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A new synthetic route to donor–acceptor porphyrins

M. John Plater,[a,*] Stuart Aiken[a] and Grant Bourhill[b,†]

[a]*Department of Chemistry, University of Aberdeen, Meston Building, Room G103, Meston Walk, Aberdeen, Scotland AB24 3UE, UK*
[b]*Defence Science and Technology Laboratory, Great Malvern, St Andrews Road, Worcs WR14 3PS, UK*

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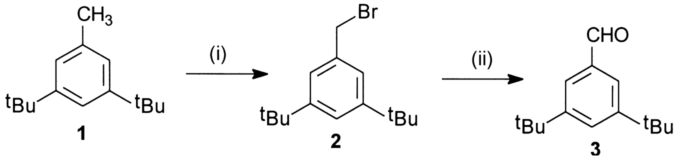
Abstract—Some new donor–acceptor porphyrins have been prepared based on a metallated bis(ethynyl) porphyrin core. 4-(Dimethylamino)phenyl was used as the donor group and 4-nitrophenyl, 4-cyanophenyl and 5-nitrothiazoyl as the acceptor groups. Dipyrrylmethane was used for large scale porphyrin ring synthesis because the absence of methylene substituents reduces the difficulty of substituent scrambling that occurs during porphyrin synthesis. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

New generations of optoelectronic devices for telecommunications, optical switching and information storage require the development of materials with exceptional nonlinear optical (NLO) responses.[1–3] This is because an NLO chromophore with a very large first-order hyperpolarisability would be desirable for incorporation into electric field poled-polymeric systems and serve as the basis for frequency doubling materials and for devices that function as waveguide switches, modulators, filters and optical limiting devices. The general approach to designing NLO chromophores with large molecular first order hyperpolarisabilities involves coupling an electron donor (D) and acceptor (A) to an organic framework that provides moderately strong electronic coupling between D and A. Previous studies have illustrated that macrocycles with extensive π-conjugation can provide a basis from which to construct D–A molecules with interesting NLO properties.[4] Recently very large first-order hyperpolarisabilities have been measured in a new class of asymmetric D–A porphyrin. These molecules are based on a porphyrin centred 5,15-bis(arylethynyl) linker topology with donor and acceptor groups attached to the ethynyl groups. One such compound [5,15-bis-(phenyl)-10-(4-*N*,*N*-dimethylaminophenylethynyl)-20-(4-nitrophenylethynyl)porphinato]-zinc(II) possesses by far the largest β value or first order hyperpolarisability yet measured for an organic based chromophore.[5] The pioneering synthesis of ethynyl substituted porphyrins was a key step towards the development of conjugated porphyrin chromophores.[6] Alkynyl groups allow conjugation to the central porphyrin whereas other groups such as aryl rings and alkenes are twisted which reduces their ability to be conjugated to the central porphyrin. Our interest in these compounds stems from the potential use of porphyrins in optical limiting devices for the attenuation of short laser pulses, owing to their desirable reverse saturation absorption characteristics, and their potential use in optical limiters for the attenuation of continuous wave laser beams, owing to their large β values and dipole moments.[7–8] This paper reports improved synthetic routes to D–A porphyrins that allows the donor and acceptor groups to be varied more easily. The solubility of the chromophores is increased by using 3,5-di-*tert*-butylphenyl side groups. Two D–A porphyrins are also described which possess different electron acceptor groups and D–D and A–A porphyrins are described.

2. Results and discussion

The key building block [5,15-bis-bromo-10,20-bis-(3,5-bis-



Scheme 1. *Reagents and conditions*: (i) NBS, $(PhCO)_2O_2$ 50% (125 g); (ii) $(CH_2)_6N_4$, c. HCl 82% (79 g).

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[*] Corresponding author. Tel.: +44-1224-272-943; fax: +44-1224-272-921; e-mail: m.j.plater@abdn.ac.uk
[†] Fax: +44-1865-747719.

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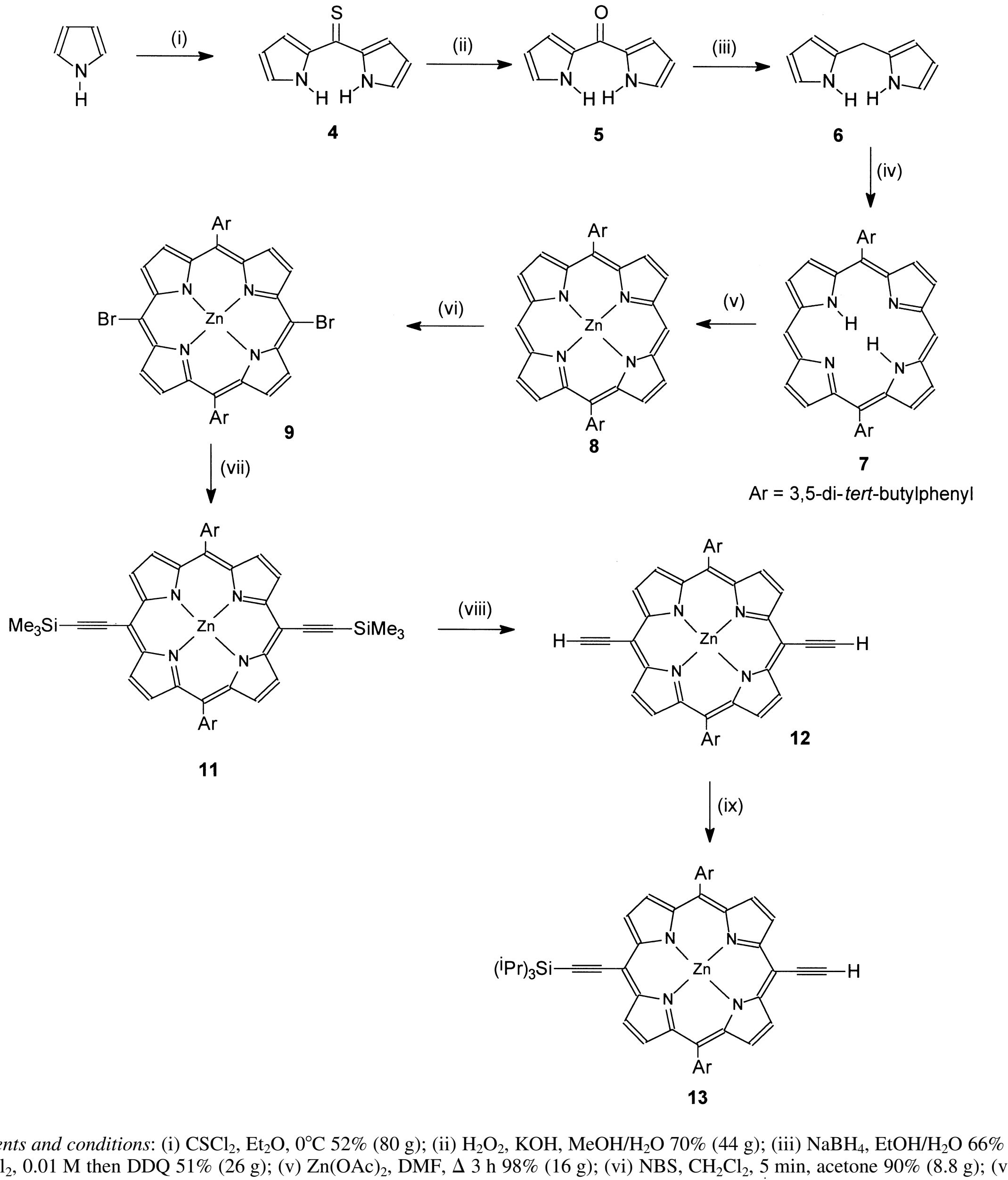
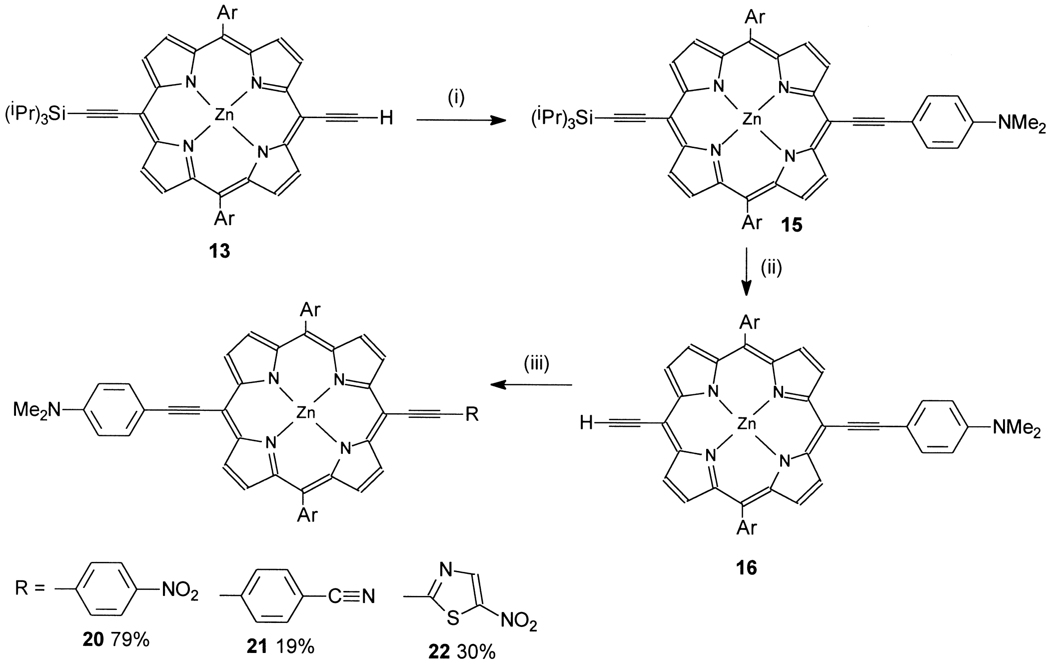
tert-butylphenyl)porphinato]zinc(II) **9** and the related compound 5,15-bis-bromo-10,20-bis-(phenyl)porphyrin have been described previously.[9,10] A variation on a synthetic route to it which can be performed on a large scale is reported here. 3,5-Di-*tert*-butylbenzaldehyde **3** was prepared from 3,5-di-*tert*-butyl(bromomethyl)benzene **2** by oxidation with hexamethylenetetraamine (Scheme 1). The intermediate 3,5-di-*tert*-butyltoluene **1** was prepared by Friedel–Crafts *tert*-butylation of toluene.[11–12] This is an interesting reaction since the methyl group activates the *ortho* and *para* sites of toluene. The isolation of the *meta* functionalised product indicates the reversibility of the reaction and that the de-*tert*-butylation of the *meta* isomer is presumably slower than that of the first formed *ortho* or *para* isomers. The second key building block for porphyrin synthesis, dipyrrylmethane **6**,[13] was prepared by reduction of dipyrrylketone **5** with $NaBH_4$ (Scheme 2). Thione **4**[14] required to prepare dipyrryl ketone **5**[15] was prepared by an uncatalysed reaction between pyrrole and thiophosgene. Porphyrin **7** was prepared on a 26 g scale by acid catalysed condensation of dipyrrylmethane **6** with 3,5-di-*tert*-butylbenzaldehyde **3** in a similar manner to a literature protocol.[9] An advantage of porphyrin synthesis using dipyrrylmethane **6** is the absence of unwanted side products arising as a consequence of acid catalysed scrambling of substituents[16,17] which can occur when methylene substituted dipyrrylmethanes are used. Substituent scrambling requires a reversal of bond formation with the formation of a pyrrylic carbocation intermediate. For porphyrin syntheses using dipyrrylmethane this fragmentation does not occur because there is no extra group to stabilise the pyrrylic carbocation. Porphyrin **7** was easily metallated by heating with $Zn(OAc)_2$ in DMF. The two *meso* positions were then brominated by treatment with NBS to give the dibrominated porphyrin **9**. It was found to be more satisfactory to brominate the metallated porphyrin **8** rather than the unmetallated porphyrin **7**

