Synthesis and Characterization of Directly Linked Salen-Porphyrin System with Constrained Geometries

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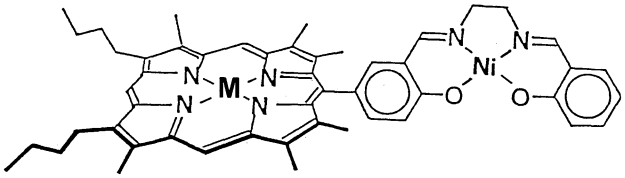
Novel heterobinucleating porphyrin complexes, in which porphyrin and salen [*N*, *N*'-disalicylideneethylenediamine] subunits were directly linked with restricted geometries, were synthesized. These complexes showed a small change in their UV-vis spectra and oxidation potentials, but the fluorescence of porphyrin was effectively quenched by the linked nickel–salen subunit.

Extensive studies of binuclear metal complexes have been made in recent years as simple chemical models for biological metalloproteins containing bimetallic centers. One of the important aspects for the model complexes is close proximity of two metal centers in a well-defined three dimensional geometry, as such in biological systems.

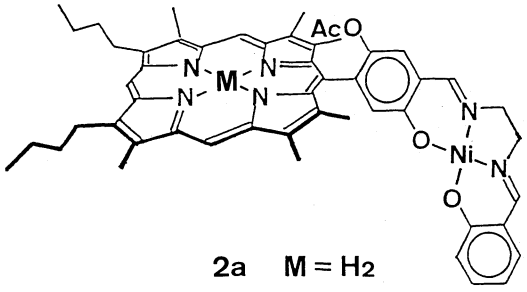
Recently we have reported the synthesis and spectroscopic investigation of salen-capped porphyrins,[1] in which salen subunits were just held over the porphyrin macrocycle. Electronic interactions between these two metal complexes, which were seen in their absorption and fluorescence spectra, and oxidation potentials, were strongly influenced by mutual geometry of the metal complexes.

Now we have synthesized another set of salen-linked porphyrins **1** and **2** as well as salen-bridged dimeric porphyrins **3** and **4**, in which the salen subunit is directly connected to the *meso* position of the porphyrin macrocycle. Since the 5-aryl group was forced to be perpendicular to the porphyrin plane due to the steric hindrance against the β-alkyl groups,[2] the geometry between the porphyrin and the salen complex can be considered to be rigidly fixed. On the basis of Corey–Pauling–Koltun (CPK) models, the metal-to-metal distances of the nickel–salen-linked zinc porphyrins **1b** and **2b** are both estimated to be ca. 10Å. In the case of the salen-bridged dimeric porphyrins **3** and **4**, the salen subunit acts as the bridging group as well as the third metal binding site. In the metal-free salen form, two porphyrins are linked only by flexible ethylene chain, while two porphyrins are expected to adopt a rather fixed geometry upon the nickel complexation at the salen site owing to a preferred planar geometry of the nickel–salen complexes.[3] On the basis of CPK models, the center-to center distances and interplane angles of two porphyrins are estimated to be 20 Å and 180° in **3b—3c**, and 13 Å and 60° in **4b—4c**, respectively.



