Synthesis and Properties of 5-(*p*-Carbomethoxyphenyl)-15-(*p*-dimethylaminophenyl)porphyrin

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An unsymmetrically substituted 5,15-diarylporphyrin **1**, with *p*-dimethylamino and *p*-carbomethoxy substituents, was synthesized *via* a MacDonald condensation of aryldipyrromethane precursors **6** and **12**, which were prepared in good yield by three or four step procedures starting from ethyl 3,4-dimethyl-1*H*-pyrrole-2-carboxylate (**2**).

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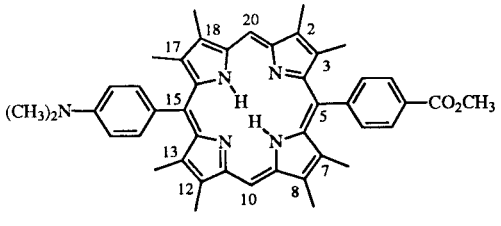
Introduction.

Although porphyrins have been synthesized by many different routes [1], one of the more attractive ways to prepare symmetrically-substituted 5,15-diarylporphyrins is by condensation of two dipyrromethanes with aromatic aldehydes [2]. Recently this method was modified to allow for the condensation of two different aromatic aldehydes to give unsymmetrically substituted 5,15-diarylporphyrins [3]. Yet, another general method involves MacDonald condensation [4] or an aminomethylation [5] of two aryldipyrromethane precursors [6]. The last pathway appeared to us to be the method of choice for the synthesis of the unsymmetrically substituted 5,15-diarylporphyrins. Our target was 5,15-diarylporphyrin **1** has a strong electron-donating group ($(CH_3)_2N$–) at the *para* position of one phenyl group and an electron-withdrawing group (–CO_2CH_3) on the other. Our interest in **1** was to explore "push-pull" charge transfer through the porphyrin core as detected by nmr and uv-visible spectroscopy.



1-H_2

Synthesis of Aryldipyrromethanes.

