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Metallated porphyrins containing lead(II), copper(II) or zinc(II)

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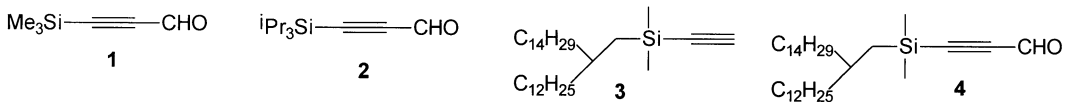
Abstract—A series of ethynyl and aryl substituted porphyrins and the corresponding metallated derivatives have been synthesised and characterised.

1. Introduction

Optical limiters or reverse saturable absorbers are materials which display diminishing transmittance with increasing incident light intensity. This attenuation of the optical throughput can be used to protect various sensors against damage from pulsed laser sources.[1–5] Porphyrins and phthalocyanines are promising candidates for certain applications. Population of triplet excited states is desirable since triplet states are longer lived than singlet states which enhances the limiter's performance. Hence dyes which contain heavy atoms are of interest because heavy atoms can promote intersystem crossing. This paper reports the synthesis and characterisation of a range of porphyrins and their metallated derivatives containing Zn(II), Cu(II) or Pb(II). The properties of lead porphyrins in particular are of interest owing to the large size of the lead atom.

2. Results and discussion

Porphyrins **8**–**9**, **11**–**12** and **14**–**17** were synthesised by documented methods. Modifications to some procedures are described in Section 3. The silylprop-2-ynal building blocks **1**,[6a] **2**[6b] and **4** required for porphyrin synthesis were prepared by treatment of the corresponding silylacetylene with ethylmagnesium bromide followed by quenching with DMF. 3-(Dimethyl-2-dodecyl-hexadecylsilyl)-propynal **4** has a large and branched alkyl side chain which was desired to make low melting porphyrins that would not aggregate in concentrated solutions. (3,5-Bis-*tert*-butylphenyl)-2,2′-dipyrrylmethane **6**[7] was prepared by condensation of 3,5-di-*tert*-butylbenzaldehyde **7** with pyrrole using pyrrole as the solvent and trifluoroacetic acid as an acid catalyst. Porphyrins **8**, **9** and **11** were prepared by reaction of dipyrrylmethane **6** with 3-trimethylsilylprop-2-ynal **1**, 3-triisopropylsilylprop-2-ynal **2** or 3-phenylprop-2-ynal **5**, respectively, using $BF_3{\cdot}OEt_2$ as catalyst.[7–10] The intermediate hexahydroporphyrins are oxidised in situ with DDQ. Some care with the length of reaction time is required because facile scrambling of *meso* ring substituents can occur.[8,11] Our studies with silylated acetylenes showed that a reaction time of just 1 min was adequate before the addition of DDQ. This short reaction time minimised porphyrin by-products and aided purification. During the synthesis of porphyrin **9** a small quantity of 5,10,15-tris-(3,5-bis-*tert*-butylphenyl)-20-triisopropylsilylethynyl-porphyrin **10** was isolated. The isolation of a similar intermediate has been reported previously.[8] Porphyrin **12**, substituted with two 4-nitrophenylethynyl groups, was prepared by demetallation of the corresponding zinc metallated derivative **13** with concentrated HCl. The synthesis of this compound has been reported previously by us.[12] Tetraethynyl substituted porphyrins **14** and **15** were prepared by condensation of pyrrole with 3-triisopropylsilylprop-2-ynal **2** and the branched silylpropynal **4**, respectively, by modification of a literature procedure.[13,14] Tetraphenylporphyrin **16** was purchased and tetra-(4-methoxyphenyl)-porphyrin **17** was prepared in a similar manner to compounds **14** and **15** using 4-methoxybenzaldehyde and pyrrole.



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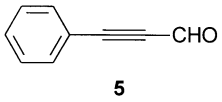

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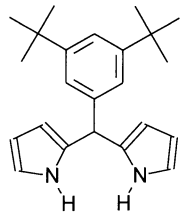

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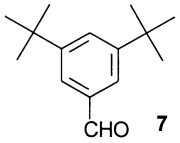

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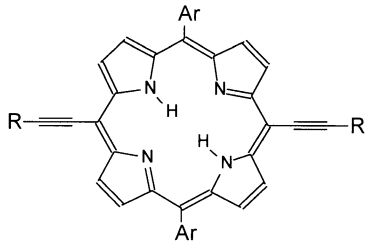
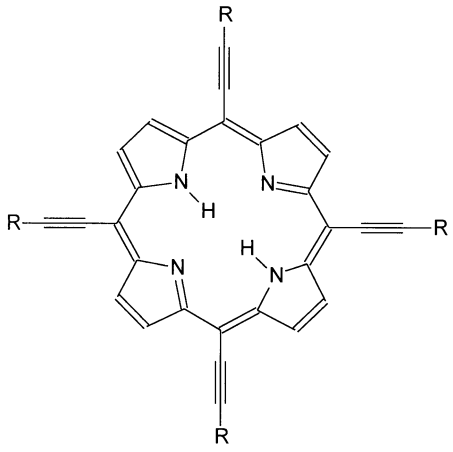
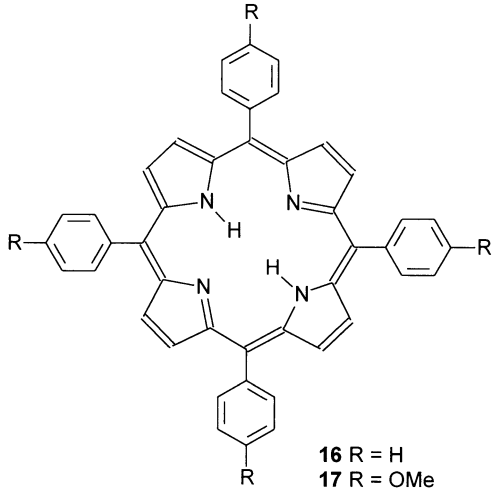


8 R = Me_3Si
9 R = $^iPr_3Si$
11 R = Ph
12 R = 4-O_2NPh



14 R = $^iPr_3Si$
15 R = $SiMe_2CH_2CH(C_{12}H_{25})(C_{14}H_{29})$



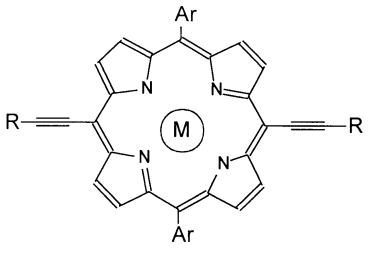
16 R = H
17 R = OMe

The metallated porphyrins **18**–**21** and **23**–**29** were easily prepared by heating the corresponding porphyrin with either $Zn(OAc)_2$, $Cu(OAc)_2$ or $Pb(OAc)_2$ in DMF. The UV–VIS data are summarised in Table 1. The UV–VIS spectrum for each porphyrin is important for optical limiting applications because a visible window is required so it is undesirable to have a strong ground state absorption in the visible region.

