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PREPARATION OF MESO-UNSUBSTITUTED PORPHYRINS SUBSTITUTED WITH MONO- AND TETRAFORMYL AND OTHER ELECTRON-WITHDRAWING GROUPS

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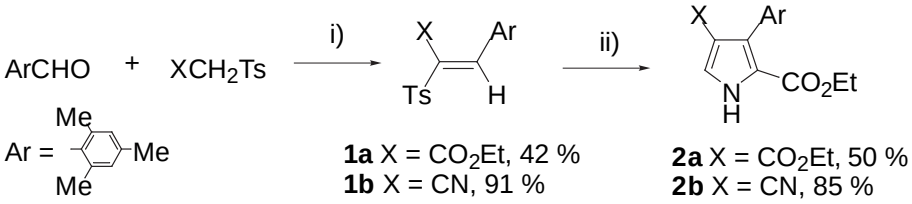
Dedicated to Professor Sho Ito on the occasion of his 77th birthday.

Abstract- A meso-unsubstituted porphyrin having a formyl group was synthesized both from a mono(ethoxycarbonyl)porphyrin by reduction with $LiAlH_4$ followed by oxidation with MnO_2 and from a monocyanoporphyrin by reduction with DIBALH. The monoethoxycarbonyl and onocyanoporphyrins were prepared by the acid catalyzed mixed condensation of the corresponding 4-ethoxycarbonyl- and 4-cyano-2-(hydroxymethyl)pyrroles with 3-mesityl-4-methyl-2-(hydroxymethyl)pyrrole. A porphyrin with four formyl groups at the β-positions was prepared from ethyl 4-(dithiolan-2-yl)-3-methylpyrrole-2-carboxylate by the sequential treatment of $LiAlH_4$, *p*-TsOH, and NBS. Cyclic voltammetry and UV-VIS spectroscopic analyses of these porphyrins revealed the highly electron-deficient property of the porphyrin chromophore.

Porphyrins have been extensively studied as key components found in a wide range of model systems of biomimetic and material chemistry.[1] In most cases, meso-substituted porphyrins rather than meso-unsubstituted ones have, so far, been employed as artificial porphyrin models because of their simple preparation,[2] although naturally occurring porphyrins such as hem, chlorophyll, and cytochrom c (oxidase) consist of meso-unsubstituted porphyrins.[3] Since molecular orbital energies between meso-substituted and unsubstituted porphyrins are quite different,[4] the studies using meso-unsubstituted porphyrins as the models would be very important for understanding the natural redox and photosynthetic systems, and conversion of substituents on the porphyrin peripheral would also help to understand the electronic structure of the active center. One of the common preparations of meso-unsubstituted porphyrins is the acid-catalyzed cyclization of 5-unsubstituted 2-(hydroxymethyl)pyrroles, which can be easily accessed by reduction of the corresponding pyrrole-2-carboxylates.[5] However, the acid catalyzed cyclic tetramerization of the pyrroles with different substituents at β-positions generally afforded a mixture of porphyrin peripheral isomers.[6] Steric requirment of a bulky β-substituent is known to lead the preferrable formation of D_{4h} symmetric porphyrin isomers (type I).[7] We have reported that substitution of electron-withdrawing groups at β-positions also enforced the formation of type I isomers.[8] In this paper, we report preparation of meso-unsubstituted porphyrins bearing ethoxycarbonyl, cyano, and formyl groups, and the effects of the porphyrin peripheral substituents are discussed.

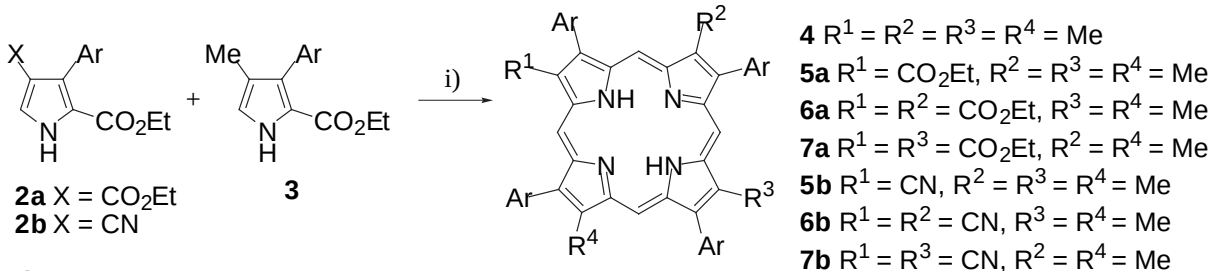


Scheme 1. Reagents:
i) AcOH, piperidine, toluene; ii) $CNCH_2CO_2Et$, DBU, THF.

Results and Discussion

The starting 4-ethoxycarbonyl- and 4-cyanopyrroles (**2a**) and (**2b**) were prepared by the modified method of Barton-Zard reaction from the α,β-unsaturated sulfones (**1a**) and (**1b**) in 50 and 85% yields, respectively[9] (Scheme 1). The sulfones (**1a**) and (**1b**) were obtained by the Knoevenagel condensation of mesitaldehyde with ethyl tosylacetate and tosylacetonitrile in 42 and 91% yields, respectively. A mixture of the pyrroles (**2a**) and (**3**) was treated with $LiAlH_4$ in THF at 0 ˚C to give a mixture of the

correponding 2-(hydroxymethyl)pyrroles. The mixture was cyclotetramerized by an acid catalyst and oxidized with chloranil to give a mixture of porphyrins, which consisted of tetramethyl-, mono(ethoxycarbonyl)- and two isomeric di(ethoxycarbonyl)porphyrins (**4**,**5**, **6**, and **7**) (Scheme 2). In order to obtain the maximum yield of the mono(ethoxycarbonyl)porphyrin (**5a**), the conditions of the cyclotetramerization were examined and the results are summarized in Table 1. The maximum yield of **5a** (27%) was obtained by starting from a 1 : 3 mixture of **2a** and **3** using $BF_3 \cdot Et_2O$ as the acid catalyst. The reaction of **2b** and **3** affording monocyanoporphyrin (**5b**) was carried out under similar conditions, though the yield of **5b** was very low (6%). Formation of type-I isomers of the porphyrins (**5a**) and (**5b**) was confirmed by the singlet signals of meso-protons in ^{1}H NMR spectra (Figure 1). The lowest signal (10.63 ppm) in **5a** is assigned as the meso-proton adjacent to the ethoxycarbonyl group due to the anisotropic effect. Contrary to **5a**, the meso-protons of **5b** appear as three singlets, the lowest one of which contains two meso-protons.



