New Journal of Chemistry

Synthesis and characterization of eight new tetraphenylporphyrins bearing one or two ferrocenes on the β-pyrrole positions

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Supplementary Information

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Experimental

General Methods. $^1$H-NMR spectra were recorded as CDCl$_3$ solutions on a Bruker AM-300 instrument using residual solvent signal as an internal standard. Chemical shifts are given as δ values. FAB mass spectra were measured on a VG-4 spectrometer using m-nitrobenzyl alcohol (NBA) as a matrix. UV/vis spectra were recorded on a Varian Cary 50 Scan spectrophotometer in dichloromethane solution. Cyclic voltammetry was carried out with an Autolab electrochemical system, Eco Chemie equipped with PG Stat-12. Current-voltage curves were recorded using GPES, Eco Chemie software. A three electrode system was used and consisted of a platinum button working electrode, a platinum wire counter electrode and a saturated calomel reference electrode (SCE). This reference electrode was separated from the bulk of the solution by a fritted-glass bridge filled with solvent/supporting electrolyte mixture. All potentials are referenced to the SCE.

Chemicals. Silica gel 60 (70-230 and 230-400 mesh, Merck) was used for column chromatography. CH$_2$Cl$_2$ for electrochemistry was purchased from Aldrich Chemical Co. and purified by several washings with conc. H$_2$SO$_4$ and distilled over P$_2$O$_5$ under vacuum prior to use. Tetra-n-butylammonium Perchlorate (TBAP), from Aldrich Chemical Co., was recrystallized from ethyl acetate and dried under vacuum at 40 °C for at least one week prior to use. High-purity-grade nitrogen gas was purchased from Rivoira. C$_{60}$ was purchased from Term-USA. All other reagents and solvents were from Fluka Chem. Co., Aldrich Chem. Co. or Carlo Erba and were used as received. All the compounds gave satisfactory elemental analysis.

4-acetylphenylferrocene (9). Ferroceneboronic acid (0.925 g, 4.02 mmol) and 4-bromoacetophenone were dissolved in dry(Na) toluene (0.4 g, 2.01 mmol) under nitrogen. Anhydrous K$_2$CO$_3$ (1.11 g, 8.04 mmol) and PPh$_3$ (0.211 g, 0.804 mmol) were added and the mixture was purged with argon bubbling for 20 minutes, after that Pd(CH$_3$CO$_2$)$_2$. (45 mg, 0.201 mmol) was added and the solution was kept at 100°C for 48 hours. The solvent was evaporated under vacuum and the residue was redissolved in CHCl$_3$. The organic solution was washed with water and dried.
on anhydrous Na$_2$SO$_4$. The residue was chromatographed on silica gel column eluting with petroleum ether/diethyl ether, 95:5. The desired product was obtained in 62% of yield.

MS (EI): $m/z$: 304 [M$^+$]; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$(ppm) 7.90 (d, 2 H, $J$=8.0 Hz), 7.55 (d, 2H $J$=8.0 Hz), 4.74(s, 2H), 4.43(s, 2H), 4.06(s, 5H), 2.62(s, 3H).

4-ethynylphenylferrocene (10). 200 mg (0.658 mmol) of compound 9 were dissolved in 15 ml of dry DMF under nitrogen and 0.6 ml of Vilsmeier reagent$^{13}$ were added at 0º C using an ice bath. The reaction was kept for 3 hours at 0º C and later at 35º C for two days. The reaction mixture was hydrolyzed with a 20% sodium acetate water solution and extracted with three 50 ml portions of chloroform. The organic solution was washed with water and dried on anhydrous Na$_2$SO$_4$. The solvent was evaporated under vacuum and the residue purified on silica gel column using hexane/diethyl ether 70:30 mixture as eluant giving an overall yield of 40%. MS (EI): $m/z$: 286 [M$^+$], $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$(ppm) 7.44 (s, 4H), 4.67 (s, 2H), 4.37 (s, 2H), 4.05 (s, 5H), 3.12 (s, 1H)

