

## Wittig Reactions on Photoporphyrin IX: New Synthetic Models for the Special Pair of the Photosynthetic Reaction Center<sup>†</sup>

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A first example of spirochlorin–chlorin dimer with fixed distances and orientations as potential model for the “special pair” of the photosynthetic reaction center is discussed. For the preparation of such a novel structure, the Wittig reagent of the desired “spacer” **5** was reacted with photoporphyrin IX dimethyl ester **3** to produce the intermediate dimer **6**, which on intramolecular [4 + 2] Diels–Alder cycloaddition gave an unexpected spirochlorin–chlorin dimer **9**. Dehydration of dimer **6** under acid-catalyzed conditions generated the corresponding spirochlorin–porphyrin dimer **16** in quantitative yield. The asymmetry in dimer **6** caused by the biphenyl-type anisotropic effect was confirmed by NMR and model studies. The formation of dihydrobenzoporphyrin **14** by reacting chlorin **3** with the phosphonium salt of *p*-methylbenzylbromide **10** and isolation of 8-phenanthrenevinylporphyrin **19** from chlorin **7** further confirmed our proposed mechanism for the formation of a spirochlorin–chlorin dimer **9**. Following a similar approach, chlorin **3** on reacting with bis-phosphonium salt of 4,4′-bischloromethylbiphenyl produced conjugated chlorin dimer **25**. The spectroscopic data obtained from these dimers suggest that, in these compounds, the individual chromophores are not behaving as an individual molecule, but as a single macrocycle. To examine whether the  $\pi$ – $\pi$  interaction exhibited by dimer **9** resembles the structural arrangement of bacteriochlorophylls in reaction center (RC), we investigated the geometrical parameters used to characterize the  $\pi$ – $\pi$  interactions in tetrapyrrolic macrocycles. Starting from the crystallographic coordinates of **9**, the molecular mechanics energy minimization was performed to obtain the model dimer structure. The geometrical parameters that measure the single pyrrole ring overlap were used to compare the model structure with the crystallographic coordinates of the special pair in photosynthetic reaction center. The results indicated that the ring A of spirochlorin and the ring C of chlorin in our model dimer **9** mimic the ring A–ring A interaction found in the crystallographic special pairs, which are strategically placed by the surrounding photosynthetic reaction center protein matrix.

### Introduction

Photosynthesis in purple photosynthetic bacteria occurs in membrane-bound pigment protein complexes known as light-harvesting (antenna) complexes (LHC)<sup>1</sup> and reaction centers (RC).<sup>2</sup> The major function of LHCs is to broaden the spectral region of the light that can be used by the bacteria, whereas RCs utilize the collected light energy for photoinduced electron transfer, which fuels cellular processes. To date, only two RCs, those from *Rd. viridis*<sup>3</sup> and *Rd. sphaeroides*,<sup>4</sup> have been characterized structurally in high resolution. Six tetrapyrrolic subunits are found at these two very similar RCs:<sup>5</sup> a dimeric

bacteriochlorophyll, the so-called “special pair”, which acts as primary electron donor; two accessory bacteriochlorophylls, which mediate ET; and two bacteriopehophytins, which are the primary electron acceptors. In addition, there are cofactors: the menaquinone, which is an electron relay, and the ubiquinone, which is the final electron acceptor in RC. All elements are held in precise distances and orientation along a  $C_2$  axis of symmetry by a protein matrix. In such RCs, the primary charge separation process is initiated from the lowest singlet excited state of the special pair.<sup>6</sup> Two bacteriochlorophyll *a* or *b* molecules, depending on the bacteria, are laterally offset by  $\sim 6$  Å from center to center and oriented such that only their unsaturated acetyl-substi-

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tuted pyrrole rings overlap at a separation of  $\sim 3.2$  Å. The resulting dimer interaction contributes to the split and red-shifted  $Q_y$  band of the special pair and makes it the better phototrap for the antenna pigments. Excitation of the special pair results in unity quantum yield electron transfer from the special pair to a bacteriopheophytin molecule in about 2.8 ps.<sup>8</sup> Within about 150 ps the electron is transferred to a quinone molecule, which in turn transfers an electron to a secondary quinone within a few microseconds. Such fast sequential electron-transfer steps are essential to overcome the back-electron-transfer processes and afford a long-lived charge separation state. A desire to understand the intricacies of natural photosynthesis has motivated many chemists and molecular biologists to synthesize and study a wide variety of arrays of covalently connected artificial models based on derivatized porphyrins,<sup>9</sup> dimeric and trimeric porphyrins,<sup>10</sup> and porphyrin arrays.<sup>11</sup>

There are two major aspects to the design of artificial RCs: the choice of chromophores and the selection of an organizing principle that will control the interactions among the chromophores. Such interactions are determined by spatial separations, angular relationships, and the nature of the intervening medium.<sup>10b</sup> Thus, it will be ideal to use chromophores found in natural photosynthesis (chlorophyll and bacteriochlorophyll) but to replace the protein with spacers with well-defined geometry and orientation. So far, besides a small group of chlorin and bacteriochlorin dimers models,<sup>12</sup> most

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artificial models are based on covalently linked porphyrin dimers to mimic either the antenna complexes<sup>13</sup> or the various sequential electron-transfer steps in reaction centers.<sup>14</sup>

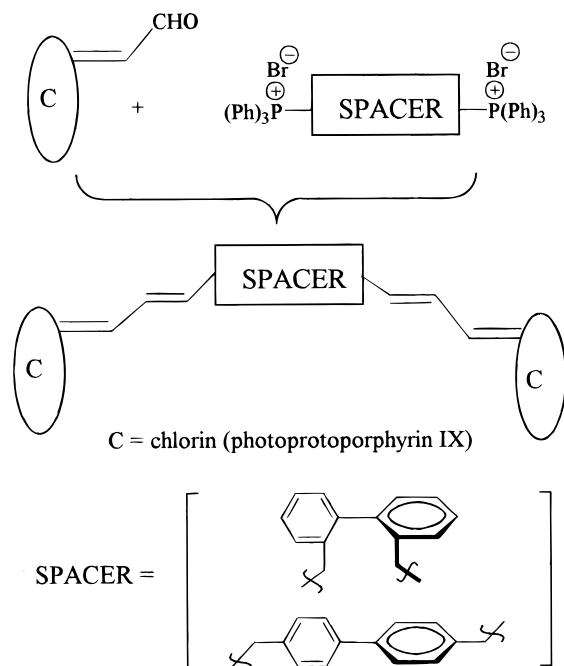
Recent studies to understand electron transfer in the special pair have shown that studies of porphyrin-based dimeric models are critical for revealing the effects of ring overlap and orientation on the full electronic structures of the special pair.<sup>15</sup> Criteria for a good model of the special pair include two tetrapyrrolic macrocycles in close proximity with fixed distance and geometry, interaction

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**Scheme 1. Strategy for Constructing Bis-chlorin Model Systems**

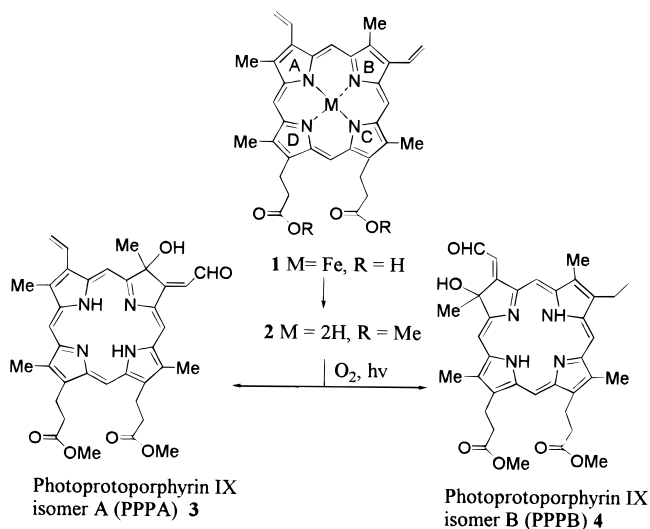
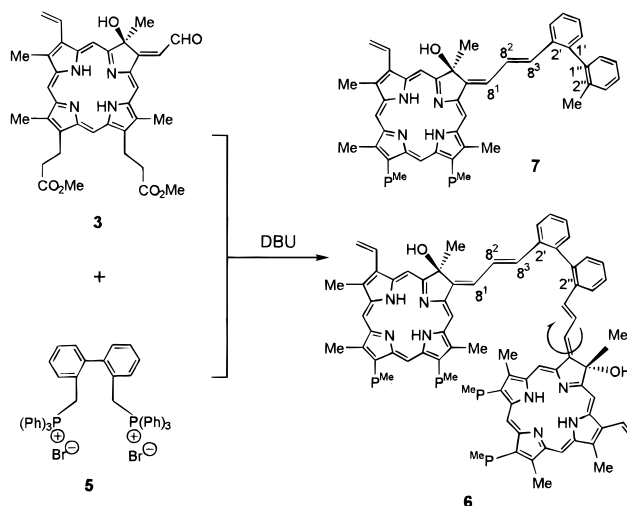
between the  $\pi$ -electron systems of the pair, and a substituent pattern as close as possible to that in natural bacteriochlorophylls. Thus, our goal has been to develop a versatile methodology for the preparation of chlorin and bacteriochlorin dimers with fixed distance and orientation.

Officer and colleagues<sup>16</sup> have recently shown that by using porphyrin-derived Wittig reagents, a variety of porphyrin dimers can be constructed. This chemistry offers a versatile approach for the preparation of a variety of porphyrin-based free base and heterometalated dimers. However, in our hands, the extension of this approach for preparing less stable chlorin and bacteriochlorin dimers mainly yielded decomposition products. Thus, we have been interested in developing an alternate method for preparing various coplanar and cofacial chlorin and bacteriochlorin dimers. In our attempts to synthesize such dimers, we thought it worthwhile to prepare the Wittig reagents of the desired linkers first and then react them individually with chlorin and bacteriochlorin monomers.

**Results and Discussions**

The basic strategy for the preparation of bis-chlorin model systems is depicted in Scheme 1. Depending on the type of Wittig reagent used, the presence of a "spacer" directly attached at the peripheral position of a chlorin gives a unique opportunity to prepare a series of chlorin dimers with fixed distances and geometry.

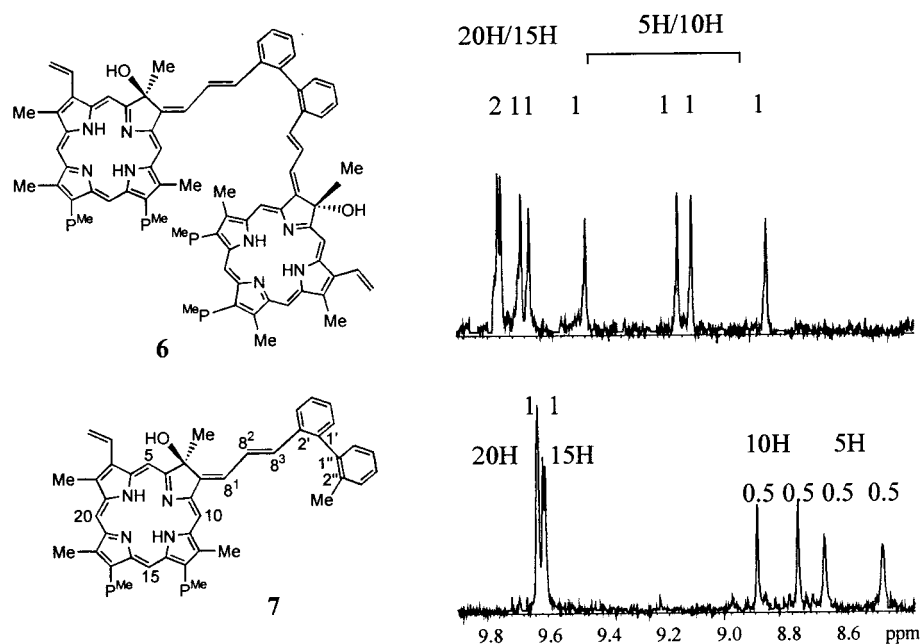
**Chlorin–Spirochlorin and Porphyrin–Spirochlorin Dimers with 2',2''-Biphenyl Bridge System.** For the preparation of the starting material, hemin **1** was first converted into protoporphyrin IX dimethyl ester **2** by following the standard methodology.<sup>17a</sup> See Scheme 2. Reaction of **2** with light and air produced the "so-called" photoporphyrin IX (a type of chlorin, PPP) as a

**Scheme 2. Starting Materials PPPA **3** and PPPB **4******Scheme 3. Formation of Bis-chlorin **6** and Monomeric Chlorin **7****

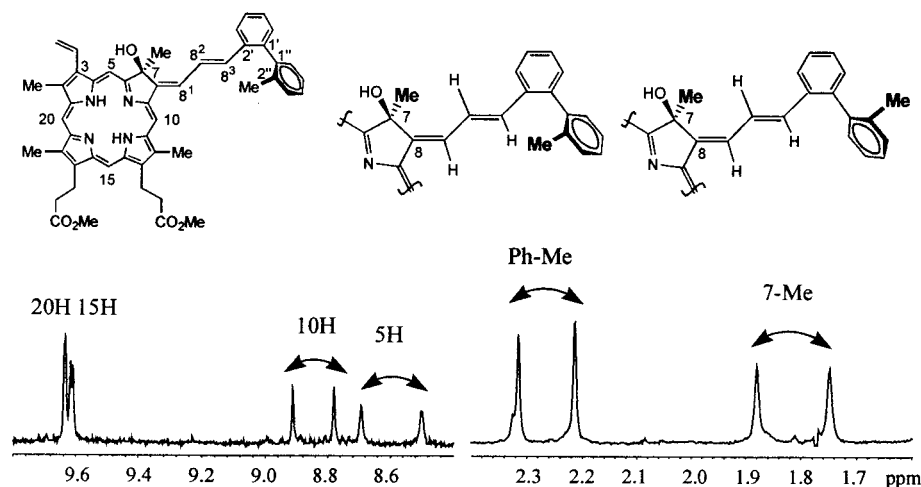
mixture of two isomers: **3** (PPPA, isomer A) and **4** (PPPB, isomer B). The isomeric mixture was separated into individual isomers by column chromatography (silica gel-G),<sup>17b</sup> and isomerically pure chlorin **3** (isomer A) was used as a substrate. The bis-phosphonium salt **5** derived from 2,2'-bisbromomethyl-1,1'-biphenyl was reacted with PPPA **3** in the presence of DBU to afford a mixture of mainly two compounds. See Scheme 3. On the basis of mass spectrometry and NMR analysis, the structure for the faster moving band obtained in 60% yield was assigned as 2',2''-bischlorin **6**, HRMS (calcd 1391.6550 for C<sub>86</sub>H<sub>87</sub>N<sub>8</sub>O<sub>10</sub>, found 1391.6540). The presence of eight meso protons in the range of 8.8–9.8 ppm clearly indicated a dimer possessing an asymmetric structure. On the basis of mass spectrometry analysis (HRMS calcd 786.3781 for C<sub>50</sub>H<sub>50</sub>N<sub>4</sub>O<sub>5</sub>, found 786.3749), the structure for the minor component (yield 20%) was initially assigned as **7**, which was further confirmed by <sup>1</sup>H NMR studies. As shown in Figure 1, the <sup>1</sup>H NMR spectrum of the monomer **7** shows an unexpected equal-splitting pattern for each meso

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**Figure 1.** Partial NMR spectra of dimer **6** and monomer **7** (a comparative study).