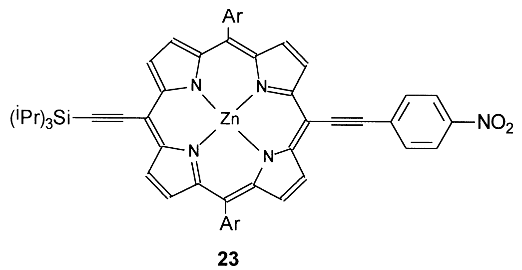


Scheme 2. *Reagents and conditions*: (i) $CSCl_2$, Et_2O, 0°C 52% (80 g); (ii) H_2O_2, KOH, $MeOH/H_2O$ 70% (44 g); (iii) $NaBH_4$, $EtOH/H_2O$ 66% (27 g); (iv) **3**, CF_3CO_2H, CH_2Cl_2, 0.01 M then DDQ 51% (26 g); (v) $Zn(OAc)_2$, DMF, Δ 3 h 98% (16 g); (vi) NBS, CH_2Cl_2, 5 min, acetone 90% (8.8 g); (vii) TMSCCH, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, 16 h 91% (13.2 g); (viii) Bu_4NF, $CHCl_3$ 90% (8.8 g); (ix) LiHMDS/THF then $(^iPr)_3SiCl$ 48% (0.3 g).



Scheme 3. *Reagents and conditions*: (i) **14**, $Pd(PPh_3)_2Cl_2$, CuI, pyrrolidine, 20 min 80% (1.0 g); (ii) Bu_4NF, THF 95% (0.73 g); (iii) **17**, **18** or **19**, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, **20** 79% (82 mg), **21** 19% (22 mg), **22** 30% (35 mg).

as reported previously for a related preparation of 5,15-bis-bromo-10,20-bis-(phenyl)porphyrin.[9] The bis(trimethylsilyl-ethynyl) porphyrin **11** was prepared by palladium catalysed coupling of dibrominated porphyrin **9** with trimethylsilyl-acetylene **10** on a 13 g scale. It was not necessary to use trimethylsilylethynylzinc chloride as reported previously by Therien on a small scale for the preparation of [5,15-bis-(phenyl)-10,20-bis-trimethylsilylethynylporphinato]zinc(II).[18] This route into bis(ethynyl) porphyrins was found by trial and error to be the most satisfactory for preparing multigram quantities of material. The two silyl groups of compound **11** were easily removed with Bu_4NF to give the bis(ethynyl) porphyrin **12**. This was monolithiated and quenched with triisopropylchlorosilane to give the mono-protected porphyrin **13** following a procedure developed by Anderson.[19] The coupling of dibromoporphyrin **9** with tri-isopropylsilylacetylene using $Pd(PPh_3)_2Cl_2$ was unsuccessful presumably owing to the steric bulk of the silyl group. Porphyrin **13** was used as a key building block to access donor–acceptor porphyrins. Palladium catalysed coupling with 4-iodo-*N*,*N*-dimethylaniline **14**[20] gave the donor functionalised porphyrin **15** (Scheme 3). This was desilylated with fluoride to give porphyrin **16** which was then coupled with three different acceptors to give the novel D–A porphyrins **20**–**22**. The D–A porphyrin **20** was also prepared by palladium catalysed coupling of mono-protected porphyrin **13** with 4-iodonitrobenzene **17** to give the acceptor functionalised porphyrin **23**. This was subsequently deprotected with fluoride to give porphyrin **24** then coupled with 4-iodo-*N*,*N*-dimethylaniline **14** to give the same D–A porphyrin **20**. This variation on the route appeared to offer no particular advantages. D–A porphyrins **20** and **21** show similar long wavelength UV absorptions at 679(4.9) and 674(5.2) nm, respectively, while D–A porphyrin **22** containing the nitrothiazoyl acceptor group showed a long wavelength UV absorption red shifted to 766(4.9) nm. The D–A compound similar to porphyrin **20** studied by Therien,[5] in which the 3,5-di-*tert*-butylphenyl groups are replaced by phenyl groups, was prepared previously by palladium catalysed coupling of [5,15-bis-bromo-10,20-bis-(phenyl)porphinato]zinc(II) firstly with *para*-(dimethylamino)phenylacetylene followed by *para*-nitrophenylacetylene. This route necessitates the synthesis of ethynyl derivatised donor and acceptor building blocks. The route published here is a more convergent approach making use of readily available bromo- and iodo- aromatic acceptors **20**–**22** for palladium coupling reactions. The D–D and A–A porphyrins **25** and **26**, respectively, were prepared in a similar manner by palladium catalysed coupling reactions of the bis(ethynyl) building block **12** with either 4-iodo-*N*,*N*-dimethylaniline **14** or 4-iodonitro-benzene **17**, respectively.



