A new convergent method for porphyrin synthesis based on a '3 + 1' condensation

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A new methodology based on the '3 + 1' acid-catalytic condensation of tripyrranes and pyrrole-2,5-dicarbaldehyde has been used, for the first time, for the synthesis of two types of porphyrins: *vic*-dipropionic ester porphyrins 30 and 31 including an analogue of the corallistin-A and *vic*-diacrylic ester porphyrins 32 and 34. For this purpose, synthesis of various tripyrranes and pyrrole-2,5-dicarbaldehydes have been reported and characterized. Studies by dynamic ^{1}H NMR of sterically hindered tripyrranes show conformational exchange, in solution. Structures of the new porphyrins have been confirmed by ^{1}H NMR spectrometry. Introduction of diacrylic ester groups in vicinal positions markedly influences the electronic spectra of compounds 32 and 34 which present an oxorhodo-type absorption pattern.

Introduction

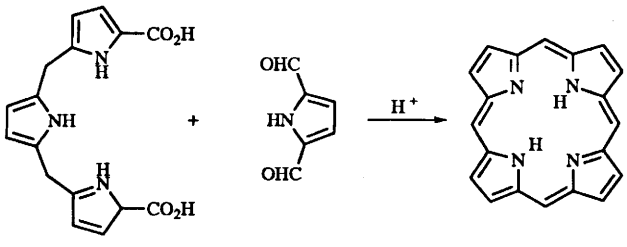
In order to satisfy either symmetry factors or the nature of the substituents, a variety of approaches have been developed and are currently employed in the synthesis of porphyrins and related macrocycles. They are as follows.

Stepwise condensation of monopyrroles with aliphatic or aromatic aldehydes. This procedure initiated and developed by Rothemund[1] and reinvestigated by Lindsey *et al.*[2] is used to prepare *meso*-arylporphyrins. Using a functionalized pyrrole, in a self-condensation reaction, this synthetic route was recently extended to the general synthesis of porphyrins bearing the same substituents at the β-positions[3] and of *meso*-tetra-alkylporphyrins.[4]

'2 + 2' Synthesis. This procedure consists of the condensation of two dipyrromethanes or dipyrromethenes units. This method has an historical value since it was initially employed by Fischer.[5] It was later developed by MacDonald *et al.*[6] and was employed to produce uro-, copro-, aetio-porphyrins and other centrosymmetric porphyrins.[7]

Cyclization of linear tetrapyrrole compounds (bilanes, bilenes or biladienes). This procedure involves cyclization of tetrapyrroles obtained by multi-step condensation of pyrroles.[8] In this method, the presence of a transition metal is often required. Limitations and advantages of these methods have been discussed by Dolphin.[9]

In a recent communication we reported the first example of the synthesis of a *vic*-diacrylic porphyrin using a new '3 + 1' condensation strategy.[10] The general path of this method consists of a condensation of a tripyrrane with a pyrrole-2,5-dicarbaldehyde in the presence of an acidic catalyst. Herein, we report the development of this new method (Scheme 1) allowing



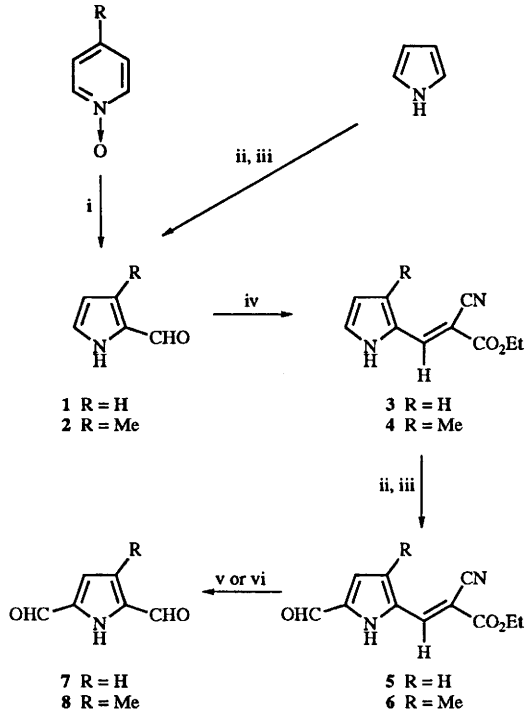
Scheme 1

the preparation of compounds that cannot be obtained using classical procedures. The synthesis and characterization of their precursors are also included.

Results and discussion

Synthesis of pyrrole-2,5-dicarbaldehydes

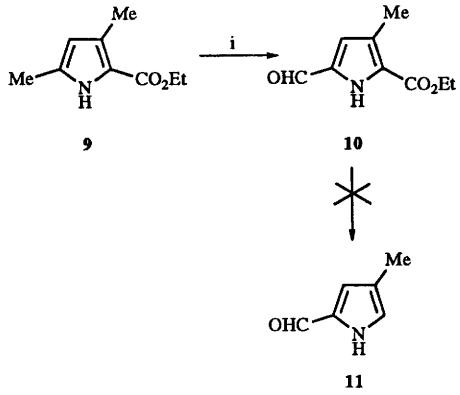
The preparation of pyrrole-2,5-dicarbaldehydes has recently been described.[11] Since, however, the method reported was only applicable to the synthesis of one of the types of pyrrole which we needed, we decided to investigate the preparation of such starting materials by two other procedures which allow the introduction of aldehyde functions onto pyrroles. Formylation can be achieved by the Vilsmeier–Haack reaction[12] or oxidation of α-methyl groups.[13] For the synthesis of porphyrins **30**–**32** and **34** we needed three types of pyrrolecarbaldehydes **7** and **8** (Scheme 2) and **14**. Synthesis of the pyrroledicarbaldehyde



Scheme 2 *Reagents and conditions:* i, *hν*, UV, $CuSO_4$–H_2O, RT; ii, $POCl_3$–DMF, $ClCH_2CH_2Cl$, 60–70 °C; iii, aqueous AcONa, reflux, 45 min; iv, $NCCH_2CO_2Et$, Et_3N, toluene, reflux; v, 3 mol dm^{-3} aq. NaOH, reflux, 3 h; vi, KOH–MeOH–H_2O, reflux, 30 min

7 has been reported by Olsson *et al.*[14] To obtain the pyrroledicarbaldelyde **8** from **11**, we investigated the synthesis

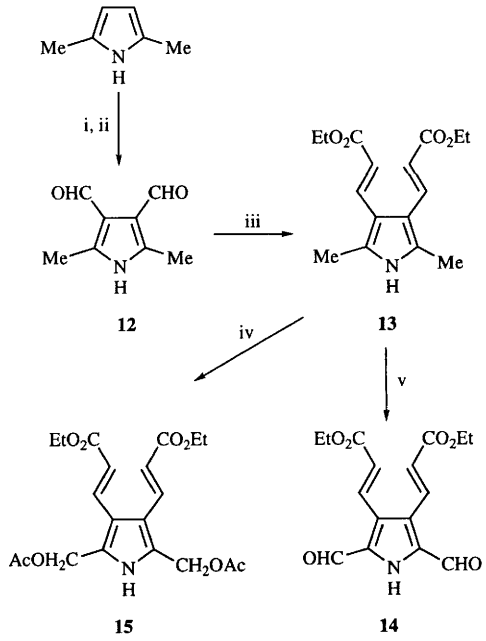
of the latter from α-methyl pyrrole **9**[15] as a starting material. Thus, treatment of **9** with $Pb(OAc)_4$–PbO_2 in acetic acid at room temperature for 3 days by the procedure described by Battersby *et al.*[13] gave compound **10** (73%) (Scheme 3). However,