2-(4'-ferrocenylethynyl)-5,10,15,20-tetraphenylporphyrin (1). 2-bromo-5,10,15,20-tetraphenylporphyrin, (96 mg, 0.140 mmol) was dissolved in 50 ml of dry THF under nitrogen and 0.3 ml of tetrabutylammonium fluoride (TBAF), 10% THF solution, were added. The solution was deaerated by argon bubbling for 10 minutes after that ethynylferrocene, (59 mg, 0.280 mmol) were added with further argon bubbling of 10 minutes. 30 mg of Pd(PPh$_3$)$_2$Cl$_2$ were added and after 20 minutes of argon bubbling, the solution was kept at 80º C for 12 hours under nitrogen. The resulting mixture was evaporated under vacuum and the residue chromatographed on a silica gel column, eluting with CHCl$_3$/hexane 30:70, affording 75 mg (0.091 mmol) of the desired compound in 65% of yield. MS(FAB): 823(M+H)$^+$; $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$(ppm) 9.02(s, 1H), 8.87(s, 2H), 8.82(m, 3H), 8.73(m, 1H), 8.24(m, 8H), 7.83(s, 12H), 4.38(s, 3H), 4.27(s, 6H), -2.66(s, 2H); UV/vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (nm): 426, 526, 566, 602, 660. Anal. Calcd. for C$_{56}$H$_{38}$N$_4$Fe: C, 81.74; H, 4.65; N, 6.80. Found: C, 82.01; H, 4.55; N, 6.90
2,3-[di-(4'-ferrocenylethynyl)]-5,10,15,20-tetraphenylporphyrin (3). 2,3-dibromo-5,10,15,20-tetraphenylporphyrin, (108 mg, 0.140 mmol) was dissolved in 50 ml of dry THF under nitrogen and 0.35 ml of tetrabutylammonium fluoride (TBAF), 10% THF solution, were added. The solution was deaerated by argon bubbling for 10 minutes after that ethynylferrocene, (118 mg, 0.56 mmol) were added with further argon bubbling of 10 minutes. 40 mg of Pd(PPh₃)₂Cl₂ were added and after 20 minutes of argon bubbling, the solution was kept at 80°C for 12 hours under nitrogen. The resulting mixture was evaporated under vacuum and the residue chromatographed on a silica gel column, eluting with CHCl₃/hexane 50:50, affording 23 mg (0.022 mmol) of the desired compound in 25% of yield. MS(FAB): 1030(M⁺); ¹H-NMR (300 MHz, CDCl₃): δ(ppm) 8.83(d, 2H, J=6.4 Hz), 8.74(d, 2H, J=6.4 Hz), 8.72(s, 2H), 8.25(m, 8H), 7.93(m, 2H), 7.84(m, 4H), 7.78(m, 6H), 4.48(s, 4H), 4.33(s, 4H), 4.28(s, 10H), -2.48(s, 2H); UV/vis (CH₂Cl₂): λₘₐₓ (nm): 436, 530, 576, 611, 665. Anal. Calcd. for C₆₈H₄₆N₄Fe₂: C, 79.23; H, 4.49; N, 5.43. Found: C, 79.02; H, 4.60; N, 5.40

2-(4'-ferrocenylphenylethynyl)-5,10,15,20-tetraphenylporphyrin (5). 2-bromo-5,10,15,20-tetraphenylporphyrin, (96 mg, 0.140 mmol) was dissolved in 50 ml of dry THF under nitrogen and 0.3 ml of tetrabutylammonium fluoride (TBAF), 10% THF solution, were added. The solution was deaerated by argon bubbling for 10 minutes after that ethynylphenylferrocene (10), (80 mg, 0.280 mmol) were added with further argon bubbling of 10 minutes. 30 mg of Pd(PPh₃)₂Cl₂ were added and after 20 minutes of argon bubbling, the solution was kept at 80°C for 12 hours under nitrogen. The resulting mixture was evaporated under vacuum and the residue chromatographed on a silica gel column, eluting with CHCl₃/hexane 40:60, affording 75.3 mg (0.091 mmol) of the desired compound in 60% of yield. MS(FAB): 899(M+H)⁺; ¹H-NMR (300 MHz, CDCl₃): δ(ppm) 9.09(s, 1H), 8.87(s, 2H), 8.82(d, 2H), 8.73(m, 2H), 8.24(m, 8H), 7.83(m, 12H), 7.42(d, 2H, J=8.3 Hz), 7.29(d, 2H, J=8.3 Hz) 4.65(s, 2H), 4.38(s, 2H), 4.27(s, 5H), -2.66(s, 2H); UV/vis (CH₂Cl₂): λₘₐₓ
anal. calcd. for C_{62}H_{42}N_{4}Fe: C, 82.84; H, 4.70; N, 6.23. found: C, 83.02; H, 4.61; N, 6.33

