Facile Peripheral Functionalization of Porphyrins via Pd-Catalyzed [3 + 2] Annulation with Alkynes

Akhila K. Sahoo, Shigeki Mori, Hiroshi Shinokubo,* and Atsuhiro Osuka*

Department of Chemistry, Graduate School of Science, Kyoto University,
PRESTO & CREST, Japan Science and Technology Agency (JST),
and International Innovation Center (IIC), Kyoto University, Kyoto 606-8502, Japan

hshino@kuchem.kyoto-u.ac.jp; osuka@kuchem.kyoto-u.ac.jp

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Instrumentation and Materials:

$^1$H NMR (600 MHz), $^{13}$C NMR (151 MHz), and $^{19}$F NMR (565 MHz) spectra were taken on a JEOL ECA-600 spectrometer. Chemical shifts were reported as delta scale in ppm relative to CHCl$_3$ ($\delta = 7.26$) and C$_2$H$_2$Cl$_4$ ($\delta = 5.91$) for $^1$H NMR and to CDCl$_3$ ($\delta = 77.0$) for $^{13}$C NMR. Hexafluorobenzene was used as external reference for $^{19}$F NMR ($\delta = -162.9$). UV-vis absorption and steady-state fluorescence spectra were recorded on a Shimadzu UV-3100 spectrometer and a Shimadzu RF-5300PC spectrometer, respectively. MALDI-TOF mass spectra were obtained with a Shimadzu/KRATOS KOMPACT MALDI 4 spectrometer, using positive-MALDI ionization method without matrix. High-resolution ESI-TOF mass spectra were taken on a Bruker microTOF using positive-mode. Recycling preparative GPC-HPLC was carried out on JAI LC-908 using preparative JAIGEL-2H, 2.5H, and 3H columns eluting with CHCl$_3$. X-Ray data were taken on a Rigaku-Raxis imaging plate system. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Symmetrical diareylethynes were prepared following the reported literature procedure.$^1$

General Procedure:

Reaction of meso-Bromo Porphyrins with Symmetrical Alkynes:

Pd$_2$(dba)$_3$ (1.37 mg, 1.5 $\mu$mol), (o-Tol)$_3$P (1.83 mg, 6.0 $\mu$mol), meso-bromoporphyrin 2 (30 $\mu$mol), and symmetrical alkynes (45 $\mu$mol) were weighted in air and transferred to a 10-mL septum-capped tube, which was evacuated and then purged with argon for five times followed by an addition of dry toluene (1.5 mL). Dicyclohexylmethylamine (Cy$_2$NMe) (29.3 mg, 0.15 mmol) was introduced via syringe
under argon atmosphere and the tube was closed and then the resulting reaction mixture
was heated at 110 °C for 16–24 h. The reaction mixture was cooled down to room
temperature, diluted with CHCl₃ (20 mL), filtered through a small plug of silica gel with
copious washings (CHCl₃). After removal of the solvent in vacuo, the residue was
purified by gel permeation chromatography (GPC) eluting with CHCl₃ to afford the
desired compounds in their respective yields as shown in Table 1.

**Compound Data for 2aNi:**

\(^1\)H NMR (600 MHz, CDCl₃, 50 °C): \(\delta = 8.91\) (s, 1H, *meso*-H), 8.41
(d, \(J = 4.6\) Hz, 1H, \(\beta\)-H), 8.34 (d, \(J = 4.6\) Hz, 1H, \(\beta\)-H), 8.15 (d, \(J =
4.6\) Hz, 1H, \(\beta\)-H), 8.09 (d, \(J = 4.6\) Hz, 1H, \(\beta\)-H), 8.06 (d, \(J = 5.0\) Hz,
1H, \(\beta\)-H), 7.72 (bs, 2H, Ar-\(o\)-H), 7.68 (bs, 1H, Ar-\(p\)-H), 7.67-7.64
(m, 2H, Ph), 7.63 (bs, 1H, Ar-\(p\)-H), 7.62 (bs, 2H, Ar-\(o\)-H),
7.54-7.48 (m, 3H, Ph), 7.42 (d, \(J = 5.0\) Hz, 1H, \(\beta\)-H), 7.40-7.37 (m, 2H, Ph), 7.36 (s, 1H,
\(\beta\)-H), 7.24-7.16 (m, 3H, Ph), 1.43 (s, 18H, tert-butyl-H), 1.39 (s, 18H, tert-butyl-H).
UV (CHCl₃): \(\lambda_{\text{max}} [\epsilon (\text{M}^{-1}\text{cm}^{-1})] = 757\) (sh) \((1.7 \times 10^3)\), 644 \((2.2 \times 10^3)\), 592 \((4.4 \times 10^3)\),
478 \((5.08 \times 10^4)\), 457 (sh) \((4.79 \times 10^4)\), 423 \((4.84 \times 10^4)\), 381 \((6.96 \times 10^4)\), 326 \((2.48 \times
10^4)\) nm.
HR-ESI-TOF MS: \(m/z = 918.4136\). Calcd for C₆₂H₆₀N₄Ni: 918.4166 [M]+

