Stacked Porphyrin Arrays from Hydrogen-Bonded Porphyrin–Resorcinol 1D Chains

Toshihiro Tanaka, Ken Endo, and Yasuhiro Aoyama*

Institute for Fundamental Research of Organic Chemistry, Kyushu University, CREST, Japan Science and Technology Corporation (JST), Hakozaki, Higashi-ku, Fukuoka 812-8581

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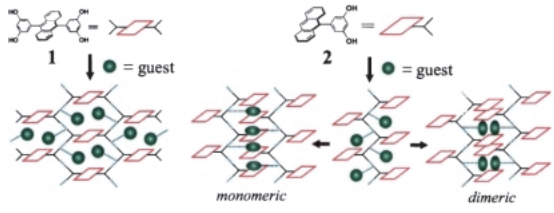
The Ni(II) complex of monoresorcinol derivative of a sterically unhindered tetraalkylporphyrin (**3**) affords adducts **3**•(methanol) and **3**•1.5(acetophenone). In the crystals, porphyrin **3** forms hydrogen-bonded (O–H···O–H) polyresorcinol chains with the porphyrin residues sticking out of the chains. The chains are self-assembled in such a manner as to give closely stacked interchain porphyrin columns, while the guest molecules are either firmly bound to the hydrogen-bonding sites (in the case of methanol) or incorporated in the channels running in parallel with the porphyrin stacks (in the case of acetophenone). The formation of such a stacked porphyrin array is not observed when the guest is changed to 4-heptanone or when the porphyrin is changed to a sterically hindered one **4** or **5** with full substitution at the *meso*- or the β-positions. The mode of interchain porphyrin stacking is discussed in light of the crystal structures of adducts **3**•(4-heptanone), **4**•pyridine, and **5**•(2-nonanone).

Manipulation of stacked aromatic columns[1] may be an important step toward rational design of (photo)electronically potential materials. Aromatic stacking is a frequently encountered motif arising from π-stacking and/or crystal packing forces. On the other hand, columnar assemblies of aromatic building blocks may also be induced through interactions of peripheral substituents.[2] We entered this field with an anthracenebisresorcinol derivative **1** as an orthogonal building block.[3] It forms a hydrogen-bonded (O–H···O–H) 2D network, thereby inducing a columnar alignment of the orthogonal anthracene residues (Scheme 1). The interplanar distance can be significantly shortened when a monoresorcinol analogue **2** is used, since it forms 1D chains which come together via a kind of self-clathration.[4] An essential problem, however, is that single-crystalline materials of hosts **1** and **2** are obtained as lattice inclusion complexes, where the guest molecules (ketones and esters) hydrogen-bonded to the host (O–H···O–H···O=C) are inserted between the anthracene rings to prevent the latter from forming a continuous stack column (Scheme 1). The present work is concerned about porphyrin–monoresorcinol derivatives **3**–**5** (Scheme 2); the bisresorcinol analogue[5] has been studied before.[6–8] The porphyrin is (photo)electronically potential and its size, as compared with that of anthracene, would give a better chance of stacking.[9] We report here that a combination of a sterically unhindered porphyrin **3** and particular guests leads to closely packed interchain porphyrin stack columns.

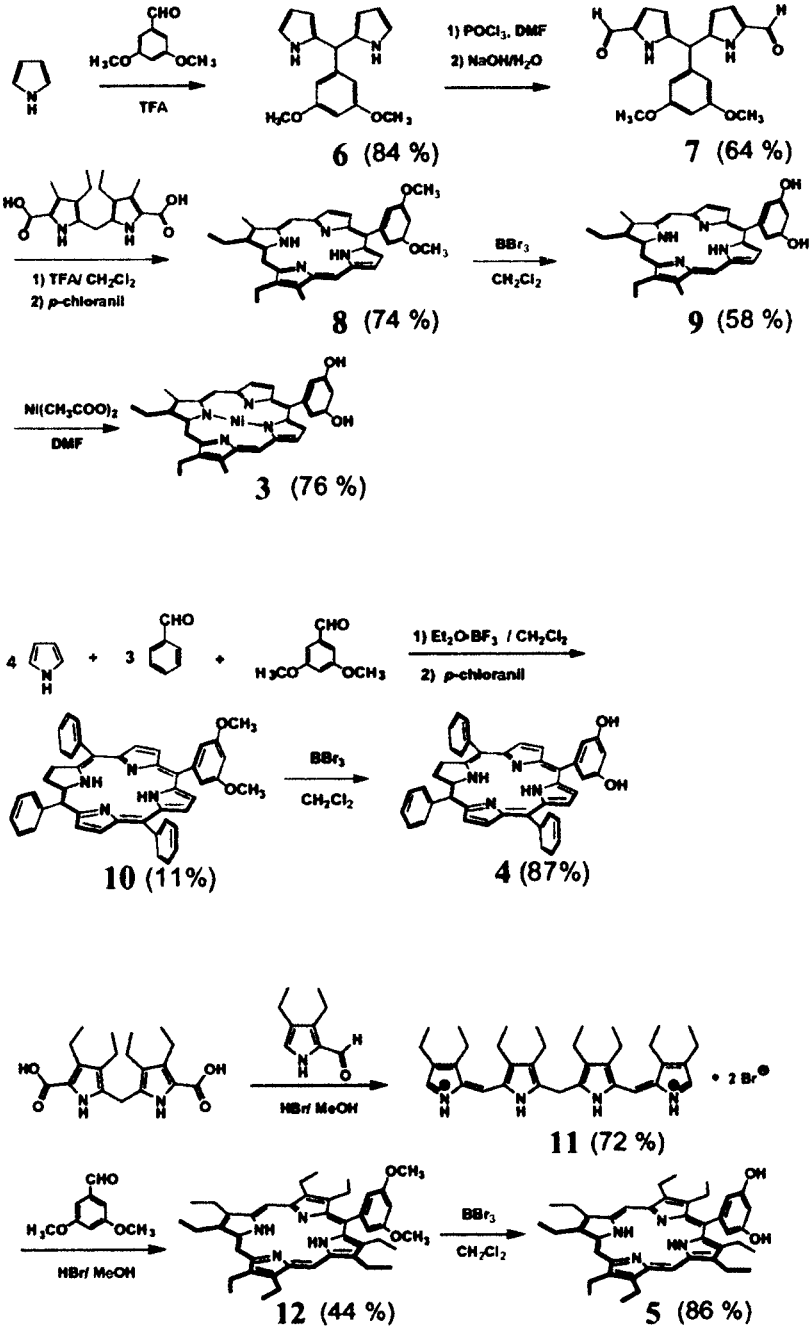


Scheme 1.