2,3-[di-(4'-ferrocenylphenylethynyl)]-5,10,15,20-tetraphenylporphyrin (7). 2,3-dibromo-5,10,15,20-tetraphenylporphyrin, (108 mg, 0.140 mmol) was dissolved in 50 ml of dry THF under nitrogen and 0.35 ml of tetrabutylammonium fluoride (TBAF), 10% THF solution, were added. The solution was deareted by argon bubbling for 10 minutes after that ethynylphenylferrocene (10), (120 mg, 0.320 mmol) were added with further argon bubbling of 10 minutes. 40 mg of Pd(PPh_{3})_{2}Cl_{2} were added and after 20 minutes of argon bubbling, the solution was kept at 50\(^{\circ}\) C for 12 hours under nitrogen. The resulting mixture was evaporated under vacuum and the residue chromatographed on a silica gel column, eluting with CHCl\(_{3}/\)hexane 50:50, affording 25 mg (0.024 mmol) of the desired compound in 25% of yield. MS(FAB): 1183(M\(^{+}\)); \(^{1}\)H-NMR (300 MHz, CDCl\(_{3}\)): \(\delta\) (ppm) 8.86(d, 2H, J=5.9 Hz), 8.82(d, 2H, J=5.9 Hz), 8.73(s, 2H), 8.29(m, 8H), 7.79(m, 12H), 7.42(d, 4H, J=10.8 Hz), 7.33(d, 4H, J=10.8 Hz), 4.70(s, 4H), 4.38(s, 4H), 4.07(s, 10H), -2.60(s, 2H); UV/vis (CH\(_{2}\)Cl\(_{2}\)): \(\lambda_{\text{max}}\) (nm): 440, 532, 573, 609, 672. Anal. calcd. for C_{80}H_{54}N_{4}Fe_{2}: C, 81.22; H, 4.60; N, 4.73. found: C, 80.98; H, 4.70; N, 4.56

General procedure for zinc insertion. To a solution of starting compound in chloroform, a saturated solution of Zn(AcO)_2 in methanol was added and the mixture was left to react at room temperature under nitrogen for 2 h. The solvent was evaporated and the product was purified using a plug of silica gel, eluting with chloroform.

[2-(4'-ferrocenylethynyl)-5,10,15,20-tetraphenylporphyrin]-Zn (2). Yield: 97%. MS(FAB), m/z: 886, [M]\(^{+}\); \(^{1}\)H-NMR (300 MHz, CDCl\(_{3}\)): \(\delta\) (ppm) 9.18(s, 1H), 8.92(m, 4H), 8.82(d, 2H, J=7.1 Hz), 8.75(d, 2H, J=7.1 Hz), 8.24(m, 8H), 7.80(m, 12H), 4.68(s, 1H), 4.42(s, 2H), 4.25(s, 6H), UV/vis...
(CH₂Cl₂): $\lambda_{\text{max}}$ (nm): 432, 566, 602. Anal. Calcd. for C₅₆H₃₆N₄FeZn: C, 75.90; H, 4.09; N, 6.32. Found: C, 75.71; H, 4.25; N, 6.50

