CHEMISTRY LETTERS, pp. 741-744, 1989.

Synthesis of a Conformationally Restricted Porphyrin Tetramer Bridged by a 9,9'-Spirobifluorene Spacer

Atsuhiro OSUKA, Kazutaka IDA, and Kazuhiro MARUYAMA*
Department of Chemistry, Faculty of Science,
Kyoto University, Kyoto 606

9, 9'-Spirobifluorene-linked porphyrin monomer, dimer, and tetramer, and their zinc-complexes have been synthesized. Intramolecular porphyrin-porphyrin interactions were shown to be greater in the dimer than in the tetramer by ^{1}H-NMR, absorption spectra and intramolecular singlet energy transfer studies.

Since X-ray structural studies of the photosynthetic reaction center from photosynthetic bacteria have revealed the presence of six interacting tetrapyrrole pigments at the active site,$^{1)}$ much attention has been focused on development of complex photosynthetic model compounds containing two or more porphyrins.$^{2)}$ A key question concerns the nature and extent of interactions between the pigments and the unique properties imparted to the aggregates beyond those found in monomeric unit. Synthetic model compounds with well-defined geometries are particularly effective in probing this problem. Recently we reported the synthesis of conformationally restricted porphyrin dimers and the geometry dependence of their absorption spectra and intramolecular singlet energy transfer.$^{3)}$ It has also been shown that diporphyrins bridged by spirobiindane spacer well duplicate the twisted and partially overlapping geometry of the special pair in the bacterial photosynthetic reaction center.$^{3)}$

Now we wish to report here the synthesis of 9,9'-spirobifluorene-linked porphyrin monomer **1**, dimer **2**, and tetramer 3, in all of which relative geometries of porphyrins and spacer can be considered to be rather restricted.

Typically, the synthesis of the tetrameric model 3 is outlined in Scheme 1. Condensation of ethyl 3,4-dimethylpyrrole-2-carboxylate **5**$^{4)}$ with the tetraaldehyde **4**$^{5)}$ in ethanol-HCl gave the tetrakis(dipyrryl)methane **6** in 85% yield. Hydrolysis and decarboxylation by Chang's procedure$^{6)}$ gave the α-unsubstituted tetrakis(dipyrryl)methane **7** in 37% yield. The final cyclization was carried out by treating **7** and 2 equiv. of **8** with p-toluenesulfonic acid for 48 h, giving **3** in 0.42% yield (FAB mass spectrum, m-nitrobenzyl alcohol matrix, 10 keV, 2559.683, $C_{177}H_{208}N_{16}$ requires 2559.697).$^{7)}$ In an analogous manner, the monomer model **1** (18.3%) and dimer model **2** (4.5%) were prepared from the corresponding aromatic aldehydes.$^{5)}$

Selected ^{1}H-NMR data and the absorption and fluorescence data of **1**, **2**, and 3 and their zinc complexes, **1(Zn)**, **2(Zn$_2$)**, and **3(Zn$_4$)**, are listed in Table 1. The protons of the peripheral methyl group (Me^a, indicated in Fig. 1) in 1 and **1(Zn)** experience a diamagnetic ring current of the aromatic spacer and thus appear at 2.42 ppm. Greater upfield shifts observed for the Me$^{a'}$ in **2** (1.77 ppm) and **2(Zn$_2$)** (1.74 ppm) are apparently due to a strong porphyrin ring cur-