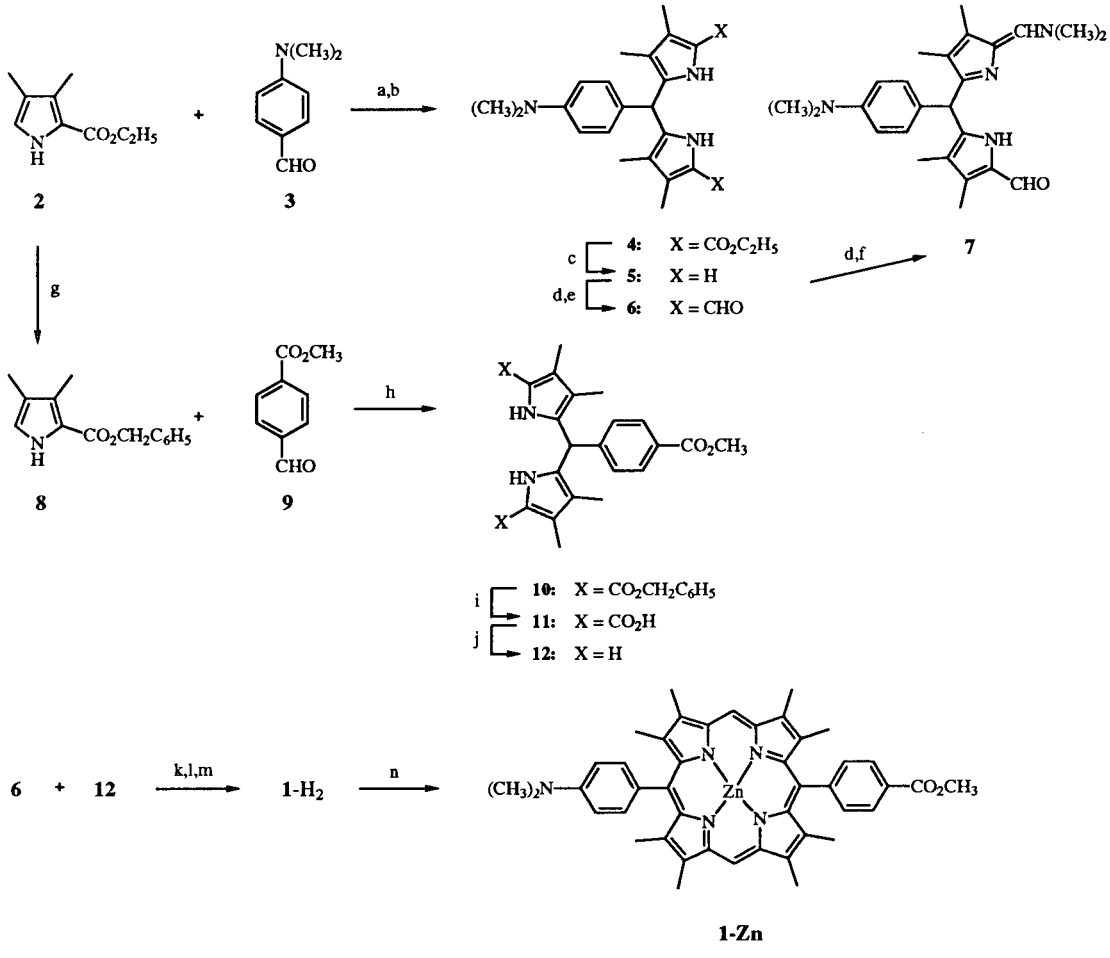
As outlined in Scheme 1, the left half of **1** was prepared in three steps from the readily available starting material, ethyl 3,4-dimethyl-1*H*-pyrrole-2-carboxylate (**2**) [7] by reaction with 4-dimethylaminobenzaldehyde (**3**) in an acid-catalyzed condensation to afford dipyrromethane ester **4**. Thus, a solution of pyrrole **2** and aldehyde **3** in ethanol was treated with concentrated hydrochloric acid and heated at reflux. After neutralization of the cooled mixture with aqueous sodium hydroxide, the crude product precipitated, and dipyrromethane ester **4** was isolated in 92% yield as a white powder after crystallization from hexane. Saponification of **4**, followed by decarboxylation, was carried out by heating at 180° in ethylene glycol containing sodium hydroxide. The resulting dipyrromethane **5** was obtained in 90% yield as a brown solid and used in the next step without additional purification. Compound **5** was formulated *via* a Vilsmeier reaction by treating with phosphorus oxychloride in cold dimethylformamide. Hydrolysis of the intermediate by heating in aqueous sodium hydroxide at reflux gave dialdehyde **6** as a white powder in 61% yield after crystallization from methanol. However, hydrolysis at room temperature afforded azafulvene **7** in 42% yield as yellow crystals after crystallization from dichloromethane/methanol (Scheme 1).

Similarly, the right half of **1** was prepared from pyrrole **2**. As outlined in Scheme 1, titanate-mediated transesterification [8] of pyrrole ethyl ester **2** in benzyl alcohol, followed by purification through a short column of silica gel and crystallization from hexane gave benzyl 3,4-dimethyl-1*H*-pyrrole-2-carboxylate (**8**) in 56% yield. A solution of pyrrole **8** and aldehyde **9** in methanol was treated with concentrated hydrochloric acid and heated at reflux to afford dipyrromethane ester **10** in 86% as a light yellow powder after crystallization from hexane. The benzyl groups of dipyrromethane ester **10** were removed in a palladium-catalyzed hydrogenolysis to give dipyrromethane acid **11** in quantitative yield as a light brown solid. It was used in the next step without additional purification. Decarboxylation of **11** was accomplished in diethylaminoethanol by heating at 160° to afford dipyrromethane **12**, isolated in 88% yield as a brown solid, which was condensed directly with dialdehyde 6 to afford 5,15-diarylporphyrin **1-H_2** following the standard MacDonald procedure [4]. The reaction was carried out in acetic acid containing hydriodic acid. After addition of sodium acetate, the mixture was aerated to oxidize the intermediates. 5,15-Diarylporphyrin **1-H_2** was isolated in 32% yield as a purple solid. Zinc insertion into the 5,15-diarylporphyrin **1-H_2** was readily achieved using zinc acetate in methanol/chloroform to give **1-Zn** in quantitative yield after purification on a short column of alumina.

