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Synthesis and Spectroscopic Investigation of Directly Conjugated Polyyne Porphyrins

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A series of conjugated polyyne porphyrin, in which porphyrin macrocycle is directly connected with one end of diarylpolyyne through aromatic ring, has been prepared and their spectroscopic behaviors were investigated. Diarylpolyynes consisting of aryl group and conjugated triple bond system have rigid and linear structure, and the two chromophores are held at a fixed geometry and a determined distance. The UV-vis absorption spectra of these compounds showed strong conjugative interaction, showing broadening of their spectra and slightly red shifted porphyrin Soret bands with increasing the number of acetylenic bond. From their fluorescence excitation spectra energy transfer efficiencies from polyyne moiety to porphyrin moiety were estimated. The energy transfer efficiencies were almost unity regardless of their substituted position, geometry, and 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. The X-ray analysis of a bacterial photosynthetic reaction center from Rhodopseudomonas viridis[1] clarified an excellent geometrical arrangement of related pigments. Distance, geometry, and orientation have been recognized more importantly to control the efficiency of energy and electron transfer process. In addition, the environment such as polypeptide, residue of amino acid, π-conjugated system, and long-chain hydrocarbon surrounding the prosthetic molecules has a crucial role for electron transport system as the intervening medium. In order to elucidate the meanings of each factor definitely, it is necessary to construct the model systems of rigidly fixed structure, geometry and orientation. In recent years numerous model systems have been investigated by many investigators in different laboratories.[2–15]

We have synthesized a series of directly conjugated polyyne porphyrins, in which porphyrin macrocycle is directly connected with one end of diarylpolyyne through meso-aromatic ring and investigated the interaction between porphyrin and π-conjugated triple bond system. Since diarylpolyynes have rigid and linear structure, two chromophores are held at a fixed geometry. Changing the substituted position of polyyne, three types of polyyne porphyrin have been synthesized. Increasing the number of conjugated triple bond, distance between both ends of diarylpolyyne can be altered systematically.

Gust et al.[7] had already prepared a variety of carotenoporphyrin and investigated the interaction between porphyrin and carotenoid polyenes, which have typical conjugated double bond system. They revealed that the geometry and distance between them much affected the efficiency of energy transfer. Especially, close proximity is the most important factor of efficient energy transfer.

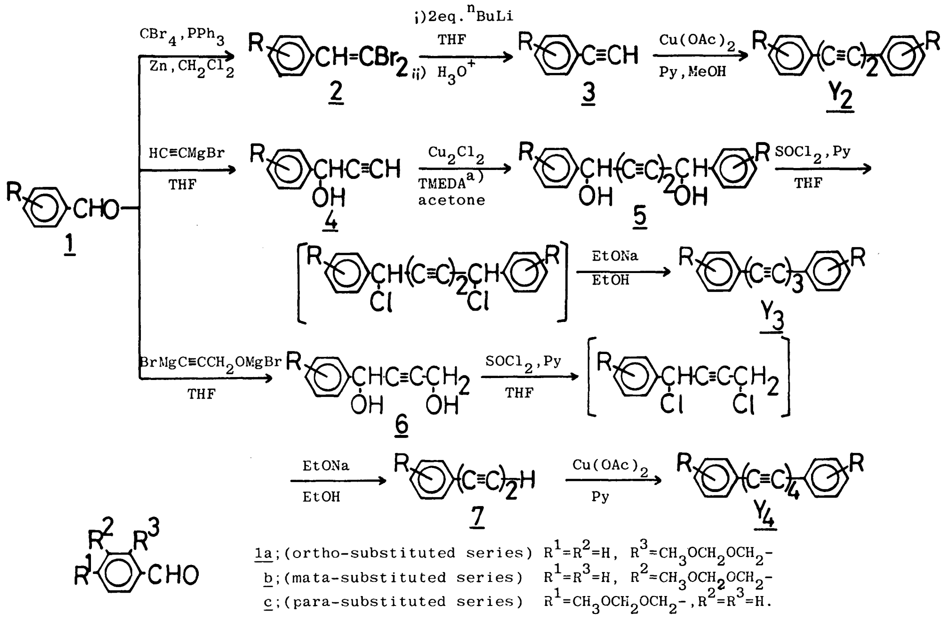
In our case, energy transfer from polyyne to porphyrin had been also observed. However, the efficiency of energy transfer is almost unity regardless of their substituted position, geometry, and orientation. Strong interaction between polyyne and porphyrin through direct conjugation have been observed with electronic absorption spectra. The excitation energy absorbed by polyyne was efficiently transferred to porphyrin and then porphyrin fluoresced. On the other hand, in the polyyne porphyrin systems in which the two chromophores were connected through ester linkage indirectly, energy transfer efficiency was dependent upon substituted position.

