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# Synthesis of Benzochlorin Monomer, Dimer, and Porphyrin–Benzochlorin Heterodimer from 5-Aryl- and 5,15-Diaryl-octaethylporphyrins

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Vinylogous Vilsmeier formylation of nickel(II) 5,15-di-*p*-tolyl-octaethylporphyrin gave the corresponding *meso*-(2-formylvinyl)porphyrin, which, on treatment with trifluoroacetic acid, provided the corresponding benzochlorin derivative. In the case of the copper(II) complex, Lewis acid such as $BF_3 \cdot Et_2O$ and $SnCl_4$ catalyzed the cyclization to the benzochlorin without demetallation. Similar vinylogous Vilsmeier formylation of the nickel(II) and copper(II) complexes of 5-*p*-tolyloctaethylporphyrin resulted in the selective formation of 5-*p*-tolyl-10-(2-formylvinyl)porphyrin. Subsequent cyclization of these metal complexes took place with marked different regioselectivity; the nickel(II) complex favors the cyclization at near the 5-*p*-tolyl substituent, while the copper(II) complex favors the cyclization at the opposite site. Application of these synthetic methods to the 4,4′-biphenylylene-bridged diporphyrin led to the synthesis of porphyrin–benzochlorin heterodimer and benzochlorin homodimer. The steady-state fluorescence spectrum of free base form of the heterodimer suggested the intramolecular singlet excitation energy transfer from the porphyrin to the benzochlorin.

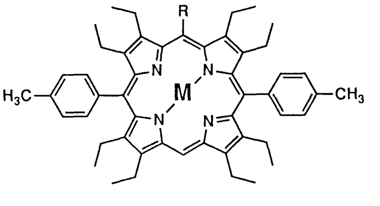
The appearance of the X-ray structure of bacterial photosynthetic reaction center has stimulated a wide range of synthetic modelling approaches towards this natural charge separation apparatus. Among these, a host of conformationally flexible or restricted porphyrin dimers and oligomers have been prepared with a view to studying intramolecular energy and electron transfer reactions and electronic interactions of porphyrin π-systems.1–9) Recently, much attention has been paid to conformationally restricted models,1,3,5–9) since it is obviously of mechanistic importance to correlate the rates of energy and electron transfer reactions with geometrical parameters such as distances and orientations, and this can be done better with models with well-defined geometries.

Recently we reported a series of porphyrin dimers, trimers, tetramers, and even pentamers involving 5-aryl- and 5,15-diaryloctaalkylporphyrins as a building block.5–7) One of key stereochemical features incorporated in these models is a restricted geometry of porphyrins which is brought about from steric hindrance between the bridging aromatic spacer and the neighboring peripheral alkyl substituents.8) In the course of our research program aiming at construction of artificial photosynthetic reaction center, we need conformationally restricted chlorin dimers and porphyrin–chlorin heterodimers as a rational extension of our porphyrin models. To the best of our knowledge, only a few examples of such compounds have appeared in the literature so far.9)

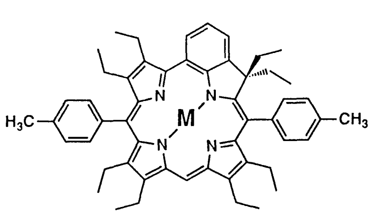
Recent papers by Smith et al. have described the transformation of nickel(II) complexes of octaalkylporphyrin to the corresponding *meso*-(2-formylvinyl)-porphyrins.10) On treatment with strong acids, these nickel(II) complexes were converted into the corresponding benzochlorin derivatives.10,11) Synthesis of benzochlorins and related purpurins pigments have attracted considerable interests from the viewpoint of the development of new green sensitizers effective for photodynamic therapy of tumors. A quite recent paper12) which described the extension of this strategy to the 5,15-diaryloctaalkylporphyrin system prompted us to report our own results on the synthesis of benzochlorin compounds from 5-*p*-tolyl- and 5,15-di-*p*-tolyl-octaethylporphyrins as well as the synthesis of porphyrin–benzochlorin heterodimer and benzochlorin homodimer.

## Results and Discussion

**Synthesis of Benzochlorin from 5,15-Ditolyloctaethylporphyrin.** Nickel(II) and copper(II) complexes of 5,15-di-*p*-tolyloctaethylporphyrin **1(H₂)**13) were treated with 3-(dimethylamino)acrylaldehyde and $POCl_3$14) to give the corresponding metal complexes of



1(M) R = H ; M = Ni, Cu
2(M) R = CH=CH-CHO ; M = Ni, Cu, $H_2$



3(Ni) M = Ni
3(Cu) M = Cu
3($H_2$) M = $H_2$

*meso*-(2-formylvinyl)porphyrin **2(Ni)** and **2(Cu)**, in yields of 65 and 60%, respectively. The porphyrin **2(Ni)** underwent cyclization to the corresponding benzochlorin **3(Ni)** with an aid of trifluoroacetic acid (TFA)-catalysis, similarly to the results reported by Gunter.[12] We tried this cyclization reaction in neat TFA, TFA–$CH_2Cl_2$, (1 : 1) and TFA–AcOH (1 : 1), and noted that virtually the similar yield of **3(Ni)** was obtained in each solvent system. Since it was difficult to remove the central nickel(II) ion from **3(Ni)**,[10,15] we attempted the acid-catalyzed cyclization of **2(Cu)** to **3(Cu)** under a variety of conditions using TFA, trichloroacetic acid, $H_2SO_4$ or even in the presence of excess amounts of Cu(II) ion.[16] In all cases attempted, demetallation of copper(II) ion from **2(Cu)** took place readily and the free base **2(H₂)** was recovered. The free base porphyrin **2($H_2$)** did not cyclize on further treatment with acid. This was also noted by Smith[10] and Gunter.[12] However, we found that Lewis acids such as $BF_3 \cdot Et_2O$ and $SnCl_4$ were effective for the cyclization of **2(Cu)** to **3(Cu)**. Thus, on treatment with $BF_3 \cdot Et_2O$ or $SnCl_4$ in $CH_2Cl_2$ under nitrogen at room temperature for 2 h, **2(Cu)** underwent smooth cyclization to form **3(Cu)**, which in turn was relatively easily demetallated to afford the free base form **3($H_2$)** with a 1 : 1 mixture of TFA and $H_2SO_4$ for 3 h at room temperature. The Lewis acid-induced cyclization of the copper complexes may constitute a new synthetic route to the free base form of benzochlorin derivatives.

In Fig. 1, the absorption spectra of **3($H_2$)** and **3(Ni)** in $CH_2Cl_2$ were presented. The benzochlorin **3($H_2$)** exhibits Soret band at 420 nm and Qy-band at 672 nm, while the nickel complex **3(Ni)** displays Soret band at 436 nm and Qy-band at 701 nm. The fluorescence peak of **3($H_2$)** was observed at 690 nm, indicating its excitation energy (*E*($S_1$)) of the lowest singlet excited state to be ca. 1.82 eV.

**Synthesis of Benzochlorin from 5-*p*-Tolyloctaethylporphyrin.** Vinylogous Vilsmeier formylation of the nickel(II) 5-*p*-tolyloctaethyl-porphyrin **4(Ni)** with 3-(dimethylamino)acrylaldehyde and $POCl_3$ produced regioselectively the corresponding 10-(2-formylvinyl)-substituted product **5(Ni)** (53% yield) along with the 15-(2-formylvinyl)-subsituted product **6(Ni)** (8% yield).[17] A slightly higher regioselectivity was observed in the reaction of **4(Cu)**, i.e., the yields of **5(Cu)** and **6(Cu)** from **4(Cu)** were 60 and 6% respectively. The acid-catalyzed cyclizations of **5(Ni)** and **5(Cu)** to the corresponding benzochlorin derivatives were studied with TFA, $BF_3 \cdot Et_2O$, and $SnCl_4$, and the results were summarized in Table 1. Interestingly, the regioselectivity of the cyclization was quite dependent on the central metal. The nickel complex **5(Ni)** gave benzochlorin

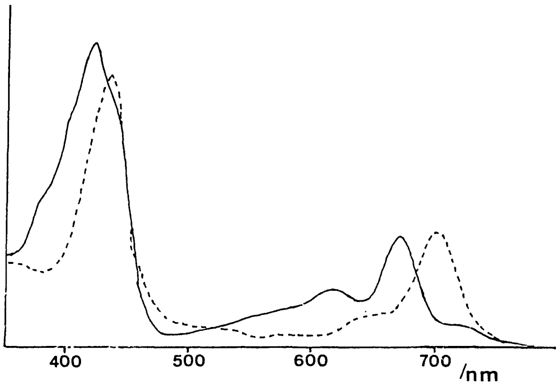
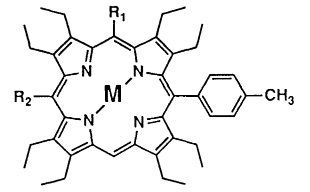


Fig. 1. Absorption spectra of **3(Ni)** (dashed line) and **3($H_2$)** (solid line) in $CH_2Cl_2$.