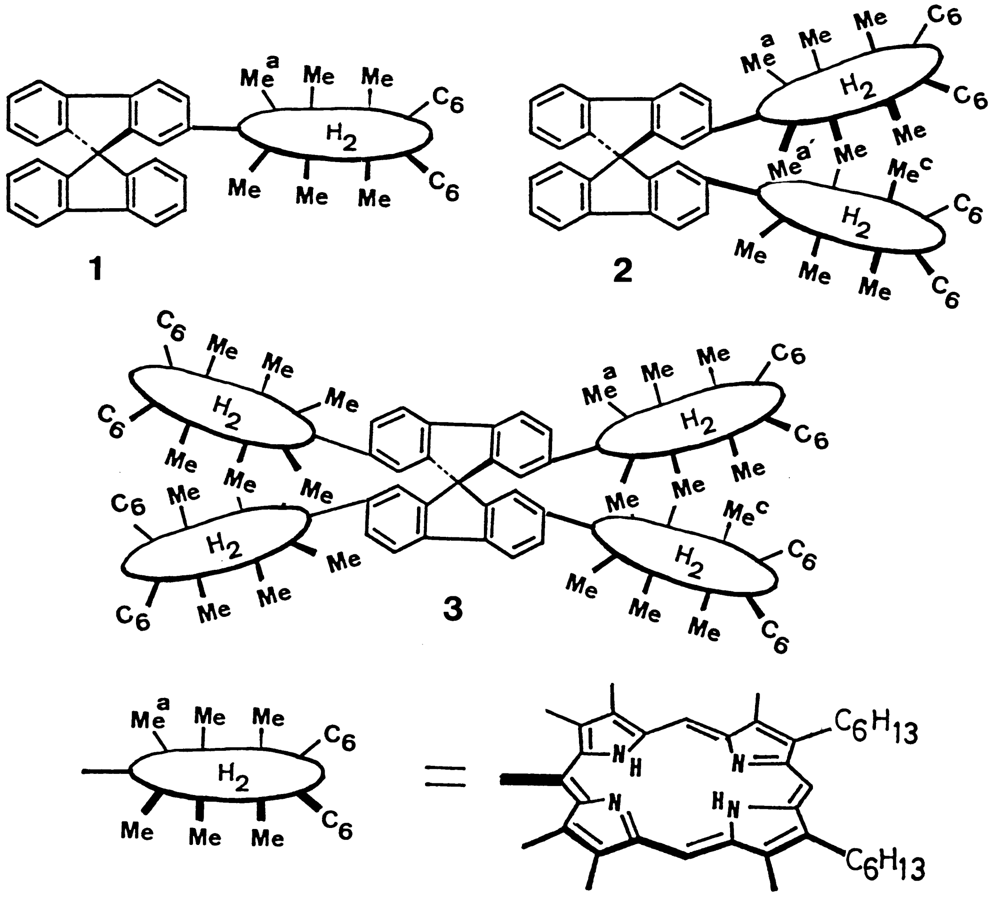
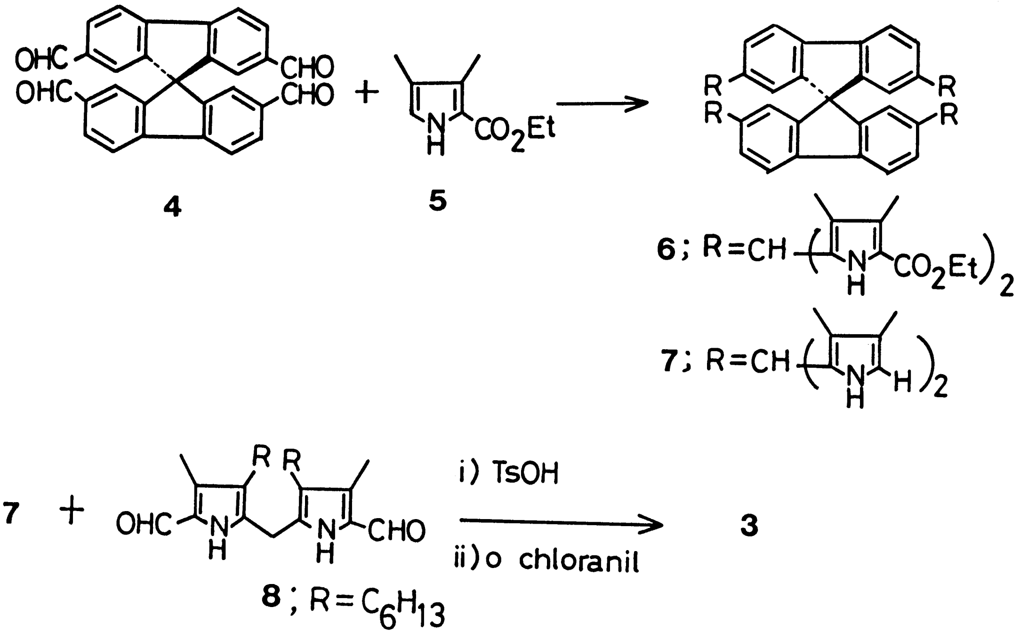


