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# Synthesis of *meso*-substituted porphyrins carrying carboranes and oligo(ethylene glycol) units for potential applications in boron neutron capture therapy †

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Selective delivery of $^{10}$B to tumours is one of the major remaining problems in boron neutron capture therapy (BNCT) of cancer. Porphyrins are selectively accumulated in tumours. Thus two series of carborane-carrying porphyrins were constructed, with additional functionality for attachment of uncharged potentially water-solubilising polyethers. 3-(1,2-Dicarba*closo*dodecaboran(12)-1-ylmethoxy)benzaldehyde was prepared by protection of the aldehyde of 3-(prop-2-ynyloxy)benzaldehyde as a dithioacetal, treatment with decaborane(14) and deprotection. Condensation with a 3-nitrophenyldipyrromethane gave a separable mixture of *meso*-(3-nitrophenyl)-*meso*-(3-carboranylmethoxyphenyl)porphyrins, resulting from extensive scrambling at the porphyrinogen stage. Similarly, condensation of 3-(1,2-dicarba*closo*dodecaboran(12)-1-yl)benzaldehyde with this dipyrromethane gave an analogous mixture of *meso*-(3-nitrophenyl)-*meso*-(3-carboranylphenyl)porphyrins. In this second series, the two regioisomeric bis(nitrophenyl)bis(carboranylphenyl)porphyrins could only be distinguished by X-ray crystallography, their NMR spectra being identical. The nitro groups of the mono(nitrophenyl)porphyrins and the bis(nitrophenyl)-porphyrins were reduced to the corresponding amines with tin(II) chloride and the monoamines were coupled with a ω-methoxy poly(ethylene glycol) chloroformate of mean MW 600 to give the MeOPEGylated tricarboranyl porphyrins.

## Introduction

Boron neutron capture therapy (BNCT) is under active investigation for the treatment of various cancers, notably gliomas and melanomas.[1] When the $^{10}$B isotope is irradiated with slow ('thermal') neutrons, an [*n*,α] reaction ensues, giving $^{7}$Li and $^{4}$He nuclei with kinetic energy (2.31 MeV). With this energy, the α-particle has a range of *ca*. one cell diameter in biological tissue and damage is limited to the cell containing the boron. Early clinical failures of BNCT were attributed[2] to inadequate concentrations of $^{10}$B in the tumour tissue or to lack of selectivity of disposition of $^{10}$B, leading to damage to normal tissue. Thus one of the remaining major issues in BNCT is the development of water-soluble boron-containing drugs that are selectively taken up or retained by tumours. Carboranes have been linked *inter alia* to nucleosides[3] and to nitroimidazoles[4,5] in attempts to target boron selectively to tumours.

The selective accumulation of porphyrins in tumours was first observed in the 1940s.[6] However, the first porphyrins carrying multiple borons (*meso*-tetrakis(*closo*-1,2-dicarbadodecaboran-(12)ylmethyl)- and *meso*-tetrakis(*nido*-1,2-dicarbaundecaboran-(12)ylmethyl)- porphyrins) were synthesised in the late 1970s by Haushalter and Rudolph[7] as catalysts for reversible multi-electron reductions. The use of porphyrins as boron carriers for BNCT arose from the photodynamic therapy studies of Dougherty[8] in 1983. Since then, several groups have prepared porphyrins carrying clusters of boron and have evaluated them in the context of BNCT. The early boron-carrying porphyrins were β-substituted *meso*-free derivatives of haem, such as BOPP **1**[9] and VCDP **2**[10] (Fig. 1). In these compounds, the lipophilicity of the *closo*carboranes and the porphyrin ring is counteracted by formation of salts of the carboxylic acids to aid water-solubility; in the latter, the carborane cages have also been degraded to the anionic *nido* clusters. Later, synthetic and biological studies were reported[11] on a *meso*-tetraphenylporphyrin with *nido*-carboranes linked to the phenyls though amides (**3**, Fig. 2). More recently, ether linkages between the carboranylmethyl unit and the phenyl of the TPP were used by Miura *et al.*[12] in carborane–porphyrin constructs **4**; in these, the water-solubility is provided by eight carboxylates and unwanted photosensitisation was suppressed by metallation. This group have also reported[13] analogous constructs **5** in which four *nido*carboranes are linked through ethers to TPP; these lack the β-acetic acids of **4**. In general, the boron-carrying TPP derivatives present less problems of toxicity than the haem derivatives and have been most successful in biodistribution studies *in vivo*. However, all of these carborane–porphyrin constructs rely on their anionic nature for solubility in water; this may adversely influence their intracellular biodistribution (accumulation near polyanionic DNA is optimum for BNCT[14]). Thus we sought to pursue other, non-ionic approaches to solubilising carborane–TPP constructs.

Our principal synthetic targets were the porphyrins **6** and **7** (Fig. 3), which carry multiple carboranes and one poly(ethylene glycol) unit. The carboranes are attached either through an ether linkage or through a direct carbon–carbon bond between the carborane and the phenyl of the TPP. The ω-methoxyPEG is designed as a non-ionic non-toxic water-solubilising group[15] for these constructs and, for ease of synthesis,[16] we chose to attach it *via* a carbamate to the carboranyl TPP.

† Electronic supplementary information (ESI) available: experimental details for the synthesis of compounds **12**–**15**, **31** and **32**. See http://www.rsc.org/suppdata/ob/b2/b209534c/

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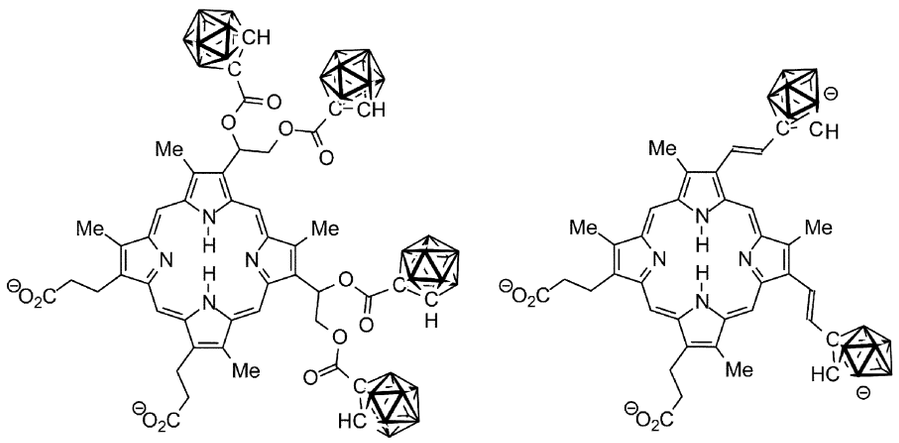



**Fig. 1** Structures of anionic β-linked carboranylporphyrins BOPP **1** and VCPP **2**, as reported by Fairchild *et al.*[9] and Miura *et al.*[10].

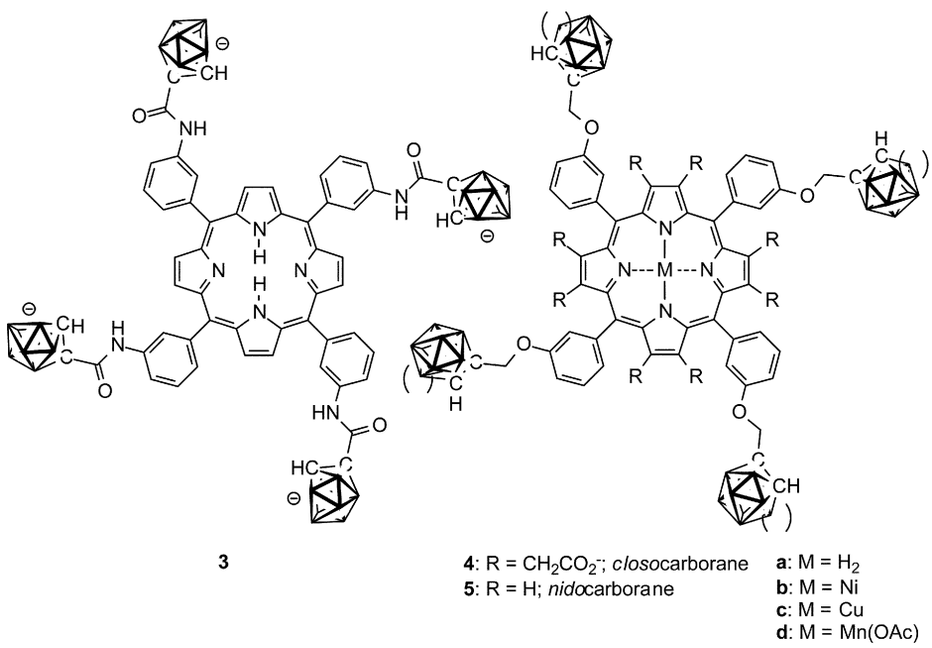



**Fig. 2** Structures of anionic *meso*-linked carboranylporphyrins **3**–**5**, as reported by Kahl *et al.*[11] and Miura *et al.*[12,13].

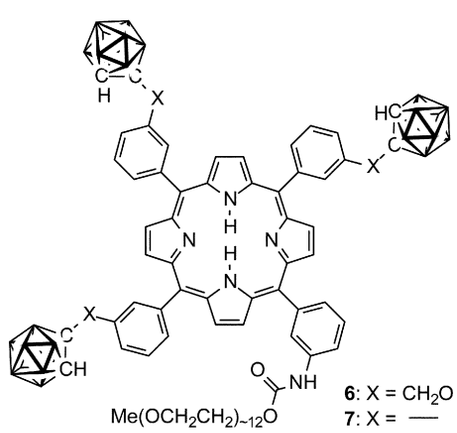
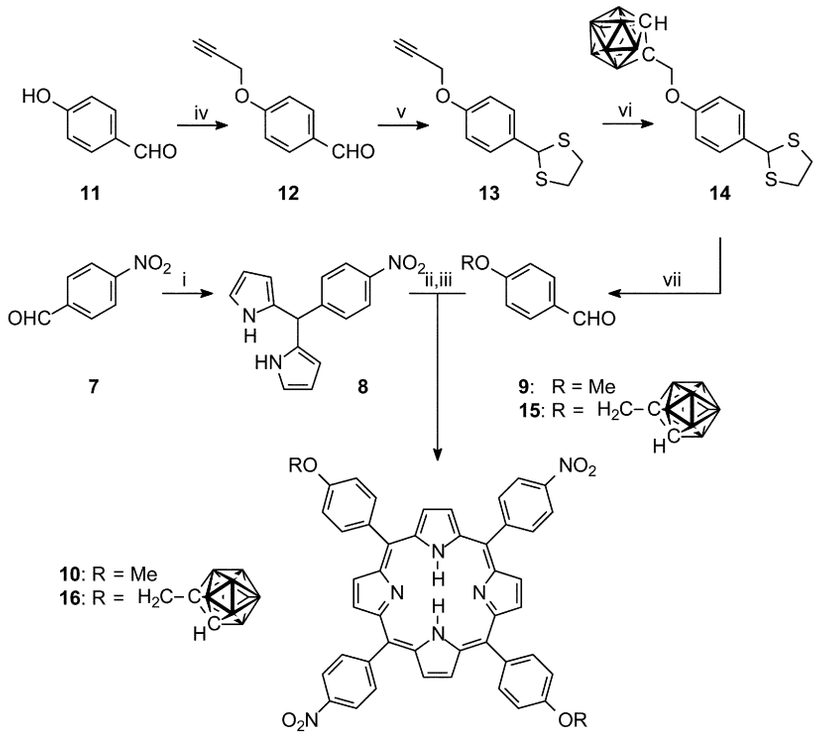



**Fig. 3** Structures of target neutral carboranylporphyrins **6**,**7**, carrying polyethers.

## Results and discussion

Thus the first targets were the tris(carboranylmethoxy)-porphyrin monoamines and the corresponding bis(carboranylmethoxy)porphyrin diamines. Initial experiments were designed to approach the 4-substituted TPP derivatives (Scheme 1). As a model for the assembly of porphyrins carrying nitrophenyl and alkoxyphenyl *meso*-substituents by the Lindsey 2 + 2 route,[17] condensation of the 4-nitrophenyldipyrromethane **8** with 4-methoxybenzaldehyde **9** was investigated. Condensation of 4-nitrobenzaldehyde **7** with excess pyrrole in the presence of trifluoroacetic acid gave the dipyrromethane **8** in high yield. This compound was remarkably stable to storage, unlike many other dipyrromethanes, remaining essentially undecomposed after 3 months at 4 °C. Condensation with 4-methoxybenzaldehyde **9** in the presence of boron trifluoride as a Lewis acid, followed by oxidation of the mixture of porphyrinogens with DDQ, gave the correct di(4-methoxyphenyl)di(4-nitrophenyl)-porphyrin **10** in 40% yield with little scrambling of the substituted arenes around the porphyrin core. Scrambling often occurs in condensations of dipyrromethanes with aldehydes, owing to the establishment of equilibria between acidolytic cleavage reactions and re-condensations.[18] In the light of this excellent yield of **10**, the process was extended to the assembly of the analogous ether-linked carborane–porphyrin **16**. The 1,2-dicarba*closo*dodecaborane(12) ("carborane") structure is most conveniently prepared by reaction of a terminal alkyne with decaborane(14) in the presence of a Lewis base, such as acetonitrile. The anion of 4-hydroxybenzaldehyde **11** was alkyl-



