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Synthesis and Atropisomerism of *meso*-Tetraarylporphyrins with Mixed *meso*-Aryl Groups Having *ortho*-Substituents.

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Abstract: *meso*-Tetraarylporphyrins having two kinds of *ortho*-substituted *meso*-aryl groups alternately at 5-, 10-, 15-, and 20-positions have been prepared by way of the modified MacDonald [2+2]-type condensation of α,α'-free aryldipyrrylmethanes with aryl aldehydes. 5,15-Di(2-acetylaminophenyl)-10,20-di-1-(2-methoxynaphthyl)porphyrin was prepared by way of two different combinations of aryldipyrrylmethanes and aryl aldehydes. The five atropisomers (αα'ββ', αα'βα', αβ'αβ', αα'αβ', αα'αα') expected for these porphyrins were separated and characterized on the basis of the ^{1}H NMR spectra and thermal isomerization behavior.

INTRODUCTION

meso-Tetraarylporphyrins with *ortho*-substituted *meso*-aryl groups have recently been utilized as building bases for modeling hemoprotein active sites and developing biomimetic catalysts, taking advantage of the ability of the *ortho* functionality to link substructures over the porphyrin plane.[1] 2-Aminophenyl and 2-hydroxyphenyl groups have frequently been used for this purpose in *meso*-tetraarylporphyrins and 5,15-diarylporphyrins.[1a,2] Since the latter has two atropisomers and the former has four atropisomers, a variety of structurally different porphyrins are available. While the four *meso*-aryl groups in these porphyrins are identical, porphyrins with mixed *meso*-aryl groups are of interest from the viewpoint of the molecular recognition, especially if the *meso*-aryl groups with different *ortho*-substituents are used. *meso*-Tetraarylporphyrins with two different aryl groups attached alternately at the 5-, 10-, 15-, and 20-positions have originally been prepared through the statistical pyrrole condensation with two different aryl aldehydes followed by the chromatographic separation of the resulting six component mixture.[3] The sequential condensation of pyrroles with the first aldehyde and then the resulting dipyrrylmethanes with the second aldehyde has recently been demonstrated to provide more elegant pathway to these C_2 symmetric porphyrins, particularly to 5,15-diarylporphyrins.[2a,2b,4] This synthetic methodology has very recently been applied to *meso*-tetraarylporphyrins, while some C_2-symmetric porphyrins have also been synthesized by modified MacDonald [2+2] condensations.[5]

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If two *ortho*-substituted aryl aldehydes (for example, *o*-nitrobenzaldehyde and 2-methoxy-1-naphthaldehyde) are used in this sequential condensation procedure, five atropisomers ($\alpha\alpha'\beta\beta'$, $\alpha\alpha'\beta\alpha'$, $\alpha\beta'\alpha\beta'$, $\alpha\alpha'\alpha\beta'$, $\alpha\alpha'\alpha\alpha'$)[6] arising from the restriction of rotation of the *meso*-aryl groups should occur for the resulting 5,15-di(2-nitrophenyl)-10,20-di-1-(2-methoxynaphthyl)porphyrin. Although the atropisomerism in *meso*-tetraarylporphyrins has been well known,[7] there has been no reports on the atropisomerism of *meso*-tetraarylporphyrins with mixed *meso*-aryl groups. The C_i symmetric atropisomer ($\alpha\alpha'\beta\beta'$) is of special interest because two sides of the porphyrin plane have opposite chirality and thus diastereomeric interaction is expected toward optically active substrates depending on which side of the porphyrin plane interacts with the substrates. This molecular recognition is relevant to the design of new biomimetic catalysts.[1f]

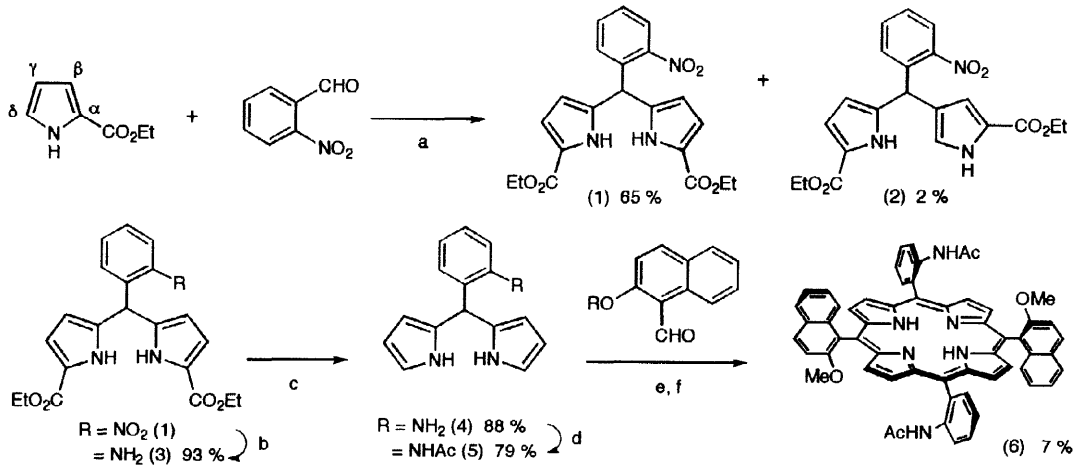
We have shown in the preliminary communication[8] that α,α'-free aryldipyrrylmethanes are better condensed with aryl aldehydes under the modified Adler-Longo conditions[9] rather than the Lindsey conditions[10] and that the resulting porphyrin is a mixture of the expected five atropisomers. In this paper is described the details of synthesis, characterization, and isomerization behavior of the mixed *meso*-tetraarylporphyrins.

RESULTS AND DISCUSSION

Multi-step synthesis:

meso-Tetraarylporphyrins with mixed *meso*-aryl groups can be prepared by the condensation of one aryl aldehyde and an α,α'-free aryldipyrrylmethane which may be synthesized by the condensation of pyrrole with another aryl aldehyde. The α,α'-free dipyrrylmethanes are more reactive towards electrophilic reagents than their parent pyrroles because of the electron-donating effect of the central methine or methylene carbon. Therefore, it is not easy to obtain dipyrrylmethanes in good yields by the condensation of pyrrole and aldehyde unless one of the two α-positions of pyrrole is protected. In this context, 5,5'-dicarboethoxy-2,2'-dipyrrylmethanes have frequently been synthesized and then the carboethoxy groups have been removed by hydrolysis and decarboxylation.[11] As a 5-carboethoxy substituent deactivates the pyrrole nucleus in the electrophilic substitution reaction, the additional 3,4-dialkyl substituents as the electron-donating groups on the pyrrole ring have been regarded necessary for this strategy. Thus, the condensation reaction between ethyl pyrrole-2-carboxylate and aryl aldehydes has never been examined in detail.

When *o*-nitrobenzaldehyde and ethyl pyrrole-2-carboxylate were allowed to react in CH_2Cl_2 in the presence of $TiCl_4$ at room temperature, a mixture of 2-nitrophenyl-5,5'-dicarboethoxy-2,2'-dipyrrylmethane (**1**) and 2-nitrophenyl-5,5'-dicarboethoxy-2,3'-dipyrrylmethane (**2**) were formed in a ratio of 5 : 2 as judged from the NMR analysis of the product mixture (see Scheme 1). The compound **1** was obtained in a 65 % yield through the repeated recrystallizations of the product mixture from ethanol. The compound **2** could be isolated by careful chromatographic separation. Three signals (6.86, 6.68, 5.88 ppm) with a 1 : 2 : 1 ratio are observed for the pyrrole ring protons of **2** in contrast to two signals (6.73 and 5.84 ppm) with a 1 : 1 ratio for those of **1**. The ring protons of ethyl pyrrole-2-carboxylate at the β- and δ-positions with respect to the carbonyl group resonate at lower magnetic fields (6.8 ppm) than that at the γ-position (6.1 ppm). Thus, the only one 1H-signal at 5.88 ppm of the compound **2** is in the chemical shift range assignable to the γ-position. This is consistent with the 5,5'-dicarboethoxy-2,3'-dipyrrylmethane structure for **2**. Although pyrroles undergo an electrophilic attack generally on the α(or δ)-position, ethyl pyrrole-2-carboxylate reacted both on the δ-pyrrole position and the γ-pyrrole position. This reactivity of ethyl pyrrole-2-carboxylate has also been noted in the Vilsmeier formylation.[5b]



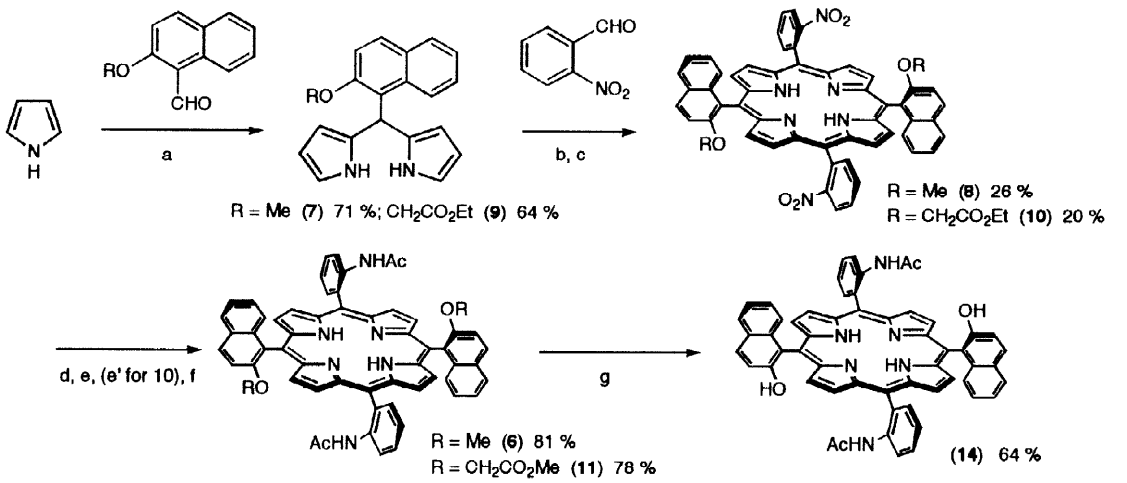
Reagents: a) $TiCl_4$, CH_2Cl_2, 0 °C, 22 hr; b) H_2, 10 % Pd-C, THF, r.t., 10 hr; c) NaOH, $(CH_2OH)_2$, reflux, 2 hr; d) Ac_2O, Et_3N, 0 °C, 2 hr; e) $EtCO_2H$, $Zn(OAc)_2$, reflux, 5 hr; f) aq. HCl, 30 min.

