Synthesis of β-Arylporphyrins and Oligophenylenediporphyrins by the Suzuki–Miyaura Reaction

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Received 9 September 2009; revised 16 September 2009

Dedicated to Professor Peter Stanetty, Vienna University of Technology, on the occasion of his 65th birthday

Abstract: Several β-aryl-substituted porphyrins were prepared in good yields by Suzuki–Miyaura cross-coupling of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,10,15,20-tetraphenylporphinatozinc(II) with various aryl bromides. Additionally, syntheses of β,β′-diporphyrins linked by biphenylene or quaterphenylene units were examined.

Key words: Suzuki–Miyaura reaction, cross-coupling, oligophenylenes, porphyrins, coupling

The search for new tetrapyrrole macrocycles with particular features for specific applications (e.g., photodynamic therapy (PDT) of cancer, catalysis, electronics, solar-cell production, etc.) has become a target for several research groups.[1] Many approaches have been explored to develop or improve methods that permit the synthesis of novel porphyrin derivatives by such reactions as macrocycle modification,[2] Diels–Alder,[3] 1,3-dipolar cycloaddition,[4] electrocyclization,[5] or cyclopropanation[6] reactions.

β-Functionalization of porphyrins merits considerable attention because of the diversity of structural features that can be introduced into the macrocycle. Of particular importance are methods that lead to reduced porphyrins (chlorins or bacteriochlorins) or to π-extended porphyrin derivatives that show strong absorption of light at wavelengths near or above 600 nm, a requirement for photosensitizers used in PDT.[1,7]

The Suzuki–Miyaura coupling reaction of organoboron compounds with aryl halides in the presence of a palladium-catalyst is one of the most versatile methods for constructing carbon–carbon bonds, particularly those in unsymmetrical bisaryl systems.[8] Suzuki–Miyaura coupling reactions have also been extensively used in the functionalization of porphyrins, mainly at the *meso* positions.[9,10]

However, there are few reports of studies involving this type of reaction in the structural modification of *meso*-tetraarylporphyrins at the β-position of the pyrrole moieties.[11–15] With this in mind, we decided to explore the versatility of the Suzuki–Miyaura coupling reaction in the preparation of *meso*-tetraarylporphyrins bearing aryl groups at the β-positions of the pyrrole rings. We found that this method can be successfully used to synthesize a range of β-aryl-substituted porphyrins, including compounds that contain two porphyrin units linked through an oligophenylene group.

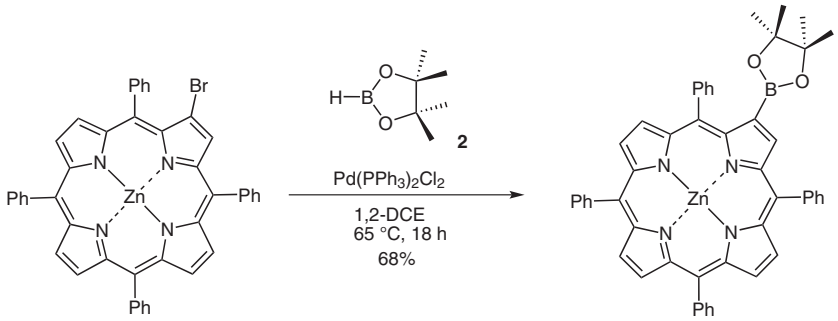
The starting porphyrin boronate **3** was prepared by a method similar to that reported by Suslick.[11] The palladium-catalyzed Suzuki coupling reaction of 2-bromo-5,10,15,20-tetraphenylporphinatozinc(II) (**1**) with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**; pinacolborane) was carried out in a sealed Schlenk tube in degassed anhydrous 1,2-dichloroethane at 65 °C overnight (Scheme 1).

The porphyrin boronate **3** was then treated with a series of aryl bromides (**4a–d**) to give high yields of the corresponding β-aryl-substituted porphyrins **5a–d** (Scheme 2). The reactions were carried out in a mixture of toluene and *N*,*N*-dimethylformamide containing tetrakis(triphenyl)palladium as a catalyst and cesium carbonate as the base.

