 8.8 Hz), 7.78 (d, 2H, $J$ = 8.0 Hz), 8.33 (br s, 2H), 8.43 (d, 4H, $J$= 8.4 Hz), 8.66 (2d, 8H, $J$= 8 and 8.4 Hz); $^{13}$C NMR (125 MHz, d$_5$-pyridine) $\delta$ 19.8, 25.9, 31.0, 43.1, 44.4, 62.0, 67.1, 68.1, 70.1, 70.9, 71.0, 71.2, 99.1, 114.9, 128.1, 128.2, 128.4, 128.46, 128.51, 129.1, 130.3, 134.5, 134.8, 140.1, 140.4, 140.7, 141.3, 141.6,
[2-Dimethylamino-3-((4-(1-butyl)oxycarbonyl)phenylmethyl)amino-7,8,12,13,17,18-
hexakis-(9-(2-tetrahydropyranoxy)-1,4,7-trioxanonyl)-phenyl]-porphyrazinato] magnesium(II) (14). (Method 1). Mg turnings (117 mg, 4.81 mmol) and I$_2$ (ca. 1 crystal) in
1-BuOH (60 mL) were heated under reflux for 24 h under N$_2$. The mixture was allowed to
cool to room temperature and dinitrile 5 (143 mg, 0.48 mmol) and pure isomer Z-10 (2.00 g,
2.88 mmol) in 1-BuOH (60 mL) was added. The mixture heated under reflux for 24 h, cooled,
filtered through celite and the solids washed with CH$_2$Cl$_2$. The combined dark turquoise
organic extracts were rotary evaporated and chromatographed (MeOH:CHCl$_3$:Et$_2$O 2:45:55)
to give the porphyrazine 15 (424 mg, 36%) as a blue-green solid. (Method 2). 2,4,6-
C$_6$H$_2$COCl (3.82 g, 15.67 mmol) in PhMe (10 mL) was added to iso-Pr$_2$NEt (2.02 g, 15.67
mmol) and porphyrazine acid 15 (15.0 g, 6.27 mmol) in THF (50 mL) at room temperature
under N$_2$. After 1.5 h, the solvent was evaporated under vacuum and the resultant blue oil
dissolved in PhMe (500 mL). n-BuOH (4.64 g, 62.7 mmol) in PhMe (10 mL) was added
followed by DMAP (7.65 g, 62.7 mmol) in PhMe (100 mL). After stirring for 1 h, EtOAc was
added and organic layers were washed with saturated aqueous NaHCO$_3$ and brine. The
organic layer was dried (Na$_2$SO$_4$), filtered, rotary evaporated and chromatographed
(CH$_2$Cl$_2$:Et$_2$O 1:1; MeOH:CH$_2$Cl$_2$:Et$_2$O 1:9:9) to give porphyrazine ester 14 (13.85 g, 90%) as
a blue oil: $R_f$ 0.63 (MeOH:CHCl$_3$:Et$_2$O 9.5:45.2:45.2); IR (film) 1719, 1606, 1511, 1499,
1459, 1285, 1250, 1179, 1125, 987, 877, 842 cm$^{-1}$; UV-vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\varepsilon$) 378 (5.04),
588 (4.56), 649 (4.71) nm; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.92 (app t, 3H, $J = 7.2, 7.6$ Hz),
1.41 (dt, 2H, $J = 7.2, 7.6$ Hz), 1.45 - 1.90 (m, 40H), 3.45 - 3.55 (m, 10H), 3.60 - 3.95 (m,
61H), 3.95 - 4.05 (m, 12H), 4.22 (app t, 2H, $J = 6.4, 6.8$ Hz), 4.25 - 4.35 (m, 10H), 4.64 (app t,
6H, $J = 3.2, 4$ Hz), 7.08 (2d, 4H, $J = 4, 8.8$ Hz), 7.13 (2d, 8H, $J = 8.8$ Hz), 7.44 (d, 2H, $J = 8.0$ Hz).