Scheme 3 *Reagents and conditions:* i, $Pb(OAc)_4$–PbO_2, AcOH, RT, 3 days

attempted saponification of the ester function and subsequent removal of the carboxylic acid group from **10** was unsuccessful. An alternative way to prepare **8** was by formylation of **2** (Scheme 2). The work of Bellamy *et al.*[16] related to the photochemistry of aromatic *N*-oxides, shows the possibility of converting 4-substituted pyridine *N*-oxides into pyrrole-2-carbaldehydes by UV irradiation. Thus, aqueous 4-methylpyridine *N*-oxide when irradiated in the presence of $CuSO_4$ with a 350 W high-pressure mercury vapour lamp effectively gave **2**. The best yield (21%) was obtained after 30 h of reaction. Protection of the aldehyde function at position 2 as an ethoxycarbonyl(cyano)vinyl group and subsequent formylation on carbon 5 were carried out as described above to give **6** (59%). Cleavage of the protecting group to give the pyrroledicarbaldehyde **8** was carried out using milder conditions than those used in the case of **5**. Thus, the compound was obtained in 39% yield by treatment of **6**, in methanol, with 1.5 mol dm^{-3} aqueous potassium hydroxide for 40 min under reflux.

A second improved method for the synthesis in good yield (> 70%),[13] of pyrrolecarbaldehydes is based on the oxidation of α-methyl groups. We have used this method to prepare pyrrole-2,5-dicarbaldehydes bearing two electron-withdrawing groups at positions 3 and 4 (Scheme 4), starting from commercially available 2,5-dimethylpyrrole. Thus, treatment with $POCl_3$–DMF (3 equiv.), in a Vilsmeier–Haack reaction, gave **12** (55%). These functions react in a Wittig-type reaction to give the diacrylic pyrrole derivative **13** (62%). Oxidation of the 2- and 5-methyl groups was carried out with $Pb(OAc)_4$–PbO_2 in acetic acid. Although this reaction is usually very slow (reaction time > 70 h),[13] 3 h was found sufficient to give the pyrrole dicarbaldehyde **14** (22%).



Scheme 4 *Reagents and conditions:* i, $POCl_3$–DMF, $ClCH_2CH_2Cl$, 60–70 °C; ii, Aqueous NaOH, reflux, 15 min; iii, $(EtO)_2POCH_2CO_2Et$–NaH, THF, 60 °C; iv, $Pb(OAc)_4$, AcOH, RT, 1 h; v, $Pb(OAc)_4$–PbO_2, AcOH, RT, 3 h

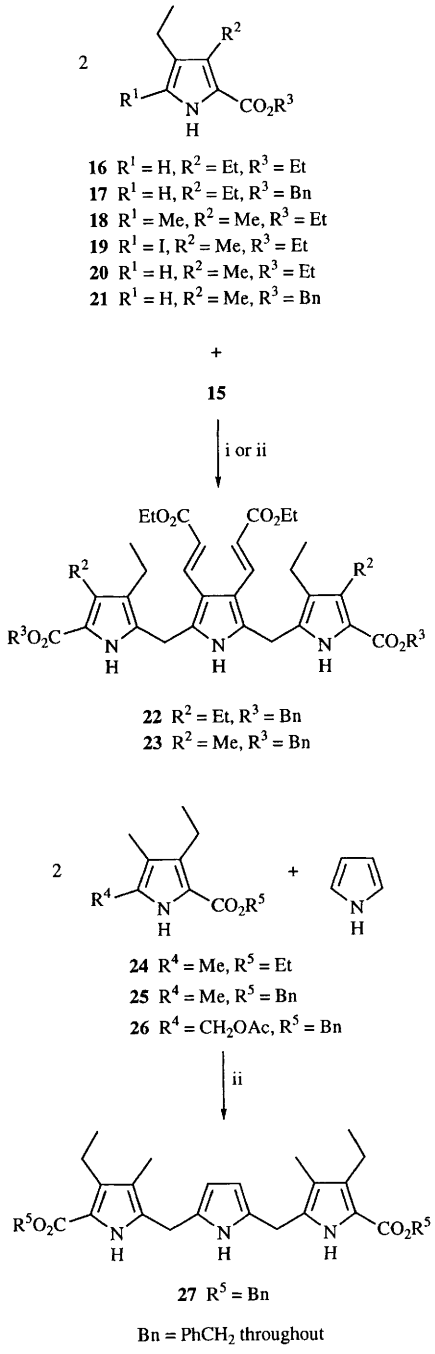
Synthesis of tripyrranes

The synthesis of tripyrranes has already been described and used for the preparation of porphyrinoid derivatives which possess a thiophene,[17] furan[17] or pyridine[18] ring as a replacement for one of the pyrrole rings and in the preparation of extended macrocycles such as sapphyrins.[19,20] As defined above, our strategy for the preparation of porphyrins is a convergent procedure which consists of condensation of tripyrrole units with pyrrole-2,5-dicarbaldehydes. We now describe the preparation of the different tripyrranes employed (Scheme 5). The pyrrole derivative **13** was converted, into the 2,5-di(acetoxymethyl)pyrrole **15**, in good yield, when treated with lead tetraacetate (2.2 equiv.) in acetic acid.

The pyrroles **16**,[21] **18**[22] and **24**[23] were prepared according to the literature. The pyrrole **16** was transesterified to afford **17**. The α-methyl group of the pyrrole **18** was oxidized to a carboxylic acid group by treatment with SO_2Cl_2 followed by hydrolysis. The resulting carboxylic acid substituent was removed by iodination to give **19**. Finally, iodine was removed by catalytic hydrogenation at 40 °C in a mixture of THF–MeOH to afford the pyrrole **20** (68.6%) which upon transesterification led to the benzyl ester **21**. Following the same procedure, **24** was converted into compound **25** which was converted into the 2-(acetoxymethyl)pyrrole **26** (68%). The tripyrrane **22** was prepared in 56% yield by a Montmorillonite K-10 catalysed condensation of the di(acetoxymethyl) pyrrole **15** with the pyrrole **17** (2 equiv.) in methylene dichloride.[24] The tripyrrane **23** was prepared in 67.5% yield by a toluene-*p*-sulfonic acid catalysed condensation of **15** with the pyrrole **21** (2 equiv.) in hot absolute ethanol (Scheme 5). Following the procedure used for compound **22**, the tripyrrane **27** was prepared in 64% yield by condensation of the pyrrole **26** with freshly distilled pyrrole.