Scheme 1. Multi-step synthesis of mixed *meso*-tetraarylporphyrin (**6**).

As shown in Scheme 1, the dipyrrylmethane **1** was then converted into 2-aminophenyl-2,2'-dipyrrylmethane (**4**) through the reduction of the nitro group to the amino group (93 % yield for (**3**))[12,13] followed by hydrolysis and decarboxylation (88 % yield) according to the standard procedure.[11] After the amino group was protected (79 % yield), 2-acetylaminophenyl-2,2'-dipyrrylmethane (**5**) was allowed to react with 2-methoxy-1-naphthaldehyde in the presence of an acid catalyst. When the condensation was done in dry CH_2Cl_2 in the presence of BF_3•OEt_2 according to the method of Lindsey,[5d] an intractable mixture of porphyrins including tetra-1-(2-methoxynaphthyl)porphyrin were obtained in a 10 % total yield after the treatment with p-chloranil. This indicates that the dipyrrylmethane **5** was hydrolyzed into pyrrole and 2-acetylaminobenzaldehyde under the acidic reaction conditions and then pyrrole was randomly condensed with the two kinds of aryl aldehydes. In contrast, the dipyrrylmethane **5** was not decomposed in a refluxing propionic acid in the presence of $Zn(OAc)_2$•$2H_2O$, under which conditions the [2+2] condensation with 2-methoxy-1-naphthaldehyde took place to give 5,15-di(2-acetylaminophenyl)-10,20-di-1-(2-methoxynaphthyl)porphyrin(**6**) as a mixture of five atropisomers in a 7 % yield after chromatographic purification on silica gel.

Two-step synthesis:

Ethyl pyrrole-2-carboxylate is deactivated towards electrophilic reagents in comparison with the parent pyrrole so that it could not be successfully used for condensation with non-activated aryl aldehydes. In fact, ethyl pyrrole-2-carboxylate did not react with 2-methoxy-1-naphthaldehyde under the standard reaction conditions as noted above. Further limitation comes from the drastic reaction conditions required for the removal of the α-carboethoxy groups of the dipyrrylmethanes which have a functionality on the *meso*-aryl moiety. In fact, it was necessary to reduce the nitro groups of **1** before the decarboxylation step in the synthesis of Scheme 1. Since the unsubstituted pyrrole is reactive enough to undergo electrophilic substitution with a non-activated aryl aldehyde, it is possible to reserve an activated aldehyde (*o*-nitrobenzaldehyde) for the condensation with aryldipyrrylmethanes to give porphyrins with mixed *meso*-aryl groups as shown in Scheme 2. Thus, the condensation of pyrrole with 2-methoxy-1-naphthaldehyde was examined under various conditions as summarized in Table 1. Whereas the



Reagents: a) $TiCl_4$, CH_2Cl_2, 0 °C, 22 h; b) $EtCO_2H$, $Zn(OAc)_2$, 0°C (2 h) ~ reflux; c) aq. HCl, 30 min; d) $SnCl_2$, HCl, 15 h; e) NH_3; e') H_2SO_4, MeOH, 45 °C, 7 h, then Na_2CO_3 ; f) Ac_2O; g) BBr_3, EtSH.

Scheme 2. Two-step synthesis of mixed meso-tetraarylporphyrins.

use of p-toluenesulfonic acid in methanol resulted in the formation of a mixture of oligomeric products, acid catalysis by 2 mol % $TiCl_4$ in CH_2Cl_2 was found to give a good yield (71 %) of 1-(2-methoxynaphthyl)-2,2'-dipyrrylmethane (**7**) at room temperature in 10 min, if 100-fold molar excess of pyrrole was used in order to suppress oligomerization. Because the most part of excess pyrrole can be recovered by distillation in the work-up process, this reaction is practically applied to a large scale synthesis. A similar procedure has already been reported in the literature.[5] The dipyrrylmethane **7** is relatively stable at room temperature in comparison with **4** and **5** so that it can be stored for months in a refrigerator.

Table 1. Synthesis of 1-(2-Methoxynaphthyl)-2,2'-dipyrrylmethane(**7**).

pyrrole (mM)	2-methoxy-1-naphth-aldehyde (mM)	catalyst (mM)	solvent	temp.	time (min)	yield of (**7**)[a] (%)
230	11	p-TsOH (11)	MeOH	r.t.	5	0
230	11	p-TsOH (1)	MeOH	r.t.	120	0
630	30	$TiCl_4$ (3)	CH_2Cl_2	-20 °C	30	36
1260	30	$TiCl_4$ (0.6)	CH_2Cl_2	r.t.	10	49
2960	30	$TiCl_4$ (0.6)	CH_2Cl_2	r.t.	10	71
5920	30	$TiCl_4$ (0.6)	CH_2Cl_2	r.t.	10	73

[a] based on 2-methoxy-1-naphthaldehyde

When the dipyrrylmethane **7** was condensed with *o*-nitrobenzaldehyde in dry CH_2Cl_2 in the presence of a catalytic amount of BF_3•OEt_2, an intractable mixture of porphyrins with random *meso*-aryl substitution patterns were also obtained (Table 2, run 1). The total yield (24 ± 4 %) of porphyrins and the reaction conditions in this case are similar to those reported by Lindsey for the condensation of an aryl aldehyde and a dipyrrylmethane having a 2,6-disubstituted aryl group on the central carbon.[5d] However, Lindsey obtained a single porphyrin product without formation of porphyrins resulting from the acid-catalyzed redistribution of the dipyrrylmethane unit.[5d] It seems that the Lindsey's aryldipyrrylmethanes are kinetically stabilized against acid-catalyzed hydrolysis owing to the bulky aryl substituents. A milder acid catalyst than BF_3•OEt_2 promoted condensation

Table 2. Condensation of 1-(2-Methoxynaphthyl)-2,2'-dipyrrylmethane(**7**) with *o*-Nitrobenzaldehyde.[a]

run	method[b]	(**7**) (mM)	catalyst (mM)	solvent	temp / time (°C / hr)	yield of (**8**) (%)
1	A	6	BF_3•OEt_2 (0.6)	CH_2Cl_2	r.t. / 24	(28.4)[c]
2	A	6	TFA (6)	CH_2Cl_2	r.t. / 17	8.6
3	A	6	TFA (6)	$C_2H_4Cl_2$	83 / 20	12.3
4	A	40	none	$EtCO_2H$ - CH_2Cl_2	r.t. / 2.5	4.2
5	A	40	$Zn(OAc)_2$ (60)	$EtCO_2H$ - CH_2Cl_2	r.t. / 2.5	10.1
6	B	40	$Cu(OAc)_2$ (60)	$EtCO_2H$ - CH_2Cl_2	50 / 3.5 → 140 / 2	4.8
7	B	40	$Zn(OAc)_2$ (60)	$EtCO_2H$ - CH_2Cl_2	50 / 3.5 → 140 / 2	13.8
8	C	40	$Zn(OAc)_2$ (60)	$EtCO_2H$ - CH_2Cl_2	50 / 3.5 → 140 / 2	18.1
9	B	40	$Zn(OAc)_2$ (60)	$EtCO_2H$ - CH_2Cl_2	0 / 2 → r.t. / 15 → 140 / 2	21.0
10	C	40	$Zn(OAc)_2$ (60)	$EtCO_2H$ - CH_2Cl_2	0 / 2 → r.t. / 15 → 140 / 2	25.8

[a] The molar ratio of *o*-nitrobenzaldehyde and **7** is 1 : 1 in every run. The volume ratio of $EtCO_2H$ - CH_2Cl_2 is 3 : 1 in the runs 4 ~ 10. [b] A: the addition of the dipyrrylmethane **7** to *o*-nitrobenzaldehyde followed by the work-up with p-chloranil. B: the addition of the dipyrrylmethane **7** to *o*-nitrobenzaldehyde followed by the air-oxidation at 140 °C. C: the addition of *o*-nitrobenzaldehyde to the dipyrrylmethane **7** followed by the air-oxidation at 140 °C. [c] A total yield of a mixture of porphyrins with random *meso*-aryl substitution patterns in the run 1.

without hydrolyzing the dipyrrylmethane **7** to afford 5,15-di(2-nitrophenyl)-10,20-di-1-(2-methoxynaphthyl)-porphyrin (**8**) in up to a 12 % yield, if the initially formed porphyrinogen was oxidized to the porphyrin by using p-chloranil. Table 2 (run 2 - 5) shows that trifluoroacetic acid (TFA) is superior to propionic acid as an acid catalyst and that the addition of $Zn(OAc)_2$•$2H_2O$ improves the yield of the porphyrin **8** in the reactions at room temperature. On the other hand, the condensation at room temperature followed by the aerobic oxidation of the formed porphyrinogen in refluxing propionic acid resulted in the formation of the porphyrin **8** in much better yields (Table 2, run 7 - 10). The progress of the reaction was monitored by the UV-vis spectral change. The 495 nm band developed initially at room temperature gradually decreased with increasing the Soret band at 428 nm when the reaction mixture was heated to 140 °C for 2 hr.