2a X = CO_2Et
2b X = CN

3

4 $R^1 = R^2 = R^3 = R^4$ = Me
5a $R^1 = CO_2Et$, $R^2 = R^3 = R^4$ = Me
6a $R^1 = R^2 = CO_2Et$, $R^3 = R^4$ = Me
7a $R^1 = R^3 = CO_2Et$, $R^2 = R^4$ = Me
5b R^1 = CN, $R^2 = R^3 = R^4$ = Me
6b $R^1 = R^2$ = CN, $R^3 = R^4$ = Me
7b $R^1 = R^3$ = CN, $R^2 = R^4$ = Me

Scheme 2. Reagents:
i) $LiAlH_4$, THF; K10, *p*-TsOH, or $BF_3 \cdot Et_2O$, $CHCl_3$; chloranil.

The monoformylporphyrin (**11**) was prepared from both **5a** and **5b** (Scheme 3). The porphyrin (**5a**) was reduced by the breaf treatment with 3 equivalents of DIBALH at 0 ˚C. The hydroxymethylporphyrin (**9**) was oxidized with activated MnO_2 in CH_2Cl_2 to give the monoformylporphyrin (**11**) in 79% yield.[10] The porphyrin (**11**) was also prepared by reduction of **5b** with DIBALH in 40% yield. The obtained porphyrins (**5a**, **5b**, **9**, and **11**) were easily transformed to zinc porphyrins (**8**, **10**, **12**, and **13**) by the metallation with $Zn(OAc)_2 \cdot 2H_2O$ in 70-85% yield.

Next, we attempted to prepare tetraformylporphyrin (**18**) by the similar protocol to **11**. Thus, tetra(ethoxycarbonyl)porphyrin (**14**) was prepared from **2a** by the reduction, acid-tetramerization, followed by oxidation. Reduction of **14** with large excess of DIBALH gave tetra(hydroxymethyl)porphyrin (**16**) in 47% yield. However, oxidation of **16** to the targeted

tetraformylporphyrin (**18**) was problematic. Oxidation of **16** with MnO_2 or CrO_2 did not proceed, and other oxidation reagents such as PCC gave no product probably due to the low solubility of **16**.

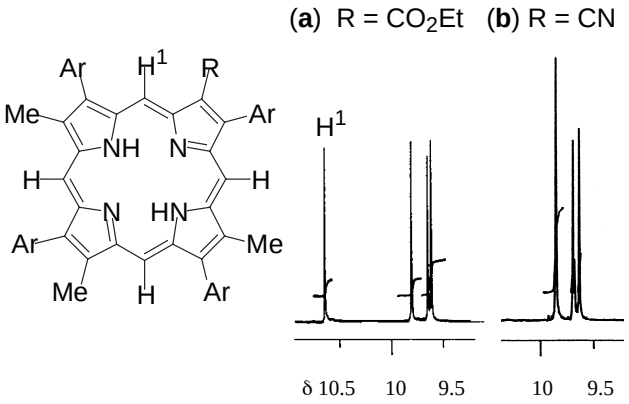
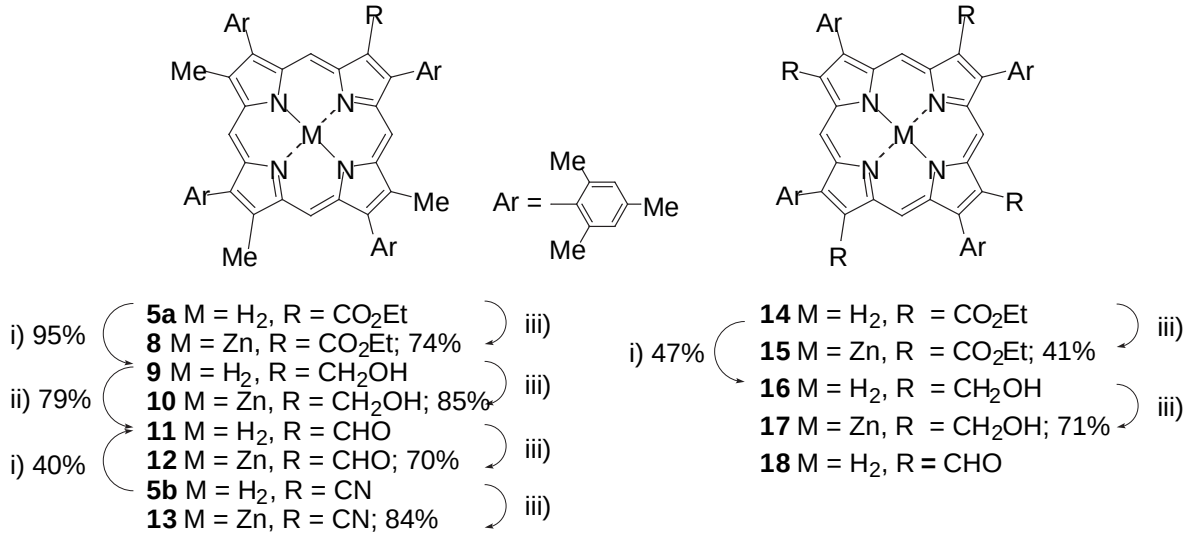


Figure 1. The ^{1}H NMR spectra of meso-H of porphyrin **5a** (**a**) and **5b** (**b**).

Table 1. Synthesis of porphyrins by the mixed condensation.

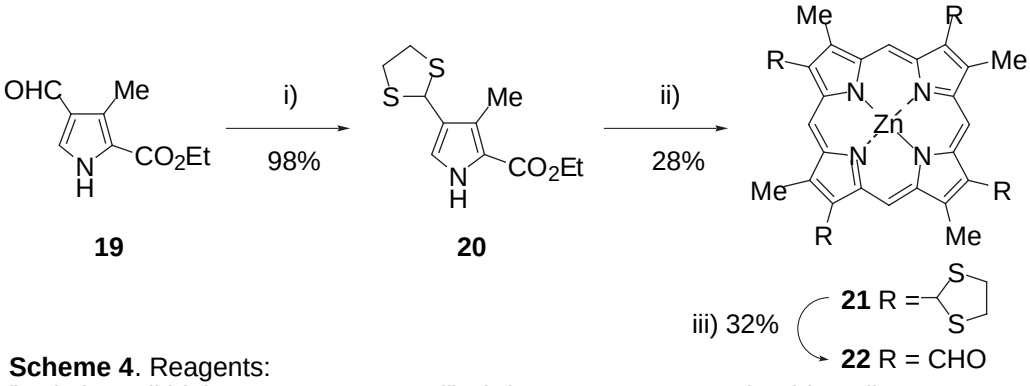
Pyrrole **2**	Ratio **3/2**	Acid	Yield (%) **4**	**5**	**6** and **7**
a	1/1	K10	40	<1	trace
a	3/1	K10	32	2	trace
a	1/1	*p*-TsOH	<1	4	2
a	3/1	*p*-TsOH	5	14	1
a	3/1	TFA	28	12	2
a	3/1	$BF_3{\cdot}Et_2O$	7	27	3
b	3/1	$BF_3{\cdot}Et_2O$	12	6	trace