Spectroscopic Properties

The ^{1}H-nmr spectra data of 5,15-diarylporphyrin **1-H_2**

Scheme 1



[a] HCl, CH_3CH_2OH, 80°C, 15h; [b] NaOH, H_2O, 0°C (92%); [c] NaOH, $(CH_2OH)_2$, 180°C, 1h (90%); [d] $POCl_3$, $(CH_3)_2NCHO$, 0°C to room temp., 3h; [e] NaOH, H_2O, 100°C, 2h (61%); [f] NaOH, H_2O, room temp., 15 min. (42%); [g] Ti $(OCH(CH_3)_2)_4$, $C_6H_5CH_2OH$, 90°C, 15h (56%); [h] HCl, CH_3OH, 60°C, 15h (86%); [i] H_2/Pd(C), CH_3OH, room temp., 5h (94%); [j] $(C_2H_5)_2N(CH_2)_2OH$, 160°C, 2h (88%); [k] HI, CH_3CO_2H, room temp., 1h; [l] CH_3CO_2Na, CH_3CO_2H, room temp.; [m] O_2, room temp., 24h (32%); [n] Zinc acetate, CH_3OH, $CHCl_3$, 60°C, 1h (95%).

are compared with those from the parent with no dimethylamino or carbomethoxy groups, 2,3,7,8,12,-13,17,18-octamethyl-5,15-diphenylporphine (**5,15-DPP**) [9,10] in Table 1. Under the influence of anisotropic effects from nearby phenyl substituents the methyl groups at the porphyrin ring carbons 3,7,13 and 17 are shifted upfield, about 1 ppm, in comparison to the methyl groups at ring carbons 2,8,12 and 18 (Table 1). Although the

Table 1

Comparison of ^{1}H-NMR, UV-visible Absorption and Fluorescent Properties of 5-*p*-Dimethylaminophenyl-15-*p*-carbomethoxyphenyl Porphyrins **1-H_2** and **1-Zn** with the Unsubstituted 1,15-Diphenylporphyrins (**5,15-DPP**).

	^{1}H-nmr Chemical Shifts [a]			Uv-visible Absorption [b]		Fluorescence [b]
Porphyrin	3,7,13,17-CH_3	2,8,12,18-CH_3	10,20-H	Soret	Q-bands	Bands
1-H_2	2.45, 2.57	3.53	10.21	407	507, 540, 574, 627	631, 693
1-Zn	2.31, 2.49	3.39, 3.44	9.98	410	539, 573	582, 633
5,15-DPP-H_2 [c]	2.27	3.29	10.26	408	508, 542, 576, 626	
5,15-DPP-H_2 [d]	2.28	3.27	10.41	408	505, 538, 576, 628	635, 698
5,15-DPP-Zn	2.44	3.49	10.12	411	538, 573	

[a] Values in δ, ppm downfield from $(CH_3)_4Si$. [b] λ max (nm). [c] Ref [9]. [d] Ref [10].

more shielded methyls in **1** split into two signals, distinguishing the 3,7 pair from the 13,17 pair, no other significant influence of the electron-donating group or the electron-withdrawing group in 5,15-diarylporphyrin **1** on the chemical shifts of the porphyrin core was noted.