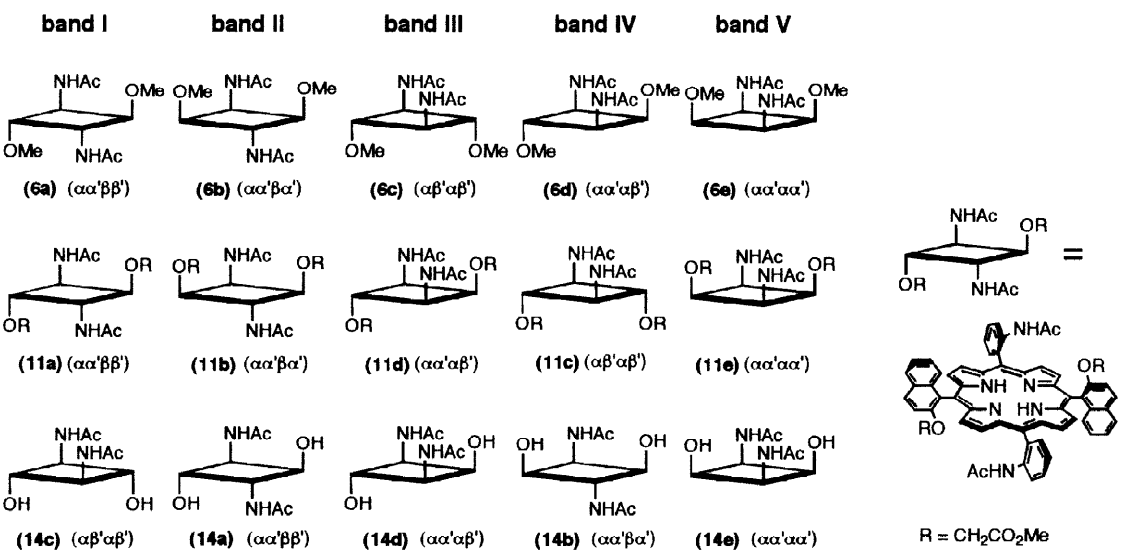
1-(2-Ethoxycarbonylmethoxynaphthyl)-2,2'-dipyrrylmethane (**9**) was similarly prepared in a 64 % yield and then condensed with *o*-nitrobenzaldehyde to afford 5,15-di(2-nitrophenyl)-10,20-di-1-(2-ethoxycarbonyl-methoxynaphthyl)porphyrin (**10**) in a 20 % yield. The porphyrin **10** was converted into 5,15-di(2-acetylamino-phenyl)-10,20-di-1-(2-methoxycarbonylmethoxynaphthyl)porphyrin (**11**) through the reduction with $SnCl_2$, reesterification of the hydrolyzed carboxyl groups with methanol, and acetylation with acetic anhydride in a 78 % overall yield. The conversion of the porphyrin **8** to the porphyrin **6** was done by a similar procedure in a 81 % overall yield.

Separation and characterization of atropisomers of the porphyrins with mixed *meso*-aryl groups:

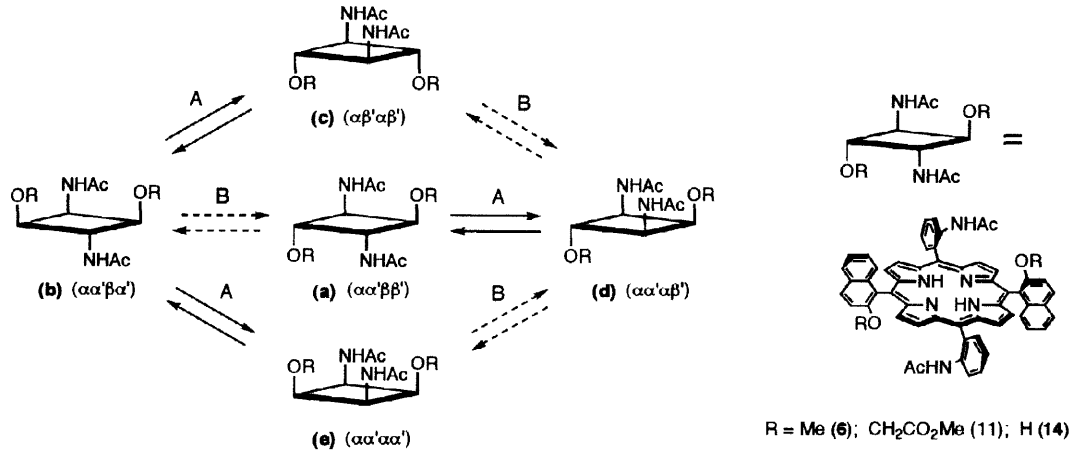
The chromatographic separation of the porphyrin **6** on silica gel using solvents with gradient from benzene to CH_2Cl_2 and finally to CH_2Cl_2 - acetone (10 : 1) afforded five fractions (**6a - 6e**) in the order of elution. The ^1H NMR spectra show that the two acetylaminophenyl groups are non-equivalent only in the second fraction **6b**, whereas the two methoxynaphthyl groups are non-equivalent only in the fourth fraction **6d**. That is, a pair of acetylamino NH signals are observed at 6.81 and 6.80 ppm and a pair of CH_3CO signals are at 1.25 and 1.24 ppm with a 1 : 1 ratio in the ^1H NMR spectrum of **6b**. A pair of methoxy signals are observed at 3.66 and 3.64

ppm with a 1 : 1 ratio and the 7- and 8-naphthyl protons appear as two pairs of signals (triplets at 7.04 and 6.99 ppm; doublets at 6.88 and 6.77 ppm) in the ^{1}H NMR spectrum of **6d**. Therefore, **6b** and **6d** are unambiguously associated to the αα'βα' and the αα'αβ' isomer, respectively, as depicted in Scheme 3. Two 2-methoxynaphthyl groups are anti in the latter and syn in the former. Although the remaining fractions, **6a**, **6c**, and **6e**, could not be differentiated on the basis of the spectral patterns in their ^{1}H NMR spectra, they were characterized on the basis of the thermal interconversion behaviors. It is known that an αααα isomer of tetra(2-pivaloylaminophenyl)porphyrin (**12**) isomerizes to other atropisomers under reflux in *m*-xylene for 45 min while an αααα isomer of tetra-1-(2-hydroxynaphthyl)porphyrin (**13**) is totally unaffected under reflux in toluene for 2 hr.[2c,7a] Therefore, the rotational barrier of the 2-methoxynaphthyl groups at the 10- and 20-*meso*-positions of **6** is expected to be much larger than that of the 2-acetylaminophenyl groups at the 5- and 15-*meso*-positions of **6**. HPLC analysis (SiO_2 / $CHCl_3$) of *m*-xylene solutions of **6b** (αα'βα') and **6d** (αα'αβ') after reflux for 1 hr showed that **6b** was isomerized to both **6c** and **6e** whereas **6d** was isomerized only to **6a**. The interconversion between the two groups, (**6b**, **6c**, **6e**) and (**6a**, **6d**), has never been observed under the above reaction conditions. This means that the rotation of the 2-methoxynaphthyl group (process B in Scheme 4) does not take place under the above conditions and that the latter two isomers have an anti 2-methoxynaphthyl arrangement whereas the former three isomers have a syn arrangement. The observed isomer ratio after equilibration based on the HPLC peak areas was 3.4 for (**6b** + **6c**) / **6e** whereas 1.0 for **6a** / **6d**. These ratios are in good accordance with the theoretical ratios (1 : 1 for **6a** / **6d**, 2 : 1 : 1 for **6b** / **6c** / **6e**), assuming that the rate of rotation of an 2-acetylaminophenyl group is independent of the arrangement of the other three *meso*-aryl substituents in an atropisomer. Thus, the fraction **6a** is assigned to a C_i-symmetric isomer (αα'ββ'), while both **6c** and **6e** are C_2-symmetric isomers (αβ'αβ' and αα'αα'). The last fraction **6e** on silica gel HPLC is considered to have all the polar substituents directed to one side of the porphyrin plane (αα'αα'), taking into account a number of reports on the separation of atropisomers of *meso*-tetraarylporphyrins including **12** and **13**.[7] Thus, the remaining fraction **6c** must possess an αβ'αβ' arrangement. The isomer distribution (**6a** / (**6b** + **6c**) / **6d** / **6e** = 0.84 : 2.1 : 1.5 : 2.5) just after the [2+2] condensation reaction was determined on the basis of the HPLC analysis.

The five atropisomers (the bands I ~ V) of **11** were also separated by column chromatography on silica gel



Scheme 3. Relative polarity of 5 atropisomers of mixed *meso*-tetraarylporphyrins (**6**), (**11**), and (**14**).



Scheme 4. Atropisomerization by the rotation of the 2-acetylaminophenyl group (process A) and the 2-alkoxy- or 2-hydroxynaphthyl group (process B) in the porphyrins (**6**), (**11**), and (**14**).

using eluents with gradient from CH_2Cl_2 finally to CH_2Cl_2 - ethyl acetate (1 : 3). The five fractions (**11a, 11b, 11d, 11c, 11e**) were obtained in the order of elution. These atropisomers were unambiguously characterized on the basis of the splitting patterns of the ^1H NMR signals due to the acetylamino group and the methoxycarbonylmethoxy group. The two acetylamino groups are non-equivalent only in the second fraction, whereas the two methoxycarbonylmethoxy groups are non-equivalent only in the third fraction. That is, a pair of the acetylamino NH singlets are observed at 6.78 and 6.87 ppm with a 1 : 1 ratio and a pair of the CH_3CO singlets are at 1.25 and 1.27 ppm in the ^1H NMR spectrum of the second fraction. A pair of the OCH_2 singlet are observed at 4.43 and 4.45 ppm with a 1 : 1 ratio and a pair of the OCH_3 singlets appear at 3.51 and 3.54 ppm in the ^1H NMR spectrum of the third fraction. Therefore, the second and the third fractions are associated to **11b** (αα'βα') and **11d** (αα'αβ'), respectively. The OCH_2 protons at the 2-naphthyl position appear as AB doublets or singlet(s) depending on whether the two acetylaminophenyl groups are in an anti or syn arrangement. The first and the second fractions show AB doublets at 4.43 and 4.45 ppm and at 4.42 and 4.44 ppm, respectively, while the fourth and the fifth fractions show singlets at 4.42 and 4.46 ppm, respectively. Therefore, the first fraction is assigned to **11a** (αα'ββ'). Although the fourth and the fifth fractions could not be differentiated on the basis of the splitting patterns in their ^1H NMR spectra, the much more polar nature of the fifth fraction than the fourth fraction ensures that the fifth fraction is the αα'αα' atropisomer **11e**.[7] Thus, the fourth fraction is associated to **11c** (αβ'αβ'). When the third fraction was heated under reflux in *m*-xylene for 4 hr, it was isomerized only to the first fraction. This means that the first and the third fractions are the atropisomers with an anti arrangement of the 1-(2-methoxycarbonylmethoxy)naphthyl groups, because only the 2-acetylaminophenyl group rotates under these conditions. When the fourth fraction was heated under reflux in *m*-xylene for 4 hr, it was mainly isomerized to the second and the fifth fraction. Therefore, the second, the fourth and the fifth fractions are the atropisomers with a syn arrangement of the 1-(2-methoxycarbonylmethoxy)naphthyl groups. These isomerization behavior is consistent with the NMR spectroscopic characterization of the atropisomers discussed above.