Results and Discussion

Preparation. Three types of porphyrin-monoresorcinol derivatives were investigated. One, as a Ni(II) complex **3**,[10] is a tetraalkylporphyrin having a methyl or ethyl substituent at the β-positions of remote (with respect to the resorcinol moiety at a *meso*-position) pyrrole rings, while those of near ones are unsubstituted. Another is a tetraarylporphyrin **4**, having extra three phenyl substituents at the remaining *meso*-positions. The third is an octaethylporphyrin **5** with exhaustive β-substitution. The preparative routes to these porphyrins are shown in Scheme 2. Crystallization of the Ni(II) complex **3** from methanol, 4-heptanone, or acetophenone affords single crystals of adduct **3**•(methanol), **3**•(4-heptanone), or **3**•1.5(acetophenone), where the stoichiometries are based on ^{1}H NMR analysis. X-ray diffraction studies reveal that they all contain hydrogen-bonded (O–H···O–H) 1D porphyrin arrays, whose packing modes are guest-dependent. The crystal data are summarized in Table 1.

Adduct 3•(Methanol). In the methanol adduct, the small alcoholic guest acting as a hydrogen-bond donor as well as an acceptor bridges the adjacent host–host O–H···O–H sites to form a cyclic array of hydrogen bonds, as schematically shown in Scheme 3. The 1D chains are thereby rendered coordinatively saturated and undergo self-clathration of the porphyrin residues to give a pseudo 2D sheet composed of closely packed interchain porphyrin stack columns and methanol-strengthened hydrogen-bonded polyresorcinol chains (Scheme 3). The actual crystal structure of the sheet is shown in Fig. 1 (front view 1a with a column-to-column distance of l_c = 21.4 Å; side



Scheme 2.

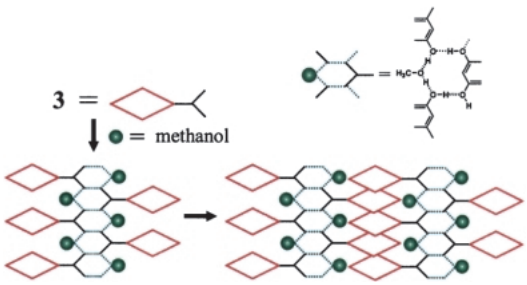
view 1b with a porphyrin–resorcinol dihedral angle of ϕ = 66°). The adjacent porphyrin rings coming from neighboring chains are l_f = 3.5 Å face-to-face apart and hence almost in contact with each other and their centers are l_l = 3.5 Å laterally slide-separated. The molecular sheets thus constructed are layered in a staggered manner with an intersheet distance of l_s = 7.0 Å, as shown in the top view 1c and side view 1d of three adjacent sheets.

Adduct 3•(4-Heptanone). In the 4-heptanone adduct, the ketonic guest serves only as a hydrogen-bond acceptor and is

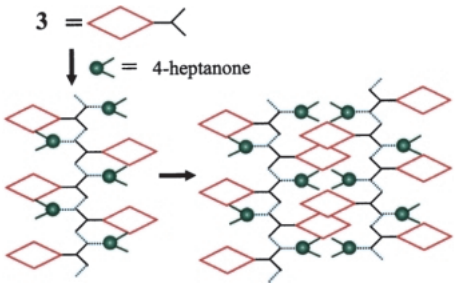
Table 1. Crystallographic Data for Adducts **3**•(methanol), **3**•(4-heptanone), **3**•1.5(acetophenone), **4**•(pyridine), and **5**•(2-nonanone)

	3•(methanol)	**3**•(4-heptanone)	**3**•1.5(acetophenone)	**4**•(pyridine)	**5**•(2-nonanone)
Formula	$C_{33}H_{32}N_4NiO_3$	$C_{39}H_{42}N_4NiO_3$	$C_{44}H_{40}N_4NiO_{3.5}$	$C_{49}H_{35}N_5O_2$	$C_{51}H_{68}N_4O_3$
F.W./g mol^{-1}	591.34	673.49	739.52	725.85	785.12
Crystal size/mm	0.15×0.10×0.15	0.20×0.20×0.20	0.20×0.20×0.20	0.10×0.10×0.05	0.20×0.40×0.40
Crystal color	Reddish purple	Reddish purple	Reddish purple	Dark red	Reddish purple
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Cc*	$P2_1/c$	*Pa*	$P2_1/a$	*Cc*
a/Å	16.525(2)	9.771(2)	9.478(2)	14.962(1)	8.494(3)
b/Å	21.385(1)	12.467(4)	20.209(1)	8.685(1)	50.443(4)
c/Å	9.503(2)	28.796(2)	9.805(2)	30.079(1)	10.835(3)
β/°	122.439(9)	91.37(1)	109.90(1)	100.889(6)	92.36(2)
V/Å^3	2834.2(7)	3506(1)	1765.9(5)	3838.1(6)	4638(1)
Z	4	4	2	4	4
d_{calc}/g cm^{-3}	1.386	1.275	1.391	1.256	1.124
F_{000}	1240.00	1424.00	776.00	1520.00	1704.00
Radiation	Mo $K\alpha$ (λ = 0.71069 Å)	Mo $K\alpha$ (λ = 0.71069 Å)	Mo $K\alpha$ (λ = 0.71069 Å)	Cu $K\alpha$ (λ = 1.54178 Å)	Mo $K\alpha$ (λ = 0.71069 Å)
μ/mm^{-1}	0.726	0.596	0.599	0.616	0.069
$2\theta_{max}$/°	55.0	55.0	55.0	120.1	55.8
Scan mode	ω-2θ	ω-2θ	ω-2θ	ω-2θ	ω-2θ
T/K	295	295	295	295	295
No. reflns measured	3548	7348	4407	6422	5739
No. unique reflns	3354 (R_{int} = 0.037)	6945 (R_{int} = 0.052)	4178 (R_{int} = 0.022)	5956 (R_{int} = 0.034)	5406 (R_{int} = 1.325)
No. reflns used ($I > 2\sigma(I)$)	1704	2893	3378	2796	2692
No. parameters	355	427	416	617	459
R[a], R_w[b]	0.050, 0.064	0.064, 0.088	0.047, 0.074	0.050, 0.066	0.088, 0.128
GOF[c]	1.30	1.31	1.26	1.29	1.93
Final diff four. map (e$^-$Å^{-3})	max 0.57, min −0.31	max 0.65, min −0.37	max 0.54, min −0.48	max 0.37, min −0.17	max 0.62, min −0.32

a) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ b) $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$ c) GOF = $[\Sigma w(|F_o| - |F_c|]^2/(\text{No. refs} - \text{No. params})]^{1/2}$



Scheme 3.



Scheme 4.

bound as such to each host–host hydrogen-bond (O–H···O–H···O=C) with their alkyl chains partially stacked on the porphyrin rings. The chains are assembled in such a manner as to give a stacked dimeric porphyrin unit and a pair of guest molecules inserted in between the units (Scheme 4); there is no continuous stacked porphyrin column as a consequence. This is what we call the dimeric lattice pattern for adducts of anthracenemonoresorcinol host **2** with relatively small guest molecules (Scheme 1).[4] While larger guests tend to give the monomeric lattice pattern, all the inclusion compounds of hosts **2** and **1** so far obtained have their guests inserted in between the parallel-aligned anthracene rings. The present crystal structure (Scheme 4 and Fig. 2 where l_c = 17.2 Å, l_f = 3.8 Å, l_1 = 3.6 Å, l_s = 8.2 Å, and ϕ = 80°) follows this general trend.

