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Synthesis and Characterization of Polyyne Porphyrins

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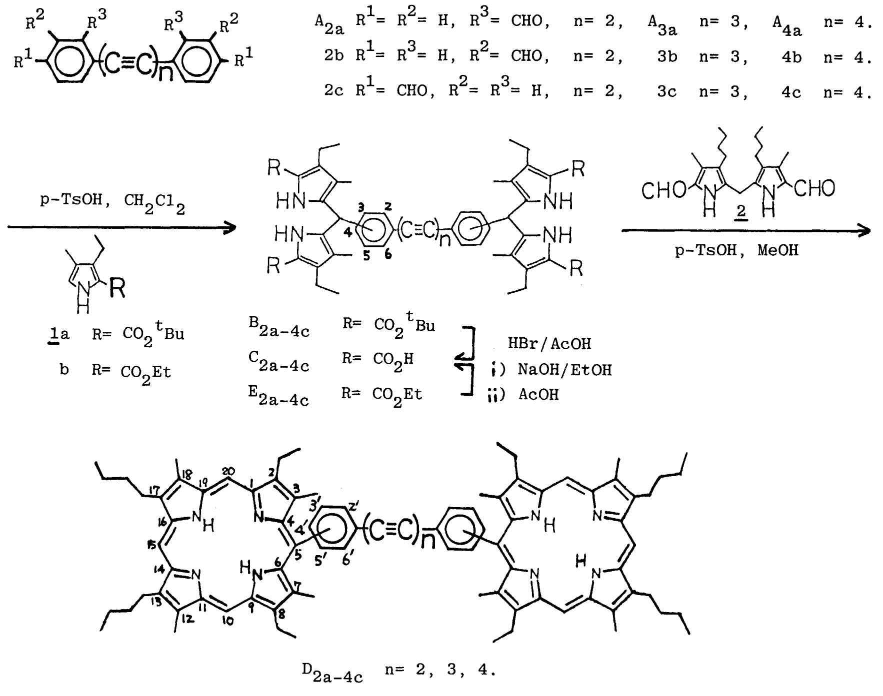
A series of conjugated polyyne porphyrins, in which two porphyrin macrocycles are connected with both ends of diarylpolyyne through aromatic ring, has been prepared and their spectroscopic behaviors were investigated. Diarylpolyyne consisting of aryl group and conjugated triple bond system have rigid and linear structure, and the two porphyrins are held at a fixed geometry and a determined distance. In their absorption spectra, porphyrin Soret bands were red- or blue-shifted depending on their edge-to-edge or face-to-face orientation.

In the primary process of natural green plant photosynthesis, energy and/or electron donor and acceptor are held at appropriate distance, geometry, and orientation, and highly effective energy transfer together with charge separation is achieved in these systems. Since the X-ray analysis of a bacterial photosynthetic reaction center from Rhodopseudomonas viridis[1] clarified an excellent geometrical arrangement of related pigments, many model systems have been investigated by many investigators in different laboratories.[2–14] The exothermicity of the process, distance, orientation, and intervening medium between donor and acceptor control the efficiency of energy and electron transfer process. In order to elucidate the meanings of related factors definitely, it is necessary to construct the model systems of rigidly fixed structure, geometry and orientation.

We have already reported the synthesis and spectroscopic investigation of directly conjugated polyyne porphyrins,[14] in which porphyrin macrocycle is directly connected with one end of diarylpolyyne through aromatic ring. Now, we have synthesized a series of polyyne porphyrins, in which two porphyrin macrocycles are directly connected with both ends of diarylpolyyne through aromatic ring. Since diarylpolyynes have rigid and linear structure, two porphyrin macrocycles are held at a fixed geometry and a determined distance. Changing the substituted position of diarylpolyyne, three types of polyyne porphyrins have been synthesized. Increasing the number of conjugated triple bonds, distance between both ends of diarylpolyyne can be altered systematically. In this report, we will describe detailed synthetic methods, characterization, and spectroscopic behaviors of a series of directly conjugated polyyne porphyrins.

Results and Discussion

Synthesis. The synthetic route of polyyne porphy-



Scheme 1. Synthesis of polyyne porphyrins.

