CHAPTER 4

Experimental Methods

4.1 GENERAL EXPERIMENTAL METHODS

All solvents were distilled before use by using standard procedures.[1] Tetrahydrofuran (THF) was distilled over sodium using benzophenone as an indicator of water content; pyridine was stored over KOH and molecular sieves (type 3 Å) for a minimum of 6 hrs and then distilled over $LiAlH_4$ and stored over KOH/molecular sieves (type 3 Å); triethylamine (Et_3N) was distilled over CaH_2; benzene was dried over sodium wire; AR grade acetonitrile (MeCN) and dimethylformamide (DMF) were both dried over type 3 Å molecular sieves. Flash column chromatography on alumina was carried out using Aldrich aluminium oxide, activated, neutral (Brockmann I standard grade) and Flash Column Chromatography on silica was carried out using Aldrich silica gel (grade 9385, 230-400 mesh). All flash column chromatography was performed using nitrogen gas. Preparative TLC was performed on 20 x 20 cm glass plates coated with 0.5 mm thick Art. 7731 Kieselgel 60 G Merck silica. Analytical TLC was carried out on Merck Silica Gel 60 G254 pre-coated aluminium sheets.

NMR spectra were acquired using a 300 MHz Bruker AC–300P FT spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual solvent. Coupling constants are reported in hertz (Hz). Deuterated solvents were purchased from Aldrich and stored over type 3Å molecular sieves after opening. Gradient COSY, one-bond C-H correlation (HMQC), long-range C-H correlation (HMBC), 2D gradient NOESY, 2D ROESY and 2D DOSY experiments utilised standard BRUKER pulse programs and standard BRUKER parameters. UV–Vis spectra were recorded on a Varian Cary IE UV–VIS spectrophotometer. IR spectra were recorded on a either a Perkin-Elmer FT-IR 1600 series or a Perkin-Elmer FT-IR 1725X series spectrophotometer. Melting points were determined using a Reichert microscopic hot-stage apparatus. Irradiations were performed using a 500W (visible) lamp. High Pressure reactions were performed using a HOFER High Pressure Apparatus Model HP14 at room temperature. High-pressure reactions and

high-resolution EI and ES mass spectrometric analyses were carried out at the Centre for Molecular Architecture, Central Queensland University, Rockhampton, Qld.

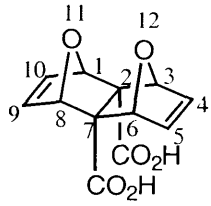
Molecular Modelling was carried out using the Spartan software package [v4.0 (MM2) or 5.0 (MMFF94 and AM1, Wavefunction Inc.] on a Silicon Graphics O_2 Computer.

Abbreviations used for reagents and solvents:

AcOH	acetic acid
Ac_2O	acetic anhydride
ADA	acetylene dicarboxylic acid
BTA	benzenetetramine tetrahydrochloride
DMAD	dimethyl acetylenedicarboxylate
EDC	1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride
Et_3N	triethylamine
EtOAc	ethyl acetate
HOBT	1-hydroxybenzotriazole
MeOH	methanol
NH_4OAc	ammonium acetate
THF	tetrahydrofuran

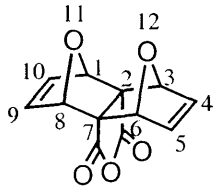
4.2 SYNTHETIC METHODS

1α,2β,3α,6α,7β,8α-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-2,7-dicarboxylic acid (1)



This compound was prepared using the literature method.[2] Acetylene dicarboxylic acid (50 g, 0.44 mol) and furan (69 g, 73 mL, ~1 mol) were dissolved in diethyl ether (250 mL) and stirred at room temperature for 3 weeks in darkness. The product gradually crystallised from solution over the reaction period and was separated by filtration, washed with diethyl ether and dried under vacuum to give cream-coloured crystals (27.4 g). Yield = 50% (lit. 65%); m.p. 156-160°C (lit. 160-162°C) Note: a further crop was obtained by the introduction of another aliquot of furan to the mother liquor with stirring over several weeks.

1α,2β,3α,6α,7β,8α-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-2,7-dicarboxylic anhydride (2)



This compound was prepared using the two different literature methods outlined below.

Method 1[3]: A solution of (**1**) in thionyl chloride (20 mL) was heated at 80°C for 2 hrs under $N_{2(g)}$. Excess thionyl chloride was evaporated off under reduced pressure giving an oil, which was taken up in a minimum of ethyl acetate, and the product crystallised as a fine, light cream coloured solid (lit. light yellow needles). Yield = 58%; m.p. 185-187°C (lit. 184-185°C); IR = ($CHCl_3$/cm^{-1}) 1779, 1850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.78 (4H, m), 5.29 (4H, m); ^{13}C NMR ($CDCl_3$) δ 167.3, 139.9, 81.5, 78.0; ^{13}C NMR (d_6-acetone) 171.7, 141.0, 82.1, 73.5.

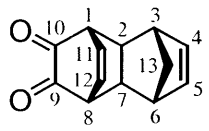
^{1}H ($CDCl_3$) and ^{13}C ($CDCl_3$) NMR spectra were both in agreement with literature.

Method 2 (translated from literature; German)[4]:

To a solution of bis-oxa-norbornene_diacylchloride (**11**) (800 mg, 2.79 mmol) in CCl_4 (50 mL) was added 50 mL of a buffer solution (1.00 g NaH_2PO_4 and 1.18 g Na_2HPO_4). This mixture was stirred for 6 hrs at room temperature. The organic layer was separated and concentrated. The aqueous layer was extracted with ether (5 x 20 mL) and the combined organic layers were dried over Na_2SO_4 (anhydrous) and the solvent removed under reduced pressure. The organic residues were dried further under vacuum for 1 hr at room temperature. The crude product was

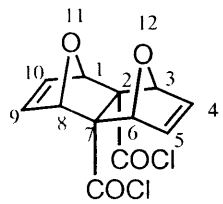
recrystallised from ethyl acetate giving a fine off-white solid (356 mg) yield = 55%. The analysis of the product by ^{1}H NMR spectroscopy was consistent with data obtained from method 1 above.

tetracyclo[6.2.2.1^{3,6}.O^{2,7}]trideca-4,11-dien-9,10-dione (7)



Iodobenzene diacetate (PiDA, 1.9 g, 5.9 mmol) was added all at once to a solution of catechol (0.50 g, 4.5 mmol) and 2,5-norbornadiene (70 mL) in acetonitrile (300 mL). The solution was stirred under $N_{2(g)}$ in darkness at room temperature changing from yellow to red after 10 mins. Stirring under the same conditions was continued for 2 days. A further 0.5 g of catechol and 1.9 g of PiDA were then added and stirring was continued under $N_{2(g)}$ in darkness for another 2 days. After a third and final addition of catechol (0.5 g) and PiDA (1.9 g) and 2 day stirring period ($N_{2(g)}$, R.T., darkness) the solvent and NBD were removed under reduced pressure using a rotary evaporator. The residue was rapidly filtered through a wet ($CHCl_3$) silica plug washing thoroughly afterwards with $CHCl_3$. The solvent was removed from the filtrate under reduced pressure and the product recrystallised from Pet.Spirit/EtOAc giving an orange/yellow crystalline product (1.5 g) with a distinct aroma. Yield = 54%; m.p. = 140-142°C (lit. 142°C)[5]; ^{1}H NMR ($CDCl_3$) δ 6.36 (2H, t, *J* = 3.9 Hz), 6.28 (2H, t, *J* = 1.8 Hz), 3.52 (2H, t, *J* = 3.5 Hz), 2.95 (2H, t, *J* = 1.8 Hz), 2.55 (1H, d, *J* = 9 Hz), 2.13 (2H, s), 1.18 (1H, d, *J* = 9 Hz); ^{13}C NMR ($CDCl_3$) δ 189.25, 140.77, 131.31, 52.02, 47.96, 43.27, 40.65. Both spectra were in agreement with literature.[5]

1α,2β,3α,6α,7β,8α-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-2,7-diacyl chloride (11)



Method translated from literature (German)[4]: Furan (1.54 g, 22.7 mmol, 1.13 eqv.) was added, under N_2, to a stirred suspension of ADA (1.14 g, 10.0 mmol) and PCl_5 (4.16 g, 20.0 mmol) in CCl_4 (100 mL). This mixture was stirred under N_2 in darkness at R.T. for 6 hrs and then a further 1.54 g of furan was added. Stirring under the same conditions was continued for 6 days. Solids were filtered off and washed with CCl_4 (20 mL). The solvent was removed from the filtrate under reduced pressure at R.T. and the residue dried overnight under vacuum leaving a dark brown crystalline solid.

Yield = 1.91 g, 67% (lit. 81%); m.p. = 113-116°C (lit. 115°C); IR = ($CHCl_3$/cm^{-1}) 1760, 1800 cm^{-1} (lit. 1760, 1800 cm^{-1}); ^{1}H NMR ($CDCl_3$) δ 6.80 (4H, m), 5.32 (4H, m) [lit.6.81 (4H, s) 5.33 (4H, s)][4].

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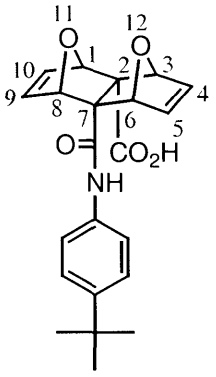
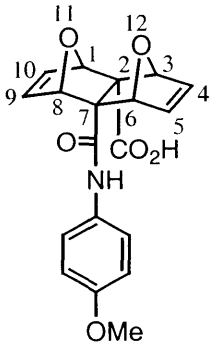
1α,2β,3α,6α,7β,8α-N-(4-*tert*-butylphenyl)-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-2,7-dicarboxamic acid (12)



A solution of the *bis*-acyl chloride **(11)** (3.60 g, 12.5 mmol), 4-*tert*-butylaniline (1.40 g, 9.4 mmol) and pyridine (2.00 g, 25.3 mmol) in $CHCl_3$ (120 mL) was stirred under N_2 for 3 days at room temperature in darkness. The reaction mixture was poured into 200 mL of water and the organic layer separated. The aqueous layer was extracted with $CHCl_3$ (3 x 30 mL) and the combined organic layers washed with water (5 x 100 mL). The organic layers were dried over Na_2SO_4 (anhydrous) and the solvent removed under reduced pressure. The remaining residue was dried under vacuum overnight giving the crude amic acid as a brown solid (4.08 g). Yield = 85%*; A sample of the product (1.2 g) was recrystallised from EtOAc/Pet.Spirit and further purified by flash column chromatography [silica, EtOAc/Pet.Spirit (1:1)] to give a white solid (160 mg). m.p. = 200-201°C; ^{1}H NMR ($CDCl_3$) δ 7.31 (2H, m, Ar), 6.96 (2H, m, Ar), 6.81(2H, m) 6.73 (2H, m), 5.39 (2H, bs), 5.26 (2H, bs), 1.29 (9H, s).

1α,2β,3α,6α,7β,8α-N-(4-methoxyphenyl)-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-2,7-dicarboxamic acid (13)

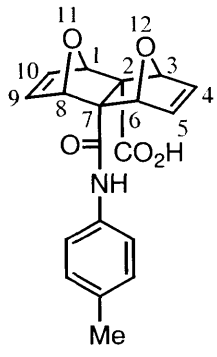


A solution of the *bis*-acyl chloride **(11)** (442 mg, 1.54 mmol), anisidine (190 mg, 1.56 mmol) and pyridine (250 mg, 3.16 mmol) in $CHCl_3$ (15 mL) was stirred under N_2 for 5 days at room temperature in darkness. The reaction mixture was poured into 20 mL of water and the organic layer separated. The aqueous layer was extracted with $CHCl_3$ (4 x 5 mL) and the combined organic layers washed with water (5 x 20 mL). The organic layers were dried over Na_2SO_4 (anhydrous) and the solvent removed under reduced pressure. The remaining residue was dried under vacuum overnight giving the crude amic acid as a cream-coloured solid (455 mg). The product was purified by recrystallisation from $CHCl_3$/ MeOH giving white needles (249 mg) Yield = 43%*; m.p. = 214-215°C; ^{1}H NMR ($CDCl_3$) δ 7.05 (2H, m, Ar) and 6.82 (2H, m, Ar), 6.80 (2H, m), 6.73 (2H, m), 5.38 (2H, bs), 5.26 (2H, bs), 3.78 (3H, s).

*A second run at the same scale under identical conditions gave the amic acid in 68% yield.

* > 85% pure by ^{1}H NMR, (**2**) present as impurity (<15%).

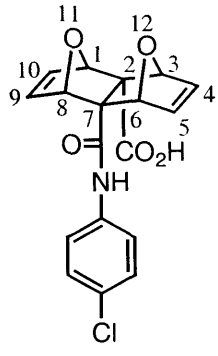
1α,2β,3α,6α,7β,8α-N-(4-methylphenyl)-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-2,7-dicarboxamic acid (14)



A solution of the *bis*-acyl chloride **(11)** (442 mg, 1.54 mmol), 4-methylaniline (165 mg, 1.54 mmol) and pyridine (250 mg, 3.16 mmol) in $CHCl_3$ (15 mL) was stirred under N_2 for 5 days at room temperature in darkness. The reaction mixture was poured into 20 mL of water and the organic layer separated. The aqueous layer was extracted with $CHCl_3$ (4 x 5 mL) and the combined organic layers washed with water (5 x 20 mL). The organic layers were dried over Na_2SO_4 (anhydrous) and the solvent removed under reduced pressure. The remaining residue was dried under vacuum overnight giving the crude amic acid as a cream-coloured solid (450 mg). Yield = 85%*; the product was further purified by recrystallisation from $CHCl_3$ giving a fine white powder after drying (203 mg) Yield (pure) = 40%; m.p. = 209-212°C; ^{1}H NMR ($CDCl_3$) δ 7.38 (2H, m, Ar), 7.08 (2H, m, Ar), 6.75 (2H, m), 6.56 (2H, m), 5.32 (2H, bs), 5.15 (2H, bs), 2.29 (3H, s).

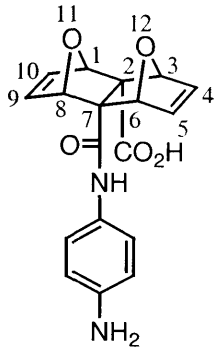
* The crude product was almost pure by NMR analysis and a conservative estimate of yield was based on this.

1α,2β,3α,6α,7β,8α-N-(4-chlorophenyl)-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-2,7-dicarboxamic acid (15)



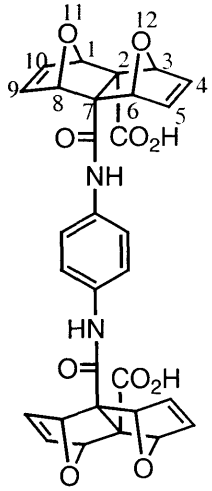
A solution of the *bis*-acyl chloride **(11)** (570 mg, 1.99 mmol), 4-chloroaniline (260 mg, 2.04 mmol) and pyridine (316 mg, 4.00 mmol) in $CHCl_3$ (20 mL) was stirred under N_2 for 4 days at room temperature in darkness. The reaction mixture was poured into 30 mL of water and the organic layer separated. The aqueous layer was extracted with $CHCl_3$ (4 x 10 mL) and the combined organic layers washed with water (5 x 40 mL). The organic layers were dried over Na_2SO_4 (anhydrous) and the solvent removed under reduced pressure. The remaining residue was dried under vacuum overnight giving the crude amic acid as a light brown solid (~800 mg). The product was purified by flash column chromatography (silica, $CHCl_3$) and dried overnight under vacuum giving a cream-coloured powder (450 mg). Yield = 63%; m.p. = 210-214°C; ^{1}H NMR ($CDCl_3$) δ 7.46 (2H, m, Ar), 7.24 (2H, m, Ar), 6.73 (2H, m), 6.57 (2H, m), 5.31 (2H, bs), 5.16 (2H, bs).

1α,2β,3α,6α,7β,8α-N-(4-aminophenyl)-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-2,7-dicarboxamic acid (16)



A solution of the *bis*-acyl chloride **(11)** (430 mg, 1.50 mmol), 4-phenylenediamine (162 mg, 1.50 mmol) and pyridine (237 mg, 3.00 mmol) in $CHCl_3/Et_2O$ [(3:2) 12.5 mL] was stirred under N_2 for 5 days at room temperature in darkness. The solvents were removed from the reaction mixture under reduced pressure at R.T. and the residues partitioned between $CHCl_3$ (50 mL) and water (50 mL) and the organic layer separated. The aqueous layer was extracted with $CHCl_3$ (4 x 10 mL) and the combined organic layers washed with water (5 x 10 mL). The organic layers were dried over Na_2SO_4 (anhydrous) and the solvent removed under reduced pressure. The remaining residue was dried under vacuum overnight giving the crude product as a cream-coloured solid (200 mg). The product was recrystallised from hot $CHCl_3$, collected and dried overnight under vacuum giving a cream-coloured powder (122 mg). Yield = 50%; m.p. = 220-224°C; ^{1}H NMR ($CDCl_3$) δ 7.06 (2H, m, Ar), 6.87 (2H, m, Ar), 6.79 (2H, m), 6.70 (2H, m), 5.35 (2H, bs), 5.23 (2H, bs), NH_2 peak not evident.

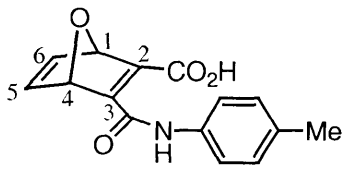
N,N'-1',4'-phenylene-bridged (1α,2β,3α,6α,7β,8α-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-2,7-dicarboxamic acid) dimer* (17)



A solution of the *bis*-acyl chloride **(11)** (112 mg, 3.9 x 10 $^{-4}$ mol), 4-phenylenediamine (22 mg, 2.0 x 10 $^{-4}$ mol) and pyridine (130 mg, 1.6 mmol) in $CHCl_3/Et_2O$ [(3:2) 5 mL] was stirred under N_2 for 5 days at room temperature in darkness. The solvents were removed from the reaction mixture under reduced pressure at R.T., the residues partitioned between $CHCl_3$ (5 mL) and water (5 mL), and the organic layer separated. The aqueous layer was extracted with $CHCl_3$ (4 x 5 mL) and the combined organic layers washed with water (5 x 10 mL). The organics were dried over Na_2SO_4 (anhydrous) and the solvent removed under reduced pressure. The remaining residue was dried under vacuum overnight giving the crude product as a brown solid (80 mg). The product was recrystallised from $CHCl_3$ and dried overnight under vacuum giving a fine light brown-coloured solid (67 mg). Yield = 59%; m.p. > 300°C (colour darkens at 170°C); ^{1}H NMR ($CDCl_3$) δ 6.95 (4H, s, Ar), 6.80 (4H, m), 6.73 (4H, m), 5.38 (4H, bs), 5.26 (4H, bs).

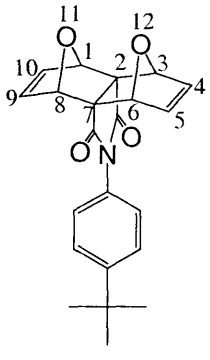
* Non-systematic nomenclature

3-*p*-tolylcarbamoyl-7-oxa-bicyclo[2.2.1]hepta-2,5-diene-2-carboxylic acid (18)



The 4-tolylamic acid (**14**) (236 mg, 6.95 x 10^{-4} mol) was stirred with NaOAc (1 g) in Ac_2O (10 mL) at 120°C for 1 hr. The acetic anhydride was distilled off under vacuum and the remaining residues were partitioned between $CHCl_3$ and H_2O. The organic layer was separated and the aqueous layer extracted with $CHCl_3$ (4 x 10 mL). The combined organics were washed with water (4 x 30 mL), dried over $NaSO_4$ (anhyd.) and the solvent removed using a rotary evaporator. The crude product was dried overnight under vacuum to give a sticky brown solid. The product was purified by flash column chromatography (silica, 20% hexane/$CHCl_3$) and obtained as a sticky brown solid (160 mg). Yield = 85%; ^{1}H NMR ($CDCl_3$) δ 10.99 (1H, bs), 7.55 (2H, m, Ar), 7.13 (2H, m, Ar), 7.25 (2H, m), 5.94 (1H, t, *J* = 1.8 Hz), 5.78 (1H, t, *J* = 1.8 Hz), 2.31 (3H, s).

1α,2β,3α,6α,7β,8α-N-(4-*tert*-butylphenyl)-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-2,7-dicarboximide (20)

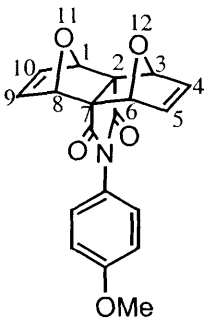


Method 1: The amic acid (**12**) (1.05g, 2.75 mmol) was added to a mixture of NaOAc (4 g) in Ac_2O (40 mL) and heated to 130°C for 12 hrs. A drying tube was attached to the reaction vessel and the mixture was allowed to cool slowly to room temperature. The acetic anhydride was removed under vacuum and the remaining residues were partitioned between $CHCl_3$ and H_2O. The aqueous layer was extracted with $CHCl_3$ (5 x 50 mL) and the combined organic layers washed with H_2O (5 x 100 mL). The organic layers were dried over Na_2SO_4 (anhyd.) and the solvent removed under reduced pressure. The residues were dried under vacuum overnight. The product was purified by flash column chromatography (silica), eluting with 50% Pet Spirit/EtOAc to obtain a light cream coloured solid (810 mg) Yield = 81%; m.p. = 232-234°C; ^{1}H NMR ($CDCl_3$) δ 7.42 (2H, m, Ar), 6.94 (2H, m, Ar), 6.74 (4H, m), 5.34 (4H, m), 1.29 (9H, s); ^{13}C NMR ($CDCl_3$) δ 173.4, 152.1, 139.2, 128.4, 126.2, 125.4, 81.6, 69.1, 34.7, 31.2; HRMS $C_{22}H_{21}NO_4$: calculated 363.1471; m/z (EI) M^+ observed 363.1482.