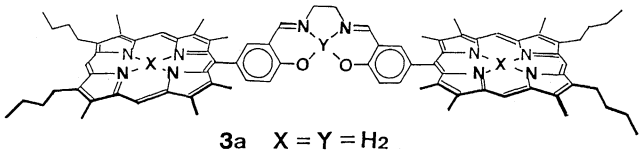
1a M = H_2

1b M = Zn



2a M = H_2

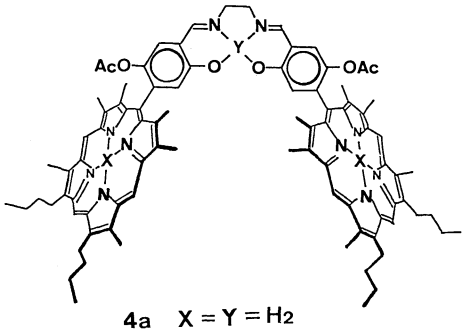
2b M = Zn



3a X = Y = H_2

3b X = H_2, Y = Ni

3c X = Zn, Y = Ni



4a X = Y = H_2

4b X = H_2, Y = Ni

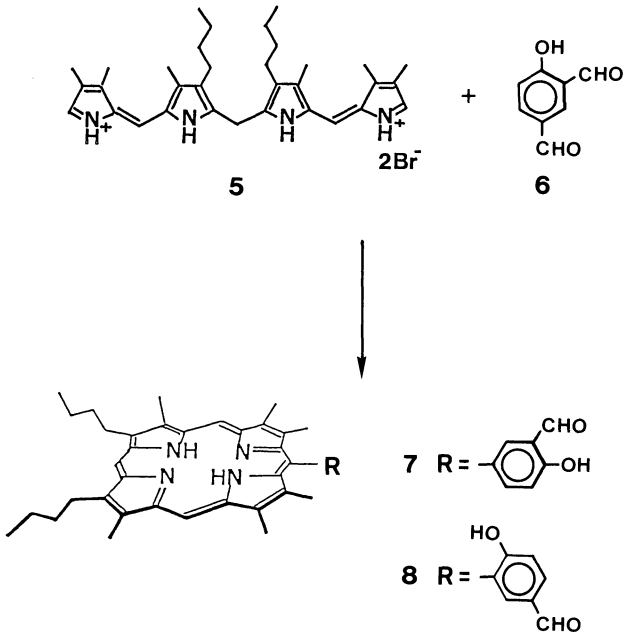
4c X = Zn, Y = Ni

Results and Discussion

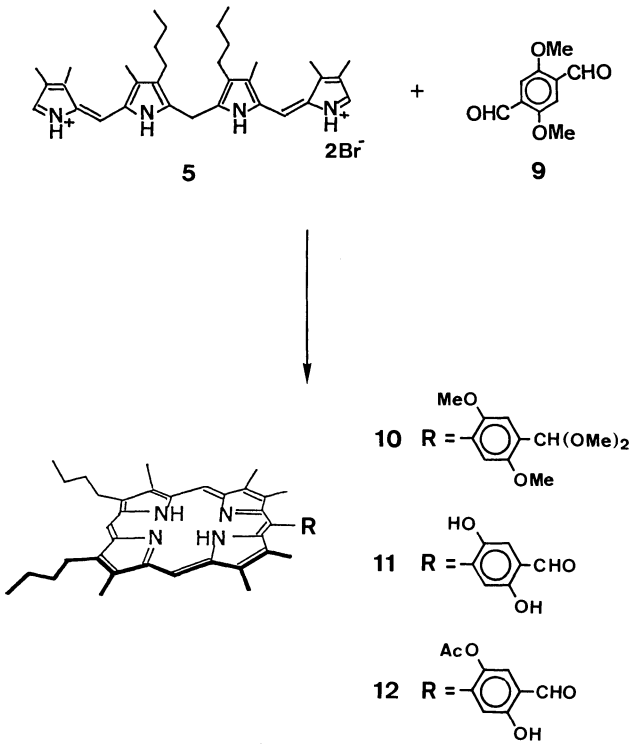
Salen-linked porphyrins **1** and **2** were prepared from

salicylaldehyde-linked porphyrins **7** and **12**, respectively. A key porphyrinic intermediate **7** was prepared by the acid-catalyzed condensation of the biladiene-*ac*-21,24-diium dibromide **5**[4] with 4-hydroxy-1,3-benzenedicarbaldehyde (**6**)[5] (HBr/MeOH, 24 h, reflux), which furnished **7** in 28% yield together with **8** (30%).[6] (Scheme 1) Another salicylaldehyde-linked porphyrinic intermediate **12** was prepared as follows:— Condensation of **5** and 2,5-dimethoxy-1,4-benzenedicarbaldehyde (**9**) afforded an acetal porphyrin **10** in 52% yield, which was treated with BBr_3 in CH_2Cl_2 at low temperature to give a deprotected porphyrin **11** in 95% yield. Selective acetylation of **11** was achieved by the reaction with small excess amounts of acetyl chloride in the presence of pyridine in CH_2Cl_2 (Scheme 2).