2,3-[di-(4'-ferrocenylethynyl)]-5,10,15,20-tetraphenylporphyrin-Zn(4). Yield: 95%. MS(FAB), 1094, [M]+; $^1$H-NMR (300 MHz, CDCl₃): δ(ppm) 8.86(d, 4H), 8.71(d, 2H), 8.22(m, 8H), 7.75(m, 12H), 4.34(s, 4H), 4.27(s, 4H), 4.19(s, 10H), UV/vis (CH₂Cl₂): $\lambda_{\text{max}}$ (nm): 445, 575, 617. Anal. Calcd. for C₈₀H₄₆N₄ZnFe₂: C, 74.64; H, 4.05; N, 5.12. Found: C, 74.42; H, 4.20; N, 5.20

2-(4'-ferrocenylphenylethynyl)-5,10,15,20-tetraphenylporphyrin-Zn(6). Yield: 96%. MS(FAB), 963, [M+H]+; $^1$H-NMR (300 MHz, CDCl₃): δ(ppm) 9.21(s, 1H), 8.84(m, 5H), 8.82(d, 2H), 8.75(d, 1H), 8.21(m, 8H), 7.75(m, 12H), 7.45(d, 2H), 4.72(s, 2H), 4.39(s, 2H), 4.10(s, 5H), UV/vis (CH₂Cl₂): $\lambda_{\text{max}}$ (nm): 436, 565, 602. Anal. Calcd. for C₆₂H₄₄N₄ZnFe: C, 77.38; H, 4.18; N, 5.82. Found: C, 77.02; H, 4.280; N, 5.60

2,3-[di-(4'-ferrocenylphenylethynyl)]-5,10,15,20-tetraphenylporphyrin-Zn(8). Yield: 95%. MS(FAB), 1246, [M]+; $^1$H-NMR (300 MHz, CDCl₃): δ(ppm) 8.78(d, 4H), 8.62(d, 2H), 8.21(m, 8H), 7, 85(d,4H), 7.25(d, 4H), 7.25(m, 12H), 4.68(s, 5H), 4.59(s, 4H), 4.12(s, 9H), UV/vis (CH₂Cl₂): $\lambda_{\text{max}}$ (nm): 449, 576, 616. Anal. Calcd. for C₈₀H₅₂N₄ZnFe₂: C, 77.09; H, 4.20; N, 4.49. Found: C, 77.02; H, 4.30; N, 4.40
UV-visible spectra of compound 1, $4.8 \cdot 10^{-6}$ M in CH$_2$Cl$_2$

UV-visible spectra of compound 2, $4.0 \cdot 10^{-6}$ M in CH$_2$Cl$_2$
UV-visible spectra of compound 3, $4.8 \cdot 10^{-6}$ M in CH$_2$Cl$_2$

UV-visible spectra of compound 4, $4.8 \cdot 10^{-5}$ M in CH$_2$Cl$_2$
UV-visible spectra of compound 5, $4.8 \cdot 10^{-6}$ M in CH$_2$Cl$_2$

UV-visible spectra of compound 6, $4.8 \cdot 10^{-6}$ M in CH$_2$Cl$_2$
UV-visible spectra of compound 7,  M in CH₂Cl₂

UV-visible spectra of compound 8,  M in CH₂Cl₂
$^1$H NMR spectrum of compound 1
$^1$H NMR spectrum of compound 2

C\textsubscript{3}D\textsubscript{3}
$^1$H NMR spectrum of compound 3
$^1$H NMR spectrum of compound 4
$^1$H NMR spectrum of compound 5
$^1$H NMR spectrum of compound 6
$^1$H NMR spectrum of compound 7
$^1$H NMR spectrum of compound 8
Cyclic voltammimtries of compound 1 in CH₂Cl₂ 0.1 M TBAP

Cyclic voltammimtries of compound 2 in CH₂Cl₂ 0.1 M TBAP
Cyclic voltammetries of compound 3 in CH$_2$Cl$_2$ 0.1 M TBAP
Cyclic voltammetries of compound 4 in CH₂Cl₂ 0.1 M TBAP
Cyclic voltammetries of compound 5 in CH₂Cl₂ 0.1 M TBAP

Cyclic voltammetries of compound 6 in CH₂Cl₂ 0.1 M TBAP
Cyclic voltammetries of compound 7 in CH$_2$Cl$_2$ 0.1 M TBAP
Cyclic voltammetries of compound 8 in CH$_2$Cl$_2$ 0.1 M TBAP