**Compound Data for 2bNi:**

\(^1\)H NMR (600 MHz, CDCl₃, 50 °C): \(\delta = 8.94\) (s, 1H, *meso*-H), 8.42 (d, \(J = 4.6\) Hz, 1H, \(\beta\)-H), 8.35 (d, \(J = 4.6\) Hz,
1H, \(\beta\)-H), 7.72 (bs, 2H, Ar-\(o\)-H), 7.68 (bs, 1H, Ar-\(p\)-H), 7.67-7.64
(m, 2H, Ph), 7.63 (bs, 1H, Ar-\(p\)-H), 7.62 (bs, 2H, Ar-\(o\)-H),
7.54-7.48 (m, 3H, Ph), 7.42 (d, \(J = 5.0\) Hz, 1H, \(\beta\)-H), 7.40-7.37 (m, 2H, Ph), 7.36 (s, 1H,
\(\beta\)-H), 7.24-7.16 (m, 3H, Ph), 1.43 (s, 18H, tert-butyl-H), 1.39 (s, 18H, tert-butyl-H).
UV (CHCl₃): \(\lambda_{\text{max}} [\epsilon (\text{M}^{-1}\text{cm}^{-1})] = 757\) (sh) \((1.7 \times 10^3)\), 644 \((2.2 \times 10^3)\), 592 \((4.4 \times 10^3)\),
478 \((5.08 \times 10^4)\), 457 (sh) \((4.79 \times 10^4)\), 423 \((4.84 \times 10^4)\), 381 \((6.96 \times 10^4)\), 326 \((2.48 \times
10^4)\) nm.
Hz, 1H, β-H), 8.17 (d, J = 4.6 Hz, 1H, β-H), 8.11 (d, J = 5.0 Hz, 2H, β-H), 7.79 (q, J = 8.3 Hz, 4H, Ar'-H), 7.71 (bd, J = 1.8 Hz, 2H, Ar-o-H), 7.69 (bd, J = 1.8 Hz, 1H, Ar-p-H), 7.65 (bd, J = 1.8 Hz, 1H, Ar-p-H), 7.61 (bd, J = 1.8 Hz, 2H, Ar-o-H), 7.49 (d, J = 8.3 Hz, 2H, Ar'-H), 7.43 (d, J = 8.3 Hz, 2H, Ar'-H), 7.37 (s, 1H, β-H), 7.35 (d, J = 5.0 Hz, 1H, β-H), 1.49 (s, 18H, tert-butyl-H), 1.43 (s, 18H, tert-butyl-H).

19F NMR (564.7 MHz, CDCl3, 50 ºC): δ = –62.39 (s), –62.53 (s).

UV (CHCl3): λmax [ε (M⁻¹ cm⁻¹)] = 760 (sh) (1.8 × 10³), 643 (2.9 × 10³), 591 (5.1 × 10³), 473 (5.89 × 10⁴), 457 (sh) (5.57 × 10⁴), 427 (4.75 × 10⁴), 381 (7.25 × 10⁴), 325 (sh) (2.57 × 10⁴) nm.