Therefore, we decided to prepare the tetraformylporphyrin (**22**) by the tetramerization of a pyrrole with a protected formyl group. Since a mild oxidative deprotection method of ethylenedithio acetals to aldehydes was reported,[11] the formyl group of **19** was converted to 4-(1,3-dithiolan-2-yl)pyrrole (**20**) by treatment with ethanedithiol (Scheme 4). The 4-(1,3-dithiolan-2-yl)pyrrole (**20**) was then reduced with $LiAlH_4$ at 0 ˚C to give the corresponding hydroxymethylpyrrole, which was successively treated with montmorillonite K10, chloranil, and $Zn(OAc)_2{\cdot}2H_2O$ to afford tetrakis(dithiolanyl)porphyrinato zinc(II) (**21**) in 28% yield.



Scheme 3. Reagents:
i) DIBALH, CH_2Cl_2; ii) activated MnO_2, CH_2Cl_2 iii) $Zn(OAc)_2{\cdot}2H_2O$, CH_2Cl_2, MeOH.

Isomeric ratio of the porphyrin (**21**) was estimated to be I : II : III : IV = 67 : 5 : 28 : trace by the NMR analysis. Regeneration of the formyl group was achieved by treatment with NBS in aqueous THF to give tetraformylporphyrin (**22**). The crude **22** was purified by the combination of column chromatography and recrystallization to give only the type I isomer of tetraformylporphyrinato zinc complex (**21**) in 32% yield (>95% isomerically pure). The obtained porphyrins (**14**) and (**16**) were also transformed to zinc porphyrins (**15**) and (**17**) by the metallation with $Zn(OAc)_2 \cdot 2H_2O$ in 41 and 71% yields, respectively (Scheme 3).



19 **20**

Scheme 4. Reagents:
i) ethylene dithiol, $BF_3 \cdot Et_2O$, MeOH; ii) $LiAlH_4$, THF; K10, $CHCl_3$; chloranil; $Zn(OAc)_2 \cdot 2H_2O$, MeOH; iii) NBS, THF, H_2O.

Table 2. Oxidation potentials[a] and UV-VIS spectral data of porphyrinato zinc complexes.

Porphyrin	$E^{OX}_{1/2}(1)$	$E^{OX}_{1/2}(2)$	λ_{max} ($\log_{10}\varepsilon$) in CH_2Cl_2 (nm)
8 (CO_2Et)	0.45	0.77	414 (5.55), 543 (4.23), 587 (4.53)
10 (CH_2OH)	0.35	0.63	407 (5.61), 534 (4.28), 584 (4.42)
12 (CHO)	0.51	0.78	423 (5.43), 553 (4.10), 599 (4.60)
13 (CN)	0.56	0.94	414 (5.49), 544 (4.12), 589 (4.56)
15 $(CO_2Et)_4$	0.55	0.79	435 (5.58), 558 (4.36), 595 (4.15)
17 $(CH_2OH)_4$	0.52	0.72	411 (5.43), 537 (4.10), 573 (4.17)
22[b] $(CHO)_4$	0.74	-	456 (5.03), 581 (3.91), 623 (3.74)

[a] The half-wave potential values are versus Fc/Fc^+ = +0.20 V. The concentrations of porphyrins were over 3.5 X 10^{-3} M in CH_2Cl_2 and 0.1 M TBAP was used as an electrolyte. The scan rate was 0.3 $V \cdot s^{-1}$. [b] in DMSO.

Cyclic voltammetry (CV) and UV-VIS spectroscopy were measured to examine the effects of the electron-withdrawing substituents of the Zn complexes (**8**, **10**, **12**, **13**, **15**, **17**, and **22**). The CV measurement was performed by using a Pt working electrode in CH_2Cl_2 (**8**, **10**, **12**, **13**, **15**, and **17**) or in DMSO (**22**), containing 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte, and a $Ag/AgNO_3$ reference electrode. The reversible oxidation peaks of **8**, **10**, **12**, **13**, **15**, **17**, and **22** are approved by the Fc/Fc^+ (+0.20 V) potential and summarized in Table 2. The oxidation peaks of the

monofunctionalized porphyrins shifted to higher potentials, as the electron-withdrawing nature of the substituent increased ($E^{ox}_{1/2}$, **13** > **12** > **8** > **10**). The oxidation potential of **22** is 0.23 V higher than that of monoformylporphyrin (**12**). Since the first oxidation potentials correspond to the HOMO energy levels, the electrochemical results indicate that the HOMO levels are lowered by accumulation of the electron-withdrawing groups.[12] The porphyrin (**22**) shows only one oxidation wave. This fact suggested that only one electron oxidation took place due to low HOMO level of the porphyrin ring. UV-VIS spectral data of **8**, **10**, **12**, **13**, **15**, and **17** in CH_2Cl_2 and **22** in DMSO are also summarized in Table 2. Soret bands of the Zn complexes appear at 423 (**12**), 414 (**13** and **8**), and 407 nm (**10**). These results are also understood based on the effect of substituents reported (CHO > CN > CO_2Et > CH_2OH).[13] As electron-withdrawing nature of the substituent increases, the Soret and Q bands appeared in longer wave numbers, The intensities around 584-599 nm of Q bands in monofunctionalized porphyrins increase their intensities, and the intensities of Soret bands decrease.

In conclusion, the monoformylporphyrin (**11**) was prepared from the mono(ethoxycarbonyl)- and monocyanoporphyrin (**5a**) and (**5b**). The tetraformylporphyrin (**22**) was prepared by the mild oxidative deprotection of the dithioacetal group of tetra(1,3-dithiolan-2-yl)porphyrin (**21**). The $E^{ox}_{1/2}$ values of the porphyrins were affected by electron-deficiency of the porphyrin rings. The formyl porphyrins (**11**) and (**22**) could be key substances both for synthesis of covalently linked porphyrin arrays[14] and for an artificial model of cytocrome c oxidase.