Table 1. ^{1}H NMR Spectral Data of Polyyne Porphyrins in $CDCl_3$ Solution

Compd	Chemical shift δ/ppm																
	Me		2,8-Et		13,17-Bu				H meso		NH	Aryl				
	3,7-	12,18-	$-CH_2-CH_3$		$-CH_2$	$-CH_2$	$-CH_2$	$-CH_3$	15	10,20		H2′	H6′	H3′	H5′	H4′
D_{2a}	2.03	3.64	3.76 —3.90	1.59	4.03 —4.11	2.26 —2.34	1.74 —1.84	1.15	9.97	10.09	−3.34	—	7.16	7.59	6.94	7.32
D_{3a}	2.13	3.59	3.73 —3.89	1.56	4.00 —4.08	2.24 —2.32	1.72 —1.82	1.15	9.91	10.01	−3.42	—	7.43 —7.50	7.62 —7.69	7.43 —7.50	7.43 —7.50
D_{4a}[a]	—	3.53	—	—	—	—	—	—	—	—	—	—	—	—	—	—
D_{2b}	2.47	3.61	3.95 —4.10	1.70 —1.82	3.95 —4.10	2.23 —2.31	1.70 —1.82	1.12	9.93	10.13	−3.29	8.27	7.96	—	7.70	8.07
D_{3b}	2.46	3.62	3.96 —4.09	1.71 —1.79	3.96 —4.09	2.23 —2.31	1.71 —1.79	1.12	9.94	10.13	−3.25 −3.34	8.27	7.96	—	7.70	8.09
D_{4b}	2.45	3.62	3.97 —4.07	1.72 —1.80	3.97 —4.07	2.21 —2.31	1.72 —1.80	1.12	9.94	10.13	−3.24 −3.34	8.27	7.96	—	7.70	8.11
D_{2c}	2.55	3.64	4.01 —4.07	1.75 —1.80	4.01 —4.07	2.25 —2.33	1.75 —1.80	1.14	9.96	10.17	−3.21	8.01		8.13		—
D_{3c}	2.51	3.64	4.00 —4.06	1.75 —1.79	4.00 —4.06	2.25 —2.33	1.75 —1.79	1.13	9.95	10.16	−3.21 −3.31	7.98		8.10		—
D_{4c}	2.49	3.63	3.98 —4.08	1.72 —1.80	3.98 —4.08	2.24 —2.32	1.72 —1.80	1.13	9.96	10.16	−3.23 −3.32	7.96		8.11		—

a) Trace, not exactly determined.

rins is shown in Scheme 1. 2,2′-(ortho, a series), 3,3′-(meta, b series), and 4,4′-(para, c series) diformyldiphenylpolyynes (**A**)[14] were used as starting materials, respectively. Most of synthetic methods of polyyne porphyrins were based on procedures reported by Chang et al.[15] and Sessler et al.,[16] but in some cases their procedures were suitably modified. Condensation of *t*-butyl (**1a**) or ethyl 3-ethyl-4-methylpyrrole-2-carboxylate (**1b**) with diarylpolyynedicarbaldehyde (**A**$_{2a-4c}$) gave bis(dipyrrylmethyl)polyynes (**B**$_{2a-4c}$, **E**$_{2b,2c}$) in good yields. Diarylbutadiyne (**E**$_2$) was relatively stable in hydrolysis under basic conditions, and therefore syntheses of polyyne porphyrins **D**$_{2b}$ (n=2, meta) and **D**$_{2c}$ (n=2, para) were attained via their ethyl esters (**E**$_{2b,2c}$). However, in the case of **E**$_{2a}$ steric hindrance prevents hydrolysis of the ethyl ester. Diarylhexatriyne (**E**$_3$) and diaryloctatetrayne (**E**$_4$) were unstable in hydrolysis under basic conditions; addition of ethoxide anion to conjugated triple bond had occurred. Consequently, synthesis of polyyne porphyrins **D**$_{2a}$ (n=2, ortho), **D**$_3$, and **D**$_4$ were not attained via their ethyl ester using hydrolysis under basic conditions. We succeeded in the syntheses of all the polyyne porphyrins (**D**$_{2a-4c}$) via their *t*-butyl ester using hydrolysis under acidic conditions. In the hydrolysis under acidic conditions, using anhydrous 25% HBr in acetic acid, bis(dipyrrylmethyl)polyynetetracarboxylic tetra-*t*-butyl ester (**B**$_{2a-4c}$) were hydrolyzed to tetracarboxylic acid (**C**$_{2a-4c}$) satisfactorily. Without decarboxylation the final double cyclization was carried out by treating **C**$_{2a-4c}$ and 2 equiv of **2** with *p*-TsOH in methanol for 48 h, and followed by air oxidation. A series of polyyne porphyrins (**D**$_{2a-4c}$) were obtained in reasonable yields, except for **D**$_{4c}$. **D**$_{4c}$ was obtained only in trace amounts.