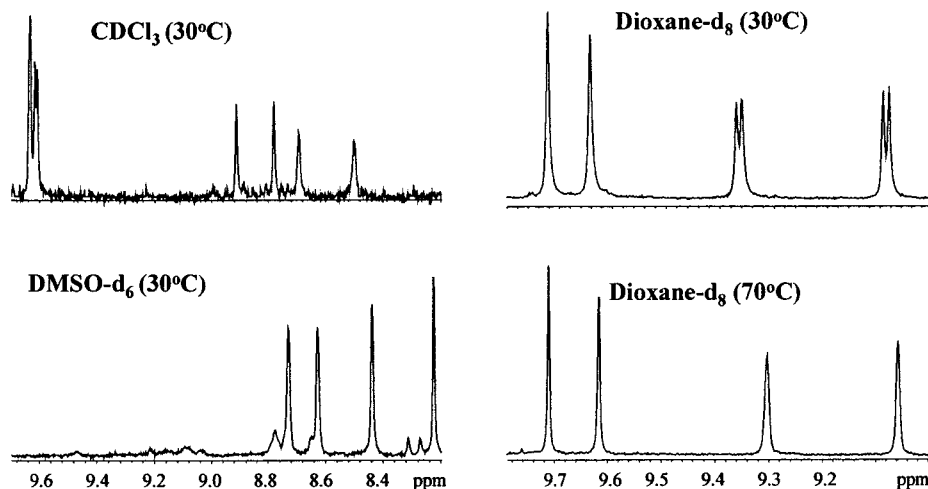


**Figure 2.** Evidence for inter-exchanging conformations in monomer **7**.

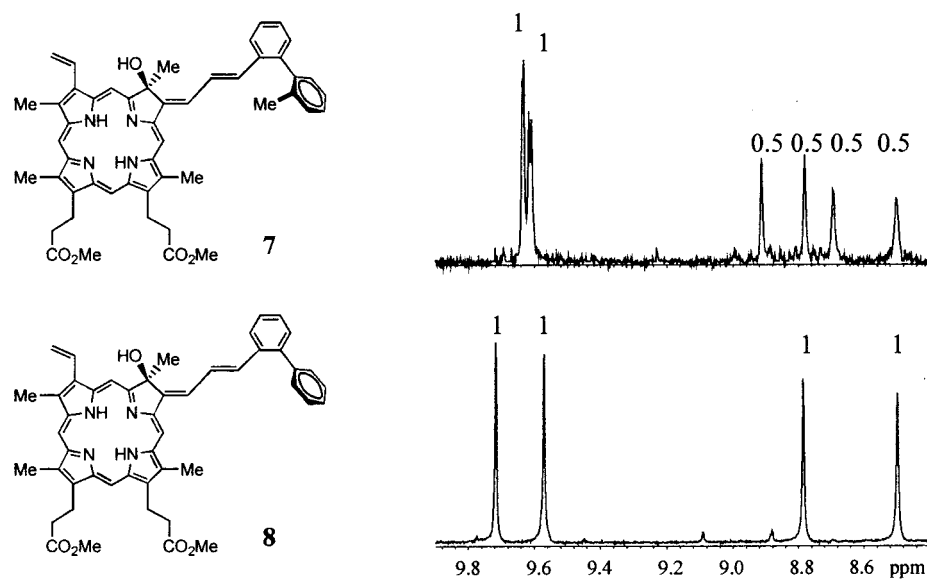
proton close to the reduced ring, which is similar to that observed in dimer **6**. To understand the reason for the asymmetry in both dimer **6** and monomer **7**, extensive NMR studies were performed on monomer **7**. In the NMR spectrum, the evidence of two inter-exchanging conformations was initially observed from a 2D ROESY experiment (Figure 2), which was further confirmed by variable temperature NMR studies. As shown in Figure 3, at 30 °C, replacing  $\text{CDCl}_3$  with dioxane- $d_8$  drastically reduced the splitting pattern, which completely disappeared in  $\text{DMSO}-d_6$ . Interestingly, raising the temperature of the dioxane- $d_8$  solution from 30 to 70 °C also eliminated such a splitting pattern. These results suggest that in monomer **7** this effect is certainly due to a slow exchange between the two possible conformations causing the biphenyl-type anisotropic effect<sup>18</sup> induced by the restricted rotation around the biphenyl bond. To confirm these results, chlorin **8**, lacking the methyl group at 2'-

position of the biphenyl substituent, was synthesized, and as expected, in the  $^1\text{H}$  NMR spectrum of chlorin **8** ( $\text{CDCl}_3$ , room temperature) no splitting pattern was observed (Figure 4). Compared to **7**, dimer **6** in which the methyl group is replaced with the much larger chlorin macrocycle will certainly generate more restricted rotation around the biphenyl bond. This was confirmed by its NMR spectrum, which produces a similar splitting pattern as observed for **7**. To our surprise, the bis-chlorin **6** was found to be unstable if the reaction was left for longer periods of time and slowly converted into an unknown chlorin dimer **9**. The rate of the transformation and thus the yield of the individual dimers **6** and **9** was found to be dependent on the reaction conditions used. Both compounds were found to have the same molecular weight as confirmed by high-resolution mass spectrometry. The NMR studies indicated that compared to dimer **6**, some of the meso protons in dimer **9** showed a significant upfield shift resulting into a complex spectrum. Figure 5 represents the partial spectra of these dimers (the spectrum of dimer **9**, shows the resonances

(18) (a) Gottwald, L. K.; Ullman, E. F. *Tetrahedron Lett.* **1969**, 36, 3071–3074. (b) Lindsey, J. S. *J. Org. Chem.* **1980**, 45, 5215. (c) Gunter, M. J.; Mander, L. N. *J. Org. Chem.* **1981**, 46, 4792–4795. (d) Young, R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, 107, 898–909.



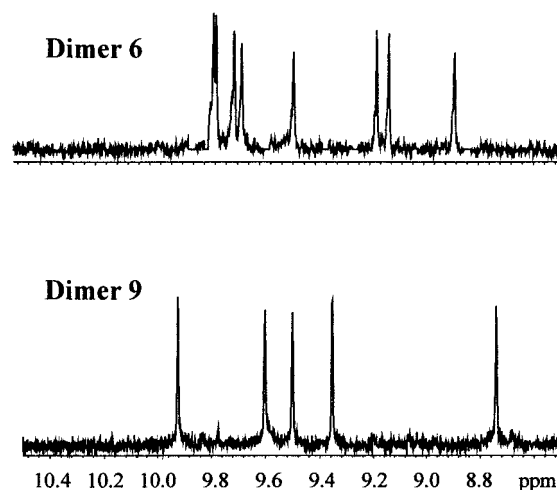
**Figure 3.** Effect of solvents and temperature on the NMR of monomer 7.



**Figure 4.** Biphenyl-type anisotropic effect induced by restricted rotation around biphenyl bond (caused by the presence of the methyl group substituted at the ortho-position of the biphenyl substituent).

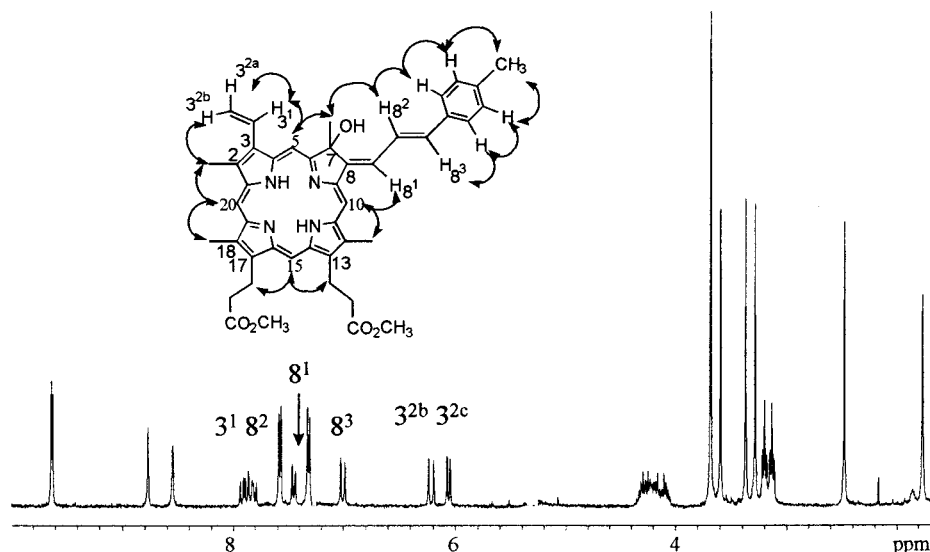
of only five of the eight meso protons appeared in the range of  $\delta$  8.7–10.0 ppm).

To provide a simple reference spectra for identifying all the resonances of dimer **9**, model studies were performed. The Wittig reagent **10**, obtained from *p*-methylbenzylbromide, was reacted with chlorin **3** under various reaction conditions. The best results were obtained when DBU was used as a base and the reaction was performed at room temperature (Scheme 4). Under these conditions, compound **11** was obtained in 90% yield. By performing 2D-ROESY experiments, the geometry of model compound **11** was established as the *E,E* isomer. The NOE connectivities and the assignments of the key protons are shown in Figure 6. To investigate the stability of the model chlorin **11**, it was dissolved in *o*-dichlorobenzene and heated at various temperatures. Surprisingly, it gave an unexpected dihydrobenzoporphyrin **14** as a sole product. The formation of porphyrin **14** suggests a two-step mechanism through an intermediate **11**, which includes a simple dehydration followed by an intramolecular [4 + 2] Diels–Alder cycloaddition (Scheme 4). The structure of porphyrin **14** was confirmed by  $^1\text{H}$



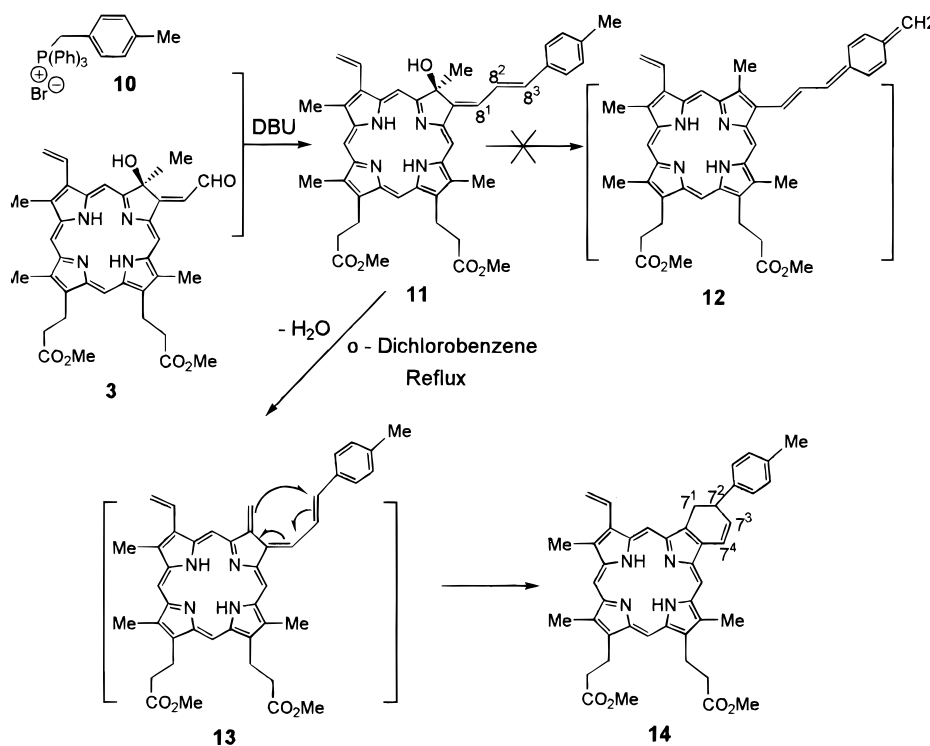
**Figure 5.** Partial NMR spectra of dimer **6** and monomer **9** (a comparative study).

NMR (Figure 7) and HRMS analysis (calcd 693.3441 for  $\text{C}_{44}\text{H}_{44}\text{N}_4\text{O}_4$ , found 693.3417).



**Figure 6.** NMR spectrum of chlorin **11**. The assignments are based on the NOE connectivities observed by 2D-ROESY experiments.

