Efficient formation of lipophilic dihydroxotin(IV) porphyrins and bis-porphyrins

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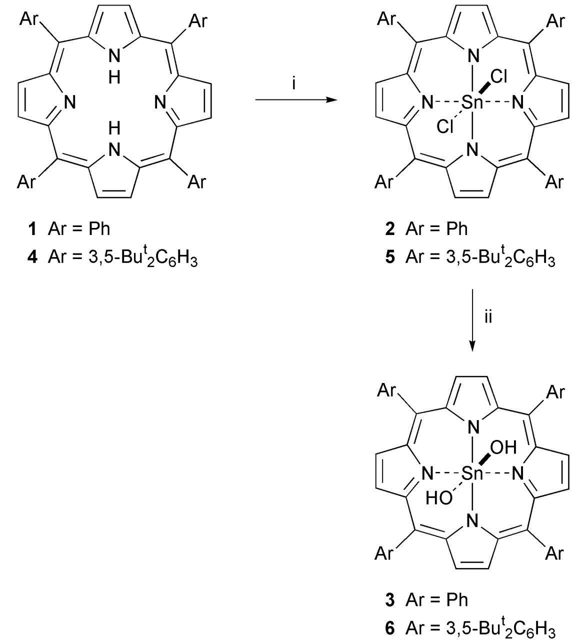
Treatment of dichloro- and dicarboxylato-tin(IV) porphyrins with K_2CO_3 in THF–H_2O (4 : 1) is a mild and highly efficient method for formation of dihydroxotin(IV) porphyrins; unlike other reported procedures, this method is especially good for lipophilic porphyrins and bis-porphyrins. The synthesis of the mixed metal dihydroxotin(IV) zinc(II) bis-porphyrins **15** and **21** from the corresponding monozinc(II) free-base bis-porphyrins **13** and **19** without loss of the coordinated zinc(II) by hydrolysis or transmetalation illustrates the usefulness and mildness of the methodology.

Introduction

Dihydroxotin(IV) porphyrins have attracted recent use in molecular recognition studies because of the ability of the tin(IV) to coordinate oxygen donor ligands preferentially.[1] Extensive studies by Arnold and co-workers have shown that hydroxo ligands of dihydroxotin(IV) porphyrins can be displaced by carboxylate, alkoxide and phenoxide.[2–6] Recently, Sanders and his colleagues have examined the scope of carboxylate binding by such dihydroxotin(IV) porphyrins[7] and have used this binding motif in the formation of supramolecular self-assembled porphyrin-based architectures.[8–11]

Dihydroxotin(IV) porphyrins are obtained by hydrolysis of dichlorotin(IV) porphyrins. Literature methods for this hydrolysis are cumbersome and, in our hands, not efficient when lipophilic porphyrins are involved.[2,3,12] We now report a relatively mild method that has provided dihydroxotin(IV) porphyrins in high yield from a range of dichlorotin(IV) porphyrins. We also report that this methodology can be used efficiently to liberate carboxylic acids from dicarboxylatotin(IV) porphyrins, a process of some importance in molecular recognition studies.

This methodology is found to be generally applicable and should facilitate wider use of tin porphyrins in supramolecular chemistry.



Scheme 1 *Reagents and conditions:* i, $SnCl_2{\cdot}2H_2O$, pyridine, reflux 3 h; ii, K_2CO_3 in THF–H_2O (4 : 1), reflux 1–3 h.

Results and discussion

The synthesis and hydrolysis of a range of dichlorotin(IV) porphyrins **2**, **5** and **8**, di[dichlorotin(IV)] bis-porphyrins **11** and **17** and dichlorotin(IV) zinc(II) bis-porphyrins **14** and **20** to give corresponding dihydroxotin(IV) porphyrins and bis-porphyrins have been studied (Schemes 1–3). These compounds have a variety of substituents and architectures, including laterally-extended conjugated quinoxalinoporphyrin and bis-porphyrins,[13] and bis-porphyrin Tröger's base analogues.[14] All of these compounds are very lipophilic and because of this fact a method that utilised organic solvents for the conversion of dichlorotin(IV) porphyrins into the corresponding dihydroxotin(IV) porphyrins had to be developed to bring about this transformation efficiently.

Synthesis of dichlorotin(IV) porphyrins

The precursor dichlorotin(IV) porphyrins were obtained by treatment of free-base porphyrins with $SnCl_2{\cdot}2H_2O$ in pyridine under aerobic conditions.[15,16] This methodology worked well for metalation of simple 5,10,15,20-tetraarylporphyrins **1** and **4** (Scheme 1) and for the laterally-extended quinoxalinoporphyrin **7** and bis-porphyrins **10** and **13** (Scheme 2), and the bis-porphyrin Tröger's base analogues **16** and **19** (Scheme 3). Under these conditions the monozinc(II) bis-porphyrins **13** and **19** were smoothly converted to the corresponding mixed metal dichlorotin(IV) zinc(II) bis-porphyrins without any loss of zinc(II) by hydrolysis or transmetalation processes.

In each case, the dichlorotin(IV) porphyrin was isolated very easily by precipitation on addition of water to the reaction mixture. Dissolution of the resultant solid in dichloromethane and washing the organic phase with aqueous HCl and water yielded essentially pure product upon drying and evaporating the solvent. When this procedure did not yield analytically pure compound directly, recrystallisation of the product from acetonitrile–dichloromethane was all that was required to achieve this level of purity. Attempts to chromatograph dichlorotin(IV) porphyrins over silica or alumina were found to be counter-productive and invariably led to the formation of mixtures of compounds. Unlike the other dichlorotin(IV)

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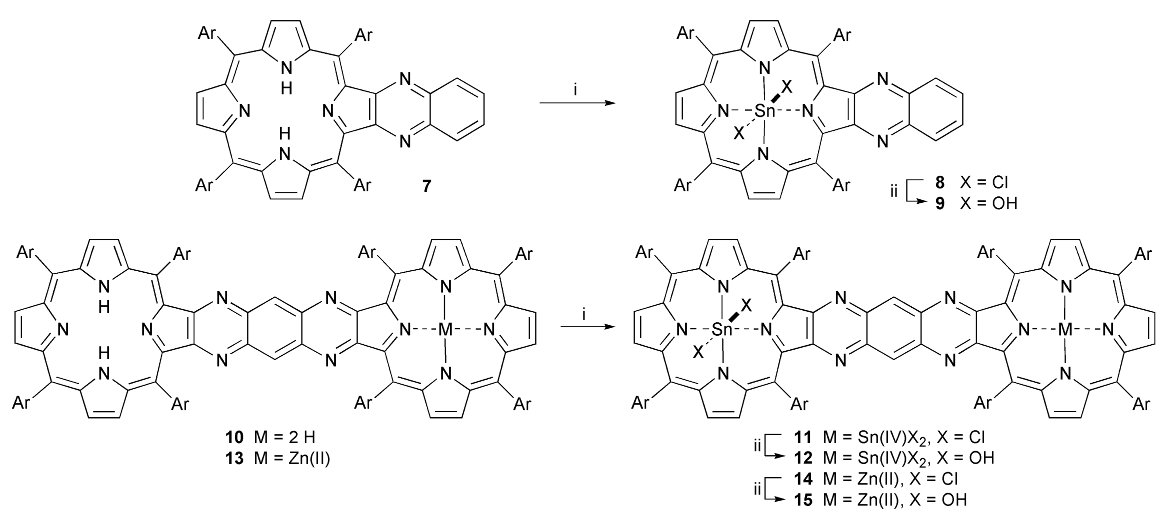
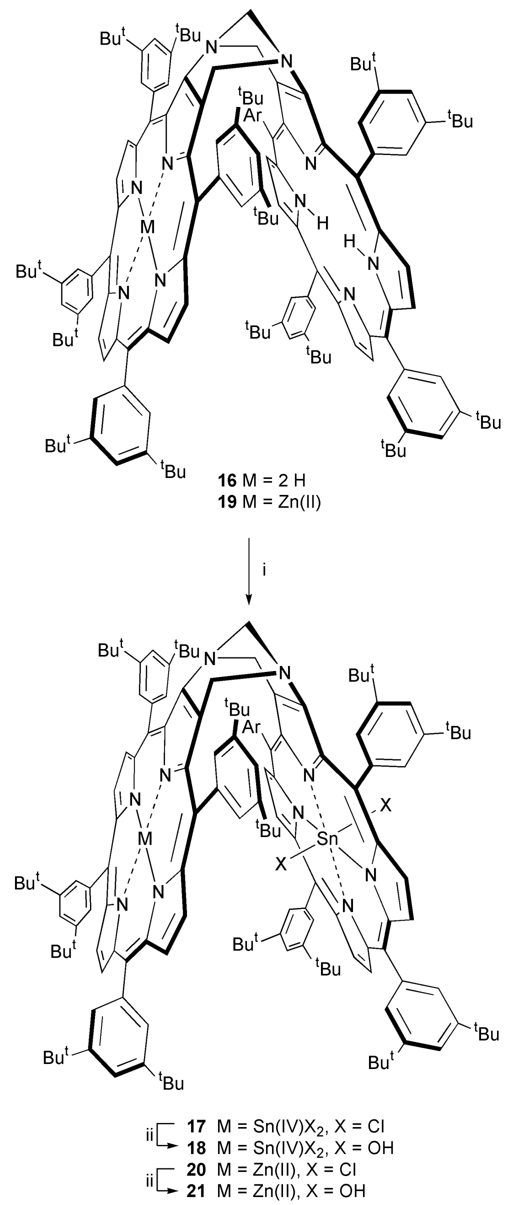


Scheme 2 *Reagents and conditions:* i, $SnCl_2 \cdot 2H_2O$, pyridine, reflux 4 h; ii, K_2CO_3 in THF–H_2O, reflux 2–4 h (Ar = 3,5-$Bu^t_2C_6H_3$).



Scheme 3 *Reagents and conditions:* i, $SnCl_2 \cdot 2H_2O$, pyridine, reflux 3 h; ii, K_2CO_3 in wet CH_2Cl_2–MeOH (4 : 1), reflux 2 h.

porphyrins described above, the Tröger's base bis-porphyrin analogues **17** and **20** were not fully characterised at this stage but were hydrolysed directly as is described below.