In this report, we will describe detailed synthetic methods of a series of polyyne porphyrins together with characterization of synthesized compounds, and strong interaction through conjugation is discussed.

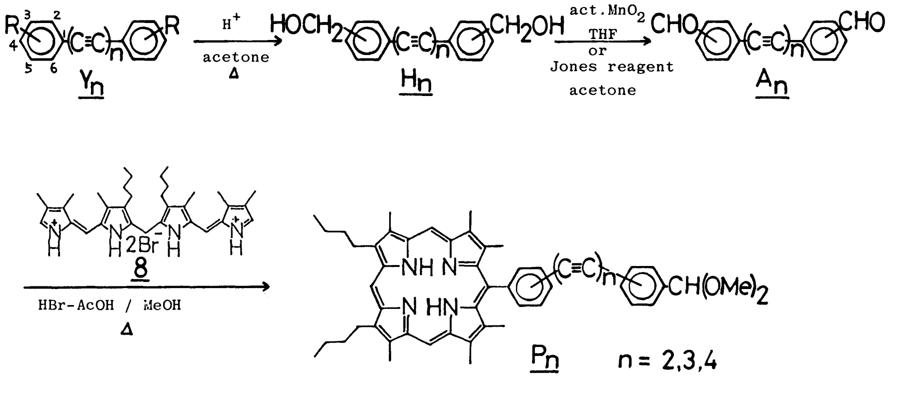
Results and Discussion

Synthesis. The synthetic route of diarylpolyynes is shown in Scheme 1. Ortho (a series), meta (b series), and para (c series) methoxymethoxymethylbenzaldehydes **1** were used as starting materials, respectively. Most of synthetic method of diarylpolyynes were based on a method reported by Armitage et al.[16] and Akiyama et al.,[17] but in some cases their methods were suitably modified.[18,19] Yields in almost all the reactions were satisfactorily high in each series. Methoxymethyl group was a good protective group of the hydroxyl group under these conditions. In these manners, each series of diarylbutadiynes ($\mathbf{Y}_2$), diarylhexatriynes ($\mathbf{Y}_3$), and diaryloctatetraynes ($\mathbf{Y}_4$) were obtained and recrystallized from ethanol. These compounds were characterized by ^{1}H NMR, IR (Table 1), and mass spectroscopy. Diarylhexatriynes and diaryloctatetraynes are heat- and light-sensitive. They gradually polymerize to give insoluble blue and green colored compounds, respectively.

These synthetic diarylpolyynes ($\mathbf{Y}_n$) were converted into polyyne porphyrins ($\mathbf{P}_n$) according to the reaction Scheme 2. Deprotection by acid hydrolysis and oxi-



Scheme 1. Synthesis of diarylpolyynes. a) TMEDA: tetramethylethylenediamine.