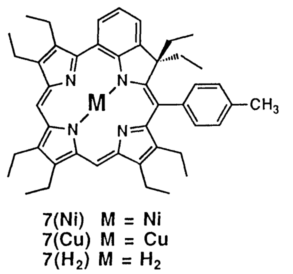
Table 1. Lewis Acid Catalyzed Cyclization of **5(Ni)** and **5(Cu)**

| Compound | Acid | **7**/**8**[a] | Total yield/% |
|---|---|---|---|
| 5(Ni) | TFA | >95/<5 | 66 |
| 5(Ni) | $SnCl_4$ | >95/<5 | 33 |
| 5(Ni) | $BF_3 \cdot Et_2O$ | 88/12 | 51 |
| 5(Cu) | TFA | Demetallated | |
| 5(Cu) | $SnCl_4$ | 12/88[b] | 43 |
| 5(Cu) | $BF_3 \cdot Et_2O$ | 29/71[b] | 61 |

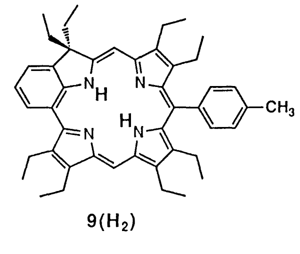
a) The ratios of **7**/**8** were determined from the $^1$H NMR signals. b) These ratios were **7($H_2$)**/**8($H_2$)** and were determined by the $^1$H NMR analysis of the products after demetallation of **7(Cu)** and **8(Cu)**.



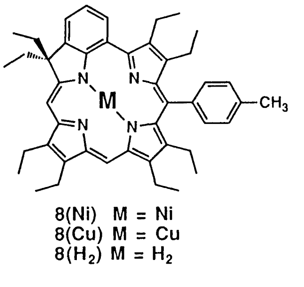
4(M) $R_1 = R_2 = H$ ; M = Ni, Cu, $H_2$
5(M) $R_1$ = CH=CH-CHO, $R_2$ = H ; M=Ni, Cu, $H_2$
6(M) $R_1$ = H, $R_2$ = CH=CH-CHO ; M=Ni, Cu, $H_2$
10(M) $R_1$ = CHO, $R_2$ = H ; M = Ni, Cu, $H_2$
11(M) $R_1$ = H, $R_2$ = CHO ; M = Ni, Cu, $H_2$



7(Ni) M = Ni
7(Cu) M = Cu
7($H_2$) M = $H_2$



9($H_2$)



8(Ni) M = Ni
8(Cu) M = Cu
8($H_2$) M = $H_2$

**7(Ni)** preferentially over **8(Ni)**. More than 20 : 1 regioselectivity was achieved either with TFA or $\mathrm{SnCl_4}$ catalyst, while the use of $\mathrm{BF_3 \cdot OEt}$ tended to drop the selectivity to 7.3 : 1. In sharp contrast, Lewis acid-mediated cyclization of **5(Cu)** provided **8(Cu)** over **7(Cu)** with selectivity of 7.3 : 1—2.3 : 1. Thus, the nickel(II) complex favors the cyclization near the *meso*-aryl substituent, while the copper(II) complex favors the cyclization at the opposite site. Quite different regioselectivity observed in these electrophilic cyclization reactions seems to reflect different electronic densities at the 10- and 15-positions of **5(Ni)** and **5(Cu)**. The free-base benzochlorins **7($\mathrm{H_2}$)** and **8($\mathrm{H_2}$)** were readily prepared from **7(Cu)** and **8(Cu)**, respectively, in a similar manner with **3(Cu)**.

Since the yield of **6(Ni)** was rather low and separation of **6(Ni)** from **5(Ni)** in a pure state was found to be difficult, we tried to prepare **6(Ni)** by a different synthetic route. First, Vilsmeier formylation of **4(Ni)** or **4(Cu)** yielded 10-formyl substituted product **10** and 15-substituted product **11**. The yield of **10(Ni)** and **11(Ni)** were 61 and 30%, and **10(Cu)** and **11(Cu)** were obtained in yields of 63 and 21%, respectively. After demetallation, the free base compounds **10($\mathrm{H_2}$)** and **11($\mathrm{H_2}$)** were easily separated by chromatography. The nickel(II) complex **11(Ni)** was transformed into **6(Ni)** by the procedure developed by Arnold et al.[11] Upon treating with TFA, **6(Ni)** provided **9($\mathrm{H_2}$)** directiy in 57% yield. The central nickel(II) ion was demetallated under the cyclization conditions in this case, in contrast to **3(Ni)** and **7(Ni)**.

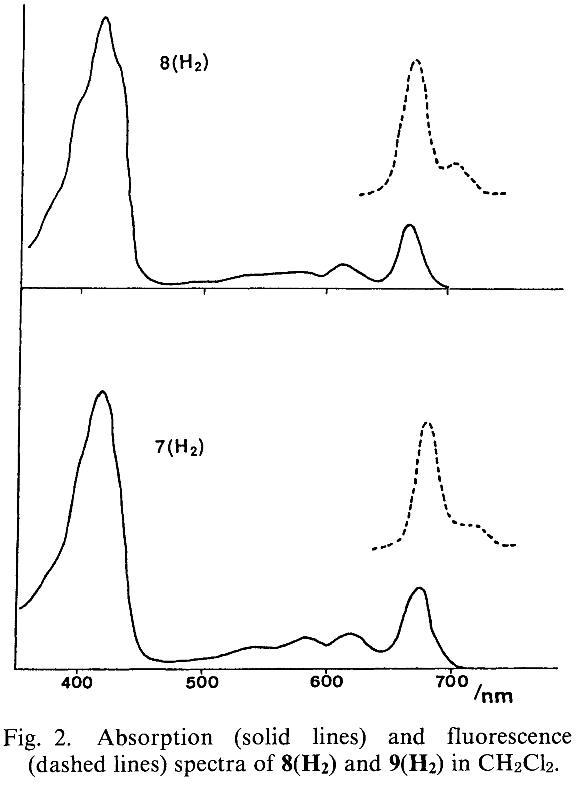
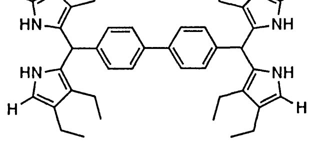


Fig. 2. Absorption (solid lines) and fluorescence (dashed lines) spectra of **8($\mathrm{H_2}$)** and **9($\mathrm{H_2}$)** in $\mathrm{CH_2Cl_2}$.

In Fig. 2, the absorption and fluorescence spectra of **7($\mathrm{H_2}$)** and **8($\mathrm{H_2}$)** in $\mathrm{CH_2Cl_2}$ were presented. The free base benzochlorins **7($\mathrm{H_2}$)** and **8($\mathrm{H_2}$)** display Soret band at 417 and 419 nm, and Q-bands at 581, 617, and 672 nm and at 607 and 662 nm, respectively, while the fluorescence emission spectra exhibit peaks at 680 and 730 (shoulder) nm for **7($\mathrm{H_2}$)** and at 668 and 718 nm for **8($\mathrm{H_2}$)**, respectively. On the basis of these spectral data, the excitation energy was estimated to be ca. 1.83 eV for **7($\mathrm{H_2}$)** and 1.87 eV for **8($\mathrm{H_2}$)**, respectively. The fluorescence lifetimes of **7($\mathrm{H_2}$)** and **8($\mathrm{H_2}$)**, which have been determined by single photon counting technique to be 7.8 and 7.3 ns, respectively, are shorter than that of **4($\mathrm{H_2}$)** (10.4 ns) but longer than that of pyropheophorbide pigments (5.8—6.0 ns).[19]