In order to give a further insight into the structure and polarity relationship in the atropisomers of the porphyrins with mixed *meso*-aryl groups, the methoxy groups of the porphyrin **6** were converted into the hydroxy groups by using BBr_3. Whereas similar demethylation reactions with BBr_3 are known to proceed quantitatively in the case of *meso*-tetraarylporphyrins with 2-methoxyphenyl and 2-methoxynaphthyl groups,

[2c,4g,4h] the presence of the acetylamino groups in the porphyrin **6** required a greater amount of BBr_3 and resulted in a low yield of 5,15-di(2-acetylaminophenyl)-10,20-di-1-(2-hydroxynaphthyl)porphyrin (**14**) under the reaction conditions using large excess amount of BBr_3 (56-fold molar) initially at -78 °C and then at room temperature. When a mixture of five atropisomers of **6** were treated with BBr_3 (17-fold molar) and ethanethiol (53-fold molar), the five atropisomers of **14** (the bands I ~ V) could be isolated in 9, 15, 22, 12, and 11 % yield in the order of decreasing R_f values on a silica gel TLC plate. Since three slowly running atropisomers (the bands III ~ V) on silica gel chromatography of **14** were converted exclusively back to the original atropisomers, **6d**, **6b**, and **6e**, by the treatment with methyl iodide in acetone containing K_2CO_3, they were unambiguosly identified as **14d**, **14b**, and **14e**, respectively. The band I and II atropisomers of **14**, however, decomposed in an attempted methylation reaction going back to the original atropisomers of **6**. When the band I atropisomer of **14** was heated in a refluxing DMF solution for 2 hr, it was isomerized to all the atropisomers (the ratio of band I / II / III(**14d**) / IV(**14b**) / V(**14e**) = 25 : 6 : 5 : 48 : 14). The preferential isomerization from the band I atropisomer to the band IV atropisomer (**14b**) suggests that the band I atropisomer has the same arrangement (syn) of 1-(2-hydroxynaphthyl) groups as **14b**. Furthermore, the identity of the band I and II atropisomers was confirmed on the basis of the fact that 5,15-syn-di-1-(2-hydroxynaphthyl)-2,3,7,8,12,13,17,18-octaethylporphyrin has a greater binding constant with anthraquinone than the corresponding 5,15-anti isomer.[2d] The observed binding constants (K_a) of the band I and II atropisomers with anthraquinone in CH_2Cl_2 are 64 M^{-1} and 1.9 M^{-1}, respectively. These values parallel the reported values for the syn and anti isomers of 5,15-di-1-(2-hydroxynaphthyl)octaethylporphyrin (220 M^{-1} vs. 5.9 M^{-1}). Therefore, the band I atropisomer is a C_2-symmetric isomer **14c** in which two *meso*-1-(2-hydroxy)naphthyl groups are syn and the band II atropisomer is a C_i-symmetric isomer **14a** in which two *meso*-1-(2-hydroxy)naphthyl groups are anti. The two 1-(2-hydroxy)naphthyl groups and also the two 2-acetylaminophenyl groups are equivalent in the ^1H NMR spectra of **14c**, **14a**, and **14e**. The atropisomer **14d** showed a pair of doublets due to the 8-naphthyl protons at 6.70 and 6.80 ppm and a pair of triplets due to the 7-naphthyl protons at 6.81 and 6.96 ppm. This is consistent solely with the αα'αβ' conformation of **14d**. The isomer **14b** showed two pairs of doublets due to the 3-phenyl protons at 8.51 and 8.55 ppm and the acetyl protons at 1.21 and 1.23 ppm in accord with its αα'βα' conformation.

In general, a porphyrin atropisomer becomes polar as its polar substituents are converged to one side of a porphyrin plane. This tendency is reported for a number of porphyrins with *meso*-tetraaryl groups.[7] For example, the order of polarity of four atropisomers of *meso*-tetra(2-aminophenyl)porphyrin is αβαβ < ααββ < ααβα < αααα,[7a] assuming that the relative polarity of atropisomers as free base forms is directly related to the order of elution from normal phase silica gel chromatography. Since an acetylamino group is a much more polar substituent than a methoxy group, the atropisomers with an anti arrangement of the 2-acetylaminophenyl groups (**6a** and **6b**) run faster than the atropisomers with a syn arrangement of the 2-acetylaminophenyl groups (**6c**, **6d**, and **6e**) in the normal phase chromatography on silica gel. The arrangement of the 2-methoxy-1-naphthyl groups makes a secondary effect on the polarity of atropisomers. Thus, the atropisomer with an anti arrangement of the 2-methoxy-1-naphthyl groups **6a** (or **6d**) runs faster than the corresponding atropisomer with a syn arrangement of the 2-methoxy-1-naphthyl groups **6b** (or **6e**). The atropisomer **6c** is less polar than **6d** and **6e** since the difference in the polarity between the two sides of the porphyrin plane is smaller in **6c** than in **6d** and **6e**. Since an acetylamino group is a more polar substituent than a methoxycarbonylmethoxy group, the order of the polarity of five atropisomers in the porphyrin **11** (**11a** < **11b** < **11d** < **11c** < **11e**) is the same as that in the porphyrin **6** (**6a** < **6b** < **6c** < **6d** < **6e**) except that **11c** follows **11d**. On the other hands, the order of the polarity of the five

Table 3. Thermal Isomerization between Five Atropisomers of (**14**).

starting isomer	solvent	temp / time (°C / hr)	isomer distribution (%)[a] (**14c**)	(**14a**)	(**14d**)	(**14b**)	(**14e**)
(**14c**)	*m*-xylene	140 / 24	0	44	16	37	0
(**14a**)	*m*-xylene	140 / 24	0	90	2	4	0
(**14d**)	*m*-xylene	140 / 24	0	78	16	5	1
(**14b**)	*m*-xylene	140 / 24	0	1	0	97	1
(**14e**)	*m*-xylene	140 / 24	0	9	1	84	1
(**14c**)	DMF	153 / 2	25	6	5	48	14
(**14b**)	DMF	153 / 8	17	11	10	36	22

[a] based on the HPLC peak areas (column: 6 x 150 mm ODS (Cosmosil 5C18-AR); eluent: MeOH-H_2O (5 : 1); flow rate: 1.0 mL/min; detection: UV at 400 nm).

atropisomers of **14** (**14c** < **14a** < **14d** < **14b** < **14e**) is consistent with the fact that a hydroxy group is more polar than an acetylamino group, if **14c** is not taken into account. The fact that **14c** is the least polar atropisomer suggests that a hydroxy group seems to be only slightly more polar than an acetylamino group.

When a single atropisomer **14b** was heated at reflux in a DMF solution, **14b** was isomerized to all the atropisomers. The observed isomer distribution between the five atropisomers (**14c** / **14a** / **14d** / **14b** / **14e** = 17 / 11 / 10 / 36 / 22) after 8 hr is explained in terms of a fast rotation of 2-acetylaminophenyl groups (process A in Scheme 4) because the ratio of **14c**, **14b**, and **14e** is close to a theoretical ratio (1 : 2 : 1) for the atropisomers with a syn arrangement of the 1-(2-hydroxy)naphthyl groups. The ratio of **14a** and **14d** is also close to a theoretical ratio (1 : 1) in the case of the free rotation of 2-acetylaminophenyl groups of the atropisomers with an anti arrangement of the 1-(2-hydroxy)naphthyl groups. However, the isomerization between these two groups is very slow because the rotation of 1-(2-hydroxy)naphthyl groups (process B in Scheme 4) is very slow under the conditions of DMF reflux. In contrast, the isomer distribution is governed by the solubility of each atropisomer when a single atropisomer of **14** is isomerized in a refluxing *m*-xylene solution for 24 hr. The atropisomers, **14a** and **14b**, were almost unchanged (90 and 97 % contents, respectively, after heating) and atropisomers, **14c**, **14d**, and **14e**, were predominantly isomerized to **14a** and **14b** as summarized in Table 3. The insoluble nature of **14a** and **14b** in *m*-xylene should be responsible for this convergent isomerization behavior. Since the structures of **14a** and **14b** are different from other three atropisomers in the sense that two 2-acetylaminophenyl groups are in an anti arrangement, it seems that 2-acetylaminophenyl groups may play a key role in the intermolecular hydrogen bondings which lead to insoluble high molecular-weight aggregates.

CONCLUSION

Aryldipyrrylmethanes were successfully used to the synthesis of *meso*-tetraarylporphyrins in which two differently *ortho*-substituted aryl groups are positioned alternately at the 5-, 10-, 15-, and 20-*meso* positions. The five atropisomers of the 5,15-di(2-acetylaminophenyl)-10,20-di-1-(2-substituted naphthyl)porphyrins, **6**, **11**, and **14**, were separated by chromatography and characterized on the basis of the ^1H NMR and thermal isomerization behaviors. The relative polarity of atropisomers of these porphyrins is governed by the relative strength of the polarity of the substituents at the 5- and 15-phenyl groups and at the 10- and 20-(1-naphthyl) groups. Two atropisomers ($\alpha\alpha'\beta\beta'$ and $\alpha\alpha'\beta\alpha'$) were obtained in greater abundance by the thermal isomerization of the five atropisomers of 5,15-di(2-acetylaminophenyl)-10,20-di-1-(2-hydroxynaphthyl)-porphyrin **14**.

Further study directed to the stereoselection using the derivatives of mixed *meso*-tetraarylporphyrins and their metal complexes is now going on.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were measured on a Bruker AC-250 (250 MHz for ^1H) spectrometer and the chemical shifts are referenced to tetramethylsilane as an internal standard. UV-vis spectra in CH_2Cl_2 solution were measured on a Shimadzu UV-2200. IR spectra were obtained in a KBr disk on a Hitachi I-2000. EI mass and FAB mass spectra were taken on Shimadzu GCMS-QP2000A and JEOL JMS-SX102. *m*-Nitrobenzyl alcohol was used as a matrix for FABMS measurement. HPLC analyses were performed on a Shim-pack PREP-SIL(H) or a Cosmosil 5C18-AR column. GC analyses were done on a Shimadzu GC-14A with a Silicon SE-30 column. Melting points are uncorrected. Wakogel C-300 (silica gel) and Merck aluminiumoxide 90 were used for column chromatography. Merck aluminiumoxide 60 F_{256} neutral, and Merck Kieselgel 60 F_{256} were used for TLC analyses. Dichloromethane was dried by distilling from calcium hydride and stored over molecular sieves 4A. Methanol, ethanol, and ether were dried and distilled before use.