Adduct 3•1.5(Acetophenone). The acetophenone adduct has an unusual stoichiometry of 1:1.5, i.e., **3**•1.5(acetophenone). It is also atypical in that the included guest molecules are disordered in crystals. As in the case of the methanol adduct, the porphyrin forms hydrogen-bonded 1D arrays which come together to give tightly packed porphyrin columns without intervention of the guests (Figs. 3a and 3b where l_c = 20.2 Å, l_f = 3.5 Å, l_1 = 2.2 Å, and ϕ = 61°). The molecular sheets are layered (l_s = 9.2 Å) in an eclipsed manner (top view 3c, as opposed to staggered (1c) in case of the methanol adduct) to

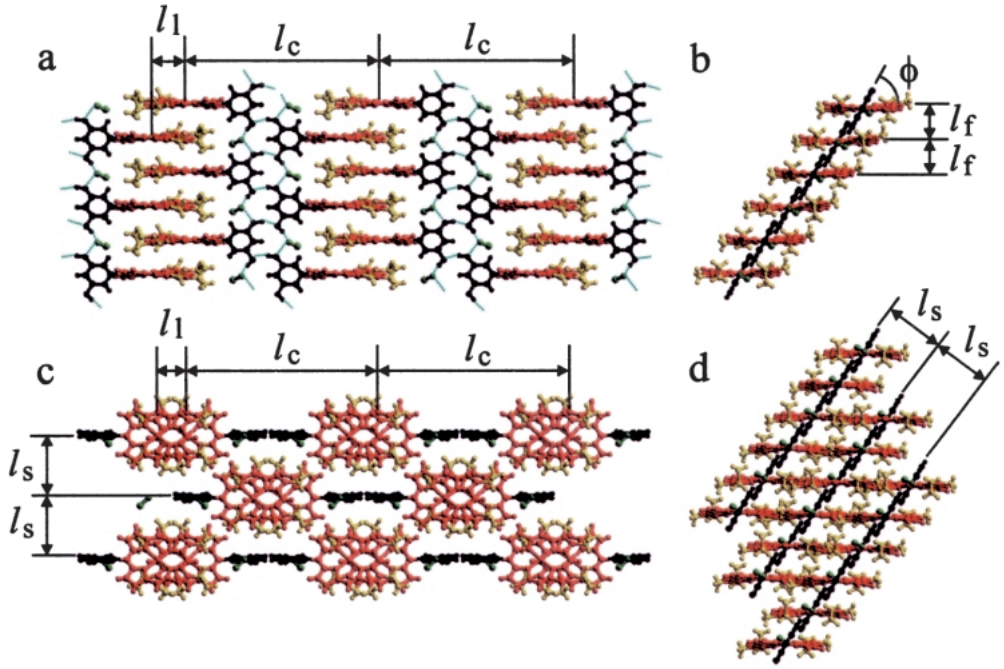


Fig. 1. Crystal structure of adduct **3**•(methanol): front view (a) and side view (b) of a pseudo 2D sheet and top view (c) and side view (d) of the arrangement of three adjacent sheets; ϕ is the porphyrin-resorcinol dihedral angle, l_f and l_l are the vertical face-to-face and lateral center-to-center distances, respectively, for stacking porphyrin rings in a column, l_c is the intercolumn distance, and l_s is the intersheet distance. The porphyrin rings, resorcinol moiety, other peripheral substituents, guest molecules, and hydrogen bonds are shown in red, black, yellow, green, and blue, respectively.

give large channels, in which disordered guest molecules (acetophenone) are included.[11] Such a packing mode of the sheets has never been noted before for the adducts of hosts **1** and **2**.[3,4]

As far as NMR-determined host-guest stoichiometries are concerned, many ketones such as acetone, 2-butanone, 2-pentanone, 3-pentanone, 3-hexanone, 2-heptanone, and 2-nonanone as guests behave similarly to 4-heptanone, giving rise to 1:1 adducts with host **3**. Propiophenone and isobutyrophenone as higher homologues of acetophenone also exhibit a 1:1 stoichiometry. As for esters, ethyl acetate affords a 1:1 adduct, while methyl benzoate apparently gives a 1:0.5 adduct. Higher-alkyl homologues, i.e., ethyl, isopropyl, isobutyl, and butyl benzoates, are not included. While many of the adducts thus obtained unfortunately lack sufficient single crystallinity to allow crystal structure determination, a survey of various guests suggests that the acetophenone adduct represents an exceptional case, whose unique crystal structure is a consequence of a delicate balance of a number of energy terms associated with porphyrin π-stacking,[8] host-guest hydrogen-bonding, and generation of channels and packing of guests therein.

Adducts 4•(Pyridine) and 5•(2-Nonanone). The characteristic crystal structures of the three adducts of porphyrin **3** are commonly based on antiparallel stacking of the porphyrin rings from neighboring chains. This geometrical arrangement brings the β-positions and the *meso*-positions of stacking porphyrin rings into close proximity, especially the remote (with respect to the resorcinol moiety) β's of one porphyrin and the near β's of the other come in contact. Intolerable steric repulsion associated therewith could be avoided in case of porphyrin **3**, which has neither extra *meso*-phenyl substituent nor near β-substituent. In order to shed light on this point, the crystal packing modes of the sterically hindered porphyrins **4** and **5** were also studied.

Single crystals of tetraarylporphyrin **4** were obtained as a 1:1 pyridine adduct **4**•(pyridine). Here too, there are hydrogen-bonded 1D arrays with pyridine molecules hydrogen-bonded to them (O–H···O–H···N) (Scheme 5, a–c). The chains are assembled not laterally as above but in the front-to-rear direction (b → d and c → e). The inter-porphyrin voids along a chain are thereby occupied by the north and south *meso*-phenyl groups of the porphyrin residues of the front and rear chains, respectively, to form a pseudo 2D sheet of a bimolecular thickness, as schematically shown in Scheme 5. There is no interchain porphyrin stack or overlap. The actual crystal structure in reference to Scheme 5 is shown in Fig. 4 (l_c = 7.5 Å, l_f = 8.5 Å, and ϕ = 64°).

Octaethylporphyrin derivative **5** forms a 1:1 adduct with 2-nonanone. The guest molecules are attached to the hydrogen-bonded chain (O–H···O–H···O=C) with their long alkyl tails stacked on the porphyrin rings. The chains undergo a front-to-rear alignment as above (Scheme 5), where the peripheral ethyl groups at the north and south β-positions act as guests to fill the inter-porphyrin voids in collaboration with the guest molecules. The crystal structure is shown in Fig. 5 (l_c = 6.6 Å, l_f = 13.8 Å, and ϕ = 80°).