Table 1 Yields of dihydroxotin(IV) porphyrin derivatives from treatment of dichlorotin(IV) porphyrin derivatives with K_2CO_3

Reactant	Product	Yield (%)
2	**3**	90[a]
5	**6**	99[a]
8	**9**	99[a]
11	**12**	74[b]
14	**15**	72[b]
17	**18**	92[c]
20	**21**	89[c]
23	**24**	91[c]
26	**3**	77[a]

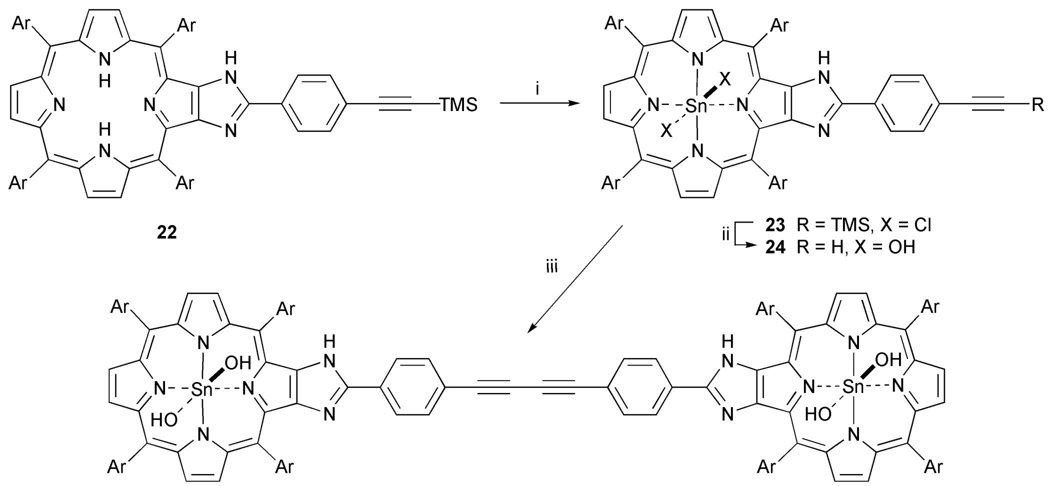
[a] THF–H_2O (4 : 1). [b] THF–H_2O (5 : 1). [c] CH_2Cl_2–MeOH (4 : 1).

Hydrolysis of dichlorotin(IV) porphyrins

Compounds **2**, **5**, **8**, **11** and **14** were all hydrolysed in very good yields by treatment with K_2CO_3 in THF–H_2O at reflux to give the corresponding dihydroxotin(IV) analogues (Schemes 1 and 2, Table 1). In each case, workup simply involved evaporation of the THF and partitioning of the product into CH_2Cl_2 which was then dried and evaporated and, if necessary, the product was recrystallised from chloroform–acetonitrile or dichloromethane–acetonitrile. The zinc(II) chelated porphyrin ring was again stable to the conditions as is seen in the smooth conversion of **14** into **15**.

The di[dichlorotin(IV)] bis-porphyrin Tröger's base analogue **17** was hydrolysed by treatment with K_2CO_3 in dichloromethane–methanol (4 : 1) at reflux for 2 hours and then the reaction mixture was washed well with water. Work-up and chromatography of the product over deactivated neutral alumina gave the di[dihydroxotin(IV)] porphyrin **18** in 92% yield after recrystallisation. The dichlorotin(IV) zinc(II) bis-porphyrin Tröger's base analogue **20** was similarly converted to the dihydroxotin(IV) zinc(II) bis-porphyrin Tröger's base analogue **21**. Presumably in these reactions, the corresponding dimethoxotin(IV) porphyrins have been formed as an intermediate. In other studies such compounds have been found to be very labile and easily hydrolysed by water.[17,18]

Dichlorotin(IV) 5,10,15,20-tetraphenylporphyrin **2** has previously been converted to **3** by treatment with concentrated ammonia[3,12] and by treatment with deactivated alumina.[2,12] Neither of these methods gave satisfactory results with the more lipophilic porphyrins used in the present study. In particular, the interior chloro groups of the Tröger's base analogues **17** and **20** are especially protected from attack



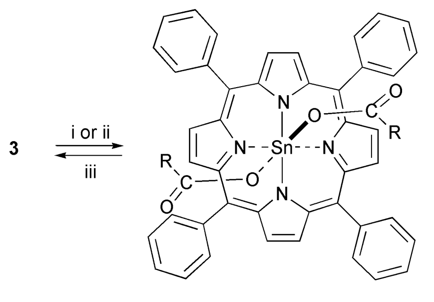
Scheme 4 *Reagents and conditions:* i, $SnCl_2·2H_2O$, DMF, reflux 5 h; ii, K_2CO_3 in wet CH_2Cl_2–MeOH (4 : 1), reflux 2 h; iii, CuCl and TMEDA in CH_2Cl_2, stir at room temperature, 100 min (Ar = 3,5-$Bu^t_2C_6H_3$).

as they lie in a tight cavity in which the metal centres are only about 6.2 Å apart (Scheme 3). At best using these older methods,[2,3,12] mixtures of dichloro-, chlorohydroxo-, and dihydroxo-tin(IV) porphyrins were obtained and these could not be easily separated. It is noteworthy that Webb and Sanders reported some difficulties in the hydrolysis of a dichlorotin(IV)–ruthenium(II)–dichlorotin(IV) cyclic porphyrin trimer using deactivated alumina; double treatment over 2 days followed by recrystallisation was required to obtain the desired product.[11]

The ease with which dichlorotin(IV) porphyrins are hydrolysed by K_2CO_3–H_2O is seen in our synthesis of the butadiyne-linked bis-porphyrin **25** (Scheme 4). We had intended to deprotect the TMS-ethynyl group of dichloro[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-2^2-{4-[(trimethylsilyl)ethynyl]-phenyl}-2^1*H*-imidazo[4,5-*b*]porphyrinato]tin(IV) **23** and then carry out a Glaser–Hay acetylene coupling[19,20] followed by hydrolysis of the resultant di[dichlorotin(IV)] bis-porphyrin to **25**. The dichlorotin(IV) porphyrin **23** was obtained in 95% yield by treatment of the corresponding free-base porphyrin[21] with $SnCl_2·2H_2O$ in DMF; the trimethylsilyl protecting group survived these conditions. However, treatment of **23** with K_2CO_3 in CH_2Cl_2–MeOH, followed by an aqueous work-up step, a method routinely used in other work to deprotect trimethylsilylethynyl groups,[21,22] accomplished both the deprotection of the ethynyl group and hydrolysis of the dichlorotin(IV) group to give **24** in 91% yield. Interestingly only small amounts of dimethoxotin(IV) porphyrins were detected by ^1H NMR spectroscopy of the residue. Glaser–Hay coupling of **24** gave the di[dihydroxotin(IV)] bis-porphyrin **25** in 63% yield.

Hydrolysis of dicarboxylatotin(IV) porphyrins

The convenience of the K_2CO_3 in THF–H_2O hydrolysis methodology led us to investigate its use on dicarboxylatotin(IV) porphyrins. An easy method for liberating a guest acid from its bound carboxylate state would be useful in molecular recognition studies in progress. Arnold has shown that dihydroxotin(IV) 5,10,15,20-tetraphenylporphyrin **3** can be converted into corresponding diacyloxotin(IV) porphyrins by treatment with carboxylic acids in $CHCl_3$.[3,6] The carboxylates bind in unidentate mode. Sanders and his co-workers have investigated the mechanism of this process. They found that an outer sphere intermediate with H-bonding between the bound hydroxo and the carboxylic acid is involved.[7]



26 R = CH_3
27 R = Ph

Scheme 5 *Reagents and conditions:* i, excess CH_3CO_2H in $CHCl_3$, stir for 35 min; ii, excess $PhCO_2H$ in $CHCl_3$, stir for 20 min; iii, K_2CO_3 in THF–H_2O (4 : 1), reflux 2 h.

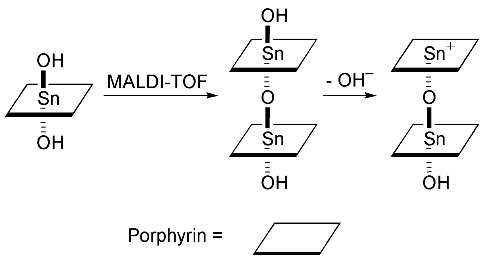


Fig. 1 Schematic diagram showing a μ-oxo type dimer formed between two dihydroxotin(IV) porphyrins.

The diacetatotin(IV) porphyrin **26** and the dibenzoatotin(IV) porphyrin **27** were prepared by Arnold's method[3,6] (Scheme 5). Treatment of each with K_2CO_3 in THF–H_2O at reflux for 2 hours gave the dihydroxotin(IV) porphyrin **3** in essentially quantitative yield (**26** ⟶ **3**; 77% after recrystallisation; **27** ⟶ **3**; 84% after recrystallisation). In the latter case, benzoic acid was also recovered in 86% yield. The only other example of a carboxylate decomplexation of tin(IV) porphyrin complexes comes from Sanders and co-workers who reported the use of excess methanol to cleave a carboxylate-catenane tin(IV) porphyrin complex, however, the tin(IV) porphyrin was not recovered in their procedure.[9]

Some observations on the mass spectrometry of tin(IV) porphyrins

In our studies we noted that mass spectrometry, in particular MALDI-TOF, showed a notable difference between the behaviour of dichlorotin(IV) porphyrins and dihydroxotin(IV) porphyrins. The dichlorotin(IV) porphyrins show a parent ion resulting from the loss of one chloro ligand. Interestingly, under the conditions of MALDI-TOF mass spectral analysis, the dihydroxotin(IV) porphyrins form an associated dimer with the loss of one or two hydroxo ligands ($M_2 - 2 \times OH$). A possible explanation is that a μ-oxo type dimer is formed in the mass spectrometer between two dihydroxotin(IV) porphyrins