**Scheme 4. Formation of a Novel Dihydrobenzoporphyrin 14 by Reacting PPPA 3 with Wittig Reagent 10**



With the reference spectra of model chlorin **11** in hand, the structure of dimer **9** was postulated as a spirochlorin–chlorin dimer linked via a tetrahydrobenzophenanthrene bridge. The HRMS and NMR ( $^1\text{H}$ , 2D-ROESY, 2D-COSY) data also confirmed the proposed structure. To the best of our knowledge, dimer **9** is the first structurally characterized chlorin–spirochlorin dimer with a remarkable  $\pi$  electron overlap. As shown in Scheme 5, the mechanism of the formation of this novel dimer is possibly due to the intramolecular [4 + 2] Diels–Alder cycloaddition of the unsaturated alkyl chain joining the two chlorin systems. The structure of dimer **9** was also confirmed by a single-crystal X-ray analysis.<sup>19</sup>

The  $^1\text{H}$  NMR spectrum of dimer **9** showed unique characteristics due to the  $\pi$  electron interactions between

the two chlorin macrocycles (Figure 8). Table 1 summarizes the assignments of all the resonances ( $\delta$  ppm) as well as changes in chemical shift compared to that of the model chlorin **11** ( $\Delta\delta$  ppm). The most notable features were as follows:

The resonances for the meso protons (5H, 10H, 15H, and 20H) in model chlorin **11** were observed in the region of 8.5–10 ppm; however, in dimer **9**, the meso proton labeled as “v” of the chlorin part shifted dramatically to 4.89 ppm, exhibiting an upfield shift of 3.86 ppm relative to the chlorin **11**. On the other hand, meso protons from the spirochlorin labeled as “k” and “n” show 0.80 and 2.08 ppm upfield shifts. Unlike the vinyl protons “g”, “s”, and

(19) Senge, M. O.; Zheng, G.; Pandey, R. K. Manuscript in preparation.

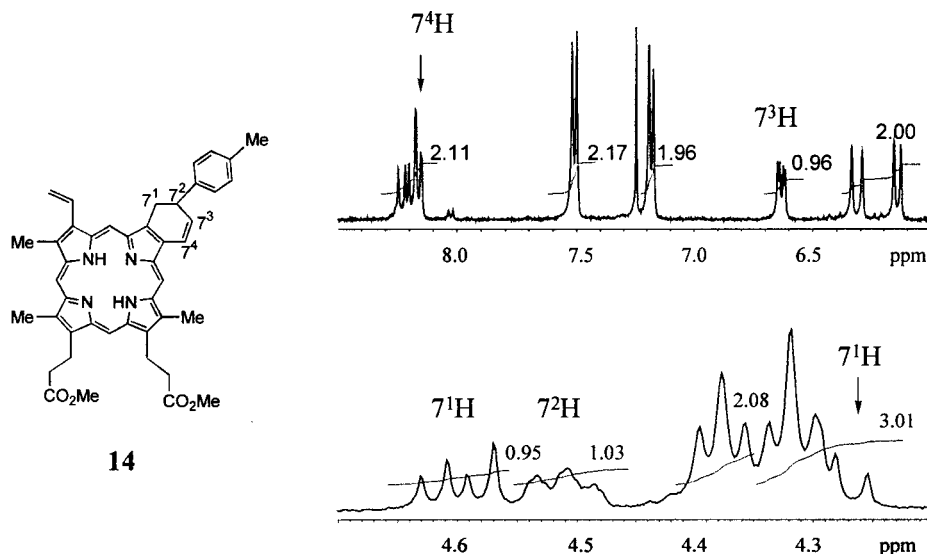
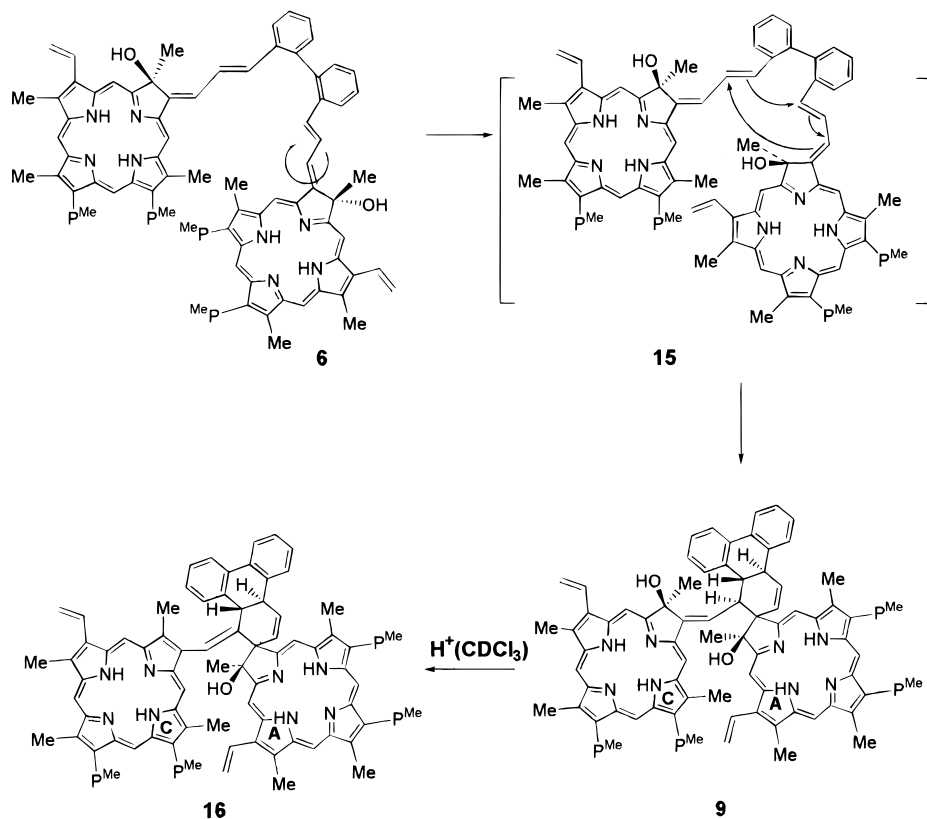


Figure 7.  $^1\text{H}$  NMR spectrum of porphyrin **14** (only the resonances observed for bridging protons are shown).

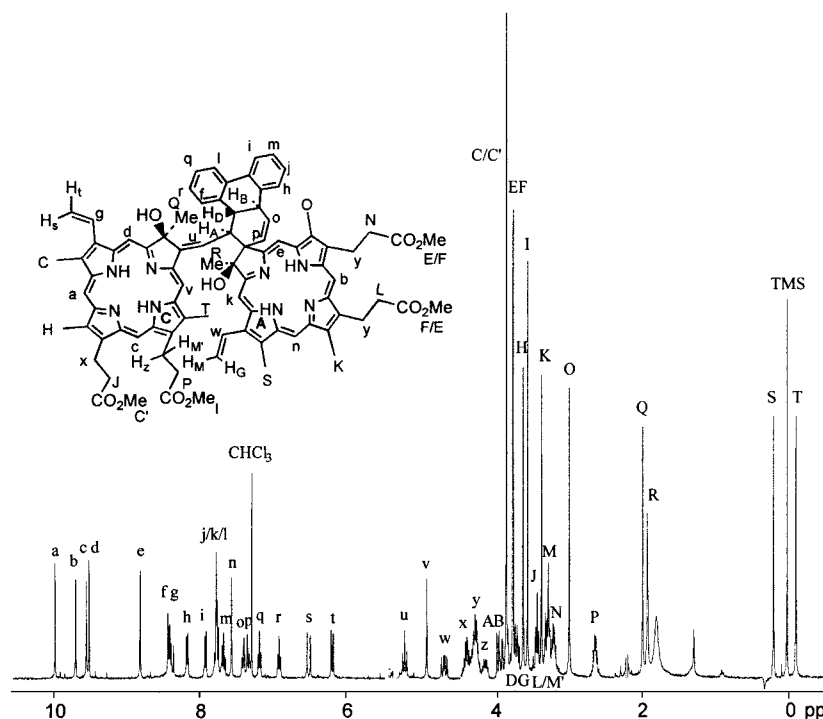
**Scheme 5. Mechanism for the Formation of an Unexpected Chlorin–Spirochlorin Dimer **9** and Its Dehydration Product **16****



“t” of the chlorin moiety that appeared at 8.35 ppm ( $\Delta\delta = +0.46$  ppm), 6.48 ppm ( $\Delta\delta = +0.28$  ppm), and 6.15 ppm ( $\Delta\delta = +0.11$  ppm), respectively, the vinyl protons “w”, “G”, and “M” from the spirochlorin showed significantly upfield resonances at 4.66 ppm ( $\Delta\delta = -3.23$  ppm), 3.66 ppm ( $\Delta\delta = -4.23$  ppm), and 3.25 ppm ( $\Delta\delta = -2.79$  ppm), respectively.

Furthermore, the 12-methyl resonance “T” in the chlorin part of dimer **9** was observed at  $-0.13$  ppm, exhibiting an upfield shift of 3.50 ppm, whereas the 2-methyl signal “S” of the spirochlorin was shifted 3.41 ppm upfield relative to chlorin **11**. On the other hand, the 18-methyl protons “K” and 7-methyl protons “R”

(attached to the reduced ring) of the spirochlorin appeared at 3.33 ppm ( $\Delta\delta = +0.05$  ppm) and 1.88 ppm ( $\Delta\delta = +0.15$  ppm), respectively. Surprisingly, two protons adjacent to ring C of the chlorin labeled as “z” and “M” have very different shifts with “M” being 0.84 ppm upfield of “z”. In dimer **9**, compared to the resonances for the  $-\text{NH}$  protons (ring A of chlorin and ring C of spirochlorin) the  $-\text{NH}$  protons of ring C (chlorin) and ring A (spirochlorin) produced upfield shifts of  $\sim 2.00$  ppm. See Figure 9. These upfield shifts are due to the large ring current produced by the system, which naturally affects the adjacent ring due to partial chlorin–spirochlorin overlap and, thus, causes a strong shielding effect. All protons



**Figure 8.**  $^1\text{H}$  NMR spectrum of chlorin-spirochlorin dimer **9** (for details see Table 1).

affected by these  $\pi$ - $\pi$  interactions are included in the circle shown in Figure 8.

The nature of the overlap between the pyrrole ring C of the chlorin and the pyrrole ring A of the spirochlorin in dimer **9** was further resolved by performing a 2D-ROESY experiment (600 MHz) at 30 °C (**9** was dissolved 0.5% pyridine- $d_5$ /CDCl $_3$ ). A few through-space cross-peaks, due to interchlorin subunit proton-proton interactions (<3.5 Å), were also observed. For example, proton "z" of the chlorin shows a cross-interaction with the 18-methyl "K" of the spirochlorin. Our observations are consistent with a structure where the chlorin units are present in such a way that the pyrrole ring A of the spirochlorin overlaps the pyrrole ring C of the opposite chlorin. This intermolecular interaction was further confirmed by the energy-optimized structure of chlorin-spirochlorin **9**, obtained by molecular modeling (Figure 10).

The presence of a hydroxy functionality in the chlorin system (ring B) of the dimer **9** was also supported by its transformation into a porphyrin-spirochlorin dimer **16**, which was formed upon leaving the NMR sample in CDCl $_3$  (without pyridine- $d_5$ ) at room temperature for an extended period (Figure 11). See Scheme 5. The dehydration product so obtained was isolated by preparative TLC, and the structure was assigned on the basis of its UV-vis, HRMS (calcd 1373.6390 for C $_{86}$ H $_{85}$ N $_8$ O $_9$ , found 1373.6520) and NMR data.

Logically, the formation of dimer **16** could be explained by the dehydration of dimer **9** caused by a trace amount of acid present in CDCl $_3$  used as a NMR solvent. In the electronic absorption spectrum of dimer **16** (Figure 12), the appearance of a new band at 578 nm with an additional 18 nm red shift for the Soret band in the dimer also indicated the presence of a porphyrin system. Furthermore, compared to **9**, the NMR spectrum of **16** showed entirely different structural features. For example, the vinyl protons attached to the porphyrin

macrocycle and those of the spirochlorin system appeared in the range of 7.5–8.5 ppm, generally reported for chlorin and porphyrin systems. In the NMR spectrum of **9** (Figures 8 and 9), the upfield resonances at -0.13 and +0.18 ppm were assigned to the 12-methyl "T" of the chlorin and 2-methyl "S" of the spirochlorin; however, in dimer **16**, they appeared in the usual range of 2–3 ppm. These results indicate that porphyrin-spirochlorin dimer **16** processes linear geometry and thus lacks cofacial  $\pi$ - $\pi$  interactions observed in dimer **9**.

The absorption and fluorescence emission spectra of dimers **9** and **16** were measured in dichloromethane. The ground-state absorption spectra of dimer **9** reveals a Soret band at 388 nm and distinct Q-bands at 505, 540, and 664 nm. Excitation of dimer **9** at 388, 505, 540, and 664 nm gave a fluorescence emission band at 672 nm. In both dimers, the long-wavelength absorption was observed at 664 nm. However, dimer **16** exhibited a remarkable red shift in the Soret band appearing at 409 nm. The Q-band at 574 nm belongs to one of the bands (etio-type) of the newly formed porphyrin system. Excitation of all the bands at 409, 505, 538, 574, and 664 nm afforded an emission at 668 nm. Interestingly, the two emission bands generally observed at 635–645 nm (strong) and 690–700 nm (weak) for a typical porphyrin macrocycle were found to be absent in the fluorescence spectrum of **16**, indicating that in this dimer porphyrin and chlorin moieties are not behaving as an individual molecule, but as a single macrocycle.