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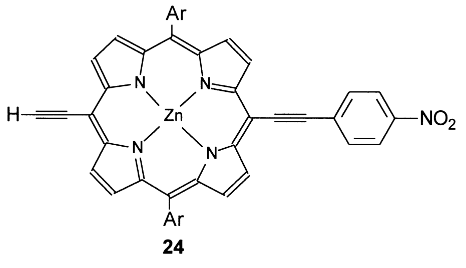

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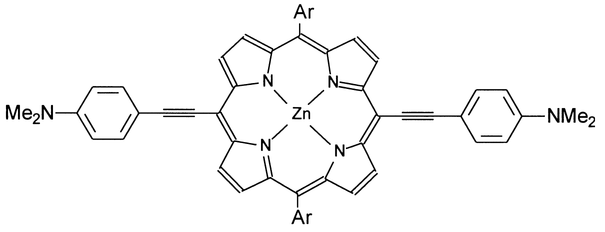

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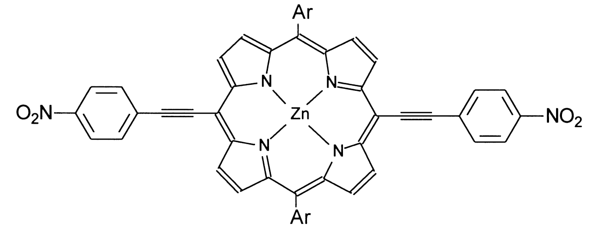

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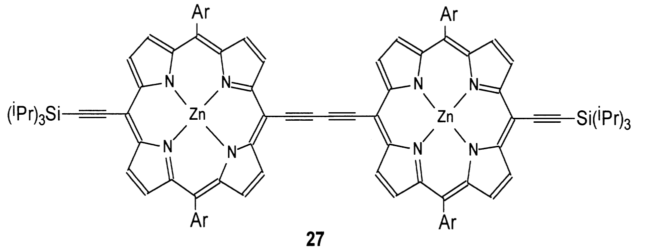

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Palladium catalysed self coupling[21] of porphyrin **13** gave the dimer **27** which has recently been studied as a template for the supramolecular assembly of a six particle hydrogen bonded aggregate using 4(3*H*)pyrimidone.[22] This report was the first example of a prototype aggregate that was co-operatively stabilised by both hydrogen bonding (4 H-bonds) and reversible pyridyl nitrogen–zinc bonding (4 N–zinc bonds).

In summary a new improved approach to bis(ethynyl) porphyrins has been developed and some new D–A porphyrins have been synthesised. Their NLO properties are currently under evaluation.

3. Experimental

3.1. General

Ultraviolet spectra were recorded on a Perkin–Elmer Lambda 15 UV–VIS spectrophotometer using dichloromethane or THF as the solvent. Infrared spectra were recorded on an ATI Mattson FTIR spectrometer. ^1H and ^{13}C NMR spectra were obtained at 250 and 62.9 MHz, respectively, on a Brucker AC 250 spectrometer. Chemical shifts, δ, are given in ppm relative to the residual solvent. Coupling constants J are given in Hz. Low resolution mass spectra were obtained using electrospray ionisation on a Finnigan Navigator Mass Spectrometer and accurate mass at the University of Wales, Swansea using fast atom bombardment methods. Butterworth Laboratories, using a PE 2400 CHN analyser, conducted elemental analyses. Melting points were carried out using a Kofler hot-stage microscope and are uncorrected. Starting materials were supplied by Aldrich and Lancaster Synthesis. Pyrrole, Et_3N, Et_2NH and pyrrolidine were dried by distillation from CaH_2. Solvents were used as supplied unless otherwise stated. THF was dried under nitrogen over CaH_2 and $LiAlH_4$ using triphenylmethane as an indicator.

3.1.1. 3,5-Di-*tert*-butyltoluene 1.[11] Aluminium trichloride (20 g, 0.14 mol) was added in 2 g portions, over a period of 12 h, to a rapidly stirred solution of 2-chloromethylpropane (400 g, 4.3 mol) in toluene (200 g, 2.1 mol) in a 1 L round bottomed flask fitted with a silicon oil bubbler. After a further 12 h, water was added and the product was extracted into Et_2O. The solvent was removed under reduced pressure and the residue purified by Vigreux distillation. The distillate was collected in 30 mL portions, which were subsequently stored in the cold for 24 h. The crude crystalline product (220 g, 50%) was filtered and used without further purification. An analytical sample was purified by crystallisation from methanol. (Found: C, 88.1; H, 12.3. $C_{15}H_{24}$ requires C, 88.2; H, 11.8%.)

3.1.2. 3,5-Di-*tert*-butyl(bromomethyl)benzene 2.[12] A mixture of 3,5-di-*tert*-butyltoluene **1** (90 g, 0.44 mol), *N*-bromosuccinimide (135 g, 0.66 mol) and benzoylperoxide (1 g, 4 mmol) in CCl_4 (800 mL) was refluxed for 3 h. The solution was cooled, filtered and concentrated under reduced pressure. The crude product (125 g) was used without further purification in the next step.

3.1.3. 3,5-Di-*tert*-butylbenzaldehyde 3. A mixture of 3,5-di-*tert*-butyl(bromomethyl)benzene **2** (crude weight 125 g, 0.44 mol) and hexamethylenetetraamine (256 g, 1.83 mol) in methanol/water (500 mL, 1:1) was refluxed for 4 h. Concentrated aqueous HCl (150 mL) was added dropwise and the mixture refluxed for a further 0.5 h. The solution was cooled and extracted into CH_2Cl_2 (3×350 mL), the solvent removed under reduced pressure and the residue recrystallised from EtOH/water to give the title compound (79 g, 82%) as a white crystalline solid, mp 88–89°C (sublimation) (lit.[12] 82–83°C) (Found: C, 82.7; H, 10.2. $C_{15}H_{22}O$ requires C, 82.5; H, 10.2%); λ_{max} ($CHCl_3$) (nm) 296 (log ε 3.2); ν_{max} (KBr) (cm^{-1}) 3365m, 2962vs, 2904s, 2866s, 2815s, 2733s, 1689vs, 1601s, 1463s, 1388s, 1364s, 1324vs, 1304m, 1278m, 1249s, 1190vs, 1126w, 998w, 947m, 899m, 882s, 817m, 706s and 514m; δ_H (250 MHz; $CDCl_3$) 1.35 (18H, s, *t*-Bu), 7.71 (3H, m, *o* and *p*-Ph) and 10.00 (1H, s, CHO); δ_C (62.9 MHz; $CDCl_3$) 31.4, 35.0, 124.2, 128.9, 136.2, 151.9 and 193.3; *m*/*z* 219.1 (M^++H, 100%) and 203 (M^+−Me, 5).

3.1.4. 2,2-Dipyrrylthione 4. A solution of pyrrole (116 g, 1.74 mol) in dry Et_2O (300 mL) was added dropwise to a stirred solution of thiophosgene (100 g, 0.87 mol) in dry Et_2O (300 mL) at 0°C under argon. After 30 min, MeOH (200 mL) was added and stirring was continued for a further 30 min. The solvent was removed under reduced pressure and the residue dissolved in $CHCl_3$ before filtering through a short plug of silica. The solvent was removed under reduced pressure to give the title compound (80 g, 52%) as a deep purple crystalline solid. An analytical sample was purified by flash chromatography on silica gel using toluene/$CHCl_3$

(9:1) as eluent, mp 98–99°C (ether/light petroleum 60–80) (lit[14] 96–98°C); $\lambda_{\max}$ ($CHCl_3$) (nm) 404 (log ε 4.5); $\nu_{\max}$ (KBr) (cm^{-1}) 3394s, 3344s, 3115m, 1523vs, 1405vs, 1386vs, 1284s, 1234w, 1129w, 1101vs, 1060m, 1028vs, 985w, 935w, 906m, 878m, 832w, 773w, 748vs, 701m, 636s and 585vs; δ_H (250 MHz; $CDCl_3$) 6.40 (2H, m), 7.04 (2H, m), 7.19 (2H, m) and 9.76 (2H, s, N–H); δ_C (62.9 MHz; $CDCl_3$) 112.5, 114.8, 127.7, 138.4 and 193.2; *m/z* 176.0405 (M^+ $C_9H_8SN_2$ requires 176.0408); *m/z* 177.0 (M^+, 100%) and 110.1 ($M^+-C_4H_4N$, 6).