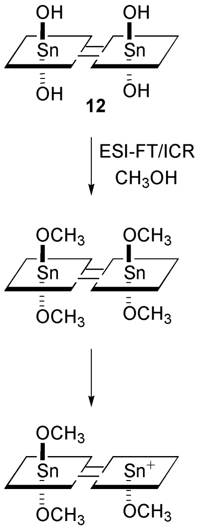


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Fig. 2 Schematic diagram showing the formation of trimethoxoditin(IV) bis-porphyrin **28**.

with loss of one water molecule. Under these MALDI-TOF conditions (20 kV, pressure $< 10^{-5}$ Pa, nitrogen laser at 337 nm) the remaining axial hydroxo ligands can also be lost (Fig. 1). In addition to these dimers, we observed that the $(M - OH)^+$ is usually the base peak in the MALDI-TOF mass spectra of the dihydroxotin(IV) complexes and that the $(M)^+$ and $(M - 2OH)^+$ and even $(M - 3OH)^+$ [in the case of ditin(IV) bis-porphyrins] mass peaks were also observed. Based on previous observations that simpler free-base and metalloporphyrins tend to form the radical ion $M^{\bullet +}$ rather than $(M + H)^+$ or related species under MALDI-TOF conditions,[23] the above observations suggest that tin(IV) porphyrins can lose more than one ligand under these conditions without forming multiply charged species. Similar observations of ligand lability were made recently by Sanders and co-workers in their study of metalloporphyrins by MALDI-TOF mass spectrometry.[23] Interestingly in their studies they detected hydrolysis to a dihydroxotin(IV) porphyrin but they did not detect the formation of μ-linked bis[tin(IV) porphyrin] in the mass spectrum of a dibenzoatotin(IV) porphyrin. Perhaps in this case, the dihydroxotin(IV) species is being formed under high dilution conditions after desorption. Differences in porphyrin structure might also account for this difference as Sanders and co-workers did observe the formation of a Ru–Ru linked dimer with loss of two carbonyl ligands in the mass spectrum of Ru(II)(CO) 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin, a closer analogue of our compounds.

In ESI mass spectrometry the exchange of the hydroxo ligands with the solvent employed (methanol) was observed. For instance the di[dihydroxotin(IV)] bis-porphyrin **12** was analysed using a high-resolution Fourier transform ion cyclotron resonance mass spectrometer fitted with an ESI source (ESI-FT/ICR). It was found that under the conditions used (methanol as the solvent), all the hydroxo ligands had been replaced with methoxo ligands. The ion envelope detected corresponded within 5 ppm to the trimethoxoditin(IV) bis-porphyrin cation **28** with the formula $[C_{159}H_{191}N_{12}O_3Sn_2]^+$ (Fig. 2).

The quinoxalinoporphyrins and laterally extended bis-porphyrins are of considerable interest in studies designed to investigate electronic coupling between porphyrin and bridging units with potential molecular electronics applications.[24–28] An analysis of the electronic spectra of the compounds synthesised in the present study will be presented elsewhere.

In order to extend our work on molecular and chiral recognition of diamines and histidines by novel chiral Tröger's base dizinc(II) bis-porphyrin cavities[14,29,30] to include recognition of α-amino acids, dicarboxylic acids, amino-alcohols and diols, we required bis-metalloporphyrin analogues in which at least one of the bound metal ions has a stronger affinity for oxygen donor ligands rather than nitrogen donor ligands. In very successful on-going work in our laboratory, the chiral dihydroxotin(IV) zinc(II) bis-porphyrin **21** is being used in molecular recognition studies on α-amino acids, the di[dihydroxotin(IV)] bis-porphyrin **18** for recognition of dicarboxylic acids and the planar bis-porphyrins **12**, **15** and **25** in complementary- and self-recognition studies. All of this work has been facilitated by the convenient and efficient hydrolysis methodology outlined in this paper.

Experimental

General procedures

Melting points were recorded on a Reichert melting point stage microscope and are uncorrected. Microanalyses were performed by the Campbell Microanalytical Laboratory, The University of Otago, New Zealand. Infrared spectra were recorded on chloroform solutions with a Perkin-Elmer Model 1600 FT-IR spectrophotometer. Electronic absorption spectra were recorded on a Cary 5E UV-vis spectrophotometer at 25 °C. ^1H NMR spectra were recorded on a Bruker AC-200F (200 MHz), a Bruker DRX-400 (400 MHz) or a Bruker DPX-400 (400 MHz) spectrometer and signals are quoted in ppm relative to tetramethylsilane ($SiMe_4$, ^1H and $^{13}C = 0$ ppm) or the solvent residue peak ($CDCl_3$; $^1H = 7.26$ and $^{13}C = 77.16$ ppm) as the internal standard. Coupling constants are reported in Hz. ^{119}Sn NMR spectra were acquired on a Bruker DPX-400 (149 MHz) spectrometer as stated, quoted in ppm relative to tetramethyltin ($SnMe_4$, $^{119}Sn = 0$ ppm) as an external standard and are reported as the fully decoupled spectra using similar parameters as previously reported in the literature.[31] Two-dimensional gradient ^1H detected H–X correlation spectra (^{119}Sn–^1H NMR HMQC from standard Bruker pulse programs, optimised to a $^4J_{1H-Sn} = 15$ Hz) were acquired at 300 K with a relaxation delay of 2 s and 2048 data points in t_2. Typically 4 scans were accumulated for 512 increments in t_1. Prior to FT, zero filling was applied to t_1 (1 K) and the data multiplied by a shifted sine-bell function in both domains. If necessary, a sample of **6** was used for external calibration of the ^{119}Sn dimension ($\delta = -569.2$ ppm relative to tetramethyltin). Deuteriated chloroform was dried and deacidified by filtration through a plug of alumina and potassium carbonate.

Matrix assisted laser desorption ionisation time of flight (MALDI-TOF) mass spectra were recorded on a VG TofSpec spectrometer in the positive linear mode. For most porphyrins under study, no matrix was required but when necessary α-cyano-4-hydroxycinnamic acid was used as the matrix. Mass spectra were obtained as an envelope of the isotope peaks of the molecular ion. The mass corresponding to the maximum of the envelope is reported and was compared with the maximum of a simulated spectrum. Electrospray ionisation (ESI) mass spectra were recorded on a ThermoQuest Finnigan LCQ Deca mass spectrometer. High resolution fast atomic bombardment (HRFAB) mass spectra were acquired at the Research School of Chemistry, Australian National University. The HRFAB mass spectra were obtained as an envelope of the isotope peaks of the molecular ion and calibrated against an external CsI standard. High resolution electrospray ionisation Fourier transform ion cyclotron resonance (ESI-FT/ICR) spectra were acquired at the School of Chemistry, The University of New South Wales on a Bruker Daltonics BioAPEX II FT/ICR mass spectrometer equipped with a 7 Tesla MAGNEX superconducting magnet and an Analytical external ESI source.

Alumina refers to Merck aluminium oxide 90 active neutral I, Type 1077 (63–200 mesh). Class IV alumina refers to the water content (10% water added).[32] Tetrahydrofuran was distilled from sodium wire and benzophenone under nitrogen prior to use, primarily to remove phenolic antioxidant present. The light petroleum used boiled in the range 60–80 °C. Other chemicals were used as obtained from commercial sources.

Dichloro(5,10,15,20-tetraphenylporphyrinato)tin(IV) 2

5,10,15,20-Tetraphenylporphyrin **1** (470 mg, 0.77 mmol) was dissolved in pyridine (100 cm^3) and tin(II) chloride dihydrate (390 mg, 1.72 mmol) was added and the mixture heated at reflux for 3 h. Excess water was added to precipitate the product which was then filtered, washed with water and air dried to give dichloro(5,10,15,20-tetraphenylporphyrinato)tin(IV) **2** (520 mg, 85%) as an amorphous solid, mp >300 °C. The compound had identical ^{1}H NMR properties to those reported by Arnold.[2,3] δ_H (200 MHz; $CDCl_3$; $SiMe_4$) 7.80–7.84 (12 H, m, Ar-H), 8.31–8.34 (8 H, m, Ar-H) and 9.22 (8 H, s, satellites $^4J_{H\text{–}Sn}$ 15.4, β-pyrrolic H); *m*/*z* (MALDI-TOF) 767.9 [$(M - Cl)^+$ requires 766.9].

Dihydroxo(5,10,15,20-tetraphenylporphyrinato)tin(IV) 3

Potassium carbonate (400 mg, 2.9 mmol) and dichloro-[5,10,15,20-tetraphenylporphyrinato]tin(IV) **2** (140 mg, 0.174 mmol) were dissolved in a mixture of tetrahydrofuran (80 cm^3) and water (20 cm^3) and heated at reflux for 3 h. The organic solvent was removed and the aqueous layer was extracted into dichloromethane (60 cm^3). The organic layer was washed with water (2 × 40 cm^3) and then dried over anhydrous sodium sulfate, filtered and then the solvent was removed to give the crude product, which was then recrystallised (hexane–dichloromethane, 1 : 1) to give dihydroxo(5,10,15,20-tetraphenylporphyrinato)tin(IV) **3** (120 mg, 90%) as a metallic purple crystalline solid, mp >300 °C. The compound had identical ^{1}H NMR properties to those reported by Arnold.[2,3] δ_H (200 MHz; $CDCl_3$; $SiMe_4$) −7.50 (2 H, br s, OH), 7.80–7.86 (12 H, m, Ar-H), 8.30–8.34 (8 H, m, Ar-H) and 9.13 (8 H, s, satellites $^4J_{H\text{–}Sn}$ 10.9, β-pyrrolic H); *m*/*z* (MALDI-TOF) 1496.9 [$(M_2 - 2OH)^+$ requires 1496.8] and 749.8 [$(M - OH)^+$ requires 748.4].

