# Conjugated Macrocycles Related to the Porphyrins. Part 3 [1]. Acid Catalyzed Condensations of Thiophenecarboxaldehydes with a Dipyrrylmethane [2]



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MacDonald condensation of a dipyrrylmethanedicarboxylic acid **3b** with 2,2'-dithienylmethane-5,5'-dicarboxaldehyde (**2b**) failed to give the expected dithiophene porphyrin analog **1b**. However, oxidation of the reaction mixtures with DDQ gave trace amounts of porphyrin-like materials. Model studies indicate that these fractions are *meso*-dithienylporphyrins. The synthesis of three related α,γ-disubstituted porphyrins is described.

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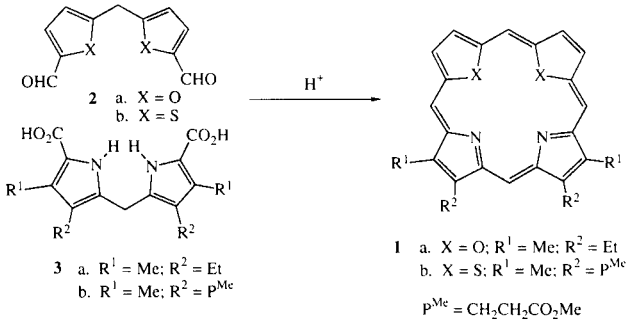
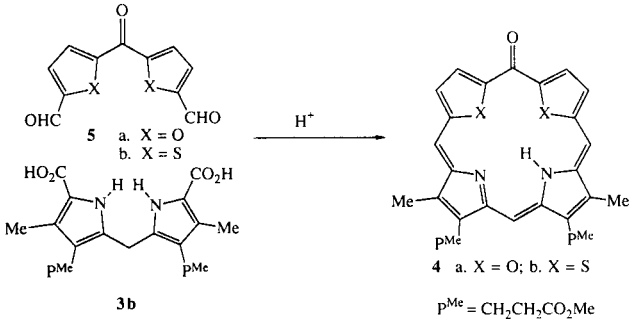
It has long been recognized that a variety of macrocyclic systems related to the porphyrins are possible [3]. In recent years, the synthesis of porphyrin analogs has received renewed interest, in part due to the potential utility of these compounds in photodynamic tumor therapy [4]. Porphyrin analogs may also form novel metal complexes that could find application as magnetic resonance imaging enhancers, electrical conductors or industrial dyes. Porphyrin-like systems with one or two furan and/or thiophene units were synthesized by Johnson and co-workers [5a,b] over twenty years ago. Using a "3 + 1" approach, porphyrin analogs containing one or two chalconide atoms were synthesized. In later studies, Ulman *et al.* prepared analogs of tetraphenylporphyrin with two thiophene units [5c], thiophene/selenophene units [5d], two selenophene rings [5d] or thiophene/tellurophene rings [5e]. In all of the above examples where two chalconide atoms are present, these atoms were placed at diagonally opposed positions in the porphyrin-like macrocycle. Few examples of porphyrin analogs with adjacent furan and/or thiophene rings have been reported.

A synthesis of a difurylporphyrin analog **1a** from the diformyl difurylmethane **2a** and dipyrrylmethane **3a**, using the MacDonald condensation, has been noted [6] (Scheme 1). More recently, the tetraoxaporphyrin dication was also prepared in this way [7]. We have previously reported the synthesis [1] of difuryl oxophlorin analogs (*e.g.*, **4a**) by the condensation of a difurylketone dialdehyde **5a** with dipyrrylmethane dicarboxylic acids (*e.g.*, **3b**) in trifluoroacetic acid (Scheme 2). Although good yields were obtained in these condensations attempts to extend this work to the dithienyl system **4b** have been unsuccessful.