No "charge transfer" bands from the dimethylamino and ester groups of 5,15-diarylporphyrin **1** could be detected by comparison of the absorption and fluorescence spectra of **1** and those of **5,15-DPP** (Table 1). Thus, the effective "push-pull" charge transfer mechanism responsible for red-shifted bands in the uv-visible spectra of, *e.g.*, *p*-dimethylaminobenzoic acid (relative to benzoic acid) is not operative in **1** due to ineffective conjugation. The planes of the phenyl rings and the flat porphyrin core are orthogonal [11].

EXPERIMENTAL

General.

All ^{1}H-nmr and ^{13}C-nmr spectra were recorded in deuteriochloroform on a General Electric QE-300 spectrometer unless otherwise noted. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer. All uv-visible spectra were recorded on a Perkin-Elmer Lambda Array 3840 spectrophotometer, and fluorescence spectra were recorded on a Perkin-Elmer MPF-44A spectrophotometer. Baker silica gel (60-200 mesh) or Woelm alumina (N32-63) was used for column chromatography. Melting points are uncorrected. Combustion analysis were carried out by the Desert Analytics Laboratory in Tucson, Arizona. *p*-Dimethylaminobenzaldehyde, *p*-carbomethoxybenzaldehyde, ethylene glycol, phosphorus oxychloride, dimethylformamide (dried over 3Å molecular sieves), titanium isopropoxide, benzyl alcohol, and dimethylaminoethanol and hydriodic acid were from Aldrich Chemical Co. The deuteriochloroform (99.9% d_1) and dimethyl sulfoxide-d_6 (99.9% d_6) were from Cambridge Isotope Labs.

Bis-(5-ethoxycarbonyl-3,4-dimethyl-2-pyrryl)(4-dimethylaminophenyl)methane (**4**).

Concentrated hydrochloric acid (10 ml) was added to a solution of ethyl 3,4-dimethyl-1*H*-pyrrole-2-carboxylate (**2**) [7] (3.34 g, 20 mmoles) and 4-dimethylaminobenzaldehyde (**3**) (1.49 g, 10 mmoles) in ethanol (100 ml). After stirring under nitrogen at 80° for 15 hours, the mixture was cooled to 0° and neutralized with a solution of sodium hydroxide (5.00 g, 125 mmoles) in water (100 ml). The resulting precipitate was collected, washed with water and dried in a desiccator. The crude product was crystallized from hexane to give 4.28 g (92%) of **4**. It had mp 109-110°, ir (potassium bromide): ν 3300 (NH), 2900, 1640 (C=O), 1430, 1240, 770 cm^{-1}; ^{1}H-nmr: δ 1.32 (t, 6H, J = 7.2 Hz, CH_3), 1.77 (s, 6H, CH_3), 2.25 (s, 6H, CH_3), 2.94 (s, 6H, $N(CH_3)_2$), 4.25 (q, 4H, J = 7.2 Hz, CH_2), 5.39 (s, 1H, CH), 6.67 (d, 2H, J_{AB} = 8.7 Hz, Ph-H), 6.93 (d, 2H, J_{AB} = 8.7 Hz, Ph-H), 8.25 (s br, 2H, NH) ppm; ^{13}C-nmr: δ 8.4 (q), 10.3 (q), 14.1 (q), 39.7 (d), 40.1 (q, $N(CH_3)_2$), 59.3 (t), 112.5 and 128.5 (d, Ar-C), 117.1, 117.2, 125.9, 127.2, 132.3 and 149.4 (s), 161.4 (s, C=O) ppm.

Anal. Calcd. for $C_{27}H_{35}N_3O_4$ (465.6): C, 69.65; H, 7.58; N, 9.03. Found: C, 69.87; H, 7.72; N, 8.88.

Bis-(5-formyl-3,4-dimethyl-2-pyrryl)(4-dimethylaminophenyl)methane (**6**).