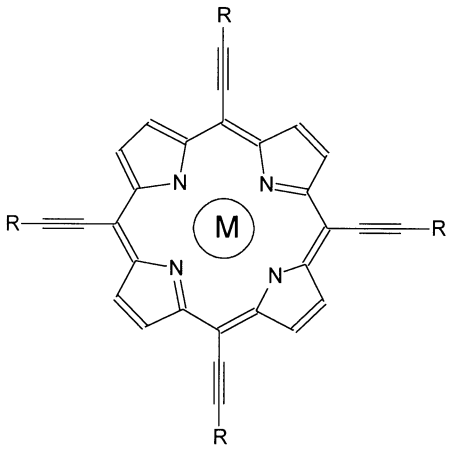
Table 1. Summary of UV data for metallated porphyrins

Porphyrin	λ_{max}, nm (log ϵ, 1000 cm^2 mol^{-1})		
18 (Zn)	438(5.7)	449(5.5)	637(4.7)
19(Cu)	432(5.8)	609(4.6)	
20(Pb)	473(5.3)	493(5.3)	704(4.6)
21(Zn)	447(5.6)	651(4.7)	
23(Pb)	477(5.4)	497(5.3)	720(4.8)
24(Pb)	485(5.3)	739(4.9)	
25(Zn)	463(5.7)	656(4.4)	
26(Pb)	500(5.8)	719(4.9)	
27(Pb)	500(5.8)	719(4.9)	
28(Pb)	353(4.8)	465(5.6)	656(4.3)
29(Pb)	468(5.2)	766(4.8)	

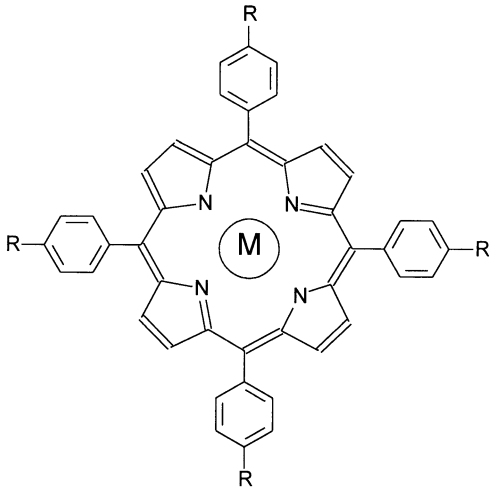
Sharp Soret and Q bands help to create a good visible window. These studies show that symmetric porphyrins often have sharper absorption peaks than unsymmetric porphyrins. For example, the lead containing metalloporphyrins **20** and **23** each have a split soret band whereas symmetric metalloporphyrins **26**–**29** have a single Soret band. The synthesis of [10,20-bis-(3,5-bis-*tert*-butylphenyl)-5,15-bis-ethynylporphinato] zinc(II) **22** has been reported previously. The peaks are sharp for tetraphenylporphyrin **28** containing lead but are broadened for (4-methoxytetraphenyl)porphyrin **29** which is substituted with methoxy groups. The lead containing metalloporphyrins show a red shifted Q band maximum typically in the region 700–720 nm. The ^1H NMR spectra of some of the lead containing metalloporphyrins shows that the lead atom is situated off centre from the mean plane of the porphyrin ring and that the *meso* aryl rings are sufficiently crowded to make rotation slow on the NMR time scale. For example, in metalloporphyrins **20** and **24** the 3,5-di-*tert*-butylphenyl groups show a peak for the two *para* hydrogens and two broad singlets for the *ortho* hydrogens. Compounds **23** and **24** show two different *tert*-butyl groups.



18 R = $^iPr_3Si$ M = Zn(II)
19 R = $^iPr_3Si$ M = Cu(II)
20 R = $^iPr_3Si$ M = Pb(II)
21 R = Ph M = Zn(II)
23 R = Ph M = Pb(II)
24 R = O_2NPh M = Pb(II)



25 R = $^{i}Pr_3Si$ M = Zn(II)
26 R = $^{i}Pr_3Si$ M = Pb(II)
27 R = $SiMe_2CH_2CH(C_{12}H_{25})(C_{14}H_{29})$ M = Pb(II)



28 R = H M = Pb
29 R = OMe M = Pb

The X-ray single crystal structures of lead containing metalloporphyrins **20** and **26** were solved. Full details of the structures will be published elsewhere.[15] The lead atoms in each are situated out of the plane of the porphyrin ring and are disordered in a similar manner. The replacement of the four twisted *meso* aryl rings with ethynyl spacers and the out of plane lead atom, might cause aggregation of this porphyrin in concentrated solution by a stacking phenomenon.

In summary a range of metallated porphyrins have been prepared in which the absorption maxima are varied by the choice of substituent and metal ion. Further properties of these compounds will be reported in due course.

3. Experimental

3.1. General

For general details see the preceding paper in this series.[12] Alkyl silanes were purchased from Aldrich. Units of ϵ are 1000 cm^2 mol^{-1}.

3.1.1. 3-Trimethylsilylprop-2-ynal 1.[6a] *General procedure*. Ethylmagnesium bromide, prepared from Mg (0.25 g, 10 mmol) and EtBr (1.1 g, 10 mmol) in THF (40 mL), was added dropwise to a solution of trimethylsilylacetylene (1 g, 10 mmol) in THF (40 mL), under argon. After the addition, the solution was refluxed for 5 min and then added dropwise to a solution of DMF (4.5 g, 61 mmol) in THF (40 mL). The solution was refluxed for 5 min before dilute aqueous HCl (20 mL) was added. The solution was poured into water and extracted with Et_2O. The solution was dried over $MgSO_4$ and the solvent removed under reduced pressure. The resulting oil was purified by vacuum distillation to give the title compound (0.92 g, 72%) as a colourless oil, bp 44–47°C (20 mmHg) δ_H (250 MHz; $CDCl_3$) 0.16 (9H, s, Si–Me) and 9.06 (1H, s, CHO).

3.1.2. 3-Triisopropylsilylprop-2-ynal 2.[6b] (11.4 g, 78%) as a pale yellow oil. δ_H (250 MHz; $CDCl_3$) 1.07–1.10 (21H, m) and 9.20 (1H, s, CHO); δ_C (62.9 MHz; $CDCl_3$) 11.0, 18.4, 100.8, 104.5 and 176.6.

