Linearly -π- Extended Porphyrins: Synthesis of Novel Tetrabenzoylporphyrins

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The π-extended porphyrins 11a – c with a λ_{max} = 644, 643 and 639 nm were synthesized by an acid catalysed reaction of the dipyrrolylmethane 10 with different aldehydes followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-quinone (DDQ). In a second approach, 10 was decarboxylated to yield 12, which was treated with DMF and benzoylchloride to give the diformyl compound 13. Acid catalysed reaction of 12 and 13 led to the porphyrin 11a after oxidation.

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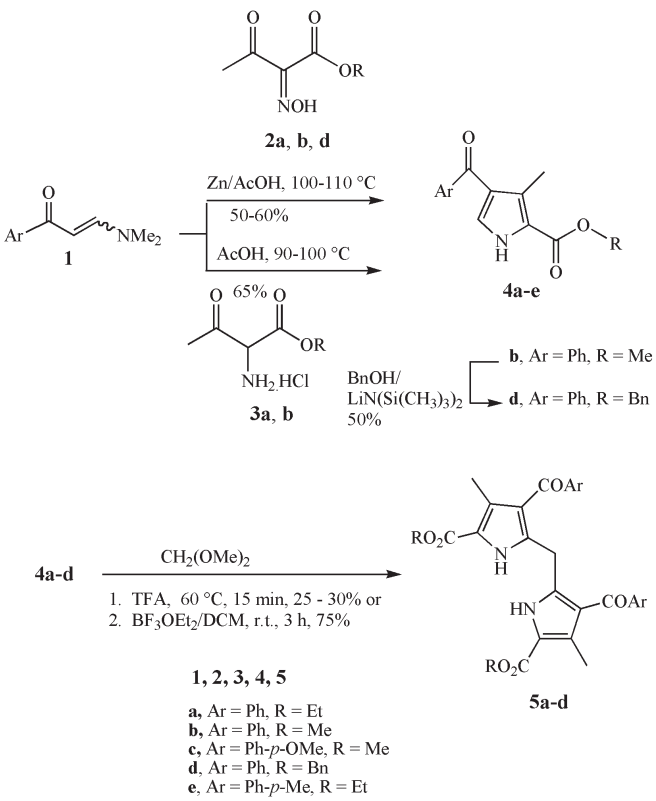
Introduction.

Highly conjugated porphyrins with a strong absorption in the far-visible/near-IR region have attracted a great level of interest in recent years due to their intrinsic value as photosensitiser for the photodynamic therapy of cancer (PDT) [1], multibit molecular-based information storage arrays [2-7], or near-IR dyes and nonlinear optical materials [8,9].

The π–electron system of the porphyrin macrocycles have been reported to be extended by peripheral substituents at the *meso*-/β-positions [10-13], or fused polycyclic ring systems [14-16]. Although extension of the chromophore by introducing fused aromatic rings or single chromophoric groups (*e.g.*, C=O, CN, or ester) was expected to produce a major bathochromic shift, in many cases the effects are actually rather small [9,10,17]. Tetraphenylporphyrin (TPP) [10] and tetraformylporphyrin (TFP) [11] give Soret bands at 409 nm and 405 nm and longest wavelength Q-bands at 624 and 623 nm, respectively; values that are only slightly higher than those reported for polyalkylporphyrins (PAP) [18,19] such as octaethylporphyrin (OEP) [19,20] (400 and 622 nm, respectively). With this in mind, we targeted the synthesis of porphyrins containing benzoyl groups as substituents; the element of both carbonyl and phenyl moieties represents a structural unit that could potentially produce a strong effect on the UV-vis absorption.

Scheme 1



Results and Discussion.

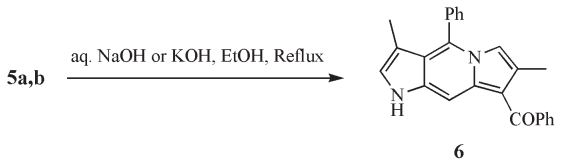
Enaminones are versatile synthetic intermediates in the synthesis of many heterocycles and natural products [21]. In a recent communication we reported a regioselective synthesis of 4-oxoaryl pyrrole-2-carboxylate **4** from enaminone **1** and 2-oximinacetoacetate **2** under Knorr-conditions in moderate yield [22]. A slight improvement for the yield was achieved by using 2-aminoacetoacetate [3] **3** instead of producing it *in situ* from the oxime **2** (Scheme 1).