^{1}H NMR characterization of tripyrranes

The ^{1}H NMR spectrum of the tripyrrane **29** showed two broad signals at 9.12 (1 H) and 10.85 (2 H) ppm, assignable to the NH resonance. β-Pyrrole protons of the central pyrrole gave a doublet at 5.85 ppm (weakly coupled with NH, J_{HH} 2.5 Hz) whilst singlets at 4.41 and 3.66 ppm (both 4 H) were identified as the benzylic CH_2 and bridge-CH_2 protons, respectively. In the case of the tripyrranes **22** and **23**, there are β-ethyl acrylate substituents which exert an additional steric hindrance and affect the ^{1}H NMR spectra. Except in the 2–5 ppm range, the spectra of these tripyrranes were well resolved. In addition to a quartet assignable to ethoxy group CH_2, these spectra showed, in the 2–5 ppm range, unresolved and unassignable signals [see Fig. 1(*a*) and (*b*), T = 295 K] the broadness and multiplicity of which, however, suggest the occurrence of slow conformational exchange. By use of ^{1}H dynamic NMR spectroscopy in [$^2H_8$]toluene rather than in $CDCl_3$, the former allowing studies over a larger temperature range than the latter, assignments in the 2–5 ppm range for the tripyrranes **22** and **23** were made. At 295 K, the spectrum of **22** showed an unresolved signal at 2.33 ppm (4 H), 4 coalescent signals at 2.75 (4 H), 3.1 (2 H), 3.9 (4 H) and 4.5 ppm (2 H). At the same temperature, the spectrum of **23** showed 3 coalescent signals at 3.2 (2 H), 4 (4 H) and 4.5 ppm (2



Scheme 5 *Reagents and conditions:* i, Montmorillonite K-10 Clay, CH_2Cl_2, 3 h, RT; ii, *p*-$MePhSO_3H$, abs. EtOH 60–70 °C

H). With an increase in temperature, in both cases, a gradual disappearance of the coalescence occurred. This was completed at 345 K where spectra were well resolved [see Fig. 1(*a*) and (*b*)]. From literature data for the ^1H chemical shifts of tripyrranes [25] and from those obtained for the tripyrrane **27**, we have assigned the signals in the spectrum of compound **22** as follows: quartets at 2.35 and 2.80 ppm correspond to β-ethyl methylene protons; singlets at *ca* 3.6 and 4.5 ppm (both 4 H) present in the spectra of **22** and **23** were assigned to bridge and benzyl methylene protons. Wishing to know if the non-equivalence resulting from conformational exchange was due to a loss of symmetry relative to the central pyrrole or to the presence of another element of symmetry, we lowered the temperature in order to reduce conformational exchange rates. As shown on the spectra at 273 K [see Fig. 1(*a*) and (*b*)], each singlet at 3.6 and 4.5 ppm on spectra recorded at 345 K, gave rise to two doublets. In addition, homonuclear coupling constant values (J_{HH} 16 Hz) determined from spectra were in agreement with those of

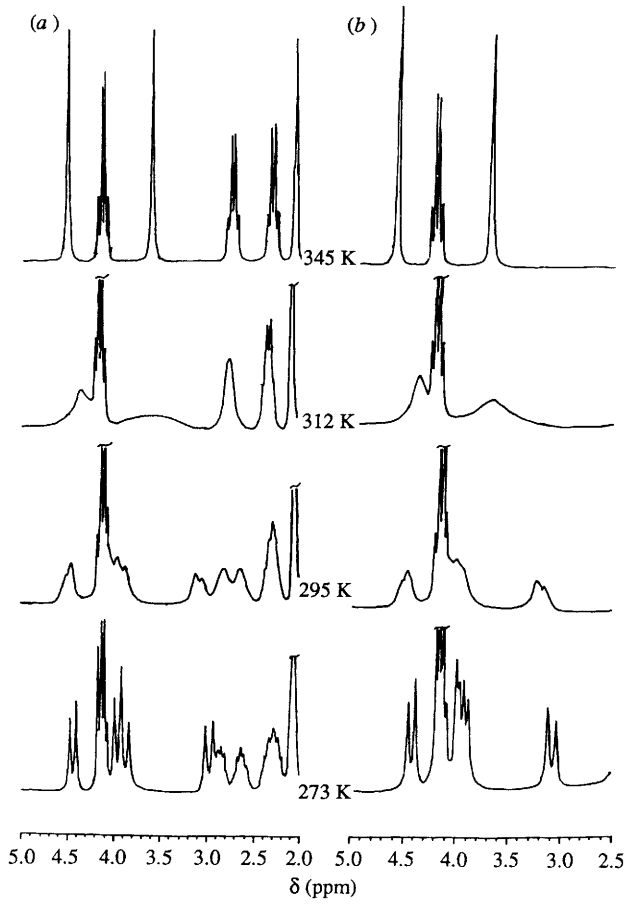


Fig. 1 2–5 ppm range ^1H DNMR spectra (200 MHz, [$^2H_8$]toluene) of the tripyrranes **22** (*a*) and **23** (*b*)

geminal protons. In order to confirm this assumption, homonuclear decoupling experiments were carried out. Couplings of the protons at 3 and 4.45 ppm have been established by selective irradiation. From ^1H DNMR studies in the case of the tripyrranes **22** and **23**, we deduced that broadening of the signals corresponding to bridge-methylene protons and those of benzylic groups was really due to slow conformational exchange. In addition, results of decoupling experiments at low temperature (273 K) suggested that the two protons of each methylene group were magnetically different. The presence of these two non-equivalent protons either for bridge-methylene groups or benzylic ester substituents could be explained by a central symmetry type with respect to the central pyrrole.

Formation of porphyrins

The cyclization involves the acid-catalysed condensation of 1,14-unsubstituted tripyrranes with 1 equiv. of pyrrole-2,5-dicarbaldehydes. In a general procedure, protected benzyl tripyrrane-1,14-dicarboxylates were deesterified by hydrogenation over Pd–C. Although decarboxylation of the resulting tripyrrane-dicarboxylic acids appears to occur spontaneously, they were used in the following step without other purification.