HR-ESI-TOF MS: m/z = 1054.3950. Calcd for C₆₄H₅₈F₆N₄Ni: 1054.3914 [M]⁺

Compound Data for 2cNi:

1H NMR (600 MHz, CDCl₃, 50 ºC): δ = 8.88 (s, 1H, meso-H), 8.39 (d, J = 4.6 Hz, 1H, β-H), 8.31 (d, J = 4.6 Hz, 1H, β-H), 8.13 (d, J = 4.6 Hz, 1H, β-H), 8.08 (d, J = 4.6 Hz, 1H, β-H), 8.05 (d, J = 5.0 Hz, 1H, β-H), 7.71 (bd, J = 1.8 Hz, 2H, Ar-o-H), 7.67 (bs, 1H, Ar-p-H), 7.624 (bs, 1H, Ar-p-H), 7.619 (bs, 2H, Ar-o-H), 7.56 (d, J = 8.7 Hz, 2H, Ar'-H), 7.48 (d, J = 5.0 Hz, 1H, β-H), 7.34 (d, J = 8.7 Hz, 2H, Ar'-H), 7.31 (s, 1H, β-H), 7.06 (d, J = 8.7 Hz, 2H, Ar'-H), 6.78 (d, J = 8.7 Hz, 2H, Ar'-H), 3.93 (s, 3H, O-Me), 3.79 (s, 3H, O-Me), 1.49 (s, 18H, tert-butyl-H), 1.43 (s, 18H, tert-butyl-H).

UV (CHCl₃): λmax [ε (M⁻¹ cm⁻¹)] = 765 (sh) (1.6 × 10³), 649 (2.1 × 10³), 596 (4.1 × 10³), 487 (4.8 × 10⁴), 460 (sh) (4.26 × 10⁴), 421 (5.04 × 10⁴), 389 (6.34 × 10⁴), 325 (2.45 × 10⁴) nm.
HR-ESI-TOF MS: $m/z = 978.4381$. Calcd for C$_{64}$H$_{64}$N$_4$NiO$_2$: 978.4377 [M]$^+$

**Compound Data for 2dNi:**

$^1$H NMR (600 MHz, CDCl$_3$, 50 °C): $\delta = 8.87$ (s, 1H, meso-H), 8.38 (d, $J = 5.0$ Hz, 1H, $\beta$-H), 8.32 (d, $J = 4.6$ Hz, 1H, $\beta$-H), 8.17 (d, $J = 4.6$ Hz, 1H, $\beta$-H), 8.08 (d, $J = 5.0$ Hz, 2H, $\beta$-H), 7.73 (bd, $J = 1.8$ Hz, 2H, Ar-o-H), 7.69 (bt, $J = 1.8$ Hz, 1H, Ar-p-H), 7.65 (d, $J = 2.3$ Hz, 1H, Th-5/5'-H), 7.63 (bd, $J = 1.8$ Hz, 1H, Ar-p-H) 7.62 (bd, $J = 1.8$ Hz, 2H, Ar-o-H), 7.50 (d, $J = 5.0$ Hz, 1H, $\beta$-H), 7.49 (s, 1H, $\beta$-H), 7.41 (d, $J = 2.3$ Hz, 1H, Th-3/3'-H), 7.32 (dd, $J = 3.7$, 5.5 Hz, 1H, Th-4/4'-H), 7.23 (dd, $J = 5.2$, 5.3 Hz, 2H, Th-5/5'-H & Th-3/3'-H), 7.01 (t, $J = 4.1$ Hz, 1H, Th-4/4'-H), 1.51 (s, 18H, tert-butyl-H), 1.43 (s, 18H, tert-butyl-H).

UV (CHCl$_3$): $\lambda_{\text{max}} [\varepsilon$ (M$^{-1}$ cm$^{-1}$)] = 783 (sh) (1.5 $\times$ 10$^3$), 651 (1.7 $\times$ 10$^3$), 599 (4.2 $\times$ 10$^3$), 487 (6.36 $\times$ 10$^4$), 458 (sh) (5.12 $\times$ 10$^4$), 427 (4.09 $\times$ 10$^4$), 385 (6.76 $\times$ 10$^4$) nm.

HR-ESI-TOF MS: $m/z = 930.3323$. Calcd for C$_{58}$H$_{56}$N$_4$NiS$_2$: 930.3294 [M]$^+$