The benzoyl pyrrole **4** as asymmetrically substituted pyrrole could be employed for the synthesis of porphyrins using a variety of routes [10,24,25] however, one of the most successful method is the '2+2' MacDonald tetramerization [26,27] followed by oxidation with DDQ [28-30]. For this purpose we prepared the dipyrrolylmethanes **5a-d**; but heating of the pyrroles **4a-d** for 15 minutes in dimethoxymethane and trifluoroacetic acid (TFA) gave only low yields (25-30%) [31]. However, when $BF_3 \cdot OEt_2$ [32] was used as a Lewis acid catalyst, the conversion was complete in 3 hours without heating and the dipyrrolylmethanes **5a-d** were obtained in high yields (75-80%) (Scheme 1).

The cleavage of an ester moiety to furnish the corresponding carboxylic acids is a common organic transformation that is usually carried out in a routine way by basic or acidic hydrolysis. However, pyrrole derivatives are very

sensitive to acidic conditions and saponification of pyrrole-2-carboxylic acid esters under basic conditions usually furnishes the corresponding α-unsubstituted pyrrole derivative by subsequent thermal decarboxylation. But saponification of the dipyrrolylmethanes **5a,b** with NaOH and KOH gave the corresponding dicarboxylic acid but in a very low yield and the main product was the pyrrolo[3,2-*f*]indolizine **6** a product of intramolecular cyclization of dipyrrolylmethane (Scheme 2). When LiOH was used only the starting material **5** was recovered even after 8 hours of reflux.

Scheme 2



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In order to avoid the intramolecular cyclization of the dipyrrolylmethane **5** under the saponification conditions, the benzyl ester **5d** was prepared and subsequently cleaved by catalytic hydrogenolysis to furnish the dicarboxylic acid.

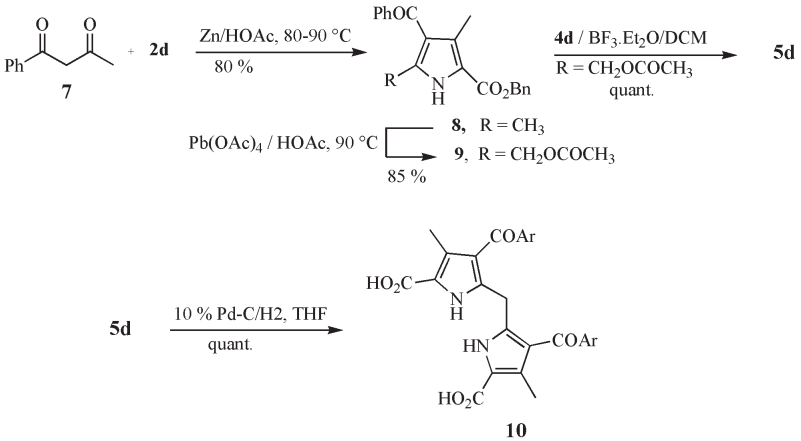
In a first attempt to synthesize **5d**, the pyrrole **4d** was synthesized by transesterification of the methyl ester **4b** in the presence of $LiN(Si(CH_3)_3)_2$/BzOH in a moderate yield of 50% [21]. A much better overall yield of 60 % of **4d** was obtained by Knorr-pyrrole synthesis employing enaminone **1** and the oxime **2d** (Scheme 1). Electrophilic substitution of the pyrrole **4d** with dimethoxymethane in the presence of $BF_3 \cdot OEt_2$ gave the dipyrrylmethane **5d** in 75% yield. In an another approach the latter compound was obtained in 85% yield by reductive condensation of 1,3-diketone **7** with oxime **2d** to yield pyrrole **8** which on oxidation with lead tetraacetate in acetic acid furnished the acetoxy pyrrole-2-carboxylate **9**. Reaction of **9** with the pyrrole **4d** in the presence of $BF_3 \cdot Et_2O$ afforded the dipyrrolylmethane **5d** in almost quantitative yield (Scheme 3). Catalytic hydrogenolysis of **5d** in the presence of 10% Pd/C gave the free diacid **10** in an excellent yield (Scheme 3). Over time, compound **10** changes from colourless to black upon exposure to air, however it is stable under argon in the refrigerator for at least 5 months.

Synthesis of Porphyrins **11a-c**.