Method 2: The amic acid (**12**) (15 mg, 3.9 x 10^{-5} mol) and HOBT (8 mg, 6 x 10^{-5} mol) were dissolved in dry THF (1.5 mL) and stirred for 5 minutes under $N_{2(g)}$. EDC (11 mg, 6 x 10^{-5} mol) and Et_3N (dry, 50 μL) were added in quick succession (under $N_{2(g)}$) and the mixture was stirred at room temperature under $N_{2(g)}$ for 3 days. THF was removed under vacuum and the residues

partitioned between $CHCl_3$ (~3 mL) and 6M $HCl_{(aq)}$ (~2 mL). The aqueous layer was neutralised with $NaHCO_{3(aq)}$(sat.) and extracted with $CHCl_3$. The combined organics were washed with water (3 x 5 mL), dried over $NaSO_4$ (anhyd.) and concentrated using a rotary evaporator. The residues were dissolved in a minimum of CH_2Cl_2 and precipitation of the product was induced by the slow addition of hexane to this solution. The fine white solid was filtered and dried under vacuum to give a white powder (12 mg). Yield = 80%. Both the melting point and ^1H NMR data were identical to results obtained from method 1 above.

1α,2β,3α,6α,7β,8α-N-(4-methoxyphenyl)-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dien-2,7-dicarboximide (21)

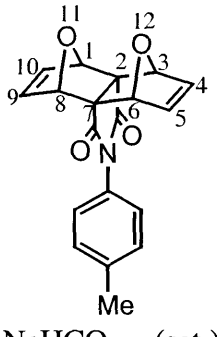


Method 1: A mixture of the anhydride (**1**) (526 mg, 2.27 mmol) and anisidine (286 mg, 2.32 mmol) in CH_2Cl_2 (4.5 mL) were placed under high pressure (13 kbar) for 3 days. The solvent was removed under reduced pressure and the residues dried under vacuum. The crude residue was treated with NaOAc (1 g) in AC_2O (5 mL) and this mixture was stirred at room temperature for 2 days and then at 60°C for another day. The acetic anhydride was removed under high vacuum and the residues were partitioned between $CHCl_3$ and H_2O. The aqueous layer was extracted with $CHCl_3$ (3 x 50 mL) and the combined organic layers washed with H_2O (3 x 100 mL). The organic layers were dried over Na_2SO_4 (anhyd) and the solvent removed under reduced pressure. The remaining residue was dried under vacuum overnight. The product was recrystallised from EtOAc/Petroleum Spirit (2:1) giving a fine off-white solid (360 mg). Yield = 47% [from (**2**)]; m.p. = 275-278°C; ^1H NMR ($CDCl_3$) δ 6.92 (4H, s, Ar), 6.74 (4H, m), 5.33 (4H, m), 3.79 (3H, s).

Method 2: The amic acid (**13**) (50 mg, 1.41 x 10^{-4} mol) was stirred with NaOAc (300 mg) in Ac_2O (3 mL) at 130°C for 3 hrs. The acetic anhydride was distilled off under vacuum and the remaining residues were partitioned between $CHCl_3$ and H_2O. The organic layer was separated and the aqueous layer extracted with $CHCl_3$ (4 x 5 mL). The combined organics were washed with water (4 x 5 mL), dried over $NaSO_4$ (anhyd.) and the solvent removed using a rotary evaporator. The residue was dissolved in a minimum of $CHCl_3$ (~2 mL) and approximately 1 mL of hexane was added down the side of the flask. A fine white precipitate formed and was filtered and dried under vacuum overnight (40 mg). Yield = 84%. Both the melting point and NMR data were identical to results obtained from method 1 above.

Method 3: The amic acid (**13**) (21 mg, 5.8 x 10^{-5} mol) and HOBT (12 mg, 8.8 x 10^{-5} mol) were dissolved in dry THF (2 mL) and stirred for 5 minutes under $N_{2(g)}$. EDC (17 mg, 8.8 x 10^{-5} mol) and Et_3N (dry, 70 μL) were added in quick succession and the mixture stirred at room temperature under $N_{2(g)}$ for 3 days. THF was removed under vacuum and the residues partitioned between $CHCl_3$ (~3 mL) and 6M $HCl_{(aq)}$ (~2 mL). The aqueous layer was neutralised with $NaHCO_{3(aq)}$(sat.) and extracted with $CHCl_3$. The combined organics were washed with water (3 x 5 mL), dried over $NaSO_4$ (anhyd.) and concentrated using a rotary evaporator. The residues were dissolved in a minimum of CH_2Cl_2 and precipitation of the product was induced by the slow addition of hexane to this solution. A fine white solid was filtered off and dried under vacuum to give a white powder (13.7 mg). Yield = 70%. Both the melting point and ^1H NMR data were identical to results obtained from method 1 above.

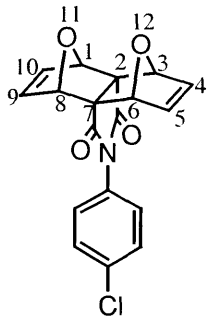
1α,2β,3α,6α,7β,8α-N-(4-methylphenyl)-11,12-dioxatetracyclo[6.2.1.$1^{3,6}$.$0^{2,7}$]dodeca-4,9-dien-2,7-dicarboximide (22)



The amic acid (**14**) (20 mg, 5.9 x 10^{-5} mol) and HOBT (12 mg, 8.8 x 10^{-5} mol) were dissolved in dry THF (2 mL) and stirred for 5 minutes under $N_{2(g)}$. EDC (17 mg, 8.8 x 10^{-5} mol) and Et_3N (dry, 70 μL) were added in quick succession and the mixture stirred at room temperature under $N_{2(g)}$ for 3 days. THF was removed under vacuum and the residues partitioned between $CHCl_3$ (~3 mL) and 6M $HCl_{(aq)}$ (~2 mL). The aqueous layer was neutralised with $NaHCO_{3(aq)}$(sat.) and extracted with $CHCl_3$. The combined organics were washed with water (3 x 5 mL), dried over $NaSO_4$ (anhyd.) and concentrated using a rotary evaporator. The residues were dissolved in a minimum of CH_2Cl_2 and precipitation of the product was induced by the slow addition of hexane to this solution. The fine white solid was filtered and dried under vacuum to give a white powder (10 mg). Yield = 50%; m.p. = 270-273°C; ^1H NMR ($CDCl_3$) δ 7.21 (2H, m, Ar), 6.88 (2H, m, Ar), 6.75 (4H, bs), 5.34 (4H, bs), 2.35 (3H, s); HRMS $C_{19}H_{15}ClNO_4$: calculated 321.1001; m/z (EI) M^+ 321.1002.

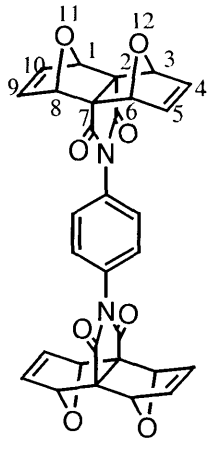
1α,2β,3α,6α,7β,8α-N-(4-chlorophenyl)-11,12-dioxatetracyclo[6.2.1.$1^{3,6}$.$0^{2,7}$]dodeca-4,9-dien-2,7-dicarboximide (23)

The amic acid (**14**) (50 mg, 1.4 x 10^{-4} mol) and HOBT (28 mg, 2.1 x 10^{-4} mol) were dissolved in dry THF (4 mL) and stirred for 5 minutes under $N_{2(g)}$. EDC (40 mg, 2.1 x 10^{-4} mol) and Et_3N (dry, 160 μL) were added in quick succession and the mixture stirred at room temperature under



$N_{2(g)}$ for 3 days. THF was removed under vacuum and the residues partitioned between $CHCl_3$ (~5 mL) and 6M $HCl_{(aq)}$ (~5 mL). The aqueous layer was neutralised with $NaHCO_{3(aq)}$(sat.) and extracted with $CHCl_3$. The combined organics were washed with water (3 x 10 mL), dried over $NaSO_4$ (anhyd.) and concentrated using a rotary evaporator. The residues were dissolved in a minimum of CH_2Cl_2 and precipitation of the product was induced by the slow addition of hexane to this solution. The white precipitate was filtered and dried under vacuum to give a white powder (30 mg). Yield = 63%; m.p. = 263-266°C; ^{1}H NMR ($CDCl_3$) δ 7.39 (2H, m, Ar), 6.97 (2H, m, Ar), 6.75 (4H, s), 5.34 (4H, s); HRMS $C_{18}H_{12}NO_4$: calculated 341.0455; m/z (EI) M^+ observed 341.0453.

N,N'-(1',4'-phenylene)-bridged (1α,2β,3α,6α,7β,8α-11,12-dioxatetracyclo [6.2.1.1^{3,6}.0^{2,7}]-dodeca-4,9-dien-2,7-dicarboximide) dimer* (24)

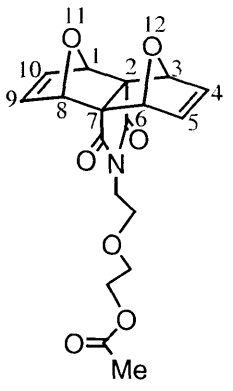


The amic acid (**16**) (34 mg, 5.9 x 10^{-5} mol) HOBT (12 mg, 8.8 x 10^{-5} mol) were dissolved in dry THF (2 mL) and stirred for 5 minutes under $N_{2(g)}$. EDC (17 mg, 8.8 x 10^{-5} mol) and Et_3N (dry, 70 μL) were added in quick succession and the mixture stirred at room temperature under $N_{2(g)}$ for 3 days. THF was removed under vacuum and the residues partitioned between $CHCl_3$ (~3 mL) and 6M $HCl_{(aq)}$ (~2 mL). The aqueous layer was neutralised with $NaHCO_{3(aq)}$(sat.) and extracted with $CHCl_3$. The combined organics were washed with water (3 x 5 mL), dried over $NaSO_4$ (anhyd.) and concentrated using a rotary evaporator. The residues were dissolved in a minimum of CH_2Cl_2 and precipitation of the product was induced by the slow addition of hexane to this solution. The fine white solid was filtered and dried under vacuum to give a white powder (9 mg). Yield = 28%; m.p. > 300°C; ^{1}H NMR ($CDCl_3$) δ 7.11 (4H, s, Ar), 6.72 (8H, bs), 5.33 (8H, bs); HRMS $C_{30}H_{20}NO_8$: calculated 536.1220; m/z (EI) M^+ observed 536.1219.

1α,2β,3α,6α,7β,8α-N-{2-(2-acetoxyethoxy)ethyl}-11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}.0^{2,7}]-dodeca-4,9-dien-2,7-dicarboximide (25)

Step 1: 2-(2-aminoethoxyethanol) (500 mg, 2.15 mmol) was added to a solution of (**2**) (500 mg, 4.76 mmol) in $CHCl_3$ and the reaction mixture stirred under N_2 at room temperature for 4 days.

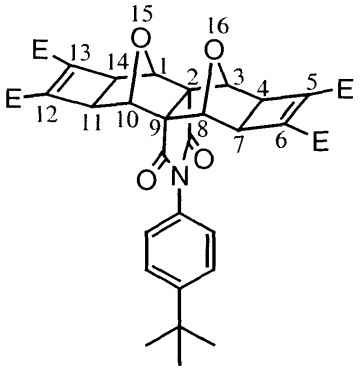
* Non-systematic nomenclature



The solvent was evaporated under reduced pressure leaving a brown oily residue (An aqueous work up was avoided as it had been previously discovered that the amic acid product is very soluble in water).

Step 2: NaOAc (1g) and AC_2O (10 mL) were added to the crude oil (step 1; 1.5g) and this mixture was stirred at 60°C for 3 days. The AC_2O was removed under reduced pressure at 40°C and the oily residue was partitioned between $CHCl_3$ and H_2O. The aqueous layer was extracted with $CHCl_3$ (3 x 50ml) and the combined organic layers washed with H_2O (3 x 100ml). The organic layers were concentrated and the remaining residue was dried under vacuum overnight giving a dark brown oil (230 mg). The crude product was purified further by column chromatography (silica), eluting with $CHCl_3$ to obtain a light brown oil (150 mg) Yield = 20%; ^{1}HNMR ($CDCl_3$) δ 6.59 (4H, s), 5.23 (4H,s), 4.16 (2H, t, J = 4.7Hz), 3.57 (2H, t, J = 4.7Hz), 3.43 (4H, m), 2.06 (3H, s).

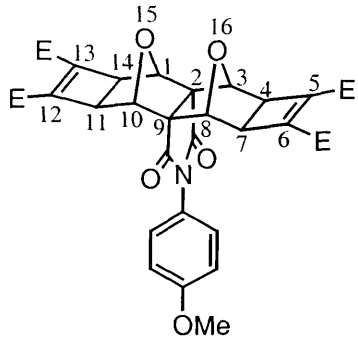
(1α,2β,3α,4β,7β,8α,9β,10α,11β,14β)-N-(4-*tert*-butylphenyl)-5,6,12,13-tetra-(methoxycarbonyl)-15,16-dioxahexacyclo[8.4.1.1^{3,8}.0^{2,9}.0^{4,7}.0^{11,14}]hexadeca-5,12-diene-2,9-dicarboximide (26)



The Ru(0) catalyst [$RuH_2CO(PPh_3)_3$] was prepared according to literature method.[6] I.R (benzene) ν(CO) 1940 cm^{-1}, ν(RuH) 1960 and 1900 cm^{-1}.

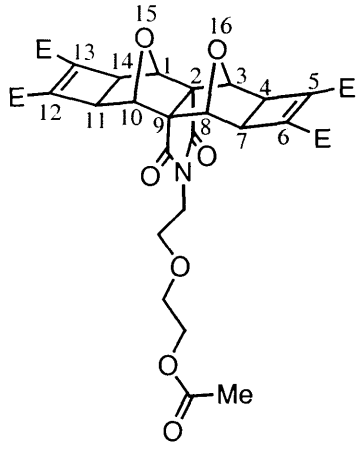
To a solution of (**20**) (85.3 mg, 2.35 x 10^{-4} mol) and DMAD (190 mg, 1.34 mmol, 5.7 eqv.) in benzene (5 mL) was added $RuH_2CO(PPh_3)_3$ (10 mol%, 21 mg). The solution was heated at reflux temperature under $N_{2(g)}$ for 3 days. The solution was taken to dryness (rotary evaporator) and the residue dissolved in EtOAc. Solids were filtered off and washed well with EtOAc. The filtrate was concentrated and the product recrystallised from EtOAc/Pet.Spirit to give a white solid (84 mg). Yield = 55%; m.p. = 284-286°C; ^{1}H NMR ($CDCl_3$) δ 7.49 (2H, m, Ar), 7.10 (2H, m, Ar), 4.84 (4H, s), 3.79 (12H, s), 3.26 (4H, s), 1.32 (9H, s); ^{13}C NMR ($CDCl_3$) δ 171.9, 160.0, 152.8, 140.1, 127.9, 126.5, 125.5, 77.2 (hidden), 70.2, 52.2, 44.8, 34.9, 31.2; HRMS $C_{34}H_{33}NO_{12}$: calculated 647.2003; m/z (EI) M^+ observed 647.1998.

(1α, 2β, 3α, 4β, 7β, 8α, 9β, 10α, 11β, 14β)-N-(4-methoxyphenyl)-5,6,12,13-tetra-(methoxycarbonyl)-15,16-dioxahexacyclo[8.4.1.1^{3,8}.0^{2,9}.0^{4,7}.0^{11,14}]hexadeca-5,12-diene-2,9-dicarboximide (27)



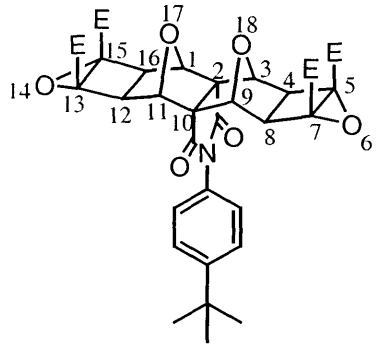
To a solution of (**21**) (200 mg, 5.93 x 10^{-4} mol) and DMAD (211 mg, 1.48 mmol, 2.5 eqv.) in benzene (8 mL) was added $RuH_2CO(PPh_3)_3$ (2 mol%, 11 mg). The solution was heated at reflux temperature under $N_{2(g)}$ for 2 days. The solution was taken to dryness (rotary evaporator) and the residue dissolved in EtOAc. Solids were filtered off and washed well with EtOAc. The filtrate was concentrated and the residue purified by flash column chromatography (silica, 50%EtOAc/Pet.Spirit) giving a white solid (111 mg). Yield = 30%; m.p. = 248-250°C; ^{1}H NMR ($CDCl_3$) δ 7.49 (2H, m, Ar), 7.10 (2H, m, Ar), 4.84 (4H, s), 3.79 (12H, s), 3.26 (4H, s), 1.32 (9H, s); HRMS $C_{31}H_{27}NO_{13}$: calculated 621.1482; m/z (EI) M^+ observed 621.1487.

(1α,2β,3α,4β,7β,8α,9β,10α,11β,14β)-N-{2-(2-acetoxyethoxy)ethyl}-5,6,12,13-tetra-(methoxycarbonyl)-15,16-dioxahexacyclo[8.4.1.1^{3,8}.0^{2,9}.0^{4,7}.0^{11,14}]hexadeca-5,12-diene-2,9-dicarboximide (28)



To a solution of (**25**) (150 mg, 4.11x 10^{-4} mol) and DMAD (146 mg, 1.02 mmol, 2.5 eqv.) in benzene (6 mL) was added $RuH_2CO(PPh_3)_3$ (2 mol%, 8 mg). The solution was heated at reflux temperature under $N_{2(g)}$ for 2 days. The solution was taken to dryness (rotary evaporator) and the residue dissolved in EtOAc. Solids were filtered off and washed well with EtOAc. The filtrate was concentrated and the residue purified by flash column chromatography (silica, 50%EtOAc/Pet.Spirit) giving a brown oil (53 mg). Yield = 20%; ^{1}H NMR ($CDCl_3$) δ 4.74 (4H, s), 4.11 (2H, t, J = 4.7 Hz), 3.78 (12H, s), 3.66 (4H, bs), 3.61 (2H, t, J = 4.7 Hz), 3.12 (4H, s), 2.04 (3H, s); HRMS $C_{30}H_{31}NO_{15}$: calculated 645.1694; m/z (EI) M^+ observed 645.1693.

(1α,2β,3α,4β,5α,7α,8β,9α,10β,11α,12β,13α,15α,16β)-N-(4-*tert*-butylphenyl)-5,7,13,15-tetra-(methoxycarbonyl)-6,14,17,18-tetraoxaoctacyclo[9.5.1.1^{3,9}.0^{2,10}.0^{4,8}.0^{5,7}.0^{12,16}.0^{13,15}]octadeca-2,9-dicarboximide (29)

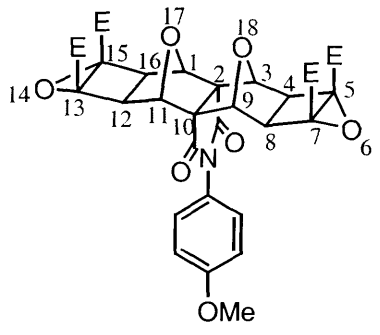


The *bis*-cyclobutenediester (**26**) (88 mg, 1.30 x 10^{-4} mol) was dissolved in dry THF (7 mL) and cooled to -8°C. ^{t}BuOOH* (3.8 M in toluene, 89 μL, 3.4 x 10^{-4} mol, ~ 1.3 eqv. per 'ene' group) was added and the solution stirred at -5°C for 10 mins. ^{t}BuOK (14.6 mg, 1.30 x 10^{-4} mol, 0.5 eqv. per 'ene' group) was added under $N_{2(g)}$ and the reaction mixture was stirred and allowed to rise gradually to +25°C over several hours. Stirring under $N_{2(g)}$ at ~25°C was continued overnight. An aqueous solution of Na_2SO_3 (10% w/v, 7 mL) was added along with 7 mL of chloroform and the mixture stirred for 5 mins. The organic layer was separated and the aqueous layer extracted with $CHCl_3$ (3 x 7 mL). The combined organics were washed with water (3 x 20 mL), dried over Na_2SO_4 (anhyd.) and the solvents removed using a rotary evaporator. The residue was dried under vacuum giving an off-white solid. The product was purified by flash column chromatography (silica, $CHCl_3$) and obtained as a white solid (68 mg). Yield = 74%; m.p. > 300°C (sample changes colour and gradually liquifies at T > 150°C possibly due to partial conversion to the 1,3-dipole); ^{1}H NMR ($CDCl_3$) δ 7.47 (2H, m, Ar), 6.99 (2H, m, Ar), 5.58 (4H, s), 3.83 (12H, s), 2.90 (4H, s), 1.31 (9H, s); ^{13}C NMR ($CDCl_3$) δ 171.4, 163.2, 152.9, 127.6, 126.6, 125.4, 80.6, 70.4, 62.7, 53.1, 48.7, 34.8, 31.2; HRMS $C_{34}H_{33}NO_{14}$: calculated 679.1901; m/z (EI) M^+ observed 679.1889.

* The 3.8M solution of ^{t}BuOOH in toluene was prepared according to literature methods.[7]

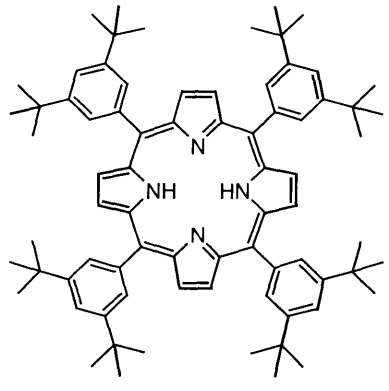
(1α,2β,3α,4β,5α,7α,8β,9α,10β,11α,12β,13α,15α,16β)-N-(4-methoxyphenyl)-5,7,13,15-tetra-(methoxycarbonyl)-6,14,17,18-tetraoxaoctacyclo[9.5.1.1^{3,9}.0^{2,10}.0^{4,8}.0^{5,7}.0^{12,16}.0^{13,15}] octadeca-2,9-dicarboximide (30)

The *bis*-cyclobutenediester (**27**) (80 mg, 1.29 x 10^{-4} mol) was dissolved in dry THF (5 mL) and cooled to -78°C (dry ice/acetone). ^{t}BuOOH (3.8 M in toluene, 110 μL, 4.2 x 10^{-4} mol, ~ 1.3 eqv. per 'ene' group) was added and the solution stirred at -78°C for 10 mins. MeLi (1.4 M, 0.278 mL) was added under $N_{2(g)}$ and the reaction mixture was stirred at –78°C for 30 mins. and allowed to rise gradually to R.T. over 2hrs. Stirring under $N_{2(g)}$ at R.T. was continued for another 6 hrs. The reaction mixture was diluted with 50 mL of CH_2Cl_2 and washed with $Na_2SO_{3(aq)}$ (10% w/v, 2 x 50



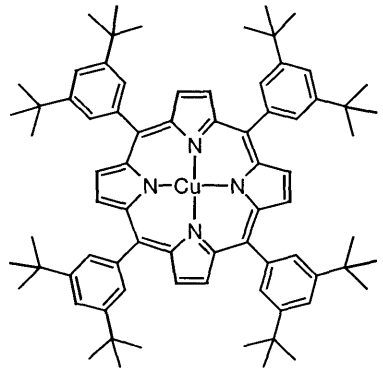
mL), water (3 x 20 mL) and dried over Na_2SO_4 (anhyd.). The solvents were removed using a rotary evaporator and the residue was dried under vacuum giving a white solid (70 mg). The product was further purified by flash column chromatography (silica, $CHCl_3$) and obtained as a white solid (63 mg). Yield = 75%; m.p. >250°C; ^{1}H NMR ($CDCl_3$) δ 6.96 (4H, s), 5.57 (4H, s), 3.83 (12H, s), 3.81 (3H, s), 2.90 (4H, s).