**Compound Data for 2eNi:**

$^1$H NMR (600 MHz, CDCl$_3$, 50 °C): $\delta = 8.89$ (s, 1H, meso-H), 8.42 (d, $J = 5.0$ Hz, 1H, $\beta$-H), 8.39 (d, $J = 4.6$ Hz, 1H, $\beta$-H), 8.31 (d, $J = 4.6$ Hz, 2H, $\beta$-H), 8.10 (dd, $J = 3.8$, 4.9 Hz, 2H, $\beta$-H), 7.69-7.64 (m, 6H, Ar-o-H & Ar-p-H), 6.90 (s, 1H, $\beta$-H), 2.74 (t, $J = 8.2$ Hz, 2H, 1/1'-H), 2.27 (t, $J = 8.2$ Hz, 2H, 1/1'-H), 1.92 (m, 2H, 2/2'-H), 1.71 (m, 2H, 2/2'-H), 1.479 (s, 18H, tert-butyl-H), 1.471 (s, 18H, tert-butyl-H), 1.19 (t, $J = 8.2$ Hz, 3H, 3/3'-H), 1.11 (t, $J = 8.2$ Hz, 3H, 3/3'-H).
UV (CHCl₃): \( \lambda_{\text{max}} [\varepsilon (\text{M}^{-1}\text{cm}^{-1})] = 643 (2.0 \times 10^3), 569 (\text{sh}) (3.5 \times 10^3), 526 (7.0 \times 10^3), 468 (\text{sh}) (2.88 \times 10^4), 418 (8.69 \times 10^4), 378 (4.59 \times 10^4) \text{ nm.} \\

HR-ESI-TOF MS: \( m/z = 850.4483 \). Calcd for C₅₆H₆₄N₄Ni: 850.4479 [M⁺]

**Compound Data for 2aCu:**

UV (CHCl₃): \( \lambda_{\text{max}} [\varepsilon (\text{M}^{-1}\text{cm}^{-1})] = 665 (\text{sh}) (2.3 \times 10^3), 606 (4.3 \times 10^3), 486 (6.88 \times 10^3), 461 (\text{sh}) (5.99 \times 10^4), 391 (7.91 \times 10^4), 326 (2.71 \times 10^4) \text{ nm.} \\

HR-ESI-TOF MS: \( m/z = 923.4100 \). Calcd for C₆₂H₆₀N₄Cu: 923.4109 [M⁺]

**Compound Data for 2eCu:**

UV (CHCl₃): \( \lambda_{\text{max}} [\varepsilon (\text{M}^{-1}\text{cm}^{-1})] = 663 (1.3 \times 10^3), 594 (3.8 \times 10^3), 549 (6.7 \times 10^3), 466 (\text{sh}) (2.76 \times 10^4), 426 (1.1 \times 10^5), 390 (4.11 \times 10^4) \text{ nm.} \\

HR-ESI-TOF MS: \( m/z = 855.4485 \). Calcd for C₅₆H₆₄N₄Cu: 855.4422 [M⁺]

**Compound Data for 2aZn:**

\( ^1\text{H NMR} \) (600 MHz, CDCl₃, 25 °C): \( \delta = 9.11 \) (s, 1H, meso-H), 8.59 (d, \( J = 4.1 \text{ Hz}, 1\text{H}, \beta\text{-H} \)), 8.50 (d, \( J = 4.1 \text{ Hz}, 1\text{H}, \beta\text{-H} \)), 8.25 (d, \( J = 4.1 \text{ Hz}, 1\text{H}, \beta\text{-H} \)), 8.21 (d, \( J = 4.1 \text{ Hz}, 1\text{H}, \beta\text{-H} \)), 8.06 (d, \( J = 4.6 \text{ Hz}, 1\text{H}, \beta\text{-H} \)), 7.85 (bs, 2H, Ar-o-H), 7.75 (d, \( J = 7.3 \text{ Hz}, 2\text{H}, \text{Ph-o-H} \)), 7.73 (bs, 2H, Ar-o-H), 7.71 (s, 1H, Ar-p-H), 7.66 (s, 1H, Ar-p-H), 7.59–7.51 (m, 3H, Ph-m-H), 7.42 (d, \( J = 7.3 \text{ Hz}, 2\text{H}, \text{Ph-o-H} \)), 7.36 (d, \( J = 4.6 \text{ Hz}, 1\text{H}, \text{Ph-m-H} \))
\[ \delta = 9.15 \text{ (s, } 1\text{H, meso-H}), 8.62 \text{ (d, } J = 4.6 \text{ Hz, } 1\text{H, } \beta-H), 8.52 \text{ (d, } J = 4.1 \text{ Hz, } 1\text{H, } \beta-H), 8.27 \text{ (d, } J = 4.1 \text{ Hz, } 1\text{H, } \beta-H), 8.23 \text{ (d, } J = 4.1 \text{ Hz, } 2\text{H, } \beta-H), 8.11 \text{ (d, } J = 4.6 \text{ Hz, } 1\text{H, } \beta-H), 7.89-7.83 \text{ (m, } 4\text{H, Ar'-H }), 7.828 \text{ (bd, } J = 1.8 \text{ Hz, } 2\text{H, Ar-}o\text{-H)}, 7.73-7.70 \text{ [m, } 3\text{H, Ar-}o\text{-H (2H) & Ar-p-H (1H)]}, 7.66 \text{ (t, } J = 1.8 \text{ Hz, } 1\text{H, Ar-p-H)}, 7.49 \text{ (d, } J = 8.3 \text{ Hz, } 2\text{H, Ar'-H}), 7.43 \text{ (d, } J = 8.3 \text{ Hz, } 2\text{H, Ar'-H)}, 7.35 \text{ (s, } 1\text{H, } \beta-H), 7.29 \text{ (d, } J = 4.6 \text{ Hz, } 1\text{H, } \beta-H), 1.52 \text{ (s, } 18\text{H, tert-butyl-H}), 1.45 \text{ (s, } 18\text{H, tert-butyl-H}).
\]