The intramolecular [4 + 2] cycloaddition that occurred in bis-chlorin **6** was not an isolated phenomenon. Such transformation was also observed in the case of 2',2''-monomer **7**. As shown in Scheme 6, when monomer **7** was kept in CDCl $_3$  for several days, it slowly converted to a dihydrophenanthrene type of porphyrin **18**, which further underwent auto-oxidation to afford fully aromatized phenanthrene-linked porphyrin **19**. Such a trans-



**Table 1.**  $^1\text{H}$  NMR Parameters<sup>a</sup> for Chlorin–Spirochlorin Dimer **9**

proton signal with integration	type	$\delta$ ppm	$\Delta\delta^{b,c}$	NOE from ROSEY	$J$ - $J$ coupling from COSY
a (1H)	s	9.91	+0.29	C, H	
b (1H)	s	9.63	+0.03	y, L, N	
c (1H)	s	9.48	-0.12	J, P, x, z, M'	
d (1H)	s	9.44	+0.91	Q, s, g, k	
e (1H)	s	8.76	+0.01	C, O, h, o, p	
f (1H)	d	8.38		Q, u, r, q, A	f-r
g (1H)	dd	8.35	+0.46	d, C, s, t	g-s, g-t
h (1H)	d	8.13		j, m, o, p, e, O	h-j
i (1H)	d	7.89		m, l	i-m
j (1H)	t	7.75		m, h	m-j, j-h
k (1H)	s	7.73	-0.80	w, d, R, M	
l (1H)	d	7.72		q, I	q-l
m (1H)	t	7.64		i, j, h	i-m, m-j
n (1H)	s	7.54	-2.08	S, K	
o (1H)	ABq with p	7.40		h, e, B	o-p, o-B
p (1H)	ABq with o	7.33		h, e, B, R	p-o, p-B
q (1H)	t	7.15		r, l	q-r, q-l
r (1H)	t	6.88		q, f, Q	r-q, r-f
s (1H)	d	6.48	+0.28	C, d, g, t	s-g
t (1H)	d	6.15	+0.11	s, g	t-g
u (1H)	t	5.18	-2.26	D, A, B, Q	u-A, u-D
v (1H)	s	4.89	-3.86	A, T	
w (1H)	dd	4.66	-3.23	G, M	w-M, w-G
x (2H)	m	4.36	+0.13	H, J	x-J
y (4H)	m	4.24	+0.01	b, K, N, O	y-L, y-N
z (1H)	m	4.10	+0.01	M', P, K	z-M', z-P
A (1H)	d	3.92		u, v, D, f, B	A-u
B (1H)	ABq with D	3.88		o, p, A	B-o, B-p, B-D
C (6H)	s	3.80	+0.21	a, g, s	
D (1H)	dd and ABq with B	3.79		A, u, B	D-u, D-B
E (3H)	s	3.73	+0.05	N	
F (3H)	s	3.72	+0.04	N	
G (1H)	d	3.66	-4.23	w, M, I	G-w
H (3H)	s	3.58	+0.30	a, x, C, J	
I (3H)	s	3.52	-0.16	C	
J (2H)	t	3.39	+0.20	x, C, H	J-x
K (3H)	s	3.33	+0.05	n, y, L, z	
L (2H)	m	3.25	+0.06	b, K	L-y
M (1H)	d	3.25	-2.79	w, k, G	M-w
M' (1H)	m	3.25	-0.84	c, C, z, P,	M'-z
N (2H)	m	3.16	+0.03	b, O, y, E/F	N-y
O (3H)	s	2.95	-0.42	e, h, j, y, N	
P (2H)	m	2.60	-0.53	c, z, M'	P-z
Q (3H)	s	1.94	+0.21	f, d, r, u	
R (3H)	s	1.88	+0.15	k, p	
S (3H)	s	0.18	-3.41	n, M	
T (3H)	s	-0.13	-3.50	v, M'	

<sup>a</sup>  $^1\text{H}$  NMR data acquired from AMX-600; assignments were based on both 2D ROESY and COSY experiments. <sup>b</sup>  $\Delta\delta = \delta$  (dimer **9**) -  $\delta$  (model monomer **7**). <sup>c</sup> NH protons observed at -2.155 (br), -4.247 (br), -2.834 (s), and -4.348 (s) ppm were not shown.

formation clearly appeared in their optical spectra (Figure 13). Interestingly, in developing the preparative TLC plates, porphyrin **18** and **19** were often partially metalated to give their zinc complexes **20** and **21**, respectively. Thus, the structures of these porphyrins as zinc complex were confirmed by NMR and HRMS analyses (calcd 830.2810 for  $\text{C}_{50}\text{H}_{46}\text{N}_4\text{O}_4\text{Zn}$  **20**, found 830.2769; calcd 828.2654 for  $\text{C}_{50}\text{H}_{44}\text{N}_4\text{O}_4\text{Zn}$  **21**, found 828.2610). For example, the resonances from  $^1\text{H}$  NMR spectrum of aromatized porphyrin **21** were assigned on the basis of NOE connectivities observed by performing the 2D-ROESY experiment in  $\text{DMSO}-d_6$  (Figure 14). Thus, similar to what happened to dimer **6**, the formation of porphyrins **18** and **19** also involves an intramolecular [4 + 2] cycloaddition followed by an acid-catalyzed dehydration and an auto-oxidation, which serves as more evi-

dence for the formation of unexpected chlorin–spirochlorin system.

**Chlorin–Chlorin Dimer with 4',4''-Biphenyl Bridge System.** In our initial efforts to prepare the bis-chlorin systems with a 4',4''-biphenyl bridge, we experienced difficulty in isolating the pure bis-Wittig reagent. Refluxing the 4,4'-bischloromethyl-1,1'-biphenyl<sup>20</sup> **22** with  $\text{Ph}_3\text{P}$  in  $\text{CHCl}_3$  overnight failed to produce the expected bisphosphonium salt **23**. Instead, a mono-Wittig reagent **24** with an unreacted chloromethyl group was mainly obtained. However, we were able to isolate the bis-Wittig reagent **23** under rigorous reaction conditions (refluxing in DMF overnight). It was then condensed with PPPA **3** (Scheme 7). After the standard workup, the reaction mixture was purified by preparative TLC, and the 4',4''-bischlorin **25** and 4',4''-monomer **26** were obtained in 50% and 20% yield, respectively. Unlike 2',2''-bischlorin **6**,  $^1\text{H}$  NMR spectrum of dimer **25** exhibited only four broad peaks in the range of 8–10 ppm for the meso protons. Replacing  $\text{CDCl}_3$  with  $\text{THF}-d_4$  as NMR solvent gave much better resolution (Figure 15). The presence of four meso protons (each as a singlet) in 4,4-bischlorin **25** clearly indicated the formation of a symmetrical dimer. Mass spectroscopy analysis gave a molecular ion peak at 1391.10 (calcd 1391.6550 for  $\text{C}_{86}\text{H}_{87}\text{N}_8\text{O}_{10}$ ), which further confirmed the dimeric structure.

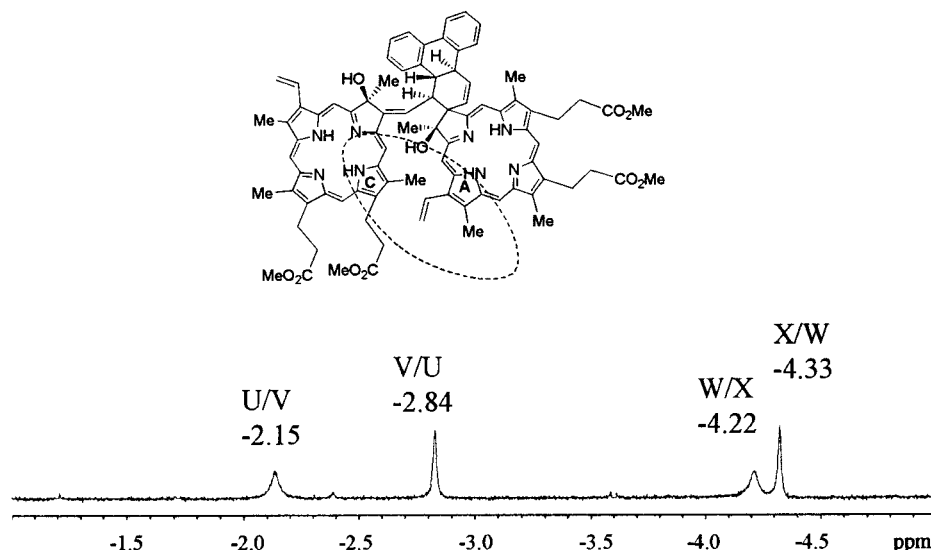
Similar to dimers **9** and **16**, in dimer **25**, excitation of the absorption bands at 357, 438, 570, or 681 afforded emission at 687 nm, suggesting that the two chlorin systems joined by an unsaturated carbon–carbon linkage are behaving as a single molecule.

**Molecular Modeling Studies.** To examine whether the  $\pi$ - $\pi$  interaction exhibited in our dimer model **9** resembles the structural arrangement of bacteriochlorophylls in RC, we investigated the geometrical parameters used to characterize the  $\pi$ - $\pi$  interactions in tetrapyrrolic macrocycles.<sup>20,21,22</sup> The parameters used are described in the method, and the results for our model dimer **9** and some special pairs from crystallographic photosynthetic reaction centers are shown in Table 2. In addition to the standard parameters, which describe the relative orientation of the whole tetrapyrrole ring systems, the additional parameters were used to measure the relative orientation of specific pair of pyrrole rings as found for the ring A–ring A overlap in the special pairs. Table 2 indicates that there are some variations in these parameters among the crystallographic special pairs depending upon the source of organisms and the crystal environment. The dimer **9** possesses more planer tetrapyrrole ring system (dihedral angle of 3°) than the special pairs (6°–11°) while the mean separation distance of the dimer **9**. (3.4 Å), falls within the range found for the special pairs (3.1–3.6 Å). Judged by the center–center separation distances (6.0 Å vs 7.4–7.7 Å), lateral shifts (4.9 Å vs 6.6–6.9 Å), and slip angles (56° vs 61–65°), it seems that the relative orientation of the tetrapyrrole rings in model dimer **9** are slightly shifted from what is found for the special pairs. Both the top and side views clearly represent this slight shift graphically. However, when we focused on the geometrical parameters describing the relative orientation and overlap between single pyrrole

(20) 4,4'-Bischloromethylbiphenyl was generously supplied by Dr. Subramaniam, Department of Chemistry, Penn State University.

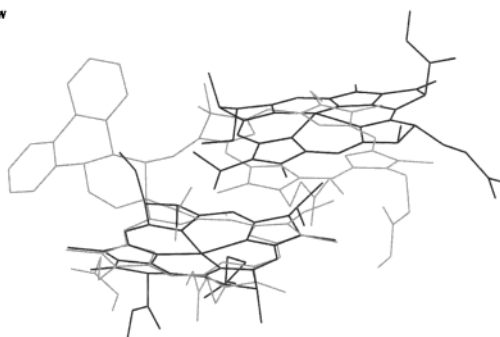
(21) Scheidt, W. R.; Lee, Y. J. *Structure Bonding* **1987**, *64*, 1–70.

(22) Kalisch, W. W.; Senge, M. O.; Ruhlandtsenge, K. *Photochem. Photobiol.* **1998**, *67*, 312–323.

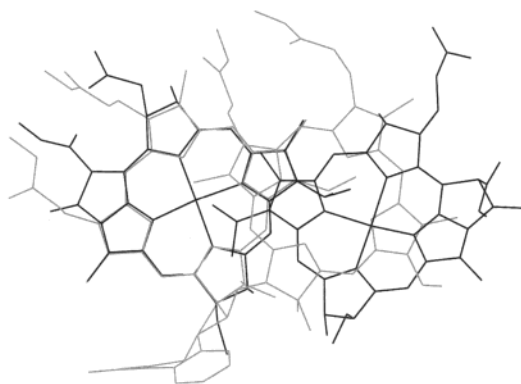


**Figure 9.**  $^1\text{H}$  NMR spectrum of chlorin–spirochlorin dimer **9**: expanded region showing all NH protons. (one proton each from two chlorin subunits (W and X) show significant upfield shifts).

Top view



Side view



**Figure 10.** Top and side views of the special pair (black line) and dimer **9** (gray line).

ring as found for the ring A–ring A interaction in the special pairs, the data in Table 2 revealed that our model dimer **9**, indeed, possesses a very similar relative orientation and overlap of pyrrole rings to that found in the crystallographic special pairs (Figure 10). All parameters, mean plane separation distance, center–center distance, lateral shift, slip angle, and dihedral angle, are close to the values obtained from the crystal structure of special pairs, while protein data bank id–1pcr is the closest to our model dimer **9**. Thus, it is evident that ring A of spirochlorin and ring C of chlorin in our model dimer **9**

mimic the ring A–ring A interaction found in the crystallographic special pairs that are strategically placed by the surrounding photosynthetic reaction center protein matrix.

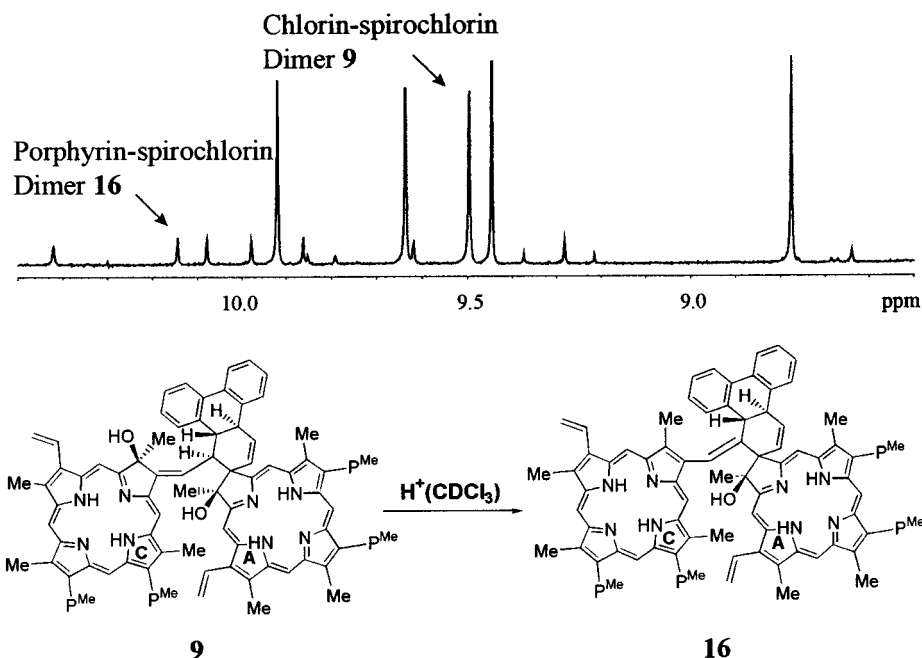
## Conclusions

In conclusion, the new class of dimeric systems discussed here are the first examples of chlorin–spirochlorin and porphyrin–spirochlorin dimers. The Wittig/Diels–Alder approach discussed here has great potential for designing a reasonable model to study the special pair which includes two chlorin macrocycles in close proximity. The modeling studies indicate that similar to the bacterial reaction center, which consists of a bacteriochlorophyll dimer with partial overlap, the spirochlorin–chlorin dimer **9** also demonstrates a partial overlap in the ring A area. These findings are very exciting because such close proximity of the two components of a pair should produce models worthy of investigation. This method also provides a unique opportunity to construct various porphyrin-based dimers, such as chlorin–chlorin, porphyrin–chlorin, bacteriochlorin–chlorin, and bacteriochlorin–bacteriochlorin dimers linked with spacers of variable distances and geometries. By using appropriate reagents, this methodology can also be used for the preparation of various conjugated porphyrins linked at the peripheral position(s) with a variety of aromatic systems, which are otherwise difficult to synthesize. The photophysical properties of dimer **9** and the related compounds are currently in progress and will be published elsewhere.