Fig. 1. 9,9'-Spirobifluorene-linked porphyrin model compounds.



Scheme 1.

rent, indicating a twisted and partially overlapping geometry for 2 and **2(Zn$_2$)**. The tetramer **3** has D_{2d} symmetry and thus displays a simple ^{1}H-NMR spectrum, in which the Me^a protons appear at 2.20 ppm, suggesting weaker interactions of the neighboring porphyrins in **3** than those in **2**. This was also inferred from comparison of the absorption spectra of the zinc-complexes, **1(Zn)**, **2(Zn$_2$)**, and **3(Zn$_4$)**. Full width at half-height of the maximum absorbance of Soret band increases in the order of **1(Zn)** < **3(Zn$_4$)** < **2(Zn$_2$)**. The bis-zinc complex **2(Zn$_2$)** showed a split Soret band (S_2) at 406.5 and 411 nm due to exciton coupling, while **3(Zn$_4$)** exhibited a broadened and red-shifted Soret band at 412.5 nm.[8)]

The fluorescence spectra, fluorescence intensities, and fluorescence lifetimes of **2**, **2(Zn$_2$)**, **3**, **3(Zn$_4$)** were unchanged relative to **1** and **1(Zn)**, respectively. In zinc-porphyrin (Zn-P) and free base porphyrin (H_2-P) hybrid complexes, efficient intramolecular singlet excitation energy transfer from the Zn-P to the H_2-P was observed.[9)] Picosecond time-resolved fluorescence spectroscopy[10)] revealed that mono-zinc complexes **2(Zn$_1$)** and **3(Zn$_1$)** in CH_2Cl_2 exhibited a singly decaying component in the fluorescence of the Zn-P at 580 nm with a lifetime of 16 ps and 12 ps, respectively. Taking the radiative lifetime of **1(Zn)** (1.4 ns, τ_0) into consideration, we can calculate the rate of energy transfer, k_E, from the equation, $k_E = 1/\tau - 1/\tau_0$, 6.2 x 10^{10} s^{-1} for **2(Zn$_1$)** and 8.2 x 10^{10} s^{-1} for **3(Zn$_1$)**, respectively. The rate for **3(Zn$_1$)** should be interpreted as a sum of $2k_E'$ and k_E'', where k_E' represents the rate of energy transfer from the Zn-P to the each neighboring H_2-P and k_E'' represents the rate from the Zn-P to the H_2-P on the opposite side. Therefore, it may be concluded that the intramolecular energy transfer is more efficient in the dimer geometry than in the tetramer geometry. In contrast to the mono-zinc complexes, the tris-zinc complex of the tetramer **3(Zn$_3$)** displayed two decaying components, 21 ps and 1.4 ns with 2:1 pre-exponential ratio. A possible explanation for this result is that the short-lifetime component corresponds to the Zn-P in the neighborhood of the H_2-P and the long-lifetime component corresponds to the central Zn-P.