2-Nitrophenyl-5,5'-dicarboethoxy-2,2'-dipyrrylmethane (1) and 2-nitrophenyl-5,5'-dicarboethoxy-2,3'-dipyrrylmethane (2). In a three-necked, round-bottomed flask equipped with a septum, a stopper, and a two way cock attached to an argon line, 5.8 g (42 mmol) of ethyl pyrrole-2-carboxylate, 3.0 g (20 mmol) of *o*-nitrobenzaldehyde, a small amount of molecular sieves 4A were placed under argon atmosphere. 300 mL of dry CH_2Cl_2 was added to this flask and the whole mixture was cooled at 0°C. Titanium tetrachloride (1 mL) was added through a septum and the mixture was stirred magnetically for 20 hr at 20°C. The reaction mixture was washed with saturated $NaHCO_3$ aqueous solution and then with water. After drying over anhydrous Na_2SO_4, the organic layer was condensed and the residue was purified by repeated recrystallizations from ethanol. The product, 2-nitrophenyl-5,5'-dicarboethoxy-2,2'-dipyrrylmethane (**1**), weighs 4.36 g (10.6 mmol; 53 % yield). M.p. 181~184°C. ^1H NMR (in $CDCl_3$) δ 1.31 (t, 6H, $OCCH_3$); 4.17 (q, 4H, OCH_2C); 5.84 (dd, 2H, pyrrole-β-H), 6.27 (s, 1H, methine); 6.73 (dd, 2H, pyrrole-β-H); 7.43, 7.53 (dtx2, 1Hx2, 4- and 5-phenyl-H); 7.62, 7.92 (ddx2, 1Hx2, 6- and 3-phenyl-H); 10.3 (bs, 2H, NH). IR 1680 (CO); 1532, 1352 cm^{-1} (NO_2). MS (m/e) 411 (M^+), 394, 348, 331, 302, 245. Elemental analysis calcd for $C_{21}H_{21}N_3O_6$: C, 61.31; H, 5.14; N, 10.21. Found: C 61.40; H, 5.26; N, 10.03.

The filtrate from the above recrystallization was evaporated and the residue was chromatographed repeatedly on silica gel. A yellow fraction eluated closely following (**1**) with benzene - acetone (40 :1) gave the isomer, 2-nitrophenyl-5,5'-dicarboethoxy-2,3'-dipyrrylmethane (**2**) as a yellow oil in a 2 % yield. ^1H NMR (in $CDCl_3$) δ 1.30 (t, 6H, $OCCH_3$); 4.25 (q, 4H, OCH_2C); 5.88 (t, 1H, pyrrole-β-H), 6.68 (mx2, 1Hx2, pyrrole-β-H); 6.86 (dd, 1H, pyrrole-β-H), 6.17 (s, 1H, methine); 7.2~8.0 (m, 4H); 9.6, 9.8 (bsx2, 1Hx2, NH). The chemical shifts, especially of NH proton, of (**1**) and (**2**) are dependent on the concentration. IR 1680 (CO); 1532, 1352 cm^{-1} (NO_2). MS (m/e) 411 (M^+), 394, 348, 331, 302, 245. Elemental analysis calcd for $C_{21}H_{21}N_3O_6$: C, 61.31; H, 5.14; N, 10.21. Found: C 61.48; H, 5.07; N, 10.33.

2-Aminophenyl-5,5'-dicarboethoxy-2,2'-dipyrrylmethane (3). According to the literature method for ordinary $TiCl_3$ reduction,[13] a mixture of 2-nitrophenyl-5,5'-dicarboethoxy-2,2'-dipyrrylmethane (**1**) (7.0 g, 17.0

mmol), acetic acid (100 mL), water (100 mL), THF (100 mL), and 20 % titanium(III) trichloride solution in hydrochloric acid (150 mL) was stirred for 1 hr at room temperature. Then, the mixture was treated with saturated aqueous sodium hydroxide, and extracted with ether until the aqueous layer becomes colorless. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and condensed under reduced pressure. The crude product was washed with a small amount of cold CH_2Cl_2 to give 5.2 g (13.6 mmol, 80 % yield). M.p. 159~160°C. ^1H NMR (in $CDCl_3$) δ 1.31 (t, 6H, $OCCH_3$); 3.6 (bs, 2H, NH_2); 4.26 (q, 4H, OCH_2C); 5.41 (s, 1H, methine); 6.00 (m, 2H, pyrrole-β-H); 6.83 (m, 2H, pyrrole-β-H); 6.74 (dd, 1H, 3-phenyl-H); 6.81 (dt, 1H, 5-phenyl-H); 6.98 (dd, 1H, 6-phenyl-H); 7.15 (dt, 1H, 4-phenyl-H); 9.5 (bs, 2H, NH). IR 1674 cm^{-1} (CO). MS (m/e) 381 (M^+), 352, 306, 260, 169. Elemental analysis calcd for $C_{21}H_{23}N_3O_4$: C, 66.13; H, 6.08; N, 11.02. Found: C 66.09; H, 6.13; N, 11.04.

Catalytic hydrogenation of NO_2 to NH_2 was performed according to the literature method.[12] A mixture of 2-nitrophenyl-5,5'-dicarboethoxy-2,2'-dipyrrylmethane (**1**) (2.0 g, 4.86 mmol), 10% palladium carbon (200 mg), and THF (100 mL) was stirred magnetically at room temperature under H_2 pressurized at 1.1 atom. The reaction was followed by TLC (R_f = 0.3 for (**1**) and 0.1 for (**3**); silica gel, CH_2Cl_2) and completed within half a day. Pd-C was filtered off with a Celite and the filtrate was evaporated. The crude product was washed with a small amount of cold CH_2Cl_2 to give 1.72 g (4.51 mmol, 93 % yield).

2-Aminophenyl-2,2'-dipyrrylmethane (4). According to the procedure of the literature[11], a mixture of 2-aminophenyl-5,5'-dicarboethoxy-2,2'-dipyrrylmethane (**3**) (8.3 g, 21.7 mmol), ethylene glycol (160 mL), and sodium hydroxide (4.0 g) was refluxed for 2 hr under argon atmosphere. The reaction mixture was cooled and then partitioned between water and CH_2Cl_2. The organic layer was washed with water, dried over anhydrous K_2CO_3, and condensed under reduced pressure. The residue was quickly passed through a short silica gel column with CH_2Cl_2. The eluent of a R_f value of 0.4 with CH_2Cl_2 on a silica gel TLC was collected. The yield of (**4**) was a 88 % yield (4.57 g, 19.3 mmol). The compound (**4**) deteriorated at room temperature. M.p. 41~43°C. ^1H NMR (in $CDCl_3$) δ 3.66 (bs, 2H, NH_2); 5.40 (s, 1H, methine); 5.98 (m, 2H, pyrrole-β-H); 6.15 (m, 2H, pyrrole-β-H); 6.68 (m, 2H, pyrrole-α-H); 6.71 (dd, 1H, 3-phenyl-H); 6.78 (dt, 1H, 5-phenyl-H); 7.00 (dd, 1H, 6-phenyl-H); 7.11 (dt, 1H, 4-phenyl-H); 8.5 (bs, 2H, NH). MS (m/e) 237 (M^+), 219, 169, 145.

2-Acetylaminophenyl-2,2'-dipyrrylmethane (5). To a mixture of 2-aminophenyl-2,2'-dipyrrylmethane (**4**) (2.3 g, 9.75 mmol), CH_2Cl_2 (80 mL), and triethylamine (5 mL) cooled at -15°C under nitrogen atmosphere, 1.5 mL of acetic anhydride was added. After magnetic stirring for 5 hr at -15°C, the reaction mixture was washed with water, dried over K_2CO_3, and condensed with rotary evaporator. The residue was quickly passed through a short silica gel column with CH_2Cl_2. The eluent of a R_f value of 0.2 with CH_2Cl_2 on a silica gel TLC was collected. The yield of (**5**) was a 79 % yield (2.15 g, 7.70 mmol). The compound (**5**) deteriorated at room temperature. M.p. 47~52°C. ^1H NMR (in $CDCl_3$) δ 2.02 (s, 3H, $COCH_3$); 5.53 (s, 1H, methine); 5.90 (m, 2H, pyrrole-β-H); 6.15 (dd, 2H, pyrrole-β-H); 6.71 (m, 2H, pyrrole-α-H); 7.15 (s, 1H, NHCO); 7.15 (m, 2H, 3- and 4-phenyl-H); 7.29 (dt, 1H, 5-phenyl-H); 7.53 (dd, 1H, 6-phenyl-H); 8.3 (bs, 2H, NH). IR 1666 cm^{-1} (CO). MS (m/e) 279 (M^+), 236, 219, 207, 169.

5,15-Di(2-acetylaminophenyl)-10,20-di-1-(2-methoxynaphthyl)porphyrin (6). A mixture of 2-acetylaminophenyl-2,2'-dipyrrylmethane (**5**) (588 mg, 2.11 mmol), 2-methoxy-1-naphthaldehyde (392 mg, 2.11

mmol), zinc acetate dihydrate (500 mg), and propionic acid (50 mL) was allowed to react at room temperature for 1 hr. It was then heated up to reflux temperature in 30 min with magnetic stirring and reflux was continued for further 2 hr in an oil bath. Then, the propionic acid was distilled off and the resulting oily resudue was cooled and solidified with addition of hexane. The black solid was collected by filtration and washed with hexane. The solid material dissolved in CH_2Cl_2 was treated with excess aqueous ammonia, dried over Na_2SO_4, and condensed under reduced pressure. The residue was chromatographed on a dry alumina column with CH_2Cl_2. The dark red fraction was collected and then treated with 10 mL of conc. HCl for 1 hr with vigorous stirring. After the organic layer was washed with excess aqueous ammonia, dried over Na_2SO_4, and condensed under reduced pressure, the residue was purified by chromatography on dry alumina. The first red band eluted with CH_2Cl_2 was further purified on silica gel with a mixture of CH_2Cl_2 and acetone (10 :1) to give the porphyrin (**6**) as a mixture of five atropisomers in a 7.0 % yield (65 mg, 0.073 mmol). M.p. > 300°C. IR 1700 cm^{-1} (CO). FABMS (m/e) 889 (M^++1). Elemental analysis calcd for $C_{58}H_{44}N_6O_4$•(1/2)H_2O: C, 77.57; H, 5.05; N, 9.36. Found: C 77.73; H, 5.13; N, 9.14.