**Synthesis of Porphyrin-Benzochlorin Heterodimer and Benzochlorin Homodimer.** 4,4′-Biphenylylene-bridged diporphyrin **12($\mathrm{H_2}$–$\mathrm{H_2}$)** was synthesized by Chang's method from the tetrapyrrole **13** and the bis(5-formyl-2-pyrrolyl)methane **14**. Subsequent partial metallation with Ni(II) acetate or Cu(II) acetate provided the corresponding mono-metallated diporphyrins **12(Ni–$\mathrm{H_2}$)** and **12(Cu–$\mathrm{H_2}$)**, respectively, which were treated with 3-(dimethylamino)acrylaldehyde and $\mathrm{POCl_3}$ gave mono *meso*-(2-formylvinyl) substituted diporphyrins **15(Ni–$\mathrm{H_2}$)** and **15(Cu–$\mathrm{H_2}$)**, respectively. The TFA-induced cyclization of **15(Ni–Ni)** afforded benzochlorin–porphyrin heterodimer **16(Ni–Ni)**, and the $\mathrm{BF_3 \cdot Et_2O}$ catalyzed reaction of **15(Cu–Cu)** gave



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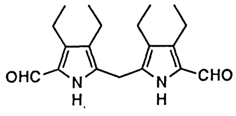

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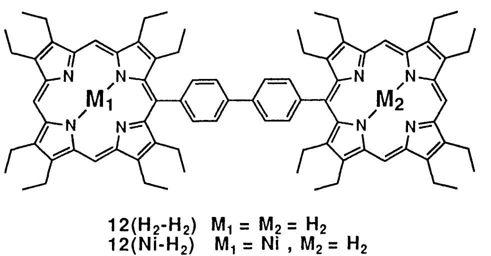
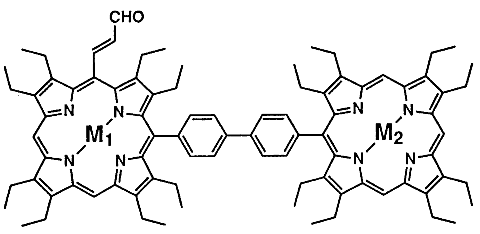
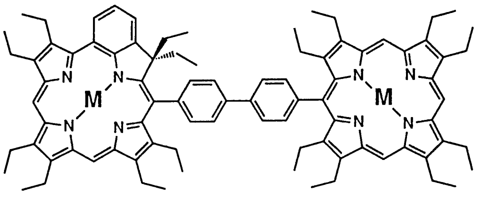


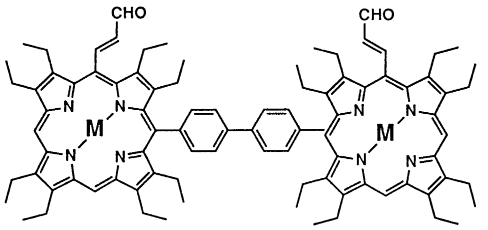
12($\mathrm{H_2}$-$\mathrm{H_2}$) $\mathrm{M_1 = M_2 = H_2}$
12(Ni-$\mathrm{H_2}$) $\mathrm{M_1}$ = Ni , $\mathrm{M_2 = H_2}$
12(Cu-$\mathrm{H_2}$) $\mathrm{M_1}$ = Cu , $\mathrm{M_2 = H_2}$
12(Ni-Ni) $\mathrm{M_1 = M_2}$ = Ni
12(Cu-Cu) $\mathrm{M_1 = M_2}$ = Cu



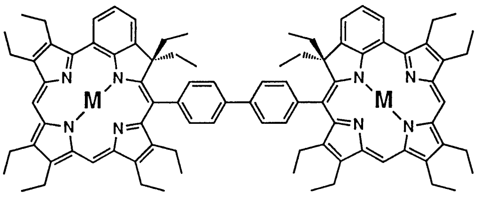
15(Ni-H$_2$) $M_1$ = Ni , $M_2$ = H$_2$
15(Cu-H$_2$) $M_1$ = Cu, $M_2$ = H$_2$
15(Ni-Ni) $M_1$ = $M_2$ = Ni
15(Cu-Cu) $M_1$ = $M_2$ = Cu



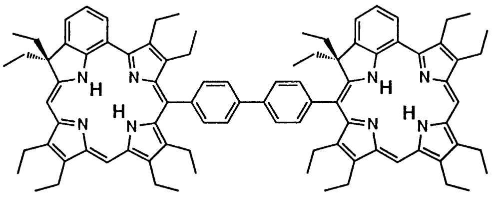
16(Ni-Ni) M = Ni
16(H$_2$-H$_2$) M = H$_2$



17(Ni-Ni) M = Ni
17(Cu-Cu) M = Cu



18(Ni-Ni) M = Ni
18(H$_2$-H$_2$) M = H$_2$



19(H$_2$-H$_2$)

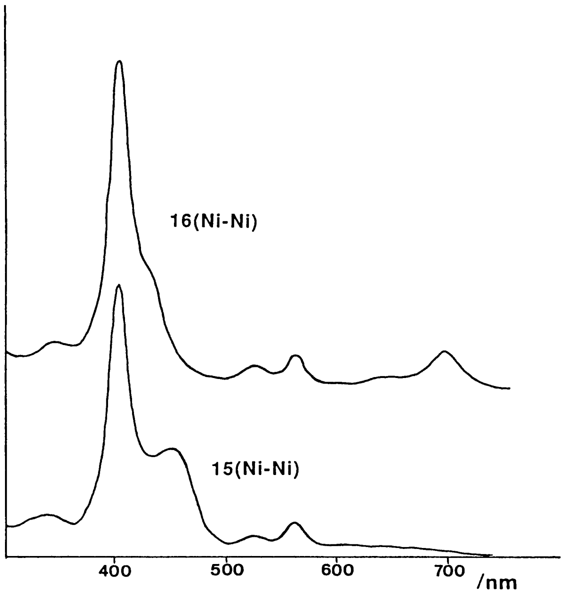


Fig. 3. Absorption spectra of **15(Ni-Ni)** and **16(Ni-Ni)** in CH$_2$Cl$_2$.

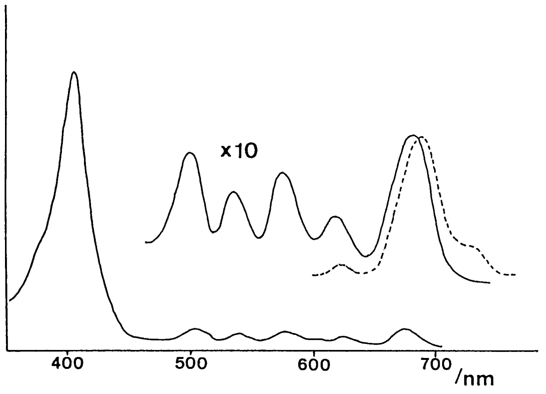


Fig. 4. Absorption (solid line) and fluorescence (dashed line) spectra of **16(H$_2$-H$_2$)** in CH$_2$Cl$_2$.

**16(Cu-Cu)**. Upon treatment with H$_2$S/TFA, the latter cyclization product gave the free base form of porphyrin-benzochlorin hybrid dimer **16(H$_2$-H$_2$)**.

Finally, benzochlorin dimers **18(Ni-Ni)**, **18(H$_2$-H$_2$)**, and **19(H$_2$-H$_2$)** were prepared as follows. The vinylogous Vilsmeier formylation of **12(Cu-Cu)** gave **17(Cu-Cu)**, which was converted to **17(Ni-Ni)**. The dinickel complex **17(Ni-Ni)** was cyclized with an aid of TFA to form **18(Ni-Ni)**, while the dicopper complex **17(Cu-Cu)**, on treatment with BF$_3$·Et$_2$O in CH$_2$Cl$_2$ followed by demetallation, provided two benzochlorin dimers **18(H$_2$-H$_2$)** and **19(H$_2$-H$_2$)** in a ratio of ca. 4 : 1.

In Fig. 3, the absorption spectra of **15(Ni-Ni)** and **16(Ni-Ni)** were shown. Both spectra can be nicely reproduced by the superposition of the respective components, indicating the electronic interactions in the ground state to be small. In Fig. 4, the absorption and fluorescence spectra of **16(H$_2$-H$_2$)** are presented. The fluorescence from the porphyrin is observed at 628 and 694 nm, and the fluorescence from the benzochlorin is observed at 680 and 730 nm. It should be noted here that the fluorescence from the porphyrin unit is substantially reduced, while the fluorescence from the benzochlorin unit is enhanced, suggesting the occurrence of the intramolecular energy transfer from the porphyrin to the benzochlorin. The preliminary measurement of the fluorescence lifetime of **16(H$_2$–H$_2$)** has revealed a rapidly decaying component with a lifetime of less than 1.5 ns at 630 nm, where the porphyrin moiety primarily emits, in line with the intramolecular singlet-singlet excitation energy transfer. More detailed time-resolved spectroscopic experiments on these models are being in progress and will be presented elsewhere.