Dipyrromethane ester **4** (2.33 g, 5 mmoles) was dissolved in a solution of ethylene glycol (50 ml) and sodium hydroxide (1.60 g, 40 mmoles), and stirred under nitrogen at 180° for 1 hour. Water (50 ml) was added at room temperature, and the resulting precipitate was collected, washed with water, and dried in a desiccator to give 1.45 g (90%) of **5** with mp 60-65° dec. It was used directly in the next step and had ir (potassium bromide): ν 3400 (NH), 2900, 1430, 1050, 860, 760 cm^{-1}; ^{1}H-nmr: δ 1.80 (s, 6H, CH_3), 2.01 (s, 6H, CH_3), 2.93 (s, 6H, $N(CH_3)_2$), 5.39 (s, 1H, CH), 6.36 (s, 2H, 5-H), 6.67 (d, 2H, J_{AB} = 8.7 Hz, Ph-H), 6.98 (d, 2H, J_{AB} = 8.7 Hz, Ph-H), 7.30 (s br, 2H, NH) ppm; ^{13}C-nmr: δ 8.5 (q), 10.1 (q), 39.8 (d), 40.3 (q, $N(CH_3)_2$), 112.5, 112.6 and 128.7 (d, Ar-C), 113.6, 118.4, 128.0, 129.3 and 149.0 (s) ppm.

To a stirred solution of dipyrromethane **5** (1.61 g, 5 mmoles) in dry dimethylformamide (10 ml), phosphorus oxychloride (1.8 ml, 20 mmoles) was added dropwise at 0°. After stirring under nitrogen at room temperature for 3 hours, a solution of sodium hydroxide (8.0 g, 200 mmoles) in water (100 ml) was added, and the mixture was heated at reflux for 2 hours. The resulting precipitate was collected, washed with water and crystallized from methanol to give 1.15 g (61%) of **6**. It had mp 205-206°; ir (potassium bromide): ν 3250 (NH), 2900, 1620 (C=O), 1510, 1430, 1225, 79 cm^{-1}; ^{1}H-nmr: δ 1.80 (s, 6H, CH_3), 2.55 (s, 6H, CH_3), 2.95 (s, 6H, $N(CH_3)_2$), 5.42 (s, 1H, CH), 6.65 (d, 2H, J_{AB} = 8.7 Hz, Ph-H), 6.92 (d, 2H, J_{AB} = 8.7 Hz, Ph-H), 8.80 (s br, 2H, NH), 9.47 (s, 2H, CHO) ppm; ^{13}C-nmr: δ 8.0 (q), 8.5 (q), 39.6 (d), 40.1 (q, $N(CH_3)_2$), 112.6 and 128.5 (d, Ar-C), 118.1, 128.0, 131.9, 132.0, 136.7 and 149.4 (s), 176.0 (s, C=O) ppm.

Anal. Calcd. for $C_{23}H_{27}N_3O_2$ (377.5): C, 73.18; H, 7.21; N, 11.13. Found: C, 73.45; H, 7.36; N, 11.15.

(5-Formyl-3,4-dimethyl-2-pyrryl)(2,3-dimethyl-6-dimethylamino-1-azafulvene)(4-dimethylaminophenyl)methane (**7**).

To a stirred solution of dipyrromethane **5** (1.61 g, 5 mmoles) in dry dimethylformamide (10 ml), phosphorus oxychloride (1.8 ml, 20 mmoles) was added dropwise at 0°. After stirring under nitrogen at room temperature for 3 hours, a solution of sodium hydroxide (8.0 g, 200 mmoles) in water (100 ml) was added, and the mixture was stirred at room temperature for 15 minutes. The resulting precipitate was collected, washed with water and crystallized from dichloromethane-methanol to give 0.85 g (42%) of **7**. It had mp 225° dec; ir (potassium bromide): ν 3200 (NH), 2900, 1630 (C=C, C=N, C=O), 1320, 1190, 930, 700 cm^{-1}; ^{1}H-nmr: δ 1.96 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.86 (s, 6H, $N(CH_3)_2$), 3.30 (s, 3H, NCH_3), 3.91 (s, 3H, NCH_3), 5.23 (s, 1H, CH), 6.62 (d, 2H, J_{AB} = 8.7 Hz, Ph-H), 6.94 (s, 1H, CH), 7.23 (d, 2H, J_{AB} = 8.7 Hz, Ph-H), 9.50 (s, 1H, CHO), 12.60 (s br, 1H, NH) ppm; ^{13}C-nmr: δ 8.3 (q), 8.4 (q), 9.4 (q), 40.2 (q, $N(CH_3)_2$), 40.3 (d), 41.0 (q, NCH_3), 46.8 (q, NCH_3), 112.5 and 128.2 (d, Ar-C), 116.6, 122.7, 127.0, 129.4, 130.2, 130.9, 137.0, 141.0, 148.7 and 160.8 (s), 141.4 (d, CH), 175.4 (s, C=O) ppm.