5,10,15,20-*tetrakis*-(3,5-di-*tert*-butylphenyl) porphyrin (32)



Freshly distilled pyrrole (1.48 g, 22.1 mmol) was added to a refluxing solution of 3,5-di-*tert*-butylbenzaldehyde (4.37 g, 20.0 mmol) in propionic acid (75 mL) and heated at reflux temperature for 2.5 hrs. The solution was allowed to cool slowly to room temperature and then refrigerated for 3 hrs. The solids were separated by filtration and washed with boiling water (500 mL) followed by cold acetone (100 mL) and again with boiling water (100 mL). The crystalline solids were dried under vacuum at room temperature overnight and the final product was obtained as lustrous purple crystals. Yield = 1.27 g (23%); m.p. > 300°C; ^{1}H NMR ($CDCl_3$) δ 8.88 (8H, s), 8.08 (8H, d, J = 1.8 Hz), 7.78 (4H, t, J = 1.8 Hz), 1.51 (72H, s), -2.67 (2H, bs).

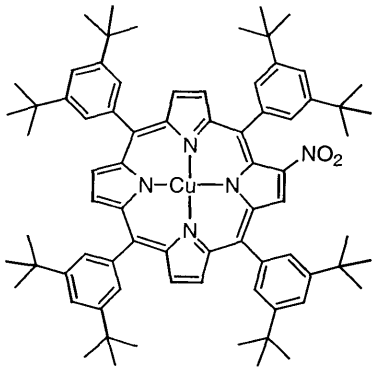
[5,10,15,20-*tetrakis*-(3,5-di-*tert*-butylphenyl) porphyrinato]copper(II) (33)



A solution of cupric acetate monohydrate (1.35 g, 6.78 mmol) in methanol (30 mL) was added to a solution of (**32**) (3.41 g), 3.39 mmol) in $CHCl_3$ (270 mL) and this mixture was heated at reflux temperature with stirring for 12 hrs. The reaction was monitored by TLC (the product gave a distinct purplish red spot with $R_f \approx 0.5$ in CCl_4) The reaction mixture was filtered and the solids washed well with $CHCl_3$. The filtrate was washed with water (2 x 100 mL) and dried over $NaSO_4$ (anhyd.) and the solvent removed using a rotary evaporator. The product was recrystallised from $CHCl_3$/MeOH (2 crops) giving purplish red crystals. Yield = 3.47 g (92%); m.p. > 300°C. This material was used for the synthesis of (**34**) below without further analysis.

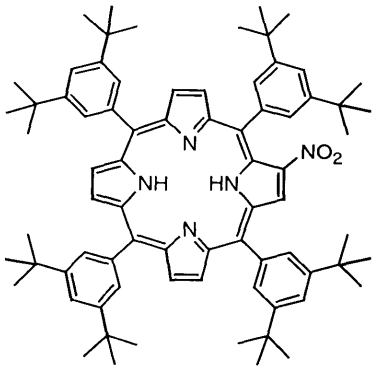
2-nitro-[5,10,15,20-*tetrakis*-(3,5-di-*tert*-butylphenyl) porphyrinato]copper(II) (34)

A stirred solution of (**33**) (3.28 g, 2.94 mmol) in CH_2Cl_2 (250 mL) was treated with small portions (~ 0.5 mL) of a NO_2/hexane solution (0.32g in 20 mL) until all starting material had been consumed as monitored by TLC (silica;$CHCl_3$). The solution was filtered through a silica plug with the silica being thoroughly washed with CH_2Cl_2. The filtrate was concentrated using a rotary evaporator and the product recrystallised from CH_2Cl_2/MeOH. Yield = 2.58 g (76%); m.p. > 300°C; IR ($CHCl_3$/cm^{-1}) 1522 (NO_2) (lit.[8] 1527 KBr).



2-nitro-5,10,15,20-*tetrakis*-(3,5-di-*tert*-butylphenyl) porphyrin (35)

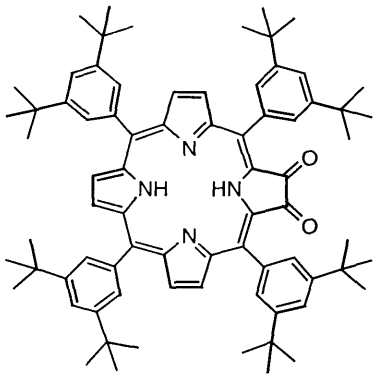
To a solution of (**34**) (2.54 g, 2.19 mmol) in CH_2Cl_2 (250 mL) was added sulfuric acid (98%, 20 mL) and this mixture was stirred vigorously at room temperature for 1.5 hrs. The reaction mixture was poured in a thin stream onto ice (300 g) and the aqueous layer was separated and extracted with CH_2Cl_2 (4 x 50 mL). The combined organics were washed with water (2 x 150 mL), $NaCO_{3(aq)}$ (sat., 3 x 300 mL) and again with water (2 x 150 mL). The organic layer was dried over $NaSO_4$ (anhyd.) and the solvent removed using a rotary evaporator. The product was recrystallised from CH_2Cl_2/MeOH. Yield = 1.60 g (65%); m.p. > 300°C; ^{1}H NMR ($CDCl_3$) δ 9.05 (1H, s), 8.93 (2H, bs), 9.04 and 8.92 (2H, broad AB_q), 8.76 and 8.75 (2H, broad AB_q), 8.07 (2H, d, J = 1.8Hz), 8.04 (6H, bs), 7.81 (1H, dd, J = 1.8 Hz), 7.79 (2H, dd, J = 1.8 Hz), 7.76 (1H, dd, J = 1.8 Hz), 1.51-1.52 (72H, m), -2.56 (2H, bs). NMR data similar* to data reported in the literature.[8]



* Published NMR data acquired on a 200 MHz spectrometer.

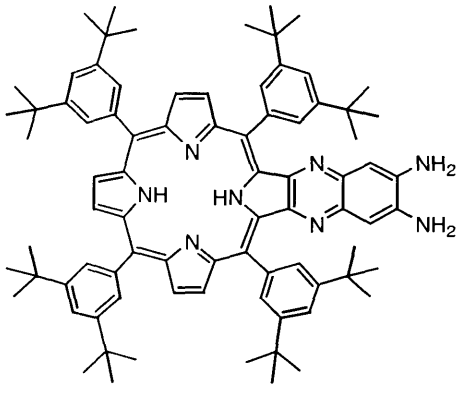
2,3-dioxo-5,10,15,20-*tetrakis*-(3,5-di-*tert*-butylphenyl)porphyrin (37)

Step 1: After bubbling $N_{2\,(g)}$ through a stirred mixture of (**35**) (0.71 g, 0.64 mmol) and 5% Pd/C (1.46 g) in CH_2Cl_2/MeOH (8:5; 600 mL) for 30 minutes, 60 mg of $NaBH_4$ was added all at once and the mixture was stirred for another 45 mins under the inert atmosphere. The mixture was filtered through Celite washing the cake thoroughly with CH_2Cl_2. The filtrate was concentrated using a rotary evaporator and the crude residue (**36**) obtained and used directly in step 2.



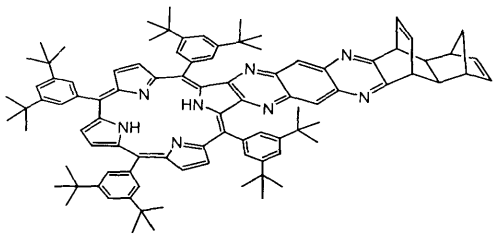
Step 2: The crude amino-porphyrin (**36**), from step 1, was dissolved in CH_2Cl_2 (750 mL) and the solution was irradiated with visible light (500 W lamp) and bubbled with $O_{2(g)}$ simultaneously for 20 hrs. Dilute hydrochloric acid (300 mL) was added and the mixture stirred vigorously for 8 hrs at R.T. The organic layer was separated and the aqueous layer extracted with $CHCl_3$ (4 x 50 mL). The combined organic layers were washed with water (3 x 200 mL), saturated $NaHCO_{3(aq)}$ (2 x 100 mL) and again with water (2 x 200 mL). The organics were dried over Na_2SO_4 (anhyd.) and the solvent removed using a rotary evaporator. The product was recrystallised from CH_2Cl_2/MeOH giving (**37**) as a fine brown solid (442 mg). Yield = 63%; m.p. > 300°C; ^{1}H NMR ($CDCl_3$) δ 8.77 (2H, d, *J* = 6 Hz) 8.60 (2H, d, *J* = 6 Hz), 8.61 (2H, s), 7.98 (4H, d, *J* = 1.8 Hz), 7.71 (4H, d, *J* = 1.8 Hz), 7.77 (2H, t, *J* = 2 Hz), 7.74 (2H, t, *J* = 2 Hz), 1.50 (36H, s), 1.46 (36H, s), -1.93 (2H, bs). NMR data identical to published data.[9]

^{t}Bu H_2TPP-q-$(NH_2)_2$ (38)



Porphyrin dione (**37**) (30 mg, 2.7 x 10^{-5} mol) was dissolved in dry deoxygenated pyridine (30 mL) and BTA (9 mg, 3.3 x 10^{-5} mol) was added all at once to the stirred solution. The solution was stirred under $N_{2(g)}$ at R.T. in darkness for 14 days. The pyridine solution was diluted with 100 mL of water and extracted with diethyl ether (3 x 100 mL). The combined organic layers were washed with water (5 x 100 mL) and dried over Na_2SO_4 (anhyd.) The solvent was removed using a rotary evaporator and the residue dried under vacuum for overnight. The residue was purified by flash column chromatography [silica, CH_2Cl_2/Pet.Spirit (1:1)] giving the product as a brown/purple solid (32 mg). The product was purified further by recrystallising from CH_2Cl_2/MeOH to give a brown/purple solid Yield = 85%; m.p. > 300 °C; ^{1}H NMR ($CDCl_3$) δ 9.04 (2H, d, *J* = 5 Hz), 8.99 (2H, d, *J* = 5 Hz), 8.81 (2H, s), 8.13 (4H, d, *J* = 2 Hz), 8.00 (4H, d, *J* = 2 Hz), 7.92 (2H, t, *J* = 2 Hz), 7.82 (2H, t, *J* = 2 Hz), 6.97 (2H, s), 3.94 (4H, bs), 1.56 (36H, s), 1.52 (36H, s), -2.45 (2H, bs).

^{t}BuPBlock (39)



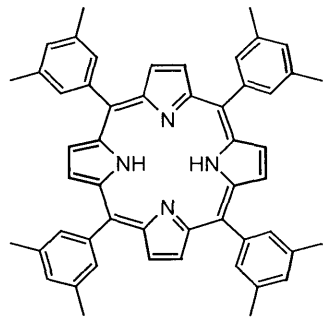
Method 1: Nitrogen gas was bubbled through a solution of the porphyrin diamine (**38**) (30 mg, 2.5 x 10^{-5} mol) in dry pyridine (3 mL) for 5 minutes. The polycycic dione (**7**) (13 mg, 6.5 x 10^{-5} mol, 2.6 eqv.) was added and the solution stirred under $N_{2(g)}$ at R.T. in darkness for 3 days then heated at 60°C for 3 hrs. After allowing the solution to cool to R.T. the solvent was removed using a rotary evaporator and the residue dried under vacuum for 2 hrs. The product was recrystallised from CH_2Cl_2/MeOH giving two crops of a fine brown solid (28 mg) Yield = 82%; m.p > 300°C; ^{1}H NMR* ($CDCl_3$) δ 9.00 (2H, d, *J* = 5 Hz), 8.95 (2H, d, *J* = 5 Hz), 8.75 (2H, s), 8.48 (2H, s), 8.08 (4H, d, *J* = 4 Hz), 7.99 (4H, d, *J* = 2 Hz), 7.92 (2H, t, *J* = 2 Hz), 7.79 (2H, t, *J* = 2 Hz), 6.66 (2H, t, *J* = 4 Hz), 6.25 (2H, bs), 4.18 (2H, bs) 2.93 (2H, bs), 2.81 (1H, d, *J* = 9 Hz), 2.20 (2H, s), 1.54 (36H, s), 1.49 (36H, s), 1.25 (1H, d, *J* = 9 Hz), -2.41 (2H, bs); HRMS $C_{95}H_{107}N_8$: calculated 1359.862; m/z (ES) $(M+H)^+$ observed 1359.863.

* NMR data in agreement with literature values.[10]

Method 2: Nitrogen gas was bubbled through a solution of porphyrin dione (**37**) (200 mg, 1.82 x 10^{-4} mol) in dry pyridine (4 mL) for 20 mins. BTA (78 mg, 2.73 x 10^{-4} mol, 1.5 eqv.) was added all at once and the solution heated at reflux temperature for 1 hr under $N_{2(g)}$ in darkness. The polycyclic dione (**7**) (73 mg, 3.64 x 10^{-4} mol, 2 eqv.) was added all at once and heating under $N_{2(g)}$ was continued for 8 hrs. The solution was allowed to cool to R.T. and the solvent was removed under reduced pressure. The residue was partitioned between CH_2Cl_2 and H_20 and the aqueous layer extracted with CH_2Cl_2. The combined organics were washed well with water, dried over Na_2SO_4 (anhyd.) and solvents removed by rotary evaporator. The residues were dried under vacuum for 12 hrs and then purified by flash column chromatography [silica, CH_2Cl_2/Pet.Spirit (1:1)]. Final purification by recrystallisation from CH_2Cl_2/MeOH gave (**39**) as a fine brown solid (214 mg). Yield = 85%; ^{1}H NMR in agreement with product from method 1.

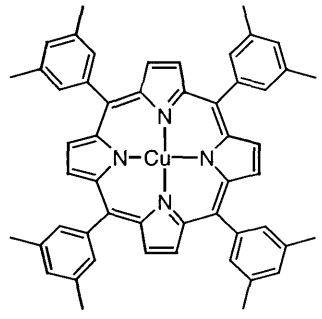
5,10,15,20-*tetrakis*-(3,5-dimethylphenyl) porphyrin (41)

Freshly distilled pyrrole (7.3 g, 0.11 mol) was added to a refluxing solution of 3,5-dimethylbenzaldehyde (14.5 g, 0.11 mol) in propionic acid (400 mL) and heated at reflux temperature for 30 mins. The solution was allowed to cool slowly to room temperature and then left to stand overnight. The solids were separated by filtration and washed with boiling water (500



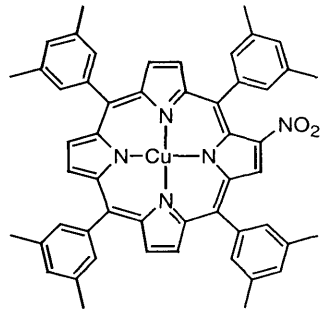
mL) followed by cold acetone (20 mL) and again with boiling water (100 mL). The crystalline solids were dried under vacuum at room temperature overnight and the final product was obtained as lustrous purple crystals. Yield = 3.5 g (18%); m.p. > 300°C; ^{1}H NMR ($CDCl_3$) δ 8.85 (8H, s), 7.82 (8H, s), 7.39 (4H, bs), 2.59 (24H, s), -2.77 (2H, bs); ^{13}C NMR ($CDCl_3$) δ 142.1, 135.8, 132.9, 130.9 (broad), 129.2, 120.3, 21.5.

[5,10,15,20-*tetrakis*-(3,5-dimethylphenyl) porphyrinato]copper(II) (42)



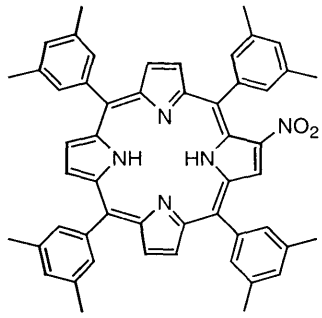
A solution of cupric acetate monohydrate (2.40 g, 12.0 mmol) in methanol (70 mL) was added to a solution of (**41**) (2.67 g), 3.67 mmol) in $CHCl_3$ (400 mL) and this mixture was heated at reflux temperature with stirring for 8 hrs. The solution was allowed to cool slightly and washed with water (300 mL). The aqeuous layer was extracted with $CHCl_3$ (2 x 50 mL) and the combined organic layers washed with water (2 x 100 mL), dried over Na_2SO_4 (anhyd.) and the solvent removed using a rotary evaporator. The product was recrystallised from $CHCl_3$/MeOH to giving a pinkish-purple crystalline solid (2.88 g). Yield = quantitative; m.p. > 300°C; UV-Vis ($CHCl_3$/nm) (logε) 417 (5.70), 539 (4.28), 571 (3.43).

2-nitro-[5,10,15,20-*tetrakis*-(3,5-dimethylphenyl) porphyrinato]copper(II) (43)



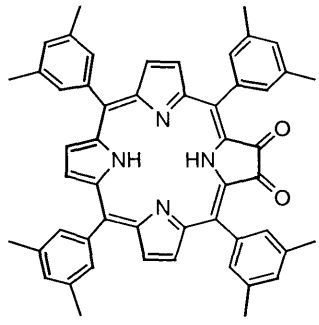
[5,10,15,20-*tetrakis*-(3,5-dimethylphenyl) porphyrinato]copper(II) (**42**) (1.00 g, 1.27 mmol) was dissolved in $CHCl_3$ (150 mL). The solution was stirred at r.t. and successively treated with small aliquots (~0.5 mL) of a chilled (ice bath) NO_2/hexane solution (0.32 g/20 mL). The reaction was monitored by TLC ($CHCl_3$) and NO_2/Pet.Spirit additions were halted after the starting material (**42**) could no longer be detected. The solution was filtered through a silica plug and the silica washed thoroughly with $CHCl_3$ (~100 mL). The solvent was removed from the filtrate using a rotary evaporator and the residues purified by recrystallisation from $CHCl_3$/MeOH to give (**43**) as purple crystals (0.83 g); Yield = 78%; m.p. > 300°C; IR ($CHCl_3$) ν(NO_2) 1513 cm^{-1}; UV-Vis ($CHCl_3$)/nm (logε) 421 (5.33), 518 (3.84), 550 (4.21), 591 (4.01).

2-nitro-5,10,15,20-*tetrakis*-(3,5-dimethylphenyl) porphyrin (44)



2-nitro-[5,10,15,20-*tetrakis*-(3,5-dimethylphenyl) porphyrinato] copper(II) (**43**) (2.65 g, 3.18 mmol) was dissolved in $CHCl_3$ (350 mL) and $H_2SO_{4(aq)}$ (98%, 15 mL) was added. The mixture was shaken vigorously for about 20 min and poured onto ice (500 g). The organic layer was separated and the aqeous layer extracted with $CHCl_3$ (6 x 25 mL). The combined organics were washed with water (3 x 200 mL), $Na_2CO_{3(aq)}$ (5%, 2 x 200 mL) and again with water (1 x 200 mL) and then dried over Na_2SO_4 (anhyd.). The solvent was removed using a rotary evaporator and the product recrystallised from $CHCl_3$/MeOH to give (**44**) as purple crystals (2.33 g). Yield = 95%; m.p. > 300 °C; ^{1}H NMR ($CDCl_3$) δ 9.06 (1H, d, J = 5 Hz), 9.05 (1H, s), 8.95-8.88 (3H, m), 8.73 (1H, s), 8.72 (1H, s), 7.86 (2H, bs), 7.81 (2H, bs), 7.80 (4H, bs), 7.41 (3H, bs), 7.38 (1H, bs), 2.60 (18H, bs), 2.58 (6H, bs), -2.64 (2H, bs).

2,3-dioxo-5,10,15,20-*tetrakis*-(3,5-dimethylphenyl)porphyrin (46)

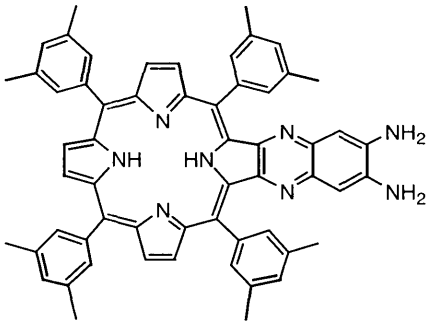


Step 1: A chloroform/methanol mixture (1:1; 500 mL) was added to nitro-porphyrin (**44**) (2.00 g, 2.59 mmol) and 10%Pd/C (~2 g). The mixture was deoxygenated by bubbling $N_{2(g)}$ through the mixture for 20 mins. Sodium borohydride (200 mg) was added all at once and the mixture stirred at R.T. under $N_{2(g)}$ for 1 hr. The reaction mixture was filtered through Celite washing thoroughly with $CHCl_3$. The filtrate was concentrated and washed with water (3 x 200 mL), dilute $HCl_{(aq)}$ (3 x 100 mL) and again with water (3 x 200 mL). The organics were dried over Na_2SO_4 (anhyd.) and the solvents removed using a rotary evaporator. The residues were dried under vacuum in darkness overnight giving the crude aminoporphyrin (**45**) as a purple solid, which was used immediately in the next step.