Initially, condensation of the tripyrrane **28** with the pyrroledicarbaldehyde **7** was carried out in absolute ethanol, in the presence of an excess of zinc acetate, at room temperature for 1 day. Such conditions were chosen because it has been reported in the literature that the presence of metallic ion appears to facilitate cyclization by the template effect.[26,27] With a catalytic amount of toluene-*p*-sulfonic acid and after addition of DDQ to oxidize porphyrinogen, the work-up of the reaction mixture furnished the zinc complex of porphyrin **30** (5.5%). The structure of Zn·**30**, as well as the other porphyrins whose synthesis is reported here, was characterized on the basis

Table 1 Optimization conditions for the preparation of the porphyrin **30**

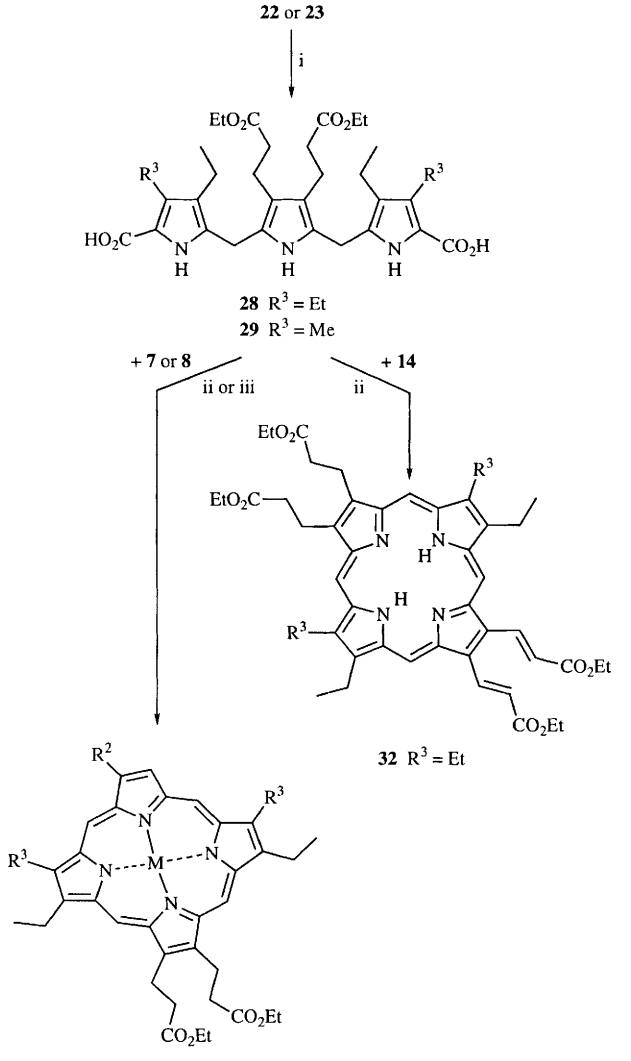
	Concentration of reagents (mmol)	Solvent	Temperature (°C)	Acidic catalyst	Duration (hours)	Yield (%)
a[a]	1.6	EtOH	RT	TSA[b]	24	5.5
b	2	CH_2Cl_2	RT	TSA	20	20
c	1.6	CH_2Cl_2	RT	TSA	20	22
d	1.6	CH_2Cl_2	RT	F_3CCO_2H	20	30
e	1.6	CH_2Cl_2	RT	F_3CCO_2H	70	53.5
f	1.6	CH_2Cl_2	RT	F_3CCO_2H	80	61.5
g	2	$(CH_2Cl)_2$	40–50	TSA	20	6.5

[a] In the presence of $Zn(OAc)_2 \cdot 2H_2O$. [b] TSA = toluene-*p*-sulfonic acid.

of ^1H NMR spectral evidence. The presence of Zn^{II} having little effect on the yield of the cyclization, we have tested different conditions but always in the absence of zinc salt; the results are reported in Table 1. The concentration range (1.6–2 mmol) used was suggested by the procedure described by Sessler in the synthesis of sapphyrins.[21] In all cases, the yields of **30** were higher after oxidation, chromatography and crystallisation than in the presence of Zn^{II}. Factors such as the nature of the acid catalyst, reaction time and temperature were varied. Use of trifluoroacetic acid instead of toluene-*p*-sulfonic acid in CH_2Cl_2 increased the yields, (from 20 to 30%) for 20 h reactions. An increase in the reaction time (from 70 to 80 h) but with no other changes, also gave increased yields; (from 53.5 and 61.5%). An increased reaction temperature (50 °C in dichloroethane which has a polarity comparable to that of methylene dichloride) significantly decreased the yield (to 6.5%). This result suggested that one of the two reactants or both are very unstable when the temperature is raised. Porphyrins **31**, **32** and **34** were prepared under the conditions corresponding to the test **f** (Table 1) in 42.5, 49 and 33% yields respectively. Porphyrin **32** is an analogue of corallistin-A. This free-base porphyrin was isolated from the demosponge *Corallistes* sp.[28] Its synthesis as a dimethyl ester derivative was reported by Scott *et al.*[29] and was obtained in 32% yield using Johnson's method by cyclization of appropriate a,c-biladiene. Our porphyrin **31** differs only by the substitution of one acetic acid side chain of the natural product by one propionic acid side chain, other peripheral substituents remaining unchanged. The porphyrins **32** and **34** bearing vicinal β-ethyl acrylic ester groups, are reported for the first time (Schemes 6 and 7), and are the first representatives of a new family which should be of interest in exploring physicochemical behaviour–electronic property relationships.

UV–visible characterization

From the UV–visible absorption patterns of the porphyrins synthesized two groups may be characterized. Porphyrins **30** and **31** show, in the visible region, an absorption spectrum of the well known etio-type (band IV > III > II > I). This is characteristic of β-alkyl substituted free-base porphyrins (see data in Experimental section). Porphyrins **32** and **34** form a second group, the visible absorption spectra of which are characterized by four bands with relative intensities III > II > IV > I. This sort of absorption pattern, known as the oxo-rhodo-type, was reported for free-base porphyrins bearing two electron-withdrawing groups on diagonally opposite pyrrole rings.[30] Thus, porphyrins with vicinal diacrylic ester groups represent a further substitution pattern which is also characterized by the same oxorhodo-type visible spectra. Moreover, we observed a bathochromic shift of *ca.* 20 nm with respect to those of the dipropionic acid porphyrins **30** and **31**, probably as the result of an extension of the π delocalized system to the adjacent acrylic side chains.

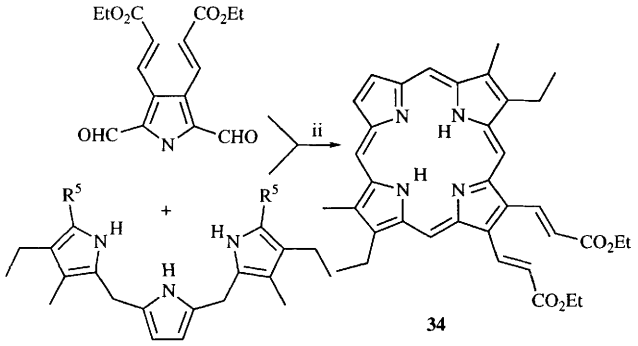


Zn•30 M = Zn, R^2 = H, R^3 = Et
30 M = 2H, R^2 = H, R^3 = Et
31 M = 2H, R^2 = Me, R^3 = Me

Scheme 6 *Reagents and conditions:* i, H_2, Pd–C (10%), THF, RT; ii, CF_3CO_2H, distilled CH_2Cl_2, 72 h, RT; iii, *p*-$MePhSO_3H$, abs. EtOH, RT

Conclusion

We have shown that a new general pathway based on a '3 + 1' condensation may conveniently afford a single porphyrin if at least one of the two components, pyrrole or tripyrrane, is symmetrical. The symmetry restriction which characterizes this method is balanced by its convergent character. By the reported technique we have directly synthesized for the first time *vic*-dipropionic and *vic*-diacrylic ester porphyrins. Porphyrins of



Scheme 7 *Reagents and conditions:* i, H_2, Pd–C (10%), THF, RT; ii, CF_3CO_2H, distilled CH_2Cl_2, RT

the latter type have unusual oxorhodo electronic absorption spectra as a result of the chemical nature of the substituents and/or their peripheral positions. Studies of the effects induced by the presence of electron-withdrawing substituents on the physicochemical properties, mainly the redox behaviour of their metal complexes, are underway.