The conversion of the dipyrrylmethane **10** into the corresponding porphyrins **11a-c** with four benzoyl groups was accomplished by two routes. First, we used a one-pot-three-step approach, which starts with decarboxylation followed by formation of the corresponding porphyrinogen with subsequent oxidation. Thus, a solution of dipyrrolylmethane **10** in dichloromethane/methanol (DCM /MeOH) (4:1) was heated under argon atmosphere at 50 °C for 1 hour in the presence of hydrobromic acid and formaldehyde and afterwards kept at room temperature for 24 hours. Subsequent addition of 3 equivalents of DDQ afforded the desired porphyrin **11a** as a violet powder in 25% yield. In a similar manner, porphyrins **11b** and **11c** were synthesized in 26% and 24% yield, respectively by reaction of **10** with benzaldehyde and *p*-phenylbenzaldehyde, respectively (Scheme 4).

In a second approach, the α,α'–dicarboxylic acid **10** was transformed into **12** by decarboxylation, which on treatment with dimethylformamide (DMF) and benzoylchloride gave the diformyl derivative **13**. Reaction of **12** and **13** according to the MacDonald procedure in the presence of an acid catalyst led, after oxidation, to the porphyrin **11a**. The decarboxylation of **10** to furnish the dipyrrylmethane **12** in a good yield was achieved by heating the compound

Scheme 3



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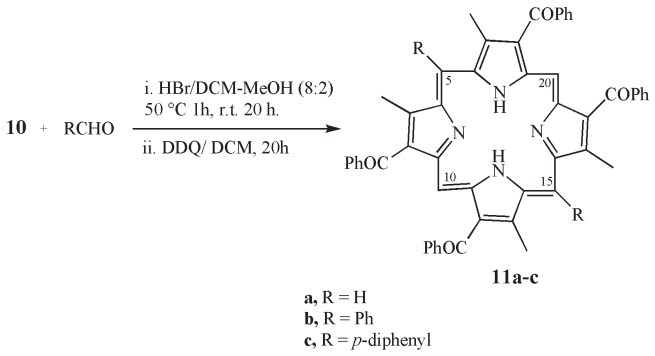
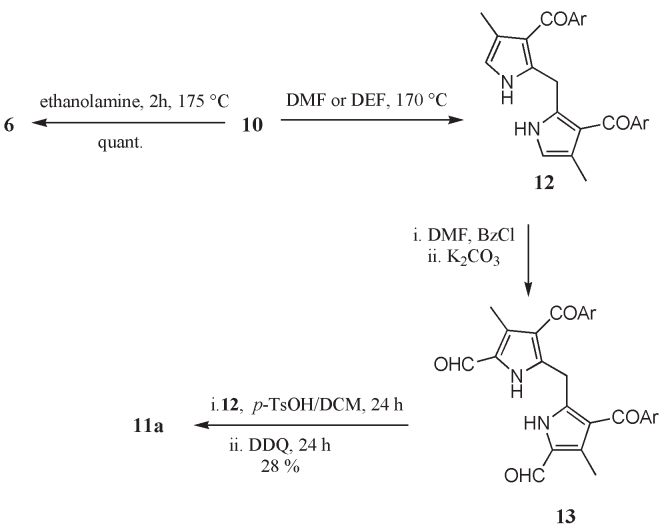
Scheme 4



Scheme 5



in DMF or DEF at 170 °C [33]. Interestingly, when the diacid **10** was heated in ethanolamine [34] the pyrolo[3,2-*f*]indololizine **6** was obtained in almost quantitative yield and no bis-α-free dipyrrylmethane was detected in the reaction mixture. Reaction of **12** with benzoyl chloride [35] in DMF and subsequent hydrolysis of the isolable iminium salt afforded the diformyl derivative **13** in a moderate yield. The condensation of **12** with **13** was accomplished at room temperature in the presence of *p*-TsOH to give the corresponding porphyrinogen, which on oxidation with DDQ afforded the porphyrin **11a** in 28% yield. (Scheme 5)

Structure elucidation of the new porphyrins was performed by EI-MS, ^{1}H-NMR, and UV-visible spectroscopy and the data were compared with those of OEP [19,20,32], TPP [10] and TFP [11] (Table 1).

In the ^{1}H NMR spectra porphyrins the internal NH protons are shielded due to a ring current effect of the aromatic macrocycle [13-16]. Thus, the NH of porphyrin **11a** containing no phenyl groups at the *meso*-position resonates at δ = –3.25. On the other hand, porphyrins **11b** and **11c** contain a phenyl and a *p*-diphenyl group at the *meso*-position, signals for the NH-group are found at lower field strengths, relative to those of **11a**, of δ = –1.95 and δ = –1.89, respectively. These can be attributed to a distortion of the planar macrocyclic structure and therefore a decrease of the ring current effect [36]. Also, the effect of the benzoyl groups on the *meso*-protons at positions 10 and 20 of porphyrins **11a-c** is noticeable. Thus, the signal for 5-H and 15-H in porphyrin **11a** is observed at δ = 10.28 as found also for the porphyrins OEP [19,20] and TPP [10] (Table 1), whereas the other two *meso*-hydrogens at positions 10 and 20 in **11a** - **c** resonate at δ = 9.91, 9.61 and 9.69, respectively due to shielding caused by the benzoyl groups.