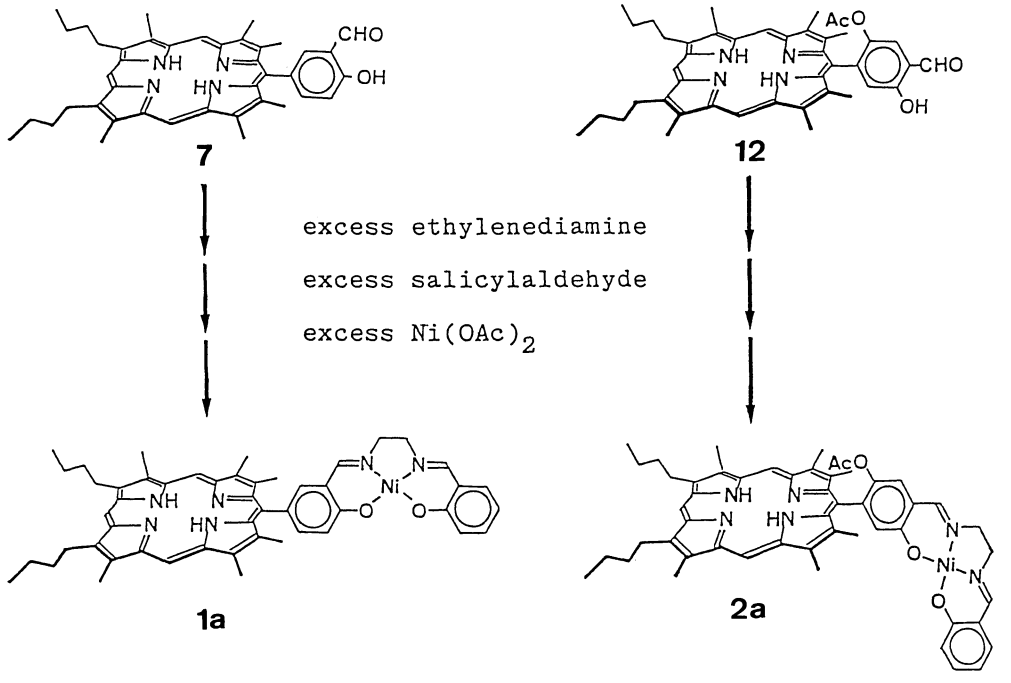
The salicylaldehyde-linked porphyrins **7** thus pre-



Scheme 1.



Scheme 2.



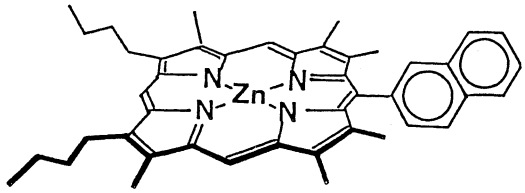
Scheme 3.

pared was dissolved in CH_2Cl_2 and treated with 5 fold excess of ethylenediamine. After 1 h, 7 fold excess of salicylaldehyde was added and the mixture was stirred overnight to yield a crude salen-linked porphyrin. Since a metal free salen moiety was acid-labile, the salen site was converted to the nickel complex by treating with nickel(II) acetate at room temperature. The resulting mixture was separated on silica-gel column eluting with CH_2Cl_2–5% ether (v/v) to yield a nickel–salen-linked porphyrin **1a** in 49% yield. The nickel–salen-linked porphyrin **2a** was prepared in the same manner from the salicylaldehyde-linked porphyrin **12** in 42% yield.

The salen-bridged dimeric porphyrins **3a** and **4a** were prepared by Schiff base condensation of salicylaldehyde-linked porphyrins **7** and **12** with ethylenediamine.[1a] The salicyllaldehyde-linked porphyrins **7** and **12** were treated with 0.5 equimolar amount of ethylenediamine in CH_2Cl_2 at room temperature for 2 weeks to allow a nearly complete transformation into the corresponding salen-bridged dimeric porphyrins **3a** and **4a**, respectively. After recrystallization from CH_2Cl_2–methanol, **3a** and **4a** were obtained in high yields (over 85% yield) in pure form.

In the nickel–salen-linked zinc porphyrin **1b** and **2b**, the absorption of the porphyrin subunit was almost unchanged by covalent linkage with the nickel–salen, but the porphyrin Soret band was slightly broadened and red-shifted (Table 1). The Soret band of dimers were more broadened and red-shifted in **3c** but slightly blue-shifted in **4c**. These additional shifts in the dimers **3c** and **4c** were in agreement with exciton coupling interactions between the two porphyrins in flat and oblique geometries, respectively.[2]

The oxidation potentials of these complexes (**1b**, **2b**, **3c**, and **4c**) were slightly lower than that of the reference zinc porphyrin **13** (Table 2). These results are in contrast to that of the salen-capped porphyrin (**14**) which showed 140 mV lower oxidation potential and red-shifted Soret band.[1b]