Dichloro[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]tin(IV) 5

Method 1[15]**.** A solution of 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin[33] **4** (180 mg, 0.17 mmol) and tin(II) chloride dihydrate (740 mg, 3.3 mmol) in pyridine (50 cm^3) was heated at reflux for 3 h. The solution was allowed to cool and then diluted with water (50 cm^3) and filtered. The precipitate collected on the filter was dissolved in dichloromethane (350 cm^3) and washed with water (100 cm^3). The aqueous phase was treated with hydrochloric acid solution (1 M, 150 cm^3) and then extracted with dichloromethane (2 × 50 cm^3). The combined organic extracts were washed with water (100 cm^3) and hydrochloric acid solution (1 M, 100 cm^3) and water again (100 cm^3), dried over anhydrous sodium sulfate and evaporated to dryness to afford *dichloro[5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)-porphyrinato]tin(IV)* **5** (190 mg, 91%) as blue–purple crystals, mp >300 °C (Found: C, 72.8; H, 7.6; N, 4.7; Cl, 5.4; $C_{76}H_{92}Cl_2N_4Sn$ requires C, 73.0; H, 7.4; N, 4.5; Cl, 5.7%); ν_{max} ($CHCl_3$)/cm^{-1} 2969s, 2875s, 1592s, 1474m, 1427w, 1362m, 1286w and 1245m; λ_{max} ($CHCl_3$)/nm 316 (log ε 4.50), 409.5sh (4.64), 431.5 (5.86), 524.5 (3.60), 564.5 (4.33), 604.5 (4.31) and 629.5 (3.42); δ_H (400 MHz; $CDCl_3$; $SiMe_4$) 1.54 (72 H, s, *tert*-butyl H), 7.87 (4 H, t, *J* 1.8, Ar-H_p), 8.18 (8 H, d, *J* 1.8, Ar-H_o) and 9.27 (8 H, s, satellites $^4J_{H\text{–}Sn}$ 15.8, β-pyrrolic H); δ_{Sn} (149 MHz; $CDCl_3$; $SnMe_4$) −589.0 (Sn); *m*/*z* (MALDI-TOF) 1252.3 (M^+ requires 1250.6) and 1216.9 [$(M - Cl)^+$ requires 1215.6]; (HRFAB) 1215.6033 [$(M - Cl)^+$, calcd for $C_{76}H_{92}ClN_4Sn$: 1215.6003].

Method 2[16]**.** A mixture of 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin[33] **4** (340 mg, 0.32 mmol) and tin(II) chloride dihydrate (600 mg, 2.7 mmol) in *N*,*N*-dimethylformamide (200 cm^3) was heated at reflux for 4 h. The reaction mixture was allowed to cool overnight. Water (150 cm^3) was added, causing the solution to warm up significantly. The mixture was allowed to cool and then filtered. The precipitate was dissolved in dichloromethane (200 cm^3), washed with water (3 × 200 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The filtrate was also extracted with dichloromethane (200 cm^3), the organic layer was separated and washed with water (6 × 200 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated. The combined residues gave dichloro[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]tin(IV) **5** (334 mg, 83%) which had identical spectroscopic properties to the sample prepared by Method 1.

Dihydroxo[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]tin(IV) 6

Method 1. A mixture of dichloro[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]tin(IV) **5** (40 mg, 0.032 mmol) and potassium carbonate (175 mg, 1.3 mmol) in tetrahydrofuran (40 cm^3) and water (10 cm^3) was heated at reflux for 1 h. The solution was concentrated on a rotary evaporator (to remove the tetrahydrofuran) and then treated with dichloromethane (100 cm^3) and water (100 cm^3). The organic phase was separated and washed again with water (100 cm^3), dried over anhydrous sodium sulfate, filtered and the solvent removed to give *dihydroxo[5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)-porphyrinato]tin(IV)* **6** (39 mg, 99%) as a blue–purple solid, mp >300 °C (Found: C, 72.4; H, 7.9; N, 4.7. $C_{76}H_{94}N_4O_2Sn + 3H_2O$ requires C, 72.0; H, 8.0; N, 4.4%); ν_{max} ($CHCl_3$)/cm^{-1} 2969s, 2864s, 1668w, 1591s, 1474m, 1427w, 1362m and 1245m; λ_{max} ($CHCl_3$)/nm 316 (log ε 4.29), 408.5sh (4.64), 428 (5.74), 525 (3.60), 564.5 (4.26), 604.5 (4.24) and 624.5sh (3.65); δ_H (400 MHz; $CDCl_3$; $SiMe_4$) −7.32 (2 H, br s, axial OH), 1.55 (72 H, s, *tert*-butyl H), 7.85 (4 H, t, *J* 1.8, Ar-H_p), 8.21 (8 H, d, *J* 1.8, Ar-H_o) and 9.18 (8 H, s, satellites $^4J_{H\text{–}Sn}$ 10.5, β-pyrrolic H); δ_{Sn} (149 MHz; $CDCl_3$; $SnMe_4$) −569.2 (Sn); *m*/*z* (MALDI-TOF) 2396.1 [$(M_2 - 2OH)^+$ requires 2395.2] and 1198.5 [$(M - OH)^+$ requires 1197.6]; (ESI) 2406.3 [$(M_2 - OH)^+$ requires 2408.3] and 1211.8 (M^+ requires 1212.6); (HRFAB) 1180.6306 [$(M - 2OH)^+$, calcd for $C_{76}H_{92}N_4Sn$: 1180.6344].

Method 2. A mixture of dichloro[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]tin(IV) **5** (159 mg, 0.127 mmol) and potassium carbonate (2.00 g, 14.5 mmol) in dichloromethane (50 cm^3) and methanol (15 cm^3) was heated at reflux for 3 h. The reaction mixture was filtered through a small plug of deactivated alumina (neutral, Class IV), washed with a saturated sodium bicarbonate solution (100 cm^3), water (100 cm^3), dried over anhydrous sodium sulfate, filtered and the solvent removed to give dihydroxo[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinato]tin(IV) **6** (150 mg, 97%) which had identical spectroscopic properties to the sample prepared by Method 1.

Dichloro[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]tin(IV) 8

A solution of 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-quinoxalino[2,3-*b*]porphyrin[34] **7** (149 mg, 0.128 mmol) and tin(II) chloride dihydrate (354 mg, 1.57 mmol) in pyridine (50 cm^3) was heated at reflux for 4 h. The mixture was allowed to cool for 30 min and water (50 cm^3) was then added and the mixture left overnight. The mixture was then filtered and the precipitate dissolved with several washings of dichloromethane (500 cm^3) and hydrochloric acid solution (1 M, 200 cm^3). The organic extract was washed with hydrochloric acid solution (1 M, 300 cm^3), water (2 × 400 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was recrystallised (dichloromethane–acetonitrile, 1 : 1) to yield *dichloro[5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)quinoxalino[2,3-b]porphyrinato]tin(IV)* **8** (158 mg, 91%) as a green–brown solid, mp >300 °C (Found: C, 72.6; H, 7.3; N, 6.3; Cl, 5.1. $C_{82}H_{94}Cl_2N_6Sn$ requires C, 72.8; H, 7.0; N, 6.2; Cl, 5.2%); ν_{max} ($CHCl_3$)/cm^{-1} 3011s, 2973s, 2899m, 1707w, 1595w, 1445w, 1389m and 1364m; λ_{max} ($CHCl_3$)/nm 347.5 (log ε 4.51), 404sh (4.64), 418 (4.70), 440sh (5.09), 456 (5.48), 541 (3.90), 577 (4.24) and 622.5 (4.32); δ_H (400 MHz; $CDCl_3$; $SiMe_4$) 1.48 (36 H, s, *tert*-butyl H), 1.54 (36 H, s, *tert*-butyl H), 7.86 (2 H, t, *J* 1.7, Ar-H_p at $C_{10,15}$), 7.88–7.92 (2 H, m, quinoxalino H), 7.90–7.97 (2 H, m, quinoxalino H), 7.99 (2 H, t, *J* 1.7, Ar-H_p at $C_{5,20}$), 8.03 (4 H, d, *J* 1.7, Ar-H_o at $C_{5,20}$), 8.16 (4 H, d, *J* 1.7, Ar-H_o at $C_{10,15}$), 9.19 (2 H, s, satellites $^4J_{H–Sn}$ 15.0, β-pyrrolic H-12 and H-13), 9.20 and 9.23 (4 H, ABq, *J* 4.9, satellites $^4J_{H–Sn}$ 12.1 and 12.8, β-pyrrolic H-8 and H-17 and β-pyrrolic H-7 and H-18); δ_{Sn} (149 MHz; $CDCl_3$; $SnMe_4$) −593.0 (Sn); *m*/*z* (MALDI-TOF) 1318.9 [$(M - Cl)^+$ requires 1317.8].

Dihydroxo[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]tin(IV) 9

A mixture of dichloro[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)quinoxalino[2,3-*b*]porphyrinato]tin(IV) **8** (44 mg, 0.033 mmol) and potassium carbonate (308 mg, 2.2 mmol) in tetrahydrofuran (40 cm^3) and water (10 cm^3) was heated at reflux for 2 h. The solution was concentrated on a rotary evaporator (to remove the tetrahydrofuran) and then treated with dichloromethane (100 cm^3) and water (100 cm^3). The organic phase was washed with aqueous sodium hydroxide (1 M, 100 cm^3) and again with water (200 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was recrystallised (dichloromethane–acetonitrile, 1 : 1) to yield *dihydroxo[5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)quinoxalino[2,3-b]porphyrinato]tin(IV)* **9** (43 mg, 99%) as a green–brown solid, mp >300 °C (Found: C, 71.5; H, 7.4; N, 6.2. $C_{82}H_{96}N_6O_2Sn + CH_2Cl_2$ requires C, 71.1; H, 7.1; N, 6.0%); ν_{max} ($CHCl_3$)/cm^{-1} 3014m, 2967s, 1708s, 1684w, 1614m, 1596m, 1443m, 1426m, 1361s and 1249s; λ_{max} ($CHCl_3$)/nm 343.5 (log ε 4.49), 406sh (4.75), 418 (4.86), 443.5sh (5.23), 454.5 (5.37), 538 (3.89), 576 (4.26) and 621 (4.26); δ_H (400 MHz; $CDCl_3$; $SiMe_4$) −6.60 (2 H, br s, axial OH), 1.49 (36 H, s, *tert*-butyl H), 1.55 (36 H, s, *tert*-butyl H), 7.85 (2 H, t, *J* 1.7, Ar-H_p at $C_{10,15}$), 7.84–7.89 (2 H, m, quinoxalino H), 7.91–7.96 (2 H, m, quinoxalino H), 7.97 (2 H, t, *J* 1.7, Ar-H_p at $C_{5,20}$), 8.06 (4 H, d, *J* 1.7, Ar-H_o at $C_{5,20}$), 8.20 (4 H, d, *J* 1.7, Ar-H_o at $C_{10,15}$), 9.12 (2 H, s, satellites $^4J_{H–Sn}$ 10.0, β-pyrrolic H-12 and H-13), 9.15 and 9.17 (4 H, ABq, *J* 4.9, β-pyrrolic H-8 and H-17 and β-pyrrolic H-7 and H-18); δ_{Sn} (149 MHz; $CDCl_3$; $SnMe_4$) −572.0 (Sn); *m*/*z* (MALDI-TOF) 2602.1 [$(M_2 - 2OH)^+$ requires 2598.8], 1316.2 (M^+ requires 1316.4), 1300.9 [$(M - OH)^+$ requires 1299.4] and 1283.7 [$(M - 2OH)^+$ requires 1282.4].