The UV-visible spectra of the new porphyrins **11a** – **c** show a bathochromic shift in both the Soret and the Q-bands compared to those of TPP and TFP (Table 1). Thus, the Soret bands of **11a-c** are red shifted and observed at λ_{max} = 424 nm, 427 nm and 428 nm, respectively while

Table 1

Selected UV-visible and ^{1}H-NMR spectroscopic data of the new porphyrins **11a-c**, as well as of OEP [19,20], TPP [10] and TFP [11].

Porphyrin	UV-visible [a], λmax/nm (logε)					^{1}H NMR [b] δ/ppm	
	Soret		Q-bands			*Meso*-H	NH
OEP	396	497	530	564	620	10.08 (s,4H)	-3.80
TPP	409	504	540	570	624	10.17 (s,4H)	-3.39
TFP	405	456	581	-	623	10.56 (s, 4H)	-3.30
11a	424	516	551	590	644	10.28 (s,2H)	-3.25
	(5.13)	(4.15)	(3.85)	(3.85)	(3.77)	9.91 (s,2H)	
11b	427	518	550	590	643.5	9.61 (s,2H)	-1.95
	(5.19)	(4.30)	(4.22)	(3.92)	(3.92)		
11c	428	518	551	589	639	9.69 (s,2H)	-1.89
	(4.89)	(3.95)	(3.62)	(3.62)	(2.88)		

[a] in chloroform: [b] in $CDCl_3$.

TPP and TFP gave Sort bands at λ_{max} = 409 nm and 405 nm, respectively. Also, the longest wavelength of the Q-bands of **11a-c** are red shifted and observed at λ_{max} = 644, 643 and 639 nm, respectively. These values are higher than those reported for TPP and TFP (Table 1).

In conclusion, new porphyrins **11a-c** were synthesized and their spectral data were measured and compared to previously reported related porphyrins. More photochemical and photophysical studies on the new synthesized porphyrins including emission spectra, the mechanism of the deactivation of the excited molecules *e.g*. electron transfer and energy transfer process are under way.

EXPERIMENTAL

General.

Melting points are uncorrected. NMR spectra were recorded on Bruker WM 300 and DRX 500 spectrometers (300 MHz and 500 MHz, respectively for ^{1}H, 75 and 125 MHz, respectively, for ^{13}C) using TMS as internal standard and the deuterated solvent as lock. IR spectra were obtained by using a Perkin-Elmer 983 spectrophotometer. Electron impact ionisation mass spectrometry (EIMS) and electrospray ionization (ESI) were performed on a Varian AMD 604 instrument using 70 eV ionization energy. All chromatographic separations were performed using Grade 3 neutral alumina 70-230 mesh silica gel. Pyrrole-2-carboxylates **4a-d** were prepared by reacting enaminone **1** with 2-oximinoacetoacetate **2** under knorr-conditions [22] or 2-aminoacetoacetate [23] under standard conditions in acetic acid.

Methyl 4-Benzoyl-3-methyl-2-carboxylate (**4b)**.

This compound was obtained as colourless crystals (methanol), mp 192.6 °C; ir: NH 3400, CO17167, (CO) 1670 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 2.51 (s, 3H, CH_3), 3.81 (s,3H, OCH_3), 7.22 (s,1H, 5-$H_{pyrr.}$), 7.45 (m, 3H, Ar-H), 7.71 (m, 2H, Ph-H), 12.21 (s,1H, NH); ^{13}C nmr: δ 11.4, 51.1, 120.6, 122.8, 128.3, 128.9, 129.8, 131.5,139.8,161.1,190.6 ppm; ms: m/z (%) 243 (M^+) (100), 210 (80), 134 (60), 77 (20).

Anal. Calcd. for $C_{14}H_{13}NO_3$C: 69.12; H, 5.39. Found: C, 68.81; H, 5.16.

Methyl 4-(*p*-Methoxybenzoyl)-3-methyl-2-carboxylate (**4c**).