Table 1. Selected physical properties of porphyrin models **1**-**3**

Porphyrin	Absorption, λ_{max}/nm			Fluorescence		^{1}H-NMR$^{c)}$
	Soret	Q bands	FWHM$^{a)}$	λ_{em}/nm	$\tau^{b)}$/ns	(δ/ppm)
1	403	500, 535	33	625	10.5	2.42, 3.46, 3.59
		569, 623		691		
2	404.5	501, 535	41.5	624	10.6	1.77, 2.51, 2.79
		569, 623		690		3.49, 3.65, 3.74
3	408.5	502, 535	33.2	625	10.2	2.26, 3.14, 3.84
		569, 623		691		
1(Zn)	407.5	536, 571	15	575	1.40	2.42, 3.42, 3.49
				627		
2(Zn$_2$)	406.5	536, 571	21	575	1.39	1.74, 2.52, 2.70
	411			625		3.50, 3.57, 3.72
3(Zn$_4$)	412.5	536, 572	18.7	581	1.42	2.29, 3.06, 3.87
				629		

a) Full width at half-height of the maximum absorbance of the Soret band, nm. b) Fluorescence lifetimes at 625 nm for H_2-P and at 580 nm for Zn-P measured by time-correlated single photon counting technique in air-saturated CH_2Cl_2 at 25 °C. c) Chemical shifts of the peripheral methyl protons in $CDCl_3$.

Investigations are continuing to explore inter-porphyrin interactions which are characteristic of conformationally restricted higher homologue of porphyrin aggregates.

We thank the Grand-in-Aid for Special Project Research (No. 63104003) from the Ministry of Education, Science and Culture of Japan and Mitsubishi Foundation for Scientific Research for financial support of this work. We also thank Professor I. Yamazaki and Dr. N. Tamai for measurement of picosecond fluorescence lifetimes.

References

1) J. Deisenhofer, O. Epp, K. Miki, R. Huber, and H. Michel, J. Mol. Biol., 180, 385 (1984); J. P. Allen, G. Feher, T. O. Yeates, H. Komiya, and D. C. Rees, Proc. Natl. Acad. Sci. U.S.A., 84, 5730 (1987); C.-H, Chang, D. Tiede, J. Tang, U. Smith, J. Norris, and M. Schiffer, FEBS Lett., 205, 82 (1986).
2) Some recent examples of covalently linked porphyrin oligomers include; M. R. Wasielewski, M. P. Niemczyk, and W. A. Svec, Tetrahedron Lett., 23, 3215 (1982); I. Abdalmuhdi and C. K. Chang, J. Org. Chem., 50, 411 (1985); J. A. Cowan, J. K. M. Sanders, G. S. Beddard, and R. J. Harrison, J. Chem. Soc., Chem. Commun., 1987, 55; G. M. Dubowchik and A. D. Hamilton, ibid., 1986, 665, 1391; J. Darila, A. Harriman, and L. R. Milgrom, Chem. Phys. Lett., 136, 427 (1987).
3) A. Osuka and K. Maruyama, Chem. Lett., 1987, 825; A. Osuka and K. Maruyama, J. Am. Chem. Soc., 110, 4454 (1988); A. Osuka, K. Maruyama, I. Yamazaki, and N. Tamai, J. Chem. Soc., Chem. Commun., 1988, 1243.
4) This pyrrole was prepared in an analogous manner to the synthesis of 4-ethyl-3-methylpyrrole-2-carboxylate. T. P. Wijeskera, J. B. Paine, III, and D. Dolphin, J. Org. Chem., 50, 3822 (1985).
5) This aldehyde was prepared in 4 steps from 2,2',7,7'-tetrakis(acetyl)-9,9'-spirobifluorene. G. Haas and V. Prelog, Helv. Chim. Acta, 52, 1202 (1969).
6) C. K. Chang and I. Abdalmuhdi, J. Org. Chem., 48, 5388 (1983).
7) All new compounds described in this paper gave satisfactory spectral data consistent with the assigned structures.
8) M. Kasha, Radiat. Res., 20, 55 (1963). The red shift observed in **3(Zn$_4$)** is predicted by application of the exciton theory to D_{2d} symmetric system consisting of four chromophores.
9) R. L. Brookfield, H. Ellul. A. Harriman, and G. Porter, J. Chem. Soc., Faraday Trans. 2, 82, 219 (1986).
10) I. Yamazaki, N. Tamai, H. Kume, H. Tsuchiya, and K. Oba, Rev. Sci. Instrum., 56, 1187 (1985).

(Received February 1, 1989)