3.1.3. 13-(Dimethylethynylsilylmethyl)heptacosane 3. *Method 1*. Ethynylmagnesium bromide was prepared by bubbling dry acetylene through a solution of EtMgBr, prepared from magnesium (160 mg, 6.6 mmol) and EtBr (1.0 g, 9 mmol), in THF (15 mL), for 1 h. This solution was added to 13-(chlorodimethylsilylmethyl)heptacosane (3.0 g, 6 mmol) in THF (15 mL). After refluxing for 10 min the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica using light petroleum 60–80 as eluent. The third fraction was collected and the solvent removed under reduced pressure to give the title compound (1.2 g, 42%) as a colourless oil. *Method 2*. A suspension of sodium acetylide (10 g, 18% w/w in xylenes, 37 mmol) was added to a stirred solution of 13-(chlorodimethylsilylmethyl)heptacosane (7.0 g, 14 mmol) in THF (30 mL) under argon. The solution was stirred overnight before water was added to quench the excess acetylide. The solution was extracted into Et_2O (3×50 mL). The combined ethereal extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure. The residue was purified by flash chromatography on silica using light petroleum 60–80 as eluent. The third fraction was collected and the solvent removed under reduced pressure to give the title compound (4.7 g, 69%) as a colourless oil. (Found: C, 80.8; H, 13.5. $C_{32}H_{64}Si$ requires C, 80.6; H, 13.5%); δ_H (250 MHz; $CDCl_3$) 0.18 (6H, s, Me–Si), 0.65 (2H, d, CH_2–Si, J=7 Hz), 0.88 (6H, m, Me), 1.25 (48H, bs, CH_2), 1.55 (1H, m, CH) and 2.36 (1H, s, CC–H); δ_C (62.9 MHz; $CDCl_3$) −0.8, 14.2, 21.1, 22.7, 26.5, 29.8, 30.0, 32.0, 34.0, 36.4, 90.1 and 93.3 (20 resonances are missing).

3.1.4. 3-(Dimethyl-2-dodecyl-hexadecylsilyl)-propynal 4. (2 g, 52%) as a pale yellow oil (Found: C, 77.9; H, 13.25. $C_{33}H_{64}OSi$ requires C, 78.5; H, 12.8%); δ_H (400 MHz; $CDCl_3$) 0.21 (6H, s, Si–Me), 0.69 (2H, d, J=6.8 Hz, Si–CH_2), 0.82 (6H, t, J=4.1 Hz, Me), 1.25 (48H, bs, CH_2), 1.55 (1H, m, CH) and 9.12 (1H, s, CHO); δ_C (100.6 MHz; $CDCl_3$) −0.5, 15.1, 21.6, 23.7, 23.7, 27.5, 30.4, 30.5,

30.7, 30.7, 31.0, 32.9, 33.0, 35.0, 37.4, 103.7, 104.4 and 177.5 (15 resonances are missing); *m/z* (EI) 503.4 (M^+, 100%).

3.1.5. (3,5-Bis-*tert*-butylphenyl)-2,2′-dipyrrylmethane 6.[7a] The method is similar to the literature procedure but with some modifications. Trifluoroacetic acid (0.1 mL) was added to a stirred solution of 3,5-di-*tert*-butylbenzaldehyde **7** (5.0 g, 23 mmol) in pyrrole (250 mL, 3.6 mol). Stirring was continued for 5 min, the solution diluted with CH_2Cl_2 (500 mL), washed with NaOH (1 M, 200 mL), dried over Na_2SO_4 and the solvent removed under reduced pressure. Excess pyrrole was removed by vacuum distillation at 40°C and the tarry residue purified by flash chromatography on silica with hexane/ethyl acetate/triethylamine (80:20:10) as eluent. The second fraction was collected and dissolved in hot MeOH/water and stored at −20°C for 2 h. The solvent was decanted into water and extracted into CH_2Cl_2. The organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure at room temperature and the resulting oil stored at −20°C for 5 days to give the title compound (5.5 g, 72%) as a pale yellow crystalline solid, mp 107–108°C (hot methanol/water) (lit.[7a] 106–107°C). $\lambda_{max}(CHCl_3)$/nm 395 (log ϵ 2.9) and 466 (2.6); ν_{max} (KBr)/cm^{-1} 3417vs, 3396vs, 3101m, 2961vs, 2904m, 2865m, 1595m, 1564m, 1472m, 1425m, 1395m, 1361m, 1304w, 1246m, 1188w, 1112m, 1092m, 1030m, 972w, 902w, 881m, 779m, 757w, 714vs, 645w, 568m and 538m; δ_H (400 MHz; $CDCl_3$) 1.26 (18H, s, *t*-Bu), 5.42 (1H, s, *meso*), 5.91 (2H, bs), 6.13 (2H, m), 6.65 (2H, m), 7.04 (2H, d, *J*=1.7 Hz, *o*-Ph), 7.29 (1H, t, *J*=1.7 Hz, *p*-Ph) and 7.89 (2H, bs, N–H); δ_C (100.6 MHz; $CDCl_3$) 32.5, 35.9, 45.6, 108.2, 109.4, 118.0, 121.9, 123.8, 134.0, 141.9 and 152.0.

3.1.6. 5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10,20-bis-trimethylsilylethynylporphyrin 8.[9] The procedure is similar to that given in Ref. 9. Under argon, $BF_3{\cdot}Et_2O$ (25 μL) was added to a solution of (3,5-bis-*tert*-butylphenyl)-2,2′-dipyrrylmethane **6** (168 mg, 0.5 mmol) and 3-trimethylsilylprop-2-ynal **1** (63 mg, 0.5 mmol) in CH_2Cl_2 (50 mL) and the solution stirred at rt for 1 min. DDQ (178 mg, 0.78 mmol) was added and stirring continued for 5 min more. Et_3N (1 mL) was added and the solution filtered through silica. The solvent was removed under reduced pressure and the residue, dissolved in light petroleum 60–80/CH_2Cl_2 (1:1), was filtered through a short plug of silica. The solvent was removed under reduced pressure to give the title compound (44 mg, 20%) as a purple crystalline solid, mp>250°C (dichloromethane/methanol) (Found: C, 77.4; H, 8.1; N, 6.4. $C_{58}H_{70}N_4Si_2{\cdot}CH_3OH$ requires C, 77.7; H, 8.2; N, 6.2%); $\lambda_{max}(CHCl_3)$/nm 433 (log ϵ 5.6); ν_{max} (KBr)/cm^{-1} 3314w, 2959vs, 2925m, 2866m, 2140m, 1591m, 1557w, 1474m, 1363m, 1246s, 1137w, 849vs, 798s and 719m; δ_H (250 MHz; $CDCl_3$) −2.12 (s, 2H, N–H), 1.55 (36H, s, *t*-Bu), 7.82 (2H, t, *J*=1.9 Hz, *p*-Ph), 8.03 (4H, d, *J*=1.9 Hz, *o*-Ph), 8.86 (4H, d, *J*=4.8 Hz) and 9.60 (4H, d, *J*=4.8 Hz); δ_C (62.9 MHz; $CDCl_3$) 0.3, 31.8, 35.1, 100.6, 102.4, 107.1, 121.3, 123.2, 129.9, 130.5br, 131.9br, 140.3 and 149.1 (two resonances are missing); *m/z* (FAB) 879 (M^+, 100%).