This compound was obtained as colourless crystals (methanol), mp 186.3 °C; ir: NH 3469, CO1716, CO 1624 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 2.61 (s, 3H, CH_3), 3.84 (s,3H, OCH_3), 3.90 (s, 3H, OCH_3),6.93 (s,1H, 5-$H_{pyrr.}$), 6.95 (m, 2H, Ar-H), 7.19(m, 1H, 5-H_{pyrr}),7.81 (m, 2H, Ar-H), 9.51 (s,1H, NH); ^{13}C nmr: δ 11.6, 51.6, 55.4, 113.5, 121.1, 124.8, 127.8, 129.9, 131.4, 132.6, 162.1, 162.7, 190.6 ppm; ms: m/z (%) 274 (M^+ +1) (20), 273 (M^+) (100), 256 (15), 240 (90),210 (50), 134(58), 92 (10), 77 (15).

Anal. Calcd for $C_{15}H_{15}NO_4$ (273.10): C, 65.92; H, 5.53. Found: C, 65.82; H, 5.33.

Benzyl 4-Benzoyl-3-methyl-2-carboxylate (**4d**).

This compound was obtained as colourless crystals (ethylacetate), mp 149.4 °C; ir: NH 3377, CO 1675, CO1633 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 2.63(s, 3H, CH_3), 5.38 (s, 2H, -CH_2-), 7.19 (s, 1H, 5-$H_{pyrr.}$) 7.41 (m, 8H, Ar-H), 7.68 (m, 2H, Ar-H), 9.60 (s, 1H, NH); ^{13}C nmr 11.7, 66.4, 121.1, 124.2, 128.1, 128.3, 128.6, 128.9, 129.0, 130.6, 131.7, 135.7, 140.0 ppm; ms: m/z (%) 320 (M^++1), (10), 319 (M^+) (65), 210 (20), 91 (100), 77 (15).

Anal. Calcd for $C_{20}H_{17}NO_3$: C, 75.22: H, 5.37. Found: C, 75.02: H, 5.24.

Ethyl 4-(*p*-Methylbenzoyl)-3-methyl-2-carboxylate (**4e**).

This compound was obtained as colourless crystals (ethanol), mp 129.4 °C; ir: NH 3318, CO 1691, CO 1620 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 1.38 (t, *J* = 7.13, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.63 (s, 3H, CH_3), 4.38 (q, 2H, *J* = 7.13, CH_2), 7.21 (s, 3H, Ar-H and 5-H_{pyrr}), 7.66 (m, 2H, Ar-H), 9.66 (s, 1H, NH); ^{13}C nmr: 11.7, 14.4, 21.6, 60.6, 121.4,124.6, 124.7, 128.9, 129.3, 130.0, 137.4, 142.4, 161.8, 191.7 ppm; ms: m/z (%) 272 (M^++1) (10), 271 (M^+) (58), 256 (100), 224 (57), 210 (95), 134 (50), 91 (20).

Anal. Calcd. for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32. Found: C, 70.63; H, 6.23.

Dipyrrolylmethanes **5a-d**.

Method 1.

A mixture of pyrrole-2-carboxylate (**4**) (1 mmol) and dimethoxymethane (0.6 mmol) was purged with Argon, 0.5 ml TFA was added. The mixture was stirred at 70-80 °C for 30 min during which the reaction mixture turned to pale green. The mixture was then poured into 100 ml ice-water and the solid so obtained was collected by filtration and washed several times with water-ethanol mixture (1:1) and recrystallized from acetone.

Method 2.

In an atmosphere of Argon, boron trifluoride diethyl etherate was added to a solution of pyrrole-2-carboxylate **4** (1 mmol) and dimethoxymethane (0.6 mmol) in dichloromethane (50 ml) and the mixture was stirred for 3 hours at room temperature. The mixture was poured into ice-water and extracted with dichloromethane. The dichloromethane layer was washed with water and dried over anhydrous $MgSO_4$. After evaporation of the solvent under vacuum, the residue was recrystallized from acetone.

Diethyl 3,3'-Dimethyl-4,4'-dibenzoylpyrroylmethane-2,2'-dicarboxylate (**5a**).

This compound was obtained as colourless crystals, mp 276.7 °C; ir: NH 3359, CO 1710, CO 1630 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 1.41 (t, *J* = 7.20, 6H, $2CH_3$), 2.12 (s, 6H, $2CH_3$), 4.15 (s, 2H, -CH_2-) 4.58 (q, 2H, *J* = 7.20, $2CH_2$), 7.51 (m, 4H, Ar-H), 7.61 (m, 2H, Ar-H), 7.81 (m,4H, Ar-H), 11.10 (s, 2H, 2NH); ^{13}C nmr: 12.9, 14.4, 24.1, 60.25, 119.0, 122.8, 127.6, 128.4, 129.7, 132.7, 137.8, 139.5, 161.0, 104.6 ppm; ms: esi (methanol) 526.7 (M^+).