\[ \delta = -63.38 \text{ (s), } -63.53 \text{ (s).}
\]

\[ \lambda_{\text{max}} = 620, 484, 419 \text{ (sh), } 398 \text{ nm}
\]

HR-ESI-TOF MS: \(m/z = 1060.3850\). Calcd for \(C_{64}H_{58}F_6N_4Zn\): 1060.3852 \([M]^+\)

**Compound Data for 2bZn:**

\[ \delta = 8.99 \text{ (s, } 1\text{H, meso-H}), 8.52 \text{ (d, } J = 4.1 \text{ Hz, } 1\text{H, } \beta-H), 8.40 \text{ (d, } J = 4.1 \text{ Hz, } 1\text{H, } \beta-H), 8.24 \text{ (d, } J = 4.1 \text{ Hz, } 1\text{H, } \beta-H), 8.21 \text{ (d, } J = 4.6 \text{ Hz, } 1\text{H, } \beta-H), 8.10 \text{ (d, } J = 5.0 \text{ Hz, } 1\text{H, } \beta-H), 7.63 \text{ (d, } J = 8.7 \text{ Hz, } 2\text{H, Ar''-H)}, 7.37 \text{ (d, } J = 5.0 \text{ Hz, } 1\text{H, } \beta-H),
\]
7.36 (d, J = 8.7 Hz, 2H, Ar'-H), 7.25 (s, 1H, β-H), 7.11–7.07 [m, 4H, Ar'-H (2H) & Ar-o-H (2H)], 7.02 (d, J = 2.3 Hz, 2H, Ar-o-H), 6.80 (d, J = 8.7 Hz, 2H, Ar'-H), 6.76 (t, J = 2.3 Hz, 1H, Ar-p-H), 6.72 (t, J = 2.3 Hz, 1H, Ar-p-H), 4.10 [t, J = 6.4 Hz, 4H, O-CH₂ (OC₈H₁₇)], 4.04 [t, J = 6.4 Hz, 4H, O-CH₂ (OC₈H₁₇)], 3.96 [s, 3H, O-Me (Ar')], 3.81 [s, 3H, O-Me (Ar')], 1.91–1.77 [m, 8H, (OC₈H₁₇)], 1.57–1.23 [m, 40H, (OC₈H₁₇)], 0.92–0.83 [m, 12H, Me (OC₈H₁₇)].

UV (CHCl₃): λmax = 692 (sh), 623, 495, 420 (sh), 402, 332 nm.

HR-ESI-TOF MS: m/z = 1272.6616. Calcd for C₈₀H₉₆N₄O₆Zn: 1272.6665 [M]+

**Compound Data for 3:**

A dilute solution of 2aZn (10 mg, 10.8 μmol) in CHCl₃ (200 mL) was stirred in an open atmosphere for overnight. The profile of the transformation was monitored through UV-spectrum, while noticing the complete change of the spectrum from purpurin-type to porphyrin-type. After removal of the solvent in vacuo, the residue was purified by silica gel chromatography eluting with CH₂Cl₂/MeOH to afford the desired compound in 87% yield.