## Experimental

**General.** Preparative separation were usually performed by flash column chromatography on silica gel (Merk, Kieselgel 60HF, Art 7739). Dichloromethane was distilled from P$_2$O$_5$ under N$_2$ before use. 1.2-Dichloroethane was distilled under N$_2$ and stored with Molecular Sieves 4A. *N,N*-Dimethylformamide (DMF) was distilled under reduced pressure and stored with Molecular Sieves 4A. Tetrahydrofuran (THF) was refluxed and distilled over sodium diphenylketyl and stored with Na wire. Other solvents and reagents were commercially available and were used as received.

The $^1$H NMR spectra were recorded on a JEOL JNM-GX-400 spectrometer, with tetramethylsilane as the internal reference. All $^1$H NMR spectra were measured in CDCl$_3$ solution. Mass spectra were recorded on a JEOL JMS-DX-300 or a JEOL JMS-HX-110 spectrometer, with positive FAB (fast atom bombardment) ionization method. The FAB matrix was *m*-nitrobenzyl alcohol/chloroform. UV-vis spectra were recorded in CH$_2$Cl$_2$ on a Shimadzu UV-160 or a Shimadzu UV-3000 spectrometer. Steady-state fluorescence spectra were recorded on a Shimadzu RF-502a spectrofluorimeter. Fluorescence lifetimes were measured on a HORIBA NAES 1100 model.

**Ni(II) 5,15-Di-*p*-tolyl-10-(2-formylvinyl)-2,3,7,8,12,13,17,18-octaethylporphyrin 2(Ni).** Phosphoryl chloride (POCl$_3$) (1.2 ml) was added dropwise to a solution of 3-(dimethylamino)acrylaldehyde (3-DMA) (2.5 ml) in 1,2-dichloroethane (15 ml) under N$_2$ atmosphere, and the resulting mixture was warmed to 50 °C and stirred for 30 min. Then to this mixture, a solution of **1(Ni)** (200 mg, 0.27 mmol) in 1,2-dichloroethane (50 ml) was added. The final mixture was stirred at 50 °C for 4 h. Saturated aqueous sodium acetate solution (200 ml) was then added, and the solution was stirred further for 4 h. The mixture was poured into water and extracted with CHCl$_3$. The combined organic layers were washed with water and dried over Na$_2$SO$_4$. After the solvent was removed by rotary evaporator, the residue was chromatographed on silica gel (elution with benzene) and the major green fraction was collected. After evaporation of the solvent, **2(Ni)** was recrystallized from CH$_2$Cl$_2$/MeOH. Yield: 138 mg (65%). Mp 223—224 °C. $^1$H NMR $\delta$=0.66, 0.83, 1.47, 1.54 (each t, 6H, 2×CH$_3$), 2.43 (overlapping q, 8H, 4×CH$_2$), 2.61 (s, 6H, ArCH$_3$), 3.51 (overlapping q, 8H, 4×CH$_2$), 5.77 (dd, 1H, vinyl H), 7.35 d, 4H, Ar H), 7.74 (d, 4H, Ar H), 9.01 (s, 1H, *meso* H), 9.13 (d, 1H, vinyl H), 9.73 (d, 1H, CHO). MS *m*/*z* 825 (M$^+$); UV-vis $\lambda_{\max}$ 458, 636 nm.

**Cu(II) 5,15-Di-*p*-tolyl-10-(2-formylvinyl)-2,3,7,8,12,13,17,18-octaethylporphyrin 2(Cu).** The same procedure was followed as for the synthesis of **2(Ni)**, using **1(Cu)** (200 mg, 0.26 mmol), 3-DMA (2.5 ml), POCl$_3$ (1.2 ml), and 1.2-dichloroethane (15 ml). Yield: 130 mg (60%). Mp 249—250 °C MS *m*/*z* 829 (M$^+$); UV-vis $\lambda_{\max}$ 455, 575, 636 nm.

**Ni(II) Di-*p*-tolyloctaethylbenzochlorin 3(Ni).** Solids of **2(Ni)** (34 mg, 0.041 mmol) were dissolved into TFA (10 ml), and the resulting solution was stirred for 2 h. The mixture was poured into water and extracted with CH$_2$Cl$_2$. The organic layer was successively washed with water, saturated aqueous NaHCO$_3$, and water, and dried over Na$_2$SO$_4$. After evaporation of the solvent, the residue was chromatographed on silica gel (elution with benzene) and the major first green fraction was collected. After evaporation of the solvent, **3(Ni)** was recrystallized from CH$_2$Cl$_2$/hexane. Yield: 14.8 mg (44%). Mp 172—173 °C. $^1$H NMR $\delta$=0.03 (t, 6H, 2×CH$_3$), 0.54, 0.56, 0.85 (each t, 3H, CH$_3$), 1.35—1.45 (overlapping t, 9H, 3×CH$_3$), 1.78, 2.02, 2.11, 2.24 (each q, 2H, CH$_2$), 2.55, 2.88 (each s, 3H, ArCH$_3$), 3.21 (overlapping q, 6H, 3×CH$_2$), 7.25, 7.31 (each d, 2H, Ar H), 7.41 (d, 1H, benzo H), 7.56 (t, 1H, benzo H), 7.63, 7.66 (each d, 2H, Ar H), 8.20 (s, 1H, *meso* H), 8.48 (d, 1H, benzo H). MS *m*/*z* 809 (M$^+$); UV-vis $\lambda_{\max}$ 436, 701 nm.

**Cu(II) Di-*p*-tolyloctaethylbenzochlorin 3(Cu).** To a solution of **2(Cu)** (10.4 mg, 0.0125 mmol) in CH$_2$Cl$_2$ (3 ml), BF$_3$·Et$_2$O (47% ether solution) (0.012 ml) was added under N$_2$ atmosphere. The mixture was stirred for 2 h at room temperature. Work-up and purification were followed as for the synthesis of **3(Ni)**. Yield: 5.3 mg (52%). MS *m*/*z* 813 (M$^+$); UV-vis $\lambda_{\max}$ 463, 632 nm.

**5,15-Di-*p*-tolyl-10-(2-formylvinyl)-2,3,7,8,12,13,17,18-octaethylporphyrin 2(H$_2$).** The same procedure as for the synthesis of **3(Ni)** was attempted in order to cyclize **2(Cu)**, but in this case demetallation proceeded smoothly and the corresponding free base **2(H$_2$)** was obtained without purification with chromatography. Starting from **2(Cu)** (10.4 mg, 0.012 mmol), we got 5.8 mg (63%) of **2(H$_2$)**. Mp 110—111 °C. $^1$H NMR $\delta$=−0.47 (br, 2H, 2×-NH), 0.56, 0.80, 1.25, 1.54 (each t, 6H, 2×CH$_3$), 2.36, 2.55 (each q ,4H, 2×CH$_2$), 2.71 (s, 6H, ArCH$_3$), 3.35, 3.62 (each q, 4H, 2×CH$_2$), 6.63 (dd, 1H, vinyl H), 7.47 (d, 4H, Ar H), 8.00 (d, 4H, Ar H), 9.35 (d, 1H, vinyl H), 10.03 (d, 1H, CHO). MS *m*/*z* 796 (M$^+$+1); UV-vis $\lambda_{\max}$ 442, 580, 700 nm.

**Di-*p*-tolyloctaethylbenzochlorin 3(H$_2$).** The copper complex **3(Cu)** (32.4 mg, 0.040 mmol) was dissolved in a mixture of TFA (2 ml) and concentrated H$_2$SO$_4$ (2 ml). The resulting mixture was stirred for 3 h at room temperature. Then the mixture was neutralized with saturated aqueous NaHCO$_3$, extracted with CH$_2$Cl$_2$. The combined organic layers were washed with water and dried over Na$_2$SO$_4$. After evaporation of the solvent, the residue was chromatographed on silica gel (elution with benzene) and the major second blue fraction was collected (the first minor green fraction was unreacted **3(Cu)**). After evaporation of the solvent, **3(H$_2$)** was recrystallized from CH$_2$Cl$_2$/hexane. Yield: 16.5 mg (56%). Mp 84—85 °C. $^1$H NMR $\delta$=0.07, (t, 6H, 2×CH$_3$), 0.59, 0.77, 0.79, 1.26, 1.35, 1.47 (each, t, 3H, CH$_3$), 1.85, 2.06, 2.10 (each q, 2H, CH$_2$) 2.14, (q, 4H, 2×CH$_2$), 2.56, 2.59 (each s, 3H, ArCH$_3$), 3.12 (q, 4H, 2×CH$_2$), 3.16 (q, 2H, CH$_2$), 7.27, 7.34 (each d, 2H, Ar H), 7.50 (d, 1H, benzo H), 7.61 (t, 3H, benzo H), 7.69, 7.76 (each d, 2H, Ar H), 7.76 (s, 1H, *meso* H), 8.65 (d, 1H, benzo H). MS *m*/*z* 753 (M$^+$+1); UV-vis $\lambda_{\max}$ 420, 618, 672 nm.