EXPERIMANTAL

Tetrahydrofuran was distilled from sodium benzophenone ketyl under an inert atmosphere. Chloroform and dichloromethane were washed with water to remove EtOH, dried with Na_2SO_4, and distilled from CaH_2 under an inert atmosphere. MeOH was distilled from CaH_2 under an inert atmosphere. Montmorilonite K10 was dried at 150 ˚C (10.0 torr). Other commercially available materials were used without further purification. Ethyl isocyanoacetate was prepared from ethyl *N*-formylglycinate using $POCl_3$ and triethylamine.[15]

Ethyl 3-Mesityl-2-tosylpropenoate (1a)

To a stirred solution of mesitylaldehyde (5 mL, 34 mmol) and ethyl tosylacetate (7.8 g, 34 mmol) in toluene (100 mL) were added piperidine (0.05 mL) and acetic acid (0.15 mL) and refluxed. After 18 h, ater (150 mL) was added. The organic layer was separated and the aqueous layer was extracted with

toluene (2 x 50 mL). The combined organic layer was washed with water (2 x 50 mL) and brine (100 mL), dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (10 %, EtOAc/hexane) to give crude **1a**. Recrystallization from EtOAc and hexane afforded 5.1 g (42%) of **1a**: pale yellow crystals; mp 112-114 °C; IR 2985, 2921, and 1728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, 3H, *J* = 7.1), 2.09 (s, 6H), 2.26 (s, 3H), 2.45 (s, 3H), 3.95 (q, 2H, *J* = 7.0), 6.83 (s, 2H), 7.36 (m, 2H), 7.89 (m, 2H), and 8.31 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.3, 19.8, 21.0, 21.6, 61.6, 128.1. 128.5, 129.3, 129.5, 134.6, 137.1, 138.3, 138.4, 144.5, 148.7, and 161.5; EI/MS 373 (M^++1, 40), 327 (100) 216 (18), and 144 (18). Anal. Calcd for $C_{21}H_{24}O_4S$: C, 67.72; H, 6.49. Found: C, 67.60; H, 6.49.

1-Cyano-3-mesityl-2-tosylate (**1b**)

The title compound was obtained in 91% yield from the reaction of mesitylaldehyde and tosylacetonitrile in the presence of piperidine and acetic acid: pale yellow crystals; mp 159-160 °C; IR 2220, 1330, and 1157 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.22 (s, 6H), 2.28 (s, 3H), 2.48 (s, 3H), 6.90 (s, 2H), 7.40 (m, 2H), 7.91 (m, 2H), and 8.48 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 20.1, 21.1, 21.8, 112.1, 122.1, 127.0, 128.6, 129.5, 130.4, 134.8, 136.3, 140.8, 146.1, and 153.9; EI/MS 325 (M^+, 18), 169 (100), and 154 (18). Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.12; H, 5.88; N, 4.30. Found: C, 69.85; H, 5.82, N, 4.38.

Diethyl 3-Mesitylpyrrole-2,4-dicarboxylate (**2a**)

To a stirred solution of **1a** (5.1 g, 13.4 mmol) in THF (50 mL) were added dropwise ethyl isocyanoacetate (1.5 mL, 13.4 mmol) and DBU (2.4 mL, 16 mmol) with cooling to 0 ˚C. After 18 h, 1 M HCl (50 mL) and $CHCl_3$ (50 mL) were added. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (2 x 50 mL). The combined organic layer was washed with water (2 x 50 mL) and brine (100 mL), dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (20%, EtOAc/hexane) to give a crude **2a**. Recrystallization from $CHCl_3$ and hexane afforded 2.2 g (50%) of **2a**: colorless crystals; mp 109-110 ˚C; IR 3292, 2983, 2916, 1726, and 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (t, 3H, *J* = 7.0), 1.07 (t, 3H, *J* = 7.0), 1.95 (s, 6H), 2.29 (s, 3H), 4.08 (q, 2H, *J* = 7.0), 4.09 (q, 2H, *J* = 7.0), 6.85 (s, 2H), 7.64 (d, 1H, *J* = 3.4), and 9.86 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ14.2, 14.4, 20.9, 21.6, 60.0, 60.8, 117.3, 121.0, 127.7, 127.8, 131.4, 131.6, 136.1, 136.4,

161.6, and 164.2; EI/MS 329 (M^+, 72), 283 (40), 238 (100), and 210 (70); Anal. Calcd for $C_{19}H_{23}NO_4$: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.35; H, 7.12; N, 4.24.

Ethyl 4-Cyano-3-mesitylpyrrole-2-carboxylate (**2b**)

The title compound was obtained in 85% yield from the reaction of **1b** and ethyl isocyanoacetate in the presence of DBU: colorless crystals; mp 112.5-113.5 ˚C; IR 3268, 3249, 3234, 2227, and 1702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (t, 3H, *J* = 7.0), 2.03 (s, 6H), 2.31 (s, 3H), 4.13 (q, 2H, *J* = 7.0), 6.91 (s, 2H), 7.3 (d, 1H, *J* = 3.7), and 10.56 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.61, 20.1, 21.0, 60.7, 96.3, 115.0, 120.2, 127.8, 128.0, 128.7, 132.8, 136.3, 137.4, and 160.2; EI/MS 283 (M^++1, 100) and 237 (25); Anal. Calcd for $C_{17}H_{18}N_2O_2$: C, 72.32; H, 6.43; N, 9.92. Found: C, 72.36; H, 6.43; N, 9.80.

Ethyl 4-Methyl-3-mesitylpyrrole-2-carboxylate (**3**)

The title compound was prepared from mesitylaldehyde and nitroethane by the reporpted procesure.[5]

Ethyl 3,8,13,18-Tetramesityl-7,12,17-trimethylporphyrin-2-carboxylate (**5a**)