3.1.5. 2,2′-Dipyrrylketone 5. Hydrogen peroxide (330 mL, 30%) was added dropwise to a solution of KOH (100 g, 1.8 mol) and 2,2′-dipyrrylthione **4** (80 g, 0.4 mol) in 95% aqueous MeOH (2.5 L) at 0°C. The mixture was refluxed for 5 min then cooled. Water (4 L) was added and the solution chilled. The product was filtered and dried to give the title compound (44 g, 69%) as pale yellow needles, mp 159–160°C (sublimation) (lit.[15] 160–161°C) (Found: C, 67.6; H, 5.0; N, 17.5. $C_9H_8N_2O$ requires C, 67.5; H, 5.0; N, 17.5%); $\lambda_{\max}$ ($CHCl_3$) (nm) 333 (log ε 4.5); $\nu_{\max}$ (KBr) (cm^{-1}) 3413s, 3364s, 3126m, 1726w, 1568vs, 1545s, 1405vs, 1120m, 1101s, 1056m, 1032s, 882m, 839vs, 753vs and 577s; δ_H (250 MHz; $CDCl_3$) 6.34 (2H, m), 7.08 (2H, m), 7.16 (2H, m) and 10.09 (2H, s, N–H); δ_C (62.9 MHz; $CDCl_3$) 111.0, 116.2, 124.2, 130.6 and 173.1; *m/z* 161.1 (M^+, 100%) and 94.1 ($M^+-C_4H_4N$, 4).

3.1.6. 2,2′-Dipyrrylmethane 6. A mixture of 2,2′-dipyrrylketone **5** (44 g, 0.27 mol) and sodium borohydride (100 g, 2.7 mol) in aqueous EtOH (500 mL, 95%) was brought to reflux. After 3 h, water (300 mL) was added and the EtOH removed under reduced pressure. The remaining solution was extracted with Et_2O (4×300 mL). The solvent was removed under reduced pressure and the residue extracted with light petroleum 40–60 until only a small amount of a dark coloured oil remained. The solvent was removed under reduced pressure in base washed glassware to yield the title compound (26.5 g, 66%) as a cream powder, mp 73–74°C (light petroleum 60–80) (lit.[13] 72–73°C); $\lambda_{\max}$ ($CHCl_3$) (nm) 334 (log ε 3.1) and 449 (3.0); $\nu_{\max}$ (KBr) (cm^{-1}) 2896m, 1716w, 1656w, 1562m, 1469m, 1438m, 1423m, 1403m, 1330m, 1261w, 1245w, 1224w, 1181m, 1112s, 1093s, 1024vs, 884m, 803vs, 726vs and 664s; δ_H (250 MHz; $CDCl_3$) 3.92 (2H, s, CH_2), 6.07 (2H, bs), 6.19 (2H, m), 6.60 (2H, m) and 7.62 (2H, m); δ_C (62.9 MHz; $CDCl_3$) 53.6, 106.6, 108.3, 117.5 and 129.3; *m/z* 147.1 (M^+, 100%).

3.1.7. 5,15-Bis-(3,5-bis-*tert*-butylphenyl)porphyrin 7.[10] A solution of dipyrrylmethane **6** (21.7 g, 0.15 mol) and 3,5-di-*tert*-butylbenzaldehyde **3** (33 g, 0.15 mol) in DCM (20 L) was stirred for 3 h, under argon, in the presence of trifluoroacetic acid (10 mL). The reaction was quenched by the addition of DDQ (51 g, 0.23 mol) and stirring continued for 0.5 h. The mixture was basified with Et_3N (50 mL) and filtered through silica. The solvent was removed under reduced pressure to give the title compound (26 g, 51%) as a purple solid, mp>250°C; $\lambda_{\max}$ ($CHCl_3$) (nm) 409 (log ε 5.7); $\nu_{\max}$ (KBr) (cm^{-1}) 3292m, 3067vs, 2959s, 2865s, 1588s, 1536w, 1469s, 1410s, 1359s, 1245vs, 1197m, 1143w, 1053w, 959m, 912m, 846s, 786vs, 737s and 686m; δ_H (250 MHz; $CDCl_3$) −3.02 (2H, s, N–H), 1.57 (36H, s), 7.83 (2H, t, J=1.8 Hz, *p*-Ph), 8.16 (4H, d, J=1.8 Hz, *o*-Ph), 9.17 (4H, d, J=4.8 Hz), 9.42 (4H, d, J=4.8 Hz) and 10.33 (2H, s, *meso*); δ_C (62.9 MHz; $CDCl_3$) 31.8, 35.1, 105.1, 120.5, 121.1, 130.3, 131.3, 131.5, 140.4, 145.0, 147.5 and 149.1; *m/z* 687.0 (M^+, 50%), 499.6 (M^+−di-*tert*-BuPh+H, 100).

3.1.8. [5,15-Bis-(3,5-bis-*tert*-butylphenyl)porphinato]zinc(II) 8.[10] A suspension of 5,15-bis-(3,5-bis-*tert*-butylphenyl)porphyrin **7** (15 g, 22 mmol) and $Zn(OAc)_2\cdot 2H_2O$ (48 g, 220 mmol) in DMF (900 mL) was refluxed for 3 h. Water (1 L) was added and the precipitate filtered and washed with water, MeOH and acetone. The residue was dissolved in $CHCl_3$ and filtered, MeOH was added and the volume reduced to precipitate the product. Filtration give the title compound (16 g, 98%) as a purple solid, mp>250°C (dichloromethane/methanol). $\lambda_{\max}$ ($CHCl_3$) (nm) 412 (log ε 5.6) and 540 (4.3); $\nu_{\max}$ (KBr) (cm^{-1}) 2958vs, 2903s, 2867s, 2362m, 2363m, 1652s, 1589s, 1517w, 1469m, 1424m, 1389s, 1360s, 1287m, 1244s, 1213m, 1059s, 987s, 926w, 855m, 822w, 784s, 707m and 670w; δ_H (250 MHz; $CDCl_3$) 1.58 (36H, s, *t*-Bu), 7.85 (2H, t, J=1.8 Hz, *p*-Ph), 8.15 (4H, d, J=1.8 Hz, *o*-Ph), 9.20 (4H, d, 4.7), 9.44 (4H, d, 4.7) and 10.31 (2H, s, *meso*); δ_C (62.9 MHz; $CDCl_3$) 31.8, 35.1, 106.0, 120.8, 121.4, 130.1, 131.6, 132.8, 141.7, 148.7, 149.4 and 150.4; *m/z* 749.3 (M^+, 100%).

3.1.9. [5,15-Bis-bromo-10,20-bis-(3,5-bis-*tert*-butylphenyl)porphinato]zinc(II) 9.[10] NBS (3.84 g, 22 mmol) was added to a stirred solution of porphyrin **8** (8.1 g, 11 mmol) in DCM (400 mL). After 5 min the reaction was quenched with acetone (50 mL), MeOH was added and the solvent was reduced to a small volume. The solution was then filtered and the residue was washed with MeOH to give the title compound (8.8 g, 90%) as a purple powder and a single spot by TLC, mp>250°C (tetrahydofuran/light petroleum); (Found: C, 63.3; H, 5.6; N, 6.0; Br, 17.0. $C_{48}H_{64}Br_2N_4Zn$ requires C, 63.5; H, 5.5; N, 6.2; Br, 17.6%); $\lambda_{\max}$ ($CHCl_3$) (nm) 426 (log ε 5.6); $\nu_{\max}$ (KBr) (cm^{-1}) 3456br, 2959s, 2862m, 1590m, 1470w, 1385m, 1360m, 1286m, 1260s, 1097s, 1074s, 1005s, 795s and 715w; δ_H (250 MHz; THF-d_8) 1.64 (36H, s, *t*-Bu), 7.99 (2H, t, J=1.8 Hz, *p*-Ph), 8.14 (4H, d, J=1.8 Hz, *o*-Ph), 8.96 (4H, d, J=4.9 Hz) and 9.73 (4H, d, J=4.9 Hz); δ_C (62.9 MHz; THF-d_8) 33.4, 37.1, 106.4, 123.4, 125.6, 132.2, 134.8, 135.6, 144.2, 150.9, 152.3 and 153.4; *m/z* 927/929/931 (M^+, 100%).