**Ni(II) 5-*p*-Tolyl-10-(2-formylvinyl)-2,3,7,8,12,13,17,18-octaethylporphyrin 5(Ni).** The same procedure was followed as for synthesis of **2(Ni)**, using **4(Ni)** (100 mg, 0.147 mmol), 3-DMA (2.0 ml), and POCl$_3$ (0.9 ml). The reaction mixture was chromatographed on silica gel (elution with $CH_2Cl_2$) and the major green fraction was collected. After the solvent was evaporated, recrystallization from $CH_2Cl_2$/MeOH gave the dark green crystals (65.8 mg, 61%), consisting of a mixture of **5(Ni)** and **6(Ni)**. Then this mixture was chromatographed again on silica gel (elution with benzene) and the slowly eluting broad band with green color was collected. After evaporation of the solvent, **5(Ni)** was recrystallized from $CH_2Cl_2$/MeOH. Yield: 45.3 mg (42%). Mp 224—225 °C. $^1$H NMR $\delta$=0.46, 1.02, 1.54, 1.57 (each t, 3H, $CH_3$), 1.63—1.76 (overlapping t, 12H, $4\times CH_3$), 2.46 (q, 4H, $CH_2$), 2.62 (s, 3H, $ArCH_3$), 3.49, 3.54 (each q, 2H, $CH_2$), 3.65 (overlapping q, 6H, $3\times CH_2$), 3.80, (q, 2H, $CH_2$), 5.63 (dd, 1H, vinyl H), 7.34, 7.75 (each d, 2H, ArH), 9.04, 9.14 (each s, 1H, *meso* H), 9.24 (d, 1H, vinyl H), 9.73 (d, 1H, CHO). MS *m*/*z* 735 ($M^+$); UV-vis $\lambda_{max}$454, 620 nm.

**Cu(II) 5-*p*-Tolyl-10-(2-formylvinyl)-2,3,7,8,12,13,17,18-octaethylporphyrin 5(Cu).** The same procedure was followed as for the synthesis of **5(Ni)**, using **4(Cu)** (100 mg, 0.146 mmol). We got a mixture of **5(Cu)** and **6(Cu)** (72 mg, 66%), which was chromatographed again, giving **5(Cu)**. Yield: 48.6 mg (45%). Mp 199—200 °C. MS *m*/*z* 740 ($M^+$); UV-vis $\lambda_{max}$ 448, 619 nm.

**5-*p*-Tolyl-10-(2-formylvinyl)-2,3,7,8,12,13,17,18-octaethylporphyrin 5($H_2$).** The same procedure was followed as for the synthesis of **3($H_2$)**, using **5(Cu)** (48.6 mg, 0.066 mmol), and TFA (5 ml). Yield: 37.4 mg (84%). Mp 124—125 °C. $^1$H NMR $\delta$=0.28, 0.90, 0.99, 1.52, 1.68, 1.73, 1.77, 1.82 (each t, 3H, $CH_3$), 2.17, 2.63 (each q, 2H, $CH_2$), 2.70 (s, 3H, $ArCH_3$), 3.17 (q, 2H, $CH_2$), 3.68 (overlapping q, 4H, $2\times CH_2$), 3.84, 3.94 (each q, 2H, $2\times CH_2$), 6.37 (dd, 1H, vinyl H), 7.48, 7.99 (each d, 2H, Ar H), 9.07, 9.30 (each s, 1H, *meso* H), 9.55 (d, 1H, vinyl H), 9.94 (d, 1H, CHO). MS *m*/*z* 679 ($M^+$+1); UV-vis $\lambda_{max}$ 450, 633, 668 nm.

**Ni(II) *p*-Tolyloctaethylbenzochlorin 7(Ni).** The same procedure was followed as for the synthesis of **3(Ni)**, using **5(Ni)** (26 mg, 0.036 mmol), and TFA (5 ml). Yield: 18.6 mg (72%). Mp 83—84 °C. $^1$H NMR $\delta$=0.01 (t, 6H, $2\times CH_3$), 0.60 (t, 3H, $CH_3$), 1.46—1.65 (overlapping t, 15H, $5\times CH_3$), 1.84, 2.12, 2.26 (each 2H, $CH_2$), 2.54 (s, 3H, $ArCH_3$), 3.22, 3.47, 3.56 (each q, 2H, $CH_2$), 3.40 (overlapping q, 4H, $2\times CH_3$), 7.22, 7.59 (each d, 2H, Ar H), 7,53 (d, 1H, benzo H), 7.70 (t, 1H, benzo H), 8.38, 8.74 (each s, 1H, *meso* H), 8.76 (d, 1H, benzo H). MS *m*/*z* 718 ($M^+$); UV-vis $\lambda_{max}$ 347, 429, 657, 692 nm. Since an isomeric product **8(Ni)** was formed in quite a low amount and it was difficult to separate **8(Ni)** from **7(Ni)**, the characterization of **8(Ni)** was only done by $^1$H NMR and mass analyses of the mixture of **7(Ni)** and **8(Ni)**. Most of the $^1$H NMR signals of **8(Ni)** were hindered in signals due to the major isomer **7(Ni)**, so only characteristic signals were reported; $^1$H NMR $\delta$=0.23 (t, 6H, $2\times CH_3$), 0.79 (t, 3H, $CH_3$), 0.83 (t, 3H, $CH_3$), 2.57 (s, 3H, $ArCH_3$). MS *m*/*z* 718 ($M^+$).

**Cu(II) *p*-Tolyloctaethylbenzochlorins 7(Cu) and 8(Cu).** The same procedure was followed as for the synthesis of **3(Cu)**, using **5(Cu)** (30 mg, 0.041 mmol), $CH_2Cl_2$ (10 ml), and Lewis acid (0.04 ml). We got a mixture of **7(Cu)** and **8(Cu)**. Yield 40—60%. MS *m*/*z* 723 ($M^+$).

***p*-Tolyloctaethylbenzochlorins 7($H_2$) and 8($H_2$).** The same procedure was followed as for the synthesis of **3($H_2$)**. The reaction mixture was chromatographed on silica gel (elution with benzene) and two blue bands were collected separately. The first fraction was **7($H_2$)** and the second fraction was **8($H_2$)**. Yield: 75—80%.

**7($H_2$).** $^1$H NMR $\delta$=0.00 (t, 6H, $2\times CH_3$), 0.90 (t, 3H, $CH_3$), 1.55—1.62 (overlapping t, $4\times CH_3$), 1.73 (t, 3H, $CH_3$), 1.98 (q, 2H, $CH_2$), 2.19 (overlapping q, 4H, $2\times CH_2$), 2.60 (s, 3H, $ArCH_3$), 3.46 (overlapping q, 6H, $3\times CH_2$), 3.64, 3.70 (each q, 2H, $CH_2$), 7.30, 7.78 (each d, 2H, Ar H), 7.70 (d, 1H, benzo H), 7.90 (t, 1H, benzo H), 8.36, 8.89 (each s, 1H, *meso* H), 9.23 (d, 1H, benzo H). MS *m*/*z* 663 ($M^+$+1); UV-vis $\lambda_{max}$ 417, 549, 581, 617, 672 nm.

**8($H_2$).** $^1$H NMR $\delta$=0.05 (t, 6H, $2\times CH_3$), 0.94, 1.08, 1.62, 1.70, 1.85 (each t, 3H, $CH_3$), 2.32, 2.51 (each q, 2H, $CH_2$), 2.65 (q, 4H, $2\times CH_2$), 2.63 (s, 3H, $ArCH_3$), 3.54 (q, 4H, $2\times CH_2$), 3.82, 3.94 (each q, 2H, $CH_2$), 7.36, 7.84 (each d, 2H, Ar H), 8.05 (d, 1H, benzo H), 8.07 (s, 1H, *meso* H), 8.12 (t, 1H, benzo H), 9.41 (s, 1H, *meso* H), 9.52 (d, 1H, benzo H). MS *m*/*z* 663 ($M^+$+1); UV-vis $\lambda_{max}$ 419, 579, 607, 662 nm.