Step 2: Crude 2-amino-5,10,15,20-*tetrakis*-(3,5-dimethylphenyl)porphyrin (**45**) was dissolved in $CHCl_3$ (500 mL). Oxygen gas was bubbled through the stirred solution whilst being irradiated using a 500 W visible lamp at R.T. for 24 hrs. Dilute $HCl_{(aq)}$ (100 mL) was added and the mixture stirred at R.T. for 1 hr. The organic layer was separated and the aqueous layer extracted with $CHCl_3$. The combined organic layers were washed with water (3 x 100 mL), saturated $NaHCO_{3(aq)}$ (2 x 100 mL) and again with water (2 x 100 mL). The organics were dried

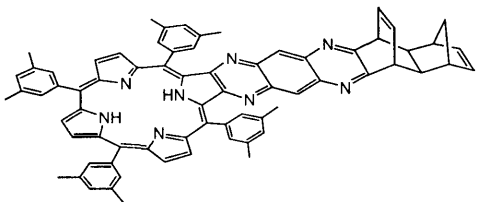
over Na_2SO_4 (anhyd.) and the solvent removed using a rotary evaporator. The crude product was dried under vacuum and purified using flash column chromatography (silica, 50% $CHCl_3$/Pet.Spirit). A distinct olive-green band with a lower R_f compared with the starting material was found to correspond to the desired product (**46**), which was obtained as a dark olive-green solid (1.38 g) after recrystallisation from $CHCl_3$/MeOH. Yield = 72%; m.p. > 300°C; ^{1}H NMR ($CDCl_3$) δ 8.75 (2H, d, *J* = 5 Hz), 8.62 (2H, d, *J* = 5 Hz), 8.57 (2H, s), 7.73 (4H, s), 7.50 (2H, s), 7.39 (2H, s), 7.36 (2H, s), 2.57 (12H, s), 2.53 (12H, s), -2.04 (2H, bs).

MeH$_2$TPP-q -(NH$_2$)$_2$ (47)



Porphyrin dione (**46**) (68 mg, 9.0 x 10^{-5} mol) was dissolved in dry deoxygenated pyridine (30 mL) and BTA (30 mg, 1.0 x 10^{-4} mol) was added all at once to the stirred solution. The solution was stirred under $N_{2(g)}$ at R.T. in darkness for 38 hrs. The pyridine solution was diluted with 150 mL of water and extracted with diethyl ether (3 x 60 mL). The combined organic layers were washed with water (6 x 100 mL) and dried over Na_2SO_4 (anhyd.) The solvent was removed using a rotary evaporator and the residue dried under vacuum for 3 hrs. The residue was purified by flash column chromatography [silica, CH_2Cl_2/Pet.Spirit (3:1)] giving the product as a purple solid (27 mg). Yield = 35%; ^{1}H NMR ($CDCl_3$) δ 8.95 (2H, d, *J* = 5 Hz), 8.90 (2H, d, *J* = 5 Hz), 8.71 (2H, s), 7.83 (4H, s), 7.77 (4H, s), 7.47 (2H, s), 7.40 (2H, s), 7.05 (2H, s), 3.98 (4H, bs), 2.59 (24H, s), -2.57 (2H, bs).

MePBlock (48)



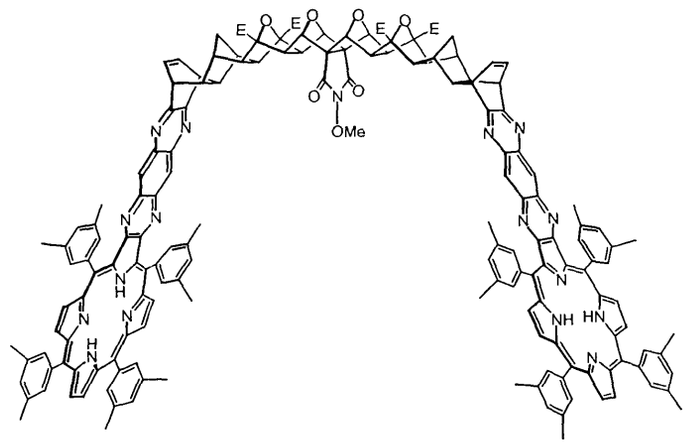
Method 1 Nitrogen gas was bubbled through a solution of the crude porphyrin diamine (**47**) (13 mg, 1.5 x 10^{-5} mol) in dry pyridine (2 mL) for 5 minutes. The polycycic dione (**7**) (4 mg, 2.0 x 10^{-5} mol) was added and the solution stirred under $N_{2(g)}$ at R.T. in darkness for 19 hrs then heated at 60°C for 2 hrs. The solvent was removed using a rotary evaporator and the residue dried under vacuum for 2 hrs. The residue was then dissolved in a minimum of a CH_2Cl_2/Pet.Spirit mixture (4:1) and purified by flash column chromatography [silica, CH_2Cl_2/Pet.Spirit (1:1)] giving a dark brown solid (15 mg). Yield = 98%; m.p > 300°C; ^{1}H NMR ($CDCl_3$) δ 9.01 (2H, d, *J* = 5 Hz), 8.93 (2H, d, *J* = 5 Hz), 8.72 (2H, s), 8.60 (2H, s), 7.83 (4H, bs),

7.77 (4H, bs), 8.04 (6H, bs), 7.51 (2H, bs), 7.41 (2H, bs), 6.68 (2H, t, J = 4 Hz), 6.27 (2H, bs), 4.18 (2H, t, J = 4 Hz) 2.96 (2H, bs), 2.82 (1H, d, J = 8 Hz), 2.60-2.58 (24H, m), 2.21 (2H, bs), 1.49 (2H, bs), 1.24 (1H, d, J = 8 Hz), -2.49 (2H, bs); ^{13}C NMR ($CDCl_3$) δ 160.7, 154.9, 153.4, 145.4, 141.8, 141.3, 140.7, 139.7, 139.6, 138.9, 138.0, 136.1, 136.0, 134.4, 133.9, 132.7, 132.0, 129.4, 129.2, 129.0, 128.1, 127.9, 122.1, 117.1, 46.8, 46.5, 45.5, 42.3, 21.6, 21.5; HRMS $C_{71}H_{59}N_8$: calculated 1023.486; m/z (ES) $(M+H)^+$ observed 1023.485.

Method 2 Porphyrin dione (**46**) (156 mg, 2.06 x 10^{-4} mol) was dissolved in dry deoxygenated pyridine (4 mL) and BTA (100 mg, 3.52 x 10^{-4} mol, 1.7 eqv.) was added all at once to the stirred solution. The solution was stirred under $N_{2(g)}$ at reflux temperature in darkness for 1.5 hrs. The polycyclic dione (**7**) (83 mg, 4.0 x 10^{-4} mol, 2 eqv.) was added all at once and the solution heated at reflux under $N_{2(g)}$ in darkness for 8 hrs. The solution was allowed to cool to R.T. and the solvent removed under reduced pressure with mild heating. The residue was partitioned between $CHCl_3$ and H_2O (10 mL of each) and the organic layer separated. The aqueous layer was extracted with $CHCl_3$ (3 x 3 mL) and the combined organics washed with H_2O (6 x 10 mL) and dried over Na_2SO_4 (anhyd.). The solvent was removed on a rotary evaporator and the residue recrystallised from $CHCl_3$/MeOH. The first crop of crystals was analysed by NMR and UV-Vis. Both spectra indicated that this material was the quinoxalino-pyrazine bridged porphyrin dimer (**49**) (54 mg). Yield = 33% (from porphyrin dione); m.p. > 300°C; UV-Vis ($CHCl_3$ (logε) 424 (5.47), 456 (5.40), 608 (4.18), 628 (4.20), 676 (3.82); ^{1}H NMR ($CDCl_3$) δ 9.14 (4H, d, J = 5 Hz), 8.98 (4H, d, J = 5 Hz), 8.74 (4H, s), 8.60 (2H, s), 7.86 (16H, bs), 7.79 (4H, bs), 7.43 (4H, bs), 2.76 (24H, s), 2.63 (24H, s), -2.37 (4H, bs). The filtrate was concentrated and the residues purified by flash column chromatography [silica, Pet.Spirit/$CHCl_3$ (1:5)]. TLC analysis of all fractions showed that none of the unwanted porphyrin dimer (**49**) was present. The product fractions were combined, concentrated and the residue recrystallised from $CHCl_3$/MeOH to give the porphyrin Block (**48**) as a brown solid (62 mg). Yield = 30%. The identity of the product was confirmed by co-spotting with a sample prepared from Method 1 (above) on a TLC plate as well as by NMR.

References, p.204

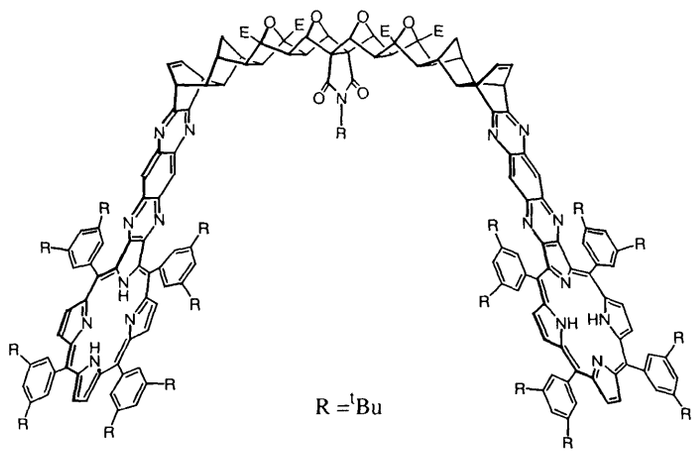
MePSP (51)



MePBlock (**48**) (29 mg, 2.8 x 10^{-5} mol) and *p*-methoxyphenyl *bis*-epoxide (**30**) (8.0 mg, 1.5 x 10^{-5} mol, 0.54 eqv.) were dissolved in 1,2-dichloroethane (1.0 mL) and heated in a sealed glass tube at 148°C for 75 hrs. The product was obtained after chromatographic purification (column: silica, $CHCl_3$) as a brown solid (~2 mg*). Yield ≈ 5%; m.p. > 300°C; ^{1}H NMR ($CDCl_3$) 8.97 (4H, d, *J* = 5 Hz), 8.90 (4H, d, *J* = 5 Hz), 8.69 (4H, s), 8.57 (4H, s), 7.80 (8H, s), 7.75 (4H, s), 7.72 (4H, s), 7.49 (4H, s), 7.39 (4H, s), 6.91 (2H, d, *J* = 8 Hz), 6.72 (2H, d, *J* = 8 Hz), 6.53 (4H, t, *J* = 3.5 Hz), 4.69 (4H, s), 4.21 (4H, t, *J* = 3.5 Hz), 3.93 (12H, s), 3.87 (3H, s), 2.58 (48H, bs), 2.42 (4H, s), 2.37 (4H, s), 2.18 (2H, d, *J* = 10 Hz), 2.04 (2H, d, *J* = 10 Hz), 1.91 (4H, s), 1.88 (4H, s), -2.52 (4H, bs). * Unknown porphyrinic impurity(s) present according to NMR spectrum (see Fig. 2.18, p100)

^{t}Bu PSP (52)

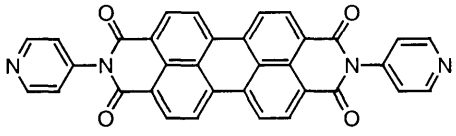
Larger-Scale Method



In a thick-walled glass reaction tube a solution of ^{t}BuPBlock (**39**) (111 mg, 8.16 x 10^{-5} mol) and *bis*-epoxide (**29**) (28 mg, 4.1 x 10^{-5} mol) in CH_2Cl_2 (3.0 mL) was degassed, by feeze-thawing (x4) under high vacuum. The reaction vessel was flame-sealed under vacuum and the solution heated and magnetically stirred at 140°C for 90 hrs. The reaction mixture was added directly to the top of a wet (2% MeOH/CH_2Cl_2) silica column and the product purified chromatographically (flash column). The product was obtained as a brown solid (80 mg) and further purified by recrystallisation from CH_2Cl_2/MeOH gave the final product (52 mg) in 38% yield. m.p. > 300°C; ^{1}H NMR ($CDCl_3$) δ 9.02 (4H, d, *J* = 5 Hz), 8.97 (4H, d, *J* = 5 Hz), 8.77 (4H,

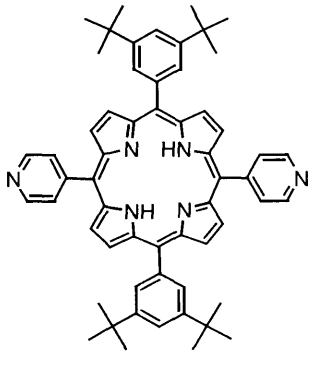
s), 8.50 (4H, s), 8.10 (8H, s), 7.99 (4H, s), 7.95 (4H, s), 7.81 (4H, s), 7.30 (2H, m), 6.95 (2H, m), 6.55 (4H, t, J = 4 Hz), 4.72 (4H, s), 4.26 (4H, t, J = 4 Hz), 3.96 (12H, s), 2.46 (4H, s), 2.39 (4H, s), 2.20 (2H, d, J = 10 Hz), 2.06 (2H, d, J = 10 Hz), 1.92 (4H, s), 1.90 (4H, s), 1.53 (36H, s), 1.52 (36H, s), 1.49 (72H, s), 0.98 (3H, s) -2.40 (4H, bs); ^{13}C NMR ($CDCl_3$) δ 172.0, 168.1, 158.5, 155.0, 153.7, 149.1, 149.0, 148.8, 145.5, 141.0, 140.7, 139.8, 139.6, 138.9, 138.1, 134.2, 133.6, 129.5, 129.0, 128.6, 128.3, 128.1, 126.5, 124.9, 123.0, 121.2, 120.7, 117.9, 89.5, 82.7, 70.6, 57.2, 52.9, 52.8, 46.7, 46.5, 43.8, 35.0, 35.0, 31.9, 31.7, 30.9.

N,N-*bis*-(4'-pyridine)-perylene-3,4:9,10-*bis*-dicarboximide (perylbipy) (79)



perylene-3,4:9,10-tetracarboxylic anhydride (1.00 g, 2.55 mmol), *p*-aminopyridine (2.00 g, 24.4 mmol) and an excess of imidazole (~20 g) were placed in a 25 mL RBF equipped with a reflux condenser and boiling chips. The mixture was heated in a microwave oven (500 W domestic) for 3 minutes on a high setting (reflux temperature) and allowed to cool to room temperature. Solids were filtered off and washed with water (300 mL), acetone (50 mL) and again with water. The solids were transferred to a conical flask and stirred with dilute $HCl_{(aq)}$ (150 mL) at R.T. for 4 hrs. The solids were filtered off, washed with water (300 mL), $NaHCO_{3(aq)}$ (100 mL) and again with water (200 mL) and dried under vacuum overnight to give a maroon-coloured solid (1.29 g). Yield = 93%; m.p. > 300°C; I.R. (nujol) ν_{CO} = 1700 and 1670 cm^{-1}; ^{1}H NMR (TFA; external $CDCl_3$ reference) δ 9.08 (4H, d, J = 6 Hz), 8.91 (8H, m), 8.35 (4H, d, J = 6 Hz).

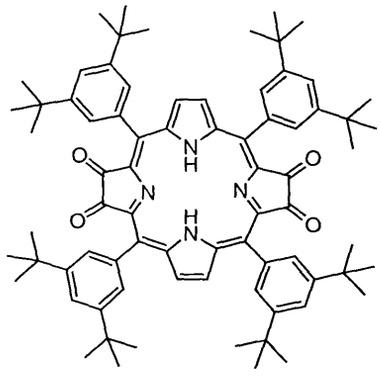
5,15-*bis*-(4-pyridyl)-10,20-*bis*-(3,5-di-*tert*butylphenyl)porphyrin (bipyP) (80)



To a refluxing solution of pyridine-4-carbaldehyde (1.00 g, 9.34 mmol) was added, all at once, dipyrromethane (**96**) (3.12 g, 9.34 mmol). Heating of the solution at reflux temperature was continued for 1 hr and then allowed to cool slowly to room temperature. Fine purple crystals were filtered off and washed with hot water (200 mL), acetone (20 mL) and again with hot water (100 mL). The product was purified using flash column chromatography (silica, $CHCl_3$) followed by recrystallisation from $CHCl_3$/MeOH giving a fine light-purple crystalline solid (30 mg). Yield = 0.8%; m.p. > 300°C; ^{1}H NMR ($CDCl_3$) δ 9.02 (4H, m), 8.93 (4H, d, J = 5 Hz), 8.80 (4H, d, J = 5 Hz), 8.17 (4H, m), 8.07 (4H, d, J = 2 Hz), 7.82 (2H, t, J = 2

Hz), 1.53 (36H, s), -2.78 (2H, bs); HRMS $C_{58}H_{61}N_6$: calculated 841.4958; m/z (ES) $(M+H)^+$ observed 841.4980

2,3,12,13-tetraoxo-5,10,15,20-*tetrakis*-(3,5-di-*tert*-butylphenyl)porphyrin (102)[8]



Step 1 [5,10,15,20-*tetrakis*-(3,5-di-*tert*-butylphenyl) porphyrinato]copper(II) (**33**) (500 mg, 6.34 x 10^{-4} mol) was dissolved in CH_2Cl_2 (100 mL) and cooled to 5°C. The solution was stirred and successively treated with small aliquots (~0.5 mL) of a chilled (ice bath) NO_2/hexane solution (0.32 g/20 mL). The reaction was monitored by TLC ($CHCl_3$) and NO_2/Pet.Spirit additions were halted after the initially formed 2-nitro-[5,10,15,20-*tetrakis*-(3,5-di-*tert*-butylphenyl) porphyrinato]copper(II) (**43**) could no longer be detected*. The solution was filtered through a silica plug and the silica washed thoroughly with $CHCl_3$ (~200 mL). The solvent was removed from the filtrate using a rotary evaporator and the residues dried under vacuum overnight giving a crude mixture of dinitro-porphyrinato copper(II) isomers (**97**) as a purple solid (620 mg) (several olive-green bands by TLC; silica, $CHCl_3$). Yield = 81%; m.p. > 300°C; IR (CH_2Cl_2) $\nu(NO_2)$ 1527 cm^{-1} (lit. 1531 cm^{-1} KBr).

Step 2 A solution of the crude dinitro-porphyrinato copper(II)s (**97**) (620 mg, 5.1 x 10^{-4} mol) in CH_2Cl_2 (40 mL) was treated with $H_2SO_{4(aq)}$ (98%, 3 mL) and stirred vigorously for 20 min and poured onto ice (50 g). The organic layer was separated and the aqeous layer extracted with CH_2Cl_2 (3 x 15 mL). The combined organics were washed with water (3 x 50 mL), $Na_2CO_{3(aq)}$ (5%, 2 x 50 mL) and again with water (3 x 50 mL) and then dried over Na_2SO_4 (anhyd.). The solvent was removed using a rotary evaporator and the crude product (**98**) dried overnight under vacuum to give a purple solid (450 mg). Yield = 77%; m.p. > 300°C; IR (CH_2Cl_2) $\nu(NO_2)$ 1477 and 1364 cm^{-1} (lit. 1477 and 1363 cm^{-1} KBr).

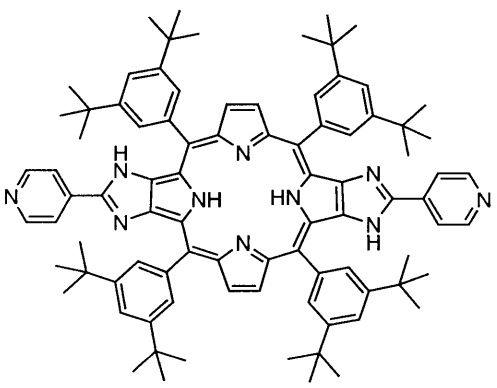
Step 3 A stirred mixture of the crude dinitro-porphyrins (**98**) (400 mg, 3.5 x 10^{-4} mol) and 5% Pd/C (520 mg) in CH_2Cl_2/MeOH (1:1, 200 mL) was deoxygenated by bubbling nitrogen gas through it for 30 min. Sodium borohydride ($NaBH_4$, 70 mg) was added all at once and the mixture stirred with continued $N_{2(g)}$ bubbling for 2 hrs at room temperature. The mixture was filtered

* cospotted (TLC) with a previously prepared sample of (**43**).

through Celite washing the cake thoroughly with CH_2Cl_2. The filtrate was concentrated using a rotary evaporator and the brown-purple residue (**99**) was used immediately in the next step.

Step 4 The crude diamino-porphyrins (**99**) were dissolved in CH_2Cl_2 (300 mL). The solution was stirred and irradiated (500 W visible lamp) whilst $O_{2(g)}$ was being continuously bubbled through it at room temperature for 24 hrs. Dilute $HCl_{(aq)}$ (120 mL) was added and the mixture stirred at r.t. for 1 hr. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic layers were washed with water (3 x 100 mL), saturated $NaHCO_{3(aq)}$ (2 x 50 mL) and again with water (2 x 100 mL). The organics were dried over Na_2SO_4 (anhyd.) and the solvent removed using a rotary evaporator. To a refluxing solution of the crude residue in $CHCl_3$ (10 mL) was added a saturated solution of zinc acetate dihydrate in MeOH (3 mL). The solution was heated at reflux temperature for 30 mins. The reaction mixture was partitioned between $CHCl_3$ and H_2O. The organic layer was separated and the aqueous layer extracted with $CHCl_3$. The combined organic layers were washed with H_2O (3 x 50 mL) and dried over Na_2SO_4 (anhyd.). The solvent was removed under reduced pressure. The product was purified using flash column chromatography (silica, 50% hexane/$CHCl_3$). Two main bands (1 x narrow olive-green and 1 x broad orange) were evident with the olive-green band (non-polar) being isolated as the product (**102**) (orange polar bands are expected to correspond to the zinc amino-dioxoporphyrins, **101**).[11] Recrystallisation from $CHCl_3$/MeOH gave the tetraoxo-porphyrin (**102**) (26 mg). Yield = 7% (from **98**); m.p. > 300°C; ^{1}H NMR ($CDCl_3$) δ 8.50 (4H, d, *J* = 2 Hz), 7.75 (4H, t, *J* = 2 Hz), 7.65 (8H, d, *J* = 2 Hz), 1.46 (72H, s), -1.78 (2H, bs); ^{13}C NMR ($CDCl_3$) δ 186.9, 149.3, 140.7, 139.6, 137.5, 128.9, 127.1, 121.7, 118.3, 35.0, 31.7.