3.1.10. Trimethylsilylacetylene 10. A suspension of sodium acetylide (80 g, 18% w/w in xylenes, 0.3 mol) was added to chlorotrimethylsilane (32.5 g, 0.3 mol) in THF (100 mL) under argon. The mixture was stirred for 24 h, the solution distilled, and the fraction boiling between 50 and 80°C collected. The crude product was washed with water, dried over $MgSO_4$ and redistilled. The fraction boiling between 50 and 65°C was collected, washed with water, dried over $MgSO_4$ and filtered to give the title compound (22 g, 75%) as a colourless oil which was spectroscopically identical to a commercial sample (Aldrich).

3.1.11. [5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10,20-bis-trimethylsilylethynylporphinato]zinc(II) 11. Triethylamine

(35 mL) was distilled, from CaH_2 under argon, into a stirred solution of dibromoporphyrin **9** (14 g, 15.4 mmol), trimethylsilylacetylene **10** (6 g, 60 mmol), $Pd(PPh_3)_2Cl_2$ (600 mg, 0.84 mmol) and CuI (150 mg, 0.78 mmol) in THF (700 mL). The resulting solution was stirred for 16 h, the solvent was removed under reduced pressure and the residue, dissolved in light petroleum 60/80–CH_2Cl_2 (1:1), was filtered through silica. The solvent was removed under reduced pressure and the butadiynyl compound formed as a side product was removed by sublimation. The residue was recrystallised from DCM/acetonitrile to yield the title compound (13.2 g, 91%) as a deep purple crystalline solid which was spectroscopically identical to the compound reported previously,[19] mp>250°C; (Found: C, 74.3; H, 7.4; N, 6.0. $C_{58}H_{68}N_4Si_2Zn$ requires C, 73.9; H, 7.3; N, 5.9%); λ_{max} ($CHCl_3$) (nm) 434 (log ε 5.8) and 633 (4.8); ν_{max} (KBr) (cm^{-1}) 2960vs, 2139s, 1590m, 1498w, 1470m, 1423w, 1360m, 1288m, 1248s, 1211s, 1163w, 1063w, 1005s, 794s, 758m and 712s; δ_H (250 MHz; $CDCl_3$) 0.60 (18H, s, Si-Me), 1.55 (36H, s, *t*-Bu), 7.82 (2H, t, *J*=1.8 Hz, *p*-Ph), 8.04 (4H, d, *J*=1.8 Hz, *o*-Ph), 8.97 (4H, d, *J*=4.8 Hz) and 9.71 (4H, d, *J*=4.8 Hz); δ_C (62.9 MHz; $CDCl_3$) 0.4, 31.8, 35.1, 101.3, 101.8, 107.5, 121.1, 124.1, 129.8, 131.2, 133.1, 141.1, 148.8, 150.6 and 152.2; *m*/*z* 941.4352 (M^++H. $C_{58}H_{69}N_4Si_2Zn$ requires 941.4352), 941.3 (M^++H, 100%).

3.1.12. [10,20-Bis-(3,5-bis-*tert*-butylphenyl)-5,15-bis-ethynylporphinato]zinc(II) 12.[19] Tetrabutylammonium fluoride (50 mL, 0.5 M in THF) was added to a stirred solution of porphyrin **11** (11.62 g, 12.3 mmol) in CH_2Cl_2 (350 mL). After 5 min acetic acid (2 mL) and MeOH (600 mL) were added and the solution chilled (∼−20°C). After 1 h the precipitate was filtered and washed with MeOH to give the title compound (8.8 g, 90%) as a purple powder, mp>250°C; (Found: C, 77.8; H, 6.6; N, 6.8. $C_{52}H_{52}N_4Zn$ requires C, 78.2; H, 6.6; N, 7.0%); λ_{max} ($CHCl_3$) (nm) 432 (log ε 5.8); ν_{max} (KBr) (cm^{-1}) 3300m, 2958vs, 2865m, 2089w, 1590s, 1499w, 1469m, 1423w, 1391w, 1361m, 1287m, 1245m, 1209m, 1062m, 1003m, 932m, 880w, 821w, 792s, 711m and 651w; δ_H (250 MHz; $CDCl_3$) 1.59 (36H, s, *t*-Bu), 4.63 (2H, s, CC–H), 7.92 (2H, s, *p*-Ph), 8.10 (4H, s, *o*-Ph), 8.90 (4H, d, *J*=4.6 Hz) and 9.68 (4H, d, *J*=4.6 Hz); δ_C (62.9 MHz; $CDCl_3$) 32.2, 35.9, 85.4, 87.3, 100.7, 122.0, 124.6, 130.9, 131.7, 133.6, 143.0, 149.7, 151.6 and 153.2; *m*/*z* 798.3 (M^+, 100%).

3.1.13. [5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10-ethynyl-20-triisopropylsilylethynylporphinato]zinc(II) 13. A solution of lithium bis(trimethylsilyl)amide (0.9 mL, 1 M in THF, 0.9 mmol) was added to a rapidly stirred solution of porphyrin **12** (0.50 g, 0.6 mmol) in dry THF (60 mL) under an argon atmosphere. After 10 min chlorotriisopropylsilane (0.4 mL, 1.8 mmol) was added. Stirring was continued for 30 min and aqueous KOH (1 M, 30 mL) was added. The solution was poured into CH_2Cl_2 and washed with water. The solvent was removed under reduced pressure and the residue purified by flash chromatography using light petroleum/CH_2Cl_2–pyridine (70:10:2) as eluent. Recrystallisation from CH_2Cl_2/MeOH gave the title compound (0.30 g, 48%) as a purple solid, mp>250°C; λ_{max} ($CHCl_3$) (nm) 434 (log ε 5.4), 445 (5.2), 580 (4.2) and 629 (4.4); δ_H (250 MHz; $CDCl_3$) 1.44 (21H, m, *i*-Pr), 1.55 (36H, s, *t*-Bu), 4.13 (1H, s, CCH), 7.81 (2H, bs, *p*-Ph), 8.04 (4H, bs, *o*-Ph), 8.98 (4H, d, *J*=4.6 Hz), 9.71 (2H, d, *J*=4.6 Hz) and 9.77 (2H, d, *J*=4.6 Hz); *m*/*z* 954.6 (M^+, 100%).

3.1.14. 4-Iodo-*N*,*N*-dimethylaniline 14. Ground mercury-(II)chloride (67 g, 248 mmol) was added to a solution of *N*,*N*-dimethylaniline (30 g, 248 mmol) in CH_2Cl_2 (1 L). Iodine (31 g, 124 mmol) was added and the mixture stirred rapidly for 9 h. The solid was removed by filtration and washed with sodium thiosulphate (500 mL, 0.1 M) and saturated KI solution (500 mL). The organic layer was dried over Na_2SO_4 and the solvent removed under reduced pressure to give the title compound (30 g, 22%) as white plates, mp 81–82°C (ethanol) (lit[20] 79–80.5°C); ν_{max} (KBr) (cm^{-1}) 2979w, 2929m, 2888m, 2853m, 2802m, 1586s, 1553m, 1498s, 1444m, 1354s, 1312m, 1227s, 1192m, 1165m, 1123m, 1062m, 983w, 942w, 801vs, 743w, 691w, 565w and 502s; δ_H (250 MHz; $CDCl_3$) 2.91 (6H, s, N-Me), 6.48 (2H, d, *J*=9 Hz) and 7.46 (2H, d, *J*=9 Hz); δ_C (62.9 MHz; $CDCl_3$) 40.4, 77.5, 114.8, 137.6 and 150.0; *m*/*z*247.9 (M^+, 100%) and 122.1 (M^+−I, 22).