3.1.7. 5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10,20-bis-triisopropylsilylethynylporphyrin 9. Under argon, $BF_3{\cdot}Et_2O$ (0.1 mL) was added to a stirred solution of aryldipyrrylmethane **6** (753 mg, 2.2 mmol) and 3-triisopropylsilylprop-2-ynal **2** (500 mg, 2.4 mmol) in CH_2Cl_2 (1 L) and the solution stirred. After 1 min, DDQ (0.768 g, 3.4 mmol) was added and stirring continued for a further 20 min. The solution was filtered through silica, the solvent removed under reduced pressure and the residue chromatographed on silica with light petroleum/dichloromethane (1:1) as eluent. The second fraction was collected and the solvent removed under reduced pressure to give the title compound (230 mg, 20%) as a purple crystalline solid, mp>300°C (dichloromethane/methanol). Larger preparations of this compound can be purified by repeated crystallisation. (Found: C, 79.2; H, 9.0; N, 5.0. $C_{70}H_{94}N_4Si_2{\cdot}CH_3OH$ requires C, 79.0; H, 9.15; N, 5.2%); $\lambda_{max}(CHCl_3)$/nm 434 (log ϵ 5.7) and 585 (4.9); ν_{max} (KBr)/cm^{-1} 2959vs, 2862s, 2139m, 1591m, 1558w, 1473m, 1427w, 1363m, 1263w, 1245m, 1136m, 1069m, 985m, 915m, 881m, 801s, 715s, 676m and 580w; δ_H (250 MHz; $CDCl_3$) −2.11 (s, 2H, N–H), 1.42 (42H, m, *i*-Pr), 1.53 (36H, s, *t*-Bu), 7.80 (2H, t, *J*=1.8 Hz, *p*-Ph), 8.01 (4H, d, *J*=1.8 Hz, *o*-Ph), 8.86 (4H, d, *J*=4.6 Hz) and 9.64 (4H, d, *J*=4.6 Hz); δ_C (62.9 MHz; $CDCl_3$) 11.9, 19.1, 31.8, 35.1, 99.1, 100.9, 108.8, 121.4, 123.1, 129.4, 130.4, 131.9, 140.4 and 148.9 (two resonances are missing); *m/z* (FAB) 1047 (M^+, 100%).

3.1.8. 5,10,15-Tris-(3,5-bis-*tert*-butylphenyl)-20-triisopropylsilylethynylporphyrin 10. Produced as an acidolysis product of **9** and separated by chromatography, mp>250°C; $\lambda_{max}(CHCl_3)$/nm 426 (log ϵ 5.4) and 565 (4.6); ν_{max} (KBr)/cm^{-1} 3414w, 2958vs, 2863m, 1590m, 1469m, 1360m, 1245m, 1066w, 983w, 912w, 881w, 800m, 727m and 691w; δ_H (250 MHz; $CDCl_3$); −2.28 (s, 2H, N–H), 1.50 (75H, m, *t*-Bu and *i*-Pr), 7.79 (3H, m), 8.50 (6H, m), 8.81 (6H, m) and 9.70 (2H, d, *J*=4.9 Hz); δ_C (62.9 MHz; $CDCl_3$) 11.9, 19.1, 31.8, 35.1, 98.0, 99.0, 109.1, 121.2, 122.3, 123.3, 129.5, 132.2, 140.9, 141.2, 148.7 and 148.8 (11 resonances are missing); *m/z* (FAB) 1055.7326 (M^+, $C_{73}H_{95}N_4Si$ requires 1055.7371).

3.1.9. 5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10,20-bis-phenylethynylporphyrin 11. *Method 1*. A solution of aryldipyrrylmethane **6** (310 mg, 0.9 mmol) and 3-phenylprop-2-ynal **5** (120 mg, 0.9 mmol) in CH_2Cl_2 (50 mL) was added to a stirred solution of $BF_3{\cdot}Et_2O$ (0.1 mL) in CH_2Cl_2 (300 mL) under argon. Stirring was continued for 2 h, DDQ (316 mg, 1.4 mmol) was added and stirring continued for a further 10 min. The solution was filtered through silica, the solvent removed under reduced pressure and the residue chromatographed on silica using light petroleum/CH_2Cl_2 (1:1) as eluent. The solvent was removed under reduced pressure and the residue crystallised from CH_2Cl_2/MeOH to give the title compound (20 mg, 5%) as purple needles. *Method 2*. Concentrated aqueous HCl (0.5 mL) was added to a stirred solution of porphyrin **27** (400 mg, 0.42 mmol) in THF (40 mL). The resultant brown solution was added to Et_2O (100 mL) and the ethereal solution washed with aqueous NaOH (100 mL, 5 M), water, dried over $MgSO_4$ and the solvent removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and filtered through silica. MeOH was added and the product allowed to crystallise by slow evaporation to give the title compound (350 mg, 95%) as purple needles, mp>250°C (dichloromethane/methanol).

$\lambda_{max}(CHCl_3)$/nm 438 (log ϵ 5.7) and 597 (4.4); ν_{max} (KBr)/cm^{-1} 2960vs, 2900m, 2865m, 1591s, 1555w, 1472s, 1426w, 1393w, 1362m, 1249s, 1155m, 1067w, 986w, 913m, 882w, 799vs, 751m, 726s and 686m; δ_H (250 MHz; $CDCl_3$) −1.90 (2H, s, N–H), 1.56 (36H, s, *t*-Bu), 7.54 (6H, m), 7.84 (2H, t, *J*=1.5 Hz, *p*-Ph), 8.05 (4H, m), 8.08 (4H, d, *J*=1.5 Hz, *o*-Ph), 8.90 (4H, d, *J*=4.9 Hz) and 9.71 (4H, d, *J*=4.9 Hz); δ_C (62.9 MHz; $CDCl_3$) 31.8, 35.1, 92.2, 97.1, 100.9, 121.4, 123.4, 124.0, 128.8, 123.0, 131.7, 140.4 and 149.1; *m/z* (FAB) 887.5062 (M^++H. $C_{64}H_{63}N_4$ requires 887.5052), 887.5 (M^++H, 100%).