Scheme 1

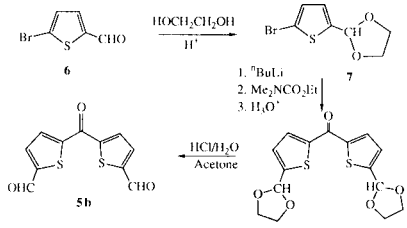



Scheme 2



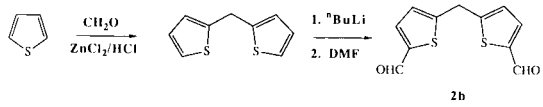

5-Bromothiophene-2-carboxaldehyde (**6**) reacted with ethylene glycol in the presence of trace *p*-toluenesulfonic acid to give the acetal **7** (Scheme 3). Reaction with *n*-butyllithium at −20° afforded the corresponding 2-thienyllithium; further reaction with ethyl *N,N*-dimethylcarbamate [8,9] and hydrolysis with an acidified aqueous acetone solution gave the dithienylketone dialdehyde **5b**. Condensation of **5b** with the dipyrrylmethane dicarboxylic acid **3b** under a variety of conditions gave unstable green pigments whose electronic spectra were not consistent with structure **4b**. It was clear from this work whether the macrocycle failed to form under the reaction conditions, or the system was too unstable to be isolated. A previously described monothienyl oxophlorin, prepared by Clezy and Diakiw [10] was very unstable and could only be isolated as the acetate derivative of the hydroxy tautomer. Attempts to trap the hydroxy tautomer of **4b** with acetic anhydride were also unsuccessful, but since the difuryl oxophlorin analog **4a** failed to give this reaction [1], this was not particularly informative.

Scheme 3



To further investigate these systems, the synthesis of porphyrin analog **1b** with two adjacent thiophene rings was investigated. 5,5'-Diformyl-2,2'-dithienylmethane **2b** was prepared in two steps from thiophene (Scheme 4). The acid catalyzed condensation of dipyrrylmethanedicarboxylic acid **3b** with dialdehyde **2b** was studied under a variety of conditions (Scheme 1). In certain cases, the formation of unstable porphyrin-like materials was noted. In one experiment, **3b** was first decarboxylated with trifluoroacetic acid and further condensed with dithienylmethane **2b** in the presence of *p*-toluenesulfonic acid. Oxidation of the crude extract with 2,3-dichloro-5,6-dicyanoquinone (DDQ), followed by immediate chromatography, afforded two red fractions which gave porphyrin-like fluorescence under longwave ultraviolet light. These fractions were very unstable and could not be fully separated from other components. The uv-visible spectra for these fractions (Figure 1) showed intense Soret bands at 408 nm and several smaller absorptions in the Q band region. These results closely resemble the spectra expected for tetrapyrrolic porphyrins and this led us to suspect that the red fractions were probably $\alpha,\gamma$-*meso*-disubstituted porphyrins.

Scheme 4



In all of our attempts to synthesize the 21,22-dithiaporphyrin **1b**, green material was observed after the reaction mixture was washed with 5% ammonium hydroxide, prior to the oxidation step. Colored fractions could be separated by column chromatography on neutal alumina, but further purification was not possible since these materials rapidly decomposed. A major green fraction was collected after chromatography which showed strong absorptions at 660, 403 and 380 nm (see Figure 2). The spectrum was similar to those reported for 1,19-dideoxybilatrienes **8a** [11] and the related furan analog **8b** [12]. It is possible that this material corresponds to the dithienyl bilatriene analog **8c**. Oxidation of this fraction with DDQ did not afford porphyrin.

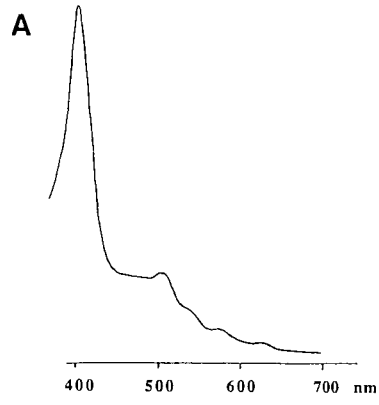



**Figure 1. The uv-visible spectra of the red porphyrin-like fractions obtained from the acid catalyzed condensation of dipyrrylmethane 3b with 2,2'-dithienylmethane-5,5'-dicarboxaldehyde (2b), followed by oxidation with DDQ and chromatography on alumina. Spectra A and B correspond to two distinct red bands obtained in a single experiment.**