3.1.15. [5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10-(4-*N*,*N*-dimethylaminophenylethynyl)-20-triisopropylsilylethynylporphinato]zinc(II) 15. Porphyrin **13** (1 g, 1 mmol) was dissolved in pyrrolidine (30 mL, freshly distilled from CaH_2), under argon. Bis-(triphenylphosphine)palladium dichloride (5 mg, 7 μmol), CuI (5 mg, 26 μmol) and 4-iodo-*N*,*N*-dimethylaniline **14** (60 mg, 0.24 mmol) were added. The solution was stirred for 20 min and the solvent removed under reduced pressure. The residue was purified by flash chromatography twice on silica using light petroleum 60/80–THF (4:1) as eluent. The crude product was crystallised from CH_2Cl_2–methanol to give the title compound (0.9 g, 80%) as a deep green, almost black, crystalline solid, mp>250°C; (Found: C, 77.0; H, 7.4; N, 6.5. $C_{69}H_{81}N_5SiZn$ requires C, 77.2; H, 7.6; N, 6.5%); λ_{max} ($CHCl_3$) (nm) 454 (log ε 5.8) and 658 (5.2); ν_{max} (KBr) (cm^{-1}) 2958vs, 2863s, 2183m, 2136m, 1601s, 1520s, 1468m, 1360s, 1287w, 1245w, 1213s, 1164w, 1113m, 1066m, 1005m, 929w, 882w, 821w, 796m, 739w, 713m and 678w; δ_H (250 MHz; THF-d_8) 1.48 (21H, m, *i*-Pr), 1.57 (36H, s, *t*-Bu), 3.09 (6H, s, N-Me), 6.91 (2H, d, *J*=8.8 Hz), 7.89 (4H, m), 8.08 (4H, d, *J*=1.8 Hz, *o*-Ph), 8.83 (2H, m, *J*=4.6 Hz), 8.84 (2H, d, *J*=4.6 Hz), 9.65 (2H, d, *J*=4.6 Hz) and 9.72 (2H, d, *J*=4.6 Hz); δ_C (62.9 MHz; THF-d_8) 13.1, 19.7, 32.2, 35.9, 40.4, 64.4, 92.1, 97.2, 99.6, 100.5, 104.5, 111.8, 112.1, 113.1, 122.0, 124.7, 130.6, 131.3, 131.6, 133.0, 133.6, 143.2, 149.7, 151.2, 151.3, 151.7, 152.6 and 153.6; *m*/*z* 1073.5 (M^+, 100%).

3.1.16. [5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10-ethynyl-20-(4-*N*,*N*-dimethylaminophenylethynyl)porphinato]-zinc(II) 16. Tetrabutylammonium fluoride (0.4 mL, 0.10 M in THF) was added to a stirred solution of porphyrin **15** (40 mg, 0.04 mmol) in THF (30 mL). The solvent was removed under reduced pressure and the resulting solid washed with MeOH, filtered, dried to give the title compound (31 mg, 90%) which was used without further purification; λ_{max} ($CHCl_3$) (nm) 456 (log ε 5.6) and 666 (4.6).

3.1.17. [5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10-(4-*N*,*N*-dimethylaminophenylethynyl)-20-(4-nitrophenylethynyl)-porphinato]zinc(II) 20. Method 1: Triethylamine (2 mL) was distilled, from CaH_2 under argon, into a mixture of porphyrin **16** (100 mg, 0.1 mmol), 4-iodonitrobenzene **17** (30 mg, 0.12 mmol), $Pd(PPh_3)_2Cl_2$ (5 mg, 7 μmol) and CuI (5 mg, 26 μmol) in THF (20 mL) with stirring. Stirring was continued for 20 h. The solvent was removed under reduced pressure and the residue, extracted into light petroleum 60/80–THF (4:1), chromatographed on silica with light petroleum/THF (3:1) as eluent to give the title compound (82 mg, 79%) as a deep green powder, mp>250°C; (Found: C, 75.4; H, 6.7; N, 6.9. $C_{66}H_{64}N_6O_2Zn{\cdot}C_4H_8O$ requires C, 75.7; H, 6.5; N, 7.6%); λ_{max} ($CHCl_3$) (nm) 458 (log ε 5.4) and 679 (4.9); ν_{max} (KBr) (cm^{-1}) 2957s, 2905m, 2868m, 2180s, 1590s, 1515s, 1361m, 1336vs, 1286m, 1261m, 1246m, 1208m, 1191m, 1109m, 1066w, 1006m, 929m, 851m, 793s and 712m; δ_H (250 MHz; $CDCl_3$) 1.65 (36H, s, *t*-Bu), 3.07 (6H, s, NMe), 6.89 (2H, d, *J*=8.2 Hz), 7.89 (2H, d, *J*=8.0 Hz), 7.97 (2H, s, *o*-Ph), 8.19 (4H, s), 8.24 (2H, d, *J*=8.2 Hz), 8.42 (2H, d, *J*=8.0 Hz), 8.95 (4H, m) and 9.78 (4H, m); δ_C (62.9 MHz; THF-d_8) 32.1, 37.1, 93.3, 96.7, 100.0, 101.4, 106.7, 113.1, 114.3, 123.2, 126.2, 126.5, 127.3, 132.4, 132.9, 133.0, 133.5, 134.2, 134.3, 135.1, 135.2, 144.2, 149.3, 151.0, 152.4, 152.7, 153.0 and 154.6 (two resonances are missing); *m*/*z* 1036.4390 (M^+. $C_{66}H_{64}N_6O_2Zn$ requires 1036.4382); *m*/*z* 1036.3 (M^+, 100%). *Method* 2. Triethylamine (20 mL) was distilled from CaH_2 under argon into a mixture of porphyrin **24** (40 mg, 0.04 mmol), 4-iodo-*N*,*N*-dimethylaniline **14** (20 mg, 0.08 mmol), $Pd(PPh_3)_2Cl_2$ (5 mg, 7 μmol) and CuI (5 mg, 26 μmol) in THF (20 mL) with stirring. Stirring was continued for 5 h. The solvent was removed under reduced pressure and the residue, extracted into light petroleum 60/80–THF (3:1), chromatographed on silica with light petroleum 60/80–THF (3:1) as eluent to give the title compound (34 mg, 75%) as a deep green powder.

3.1.18. [5,15-Bis-(3,5-di-*tert*-butylphenyl)-10-(4-cyanophenylethynyl)-20-(4-*N*,*N*-dimethylphenylethynyl) porphinato]zinc(II) 21. A mixture of porphyrin **16** (100 mg, 0.1 mmol), 4-bromobenzonitrile **18** (100 mg, 0.6 mmol), $Pd(PPh_3)_2Cl_2$ (5 mg, 7 μmol), CuI (5 mg, 26 μmol) and triethylamine (2 mL, distilled from CaH_2 under argon) in dry THF (20 mL) was stirred for 12 h. The solvent was removed under reduced pressure and the residue, extracted into light petroleum 60/80–THF (3:1, pyridine (1%)), chromatographed on silica with light petroleum/THF (3:1, pyridine (1%)) as eluent to give the title compound (22 mg, 19%) as a deep green–blue powder, mp>250°C; λ_{max} ($CHCl_3$) (nm) 457 (log ε 5.7) and 674 (5.2); ν_{max} (KBr) (cm^{-1}) 709w, 792s, 875w, 931w, 1008m, 1062m, 1108m, 1203m, 1255m, 1351s, 1508s, 1598vs, 2179s, 2863m, 2902m, 2954s, 3411s, 3467s and 3554m; δ_H (250 MHz; $CDCl_3$) 1.55 (36H, s, *t*-Bu), 3.08 (6H, s, N-Me), 6.84 (2H, d, *J*=8.8 Hz), 7.81 (6H, m), 8.02 (6H, m), 8.89 (4H, 2×d, *J*=4.6 Hz), 9.62 (2H, d, *J*=4.6 Hz) and 9.72 (2H, d, *J*=4.6 Hz); δ_C (62.9 MHz; $CHCl_3$) 31.8, 35.1, 91.6, 94.3, 97.7, 98.5, 99.0, 103.9, 110.8, 111.2, 112.2, 118.9, 120.8, 124.5, 129.9, 130.8, 131.7, 132.3, 132.5, 132.8, 133.1, 141.7, 148.3, 148.6, 148.8, 149.2, 150.1, 150.3, 150.5, 151.6 and 152.1; *m*/*z* 1016.4478 (M^+ $C_{67}H_{64}N_4Zn$ requires 1016.4484); *m*/*z* 1017.3 ($[M+H]^+$, 20%).