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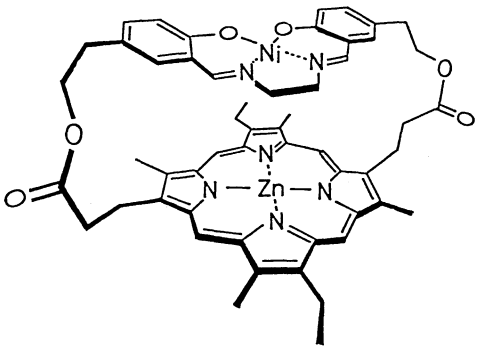

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Table 1. UV-Vis Spectral Data[a]

Compound	λ_{max}/nm	
	Soret	Q-bands
1b	407 (15)	535 571
2b	407 (15)	535 571
3c	408 (18)	535 571
4c	404 (18)	534 571
13	405 (12)	534 570
14	410 (28)	538 574

a) Measured in CH_2Cl_2 solution. Numbers given in parentheses show full width at half-height of the maximum absorbance of the Soret band (nm).

Table 2. Oxidation Potentials[a]

Compound	$E^{ox}_{1/2}$/mV	
1b	145	380
2b	160	435
3c	140	385
4c	165	420
13	170	415
14	30	460

a) Oxidation potentials (mV vs. ferrocene/ferrocenium, +0.45 V vs. SCE) were measured by cyclic voltammetry at a Pt electrode, in CH_2Cl_2 containing 0.1 M (1 M= 1 mol dm^{-3}) tetrabutylammonium perchlorate at 20 °C; accuracy ±10 mV.

Since it has been well established that porphyrins generally show red-shifted Soret bands and lower oxidation potentials in electron donating solvents or with electron donating axial ligands,[7] these spectral red shift and low oxidation potential of **14** can be ascribed to electron donation from the nickel(II)–salen to the zinc–porphyrin in the ground state, indicating the important role of electron-filled d orbitals (especially

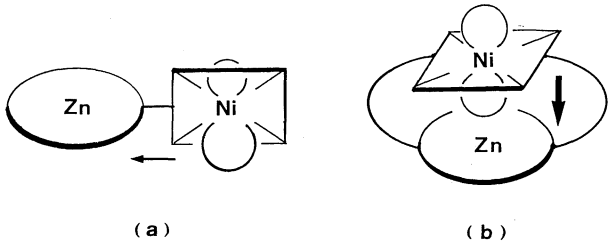

Fig. 1. Schematic representation of molecular geometry and dz^2 orbital of Ni(II) for the salen-linked porphyrin **1b** (a), and the salen-capped porphyrin **14** (b).

dz^2) of nickel(II) to the ground state interactions between zinc porphyrin and nickel-salen moieties (Fig. 1). In contrast, the interactions between the zinc porphyrin and the nickel-salen of **1b**, **2b**, **3c**, and **4c** in their ground states were small. The expected d-orbital interactions shown in Fig. 1b are presumably impossible in the molecules **1b**, **2b**, **3c**, and **4c** (Fig. 1a).

On the other hand, the fluorescence of the zinc porphyrins **1b**, **2b**, **3c**, and **4c** were all strongly quenched by the appended nickel-salen moieties (Table 3). The effective fluorescence quenching and extremely short-lived fluorescence lifetimes of **1b**, **2b**, **3c**, and **4c** suggest the strong interactions between the singlet excited state of the zinc porphyrin and the directly bound nickel-salen. The observed fluorescence lifetimes of **1b**, **2b**, **3c**, and **4c** are much shorter than the salen-capped porphyrins **14**, even though the orbital overlap between the Zn porphyrin π-system and the d-orbitals on Ni(II) seems more favorable in the latter molecule. The fact that a rapid decay of the $S_n \leftarrow S_1$ obsorption observed in the picosecond time-resolved spectra of **14** was followed by no enhancement of the $T_n \leftarrow T_1$ absorption[1b] indicates that the intersystem crossing of the singlet excited state of zinc-porphyrin was not accelerated by the Ni-salen. Although it was difficult to detect clearly the ion pair state presumably due to its rapid charge recombination, the electron transfer mechanism was expected to play a predominant role for the fluorescence quenching in these zinc-porphyrin-nickel-salen linked molecules.