**Ni(II) 5-*p*-Tolyl-10-formyl-2,3,7,8,12,13,17,18-octaethylporphyrin 10(Ni) and Ni(II) 5-*p*-Tolyl-15-formyl-2,3,7,8,12,13,17,18-octaethylporphyrin 11(Ni).** The synthetic methods developed by Inhoffen et al.[18)] were used for preparation of **10(Ni)**. Starting from **4(Ni)** (26.1 mg, 0.038 mmol), $POCl_3$ (0.7 ml), DMF (2.0 ml), and 1.2-dichloroethane (35 ml), we got a mixture of **10(Ni)** and **11(Ni)**. Yield: 24.7 mg (91%) of the mixture **10(Ni)** and **11(Ni)**. MS *m*/*z* 709 ($M^+$).

**10(Ni).** $^1$H NMR $\delta$=0.46, 0.99 (each t, 3H, $CH_3$), 1.51—1.80 (overlapping t, 18H, $6\times CH_3$), 2.40, 2.47 (each q, 2H, $CH_2$), 2.61 (s, 3H, $ArCH_3$), 3.50—3.59 (overlapping q, 4H, $2\times CH_2$), 3.60—3.65 (overlapping q, 6H, $3\times CH_2$), 3.74 (q, 2H, $CH_2$), 7.35, 7.74 (d, 2H, Ar H), 8.99, 9.13 (s, 1H, *meso* H), 11.42 (s, 1H, CHO).

**11(Ni).** $^1$H NMR $\delta$=0.98, 1.65 (each, 6H, $2\times CH_3$), 1.72—1.80 (overlapping t, 12H, $2\times CH_3$), 2.52 (q, 4H, $2\times CH_2$), 2.61 (s, 3H, $ArCH_3$), 3.50, 3.62, 3.71 (each q, 4H, $2\times CH_2$), 7.35, 7.72 (each d, 2H, Ar H), 9.07 (s, 2H, 2$\times$*meso* H), 11.60 (s, 1H, CHO).

**Cu(II) 5-*p*-Tolyl-10-formyl-2,3,7,8,12,13,17,18-octaethylporphyrin 10(Cu) and Cu(II) 5-*p*-Tolyl-15-formyl-2,3,7,8,12,13,17,18-octaethylporphyrin 11(Cu).** These copper complexes were prepared by the same method of the corresponding nickel complexes. Using **4(Cu)** (20.0 mg, 0.029 mmol), $POCl_3$ (0.25 ml), DMF (0.75 ml), and 1.2-dichloroethane (30 ml), we got a mixture **11(Cu)** and **12(Cu)**. Yield: 17.5 mg (84%). MS *m*/*z* 713 ($M^+$).

**5-*p*-Tolyl-10-formyl-2,3,7,8,12,13,17,18-octaethylporphyrin 10($H_2$) and 5-*p*-Tolyl-15-formyl-2,3,7,8,12,13,17,18-octaethylporphyrin 11($H_2$).** Mixture of **10(Cu)** and **11(Cu)** (22 mg, 0.031 mmol) was dissolved in TFA (5 ml) and stirred for 2 h. The mixture was poured into water and extracted with $CH_2Cl_2$. Combined organic layers were washed with saturated aqueous $NaHCO_3$ and water, and dried over $Na_2SO_4$. After the solvent was evaporated, the residue was chromatographed on silica gel (elution with $CH_2Cl_2$) and two green bands were collected separately. The first fraction was **11($H_2$)** and the second fraction was **11($H_2$)**. Each fraction was recrystallized from $CH_2Cl_2$/hexane after evaporation of the solvent. Yield: **10($H_2$)**: 13.0 mg (66%); **12($H_2$)**: 3.7 mg (19%).

**10($H_2$).** Mp 194—195 °C. $^1$H NMR $\delta$=−0.10 (br, 2H, $2\times NH$), 0.34, 0.86, 1.23, 1.53, 1.73, 1.78, 1.85, 1.91 (each t, 3H, $CH_3$), 2.21, 2.48 (each q, 2H, $CH_2$), 2.68 (s, 3H, $ArCH_3$), 3.28 (q, 2H, $CH_2$), 3.62—3.69 (overlapping q, 6H, $3\times CH_2$), 3.78, 3.85 (each q, 2H, $2\times CH_3$), 7.43, 7.96 (each d, 2H, Ar H), 9.12, 9.35 (each s, 1H, *meso* H), 11.83 (s, 1H, CHO). MS *m*/*z* 653 ($M^+$+1); UV-vis $\lambda_{max}$ 428, 609, 668 nm.

**11($H_2$).** Mp 220—221 °C. $^1$H NMR $\delta$=−1.62, −1.13, (each br, 1H, NH), 1.13, 1.73 (t, 6H, 2×$CH_3$), 1.78—1.82 (overlapping t, 12H, 4×$CH_3$), 2.71 (s, 3H, Ar$CH_3$), 2.73, 3.83, 3.90, 3.98 (each q, 4H, 2×$CH_2$), 7.46, 7.99 (each d, 2H, Ar H), 10.02 (s, 2H, 2×*meso* H), 12.58 (s, 1H, CHO). MS *m*/*z* 653 ($M^+$+1); UV-vis $\lambda_{max}$ 411, 510, 579, 637 nm.

**Ni(II) 5-*p*-Tolyl-15-(2-formylvinyl)-2,3,7,8,12,13,17,18-octaethylporphyrin 6(Ni).** Synthetic conditions were the same as Arnold et al.[11] except that equivalent molar amount of *n*-BuLi (1.5 M in hexane solution, 1 M=1 mol dm$^{-3}$) was used instead of PhLi (3 M in ether solution) and crude Ni-vinylporphyrin was used to the next reaction without purification. Starting from **11(Ni)** (20 mg, 0.028 mmol), Methyltriphenylphosphonium iodide (130 mg), 1.5 M butyllithium (0.25 ml), THF (10 ml), $POCl_3$ (0.6 ml), DMF (0.6 ml), and 1,2-dichloroethane (12 ml), we got **7(Ni)** (14.1 mg, 68%). $^1$H NMR $\delta$=0.89, 1.63, 1.65, 1.69 (each t, 6H, 2×$CH_3$), 2.57 (q, 4H, 2×$CH_2$), 2.61 (s, 3H, Ar$CH_3$), 3.60, 3.64, 3.68 (each q, 4H, 2×$CH_2$), 5.55 (dd, 1H, vinyl H), 7.36, 7.72 (each d, 2H, Ar H), 9.16 (s, 2H, 2×*meso* H), 9.46 (d, 2H, vinyl H), 9.77 (d, 2H, CHO). MS *m*/*z* 735 ($M^+$+1); UV-vis $\lambda_{max}$ 446, 609 nm.

***p*-Tolyloctaethylbenzochlorin 9($H_2$).** The same procedure was followed as for the synthesis of **3(Ni)**, using **6(Ni)** (14.1 mg, 0.019 mmol) and TFA (3 ml). Yield: 7.8 mg (57%). $^1$H NMR $\delta$=0.04 (t, 6H, 2×$CH_3$), 0.89, 1.04, 1.58, 1.66, 1.83 (each t, 3H, $CH_3$), 2.28, 2.51 (each q, 2H, $CH_2$), 2.63 (s, 1H, Ar$CH_3$), 3.54, 3.82, 3.93 (each q, 2H, $CH_2$), 4.23 (q, 4H, 2×$CH_2$), 7.36, 7.82 (each d, Ar H), 8.06 (d, 1H, benzo H), 8.08 (s, 1H, *meso* H), 8.10 (t, 1H, benzo H), 9.40 (s, 1H, *meso* H), 9.51 (d, 1H, benzo H). MS *m*/*z* 718 ($M^+$); UV-vis $\lambda_{max}$ 418, 542, 579, 608, 662 nm.

**4,4′-Bis(octaethyl-5-porphynyl)biphenyl 12($H_2$-$H_2$).** The tetrapyrrole **13** (1.17 g, 1.75 mmol) and bis(5-formyl-2-pyrrolyl)methane **14** (1.1 g, 3.5 mmol) were dissolved in $CH_2Cl_2$ (140 ml) and MeOH (350 ml). Then *p*-toluenesulfonic acid (7.7 g) was added to the mixture and the resulting mixture was stirred for 48 h in the dark. Then sodium acetate (8.4 g) and *o*-chloranil (1.4 g) were added and the mixture was stirred further for 4 h. Solvent was removed by rotary evaporator. The mixture was poured into water and extracted with $CHCl_3$. Combined organic layers were washed with water and dried over $Na_2SO_4$. To this solution, $Zn(OAc)_2$ in MeOH was added and the resulting mixture was refluxed for 1 h. The mixture was washed with water and dried over $Na_2SO_4$. After evaporation of the solvent, **12(Zn-Zn)** was recrystallized from $CH_2Cl_2$/MeOH. (Yield 485 mg, 21%). The dizinc complex **12(Zn-Zn)** was dissolved in $CH_2Cl_2$ and washed successively with 3 M-aqueous HCl, water and saturated aqueous $NaHCO_3$, and dried over $Na_2SO_4$. After evaporation of the solvent, **2($H_2$-$H_2$)** was recrystallized from $CH_2Cl_2$/MeOH quantitatively. Yield: 447 mg (21%).