Separation of 5 atropisomers of (6). A mixture of five atropisomers of the porphyrin (**6**) was separated into three bands by a silica gel column chromatography. The first and the second bands eluted with CH_2Cl_2 and the third band eluted with CH_2Cl_2 - acetone (10 :1). The first band dissolved in benzene solution was loaded on the top of a silica gel column and eluted with CH_2Cl_2 - benzene (1 :1) to give three separated fractions, an αα'ββ' isomer (**6a**), an αα'βα' isomer (**6b**), and an αβ'αβ' isomer (**6c**), in the order of elution. The second band of the first column was dissolved in benzene and chromatographed on silica gel. The main red fraction eluted with CH_2Cl_2 gave an αα'αβ' isomer (**6d**). The third band of the first column was dissolved in CH_2Cl_2 and chromatographed on silica gel. The main red fraction eluted with CH_2Cl_2 - acetone (10 :1) gave an αα'αα' isomer (**6e**). The five fractions showed the R_f values (0.17, 0.15, 0.10, 0.04, and 0.015) on Merck Kiesel Gel 60PF_{254} with CH_2Cl_2 elution. The HPLC elution volumes of these atropisomers (column: 4.6 x 250 mm SiO_2 (Shim-pack PREP-SIL(H)); eluent: $CHCl_3$; detection: UV at 400 nm) are 4.4, 4.7, 4.7 (overlapped), 8.3, 23 mL. UV-vis (λ_{max}(logε) in CH_2Cl_2) (**6a**): 422 (5.39), 515 (4.27), 547 (3.70), 591 (3.74), 654 (3.90). ^1H NMR (in $CDCl_3$) (**6a**): δ -2.40 (bs, 2H, NH); 1.26 (s, 6H, CH_3CO); 3.66 (s, 6H, OCH_3); 6.78 (s, 2H, NHCO); 6.83 (d, 2H, naphthyl-8-H); 7.02 (t, 2H, naphthyl-7-H); 7.36 (t, 2H, naphthyl-6-H); 7.75 (d, 2H, naphthyl-3-H); 8.09 (d, 2H, naphthyl-5-H); 8.36 (d, 2H, naphthyl-4-H); 7.97 (d, 2H, phenyl-6-H); 7.44 (t, 2H, phenyl-5-H); 7.76 (t, 2H, phenyl-4-H); 8.62 (d, 2H, phenyl-3-H); 8.60, 8.67 (dx2, 4Hx2, pyrrole-β-H). (**6b**): δ -2.39 (bs, 2H, NH); 1.24, 1.25 (sx2, 3Hx2, CH_3CO); 3.63 (s, 6H, OCH_3); 6.80, 6.81 (sx2, 1Hx2, NHCO); 6.88 (d, 2H, naphthyl-8-H); 7.01 (t, 2H, naphthyl-7-H); 7.35 (t, 2H, naphthyl-6-H); 7.71 (d, 2H, naphthyl-3-H); 8.07 (d, 2H, naphthyl-5-H); 8.33 (d, 2H, naphthyl-4-H); 7.97 (d, 2H, phenyl-6-H); 7.43 (t, 2H, phenyl-5-H); 7.74 (t, 2H, phenyl-4-H); 8.59 (d, 2H, phenyl-3-H); 8.60, 8.67 (dx2, 4Hx2, pyrrole-β-H). (**6c**): δ -2.43 (bs, 2H, NH); 1.25 (s, 6H, CH_3CO); 3.65 (s, 6H, OCH_3); 6.79 (s, 2H, NHCO); 6.85 (d, 2H, naphthyl-8-H); 7.00 (t, 2H, naphthyl-7-H); 7.36 (t, 2H, naphthyl-6-H); 7.74 (d, 2H, naphthyl-3-H); 8.09 (d, 2H, naphthyl-5-H); 8.36 (d, 2H, naphthyl-4-H); 8.02 (d, 2H, phenyl-6-H); 7.46 (t, 2H, phenyl-5-H); 7.76 (t, 2H, phenyl-4-H); 8.62 (d, 2H, phenyl-3-H); 8.60, 8.68 (dx2, 4Hx2, pyrrole-β-H). (**6d**): δ -2.41 (bs, 2H, NH); 1.25 (s, 6H, CH_3CO); 3.64, 3.66 (sx2, 3Hx2, OCH_3); 6.78 (s, 2H, NHCO); 6.77, 6.88 (dx2, 1Hx2, naphthyl-8-H); 6.99, 7.04 (t, 1Hx2, naphthyl-7-H); 7.35 (t, 2H, naphthyl-6-H); 7.74 (d, 2H, naphthyl-3-H); 8.08 (d, 2H, naphthyl-5-H); 8.35 (d, 2H, naphthyl-4-H); 8.02 (d, 2H, phenyl-6-H); 7.45 (t, 2H, phenyl-5-H); 7.76 (t, 2H, phenyl-4-

H); 8.61 (d, 2H, phenyl-3-H); 8.62, 8.68 (dx2, 4Hx2, pyrrole-β-H). (**6e**): -2.40 (bs, 2H, NH); 1.24 (s, 6H, CH_3CO); 3.62 (s, 6H, OCH_3); 6.77 (s, 2H, NHCO); 6.92 (d, 2H, naphthyl-8-H); 7.04 (t, 2H, naphthyl-7-H); 7.35 (t, 2H, naphthyl-6-H); 7.72 (d, 2H, naphthyl-3-H); 8.07 (d, 2H, naphthyl-5-H); 8.34 (d, 2H, naphthyl-4-H); 8.03 (d, 2H, phenyl-6-H); 7.44 (t, 2H, phenyl-5-H); 7.77 (t, 2H, phenyl-4-H); 8.60 (d, 2H, phenyl-3-H); 8.60, 8.67 (dx2, 4Hx2, pyrrole-β-H).

1-(2-Methoxynaphthyl)-2,2'-dipyrrylmethane (7) and 1-(2-ethoxycarbonylmethoxynaphthyl)-2,2'-dipyrrylmethane (9). To a mixture of 2-methoxy-1-naphthaldehyde(10 g, 53.7 mmol), pyrrole (370 mL, 5.33 mol), dry CH_2Cl_2 (1.8 L), and a small amount of molecular sieves 3A under nitrogen was added $TiCl_4$ (0.1 mL). After stirring at room temperature for 10 min, the reaction mixture was made basic with aqueous Na_2CO_3. The organic layer was separated, dried over anhydrous K_2CO_3, and condensed with a rotary evaporator. The excess pyrrole was removed by distillation under reduced pressure with an aspirator (ca. 20 mmHg, 50~60°C). The oily residue was free from pyrrole by heating under vacuum and then chromatographed quickly on a short column of silica gel with benzene as an eluent. The first yellow band was collected and the solvent was stripped off with a rotary evaporator. The residue was dissolved in 30 mL of CH_2Cl_2, and then allowed to stand in a refrigerator for 3 hr. The formed precipitate was filtered, washed with ether, and dried under vacuum. The filtrate was purified by silica gel chromatography. The combined product (**7**) weighs 10.76 g (35.6 mmol, 66 %). M.p. 139~140 °C. ^{1}H NMR (in $CDCl_3$) δ 3.74 (s, 3H, OCH_3); 6.50 (s, 1H, methine); 6.01 (m, 2H, pyrrole-β-H); 6.11 (m, 2H, pyrrole-β-H); 6.60 (m, 2H, pyrrole-α-H); 7.2~7.4 (m, 3H, naphthyl-3,6,7-H); 7.79 (m, 2H, naphthyl-4,5-H); 8.01 (d, 1H, naphthyl-8-H); 8.30 (bs, 2H, NH). MS (m/e) 302 (M^+), 301, 145. Elemental analysis calcd for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.26. Found: C 79.32; H, 6.02; N, 9.29. The compound (**9**) was obtained in a 64 % yield through a similar procedure. M.p. 138~139 °C. ^{1}H NMR (in $CDCl_3$) δ 1.32 (t, 3H, CH_3), 4.27 (q, 2H, CH_2), 4.46 (bs, 2H, OCH_2); 6.54 (bs, 1H, methine); 6.01 (m, 2H, pyrrole-β-H); 6.10 (m, 2H, pyrrole-β-H); 6.67 (m, 2H, pyrrole-α-H); 7.18 (d, 1H, naphthyl-3-H), 7.38 (t, 1H, naphthyl-6-H), 7.48 (t, 1H, naphthyl-7-H), 7.78 (d, 1H, naphthyl-4-H), 7.80 (d, 1H, naphthyl-5-H), 8.25 (d, 1H, naphthyl-8-H), 9.10 (bs, 2H, NH). IR (KBr) 1732, 1226 cm^{-1}. MS (m/e) 374 (M^+), 285, 269, 220, 145. Elemental analysis calcd for $C_{23}H_{22}N_2O_3$: C, 73.78; H, 5.92; N, 7.48. Found: C 73.69; H, 6.00; N, 7.62.