Anal. Calcd. for $C_{25}H_{32}N_4O$ (404.6): C, 74.22; H, 7.97; N, 13.84. Found: C, 73.94; H, 7.89; N, 13.80.

Benzyl 3,4-Dimethyl-1*H*-pyrrole-2-carboxylate (**8**).

A solution of ethyl 3,4-dimethyl-1*H*-pyrrole-2-carboxylate (**2**) [7] (6.69 g, 40 mmoles) and titanium(IV) isopropoxide (3.0 ml,

10 mmoles) in benzyl alcohol (40 ml) was heated under reflux for 15 hours at 15 Torr. The solvent was removed under reduced pressure, and the residue was purified by chromatography on a short column of silica gel, eluting with dichloromethane-hexane (1:1 by vol) followed by crystallization from hexane to give 5.09 g (56%) of **8**. It had mp 73-74° (lit mp 73-75° [12], 74-76° [13]; ir (potassium bromide): ν 3300 (NH), 2900, 1670 (C=O), 1395, 1270, 1145, 725 cm^{-1}; ^1H-nmr: δ 2.01 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 5.31 (s, 2H, CH_2), 6.66 (d, 1H, J = 2.4 Hz, 5-H), 7.30-7.45 (m, 5H, Ph-H), 8.75 (s br, 1H, NH) ppm; ^{13}C-nmr: δ 9.5 (q), 10.0 (q), 65.2 (t), 118.5, 120.2, 126.7 and 136.1 (s, Ar-C), 120.1, 126.6, 127.7 and 128.1 (d, Ar-C), 161.0 (s, C=O) ppm.

Bis-(5-benzyloxycarbonyl-3,4-dimethyl-2-pyrryl)(4-methoxycarbonylphenyl)methane (**10**).

Concentrated hydrochloric acid (1 ml) was added to a solution of pyrrole **8** (4.59 g, 20 mmoles) and methyl 4-formylbenzoate (**9**) (1.64 g, 10 mmoles) in methanol (100 ml). After stirring under nitrogen at 60° for 15 hours, the mixture was cooled to room temperature. The resulting precipitate was collected by filtration, dissolved in ether, and dried over anhydrous magnesium sulfate. After filtration and evaporation of the solvent under reduced pressure, the crude product was crystallized from hexane to give 3.84 g (86%) of **10**. It had mp 75-80°; ir (potassium bromide): ν 3300 (NH), 2925, 1680 (C=O), 1640 (C=O), 1430, 1275, 1110, 730 cm^{-1}; ^1H-nmr: δ 1.81 (s, 6H, CH_3), 2.24 (s, 6H, CH_3), 3.91 (s, 3H, OCH_3), 5.21 (s, 4H, CH_2), 5.58 (s, 1H, CH), 7.15 (d, 2H, J_{AB} = 8.4 Hz, Ph-H), 7.30-7.40 (m, 10H, Ph-H), 7.94 (d, 2H, J_{AB} = 8.4 Hz, Ph-H), 8.77 (s br, 2H, NH) ppm; ^{13}C-nmr: δ 8.6 (q), 10.4 (q), 40.1 (d), 51.7 (q, OCH_3), 65.3 (t, CH_2), 117.9, 117.7, 127.7, 128.7, 131.2, 135.9 and 144.4 (s, Ar-C), 127.5, 127.6, 127.8, 128.1 and 129.7 (d, Ar-C), 161.3 and 166.2 (s, C=O) ppm.