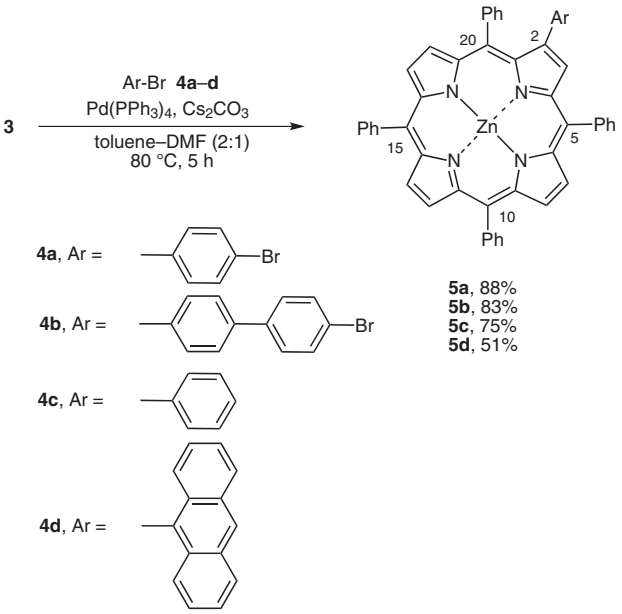
The method was also used to functionalize the bromoporphyrin derivative **5b**. In this way, the Suzuki coupling reaction of **5b** with porphyrin **3** gave the β,β-diporphyrin **6** in 18% yield (Scheme 3). Most of the unreacted porphyrin **5b** was recovered from the reaction mixture. All attempts to react the bromoporphyrin **5a** with porphyrin **3** to afford the corresponding phenylenediporphyrin were unsuccessful, probably as a result of steric hindrance.

The use of bromoaryl porphyrins **5a** and **5b** as aryl bromides in Suzuki coupling reactions with other pinacol boranes was also studied. We found that these porphyrins react with the commercially available 4-hydroxy-3,5-dimethylphenylboronic acid pinacol ester **7** under conventional Suzuki coupling conditions (Scheme 4) to give the expected cross-coupling products **8a** and **8b** in 37% and 26% yields, respectively. In these reactions, the dimeric products **6** and **9** were also formed in 19% and 41% yields, respectively, through self-coupling of the aryl bromide. The self-coupling of aryl bromides under the Suzuki–Miyaura coupling conditions has been previously reported.[16]

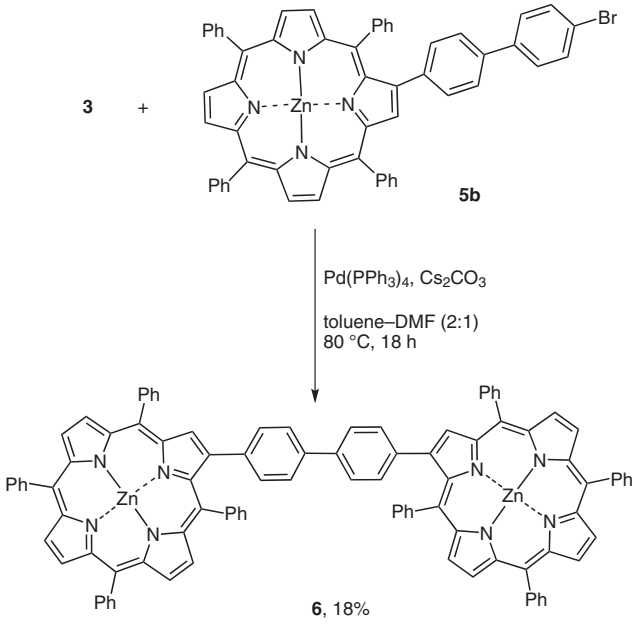
SYNTHESIS 2010, No. 3, pp 0510–0514
Advanced online publication: 20.11.2009
DOI: 10.1055/s-0029-1217114; Art ID: Z19309SS