Experimental

^{1}H NMR spectra were obtained in the indicated solvents, with a Bruker AC 200 instrument. Chemical shifts are given in ppm relative to TMS. Coupling constants are given in Hz. Optical spectra were recorded using a Varian DMS 200 spectrophotometer. When dry CH_2Cl_2 or $(CH_2Cl)_2$ is specified, these were distilled over CaH_2. THF and diethyl oxide were respectively distilled over Na–PhCOPh and sodium. Ether refers to diethyl ether.

3-Methylpyrrole-2-carbaldehyde 2

A solution of 4-methylpyridine-*N*-oxide (2 g, 18.3 mmol) and hydrated copper sulfate ($CuSO_4 \cdot 5H_2O$; 45.2 g, 10 equiv.) in distilled water (800 cm^3) was irradiated, at 24–27 °C for 24 h with a high-pressure Vapors-mercury Lamp (350 W, 1.6 A) after which it was saturated with sodium chloride and extracted with ether (450 cm^3). The extract was dried (Na_2SO_4) and evaporated to give the title compound **2** (0.42 g, 21%) after chromatography on a silica gel column (Found: C, 60.94; H, 5.25; N, 9.75. Calc. for $C_7H_7NO_2$: C, 61.31; H, 5.10; N, 10.22%); δ_H(200 MHz, $CDCl_3$) 9.65 (1 H, br, NH), 9.60 (1 H, s, CHO), 7.24 (1 H, t, 2-H), 6.11 (1 H, t, 3-H) and 2.37 (3 H, s, CH_3).

2-(2-Cyano-2-ethoxycarbonylvinyl)-3-methylpyrrole 4

A mixture of the pyrrole **2** (2 g, 18.4 mmol), ethyl cyanoacetate (2 equiv.) and triethylamine (0.8 cm^3) was heated under reflux in dry toluene (30 cm^3) for 4 h after which it was evaporated. The residue was dissolved in the minimum of absolute ethanol and the solution frozen to give the product as yellow needles (2.52 g, 67.5%); δ_H(200 MHz, $CDCl_3$), 9.80 (1 H, br, NH), 8.01 (1 H, s, CH=), 7.12 (1 H, t, 5-H), 6.22 (1 H, t, 4-H), 4.25 (2 H, q, OCH_2CH_3), 2.26 (3 H, s, CH_3) and 1.34 (3 H, t, OCH_2CH_3).

5-(2-Cyano-2-ethoxycarbonylvinyl)-4-methylpyrrole-2-carbaldehyde 6

A suspension of compound **4** (1.5 g, 7.35 mmol) in distilled dichloroethane (20 cm^3) was added to a Vilsmeier complex generated by treating DMF (1.5 cm^3) with $POCl_3$ (1.3 cm^3). After the mixture had been heated under reflux for 0.5 h it was cooled and treated with saturated aqueous sodium acetate (50 cm^3) and again heated to reflux for 1 h. After work-up, the crude product was chromatographed on a silica gel column eluted with CH_2Cl_2 to give compound **6** (1.01 g, 59.5%) as a yellow powder (Found: C, 61.8; H, 5.0; N, 11.8. Calc. for $C_{12}H_{12}N_2O_3$: C, 62.07; H, 5.17; N, 12.07%); δ_H(200 MHz, $CDCl_3$) 10.22 (1 H, br, NH), 9.68 (1 H, s, CHO), 8.07 (1 H, s, HC=), 6.81 (1 H, d, 3-H), 4.35 (2 H, q, OCH_2CH_3), 2.30 (3 H, s, CH_3) and 1.37 (3 H, t, OCH_2CH_3).

3-Methylpyrrole-2,5-dicarbaldehyde 8

The procedure described for compound **5** was used to prepare compound **6** in 59.5% yield, starting from the pyrrole **2**. Cleavage of the aldehyde protecting group was carried out under mild conditions compared with those used for **5**. A solution of the intermediate **6** (0.6 g, 2.6 mmol) in methanol (25 cm^3) was treated with a solution of potassium hydroxide (3.4 g) in water (35 cm^3) and the mixture was heated under reflux for 40 min under argon. The mixture was then evaporated to remove the methanol and the residue was diluted with water, acidified to pH 4.5 with 6 mol dm^{-3} hydrochloric acid and extracted with ethyl acetate (*ca.* 300 cm^3). The extract was dried (Na_2SO_4) and evaporated and the crude product was chromatographed on a silica gel column with CH_2Cl_2–Et_2O (100:5, v/v) as eluent the pure title compound **8** as a white powder (137 mg, 39%) (Found: C, 60.9; H, 5.25; N, 9.75. Calc. for $C_7H_7NO_2$: C, 61.31; H, 5.10; N, 10.22%). δ_H(200 MHz, $CDCl_3$) 9.87 (1 H, s, CHO), 9.68 (1 H, s, CHO), 6.76 (1 H, d, 3-H) and 2.41 (3 H, s, CH_3).

2,5-Dimethylpyrrole-3,4-dicarbaldehyde 12

Distilled 2,5-dimethylpyrrole (10.1 g, 0.105 mmol) was added dropwise at room temperature to a Vilsmeier complex prepared from distilled DMF (50 cm^3) and $POCl_3$ (34 cm^3, 0.36 mol) added at 0 °C under argon, and then stirred at room temperature for 1 h. The reaction mixture was warmed to and held at 50 °C for 2 h after which it was cooled (ice water-bath) and treated cautiously with 2 mol dm^{-3} aqueous NaOH. This mixture was briefly heated under reflux and finally poured into ice–water (2 dm^3). The title pyrrole **12** was filtered off and dried (P_2O_5) overnight (9.2 g, 62%); δ_H(200 MHz, $CDCl_3$) 9.90 (1 H, br, NH), 10.22 (2 H, s, CHO) and 2.54 (6 H, s, CH_3).

3,4-Di(2-ethoxycarbonylvinyl)-2,5-dimethylpyrrole 13

Triethyl phosphonoacetate (68 g) in freshly distilled THF (40 cm^3) was added at room temperature to a dispersion of sodium hydride (60%; 12 g) suspended in THF (60 cm^3) under argon. A solution of compound **12** (4.58 g, 30.3 mmol) in distilled THF (120 cm^3) was added dropwise at room temperature to the reaction mixture which was then heated at 60 °C overnight. The solution when poured into ice–water (1.5 dm^3) gave the diacrylic pyrrole **13** as a precipitate which was filtered off and recrystallized from hot absolute ethanol (6.75 g, 83.5%) (Found: C, 65.7; H, 7.1; N, 4.7. Calc. for $C_{16}H_{21}NO_4$: C, 65.98; H, 7.21; N, 4.81%); δ_H(200 MHz, $CDCl_3$) 9.12 (1 H, br, NH), 7.75 (2 H, d, J_{HH} 16, CH=), 5.95 (2 H, d, J_{HH} 16, =CH), 9.22 (4 H, q, OCH_2CH_3), 2.31 (6 H, s, CH_3) and 1.30 (6 H, t, OCH_2CH_3).