To a stirred solution of **2a** (1.2 g, 1.2 mmol) and **3** (0.99 g, 3.6 mmol) in THF (10 mL) was added carefully $LiAlH_4$ (0.46 g) with cooling to 0 ˚C. After 2 h, water (2 mL) and $CHCl_3$ (10 mL) were added. The mixture was filtered through a Celite pad which was washed with $CHCl_3$ (3 x 20 mL). The filtrate and washings were dried over Na_2SO_4 and concentrated to a give crude mixture of 2-(hydroxymethyl)pyrroles. To a stirred solution of the crude 2-(hydroxymethyl)pyrroles in $CHCl_3$ (30 mL) was added $BF_3 \cdot Et_2O$ (0.1 mL, 3 x 10^{-3} M). After 24 h, chloranil (0.6 g, 2.4 mmol) was added. After 15 h, the reaction mixture was concentrated and the residue was put on an alumina column. The column was eluted with $CHCl_3$ (1 L) and the eluate was concentrated. The residue was chromatographed on silca gel (5% $CHCl_3$/hexane). Porphyrin (**5a**) was obtained from the second fraction, 3,8,13,18-tetramesityl-2,7,12,17-tetramethylporphyrin (**4**) was obtained from the first fraction, and the mixture of diethyl 3,8,13,18-tetramesityl-12,17-dimethyl porphyrin-2,7-dicarboxylate (**6a**) and diethyl 3,8,13,18-tetramesityl-7,15-dimethyl porphyrin-2,12-dicarboxylate (**7a**) was obtained from the third fraction. Recrystallization from $CHCl_3$ and MeOH afforded 0.07 g (27%) of **4**, 0.29 g (7%) of **5a**, and 0.03 g (3%) of the mixture of **6a** and **7a** (ratio = 1 : 2).

5a: purple crystals; mp >250 ˚C; UV-VIS (CH_2Cl_2) λ_{max} ($\log_{10}$ ε) 412 (5.42), 511 (4.19), 550 (4.33), 575 (3.09), and 633 (3.56) nm; IR 3438, 3423, and 1712 cm^{-1}; FAB/MS 897 (M^++1); ^{1}H NMR ($CDCl_3$) δ -3.18 (br s, 2H), 1.20 (t, 3H, *J* = 7.3), 2.12 (s, 16H), 2.13 (s, 8H), 2.561 (s, 3H), 2.569 (s, 3H), 2.58 (s, 3H), 2.59 (s, 3H), 3.19 (s, 3H), 3.27 (s, 3H), 3.28 (s, 3H), 4.47 (q, 2H, *J* = 7.3), 7.23, (s, 2H), 7.24 (m, 4H), 7.30 (s, 2H), 9.61 (s, 1H), 9.64 (s, 1H), 9.80 (s, 1H), and 10.64 (s, 1H); ^{13}C NMR ($CDCl_3$, typical signals) δ 12.1, 12.2, 13.6, 21.1, 21.3, 21.4, 21.5, 21.5, 60.7, 97.8, 98.1, 100.6, 102.8, 128.0, 128.3, 128.4, 128.5, 131.0, 132.0, 132.1, 132.9, 137.2, 137.4, 137.5, 137.9, 138.5, 138.6, and 165.5; Anal. Calcd for $C_{62}H_{64}N_4O_2$: C, 83.00; H, 7.19; N, 6.24. Found: C, 82.72; H, 7.20; N, 6.19.

6a and **7a**: purple crystals; mp >250 ˚C; UV-VIS (CH_2Cl_2) λ_{max} ($\log_{10}$ ε) 415 (5.50), 518 (3.97), 561 (4.45), 586 (4.14), and 369 (3.59) nm; IR 3417, 3332, and 1714 cm^{-1}; FAB/MS 955 (M^++1); Anal. Calcd for $C_{64}H_{66}N_4O_4$: C, 80.47; H, 6.96; N, 5.87. Found: C, 80.25; H, 7.12; N, 5.61.

2-Cyano-3,8,13,18-tetramesityl-7,12,17-trimethylporphyrin (5b)

The title compound was obtained in 6% yield from the reactions of **2b** and **3** in the presence of $BF_3{\cdot}Et_2O$. This reaction also gave **4** (12%), **5b** (6%), and the mixture of 1,3-dicyano-2,4,6,8-tetramesityl-5,7-dimethyl porphyrin (**6b**) and 2,7-dicyano-3,8,13,18-tetramesityl-12,17-dimethyl porphyrin (**7b**) was obtained trace.

5b: purple crystals; mp >250 ˚C; UV-VIS (CH_2Cl_2) λ_{max} ($\log_{10}$ ε) 411 (4.37), 513 (4.03), 553 (4.34), 573 (4.07), and 624 (3.04) nm; IR 3315, 2915, and 2217 cm^{-1}; FAB/MS 850 (M^++1); ^{1}H NMR ($CDCl_3$) δ -3.24 (br s, 2H), 2.10 (s, 9H), 2.11 (s, 9H) 2.18 (s, 3H), 2.23 (s, 3H), 2.58 (s, 9H), 2.60 (s, 3H), 3.18 (s, 3H), 3.30 (s, 3H), 3.33 (s, 3H), 7.30 (m, 6H), 7.32 (m, 2H), 9.65 (s, 1H), 9.69 (s, 1H), and 9.86 (s, 2H); ^{13}C NMR δ ($CDCl_3$, typical signals) 12.0, 12.1, 12.3, 21.0, 21.1, 21.3, 21.4, 21.5, 98.4, 98.7, 99.7, 101.0, 113.3, 117.3, 128.4. 128.6, 128.7, 129.9, 130.4, 132.0, 135.5, 136.0, 136.6, 137.6, 137.7, 137.9, 138.3, 138.4, 138.6, 138.7, 138.8, 139.4, 140.6, 141.4, 145.0, 148.1, 149.1, 155.0, 155.3, and 156.1; Anal. Calcd for $C_{60}H_{59}N_5{\cdot}H_2O$: C, 83.01; H, 7.08; N, 8.07. Found: C, 82.69; H, 7.02; N, 7.62.

Tetraethyl 3,8,13,18-Tetramesitylporphyrin-2,7,12,17-tetracarboxylate (**14**)

The title compound was obtained in 17% yield from the reaction of **2a** and excess $BF_3 \cdot Et_2O$ (1×10^{-2} M) and DDQ instead of chloranil: purple crystals; mp >250 ˚C; UV-VIS (CH_2Cl_2) λ_{max} ($\log_{10}$ ε) 432 (5.48), 523 (4.32), 559 (3.80), 596 (3.85), and 652 (3.49) nm; IR 3444, 3307, 2977, 1718, 1226, and 1184 cm^{-1}; FAB/MS 1071 (M^++1); ^{1}H NMR ($CDCl_3$) δ -2.74 (br s, 2H), 1.22 (t, 12H, *J* = 7.3), 2.11 (s, 24H), 2.55 (s, 12H), 4.5 (q, 8H, *J* = 7.3), 7.26 (s, 8H), and 10.69 (s, 4H); ^{13}C NMR ($CDCl_3$, typical signals) δ 13.6, 21.3, 21.4, 61.3, 104.5, 128.2, 132.7, 137.3, 137.5, 137.3, 137.9, 139.6, and 164.6; Anal. Calcd for $C_{68}H_{70}N_4O_8 \cdot H_2O$: C, 74.98; H, 6.66; N, 5.14. Found: C, 75.06; H, 6.65; N, 5.23.