Anal. Calcd. for $C_{37}H_{36}N_2O_6$ (604.7): C, 73.49; H, 6.00; H, 4.63. Found: C, 73.43; H, 6.15; N, 4.66.

5-(4Methoxycarbonylphenyl)-2,3,7,8,12,13,17,18-octamethyl-15-(4-dimethylaminophenyl)porphine (**1-H_2**).

A solution of dipyrromethane ester **10** (3.02 g, 5 mmoles) in methanol (100 ml) was treated with Pd(C) (100 mg, 10% Pd-C) and stirred under hydrogen at room temperature for 5 hours. After filtration, water (100 ml) was added, and the resulting precipitate was collected, washed with water and dried in a desiccator to give 2.00 g (94%) of **11**, mp 137° dec. It was used directly in the next step and had ir (potassium bromide): ν 3300 (NH and OH), 2900, 1650 (C=O), 1450, 1280, 1090, 750 cm^{-1}; ^1H-nmr (dimethyl sulfoxide-d_6): δ 1.94 (s, 6H, CH_3), 2.15 (s, 6H, CH_3), 3.79 (s, 3H, (OCH_3), 5.73 (s, 1H, CH), 7.05 (d, 2H, J_{AB} = 8.1 Hz, Ph-H), 7.85 (d, 2H, J_{AB} = 8.1 Hz, Ph-H), 11.04 (s, 2H, NH), 12.10 (s br, 2H, CO_2H) ppm; ^{13}C-nmr (dimethyl sulfoxide-d_6): δ 8.8 (q), 10.5 (q), 38.1 (d), 52.0 (q, OCH_3), 117.2, 118.6, 125.1, 127.7, 131.7 and 147.0 (s, Ar-C), 128.2 and 129.1 (d, Ar-C), 162.5 and 166.2 (s, C=O) ppm.

A solution of dipyrromethane acid **11** (1.70 g, 4 mmoles) in diethylaminoethanol (5 ml) was stirred under nitrogen at 160° for 2 hours. The mixture was poured into water (200 ml) and extracted with ether (50 ml) three times. The combined organic layers were washed with water (100 ml) three times and dried over anhydrous sodium sulfate. Filtration and evaporation of the solvent under reduced pressure gave 1.18 g (88%) of **12**, mp 60-65° dec. It was used directly in the next step and had ir (potassium bromide): ν 3400 (NH), 2900, 1710 (C=O), 1430, 1270, 1110, 740 cm^{-1}; ^1H-nmr: δ 1.78 (s, 6H, CH_3), 2.02 (s, 6H, CH_3), 3.90 (s, 3H, OCH_3), 5.53 (s, 1H, CH), 6.40 (s, 2H, 5-H), 7.20 (d, 2H, J_{AB} = 8.4 Hz, Ph-H), 7.30 (s br, 2H, NH), 7.96 (d, 2H, J_{AB} = 8.4 Hz, Ph-H) ppm; ^{13}C-nmr: δ 8.5 (q), 10.0 (q), 40.7 (d), 51.5 (q, OCH_3), 113.6, 128.0 and 129.5 (d, Ar-C), 114.2, 118.3, 126.5, 127.9 and 147.5 (s, Ar-C), 166.6 (s, C=O) ppm.