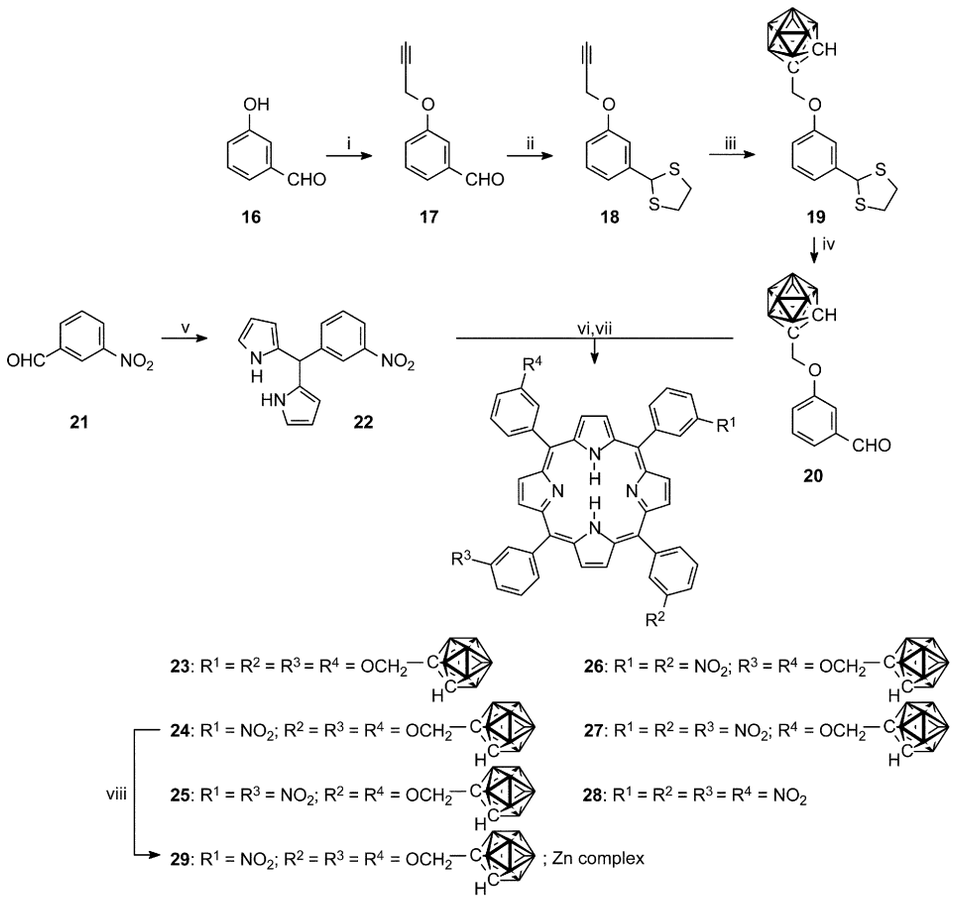

**Scheme 1** Syntheses of 5,15-bis(4-nitrophenyl)-10,20-bis(4-methoxyphenyl)porphyrin **10** and 5,15-bis(4-nitrophenyl)-10,20-bis[4-(carboranylmethoxy)phenyl]porphyrin **16**. *Reagents and conditions*: i, pyrrole (70 equiv.), $CF_3CO_2H$, $CH_2Cl_2$, Ar, 87%; ii, $BF_3.OEt_2$, $CHCl_3$; iii, DDQ, $CHCl_3$, 40% (**10**), 0.5% (**16**); iv, NaOEt, $BrCH_2C{\equiv}CH$, EtOH, reflux, 70%; v, $HSCH_2CH_2SH$, $BF_3{\cdot}OEt_2$, $CH_2Cl_2$, 83%; vi, $B_{10}H_{14}$, dry MeCN, reflux, 47%; vii, $Hg(ClO_4)_2{\cdot}H_2O$, THF, 76%.

ated with propargyl bromide, giving the ether **12** in good yield. Many functional groups are sensitive to decaborane(14),[5,19] since it is a Lewis acid and a powerful reducing agent. Aldehydes and acetals are amongst these sensitive groups, so the aldehyde function was protected as the dithioacetal **13**. Now the carborane **14** could be constructed in the relatively good yield of 47%. Rapid deprotection, catalysed by $Hg^{2+}$, gave the required 4-(carboranylmethoxy)benzaldehyde **15**. Surprisingly, in contrast to the good yield and low scrambling achieved for the model compound **10**, condensation of the (4-nitrophenyl)dipyrromethane **8** with **15** under a variety of conditions resulted in extensive scrambling and formation of only a trace (0.5%) of the target dicarborane–porphyrin **16**; indeed, this material was only formed in sufficient amount for characterisation by HRMS.

Rationalising that electronic effects from the *para*-substituents may be responsible for instability of the intermediate polypyrranes and thus for the very low yield of **16**, the effect of moving the nitro and carboranylmethoxy groups to the positions *meta* to the point of attachment to the porphyrin was investigated (Scheme 2). *Meta*-substituents may also decrease the potential for π-stacking of the target carboraneporphyrins and contribute to their solubility. Using methods analogous to those for the preparation of the *para*-substituted series, 3-hydroxybenzaldehyde **16** was propargylated and the aldehyde **17** was protected as the dithioacetal **18**. The carborane **19** was constructed in the very good yield of 58%, under the usual conditions ($B_{10}H_{14}$, boiling MeCN) and the aldehyde **20** was revealed by treatment with mercury(II) perchlorate. Similarly, condensation of 3-nitrobenzaldehyde **21** with excess pyrrole gave the (3-nitrophenyl)dipyrromethane **22** in high yield. Now, condensation of **22** with **20** in the presence of boron trifluoride gave a mixture of porphyrins in good total yield. Thus the scrambling observed with the *para*-series was maintained in the *meta*-series but the yield was greatly enhanced. Careful chromatography allowed the isolation of five porphyrins from the product mixture; the sixth (and most polar) was identified as the 5,10,15,20-tetrakis(3-nitrophenyl)porphyrin **28** only by chromatographic comparison with an authentic sample. The first porphyrin (2% yield) to be eluted was readily identified as the 5,10,15,20-tetrakis(3-carboranylmethoxyphenyl)porphyrin **23** by NMR spectroscopy. As expected, the carborane 2-H signal was observed at $\delta$ 4.17 and the carborane B–H signals appeared as a broad 1 : 1 : 1 : 1 quartet at $\delta$ 2.6 with $^1J_{B-H}$ 150 Hz. The $^1H$ and $^{13}C$ NMR spectra also reflected the high symmetry of this porphyrin. The 5-(3-nitrophenyl)-10,15,20-tris(3-carboranylmethoxyphenyl)porphyrin **24** was then isolated in 14% yield; this was also converted to its zinc complex **29**. The two regioisomeric bis(carboranylmethoxyphenyl)bis(nitrophenyl)porphyrins **25** and **26** were separable by very careful and repeated chromatography.

Identification of these compounds was achieved by consideration of their symmetries with respect to their $^1H$ NMR spectra. The presence of two orthogonal planes of symmetry in **25** suggests that the porphyrin β-protons are in only two magnetic environments, either adjacent to a *meso*-nitrophenyl or a *meso*-carboranylmethoxyphenyl group. Fortunately, in this case, the two types of *meso*-substituent are electronically significantly different and the two sets of signals are distinct, forming two doublets at $\delta$ 8.76 and $\delta$ 8.89 ($J$ 4.9 Hz). Assuming free rotation about the porphyrin–phenyl bond, porphyrin **26** has only one plane of symmetry (in addition to the porphyrin plane) and thus its β-protons would be expected to resonate in four magnetically inequivalent groups. In practice, these are observed as doublets ($J$ 4.9 Hz) at $\delta$ 8.77 and $\delta$ 8.97 and singlets at $\delta$ 8.79 and $\delta$ 8.87. Porphyrins **25** and **26** were each formed in 9% yield. Finally, the mono(carboranylmethoxyphenyl)tris(nitrophenyl)porphyrin **27** was isolated in 2% yield.

Carborane–porphyrins **23**–**27** have an ether link between the carborane and the tumour-targeting porphyrin core; such a link may possibly be metabolically labile. Thus analogous porphyrins **7** with the carboranes directly linked by carbon–carbon bonds to the porphyrin core were investigated. We have previously reported the direct coupling of 1,2-dicarba*closo*-dodecaboran(12)-1-yl copper(I) with a TPP–zinc complex carrying iodine in the *para* position of one of the phenyl rings.[20]

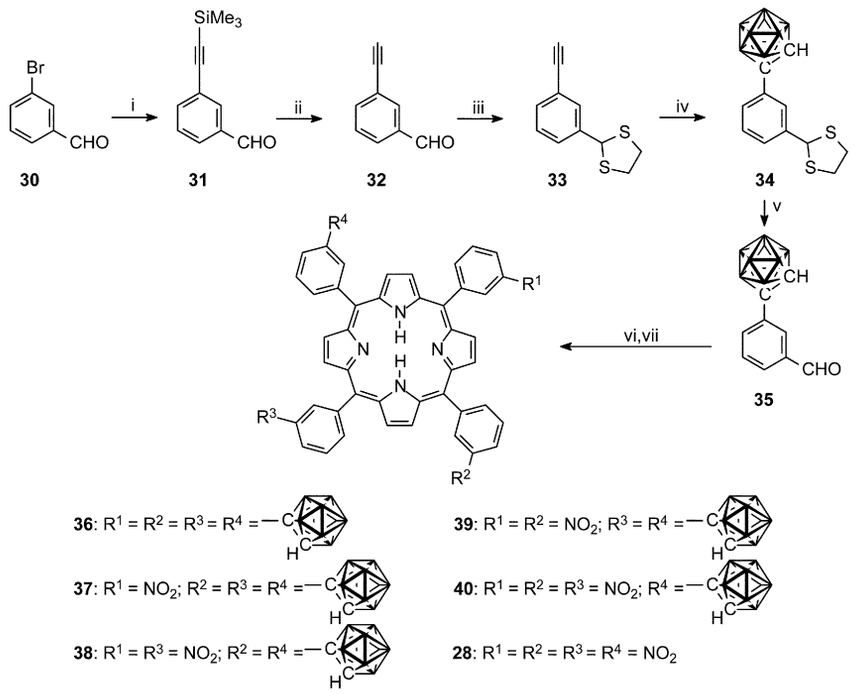



**Scheme 2** Syntheses of ether-linked *meso*-(3-nitrophenyl)-*meso*-[3-(carboranylmethoxy)phenyl]porphyrins. *Reagents and conditions*: i, NaOEt, $BrCH_2C{\equiv}CH$, EtOH, reflux, 78%; ii, $HSCH_2CH_2SH$, $BF_3{\cdot}OEt_2$, $CH_2Cl_2$, 55%; iii, $B_{10}H_{14}$, dry MeCN, reflux, 58%; iv, $Hg(ClO_4)_2{\cdot}H_2O$, THF, 81%; v, pyrrole (70 equiv.), $CF_3CO_2H$, $CH_2Cl_2$, Ar, 74%; v, $BF_3{\cdot}OEt_2$, $CH_2Cl_2$; vii, DDQ, $CH_2Cl_2$, 2% (**23**), 14% (**24**), 9% (**25**), 9% (**26**), 2% (**27**); viii, $Zn(OAc)_2$, AcOH, reflux, 71%.

However, this process gave a coupling yield of only 8% after 12 d in boiling bis(2-methoxyethyl)ether; thus a similar coupling with a tris(iodophenyl)porphyrin is likely to give <0.1% overall yield, even under these highly forcing conditions. Lacking a suitable methodology for this direct attachment of the boron cages after the assembly of the porphyrin macrocycle, a route involving condensation of a carboranylbenzaldehyde with a nitrophenyldipyrromethane was again employed. Sonogashira coupling of trimethylsilylethyne with 3-bromobenzaldehyde **30** gave the protected intermediate **31** in good yield but deprotection was more troublesome, affording the required 3-ethynylbenzaldehyde **32** in moderate yield through treatment with potassium carbonate in methanol, as shown in Scheme 3. Other deprotection systems were less effective. As with the ether-linked series above, it was necessary to protect the aldehyde function as a dithioacetal during the construction of the carborane. Thus the dithioacetal **33**, carrying the alkyne, was converted to the corresponding carborane **34** efficiently using decaborane(14) in boiling acetonitrile. As before, deprotection was achieved with mercury(II) perchlorate in wet tetrahydrofuran, giving the 3-carboranylbenzaldehyde **35**. 2 + 2 Cyclocondensations of **35** with the nitrophenyldipyrromethane **22** were investigated, using boron trifluoride or trifluoroacetic acid as catalysts. The optimum yield of porphyrins was achieved with the former catalyst but at the expense of extensive scrambling. The reaction was optimised by variation of the concentration and of the reaction time for the initial equilibrating condensations before the mixed porphyrinogens were oxidised to porphyrins, terminating the equilibration. Chromatography allowed the isolation of the expected range of porphyrins: the tetracarboranylporphyrin **36** (2%), the mononitro tricarboranyl porphyrin **37** (18%), the trinitro monocarboranyl porphyrin **40** (1%) and a mixture of the regioisomeric dinitro dicarboranyl porphyrins **38** and **39**. The latter mixture was separated by repeated chromatography, giving the 5,15-bis(4-nitrophenyl) compound **38** in 10% yield and the 5,10-bis(4-nitrophenyl) isomer **39** (9%), giving a total isolated yield of carboranylporphyrins of 40%, in addition to identification of a trace of the tetra(nitrophenyl)porphyrin **28** in the crude product mixture.

As in the ether-linked series, the tetracarborane **36**, the mononitro tricarboranyl porphyrin **37** and the trinitro monocarboranyl porphyrin **40** were readily characterised by $^1H$ and $^{13}C$ NMR spectroscopy, although it was notable that the effects of the 3-nitrophenyl and 3-carboranylphenyl *meso*-substituents on the chemical shifts of the adjacent β-protons were identical. For **37**, the 2,3,7,8,12,13,17,18-protons resonated as one singlet at $\delta$ 8.80 and in the spectrum of **40**, the corresponding singlet was at $\delta$ 8.81. Since the regiochemical assignment of the ether-linked analogues **25** and **26** above was based on the differences in electronic effect of the two types of *meso*-substituent and the corresponding effects are apparently identical in the directly linked series here, it could be predicted that regioisomeric assignment of **38** and **39** would be challenging. Indeed the $^1H$ spectra of these compounds were identical and superimposable. Moreover, the $^{13}C$ spectra were very similar and could not be used predictively.

A crystal of the less-polar regioisomer was grown by slow evaporation from a solution in a chloroform–hexane mixture. X-Ray analysis confirmed that the structure was the symmetrical 5,15-bis(3-nitrophenyl)-10,20-bis(3-carboranylphenyl)porphyrin **38**. The structure of **38** was notable in several respects. Firstly, it is the first report of the structure of a metal-free carbon-linked carboranylporphyrin; a previous report[21] was of a structure where the carborane was linked to the




**Scheme 3** Syntheses of directly linked *meso*-(3-nitrophenyl)-*meso*-(3-carboranyl)phenylporphyrins. *Reagents and conditions*: i, $Et_3N$, $Pd(OAc)_2$, $PPh_3$, $Me_3SiC{\equiv}CH$, reflux, 72%; ii, $K_2CO_3$, MeOH, 58%; iii, $HSCH_2CH_2SH$, $BF_3{\cdot}OEt_2$, $CH_2Cl_2$, 52%; iv, $B_{10}H_{14}$, dry MeCN, reflux, 57%; v, $Hg(ClO_4)_2{\cdot}H_2O$, THF, 97%; vi, $BF_3{\cdot}OEt_2$, $CH_2Cl_2$; vii, DDQ, $CH_2Cl_2$, 2% (**36**), 18% (**37**), 10% (**38**), 9% (**39**), 1% (**40**).