Characterization. By applying fast-atom-bombardment mass spectrometry to these polyyne porphyrins, characteristic peaks just corresponding to the expected $M^{+}+nH$ (n=0—4) ions were observed without contamination by others. Their ^1H NMR spectral data are shown in Table 1. In ortho-substituted polyyne porphyrins two porphyrin macrocycles were rigidly held at face-to-face geometry. Most of all protons upfield shifted relative to those of meta- and para-substituted polyyne porphyrins due to shielding by porphyrin ring current. Especially, chemical shifts of methyl groups in positions 3 and 7 and aryl groups were outstanding ($\Delta\delta$=0.3—1.0 ppm). Among the spectra of meta- and para-substituted polyyne porphyrins significant differences were not observed. The typical absorption spectra and electronic spectral data of polyyne porphyrins are shown in Fig. 1 and Table 2. Diarylpolyynes have a remarkable vibrational fine structure in their electronic absorption spectra.[14,17,18]

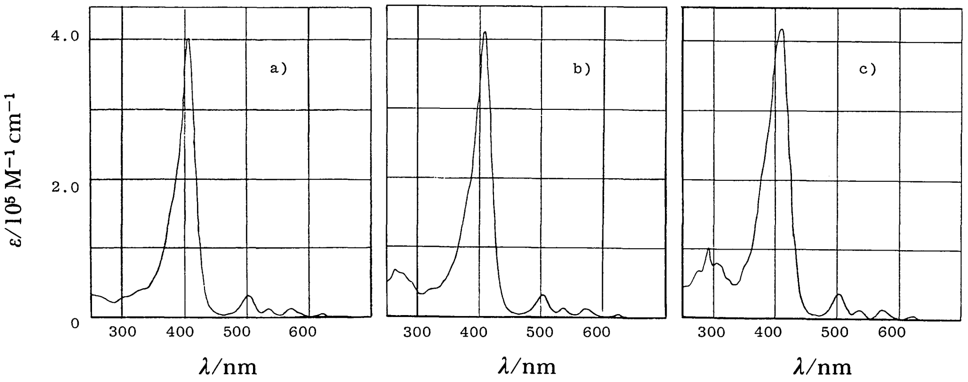


Fig. 1. UV-vis absorption spectra of polyyne porphyrins. a) **D**$_{2c}$, b) **D**$_{3c}$, c) **D**$_{4c}$. Solvent; CH_2Cl_2.

Table 2. UV-Vis Absorption Spectral Data of Polyyne Porphyrins

Compd	λ_{max}/nm (log (ε/M^{-1} cm^{-1}))$^{b)}$					
		Soret				
3		403.0 (5.32)	502 (4.25)	535 (3.90)	570 (3.87)	623 (3.39)
D$_{2a}$		407.0 (5.6)	503 (4.6)	537 (4.2)	571 (4.2)	624 (3.8)
D$_{3a}$	271 (4.9)	405.5 (5.6)	503 (4.6)	536 (4.2)	571 (4.2)	624 (3.8)
D$_{4a}$$^{a)}$	291 (5.0)	404.0 (5.5)	503 (4.6)	536 (4.3)	572 (4.2)	623 (3.8)
D$_{2b}$		404.5 (5.6)	502 (4.6)	535 (4.2)	570 (4.2)	623 (3.6)
D$_{3b}$	261 (4.9)	405.5 (5.6)	502 (4.6)	536 (4.2)	570 (4.2)	622 (3.7)
D$_{4b}$	290 (5.1)	406.5 (5.6)	502 (4.6)	535 (4.2)	570 (4.2)	622 (3.7)
D$_{2c}$		406.5 (5.7)	501 (4.6)	535 (4.2)	571 (4.2)	623 (3.7)
D$_{3c}$	264 (4.8)	407.5 (5.6)	502 (4.6)	535 (4.2)	571 (4.2)	623 (3.7)
D$_{4c}$	292 (5.0)	409.0 (5.6)	502 (4.6)	535 (4.1)	571 (4.1)	623 (3.6)

a) Crude. b) The extinction coefficients were not exactly determined. Solvent; CH_2Cl_2.