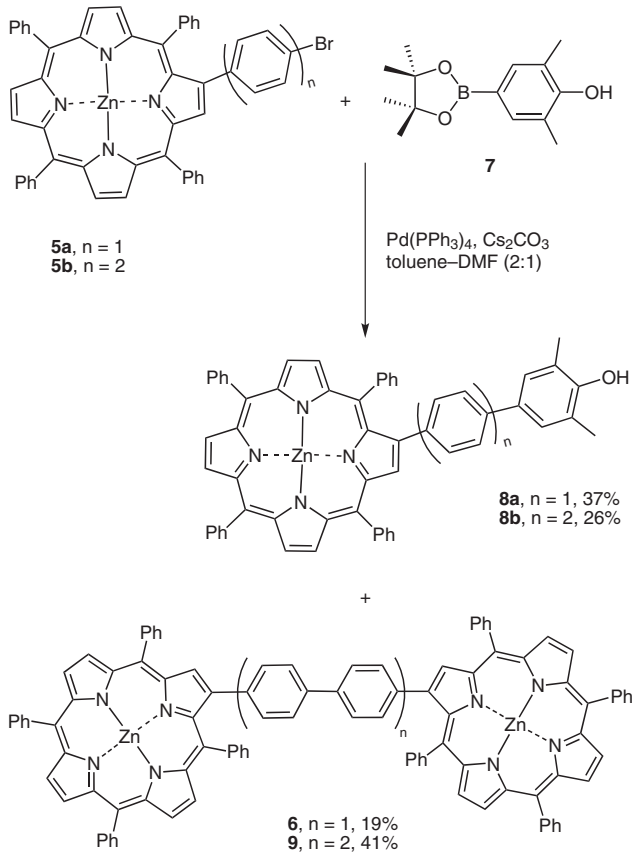
Scheme 1 Synthesis of the starting porphyrin boronate **3** by a Suzuki–Miyaura Reaction



Scheme 2 The Suzuki–Miyaura reaction of porphyrin boronate **3** and with aryl bromides **4**

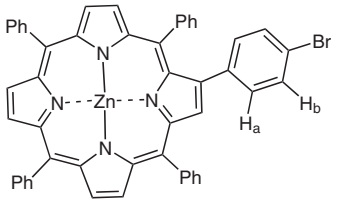


Scheme 3 Synthesis of phenylenediporphyrin **6**

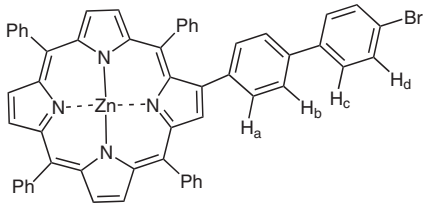


Scheme 4 Suzuki–Miyaura reaction between β-bromoarylporphyrins **5** and 4-hydroxy-3,5-dimethylphenylboronic acid pinacol ester (**7**)

The structures of the new compounds were assigned on the basis of their ^{1}H and ^{13}C NMR spectra, and their molecular formulas were confirmed by high-resolution mass spectroscopy. 2-D NMR correlation spectroscopy (COSY), heteronuclear multiple bond correlation (HMBC) spectroscopy, and heteronuclear single quantum coherence (HSQC) spectroscopy were also obtained to identify the resonances of some protons unequivocally. Because compounds **5c** and **5d** have already been prepared by another method,[17] their spectral data are not reported (their NMR spectra were identical to those already reported).



5a



5b

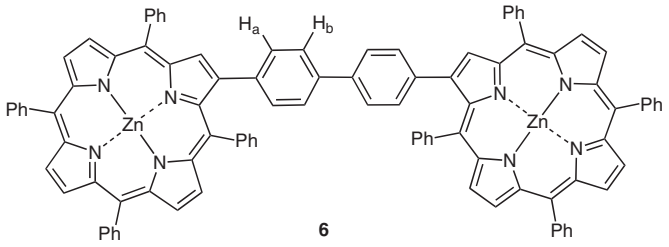
Figure 1 Structures of β-bromophenyl- and β-bromobiphenylporphyrins