Tetrachloro[5,5′,10,10′,15,15′,20,20′-octakis(3,5-di-*tert*-butylphenyl)[1″,4″,5″,8″]tetraazaanthraceno[2″,3″-*b*:6″,7″-*b*′]bisporphyrinato]ditin(IV) 11

A solution of 5,5′,10,10′,15,15′,20,20′-octakis(3,5-di-*tert*-butylphenyl)[1″,4″,5″,8″]tetraazaanthraceno[2″,3″-*b*:6″,7″-*b*′]-bisporphyrin[13] **10** (210 mg, 0.093 mmol) and tin(II) chloride dihydrate (476 mg, 2.11 mmol) in pyridine (50 cm^3) was heated at reflux for 4 h. The solution was allowed to cool to room temperature, water (50 cm^3) was added and the solution was left overnight. The mixture was filtered and the precipitate washed with water (50 cm^3). The aqueous filtrate was refiltered twice and the combined filtrates were washed with water (200 cm^3). The precipitate was dissolved (with difficulty) in several small portions of dichloromethane (500 cm^3) and hydrochloric acid solution (1 M, 500 cm^3). The organic extract was washed with hydrochloric acid solution (1 M, 500 cm^3), water (2 × 500 cm^3), dried over anhydrous sodium sulfate and evaporated to dryness to yield crude *tetrachloro[5,5′,10,10′,15,15′,20,20′-octakis(3,5-di-tert-butylphenyl)[1″,4″,5″,8″]tetraazaanthraceno[2″,3″-b:6″,7″-b′]bisporphyrinato]ditin(IV)* **11** (218 mg, 89%) as a brown–purple solid, mp >300 °C. An analytical sample was prepared by recrystallisation (dichloromethane–acetonitrile, 1 : 1) (Found: C, 72.3; H, 7.2; N, 6.1; Cl, 5.0. $C_{158}H_{182}Cl_4N_{12}Sn_2$ requires C, 72.2; H, 7.0; N, 6.4; Cl, 5.4%); ν_{max} ($CHCl_3$)/cm^{-1} 2966s, 2861s, 1719w, 1590s, 1478s and 1361s; λ_{max} ($CHCl_3$)/nm 320.5sh (log ε 4.60), 434.5 (5.46), 469 (5.35), 510sh (4.93), 541.5sh (4.75), 577sh (4.61), 647.5 (4.41) and 697 (4.60); δ_H (400 MHz; $CDCl_3$; $SiMe_4$) 1.54 (72 H, s, *tert*-butyl H), 1.58 (72 H, s, *tert*-butyl H), 7.87 (4 H, t, *J* 1.5, Ar-H_p at $C_{10,15}$), 8.06 (4 H, t, *J* 1.5, Ar-H_p at $C_{5,20}$), 8.13 (8 H, d, *J* 1.5, Ar-H_o at $C_{5,20}$), 8.14 (8 H, d, *J* 1.5, Ar-H_o at $C_{10,15}$), 8.84 (2 H, s, bridging H-9″ and H-10″), 9.12 (4 H, s, satellites $^4J_{H–Sn}$ 14.7, β-pyrrolic H-12 and H-13), 9.00 and 9.14 (8 H, ABq, *J* 4.8, satellites $^4J_{H–Sn}$ 16.8, β-pyrrolic H-8 and H-17 and β-pyrrolic H-7 and H-18); δ_{Sn} (149 MHz; $CDCl_3$; $SnMe_4$) −592.4 (Sn); *m*/*z* (MALDI-TOF) 2628.4 (M^+ requires 2628.5), 2594.9 [$(M - Cl)^+$ requires 2593.0], 2557.7 [$(M - 2Cl)^+$ requires 2557.5] and 2522.0 [$(M - 3Cl)^+$ requires 2522.1].

Tetrahydroxo[5,5′,10,10′,15,15′,20,20′-octakis(3,5-di-*tert*-butylphenyl)[1″,4″,5″,8″]tetraazaanthraceno[2″,3″-*b*:6″,7″-*b*′]-bisporphyrinato]ditin(IV) 12

A solution of tetrachloro[5,5′,10,10′,15,15′,20,20′-octakis(3,5-di-*tert*-butylphenyl)][1″,4″,5″,8″]tetraazaanthraceno[2″,3″-*b*:6″, 7″-*b*′]bisporphyrinato]ditin(IV) **11** (198 mg, 0.075 mmol) and potassium carbonate (1.24 g, 9.00 mmol) in tetrahydrofuran (50 cm^3) and water (10 cm^3) was heated at reflux for 4 h and the solvents removed. The residue was dissolved in dichloromethane (200 cm^3) and washed with sodium hydroxide solution (1 M, 100 cm^3), water (200 cm^3), sodium hydroxide solution (150 cm^3) and again with water (250 cm^3), dried over anhydrous sodium sulfate, filtered and the solvent removed. The product was then purified by recrystallisation (dichloromethane–acetonitrile, 1 : 1) to yield *tetrahydroxo[5,5′,10,10′,15,15′,20,20′-octakis(3,5-di-tert-butylphenyl)[1″,4″,5″,8″]tetraazaanthraceno[2″,3″-b:6″,7″-b′]bisporphyrinato]ditin(IV)* **12** (142 mg, 74%) as a dark purple solid, mp >300 °C (Found: C, 70.7; H, 7.5; N, 6.2. $C_{158}H_{186}N_{12}O_4Sn_2 + 2CH_2Cl_2$ requires C, 70.5; H, 7.0; N, 6.2%); ν_{max} ($CHCl_3$)/cm^{-1} 3013m, 2966s, 1719w, 1596s, 1478m, 1390m, 1361m, 1296w and 1249s; λ_{max} ($CHCl_3$)/nm 338 (log ε 4.59), 430.5 (5.49), 468 (5.41), 514 (4.94), 539sh (4.71), 571.5sh (4.46), 635.5 (4.37) and 689 (4.56); δ_H (400 MHz; $CDCl_3$; $SiMe_4$) −6.46 (4 H, br s, axial OH), 1.55 (72 H, s, *tert*-butyl H), 1.59 (72 H, s, *tert*-butyl H), 7.85 (4 H, t, *J* 1.8, Ar-H_p at $C_{10,15}$), 8.04 (4 H, t, *J* 1.7, Ar-H_p at $C_{5,20}$), 8.17 (8 H, d, *J* 1.7, Ar-H_o at $C_{5,20}$), 8.18 (8 H, d, *J* 1.7, Ar-H_o at $C_{10,15}$), 8.82 (2 H, s, bridging H-9″ and H-10″), 9.06 (4 H, s, satellites $^4J_{H–Sn}$ 10.4, β-pyrrolic H-12 and H-13), 8.92 and 9.08 (8 H, ABq, *J* 4.7, satellites $^4J_{H–Sn}$ 9.8 and 11.0, β-pyrrolic H-8 and H-17 and β-pyrrolic H-7 and H-18); δ_{Sn} (149 MHz; $CDCl_3$; $SnMe_4$) −571.7 (Sn); *m*/*z* (MALDI-TOF) 5104.8 [$(M_2)^+$ requires 5108.6], 2553.2 (M^+ requires 2554.3), 2537.8 [$(M - OH)^+$ requires 2537.3], 2520.1 [$(M - 2OH)^+$ requires 2520.3] and 2503.6 [$(M - 3OH)^+$ requires 2503.3]; *m*/*z* (ESI) 2578.2 [$(M - 4OH + 3CH_3O)^+$ requires 2579.3] and 1274.8 [$(M - 4OH + 2CH_3O)^{2+}$ requires *m*/*z* 1274.2]; *m*/*z* (HR-ESI-FT/ICR) Envelope [$(M - 4OH + 3CH_3O)^+$ requires] 2576.238/50% (2576.323/60%), 2577.245/78 (2577.345/80), 2578.245/99 (2578.325/95), 2579.249/100 (2579.326/100), 2580.249/98 (2580.326/97), 2581.249/88 (2581.327/85), 2582.251/60 (2582.328/58), [$(M - 4OH + 2CH_3O)^{2+}$ requires] 1273.131/86% (1273.153/80%), 1273.631/100 (1273.653/95), 1274.131/97 (1274.153/100), 1274.632/90 (1274.654/97) and 1275.133/73 (1275.154/80).