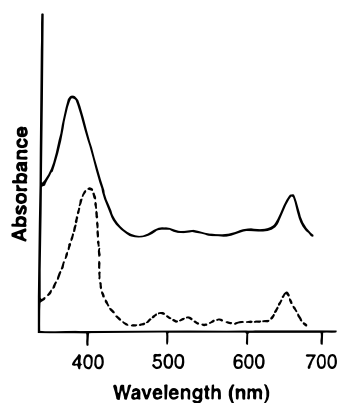
## Experimental Section

Reagents were purchased from Aldrich, Lancaster, and Porphyrin Products and used without further purification. Reactions were monitored spectrophotometrically and/or by analytical thin-layer chromatography using 250 mm Whatman precoated silica gel plates. Mass spectral analyses was performed at the department of Molecular and Cellular Biophysics, RPCI, Buffalo, and at the University of Michigan, East Lansing. Where necessary, solvents were dried before use.

**Separation of the Mixture of Photoporphyrin IX into Individual Isomers 3 and 4.** Photoporphyrin IX



**Figure 11.** Transformation of chlorin–spiroschlorin dimer **9** to porphyrin–spiroschlorin dimer **16** observed in  $^1\text{H}$  NMR spectrum.



**Figure 12.** Electronic absorption spectra (in  $\text{CH}_2\text{Cl}_2$ ) of dimer **9** (—) and dimer **16** (---).

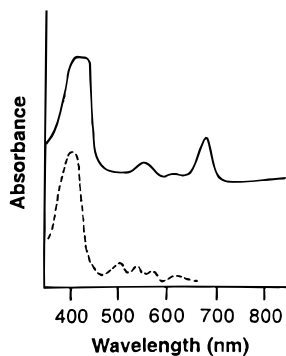
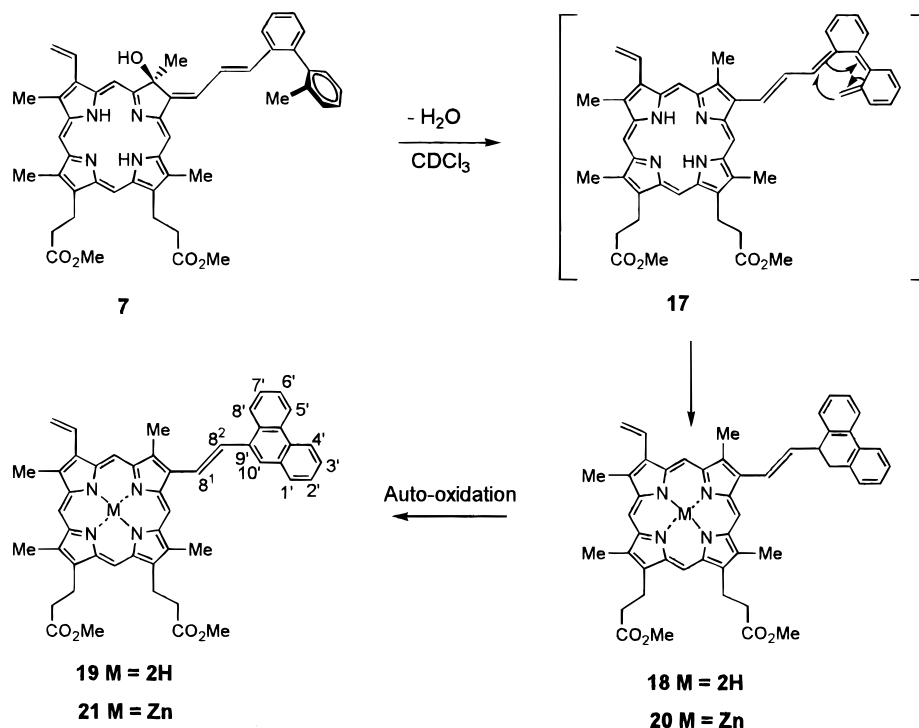
as an isomeric mixture was obtained by following the method reported by Inhoffen et al.<sup>17b</sup> The individual isomers: isomer A (**3**) (8-vinyl analogue) and isomer B (**4**) (3-vinyl analogue) were separated by repeated column chromatography on silica gel 60 eluting with the gradient acetone/ $\text{CH}_2\text{Cl}_2$  solvent system (5–12% v/v). For our studies, isomer A (**3**) was used as a substrate. Mp of **3**: 225–227 °C (lit.<sup>17b</sup> mp 222–223 °C).  $^1\text{H}$  NMR of **3** (400 MHz, 3 mg/1 mL  $\text{CDCl}_3$ ,  $\delta$  ppm): 10.23 (splitting s, 1H, CHO); 9.78, 9.70, 8.70, 8.15 (each s, 1H, 5H, 10H, 15H and 20H); 7.75 (dd, 1H, 3- $\text{CH}=\text{CH}_2$ ); 6.85 (d, 1H, 8<sup>1</sup>-H); 6.17 (d, 1H, *trans*-3- $\text{CH}=\text{CH}_2$ ); 6.10 (d, 1H, *cis*-3- $\text{CH}=\text{CH}_2$ ); 4.30 (m, 4H, 13 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  and 17 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 3.69 and 3.67 (each s, 3H, 13 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  and 17 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 3.62, 3.49 and 3.46 (each s, 3H, 2 $\text{CH}_3$ , 12 $\text{CH}_3$  and 18 $\text{CH}_3$ ); 2.75 (two t, 4H, 17 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  and 13 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 1.47 (s, 3H, 7 $\text{CH}_3$ ); -0.35 and -0.70 (each br s, 1H, 2NH). UV–vis ( $\lambda_{\text{max}}$  ( $\epsilon$ ) in  $\text{CH}_2\text{Cl}_2$ ) 669 ( $2.60 \times 10^4$ ), 612 ( $5.65 \times 10^3$ ), 567 ( $9.75 \times 10^3$ ), 429 ( $6.51 \times 10^4$ ), 390 ( $5.34 \times 10^4$ ).

**8-Deformylvinyl-8-[8<sup>3</sup>-(*p*-methyl)phenyl]dienylphotoporphyrin IX Dimethyl Ester (**11**).** *p*-Methylbenzylbromide (226 mg, 1.22 mmol) dissolved in  $\text{CHCl}_3$  (40 mL) was treated with triphenyl phosphine (711 mg, 2.71 mmol) at refluxing temperature for 3 h. The Wittig reagent so obtained was reacted with photoporphyrin IX isomer A **3** (200 mg, 0.32 mmol) at room temperature in the presence of DBU (1 mL) to afford 205 mg (0.29 mmol) of model chlorin **11** in 90%

yield. Mp: >300 °C.  $^1\text{H}$  NMR (400 MHz, 3.0 mg/mL  $\text{CDCl}_3$ ,  $\delta$  ppm): 9.62 (s, 1H, 20-H); 9.60 (s, 1H, 15-H); 8.75 (s, 1H, 10-H); 8.53 (s, 1H, 5-H); 7.88 (dd,  $J = 17.7, 11.4$  Hz, 1H, 3- $\text{CH}=\text{CH}_2$ ); 7.81 (dd,  $J = 14.5, 11.4$  Hz, 1H, 8<sup>2</sup>-H); 7.56 (d,  $J = 8.4$  Hz, 2H, phenyl-H); 7.43 (d,  $J = 11.2$  Hz, 1H, 8<sup>1</sup>-H); 7.30 (d,  $J = 7.7$  Hz, 2H, phenyl-H); 6.99 (d,  $J = 14.9$  Hz, 1H, 8<sup>3</sup>-H); 6.20 (d,  $J = 17.7$  Hz, 1H, *trans*-3- $\text{CH}=\text{CH}_2$ ); 6.04 (d, 1H, *cis*-3- $\text{CH}=\text{CH}_2$ ); 4.18 (m, 4H, 13 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  and 17 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 3.67 and 3.66 (each s, 3H, 13 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  and 17 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 3.58 (s, 3H, 2 $\text{CH}_3$ ); 3.35 (s, 3H, 12 $\text{CH}_3$ ); 3.27 (s, 3H, 18 $\text{CH}_3$ ); 3.18 (t,  $J = 7.9$  Hz, 2H, 17 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 3.12 (t,  $J = 7.7$  Hz, 2H, 13 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 2.46 (s, 3H, phenyl- $\text{CH}_3$ ); 1.75 (s, 3H, 7 $\text{CH}_3$ ); -1.25 and -1.30 (each br s, 1H, 2NH). Mass spectrum: 711.3 (100,  $\text{M}^+ + 1$ ). UV–vis ( $\lambda_{\text{max}}$  ( $\epsilon$ ) in  $\text{CH}_2\text{Cl}_2$ ): 681 ( $1.01 \times 10^4$ ), 624 ( $1.92 \times 10^3$ ), 558 ( $5.52 \times 10^3$ ), 438 ( $2.94 \times 10^4$ ). HRMS ( $\text{C}_{44}\text{H}_{46}\text{N}_4\text{O}_5$ ):  $\text{M} + 1$  requires 711.3547, found 711.3533.

**7-Demethyl-8-deformylvinyl-7<sup>2</sup>-(*p*-methyl)phenyl-7<sup>1</sup>,7<sup>2</sup>-dihydrobenzoporphyrin IX Dimethyl Ester (**14**).** Chlorin **11** (35 mg) was refluxed in *o*-dichlorobenzene (30 mL) under a nitrogen atmosphere at 170 °C for 2 h. The reaction mixture was passed through the silica column (eluted with petroleum ether) to remove the *o*-dichlorobenzene. The crude product was further chromatographed on a silica column with 2% acetone/dichloromethane. After evaporation of the solvents, the residue was crystallized from dichloromethane/hexanes and the title compound was obtained in 65% yield (22 mg). Mp: >300 °C.  $^1\text{H}$  NMR (400 MHz, 3.0 mg/mL  $\text{CDCl}_3$ ,  $\delta$  ppm): 10.10, 10.09, 10.04 and 10.02 (each s, 1H, 5-H, 10-H, 15-H and 20-H); 8.22 (d,  $J = 9.7$  Hz, 1H, 7<sup>4</sup>-H); 8.19 (dd,  $J = 18.0, 11.4$  Hz, 1H, 3- $\text{CH}=\text{CH}_2$ ); 7.54 (d,  $J = 7.9$  Hz, 2H, phenyl-H); 7.21 (d,  $J = 7.9$  Hz, 2H, phenyl-H); 6.66 (d,  $J = 9.5$  Hz, 1H, 7<sup>3</sup>-H); 6.31 (d,  $J = 17.7$  Hz, 1H, *trans*-3- $\text{CH}=\text{CH}_2$ ); 6.12 (d,  $J = 11.7$  Hz, 1H, *cis*-3- $\text{CH}=\text{CH}_2$ ); 4.65 and 4.33 (each m, 1H, 2  $\times$  7<sup>1</sup>-H); 4.55 (m, 1H, 7<sup>2</sup>-H); 4.43 and 4.38 (each t, 2H, 13 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  and 17 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 3.69 (s, 3H, 1  $\times$  ring  $\text{CH}_3$ ); 3.67 (s, 6H, 13 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  and 17 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 3.65 and 3.61 (each s, 3H, 2  $\times$  ring  $\text{CH}_3$ ); 3.30 and 3.29 (each t,  $J = 8.0$  Hz, 2H, 17 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  and 13 $\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 2.38 (s, 3H, phenyl- $\text{CH}_3$ ); -0.30 (br s, 2H, 2NH). UV–vis ( $\lambda_{\text{max}}$  ( $\epsilon$ ) in  $\text{CH}_2\text{Cl}_2$ ): 633 ( $3.61 \times 10^3$ ), 578 ( $4.12 \times 10^3$ ), 543 ( $7.46 \times 10^3$ ), 507 ( $9.23 \times 10^3$ ), 408 ( $4.39 \times 10^4$ ). Mass spectrum: 693.3 (100,  $\text{M}^+ + 1$ ). HRMS ( $\text{C}_{44}\text{H}_{43}\text{N}_4\text{O}_4$ ):  $\text{M} + 1$  requires 693.3441, found 693.3409.

**2',2''-Bis(8-deformylvinyl-8-dienylphotoporphyrin IX dimethyl ester)-1',1''-biphenyl (**6**).** Following the

**Scheme 6. 8-[8<sup>2</sup>-(9'-Phenanthrene)]vinylprotoporphyrin via Intramolecular Diels–Alder Cycloaddition**

**Figure 13.** Electronic absorption spectra (in CH<sub>2</sub>Cl<sub>2</sub>) of chlorin **7** (—) and the Related porphyrin **19** (---).