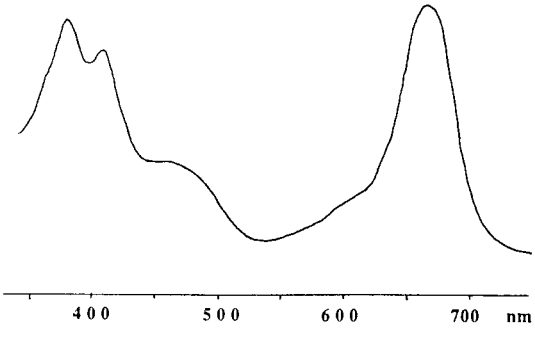
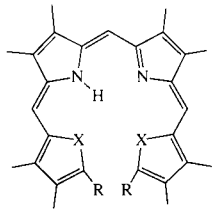
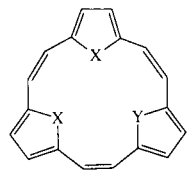



**Figure 2. The uv-visible spectrum of the crude green fraction obtained from the acid catalyzed condensation of 2b and 3b.**

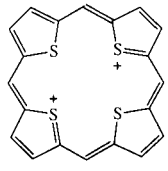
It seems likely that a related dithiophene biladiene analog **9** is involved in the formation of trace amounts of porphyrin in our experiments. Condensation with another dipyrrylmethane unit would then lead to the formation of a porphyrinogen **10** (Scheme 5). The *meso*-thienyl substituents would sterically inhibit oxidation to porphyrin **11**, although DDQ would be expected to carry out this transformation.



8 a. X = NH
b. X = O
c. X = S



12 a. X = Y = O
b. X = O; Y = S
c. X = S; Y = O
d. X = Y = S



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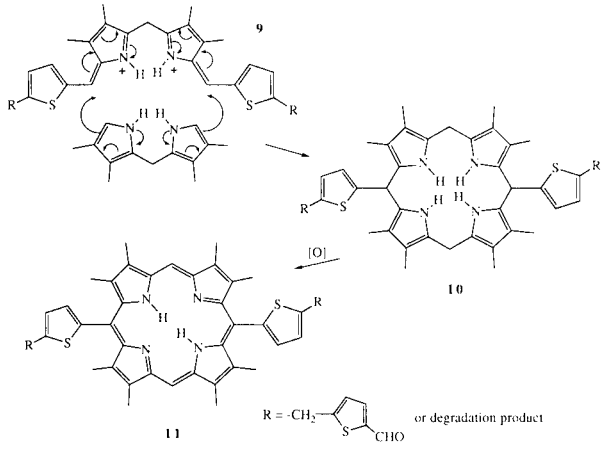
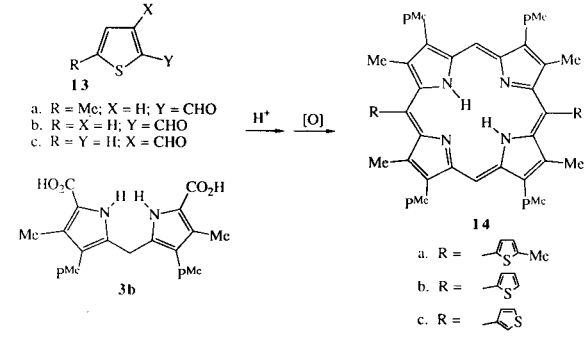
Scheme 5




Our study does not preclude the possibility that the 21,22-dithiaporphyrin **1b** was formed under the MacDonald condensation conditions, since the system might well be unstable due to the proximity of the two sulfur atoms. Similar reasoning has been invoked to explain the inability of [18]annulenes with two or three bridging sulfur atoms to attain planarity [13]. The trifuryl **12a** and difuryl **12b** systems were shown to be fully aromatic, as evidenced by their nmr spectra, but **12c** and **12d** did not support macrocyclic ring currents.