Anal. Calcd. for $C_{31}H_{30}N_2O_6$ .C: 70.71; H, 5.74. Found: C, 70.51; H, 5.44.

Dimethyl 3,3'-Dimethyl-4,4'-dibenzoylpyrroylmethane-2,2'-dicarboxylate (**5b**).

This compound was obtained as colourless crystals, mp > 300 °C; ir: NH 3363, CO 1719, CO 1631 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 1.91 (s, 6H, $2CH_3$), 3.73 (s, 6H, $2CH_3$), 3.95 (s, 2H, -CH_2-), 7.51 (m, 8H, Ar-H), 7.64 (m, 2H, Ar-H), 11.75 (s, 2H, 2NH); ^{13}C nmr: 11.8, 24.08, 50.9, 81.9, 117.98, 122.2, 126.9, 128.2, 128.7, 132.1, 136.2, 139.2, 160.8, 192.42 ppm; ms: m/z (%): 498 (M^+) (40), 393 (100), 361 (38), 329 (10), 105 (45), 77 (10).

Anal. Calcd. for $C_{29}H_{26}N_2O_6$: C, 69.87; H, 5.26. Found: C, 69.67; H, 5.17.

Dimethyl 3,3'-Dimethyl-4,4'-(*p*-methoxybenzoyl)pyrroylmethane-2,2'-dicarboxylate (**5c**).

This compound was obtained as colourless crystals, mp > 250 °C; ir: NH 3360, CO 1720, CO 1640 cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.11 (s, 6H, $2CH_3$), 3.85 (s, 6H, $2CH_3$), 3.91 (s, 6H, 2-OCH_3), 4.05 (s, 2H, -CH_2-), 6.98 (d, *J* = 14 Hz, 4H), 7.85 (d, *J* = 14 Hz, 2H), 11.10 (s, 2H, 2NH); ^{13}C nmr: 12.8, 24.0, 51.4, 55.4, 113.5, 113.8, 118.7, 123.1, 127.6, 132.1, 132.2, 132.3, 137.5, 161.4, 163.5, 193.3 ppm; ms: EI, m/z (%): 558 (M^+) (25), 423 (48), 406 (25), 359 (20), 135 (100).

Anal. Calcd for $C_{31}H_{30}N_2O_8$: C, 66.66; H, 5.41. Found: C, 66.45; H, 5.11.

Dibenzyl 3,3'-Dimethyl-4,4'-dibenzoylpyrroylmethane-2,2'-Dicarboxylate (**5d**).

This compound was obtained as colourless crystals, mp 198.4 °C; ir: NH 3362, CO 1719, CO 1628 cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.05 (s, 6H, $2CH_3$), 4.11 (s, 2H, -CH_2), 5.93 (s, 4H, 2 -CH_2-Ph), 7.44 (m, 16H, Ar-H), 7.81(m, 4H, Ar-H), 11.15 (s, 2H, 2NH); ^{13}C nmr: 12.9, 24.19, 65.9, 118.7, 122.9, 127.9, 128.1, 128.2, 128.4, 128.5, 129.7, 132.7, 136.1, 138.2, 139.5, 160.7, 194.6ppm; ms: esi 650.5 (M^+) for $C_{41}H_{34}N_2O_6$.

Anal. Calcd for $C_{41}H_{34}N_2O_6$: C, 75.68; H, 5.27. Found: C, 75.55; H, 5.22.

8-Benzoyl-3,7-dimethyl-4-phenyl-1*H*-pyrrolo[3,2-*f*]indolizine (**6**).

This compound was obtained as pale yellow crystals, mp > 300 °C; ir: NH 3364, CO 1680 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 1.59 (s, 3H, -CH_3), 1.81 (s, 3H, -CH_3), 6.61 (s, 1H), 7.21 (s, 1H), 7.45 (m, 10H, Ar-H), 8.10 (s, 1H), 10.85 (s, 1H); ^{13}C nmr: 11.23, 13.47, 96.1, 107.1, 108.1, 109.6, 119.6, 127.1, 127.4, 128.0, 128.2, 128.7, 128.9, 129.7, 130.1, 132.2, 137.7, 138.5, 144.0, 188.0 ppm; ms: EI, m/z (%): 364 (M^+) (100), 287 (20), 259 (10), 232 (10), 182 (5).