The ^{1}H NMR spectrum of compound **5a** shows two doublets at 8.80 and 8.87 ppm, one singlet at 8.86 ppm, and one multiplet at 8.92–8.97 ppm corresponding to the seven β-pyrrolic protons. The *ortho* protons of the 5-, 10-, and 15-phenyl groups give a multiplet between 8.20 and 8.23 ppm, whereas the *ortho* protons of the 20-phenyl group appear as a multiplet at 7.84–7.86 ppm. The *meta* and *para* protons of the 5-, 10-, and 15-phenyl groups appear as multiplets at 7.71–7.77 ppm, whereas the *meta* and *para* protons of the 20-phenyl group appear as multiplets at 7.25–7.28 and 7.38–7.40 ppm, respectively. The resonance of the H_a protons of the 2-aryl group (Figure 1) appear as a doublet at 7.25 ppm (J = 8.4 Hz), whereas the doublet at 7.20 ppm (J = 8.4 Hz) is due to the resonance of protons H_b. The ^{1}H NMR spectrum of compound **5b** shows a similar profile to that of **5a**, both for the signals corresponding to the β-pyrrolic protons and the *meso*-phenyl protons. The main differences are the signals related to the resonances of the biphenyl protons. The signal that appears as a doublet at 7.64 ppm (J = 8.2 Hz) is due to the resonance of H_d and the doublet at 7.49 ppm (J = 8.2 Hz) is due to the resonance of H_c. The signals related to the resonances of the protons H_b and H_a appear as two multiplets at 7.40–7.42 and 7.55–7.57 ppm, respectively. The resonances of these protons were identified by the COSY, HMBC, and HSQC spectroscopy.

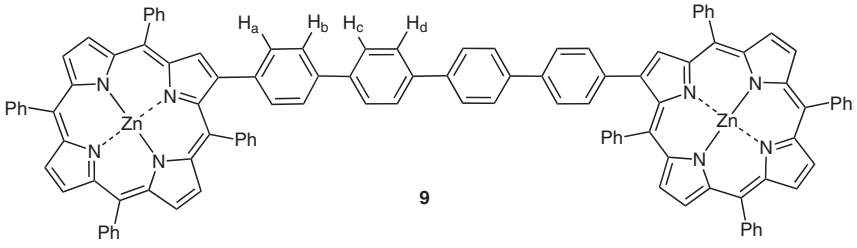
The ^{1}H NMR spectra of porphyrins **8a** and **8b** are quite similar. Their distinctive signals are those corresponding to the OH proton (singlets at 4.51 ppm for **8a** and 4.47 ppm for **8b**) and the methyl groups (singlets at 2.35 and at 2.31 ppm, respectively, for **8a** and **8b**). The resonance of the OH proton disappeared when deuterium oxide was added to the NMR tube. The ^{1}H NMR spectra of dimers **6** and **9** are very similar to those of the corresponding bromo-substituted porphyrins **5a** and **5b**. These spectra show that the two molecules have a high symmetry (Figure 2).

Interest in the synthesis of multiporphyrin materials (dimers and oligomers) is growing because of their potential applications[18] as models in light harvesting,[19] as molecular photonic and electronic wires,[20] as catalysts,[21] and as photosensitizers for PDT.[22] We have shown that new β-aryl *meso*-tetraphenylporphyrins can be obtained in high yields by Suzuki–Miyaura coupling. We have also shown that this approach is a powerful tool for preparing novel compounds containing two porphyrin moieties linked by an oligophenylene unit. The new compounds are potentially useful for the applications discussed above.

2-Bromo-5,10,15,20-tetraphenylporphyrinatozinc(II) was prepared according to the literature.[23] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300.13 and 75.47 MHz, respectively or on a Bruker Avance 500 spectrometer at 500.13 and 125.77 MHz for ^{1}H and ^{13}C, respectively. $CDCl_3$ was used as the solvent and TMS as the internal reference, and the chemical shifts are expressed in δ (ppm). Unequivocal ^{1}H assignments were made by 2D COSY and NOESY experiments (mixing time 800 ms),



6



9

Figure 2 Structures of phenylenediporphyrins **6** and **9**

whereas ^{13}C assignments were made on the basis of 2D HSQC and HMBC experiments (the delay for long-range *J* C/H couplings were optimized for 7 Hz). HRMS were recorded on a VG AutoSpec M mass spectrometer using $CHCl_3$ as the solvent and 3-nitrobenzyl alcohol (NBA) as the matrix. The UV/Vis spectra were recorded on an UV-2501 PC Shimatzu spectrophotometer with $CHCl_3$ as the solvent. Flash chromatography was carried out on silica gel (230–400 mesh). Preparative TLC was carried out on 20 × 20 cm glass plates coated with silica gel (1 mm thick). Analytical TLC was carried out on plastic sheets precoated with silica gel (Merck 60, 0.2 mm thick).