3,4-Di(2-ethoxycarbonylvinyl)pyrrole-2,5-dicarbaldehyde 14

A suspension of compound **13** (0.5 g, 17.2 mmol) in glacial acetic acid (15 cm^3) was added to a mixture of $Pb(OAc)_4$ (0.5 g, 2.2 equiv.) and of PbO_2 (0.98 g, 2.28 equiv.) in the same solvent (20 cm^3) at room temperature. After being stirred at room temperature for 3 h, the mixture was treated with distilled water (20 cm^3) and then heated under reflux for 20–30 min. It was then diluted with water (100 cm^3) and CH_2Cl_2 (100 cm^3) and the phases were separated. The aqueous layer was extracted several times with CH_2Cl_2. The combined organic phase and extracts were neutralized, washed with water, dried (Na_2SO_4) and evaporated. Chromatography of the residue on a silica gel column gave the pyrrole (0.12 g, 22%) (Found: C, 59.2; H, 5.78; N, 3.91. Calc. for $C_{16}H_{17}NO_6$:

C, 60.18; H, 5.33; N, 4.38%); δ_H(200 MHz, $CDCl_3$) 10.62 (1 H, br, NH), 9.96 (2 H, s, CHO), 7.86 (2 H, d, J_{HH} 16, CH=), 6.27 (2 H, d, J_{HH} 16, =CH), 4.26 (4 H, q, OCH_2CH_3) and 1.32 (6 H, t, OCH_2CH_3).

3,4-*Di*(2-ethoxycarbonylvinyl)-2,5-di(acetoxymethyl)pyrrole 15

Compound **13** (3 g, 10.3 mmol) in glacial acetic acid (50 cm^3) was added dropwise at room temperature to a solution of lead tetraacetate (9.6 g, 2.1 equiv.) in the same solvent (80 cm^3). The mixture was stirred at room temperature for 90 min after which it was evaporated under reduced pressure. Work-up followed by precipitation in CH_2Cl_2–heptane gave the pyrrole **15** (3.12 g, 74.5%) (Found: C, 58.3; H, 5.9; N, 3.5. Calc. for $C_{20}H_{25}NO_8$: C, 58.96; H, 6.14; N, 3.43%); δ_H(200 MHz, $CDCl_3$) 9.42 (1 H, br, NH), 7.71 (2 H, d, J_{HH} 16, CH=), 6.04 (2 H, d, J_{HH} 16, =CH), 5.05 (4 H, s, CH_2-pyrrol.), 4.24 (4 H, q, OCH_2CH_3), 2.08 (6 H, s, OCH_3) and 1.31 (6 H, t, OCH_2CH_3);

Benzyl-4-ethyl-3-methylpyrrole-2-carboxylate 21

Sulfonyl chloride (6.6 cm^3, 3.2 equiv.) was added dropwise to a solution of the pyrrole **18** (5 g, 25 mmol) (prepared according to the method described by Inhoffen *et al.*,[23] based on a Knorr cyclization, and obtained in 52% yield) in freshly distilled ether (200 cm^3). The mixture was stirred for 24 h, under argon, at room temperature after which it was evaporated. The residue was dissolved in acetone (100 cm^3) and the solution diluted with distilled water (50 cm^3). After the mixture had been heated under reflux for 45 min, the acetone was removed under reduced pressure and the aqueous layer was extracted several times with CH_2Cl_2 until no suspension remained. The combined extracts were evaporated and the residue was dissolved again in ether (300 cm^3). This solution was then extracted with 10% aqueous $NaHCO_3$ (300 cm^3) to remove the aldehyde by-product resulting from the non-quantitative formation of the trichloromethyl derivative. The aqueous solution was finally acidified with 6 mol dm^{-3} hydrochloric acid to the pyrrolecarboxylic acid. This was filtered off and dried over P_2O_5; yield 4.42 g (76.5%). The carboxylic acid (3 g, 13.33 mmol) was added to a solution of $KHCO_3$ (8 g) in water (100 cm^3) to which a similar volume of ethanol was then added. Iodine (8 g, 2 equiv.) previously dissolved in a minimum of absolute ethanol, was then added dropwise at room temperature to the solution. This mixture was stirred for 2.5 h at 40 °C before being heated at 90 °C to remove the excess of iodine. When poured into ice–water the mixture gave the iodide derivative **19** which was filtered off and dried over P_2O_5 overnight; yield 3.74 g (91.5%). Magnesium oxide (1 g) was added to a solution of compound **19** (3.5 g, 11.4 mmol) in THF–EtOH (1:1; 60 cm^3) and this was followed by Pd–C (10%; 1 g). Hydrogen was bubbled into the vigorously stirred mixture and the reaction was monitored by TLC. On completion of the reaction, the catalyst was removed by filtration through Celite and the filtrate evaporated to give compound **21** (2.03 g, 98%). Sodium (0.06 g) was added to benzyl alcohol (20 cm^3) under argon and the solution was stirred for some minutes. After this the pyrrole **20** (2 g, 11 mmol) in benzyl alcohol (5 cm^3) was added to it. The mixture was heated at 100 °C under reduced pressure (10 mmHg) for 4 h after which the alcohol was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and the solution neutralized, dried (Na_2SO_4) and evaporated to give the pyrrole **21** in quantitative yield (2.6 g). Compound **20**: δ_H(200 MHz, $CDCl_3$) 8.78 (1 H, br, NH), 6.65 (1 H, d, J_{HH} 2.5, 5-H), 4.29 (2 H, q, OCH_2CH_3), 2.41 (2 H, q, CH_2CH_3), 2.27 (3 H, s, CH_3), 1.33 (3 H, t, OCH_2CH_3), 1.15 (3 H, t, CH_2CH_3). Compound **21**: δ_H(200 MHz, $CDCl_3$) 8.80 (1 H, br, NH), 7.45 (5 H, m, Ph), 6.65 (1 H, d, J_{HH} 2.5), 5.29 (2 H, s, OCH_2), 2.41 (2 H, q, CH_2CH_3), 2.28 (3 H, s, CH_3) and 1.15 (3 H, t, CH_2CH_3).

Benzyl-3,4-diethylpyrrole-2-carboxylate 17

The pyrrole **16** (9.1 g, 46.6 mmol), prepared according to the method described by Sessler[22] and obtained in 84% yield, was transesterified under similar conditions to those used for the preparation of **21** to give the pyrrole **17** (11.4 g, 96%) as a brown oil; δ_H(200 MHz, $CDCl_3$) 9.29 (1 H, br, NH), 7.42 (5 H, m, Ph), 6.68 (1 H, d, J_{HH} 2.5, 5-H), 5.37 (2 H, s, OCH_2Ph), 2.85 (2 H, q, CH_2CH_3), 2.51 (2 H, q, CH_2CH_3) and 2.25 and 2.21 (6 H, 2 t, 2 CH_2CH_3).