**12(Zn-Zn).** $^1$H NMR $\delta$=1.39 (t, 12H, 4×$CH_3$), 1.92—2.03 (overlapping t, 36H, 12×$CH_3$), 3.04 (q, 8H, 4×$CH_2$), 4.09—4.18 (overlapping q, 24H, 12×$CH_3$), 8.36, 8.50 (each d, 4H, biphenyl H), 10.11 (s, 2H, *meso* H), 10.26 (s, 4H, 2×*meso* H).

**12($H_2$-$H_2$).** Mp>300 °C. $^1$H NMR $\delta$=−2.9 (br, 4H, 4×NH), 1.38 (t, 12H, 4×$CH_3$), 1.98 (overlapping t, 36H, 12×$CH_3$), 3.05 (q, 8H, 4×$CH_2$), 4.22 (overlapping q, 24H, 12×$CH_2$), 8.24, 8.49 (each d, 4H, biphenyl H), 9.96 (s, 2H, *meso* H), 10.22 (s, 4H, 2×*meso* H). MS *m*/*z* 1220 ($M^+$+2); UV-vis $\lambda_{max}$408, 505, 538, 572, 625 nm.

**4,4′-Mono-Ni(II) Bis-(octaethyl-5-porphynyl)biphenyl 12(Ni-$H_2$).** The free base diporphyrin **12($H_2$-$H_2$)** (46.8 mg, 0.038 mmol) was dissolved in $CHCl_3$ (50 ml). Then 0.75 equiv of $Ni(OAc)_2$ (7.1 mg, 0.029 mmol) was dissolved in a minimum amount of MeOH and was added to the above solution. The mixture was refluxed for 3 h and poured into water, extracted with $CHCl_3$. The combined organic layers were washed with water, and dried over $Na_2SO_4$. After evaporation of solvent, the residue was chromatographed on silica gel (elution with $CH_2Cl_2$). The second fraction was collected separately (the first fraction was **12(Ni-Ni)**). After the solvent was evaporated, **12(Ni-$H_2$)** was recrystallized from $CH_2Cl_2$/MeOH. Yield: 21.6 mg (44%). $^1$H NMR $\delta$=−3.05, −2.95 (each br, 1H, NH), 1.22, 1.30 (each t, 6H, 2×$CH_3$), 1.78, 1.91 (each overlapping t, 18H, 6×$CH_3$), 2.89, 3.00 (each q, 4H, 2×$CH_2$), 3.86, 4.10 (each overlapping q, 12H, 6×$CH_2$), 8.15, 8.18, 8.23, 8.41 (each d, 2H, biphenyl H), 9.54 (s, 1H, *meso* H), 9.61 (s, 2H, *meso* H), 9.95 (s, 1H, *meso* H), 10.21 (s, 2H, *meso* H). MS *m*/*z* 1276 ($M^+$+1); UV-vis $\lambda_{max}$ 407, 507, 560, 625 nm.

**4,4′-Mono-Cu(II) Bis-(octaethyl-5-porphynyl)biphenyl 12(Cu-$H_2$).** The same procedure was followed as for the synthesis of **13(Ni-$H_2$)**, using **13($H_2$-$H_2$)** (50 mg, 0.041 mmol), $Cu(OAc)_2$ (0.75 equiv, 5.6 mg, 0.031 mmol). Yield: 21.5 mg, (41%). MS *m*/*z* 1280 ($M^+$+1).

**4-[Ni(II)-octaethyl-5-porphynyl]-4′-[Ni(II)-octaethyl-20-(2-formylvinyl)-5-porphynyl]biphenyl 15(Ni-Ni).** The same reaction conditions were followed as for the synthesis of **2(Ni)**, but after the reaction mixture was washed with water and dried over $Na_2SO_4$, $Ni(OAc)_2$ in MeOH was added to the mixture and the resulting was refluxed for 3 h. After usual work up, the residue was chromatographed on silica gel (elution with $CH_2Cl_2$). The major brown fraction was collected. After evaporation of the solvent, **15(Ni-Ni)** was recrystallized from $CH_2Cl_2$/MeOH. Using **12(Ni-Ni)** (20.9 mg, 0.016 mmol), 3-DMA (0.3 ml), $POCl_3$ (0.15 ml), and 1,2-dichloroethane (35 ml). Yield: 17.8 mg (82%). Mp 274—275 °C. $^1$H NMR $\delta$=0.61 (t, 3H, $CH_3$), 1.05 (t, 6H, 2×$CH_3$), 1.18 (t, 3H, $CH_3$), 1.60—1.80 (overlapping t, 36H, 12×$CH_3$), 2.63 (q, 4H, 2×$CH_2$), 2.82 (q, 8H, 4×$CH_2$), 3.55—3.88 (overlapping q, 20H, 10×$CH_2$), 5.69 (dd, 1H, vinyl H), 8.06—8.08 (overlapping d, 6H, biphenyl H), 8.18 (d, 2H, biphenyl H), 9.08, 9.20 (each s, 1H, *meso* H), 9.29 (d, 1H, vinyl H), 9.53 (s, 1H, *meso* H), 9.59 (s, 2H, *meso* H), 9.77 (d, 1H, CHO). MS *m*/*z* 1386 ($M^+$); UV-vis $\lambda_{max}$ 338, 403, 451, 524, 560, 621 nm.

**4-[Cu(II)-octaethyl-5-porphynyl]-4′-[Cu(II)-octaethyl-20-(2-formylvinyl)-5-porphynyl]biphenyl 15(Cu-Cu).** The same procedure was followed as for the synthesis of **15(Ni-Ni)** using **12(Cu-Cu)** (23.0 mg, 0.017 mmol), 3-DMA (0.5 ml), $POCl_3$ (0.25 ml), and 1,2-dichloroethane (40 ml). Yield: 15.5 mg (65%). Mp>300 °C. MS *m*/*z* 1394 ($M^+$); UV-vis $\lambda_{max}$ 404, 445, 530, 565 nm.

**4-[Ni(II)-octaethyl-5-porphynyl]-4′-[Ni(II)-octaethylbenzochlorin-20-yl]-biphenyl 16(Ni-Ni).** The dinickel complex **15(Ni-Ni)** (9.8 mg, 0.007 mmol) was dissolved in TFA (5 ml) and $CH_2Cl_2$ (5 ml). The mixture was stirred for 2 h, then poured into water and extracted with $CH_2Cl_2$. The combined organic layers were washed with water and saturated aqueous $NaHCO_3$, and dried over $Na_2SO_4$. After evaporation of the solvent, the residue was chromatographed on silica gel (elution with $CH_2Cl_2$). The major brown fraction was collected. Yield: 5.6 mg (58%). $^1$H NMR $\delta$=0.12 (t, 6H, 2×$CH_3$), 0.78 (t, 3H, $CH_3$), 1.04 (t, 6H, 2×$CH_3$), 1.50—1.65 (overlapping t, 15H, 5×$CH_3$), 1.65—1.82 (overlapping t, 18H, 6×$CH_3$), 2.00, 2.41, 2.45 (each q, 2H, $CH_2$), 2.79 (q, 4H, 2×$CH_2$), 3.34—3.62

(overlapping q, 10H, 5×$CH_2$), 3.73—3.90 (overlapping q, 12H, 6×$CH_2$), 7.61 (d, 1H, benzo H), 7.75 (t, 1H, benzo H), 7.9 (overlapping d, 4H, biphenyl H), 8.01, 8.14 (each d, 2H, biphenyl H), 8.80 (d, 1H, benzo H), 8.45, 8.77, 9.52 (each 1H, *meso* H), 9.59 (s, 2H, *meso* H). MS *m*/*z* 1370 ($M^+$); UV-vis $\lambda_{max}$402, 524, 559, 694 nm.

**4-[Cu(II)-octaethyl-5-porphynyl]-4′-[Cu(II)-octaethylbenzochlorin-20-yl]-biphenyl 16(Cu–Cu).** The same procedure was followed as for the synthesis of **3(Cu)**, using **15(Cu–Cu)** (27 mg, 0.019 mmol), $BF_3 \cdot Et_2O$ (2 drops), and $CH_2Cl_2$ (20 ml). Yield: 13.9 mg (52%). MS *m*/*z* 1378 ($M^+$).