3.1.19. [5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10-(4-*N*,*N*-dimethylaminophenylethynyl)-(2-(5-nitrothiazoyl)ethynyl)-20-porphinato]zinc(II) 22. A mixture of porphyrin **13** (100 mg, 0.1 mmol), 2-bromo-5-nitrothiazole **19** (100 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (5 mg, 7 μmol), CuI (5 mg, 26 μmol) and triethylamine (2 mL, distilled from CaH_2 under argon) in dry THF (20 mL) was stirred for 12 h. The solvent was removed under reduced pressure and the residue, extracted into light petroleum 60/80–THF (3:1, pyridine (1%)), was chromatographed on silica with light petroleum–THF (3:1, pyridine (1%)). The green brown band was collected and the solvent removed under reduced pressure. The residue was triturated successively with MeOH and then chloroform to give the title compound (35 mg, 30%) as a deep green powder, mp>250°C; λ_{max} ($CHCl_3$) (nm) 288 (log ε 5.5), 468 (5.2) and 766 (4.9); ν_{max} (KBr) (cm^{-1}) 711m, 790m, 929w, 1004w, 1108m, 1205s, 1280m, 1351s, 1513s, 1513s, 1596vs, 2176m, 2858m, 2912m, 2952vs, 3397s, 3428s and 3498s; δ_H (250 MHz; $CDCl_3$ (1% pyridine d_5)) 1.58 (36H, s, *t*-Bu), 3.09 (6H, s, N-Me), 6.86 (2H, d, *J*=8.8 Hz), 7.26 (1H, s, C–H), 7.81 (2H, t, *J*=3.8 Hz), 7.90 (2H, d, *J*=8.8 Hz), 8.07 (4H, t, *J*=3.8 Hz), 8.88 (2H, d, *J*=4.3 Hz), 8.97 (2H, d, *J*=4.3 Hz), 9.72 (2H, d, *J*=4.3 Hz), and 9.86 (2H, d, *J*=4.3 Hz); δ_C (62.9 MHz; $CDCl_3$/1% pyridine d_5) 31.8, 35.1, 40.4, 82.2, 88.7, 91.7, 98.3, 103.6, 111.2, 112.2, 120.8, 124.4, 130.0, 130.4, 130.7, 132.4, 132.8, 133.3, 141.8, 148.5, 150.0, 150.3, 150.4, 151.6 and 153.2 (3 resonances are missing); *m*/*z* 1044 (M^+, 25%).

3.1.20. [5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10-(4-nitrophenylethynyl)-20-triisopropylsilylethynylporphinato]-zinc(II) 23. Bis-(triphenylphosphine)palladium dichloride (5 mg, 7 μmol), CuI (5 mg, 26 μmol) and 4-iodonitrobenzene (60 mg, 0.24 mmol) and Et_3N (5 mL) were added to a solution of porphyrin **13** (50 mg, 0.05 mmol) in THF (40 mL). The solution was stirred for 40 min and the solvent removed under reduced pressure. The residue was purified by flash chromatography four times on silica using light petroleum 60/80–THF (4:1) as eluent. The fraction R_f~0.83 was crystallised from THF–propanol to give the title compound (39 mg, 80%) as a green solid, mp>250°C; λ_{max} ($CHCl_3$) (nm) 453 (log ε 5.7) and 653 (4.6); ν_{max} (KBr) (cm^{-1}) 3640s, 2958vs, 2868s, 2185w, 2139w, 1750w, 1697w, 1592m, 1519w, 1433s, 1393m, 1363m, 1342m, 1311m, 1230s, 1154s, 1120m, 859m, 771m, 575w and 502w; δ_H (250 MHz; $CDCl_3$) 1.43 (21H, m, *i*-Pr), 1.56 (36H, s, *t*-Bu), 7.83 (2H, t, *p*-Ph), 7.92 (2H, d, Ph), 8.05 (4H, d, *o*-Ph), 8.36 (2H, d, Ph), 8.96 (2×2H, 2×d, β-pyrrolic), 9.54 (2H, d, β-pyrrolic) and 9.72 (2H, d, β-pyrrolic); δ_C (62.9 MHz; $CHCl_3$) 11.9, 19.1, 31.8, 35.1, 94.5, 97.2, 98.9, 99.6, 121.2, 124.0, 124.6, 129.5, 131.4, 131.8, 133.2, 133.4, 133.5, 141.1, 148.8, 150.4, 150.8, 151.8 and 152.3 (four resonances are missing); *m*/*z* 1075 (M^++H, 100%).

3.1.21. [5-Ethynyl-10,20-bis-(3,5-bis-*tert*-butylphenyl)-15-(4-nitrophenylethynylporphinato]zinc(II) 24. Tetrabutylammonium fluoride (0.3 mL, 0.10 M in THF) was added to a stirred solution of porphyrin **23** (15 mg, 0.016 mmol) in THF (20 mL). The solvent was removed under reduced pressure and the residue crystallised from THF–propanol to give the title compound (15 mg, 90%) as a green powder, mp>250°C (THF–propanol) (Found: C, 76.3; H, 6.4; N, 7.4. $C_{58}H_{55}N_5O_2SiZn$ requires C, 75.8; H, 6.0; N, 7.6%); λ_{max} ($CHCl_3$) (nm) 449 (log ε 5.7); ν_{max} (KBr) (cm^{-1}) 3296w, 2958s, 2866w, 2187m, 1592s, 1514m, 1338vs, 1288w, 1210m, 1104w, 1065w, 1006m, 934m, 851m, 793m and 711m; δ_H (250 MHz; $CDCl_3$) 1.52 (36H, s), 4.14 (1H, s), 7.78 (2H, t, J=1.8 Hz), 7.99 (4H, d, J=1.8 Hz), 8.09 (2H, d, J=2.1 Hz), 8.37 (2H, d, J=2.1 Hz), 8.90 (4H, m) and 9.65 (4H, m); δ_C (62.9 MHz; $CHCl_3$) 31.8, 35.0, 122.8, 123.2, 123.5, 124.1, 130.0, 131.8, 133.0, 133.2, 135.0, 135.4, 135.8, 141.5, 148.6, 149.0, 149.4 and 149.8 (five resonances are missing); *m/z* 919.2 (M^+, 100%).

3.1.22. [5,15-Bis-(4-*N*,*N*-dimethylaminophenylethynyl)-10,20-bis-(3,5-bis-*tert*-butylphenyl)porphinato]zinc(II) 25. Tetrakis(triphenylphosphine)palladium(0) (34 mg, 0.03 mmol) and CuI (5 mg, 0.03 mmol) were added to a stirred solution of porphyrin **12** (65 mg, 0.08 mmol) and 4-iodo-*N*,*N*-dimethylaniline **14** (40 mg, 0.16 mmol) under argon in pyrrolidine (20 mL) freshly distilled from CaH_2. The solution was stirred for 1 h and the solvent removed under reduced pressure. The residue was chromatographed on silica using light petroleum 60/80–THF (3:1) as eluent. The fraction $R_f\sim0.7$ was collected, the solvent removed under reduced pressure and the product washed with three portions of MeOH to give the title compound (58 mg, 69%) as a green powder, mp>250°C; λ_{max} (THF) (nm) 467 (log ε 5.5) and 683 (5.1); ν_{max} (KBr) (cm^{-1}) 2957s, 2901m, 2865m, 2182m, 1603vs, 1521s, 1444m, 1358m, 1285w, 1245w, 1211m, 1190m, 1109m, 1062w, 1006w, 933w, 817w, 794m and 713w; δ_H (250 MHz; THF-d_8) 1.59 (36H, s, *t*-Bu), 3.09 (6H, s, N-Me), 6.91 (4H, d, J=8.9 Hz), 7.88 (6H, m), 8.11 (4H, d, J=8.6 Hz), 8.84 (4H, d, J=4.3 Hz) and 9.70 (4H, d, J=4.3 Hz); δ_C (62.9 MHz; THF-d_8) 32.4, 36.0, 40.6, 92.3, 99.1, 103.5, 112.5, 113.2, 121.9, 124.6, 131.2, 131.4, 133.2, 133.7, 143.4, 149.8, 151.1, 151.7 and 153.0; *m/z* (FAB) 1035.4 (M^+, 100%) and 517 (M^{2+}, 70) EI 1034.4931 (M^+ $C_{68}H_{70}N_6Zn$ requires 1034.4953).