Table 3. Fluorescence Spectral Data[a]

Compd	λ_{em}/nm	Φ_f, rel[b]	τ/ns[c]
1b	577 627	0.01	<0.05
2b	576 626	0.01	0.032 (100%)
3c	574 626	0.04	0.056 (97%)
			1.06 (3%)
4c	576 626	0.03	0.048 (95%)
			1.14 (5%)
13	575 626	1.0	1.5 (100%)
14	569 622	—	0.108 (88%)
			0.710 (12%)

a) Measured in CH_2Cl solution. b) Relative fluorescence intensities of Q(00) bands with respect to **13**; excitation at Soret wavelength. c) Fluorescence lifetime measured by time-correlated single photon counting technique (Ref. 8); excited at 514.5 nm by Ar laser pulse. Numbers in parentheses indicate the normalized pre-exponential factor.

An additional unique character of the salen-bridged dimeric porphyrins **3** and **4** was also observed in their ^{1}H NMR spectra. The changes in the ^{1}H NMR spectra of salen-bridged porphyrin dimers upon complexation of nickel(II) into the salen sites are summarized in Table 4. Nickel(II) complexation can be seen clearly in their up-field shifts of salen protons ($CH{=}N{-}CH_2$). In the metal free salen form, the chemical shifts of the peripheral protons of the porphyrin (*meso*-H, β-CH_3, β-Bu) of **3a** and **4a** were comparable. Upon complexation of nickel(II), these protons were not shifted or slightly downfield shifted in **3b**, but were instead upfield shifted by 0.1 ppm in **4b**, reflecting the ring current effect of the other porphyrin ring in the oblique geometry.

In summary, the directly linked porphyrin-salen system described herein showed only weak interactions in the ground state, while strong interactions were observed in the singlet excited state.

Experimental

The ^{1}H NMR spectra were recorded at 400 MHz on a JEOL JNM-GX-400 spectrometer, with tetramethylsilane or $CHCl_3$ as internal reference. All spectra were measured in $CDCl_3$ solution. Fast atom bombardment mass spectra were recorded on a JEOL JMS-DX-300 (1.5 kV) with *m*-nitrobenzyl alcohol as the matrix. UV-vis spectra were recorded in dichloromethane on a Shimadzu UV-200 and a Shimadzu UV-3000 spectrophotometer. Steady-state fluorescence spectra were recorded by using a Shimadzu RF-502a spectrofluorometer. Fluorescence lifetimes were measured by picosecond time-correlated single photon counting technique.[8] Cyclic Voltammetry was performed with a PAR Model 174.

Flash column chromatography was carried out using Merck Kieselgel 60H Art. 7736.

Unless othewise stated all reactions were performed under an atmosphere of dry nitrogen. All organic extracts were dried over anhydrous sodium sulfate.

5-(3-Formyl-4-hydroxyphenyl)-13,17-dibutyl-2,3,7,8,12,18-hexamethylporphine (7). A suspension of 8,12-dibutyl-2,3,7,13,17,18-hexamethylbiladiene-*ac*-21,24-diium dibromide

Table 4. ^{1}H NMR Data for Salen-Bridged Dimeric Porphyrins

Compd	Chemical shift/ppm										
	meso-H			β-Me			β-Bu			$CH{=}N{-}CH_2$	
3a	10.13	9.96	3.62	3.47	2.56	4.05	2.29	1.78	1.13	8.68	4.17
3b	10.17	9.95	3.65	3.57	2.69	4.05	2.29	1.78	1.14	7.77	3.6
$\Delta\delta$[a]	0.04	−0.01	0.03	0.10	0.13	0	0	0	0.01	−0.91	−0.6
4a	10.15	9.98	3.63	3.52	2.75	4.06	2.27	1.76	1.12	8.84	4.31
4b	10.04	9.85	3.54	3.46	2.73	3.96	2.18	1.67	1.04	7.95	3.78
$\Delta\delta$[a]	−0.11	−0.13	−0.09	−0.06	−0.02	−0.10	−0.09	−0.09	−0.08	−0.89	−0.53

a) Chemical shift changes induced by nickel(II) complexation into the salen site. Negative value shows the upfield shift.