We anticipated that monothiophene aldehydes would also give porphyrins under our reaction conditions. Indeed, aromatic aldehydes have been widely utilized in the synthesis of $\alpha,\gamma$-disubstituted porphyrins [14]. In a model study, we condensed dipyrrylmethanedicarboxylic acid **3b** with 5-methylthiophene-2-carboxaldehyde **13a** under the same reaction conditions (Scheme 6). The crude green extract was oxidized with DDQ and following chromatography, a red porphyrin fraction was isolated. The yield was low and attempts to purify the material were unsuccessful. Considerably better results were obtained when the reaction was carried out in the presence of trichloroacetic acid [14d]. The crude product thereby obtained was oxidized with DDQ, and following chromatography, a red fraction was isolated which showed red porphyrin fluorescence under longwave ultraviolet light. After crystallization from dichloromethane-methanol, the *meso*-disubstituted porphyrin **14a** was obtained in 25% yield. Thiophene-2-carboxaldehyde **13b** condensed with **3b** similarly to give the bis(2-thienyl)porphyrin **14b** in 20% yield and thiophene-3-carboxaldehyde **13c** gave the related porphyrin **14c** in 16% yield (Scheme 6). Under these conditions, **2b** gave a substantially larger proportion of porphyrinic material, although these fractions still could not be fully purified.

Scheme 6




Our results show that dithienyporphyrin analogs cannot be prepared by this approach. The bulky sulfur atoms presumably inhibit macrocyclic ring formation and further condensation probably leads to polymer along with trace amounts of *meso*-disubstituted porphyrins. Earlier attempts to prepare tetrathiophene analogs **15** of porphyrins by ring synthesis were also unsuccessful [15]. It is noteworthy, however, that Vogel and co-workers recently reported [16] an indirect synthesis of **15** from a tetrafuryl macrocycle.

## EXPERIMENTAL

Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. The ir spectra were recorded on a Perkin-Elmer 710B spectrometer or a Perkin-Elmer 1600 Series FT-IR Spectrometer. The uv spectra were obtained on a Perkin-Elmer 330 or a Beckmann DU-40 spectrophotometer. The nmr spectra were recorded on a Hitachi-Perkin Elmer R24B 60 MHz nmr spectrometer or a Varian Gemini-300 nmr spectrometer. Mass spectral data were obtained at the Midwest Center for Mass Spectrometry at the University of Nebraska-Lincoln or at the Washington University Mass Spectrometry Resource, which is supported by a grant from the National Institutes of Health (RR00954). Fast atom bombardment mass spectra were run in a thioglycerol matrix; porphyrin samples consistently gave the $[M+H]^+$ ion. High resolution fast atom bombardment measurements were performed by peak matching sample ions against appropriate ions from a spectrum of mixed

CsI and RbI. Mass resolution was MΔM 4000. Elemental analyses were obtained from Micro-Analysis, Inc., Wilmington, DE 19808.

2-(5-Bromo-2-thienyl)-1,3-dioxalan (**7**).

*p*-Toluenesulfonic acid monohydrate (5 mg) was added to a mixture of 5-bromothiophene-2-carboxaldehyde (Aldrich Chemical Company) (25.00 g) and ethylene glycol (10.3 g) in toluene (100 ml). The solution was refluxed using a Dean and Stark apparatus to azeotropically removed the water as it formed in the reaction. The mixture was cooled, diluted with ether, and washed successively with saturated sodium bicarbonate, water and saturated sodium chloride solution. The etherial phase was dried over anhydrous sodium sulfate, filtered and evaporated under reduced pressure. The residue was distilled *in vacuo* to give the dioxalan as a pale yellow oil (28.84 g, 94%) bp 157-159° at 15 torr (lit bp [17] 138-139° at 10 torr); pmr (deuteriochloroform): 3.88 (4H, m, $-OCH_2CH_2O-$), 5.86 (1H, s, -CH-O), 6.70-6.85 (2H, AB quartet, 2 x thiophene-H).

5,5'-Diformyl-2,2'-dithienylmethanone (**5b**).