3.1.23. [5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10,20-bis-(4-nitrophenylethynyl)porphinato]zinc(II) 26. Triethylamine (2 mL) was distilled from CaH_2 under argon into a stirred mixture of porphyrin **12** (100 mg, 0.13 mmol), 4-iodonitrobenzene (100 mg, 0.4 mmol), $Pd(PPh_3)_4$ (10 mg, 14 μmol) and CuI (10 mg, 52 μmol) in THF (40 mL). Stirring was continued for 16 h under argon and the solvent removed under reduced pressure. The residue was dissolved in light petroleum 60/80–THF (1:1) and filtered through silica. The solvent was removed under reduced pressure and the residue crystallised from THF–light petroleum 60/80 to give the title compound (110 mg, 77%) as a deep blue–green crystalline solid, mp>250°C; λ_{max} (THF) (nm) 461 (log ε 5.6) and 669 (5.0); ν_{max} (KBr) (cm^{-1}) 2958m, 2904w, 2867w, 2388w, 2187m, 1590s, 1514m, 1423w, 1338s, 1289w, 1258m, 1208m, 1102w, 1065w, 1007w, 937w, 851m, 793m, 747w and 711w; δ_H (250 MHz; THF-d_8) 1.67 (36H, s, *t*-Bu), 8.01 (2H, t, J=1.8 Hz, *p*-Ph), 8.20 (4H, d, J=1.8 Hz, *o*-Ph), 8.37 (4H, d, J=8.8 Hz), 8.53 (4H, d, J=8.8 Hz), 9.03 (4H, d, J=4.6 Hz) and 9.86 (4H, d, J=4.6 Hz); δ_C (62.9 MHz; THF-d_8) 33.7, 37.1, 97.2, 100.7, 102.0, 123.4, 126.2, 127.0, 132.9, 132.8, 133.2, 134.4, 135.3, 135.3, 144.0, 149.6, 151.2, 153.0, 153.1 and 154.2; *m/z* (FAB) 1040.3 (M^+, 100%) EI 1038.3815 (M^+ $C_{64}H_{58}N_6O_4Zn$ requires 1038.3811).

3.1.24. [5,5′-Bis-[10,20-bis(3,5-di-*tert*-butylphenyl)-15-triisopropylsilylethynyl-porphinyl]-1,3-butyn-1,4-diyl]-dizinc(II) 27. Porphyrin **13** (250 mg, 0.3 mmol), $Pd(PPh_3)_2Cl_2$ (108 mg, 0.15 mmol), CuI (30 mg, 0.15 mmol) and Et_3N (1 mL) in dry THF (40 mL) were stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue, dissolved in DCM–light petroleum (1:6) filtered through a short plug of silica. The solvent was removed under reduced pressure and the residue crystallised from CH_2Cl_2–MeOH to give the title compound (240 mg, 95%) as a green solid with a metallic lustre, mp>300°C; (Found: C, 76.2; H, 7.8; N, 5.8. $C_{122}H_{142}N_8Si_2Zn_2$ requires C, 76.8; H, 7.5; N, 5.9%); λ_{max} ($CHCl_3$) (nm) 455 (log ε 5.7), 491 (5.3), 727 (5.1); ν_{max} (KBr) (cm^{-1}) 622w, 707m, 792m, 829w, 881w, 1002m, 1062w, 1207s, 1245w, 1284m, 1357w, 1461m, 1492m, 1589m, 2130m, 2861s, 2954vs, 3413s, 3469s and 3546m; δ_H (250 MHz; $CDCl_3$) 1.44 (42H, m, *i*-Pr), 1.57 (72H, s, *t*-Bu), 7.84 (4H, bs), 8.09 (8H, bs), 8.98 (4H, d, J=4.6 Hz), 9.06 (4H, d, J=4.6 Hz), 9.74 (4H, bd, J=4.3 Hz) and 9.92 (4H, bd, J=4.3 Hz); δ_C (62.9 MHz; $CDCl_3$) 11.9, 19.1, 31.8, 35.1, 82.4, 87.6, 98.8, 99.8, 102.4, 109.2, 121.2, 124.6, 129.6, 130.9, 131.3, 133.2, 133.6, 141.1, 148.8, 150.4, 150.8, 152.3 and 153.0; *m/z* 1908 (M^+, 100%).

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References

1. Chemla, D. S.; Zyss, J. *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vols. 1 and 2; Academic: Orlando, FL, 1987 23.
2. Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991.
3. Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31–75.
4. (a) Priyadarshy, S.; Therien, M. J.; Beratan, D. N. *J. Am. Chem. Soc.* **1996**, *118*, 1504–1510. (b) Lin, V. S.-Y.; Therien, M. J. *Chem. Eur. J.* **1995**, *9*, 645–651. (c) LeCours, S. M.; DiMagno, S. G.; Therien, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 11854–11864.
5. LeCours, S. M.; Guan, H.-W.; DiMagno, S. G.; Wang, C. H.; Therien, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 1497–1503.
6. Anderson, H. L. *Tetrahedron Lett.* **1992**, *33*, 1101–1104.
7. *Materials for Optical Limiting*; Crane, R., Lewis, K., van Stryland, E., Khoshnevisan, M., Eds.; 1996; p 374.
8. (a) Mansour, K.; Alvarez, D.; Perry, K. J.; Choong, I.; Marder, S. R.; Perry, J. W. *Proc. SPIE* **1993**, *1853*, 132–141. (b) Mansour, K.; Fuqua, P.; Marder, S. R.; Dunn, B.; Perry,

J. W. *Proc. SPIE* **1994**, *2143*, 239–250. (c) Perry, J. W.; Mansour, K.; Marder, S. R.; Chen, C.-T.; Miles, P.; Kenney, M. E.; Kwag, G. *Proc. MRS* **1996**, *374*, 257–265. (d) Le Barny, P.; Dentan, V.; Robin, P.; Soyer, F.; Vergnolle, M. *Proc. SPIE* **1996**, *2852*, 201–210.

9. DiMagno, S. G.; Lin, V. S. Y.; Therien, M. J. *J. Org. Chem.* **1993**, *58*, 5983–5993.
10. Blake, I. M.; Anderson, H. L.; Beljonne, D.; Luc Bredas, J.; Clegg, W. *J. Am. Chem. Soc.* **1998**, *120*, 10764–10765.
11. (a) Geuze, J.; Ruinard, C.; Soeterbroek, J.; Verkade, P. E.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 301–310. (b) Bologa, U.; Balaban, A. T.; Grecu, N.; Negoita, N.; Caproiu, M. T.; Walter, R. I. *J. Org. Chem.* **1987**, *52*, 4176–4179.
12. Quast, H.; Mueller, B.; Peters, Eva-M.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1982**, *115*, 3631–3652.
13. Chong, R.; Clezy, P. S.; Liepa, A. J.; Nichol, A. W. *Aust. J. Chem.* **1969**, *22*, 229–238.
14. Clezy, P. S.; Smythe, G. A. *Aust. J. Chem.* **1969**, *22*, 239–249.
15. Ref. 14 Rappoport, W. *J. Am. Chem. Soc.* **1962**, *84*, 630–635.
16. Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864–2872.
17. Scott Wilson, G.; Anderson, H. L. *Synlett* **1996**, 1039–1040.
18. Lin, V. S.-Y.; DiMagno, S. G.; Therien, M. J. *Science* **1994**, *264*, 1105–1111.
19. Taylor, P. N.; Anderson, H. L. *J. Am. Chem. Soc.* **1999**, *121*, 11538–11545.
20. Marsden, R. J. B.; Sutton, L. E. *J. Chem. Soc.* **1936**, 599–606.
21. Taylor, P. N.; Huuskonen, J.; Rumbles, G.; Aplin, R. T.; Williams, E.; Anderson, H. L. *Chem. Commun.* **1998**, 909–910.
22. Plater, M. J.; Aiken, S.; Bourhill, G. *Tetrahedron Lett.* **2001**, *42*, 2225–2228.