(**5**)[4] (230 mg, 0.35 mmol) and 4-hydroxy-1,3-benzenedicarbaldehyde (**6**)[5] (515 mg, 3.4 mmol) in methanol containing acetic acid (four drops) saturated with hydrogen bromide was heated under reflux for 24 h.[6] The mixture was cooled and poured into water, and extracted with $CHCl_3$. The organic layer was washed with aqueous sodium hydrogencarbonate, with water, and then evaporated. The residue was flash chromatographed on silica gel eluted with CH_2Cl_2–5% ether. The first band eluted was the desired porphyrin **7**. Recrystallization from CH_2Cl_2–methanol gave purple microcrystals (61 mg, 0.097 mmol, 28%).

^1H NMR ($CDCl_3$) δ=11.43 (1H, s, OH), 10.16+9.97 (2H+1H, s+s, *meso*-H), 10.07 (1H, s, CHO), 8.22+7.40 (2H+1H, m+d, ArH), 4.04 (4H, t, Bu), 3.63+3.54+2.52 (6H+6H+6H, s+s+s, β-Me), 2.28+1.77+1.13 (4H+4H+6H, m+m+t, Bu), −3.18+−3.30 (1H+1H, br, NH). MS (FAB) *m/z* 627 ($M+H^+$).

5-(2,5-Dimethoxy-4-(dimethoxymethyl)phenyl)-13,17-dibutyl-2,3,7,8,12,18-hexamethylporphine (10). A suspension of the biladiene-*ac*-21,24-diium dibromide (**5**) (206 mg, 0.31 mmol) and 2,5-dihydroxy-1,4-benzenedicarbaldehyde (**9**) (304 mg, 1.57 mmol) in methanol containing acetic acid (four drops) saturated with hydrogen dromide was heated under reflux for 41 h and the product worked up as in the previous experiment. (116 mg, 0.16 mmol, 52%)

^1H NMR ($CDCl_3$) δ=10.13+9.94 (2H+1H, s+s, *meso*-H), 7.54+7.31 (1H+1H, s+s, ArH), 6.05 (1H, s, C<u>H</u>$(OMe)_2$), 4.04 (4H, t, Bu), 3.78+3.71+3.61 (3H+3H+6H, s+s+s, OMe), 3.63+3.54+2.60 (6H+6H+6H, s+s+s, β-Me), 2.29+1.78+1.13 (4H+4H+6H, m+m+t, Bu), −3.14+−3.29 (1H+1H. br, NH). MS(FAB) *m/z* 717 ($M+H^+$).

5-(2,5-Dihydroxy-4-formylphenyl)-13,17-dibutyl-2,3,7,8,12,18-hexamethylporphine (11). The porphyrin **10** (77 mg, 0.11 mmol) was dissolved in dry CH_2Cl_2 (45 ml) and treated with BBr_3 (0.5 ml) at −78 °C. The mixture was stirred overnight and gradually warmed to room temperature, and then poured into water. The product was extracted with CH_2Cl_2 and the extract was washed with aqueous sodium hydrogencarbonate, with water, and then evaporated. Recrystallization from CH_2Cl_2–hexane gave purple microcrystals (68 mg, 0.11 mmol, 99%).

^1H NMR ($CDCl_3$) δ=10.82 (1H, br, OH), 10.21 (1H, s, CHO), 10.19+10.01 (2H+1H, s+s, *meso*-H), 7.53+7.48 (1H+1H, s+s, ArH), 4.04 (4H, t, Bu), 3.64+3.56+2.70 (6H+6H+6H, s+s+s, β-Me), 2.28+1.77+1.13 (4H+4H+6H, m+m+t, Bu). MS (FAB) *m/z* 643 ($M+H^+$).

5-(2-Acetoxy-4-formyl-5-hydroxyphenyl)-13,17-dibutyl-2,3,7,8,12,18-hexamethylporphine (12). The dihydroxy porphyrin **11** (68 mg, 0.11 mmol) was dissolved in dry CH_2Cl_2 (25 ml) containing pyridine (50 µl) and acetyl chloride (50 µl) in CH_2Cl_2 (10 ml) was added. The mixture was stirred for 2 days and then poured into water. The organic layer was washed with water, dried, and evaporated. The residue was purified by flash column chromatography (CH_2Cl_2). The first band eluted was the desired porphyrin **12**. Recrystallization from CH_2Cl_2–methanol gave purple microcrystals (23 mg, 0.033 mmol, 32%).