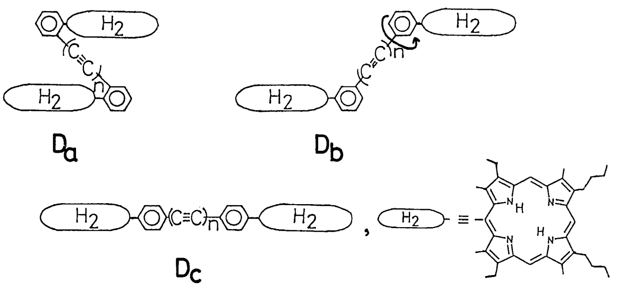


Fig. 2. Geometry of polyyne porphyrins.

In general, extending the terminal π-conjugated aromatic system, the fine structures of their spectra become more broad.[18] These synthetic polyyne porphyrins, in which very large π-conjugated porphyrin macrocycle was connected with both ends of polyyne, showed highly broadening spectra in the region of those of diarylpolyynes. Porphyrin Soret bands were slightly red shifted in each series of polyyne porphyrins (Table 2). In the meta- and para-substituted series their λ_{max}'s were gradually red shifted with increasing the number of acetylenic linkage. Especially, in the para-substituted series this trend was characteristic. On the other hand, in the ortho-substituted series they were gradually blue shifted with increasing the number of the acetylenic linkage. This can be understood taking into consideration of the inter-relating porphyrin geometry. As shown in Fig. 2, in the ortho-substituted series two porphyrin macrocycles were fixed at face-to-face geometry and two rings were exactly overlapping with increasing the number of acetylenic linkage. In the para-substituted series, however, they were fixed at edge-to-edge configuration. Therefore, their λ_{max}'s of Soret band red shifted more with the number of acetylenic linkage. In addition, interaction between the porphyrin and the polyyne was so large in ortho-substituted series that porphyrin Soret bands became exceedingly broader than those of the other series.

These diporphyrin substituted polyynes showed usual fluorescence emission spectra compared with that of the reference porphyrin **3**. Fluorescence emission maxima and total emission intensity were not significantly perturbed by direct conjugation with polyyne functionality (Table 3). Relative emission intensities (I_b/I_a) were different in each series. Difference in substituted position was presumed to alter the overlap of 0–0 and 0–1 bands, similar to that in mono porphyrin substituted polyyne series.[14]

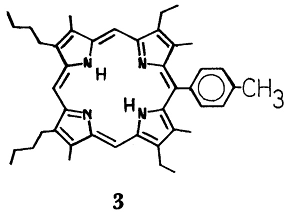


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Table 3. Fluorescence Emission Spectral Data of Polyyne Porphyrins

Compd	$\lambda_{Em\,max}$/nm a ; Q (0–0)	 b ; Q (0–1)	I_b/I_a
3	625	689	0.72
D_{2a}	625	691	0.60
D_{3a}	626	692	0.58
D_{4a}[a)]	626	692	0.59
D_{2b}	625	691	0.66
D_{3b}	625	690	0.65
D_{4b}	625	690	0.65
D_{2c}	625	690	0.75
D_{3c}	626	690	0.74
D_{4c}	624	691	0.75

a) Crude. Solvent; CH_2Cl_2.