Hz), 7.82 (d, 2H, J= 8.4 Hz), 8.15 (2d, 4H, J= 8.4, 8.8 Hz), 8.32 (2d, 8H, J= 8.4, 8.8 Hz); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 13.7, 19.2, 19.5, 25.4, 30.1, 30.5, 38.7, 43.4, 48.1, 62.2, 64.5, 66.6, 67.4, 69.9, 70.7, 70.9, 98.9, 105.7, 127.6, 127.7, 128.1, 128.2, 128.5, 128.7, 129.2, 129.5, 133.7, 133.8, 134.1, 139.2, 139.5, 139.7, 140.3, 142.7, 146.3, 153.9, 155.4, 155.8, 156.2, 156.9, 157.5, 158.1, 158.6, 166.6; MS (MALDI) m/z 2450 [M$^+$]; HRMS (MALDI), calcd. for C$_{133}$H$_{174}$MgN$_{10}$O$_{32}$: [M$^+$], 2449.16, found: [M$^+$], 2449.62.

2-Dimethylamino-3-((4-(1-butyl)oxycarbonyl)phenylmethyl)amino-7,8,12,13,17,18-hexakis-(9-(2-tetrahydropyranoxy)-1,4,7-trioxanonyl)-phenyl-porphyrazine (16).

AcOH (35.0 mL, 0.56 mol) was added to porphyrazine 14 (10.0 g, 4.08 mmol) in CH$_2$Cl$_2$ (1 mL) at 0 °C under N$_2$. After standing overnight at room temperature, the mixture was added to aqueous NaOH (1M; 500 ml) and extracted with CH$_2$Cl$_2$ (2X) until the aqueous layer became colorless. The combined organic extracts were dried (MgSO$_4$), filtered, and rotary evaporated yielding porphyrazine 16 as a blue-purple solid, which was used without further purification: $R_f$ 0.64 (MeOH:CHCl$_3$:Et$_2$O 9.5:45.3:45.3); IR (film) 1719, 1657, 1606, 1513, 1491, 1459, 1281, 1251, 1179, 1121, 1074, 1034, 987 cm$^{-1}$; UV-vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\varepsilon$) 340 (4.65), 379 (4.54), 531 (4.39), 573 (4.34), 692 (4.40), 738 (4.50) nm; $^1$H NMR (400 MHz, CDCl$_3$) δ –0.88 (s, 2H), 0.91 (t, 3H, J = 7.6 Hz), 1.40 - 1.83 (m, 40H), 3.45 - 3.66 (m, 14H), 3.65 - 4.05 (m, 69H), 4.19 (t, 2H, J = 7.0 Hz), 4.30 - 4.38 (m, 12H), 4.65 - 4.70 (m, 6H), 7.08 - 7.20 (m, 12H), 7.41 (d, 2H, J = 8.0 Hz), 7.87 (d, 2H, J = 8.0 Hz), 8.04 - 8.10 (m, 4H), 8.23 - 8.30 (m, 8H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 13.7, 19.2, 19.5, 25.4, 29.7, 30.6, 30.7, 59.8, 62.3, 64.6, 66.7, 67.5, 69.9, 70.6, 70.7, 70.9, 99.0, 114.4, 114.5, 126.6, 128.6, 129.5, 133.5, 133.6, 134.1, 158.6, 158.7, 166.5; MS (MALDI) m/z 2428 [M + H]$^+$; HRMS (MALDI), calcd. for C$_{133}$H$_{172}$MgN$_{10}$O$_{32}$: [M + H]$^+$, 2427.87, found: [M + H]$^+$, 2428.10.