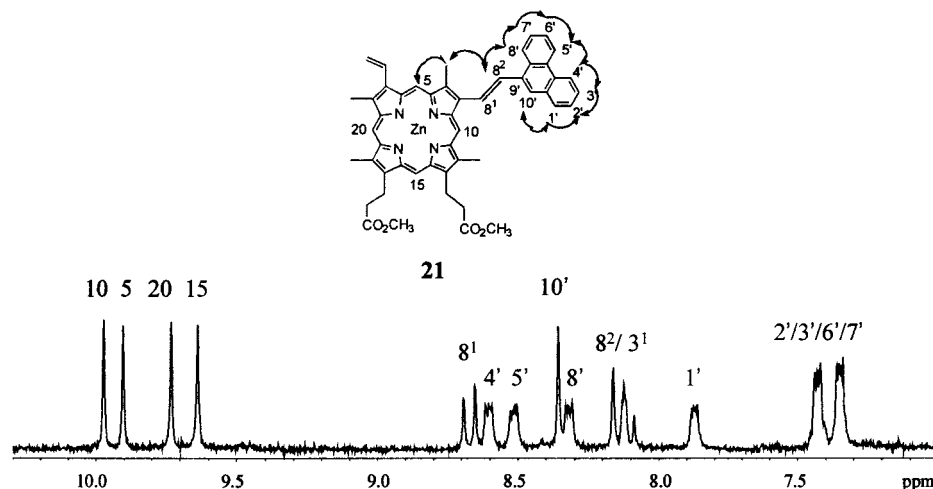
methodology discussed for the preparation of model chlorin **11**, bis-phosphonium salt **5** was obtained by reacting 2,2-dibromobisphenyl (35 mg, 0.05 mmol) and condensed with chlorin **3** (50 mg, 0.10 mmol), dissolved in dichloromethane. The 2,2-bis-chlorin **6** was isolated in 60% yield (42 mg, 0.03 mmol). Mp: > 300 °C. <sup>1</sup>H NMR (400 MHz, 3.0 mg/mL CDCl<sub>3</sub>, δ ppm): 9.77, 9.76, 9.69, 9.67, 9.48, 9.17, 9.13 and 8.89 (each s, 1H, 2 × (5H, 10H, 15H, 20H)); 8.36–7.16 (each d or dd, total 14H, 2 × (8<sup>1</sup>-, 8<sup>2</sup>- and 8<sup>3</sup>-H) and 8H from biphenyl); 8.04 and 7.94 (each dd, *J* = 17.4, 10.8 Hz, 1H, 2 × 3-CH=CH<sub>2</sub>); 6.21 and 6.10 (each d, *J* = 17.4 Hz, 1H, 2 × *trans*-3-CH=CH<sub>2</sub>); 6.02 and 5.90 (each d, *J* = 10.8 Hz, 1H, 2 × *cis*-3-CH=CH<sub>2</sub>); 4.62–4.06 (each m, total 8H, 2 × 13CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> and 2 × 17CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>); 3.69, 3.65, 3.64, 3.60, 3.56, 3.53, 3.49, 3.44, 3.43 and 3.34 (each s, 3H, 10 CH<sub>3</sub>); 3.25, 3.20, 3.06 and 2.72 (each m, 2H, 2 × 17CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> and 2 × 13CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>); 2.17 (s, 6H, 2 × 7CH<sub>3</sub>); -1.36, -1.59 and -1.73 (each br s, total 4H, 2 × 2N-H). Mass spectrum: 1391.8 (100, M<sup>+</sup>). UV-vis (λ<sub>max</sub> (ε) in CH<sub>2</sub>Cl<sub>2</sub>): 663 (2.04 × 10<sup>5</sup>), 540 (5.00 × 10<sup>3</sup>), 504 (7.36 × 10<sup>3</sup>), 390 (6.72 × 10<sup>4</sup>). HRMS (C<sub>86</sub>H<sub>87</sub>N<sub>8</sub>O<sub>10</sub>): requires 1391.6550, found 1391.6540.

**2'-Methyl-2'-(8-deformylvinyl-8-dienyl-photoporphyrin IX dimethyl ester)-1',1'-biphenyl (7)**. The title chlorin was isolated as a byproduct in 20% yield (15 mg). <sup>1</sup>H NMR (400 MHz, 3.0 mg/mL CDCl<sub>3</sub>, δ ppm): 9.637 and 9.634 (splitting s, 1H, 20-H); 9.62 and 9.61 (splitting s, 1H, 15-H);

8.92 and 8.78 (splitting s, 1H, 10-H); 8.69 and 8.50 (splitting s, 1H, 5-H); 7.89 (dd, *J* = 18.0, 11.2 Hz, 1H, 3-CH=CH<sub>2</sub>); 7.66 (dd, *J* = 11.6, 7.2 Hz, 1H, 8<sup>2</sup>-H); 7.56–7.33 (each d or dd, total 8H, biphenyl-H); 7.29 (splitting d, 3H, 8<sup>1</sup>-H); 6.84 and 6.78 (splitting d, *J* = 15.8 Hz, 1H, 8<sup>3</sup>-H); 6.20 and 6.18 (splitting d, *J* = 18.0 Hz, 1H, *trans*-3-CH=CH<sub>2</sub>); 6.05 and 6.04 (splitting d, *J* = 11.2 Hz, 1H, *cis*-3-CH=CH<sub>2</sub>); 4.25 and 4.15 (each m, 4H, 13CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> and 17CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>); 3.67 and 3.66 (each s, 3H, 13CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> and 17CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>); 3.57 and 3.56 (splitting s, 3H, 2CH<sub>3</sub>); 3.39 and 3.38 (s, 3H, 12CH<sub>3</sub>); 3.30 (s, 3H, 18CH<sub>3</sub>); 3.18 and 3.13 (each t, *J* = 7.6 Hz, 2H, 17CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> and 13CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>); 2.32 and 2.22 (splitting s, 3H, biphenyl-CH<sub>3</sub>); 1.88 and 1.75 (splitting s, 3H, 7CH<sub>3</sub>); -1.15, -1.24, -1.26 and -1.35 (each splitting br s, 1H, 2N-H). (Note: all splitting peaks are in a ratio of 1:1). Mp: > 300 °C. UV-vis (λ<sub>max</sub> (ε) in CH<sub>2</sub>Cl<sub>2</sub>): 681 (1.56 × 10<sup>4</sup>), 624 (5.42 × 10<sup>3</sup>), 561 (8.66 × 10<sup>3</sup>), 435 (3.91 × 10<sup>4</sup>), 408 (4.5 × 10<sup>4</sup>). Mass: 787.3 (100, M<sup>+</sup> + 1, bp). HRMS (C<sub>50</sub>H<sub>50</sub>N<sub>4</sub>O<sub>5</sub>): requires 786.3781, found 786.3749.

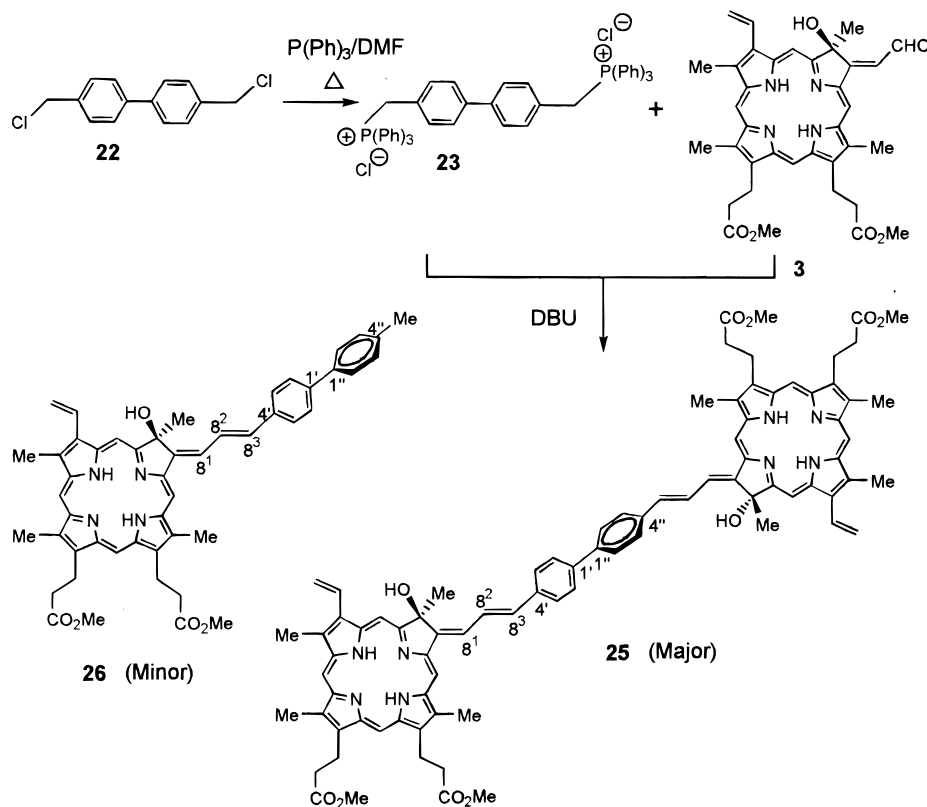
<sup>1</sup>H NMR (400 MHz, 3 mg/mL in DMSO-*d*<sub>6</sub>, all δ values are relative to the CH<sub>2</sub>Cl<sub>2</sub> which is 5.30 ppm): 9.40, 9.30, 9.11 and 8.90 (each s, 1H, 5-H, 10-H, 15-H and 20-H); 7.83 (dd, *J* = 18.6, 11.5 Hz, 1H, 3-CH=CH<sub>2</sub>); 7.78 and 7.63 (each d, *J* = 8.4 Hz, 1H, 2 × biphenyl-H); 7.22–7.20 (total 8H, 6 × biphenyl-H and 8<sup>1</sup>-H and 8<sup>2</sup>-H); 6.44 (splitting d, *J* = 15.6 Hz, 1H, 8<sup>3</sup>-H); 5.98 (d, *J* = 18.6 Hz, 1H, *trans*-3-CH=CH<sub>2</sub>); 5.75 (d, *J* = 11.5 Hz, 1H, *cis*-3-CH=CH<sub>2</sub>); 3.83 and 3.67 (each t, *J* = 7.5 Hz, 2H, 13CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> and 17CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>); 3.21, 3.13, 3.11, 3.03 and 2.94 (each s, 3H, 13CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>-CH<sub>3</sub>, 17CH<sub>2</sub>CH<sub>2</sub>-CO<sub>2</sub>CH<sub>3</sub>, 2 CH<sub>3</sub>, 12 CH<sub>3</sub> and 18CH<sub>3</sub>); 2.77 and 2.71 (each t, *J* = 7.6 Hz, 2H, 17CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> and 13CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>); 2.07 (s, 3H, biphenyl-CH<sub>3</sub>); 1.66 (s, 3H, 7CH<sub>3</sub>); 0.49 and 0.42 (each br s, 1H, 2NH).

<sup>1</sup>H NMR (400 MHz, 303 K, 3.0 mg/mL dioxane-*d*<sub>6</sub>, δ ppm relative to CHCl<sub>3</sub>: 7.26 ppm): 9.68, 9.60 (each s, 1H, 2 × meso-H); 9.323 and 9.316 (splitting s, 1H, 1 × meso-H); 9.048 and 9.037 (splitting s, 1H, 1 × meso-H); 8.38 and 8.34 (dd, *J* = 11.3, 6.8 Hz, 1H, 8<sup>2</sup>-H); 8.10 (dd, *J* = 18.0, 12.0 Hz, 1H, 3-CH=CH<sub>2</sub>); 7.85 (splitting d, *J* = 11 Hz, 1H, 8<sup>1</sup>-H); 7.97, 7.41, 7.31 and 7.23 (each t, *J* = 7.4 Hz, 1H, 4 × biphenyl-H); 7.28, 7.25, 7.16 and 7.13 (each d, *J* = 8.2 Hz, 1H, 4 × biphenyl-H); 6.73 (splitting d, *J* = 15.8 Hz, 1H, 8<sup>3</sup>-H); 6.25 (d, *J* = 18.0 Hz, 1H, *trans*-3-CH=CH<sub>2</sub>); 5.99 (d, *J* = 12.0 Hz, 1H, *cis*-3-CH=CH<sub>2</sub>);



**Figure 14.**  $^1\text{H}$  NMR spectrum of porphyrin **21** [only the downfield region ( $\delta$  7.0–10.3 ppm) is shown].

**Scheme 7. Conjugated Chlorin Dimer 25 and Related Monomer 26 from Chlorin 3**

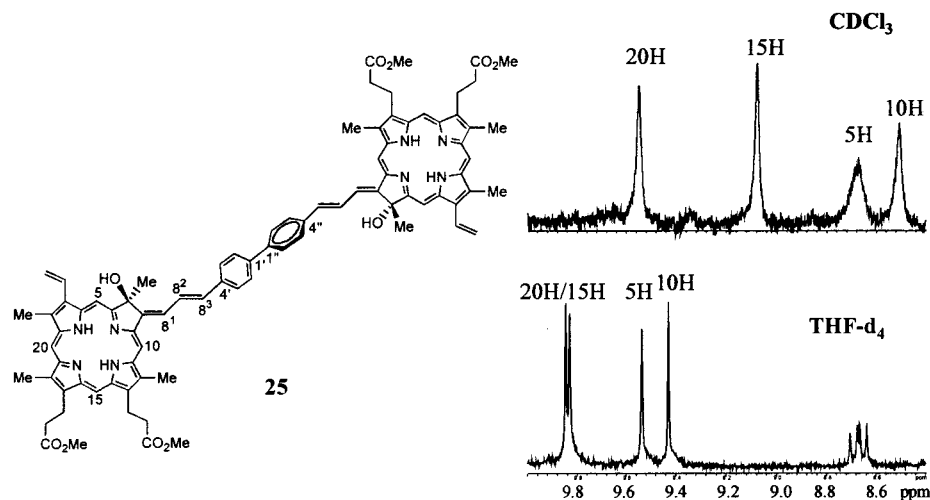


4.18 and 4.00 (each m, 2H,  $13\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  and  $17\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 3.45 (s, 6H,  $13\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  and  $17\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 3.43, 3.39 and 3.23 (each s, 3H,  $3 \times$  ring  $\text{CH}_3$ ); 3.10 and 3.02 (each t,  $J = 7.6$  Hz, 2H,  $17\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  and  $13\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 2.05 (s, 6H, biphenyl- $\text{CH}_3$  and 7 $\text{CH}_3$ ); -2.50 and -2.58 (each br s, 1H, 2NH).