Both crystal structures exhibit a kind of self-clathration by

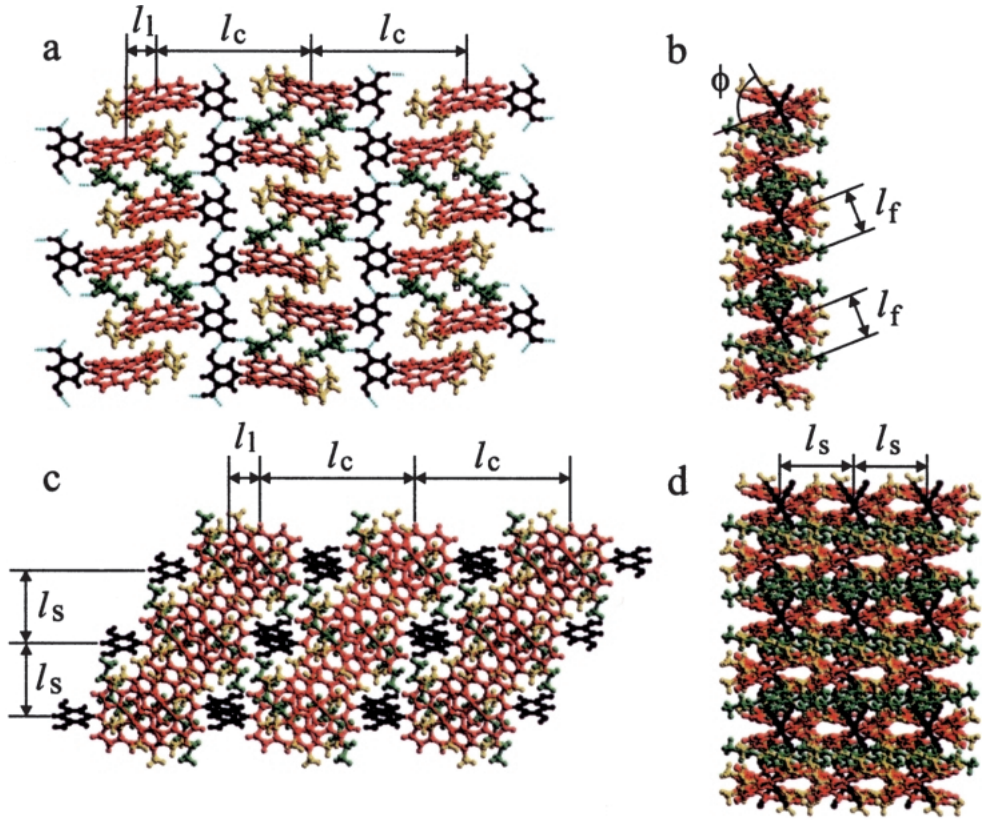
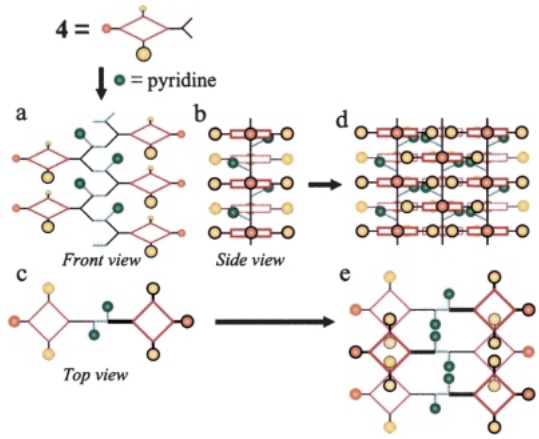


Fig. 2. Crystal structure of adduct **3**•(4-heptanone): front view (a) and side view (b) of a pseudo 2D sheet and top view (c) and side view (d) of the arrangement of three adjacent sheets. The angle and distances and different colors have the same meanings as in Fig. 1.



Scheme 5.

the peripheral substituents, although rigorous comparison with unhindered porphyrin **3** is by no means allowed because of the difference in coordination states (**3** as a Ni(II) complex and **4** and **5** as free bases) and that in guest molecules.

Conclusions

In view of applications of the monoresorcinol strategy to the porphyrin compounds, the present work may be summarized as follows. (1) All the porphyrin–resorcinol derivatives investigated here form hydrogen-bonded polyresorcinol chains with included guest molecules attached thereto. The porphyrin residues sticking out of the chains form interplanar (inter-porphyrin) voids which are filled via assembly of the chains in various ways. (2) The voids are filled by peripheral substituents as a kind of guests when the porphyrin (**4** or **5**) has such substituents at all the *meso*-positions or all the β-positions. In this case, there is no porphyrin stack in the crystals. (3) Sterically unhindered porphyrin **3**, having neither extra *meso*- nor near β-substituents, allows the chains to come close enough to give interchain porphyrin stacks with intervention of the guest molecules. (4) In the particular two cases of methanol and acetophenone as guest, interchain stacking of the porphyrin rings leads to closely packed columns without interference of the guests, the latter being either bound in case of methanol to the hydrogen-bonded chains or accomodated in case of acetophenone in the channels running along the porphyrin stacks. (5) Thus, the self-assembly of hydrogen-bonded chains is still un-

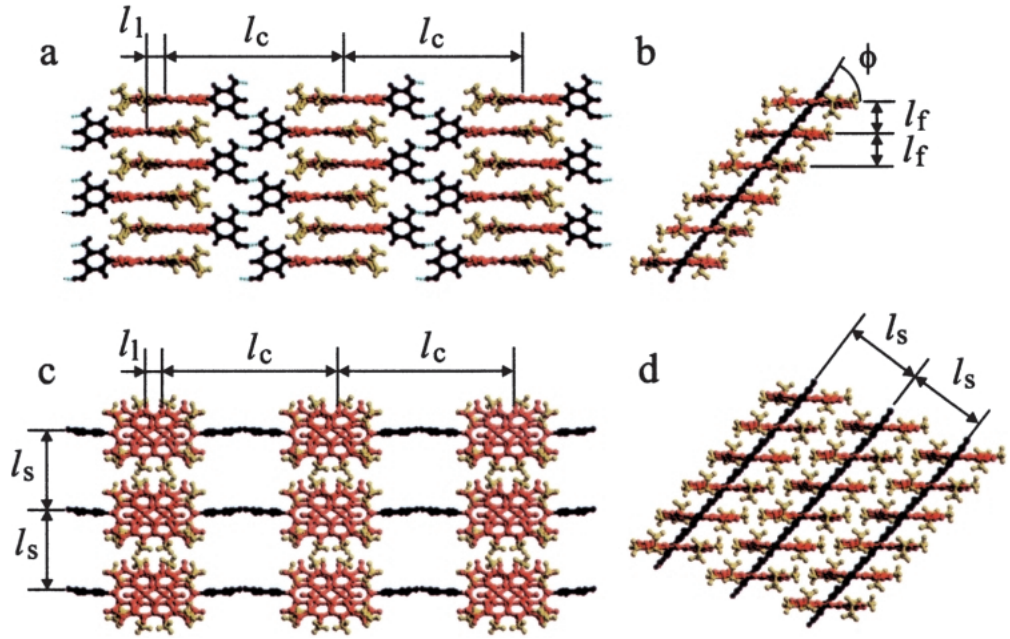


Fig. 3. Crystal structure of adduct **3**•1.5(acetophenone): front view (a) and side view (b) of a pseudo 2D sheet and top view (c) and side view (d) of the arrangement of three adjacent sheets. The angle and distances and different colors have the same meanings as in Fig. 1. Disordeed guest molecules incorporated in the channels are not shown.

predictably guest-dependent. Choice of shorter bridging units other than the resorcinol would allow a better chance of porphyrin stacking. Inclusion of redox-active guest molecules such as quinones may also be an interesting extension of this study. Further work is now under way along this line to shed light on the dynamics of photo-excited and charge-separated states of induced porphyrin arrays in crystals.