^1H NMR ($CDCl_3$) δ=11.20 (1H, br, OH), 10.24 (1H, s, CHO), 10.17+9.99 (2H+1H, s+s, *meso*-H), 7.85+7.79 (1H+1H, s+s, ArH), 4.05 (4H, t, Bu), 3.64+3.55+2.69 (6H+6H+6H, s+s+s, β-Me), 2.28+1.77+1.13 (4H+4H+6H, m+m+t, Bu), 1.03 (3H, s, CH_3CO), −3.20 (2H, br, NH). MS (FAB) *m/z* 685 ($M+H^+$).

Salen-Linked Porphyrin 1a. The salicylaldehyde-linked porphyrin **7** (4.7 mg, 0.007 mmol) was dissolved in CH_2Cl_2 (7 ml) and ethylenediamine (0.15 M solution in methanol, 0.2 ml) was added. After the solution was stirred at room temperature for 1 h, salicylaldehyde (0.1 M solution in CH_2Cl_2, 0.65 ml) was added and stirring was continued overnight. To this solution, a saturated methanolic solution of nickel(II) acetate (ca. 1 ml) was added, and the mixture was stirred for 2 h at room temperature. The solvent was removed, and the residue was purified by flash column chromatography (CH_2Cl_2). Recrystallization from CH_2Cl_2–methanol gave purple crystals (3.0 mg, 0.004 mmol, 49%).

1a: ^1H NMR ($CDCl_3$) δ=10.14+9.94 (2H+1H, s+s, *meso*-H), 7.69+7.61 (1H+1H, s+s, CH=N), 7.90+7.68+7.45+7.30+7.17+6.62 (7H, dd+d+d+d+t+t, Ar-H), 4.04 (4H, t, Bu) 3.62+3.53+2.61 (6H+6H+6H, s+s+s, β-Me), 3.49 (4H, s, NCH_2), 2.28+1.77+1.12 (4H+4H+6H, m+m+t, Bu), −3.3 (2H, br, NH). UV-vis (CH_2Cl_2) 407, 504, 537, 572, and 624 nm. MS (FAB) *m/z* 829 ($M+H^+$).

1b: ^1H NMR ($CDCl_3$) δ=10.14+10.05 (2H+1H, s+s, *meso*-H), 7.69+7.64 (1H+1H, s+s, CH=N), 7.91+7.68+7.45+7.3+7.18+6.62 (7H, dd+d+d+d+m+t, Ar-H), 4.06 (4H, t, Bu), 3.63+3.53+2.62 (6H+10H+6H, s+s+s, β-Me and NCH_2), 2.30+1.80+1.15 (4H+4H+6H, m+m+t, Bu). UV-vis (CH_2Cl_2) 407, 535, and 571 nm.

Salen-Linked Porphyrin 2a. From the salicylaldehyde-linked porphyrin **12** (5.0 mg, 0.007 mmol, in CH_2Cl_2 20 ml), the salen-linked porphyrin **2a** was synthesized by the same procedure as described above to give purple crystals (2.7 mg, 0.003 mmol, 42%).

2a: ^1H NMR ($CDCl_3$) δ=10.14+9.95 (2H+1H, s+s, *meso*-H), 7.86+7.58 (1H+1H, s+s, CH=N), 7.73+7.41+7.13+6.95+6.54 (6H, s+s+m+d+t, Ar-H), 4.04 (4H, t, Bu) 3.63+3.53+2.77 (6H+6H+6H, s+s+s, β-Me), 3.6 (4H, m, NCH_2), 2.26+1.75+1.11 (4H+4H+6H, m+m+t, Bu), 0.94 (3H, s, CH_3CO), −3.30 (2H, br, NH). UV-vis (CH_2Cl_2) 405, 503, 537, 572, and 625 nm.

2b: ^1H NMR ($CDCl_3$) δ=10.14+10.05 (2H+1H, s+s, *meso*-H), 7.88+7.62 (1H+1H, s+s, CH=N), 7.78+7.41+7.13+6.95+6.54 (6H, s+s+m+d+t, Ar-H), 4.06 (4H, t, Bu) 3.63+3.53+2.77 (6H+6H+6H, s+s+s, β-Me), 3.58 (4H, m, NCH_2), 2.28+1.78+1.13 (4H+4H+6H, m+m+t, Bu), 0.80 (3H, s, CH_3CO). UV-vis (CH_2Cl_2) 407, 535, and 571 nm.