*meso*-phenyl through a $CH_2$ and the porphyrin contained a central zinc. Both of these features will affect the rigidity and thus the conformation of the molecule. Clearly, whereas Vicente *et al.*[21] observed intermolecular co-ordination of a B–H hydrogen to the zinc of an adjacent porphyrin, such co-ordination is unavailable to porphyrin **38**. Secondly, the crystal contains two different atropisomers of **38**. Approximately 80% of the molecules have the α,α,β,β conformation shown in Fig. 4,

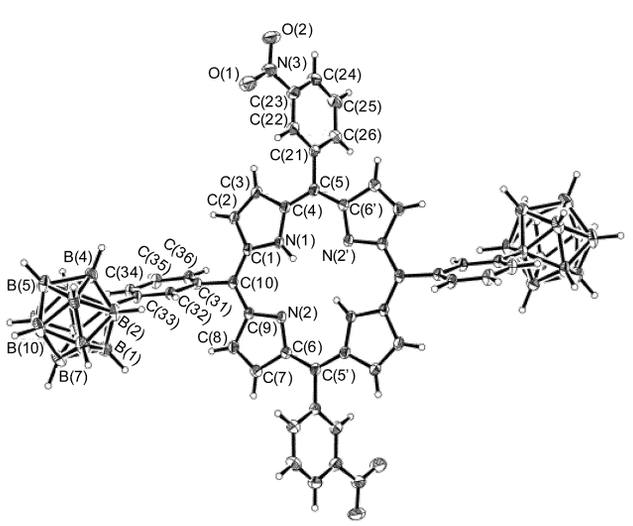



**Fig. 4** Crystal structure of 5,15-bis(3-nitrophenyl)-10,20-bis(3-carboranylphenyl)porphyrin **38**.

whereas 20% have the α,α,α,β conformation where the α-carborane is flanked by two α-nitro substituents (Fig. 5). No molecules have both carboranes on the same face. Thirdly, in the major atropisomer, the porphyrin ring is deformed out of plane in the regions of the carboranylphenyl substituents but not in the other *meso* regions bearing the nitrophenyl groups. For example, near the carboranylphenyl *meso* position, the dihedral angle N(2)–C(9)–C(10)–C(1) is −3.9°, N(2)–C(9)–C(10)–C(31) is +173.0°, C(8)–C(9)–C(10)–C(31) is −6.2°, C(8)–C(9)–C(10)–C(1) is +176.0°, N(1)–C(1)–C(10)–C(9) is −7.7°, N(1)–C(1)–C(10)–C(31) is +170.2°, C(2)–C(1)–C(10)–C(31) is −9.3° and C(2)–C(1)–C(10)–C(9) is +172.9°. By contrast, near the carboranylphenyl *meso* position, the dihedral angle N(1)–C(4)–C(5)–C(6) is +2.2°, N(1)–C(4)–C(5)–C(21) is −179.7°, C(3)–C(4)–C(5)–C(6) is −177.0°, C(3)–C(4)–C(5)–C(21) is +1.2° and N(2)–C(6)–C(5)–C(4) is +1.6°. Fourthly, the phenyl rings, as expected, are not in the plane of the porphyrin. The dihedral angle between the porphyrin and the carborane-carrying phenyl ring is illustrated by the C(1)–C(10)–C(31)–C(36) angle which is +71.2°. The corresponding angle at the *meso* position carrying the nitrophenyl unit is C(6)–C(5)–C(21)–C(26), which is +84.4°. Thus the substituent on the phenyl has an effect on this twist angle. Fifthly, the carborane is ordered with respect to the orientation of its C–H bond. The dihedral angle to this carborane C–H, C(34)–C(33)–C(41)–C(42), is +36.8°.

The observation of atropisomers in the crystal helps rationalisation of phenomena in the $^1$H NMR spectra. As noted above, the highly symmetrical tetracarborane–porphyrin **36** gives a sharp $^1$H NMR spectrum in $CDCl_3$ at 20 °C, in which the 2,3,7,8,12,13,17,18-protons gave a singlet at $\delta$ 8.80, suggesting either that only one atropisomer is present (presumably the least crowded α,β,α,β,atropisomer) or that the atropisomers of this compound are in rapid equilibrium at this temperature. This contrasts markedly with the NMR spectrum reported by Vicente *et al.*[21] for this compound in the same solvent. These authors report multiple signals for these protons and suggest that the presence of slowly interconverting atropisomers may be responsible; they also report coalescence of these signals at 50 °C. However, in the proton NMR spectrum of **38**, it was notable that the resonances for the phenyl rings bearing the nitro groups were sharp at 25 °C, whereas those for the carborane-carrying phenyls were markedly broader. These signals sharpened upon heating to 50 °C, indicating the presence of slowly interconverting atropisomers at the lower temperature. Atropisomers are well known in the cases of porphyrins carrying *ortho*-substituents on the *meso*-phenyl rings.[22] Such atropisomers are separable and do not usually interconvert at room temperature, requiring >100 °C for rapid equilibration. Atropisomers from *meta*-substituted *meso*-phenylporphyrins normally interconvert much more rapidly,[23] as there would be much less steric clash between the substituent and the adjacent porphyrin β-proton

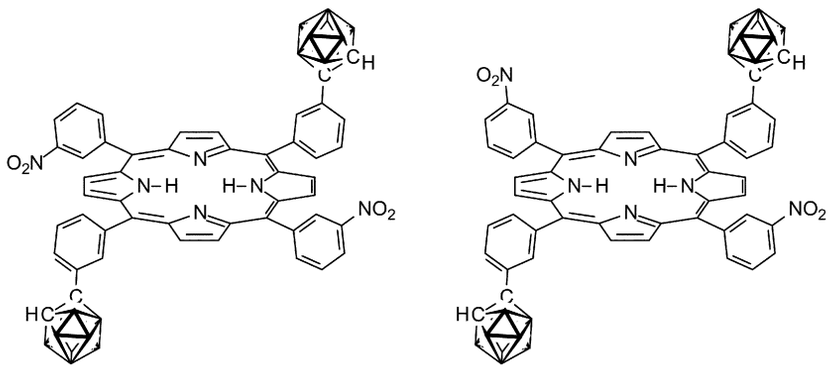



**Fig. 5** Structures of the α,α,β,β and α,α,α,β atropisomers of 5,15-bis(3-nitrophenyl)-10,20-bis(3-carboranylphenyl)porphyrin **38**.

during rotation about the porphyrin–phenyl bond. However, the carborane represents a locally very bulky substituent and this may lead to a higher energy barrier to rotation between atropisomers than is normal for *meta* substitution.

To provide a point of attachment for the poly(ethylene glycol) units, the nitro groups of the nitrophenyl carboranyl porphyrins were reduced to amines. 5-(4-Nitrophenyl)-10,15,20-triphenylporphyrin **41** was synthesised by nitration of *meso*-tetraphenylporphyrin and, as shown in Scheme 4, was reduced to the corresponding amine **42** with tin(II) chloride in boiling hydrochloric acid, as previously reported by us.[20,24] This process also successfully reduced the nitro groups of the bis-(4-nitrophenyl)bis(4-methoxyphenyl)porphyrin **10** to give the diamine **43** in moderate yield. However, this process was ineffective for the carborane-bearing porphyrins, largely owing to their limited solubility in aqueous media. However, reduction of the mono(nitrophenyl) tris(carboranylmethoxyphenyl) porphyrin **24** with the same reductant in acetic acid was successful in giving the required monoamine **44** in 72% yield. A similar reaction converted the mono(nitrophenyl)tris(carboranylphenyl)porphyrin **37** to the analogous amine **47**. An alternative reduction, a transfer hydrogenation with cyclohexene in the presence of Raney nickel, only afforded a 14% yield of **44**. Owing to the difficulty in separating individual dinitro regioisomers from the pairs **25/26** and **38/39**, the nitro to amine reductions were carried out on equimolar mixtures of isomers. After reduction with tin(II) chloride in hydrochloric acid by prolonged treatment at ambient temperature, the symmetrical diamine **45** could be separated readily by chromatography from its less symmetrical isomer **46**. Similarly, the product mixture from **38/39** was separated to give the required diamines **48** and **49** in high yields.

Since we have previously noted that the amines of *meso*-(4-aminophenyl)porphyrins are relatively weak nucleophiles,[24] the formation of the carbamate link between the aminophenylporphyrins and the PEG unit was tested in a model system (Scheme 4). Poly(ethylene glycol) monomethyl ether of mean MW 550 Da (MeOPEG550) was selected as a suitable polyether mono-alcohol and was converted to the corresponding chloroformate by treatment[16] with phosgene in dichloromethane. Whereas the *meso*-(4-aminophenyl)porphyrin **42** required prolonged treatment with "active" esters to achieve efficient acylation,[24] the MeOPEG550 chloroformate reacted rapidly with this amine to give the MeOPEGylated derivative **50** in excellent yield, after chromatography to separate it from excess polyether. Similar high yields were obtained in couplings of the MeOPEG550 chloroformate with **44** (giving **51**) and **45** (giving **52**). Considerable difficulty was experienced in separating **51** and **52** from excess polyether. The FAB mass spectra of **50**–**52** showed the expected distribution of *pseudo*molecular ions corresponding to the mixture of MeOPEG oligomers present. Fig. 6 illustrates part of the FAB negative ion mass spectrum of **52**;

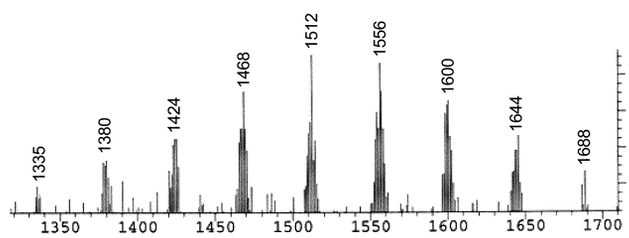



**Fig. 6** Part of the FAB negative ion mass spectrum of mono-(MeOPEG) tricarboranyl porphyrin **52**. The individual clusters correspond to the *pseudo*molecular ions of the different MeOPEG oligomers present whereas the envelope of each individual cluster corresponds to the statistical distribution of the $^{11}B$ and $^{10}B$ isotopes present at natural abundance.

the individual clusters correspond to the different MeOPEG oligomers present whereas the envelope of each individual cluster corresponds to the statistical distribution of the $^{11}B$ and $^{10}B$ isotopes present at natural abundance. Surprisingly, the individual oligomers of **51** and **52** were separable by thin layer chromatography on silica gel (Fig. 7); selected oligomers of **51**

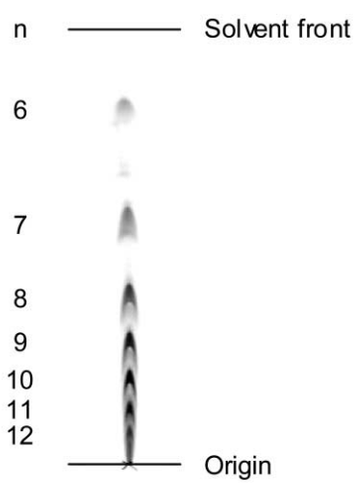
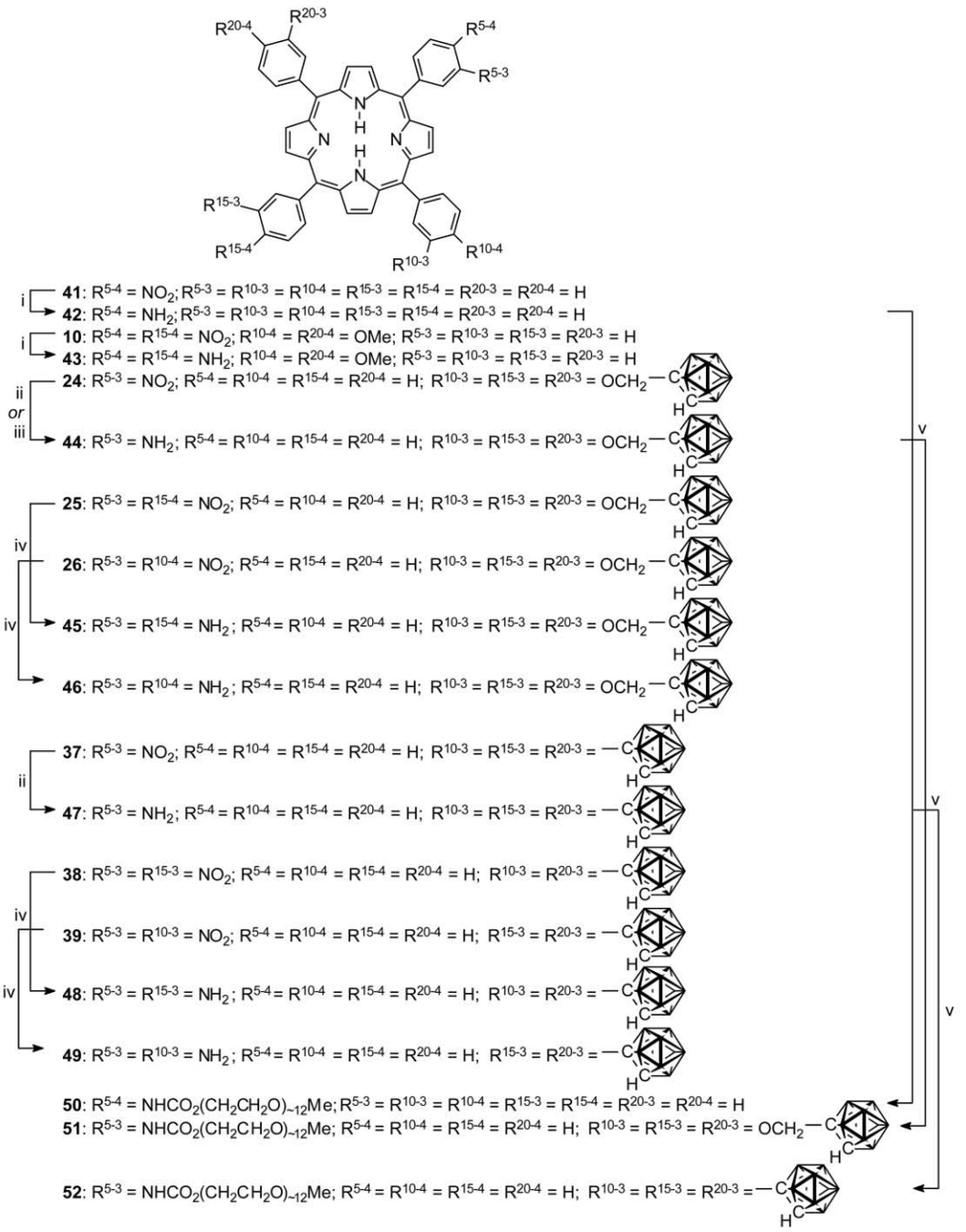



**Fig. 7** Thin layer chromatogram (silica gel, ethyl acetate) of the mono(MeOPEG) tricarboranyl porphyrin **52**. Each spot corresponds to an individual oligomer of the MeOPEG unit. *n* refers to the number of oxyethylene units in the oligomers $(MeO(CH_2CH_2O)_nCOHNPh)$-$(carboranylphenyl)_3$porphyrin.

were characterised by mass spectrometry. Straightforward chromatographic separation of PEG oligomers (of more than five repeating $OCH_2CH_2$ units) is unusual and this observation may point to a potential method for fractionating PEG derivatives into individual oligomers. In contrast, the reactions of the diamines **43**, **45**, **48** and **49** gave rise to intractable mixtures of MeOPEGylated porphyrins and unreacted MeOPEG derivatives.