Benzyl 5-acetoxymethyl-3-ethyl-4-methylpyrrole-2-carboxylate 26

The pyrrole **24**[24] (5 g, 25.6 mmol), transesterified by the method described above, gave the ester **25** which was then treated with lead tetraacetate in acetic acid according to the preparation of the pyrrole **15** to afford compound **26** (5.35 g, 78%) (Found: C, 68.41; H, 6.45; N, 4.44. Calc. for $C_{18}H_{21}NO_4$: C, 68.57; H, 6.66; N, 4.44%); δ_H(200 MHz, $CDCl_3$) 8.92 (1 H, br, NH), 4.65 (2 H, q, OCH_2CH_3), 2.70 (2 H, q, CH_2CH_3), 2.16 and 1.91 (6 H, 2 s, 2 CH_3), 1.31 (3 H, t, OCH_2CH_3) and 1.08 (3 H, t, CH_2CH_3).

2,5-Bis(5′-benzyloxycarbonyl-3′,4′-diethylpyrrol-2′-ylmethyl)-3,4-di(2-ethoxycarbonylvinyl)pyrrole 22

A solution of compounds **17** (2.52 g, 9.8 mmol) and **15** (2 g, 4.9 mmol) in CH_2Cl_2 (40 cm^3) was stirred at room temperature in the presence of acidic Montmorillonite K-10 clay (4 g). After 3 h, the clay was filtered off and the solution was first shaken in the presence of aqueous $NaHCO_3$ and then washed with water and dried (Na_2SO_4). Evaporation gave the crude product which was chromatographed on a silica gel column. The starting pyrrole **17** was eluted with CH_2Cl_2 followed by elution of the tripyrrane **22** (2.21 g, 56%) with a mixture of CH_2Cl_2–Et_2O (100:3, v/v) (Found: C, 71.8; H, 6.7; N, 5.4. Calc. for $C_{48}H_{55}N_3O_8$: C, 71.91; H, 6.86; N, 5.24%); δ_H(200 MHz, [$^2H_8$]toluene) 11.51 (2 H, s, 2NH), 10.09 (1 H, s, NH), 8.31 (2 H, d, J_{HH} 16, CH=), 7.11–6.94 (10 H, 2 m, Ph), 6.39 (2 H, d, J_{HH} 16, =CH), 4.4 and 4.1 (4 H, br, OCH_2Ph), 4.27 (4 H, q, OCH_2CH_3), 4.1 and 3.2 (4 H, br, 2 bridge-CH_2), 2.85 and 2.66 (4 H, m, CH_2CH_3), 2.33 (4 H, br, CH_2CH_3) and 1.22, 1.11 and 1.01 (18 H, 3 t, OCH_2CH_3 and CH_2CH_3).

2,5-Bis(5′-benzyloxycarbonyl-3′-ethyl-4′-methylpyrrol-2′-ylmethyl)-3,4-di(2-ethoxycarbonylvinyl)pyrrole 23

A mixture of compounds **15** (0.84 g, 2.06 mmol) and **21** (1 g, 4.12 mmol) in absolute ethanol (30 cm^3) was heated under reflux in the presence of toluene-*p*-sulfonic acid (0.5 g) for 1.5 h. The solution was then concentrated and frozen to give the tripyrrane **23** as crystals which were filtered off (1.07 g, 67.5%) (Found: C, 71.3; H, 6.7; N, 5.2. Calc. for $C_{46}H_{51}O_8N_3$: C, 71.41; H, 6.59; N, 5.43%); δ_H(200 MHz, [$^2H_8$]toluene) 11.44 (2 H, s, 2NH), 9.95 (1 H, s, NH), 8.33 (2 H, d, J_{HH} 16, CH=), 7.2–6.9 (10 H, m, Ph), 6.43 (2 H, d J_{HH} 16, =CH), 4.4 and 4.1 (4 H, br, OCH_2Ph), 4.28 (4 H, q, OCH_2CH_3), 4.1 and 3.2 (4 H, br, bridge-CH_2), 2.29 (10 H, br, CH_2CH_3 and CH_3) and 1.10 and 0.95 (12 H, 2 t, CH_2CH_3 and OCH_2CH_3).

2,5-Bis(5′-benzyloxycarbonyl-4′-ethyl-3′-methylpyrrol-2′-ylmethyl)pyrrole 27

A mixture of the pyrrole **26** (1 g, 3.17 mmol) and the pyrrole (0.11 g, 1.58 mmol) in CH_2Cl_2 (25 cm^3) was stirred at room temperature in the presence of Montmorillonite K-10 clay (1 g). After 3 h, the clay was filtered off and the filtrate was evaporated. Recrystallization of the residue from hot absolute ethanol gave the tripyrrane **27** (0.61 g, 64%) (Found: C, 74.7; H, 6.7; N, 7.3. Calc. for $C_{36}H_{39}N_3O_4$: C, 74.87; H, 6.76; N, 7.28%); δ_H(200 MHz, $CDCl_3$) 10.85 (2 H, br, NH), 9.12 (1 H, br, NH), 7.23–7.06 (10 H, m, Ph), 5.21 (2 H, d, J_{HH} 2.5, H_β), 4.41 (4 H, s, OCH_2Ph), 3.66 (4 H, s, bridge-CH_2), 2.64 (4 H, q, OCH_2CH_3), 1.87 (6 H, s, CH_3) and 0.99 (6 H, t, CH_2CH_3).

Zinc 7,8-di(2-ethoxycarbonylethyl)-2,3,12,13-tetraethylporphyrinate (Zn 30)

Pd–C (10%; 0.2 g) was added under argon to a solution of the tripyrrane **22** (0.325 g, 0.41 mmol) in distilled THF (25 cm^3). Hydrogenation at room temperature was followed by measuring the hydrogen volume used. Removal of the catalyst by filtration through Celite and evaporation of the THF under reduced pressure gave the tripyrranedicarboxylic acid as a brown oil which was immediately dissolved in absolute ethanol (250 cm^3). The pyrrole **7** (0.05 g, 1 equiv.) was then added to this solution followed by toluene-*p*-sulfonic acid (0.38 g, 5 equiv.) and hydrated zinc acetate $Zn(OAc)_2 \cdot 2H_2O$ (0.27 g, 3 equiv.). This mixture was stirred at room temperature for 1 day, after which it was neutralized with triethylamine (1 cm^3), and treated with DDQ (93 mg, 1 equiv.) for 1 h with stirring at 40 °C. After this, the mixture was evaporated and diluted with CH_2Cl_2. The solution was washed with water several times to remove the oxidation reagent before it was dried (Na_2SO_4) and evaporated. The resulting crude product was chromatographed on a silica gel column with CH_2Cl_2 as eluent to give pure zinc porphyrin **Zn 30** (0.015 g, 5.5%) (Found: C, 65.6; H, 6.6; N, 7.6. Calc. for $C_{38}H_{44}N_4O_4$ Zn: C, 66.53; H, 6.42; N, 8.17%); δ_H(200 MHz, $CDCl_3$) 9.94 and 9.85 (4 H, 2 s, 4 H, *meso*), 9.32 (2 H, s, $2H_\beta$), 4.33 (4 H, q, OCH_2CH_3), 4.25 (4 H, t, $CH_2CH_2CO_2$), 3.96 (8 H, q, CH_2CH_3), 3.23 (4 H, t, $CH_2CH_2CO_2$), 1.85 (6 H, t, CH_2CH_3) and 1.23 (12 H, t, CH_2CH_3); λ_{max}/nm 401 (ε 166 400), 531 (7340) and 570 (7750).