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-5,10,15,20-tetraphenylporphyrinatozinc(II) (3)

2-Bromo-5,10,15,20-tetraphenylporphyrinatozinc(II) (37.6 mg, 49.7 μmol), $Pd(PPh_3)_2Cl_2$ (8.92 mg, 12.7 μmol), anhyd DCE (12 mL), Et_3N (0.17 mL), and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.3 mL, 2079 μmol) were placed in a 50-mL Schlenk tube. The solvent was degassed by repeated sonication for 0.5–1 min under reduced pressure and then the mixture was stirred for 18 h at 65 °C. The reaction was quenched with aq NaCl (25 mL) and the mixture was extracted with CH_2Cl_2 (2 × 25 mL). The organic layer was washed with H_2O (25 mL), dried (Na_2SO_4), and concentrated. The residue was purified by flash chromatography ($CHCl_3$); yield: 68%. The NMR data were identical to those previously reported.[11]

Coupling of Boranes 3 or 7 with Aryl Halides 4 or 5; General Procedure

A 25-mL Schlenk tube was charged with borane **3** or **7** (47.3 μmol), aryl bromide **4** or **5** (144 μmol), Cs_2CO_3 (42 mg, 128.9 μmol), $Pd(PPh_3)_4$ (25 mg, 21.6 μmol), DMF (1 mL), and toluene (2 mL). The solvent was degassed by repeated sonication for 0.5–1 min under reduced pressure, and the mixture was stirred for 5 h (or 18 h) at 80 °C. The reaction was quenched with aq NaCl (25 mL) and the mixture was extracted with CH_2Cl_2 (2 × 25 mL). The organic layer was washed with H_2O (25 mL), dried (Na_2SO_4), and concentrated. The residue was purified by preparative TLC [gradient: hexane–$CHCl_3$ (2:1) to $CHCl_3$].

2-(4-Bromophenyl)-5,10,15,20-tetraphenylporphyrinatozinc(II) (5a)

Yield: 88%.

UV/Vis ($CDCl_3$): λ_{max} (log ε) = 422 (5.72), 511 (3.52), 549 (4.32), 586 nm (3.49).

^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.20 (d, *J* = 8.4 Hz, 2 H, H_b), 7.25–7.28 (m, 2 H, 20-Ph-H_m), 7.25 (d, *J* = 8.4 Hz, 2 H, H_a), 7.38–7.40 (m, 1 H, 20-Ph-H_p), 7.71–7.77 (m, 9 H, 5,10,15-Ph-$H_{m,p}$), 7.84–7.86 (m, 2 H, 20-Ph-H_o), 8.20–8.23 (m, 6 H, 5,10,15-Ph-H_o), 8.80 (d, *J* = 4.7 Hz, 1 H, H-12 or H-13), 8.86 (s, 1 H, H-3), 8.87 (d, *J* = 4.7 Hz, 1 H, H-13 or H-12), 8.92–8.97 (m, 4 H, H-7,8,17,18).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 119.8, 121.6, 126.0, 126.5, 126.6, 127.1, 127.5, 130.2, 131.5, 131.8, 132.0, 132.1, 132.2, 132.7, 134.3, 134.4, 135.1 (C-3), 135.6, 138.2, 141.3, 142.6, 142.8, 146.3, 147.7, 150.2, 150.3, 151.2.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{50}H_{32}BrN_4Zn$: 831.1096; found: 831.1121.

2-(4′-Bromobiphenyl-4-yl)-5,10,15,20-tetraphenylporphyrinatozinc(II) (5b)

Yield: 83%.

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 422 (5.61), 511 (3.42), 549 (4.24), 586 (3.36) nm.