5,15-Di(2-nitrophenyl)-10,20-di-1-(2-methoxynaphthyl)porphyrin (8) and 5,15-di(2-nitrophenyl)-10,20-di-1-(2-ethoxycarbonylmethoxynaphthyl)porphyrin (10). *o*-Nitrobenzaldehyde (5.36 g, 35.5 mmol) in CH_2Cl_2 (200 mL) was slowly added in 1 hr to a mixture of 1-(2-methoxynaphthyl)-2,2'-dipyrrylmethane (**7**) (10.67 g, 35.3 mmol), zinc acetate dihydrate (10 g), and propionic acid (500 mL) at 0 °C. After the stirring was continued for 2 hr at 0 °C and then for 15 hr at room temperature, the reaction mixture was heated until propionic acid goes into reflux. After refluxing for further 2 hr in an oil bath, the propionic acid was distilled off and the resulting oily resudue was cooled and solidified with addition of hexane. The black solid was collected by filtration and washed with hexane. The solid material dissolved in CH_2Cl_2 was treated with excess aqueous ammonia, dried over Na_2SO_4, and condensed under reduced pressure. The residue was chromatographed on a dry alumina column with CH_2Cl_2. The dark red fraction was collected and then treated with 10 mL of conc. HCl for 4 hr with vigorous stirring. After the organic layer was washed with excess aqueous ammonia, dried over Na_2SO_4, and condensed under reduced pressure, the residue was purified by

chromatography. The first red band eluted with CH_2Cl_2 on dry alumina was further purified on silica gel with a mixture of CH_2Cl_2 and acetone (10 :1) to give the porphyrin (**8**) as a mixture of five atropisomers in a 26 % yield (3.94 g, 4.55 mmol). The αα'ββ' atropisomer (**8a**) was separated as the first band in a silica gel column chromatography using CH_2Cl_2 as an eluent and characterized as follows. M.p. > 300°C. ^1H NMR (in $CDCl_3$) δ -2.35 (bs, 2H, NH); 3.64 (s, 6H, OCH_3); 6.88 (d, 2H, naphthyl-8-H); 7.03 (t, 2H, naphthyl-7-H); 7.34 (t, 2H, naphthyl-6-H); 7.69 (d, 2H, naphthyl-3-H); 8.05 (d, 2H, naphthyl-5-H); 8.30 (d, 2H, naphthyl-4-H); 7.82 (d, 2H, phenyl-6-H); 7.87 (t, 2H, phenyl-4-H); 8.17 (t, 2H, phenyl-5-H); 8.41 (d, 2H, phenyl-3-H); 8.51 (m, 8H, pyrrole-β-H). IR 1530, 1348 cm^{-1} (NO_2). Elemental analysis calcd for $C_{54}H_{36}N_6O_6$: C, 74.99; H, 4.20; N, 9.72. Found: C 75.64; H, 4.43; N, 9.94. UV-vis (λ_{max}(logε) in CH_2Cl_2) 422 (5.36), 525 (4.30), 548 (3.66), 596 (3.78), 656 (3.26) nm. The porphyrin (**10**) was obtained in a 20 % yield through a similar procedure. The αα'ββ' atropisomer (**10a**) was separated as the first band in a silica gel column chromatography using CH_2Cl_2 as an eluent and characterized as follows. M.p. > 300 °C. ^1H NMR (in $CDCl_3$) δ -2.37 (bs, 2H, NH); 0.98 (t, 6H, CH_3); 3.98 (q, 4H, OCH_2); 4.34, 4.43 (dx2, 2Hx2, J = 16.9 Hz, OCH_2CO); 6.85 (d, 2H, J = 8.8 Hz, naphthyl-8-H); 7.04 (t, 2H, naphthyl-7-H), 7.37 (t, 2H, naphthyl-6-H); 7.56 (d, 2H, J = 9.2 Hz, naphthyl-3-H); 8.05 (d, 2H, J = 8.1 Hz, naphthyl-5-H), 8.28 (d, 2H, J = 9.0 Hz, naphthyl-4-H); 7.91 (m, 4H, phenyl-4,5-H); 8.21 (dd, 2H, J = 7.2 and 1.9 Hz, phenyl-6-H); 8.42 (dd, 2H, J = 8.0 and 1.5 Hz, phenyl-3-H); 8.51, 8.53, 8.57, 8.65 (dx4, 2Hx4, J = 4.7 Hz, pyrrole-β-H). IR 1756 (CO), 1198 (COC), 1526, 1348 cm^{-1} (NO_2). Elemental analysis calcd for $C_{60}H_{44}N_6O_{10}$: C, 71.42; H, 4.40; N, 8.33. Found: C 71.74; H, 4.33; N, 8.51. UV-vis (λ_{max}(logε) in CH_2Cl_2) 422 (5.43), 517 (4.32), 550 (3.71), 592 (3.81), 648 (3.32).

5,15-Di(2-acetylaminophenyl)-10,20-di-1-(2-methoxycarbonylmethoxynaphthyl)porphyrin (11). A conc. HCl solution (5 mL) was added dropwisely to a dioxane solution (60 mL) of 5,15-bis-(2-nitrophenyl)-10,20-bis-1-(2-ethoxycarbonylmethoxynaphthyl)porphyrin (**10**) (595 mg, 0.59 mmol) and $SnCl_2$•$2H_2O$ (1.59 g, 7.0 mmol). After stirring for 15 hr at room temperature, water was added. The precipitates was filtered, washed with water and then dried under vacuum. The filtrate was extracted with CH_2Cl_2 repeatedly and the organic layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The combined crude porphyrin product was dissolved in a mixture of methanol (140 ml) and sulfric acid (0.7 ml). After heating at 45 °C for 7 hr, the reaction mixture was poured into a 5 % Na_2CO_3 aqueous solution (150 mL). The porphyrin was extracted into CH_2Cl_2 and then the CH_2Cl_2 layer was dried over anhydrous Na_2SO_4. After the solvent was stripped off, the residue was passed through a silica gel column using ethyl acetate as an eluent. A mixture of thus obtained 5,15-bis-(2-aminophenyl)-10,20-bis-1-(2-methoxycarbonylmethoxynaphthyl)porphyrin (463 mg, 0.50 mmol), triethylamine (2 mL), CH_2Cl_2 (40 mL), and acetic anhydride (1.08 g, 10.6 mmol) was stirred overnight at room temperature. Then, water (15 mL) was added and the mixture was stirred for 1 hr. The organic layer was separated, washed with a 5 % Na_2CO_3 aqueous solution and then with water, dried over anhydrous Na_2SO_4, and evaporated to dryness. Chromatography on silica gel with CH_2Cl_2 afforded 462 mg (0.46 mmol) of 5,15-di(2-acetylaminophenyl)-10,20-di-1-(2-methoxycarbonylmethoxynaphthyl)porphyrin (**11**) as a mixture of five atropisomers in a 78 % overall yield based on (**10**).

A mixture of five atropisomers of the porphyrin (**11**) was separated into three bands by a silica gel column chromatography. The first and the second bands eluted with CH_2Cl_2 and the third band eluted with ethyl acetate. The first band was further chromatographed on silica gel with CH_2Cl_2 to give two fractions, an αα'ββ' atropisomer (**11a**) and an αα'βα' atropisomer (**11b**), in the order of elution. The second band of the first

column was chromatographed again on silica gel using eluent with gradient from CH_2Cl_2 to CH_2Cl_2 - ethyl acetate (15 : 1) to result in the separation of very close two bands, an αα'αβ' atropisomer (**11d**) and an αβ'αβ' atropisomer (**11c**), in the order of elution. The third band of the first column was chromatographed again on silica gel using CH_2Cl_2 - ethyl acetate (1 : 3) to give an αα'αα' atropisomer (**11e**). The five fractions showed the R_f values (0.77, 0.72, 0.63, 0.38, and 0.09) on Merck Kiesel Gel $60PF_{254}$ with CH_2Cl_2 - ethyl acetate (1 : 1) elution. IR (**11a**): 1760, 1690 (CO), 1202 cm^{-1} (COC). Elemental analysis calcd for $C_{62}H_{48}N_6O_8$: C, 74.09; H, 4.81; N, 8.36. Found: C 74.13; H, 4.96; N, 8.19. UV-vis (λ_{max}(log ε) in CH_2Cl_2) (**11a**): 422 (5.80), 515 (4.35), 547 (3.64), 589 (3.81), 644 (3.07). ^1H NMR (in $CDCl_3$) (**11a**): δ -2.44 (bs, 2H, NH); 1.26 (s, 6H, CH_3CO); 3.51 (s, 6H, OCH_3); 4.42 (d, 2H, -CH_2-); 4.47 (d, 2H, -CH_2-); 6.84 (s, 2H, NHCO); 6.81 (d, 2H, naphthyl-8-H); 7.02 (t, 2H, naphthyl-7-H); 7.38 (t, 2H, naphthyl-6-H); 7.58 (d, 2H, naphthyl-3-H); 8.08 (d, 2H, naphthyl-5-H); 8.32 (d, 2H, naphthyl-4-H); 7.45 (t, 2H, phenyl-5-H); 7.77 (t, 2H, phenyl-4-H); 7.98 (d, 2H, phenyl-6-H); 8.61 (d, 2H, phenyl-3-H); 8.70 (bs, 8H, pyrrole-β-H). (**11b**): δ -2.44 (bs, 2H, NH); 1.25 (s, 3H, CH_3CO); 1.27 (s, 3H, CH_3CO); 3.48 (s, 6H, OCH_3); 4.41 (d, 2H, -CH_2-); 4.46 (d, 2H, -CH_2-); 6.78 (s, 1H, NHCO); 6.87 (s, 1H, NHCO); 6.82 (d, 2H, naphthyl-8-H); 7.01(t, 2H, naphthyl-7-H); 7.39 (t, 2H, naphthyl-6-H); 7.59 (d, 2H, naphthyl-3-H); 8.09 (d, 2H, naphthyl-5-H); 8.33 (d, 2H, naphthyl-4-H); 7.44 (t, 1H, phenyl-5-H); 7.46 (t, 1H, phenyl-5-H); 7.77 (t, 2H, phenyl-4-H); 7.97 (d, 1H, phenyl-6-H); 7.99 (d, 1H, phenyl-6-H); 8.60 (d, 1H, phenyl-3-H); 8.62 (d, 1H, phenyl-3-H); 8.68 (bs, 8H, pyrrole-β-H). (**11c**): δ -2.46 (bs, 2H, NH); 1.23 (s, 6H, CH_3CO); 3.51 (s, 3H, OCH_3); 3.54 (s, 3H, OCH_3); 4.43 (d, 2H, -CH_2-); 4.45 (d, 2H, -CH_2-); 6.79 (s, 2H, NHCO); 6.76 (d, 1H, naphthyl-8-H); 6.85 (d, 1H, naphthyl-8-H); 6.99 (t, 1H, naphthyl-7-H); 7.05 (t, 1H, naphthyl-7-H); 7.38 (t, 2H, naphthyl-6-H); 8.09 (d, 2H, naphthyl-5-H); 8.33 (d, 2H, naphthyl-4-H); 7.46 (t, 2H, phenyl-5-H); 7.59 (d, 2H, naphthyl-3-H); 7.77 (t, 2H, phenyl-4-H); 8.03 (d, 2H, phenyl-6-H); 8.60 (d, 2H, phenyl-3-H); 8.68 (bs, 8H, pyrrole-β-H). (**11d**): δ -2.44 (bs, 2H, NH); 1.24 (s, 6H, CH_3CO); 3.50 (s, 6H, OCH_3); 4.42 (s, 4H, -CH_2-); 6.80 (s, 2H, NHCO); 6.84 (d, 2H, naphthyl-8-H); 7.04 (t, 2H, naphthyl-7-H); 7.38 (t, 2H, naphthyl-6-H); 7.60 (d, 2H, naphthyl-3-H); 8.08 (d, 2H, naphthyl-5-H); 8.33 (d, 2H, naphthyl-4-H); 7.45 (t, 2H, phenyl-5-H); 7.77 (t, 2H, phenyl-4-H); 8.04 (d, 2H, phenyl-6-H); 8.61 (d, 2H, phenyl-3-H); 8.68 (bs, 8H, pyrrole-β-H). (**11e**): δ -2.44 (bs, 2H, NH); 1.07 (s, 6H, CH_3CO); 3.34 (s, 6H, OCH_3); 4.46 (s, 4H, -CH_2-); 6.77 (s, 2H, NHCO); 6.86 (d, 2H, naphthyl-8-H); 7.02 (t, 2H, naphthyl-7-H); 7.38 (t, 2H, naphthyl-6-H); 7.61 (d, 2H, naphthyl-3-H); 8.08 (d, 2H, naphthyl-5-H); 8.32 (d, 2H, naphthyl-4-H); 7.45 (t, 2H, phenyl-5-H); 7.75 (t, 2H, phenyl-4-H); 8.08 (d, 2H, phenyl-6-H); 8.53 (d, 2H, phenyl-3-H); 8.70 (bs, 8H, pyrrole-β-H).