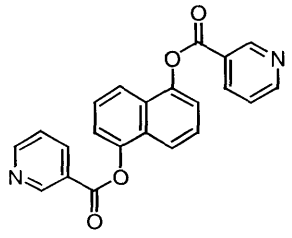
***bis*-[2-(4-pyridyl)-1*H*-imidazo]porphyrin (imibipyP) (81)**



2,3,12,13-tetraoxo-5,10,15,20-*tetrakis*-(3,5-di-*tert*-butylphenyl)porphyrin (**102**) (26 mg, 2.3 x 10^{-5} mol), pyridine-4-carbaldehyde (6.5 mg, 6.0 x 10^{-5} mol) and NH_4OAc (50 mg) were stirred in refluxing AcOH (glacial)/$CHCl_3$ (1:1, 5 mL) for 4 hrs. The reaction mixture was washed with water (3 x 10 mL), $NaHCO_{3(aq)}$ (3 x 10 mL) and again with water (2 x 10 mL), dried over $NaSO_4$ (anhyd.) and the solvent removed using a rotary evaporator. The residue was purified using flash column chromatography (silica, $CHCl_3$) giving

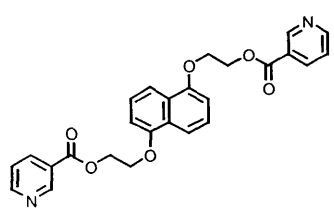
imibipyP (**81**) (10 mg). Yield = 34%; m.p. > 300°C; ^{1}H NMR ($CDCl_3$) broad unresolved spectrum described in Chapter 3 (Section 3.2.2.3); UV-Vis (CH_2Cl_2) λ_{max} (logε)/nm 423 (5.15), 516 (4.03), 551 (3.93), 587 (3.87), 638 (3.54), 659 (3.53); HRMS $C_{88}H_{100}N_{10}$: calculated 1297.821; m/z (ES) $(M+H)^+$ observed 1297.820

Nicotinic acid 5-nicotinoyloxy-naphthalen-1-yl ester ($f_0$bipy) (82)



Naphthalene-1,5-diol (160 mg, 1.0 mmol), nicotinic acid (369 mg, 3.0 mmol) and HOBT (405 mg, 3.0 mmol) were placed in a two-necked RBF fitted with a septum and the flask flushed with $N_{2(g)}$ for 60 secs. Dry THF (20 mL) was added under $N_{2(g)}$ (canula) and the solution stirred for 5 mins. EDC (575 mg, 3.0 mmol) was added followed by Et_3N (dry, 800 μL). The solution was stirred under $N_{2(g)}$ at R.T. in darkness for 5 days. The solvents were removed under reduced pressure and the residue was partitioned between $CHCl_3$ and H_2O. The aqueous layer was extracted with $CHCl_3$ and the combined organics washed with water, dried over $NaSO_4$ (anhyd.) and the solvent removed on a rotary evaporator. The product was dried under vacuum overnight giving a reddish-brown solid (320 mg). Yield = 87%; m.p. = 189-192°C; ^{1}H NMR ($CDCl_3$) δ 9.55 (2H, s), 8.92 (2H, d, *J* = 4 Hz), 8.57 (2H, m), 7.89 (2H, d, *J* = 8 Hz), 7.59-7.51 (4H, m), 7.46 (2H, d, *J* = 8 Hz); HRMS $C_{22}H_{14}N_2O_4$: calculated 370.0954; m/z (EI) M^+ observed 370.0952.

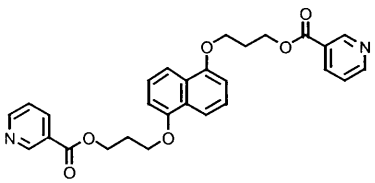
Nicotinic acid 2-[5-(2-nicotinoyloxyethoxy)-naphthalen-1-yloxy]-ethyl ester ($f_2$bipy) (83)



Step 1: A solution of 2-chloroethanol (3.2 g, 34 mmol) in MeCN (15 mL) was added, all at once, to a refluxing mixture of naphthalene-1,5-diol (1.6 g, 10 mmol) and K_2CO_3 (7 g) in MeCN (25 mL) . Heating was continued at reflux temperature under $N_{2(g)}$ for 7 days. The reaction mixture was allowed to cool to R.T. and the solids filtered off and washed with $CHCl_3$ (30 mL). The filtrate was concentrated and the residues were partitioned between $CHCl_3$ and H_2O. The organic layer was washed with $NaHCO_{3(aq)}$ (sat.), dil. $HCl_{(aq)}$, and finally with H_2O. The organics were dried over Na_2SO_4 and the solvent removed using a rotary evaporator. The residues were dried under vacuum overnight giving the crude product (**57**) (482 mg) as a white solid. Yield (crude) = 15%

Step 2: Crude 1,5-*bis*-(2-hydroxy-ethoxy)-naphthalene (**57**) (355 mg, 1.43 mmol), nicotinic acid (1.0 g, 8.1 mmol) and HOBT (1.1 g, 8.1 mmol) were placed in a two-necked RBF fitted with a septum and the flask flushed with $N_{2(g)}$ for 60 secs. Dry THF (24 mL) and $CHCl_3$ (12 mL) were added under $N_{2(g)}$ (canula) and the solution stirred for 5 mins. EDC (1.2 g, 6.0 mmol) was added followed by Et_3N (dry, 830 μL). A white precipitate formed immediately upon the addition of triethylamine. The mixture was stirred under $N_{2(g)}$ at R.T. in darkness for 3 days. The solvents were removed under reduced pressure and the residue was partitioned between $CHCl_3$ and $HCl_{(aq)}$ (6 M). The aqueous layer was neutralised and extracted with $CHCl_3$ and the combined organics washed with water and dried over $NaSO_4$ (anhyd.). A small sample was purified by recrystallisation from $CHCl_3$/hexane giving the product as a light-red solid (20.0 mg). Yield = 3%; m.p. = 128-130°C; ^{1}H NMR (d_6-acetone) δ 9.17 (2H, d, *J* = 2Hz), 8.78 (2H, s), 8.35-8.31 (2H, m), 7.86 (2H, d, *J* = 8.5 Hz), 7.53-7.49 (2H, m), 7.37 (2H, t, *J* = 8 Hz), 7.05 (2H, d, *J* = 8 Hz), 4.88 (4H, t, *J* = 5 Hz), 4.59 (4H, t, *J* = 5 Hz); HRMS $C_{26}H_{22}N_2O_6$: calculated 458.1478; m/z (M^+) EI observed 458.1471.

Nicotinic acid 3-[5-(3-nicotinoyloxypropoxy)-naphthalen-1-yloxy]-propyl ester ($f_3$bipy) (84)

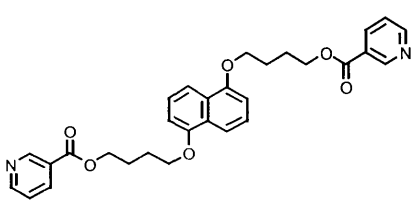


Step 1: A solution of 3-bromopropan-1-ol (5.6 g, 40 mmol) in MeCN (15 mL) was added, all at once, to a mixture of naphthalene-1,5-diol (1.6 g, 10 mmol) and K_2CO_3 (7 g) in MeCN (25 mL) . The mixture was stirred under $N_{2(g)}$ at R.T. for 3 days and then heated at reflux temperature for 1 hr. After cooling to R.T. the solids were filtered off and washed with $CHCl_3$ (30 mL). The filtrate was concentrated and the residues were partitioned between $CHCl_3$ and H_2O. The organic layer was washed with $NaHCO_{3(aq)}$ (sat.), dil. $HCl_{(aq)}$, and finally with H_2O. The organics were dried over Na_2SO_4 and the solvent removed using a rotary evaporator. The residues were dried under vacuum overnight. Yield (crude) = 25%

Step 2: A sample of the crude 1,5-*bis*-(3-hydroxy-propoxy)-naphthalene (**58**) (204 mg, 0.74 mmol), nicotinic acid (0.37 g, 3.0 mmol) and HOBT (0.40 g, 3.0 mmol) were placed in a two-necked RBF fitted with a septum and the flask flushed with $N_{2(g)}$ for 60 secs. Dry THF (15 mL) and $CHCl_3$ (5 mL) were added under $N_{2(g)}$ (canula) and the solution stirred for 5 mins. EDC (0.43 g, 2.2 mmol) was added followed by Et_3N (dry, 500 μL). A precipitate formed immediately upon the addition of triethylamine. The mixture was stirred under $N_{2(g)}$ at R.T. in darkness for 6 days. The solvents were removed under reduced pressure and the residue was partitioned between

$CHCl_3$ and $HCl_{(aq)}$ (6 M). The aqueous layer was neutralised and extracted with $CHCl_3$ and the combined organics washed with water and dried over $NaSO_4$ (anhyd.). A small sample was purified by recrystallisation from $CHCl_3$ giving the product as a pink solid (57 mg). Yield = 16%; m.p. = 151-153°C; ^{1}H NMR ($CDCl_3$) δ 9.22 (2H, m), 8.76 (2H, s), 8.29-8.25 (2H, m), 7.86 (2H, d, J = 8 Hz), 7.38-7.30 (4H, m), 6.85 (2H, d, J = 7.3 Hz), 4.67 (4H, t, J = 6 Hz), 4.30 (4H, t, J = 6 Hz), 2.41 (4H, t, J = 6 Hz); HRMS $C_{28}H_{26}N_2O_6$: calculated 486.1791; m/z (M^+) EI observed 486.1786.

Nicotinic acid 4-[5-(4-nicotinoyloxybutoxy)-naphthalen-1-yloxy]-butyl ester ($f_4$bipy) (85)

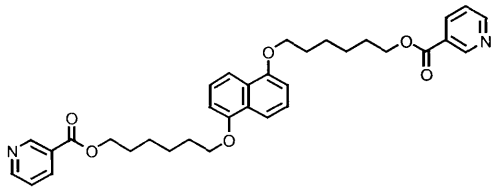


Step 1: A solution of 4-chlorobutan-1-ol (85% tech. grade, 5.0 g, 28 mmol) in MeCN (15 mL) was added, all at once, to a refluxing mixture of naphthalene-1,5-diol (1.6 g, 10 mmol) and K_2CO_3 (7 g) in MeCN (25 mL). Heating was continued at reflux temperature under $N_{2(g)}$ for 7 days. The reaction mixture was allowed to cool to R.T. and the solids filtered off and washed with $CHCl_3$ (30 mL). The filtrate was concentrated and the residues were partitioned between $CHCl_3$ and H_2O. The organic layer was washed with $NaHCO_{3(aq)}$ (sat.), dil. $HCl_{(aq)}$, and finally with H_2O. The organics were dried over Na_2SO_4 and the solvent removed using a rotary evaporator. The residues were dried under vacuum overnight to give the product (**59**) as a white solid (700 mg). Yield (crude) = 23%.

Step 2: The crude *bis*-(hydroxybutoxy)naphthalene (**59**) (700 mg, 2.3 mmol), nicotinic acid (1.2 g, 9.7 mmol) and HOBT (1.30 g, 9.7 mmol) were placed in a two-necked RBF fitted with a septum and the flask flushed with $N_{2(g)}$. Dry THF (24 mL) and $CHCl_3$ (12 mL) were added under $N_{2(g)}$ and the solution stirred for 5 mins. EDC (1.15 g, 6.0 mmol) and Et_3N (dry, 1.0 mL) were added and the solution stirred under $N_{2(g)}$ for 3 days. A precipitate formed immediately upon the addition of triethylamine. The solvents were removed under reduced pressure and the residue was partitioned between $CHCl_3$ and $HCl_{(aq)}$ (6 M). The aqueous layer was neutralised and extracted with $CHCl_3$ and the combined organics washed with water and dried over $NaSO_4$ (anhyd.). The solvent was removed on a rotary evaporator and the residue dried under vacuum overnight giving the crude product as a thick red oil. A small quantity (30 mg) of the pure product (red oil) was obtained by preparative TLC (alumina, $CHCl_3$/EtOAc 9:1). Yield = 3%; ^{1}H NMR ($CDCl_3$) δ 9.22 (2H, d, 2 Hz), 8.75 (2H, s), 8.28-8.24 (2H, m), 7.82 (2H, d, J = 8.5 Hz), 7.37-7.30

(4H, m), 6.82 (2H, d, J = 7.6 Hz), 4.49 (4H, t, J = 6 Hz), 4.20 (4H, t, J = 6 Hz), 2.09 (8H, m); HRMS $C_{30}H_{30}N_2O_6$: calculated 514.2104; m/z (M^+) EI observed 514.2107.

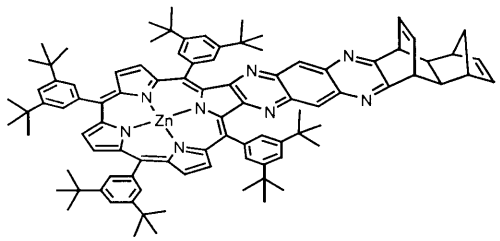
Nicotinic acid 6-[5-(6-nicotinoyloxyhexoxy)-naphthalen-1-yloxy]-hexyl ester ($f_6$bipy) (86)



Step 1: A solution of 6-bromohexan-1-ol (5.0 g, 28 mmol) in MeCN (15 mL) was added, all at once, to a mixture of naphthalene-1,5-diol (1.60 g, 10 mmol) and K_2CO_3 (7 g) in MeCN (25 mL). The mixture was heated at reflux temperature under $N_{2(g)}$ for 6hrs. After cooling to R.T. the solids were filtered off and washed with $CHCl_3$ (30 mL). The filtrate was concentrated and the residues were partitioned between $CHCl_3$ and H_2O. The organic layer was washed with $NaHCO_{3(aq)}$ (sat.), dil. $HCl_{(aq)}$, and finally with H_2O. The organics were dried over Na_2SO_4 and the solvent removed using a rotary evaporator. The residues were dried under vacuum overnight. Yield (crude) = 60%.

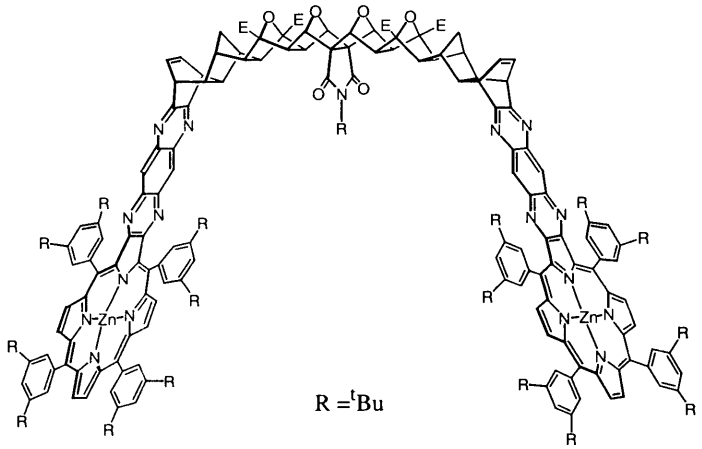
Step 2: A sample of the crude 1,5-*bis*-(6-hydroxy-hexyloxy)-naphthalene (**58**) (1.29 g, 3.58 mmol), nicotinic acid (1.76 g, 14.3 mmol) and HOBT (1.93 g, 14.3 mmol) were placed in a two-necked RBF fitted with a septum and the flask flushed with $N_{2(g)}$ for 1 min. Dry THF (40 mL) and $CHCl_3$ (20 mL) were added under $N_{2(g)}$ (canula) and the solution stirred for 5 mins. EDC (2.05 g, 10.74 mmol) was added followed by Et_3N (dry, 2.0 mL). A gel formed immediately upon the addition of triethylamine. The mixture was stirred under $N_{2(g)}$ at R.T. in darkness for 6 days. The solvents were removed under reduced pressure and the residue was partitioned between $CHCl_3$ and $HCl_{(aq)}$ (6 M). The aqueous layer was neutralised and extracted with $CHCl_3$ and the combined organics washed with water and dried over $NaSO_4$ (anhyd.). The product was purified by flash column chromatography (alumina, $CHCl_3$) giving a red sticky oil (1.4 g). Yield = 69%; ^{1}H NMR ($CDCl_3$) δ 9.20 (2H, bs), 8.75 (2H, bs), 8.31-8.24 (2H, m), 7.82 (2H, d, J = 8.5 Hz), 7.40-7.29 (4H, m), 6.80 (2H, d, J = 7.6 Hz), 4.39 (4H, t, J = 6 Hz), 4.11 (4H, t, J = 6 Hz), 1.99-189 (8H, m), 1.68-1.56 (8H, m); HRMS $C_{34}H_{38}N_2O_6$: calculated 570.2730; m/z (M^+) EI observed 570.2730.

Zn^{t}BuPBlock (103)



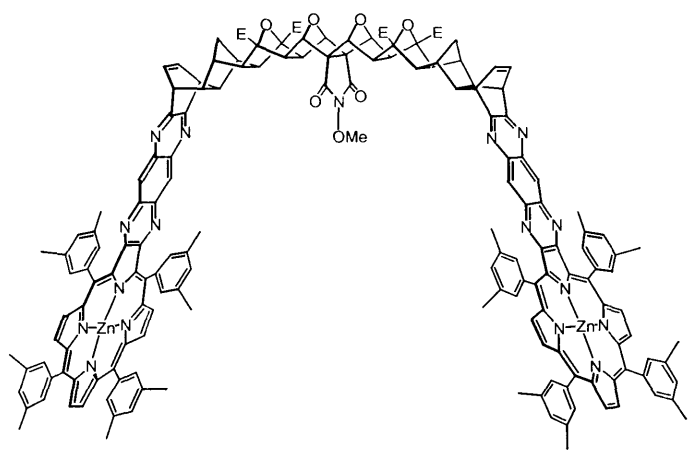
To a refluxing solution of ^{t}BuPBlock (**39**) (50 mg, 3.7 x 10^{-5} mol) in $CHCl_3$ (5 mL) was added a saturated solution of zinc acetate dihydrate in MeOH (2 mL). The solution was heated at reflux temperature for 30 mins. The reaction mixture was partitioned between $CHCl_3$ and H_2O. The organic layer was separated and the aqueous layer extracted with $CHCl_3$. The combined organic layers were washed with H_2O (3 x 10 mL) and dried over Na_2SO_4 (anhyd.). The solvent was removed under reduced pressure. The product was recrystallised from $CHCl_3$/MeOH giving (**103**) as a greenish brown solid (46 mg). Yield = 87%; m.p. > 300°C; ^{1}H NMR ($CDCl_3$) δ 8.96 (4H, s), 8.86 (2H, s), 8.57 (2H, s), 8.07 (4H, d, *J* = 2 Hz), 7.97 (4H, d, *J* = 2 Hz), 7.92 (2H, t, *J* = 2 Hz), 7.78 (2H, t, *J* = 2 Hz), 6.68 (2H, t, *J* = 4 Hz), 6.25 (2H, t, *J* = 2 Hz), 4.20 (2H, t, *J* = 4 Hz), 2.96 (2H, t, 2Hz), 2.82 (1H, d, *J* = 9 Hz), 2.22 (2H, s), 1.52 (36H, s), 1.489 (18H, s), 1.485 (18H,s).

Zn$_2$^{t}BuPSP (104)



To a refluxing solution of ^{t}BuPSP (**52**) (12.0 mg, 3.53 μmol) in $CHCl_3$ (500 μL) was added a saturated solution of zinc acetate dihydrate in MeOH (150 μL). The mixture was heated at reflux temperature for 30 mins. The reaction mixture was partitioned between $CHCl_3$ and H_2O. The organic layer was separated and the aqueous layer extracted with $CHCl_3$. The combined organic layers were washed with H_2O (3 x 10 mL), dried over Na_2SO_4 (anhyd.) and the solvent removed under reduced pressure. The product was recrystallised from $CHCl_3$/MeOH giving the product (**104**) as a brown solid (11.1 mg). Yield = 90%; m.p. > 300°C; ^{1}H NMR ($CDCl_3$) δ 8.94 (8H, s), 8.84 (4H, s), 8.56 (4H, s), 8.06 (8H, bs), 7.95 (8H, bs), 7.92 (4H, bs), 7.27 (2H, m), 6.93 (2H, m), 6.54 (4H, t, *J* = 4 Hz), 4.70 (4H, s), 4.25 (4H, bs), 3.94 (12H, s), 2.44 (4H, s), 2.38 (4H, s), 2.19 (2H, d, *J* = 10 Hz), 2.04 (2H, d, *J* = 10 Hz), 1.92 (4H, s), 1.88 (4H, s), 1.52 (36H, s), 1.51 (36H, s), 1.47 (72H, s), 0.96 (3H, s); HRMS $C_{224}H_{241}N_{17}O_{14}Zn_2$: calculated 3522.741; m/z (ES) $(M+2H)^{2+}$ observed 1761.369.

Zn_2MePSP (105)



To a refluxing solution of MePSP (**51**) (2 mg, 0.74 μmol) in $CHCl_3$ (500 μL) was added a saturated solution of zinc acetate dihydrate in MeOH (150 μL). The mixture was heated at reflux temperature for 30 mins. The reaction mixture was partitioned between $CHCl_3$ and H_2O. The organic layer was separated and the aqueous layer extracted with $CHCl_3$. The combined organic layers were washed with H_2O (3 x 3 mL), dried over Na_2SO_4 (anhyd.) and the solvent removed under reduced pressure. The product (**105**) was obtained as a brown solid (2 mg). Yield ≈ 95% (impure); m.p. > 300°C; ^{1}H NMR ($CDCl_3$) 8.90 (8H, bs), 8.79 (4H, s), 8.65 (4H, s), 7.80 (8H, bs), 7.70 (8H, bs), 7.49 (4H, bs), 7.37 (4H, bs), 6.91 (2H, d, J = 8 Hz), 6.72 (2H, d, J = 8 Hz), 6.53 (4H, t, J = 4 Hz), 4.69 (4H, s), 4.21 (4H, bs), 3.94 (12H, s), 3.87 (3H, s), 2.58 (48H, bs), 2.42 (4H, s), 2.38 (4H, s), 2.18 (2H, d), 2.04 (2H, d), 1.92 (4H, s), 1.88 (4H, s); HRMS $C_{173}H_{141}N_{17}O_{15}Zn_2$: calculated 2823.938; m/z (ES) $(M+2H)^{2+}$ observed 1412.952.