Dichloro[5,5′,10,10′,15,15′,20,20′-octakis(3,5-di-*tert*-butylphenyl)[1″,4″,5″,8″]tetraazaanthraceno[2″,3″-*b*:6″,7″-*b*′]bisporphyrinato]tin(IV)zinc(II) 14

A solution of [5,5′,10,10′,15,15′,20,20′-octakis(3,5-di-*tert*-butylphenyl)[1″,4″,5″,8″]tetraazaanthraceno[2″,3″-*b*:6″,7″-*b*′]bisporphyrinato]zinc(II) **13** (181 mg, 0.078 mmol) and tin(II) chloride dihydrate (371 mg, 1.64 mmol) in pyridine (50 cm^3) was heated at reflux for 4 h. The solution was allowed to cool to room temperature, water (50 cm^3) was added and the solution left overnight. The mixture was filtered and the precipitate washed with water (50 cm^3). The crude product was dissolved in dichloromethane (200 cm^3) and set aside. The aqueous filtrate was filtered twice more and washed with water (200 cm^3). The precipitates were dissolved (with difficulty) in dichloromethane (700 cm^3). The two organic extracts were combined and washed with water (4 × 300 cm^3), dried over anhydrous sodium sulfate and evaporated to dryness to yield *dichloro[5,5′,10,10′,15,15′, 0,20′-octakis(3,5-di-tert-butylphenyl)[1″,4″,5″,8″]tetraaza-anthraceno[2″,3″-b:6″,7″-b′]bisporphyrinato]tin(IV)zinc(II)* **14** (187 mg, 96%) as a dark purple solid, mp >300 °C. Further purification was achieved by recrystallisation (dichloromethane–acetonitrile, 1 : 1). ν_{max} ($CHCl_3$)/cm^{-1} 2966s, 2861s, 1713w, 1642w, 1590s, 1478m, 1361m and 1296w; λ_{max} ($CHCl_3$)/nm 302 (log ε 4.69), 430.5 (5.70), 488 (5.18), 514.5sh (5.00), 598.5sh (4.51) and 665 (4.51); δ_H (400 MHz; $CDCl_3$; $SiMe_4$, a very complex mixture, assignments difficult) 1.51–1.60 (144 H, m, *tert*-butyl H), 7.75–8.20 (24 H, m, Ar-H), 9.11 (4 H, s, satellites $^4J_{H\text{–}Sn}$ not resolved, β-pyrrolic H-12 and H-13), 8.75–9.15 (10 H, m, 8 × β-pyrrolic H and 2 × bridging H-9″ and H-10″); δ_{Sn} (149 MHz; $CDCl_3$; $SnMe_4$, from two-dimensional ^{1}H–^{119}Sn NMR HMQC) −592.9 (Sn); *m*/*z* (MALDI-TOF) 2468.4 [(M − Cl)$^+$ requires 2468.3]; *m*/*z* (ESI) 2465.4 (75%) [(M − Cl)$^+$ requires 2468.3] and 1232.9 (100) [(M − Cl)$^{2+}$ requires 1233.7].

Dihydroxo[5,5′,10,10′,15,15′,20,20′-octakis(3,5-di-*tert*-butylphenyl)[1″,4″,5″,8″]tetraazaanthraceno[2″,3″-*b*:6″,7″-*b*′]bisporphyrinato]tin(IV)zinc(II) 15

A mixture of dichloro[5,5′,10,10′,15,15′,20,20′-octakis(3,5-di-*tert*-butylphenyl)[1″,4″,5″,8″]tetraazaanthraceno[2″,3″-*b*:6″,7″-*b*′]-bisporphyrinato]tin(IV)zinc(II) **14** (167 mg, 0.067 mmol) and potassium carbonate (1.22 g, 8.83 mmol) in tetrahydrofuran (50 cm^3) and water (10 cm^3) was heated at reflux for 4 h. The solution was concentrated on a rotary evaporator (to remove the tetrahydrofuran) and then treated with dichloromethane (200 cm^3). The organic phase was washed with sodium hydroxide solution (1 M, 100 cm^3), water (200 cm^3), sodium hydroxide solution (150 cm^3) and again with water (250 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The product was purified by recrystallisation (dichloromethane–acetonitrile, 1 : 1) to yield *dihydroxo[5,5′,10,10′,15,15′, 20,20′-octakis(3,5-di-tert-butylphenyl)[1″,4″,5″,8″]tetraaza-anthraceno[2″,3″-b:6″,7″-b′]bisporphyrinato]tin(IV)zinc(II)* **15** (119 mg, 72%) as a dark-purple solid, mp >300 °C (Found: C, 75.5; H, 7.8; N, 6.4; Cl, < 0.2. $C_{158}H_{184}N_{12}O_2SnZn + 2H_2O$ requires C, 75.8; H, 7.6; N, 6.7%); ν_{max} ($CHCl_3$)/cm^{-1} 3023s, 2973s, 1726w, 1595w, 1445w, 1389m, 1364m, 1295w and 1245s; λ_{max} ($CHCl_3$)/nm 429.5 (log ε 5.59), 463sh (5.22), 492sh (5.00), 529.5 (4.85), 596.5 (4.34) and 668.5 (4.43); δ_H (400 MHz; $CDCl_3$; $SiMe_4$) −6.49 (2 H, br s, axial OH), 1.53 (36 H, s, *tert*-butyl H), 1.55 (36 H, s, *tert*-butyl H), 1.58 (36 H, s, *tert*-butyl H), 1.59 (36 H, s, *tert*-butyl H), 7.79 (2 H, t, *J* 1.7, Ar-H$_p$ at $C_{10′,15′}$), 7.84 (2 H, t, *J* 1.7, Ar-H$_p$ at $C_{10,15}$), 7.99 (2 H, t, *J* 1.7, Ar-H$_p$ at $C_{5′,20′}$), 8.03 (2 H, t, *J* 1.7, Ar-H$_p$ at $C_{5,20}$), 8.04 (4 H, d, *J* 1.7, Ar-H$_o$ at $C_{5′,20′}$), 8.07 (4 H, d, *J* 1.7, Ar-H$_o$ at $C_{10′,15′}$), 8.16 (8 H, d, *J* 1.7, Ar-H$_o$ at $C_{5,10}$), 8.18 (8 H, d, *J* 1.7, Ar-H$_o$ at $C_{10,15}$), 8.78 (2 H, s, bridging H-9″ and H-10″), 8.83 (2 H, s, β-pyrrolic H-12′ and H-13′), 8.81 and 8.95 (4 H, ABq, *J* 4.7, β-pyrrolic H-8′ and H-17′ and β-pyrrolic H-7′ and H-18′), 9.05 (2 H, s, satellites $^4J_{H\text{–}Sn}$ 9.8, β-pyrrolic H-12 and H-13), 8.90 and 9.07 (4 H, ABq, *J* 4.8, satellites $^4J_{H\text{–}Sn}$ 11.8 and 11.6, β-pyrrolic H-8 and H-17 and β-pyrrolic H-7 and H-18); δ_{Sn} (149 MHz; $CDCl_3$; $SnMe_4$) −571.7 (Sn); *m*/*z* (MALDI-TOF) 2467.7 (M$^+$ requires 2467.4) and 2452.1 [(M − OH)$^+$ requires 2450.3]; *m*/*z* (ESI) 2450.3 [(M − OH)$^+$ requires 2450.3].

Tetrahydroxo[5,5′,10,10′,15,15′,20,20′-octakis(3,5-di-*tert*-butylphenyl)-4″*H*, 8″*H*-1″,5″-methano[1″,5″]diazocino[2″,3″-*b*:6″,7″-*b*′]bisporphyrinato]ditin(IV) 18

Tin(II) chloride dihydrate (382 mg, 1.68 mmol) was added to 5,5′,10,10′,15,15′,20,20′-octakis(3,5-di-*tert*-butylphenyl)-4″*H*, 8″*H*-1″,5″-methano[1″,5″]diazocino[2″,3″-*b*:6″,7″-*b*′]bisporphyrin[14] **16** (372 mg, 0.170 mmol) dissolved in pyridine (300 cm^3) and the mixture heated at reflux for 3 h. The solution was cooled and water was added to precipitate a dark purple solid which was collected by filtration and washed with water until there was no trace of pyridine. The product was dissolved in dichloromethane (100 cm^3) and dried over anhydrous sodium sulfate, filtered and evaporated to give tetrachloro[5,5′,10, 10′,15,15′,20,20′-octakis(3,5-di-*tert*-butylphenyl)-4″*H*,8″*H*-1″, 5″-methano[1″,5″]diazocino[2″,3″-*b*:6″,7″-*b*′]bisporphyrinato]-ditin(IV) **17** (380 mg, 85%) which was used directly in the next step.

The foregoing material **17** (210 mg, 0.082 mmol) was dissolved in a mixture of dichloromethane (80 cm^3) and methanol (20 cm^3) and potassium carbonate (1.0 g, 7.2 mmol) was added. The solution was heated at reflux for 2 h. The mixture was washed with water (2 × 100 cm^3) and then dried over anhydrous sodium sulfate. The solution was evaporated and the residue purified by chromatography over alumina (neutral, Class IV, dichloromethane–light petroleum, 2 : 1). The major purple band was collected and recrystallised (chloroform–acetonitrile, 1 : 1) to give *tetrahydroxo[5,5′,10,10′,15,15′,20,20′-octakis(3,5-di-tert-butylphenyl)-4″H,8″H-1″,5″-methano[1″,5″]diazocino-[2″,3″-b:6″,7″-b′]bisporphyrinato]ditin(IV)* **18** (121 mg, 92%) as a purple microcrystalline solid, mp >300 °C (Found: C, 72.3; H, 7.6; N, 5.2. $C_{155}H_{190}N_{10}O_4Sn_2 + 0.75CHCl_3$ requires C, 72.4; H, 7.4; N, 5.4%); ν_{max} ($CHCl_3$)/cm^{-1} 3692, 3609, 3019, 2964, 2360, 1592 and 1477; λ_{max} ($CHCl_3$)/nm 322 (log ε 4.59), 428.5 (5.63), 532 (3.96), 573 (4.64) and 613.5 (4.40); δ_H (400 MHz; $CDCl_3$; $SiMe_4$) −7.50 (2 H, s, OH), −7.45 (2 H, s, OH), 1.15–1.82 (144 H, m, *tert*-butyl H), 4.34 (2 H, d, *J* 17.5, H-4″ and H-8″), 4.44 (2 H, d, *J* 17.5, H-4″ and H-8″), 4.81 (2 H, s, H-9″), 6.43 (2 H, t, *J* 1.4, Ar-H), 7.41 (2 H, t, *J* 1.5, Ar-H), 7.53 and 8.33 (4 H, ABq, *J* 4.8, satellites $^4J_{H\text{–}Sn}$ 11.0, β-pyrrolic H), 7.54 (2 H, t, *J* 1.7, Ar-H), 7.59 (2 H, t, *J* 1.5, Ar-H), 7.65 (2 H, t, *J* 1.5, Ar-H), 7.82 (2 H, t, *J* 1.5, Ar-H), 7.84–7.85 (4 H, m, Ar-H), 7.96 (2 H, t, *J* 1.5, Ar-H), 8.13 (2 H, t, *J* 1.5, Ar-H), 8.21 (2 H, t, *J* 1.5, Ar-H), 8.50 (2 H, t, *J* 1.5, Ar-H), 8.82 and 8.92 (4 H, ABq, *J* 4.8, satellites $^4J_{H\text{–}Sn}$ 14.6 and 14.3, β-pyrrolic H), 9.09 and 9.17 (4 H, ABq, *J* 4.8, satellites $^4J_{H\text{–}Sn}$ 10.7 and 10.1, β-pyrrolic H); δ_{Sn} (149 MHz; $CDCl_3$; $SnMe_4$) −570.7 (Sn); *m*/*z* (MALDI-TOF) 2462.7 [(M − OH)$^+$ requires 2460.5].