2-Hydroxymethyl-3,8,13,18-tetramesityl-7,12,17-trimethylporphyrin (**9**)

To a stirred solution of **5a** (0.29 g, 0.3 mmol) in CH_2Cl_2 (5 mL) was added slowly DIBALH (0.58 mL, 0.9 mmol) with cooling to 0 ˚C. After 4 h, 1 M HCl (5 mL) and $CHCl_3$ (10 mL) were added. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (2 x 10 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (20 mL), water (2 x 30 mL), and brine (30 mL), dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (5% $CHCl_3$/hexane) to give crude **9**. Recrystallization from $CHCl_3$ and hexane afforded 0.24 g (95%) of **9**: purple crystals; mp >250 ˚C; UV-VIS (CH_2Cl_2) λ_{max} ($\log_{10}$ ε) 405 (5.37), 502 (4.20), 537 (4.08), 569 (3.89), and 623 (3.64) nm; IR 3552, 3309, 2913, and 1606 cm^{-1}; FAB/MS 855 (M^++1); ^{1}H NMR ($CDCl_3$) δ -3.35 (br s, 2H), 2.00 (t, 1H, *J* = 5.5), 2.12 (s, 12H), 2.16 (s, 12H), 2.59 (s, 12H), 3.23 (s, 3H), 3.27 (s, 6H), 5.72 (d, 2H, *J* = 5.5), 7.29 (s, 8H), 9.67 (s, 1H), 9.7 (s, 1H), 9.73 (s, 1H), and 9.86 (s, 1H); ^{13}C NMR ($CDCl_3$, typical signals) δ 12.1, 12.2, 21.2, 21.3, 21.5, 57.8, 98.3, 98.4, 99.1, 128.4, 128.5, 131.4, 131.5, 132.1, 136.2, 136.5, 137.5, 137.8, 137.9, 138.5, 138.6, 139.3, 140.1, 140.6, 142.4, and 143.5; Anal. Calcd for $C_{66}H_{62}N_4O$: C, 84.27; H, 7.31; N, 6.46. Found: C, 83.98; H, 7.28; N, 6.46.

2,7,12,17-Tetra(hydroxymethyl)-3,8,13,18-tetramesitylporphyrin (**16**)

The title compound was obtained in 47% yield from **14** and DIBALH: purple crystals; mp >250 ˚C; UV-VIS λ_{max} ($\log_{10}$ ε) 409 (5.69), 503 (4.21), 537 (3.97), 573 (3.85), and 627 (3.57) nm; IR 3419, 3309,

2917, and 1610 cm^{-1}; FAB/MS 903 (M^++1); ^1H NMR ($CDCl_3$) δ -3.41 (br s, 2H), 2.13 (s, 24H), 3.37 (s, 12H), 5.42 (d, 8H, *J* = 4.6), 5.69 (m, 4H), 5.69 (s, 8H), and 10.10 (s, 4H); ^{13}C NMR ($CDCl_3$, typical signals) δ 21.1, 21.2, 55.7, 100.4, 128.3, 130.8, 137.3, 137.9, 140.4 and 141.5; Anal. Calcd for $C_{60}H_{62}N_4O_4 \cdot H_2O$: C, 78.23; H, 7.00; N, 6.20. Found: C, 78.64; H, 6.78; N, 6.12.

3,8,13,18-Tetramesityl-7,12,17-trimethylporphyrin-2-carbaldehyde (**11**)

Method A: To a stirred solution of **9** (0.2 g, 0.23 mmol) in CH_2Cl_2 (30 mL) was added activated MnO_2 (0.1 g). After 30 h, the reaction mixture was filtered through a Celite pad which was washed with $CHCl_3$ (3 x 30 mL). The filtrate and washings were concentrated. The residue was chromatographed on silca gel ($CHCl_3$) to give crude **11**. Recrystallization from $CHCl_3$ and MeOH afforded 0.16 g (79%) of **11**.

Method B: To a stirred solution of **5b** (0.38 g, 0.045 mmol) in CH_2Cl_2 (4 mL) was added slowly DIBALH (0.18 mL, 0.75 mmol) with cooling to 0 ˚C. After 4 h, 1 M HCl (0.5 mL) and $CHCl_3$ (5 mL) were added. The mixture was filtered through a Celite pad which was washed with $CHCl_3$ (2 x 10 mL). The filtrate and washings were concentrated. The residue was chromatographed on silca gel (5% $CHCl_3$/hexane). Monoformylporphyrin (**11**) was obtained from the second fraction and the starting porphyrin (**5b**) was obtained from the first fraction. Rrecrystalization fom $CHCl_3$ and MeOH afforded 20 mg (40%) of **11** and 8 mg (20%) of **5b**.

11: purple crystals; mp >250 ˚C; UV-VIS (CH_2Cl_2) λ_{max} ($\log_{10}$ ε) 420 (5.33), 519 (4.01), 560 (4.34), 582 (4.12), and 639 (3.40) nm; IR 3315, 2915, and 1675 cm^{-1}; FAB/MS 853 (M^++1); ^1H NMR ($CDCl_3$) δ -3.01 (br s, 2H), 2.12 (s, 12H), 2.18 (s, 12H), 2.58 and 2.59 (s and s, 12H), 3.17 (s, 3H), 3.28 (s, 3H), 3.30 (s, 3H), 7.28 and 7.30 (s and s, 8H), 9.58 (s, 1H), 9.62 (s, 1H), 9.81 (s, 1H), 10.66 (s, 1H), and 10.74 (s, 1H); ^{13}C NMR ($CDCl_3$, typical signals) δ 12.0, 12.1, 12.3, 21.1, 21.3, 21.5, 21.7, 98.0, 98.3, 100.7, 103.6, 130.2, 130.5, 130.7, 132.1, 135.3, 135.5, 136.3, 137.5, 138.1, 138.3, 138.4, 138.4, 138.5, 138.6, 138.7, 140.8, 141.1, 144.4, and 189.9; Anal. Calcd for $C_{60}H_{60}N_4O$: C, 84.47; H, 7.09; N, 6.57. Found: C, 84.39; H, 7.09; N, 6.56.