$^1\text{H}$  NMR (400 MHz, 323 K, 3.0 mg/mL dioxane- $d_6$ ,  $\delta$  ppm relative to  $\text{CHCl}_3$ ): 7.26 ppm): 9.67, 9.59 (each s, 1H,  $2 \times$  meso-H); 9.301 and 9.292 (splitting s, 1H,  $1 \times$  meso-H); 9.039 and 9.033 (splitting s, 1H,  $1 \times$  meso-H); 8.36 and 8.32 (dd,  $J = 11.3, 6.8$  Hz, 1H,  $8^2$ -H); 8.09 (dd,  $J = 18.0, 12.0$  Hz, 1H, 3- $\text{CH}=\text{CH}_2$ ); 7.82 (splitting d,  $J = 11$  Hz, 1H,  $8^1$ -H); 7.95, 7.40, 7.31 and 7.21 (each t,  $J = 7.4$  Hz, 1H,  $4 \times$  biphenyl-H); 7.28, 7.25, 7.16 and 7.12 (each d,  $J = 8.2$  Hz, 1H,  $4 \times$  biphenyl-H); 6.73 (splitting d,  $J = 15.8$  Hz, 1H,  $8^3$ -H); 6.25 (d,  $J = 18.0$  Hz, 1H,  $\text{trans-3CH}=\text{CH}_2$ ); 5.99 (d,  $J = 12.0$  Hz, 1H,  $\text{cis-3CH}=\text{CH}_2$ ); 4.19 and 4.01 (each m, 2H,  $13\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  and  $17\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 3.46 (s, 6H,  $13\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  and  $17\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ );

$3.43, 3.39$  and  $3.23$  (each s, 3H,  $3 \times$  ring  $\text{CH}_3$ ); 3.10 and 3.02 (each t,  $J = 7.6$  Hz, 2H,  $17\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  and  $13\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 2.05 (s, 6H, biphenyl- $\text{CH}_3$  and 7 $\text{CH}_3$ ); -2.50 and -2.58 (each br s, 1H, 2NH).

$^1\text{H}$  NMR (400 MHz, 343 K, 3.0 mg/mL dioxane- $d_6$ ,  $\delta$  ppm relative to  $\text{CHCl}_3$ ): 7.26 ppm): 9.69, 9.60 (each s, 1H,  $2 \times$  meso-H); 9.29 (s, 1H,  $1 \times$  meso-H); 9.039 and 9.04 (s, 1H,  $1 \times$  meso-H); 8.35 and 8.31 (splitting dd,  $J = 11.3, 6.8$  Hz, 1H,  $8^2$ -H); 8.09 (dd,  $J = 18.0, 12.0$  Hz, 1H, 3- $\text{CH}=\text{CH}_2$ ); 7.85 (d,  $J = 11$  Hz, 1H,  $8^1$ -H); 7.95 (splitting d,  $J = 7.6$  Hz, 1H,  $1 \times$  biphenyl-H); 7.40, 7.31 and 7.21 (each t,  $J = 7.4$  Hz, 1H,  $3 \times$  biphenyl-H); 7.28, 7.25, 7.16 and 7.12 (each d,  $J = 8.2$  Hz, 1H,  $4 \times$  biphenyl-H); 6.74 (splitting d,  $J = 15.8$  Hz, 1H,  $8^3$ -H); 6.26 (splitting d,  $J = 18.0$  Hz, 1H,  $\text{trans-3CH}=\text{CH}_2$ ); 6.01 (splitting d,  $J = 12.0$  Hz, 1H,  $\text{cis-3CH}=\text{CH}_2$ ); 4.20 and 4.02 (each t,  $J = 6.9$  Hz, 2H,  $13\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  and  $17\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 3.49 (s, 6H,  $13\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$  and  $17\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_3$ ); 3.44, 3.39 and 3.25 (each s, 3H,  $3 \times$  ring  $\text{CH}_3$ ); 3.12 and 3.04 (each t,  $J$



**Figure 15.** NMR of 4',4''-bischlorin **25** (effect of solvents).

**Table 2.** Geometrical Parameters<sup>a</sup> for  $\pi$ - $\pi$  Interaction in Special Pairs Found in Crystal Structures and Synthetic Dimer **9**

PDB ID	tetrapyrrole macrocycle					single pyrrole ring				
	MPS	Ct-Ct	LS	SA	dihed	MPS	Ct-Ct	LS	SA	dihed
1aij	3.63	7.52	6.59	61.1	9.6	3.58	3.64	0.69	10.8	5.2
1pcr	3.56	7.72	6.85	62.5	5.7	3.23	3.45	1.21	20.5	5.8
1prc	3.07	7.37	6.70	65.4	11.1	3.28	3.34	0.64	11.0	5.1
2prc	3.14	7.48	6.79	65.2	11.3	3.45	3.51	0.66	10.8	1.0
<b>9</b>	3.37	5.97	4.92	55.6	3.0	3.20	3.52	1.44	24.2	7.0

<sup>a</sup> Key: MPS, mean plane separation distance; ct-ct, distance between two centers; LS, lateral shift of two planes; SA, slip angle; dihed, angle between two planes. For a completely overlapped ring system, MPS = Ct-Ct and LS = SA = dihed = 0 (see method for definition).

= 7.6 Hz, 2H, 17CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> and 13CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>); 2.07 (s, 6H, biphenyl-CH<sub>3</sub> and 7CH<sub>3</sub>); -2.43 (br s, 2H, 2NH).

**2'-(8-Deformylvinyl-8-dienyl-photoporphyrin IX dimethyl ester)-1',1''-biphenyl (8).** 2-Phenylbenzylbromide (170 mg, 0.70 mmol) dissolved in chloroform (40 mL) was treated with triphenyl phosphine (320 mg, 1.2 mmol) at refluxing temperature for 24 h. The Wittig reagent obtained after removal of chloroform was redissolved in dichloromethane (30 mL) and reacted with photoporphyrin IX isomer A (**3**) (60 mg, 0.1 mmol) at room temperature in the presence of DBU (0.75 mL) to afford the title compound in 80% yield (62 mg). Mp: >300 °C. <sup>1</sup>H NMR (400 MHz, 3.0 mg/mL CDCl<sub>3</sub>,  $\delta$  ppm): 9.72 (s, 1H, 20-H); 9.57 (s, 1H, 15-H); 8.79 (s, 1H, 10-H); 8.50 (s, 1H, 5-H); 8.07 (dd,  $J$  = 18.1, 11.6 Hz, 1H, 3-CH=CH<sub>2</sub>); 7.97 (d,  $J$  = 8.1 Hz, 1H, 1  $\times$  biphenyl-H); 7.96 (dd,  $J$  = 15.7, 11.6 Hz, 1H, 8<sup>2</sup>-H); 7.59 (m, total 8H, 6  $\times$  biphenyl-H); 7.45 (m, 2H, 2  $\times$  biphenyl-H); 7.38 (d,  $J$  = 11.4 Hz, 3H, 8<sup>1</sup>-H); 7.07 (d,  $J$  = 15.5 Hz, 1H, 8<sup>3</sup>-H); 6.31 (d,  $J$  = 18.1 Hz, 1H, *trans*-3-CH=CH<sub>2</sub>); 6.13 (d,  $J$  = 11.6 Hz, 1H, *cis*-3-CH=CH<sub>2</sub>); 4.23 and 4.08 (each m, 2H, 13CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> and 17CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>); 3.67 and 3.66 (each s, 3H, 13CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> and 17CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>); 3.44, 3.31 and 3.30 (each s, 3H, 2CH<sub>3</sub>, 12CH<sub>3</sub> and 18CH<sub>3</sub>); 3.16 and 3.10 (each t,  $J$  = 7.9 Hz, 2H, 17CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> and 13CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>); 1.85 (s, 3H, 7CH<sub>3</sub>); -1.00 and -1.20 (each br s, 1H, 2NH). UV-vis ( $\lambda_{\max}$  ( $\epsilon$ ) in CH<sub>2</sub>Cl<sub>2</sub>): 678 (1.52  $\times$  10<sup>4</sup>), 621 (2.06  $\times$  10<sup>3</sup>), 558 (8.20  $\times$  10<sup>3</sup>), 435 (4.20  $\times$  10<sup>4</sup>). Mass spectrum: 773.8 (100, M<sup>+</sup> + 1). HRMS (C<sub>49</sub>H<sub>48</sub>N<sub>4</sub>O<sub>5</sub>): requires 772.3623, found 772.3614.

**Spirochlorin-Chlorin Dimer (9).** The bischlorin **6** was found to be unstable if the reaction was left for a longer period of time and slowly converted into an unexpected chlorin-spirochlorin dimer linked via a tetrahydrobenzophenanthrene bridge **9**. The rate of this transformation was found to be dependent on the reaction conditions used. Mp: >300 °C. UV-vis spectrum in dichloromethane: 664 (1.77  $\times$  10<sup>4</sup>), 613 (1.78  $\times$  10<sup>3</sup>), 504 (4.46  $\times$  10<sup>3</sup>), 388 (5.55  $\times$  10<sup>4</sup>). Mass spectrum: 1391.8 (100, M<sup>+</sup>, bp), 1373.7 (30, M<sup>+</sup>, H<sub>2</sub>O). HRMS: C<sub>86</sub>H<sub>87</sub>N<sub>8</sub>O<sub>10</sub> requires 1391.6550, found 1391.6540; C<sub>86</sub>H<sub>87</sub>N<sub>8</sub>O<sub>10</sub> - H<sub>2</sub>O

requires 1373.6440, found 1373.6520. <sup>1</sup>H NMR (400 MHz, 3 mg/mL CDCl<sub>3</sub>,  $\delta$  ppm): see Table 1.

**Porphyrin-Chlorin Dimer (16).** This dimer was formed upon leaving the NMR sample of **9** in CDCl<sub>3</sub> (without pyridine) at room temperature for an extended period of time. Mp: >300 °C. <sup>1</sup>H NMR (400 MHz, 3.0 mg/mL CDCl<sub>3</sub>,  $\delta$  ppm): 10.41, 10.13, 10.07, 9.98, 9.86, 9.62, 9.28 and 7.49 (each s, 1H, 2  $\times$  (5H, 10H, 15H, 20H)); 8.18 and 8.09 (each dd,  $J$  = 17.9, 11.8 Hz, 1H, 2  $\times$  3-CH=CH<sub>2</sub>); total 13 bridge protons [8.37 (d,  $J$  = 8.0 Hz, 1H); 7.98 (d,  $J$  = 8.0 Hz, 1H); 7.60 (t, 1H); 7.48 (dd,  $J$  = 7.5 Hz, 1H); 7.33 (d,  $J$  = 9.9 Hz, 1H); 7.19 (d,  $J$  = 7.6 Hz, 1H); 6.79 (d,  $J$  = 7.8 Hz, 1H); 6.36 (d,  $J$  = 8.0 Hz, 1H); 5.91 (d,  $J$  = 8.0 Hz, 1H); 5.86 (d,  $J$  = 9.9 Hz, 1H); 5.77 (d,  $J$  = 8.0 Hz, 1H); 4.91 (d,  $J$  = 14.0 Hz, 1H); 3.97 (d,  $J$  = 13.8 Hz, 1H)]; 6.40 and 6.19 (each d,  $J$  = 17.9 Hz, 1H, 2  $\times$  *trans*-3-CH=CH<sub>2</sub>); 6.12 and 5.94 (each d,  $J$  = 11.8 Hz, 1H, 2  $\times$  *cis*-3-CH=CH<sub>2</sub>); 4.47, 4.34 and 4.18 (each t, total 6H, 3  $\times$  CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>); 3.68 (s and t merged, 8H, 2  $\times$  CH<sub>3</sub> and 1  $\times$  CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>); 3.73, 3.71, 3.64, 3.47, 3.20, 3.10, 2.62, 2.26, 1.81 and 1.45 (each s, 3H, 10  $\times$  CH<sub>3</sub>); 3.30, 3.24, 3.14 and 2.62 (each t, 2H, 2  $\times$  17CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> and 2  $\times$  13CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>); 2.17 (s, 6H, 2  $\times$  7CH<sub>3</sub>); -0.40, -1.21 and -1.73 (each br s, total 4H, 2  $\times$  2N-H). UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): 664 (1.17  $\times$  10<sup>4</sup>), 628 (1.37  $\times$  10<sup>3</sup>), 574 (2.30  $\times$  10<sup>3</sup>), 538 (5.18  $\times$  10<sup>3</sup>), 505 (5.95  $\times$  10<sup>3</sup>), 409 (5.31  $\times$  10<sup>4</sup>). Mass: 1373.8 (100, M<sup>+</sup>, bp). HRMS: C<sub>86</sub>H<sub>85</sub>N<sub>8</sub>O<sub>9</sub> requires 1373.6440, found 1373.6446.

**8-Devinyl-8-[8<sup>2</sup>-(9', 10'-dihydrophenanthrene)]vinyl-porphyrin IX Dimethyl Ester (18) and the Related Phenanthrene Analogue (19).** Chlorin **7** was found to be unstable in CDCl<sub>3</sub> if left for an extended period of time and converted into porphyrin **18**, which on further oxidation produced an aromatized phenanthrene linked porphyrin **19**. The separation of these two porphyrins in their free base form were not successful; however, they were separated into individual analogues as the related Zn(II) complexes **20** and **21**, respectively. UV-vis spectrum in dichloromethane (mixture of **18** and **19**): 633 (1.44  $\times$  10<sup>3</sup>), 576 (2.00  $\times$  10<sup>3</sup>), 543 (3.22  $\times$  10<sup>3</sup>), 507 (3.41  $\times$  10<sup>3</sup>), 408 (3.88  $\times$  10<sup>4</sup>). Mass spectrum: 767.3

(100,  $M^+ + 1$ ) for  $C_{50}H_{46}N_4O_4Zn(II)$ . **8-Devinylnyl-8-[8<sup>2</sup>-(9',10'-dihydrophenanthrene)]vinylprotoporphyrin IX Dimethyl ester (20)**:  $^1H$  NMR (400 MHz, 3.0 mg/mL  $CDCl_3$ ,  $\delta$  ppm): 9.70, 9.68, 9.56 and 9.55 (each s, 1H, 5-H, 10-H, 15-H and 20-H); 8.11 (dd,  $J = 17.6$ , 11.1 Hz, 1H, 3- $CH=CH_2$ ); 8.02–7.39 (total 8H, 1', 2', 3', 4', 5', 6', 7' and 8'-H); 7.83 (d,  $J = 15.3$  Hz, 1H, 8<sup>1</sup>-H); 6.88 (dd,  $J = 16.1$ , 8.8 Hz, 1H, 8<sup>2</sup>-H); 6.25 (d,  $J = 17.6$  Hz, 1H, *trans*-3- $CH=CH_2$ ); 6.11 (d,  $J = 11.1$  Hz, 1H, *cis*-3- $CH=CH_2$ ); 4.86 and 4.23 (each t,  $J = 6.5$  Hz, 2H, 13 $CH_2$ - $CH_2CO_2CH_3$  and 17 $CH_2$ - $CH_2CO_2CH_3$ ); 4.32 (dd and t merged,  $J = 9.9$ , 5.9 Hz, 3H, 9'-H and 2  $\times$  10'-H); 3.67 and 3.65 (each s, 3H, 13 $CH_2$ - $CH_2CO_2CH_3$  and 17 $CH_2$ - $CH_2CO_2CH_3$ ); 3.54, 3.48, 3.46 and 3.41 (each s, 3H, 4  $\times$  ring  $CH_3$ ); 3.16 and 3.14 (each t,  $J = 8.8$  Hz, 2H, 17 $CH_2$ - $CH_2CO_2CH_3$  and 13 $CH_2$ - $CH_2CO_2CH_3$ ). Mass spectrum: 830.4 (100,  $M^+$ , bp). HRMS:  $C_{50}H_{46}N_4O_4Zn$  requires: 830.2810, found 830.2769.