Experimental

General Procedures and Host–Guest Stoichiometries. Dichloromethane and methanol were distilled from calcium hydride and magnesium, respectively. Analytical TLC was performed on silica gel 60 F_{254} plates (Merck). Wakogel C-200 was used for column chromatography. ^{1}H NMR spectra at 400 MHz were recorded on a Bruker DPX 400 or a JEOL JNM-EX 400 spectrometer. Melting points were measured with a Yanako MP-500D apparatus. Microanalyses were performed at the microanalysis center of Kyushu University. The host-guest stoichiometries of all the adducts obtained upon crystallization were determined by ^{1}H NMR integration after dissolving them in DMSO-d_6.

General Preparations. Porphyrins **3**, **4**, and **5** were obtained according to the general procedures involving [2 + 2] dipyrrole–dipyrrole coupling[12] (aryl-substituted dipyrromethanedicarboxaldehyde[13] + dipyrromethanedicarboxylic acid), [1 + 1 + 1 + 1] pyrrole cyclooligomerization[14] (substituted and unsubstituted arenecarboxaldehyde + pyrrole), and [4 + 0] tetrapyrrole cyclization[15] (arenecarboxyaldehyde + biladiene), respectively, as key steps.

***α*-(3,5-Dimethoxyphenyl)dipyrromethane (6).** To a solution of 3,5-dimethoxybenzaldehyde (2.21 g, 13.3 mmol) and pyrrole (25 mL, 0.36 mol) was added trifluoroacetic acid (0.10 mL, 1.3 mmol) under nitrogen.[16] The mixture was stirred for 15 min at room temperature, diluted with CH_2Cl_2 (300 mL), washed successively with a saturated aqueous $NaHCO_3$ solution and water, and then dried over Na_2SO_4. The solvent was removed in vacuo and unreacted pyrrole was distilled off at room temperature. The resulting brown oil was dissolved in a minimal amount of the eluant and was purified by flash chromatography with a mixture of cyclohexane, ethyl acetate, and triethylamine (80:20:1) as an eluant to give dipyrromethane **6** (3.17 g, 11.2 mmol, 84% yield): ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 6 H, OCH_3), 5.38 (s, 1 H, *meso*-H), 5.95 (m, 2 H, pyrrolic-H), 6.19 (dd, 2 H, pyrrolic-H), 6.35 (t, 1 H, J = 2.2 Hz, dimethoxyphenyl-H), 6.38 (d, 2 H, J = 2.2 Hz, dimetoxyphenyl-H), 6.66 (dd, 2 H, pyrrolic-H) , 7.92 (bs, 2 H, NH).

5,5′-Diformyl-*meso*-(3,5-dimethoxyphenyl)dipyrromethane (7). Into a solution of compound **6** (2.53 g, 8.97 mmol) in a mixture of diethyl ether (50 mL) and DMF (3.7 mL, 47 mmol) was slowly added phosphoryl chloride (2.5 mL, 27 mmol) at −15 °C.[17] The mixture was further stirred at room temperature for 30 min, evaporated, and poured onto ice water (15 mL). Addition of an aqueous 2 M-NaOH solution (50 mL) caused precipitates, which were collected by filtration and washed with water and then with ethanol to give dialdehyde **7** as a pale yellow solid (1.95 g, 5.77 mmol, 64% yield): ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 6 H, OCH_3), 5.43 (s, 1 H, *meso*-H), 6.10 (m, 2 H, pyrrolic-H), 6.38 (t, 1 H, J = 2.2 Hz, dimethoxyphenyl-H), 6.45 (d, 2 H, J = 2.2 Hz, dimethoxyphenyl-H), 6.87 (dd, 2 H, J = 3.8 and 0.6 Hz, pyrrolic-H), 9.23 (s, 2 H, CHO), 10.28 (bs, 2 H, NH).

5-(3,5-Dimethoxyphenyl)-13,17-diethyl-12,18-dimethylporphyrin (8). Trifluoroacetic acid (0.080 mL, 1.1 mmol) was added to a solution of 3,3′-diethyl-4,4′-dimethyldipyrromethane-5,5′-dicarboxylic acid[18] (113 mg, 0.355 mmol) and diformyldipyrromethane **7** (120 mg, 0.355 mmol) in CH_2Cl_2 (120 mL) under ni-

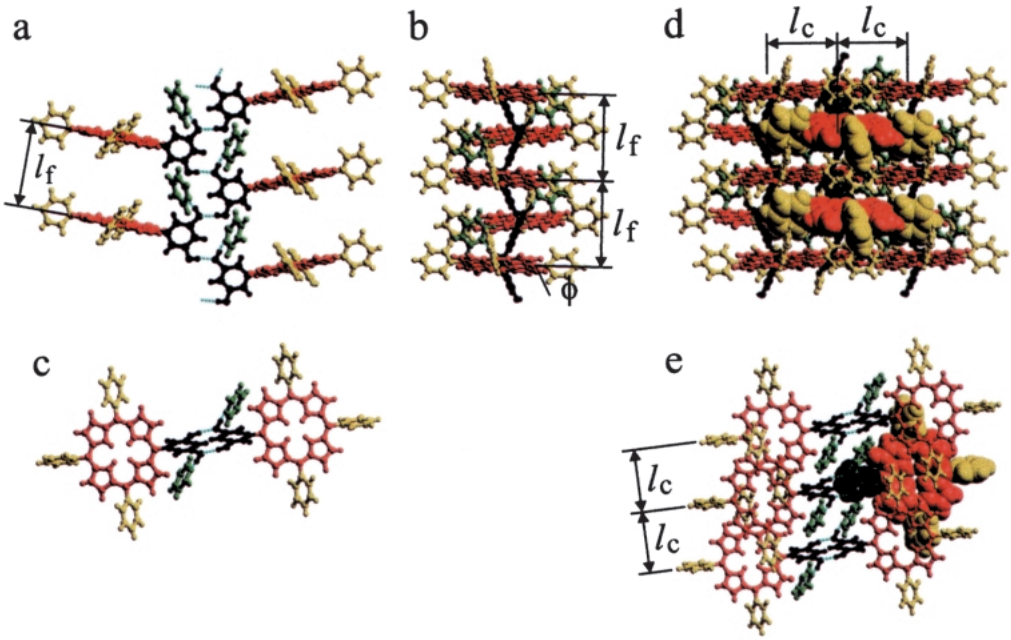


Fig. 4. Crystal structure of adduct **4**•(pyridine) in reference to the schematic representation in Scheme 5: front view (a), side view (b), and top view (c) of a hydrogen-bonded 1D chain and the front-to-rear arrangement of three neighboring chains to form a pseudo 2D sheet (d and e); ϕ is the porphyrin-resorcinol dihedral angle, l_f is the face-to-face distance for adjacent porphyrin rings in a porphyrin column or ladder along a chain, and l_c is the intercolumn or interladder distance in a sheet. Different colors have the same meanings as in Fig. 1, the peripheral phenyl substituents at the north and south *meso*-positions and the west *meso*-position being shown in yellow and orange, respetively, just for the sake of distinction. A set of porphyrin and guest molecules oriented in the same direction along a chain are shown in space-filling models to illustrate that the inter-porphyrin voids along a chain are occupied by the phenyl substituents of the porphyrin building blocks in the neighboring chains.