Ethyl 4-(1,3-Dithiolan-2-yl)-3-methylpyrrole-2-carboxylate (**20**)

To a stirred solution of **19** (2.0 g, 11 mmol) in MeOH (15 mL) were added ethylenedithiol (1 mL, 12.1 mmol) and $BF_3 \cdot Et_2O$ (0.05 mL). After 1.5 h, water (50 mL) and $CHCl_3$ (50 mL) were added. The

organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (3 x 30 mL). The combined organic layer was washed with water (2 x 30 mL), saturated $NaHCO_3$ (50 mL), water (2 x 30 mL), and brine (50 mL), dried over Na_2SO_4, and concentrated. The residual solid was recrystallized from EtOAc and hexane to give 2.8 g (98%) of **20**: colorless crystals; mp 76-78 °C; IR 3276, 2979, 2921, and 1978 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (t, 3H, *J* = 7.2), 2.39 (s, 3H), 6.72 (m, 4H), 4.31 (q, 2H, *J* = 7.2), 5.65 (s, 1H), 7.07 (d, 1H, *J* = 3.4), and 8.98 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 10.5, 14.4, 39.3, 47.9, 60.0, 120.2, 120.9, 124.1, 125.6 and 161.6; EI/MS 257 (M^+, 84), 196 (100), and 150 (74); Anal. Calcd for $C_{11}H_{15}NO_2S_2$: C, 51.33: H, 5.87: N, 5.44. Found: C, 51.10; H, 5.90; N, 5.41.

2,7,12,17-Tetra(1,3-dithiolan-2-yl)-3,8,13,18-tetramethylporphyrinato Zinc(II) (**21**) To a stirred solution of **20** (0.3 g, 1.1 mmol) in THF (5 mL) was added carefully $LiAlH_4$ (0.1 g, 2.75 mmol) with cooling to 0˚C. After 3 h, water (1 mL) and $CHCl_3$ (5 mL) were added. The mixture was filtered through a Celite pad which was washed with $CHCl_3$ (3 x 10 mL). The filtrate and washings were dried over Na_2SO_4 and concentrated to give crude 2-(hydroxymethyl)pyrrole. To a stirred solution of the 2-(hydroxymethyl)pyrrole was added K10 (1.4 g). After 24 h, the reaction mixture was neutralized with Et_3N (0.5 mL), chloranil (0.15 g, 0.6 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (0.6 g, 2.7 mmol) and MeOH (5 mL) were added. After 18h, saturated $NaHCO_3$ (30 mL) was added. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (3 x10 mL). The combined organic layer was washed with saturated $NaHCO_3$ (3 x 30 mL), water (30 mL), and brine (30 mL), dried over Na_2SO_4, and concentrated. The residue was put on an alumina column. The column was eluted with $CHCl_3$ (50 mL) and the eluate was concentrated. The residue was chromatographed on silca gel (5% $CHCl_3$/hexane) to give crude **21**. Recrystallization from $CHCl_3$ and MeOH afforded 82.4 mg (28%) of **21**: green crystals; mp > 250 °C; FAB/MS 845 (M^++1); UV-VIS (CH_2Cl_2) λ_{max} ($\log_{10}$ ε) 416 (5.41), 543 (4.18), and 580 (4.20) nm; ^1H NMR ($CDCl_3$, signals for type I isomer) δ 3.76 (s, 12H), 3.85 (m, 8H), 4.11 (m, 8H), 7.59 (s, 4H), and 10.66 (s, 4H); Anal. Calcd for $C_{36}H_{36}N_4S_8Zn$: C, 51.07: H, 4.29: N, 6.62. Found: C, 50.88; H, 4.28; N, 6.58.

3,8,13,18-Tetramethyl-2,7,12,17-tetraformylporphyrinato Zinc(II) (**22**)

To a stirred solution of **21** (82.4 mg, 0.12 mmol) in THF (5 mL) was added NBS (0.26 g, 1.52 mmol) in a solution of THF (10 mL) and water (5 mL) with cooling to 0 ˚C. After 4 h, saturated $NaHSO_3$ (20

mL) and $CHCl_3$ (20 mL) were added. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (3 x 10 mL). The combined organic layer was washed with water (2 x 30 mL) and brine (50 mL), dried over Na_2SO_4, and concentrated. The residual solid was recrystallized from THF and MeOH to give 21.4 mg (32%) of **22**: green crystals; mp >250 °C; IR 3645, 2958, 2920, and 1664 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.93 (s, 12H), 9.13 (s, 4H), and 10.56 (s, 4H); FAB/MS 542 (M^+); Anal. Calcd for $C_{28}H_{20}N_4O_4Zn \cdot 3/4CHCl_3$: C, 50.26: H, 3.06: N, 7.99. Found: C, 50.96; H, 3.84; N, 7.44.

2-Ethoxycarbonyl-3,8,13,18-tetramesityl-7,12,17-trimethylporphyrinato Zinc(II) (**8**)

To a stirred solution of **5a** (0.06 g, 0.07 mmol) in CH_2Cl_2 (4 mL) and MeOH (1 mL) was added $Zn(OAc)_2 \cdot 2H_2O$ (0.26 g, 1.1 mmol). After 2 h, water (10 mL) and CH_2Cl_2 (10 mL) were added. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (3 x 5 mL). The combined organic layer was washed with water (2 x 30 mL) and brine (30 mL), dried over Na_2SO_4, and concentrated. The residual solid was recrystallized from $CHCl_3$ and MeOH to give 0.036 g (74%) of **8**: purple crystals; mp >250 °C; ^1H NMR ($CDCl_3$) δ 1.23 (t, 3H, J = 7.3), 2.11 (s, 6H), 2.17 (s, 6H), 2.17 (s, 12H), 2.57 (s, 3H), 2.58 (s, 3H), 2.60 (s, 6H), 3.24 (s, 6H), 3.26 (s, 3H), 4.50 (q, 2H, J = 7.3), 7.29 (s, 2H), 7.30 (s, 6H), 9.65 (s, 1H), 9.66 (s, 1H), 9.83 (s, 1H), and 10.63 (s, 1H); ^{13}C NMR ($CDCl_3$, typical signals) δ 12.2, 13.6, 21.3, 21.4, 21.5, 60.7, 98.6, 99.2, 101.8, 103.6, 128.0, 128.4, 128.6, 132.1, 132.18, 132.25, 132.9, 137.1, 137.4, 137.5, 138.0, 138.41, 138.44, 138.5, 139.0, 139.2, 141.8, 142.6, 143.8, 144.1, 146.0, 148.0, 148.4, 149.1, 149.4, 149.7, 150.4, 151.2 ,and 165.8; FAB/MS 959 (M^++1); Anal. Calcd for $C_{62}H_{62}N_4O_2Zn$: C, 77.52: H, 6.51: N, 5.83. Found: C, 77.34; H, 6.47; N, 5.75.