**Zn(II) 8-devinylnyl-8-[8<sup>2</sup>-(9'-phenanthrene)]vinylprotoporphyrin IX dimethyl ester (21)**:  $^1H$  NMR (400 MHz, 3.0 mg/mL  $CDCl_3$ ,  $\delta$  ppm): 9.52 (s, 1H, 10-H); 9.51 (s, 1H, 5-H); 9.36 (s, 1H, 20-H); 9.32 (s, 1H, 15-H); 8.91 (d, 1H, 4'-H); 8.84 (d, 1H, 5'-H); 8.57 (d, 1H, 8'-H); 8.44 (s, 1H, 10'-H); 8.39 (d, 1H, 8<sup>1</sup>-H); 8.22 (d, 1H, 1'-H); 8.13 (d, 1H, 8<sup>2</sup>-H); 8.12 (dd, 1H, 3- $CH=CH_2$ ); 7.79 (m, 4H, for 2', 3', 6' and 7'-H); 6.30 (d,  $J = 18.1$  Hz, 1H, *trans*-3- $CH=CH_2$ ); 6.16 (d,  $J = 11.6$  Hz, 1H, *cis*-3- $CH=CH_2$ ); 4.21 (m, 4H, 13 $CH_2$ - $CH_2CO_2CH_3$  and 17 $CH_2$ - $CH_2CO_2CH_3$ ); 3.67 (s, 6H, 13 $CH_2$ - $CH_2CO_2CH_3$  and 17 $CH_2$ - $CH_2CO_2CH_3$ ); 3.52 (s, 3H, 2 $CH_3$ ); 3.51 (s, 3H, 7 $CH_3$ ); 3.43 (s, 3H, 12 $CH_3$ ); 3.38 (s, 3H, 18 $CH_3$ ); 3.10 (m, 4H, 17 $CH_2$ - $CH_2CO_2CH_3$  and 13 $CH_2$ - $CH_2CO_2CH_3$ ). Mass spectrum: 828.4 (100,  $M^+$ , bp). HRMS:  $C_{50}H_{44}N_4O_4Zn$  requires 828.2654, found 828.2610.

$^1H$  NMR (400 MHz, 3.0 mg/mL  $DMSO-d_6$ ,  $\delta$  ppm): 10.40, 10.32, 10.17 and 10.08 (each s, 1H, 5-H, 10-H, 15-H and 20-H); 9.10 (d,  $J = 15.8$  Hz, 1H, 8<sup>1</sup>-H); 9.04 (d, 1H, 4'-H); 8.95 (d, 1H, 5'-H); 8.80 (s, 1H, 10'-H); 8.76 (d, 1H, 8'-H); 8.58 (d,  $J = 15.8$  Hz, 1H, 8<sup>2</sup>-H); 8.56 (dd,  $J = 17.9$ , 11.5 Hz, 1H, 3- $CH=CH_2$ ); 8.30 (d, 1H, 1'-H); 7.85 and 7.78 (each m, 2H, for 2', 3', 6' and 7'-H); 6.43 (d,  $J = 17.9$  Hz, 1H, *trans*-3- $CH=CH_2$ ); 6.16 (d,  $J = 11.6$  Hz, 1H, *cis*-3- $CH=CH_2$ ); 4.38 (t, 4H, 13 $CH_2$ - $CH_2CO_2CH_3$  and 17 $CH_2$ - $CH_2CO_2CH_3$ ); 3.95 and 3.78 (each s, 3H, 13 $CH_2$ - $CH_2CO_2CH_3$  and 17 $CH_2$ - $CH_2CO_2CH_3$ ); 3.65 and 3.64 (each s, 3H, 2  $\times$  ring  $CH_3$ ); 3.60 (s, 6H, 2  $\times$  ring  $CH_3$ ); ~3.29 (m, 4H, 17 $CH_2$ - $CH_2CO_2CH_3$  and 13 $CH_2$ - $CH_2CO_2CH_3$ ).

**Reaction of Photoporphyrin IX 3 with the Wittig Reagent Derived from 4,4'-Bis(chloromethyl)-1,1'-biphenyl (22)**. 4,4'-Bis(chloromethyl)-1,1'-biphenyl **22** (30 mg, 0.12 mmol) dissolved in DMF (15 mL) along with triphenyl phosphine (150 mg, 0.57 mmol). The reaction mixture was stirred at refluxing temperature for 24 h under a nitrogen atmosphere. The Wittig reagent so obtained, **23**, was reacted with photoporphyrin IX isomer A **3** (160 mg, 0.26 mmol) at room temperature in the presence of DBU (1 mL) to afford 84 mg (yield, 25%) of bischlorin **25** and monomer **26** in 40% yield, 40% (38 mg).

**4',4''-Bis(8-deformylvinyl-8-dienyl-photoporphyrin IX dimethyl ester)-1',1''-biphenyl (25)**:  $^1H$  NMR (400 MHz, 3.0 mg/mL  $CDCl_3$ ,  $\delta$  ppm): 9.58 (s, 1H, 20-H); 9.10 (s, 1H, 15-H); 9.00 (br s, 1H, 5-H); 8.6 (s, 1H, 10-H); 8.15 (dd,  $J = 18.1$ , 11.6 Hz, 2H, 2  $\times$  3- $CH=CH_2$ ); 8.15 (dd,  $J = 15.5$ , 11.9 Hz, 2H, 2  $\times$  8<sup>2</sup>-H); 8.03 (d,  $J = 11.4$  Hz, 2H, 2  $\times$  8<sup>1</sup>-H); 7.67 (s, 8H, 8  $\times$  biphenyl-H); 7.06 (d,  $J = 15.9$  Hz, 2H, 2  $\times$  8<sup>3</sup>-H); 6.20 (d,  $J = 17.5$  Hz, 2H, 2  $\times$  *trans*-3- $CH=CH_2$ ); 5.93 (d,  $J = 11.4$  Hz, 2H, 2  $\times$  *cis*-3- $CH=CH_2$ ); 4.17 and 3.98 (each m, 4H, 2  $\times$  13 $CH_2$ - $CH_2CO_2CH_3$  and 2  $\times$  17 $CH_2$ - $CH_2CO_2CH_3$ ); 3.48, 3.41, 3.40, 3.32 and 3.23 (each s, 6H, 2  $\times$  13 $CH_2$ - $CH_2CO_2CH_3$ , 2  $\times$  17 $CH_2$ - $CH_2CO_2CH_3$ , 2  $\times$  2 $CH_3$ , 2  $\times$  12 $CH_3$  and 2  $\times$  18 $CH_3$ ); 3.06 and 2.97 (each t,  $J = 7.9$  Hz, 2H, 17 $CH_2$ - $CH_2CO_2CH_3$  and 13 $CH_2$ - $CH_2CO_2CH_3$ ); 2.01 (s, 6H, 2  $\times$  7 $CH_3$ ). (Note: NH resonances were not identified). Mp: >300 °C. UV-vis ( $\lambda_{max}$  (e) in  $CDCl_3$ ): 681 ( $3.04 \times 10^4$ ), 624 ( $7.19 \times 10^3$ ), 570 ( $2.07 \times 10^4$ ), 438 ( $6.45 \times 10^4$ ), 357 ( $2.72 \times 10^4$ ). Mass: 1392.1 (100,  $M^+ + 1$ , b.) as calculated for  $C_{86}H_{87}N_8O_{10}$ .

$^1H$  NMR (400 MHz, 3 mg/mL THF- $d_4$ ,  $\delta$  value relative to  $CH_2Cl_2$ : 5.30 ppm): 9.62 and 9.61 (each s, 2H, 2  $\times$  15-H and 2  $\times$  20-H); 9.31 and 9.20 (each s, 2H, 2  $\times$  5-H and 2  $\times$  10-H); 8.45 (dd,  $J = 15.5$ , 11.9 Hz, 2H, 2  $\times$  8<sup>2</sup>-H); 8.09 (dd,  $J = 17.5$ , 11.4 Hz, 2H, 2  $\times$  3- $CH=CH_2$ ); 8.03 (d,  $J = 11.4$  Hz, 2H, 2  $\times$  8<sup>1</sup>-H); 7.67 (s, 8H, 8  $\times$  biphenyl-H); 7.06 (d,  $J = 15.9$  Hz, 2H, 2  $\times$  8<sup>3</sup>-H); 6.20 (d,  $J = 17.5$  Hz, 2H, 2  $\times$  *trans*-3- $CH=CH_2$ ); 5.93 (d,  $J = 11.4$  Hz, 2H, 2  $\times$  *cis*-3- $CH=CH_2$ ); 4.17 and 3.98 (each m, 4H, 2  $\times$  13 $CH_2$ - $CH_2CO_2CH_3$  and 2  $\times$  17 $CH_2$ - $CH_2CO_2CH_3$ ); 3.48, 3.41, 3.40, 3.32 and 3.23 (each s, 6H, 2  $\times$  13 $CH_2$ - $CH_2CO_2CH_3$ , 2  $\times$  17 $CH_2$ - $CH_2CO_2CH_3$ , 2  $\times$  2 $CH_3$ , 2  $\times$  12 $CH_3$  and 2  $\times$  18 $CH_3$ ); 3.06 and 2.97 (each t,  $J = 7.9$  Hz, 2H, 17 $CH_2$ - $CH_2CO_2CH_3$  and 13 $CH_2$ - $CH_2CO_2CH_3$ ); 2.01 (s, 6H, 2  $\times$  7 $CH_3$ ). (Note: the NH resonances were not identified.)

**4''-Methyl-4'-(8-deformylvinyl-8-dienylphotoporphyrin IX dimethyl ester)-1',1''-biphenyl (26)**:  $^1H$  NMR (400 MHz, 3.0 mg/mL  $CDCl_3$ ,  $\delta$  ppm): 9.57, 9.51 and 8.36 (each s, 1H, 3  $\times$  Meso-H); 8.03 and 8.02 (splitting s, 1H, 1  $\times$  Meso-H); 7.74–6.83 (m, total 12H, 3- $CH=CH_2$ , 8  $\times$  biphenyl-H, 8<sup>1</sup>-H, 8<sup>2</sup>-H and 8<sup>3</sup>-H); 6.12 (d,  $J = 18.1$  Hz, 1H, *trans*-3- $CH=CH_2$ ); 6.01 (d,  $J = 11.6$  Hz, 1H, *cis*-3- $CH=CH_2$ ); 4.25 and 4.15 (each m, 2H, 13 $CH_2$ - $CH_2CO_2CH_3$  and 17 $CH_2$ - $CH_2CO_2CH_3$ ); 3.70, 3.68, 3.52, 3.24 and 3.17 (each s, 3H, 13 $CH_2$ - $CH_2CO_2CH_3$ , 17 $CH_2$ - $CH_2CO_2CH_3$ , 2 $CH_3$ , 12 $CH_3$  and 18 $CH_3$ ); 3.19 and 3.11 (each t,  $J = 7.9$  Hz, 2H, 17 $CH_2$ - $CH_2CO_2CH_3$  and 13 $CH_2$ - $CH_2CO_2CH_3$ ); 2.47 (s, 3H, biphenyl- $CH_3$ ); 1.56 (s, 3H, 7 $CH_3$ ); -0.82 and -0.98 (each br s, 1H, 2NH). Mp: >300 °C. UV-vis (in  $CH_2Cl_2$ ): 681 ( $1.76 \times 10^4$ ), 624 ( $2.92 \times 10^3$ ), 561 ( $9.38 \times 10^3$ ), 444 ( $4.80 \times 10^4$ ). Mass: 788.4 (100,  $M^+ + 2$ , bp) for  $C_{50}H_{50}N_4O_5$ .

**Molecular Modeling. Model Structure of Spirochlorin-Chlorin Dimer 9**. Starting from the crystallographic coordinate,<sup>19</sup> the energy optimization was performed using the stand SYBYL force field parameters with Del Re  $\sigma$  and Huckel  $\pi$  charges using the molecular modeling package SYBYL 6.2 running on Silicon Graphics Indigo 2 (R10000).

**Geometrical Parameters**. Geometrical parameters describing the  $\pi$ - $\pi$  interactions in porphyrin derivatives are described in Scheidt and Lee.<sup>21</sup> All 24 atoms of the core macrocyclic rings are used to define the best plane. The center of the core macrocyclic rings is defined as a centroid of four pyrrole nitrogens. The mean plane separation (MPS) is measured as an average of two perpendicular distances from the centroids to opposing best planes. The lateral shift (LS) is an average of two projections of a vector connecting two centers onto the best planes. The slip angle (SA) is an average of the angles between the vector connecting two centers and the vectors from the centers to opposing best planes. The dihedral angle is the angle between the best planes. Similar parameters were created for a measure of the single pyrrole ring overlap. All five atoms in a specified pyrrole ring were used to define the best plane and the centroid for this case. All calculations were performed with the SYBYL 6.2 package. In addition to our model dimer **9**, several special pair coordinates, obtained from the crystallographic coordinates of photosynthetic reaction centers (Protein Data Bank ID codes, 1aig, 1aij, 1pcr, 1pps, 1yst, 2rcr, 4rcr, 1pcr, 2pcr, 3pcr, 4pcr, 5pcr, 6pcr, 7pcr) were included in our calculations.

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