Anal. Calcd. for $C_{25}H_{20}N_2O$: C, 82.39; H, 5.53. Found: C, 82.31; H, 5.43.

Benzyl 4-benzoyl-3,5-dimethyl pyrrole 2-carboxylate (**8**).

Was prepared from benzoylacetone (**7**) and benzyl 2-oximinacetoacetate (**2d**) as mentioned [22]. This compound was obtained as colourless crystals (petroleum ether/ethylacetate, 4:1), mp 120-121 °C; ir: NH 3277, CO 1669, CO 1644; ^1H nmr ($CDCl_3$): 2.20 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 5.28 (s,2H, -CH_2-), 7.41 (m, 8H), 7.75 (m, 2H), 9.21 (s,1H, NH). ^{13}C nmr: 12.4, 13.5, 66.1, 118.1, 123.3, 128.1, 128.3, 128.4, 128.6, 129.15, 129.8, 132.2, 135.9, 137.0, 140.18, 161.3, 193.8; ms, esi: 333.3 (M^+).

Anal. Calcd. for $C_{21}H_{19}NO_3$: C, 75.66; H, 5.74. Found: C, 75.55; H, 5.48.

Benzyl 5-Acetoxymethyl-4-benzoyl-3-methylpyrrole-2-carboxylate (**9**).

In a stream of Ar, lead(IV) acetate (1.00 g, 2.26 mmol) was added to a solution of benzylpyrrole 2-carboxylate (**8**) (300 mg, 0.77 mmol) in acetic acid (10 ml), and the mixture was stirred for 7 h at 90 °C. After the excess lead(IV) acetate was decomposed by ethylene glycol, the mixture was poured into ice-water and extracted with dichloromethane. The dichloromethane layer was washed with H_2O and dried over anhydrous $MgSO_4$. After evaporation of the solvent under vacuum, the residue was purified by column chromatography (petroleum ether/ethylacetate, 4:1) to give **9** (300 mg, 85%) as white crystals from ethanol mp 123.3 °C; ir: NH 3272, CO 1733, CO 1666, CO 1645 cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.12 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 5.11 (s, 2H, -CH_2-), 5.38 (s, 2H, -CH_2-), 7.45 (m, 8H, Ar-H), 7.77 (m, 2H, Ar-H), 9.62 (s, 1H, NH). ^{13}C nmr: 12.3, 20.8, 57.4, 66.3, 119.8, 124.7, 128.2, 128.3, 128.4, 128.6, 129.3, 132.7, 133.5, 135.8, 139.5, 160.9, 171.5, 193.1 ppm; ms: ei, m/z (%): 391 (M^+) (25), 331 (45), 240 (58), 91(100).

Anal. Calcd. for $C_{23}H_{21}NO_5$: C, 70.58; H, 5.41. Found: C, 70.45; H, 5.38.

3,3'-Dibenzoyl-4,4'-dimethyl-2,2'-dipyrrolylmethane-5,5'-dicarboxylic Acid (**10**).

A solution of **5d** (100 mg, 0.18 mmol), in tetrahydrofurane (10 ml) was shaken in an atmosphere of hydrogen in the presence of 10% Pd-C (50 mg) until absorption of hydrogen was no longer observed. After removal of the catalyst by filtration and evaporation of the solvent, the residue was crystallised from dichloromethane to give **10** (72 mg, 99%) as colourless crystals mp (decomp.) >200 °C; ^1H nmr (dimethyl sulfoxide-d_6): δ 1.06 (s, 6H, $2CH_3$), 3.94 (s, 2H, -CH_2), 7.39 (m, 4H, Ar-H), 7.51 (m, 6H, Ar-H), 11.67 (s, 2H, 2NH), 12.30 (s, 2H, carboxylic acid); ^{13}C nmr: 11.8, 59.6, 119.0, 122.2, 122.3, 126.3, 128.2, 128.7, 128.8, 132.1, 135.8, 139.4, 162.1, 192.6 ppm.

2,8,12,18-Tetrabenzoyl-3,7,13,17-tetramethylporhyrin (**11a**).

Method A.