Dihydroxo[5,5′,10,10′,15,15′,20,20′-octakis(3,5-di-*tert*-butylphenyl)-4″*H*, 8″*H*-1″,5″-methano[1″,5″]diazocino[2″,3″-*b*:6″,7″-*b*′]bisporphyrinato]tin(IV)zinc(II) 21

Tin(II) chloride dihydrate (33 mg, 0.153 mmol) and [5,5′,10, 10′,15,15′,20,20′-octakis(3,5-di-*tert*-butylphenyl)-4″*H*,8″*H*-1″,5″-methano[1″,5″]diazocino[2″,3″-*b*:6″,7″-*b*′]bisporphyrinato]-zinc(II) **19** (370 mg, 0.163 mmol) was dissolved in pyridine (30 cm^3) and the mixture heated at reflux for 3 h. Water was added to precipitate the product which was then collected by filtration and washed with water until there was no trace of pyridine. The product was dissolved in dichloromethane (200 cm^3) which was then dried over anhydrous sodium sulfate and filtered. Evaporation of the solvent left dichloro[5,5′, 10,10′,15,15′,20,20′-octakis(3,5-di-*tert*-butylphenyl)-4″*H*,8″*H*-1″,5″-methano[1″,5″]diazocino[2″,3″-*b*:6″,7″-*b*′]bisporphyrinato]tin(IV)zinc(II) **20** (470 mg, 94%) as a purple amorphous solid, which was used directly in the next step.

The foregoing material **20** (380 mg, 0.156 mmol) was dissolved in a mixture of dichloromethane (80 cm^3) and methanol (20 cm^3). Potassium carbonate (2.0 g, 14 mmol) was added to the solution that was then heated at reflux for 2 h, allowed to cool, and then washed with water (2 × 100 cm^3) and dried over anhydrous sodium sulfate. The solution was evaporated and the residue purified by chromatography over alumina (neutral, Class IV, dichloromethane–light petroleum, 1 : 2). The major purple band was collected and recrystallised (acetonitrile–chloroform, 1 : 1) to give *dihydroxo[5,5′,10,10′,15,15′,20,20′-octakis(3,5-di-tert-butylphenyl)-4″H,8″H-1″,5″-methano[1″,5″]-diazocino[2″,3″-b:6″,7″-b′]bisporphyrinato]tin(IV)zinc(II)* **21** (253 mg, 89%) as a purple microcrystalline solid, mp >300 °C (Found: C, 75.7; H, 7.9; N, 5.7. $C_{155}H_{188}N_{10}O_2SnZn$ + 0.5CHCl$_3$ requires C, 75.7; H, 7.7; N, 5.7%); ν_{max} (CHCl$_3$)/cm^{-1} 3615, 3452, 2894, 1702, 1389 and 1238; λ_{max} (CHCl$_3$)/nm 320 (log ε 4.40), 426.5 (5.40), 570 (4.30) and 614 (4.00); δ_H (400 MHz; CDCl$_3$; SiMe$_4$) −8.06 (1 H, s, OH), −7.44 (1 H, s, OH), 0.71–1.84 (144 H, m, *tert*-butyl H), 4.06 (1 H, d, *J* 17.2, H-4″ or H-8″), 4.08 (1 H, d, *J* 17.2, H-4″ or H-8″), 4.34 (1 H, d, *J* 17.2, H-4″ or H-8″), 4.37 (1 H, d, *J* 17.2, H-4″ or H-8″), 4.81 and 4.77 (2 H, ABq, *J* 11.6, H-9″), 6.28 (1 H, br s, Ar-H), 6.47 (1 H, br s, Ar-H), 7.29 (2 H, br s, Ar-H), 7.37 and 8.03 (2 H, ABq, *J* 4.4, β-pyrrolic H′), 7.47 (1 H, br s, Ar-H), 7.49 (1 H, br s, Ar-H), 7.49 and 8.38 (2 H, ABq, *J* 5.2, satellites $^4J_{H\text{–}Sn}$ 11.6 and 11.6, β-pyrrolic H), 7.57 (2 H, m, Ar-H), 7.66 (2 H, m, Ar-H), 7.71 (1 H, m, Ar-H), 7.76–7.80 (5 H, m, Ar-H), 7.84 (1 H, br s, Ar-H), 7.93 (1 H, br s, Ar-H), 7.99 (1 H, br s, Ar-H), 8.11 (2 H, br s, Ar-H), 8.17 (1 H, br s, Ar-H), 8.43 (1 H, br s, Ar-H), 8.50 (1 H, br s, Ar-H), 8.55 and 8.69 (2 H, ABq, *J* 4.8, β-pyrrolic H′), 8.78 and 8.84 (2 H, ABq, *J* 4.4, β-pyrrolic H), 8.79 and 8.90 (2 H, ABq, *J* 4.6, satellites $^4J_{H\text{–}Sn}$ 11.4 and 11.4, β-pyrrolic H′), 9.05 and 9.17 (2 H, ABq, *J* 4.8, satellites $^4J_{H\text{–}Sn}$ 11.1 and 11.7, β-pyrrolic H); δ_{Sn} (149 MHz; CDCl$_3$; SnMe$_4$) −572.6 (Sn); *m*/*z* (MALDI-TOF) 2391.8 [(M − OH)$^+$ requires 2390.2].

Dichloro[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-2^2-{4-[(trimethylsilyl)ethynyl]phenyl}-2^1*H*-imidazo[4,5-*b*]porphyrinato]tin(IV) 23

A solution of 5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-2^2-{4-[(trimethylsilyl)ethynyl]phenyl}-2^1*H*-imidazo[4,5-*b*]porphyrin[21] **22** (235 mg, 0.184 mmol) and tin(II) chloride dihydrate (548 mg, 2.43 mmol) in *N*,*N*-dimethylformamide (200 cm^3) was heated at reflux for 5 h. The reaction mixture was allowed to cool and water (30 cm^3) was added to the warm mixture which was then left overnight. The mixture was filtered and the filtrate extracted with dichloromethane (200 cm^3). The organic layer was separated and washed with water (6 × 200 cm^3), dried over anhydrous sodium sulfate, filtered and the solvent removed. The residue was dissolved in dichloromethane (200 cm^3) which was then washed with water (3 × 200 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The combined crude residues gave *dichloro[5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)-2^2-{4-[(trimethylsilyl)ethynyl]-phenyl}-2^{1}H-imidazo[4,5-b]porphyrinato]tin(IV)* **23** (257 mg, 95%) as a blue–purple solid, mp >300 °C. ν_{max} (CHCl$_3$)/cm^{-1} 3439w (NH), 3005w, 2969s, 2864m, 2159w (C≡C), 1674w, 1591s, 1480s, 1427m, 1362m and 1245m; λ_{max} (CHCl$_3$)/nm 311.5 (log ε 4.47), 343sh (4.27), 435.5 (5.48), 526 (3.72), 563 (4.30) and 605 (4.28); δ_H (400 MHz; CDCl$_3$; SiMe$_4$) 0.34 (9 H, s, Si(CH$_3$)$_3$), 1.59 (72 H, s, *tert*-butyl H), 7.66 (2 H, d, *J* 8.2, AA′ of AA′BB′ system, phenyl H), 7.79 (2 H, d, *J* 8.2, BB′ of AA′BB′ system, phenyl H), 7.92 (2 H, d, *J* 1.1, Ar-H$_o$), 7.98 (1 H, t, *J* 1.6, Ar-H$_p$), 8.18 (1 H, t, *J* 1.6, Ar-H$_p$), 8.22–8.26 (6 H, m, 4 × Ar-H$_o$ and 2 × Ar-H$_p$), 8.27 (2 H, d, *J* 1.6, Ar-H$_o$), 8.81 (1 H, br s, imidazo H), 9.31 (2 H, s, satellites $^4J_{H\text{–}Sn}$ 15.0, β-pyrrolic H-12 and H-13) and 9.27–9.40 (4 H, m, β-pyrrolic H); δ_{Sn} (149 MHz; CDCl$_3$; SnMe$_4$) −595.1 (Sn); *m*/*z* (MALDI-TOF) 1427.7 [(M − Cl)$^+$ requires 1427.7]; (HRFAB) 1427.6816 [(M − Cl)$^+$, calcd for $C_{88}H_{104}ClN_6SiSn$: 1427.6802].