[2-Dimethylamino-3-((4-(1-butyl)oxycarbonyl)phenylmethyl)amino-7,8,12,13,17,18-
hexakis-(9-(2-tetrahydropyranoyloxy)-1,4,7-trioxanonyl)-phenyl]-porphyrazinato]
zinc(II) (17). The previous porphyrazine 16 and Zn(OAc)$_2$ (1.501 g, 8.16 mmol) in DMF (1.0 L) were heated to 90 °C for 16 h. Rotary evaporation and chromatography (MeOH:Et$_2$O:CHCl$_3$ 1:9:9) gave porphyrazine 17 (6.95 g, 75% for 2 steps) as a blue-green solid:

$R_f$ 0.55 (MeOH:CHCl$_3$:Et$_2$O 9.5:45.3:45.3); IR (film) 1714, 1607, 1580, 1514, 1497, 1453, 1368, 1284, 1248, 1178, 1123, 1074, 1034, 988, 874, 835, 812 cm$^{-1}$; UV-vis (CH$_2$Cl$_2$) $\lambda$$_{max}$ (log $\varepsilon$) 363 (5.01), 446 (4.54), 466 (4.55), 586 (4.67), 650 (4.77) nm; $^1$H NMR (400 MHz, d$_5$-pyridine) $\delta$ 0.76 (app t, 3H, $J$ = 7.2, 7.6 Hz), 1.25 (app-sextet, 2H, $J$ = 7.2, 7.6 Hz), 1.30 - 1.85 (m, 38H), 3.40 - 3.52 (m, 6H), 3.60 - 4.10 (m, 77H), 4.24 (app t, 2H, $J$ = 6.4, 6.8 Hz), 4.30 - 4.45 (m, 10H), 4.74 (app t, 6H, $J$ = 3.2, 3.6 Hz), 7.48 - 7.50 (m, 12H), 7.73 (d, 2H, $J$ = 8.0 Hz), 8.12 (d, 2H, $J$ = 8.0 Hz), 8.40 - 8.50 (m, 4H), 8.64 - 8.70 (m, 8H); $^{13}$C NMR (125 MHz, d$_5$-pyridine) $\delta$ 13.8, 19.4, 19.7, 25.8, 30.8, 31.0, 43.5, 44.1, 55.0, 60.3, 61.9, 64.7, 67.0, 68.0, 68.1, 70.1, 70.9, 71.0, 71.1, 99.0, 114.9, 127.7, 127.9, 128.09, 128.14, 128.2, 129.4, 129.5, 128.8, 133.0, 134.4, 134.5, 134.7, 134.8, 135.1, 140.0, 140.1, 140.4, 140.6, 141.2, 141.6, 143.1, 146.6, 155.9, 156.3, 156.4, 156.7, 157.5, 157.6, 158.2, 159.2, 159.3, 159.4, 166.5; MS (MALDI) m/z 2490, [M$^+$]; HRMS (MALDI) calcd. for C$_{133}$H$_{174}$ZnN$_{10}$O$_{32}$: [M$^+$], 2490.24, found: [M$^+$], 2490.58.

[2-Dimethylamino-3-((4-(1-butyl)oxycarbonyl)phenylmethyl)amino-7,8,12,13,17,18-
hexakis-(9-(2-tetrahydropyranoyloxy)-1,4,7-trioxanonyl)-phenyl]-2-seco-2,3-
dioxoporphyrizinato]zinc(II) (18). Porphyrazine 17 (580 mg, 0.23 mmol) in CH$_2$Cl$_2$ (1000 mL) was stirred opened to the air for 24 h and irradiated with a 40 W desk lamp. The solvent was evaporated under reduced pressure and the residue chromatographed (MeOH:Et$_2$O:CHCl$_3$, 3:46:46) to give seco-porphyrazine 18 (560 mg, 97%) as a blue-green solid: $R_f$ 0.47 (MeOH:CHCl$_3$:Et$_2$O 9.5:45.2:45.2); IR (film) 1718, 1642, 1607, 1513, 1495, 1454, 1377,
1249, 1179, 1124, 1035, 976 cm$^{-1}$; UV-vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (log $\epsilon$) 338 (4.88), 385 (4.89), 600 (4.62), 708 (4.84) nm; $^1$H NMR (400 MHz, d$_5$-pyridine) $\delta$ 0.90 (app t, 3H, $J = 7.2, 7.6$ Hz), 1.40 - 1.50 (m, 20H), 1.60 - 1.85 (m, 20H), 3.35 (s, 2H), 3.43 - 3.51 (m, 8H), 3.70 - 4.09 (m, 67H), 4.14 (s, 3H), 4.22 (s, 3H), 4.27 - 4.34 (m, 2H), 4.34 - 4.45 (m, 12H), 4.71 - 4.76 (m, 6H), 7.32 - 7.43 (m, 12H), 7.85 (d, 2H, $J = 8.0$ Hz), 8.19 (2d, 4H, $J = 9.2$), 8.26 (d, 2H, $J = 8.4$ Hz), 8.47 - 8.60 (m, 8H); $^{13}$C NMR (125 MHz, d$_5$-pyridine) $\delta$ 13.9, 19.5, 19.7, 25.8, 31.0, 31.1, 35.1, 38.6, 40.0, 61.9, 65.0, 67.0, 67.9, 68.0, 68.1, 70.9, 71.0, 71.1, 99.0, 114.7, 114.9, 115.0, 127.2, 127.3, 127.9, 128.1, 130.0, 130.5, 134.1, 134.2, 134.5, 134.6, 138.8, 139.7, 139.8, 142.1, 142.2, 143.4, 154.6, 154.9, 155.3, 155.4, 156.2, 156.3, 157.5, 158.2, 159.1, 159.2, 159.3, 159.4, 159.5, 166.5, 168.8, 169.4; MS (MALDI) $m/z$ 2522 [M$^+$]; HRMS (MALDI) calcd. for C$_{133}$H$_{174}$ZnN$_{10}$O$_{34}$: [M$^+$], 2522.24, found: [M$^+$], 2522.56.