¹H NMR (600 MHz, CDCl₃, 60 °C): δ = 10.28 (s, 1H, meso-H), 9.41–9.38 (m, 2H, β-H), 9.13 (d, J = 4.6 Hz, 1H, β-H), 9.10 (d, J = 4.6 Hz, 1H, β-H), 9.07 (bs, 1H, β-H), 8.97 (bs, 1H, β-H), 8.92 (bd, J = 3.7 Hz, 1H, β-H), 8.08 (s, 2H, Ar-o-H), 8.06 (s, 2H, Ar-o-H), 8.05–7.94 (m, 2H, Ph-H), 7.83 (s, 1H, Ar-p-H), 7.76 (s, 1H, Ar-p-H), 7.74–7.63 (m, 2H, Ph-H), 7.57–7.48 (m, 1H, Ph-H), 7.38 (t, J = 7.3 Hz, 2H, Ph-H), 7.35–7.29 (m, 1H, Ph-H), 7.21–7.11 (m, 2H, Ph-H), 1.54 (s, 18H, tert-butyl-H), 1.53 (s, 18H, tert-butyl-H).
\(^1\)H NMR (600 MHz, C\(_2\)D\(_2\)Cl\(_4\), 100 °C): \(\delta = 10.24\) (s, 1H, meso-H), 9.36-9.35 (m, 2H, \(\beta\)-H), 9.10 (d, \(J = 4.5\) Hz, 1H, \(\beta\)-H), 9.06 (d, \(J = 4.5\) Hz, 2H, \(\beta\)-H), 8.96 (s, 1H, \(\beta\)-H), 8.91 (d, \(J = 4.4\) Hz, 1H, \(\beta\)-H), 8.04 (s, 2H, Ar-\(\alpha\)-H), 8.02 (s, 2H, Ar-\(\alpha\)-H), 7.95 (d, \(J = 7.6\) Hz, 2H, Ph-H), 7.80 (s, 1H, Ar-\(p\)-H), 7.73 (s, 1H, Ar-\(p\)-H), 7.65 (d, \(J = 7.6\) Hz, 2H, Ph-H), 7.49 (t, \(J = 7.7\) Hz, 1H, Ph-H), 7.33 (t, \(J = 7.7\) Hz, 2H, Ph-H), 7.28 (t, \(J = 7.7\) Hz, 1H, Ph-H), 7.12 (t, \(J = 7.7\) Hz, 2H, Ph-H), 1.52 (s, 18H, tert-butyl-H), 1.47 (s, 18H, tert-butyl-H).

\(^{13}\)C NMR (600 MHz, CDCl\(_3\), 25 °C): \(\delta = 198.88, 194.11\) (carbonyl)

HR-ESI-TOF MS: \(m/z = 957.4103\). Calcd for C\(_{62}\)H\(_{61}\)N\(_4\)O\(_2\)Zn: 957.4081 [M + H]\(^+\)

UV (CHCl\(_3\)): \(\lambda_{max} = 599, 556, 431\) nm.

Reference:

$^1$H NMR for Compound 2aNi:
COSY for Compound 2aNi:
$^1$H NMR for Compound 2bNi:
$^1$H NMR for Compound 2cNi:
$^{1}H$ NMR for Compound 2dNi:
$^1$H NMR for Compound 2eNi:
$^1$H NMR for Compound 2aZn:
$^1$H NMR for Compound 2bZn:
$^1$H NMR for Compound 2fZn:
$^1$H NMR for Compound 3Zn at 60 °C:
$^1$H NMR for Compound 3Zn in C$_2$D$_2$Cl$_4$ at 100 °C:
$^{13}$C NMR for Compound 3:
COSY for Compound 3:
UV-vis Spectra of 2aNi, 2bNi, 2cNi, and 2dNi

![UV-vis Spectra Graph]

2aNi $\text{Ar} = \text{phenyl}$
2bNi $\text{Ar} = \text{phenyl-}CF_3$
2cNi $\text{Ar} = \text{phenyl-}OMe$
2dNi $\text{Ar} = \text{thiophene}$
**Computational Method**  All calculations were carried out using the *Gaussian03* program.\(^1\) All structures were optimized with Becke’s three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP),\(^2\) employing a basis set consisting of SDD\(^3\) for Ni and 6-31G(d) for the rest.

**Calculated Molecular Orbitals of Ni(II) Porphyrin and Ni(II) Dehydropurpurin**