**Scheme 4** Reduction of *meso*-(nitrophenyl)porphyrins and attachment of the polyether units. *Reagents and conditions*: i, $SnCl_2$, aq. HCl, 65 °C, 84% (**42**), 56% (**43**); ii, $SnCl_2$, AcOH, 72% (**44**), 39% (**47**); iii, Raney Ni, cyclohexene, MeOH, 14%; iv, $SnCl_2$, aq. HCl, 76% (**45**), 76% (**46**), 80% (**48**), 72% (**49**); v, $Et_3N$, $MeO(CH_2CH_2O)_{\sim 12}COCl$, 4-dimethylaminopyridine, $CHCl_3$, 99% (**50**), 96% (**51**), 90% (**52**).

## Conclusions

In this paper, we report the synthesis of two porphyrins **51** and **52** carrying methoxyPEG units and three carboranes, these compounds having potential for the selective delivery of boron to tumours for use in BNCT. Although the additional aqueous solubility conferred by the MeOPEG was very limited, these compounds are currently under investigation for their boron-delivering properties in experimental BNCT models. In the synthesis of these constructs, several *meso*-(aminophenyl)-*meso*-(carboranylphenyl) porphyrins were made available; these compounds have the amino functions available for attachment of alternative solubilising groups or tissue-targeting entities. Useful conformational and structural information for carboranylporphyrins is given by the first reported crystal structure of a metal-free carborane–porphyrin. We are actively pursuing these developments.

## Experimental

NMR spectra were recorded on samples in $CDCl_3$, unless otherwise stated. Mass spectra were obtained by fast atom bombardment (FAB) in the positive ion mode, unless otherwise stated. The stationary phase for chromatography was silica gel; column chromatography of porphyrins was performed at atmospheric pressure. Melting points are uncorrected. Solutions in organic solvents were dried with $MgSO_4$. Solvents were evaporated under reduced pressure. Experiments were conducted at ambient temperature, unless otherwise stated. The brine was saturated. The pyrrole was distilled from potassium hydroxide pellets under argon. †

### Di(pyrrol-2-yl)(4-nitrophenyl)methane 8

Trifluoroacetic acid (230 mg, 2.0 mmol) in dichloromethane (4.6 $cm^3$) was added to 4-nitrobenzaldehyde **7** (3.20 g, 20 mmol)

in pyrrole (freshly distilled under argon) (94 g, 1.4 mol) under Ar and the mixture was stirred for 20 min. Evaporation and recrystallisation (aq. methanol) gave **8** (4.65 g, 87%) as a pale yellow solid: mp 158–160 °C (lit.[25] mp 159–160 °C); $\delta_H$ 5.59 (1 H, m, methine-H), 5.87 (2 H, m, 2 × pyrrole 3-H), 6.18 (2 H, q, *J* 2.9 Hz, 2 × pyrrole 4-H), 6.75 (2 H, m, 2 × pyrrole 5-H), 7.37 (2 H, d, *J* 8.6 Hz, Ph 2,6-$H_2$), 8.01 (2 H, br s, 2 × NH), 8.17 (2 H, d, *J* 8.6 Hz, Ph 3,5-$H_2$); *m*/*z* 267 (*M* + H), 201 (M-pyrrole), 145 (M–$C_6H_4NO_2$).

### 5,15-Bis(4-methoxyphenyl)-10,20-bis(4-nitrophenyl)-21*H*,23*H*-porphine 10

Boron trifluoride diethyl etherate (2.5 $cm^3$, 20 mg $cm^{-3}$ in chloroform, 140 μmol) was added to **8** (118 mg, 440 μmol) and 4-methoxybenzaldehyde **9** (63 mg, 460 μmol) in chloroform (44 $cm^3$) and the mixture was stirred for 2 h. 2,3-Dichloro-5,6-dicyanobenzoquinone (100 mg, 440 μmol) was added and the mixture was stirred for 6 h. Evaporation and chromatography (hexane–dichloromethane 1 : 2) gave **10** (68 mg, 40%) as a dark purple powder: mp >350 °C; (Found: C, 70.30; H, 4.37; N, 10.50. $C_{46}H_{32}N_6O_6.H_2O$ requires C, 70.58; H, 4.37; N, 10.73%); $\delta_H$ −2.78 (2 H, s, 21,23-$H_2$), 4.11 (6 H, s, 2 × $OCH_3$), 7.31 (4 H, d, *J* 8.5 Hz, 2 × MeOAr 3,5-$H_2$), 8.12 (4 H, d, *J* 8.5 Hz, 2 × MeOAr 2,6-$H_2$), 8.40 (4 H, d, *J* 8.5 Hz, 2 × $O_2$NAr 2,6-$H_2$), 8.65 (4 H, d, *J* 8.5 Hz, 2 × $O_2$NAr 3,5-$H_2$), 8.75 (4 H, d, *J* 4.6 Hz, 2,8,12,18-$H_4$), 8.94 (4 H, d, *J* 4.6 Hz, 3,7,13,17-$H_4$); *m*/*z* 765 (*M* + H).

### 5,15-Bis[4-(1,2-dicarba*closo*dodecaborane(12)-1-ylmethoxyphenyl)]-10,20-bis(4-nitrophenyl)-21*H*,23*H*-porphine 16

Boron trifluoride diethyl etherate (0.9 $cm^3$, 20 mg. $cm^{-3}$ in chloroform, 120 μmol) was added to **8** (93 mg, 350 μmol) and **15** (108 mg, 350 μmol) in chloroform (35 $cm^3$). The solution was stirred for 80 min before 2,3-dichloro-5,6-dicyanobenzoquinone (80 mg, 350 μmol) was added. The mixture was stirred for a further 90 min. Evaporation and chromatography (hexane–dichloromethane 1 : 2) gave **16** (2 mg, 0.5%) as a purple powder: *m*/*z* 1053.6002 (*M* + H $^{13}C_1{}^{12}C_{49}H_{53}{}^{11}B_{19}{}^{10}B_1N_6O_6$ requires 1053.5957), 1052.5990 (*M* + H $^{13}C_1{}^{12}C_{49}H_{53}{}^{11}B_{18}{}^{10}B_2N_6O_6$ requires 1052.5994), 1051.5981 (*M* + H $^{12}C_{50}H_{53}{}^{11}B_{18}{}^{10}B_2N_6O_6$ requires 1051.5960), 1050.6031 (*M* + H $^{12}C_{50}H_{53}{}^{11}B_{17}{}^{10}B_3N_6O_6$ requires 1050.6000), 1049.6081 (*M* + H $^{12}C_{50}H_{53}{}^{11}B_{16}{}^{10}B_4N_6O_6$ requires 1049.6033), 1047.6070 (*M* + H $^{12}C_{50}H_{53}{}^{11}B_{14}{}^{10}B_6N_6O_6$ requires 1047.6106), 1046.6094 (*M* + H $^{12}C_{50}H_{53}{}^{11}B_{13}{}^{10}B_7N_6O_6$ requires 1046.6142), 1045.3132 (*M* + H $^{12}C_{50}H_{53}{}^{11}B_{12}{}^{10}B_8N_6O_6$ requires 1045.6179).

### 3-(Prop-2-ynyloxy)benzaldehyde 17

Sodium (2.40 g, 100 mmol) was stirred in dry ethanol (200 $cm^3$) for 30 min. 3-Hydroxybenzaldehyde **16** (12.2 g, 100 mmol), was added, followed by 3-bromopropyne (16.4 g, 80% w/v in toluene, 110 mmol). The mixture stirred for 18 h, then filtered. The evaporation residue, in chloroform, was washed with water and brine. Drying, evaporation and chromatography (hexane–chloroform 1 : 1) gave **17** (12.6 g, 78%) as a pale yellow oil (lit.[26] oil): $\delta_H$ 2.55 (1 H, d, *J* 2.4 Hz, C≡CH), 4.77 (2 H, d, *J* 2.4 Hz, $CH_2O$), 7.24–7.52 (4 H, m, Ar 2,4,5,6-$H_4$), 9.99 (1 H, s, CHO); *m*/*z* ($EI^+$) 159 (M).

### 2-[3-(Prop-2-ynyloxy)phenyl]-4,5-dihydro-1,3-dithiole 18

Boron trifluoride diethyl etherate (9.4 $cm^3$, 77 mmol) was added to **17** (12.3 g, 77 mmol) and ethane-1,2-dithiol (14.5 g, 154 mmol) in dry dichloromethane (390 $cm^3$) at 0 °C and the mixture was stirred at 20 °C for 16 h. Evaporation and chromatography (hexane–dichloromethane 3 : 1 ⟶ 2 : 1) gave **18** (10.1 g, 55%) as a colourless oil: $\delta_H$ 2.53 (1 H, d, *J* 2.6 Hz, C≡CH), 3.32 (2 H, m) and 3.46 (2 H, m) (dithiole 4,5-$H_4$), 4.68 (2 H, d, *J* 2.6 Hz, $CH_2O$), 5.60 (1 H, s, dithiole 2-H), 6.86 (1 H, m, Ph 4-H), 7.15 (2 H, m, Ph 2,6-$H_2$), 7.22 (1 H, t, *J* 7.8 Hz, Ph 5-H); $\delta_C$ 40.0, 55.5, 55.9, 75.5, 78.3, 114.2, 114.4, 121.0, 129.3, 142.1, 157.4; *m*/*z* ($EI^+$) 238.0291 (*M* $^{12}C_{12}H_{12}O_1{}^{34}S_1{}^{32}S_1$ requires 238.0287), 237.0357 (*M* $^{13}C_1{}^{12}C_{11}H_{12}O_1{}^{32}S_2$ requires 237.0363), 236.0328 (*M* $^{12}C_{12}H_{12}O_1{}^{32}S_2$ requires 236.0330).

### 1-[3-(4,5-Dihydro-1,3-dithiol-2-yl)phenoxymethyl]-1,2-dicarba*closo*dodecaborane(12) 19

Decaborane(14) (5.0 g, 41 mmol) in dry acetonitrile (100 $cm^3$) was stirred under argon for 4 h before **18** (10.0 g, 42 mmol) in dry acetonitrile (10 $cm^3$) was added. The mixture was boiled under reflux for 3 d. Evaporation and chromatography (hexane–chloroform 3 : 2) gave **19** (8.34 g, 58%) as a white powder: mp 122–123 °C; $\delta_H$ 1.4–3.2 (10 H, br q, $J_{B-H}$ 150 Hz, $B_{10}H_{10}$), 3.35 (2 H, m) and 3.49 (2 H, m) (dithiole 4,5-$H_4$), 4.09 (1 H, br s, carborane 2-H), 4.40 (2 H, d, *J* 4.1 Hz, $OCH_2$), 6.73 (1 H, m, Ph 4-H), 7.05 (1 H, t, *J* 1.9 Hz, Ph 2-H), 7.14 (1 H, m, Ph 6-H), 4.22 (1 H, td, *J* 7.8, 4.1 Hz, Ph 6-H); $\delta_C$ 40.3, 55.8, 57.7, 69.0, 71.3, 113.9, 114.1, 122.1, 129.6, 142.4, 156.8; *m*/*z* ($EI^+$) 356.2057 (*M* $C_{12}H_{22}{}^{11}B_{10}O_1S_2$ requires 356.2042), 355.2083 (*M* $C_{12}H_{22}{}^{11}B_9{}^{10}B_1O_1S_2$ requires 355.2079), 354.2115 (*M* $C_{12}H_{22}{}^{11}B_8{}^{10}B_2O_1S_2$ requires 354.2115) 353.2145 (*M* $C_{12}H_{22}{}^{11}B_7{}^{10}B_3O_1S_2$ requires 353.2145), 352.2172 (*M* $C_{12}H_{22}{}^{11}B_6{}^{10}B_4O_1S_2$ requires 352.2189).