3.1.10. 5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10,20-bis-(4-nitrophenylethynyl)porphyrin 12. Concentrated aqueous HCl (1 mL) was added to a stirred solution of [5,15-bis-(3,5-bis-*tert*-butylphenyl)-10,20-bis-(4-nitrophenylethynyl)-porphinato]zinc(II) **13**[12] (5 mg, 0.5 mmol) in THF (40 mL). The resultant solution was added to CH_2Cl_2 (100 mL), washed with aqueous NaOH (100 mL, 5 M), water, dried over $MgSO_4$ and the solvent removed under reduced pressure. The residue was dissolved in DCM and filtered through silica. MeOH was added and the product allowed to crystallise by slow evaporation to give the title compound (0.45 g, 95%) as a purple powder, mp>300°C (dichloromethane/methanol); $\lambda_{max}(CH_2Cl_2)$/nm 449 (log ϵ 5.4) and 607 (4.5); ν_{max} (KBr)/cm^{-1} 719w, 792m, 848w, 1103w, 1151m, 1247m, 1332vs, 1469m, 1511m, 1587s, 2186m, 2861m, 2900m, 2954s, 3415s, 3478m and 3552m; δ_H (250 MHz; $CDCl_3$) −2.07 (2H, s, N–H), 1.67 (36H, s, *t*-Bu), 7.86 (2H, s, br), 7.92 (4H, s, br), 8.08 (4H, s, br), 8.30 (4H, s, br), 8.92 (4H, s, br) and 9.57 (4H, s, br); δ_C (62.9 MHz; $CDCl_3$) 95.3, 97.6, 99.7, 121.6, 124.0, 124.2, 130.0, 130.2, 130.6, 132.1, 132.3, 132.4, 132.7, 140.0, 140.1, 147.0 and 149.3 (one resonance is missing); *m/z* (FAB) 977 (M^+, 100%); (EI) 976.4676 (M^+ $C_{64}H_{60}N_6O_4$ requires 976.4672).

3.1.11. 5,10,15,20-*tetrakis*-Triisopropylsilylethynylporphyrin 14. Borontrifluoride etherate (1.1 mL) was added to a stirred solution of pyrrole (3.80 g, 10 mmol) and 3-triisopropylsilylprop-2-ynal **2** (11.95 g, 10 mmol) in CH_2Cl_2 (5 L), cooled to −78°C. The solution was allowed to warm to rt over 2 h. Stirring was continued for a further 1 h, DDQ (9.7 g, 7.5 mmol) was added, stirring continued for 10 min and the solution filtered through silica. The solvent was removed under reduced pressure and the residue, dissolved in light petroleum/CH_2Cl_2 (1:1), filtered through silica. The solvent was removed under reduced pressure and the residue was crystallised form CH_2Cl_2/MeOH to give the title compound (3.96 g, 27%) as a purple solid with a metallic lustre, mp>250°C; (Found: C, 74.7; H, 9.1; N, 5.6. $C_{64}H_{94}N_4Si_4$ requires C, 74.5; H, 9.2; N, 5.4%); $\lambda_{max}(CHCl_3)$/nm 450 (log ϵ 5.7), 607 (4.9) and 710 (4.3); ν_{max} (KBr)/cm^{-1} 457m, 572m, 669s, 705vs, 794m, 877m, 914w, 987m, 1058w, 1132m, 1238m, 1342w, 1459s, 1502w, 1616w, 2136s, 2356w, 2858s, 2942s, 3407m, 3478m and 3544m; δ_H (250 MHz; $CDCl_3$) −1.76 (2H, s, N–H), 1.44 and 1.46 (84H, m, *i*-Pr), 9.55 (8H, s, β-pyrrolic); δ_C (62.9 MHz; $CDCl_3$) 11.9, 19.1, 100.3, 102.6 and 107.7 (two resonances are missing); *m/z* (FAB) 1031.8 (M^+, 100%).

3.1.12. 5,10,15,20-*tetrakis*-[Dimethyl-(2-dodecylhexadecyl)-silylethynyl]porphyrin 15. Borontrifluoride etherate (10 μL) was added to a stirred solution of pyrrole (66 mg, 1 mmol) and 3-(dimethyl-2-dodecyl-hexadecylsilyl)-prop-2-ynal **4** (495 mg, 1 mmol) in DCM (20 mL), cooled to −30°C. After 2 h the solution was allowed to warm to rt, stirred for a further 2 h and DDQ (167 mg, 0.74 mmol) added. Stirring was continued for 10 min before the solution was filtered through silica. The solvent was removed under reduced pressure and the residue purified by flash chromatography on silica using light petroleum/CH_2Cl_2 (9:1) as eluent. The green band was collected and the solvent removed under reduced pressure to give the title compound (41 mg, 12%) as a deep green amorphous solid; $\lambda_{max}(CHCl_3)$/nm 449 (log ϵ 5.6), 607 (4.9) and 708 (4.4); δ_H (250 MHz; $CDCl_3$) −1.73 (2H, s, N–H), 0.23 (8H, d, *J*=7.6 Hz, Si–CH_2), 0.63 (24H, s, Si–Me), 0.86 (24H, t, *J*=8.2 Hz, Me), 1.27 (192H, bs, CH_2), 1.95 (4H, m, CH) and 9.53 (8H, s, β-pyrrolic); δ_C (62.9 MHz; $CDCl_3$) −0.3, 14.15, 22.7, 26.6, 29.6, 32.0, 36.8, 102.5, 103.4, 106.4 and 130.9 (22 resonances are missing); *m/z* (FAB) 2209.5 (M^+, 100%).

3.1.13. 5,10,15,20-Tetra-(*p*-methoxyphenyl)porphyrin 17. Borontrifluoride etherate (0.1 mL) was added to a stirred solution of pyrrole (3.3 g, 49 mmol) and *p*-methoxybenzaldehyde (6.6 g, 49 mmol) in CH_2Cl_2 (250 mL) under argon. Stirring was continued for 44 h and DDQ (8.3 g, 37 mmol) added. Stirring was continued for 10 min more. The solvent was removed under reduced pressure and the residue dissolved in $CHCl_3$ before filtration. The insoluble product was washed with $CHCl_3$ to give the title compound (1.7 g, 27%) as a mauve solid, mp>250°C; $\lambda_{max}(CHCl_3)$/nm 422 (log ϵ 5.8); ν_{max} (KBr)/cm^{-1} 3311w, 2955w, 2928w, 2899w, 2832w, 1604m, 1552w, 1506s, 1464m, 1404w, 1348m, 1288m, 1246vs, 1173s, 1104m, 1071m, 1032s, 985w, 961m, 840w, 802s, 736m and 638w; δ_H (250 MHz; $CDCl_3$) −2.76 (2H, s, N–H); 4.09 (12H, s, OMe), 7.28 (8H, d, *J*=8.5 Hz), 8.11 (8H, d, *J*=8.5 Hz) and 8.85 (8H, s, β-pyrrolic); δ_C (62.9 MHz; $CDCl_3$) 55.6, 112.2, 119.8, 131.0, 134.7, 135.6 and 159.4 (1 resonance is missing); *m/z* (FAB) 735.2958 (M^++H. $C_{48}H_{39}N_4O_4$ requires 735.2958), 735.2 (M^++H, 100%).