[2-Dimethylamino-3-(((4-hydroxycarbonyl)phenylmethyl)amino)-7,8,12,13,17,18-hexakis-(9-hydroxy-1,4,7-trioxanonyl)-phenyl]-2-seco-2,3-dioxoporphyrinato]zinc(II) (1).

Porphyrazine 18 (73 mg, 0.029 mmol), NaOH in H$_2$O and n-PrOH (4:16; 1M; 20 mL) and MeOH (0.5 mL) was stirred at 0 ºC for 60 h. The two phases were separated and the organic layer was washed with H$_2$O (3 x 30 mL) to pH 10 (brine was used to facilitate phase separations). During this time, partial precipitation of a blue residue occurred. The final H$_2$O and brine phase was extracted was washed with CHCl$_3$ (40 mL) and the combined organic extracts were rotary evaporated and residual H$_2$O was removed by azeotrope with PhMe (2 x 30 mL) to give porphyrazine acid 19 as a blue solid which was used without further purification. Concentrated HCl (27 µL, 0.86 mmol) was added to porphyrazine acid 19 (71 mg, 0.0288 mmol) in CHCl$_3$ (7 mL) and MeOH (2 mL) at 0 ºC. The mixture was allowed to warm to ambient temperature and stirred for 1.5 h, during which time the mixture turned purple. The mixture was cooled to 0 ºC and Et$_3$N (0.14 mL, 1.03 mmol) was added dropwise. The mixture was allowed to warm to ambient temperature and stirred for 50 min, during
which time the mixture turned blue. Rotary evaporation and chromatography (MeOH:CHCl₃ 1:9 - MeOH) and gel permeation chromatography on Lipophilic Sephadex (MeOH:CHCl₃ 1:9) gave porphyrazine 1 (31 mg, 55 % over two steps) as a blue solid: IR (film) 3419 (br), 1713, 1641, 1606, 1494, 1453, 1376, 1287, 1247, 1178, 1113, 1062, 975, 836 cm⁻¹; UV-vis (CH₂Cl₂) λₘₚₙ (log ε) 345(4.97), 391 (5.04), 603 (4.80), 712 (5.05) nm; ¹H NMR (500 MHz, d₅-pyridine) δ 3.35 (s, 3H), 3.60 - 3.85 (m, 43H), 3.90 - 4.07 (m, 22H), 4.24 (s, 3H), 4.24 - 4.33 (m, 2H), 4.33 - 4.43 (m, 8H), 7.16 (d, 2H, J = 9.0 Hz), 7.33 (2d, 8H, J = 7.0, 8.0 Hz), 7.38 (d, 4H, J = 8.5 Hz), 7.84 (d, 2H, J = 8.0 Hz), 8.15 (d, 2H, J = 8.0 Hz), 8.24 (d, 2H, J = 8.0 Hz), 8.49 (d, 4H, J = 7.0 Hz), 8.56 (2d, 4H, J = 8.0 Hz). ¹³C NMR (125 MHz, d₅-pyridine) δ 35.0, 38.1, 40.0, 50.5, 62.0, 68.0, 70.0, 70.9, 71.1, 73.9, 114.9, 127.0, 127.2, 127.3, 127.9, 128.0, 130.1, 134.0, 134.2, 134.5, 138.7, 139.6, 139.8, 142.1, 154.7, 154.9, 155.4, 156.2, 156.7, 157.4, 159.1, 159.3, 159.4, 168.8, 169.3; MS (MALDI) m/z 1961 [M⁺]; HRMS (MALDI) calcd. for C₉₉H₁₁₀N₁₀O₂₈Zn: [M + H]⁺, 1962.44, found: [M + H]⁺, 1962.41.