2-Hydroxymethyl-3,8,13,18-tetramesityl-7,12,17-trimethylporphyrinato Zinc(II) (**10**)

The title compound was obtained in 85% yield from the reaction of **9** and $Zn(OAc)_2 \cdot 2H_2O$: purple crystals; mp >250 °C; ^1H NMR ($CDCl_3$) δ 2.12 (t, 1H, J = 5.9), 2.16 (s, 24H), 2.59 (s, 12H), 3.27 (s, 9H), 5.77 (d, 2H, J = 5.9), 7.24 (s, 2H), 7.28 (s, 2H), 7.30 (s, 4H), 9.73 (s, 1H) 9.74 (s, 1H), 9.78 (s, 1H), and 9.88 (s, 1H); ^{13}C NMR ($CDCl_3$,typical signals) δ12.2, 21.29, 21.33, 21.45, 21.54, 57.8, 99.2, 99.4, 99.9, 100.1, 128.3, 128.4, 128.5, 131.8, 132.3, 132.4, 137.4, 137.8, 138.2, 138.4, 138.48, 138.54, 139.0, 141.9, 142.2, 142.4, 143.1, 146.1, 147.0, 147.6, 148.0, 148.1, 148.8, 149.5,

and 149.8; FAB/MS 959 (M^++1); Anal. Calcd for $C_{60}H_{60}N_4OZn$: C, 78.46: H, 6.58: N, 6.10. Found: C, 77.92; H, 6.38; N, 6.08.

2-Formyl-3,8,13,18-tetramesityl-7,12,17-trimethylporphyrinato Zinc(II) (**12**)

The title compound was obtained in 70% yield from the reaction of **11** and $Zn(OAc)_2 \cdot 2H_2O$: purple crystals; mp >250 °C; ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 24H), 2.59 (s, 12H), 3.215 (s, 6H), 3.221 (s, 3H), 7.29 (s, 8H), 9.58 (s, 1H) 9.60 (s, 1H), 9.82 (s, 1H) 10.58 (s, 1H), and 10.84 (s, 1H); ^{13}C NMR ($CDCl_3$,typical signals) δ12.6, 21.8, 21.9, 22.0, 22.2, 99.1, 99.9, 102.7, 104.5, 128.85, 128.91, 130.7, 132.2, 132.35, 132.44, 133.5, 138.0, 138.6, 138.7, 138.8, 138.9, 139.1, 139.8, 140.0, 142.4, 143.3, 143.9, 144.7, 145.8, 148.9, 149.5, 150.6, 151.3, 152.3, 152.6, and 19.24; FAB/MS 915 (M^++1); Anal. Calcd for $C_{60}H_{58}N_4OZn$: C, 78.63: H, 6.38: N, 6.11. Found: C, 78.30; H, 6.47; N, 6.01.

2-Cyano-3,8,13,18-tetramesityl-7,12,17-trimethylporphyrinato Zinc(II) (**13**)

The title compound was obtained in 84% yield from the reaction of **5b** and $Zn(OAc)_2 \cdot 2H_2O$: purple crystals; mp >250 °C; ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 6H), 2.15 (s, 12H), 2.21 (s, 6H), 2.57 (s, 3H), 2.59 (s, 9H), 3.23 (s, 6H), 3.26 (s, 3H), 7.25 (s, 4H), 7.27 (s, 4H), 9.63 (s, 1H) 9.66 (s, 1H), 9.82 (s, 1H), and 9.86 (s, 1H); ^{13}C NMR ($CDCl_3$, typical signals) δ12.2, 21.2, 21.3, 21.4, 21.5, 98.9, 99.6, 100.6, 102.3, 110.2, 117.3, 128.4, 128.6, 128.7, 129.9, 131.3, 131.7, 131.8, 137.7, 137.9, 138.1, 138.4, 138.138.6, 139.0, 139.7, 139.8, 142.3, 143.1, 143.2, 144.0, 145.9, 148.3, 148.6, 150.0, 150.2, 150.7, 151.1, and 152.1; FAB/MS 912 (M^+); Anal. Calcd for $C_{60}H_{57}N_5Zn \cdot 1/2H_2O$: C, 78.12: H, 6.34: N, 7.59. Found: C, 78.18; H, 6.39; N, 7.40.

2,7,12,17-Tetra(ethoxycarbonyl)-3,8,13,18-tetramesitylporphyrinato Zinc(II) (**15**)

The title compound was obtained in 41% yield from the reaction of **14** and $Zn(OAc)_2 \cdot 2H_2O$: purple crystals; mp >250 °C; ^{1}H NMR ($CDCl_3$) δ 1.22 (t, 12H, *J* =7.3), 2.11 (s, 24H), 2.54 (s, 12H), 4.5 (q, 8H, *J* = 7.3), 7.26 (s, 8H), and 10.73 (s, 4H); ^{13}C NMR ($CDCl_3$) δ13.6, 21.36, 21.43, 61.1, 76.5,

105.5, 128.2, 130.8, 132.0, 137.2, 137.7, 147.6, 147.7, 153.0, and 165.0; FAB/MS 1133 (M^++1); Anal. Calcd for $C_{68}H_{68}N_4O_8Zn \cdot 1/2CHCl_3$: C, 68.89: H, 5.78: N, 4.69. Found: C, 68.95; H, 5.99; N, 4.69.

2,7,12,17-Tetra(hydroxymethyl)-3,8,13,18-tetramesitylporphyrinato Zinc(II) (**17**)

The title compound was obtained in 71% yield from the reaction of **16** and $Zn(OAc)_2 \cdot 2H_2O$: purple crystals; mp >250 °C; ^{1}H NMR ($CDCl_3$) δ 2.04 (t, 4H, *J* = 5.4), 2.17 (s, 24H), 2.59 (s, 12H), 5.77 (d, 8H, *J* = 5.4), 7.30 (s, 8H), and 9.97 (s, 4H); ^{13}C NMR ($CDCl_3$, typical signals) δ21.5, 57.7, 128.7, 138.1, 138.3, and 147.4; FAB/MS 964 (M^+); Anal. Calcd for $C_{60}H_{60}N_4O_4Zn \cdot 2H_2O$: C, 71.88: H, 6.43: N, 5.59. Found: C, 71.58; H, 6.19; N, 5.50.

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