3.1.14. [5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10,20-bis-triisopropylsilylethynylporphinato]zinc(II) 18. *Method 1*. A suspension of porphyrin **9** (40 mg, 0.04 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (670 mg, 3 mmol) in DMF (15 mL) was refluxed for 1 h, under argon. The resulting deep green solution was poured into water (50 mL). The precipitate was filtered and washed with water, MeOH and recrystallised from CH_2Cl_2/MeOH to give the title compound (41 mg, 98%) as a purple crystalline solid. *Method 2*. A solution of lithium bis-trimethylsilylamide (1.2 mL, 1 M in THF, 1.2 mmol) was added to a rapidly stirred solution of [10,20-bis-(3,5-bis-*tert*-butylphenyl)-5,15-bis-ethynylporphinato]zinc(II) **22**[9,12] (0.5 g, 0.6 mmol) in dry THF (pyridine 1%) (60 mL) under an argon atmosphere. After 10 min chlorotriisopropylsilane (0.27 mL, 1.2 mmol) was added. Stirring was continued for 30 min, aqueous potassium hydroxide (1 M, 30 mL) was added and the solution poured into $CHCl_3$. The solution was washed with water and the organic layer dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue washed with MeOH. The residue was crystallised from

CH_2Cl_2/MeOH to give the title compound (0.55 g, 79%), mp>250°C (dichloromethane/methanol). $\lambda_{max}(CHCl_3)$/nm 438 (log ϵ 5.7), 449 (5.5) and 637 (4.7); ν_{max} (KBr)/cm^{-1} 2956vs, 2863s, 2138m, 1591m, 1498m, 1462m, 1362m, 1288m, 1246m, 1212m, 1163m, 1063m, 1005m, 929m, 881m, 825w, 797m, 721s, 675m, 620w and 507w; δ_H (250 MHz; $CDCl_3$) 1.46 (42H, m, *i*-Pr), 1.57 (36H, s, *t*-Bu), 7.83 (2H, t, *J*=2 Hz, *p*-Ph), 8.05 (4H, d, *J*=2 Hz, *o*-Ph), 9.00 (4H, d, *J*=5 Hz) and 9.78 (4H, d, *J*=5 Hz); δ_C (62.9 MHz; $CDCl_3$) 11.9, 19.2, 31.8, 35.1, 98.5, 101.7, 109.3, 121.2, 124.1, 129.3, 131.2, 133.2, 141.2, 148.8, 150.5 and 152.4; *m/z* (FAB) 1108.6139 (M^+ $C_{70}H_{92}N_4Si_2Zn$ requires 1108.6152), 1108.6 (M^+, 100%).

3.1.15. [5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10,20-bis-triisopropylsilylethynylporphinato]copper(II) 19. A suspension of porphyrin **9** (40 g, 0.04 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (650 mg, 3 mmol) in DMF (20 mL) was refluxed for 4 h under argon. The resulting green solution was poured into water and extracted with CH_2Cl_2. The solution was dried over $MgSO_4$ and the solvent removed under reduced pressure to leave a green oil. MeOH was added and the precipitate filtered to give the title compound (10 mg, 24%) as a green powder, mp>250°C; $\lambda_{max}(CHCl_3)$/nm 432 (log ϵ 5.8) and 609 (4.6); ν_{max} (KBr)/cm^{-1} 2960vs, 2863m, 2144m, 1592m, 1520w, 1460m, 1346w, 1293w, 1260m, 1214m, 1167w, 1069m, 1010m, 928w, 881w, 799m, 723m and 676w; *m/z* (FAB) 1107.6129 (M^+. $C_{70}H_{92}N_4Si_2Cu$ requires 1107.6157), 1107.6 (M^+, 100%).

3.1.16. [5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10,20-bis-triisopropylsilylethynylporphinato] lead(II) 20. A suspension of porphyrin **9** (40 mg, 0.04 mmol) and $Pb(OAc)_2{\cdot}3H_2O$ (1.2 g, 3 mmol) in DMF (20 mL) was refluxed for 4 h under argon. The resulting deep green solution was poured into water (50 mL). The precipitate was filtered, washed with water, MeOH and recrystallised from CH_2Cl_2/MeOH to give the title compound (30 mg, 63%) as a deep green, almost black, solid, mp>300°C (dichloromethane/methanol) (Found: C, 67.9; H, 7.5; N, 4.35. $C_{70}H_{92}N_4PbSi_2$ requires C, 67.1; H, 7.4; N, 4.5%); $\lambda_{max}(CHCl_3)$/nm 473 (log ϵ 5.3), 493 (5.3) and 704 (4.6); ν_{max} (KBr)/cm^{-1} 2955vs, 2862s, 2361w, 2332w, 2134m, 1589m, 1470m, 1389w, 1361m, 1280m, 1244m, 1207s, 1157m, 1062w, 995m, 923m, 880m, 794m, 717vs, 670m and 565w; δ_H (400 MHz; $CDCl_3$) 1.55 (78H, m, *t*-Bu and *i*-Pr), 7.82 (2H, t, *J*=2 Hz, *p*-Ph), 7.87 (2H, bs, *o*-Ph), 8.19 (2H, bs, *o*-Ph), 8.99 (4H, d, *J*=4 Hz) and 9.78 (4H, d, *J*=4 Hz); δ_C (100.6 MHz; $CDCl_3$) 13.0, 20.2, 32.8, 36.0, 99.5, 103.4, 110.7, 122.2, 126.6, 131.0, 132.0, 134.2, 142.3, 150.3 and 152.5 (2 resonances are missing); *m/z* (FAB) 1252.6623 (M^+. $C_{70}H_{92}N_4Si_2Pb$ requires 1252.6627), 1252.7 (M^+, 100%).

