Electronic Supporting Information

Benzoporphyrins via olefin ring-closure metathesis methodology

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Instrumentation and Materials

All reactions were monitored by TLC using 0.25 mm silica gel plates with or without UV indicator (60F-254). Silica gel (Sorbent Technologies 32-63 μm) was used for flash column chromatography. $^1$H- and $^{13}$C-NMR spectra were obtained on either a DPX-250 or an ARX-300 Bruker spectrometer. Chemical shifts (δ) are given in ppm relative to residual CHCl$_3$ (7.26 ppm, $^1$H), or CH$_2$Cl$_2$ (5.32 ppm, $^1$H) unless otherwise indicated. Electronic absorption spectra were measured on a Perkin Elmer Lambda 35 UV-Vis spectrophotometer. MALDI-TOF mass spectra were obtained on an Applied Biosystems QSTAR XL, using positive method with dithranol as matrix. Materials obtained from commercial suppliers were used without further purification.

General Procedures for olefin ring-closure metathesis:

The allyl-substituted porphyrins (0.1 mmol) from the various Suzuki-coupling reactions were dissolved into anhydrous dichloromethane (90 ml). Grubbs II catalyst (0.0025 mmol/allyl group) in anhydrous dichloromethane (10 ml) was added dropwise into the above porphyrin solutions. The solution was then heated under reflux overnight in an atmosphere of argon. After cooling to room temperature and concentration, a silica gel
column was used for purification, using a mixture of dichloromethane/hexane as the mobile phase.

**11:**
MALDI-TOF calc. for C$_{48}$H$_{33}$N$_{4}$ [M+H]$^+$ 665.271, found 665.201. UV-vis (dichloromethane) $\lambda_{\text{max}}$ (nm): 407 (log $\varepsilon$ 4.95), 425 (5.70), 518 (4.38), 596 (3.88) and 650 (3.01). $\delta$$_H$ (300 MHz, CDCl$_3$) 8.87 (2H, d, J = 5.9 Hz), 8.77 (2H, d, J = 5.9 Hz), 8.71 (2H, s), 8.19-8.24 (8H, m), 7.74-7.93 (12H, m), 7.36-7.39 (2H, m), 7.12-7.16 (2H, m), -2.61 (2H, s). m.p. > 300 ºC.

**12:**
MALDI-TOF calc. for C$_{52}$H$_{35}$N$_{4}$ [M+H]$^+$ 715.286, found 715.798. UV-vis (dichloromethane) $\lambda_{\text{max}}$ (nm): 413 (log $\varepsilon$ 4.76), 435 (5.67), 525 (4.37), 618 (3.75) and 675 (3.85). $\delta$$_H$ (300 MHz, CD$_2$Cl$_2$) 8.76 (4H, d, J = 7.38), 8.53 (4H, d, J = 6.99), 8.28 (4H, s), 8.12-8.17 (4H, m), 8.00-8.05 (4H, m), 7.84-7.89 (4H, m), 7.56 (8H, s). m.p. > 300 ºC.

**13:**
MALDI-TOF calc. for C$_{56}$H$_{37}$N$_{4}$ [M+H]$^+$ 765.302, found 765.670. UV-vis (dichloromethane) $\lambda_{\text{max}}$ (nm): 428 (log $\varepsilon$ 4.97), 450 (5.70), 553 (4.31), 590 (4.37), 628 (4.04), 685 (3.86). $\delta$$_H$ (250 MHz, CD$_2$Cl$_2$) 8.44 (2H, s), 8.21-8.30 (10H, m), 7.82-7.97 (12H, m), 7.42-7.45 (2H, m), 7.30-7.34 (2H, m), 7.14-7.20 (4H, m), 7.02-7.05 (1H, m), 6.93 (1H, d, J = 7.24), -1.2 (2H, brs). m.p. >300 ºC.
16:
MALDI-TOF calc. for C_{48}H_{33}N_5O_2 [M+H]^+ 712.271, found 712.149. UV-vis (dichloromethane) $\lambda_{\text{max}}$ (nm): 383 (log $\varepsilon$ 5.10), 439 (5.72), 536 (4.64), 614 (4.11), 680 (4.32). $\delta_H$ (300 MHz, CDCl$_3$) 8.97 (1H, s), 8.85-8.88 (2H, m), 8.63-8.67 (2H, m), 8.21-8.25 (4H, m) 8.09-8.12 (4H, m), 7.68-7.81 (12H, m), 5.73 (2H, s), 3.27 (4H, s), -2.62 (2H, s). m.p. >300 ºC.

17:
MALDI-TOF calc. for C_{56}H_{35}N_5O_2 [M+H]^+ 809.279, found 809.422. UV-vis (dichloromethane) $\lambda_{\text{max}}$ (nm): 394 (log $\varepsilon$ 5.02), 448 (5.73), 543 (4.62), 615 (4.26), 682 (4.09). $\delta_H$ (300 MHz, CD$_2$Cl$_2$) 8.93 (1H, s), 8.88-8.92 (2H, m), 8.71-8.73 (2H, d, J = 6.03), 8.16-8.27 (8H, m), 7.73-7.91 (12H, m), 7.30-7.34 (2H, d, J = 11.0 ), 7.08 (2H, s), -2.35 (2H, s). m.p. > 300 ºC.