trogen and the mixture was stirred at room temperature for 9 h. *p*-Chloranil (15 mg, 0.061 mmol) was added and the mixture was refluxed under stirring for 1 h, treated with triethylamine (0.80 mL, 5.8 mmol), and evaporated. The residue was chromatographed with $CHCl_3$ as an eluant. The main porphyrin fraction obtained was successively washed with aqueous Na_2CO_3–$Na_2S_2O_4$, water, and saturated aqueous NaCl. The organic layer was evaporated and the residue washed with methanol to give porphyrin **8** as purple powder (140 mg, 0.264 mmol, 74% yield): mp > 300 °C (dec); TLC R_f = 0.64 ($CHCl_3$); UV-vis (CH_2Cl_2) λ_{max} (ε) 403 (132000), 500 (8250), 532 (2100), 569 (3120), 622 nm (571); ^{1}H NMR ($CDCl_3$) δ −3.40 (bs, 2 H, NH), 1.90 (t, 6 H, CH_2CH_3), 3.63 (s, 6 H, CH_3), 3.99 (s, 6 H, OCH_3), 4.09 (q, 4 H, CH_2CH_3), 6.92 (t, 1 H, J = 2.3 Hz, dimethoxyphenyl-H), 7.45 (d, 2 H, J = 2.3 Hz, dimethoxyphenyl-H), 9.12 (d, 2 H, J = 4.5 Hz, β-H), 9.31 (d, 2 H, J = 4.5 Hz, β-H), 10.03 (s, 1 H, *meso*-H), 10.16 (s, 1 H, *meso*-H). Found: C, 76.46; H, 6.48; N, 10.50%. Calcd for $C_{34}H_{34}N_4O_2$: C, 76.95; H, 6.45; N, 10.56%.

5-(3,5-Dihydroxyphenyl)-13,17-diethyl-12,18-dimethylporphyrin (9). Into a CH_2Cl_2 solution (250 mL) of the dimethoxy derivative **8** (827 mg, 1.56 mmol) was added dropwise a CH_2Cl_2 solution (20 mL) of BBr_3 (4.5 g, 18 mmol) at 0 °C in the period of 30 min.[19] The mixture was stirred for 9 h at room temperature, poured onto a saturated aqueous $NaHCO_3$ solution, and extracted with ethyl acteate. The extracts were combined, washed with saturated aqueous NaCl, dried on Na_2SO_4, and evaporated. The residue was chromatographed. The crude porphyrin product eluted with ethyl acetate was recrystallized from hexane/ethyl acetate and dried at 180 °C in vacuo to give the dihydroxy derivative **9** (462 mg, 0.92 mmol, 58% yield) as purple powder: mp > 250 °C (dec); TLC R_f = 0.51 (9:1 $CHCl_3$/methanol); UV-vis (ethyl acetate) λ_{max} (ε) 401 (128000), 498 (7240), 528 (1750), 570 (2640), 624 nm (536); ^{1}H NMR (DMSO-d_6) δ −3.8 (bs, 2 H, NH), 1.82 (t, 6 H, CH_2CH_3), 3.60 (s, 6 H, CH_3), 4.09 (q, 4 H, CH_2CH_3), 6.69 (t, 1 H, J = 2.1 Hz, dihydroxyphenyl-H), 7.90 (d, 2 H, J = 2.1 Hz, dihydroxyphenyl-H), 9.08 (d, 2 H, J = 4.5 Hz, β-H), 9.54 (d, 2 H, J = 4.5 Hz, β-H), 9.75 (bs, 2 H, OH), 10.12 (s, 1 H, *meso*-H), 10.42 (s, 2 H, *meso*-H). Found: C, 76.10; H, 5.78; N, 10.98%. Calcd for $C_{32}H_{30}N_4O_2$: C, 76.47; H, 6.01; N, 11.15%.

5-(3,5-Dihydroxyphenyl)-13,17-diethyl-12,18-dimethylporphyrinatonickel(II) (3) and its Adducts. A mixture of free base porphyrin **9** (462 mg, 0.92 mmol) and [Ni($CH_3COO)_2$]-($4H_2O$) (332 mg, 1.33 mmol) in DMF (100 mL) was stirred at 120 °C for 2 h, allowed to cool to room temperature, poured onto ice water (100 mL), and extracted with ethyl acetate (100 mL).[20] The extract was washed with water and evaporated. The crude product was purified by means of column chromatography (9:1 $CHCl_3$/methanol) and recrystallization from hexane/ethyl acetate; the solvent was removed at 150 °C in vacuo to give the nickel complex **3** (392 mg, 0.70 mmol, 76% yield) as reddish purple powder: mp > 250 °C (dec); TLC R_f = 0.43 (9:1 $CHCl_3$/methanol); UV-vis (ethyl acetate) λ_{max} (ε) 393 (198000), 513 (117000), 546 (17600); ^{1}H NMR ($CDCl_3$) δ 1.96 (t, 6 H, CH_2CH_3) , 3.63 (s, 6 H, CH_3) , 4.01 (q, 4 H, CH_2CH_3), 5.24 (s, 2 H, OH), 6.83 (t, 1 H, J = 2.1 Hz, di-