3.1.17. [5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10,20-bisphenylethynylporphinato]zinc(II) 21. Et_3N (4 mL distilled from CaH_2) was added to a stirred solution of [10,20-bis-(3,5-bis-*tert*-butylphenyl)-5,15-bis-ethynylporphinato]zinc(II) **22** (510 mg, 0.64 mmol), iodobenzene (750 mg, 3.7 mmol), $Pd(PPh_3)_2Cl_2$ (10 mg, 14 μmol) and CuI (10 mg, 52 μmol) in THF (40 mL) under argon. Stirring was continued for 16 h before the solvent was removed under reduced pressure. The residue was chromatographed on silica with light petroleum 60–80/THF (3:1) as eluent. The first fraction was collected and the solvent removed under reduced pressure. The residue was recrystallised from CH_2Cl_2/MeOH and dried under vacuum to give the title compound (470 mg, 73%) as a purple crystalline solid, mp>250°C (dichloromethane/methanol) (Found: C, 81.1; H, 6.2; N, 5.6. $C_{64}H_{62}N_4Zn$ requires C, 80.7; H, 6.6; N, 5.9%); ($\lambda_{max}(CHCl_3)$/nm 447 (log ϵ 5.6) and 651 (4.7); ν_{max} (KBr)/cm^{-1} 2956vs, 2904s, 2865s, 1591s, 1499s, 1473m, 1423w, 1362m, 1286m, 1246m, 1208s, 1062w, 1005m, 933w, 791m, 749m, 710m and 685m; δ_H (250 MHz; $CDCl_3$) 1.57 (36H, s, *t*-Bu), 7.52 (6H, m), 7.84 (2H, t, *J*=1.8 Hz, *p*-Ph), 8.01 (4H, m), 8.09 (4H, d, *J*=1.8 Hz, *o*-Ph), 9.00 (4H, d, *J*=4.6 Hz) and 9.77 (4H, d, *J*=4.6 Hz); δ_C (62.9 MHz; $CDCl_3$) 31.8, 35.1, 92.5, 96.7, 101.6, 121.1, 124.2, 124.3, 128.5, 128.7, 129.8, 130.9, 131.7, 133.1, 141.2, 148.8, 150.5 and 152.0; *m/z* (FAB) 950.4 (M^+, 100%).

3.1.18. [5,15-Bis-(3,5-bis-*tert*-butylphenyl)-10,20-bisphenylethynylporphinato]lead(II) 23. *Method 1*. A suspension of porphyrin **11** (20 mg, 0.023 mmol) and $Pb(OAc)_2{\cdot}3H_2O$ (1.0 g, 2.6 mmol) in DMF (20 mL) was refluxed for 2 h. The resultant solution was poured into water and filtered to give the title compound (24 mg, 98%) as a deep green solid. *Method 2*. A solution of porphyrin **11** (195 mg, 0.22 mmol) in THF/MeOH (20 mL, 1:1) and $Pb(OAc)_2{\cdot}3H_2O$ (1 g, 2.6 mmol) was refluxed for 4 h and allowed to cool. Water was added and the mixture extracted with Et_2O (3×20 mL). The ethereal layer was dried over $MgSO_4$ and MeOH (30 mL) added. The solvent was reduced to a small volume and the precipitate filtered. The residue was recrystallised from CH_2Cl_2/MeOH to give the title compound (190 mg, 79%) as a deep green solid, mp>300°C; $\lambda_{max}(CH_2Cl_2)$/nm 477 (log ϵ 5.4), 497 (5.3) and 720 (4.8); ν_{max} (KBr)/cm^{-1} 620m, 794m, 923m, 997w, 1203m, 1245m, 1475m, 1589m, 1616m, 2954m, 3413vs, 3475s and 3552s; δ_H (250 MHz; $CDCl_3$) 1.52 (18H, s, *t*-Bu), 1.60 (18H, s, *t*-Bu), 7.54 (6H, m), 7.83 (2H, t, *J*=1.8 Hz, *p*-Ph), 7.91 (2H, bs, *o*-Ph), 8.03 (4H, m), 8.21 (2H, bs, *o*-Ph), 9.00 (4H, d, *J*=4.6 Hz) and 9.81 (4H, d, *J*=4.6 Hz); δ_C (62.9 MHz; $CDCl_3$) 31.8, 35.1, 96.7, 102.4, 121.11, 124.3, 125.9, 128.5, 128.7, 129.6, 130.6, 130.9, 131.7, 133.2, 141.3, 148.7, 148.9, 149.3 and 151.1; *m/z* (FAB) 1093.4668 (M^++H. $C_{64}H_{61}N_4Pb$ requires 1093.4662), 1092.3 (M^+, 25%) and 887.4 (M^+−Pb+2H, 100).

3.1.19. [5,15-Bis-(3,5-di-*tert*-butylphenyl)-10,20-bis-(*p*-nitrophenylethynyl)porphinato]lead(II) 24. A mixture of porphyrin **12** (100 mg, 0.1 mmol) and $Pb(OAc)_2{\cdot}3H_2O$ (0.5 g, 1.3 mmol) in DMF was refluxed for 2 h. The solution was poured into water, filtered and the residue washed with water. The residue was dissolved in THF, filtered, the solvent removed under reduced pressure and the residue washed with MeOH to give the title compound (110 mg, 90%) as a brown solid, mp>250°C; $\lambda_{max}(CHCl_3)$/nm 485 (log ϵ 5.3) and 739 (4.9); ν_{max} (KBr)/cm^{-1} 709m, 786s, 844s, 927m, 993w, 1099m, 1199s, 1243s, 1328vs, 1423m, 1479s, 1508s, 1583s, 2181vs, 2861m and 2948vs; δ_H (250 MHz; $CDCl_3$) 1.54 and 1.60 (2×18H, s, *t*-Bu), 7.86 (2H, bs), 7.93 (2H, bs), 8.03 (4H, d, *J*=8.6 Hz), 8.22 (2H, bs), 8.31 (4H, d, *J*=8.6 Hz), 9.04 (4H, d, *J*=4.6 Hz) and

9.76 (4H, d, J=4.6 Hz); δ_C (62.9 MHz; $CDCl_3$) 31.8, 35.1, 95.1, 98.7, 101.2, 121.4, 124.0, 126.8, 129.6, 130.6, 130.8, 130.9, 132.0, 133.7, 140.9, 146.9, 148.9, 149.1, 149.7 and 151.2 (2 resonances are missing); *m/z* (FAB) 1182.9 (M^+, 100%).