### 3-(1,2-Dicarba*closo*dodecaboran(12)-1-ylmethoxy)benzaldehyde 20

Dithiole **19** (4.90 g, 13.9 mmol) was stirred with mercury(II) perchlorate hydrate (12.2 g, 31 mmol) in tetrahydrofuran (115 $cm^3$) for 10 min. The suspension was filtered. The evaporation residue, in dichloromethane, was washed with aq. sodium carbonate, water and brine and was dried. Evaporation gave **20** (3.14 g, 81%) as a white powder: mp 101–103 °C; (Found: C, 43.30; H, 6.41. $C_{10}H_{18}B_{10}O_2$ requires C, 43.15; H, 6.52%); $\delta_H$ 1.4–3.2 (10 H, br q, $J_{B-H}$ 150 Hz, $B_{10}H_{10}$), 4.08 (1 H, br s, carborane 2-H), 4.49 (2 H, s, $CH_2$), 7.16 (1 H, m, 4-H), 7.33 (1 H, dd, *J* 2.7, 1.2 Hz, 2-H), 7.50 (1 H, m, 5-H), 7.56 (1 H, dd, *J* 7.4, 1.2 Hz, 6-H); $\delta_C$ 57.9, 69.3, 71.0, 112.4, 121.7, 125.3, 130.5, 137.8, 157.3, 191.1; *m*/*z* ($EI^+$) $^{11}B/^{10}B$ cluster centred at 278 (M).

### Di(pyrrol-2-yl)(3-nitrophenyl)methane 22

3-Nitrobenzaldehyde was treated with pyrrole and trifluoroacetic acid, as for the synthesis of **8**, to give **22** (5.96 g, 74%) as a pale yellow solid: mp 124–127 °C; $\delta_H$ 5.58 (1 H, m, methine-H), 5.87 (2 H, m, 2 × pyrrole 3-H), 6.17 (2 H, m, 2 × pyrrole 4-H), 6.75 (2 H, m, 2 × pyrrole 5-H), 7.48 (1 H, t, *J* 7.8 Hz, Ph 5-H), 7.55 (1 H, d, *J* 7.8 Hz, Ph 6-H), 8.00 (2 H, br s, 2 × NH), 8.11 (2 H, m, Ph 2,4-$H_2$); *m*/*z* 267 (*M* + H), 201 (*M* − pyrrole), 145 (*M* − $C_6H_4NO_2$).

### 5,10,15,20-Tetrakis[3-(1,2-dicarba*closo*dodecaboran(12)-1-ylmethoxy)phenyl]-21*H*,23*H*-porphine 23, 5-(3-nitrophenyl)-10,15,20-tris[3-(1,2-dicarba*closo*dodecaboran(12)-1-ylmethoxy)phenyl]-21*H*,23*H*-porphine 24, 5,15-bis(3-nitrophenyl)-10,20-bis[3-(1,2-dicarba*closo*dodecaboran(12)-1-ylmethoxy)-phenyl]-21*H*,23*H*-porphine 25, 5,10-bis(3-nitrophenyl)-15,20-bis[3-(1,2-dicarba*closo*dodecaboran(12)-1-ylmethoxy)phenyl]-21*H*,23*H*-porphine 26 and 5,10,15-tris(3-nitrophenyl)-20-[3-(1,2-dicarba*closo*dodecaboran(12)-1-ylmethoxy)phenyl]-21*H*,23*H*-porphine 27

Dipyrromethane **22** (1.30 g, 4.9 mmol) and aldehyde **20** (1.35 g, 4.9 mmol) in dry dichloromethane (490 $cm^3$) were bubbled with argon before boron trifluoride diethyl etherate (70 mg, 500 μmol) was added. The mixture was stirred for 1.5 h before 2,3-dichloro-5,6-dicyanobenzoquinone (1.23 g, 5.4 mmol) was added. The mixture was stirred for 2 h, washed with water and brine. Drying, evaporation and chromatography (hexane–

chloroform–dichloromethane 3 : 1 : 1 ⟶ 2 : 3 : 3) gave **23** (35 mg, 2%) as a purple solid: mp >350 °C (decomp.); $\delta_H$ −2.86 (2 H, s, 21,23-$H_2$), 2.6 (10 H, br q, $J_{B-H}$ 150 Hz, $B_{10}H_{10}$), 4.17 (4 H, br s, 4 × carborane 2-H), 4.61 (8 H, s, 4 × $CH_2$), 7.29 (4 H, m, 4 × Ph 4-H), 7.68 (8 H, m, 4 × Ph 2,5-$H_2$), 7.90 (4 H, d, *J* 6.6 Hz, 4 × Ph 6-H), 8.84 (8 H, s, 2,3,7,8,12,13,17,18-$H_8$); $\delta_C$ 58.2, 69.7, 71.7, 114.5, 119.5, 121.3, 128.2, 129.3, 131.5, 143.9, 155.6; *m*/*z* 1304 (*M* + H). Further elution gave **24** (268 mg, 14%) as a purple solid: mp >350 °C (decomp.); $\delta_H$ (50 °C) −2.79 (2 H, s, 21,23-$H_2$), 1.6–3.2 (10 H, br m, $B_{10}H_{10}$), 4.12 (3 H, br s, 3 × carborane 2-H), 4.61 (6 H, s, 3 × $CH_2$), 7.29 (3 H, m, $Ph^{10,15,20}$ 4-$H_3$), 7.68 (6 H, m, $Ph^{10,15,20}$ 2,5-$H_6$), 7.90 (3 H, d, *J* 7.2 Hz, $Ph^{10,15,20}$ 6-$H_3$), 7.94 (1 H, t, *J* 7.9 Hz, $Ph^5$ 5-H), 8.52 (1 H, d, *J* 7.9 Hz, $Ph^5$ 6-H), 8.67 (1 H, m, $Ph^5$ 4-H), 8.72 (2 H, d, *J* 4.9 Hz, 2,8-$H_2$), 8.83 (4 H, s, 12,13,17,18-$H_4$), 8.86 (2 H, d, *J* 4.9 Hz, 3,7-$H_2$), 9.04 (1 H, s, $Ph^5$ 2-H); $\delta_C$ 57.7, 69.2, 71.2, 114.0, 116.7, 119.3, 120.8, 122.8, 128.0, 128.3, 128.5, 129.3, 131.5, 139.4, 143.2, 143.3, 146.7, 155.1; *m*/*z* 1179.7940 (*M* + H $C_{53}H_{66}{}^{11}B_{27}{}^{10}B_3N_5O_5$ requires 1179.7964), 1178.7943 (*M* + H $C_{53}H_{66}{}^{11}B_{26}{}^{10}B_4N_5O_5$ requires 1178.8001), 1177.8007 (*M* + H $C_{53}H_{66}{}^{11}B_{25}{}^{10}B_5N_5O_5$ requires 1177.8037), 1176.8033 (*M* + H $C_{53}H_{66}{}^{11}B_{24}{}^{10}B_6N_5O_5$ requires 1176.8073), 1175.8068 (*M* + H $C_{53}H_{66}{}^{11}B_{23}{}^{10}B_7N_5O_5$ requires 1175.8110), 1174.8107 (*M* + H $C_{53}H_{66}{}^{11}B_{22}{}^{10}B_8N_5O_5$ requires 1174.8146). Further elution gave **25** (230 mg, 9%) as a purple solid: mp >350 °C (decomp.); $\delta_H$ −2.85 (2 H, s, 21,23-$H_2$), 1.6–3.2 (10 H, br m, $B_{10}H_{10}$), 4.18 (2 H, br s, 2 × carborane 2-H), 4.62 (4 H, s, 2 × $CH_2$), 7.30 (2 H, m, $Ph^{10,20}$ 4-$H_2$), 7.69 (4 H, m, $Ph^{10,20}$ 2,5-$H_4$), 7.91 (2 H, m, $Ph^{10,20}$ 6-$H_2$), 7.98 (2 H, t, *J* 7.3 Hz, $Ph^{5,15}$ 5-$H_2$), 8.55 (2 H, d, *J* 7.3 Hz, $Ph^{5,15}$ 6-$H_2$), 8.70 (2 H, m, $Ph^{5,15}$ 4-$H_2$), 8.76 (4 H, d, *J* 4.9 Hz, 2,8,12,18-$H_4$), 8.89 (4 H, d, *J* 4.9 Hz, 3,7,13,17-$H_4$), 9.07 (2 H, s, $Ph^{5,15}$ 2-$H_2$); $\delta_C$ 58.2, 69.7, 71.7, 114.6, 117.7, 120.1, 121.3, 123.4, 128.0, 128.5, 129.0, 131.1, 139.8, 143.6, 143.7, 147.2, 155.3; *m*/*z* 1052.5951 (*M* + H $C_{50}H_{53}{}^{11}B_{19}{}^{10}B_1N_6O_6$ requires 1052.5924), 1051.5991 (*M* + H $C_{50}H_{53}{}^{11}B_{18}{}^{10}B_2N_6O_6$ requires 1051.5960). Further elution gave **26** (230 mg, 9%) as a purple solid: mp >350 °C (decomp.); $\delta_H$ −2.84 (2 H, s, 21,23-$H_2$), 1.6–3.2 (10 H, br m, $B_{10}H_{10}$), 4.18 (2 H, br s, 2 × carborane 2-H), 4.62 (4 H, s, 2 × $CH_2$), 7.31 (2 H, m, $Ph^{10,20}$ 4-$H_2$), 7.71 (4 H, m, $Ph^{10,20}$ 2,5-$H_4$), 7.93 (2 H, m, $Ph^{10,20}$ 6-$H_2$), 7.97 (2 H, t, *J* 7.9 Hz, $Ph^{5,15}$ 5-$H_2$), 8.55 (2 H, m, $Ph^{5,15}$ 6-$H_2$), 8.70 (2 H, d,*J* 7.9 Hz $Ph^{5,15}$ 4-$H_2$), 8.77 (2 H, d, *J* 4.9 Hz) and 8.79 (2 H, s) (2,8,12,18-$H_4$), 8.87 (2 H, s) and 8.97 (2 H, d, *J* 4.9 Hz) (3,7,13,17-$H_4$), 9.08 (2 H, s, $Ph^{5,15}$ 2-$H_2$); $\delta_C$ 57.7, 69.2, 71.1, 114.1, 117.0, 119.8, 120.8, 122.9, 127.6, 127.9, 128.5, 128.9, 131.5, 139.4, 143.1, 146.7, 155.1; *m*/*z* 1053.5996 (*M* + H $^{13}C_1{}^{12}C_{49}H_{53}{}^{11}B_{19}{}^{10}B_1N_6O_6$ requires 1053.5957), 1052.5995 (*M* + H $^{13}C_1{}^{12}C_{49}H_{53}{}^{11}B_{18}{}^{10}B_2N_6O_6$ requires 1052.5994), 1051.5980 (*M* + H $^{12}C_{50}H_{53}{}^{11}B_{18}{}^{10}B_2N_6O_6$ requires 1051.5960), 1050.6084 (*M* + H $^{13}C_1{}^{12}C_{49}H_{53}{}^{11}B_{16}{}^{10}B_4N_6O_6$ requires 1050.6066). Further elution gave **27** (30 mg, 2%) as a purple solid: mp >350 °C (decomp.); $\delta_H$ −2.84 (2 H, s, 21,23-$H_2$), 1.5–3.2 (10 H, br m, $B_{10}H_{10}$), 4.18 (1 H, br s, carborane 2-H), 4.62 (2 H, s, $OCH_2$), 7.31 (2 H, dd, *J* 8.4, 2.2 Hz, carboraneAr 4-H), 7.70 (2 H, m, carboraneAr 2,5-$H_2$), 7.92 (1 H, br m, carboraneAr 6-H), 7.98 (3 H, t, *J* 7.9 Hz, 3 × $O_2$NAr 5-H), 8.55 (3 H, m, 3 × $O_2$NAr 6-H), 8.71 (3 H, m, 3 × $O_2$NAr 4-H), 8.77 (2 H, d, *J* 4.8 Hz) and 8.80 (4 H, s) (3,7,8,12,13,17-$H_6$), 8.90 (2 H, d, *J* 4.9 Hz, 2,18-$H_2$), 9.08 (3 H, s, 3 × $O_2$NAr 2-H) $\delta_C$ 57.8, 69.4, 71.2, 114.4, 117.8, 120.4, 121.1, 123.2, 127.9, 128.5, 131.3, 139.7, 143.4, 147.1, 155.1; *m*/*z* 924.3969 (*M* + H $C_{47}H_{40}{}^{11}B_{10}N_7O_7$ requires 924.3920), 923.3972 (*M* + H $C_{47}H_{40}{}^{11}B_9{}^{10}B_1N_7O_7$ requires 923.3956), 922.3962 (*M* + H $C_{47}H_{40}{}^{11}B_8{}^{10}B_2N_7O_7$ requires 922.3992), 921.4068 (*M* + H $C_{47}H_{40}{}^{11}B_7{}^{10}B_3N_7O_7$ requires 921.4029), 920.3998 (*M* + H $C_{47}H_{40}{}^{11}B_6{}^{10}B_4N_7O_7$ requires 920.4065).

### 5-(3-Nitrophenyl)-10,15,20-tris[3-(1,2-dicarba*closo*dodecaboran(12)-1-ylmethoxyphenyl)]-21*H*,23*H*-porphinatozinc(II) 29

Porphyrin **24** (80 mg, 68 μmol) was boiled under reflux with zinc(II) acetate dihydrate (154 mg, 700 μmol) in acetic acid (3 $cm^3$) under argon for 30 min. The mixture was added to aqueous sodium hydroxide (2 M) and was extracted with chloroform. The extract was washed with water and brine. Drying, evaporation, chromatography (chloroform–hexane 1 : 1 ⟶ 4 : 1) and drying at 160 °C under reduced pressure (3 torr) for 3 h gave **29** (60 mg, 71%) as a bright pink–purple glass: $\delta_H$ 2.4 (30 H, br q, *J* 145 Hz, 3 × $B_{10}H_{10}$), 4.15 (3 H, br s, 3 × carborane 2-H), 4.61 (6 H, m, 3 × $OCH_2$), 7.28 (3 H, m, 3 × $Ph^{10,15,20}$ 4-H), 7.68 (6 H, m, 3 × $Ph^{10,15,20}$ 2,5-$H_2$), 7.92 (3 H, m, 3 × $Ph^{10,15,20}$ 6-H), 7.95 (1 H, m, $Ph^5$ 5-H), 8.54 (1 H, m, $Ph^5$ 6-H), 8.67 (1 H, m, $Ph^5$ 4-H), 8.83 (2 H, d, *J* 4.8 Hz, 2,8-$H_2$), 8.94 (4 H, s, 12,13,17,18-$H_4$), 8.96 (2 H, d, *J* 4.8 Hz, 3,7-$H_2$), 9.03 (1 H, s, $Ph^5$ 2-H); $\delta_C$ 57.7, 69.2, 71.2, 113.9, 117.7, 120.3, 120.4, 120.6, 127.3, 127.6, 127.9, 128.7, 128.8, 131.2, 131.9, 132.0, 132.2, 139.2, 143.9, 144.0, 146.5, 149.3, 149.7, 149.8, 149.9, 155.0; *m*/*z* 1242.7146 (*M* + H $C_{53}H_{64}{}^{11}B_{26}{}^{10}B_4N_5O_5{}^{66}Zn$ requires 1242.7105), 1241.7179 (*M* + H $C_{53}H_{64}{}^{11}B_{25}{}^{10}B_5N_5O_5{}^{66}Zn$ requires 1241.7141), 1240.7198 (*M* + H $C_{53}H_{64}{}^{11}B_{24}{}^{10}B_6N_5O_5{}^{66}Zn$ requires 1240.7177), 1239.7189 (*M* + H $C_{53}H_{64}{}^{11}B_{23}{}^{10}B_7N_5O_5{}^{66}Zn$ requires 1239.7214), 1238.7225 (*M* + H $C_{53}H_{64}{}^{11}B_{22}{}^{10}B_8N_5O_5{}^{66}Zn$ requires 1238.7250), 1237.7241 (*M* + H $C_{53}H_{64}{}^{11}B_{21}{}^{10}B_9N_5O_5{}^{66}Zn$ requires 1237.7286), 1236.7279 (*M* + H $C_{53}H_{64}{}^{11}B_{20}{}^{10}B_{10}N_5O_5{}^{66}Zn$ requires 1236.7278), 1235.7272 (*M* + H $C_{53}H_{64}{}^{11}B_{19}{}^{10}B_{11}N_5O_5{}^{66}Zn$ requires 1235.7314), 1234.7348 (*M* + H $C_{53}H_{64}{}^{11}B_{18}{}^{10}B_{12}N_5O_5{}^{66}Zn$ requires 1234.7395).