4.3 UV-VIS BINDING STUDIES: METHODS

Stock host solutions were prepared by weighing a small sample (~20 mg) of porphyrin followed by quantitative transfer to a volumetric flask (100 mL). The stock solution was serially diluted until the intensity (absorbance) of the Soret band (~425 nm) was measured to be between 0.6 and 1.2 corresponding to a pale straw colour. Small aliquots of the guest solution were then transferred, by pipette, to the known mass of host (porphyrin). After each aliquot was added the solutions were diluted to a volume of 10.00 mL. A batch of between 10 and 20 solutions, with a constant concentration of host and various concentrations of the same guest, were thus prepared. Pure host and guest solutions were also analysed under identical conditions. Room temperature was kept at (25±3)°C and each solution was equilibrated in a water bath at (25±1)°C for 3-4 minutes before a UV-Vis spectrum was recorded. All spectra in each batch were recorded immediately, one after the other, using a Cary 100 (version 9.00) UV-visible spectrophotometer

with each full scan taking approximately one minute to complete. Absorbances of each solution were recorded over a range of wavelengths (800 – 300 nm). The spectrophotometer was set to record at 1 nm intervals using a spectral bandwidth of 1 nm in double beam mode relative to a solvent baseline. The absorbance was recorded specifically at two wavelengths corresponding to the host (λ_H) and complex (λ_C) absorption maxima respectively.

References, p.204

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(5) Warrener, R. N.; Johnston, M. R.; Schultz, A. C.; Golic, M.; Houghton, M. A.; Gunter, M. J. *Synlett* **1998**, *6*, 590.

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(8) Promarak, V.; Burn, P. L. *J. Chem. Soc., Perkin Trans. 1* **2001**, 14.

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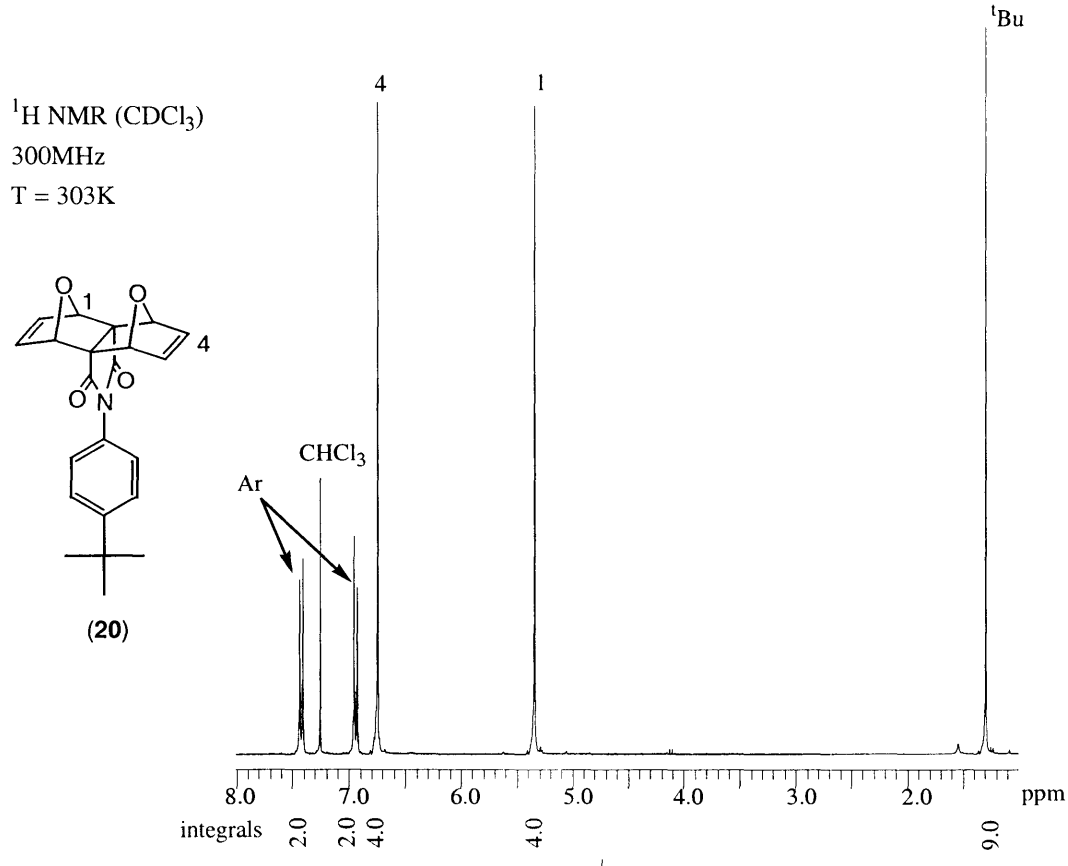
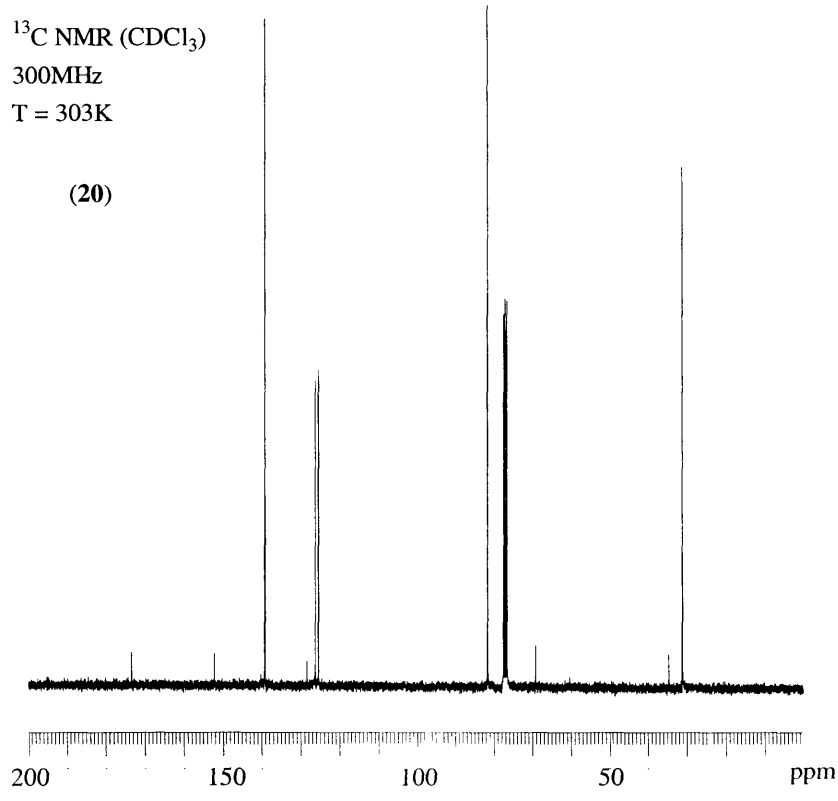
(10) Warrener, R. N.; Johnston, M. R.; Gunter, M. J. *Synlett* **1998**, *6*, 593.

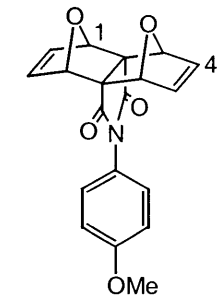
(11) Crossley, M. J.; Govenlock, L. J.; Prashar, J. K. *J. Chem. Soc., Chem. Commun.* **1995**, 2379.

Appendix A: Selected ^{1}H and ^{13}C NMR spectra

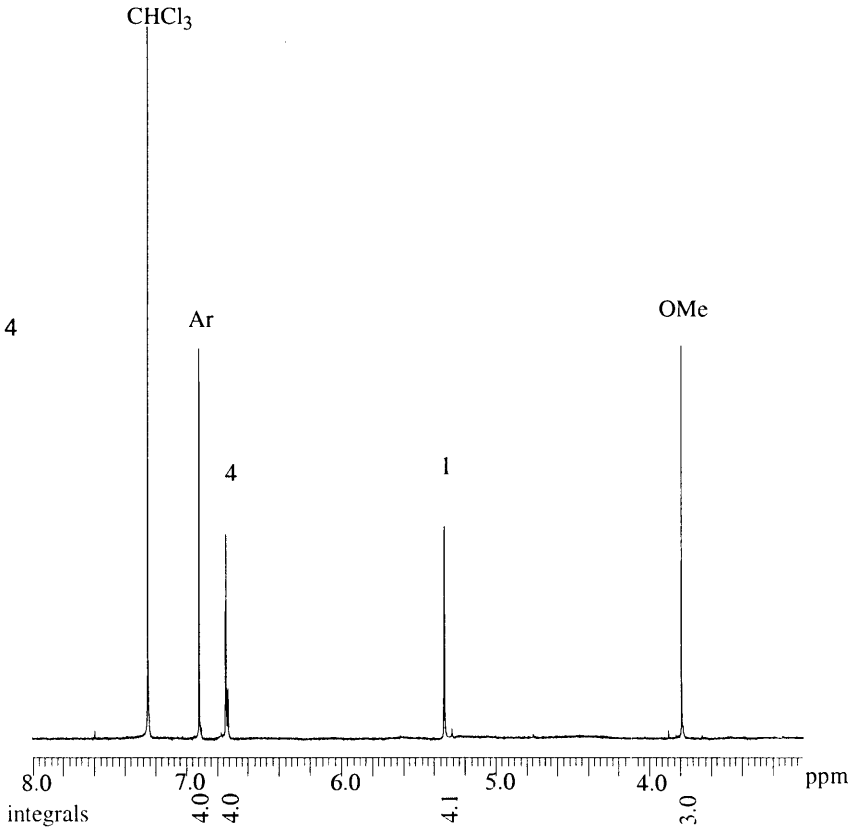




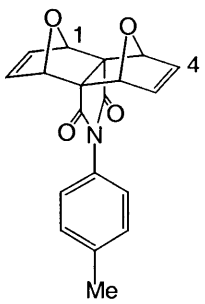
^{1}H NMR ($CDCl_3$)
300MHz
T = 303K



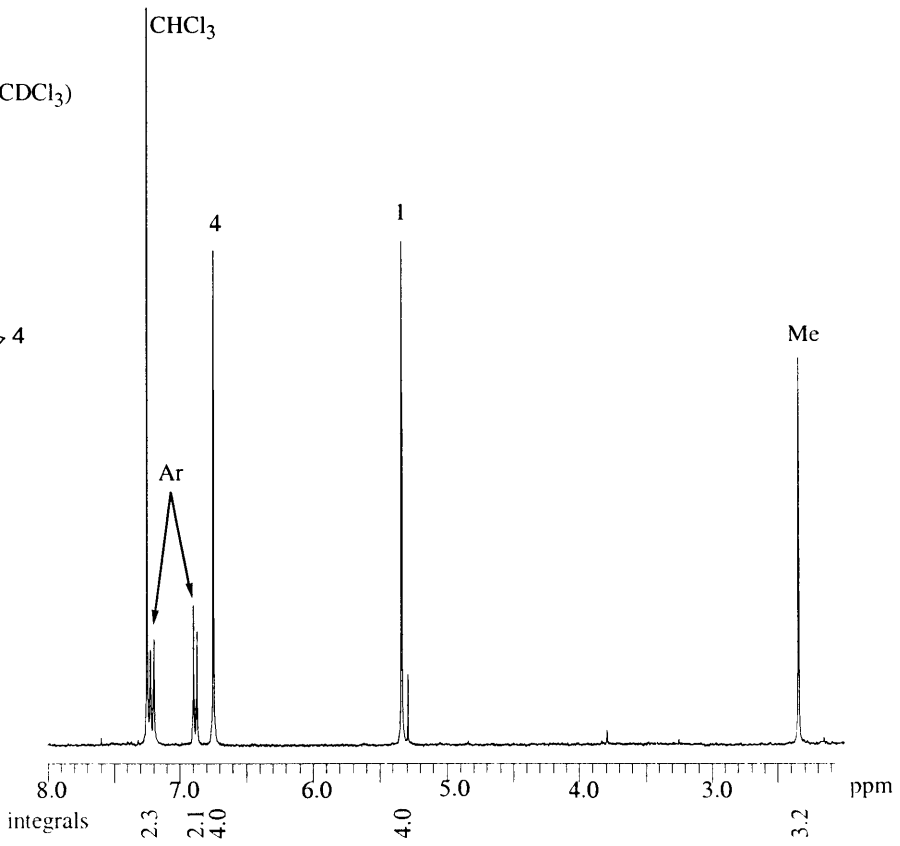
(21)

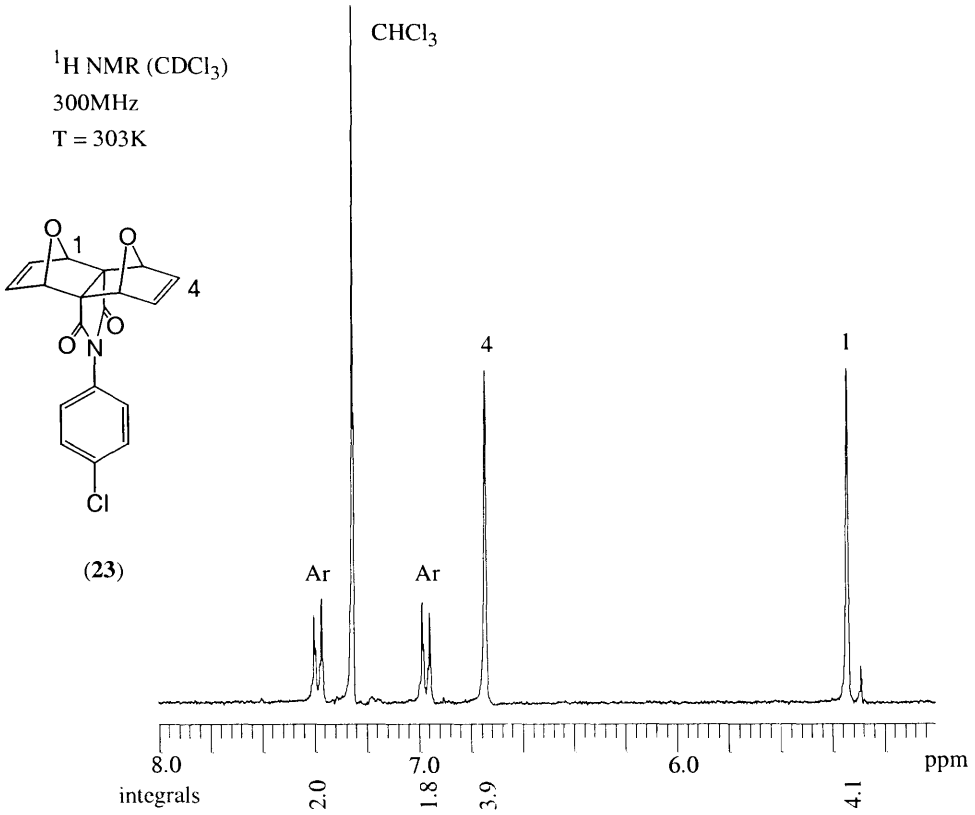


^{1}H NMR ($CDCl_3$)
300MHz
T = 303K

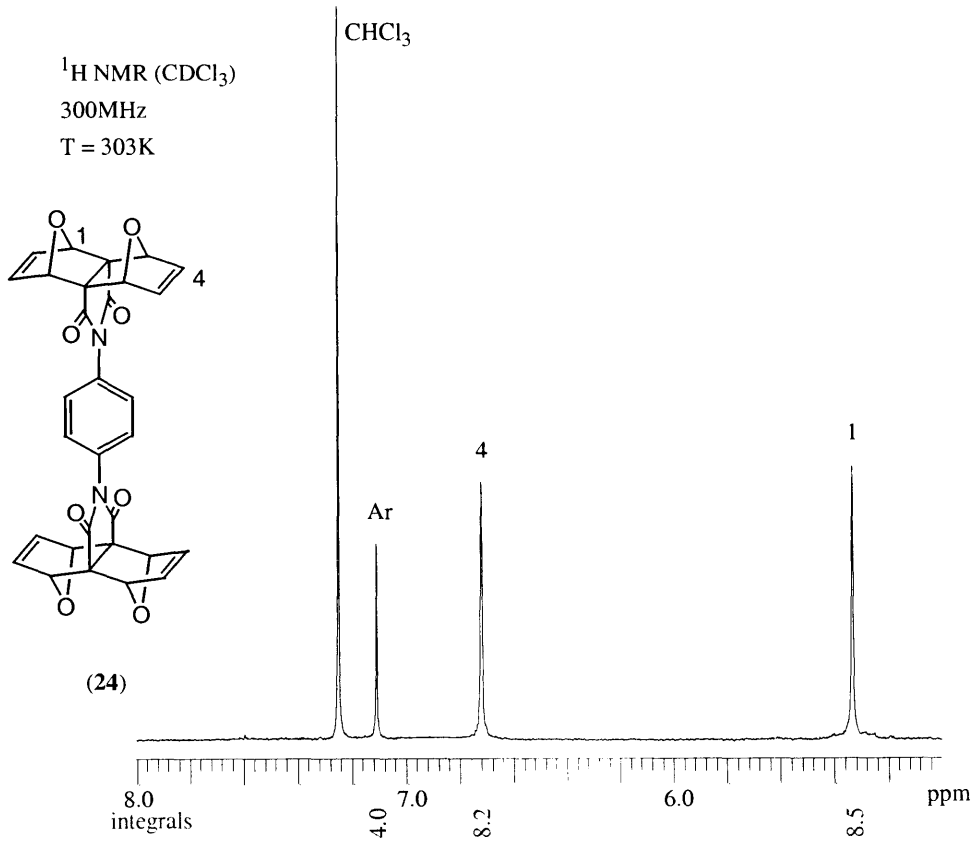


(22)

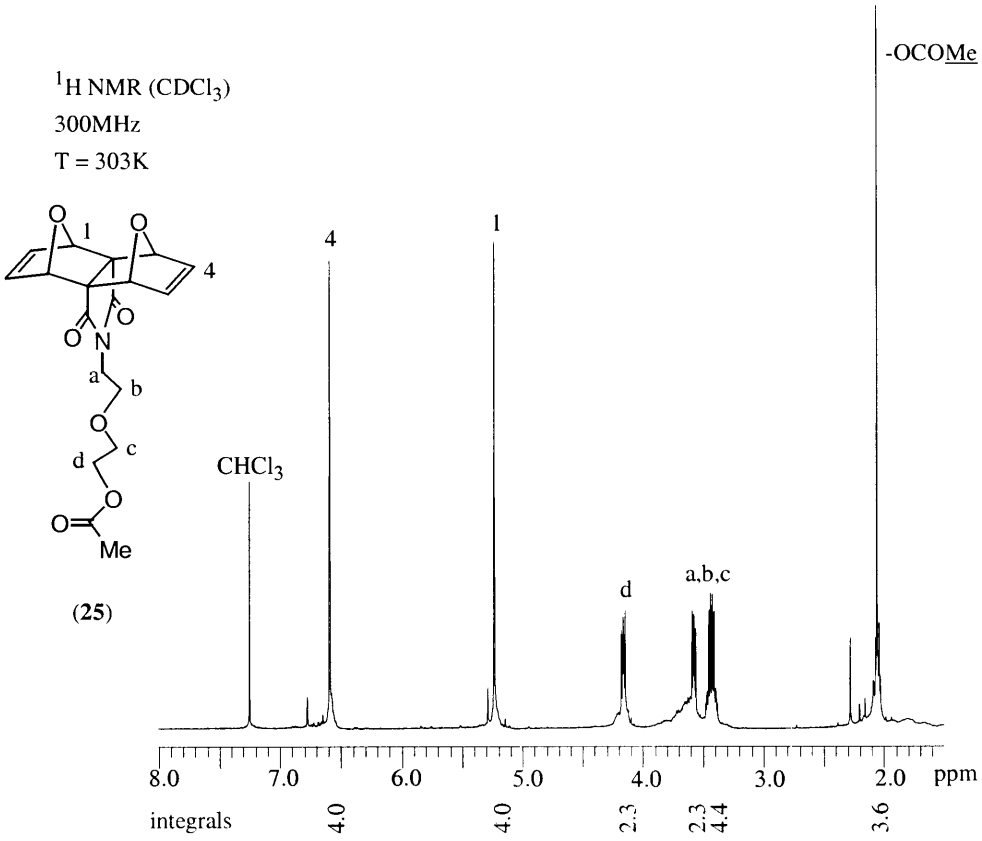



^{1}H NMR ($CDCl_3$)
300MHz
T = 303K
$CHCl_3$
Ar
Ar
4
1
8.0
7.0
6.0
ppm
integrals
2.0
1.8
3.9
4.1

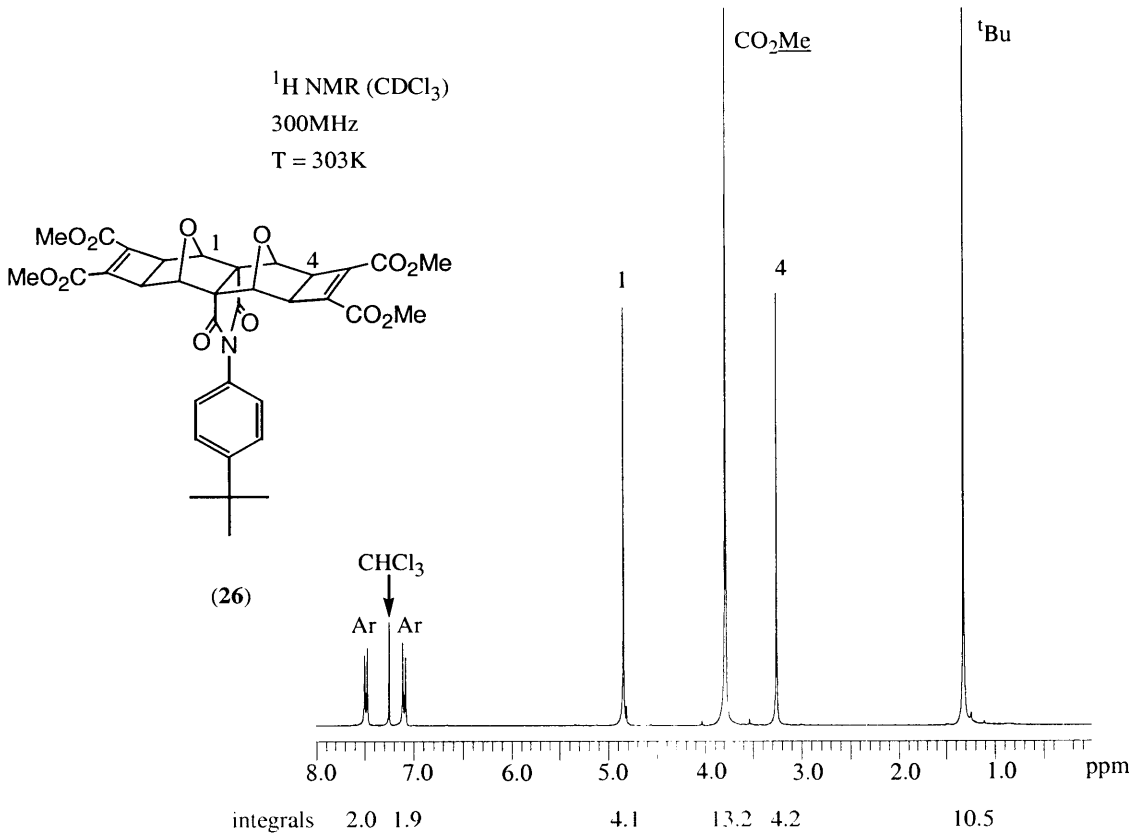
(**23**)