3.1.20. [5,10,15,20-*tetrakis*-Triisopropylsilylethynylporphinato]zinc(II) 25. A mixture of porphyrin **14** (0.71 g, 0.7 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (1 g, 4.6 mmol) in DMF (60 mL) was heated at reflux. After 1 h water was added and the precipitate filtered, washed with water, MeOH and recrystallised from CH_2Cl_2/MeOH to give the title compound (0.71 g, 95%) as a purple solid, mp>250°C; (Found: C, 70.8; H, 8.5; N, 4.8. $C_{64}H_{92}N_4Si_4Zn$ requires C, 70.2; H, 8.5; N, 5.1%); λ_{max}($CHCl_3$)/nm 463 (log ϵ 5.7) and 656 (4.4); ν_{max} (KBr)/cm^{-1} 2937vs, 2860vs, 2137s, 1496m, 1459s, 1381w, 1336w, 1212m, 1158s, 1062m, 1003m, 879m, 792m, 714vs, 669s, 577m and 459w; δ_H (250 MHz; $CDCl_3$) 1.51 and 1.53 (84H, m, *i*-Pr) and 9.62 (8H, s, β-pyrrolic); δ_C (62.9 MHz; $CDCl_3$) 11.9, 19.2, 99.2, 103.1, 108.6, 131.9 and 152.3; *m/z* (FAB) 1094.7 (M^+, 100%).

3.1.21. [5,10,15,20-*tetrakis*-Triisopropylsilylethynylporphinato]lead(II) 26. A mixture of porphyrin **14** (0.71 g, 0.5 mmol) and $Pb(OAc)_2{\cdot}3H_2O$ (2 g, 5 mmol) in DMF (60 mL) was heated at reflux. After 2 h water was added and the precipitate filtered, washed with water, MeOH and recrystallised from CH_2Cl_2/MeOH to give the title compound (0.54 g, 90%) as a green solid, mp>250°C; (Found: C, 62.0; H, 7.4; N, 4.4. $C_{64}H_{92}N_4Si_4Pb$ requires C, 62.1; H, 7.5; N, 4.5%); λ_{max}($CHCl_3$)/nm 500 (log ϵ 5.8) and 719 (4.9); ν_{max} (KBr)/cm^{-1} 457m, 516w, 572m, 665s, 709vs, 788m, 877m, 993m, 1058m, 1149s, 1203m, 1238w, 1315w, 1380w, 1463s, 2130s, 2858s, 2935s, 3408m, 3476m and 3547w; δ_H (250 MHz; $CDCl_3$) 1.50 and 1.51 (84H, m, *i*-Pr) and 9.67 (8H, s, β-pyrrolic); δ_C (62.9 MHz; $CDCl_3$) 12.0, 19.3, 99.3, 104.1, 108.7, 131.9 and 151.2; *m/z* (FAB) 1236.2 ($[M+H]^+$, 100%).

3.1.22. [5,10,15,20-*tetrakis*-[Dimethyl-(2-dodecylhexadecyl)-silylethynyl]porphinato]lead(II) 27. A solution of porphyrin **15** (100 mg, 0.045 mmol) and $Pb(OAc)_2{\cdot}3H_2O$ (0.5 g, 1.3 mmol) in CH_2Cl_2/MeOH (100 mL, 4:6) was refluxed for 4 h. Water was added and the solution extracted with CH_2Cl_2 (2×50 mL). The solvent was removed under reduced pressure and the residue purified by thin layer chromatography. Elution with light petroleum/CH_2Cl_2 (25:1) gave the title compound (108 mg, 99% as a deep green amorphous solid, λ_{max}($CHCl_3$)/nm 500 (log ϵ 5.8) and 719 (4.9); δ_H (250 MHz; $CDCl_3$) 0.24 (8H, d, J=7.6 Hz, Si–CH_2), 0.64 (24H, s, Si–Me), 0.87 (24H, m, Me), 1.28 (192H, bs, CH_2), 1.96 (4H, m, CH) and 9.68 (8H, s, β-pyrrolic); δ_C (62.9 MHz; $CDCl_3$) −0.2, 14.2, 21.9, 22.7, 26.9, 29.4, 29.7, 29.8, 30.2, 32.0, 34.6, 36.6, 36.8, 102.7, 104.3, 107.3, 132.0 and 151.3 (15 resonances are missing); *m/z* (FAB) 2415.7 (M^+, 100%).

3.1.23. [5,10,15,20-Tetraphenylporphinato]lead(II) 28. A suspension of 5,10,15,20-tetraphenylporphyrin (400 mg, 0.65 mmol) and $Pb(OAc)_2{\cdot}3H_2O$ (8.0 g, 21 mmol) in DMF (120 mL) was refluxed for 36 h. The resulting solution was poured into water and filtered. The residue was extracted with THF, filtered and the solvent removed under reduced pressure to give the title compound (320 mg, 60%) as a dark purple solid, mp>250°C; λ_{max}($CHCl_3$)/nm 353 (log ϵ 4.8), 465 (5.6) and 656 (4.3); ν_{max} (KBr)/cm^{-1} 3051w, 3018w, 1803w, 1593m, 1512m, 1472m, 1437m, 1324m, 1198m, 1176w, 1070m, 1004m, 982vs, 792s, 750s, 704s and 659w; δ_H (250 MHz; $CDCl_3$) 7.76 (12H, m), 8.10 (8H, bm) and 8.95 (8H, s, β-pyrrolic); δ_C (62.9 MHz; $CDCl_3$) 122.32, 126.47, 127.48, 132.03, 134.71, 143.03 and 149.32; *m/z* (FAB) 821.2157 (M^++H. $C_{44}H_{29}N_4Pb$ requires 821.2158), 820.2 (M^+, 28%).

3.1.24. [5,10,15,20-Tetra-(*p*-methoxyphenyl)-porphinato]lead(II) 29. A suspension of porphyrin **17** (190 mg, 0.26 mmol) and $Pb(OAc)_2{\cdot}3H_2O$ (2.0 g, 5 mmol) in DMF (40 mL) was refluxed for 24 h. The resulting solution was poured into water and filtered. The residue was dissolved in THF, filtered and the solvent removed under reduced pressure to give the title compound (157 mg, 65%) as a mauve powder, mp>250°C; λ_{max}($CHCl_3$/pyridine (1%))/nm 468 (log ϵ 5.2) and 766 (4.8); ν_{max} (KBr)/cm^{-1} 3470w, 3424w, 2997w, 2950w, 2900w, 2830w, 1601m, 1508vs, 1463s, 1405m, 1323m 1285m, 1243vs, 1172s, 1105w, 1030m, 982s, 843w, 796s, 751m, 719w and 634w; δ_H (250 MHz; $CDCl_3$) 4.10 (12H, s, O–Me), 7.28 (8H, d, J=5.2 Hz, Ph), 8.12 (8H, bd, J=5.2 Hz, Ph) and 8.97 (8H, s, β-pyrrolic); δ_C (62.9 MHz; $CDCl_3$) 55.6, 112.0, 121.8, 131.9, 135.5, 135.7, 149.6 and 159.2; *m/z* (FAB) 941.2590 (M^++H. $C_{48}H_{36}N_4O_4Pb$ requires 941.2581), 940 (M^+, 6%) and 735 (M^+Pb, 100).

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