Concentrated hydriodic acid (5 ml) dissolved in acetic acid (200 ml) was added to combined solutions of dialdehyde **6** (755 mg, 2 mmoles) in acetic acid (250 ml) and dipyrromethane **12** (673 mg, 2 mmoles) in acetic acid (250 ml). After standing in the dark for 1 hour, a solution of sodium acetate (12.3 g, 150 mmoles) in acetic acid (200 ml) was added to the mixture, and air was bubbled in through a gas dispersion tube during 24 hours. After evaporation of the solvent under reduced pressure, the residue was washed with a 0.5 *N* sodium bicarbonate solution, water and hot methanol. The resulting solid was collected by filtration, dried in a desiccator, and dissolved in chloroform. After filtration and evaporation of the solvent under reduced pressure, 430 mg (32%) of **1-H_2** was isolated. It had mp >300°; ^1H-nmr: δ -2.42 (s br, 2H, NH), 2.45 (s, 6H, CH_3), 2.57 (s, 6H, CH_3), 3.24 (s, 6H, $N(CH_3)_2$), 3.53 (s, 12H, CH_3), 4.13 (s, 3H, OCH_3), 7.08 (d, 2H, J_{AB} = 8.4 Hz, Ph-H), 7.81 (d, 2H, J_{AB} = 8.4 Hz, Ph-H), 8.17 (d, 2H, J_{AB} = 8.1 Hz, Ph-H), 8.43 (d, 2H, J_{AB} = 8.1 Hz, Ph-H), 10.21 (s, 2H, 10-H and 20-H) ppm; uv-visible (dichloromethane): λ max 241 nm, ε 23,400, λ max 407 nm, ε 224,500, λ max 507 nm, ε 15,300, λ max 540 nm, ε 7,000, λ max 574 nm, ε 7,800, λ max 627 nm, ε 3,200.

Anal. Calcd. for $C_{44}H_{45}N_5O_2$ (675.9): C, 78.19; H, 6.71; N, 10.36. *Anal.* Calcd. for $C_{44}H_{45}N_5O_2 \cdot 2H_2O$ (711.9): C, 74.24; H, 6.94; N, 9.84. Found: C, 74.20; H, 6.87; N, 9.56.

5-(4-Methoxycarbonylphenyl)-2,3,7,8,12,13,17,18-octamethyl-15-(4-dimethylaminophenyl)porphine Zinc (**1-Zn**).

A stirred solution of 5,15-diarylporphyrin **1-H_2** (338 mg, 0.5 mmole) and zinc acetate dihydrate (2.20 g, 10 mmoles) in chloroform (100 ml) and methanol (100 ml) was heated at reflux for 1 hour. After the solvents were removed under reduced pressure, the residue was purified by chromatography on a short column of alumina, eluting with dichloromethane to give 350 mg (95%) of **1-Zn**. It had ^1H-nmr: δ 2.31 (s, 6H, CH_3), 2.49 (s, 6H, CH_3), 3.22 (s, 6H, $N(CH_3)_2$), 3.39 (s, 6H, CH_3), 3.44 (s, 6H, CH_3), 4.13 (s, 3H, OCH_3), 7.05 (d, 2H, J_{AB} = 8.4 Hz, Ph-H), 7.75 (d, 2H, J_{AB} = 8.4 Hz, Ph-H), 8.08 (d, 2H, J_{AB} = 8.1 Hz, Ph-H), 8.40 (d, 2H, J_{AB} = 8.1 Hz, Ph-H), 9.98 (s, 2H, 10-H and 20-H) ppm; uv-visible (dichloromethane): λ max 240 nm, ε 27,100, λ max 341 nm, ε 20,500, λ max 410 nm, ε 393,700, λ max 498 nm, ε 3,500, λ max 539 nm, ε 19,700, λ max 573 nm, ε 10,500.

Anal. Calcd. for $C_{44}H_{43}N_5O_2Zn$ (739.2): C, 71.49; H, 5.86; N, 9.47. Anal. Calcd. for $C_{44}H_{43}N_5O_2Zn \cdot 2H_2O$ (775.3): C, 68.17; H, 6.11; N, 9.03. Found: C, 68.17; H, 5.96; N, 8.76.

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