7,8-Di(2-ethoxycarbonylethyl)-2,3,12,13-tetraethylporphyrin 30

A solution of the tripyrrane **22** (1.17 g, 1.47 mmol) was hydrogenated following the procedure described above. The resulting brown oil was immediately dissolved in distilled CH_2Cl_2 (900 cm^3) to which the pyrrole **7** (0.18 g, 1 equiv.) was then added. After the solution had been acidified with trifluoroacetic acid (0.6 cm^3), it was stirred at room temperature, under argon, in dark for 80 h. The reaction mixture was then neutralized with triethylamine (6 cm^3) to oxidize the porphyrinogen and treated with DDQ (0.3 g, 1 equiv.), with stirring at 40 °C for 1 h. After work-up, the crude product was chromatographed on a silica gel column with CH_2Cl_2 as eluent to give, after evaporation of the solvent, the pure porphyrin **30** (0.56 g, 61.5%) (Found: C, 73.1; H, 7.3; N, 8.9. Calc. for $C_{38}H_{46}N_4O_4$: C, 73.31; H, 7.39; N, 9.00%); δ_H(200 MHz, $CDCl_3$) 10.18 and 10.15 (4 H, 2 s, 4 H *meso*), 9.38 (2 H, s, $2H_\beta$), 4.42 (4 H, t, $CH_2CH_2CO_2$), 4.21 (12 H, m, CH_2CH_3 and OCH_2CH_3), 3.28 (4 H, t, $CH_2CH_2CO_2$), 1.93 (12 H, t, CH_2CH_3), 1.19 (6 H, t, OCH_2CH_3) and −3.85 (2 H, s, NH); λ_{max}/nm 398 (ε 207 600), 499 (12 720), 535 (10 140), 564 (7024) and 619 (1679).

12,13-Di(2-ethoxycarbonylethyl)-8,17-diethyl-2,7,18-trimethylporphyrin 31

The conditions used for the preparation of the porphyrin **30** were used for the reaction of the tripyrrane **29** (0.36 g, 0.47 mmol) with the pyrrole **8** (0.06 g, 1 equiv.). Chromatography of the product on a silica gel column with CH_2Cl_2 as eluent gave the pure porphyrin **31** (0.12 g, 42.5%) (Found: C, 71.5; H, 7.35; N, 8.8. Calc. for $C_{47}H_{44}N_4O_4 \cdot CH_3OH$: C, 71.21; H, 7.55; N, 8.75%); δ_H(200 MHz, $CDCl_3$) 10.15 (2 H, s, 10-CH and 15-CH), 10.12 (1 H, s, 20-CH), 10.0 (1 H, s, 5-CH), 9.02 (1 H, s, 3-CH), 4.42 (4 H, t, $CH_2CH_2CO_2$), 4.24–4.11 (8 H, m, OCH_2CH_3 and CH_2CH_3), 3.71, 3.66 and 3.63 (9 H, 3 s, 2-CH_3, 7-CH_3, and 18-CH_3), 3.27 (4 H, t, $CH_2CH_2CO_2$), 1.87 (6 H, t, CH_2CH_3), 1.19 (6 H, t, OCH_2CH_3) and −3.84 (2 H, s, NH); λ_{max}/nm 400 (ε 192 600), 498 (13 600), 535 (10 400), 566 (7050) and 620 (3300).

12,13-Di(2-ethoxycarbonylethyl)-2,3-di(2-ethoxycarbonylvinyl)-7,8,17,18-tetraethylporphyrin 32

The conditions used for the preparation of the porphyrin **30** were used for the condensation of the tripyrrane **28** (0.1 g, 0.12 mmol) with the pyrrole **14** (0.04 g, 1 equiv.). Chromatography of the product on a silica gel column with CH_2Cl_2–Et_2O (100:3, v/v) as eluent gave the pure porphyrin **32** (0.05 g, 49%) (Found: C, 69.7; H, 7.3; N, 6.8. Calc. for $C_{48}H_{58}N_4O_8$: C, 70.41; H, 7.09; N, 6.84%); δ_H(200 MHz, $CDCl_3$) 10.25 and 10.06 (4 H, 2 s, 4 H *meso*), 9.28 (2 H, d, J_{HH} 16, $CH{=}CHCO_2$), 7.03 (2 H, d, J_{HH} 16, $CH{=}CHCO_2$), 4.53 (4 H, q, CH_2CH_3), 4.30 (4 H, t, $CH_2CH_2CO_2$), 3.25 (4 H, t, $CH_2CH_2CO_2$), 1.92 (12 H, t, 4 OCH_2CH_3), 1.53 and 1.19 (12 H, 2 t, 4 CH_2CH_3) and −3.63 (2 H, s, NH); λ_{max}/nm 427 (ε 146 800), 523 (6700), 567 (23 600), 584 (20 200) and 641 (1600).

7,8-Di(2-ethoxycarbonylvinyl)-3,12-diethyl-2,13-dimethylporphyrin 34

The conditions used for the preparation of porphyrin **30** were used for the reaction of the tripyrrane **33** (0.082 g, 0.14 mmol) with the pyrrole **14** (0.045 g, 1 equiv.) except that the reaction time was 42 h. Chromatography of the product on a silica gel column with CH_2Cl_2–Et_2O (100:5; v/v) as eluent gave the pure porphyrin **34** (0.03 g, 33.5%) (Found: C, 72.3; H, 6.6; N, 8.8. Calc. for $C_{36}H_{38}N_4O_4 \cdot 0.5H_2O$: C, 72.1; H, 6.55; N, 9.34%); δ_H(200 MHz, $CDCl_3$) 10.11 and 10.0 (4 H, 2 s, H *meso*), 9.28 (2 H, s, H_β), 9.22 (2 H, d, J_{HH} 16, CH=), 7.01 (2 H, d, J_{HH} 16, =CH), 4.55 (4 H, q, OCH_2CH_3), 4.09 (4 H, q, CH_2CH_3), 3.63 (6 H, s, CH_3), 1.84 (6 H, t, OCH_2CH_3), 1.55 (6 H, t, CH_2CH_3) and −4.17 (2 H, s, NH); λ_{max}/nm 422 (ε 134 600), 518 (5600) 563 (18 800), 588 (16 000) and 630 (1900).

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