^{1}H NMR ($CDCl_3$)
300MHz
T = 303K
$CHCl_3$
Ar
4
1
8.0
7.0
6.0
ppm
integrals
4.0
8.2
8.5

(**24**)


^{1}H NMR ($CDCl_3$)
300MHz
T = 303K
-OCOMe
4
1
$CHCl_3$
d
a,b,c
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm
integrals
4.0
4.0
2.3
2.3
4.4
3.6

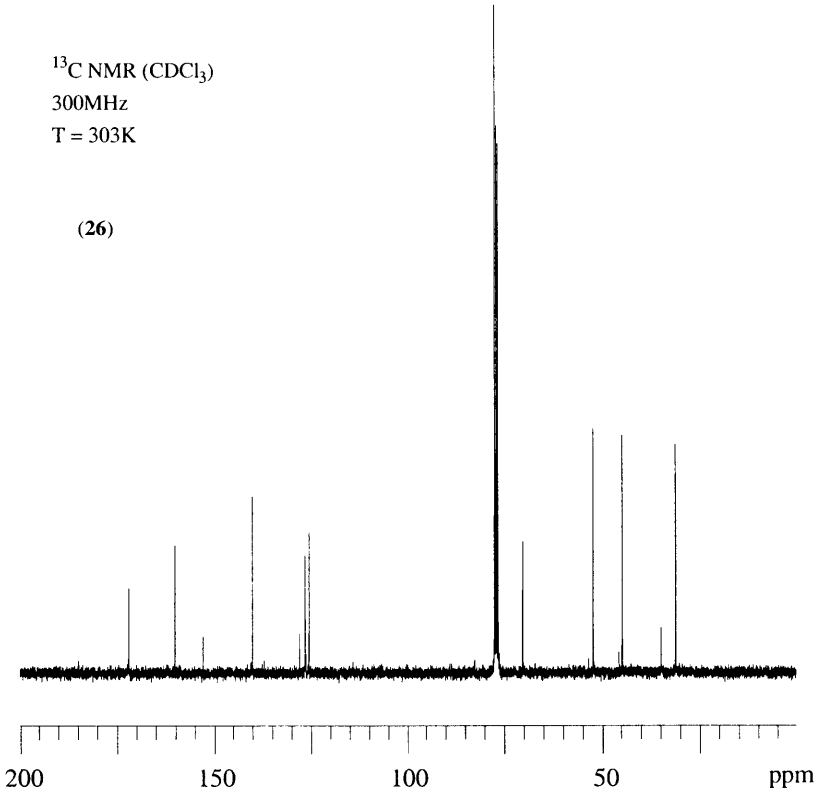
(25)


^{1}H NMR ($CDCl_3$)
300MHz
T = 303K
CO_2Me
^{t}Bu
MeO_2C
MeO_2C
CO_2Me
CO_2Me
1
4
$CHCl_3$
Ar
Ar
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm
integrals
2.0
1.9
4.1
13.2
4.2
10.5

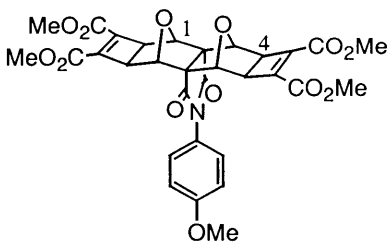
(26)

^{13}C NMR ($CDCl_3$)
300MHz
T = 303K

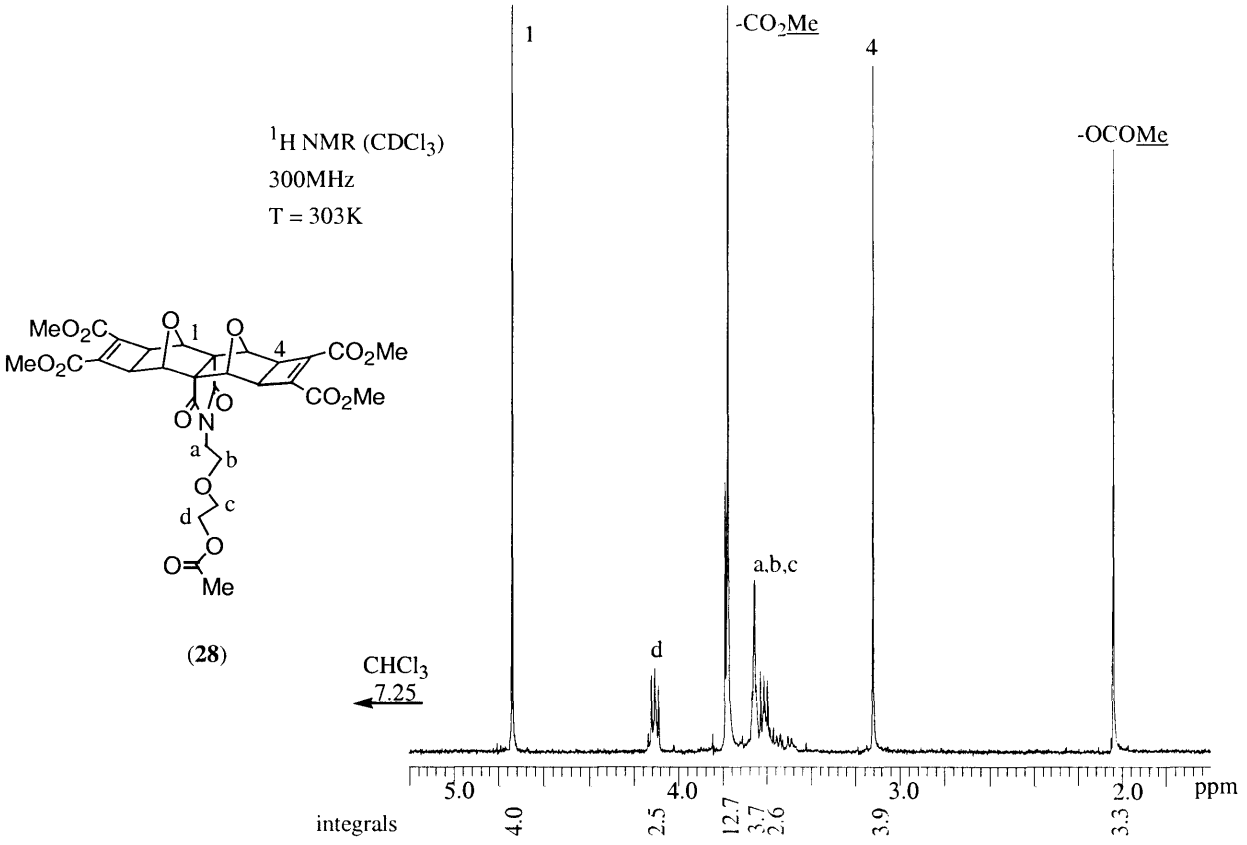
(**26**)



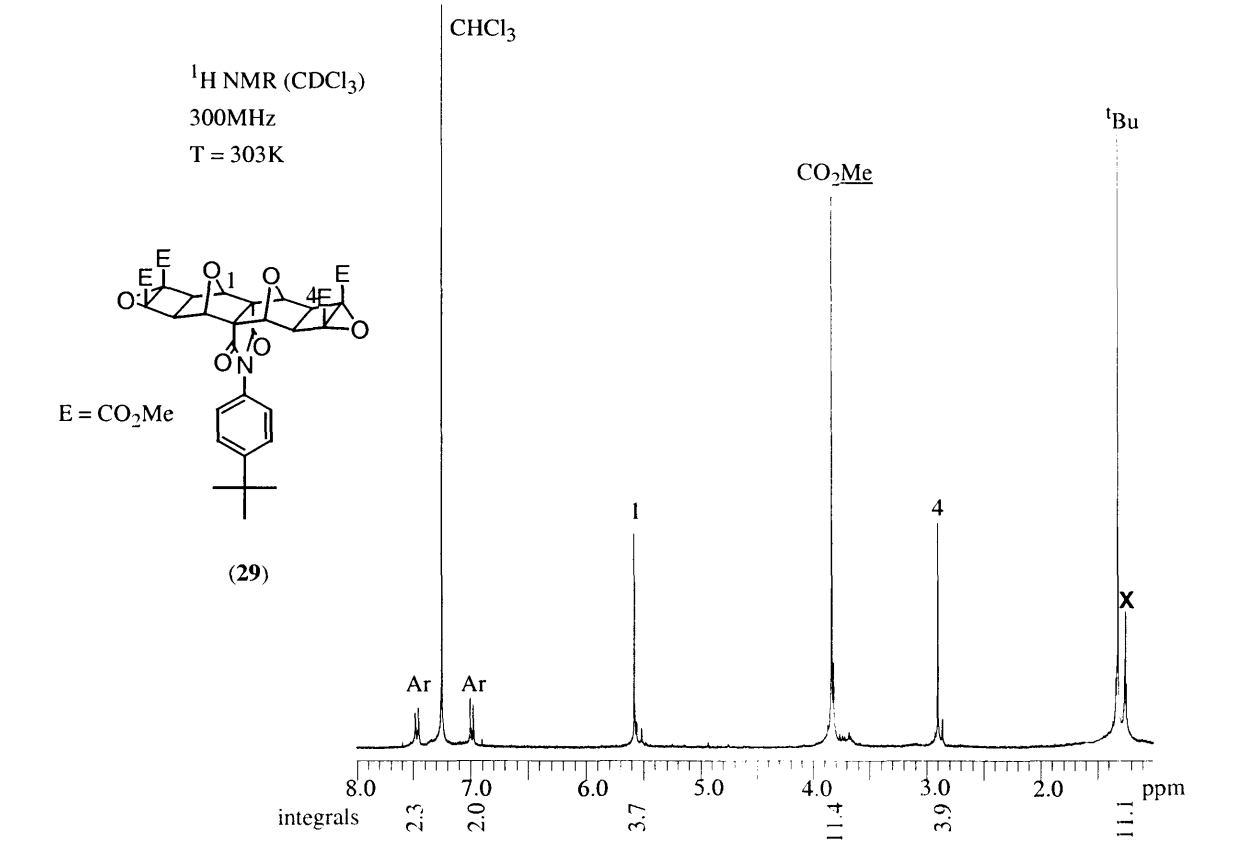
^{1}H NMR ($CDCl_3$)
300MHz
T = 303K



(**27**)


1H NMR (CDCl3)
300MHz
T = 303K
MeO2C
MeO2C
CO2Me
CO2Me
Me
1
4
a
b
c
d
1
-CO2Me
4
-OCOMe
a,b,c
d
CHCl3
7.25
5.0
4.0
3.0
2.0
ppm
integrals
4.0
2.5
12.7
3.7
2.6
3.9
3.3

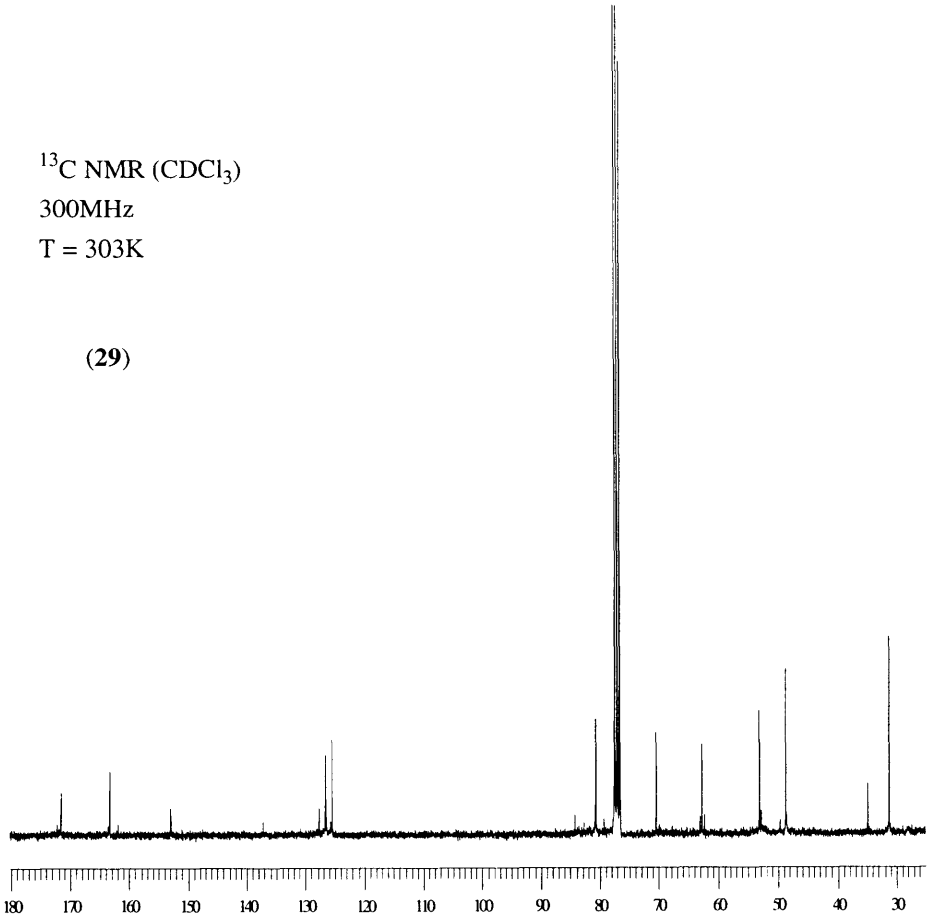
(28)


1H NMR (CDCl3)
300MHz
T = 303K
E = CO2Me
CHCl3
tBu
CO2Me
1
4
X
Ar
Ar
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm
integrals
2.3
2.0
3.7
11.4
3.9
11.1

(29)

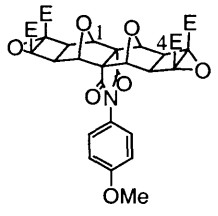
^{13}C NMR ($CDCl_3$)
300MHz
T = 303K

(**29**)

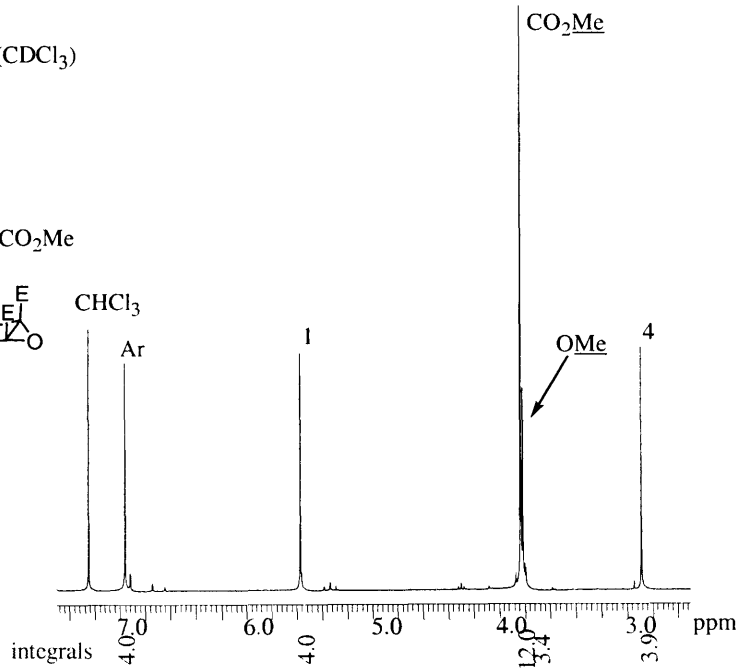


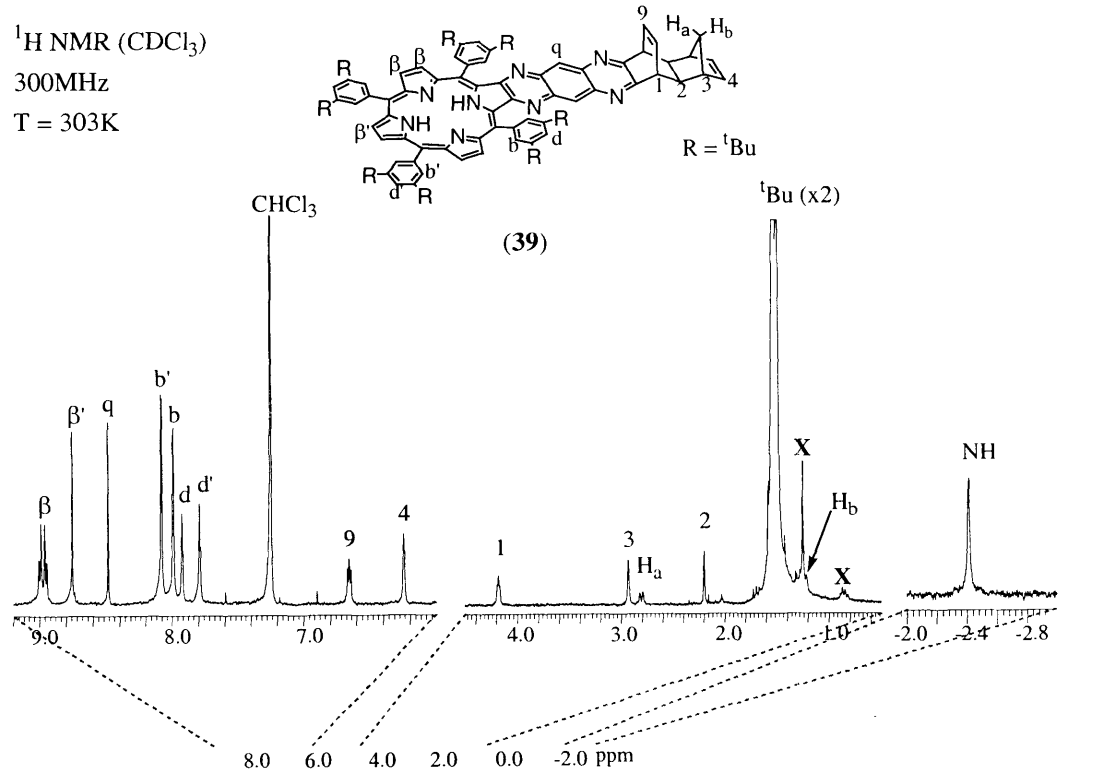
^{1}H NMR ($CDCl_3$)
300MHz
T = 303K

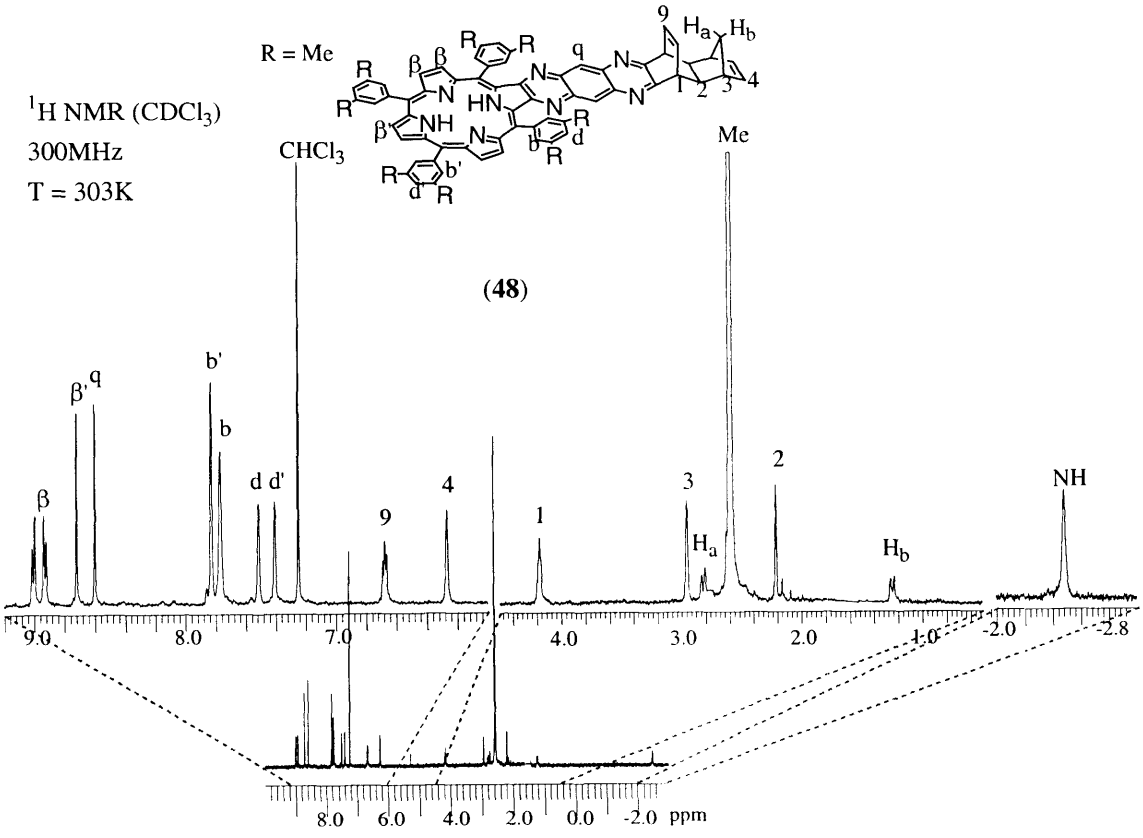
E = CO_2Me



(**30**)