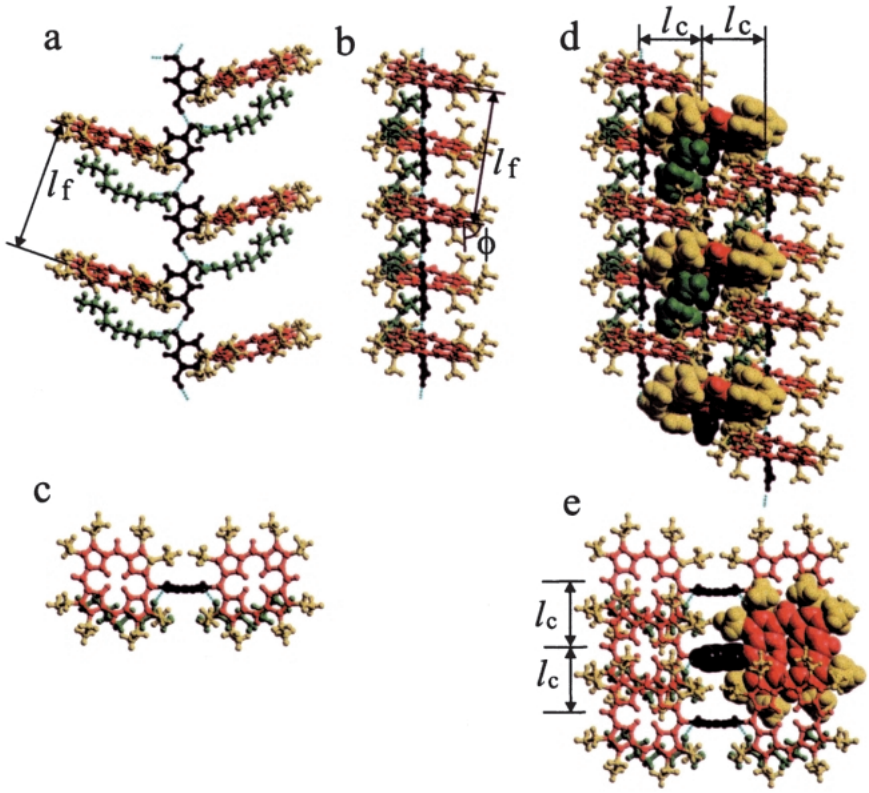


Fig. 5. Crystal structure of adduct **5**•(2-nonanone) in reference to Scheme 5, where porphyrin **4** and guest pyridine should read as **5** and 2-nonanone, respectively, and the two yellow and one orange circles for the three phenyl substitunets at the meso-positions should stand for the eight ethyl substituents at the β-positions. Otherwise, the definitions are the same as in Fig. 4.

hydroxyphenyl-H), 7.22 (d, 2 H, J = 2.1 Hz, dihydroxyphenyl-H), 9.15 (d, 2 H, J = 4.6 Hz, β-H), 9.29 (d, 2 H, J = 4.6 Hz, β-H), 9.92 (s, 1 H, *meso*-H), 9.99 (s, 2 H, *meso*-H). Found: C, 68.62; H, 5.17; N, 9.95%. Calcd for $C_{32}H_{28}N_4NiO_2$: C, 68.72; H, 5.05; N, 10.02%.

Slow diffusion of gaseous hexane into a solution of porphyrin **3** in an appropriate guest liquid afforded the corresponding adduct. The methanol adduct **3**•(methanol). Found: C, 67.42; H, 5.56; N, 9.78%. Calcd for $C_{33}H_{32}N_4NiO_3$: C, 67.03; H, 5.45; N, 9.47%. The 4-heptanone adduct **3**•(4-heptanone). Found: C, 69.56; H, 6.25; N, 8.29%. Calcd for $C_{39}H_{42}N_4NiO_3$: C, 69.55; H, 6.29; N, 8.32%. The acetophenone adduct **3**•1.5(acetophenone). Found: C, 71.06; H, 5.68; N, 7.48%. Calcd for $C_{44}H_{40}N_4NiO_{3.5}$: C, 71.46; H, 5.45; N, 7.58%.

5-(3,5-Dimethoxyphenyl)-10,15,20-triphenylporphyrin (10). A solution of 3,5-dimethoxybenzaldehyde (830 mg, 5.0 mmol), benzaldehyde (1.62 g, 15 mmol), and pyrrole (1.34 g, 20 mmol) in CH_2Cl_2 (2 L) containing diethyl ether–boron trifluoride (1/1) (0.83 mL, 6.7 mmol) was stirred at room temperature for 1.5 h under nitrogen. *p*-Chloranil (3.94 g, 16.0 mmol) was added and the mixture was stirred under reflux for 1 h and evaporated. The residue was purified by means of chromatography (1:1 CH_2Cl_2/hexane). The second porphyrin fraction out of four was washed successively with aqueous Na_2CO_3–$Na_2S_2O_4$, aqueous $NaHCO_3$, water, and saturated aqueous NaCl. The organic layer was evaporated and the residue washed with methanol to give the dimethoxy porphyrin derivative **10** (373 mg, 0.55 mmol, 11% yield): mp > 300 °C; TLC R_f = 0.44 (1:1 CH_2Cl_2/hexane): UV-vis (CH_2Cl_2) λ_{max} (ε) 418 (464000), 514 (18700), 549 (6760), 590 (5300), 645 nm (3490); ^{1}H NMR ($CDCl_3$) δ −2.78 (s, 2 H, NH), 3.96 (s, 6 H, OCH_3) , 6.90 (t, 1 H, J = 2.4 Hz, dimethoxyphenyl-H) , 7.77 (d, 2 H, J = 2.4 Hz, dimethoxyphenyl-H), 7.65–7.85 (m, 9 H, phenyl-H), 8.10–8.30 (m, 6 H, phenyl-H), 8.83 (s, 6 H, β-H), 8.95 (s, 2 H, β-H). Found: C, 81.80; H, 5.13; N, 8.28%. Calcd for $C_{46}H_{39}N_4O_2$: C, 81.88; H, 5.08; N, 8.30%.

5-(3,5-Dihydroxyphenyl)-10,15,20-triphenylporphyrin (4) and its Adduct. Into a solution of the dimethoxy derivative **10** (1.65 g, 2.44 mmol) in CH_2Cl_2 (400 mL) was added BBr_3 (10 g, 40 mmol) at 0 °C over a period of 30 min.[19] The mixture was stirred for 17 h at room temperature, poured onto saturated aqueous $NaHCO_3$ (500 mL), and extracted with ethyl acetate (2 × 300 mL). The extracts were combined, washed with saturated aqueous NaCl (300 mL), dried over Na_2SO_4, and evaporated. The usual workup procedure involving chromatography ($CHCl_3$/ethyl acetate), recrystallization from hexane/ethyl acteate, and solvent removal at 150 °C in vacuo gave the dihydroxy derivative **4** (1.38 g, 2.13 mmol, 87% yield) as violet powder: mp > 300 °C; TLC R_f = 0.55 (9:1 $CHCl_3$/methanol); UV-vis (ethyl acetate) λ_{max} (ε) 415 (550000), 512 (21200), 547 (8190), 589 (5920), 645 nm (3840); ^{1}H NMR (DMSO-d_6) δ −2.96 (s, 2 H, NH), 6.67 (t, 1 H, J = 2.0 Hz, dihydroxyphenyl-H), 7.05 (d, 2 H, J = 2.0 Hz, dihydroxyphenyl-H), 7.75–7.90 (m, 9 H, phenyl-H), 8.15–8.30 (m, 6 H, phenyl-

H), 8.81 (s, 6 H, β-H), 8.98 (s, 2 H, β-H), 9.70 (s, 2 H, OH). Found: C, 81.59; H, 4.70; N, 8.55%. Calcd for $C_{44}H_{30}N_4O_2$: C, 81.71; H, 4.68; N, 8.66%.

Slow diffusion of gaseous hexane into a pyridine solution of porphyrin **4** afforded adduct **4**•(pyridine). Found: C, 80.84; H, 5.01; N, 9.71%. Calcd for $C_{49}H_{35}N_5O_2$: C, 81.08; H, 4.86; N, 9.65%.