Dihydroxo[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-2^2-[(4-ethynyl)phenyl]-2^1*H*-imidazo[4,5-*b*]porphyrinato]tin(IV) 24

A mixture of dichloro[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-2^2-{4-[(trimethylsilyl)ethynyl]phenyl}-2^1 *H*-imidazo-[4,5-*b*]porphyrinato]tin(IV) **23** (122 mg, 0.083 mmol) and potassium carbonate (1.04 g, 7.53 mmol) in dichloromethane (40 cm^3) and methanol (10 cm^3) was heated at reflux for 2 h. The solvent was evaporated and the residue was dissolved in dichloromethane (150 cm^3) which was then washed with water (3 × 100 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The crude residue was dissolved in dichloromethane (200 cm^3), washed with water (3 × 200 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness to give *dihydroxo[5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)-2^2-[(4-ethynyl)phenyl]-2^{1}H-imidazo[4,5-b]porphyrinato]tin(IV)* **24** (103 mg, 91%) as a blue–purple solid, mp >300 °C. ν_{max} (CHCl$_3$)/cm^{-1} 3439w (NH), 3298w, 2969s, 2864s, 1668w, 1591s, 1474m, 1427w, 1362m and 1245m; λ_{max} (CHCl$_3$)/nm 311.5 (log ε 4.44), 343.5sh (4.25), 434 (5.56), 525.5 (3.72), 561.5 (4.31) and 604.5 (4.26); δ_H (400 MHz; CDCl$_3$; SiMe$_4$) −7.19 (2 H, br s, axial OH), 1.56 (24 H, s, *tert*-butyl H), 1.57 (48 H, s, *tert*-butyl H), 3.24 (1 H, s, acetylenic H), 7.64 (2 H, d, *J* 8.3, AA′ of AA′BB′ system, phenyl H), 7.79 (2 H, d, *J* 8.3, BB′ of AA′BB′ system, phenyl H), 7.93 (2 H, d, *J* 1.1, Ar-H$_o$), 7.94 (1 H, t, *J* 1.7, Ar-H$_p$), 8.13 (1 H, t, *J* 1.7, Ar-H$_p$), 8.22–8.27 (6 H, m, 4 × Ar-H$_o$ and 2 × Ar-H$_p$), 8.28 (2 H, d, *J* 1.7, Ar-H$_o$), 8.77 (1 H, br s, imidazo H), 9.21 (2 H, s, satellites $^4J_{H\text{–}Sn}$ 10.4, β-pyrrolic H-12 and H-13) and 9.19–9.28 (4 H, m, β-pyrrolic H); δ_{Sn} (149 MHz; CDCl$_3$; SnMe$_4$) −573.8 (Sn); *m*/*z* (MALDI-TOF): 2675.1 [(M$_2$ − 2OH)$^+$ requires 2675.4], 1355.5 (M$^+$ requires 1354.7) and 1138.5 [(M − OH)$^+$ requires 1337.7]; (HRFAB): 1354.6849 (M$^+$, calcd for $C_{85}H_{98}N_6O_2Sn$: 1354.6773).

μ-[2^2,2$^{2'}$-(1,4-Diphenylenebuta-1,3-diyne-1,4-diyl)]bis{dihydroxo[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-2^1*H*-imidazo[4,5-*b*]porphyrinato}tin(IV) 25

A mixture of dihydroxo[5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl)-2^2-[(4-ethynyl)phenyl]-2^1*H*-imidazo[4,5-*b*]porphyrinato]tin(IV) **24** (88 mg, 0.063 mmol), freshly prepared copper(I) chloride (514 mg, 5.19 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.75 cm^3, 5.03 mmol) in dichloromethane (90 cm^3) was stirred in the dark at room temperature for 100 min. The mixture was filtered through a small plug of deactivated alumina (neutral, Class IV), the filtrate washed with water (2 × 100 cm^3), dried over anhydrous sodium sulfate, filtered and the solvent removed. The crude residue was dissolved in dichloromethane (200 cm^3) which was then washed with water (3 × 200 cm^3), dried over anhydrous sodium sulfate, filtered and evaporated to dryness. The residue was purified by column chromatography over deactivated alumina (neutral, Class IV, dichloromethane–light petroleum, 2 : 3) and the resultant was subsequently recrystallised (dichloromethane–light petroleum, 1 : 1) to give *μ-[2^2,2$^{2'}$-(1,4-diphenylenebuta-1,3-diyne-1,4-diyl)]-bis{dihydroxo[5,10,15,20-tetrakis(3,5-di-tert-butylphenyl)-2^{1}H-imidazo[4,5-b]porphyrinato]tin(IV)* **25** (54 mg, 63%) as a blue–purple solid, mp >300 °C (Found: C, 72.3; H, 7.0; N, 5.4. $C_{170}H_{194}N_{12}O_4Sn_2$ + 1.5CH$_2$Cl$_2$ requires C, 72.7; H, 7.0; N, 5.9%); ν_{max} (CHCl$_3$)/cm^{-1} 3428w (NH), 2958s, 2864s, 1733w, 1591s, 1474s, 1427m, 1362m and 1245w; λ_{max} (CHCl$_3$)/nm 334 (log ε 4.50), 365.5sh (4.67), 434.5 (5.79), 525.5 (4.13), 562.5 (4.71) and 605 (4.68); δ_H (400 MHz; CDCl$_3$; SiMe$_4$) −7.18 (4 H, br s, axial OH), 1.57 (108 H, s, *tert*-butyl H), 1.59 (36 H, s, *tert*-butyl H), 7.70 (4 H, d, *J* 8.2, AA′ of AA′BB′ system, phenyl H), 7.87 (4 H, d, *J* 8.2, BB′ of AA′BB′ system, phenyl H), 7.87

(4 H, d, J 0.9, Ar-H$_o$), 7.96 (2 H, t, J 1.7, Ar-H$_p$), 8.15 (2 H, t, J 1.7, Ar-H$_p$), 8.21–8.26 (12 H, m, 8 × Ar-H$_o$ and 4 × Ar-H$_p$), 8.29 (4 H, d, J 1.7, Ar-H$_o$), 8.80 (2 H, br s, imidazo H), 9.20 (4 H, s, satellites $^4J_{\text{H–Sn}}$ 10.0, β-pyrrolic H-12 and H-13) and 9.18–9.28 (8 H, m, β-pyrrolic H); δ_{Sn} (149 MHz; CDCl$_3$; SnMe$_4$) −573.4 (Sn); m/z (MALDI-TOF) 2690.2 [(M − OH)$^+$ requires 2689.3].

Diacetato(5,10,15,20-tetraphenylporphyrinato)tin(IV) 26

Acetic acid (0.040 cm^3, 0.65 mmol) was added to dihydroxo-[5,10,15,20-tetraphenylporphyrinato]tin(IV) **3** (126 mg, 0.164 mmol) in chloroform (10 cm^3) and stirred for 35 min. The reaction mixture was then passed through a plug of anhydrous sodium sulfate, the organic solvent was removed to give the crude product, which was then recrystallised (hexane–dichloromethane, 1 : 1) to give diacetato(5,10,15,20-tetraphenylporphyrinato)tin(IV) **26** (76.6 mg, 53%) as a violet crystalline solid, mp >300 °C. This compound had identical ^{1}H NMR spectroscopic properties to those reported by Arnold.[6] δ_{H} (200 MHz; CDCl$_3$; SiMe$_4$) −1.03 (6 H, s, CH$_3$), 7.77–7.85 (12 H, m, Ar-H), 8.30–8.34 (8 H, m, Ar-H) and 9.19 (8 H, s, satellites $^4J_{\text{H–Sn}}$ 14.8, β-pyrrolic H); m/z (MALDI-TOF) 790.6 [(M − CH$_3$COO)$^+$ requires 790.4].

Dibenzoato(5,10,15,20-tetraphenylporphyrinato)tin(IV) 27

Dihydroxo(5,10,15,20-tetraphenylporphyrinato)tin(IV) **3** (100 mg, 0.13 mmol) was dissolved in chloroform (10 cm^3) and benzoic acid (40.3 mg, 0.33 mmol) was added and the mixture stirred for 20 min. The mixture was passed through a plug of anhydrous sodium sulfate and the solvent was removed to give the crude product which was then recrystallised (hexane–dichloromethane, 1 : 1) to give dibenzoato(5,10,15,20-tetraphenylporphyrinato)tin(IV) **27** (83 mg, 65%) as a purple microcrystalline solid, mp >300 °C. This compound had identical ^{1}H NMR spectroscopic properties to those reported by Arnold.[6] δ_{H} (200 MHz; CDCl$_3$; SiMe$_4$) 4.87–4.93 (4 H, m, Ar-H$_o$), 6.29–6.36 (4 H, m, Ar-H$_m$), 6.64–6.67 (2 H, m, Ar-H$_p$), 7.77–7.84 (12 H, m, Ar-H), 8.23–8.25 (8 H, m, Ar-H) and 9.19 (8 H, s, satellites $^4J_{\text{H–Sn}}$ 16.2, β-pyrrolic H); m/z (MALDI-TOF) 853.1 [(M − C$_6$H$_5$COO)$^+$ requires 852.3].

Hydrolysis of diacetato(5,10,15,20-tetraphenylporphyrinato)-tin(IV) 26

Diacetato(5,10,15,20-tetraphenylporphyrinato)tin(IV) **26** (48.4 mg, 54.9 µmol) and potassium carbonate (330 mg, 2.4 mmol) were dissolved in a mixture of tetrahydrofuran (40 cm^3) and water (10 cm^3) and heated at reflux for 2 h. The solvent was evaporated and the aqueous layer was extracted with dichloromethane (2 × 40 cm^3). The organic layer was washed with water (2 × 40 cm^3) and the organic layer was dried over anhydrous sodium sulfate, filtered and evaporated to give the crude product, which was then recrystallised (hexane–dichloromethane, 1 : 1) to give dihydroxo(5,10,15,20-tetraphenylporphyrinato)-tin(IV) **3** (33.1 mg, 77%) which had identical spectroscopic properties to that reported above.

Hydrolysis of dibenzoato(5,10,15,20-tetraphenylporphyrinato)-tin(IV) 27

Dibenzoato(5,10,15,20-tetraphenylporphyrinato)tin(IV) **27** (52 mg, 53.4 µmol) and potassium carbonate (360 mg, 2.6 mmol) were dissolved in tetrahydrofuran (40 cm^3) and water (10 cm^3) and heated at reflux for 2 h. The organic solvent was evaporated and the aqueous layer was extracted with dichloromethane (2 × 40 cm^3). The organic layer was washed with water (2 × 40 cm^3), dried over anhydrous sodium sulfate, filtered and the solvent removed to give the crude product, which was then recrystallised (hexane–dichloromethane, 1 : 1) to give dihydroxo(5,10,15,20-tetraphenylporphyrinato)tin(IV) **3** (34.7 mg, 84%) which had identical spectroscopic properties to that reported above.

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