These observations in the absorption and the fluorescence spectra of polyyne porphyrins seemed to indicate that direct connection between porphyrin macrocycle and diarylpolyyne had a little perturbation to the electronic state of porphyrin π-conjugated system. Fixation of two chromophores in both ends of rigid diarylpolyyne appeared to be rather important. However, porphyrin Q-bands of absorption spectra and fluorescence emission were correlated to the porphyrin lowest excited singlet state (S_1). This state was, presumably, so stabilized by huge porphyrin π-conjugated system that polyyne porphyrin S_1 state localized predominantly porphyrin inherent lowest excited singlet state. Further, porphyrin π-plane is perpendicular to the terminal aryl group of diarylpolyyne, so the electronic coupling between them are not sufficiently large.

As described in previous paper[14] in the mono porphyrin substituted polyynes polyyne excitation energy transferred efficiently to the porphyrin S_1 state through direct conjugation. The excitation energy of diarylpolyynes, however, was so high ($>2.5\times10^4$ cm^{-1}) relative to the porphyrin S_1 state that downhill energy transfer or internal conversion within the porphyrin moiety could occur. Practical information of the higher excited state of polyyne porphyrins with more sophisticated methods would possibly show significant interaction between porphyrin and diarylpolyyne. Actually, the spectra in the higher energy region, porphyrin Soret bands (S_2) and the absorbed region of diarylpolyyne, were more perturbed to be broadening.

These synthetic polyyne porphyrins are symmetric and have two sites in the molecule of changeable redox and of changeable energy-level. Replacing the NH hydrogen of each porphyrin center with a different metal, unsymmetric long-range reaction system could be constructed. Fortunately, since diarylpolyynes have rigid and linear structure, two porphyrin reactive sites are held at a fixed distance. These synthetic polyyne porphyrins have great advantage in investigating

Table 4. ^{1}H NMR Chemical Shifts of Bis(dipyrrylmethyl)polyynes in $CDCl_3$ Solution

Compd	Chemical shift δ/ppm											
	NH	Me	Et–		EtO–		Aryl					
							H2	H6	H3	H5	H4	CH
E$_{2b}$	8.41	1.80	2.72	1.10	4.23	1.30	7.23	7.41	—	7.28	7.07	5.47
E$_{2c}$	8.23	1.78	2.72	1.10	4.25	1.30	7.49		7.06		—	5.48
					t-Bu							
B$_{2a}$	8.17	1.78	2.66	1.08	1.50		—	7.52	7.01	7.32	7.24	5.91
B$_{3a}$	8.34	1.78	2.68	1.10	1.50		—	7.52	7.03	7.33	7.23	5.90
B$_{4a}$	8.10	1.81	2.68	1.11	1.52		—	7.54	6.99	7.35	7.24	5.86
B$_{2b}$	8.15	1.79	2.71	1.11	1.54		7.25—7.30	7.43	—	7.25—7.30	7.10	5.45
B$_{3b}$	8.13	1.77	2.67	1.10	1.52		7.27	7.43	—	7.29	7.09	5.43
B$_{4b}$	8.24	1.79	2.70	1.14	1.55		7.27	7.43	—	7.27—7.31	7.12	5.47
B$_{2c}$	8.23	1.78	2.68	1.10	1.54		7.47		7.07		—	5.47
B$_{3c}$	8.16	1.78	2.69	1.11	1.53		7.48		7.06		—	5.46
B$_{4c}$	8.14	1.77	2.67	1.11	1.54		7.48		7.06		—	5.46

systematically the through-space and through-bond interaction. These investigations are now under way.

Experimental

All melting points were measured with a Yanagimoto micro melting point apparatus and uncorrected. The ^{1}H NMR spectra were recorded on 400 MHz JEOL JNM-GX-400 instrument, with tetramethylsilane as an internal reference. Mass spectra were recorded with a JEOL DX-300 spectrometer. UV-vis absorption spectra were measured with Shimadzu UV-3000 and UV-160 spectrometer. Fluorescence spectra were taken on a Shimadzu RF-502A spectrofluorometer.

Synthetic methods of nine compounds (**B**$_{2a-4c}$, **C**$_{2a-4c}$, and **D**$_{2a-4c}$) were similar.