^1H NMR (500.13 MHz, $CDCl_3$): δ = 7.14–7.16 (m, 1 H, 20-Ph-H_p), 7.20–7.22 (m, 2 H, 20-Ph-H_m), 7.40–7.42 (m, 2 H, H_b), 7.49 (d, *J* = 8.2 Hz, 2 H, H_c), 7.55–7.57 (m, 2 H, H_a), 7.64 (d, *J* = 8.24 Hz, 2 H, H_d), 7.71–7.77 (m, 9 H, 5,10,15-Ph-$H_{m,p}$), 7.88 (d, 2 H, *J* = 7.5 Hz, 20-Ph-H_o), 8.21–8.24 (m, 6 H, 5,10,15-Ph-H_o), 8.81 (d, *J* = 4.6 Hz, 1 H, H-12 or H-13), 8.87 (d, *J* = 4.6 Hz, 1 H, H-13 or H-12), 8.94–8.97 (m, 5 H, H-3,7,8,17,18).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 121.9, 125.3, 125.7, 125.9, 126.6, 127.5, 128.2, 128.5, 128.6, 129.0, 130.5, 130.7, 131.9, 132.0, 132.2, 134.4, 135.5, 135.8, 136.4, 137.9, 141.4, 147.0, 150.3.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{56}H_{36}BrN_4Zn$ 907.1409; found: 907.1401.

2,2′-(Biphenyl-4,4′-diyl)bis[(5,10,15,20-tetraphenylporphyrinatozinc(II)] (6)

^1H NMR (500.13 MHz, $CDCl_3$): δ = 7.28–7.29 (m, 2 H, 20-Ph-H_p), 7.36–7.39 (m, 8 H, H_b and 20-Ph-H_m), 7.46 (d, *J* = 8.0 Hz, 4 H, H_a), 7.70–7.74 (m, 18 H, 5,10,12-Ph-$H_{m,p}$), 7.94–7.95 (m, 4 H, 20-Ph-H_o), 8.82–8.27 (m, 12 H, 5,10,15-Ph-H_o), 8.81 (d, *J* = 4.6 Hz, 2 H, H-12 or H-13), 8.83 (d, *J* = 4.6 Hz, 2 H, H-13 or H-12), 8.87–8.89 (m, 4 H, H-β) 8.90–8.91 (m, 6 H, H-β) ppm.

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 119.9, 120.2, 120.7, 125.58, 125.6, 126.9, 130.4, 126.9, 130.4, 131.4, 131.6, 132.8, 134.3, 134.4, 134.7, 135.5, 135.8, 137.4, 138.7, 142.0, 143.3, 143.5, 145.4, 146.5, 147.6, 148.0, 149.8, 149.9, 150.0, 150.1, 150.9 ppm.

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 425 (5.07), 551 (3.81), 587 (3.16), 632 (2.89) nm.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{100}H_{63}N_8Zn_2$: 1503.3753; found: 1503.3730.

2-(4′-Hydroxy-3′,5′-dimethylbiphenyl-4-yl)-5,10,15,20-tetraphenylporphyrinatozinc(II) (8a)

Yield: 37%.

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 425 (5.09), 552 (3.80), 593 (3.13), 652 nm (2.15).

^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.35 (s, 6 H, CH_3), 4.51 (s, 1 H, OH), 7.13–7.38 (m, 9 H, H_a, H_b, H_c, 20-Ph-$H_{m,p}$), 7.71–7.77 (m, 9 H, 5,10,15-Ph-$H_{m,p}$), 7.87–7.90 (m, 2 H, 20-Ph-H_o), 8.23–8.25 (m, 6 H, 5,10,15-Ph-H_o), 8.81 (d, *J* = 4.6 Hz, 1 H, H-12 or H-13), 8.87 (d, *J* = 4.6 Hz, 1 H, H-13 or H-12), 8.92–8.97 (m, 5 H, H-3,7,8,17,18).

^{13}C NMR (75.47 MHz, $CDCl_3$–Py-d_5): δ = 16.8 (CH_3), 119.7, 120.0, 120.5, 121.6, 124.7, 125.1, 125.6, 125.9, 126.2, 126.7, 126.8, 127.9, 130.1, 130.7, 131.1, 131.3, 131.4, 132.0, 132.36, 134.2, 137.6, 137.7, 141.7, 143.1, 143.1, 143.3, 146.4, 146.5, 147.4, 150.0, 152.9.

HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{58}H_{40}N_4OZn$: 872.24936; found: 872.24881.

2-(4″-Hydroxy-3″,5″-dimethyl-1,1′:4′,1″-terphenyl-4-yl)-5,10,15,20-tetraphenylporphyrinatozinc(II) (8b)

UV/Vis ($CHCl_3$): λ_{max} (log ε) = 422 (5.73), 508 (3.52), 550 (4.34), 586 nm (2.60).

^1H NMR (500.13 MHz, $CDCl_3$): δ = 2.32 (s, 6 H, CH_3), 4.47 (s, 1 H, OH), 7.22–7.24 (m, 1 H, 20-Ph-H_p), 7.30–7.32 (m, 2 H, 20-Ph-H_m), 7.33–7.34 (s, 2 H, H_e), 7.38–7.43 (m, 8 H, $H_{a,b,c,d}$), 7.71–7.77 (m, 9 H, 5,10,15-Ph-$H_{m,p}$), 7.89–7.90 (m, 2 H, 20-Ph-H_o), 8.21–8.25 (m, 6 H, 5,10,15-Ph-H_o), 8.82 (d, *J* = 4.6 Hz, 1 H, H-12 or H-13), 8.87 (d, *J* = 4.6 Hz, 1 H, H-12 or H-13), 8.95–8.97 (m, 5 H, H-3,7,8,17,18).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 16.1 (CH_3), 29.7, 34.8, 78.3, 81.4, 120.9, 123.1, 123.6, 125.8, 125.9, 126.5, 126.7, 126.8, 127.1, 127.2, 127.3, 127.5, 128.6, 128.7, 130.6, 131.4, 131.9, 132.7, 134.3, 134.4, 135.7, 142.7, 142.9, 150.1, 153.2.

HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{64}H_{44}N_4OZn$: 948.28066; found: 948.27976.

2,2′-(1,1′:4′,1″:4″,1‴-Quaterphenyl-4,4‴-diyl)bis[5,10,15,20-tetraphenylporphyrinatozinc(II)] (9)
Yield: 14%.

UV/Vis ($CHCl_3$–MeOH, 1:99): λ_{max} (log ε) = 423 (5.33), 508 (3.40), 550 (4.02), 586 nm (3.31).

^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 7.21–7.30 (m, 4 H, 20-Ph-H_m), 7.30–7.31 (m, 2 H, 20-Ph-H_p), 7.38–7.43 (m, 4 H, H_b), 7.52–7.53 (m, 4 H, H_a), 7.68–7.69 (m, 8 H, $H_{a,b}$), 7.18–7.77 (m, 18 H, 5,10,15-Ph-$H_{m,p}$), 7.89–7.90 (m, 4 H, 20-Ph-H_o), 8.21–8.25 (m, 12 H, 5,10,15-Ph-H_o), 8.82 (d, *J* = 4.6 Hz, 2 H, H-12 or H-13), 8.89 (d, *J* = 4.6 Hz, 2 H, H-12 or H-13), 8.94–8.97 (m, 10 H, H-3,7,8,17,18).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 120.1, 120.6, 120.9, 121.5, 122.4, 122.9, 123.2, 123.3, 125.3, 125.8, 125.9, 126.4, 126.5, 126.6, 126.7, 126.8, 127.1, 127.2, 127.3, 127.4, 127.5, 128.2, 128.6, 129.0 130.6, 131.4, 131.9, 132.0, 132.1, 132.2, 132.7, 134.3, 134.4, 135.7, 137.7, 138.6, 139.6, 139.8, 141.0, 141.4, 142.7, 142.7.

HRMS (ESI): *m/z* $[M + 2H]^+$ calcd for $C_{112}H_{72}N_8Zn_2$: 1656.44629; found: 1656.44582.

Acknowledgment

Thanks are due to Universidade de Aveiro, Fundação para a Ciência e a Tecnologia (FCT), FEDER and the GRICES-CAPES collaborative programme for funding this work. A.T.P.C.G.and A.C.C. thank FCT (SFRH/BD/38528/2007) and CAPES, respectively, for their research grants.

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