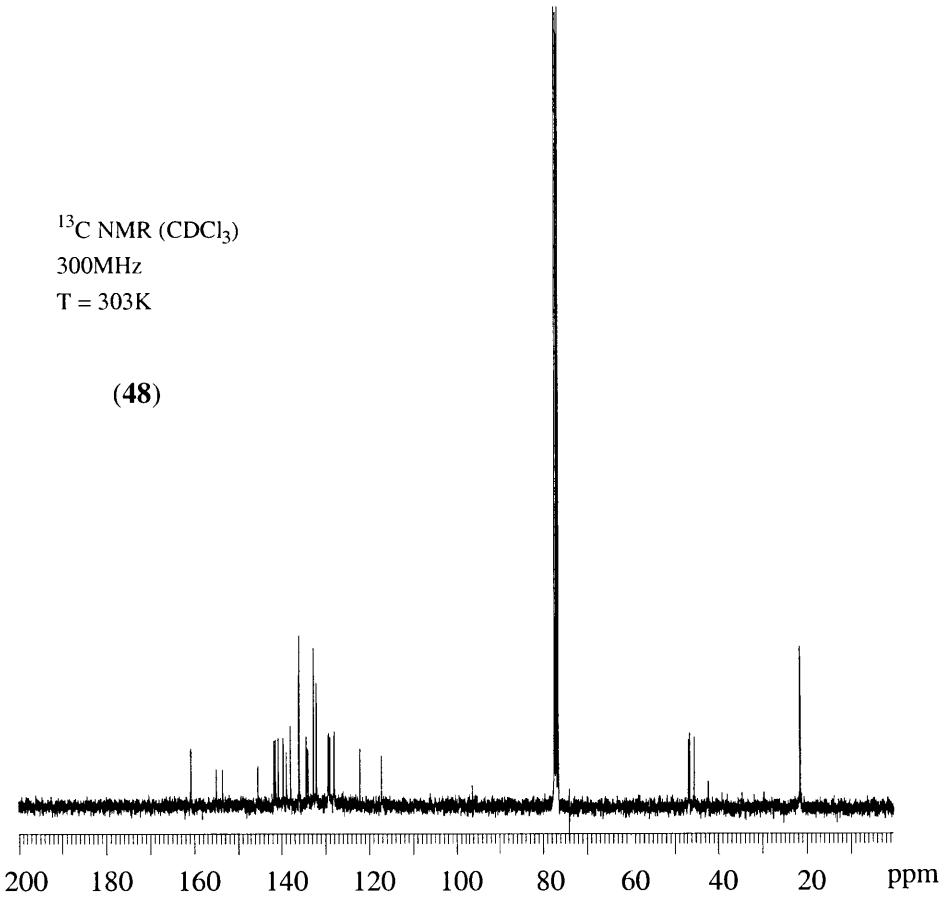



^{1}H NMR ($CDCl_3$)
300MHz
T = 303K
R = ^{t}Bu
(39)
$CHCl_3$
^{t}Bu (x2)
β
β'
q
b'
b
d
d'
9
4
1
3
H_a
2
X
H_b
NH
9.0
8.0
7.0
4.0
3.0
2.0
1.0
-2.0
-2.4
-2.8
8.0
6.0
4.0
2.0
0.0
-2.0 ppm

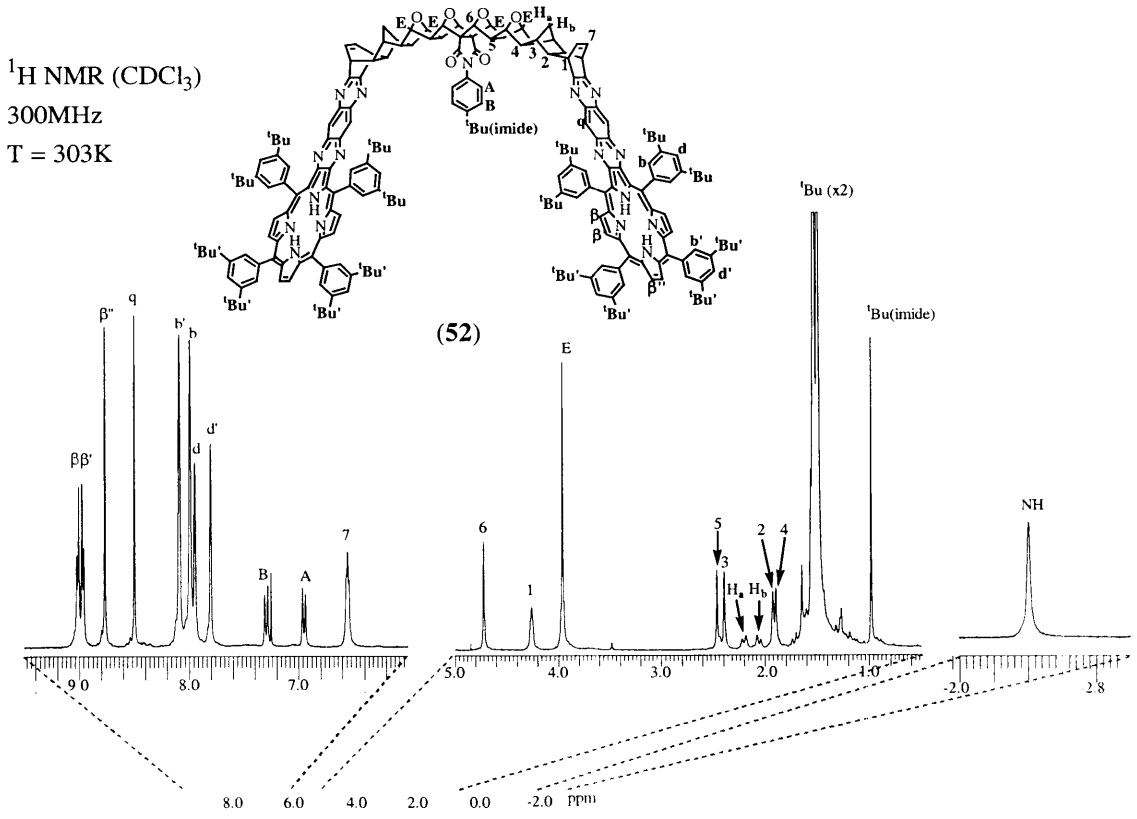

R = Me
^{1}H NMR ($CDCl_3$)
300MHz
T = 303K
(48)
$CHCl_3$
Me
β
β'
q
b'
b
d d'
9
4
1
3
H_a
2
H_b
NH
9.0
8.0
7.0
4.0
3.0
2.0
1.0
-2.0
-2.8
8.0
6.0
4.0
2.0
0.0
-2.0 ppm

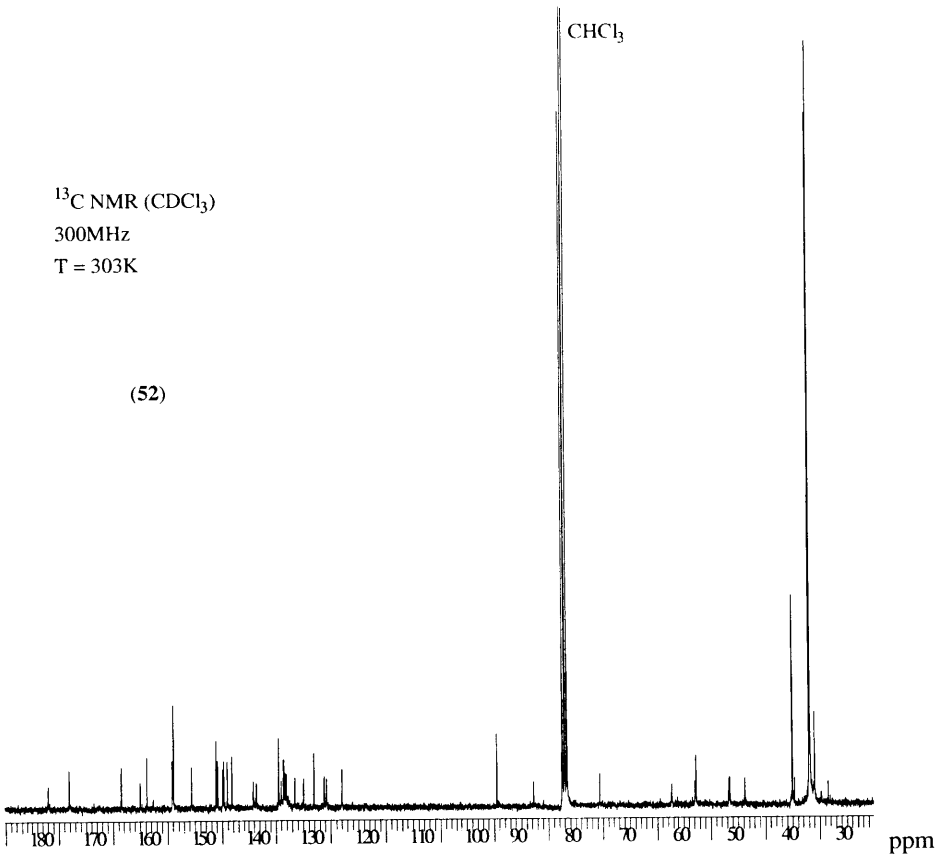
^{13}C NMR ($CDCl_3$)
300MHz
T = 303K

(48)



^{1}H NMR ($CDCl_3$)
300MHz
T = 303K



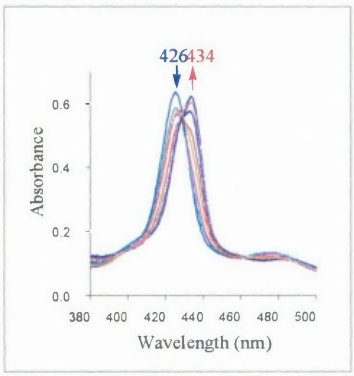

^{13}C NMR ($CDCl_3$)
300MHz
T = 303K
(52)
$CHCl_3$
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

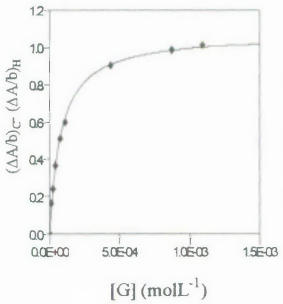
Appendix B: UV-Vis Binding Curves

UV-Vis binding studies: ZnPBlock (**103**) and Zn_2PSP (**104**) with pyridine and flexible *bis*-pyridine Guests ($f_n$bipy: **82-86**)

All titrations (constant porphyrin host concentration + variable guest) done in DCM at 25°C. UV-Vis traces (λ = 380 to 500 nm) shown on left and NLLS curve fits shown on right.

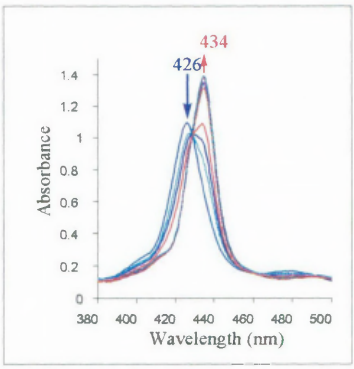
Zn^{t}BuPBlock (**103**) + Pyridine

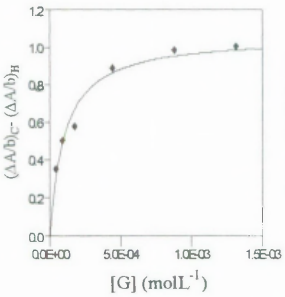




H_t =5.17 x 10^{-6} M
solvent = DCM
T = 25°C
K_{LM} = (1.26 ± 0.06) x 10^4 M^{-1}
SSE = 0.00303
r^2 = 0.99804

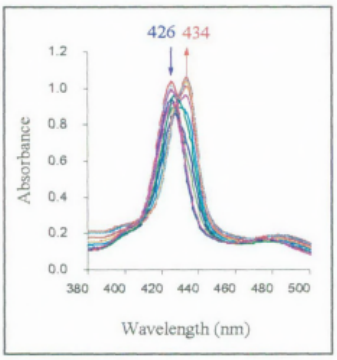
Zn_2PSP (**104**) + Pyridine

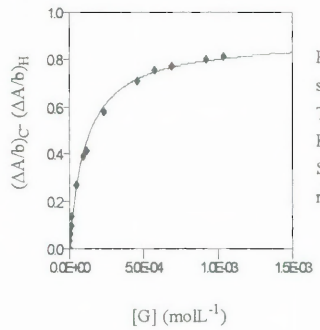




H_t =2.88 x 10^{-6} M
solvent = DCM
T = 25°C
K_{11} = (9.8 ± 0.9) x $10^3$$M^{-1}$
SSE = 0.01267
r^2 = 0.99007

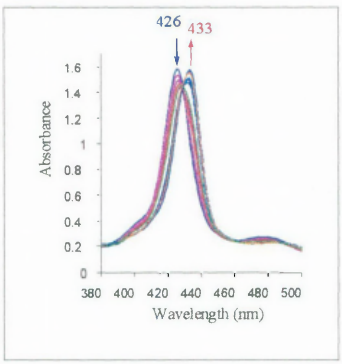
ZnPBlock(**103**) + $f_0$bipy (**82**)

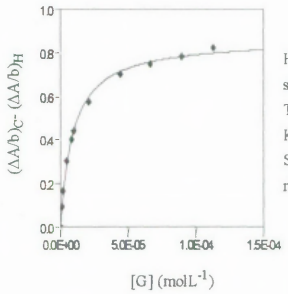




H_t =4.06 x 10^{-6} M
solvent = DCM
T = 25°C
K_{11} = (9.1 ± 1.1) x 10^3 M^{-1}
SSE = 0.01521
r^2 = 0.98973

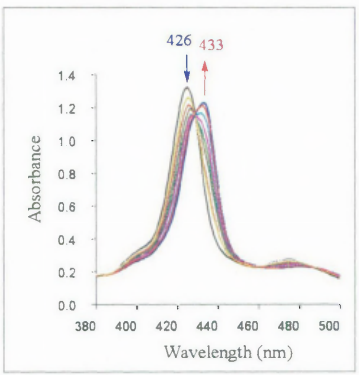
Zn_2PSP (**104**) + f_0bipy (**82**)

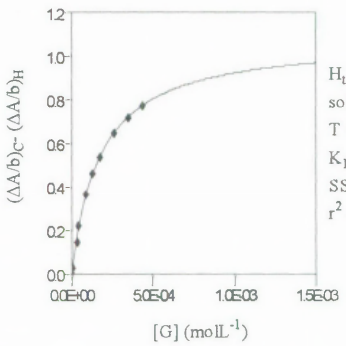




H_t =2.91 x 10^{-6} M
solvent = DCM
T = 25°C
K_{11} = (1.09 ± 0.06) x $10^5 M^{-1}$
SSE = 0.00225
r^2 = 0.99736

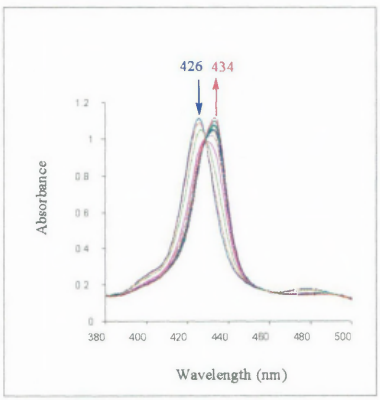
ZnPBlock (**103**) + f_2bipy (**83**)

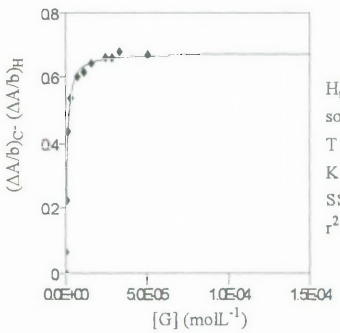




H_t =4.94 x 10^{-6} M
solvent = DCM
T = 25°C
K_{11} = (5.8 ± 0.4) x 10^3 M^{-1}
SSE = 0.00127
r^2 = 0.99825

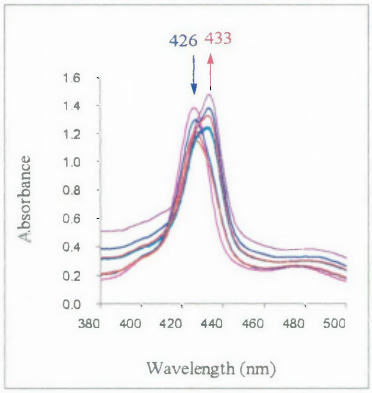
Zn_2PSP (**104**) + f_2bipy (**83**)

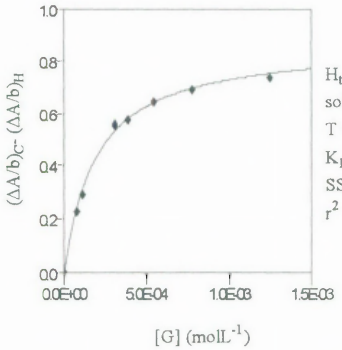




H_t =2.05 x 10^{-6} M
solvent = DCM
T = 25°C
K_{11} = (1.34 ± 0.07) x $10^6 M^{-1}$
SSE = 0.00131
r^2 = 0.99805

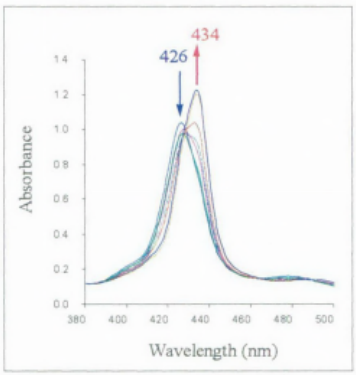
ZnPBlock (**103**) + $f_3$bipy (**84**)

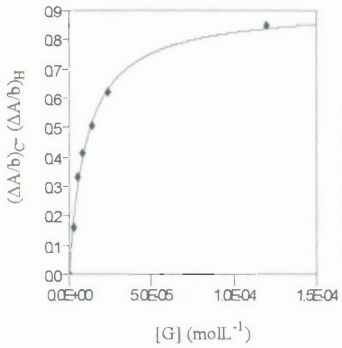




H_t =5.18 x 10^{-6} M
solvent = DCM
T = 25°C
K_{11} = (5.2 ± 0.4) x 10^3 M^{-1}
SSE = 0.00175
r^2 = 0.99640

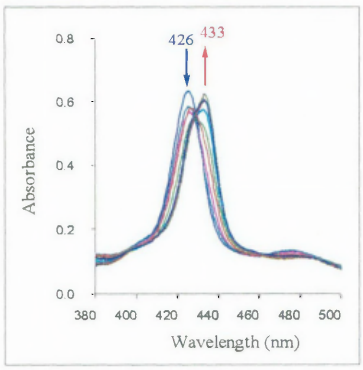
Zn_2PSP (**104**) + $f_3$bipy (**84**)

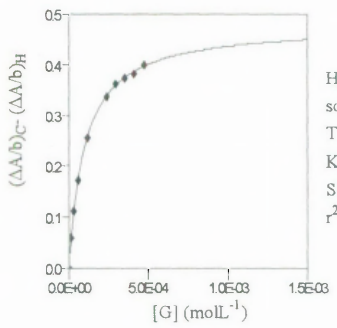




H_t =2.00 x 10^{-6} M
solvent = DCM
T = 25°C
K_{11} = (9.5 ± 0.5) x $10^4 M^{-1}$
SSE = 0.00152
r^2 = 0.99773

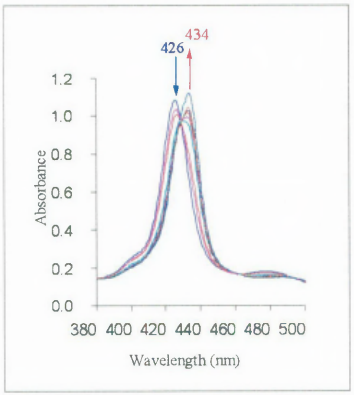
ZnPBlock (**103**) + $f_4$bipy (**85**)

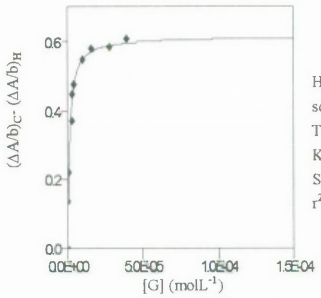




H_t =2.37 x 10^{-6} M
solvent = DCM
T = 25°C
K_{11} = (1.00 ± 0.04) x $10^4 M^{-1}$
SSE = 0.00018
r^2 = 0.99912

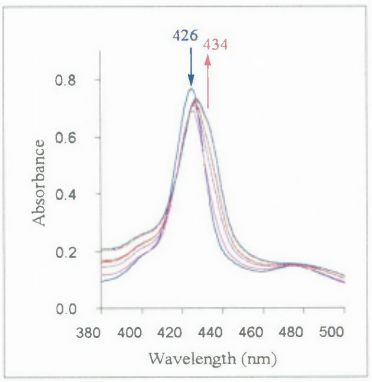
Zn_2PSP (**104**) + $f_4$bipy (**85**)

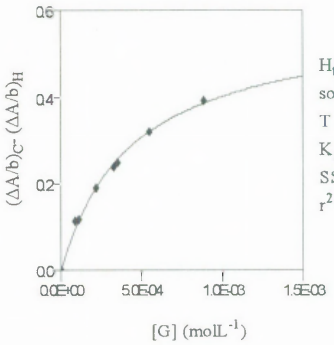




H_t =2.00 x 10^{-6} M
solvent = DCM
T = 25°C
K_{11} = (8.0 ± 1.3) x 10^5 M^{-1}
SSE = 0.00648
r^2 = 0.98382

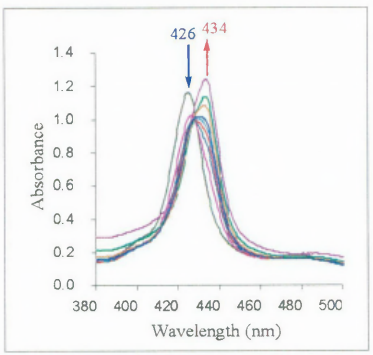
ZnPBlock (**103**) + $f_6$bipy (**86**)

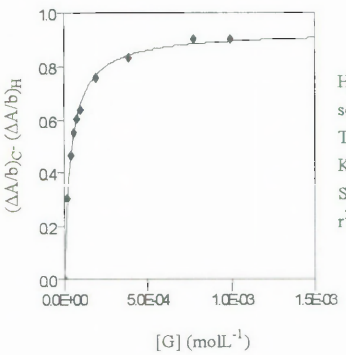




H_t =2.87 x 10^{-6} M
solvent = DCM
T = 25°C
K_{11} = (2.2 ± 0.3) x 10^3 M^{-1}
SSE = 0.00062
r^2 = 0.99430

Zn_2PSP (**104**) + $f_6$bipy (**86**)





H_t =2.14 x 10^{-6} M
solvent = DCM
T = 25°C
K_{11} = (2.5 ± 0.1) x 10^4 M^{-1}
SSE = 0.00152
r^2 = 0.9979