2,3,7,8,12,13,17,18-Octaethylbiladiene-*ac* Dihydrobromide (11). A mixture of 3,3′,4,4′-tetraethyldipyrromethane-5,5′-dicarboxylic acid[21] (1.80 g, 5.20 mmol) and 3,4-diethylpyrrole-2-carboxyaldehyde[22,23] (1.42 g, 9.38 mmol) in methanol (90 mL) was warmed to give a solution.[24] Hydrobromic acid (47% in water, 7 mL) was added and the solution was allowed to cool to room temperature and then kept at 0 °C for 1 h. The crystalline product which separated was collected, washed with methanol containing a small amount of hydrobromic acid and then with ether, and dried to give biladiene dihydrobromide **11** (2.32 g, 3.37 mmol, 72% yield) as brown powder: ^{1}H NMR (DMSO-d_6) δ 1.00–1.35 (a set of t, 24 H, CH_3), 2.49–2.85 (a set of q, 16 H, CH_2), 5.63 (s, 2 H, CH_2), 6.75 (s, 2 H, C=CH), 7.25 (s, 2 H, + N=H), 10.3 and 10.75 (both s, both 2 H, + NH and NH).

5-(3,5-Dimethoxyphenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (12). A suspension of salt **11** (2.32 g, 3.37 mmol) in methanol (450 mL) containing 3,5-dimethoxybenzaldehyde (3.42 g, 20.6 mmol) and a 30% HBr solution in acetic acid (3 mL) was heated under reflux for 48 h. The mixture was cooled and treated with an excess amount of Na_2CO_3. The precipitates which separated were collected, washed with water and methanol, dried, and recrystallized from CH_2Cl_2/methanol to give the dimethoxy porphyrin derivative **12** (985 mg, 1.47 mmol, 44% yield) as purple prisms: mp 257–258 °C, TLC R_f = 0.81 (CH_2Cl_2): UV-vis (ethyl acetate) λ_{max} (ε) 401 (195000), 501 (16100), 532 (7470), 572 (6390), 626 nm (3190); ^{1}H NMR ($CDCl_3$) δ −3.17 (s, 1 H, NH), −3.04 (s, 1 H, NH), 1.29 (t, 6 H, CH_3), 1.86–1.94 (a set of t, 18 H, CH_3), 2.93 (q, 4 H, CH_2), 3.94 (s, 6 H, OCH_3), 4.02–4.13 (a set of q, 12 H, CH_2), 6.93 (t, 1 H, J = 2.0 Hz, dimethoxyphenyl-H), 7.41 (d, 2 H, J = 2.0 Hz, dimethoxyphenyl-H), 9.93 (s, 1 H, *meso*-H), 10.18 (s, 2 H, *meso*-H). Found: C, 78.52; H, 8.06; N, 8.23%. Calcd for $C_{44}H_{54}N_4O_2$: C, 78.77; H, 8.11; N, 8.35%.

5-(3,5-Dihydroxyphenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (5) and its Adduct. Into a CH_2Cl_2 solution (250 mL) of the dimethoxy derivative **12** (985 mg, 1.47 mmol) was added dropwise a CH_2Cl_2 solution (20 mL) of BBr_3 (2.5 g, 10 mmol) at 0 °C over a period of 30 min.[19] The mixture was stirred for 12 h at room temperature, poured onto saturated aqueous $NaHCO_3$, and extracted with ethyl acetate. The extract was washed with water and saturated aqueous NaCl, dried over Na_2SO_4, and evaporated. Workup with chromatography ($CHCl_3$/ethyl acetate), recrystallization from hexane/ethyl acetate, and solvent removal at 180 °C in vacuo gave the dihydroxy derivative **5** (809 mg, 1.26 mmol, 86% yield) as purple powder: mp > 250 °C (dec); TLC R_f 0.56 (9:1 $CHCl_3$/methanol); UV-vis (ethyl acetate) λ_{max} (ε) 402 (187000), 501 (15500), 534 (7110), 572 (6150), 626 nm (2970); ^{1}H NMR (DMSO-d_6) δ −3.41 (s, 1 H, NH), −3.27 (s, 1 H, NH), 1.31 (t, 6 H, CH_3) ,1.81–1.89 (a set of t, 18 H, CH_3), 2.98 (q, 4 H, CH_2), 4.01–4.14 (a set of q, 12 H, CH_2), 6.67 (t, 1 H, J = 2.0 Hz, dihydroxyphenyl-H), 7.00 (d, 2 H, J = 2.0 Hz, dihydroxyphenyl-H), 9.60 (s, 2 H, OH), 10.06 (s, 1 H, *meso*-H), 10.19 (s, 2 H, *meso*-H). Found: C, 78.34; H, 7.81; N, 8.71%. Calcd for $C_{42}H_{50}N_4O_2$: C, 78.47; H, 7.84; N, 8.71%.

Slow diffusion of hexane into a 2-nonanone solution of porphyrin **5** afforded adduct **5**•(2-nonanone). Found: C, 78.06; H, 8.73; N, 7.13%. Calcd for $C_{51}H_{68}N_4O_3$: C, 78.02; H, 8.73; N, 7.14%.

X-Ray Crystal Structure Determinations. A selected single crystal was mounted on a glass fiber. Diffraction data were collected on a Rigaku AFC7R four-circle automated diffractometer with graphite-monochromated Mo $K\alpha$ or Cu $K\alpha$ radiation. The unit cell parameters used for refinement were determined by least-squares calculations on the setting angles of 25 reflections in the range of 2θ = 28.0–29.9, 28.0–29.6, 29.7–30.0, 45.1–56.4, and 29.7-30.4° for adducts **3**•(methanol), **3**•(4-heptanone), **3**•1.5(acetophenone), **4**•(pyridine), and **5**•(2-nonanone), respectively. Reflection data were corrected for both Lorentz and polarization effects, while no absorption correction was applied. The structures were solved by the direct methods with the programs SIR92 and the Fourier techniques DIRDIF94. Some nonhydrogen atoms were refined anisotropically, while the rest were refined isotropically. Some hydrogen atoms were located by differential Fourier calculations and their positions refined isotropically. The remaining hydrogen atoms were located on the calculated positions and were treated as riding atoms with a distance of 0.95 Å and U_{iso}(H) = 1.2U_{eq} of attached atom. Refinements were carried out by a full-matrix least squares method based on F. The weighting scheme was $w = 1/[\sigma_c^2(F_o) + 0.00090F_o^2]$ for **3**•(methanol), $w = 1/[\sigma_c^2(F_o) + 0.0025F_o^2]$ for **3**•(4-heptanone) and **3**•1.5(acetophenone), $w = 1/[\sigma_c^2(F_o + 0.0012F_o^2]$ for **4**•(pyridine), and $w = 1/[\sigma_c^2(F_o) + 0.0030F_o^2]$ for **5**•(2-nonanone). Atomic scattering factors and anomalous dispersion terms were taken from International Tables for X-Ray Crystallography.[25] Calculations were performed on an INDY workstation with the teXsan crystallographic software package from Molecular Structure Corporation. The crystal structures were visualized with the Cerius 2 set of computer programs of Molecular Simulations Incorporated.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the depositon numbers 157852–157856. The detail of structures have been deposited as Document No. 74029 at Office of the Editor of Bull. Chem. Soc. Jpn.

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