Synthesis of Bis(dipyrrylmethyl)polyynes (B$_{2a-4c}$, E$_{2b,2c}$). Corresponding diarylpolyynedicarbaldehyde (**A**$_n$)[14] (0.4 mmol) and **1a** or **1b** (1.6 mmol) were dissolved in 20 ml of dry CH_2Cl_2 with stirring. *p*-Toluenesulfonic acid (0.1 g) was added and the mixture was stirred overnight under nitrogen at the room temperature. The mixture was washed with aqueous $NaHCO_3$ solution and dried over Na_2SO_4. The solvent was evaporated and residue was purified with column chromatography on silica gel quickly, using CH_2Cl_2 as an eluent. The ^{1}H NMR chemical shifts of bis(dipyrrylmethyl)polyynes and yields of preparation were shown in Tables 4 and 5.

Synthesis of Bis(dipyrrylmethyl)polyynetetracarboxylic Acids (C$_{2a-4c}$). Method A.[19] Bis(dipyrrylmethyl)polyynetetracarboxylic tetraester (**B**$_{2a-4c}$) (0.3 mmol) was dissolved in 10 ml anhydrous 25% HBr–acetic acid solution. This was irradiated with ultrasonic wave and stirred for 10 min at the room temperature, and added 40 ml ice-cooled water, and the stirred for 10 min. The precipitate was filtered off and washed thoroughly, and completely dried in vacuo. This was used for synthesis of polyyne porphyrins without further purification. The yields of preparation were shown in Table 5.

Method B. To a solution of bis(dipyrrylmethyl)polyynetetracarboxylic tetraester (**E**$_{2b,2c}$) (0.4 mmol) in 20 ml of ethanol was added a 12 ml of 3 mol dm^{-3} NaOH solution, and resulting solution was refluxed for 4 h. The solvent was evaporated to remove ethanol and then acidified with acetic acid. The precipitate was filtered off and washed thoroughly, and dried in vacuo. The yields were shown in Table 5.

Table 5. Yields of Bis(dipyrrylmethyl)polyynes

Compd	Yield/%[a)]	Compd	Yield/%[b)]
E$_{2b}$	93	**C**$_{2b}$	>50
E$_{2c}$	>70	**C**$_{2c}$	89
B$_{2a}$	74	**C**$_{2a}$	65
B$_{3a}$	70	**C**$_{3a}$	81
B$_{4a}$	>70	**C**$_{4a}$	>70
B$_{2b}$	44	**C**$_{2b}$	65
B$_{3b}$	25	**C**$_{3b}$	50
B$_{4b}$	50	**C**$_{4b}$	>60
B$_{2c}$	>75	**C**$_{2c}$	84
B$_{3c}$	21	**C**$_{3c}$	Quant.
B$_{4c}$	64	**C**$_{4c}$	>70

a) Yield based on diarylpolyynedicarbaldehyde (**A**).
b) Yield based on bis(dipyrrylmethyl)polyynetetracarboxylic tetraester (**E**, **B**).

Table 6. Melting Points and Yields of Polyyne Porphyrins

Compd	Mp/°C	Yield/%[a)]
D$_{2a}$	>300	0.5
D$_{3a}$	>300	0.74
D$_{4a}$	—	Trace
D$_{2b}$	>300	0.5
D$_{3b}$	>300	1.5
D$_{4b}$	>300	0.5
D$_{2c}$	>300	1.8
D$_{3c}$	>300	0.5
D$_{4c}$	>300	1.5

a) Yield based on bis(dipyrrylmethyl)polyynetetracarboxylic acid (**C**).

Synthesis of Polyyne Porphyrins (D$_{2a-4c}$). Bis(dipyrrylmethyl)polyynetetracarboxylic acid (0.2 mmol) and **2** (0.4 mmol) were dissolved in 30 ml of methanol. *p*-Toluenesulfonic acid (0.2 g) was added and then the mixture was stirred for 2—3 d under nitrogen at the room temperature in the dark. Then the mixture was treated with the air oxidation. The solvent was evaporated in vacuo. The residue was dissolved in $CHCl_3$ and washed with aqueous $NaHCO_3$ solution, and dried over Na_2SO_4. The solvent was evaporated and the residue was purified with flash column chromatography on silica gel, using alcohol-free $CHCl_3$ as an eluent. The second fraction was collected and evaporated in vacuo. In some cases, solid was recrystallized from CH_2Cl_2–MeOH. The melting points and the yields of preparation of polyyne porphyrins were shown in Table 6.

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