Conversion of 5,15-di(2-nitrophenyl)-10,20-di-1-(2-methoxynaphthyl)porphyrin (8) to 5,15-di(2-acetylaminophenyl)-10,20-di-1-(2-methoxynaphthyl)porphyrin (6). To a warm dioxane solution (15 mL) of 5,15-bis-(2-nitrophenyl)-10,20-bis-1-(2-methoxynaphthyl)porphyrin (**8**) (1.69 g, 1.95 mmol) and $SnCl_2$•$2H_2O$ (4 g, 17.7 mmol) was dropwisely added conc. HCl solution (38 mL). After stirring for 15 hr at room temperature, water was added. The precipitates was filtered, washed with aqueous NH_3 and water, and extracted into CH_2Cl_2. The solution was dried over anhydrous Na_2SO_4, condensed with a rotary evaporator, and passed through a short silica gel column. The fractions eluated with CH_2Cl_2 - acetone (50 : 1) were collected, evaporated, and dried under vacuum. Acetic anhydride (10 mL) was added to the porphyrin mixture dissolved in CH_2Cl_2 (28 mL). After stirring for 48 hr at room temperature, water (100 mL) was added and stirring was continued for additional 1 hr. The reaction mixture was neutralized with aqueous ammonia and

the organic layer was separated, washed with water, and dried over Na_2SO_4. Chromatography on silica gel with CH_2Cl_2 afforded 1.40 g (1.57 mmol) of 5,15-di(2-acetylaminophenyl)-10,20-di-1-(2-methoxynaphthyl)-porphyrin (**6**) as a mixture of five atropisomers in a 81 % total yield.

5,15-Di(2-acetylaminophenyl)-10,20-di-1-(2-hydroxynaphthyl)porphyrin (14). To a mixture of 5,15-di(2-acetylaminophenyl)-10,20-di-1-(2-methoxynaphthyl)porphyrin (**6**) (100 mg, 0.12 mmol) and ethanethiol (0.47 mL) in CH_2Cl_2 (50 mL) was added BBr_3 (0.19 mL) at -78 °C. The temperature was gradually raised to room temperature in 5 hr and the reaction mixture was stirred at room temperature for 12 hr. The precipitate formed by the addition of hexanes was filtered and washed with aqueous ammonia and then with water. The porphyrin was dissolved in a mixture of CH_2Cl_2 - MeOH and dried over anhydrous Na_2SO_4. The porphyrin solution was evaporated and chromatographed on a preparative TLC using $CHCl_3$ - acetone (10 : 1) as an eluent. Five fractions, (**14c**), (**14a**), (**14d**), (**14b**), and (**14e**), were separated and recrystallized from CH_2Cl_2 - hexanes to give 9, 15, 22, 12, 11 % yield, respectively. Each atropisomer is converted into a monoprotonated form by the treatment with CF_3CO_2H and analyzed by a reverse phase HPLC. Elution volumes for these atropisomers (column: 6 x 150 mm ODS (Cosmosil 5C18-AR); eluent: MeOH / H_2O (5 : 1); detection: UV at 400 nm) are 7.4, 9.8, 14.6, 17.6, 24.8 mL. IR (**14c**): 1670 cm^{-1} (CO). Elemental analysis calcd for $C_{56}H_{40}N_6O_4$: C, 78.12; H, 4.68; N, 9.76. Found: C 78.48; H, 4.41; N, 9.66. UV-vis (λ_{max}(logε) in CH_2Cl_2) (**14c**): 422 (5.23), 515 (4.29), 548 (3.65), 589 (3.81), 645 (3.23). ^1H NMR (in $CDCl_3$) (**14c**): δ -2.50 (bs, 2H, NH); 1.20 (s, 6H, CH_3CO); 5.20 (bs, 2H, OH); 6.69 (s, 2H, NHCO); 6.73 (d, 2H, naphthyl-8-H); 6.97 (t, 2H, naphthyl-7-H); 7.35 (t, 2H, naphthyl-6-H); 7.54 (d, 2H, naphthyl-3-H); 8.06 (d, 2H, naphthyl-5-H); 8.23 (d, 2H, naphthyl-4-H); 7.88 (d, 2H, phenyl-6-H); 7.42 (t, 2H, phenyl-5-H); 7.73 (t, 2H, phenyl-4-H); 8.49 (d, 2H, phenyl-3-H); 8.65, 8.70 (dx2, 4Hx2, pyrrole-β-H). (**14a**) as a diprotonated form in the presence of excess TFA (25 fold molar excess): δ -0.21 (bs, 3H, NH); 1.39 (s, 6H, CH_3CO); 7.53 (s, 2H, NHCO); 7.11 (d, 2H, naphthyl-8-H); 7.23 (t, 2H, naphthyl-7-H); 7.50 (t, 2H, naphthyl-6-H); 7.59 (d, 2H, naphthyl-3-H); 8.16 (d, 2H, naphthyl-5-H); 8.35 (d, 2H, naphthyl-4-H); 8.27 (d, 2H, phenyl-6-H); 7.78 (t, 2H, phenyl-5-H); 7.96 (t, 2H, phenyl-4-H); 8.44 (d, 2H, phenyl-3-H); 8.70 (s, 8H, pyrrole-β-H). (**14d**): δ -2.50 (bs, 2H, NH); 1.21 (s, 6H, CH_3CO); 5.24 (bs, 2H, OH); 6.72 (s, 2H, NHCO); 6.70, 6.80 (dx2, 1Hx2, naphthyl-8-H); 6.81, 6.96 (tx2, 1Hx2, naphthyl-7-H); 7.37 (t, 2H, naphthyl-6-H); 7.55 (d, 2H, naphthyl-3-H); 8.08 (d, 2H, naphthyl-5-H); 8.24 (d, 2H, naphthyl-4-H); 7.90 (d, 2H, phenyl-6-H); 7.45 (t, 2H, phenyl-5-H); 7.75 (t, 2H, phenyl-4-H); 8.51 (d, 2H, phenyl-3-H); 8.66, 8.71 (dx2, 4Hx2, pyrrole-β-H). (**14b**): δ -2.50 (bs, 2H, NH); 1.21, 1.23 (sx2, 3Hx2, CH_3CO); 5.14 (bs, 2H, OH); 6.71 (s, 2H, NHCO); 6.79 (d, 2H, naphthyl-8-H); 7.01 (t, 2H, naphthyl-7-H); 7.38 (t, 2H, naphthyl-6-H); 7.55 (d, 2H, naphthyl-3-H); 8.09 (d, 2H, naphthyl-5-H); 8.25 (d, 2H, naphthyl-4-H); 7.89 (d, 2H, phenyl-6-H); 7.44 (t, 2H, phenyl-5-H); 7.75 (t, 2H, phenyl-4-H); 8.51, 8.55 (dx2, 1Hx2, phenyl-3-H); 8.66, 8.71 (dx2, 4Hx2, pyrrole-β-H). (**14e**): δ -2.52 (bs, 2H, NH); 1.22 (s, 6H, CH_3CO); 5.24 (bs, 2H, OH); 6.74 (s, 2H, NHCO); 6.80 (d, 2H, naphthyl-8-H); 7.03 (t, 2H, naphthyl-7-H); 7.38 (t, 2H, naphthyl-6-H); 7.57 (d, 2H, naphthyl-3-H); 8.09 (d, 2H, naphthyl-5-H); 8.27 (d, 2H, naphthyl-4-H); 7.91 (d, 2H, phenyl-6-H); 7.46 (t, 2H, phenyl-5-H); 7.78 (t, 2H, phenyl-4-H); 8.53 (d, 2H, phenyl-3-H); 8.69, 8.74 (dx2, 4Hx2, pyrrole-β-H).

Methylation of 5,15-Di(2-acetylaminophenyl)-10,20-di-1-(2-hydroxynaphthyl)porphyrin (14). A mixture of a single atropisomer of (**14**) (8.6 mg, 0.010 mmol), methyl iodide (0.1 mL), K_2CO_3 (30 mg), and

dry acetone (4 mL) were heated to reflux for 12 hr with stirring. The reaction mixture was filtered and the porphyrin product was extracted into CH_2Cl_2. Column chromatography on silica gel with CH_2Cl_2 or with CH_2Cl_2 - acetone (10 :1) afforded **66**, **63**, and 65 % yield of (**6b**), (**6d**), and (**6e**), respectively.

Determination of the binding constants between anthraquinone and the porphyrins, (14a) and (14c). Anthraquinone was added to a $CHCl_3$ solution of (**14a**) or (**14c**) (1.0 x 10^{-4} mol / L) at 26 °C. The intensity of the Q-band at 514 nm in the UV-vis spectrum decreased with increasing concentration of anthraquinone (C_X = 0, 5.0 x 10^{-4}, 1.0 x 10^{-3}, 2.0 x 10^{-3}, 5.0 x 10^{-3}, 1.0 x 10^{-2}, and 2.0 x 10^{-2} mol / L). The binding constants (K_{eq}) were calculated on the basis of a reciprocal plot of the absorbance change ($1/(A_0-A_X)$) at 514 nm against the anthraquinone concentrations ($1/C_X$) under Benesi-Hildebrand conditions.[14]

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6. A dash notation in αα'ββ' refers to the arrangement of 2-methoxynaphthyl groups.

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