### 2-(3-Ethynylphenyl)-4,5-dihydro-1,3-dithiole 33

Aldehyde **32** (1.95 g, 15 mmol) and 1,2-ethanedithiol (2.5 $cm^3$, 30 mmol) in dry dichloromethane (80 $cm^3$) were stirred with boron trifluoride diethyl etherate (1.85 $cm^3$, 15 mmol) at 0 °C for 30 min and at 20 °C for 1 h. The mixture was washed with water and brine and dried. Evaporation and chromatography (chloroform–hexane 1 : 6 ⟶ 1 : 4) gave **33** (1.60 g, 52%) as a colourless oil: $\delta_H$ 3.17 (1 H, s, C≡CH), 3.32 (2 H, m) and 3.47 (2 H, m) (dithiole 4,5-$H_4$), 5.57 (1 H, s, dithiole 2-H), 7.25 (1 H, t, *J* 7.8 Hz, Ph 5-H), 7.37 (1 H, ddd, *J* 7.8, 1.6, 1.2 Hz, Ph 4-H), 7.49 (1 H, ddd, *J* 7.8, 1.6, 1.2 Hz, Ph 6-H), 7.65 (1 H, dd, *J* 1.6, 1.2 Hz, Ph 2-H); *m*/*z* ($EI^+$) 206 (M).

### 1-[3-(4,5-Dihydro-1,3-dithiol-2-yl)phenyl]-1,2-dicarba*closo*-dodecaborane(12) 34

Alkyne **33** was treated with decaborane(14) and acetonitrile, as for the synthesis of **19** except that the chromatographic eluant was chloroform–hexane 2 : 3 ⟶ 1 : 1, to give **34** (57%) as a white glass: $\delta_H$ 2.4 (10 H, br q, $J_{B-H}$ 150 Hz, $B_{10}H_{10}$), 3.37 (2 H, m) and 3.50 (2 H, m) (dithiole 4,5-$H_4$), 3.96 (1 H, br s, carborane 2-H), 5.57 (1 H, s, dithiole 2-H), 7.27 (1 H, t, *J* 7.8 Hz, Ph 5-H), 7.38 (1 H, m, Ph 4-H), 7.54 (1 H, d, *J* 7.8 Hz, Ph 6-H), 7.62 (1 H, m, Ph 2-H); $\delta_C$ 40.8, 56.0, 60.5, 76.5, 127.3, 127.4, 129.2, 129.8, 133.8, 141.9; *m*/*z* ($EI^+$) $^{11}B/^{10}B$ cluster centred at 324 (M).

### 3-(1,2-Dicarba*closo*dodecaboran(12)-1-yl)benzaldehyde 35

Dithiole **34** was treated with mercury(II) perchlorate hydrate, as for the synthesis of **20** except that the reaction time was 5 min, to give **35** (97%) as a white powder: mp 105–107 °C, $\delta_H$ 2.3 (10 H, br q, $J_{B-H}$ 150 Hz, $B_{10}H_{10}$), 4.05 (1 H, br s, carborane 2-H), 7.56 (1 H, t, *J* 7.8 Hz, Ph 5-H), 7.78 (1 H, m, Ph 4-H), 7.91 (1 H, m, Ph 6-H), 7.96 (1 H, m, Ph 2-H); $\delta_C$ 59.8, 75.0, 127.3, 129.5, 131.1, 133.0, 134.5, 136.4, 190.4.

### 5,10,15,20-Tetrakis[3-(1,2-dicarba*closo*dodecaboran(12)-1-yl)-phenyl]-21*H*,23*H*-porphine 36, 5-(3-nitrophenyl)-10,15,20-tris-[3-(1,2-dicarba*closo*dodecaboran(12)-1-yl)phenyl]-21*H*,23*H*-porphine 37, 5,15-bis(3-nitrophenyl)-10,20-bis[3-(1,2-dicarba*closo*-dodecaboran(12)-1-yl)phenyl]-21*H*,23*H*-porphine 38, 5,10-bis(3-nitrophenyl)-15,20-bis[3-(1,2-dicarba*closo*dodecaboran(12)-1-yl)-

**phenyl]-21*H*,23*H*-porphine 39 and 5,10,15-tris(3-nitrophenyl)-20-[3-(1,2-dicarba*closo*dodecaboran(12)-1-yl)phenyl]-21*H*,23*H*-porphine 40**

Compounds **22** (2.09 g, 8.4 mmol) and **35** (2.26 g, 8.4 mmol) in dry dichloromethane (845 $cm^3$) were bubbled with argon before boron trifluoride diethyl etherate (0.17 $cm^3$, 1.4 mmol) was added. The mixture was stirred for 2.5 h. 2,3-Dichloro-5,6-dicyanobenzoquinone (2.11 g, 9.3 mmol) was added and the mixture was stirred for 16 h. The organic layer was washed with water and brine and was dried. Chromatography (hexane–chloroform–dichloromethane 3 : 1 : 1 ⟶ 4 : 5 : 5) gave **36** (50 mg, 2%) as a purple solid: mp >350 °C (decomp.); $\delta_H$ −2.87 (2 H, s, 21,23-$H_2$), 1.3–3.6 (40 H, br m, 4 × $B_{10}H_{10}$), 4.19 (4 H, s, 4 × carborane 2-H), 7.75 (4 H, br t, *J* 7.9 Hz, 4 × Ph 5-H), 7.94 (4 H, d, *J* 7.9 Hz, 4 × Ph 4-H), 8.28 (4 H, m, 4 × Ph 6-H), 8.34 (4 H, m, 4 × Ph 2-H), 8.80 (8 H, s, 2,3,7,8,12,13,17,18-$H_8$); $\delta_C$ 60.1, 76.5, 118.9, 127.0, 127.4, 131.3, 132.5, 133.3, 135.7, 142.5; *m*/*z* $^{11}B/^{10}B$ cluster centred at 1184 (*M* + H). Further elution gave **37** (507 mg, 18%) as a purple solid: mp >350 °C (decomp.); $\delta_H$ −2.86 (2 H, s, 21,23-$H_2$), 1.5–3.5 (30 H, br m, 3 × $B_{10}H_{10}$), 4.19 (3 H, s, 3 × carborane 2-H), 7.78 (3 H, br t, *J* 7.9 Hz, $Ph^{10,15,20}$ 5-$H_3$), 7.94 (3 H, br d, *J* 7.9 Hz, $Ph^{10,15,20}$ 4-$H_3$), 7.99 (1 H, m, $Ph^5$ 5-H), 8.26 (3 H, m, $Ph^{10,15,20}$ 6-$H_3$), 8.34 (3 H, s, $Ph^{10,15,20}$ 2-$H_3$), 8.57 (1 H, m, $Ph^5$ 6-H), 8.71 (1 H, m, $Ph^5$ 4-H), 8.80 (8 H, s, 2,3,7,8,12,13,17,18-$H_8$), 9.08 (1 H, m, $Ph^5$ 2-H); $\delta_C$ 59.9, 77.0, 117.2, 118.8, 122.9 ($NO_2$Ph 4-C), 126.7, 127.2, 127.6, 128.0, 131.1, 132.1, 133.1, 135.4, 139.5, 142.0, 143.1, 146.7; *m*/*z* 1090.7656 (*M* + H $C_{50}H_{60}{}^{11}B_{28}{}^{10}B_2N_5O_2$ requires 1090.7611), 1089.7669 (*M* + H $C_{50}H_{60}{}^{11}B_{27}{}^{10}B_3N_5O_2$ requires 1089.7648), 1088.7690 (*M* + H $C_{50}H_{60}{}^{11}B_{26}{}^{10}B_4N_5O_2$ requires 1088.7684), 1087.7700 (*M* + H $C_{50}H_{60}{}^{11}B_{25}{}^{10}B_5N_5O_2$ requires 1087.7720), 1086.7725 (*M* + H $C_{50}H_{60}{}^{11}B_{24}{}^{10}B_6N_5O_2$ requires 1086.7757), 1085.7750 (*M* + H $C_{50}H_{60}{}^{11}B_{23}{}^{10}B_7N_5O_2$ requires 1085.7793). Further elution gave **38** (422 mg, 10%) as a purple solid: mp >350 °C (decomp.); $\delta_H$ (50 °C) −2.77 (2 H, s, 21,23-$H_2$), 1.5–3.5 (20 H, br m, 2 × $B_{10}H_{10}$), 4.16 (2 H, s, 2 × carborane 2-H), 7.76 (2 H, br t, *J* 7.3 Hz, $Ph^{10,20}$ 5-$H_2$), 7.95 (2 H, d, *J* 7.3 Hz, $Ph^{10,20}$ 4-$H_2$), 7.98 (2 H, d, *J* 8.5 Hz, $Ph^{5,15}$ 5-$H_2$), 8.26 (2 H, d, *J* 7.3 Hz, $Ph^{10,20}$ 6-$H_2$), 8.34 (2 H, s, $Ph^{10,20}$ 2-$H_2$), 8.54 (2 H, m, $Ph^{5,15}$ 6-$H_2$), 8.69 (2 H, d, *J* 8.5 Hz, $Ph^{5,15}$ 4-$H_2$), 8.78 (8 H, s, 2,3,7,8,12,13,17,18-$H_8$), 9.06 (2 H, s, $Ph^{5,15}$ 2-$H_2$); $\delta_C$ 60.3, 76.4, 117.5, 119.2, 123.1, 127.0, 127.4, 127.9, 128.1, 131.8, 132.5, 133.1, 135.4, 139.7, 141.8, 143.0, 146.8; *m*/*z* 993.5777 (*M* + H $^{13}C_1{}^{12}C_{47}H_{49}{}^{11}B_{19}{}^{10}B_1N_6O_4$ requires 993.5746), 992.5739 (*M* + H $^{12}C_{48}H_{49}{}^{11}B_{19}{}^{10}B_1N_6O_4$ requires 992.5713), 990.5747 (*M* + H $^{12}C_{48}H_{49}{}^{11}B_{17}{}^{10}B_3N_6O_4$ requires 990.5785), 987.5856 (*M* + H $^{12}C_{48}H_{49}{}^{11}B_{14}{}^{10}B_6N_6O_4$ requires 987.5894). Further elution gave **39** (380 mg, 9%) as a purple solid: mp >350 °C (decomp.); $\delta_H$ −2.84 (2 H, s, 21,23-$H_2$), 1.5–3.5 (40 H, br m, 2 × $B_{10}H_{10}$), 4.19 (2 H, s, 2 × carborane 2-H), 7.77 (2 H, m, $Ph^{15,20}$ 5-$H_2$), 7.98 (2 H, d, *J* 7.3 Hz, $Ph^{15,20}$ 4-$H_2$), 8.01 (2 H, d, *J* 8.5 Hz, $Ph^{5,10}$ 5-$H_2$), 8.29 (2 H, br s, $Ph^{15,20}$ 6-$H_2$), 8.34 (2 H, s, $Ph^{15,20}$ 2-$H_2$), 8.55 (2 H, m, $Ph^{5,10}$ 6-$H_2$), 8.70 (2 H, d, *J* 8.5 Hz, $Ph^{5,10}$ 4-$H_2$), 8.81 (8 H, s, 2,3,7,8,12,13,17,18-$H_8$), 9.09 (2 H, s, $Ph^{5,10}$ 2-$H_2$); $\delta_C$ 60.4, 76.5, 117.9, 119.6, 123.5, 127.3, 127.7, 128.1, 128.5, 131.9, 132.7, 133.6, 135.9, 139.9, 142.5, 143.5, 147.2; *m*/*z* 993.5741 (*M* + H $^{13}C_1{}^{12}C_{47}H_{49}{}^{11}B_{19}{}^{10}B_1N_6O_4$ requires 993.5746), 992.5762 (*M* + H $^{12}C_{48}H_{49}{}^{11}B_{19}{}^{10}B_1N_6O_4$ requires 992.5713), 991.5756 (*M* + H $^{12}C_{48}H_{49}{}^{11}B_{18}{}^{10}B_2N_6O_4$ requires 991.5749), 990.5771 (*M* + H $^{12}C_{48}H_{49}{}^{11}B_{17}{}^{10}B_3N_6O_4$ requires 990.5785), 989.5801 (*M* + H $^{12}C_{48}H_{49}{}^{11}B_{16}{}^{10}B_4N_6O_4$ requires 989.5822), 988.5838 (*M* + H $^{12}C_{48}H_{49}{}^{11}B_{15}{}^{10}B_5N_6O_4$ requires 988.5858), 987.5877 (*M* + H $^{12}C_{48}H_{49}{}^{11}B_{14}{}^{10}B_6N_6O_4$ requires 987.5894). Further elution gave **40** (30 mg, 1%) as a purple solid: mp >350 °C (decomp.); $\delta_H$ −2.84 (2 H, s, 21,23-$H_2$), 1.4–3.6 (10 H, br m, $B_{10}H_{10}$), 4.19 (1 H, s, carborane 2-H), 7.79 (1 H, m, $Ph^{20}$ 5-H), 7.99 (4 H, m, $Ph^{20}$ 4-H and $Ph^{5,10,15}$ 5-$H_3$), 8.28 (1 H, br m, $Ph^{20}$ 6-H), 8.34 (1 H, s, $Ph^{20}$ 2-H), 8.56 (3 H, m, $Ph^{5,10,15}$ 6-$H_3$), 8.71 (3 H, dt, *J* 1.1, 8.4 Hz, $Ph^{5,10,15}$ 4-$H_3$), 8.81 (8 H, s, 2,3,7,8,12,13,17,18-$H_8$), 9.08 (3 H, s, 3 × $O_2$NAr 2-H); *m*/*z* 893.3917 (*M* + H $^{13}C_1{}^{12}C_{45}H_{38}{}^{11}B_8{}^{10}B_2N_7O_6$ requires 893.3920), 892.3904 (*M* + H $^{12}C_{46}H_{38}{}^{11}B_8{}^{10}B_2N_7O_6$ requires 892.3887), 891.3905 (*M* + H $^{12}C_{46}H_{38}{}^{11}B_7{}^{10}B_3N_7O_6$ requires 891.3923), 890.3962 (*M* + H $^{12}C_{46}H_{38}{}^{11}B_6{}^{10}B_4N_7O_6$ requires 890.3959), 889.3981 (*M* + H $^{12}C_{46}H_{38}{}^{11}B_5{}^{10}B_5N_7O_6$ requires 889.3996).