Salen-Bridged Dimeric Porphyrin 3a. The salicylaldehyde-linked porphyrin **7** (8.9 mg, 0.014 mmol) was dissolved in CH_2Cl_2 (20 ml) and ethylenediamine (0.15 M solution in methanol, 50 µl) was added. The solution was stirred for 2 weeks. Evaporation of the solvent and subsequent recrystallization (CH_2Cl_2–methanol) gave the porphyrin **3a** as purple crystals (8 mg, 0.006 mmol, 88%).

3a: ^1H NMR ($CDCl_3$) δ=10.13+9.96 (4H+2H, s+s, *meso*-H), 8.68 (2H, s, CH=N), 8.01+7.40 (4H+2H, m+d, Ar-H), 4.17 (4H, s, NCH_2), 4.05 (8H, t, Bu), 3.62+3.47+2.56 (12H+12H+12H, s+s+s, β-Me), 2.29+1.78+1.13 (8H+8H+12H, m+m+t, Bu), −3.2 (4H, br, NH). UV-vis (CH_2Cl_2) 405, 503, 536, 570, and 623 nm. MS (FAB) *m/z* 1278 ($M+H^+$).

3b: ^1H NMR ($CDCl_3$) δ=10.17+9.95 (4H+2H, s+s, *meso*-H), 7.77 (2H, s, CH=N), 7.89+7.76+7.57 (2H+2H+2H, dd+d+d, Ar-H), 4.05 (8H, t, Bu), 3.65+3.57+2.69 (12H+12H+12H, s+s+s, β-Me), 3.6 (4H, br, NCH_2), 2.29+1.78+1.14 (8H+8H+12H, m+m+t, Bu), −3.23 (4H, br, NH). UV-vis

(CH_2Cl_2) 406, 503, 536, 571, and 623 nm. MS (FAB) *m/z* 1333—1338 ($M+H^+$).

3c: UV-vis (CH_2Cl_2) 408, 535, and 571 nm. MS (FAB) *m/z* 1457—1464 ($M+H^+$).

Salen-Bridged Dimeric Porphyrin 4a. The salicylaldehyde-linked porphyrin **12** (8.8 mg, 0.013 mmol) was treated with ethylenediamine (0.15 M solution in methanol, 40 μl) by the same procedure as **3a** to give purple crystals (8 mg, 0.006 mmol, 88%).

4a: ^1H NMR ($CDCl_3$) δ=13.46 (2H, br, OH), 10.15+9.98 (4H+2H, s+s, *meso*-H), 8.84 (2H, s, CH=N), 7.79+7.62 (2H+2H, s+s, Ar-H), 4.31 (4H, s, NCH_2), 4.06 (8H, m, Bu), 3.63+3.52+2.75 (12H+12H+12H, s+s+s, β-Me), 2.27+1.76 +1.12 (8H+8H+12H, m+m+m, Bu), 0.95 (6H, s, CH_3CO), −3.18+−3.33 (4H, br, NH). MS (FAB) *m/z* 1392—1398 (M^+).

4b: ^1H NMR ($CDCl_3$) δ=10.04+9.85 (4H+2H, s+s, *meso*-H), 7.95(2H, s, CH=N), 7.64+7.45 (2H+2H, s+s, Ar-H), 3.96 (8H, m, Bu), 3.78(4H, s, NCH_2), 3.54+3.46+2.73 (12H+12H+ 12H, s+s+s, β-Me), 2.18+1.67+1.04 (8H+8H+12H, m+m+ m, Bu), 0.91 (6H, s, CH_3CO), −3.4 (4H, br, NH). UV-vis (CH_2Cl_2) 404, 503, 537, 572, and 624 nm. MS (FAB) *m/z* 1448—1455 (M^+).

4c: ^1H NMR ($CDCl_3$) δ=10.04+9.97 (4H+2H, s+s, *meso*-H), 7.96 (2H, s, CH=N), 7.65+7.45 (2H+2H, s+s, Ar-H), 3.98 (8H, m, Bu), 3.80 (4H, br, NCH_2), 3.55+3.47+2.74 (12H+12H+ 12H, s+s+s, β-Me), 2.20+1.69+1.06 (8H+8H+12H, m+m+ m, Bu), 0.81 (6H, s, CH_3CO). UV-vis (CH_2Cl_2) 404, 534, and 571 nm. MS (FAB) *m/z* 1572—1580 (M^+).

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