A solution of the foregoing dioxalan (2.00 g) in anhydrous ether (5 ml) was added dropwise over 15 minutes to a stirred solution of *n*-butyllithium (5.4 ml, 1.6*M* solution in hexane) in ether (6 ml), under nitrogen, maintaining the temperature at −20°. After 10 minutes a solution of ethyl *N,N*-dimethylcarbamate [9] (0.53 g) in anhydrous ether (5 ml) was added over a 10 minute period. The mixture was stirred for 2 hours at −20° to −30°. A solution of saturated aqueous ammonium chloride (20 ml) was cautiously added to the mixture. After several minutes of stirring a brown precipitate formed. The solid was filtered off, dissolved in acetone (10 ml)-10% aqueous hydrochloric acid (8 ml) and stirred overnight. The resulting precipitate was filtered off, dried *in vacuo* and recrystallized from acetone to give an off-white powder (0.56 g, 55%), mp 199-200° (lit mp [9] 202-203°); eims: (relative intensity) m/z 250 ($M^+$, 37%), 249 (10%), 221 (4%), 139 (100%), 111 (26%), 83 (23%); ir (Nujol mull): $\nu$ 1667 (aldehyde C=O str), 1596 (bridging C=O str) $cm^{-1}$; pmr (DMSO-$d_6$-deuteriochloroform): 8.09 (2H, d, J = 4.0 Hz, 3,3'-H), 8.13 (2H, d, J = 4.0 Hz, 4,4'-H), 10.08 (2H, s, 2 x CHO); cmr (DMSO-$d_6$-deuteriochloroform): 134.34, 136.70 (4 x $\beta$-thienyl C), 147.12, 148.41 (4 x $\alpha$-thienyl C), 178.78 (bridge C=O), 184.60 (2 x CHO).

*Anal.* Calcd. for $C_{11}H_6O_3S_2 \cdot 1/8H_2O$ (252.54): C, 52.32; H, 2.49; S, 25.39. Found: C, 52.14; H, 2.56; S, 25.69.

2,2'-Dithienylmethane.

Thiophene (75.6 g) was added over a few minutes to a stirred solution of zinc chloride (81 g) in concentrated hydrochloric acid (62 ml) at −10°. Formaldehyde solution (37%, 56.5 g) was then added dropwise over 90 minutes to the vigorously stirred cloudy yellow solution, maintaining the temperature throughout between −15° and −10°. The mixture was stirred for a further 1 hour between −5° and −10°. The mixture was diluted with water, extracted with ether, washed with 5% sodium bicarbonate solution, dried over magnesium sulfate, filtered and evaporated under reduced pressure to give a yellow oil. Distillation under reduced pressure gave the dithienylmethane as a pale yellow oil (49.1 g, 58%) which solidified on standing, bp 158-163° at 15 torr (lit bp [18] 131-133° at 11 torr). A sample was recrystallized from hexane to give white needles, mp 45-46° (lit mp [42] 44.5-46.5°); pmr (deuteriochloroform): $\delta$ 4.33 (2H, bridge $CH_2$), 6.87 (2H, m), 6.92 (2H, m), 7.25 (2H, m) (6 x thiophene-H); cmr (deuteriochloroform): 30.27 (bridge $CH_2$), 124.25, 125.37, 126.92 (thiophene methines), 143.26 (quaternary thiophene C).

*Anal.* Calcd. for $C_9H_8S_2$ (180.28): C, 59.96; H, 4.47. Found: C, 59.65; H, 4.59.

2,2'-Dithienylmethane-5,5'-dicarboxaldehyde (**2b**).