A solution of dipyrrolylmethanedicarboxylic acid **10** (125 mg, 0.26 mmol) and formaldehyde (37%) (3.5 ml) in dichloromethane/methanol mixture (120 ml) (4:1) was refluxed for 5 min under an atmosphere of Argon. After the addition of hydrobromic acid (48%) (1 ml) as one portion the solution turned immediately to deep pink then was allowed to reflux for 1 h. The reaction mixture was then allowed to stirr at room temperature for 20 h. DDQ was added (180 mg, 0.8 mmol) and the cloudy mixture was stirred at room temperature for additional 20 h. The mixture was concentrated under vacuum and the residue was dissolved in 500 ml dichloromethane and washed with water. The dichloromethane layer was dried over $MgSO_4$ and chromatographed on a Grade 3 alumina column. A deep violet fraction was collected and evaporation under vacuum gave **11a** as a violet powder (26 mg, 25%) from $CHCl_3$/methanol mp > 300 °C; ^1H nmr ($CDCl_3$): δ -3.25 (s, 2H), 1.58 (s, 12H), 7.95 (m, 8H), 7.42 (m, 4H), 7.62 (m, 4H) 8.15 (m, 4H), 9.91 (s, 2H), 10.28 (s, 2H); ms: ei, m/z (%): 782 (M^+) (55), 105 (50), 77 (25), 44 (100).

Anal. Calcd. for $C_{52}H_{38}N_4O_4$: C, 79.78; H, 4.89. Found: C, 79.56; H, 4.65.

2,8,12,18-Tetrabenzoyl-3,7,13,17-tetramethyl-5,10,15,20-tetraphenylporhyrin (**11b**).

This compound was prepared using **10** and benzaldehyde by the previous procedure. Following chromatography as described for **11a**, the product was recrystallised from chloroform-methanol to give the title porphyrin (32 mg, 26%) as dark violet crystals mp > 300 °C; ^1H nmr ($CDCl_3$): δ -1.95 (s, 2H), 2.41 (s, 12H), 7.38 (m, 8H), 7.51 (m, 4H), 7.71 (m, 6H), 7.81 (m, 8H), 8.15 (m, 4H), 9.61 (s, 2H); ms: ei, m/z (%): 936 (M^+ +2) (40), 935 (M^+ +1) (8), 934 (M^+) (100), 105 (95).

Anal. Calcd. for $C_{64}H_{46}N_4O_4$: C, 82.21; H, 4.96. Found: C, 82.01; H, 4.78.

2,8,12,18-Tetrabenzoyl-3,7,13,17-tetramethyl-5,10,15,20-tetra(*p*-diphenyl)porhyrin (**11c**).

This compound was prepared using **10** and *p*-phenylbenzaldehyde by the procedure given above and by using the chromatography conditions described for **11a**. The product was recrystallised from chloroform-methanol to give the title porphyrin (34 mg, 24%) as dark violet crystals mp> 300 °C; ^{1}H nmr ($CDCl_3$): δ -1.89 (s, 2H), 2.48 (s, 12H), 7.41 (m, 18H), 7.59 (m, 4H), 7.81 (m, 8H), 8.11 (m, 4H), 8.20 (m, 4H), 9.69 (s, 2H); ms, ei, m/z (%): 1088 (M^+ +2) (10), 1087 (M^+ +1) (10), 1086 (M^+) (5), 168 (25), 105 (38), 44 (100).

Anal. Calcd. for $C_{76}H_{54}N_4O_4$: C, 83.95; H, 5.15. Found: C, 83.88; H, 5.10.

2,8,12,18-Tetrabenzoyl-3,7,13,17-tetramethylporhyrin (**11a**).

Method B.

A solution of dipyrrolylmethanedicarboxylic acid **10** (200 mg, 0.43 mmol) in dimethylformaamide (DMF) (10 ml) was refluxed for 2 h under an atmosphere of Argon. The solution was left to cool and divided into two equal portions. The first portion was poured into an ice-brine mixture and extracted with ethyl acetate. The organic layer was taken and dried over anhydrous magnesium sulphate then evaporated under reduced pressure to give the crude dipyrrylmethane **12**. The second portion was chilled on ice-bath and an excess of benzoyl chloride (3 ml, 24.6 mmol) was added drop wise over a two min period, and left overnight at room temperature. The iminium salt crystallised out, was collected by filtration, rinsed with DMF and diethyl ether, taken in water and basified then boiled with potassium carbonate for 10 min. An oil separated immediately which quickly solidified. The solid diformyl **13** was recovered and recrystallised from ethanol mp> 220 °C. A solution of *p*-toluene sulphonic acid (PTA) (350 mg) in methanol (15 ml) was added to a stirred mixture of **12** (95 mg) and diformyl **13** (100 mg) in dichloromethane (300 ml) the resulting solution was stirred in the dark under an atmosphere of Argon for 24 h. DDQ (170 mg) was added and the mixture was stirred for an additional 24 h. Then the chromatography conditions described in method A were used to give **11a** (35 mg, 28%).

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