**4-(Octaethyl-5-porphynyl)-4′-(octaethylbenzochlorin-20-yl)biphennyl 16($H_2$–$H_2$).** The hybrid dicopper complex **16(Cu–cu)** (10.5 mg, 0.007 mmol) was dissolved into TFA (4 ml) saturated with $H_2S$ gas and stirred for 3 d. The mixture was poured into water and extracted with $CH_2Cl_2$. The combined organic layers were washed with water, saturated aqueous $NaHCO_3$, and dried over $Na_2SO_4$. After evaporation of the solvent, the residue was chromatographed on silica gel (elution with $CH_2Cl_2$). The second bluish purple fraction was collected (the first fraction was unreacted **16(Cu–Cu)**). Yield: 3.9 mg (41%). $^1$H NMR $\delta$=0.14 (t, 6H, 2×$CH_3$), 1.09 (t, 3H, $CH_3$), 1.23 (t, 6H, 2×$CH_3$), 1.51—1.65 (overlapping t, 12H, 4×$CH_3$), 1.78 (t, 3H, $CH_3$), 1.83—1.98 (overlapping t, 18H, 6×$CH_3$), 2.15 (q, 2H, $CH_2$), 2.43 (q, 6H, 3×$CH_2$), 2.99 (q, 4H, 2×$CH_2$), 3.41—3.58 (overlapping q, 4H, 2×$CH_2$), 3.65, 3.74 (each q, 2H, $CH_2$), 4.01—4.20 (overlapping q, 12H, 6×$CH_2$), 7.80 (d, 1H, benzo H), 7.97 (t, 1H, benzo H), 8.09 (d, 2H, biphenyl H), 8.16 (d. 4H, biphenyl H), 8.40 (d, 2H, biphenyl H), 8.45, 8.94 (each s, 1H, *meso* H), 9.30 (d, 1H, benzo H), 9.95 (s, 1H, *meso* H), 10.21 (s, 2H, 2×*meso* H). MS *m*/*z* 1258 ($M^+$+2); UV-vis $\lambda_{max}$ 407, 505, 538, 573, 622, 675 nm.

**4,4′-Bis-[Cu(II)-octaethyl-20-(2-formylvinyl)-5-porphynyl]-biphenyl 17(Cu–Cu).** The same procedure was followed as for the synthesis of **2(Cu)**, using **12(Cu–Cu)** (46.4 mg, 0.035 mmol), 3-DMA (0.8 ml), and $POCl_3$ (0.35 ml). Yield: 24.0 mg (48%). MS *m*/*z* 1448 ($M^+$).

**4,4′-Bis-[Ni(II)-octaethyl-20-(2-formylvinyl)-5-porphynyl]-biphenyl 17(Ni–Ni).** The dicopper complex **17(Cu–Cu)** (24.0 mg, 0.017 mmol) was dissolved in TFA (5 ml) and stirred for 2 h. The mixture was poured into water, extracted with $CH_2Cl_2$. The combined organic extracts were washed with water and saturated aqueous $NaHCO_3$, and dried over $Na_2SO_4$. To this solution, $Ni(OAc)_2$ in MeOH was added and refluxed for 3 h. After usual work up procedure, the residue was chromatographed on silica gel (elution with $CH_2Cl_2$). The main green fraction was collected. After evaporation of the solvent, **17(Ni–Ni)** was recrystallized from $CH_2Cl_2$/MeOH. Yield; 13.5 mg (55%). Mp 250—251 °C. $^1$H NMR $\delta$=0.58 (t, 6H, 2×$CH_3$), 1.16 (t, 6H, 2×$CH_3$), 1.50—1.80 (overlapping t, 36H, 12×$CH_3$), 2.62 (q, 8H, 4×$CH_2$), 3.55 (q, 2H, $CH_2$), 3.57—3.75 (overlapping, q, 18H, 9×$CH_2$), 3.83 (q, 4H, 2×$CH_2$), 5.68 (dd, 2H, 2×vinyl H), 8.04 (overlapping d, 8H, biphenyl H), 9.07, 9.19 (each s, 2H, 2×*meso* H), 9.28 (d, 2H, 2×vinyl H), 9.76 (d, 2H, 2×CHO). MS *m*/*z* 1440 ($M^+$); UV-vis $\lambda_{max}$ 452,619 nm.

**4,4′-Bis-[Ni(II)-octaethylbenzochlorin-20-yl]biphenyl 18(Ni–Ni).** The same procedure was followed as for the synthesis of **16(Ni–Ni)**, using **17(Ni–Ni)** (10 mg, 0.007 mmol), TFA (6 ml), and $CH_2Cl_2$ (6 ml). Yield: 6.4 mg (65%). $^1$H NMR $\delta$=0.07 (t, 12H, 4×$CH_3$), 0.75 (t, 6H, 2×$CH_3$), 1.43—1.65 (overlapping t, 30H, 10×$CH_3$), 1.94, 2.27, 2.40 (each q, 4H, 2×$CH_2$), 3.30—3.62 (overlapping q, 20H, 10×$CH_2$), 7.58 (d, 2H, 2×benzo H), 7.74 (t, 2H, 2×benzo H), 7.88 (br, 8H, biphenyl H), 8.43, 8.76 (each s, 2H, 2×*meso* H), 8.78 (d, 2H, 2×benzo H). MS *m*/*z* 1408 ($M^+$); UV-vis $\lambda_{max}$ 429, 524, 581, 697 nm.

**4,4′-Bis-(5-octaethylbenzochlorin-20-yl]biphenyl 18($H_2$–$H_2$) and 4-(Octaethylbenzochlorin-10-yl]-4′-(octaethylbenzochlorin-20-yl)biphenyl 19($H_2$–$H_2$).** The same procedure was followed as for the synthesis of **16(Cu–Cu)** and **16($H_2$–$H_2$)**. After usual work up procedure, the residue was chromatographed on silica gel (elution with benzene). The second and third blue bands were collected separately. The second fraction was **18($H_2$–$H_2$)** and the third fraction was **19($H_2$–$H_2$)**. Yield: 55—60%.

**18($H_2$–$H_2$).** $^1$H NMR $\delta$=0.11 (t, 12H, 4×$CH_3$), 1.06 (t, 6H, 2×$CH_3$), 1.55—1.70 (overlapping t, 24H, 8×$CH_3$), 1.77 (t, 6H, 2×$CH_3$), 2.14 (q, 4H, 2×$CH_2$), 2.17 (overlapping q, 8H, 4×$CH_2$), 3.47 (overlapping q, 12H, 6×$CH_2$), 3.66, 3.73 (each q, 4H, 2×$CH_2$), 7.78 (d, 2H, 2×benzo H), 7.95 (t, 2H, 2×benzo H), 8.01, 8.11 (each d, 4H, biphenyl H), 8.43, 8.94 (each s, 2H, 2×*meso* H), 9.30 (t, 2H, 2×benzo H). MS *m*/*z* 1296 ($M^+$+2); UV-vis $\lambda_{max}$419, 548, 584, 622, 676 nm.

**19($H_2$–$H_2$).** $^1$H NMR $\delta$=0.08 (t, 6H, 2×$CH_3$), 0.12 (t, 3H, $CH_3$), 1.06, 1.13, 1.19 (each t, 3H, $CH_3$), 1.50—1.80 (overlapping t, 27H, 9×$CH_3$), 1.88 (t, 3H, $CH_3$), 2.12 (q, 2H, $CH_2$), 2.27—2.54 (overlapping q, 6H, 3×$CH_2$), 2.62—2.76 (overlapping q, 6H, 3×$CH_2$), 3.51 (overlapping q, 4H, 2×$CH_2$), 3.60 (overlapping q, 4H, 2×$CH_2$), 3.65, 3.74, 3.85, 3.96 (each q, 2H, $CH_2$),7.78 (d, 1H, benzo H), 7.95 (t, 1H, benzo H), 8.01 (d, 1H, benzo H), 8.06 (s, 1H, *meso* H), 8.07 (t, 1H, benzo H), 8.10—8.19 (overlapping d, 8H, biphenyl H), 8.43, 8.93 (each s, 1H, *meso* H), 9.29 (d, 1H, benzo H), 9.46 (s, 1H, benzo H), 9.54 (d, 1H, benzo H). MS *m*/*z* 1296 ($M^+$+2); UV-vis $\lambda_{max}$ 420, 579, 612, 667 nm.

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