A solution of *n*-butyllithium in hexane (3.2 ml, 10.1*M*) was added dropwise to a stirred solution of 2,2'-dithienylmethane (2.64 g) in anhydrous ether (100 ml) under an atmosphere of nitrogen, maintaining the temperature at 20°. The mixture was stirred at room temperature for a further 15 minutes. A solution of *N,N*-dimethylformamide (2.55 g) in anhydrous ether (25 ml) was then added dropwise over 20 minutes and the resulting green mixture allowed to stir at room temperature for an additional 2 hours. Water (100 ml) was cautiously added, and the organic phase washed with water (100 ml), 2*M* hydrochloric acid (150 ml), 5% sodium bicarbonate solution (150 ml) and water (150 ml). The etherial solution was dried over anhydrous magnesium sulfate, filtered and evaporated under reduced pressure. Crystallization from 95% ethanol gave the dialdehyde as off-white crystals (2.35 g, 68%), mp 93.5-95° (lit mp [15] 95°); ir (Nujol mull) $\nu$ 1650 $cm^{-1}$ (C=O str); pmr (deuteriochloroform): $\delta$ 4.44 (2H, s, bridge $CH_2$), 7.03 (2H, d, J = 3.7 Hz, 3,3'-H), 7.65 (2H, d, J = 3.7 Hz, 4,4'-H), 9.84 (2H, s, 2 x CHO); cmr (deuteriochloroform): 31.58 (bridge $CH_2$), 127.37 (3,3'-C), 136.74 (4,4'-C), 143.17 (2,2'-C), 151.86 (5,5'-C), 182.66 (2 x CHO).

3,7,13,17-Tetrakis(2-methoxycarbonylethyl)-2,8,12,18-tetramethyl-10,20-bis(5-methyl-2-thienyl)porphyrin (**14a**).

Dipyrrylmethanedicarboxylic acid **3b** [1,19] (90 mg) was dissolved in trifluoroacetic acid (5.6 ml) and the resulting purple solution stirred at room temperature for 10 minutes. Evaporation of the trifluoroacetic acid under reduced pressure afforded a red oil, which was dissolved in dichloromethane (11 ml) and washed successively with 5% sodium bicarbonate solution (10 ml) and water (10 ml). The organic solution was dried over anhydrous magnesium sulfate, evaporated under reduced pressure and the resulting yellow oil dissolved in absolute ethanol (3 ml). 5-Methyl-2-thiophenecarboxaldehyde (25 mg) and trichloroacetic acid (10 mg) were added to the stirred solution. The mixture was stirred for a further 1 hour at room temperature. Dichloromethane (10 ml) was then added, and the solution washed successively with water (2 x 20 ml), 5% ammonia solution (10 ml) and water (10 ml). The solution was dried over sodium sulfate, filtered and evaporated under reduced pressure. The green residue was dissolved in tetrahydrofuran (5 ml), DDQ (65 mg) was added and the resulting mixture stirred at room temperature for 1 hour. The solution was evaporated to dryness under reduced pressure and the dark residue taken up in a minimal volume of dichloromethane and chromatographed on Grade 2 alumina, eluting with dichloromethane-petroleum ether (60-90°) (1:1 v/v). The $\alpha,\gamma$-dithienylporphyrin was collected as a red fraction; crystallization from dichloromethane-methanol gave purple crystals (22 mg, 25%), mp >300°; ms: (fast atom bombardment) m/z (relative intensity) 903 (100) ($M+H]^+$), 902 (20) ($M^+$), 845 (10); hrms: (fast atom bombardment) Calcd. for $C_{50}H_{54}N_4O_8S_2+H$: 903.3458. Found: 903.3472; uv (chloroform): $\lambda$ max nm ($\log_{10}\epsilon$) 412 (5.35), 511 (4.21), 545 (3.85), 579 (3.84), 630 (3.49); pmr (deuteriochloroform): $\delta$ −2.4 (2H, br, NH), 2.83 (18H, s, 4 x porphyrin-$CH_3$ + 2 x thiophene-$CH_3$), 3.17 (8H, t, J = 7.7 Hz, 4 x $CH_2CH_2CO$), 3.67 (12H, s, 4 x $OCH_3$), 4.39 (8H, t, J = 7.7 Hz, 4 x $CH_2CH_2CO$), 7.15 (2H, d, J =

2.5 Hz, 2 x thienyl 4H), 7.51 (2H, d, J = 2.5 Hz, 2 x thienyl 3H), 10.28 (2H, s, 2 x *meso*-H); pmr (25% trifluoroacetic acid-d-deuteriochloroform); δ 2.51 (12H, s, 4 x porphyrin-$CH_3$), 2.78 (8H, t, $CH_2CH_2CO$), 2.97 (6H, s, 2 x thiophene-$CH_3$), 3.78 (12H, s, 4 x $OCH_3$), 4.13 (8H, t, $CH_2CH_2CO$), 7.45 (2H), 7.82 (2H) (4 x thiophene-H), 10.47 (2H, s, 2 x *meso*-H).