**5,15-Bis(4-aminophenyl)-10,20-bis(4-methoxyphenyl)-21*H*,23*H*-porphine 43**

Porphyrin **10** (10 mg, 13 μmol) was heated with tin(II) chloride hydrate (15.0 mg, 78 μmol) in hydrochloric acid (9 M, 60 $cm^3$) for 4 h at 65 °C. Water (100 $cm^3$) was added and the pH was adjusted to 8 with aqueous ammonia (35%) before extraction with chloroform (120 $cm^3$). Drying and evaporation gave **43** (5.0 mg, 56%) as a purple solid: mp >350 °C (decomp.); $\delta_H$ −2.74 (2 H, s, 21,23-$H_2$), 0.91 (4 H, s, 2 × Ar–$NH_2$), 4.10 (6 H, s, 2 × $OCH_3$), 7.07 (4 H, d, *J* 8.5 Hz, 2 × $H_2$NAr 3,5-$H_2$), 7.32 (4 H, d, *J* 8.5 Hz, 2 × MeOAr 3,5-$H_2$), 8.00 (4 H, d, *J* 8.5 Hz, 2 × $H_2$NAr 2,6-$H_2$), 8.12 (4 H, d, *J* 8.5 Hz, 2 × MeOAr 2,6-$H_2$), 8.85 (4 H, d, *J* 4.9 Hz, 2,8,12,18-$H_4$), 8.92 (4 H, d, *J* 4.9 Hz, 3,7,13,17-$H_4$); *m*/*z* 706.3014 (*M* + H $^{13}C_1{}^{12}C_{45}H_{37}N_6O_2$ requires 706.3012), 705.2959 (*M* + H $C_{46}H_{37}N_6O_2$ requires 705.2978).

**5-(3-Aminophenyl)-10,15,20-tris[3-(1,2-dicarba*closo*dodecaborane(12)-1-ylmethoxy)phenyl]-21*H*,23*H*-porphine 44**

**Method A.** Porphyrin **24** (156 mg, 137 μmol) was stirred with tin(II) chloride hydrate (550 mg, 2.9 mmol) in acetic acid (140 $cm^3$) for 7 d. The evaporation residue was stirred with aqueous sodium hydroxide (2 M) and chloroform. The organic layer was washed with aqueous sodium hydroxide (2 M), water and brine and was dried. Evaporation and chromatography (chloroform ⟶ chloroform–ethyl acetate 99 : 1) gave **44** (110 mg, 72%) as a purple solid: mp >350 °C (decomp.); $\delta_H$ −2.86 (2 H, s, 21,23-$H_2$), 1.6–3.2 (30 H, br m, $B_{10}H_{10}$), 3.96 (2 H, s, $NH_2$), 4.17 (3 H, br s, 3 × carborane 2-H), 4.61 (6 H, s, 3 × $CH_2$), 7.11 (1 H, dd, *J* 1.2, 7.2 Hz, $Ph^5$ 4-H), 7.28 (3 H, m, $Ph^{10,15,20}$ 4-$H_3$), 7.52 (2 H, m, $Ph^5$ 2,5-$H_2$), 7.60 (1 H, d, *J* 7.2 Hz, $Ph^5$ 6-H), 7.69 (6 H, m, $Ph^{10,15,20}$ 2,5-$H_6$), 7.91 (3 H, d, *J* 6.6 Hz, $Ph^{10,15,20}$ 6-$H_3$), 8.81 (6 H, m, 2,8,12,13,17,18-$H_4$), 8.96 (2 H, d, *J* 4.9 Hz, 3,7-$H_2$); $\delta_C$ 58.2, 69.6, 71.7, 114.4, 114.8, 119.1, 119.3, 121.2, 122.2, 126.2, 127.7, 128.2, 129.4, 131.5, 143.0, 144.0, 144.8, 155.6.

**Method B.** Porphyrin **24** (59 mg, 52 μmol) was stirred with Raney nickel (50 mg) in methanol (16 $cm^3$) and cyclohexene (24 $cm^3$) for 30 h and filtered. Evaporation, chromatography (chloroform ⟶ chloroform–ethyl acetate 99 : 1) and drying at 120 °C under reduced pressure (3 torr) for 4 h gave **44** (8 mg, 14%) as a bright purple solid with properties as above.

**5,15-Bis(3-aminophenyl)-10,20-bis[3-(1,2-dicarba*closo*dodecaborane(12)-1-yl-methoxyphenyl]-21*H*,23*H*-porphine 45 and 5,10-bis(3-aminophenyl)-15,20-bis[3-(1,2-dicarba*closo*dodecaborane(12)-1-yl-methoxyphenyl]-21*H*,23*H*-porphine 46**

An equimolar mixture of **25** and **26** (89 mg, 85 μmol) was stirred vigorously with tin(II) chloride hydrate (484 mg, 2.5 mmol) in hydrochloric acid (9 M, 2 $cm^3$) for 7 d. The mixture was poured into aqueous sodium hydroxide (2 M, 200 $cm^3$) and was extracted with chloroform. The extract was washed with aqueous sodium hydroxide (2 M), water and brine. Drying, evaporation and chromatography (chloroform ⟶ chloroform–ethyl acetate 12 : 1) gave **45** (from **25**) (31 mg, 76%) as a purple glass: $\delta_H$ −2.85 (2 H, s, 21,23-$H_2$), 1.5–3.1 (20 H, br m, 2 × $B_{10}H_{10}$), 3.92 (4 H, s, 2 × $NH_2$), 4.14 (2 H, br s, 2 × carborane 2-H), 4.58 (4 H, s, 2 × $OCH_2$), 7.09 (2 H, ddd, *J* 8.2, 2.4, 1.0 Hz, 2 × $Ph^{5,15}$ 4-H), 7.28 (2 H, m, 2 × $Ph^{10,20}$ 4-H), 7.50 (4 H, m, 2 × $Ph^{5,15}$ 2,5-$H_2$), 7.59 (2 H, d, *J* 7.5 Hz, 2 × $Ph^{5,15}$ 6-H), 7.66 (4 H, m, 2 × $Ph^{10,20}$ 2,5-$H_2$), 7.91 (2 H, d, *J* 7.5 Hz,

2 × $Ph^{10,20}$ 6-H), 8.79 (4 H, d, *J* 4.6 Hz, 2,8,12,18-$H_4$), 8.94 (2 H, d, *J* 4.6 Hz, 3,7,13,17-$H_4$); $\delta_C$ 57.7, 69.1, 71.2, 113.8, 114.3, 118.5, 120.3, 120.7, 121.7, 125.7, 127.2, 127.6, 128.9, 131.0, 142.6, 143.7, 144.3, 155.0; *m*/*z* 993.6485 (*M* + H $^{13}C_1{}^{12}C_{49}H_{57}{}^{11}B_{19}{}^{10}BN_6O_2$ requires 993.6473), 992.6491 (*M* + H $^{13}C_1{}^{12}C_{49}H_{57}{}^{11}B_{18}{}^{10}B_2N_6O_2$ requires 992.6510), 991.6484 (*M* + H $^{12}C_{50}H_{57}{}^{11}B_{18}{}^{10}B_2N_6O_2$ requires 991.6477), 990.6504 (*M* + H $^{12}C_{50}H_{57}{}^{11}B_{17}{}^{10}B_3N_6O_2$ requires 990.6513), 989.6511 (*M* + H $^{12}C_{50}H_{57}{}^{11}B_{16}{}^{10}B_4N_6O_2$ requires 989.6549), 988.6535 (*M* + H $^{12}C_{50}H_{57}{}^{11}B_{15}{}^{10}B_5N_6O_2$ requires 988.6586). Further elution gave **46** (from **26**) (31 mg, 76%) as a purple glass: $\delta_H$ −2.85 (2 H, s, 21,23-$H_2$), 1.6–3.1 (20 H, br m, $B_{10}H_{10}$), 3.95 (4 H, s, $NH_2$), 4.17 (2 H, br s, 2 × carborane 2-$H_2$), 4.60 (4 H, s, 2 × $OCH_2$), 7.11 (2 H, m, 2 × $Ph^{5,10}$ 4-H), 7.28 (2 H, m, 2 × $Ph^{15,20}$ 4-H), 7.51 (4 H, m, 2 × $Ph^{5,10}$ 2,5-$H_2$), 7.61 (2 H, d, *J* 7.0 Hz, $Ph^{5,10}$ 6-H), 7.67 (4 H, m, 2 × $Ph^{15,20}$ 2,5-$H_2$), 7.91 (2 H, d, *J* 7.0 Hz, 2 × $Ph^{15,20}$ 6-H), 8.80 (4 H, m, 12,13,17,18-$H_4$), 8.95 (2 H, m, 2,3,7,8-$H_4$); $\delta_C$ 58.2, 69.6, 71.7, 114.3, 114.8, 118.8, 121.0, 121.2, 122.2, 126.2, 127.7, 128.1, 129.4, 131.5, 143.1, 144.2, 144.8, 155.6; *m*/*z* 992.6495 (*M* + H $^{13}C_1{}^{12}C_{49}H_{57}{}^{11}B_{18}{}^{10}B_2N_6O_2$ requires 992.6510), 991.6486 (*M* + H $^{12}C_{50}H_{57}{}^{11}B_{18}{}^{10}B_2N_6O_2$ requires 991.6477), 990.6506 (*M* + H $^{12}C_{50}H_{57}{}^{11}B_{17}{}^{10}B_3N_6O_2$ requires 990.6513), 989.6517 (*M* + H $^{12}C_{50}H_{57}{}^{11}B_{16}{}^{10}B_4N_6O_2$ requires 989.6549).

### 5-(3-Aminophenyl)-10,15,20-tris[3-(1,2-dicarba*closo*dodecaboran(12)-1-yl)phenyl]-21*H*,23*H*-porphine 47

Porphyrin **37** (159 mg, 146 μmol) was stirred with tin(II) chloride hydrate (554 mg, 2.9 mmol) in acetic acid (140 $cm^3$) for 8 d. The evaporation residue, in chloroform, was washed with aqueous sodium hydrogen carbonate (2 M) (2 (), water and brine and was dried. Chromatography (chloroform–hexane 1 : 1 ⟶ chloroform) gave **47** (60 mg, 39%) as a bright purple solid: mp >350 °C (decomp.); $\delta_H$ (50 °C) −2.79 (2 H, s, 21,23-$H_2$), 1.4–3.2 (10 H, br q, $J_{B-H}$ 145 Hz, $B_{10}H_{10}$), 3.95 (2 H, br s, $NH_2$), 4.15 (1 H, br s, carborane 2-H), 7.10 (1 H, m, $Ph^5$ 4-H), 7.52 (2 H, m, $Ph^5$ 2,5-$H_2$), 7.59 (1 H, m, $Ph^5$ 6-H), 7.73 (3 H, t, *J* 7.7 Hz, $Ph^{10,15,20}$ 5-$H_3$), 7.92 (3 H, d, *J* 7.7 Hz, $Ph^{10,15,20}$ 4-$H_3$), 8.24 (3 H, s, $Ph^{10,15,20}$ 6-$H_3$), 8.33 (3 H, s, $Ph^{10,15,20}$ 2-$H_3$), 8.70 (2 H, m, 2,8-$H_2$), 8.74 (4 H, s, 12,13,17,18-$H_6$), 9.00 (2 H, d, *J* 4.8 Hz, 3,7-$H_2$); $\delta_C$ 60.1, 76.3, 114.7, 118.3, 118.5, 121.6, 122.0, 126.0, 127.4, 127.6, 131.0, 132.4, 133.4, 135.7, 142.6, 142.7, 144.7; *m*/*z* 1060.7899 (*M* + H $C_{50}H_{62}{}^{11}B_{28}{}^{10}B_2N_5$ requires 1060.7869), 1059.7960 (*M* + H $C_{50}H_{62}{}^{11}B_{27}{}^{10}B_3N_5$ requires 1059.7906), 1058.7955 (*M* + H $C_{50}H_{62}{}^{11}B_{26}{}^{10}B_4N_5$ requires 1058.7942), 1057.7989 (*M* + H $C_{50}H_{62}{}^{11}B_{25}{}^{10}B_5N_5$ requires 1057.7978), 1056.8024 (*M* + H $C_{50}H_{62}{}^{11}B_{24}{}^{10}B_6N_5$ requires 1056.8015), 1055.8060 (*M* + H $C_{50}H_{62}{}^{11}B_{23}{}^{10}B_7N_5$ requires 1055.8051).