*Anal.* Calcd. for $C_{50}H_{54}N_4O_8S_2 \cdot H_2O$ (921.13): C, 65.20; H, 6.13; N, 6.08. Found: C, 65.53; H, 6.01; N, 6.09.

3,7,13,17-Tetrakis(2-methoxycarbonylethyl)-2,8,12,18-tetramethyl-10,20-bis(2-thienyl)porphyrin (**14b**).

The title porphyrin was prepared by the foregoing procedure from **3b** (180 mg) and 2-thiophenecarboxaldehyde (48 mg). After chromatography on Grade 3 alumina and recrystallization from chloroform-methanol, **14b** was obtained as purple needles (38 mg, 20%), mp >300°; ms: (fast atom bombardment) m/z (relative intensity) 983 (17) ([M + H + Thioglycerol]$^+$), 875 (100) ([M + H]$^+$), 874 (16), ($M^+$), 817 (10), 769 (6), 578 (10), 530 (25), 472 (18); hrms: (fast atom bombardment) Calcd. for $C_{48}H_{50}N_4O_8S_2$ + H: 875.3145. Found: 875.3134; uv (chloroform): λ max 411 (5.32), 510 (4.18), 545 (3.85), 578 (3.81), 630 (3.48) nm; pmr (deuteriochloroform): δ −2.4 (2H, br, NH), 2.74 (12H, s, 4 x porphyrin-$CH_3$), 3.17 (8H, t, J = 7.7 Hz, 4 x $CH_2CH_2CO$), 3.67 (12H, s, 4 x $OCH_3$), 4.39 (8H, t, J = 7.7 Hz, 4 x $CH_2CH_2CO$), 7.50 (2H, m, 2 x thienyl 4H), 7.75 (2H, m, 2 x thienyl 3H), 7.85 (2H, m, 2 x thienyl 5H), 10.30 (2H, s, *meso*-H).

*Anal.* Calcd. for $C_{48}H_{50}N_4O_8S_2 \cdot H_2O$ (893.08): C, 64.55; H, 5.87; N, 6.27. Found: C, 64.41; H, 5.80; N, 6.14.

3,7,13,17-Tetrakis(2-methoxycarbonylethyl)-2,8,12,18-tetramethyl-10,20-bis(3-thienyl)porphyrin (**14c**).

The title porphyrin was prepared by the previous procedure from **3b** (180 mg) and 3-thiophenecarboxaldehyde (48 mg). After chromatography on Grade 3 alumina and crystallization from dichloromethane-ethanol, **14c** was obtained as a maroon solid (30 mg, 16%), mp >300°; uv (chloroform): λ max nm ($\log_{10}\epsilon$) 410 (5.33), 508 (4.20), 543 (3.67), 575 (3.80), 627 (3.13); pmr (deuteriochloroform): δ −2.4 (2H, br, NH), 2.66 (12H, s, 4 x porphyrin-$CH_3$), 3.17 (8H, t, $CH_2CH_2CO$), 3.67 (12H, s, 4 x $OCH_3$), 4.38 (8H, t, $CH_2CH_2CO$), 7.76 (6H, m, 6 x thiophene-H), 10.27 (2H, m, 2 x *meso*-H).

*Anal.* Calcd. for $C_{48}H_{50}N_4O_8S_2 \cdot H_2O$ (893.08): C, 64.55; H, 5.87; N, 6.27. Found: C, 64.70; H, 5.86; N, 6.38.

Acknowledgements.

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## REFERENCES AND NOTES

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