### 5,15-Bis(3-aminophenyl)-10,20-bis[3-(1,2-dicarba*closo*dodecaboran(12)-1-yl)phenyl]-21*H*,23*H*-porphine 48 and 5,10-bis(3-aminophenyl)-15,20-bis[3-(1,2-dicarba*closo*dodecaboran(12)-1-yl)phenyl]-21*H*,23*H*-porphine 49

An equimolar mixture of **38** and **39** was treated with tin(II) chloride hydrate, as for the synthesis of **45** and **46**. Chromatography (chloroform ⟶ chloroform–ethyl acetate 16 : 1) gave **48** (80%) as a purple glass: $\delta_H$ ($CDCl_3$/$(CD_3)_2SO$) 19:1) −2.90 (2 H, s, 21,23-$H_2$), 1.5–3.5 (20 H, m, 2 × $B_{10}H_{10}$), 4.61 (4 H, s, 2 × $NH_2$), 5.04 (2 H, s, 2 × carborane 2-H), 7.11 (2 H, m, $Ph^{5,15}$ 4-$H_2$), 7.48 (4 H, br m, $Ph^{5,15}$ 2,5-$H_4$), 7.52 (2 H, br s, $Ph^{5,15}$ 6-$H_2$), 7.66 (2 H, t, *J* 7.4 Hz, $Ph^{10,20}$ 5-$H_2$), 7.98 (2 H, d, *J* 7.4 Hz, $Ph^{10,20}$ 4-$H_2$), 8.26 (2 H, d, *J* 7.4 Hz, $Ph^{10,20}$ 6-$H_2$), 8.38 (2 H, s, $Ph^{10,20}$ 2-$H_2$), 8.74 (4 H, br s, 2,8,12,18-$H_4$), 9.00 (4 H, d, *J* 4.6 Hz, 3,7,13,17-$H_4$); *m*/*z* 932.6319 (*M* + H $^{13}C_1{}^{12}C_{47}H_{53}{}^{11}B_{18}{}^{10}B_2N_6$ requires 932.6299), 931.6332 (*M* + H $^{13}C_1{}^{12}C_{47}H_{53}{}^{11}B_{17}{}^{10}B_3N_6$ requires 931.6335), 930.6338 (*M* + H $^{12}C_{48}H_{53}{}^{11}B_{17}{}^{10}B_3N_6$ requires 930.6302), 929.6360 (*M* + H $^{12}C_{48}H_{53}{}^{11}B_{16}{}^{10}B_4N_6$ requires 929.6338), 928.6383 (*M* + H $^{12}C_{48}H_{53}{}^{11}B_{15}{}^{10}B_5N_6$ requires 928.6374), 927.6378 (*M* + H $^{12}C_{48}H_{53}{}^{11}B_{14}{}^{10}B_6N_6$ requires 927.6411). Further elution gave **49** (72%) as a purple glass: $\delta_H$ −2.85 (2 H, s, 21,23-$H_2$), 1.6–3.6 (20 H, m, 2 × $B_{10}H_{10}$), 3.95 (4 H, s, 2 × $NH_2$), 4.19 (2 H, s, 2 × carborane 2-H), 7.10 (2 H, ddd, *J* 8.1, 2.2, 1.1 Hz, $Ph^{5,10}$ 4-$H_2$), 7.51 (4 H, br m, $Ph^{5,10}$ 2,5-$H_4$), 7.60 (2 H, m, $Ph^{5,10}$ 6-$H_2$), 7.72 (1 H, t, *J* 7.4 Hz, $Ph^{15}$ 5-H), 7.73 (1 H, t, *J* 7.4 Hz, $Ph^{20}$ 5-H), 7.91 (2 H, d, *J* 7.4 Hz, $Ph^{15,20}$ 4-$H_2$), 8.26 (2 H, m, $Ph^{15,20}$ 6-$H_2$), 8.32 (2 H, s, $Ph^{15,20}$ 2-$H_2$), 8.69 (1 H, d, *J* 5.0 Hz) and 8.71 (1 H, d, *J* 5.0 Hz) (3,12-$H_2$), 8.75 (2 H, s, 7,8-$H_2$), 8.96 (2 H, s, 17,18-$H_2$), 8.99 (2 H, d, *J* 5.0 Hz, 2,13-$H_2$); $\delta_C$ 60.4, 76.6, 114.8, 118.1, 121.4, 122.2, 126.2, 127.1, 127.5, 127.7, 131.5, 132.4, 133.5, 136.0, 143.0, 143.1, 144.7; *m*/*z* 933.6219 (*M* + H $^{13}C_1{}^{12}C_{47}H_{53}{}^{11}B_{19}{}^{10}B_1N_6$ requires 933.6263), 932.6251 (*M* + H $^{13}C_1{}^{12}C_{47}H_{53}{}^{11}B_{18}{}^{10}B_2N_6$ requires 932.6299), 931.6334 (*M* + H $^{13}C_1{}^{12}C_{47}H_{53}{}^{11}B_{17}{}^{10}B_3N_6$ requires 931.6335), 930.6336 (*M* + H $^{12}C_{48}H_{53}{}^{11}B_{17}{}^{10}B_3N_6$ requires 930.6302), 929.6325 (*M* + H $^{12}C_{48}H_{53}{}^{11}B_{16}{}^{10}B_4N_6$ requires 929.6338), 928.6343 (*M* + H $^{12}C_{48}H_{53}{}^{11}B_{15}{}^{10}B_5N_6$ requires 928.6374).

### 5-[3-(MeOPEG550carbonylamino)phenyl]-10,15,20-triphenyl-21*H*,23*H*-porphine 50

Dry triethylamine (42 mg, 420 μmol) was added to porphyrin **42**[24] (130 mg, 210 μmol) and 4-dimethylaminopyridine (3.5 mg) in dry chloroform (12 $cm^3$) under argon, followed by MePEG550 chloroformate (258 mg, 420 μmol, derived from polyethylene glycol 550 monomethyl ether by treatment with phosgene[16]). The mixture was stirred for 2.5 h, then diluted with chloroform to 300 $cm^3$and washed with aqueous sodium hydroxide (2 M), water and brine. Drying, evaporation, chromatography (chloroform ⟶ ethyl acetate–methanol 9 : 1) and drying at 180 °C under reduced pressure (3 torr) for 3 h gave **50** (250 mg, 99%) as a bright purple wax: $\delta_H$ −2.78 (2 H, s, 21,23-$H_2$), 3.35 (3 H, s, $CH_3O$), 3.54–3.78 (m, $(OCH_2CH_2)_n$), 4.47 (2 H, m, $CH_2O_2C$), 7.77 (9 H, m, 3 × $Ph^{10,15,20}$ 3,4,5-$H_3$), 7.82 (2 H, d, *J* 8.2 Hz, $Ph^5$ 3,5-$H_2$), 8.15 (2 H, d, *J* 8.2 Hz, $Ph^5$ 2,6-$H_2$), 8.22 (6 H, m, 3 × $Ph^{10,15,20}$ 2,6-$H_2$), 8.84 (6 H, m, 2,8,12,13,17,18-$H_6$), 8.88 (2 H, d, *J* 4.9 Hz, 3,7-$H_2$); *m*/*z* 1282 (*M* + Na, *n* = 13, 14%), 1238 (*M* + Na, *n* = 12, 22%), 1194 (*M* + Na, *n* = 11, 30%), 1150 (*M* + Na, *n* = 10, 37%), 1106 (*M* + Na, *n* = 9, 30%), 1062 (*M* + Na, *n* = 8, 22%), 1018 (*M* + Na, *n* = 7, 20%), 974 (*M* + Na, *n* = 6, 12%).

### 5-[3-(MeOPEG550carbonylamino)phenyl]-10,15,20-tris[3-(1,2-dicarba*closo*-dodecaboran(12)-1-ylmethoxy)phenyl]-21*H*,23*H*-porphine 51

Porphyrin **44** was treated with MePEG550 chloroformate, as for the synthesis of **50** except that the chromatographic eluant was chloroform ⟶ ethyl acetate, to give **51** (96%) as a bright purple wax: $\delta_H$ −2.86 (2 H, s, 21,23-$H_2$), 1.5–3.2 (30 H, br m, 3 × $B_{10}H_{10}$), 3.4–4.0 (m, $(OCH_2CH_2)_nOMe$), 4.18 (3 H, br s, 3 × carborane 2-H), 4.61 (6 H, m, 3 × $OCH_2$), 7.60–7.72 (8 H, m, 3 × $Ph^{10,15,20}$ 2,5-$H_2$ and $Ph^5$ 5,6-$H_2$), 7.84–7.91 (4 H, m, 3 × $Ph^{10,15,20}$ 6-H and $Ph^5$ 4-H), 8.30 (1 H, br s, $Ph^5$ 2-H), 8.82 (6 H, m, 2,8,12,13,17,18-$H_4$), 8.90 (2 H, d, *J* 4.6 Hz, 3,7-$H_2$); $\delta_C$ 58.2, 59.3 ($OCH_3$), 64.5, 69.6, 70.6–70.9 ($(OCH_2CH_2)_n$), 71.7, 110.1, 114.4, 119.2, 119.3, 121.2, 124.9, 127.5, 128.2, 129.3, 144.0, 155.6; *m*/*z* cluster centred at 1911 (*M* + H, *n* = 16, 0.5%), cluster centred at 1867 (*M* + H, *n* = 15, 0.7%), cluster centred at 1823 (*M* + H, *n* = 14, 1.2%), cluster centred at 1779 (*M* + H, *n* = 13, 1.5%), cluster centred at 1735 (*M* + H, *n* = 12, 2.5%), cluster centred at 1690 (*M* + H, *n* = 11, 4.2%), 1694.1044 (*M* + H $C_{77}H_{114}{}^{11}B_{29}{}^{10}BN_5O_{16}$ requires 1694.1088), 1689.1268 (*M* + H $C_{77}H_{114}{}^{11}B_{24}{}^{10}B_6N_5O_{16}$ requires 1689.1270), 1688.1320 (*M* + H $C_{77}H_{114}{}^{11}B_{23}{}^{10}B_7N_5O_{16}$ requires 1688.1306), cluster centred at 1647 (*M* + H, *n* = 10, 4%), cluster centred at 1603 (*M* + H, *n* = 9, 3.5%), cluster centred at 1559 (*M* + H, *n* = 8, 3.7%), cluster centred at 1514 (*M* + H, *n* = 7, 2.7%), cluster centred at 1471 (*M* + H, *n* = 6, 2%), cluster centred at 1425 (*M* + H, *n* = 5, 1.2%), cluster centred at 1381 (*M* + H, *n* = 4, 1%), 59 ($CH_3OCH_2CH_2$, 100%).

**5-[3-(MeOPEG550carbonylamino)phenyl]-10,15,20-tris[3-(1,2-dicarba*closo*-dodecaboran(12)-1-yl)phenyl]-21*H*,23*H*-porphine 52**

Porphyrin **47** was treated with MePEG550 chloroformate, as for the synthesis of **50** except that the chromatographic eluant was chloroform ⟶ chloroform–acetone (2 : 3), to give **52** (90%) as a bright purple wax: $\delta_H$ −2.80 (2 H, s, 21,23-$H_2$), 1.6–3.2 (30 H, m, 3 × $B_{10}H_{10}$), 3.4–4.0 (m, $(OCH_2CH_2)_nOMe$), 4.21 (3 H, s, 3 × carborane 2-H), 4.60 (6 H, m, 3 × $OCH_2$), 7.10 (1 H, m, $Ph^5$ 4-H), 7.52 (2 H, m, $Ph^5$ 2,5-$H_2$), 7.59 (1 H, m, $Ph^5$ 6-H), 7.73 (3 H, t, *J* 7.7 Hz, $Ph^{10,15,20}$ 5-$H_3$), 7.92 (3 H, d, *J* 7.7 Hz, $Ph^{10,15,20}$ 4-$H_3$), 8.24 (3 H, s, $Ph^{10,15,20}$ 6-$H_3$), 8.33 (3 H, s, $Ph^{10,15,20}$ 2-$H_3$), 8.70 (2 H, m, 2,8-$H_2$), 8.74 (4 H, s, 12,13,17,18-$H_4$), 9.00 (2 H, d, *J* 4.8 Hz, 3,7-$H_2$); *m*/*z* 1687 (*M* + H, *n* = 12, 0.6%), 1643 (*M* + H, *n* = 11, 1.4%), 1598 (*M* + H, *n* = 10, 1.6%), 1556 (*M* + H, *n* = 9, 1.7%), 1511 (*M* + H, *n* = 8, 2%), 1467 (*M* + H, *n* = 7, 1.7%), 1423 (*M* + H, *n* = 6, 1.2%), 1378 (*M* + H, *n* = 5, 0.9%), 1333 (*M* + H, *n* = 4, 0.4%), 59 ($CH_3OCH_2CH_2$, 100%).

**Crystal structure determination of compound 38**

A crystal of **38** was grown by slow evaporation of a solution in chloroform/hexane.

**Crystal data.** $C_{48}H_{48}B_{20}N_6O_4$, *M* = 989.12, wavelength = 0.71073 Å, monoclinic, space group $P2_1/n$, *a* = 14.5870(2), *b* = 7.0000(1), *c* = 27.8680(4)Å, *U* = 2748.01(7) Å$^3$, *Z* = 2, $D_c$ = 1.195 Mg m$^{-3}$, $\mu$ = 0.070 mm$^{-1}$, *F*(000) = 1020, crystal size 0.13 × 0.13 × 0.08 mm. A hemisphere of data (36917 reflections) were collected on a Nonius(kappaCCD diffractometer at 150 K, of which 5373 were unique, [*R*(int) = 0.0687] and 1863 observed with $I>2\sigma(I)$. Data were treated for Lorentz and polarisation but not for absorption. All non-hydrogen atoms were treated anisotropically in the final least squares cycles. Hydrogen atoms were included at calculated positions with the exception of H1 (attached to N1), which was located and refined at a distance of 0.89 Å from the parent atom. Final residuals *R1* and *wR2* were 0.0757 and 0.2287, respectively, with max peak/hole in the difference Fourier map of 0.624 and −0.309 eÅ$^{-3}$. Structural solution was effected using SHELXS-86[27] and refinement completed using SHELXL-97.[28] Fig. 4 was produced using ORTEX.[29] CCDC 195567. See http://www.rsc.org/suppdata/ob/b2/b209534c/ for crystallographic files in CIF or other electronic format.

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