Scheme 2. Synthesis of directly conjugated polyyne porphyrins.

dation with active MnO_2,[20] in some cases with Jones reagent,[21] gave diarylpolyyne dicarbaldehydes (**A**$_n$) in satisfactory yields. Melting points, yields, and other spectral data are shown in Table 1. In the dark diarylpolyynes are relatively stable under acidic conditions. The desired conformationally restricted polyyne porphyrins conjugated directly (**P**$_n$) could be synthesized by the acid-catalyzed condensation reaction[22] of the corresponding ac-biladiene (**8**)[23] and diarylpolyyne dicarbaldehydes (**A**$_n$) in reasonable yields (Table 2). The yields of ortho-substituted polyyne porphyrins were slightly low because of the steric hindrance. Double condensation products of both ends, polyyne porphyrin dimers,[24] could not be produced under these conditions. All these synthesized polyyne porphyrins were recrystallized from dichloromethane-methanol.

Characterization. The structures of directly conjugated polyyne porphyrins are shown in Fig. 1 and melting points, IR, ^{1}H NMR spectral data are shown in Tables 2 and 3. By applying fast-atom-bombardment mass spectrometry to these polyyne porphyrins only characteristic peaks corresponding to the expected $M^+ + nH$ (n=0—4) ions were observed. One end of diarylpolyyne was directly connected with the meso position of porphyrin macrocycle and at the other end aldehyde group was converted into dimethyl acetal group. This dimethyl acetal group was held at fixed geometry toward porphyrin ring, because diarylpolyynes had rigid and linear structure. Especially, in ortho-substituted series its methyl and methine proton were held just on the porphyrin plane and showed upfield shift ($\Delta\delta$=1.2—1.5 ppm) in the ^{1}H NMR spectrum due to the ring current. This upfield shift increases with decreasing the number of acetylenic bond. In para-substituted series dimethyl acetal group

Table 1. Melting Points, Yields of Preparation, ^{1}H NMR Chemical Shift in $CDCl_3$ Solution, and Infrared Spectral Data of Diarylpolyynes

Compd	Mp/°C	Yield/%[a]	Chemical shift δ/ppm								IR/cm^{-1}[e]							
			Aryl					Other protons										
			H2	H6	H3	H5	H4											
								$CH_3OCH_2OCH_2$–				$\nu_{C≡C}$						
$\mathbf{Y}_{2a}$	Oil	68	—	7.55	7.50	7.38	7.27	3.46	4.79	4.79	2820—3020	2230,2150		1160	1120	1050	760	
$\mathbf{Y}_{3a}$	60—61	51	—	7.54	7.49	7.40	7.27	3.44	4.77	4.75	2820—2980	2205		1160	1115	1060	760	
$\mathbf{Y}_{4a}$	72—73	15	—	7.55	7.48	7.41	7.27	3.44	4.76	4.74	2890,2940	2210,2160		1155	1110	1055	760	
$\mathbf{Y}_{2b}$	Oil	55	7.51	7.44	—	7.30—7.36		3.41	4.70	4.57	2820—3100	2240,2160		1160	1110	1050	790	690
$\mathbf{Y}_{3b}$	Oil	42	7.54	7.46	—	7.30—7.38		3.40	4.70	4.56	2780—3080	2210		1160	1110	1060	790	690
$\mathbf{Y}_{4b}$	68—72	7	7.54	7.46	—	7.32	7.39	3.40	4.70	4.56	2900,2960	2220		1155	1100	1050	795	700
$\mathbf{Y}_{2c}$	58—60	Quant.	7.62		7.40		—	3.44	4.70	4.60	2800—3000	2145		1170	1120	1070	830	
$\mathbf{Y}_{3c}$	113—114	59	7.57		7.37		—	3.43	4.72	4.62	2760—2960	2200		1150	1110	1050	810	
$\mathbf{Y}_{4c}$	275(decomp)[b]	9	7.52		7.32		—	3.40	4.70	4.59	2950	2210		1150	1115	1050	815	
								-CH_2OH			$\nu_{O\text{-}H}$	$\nu_{C≡C}$						
$\mathbf{H}_{2a}$	176	70	—	7.55	7.50	7.40	7.28	4.89		1.93	3100—3500	d)		1060		750		
$\mathbf{H}_{3a}$	200—203	Quant.	—	7.55	7.50	7.42	7.25—7.27	4.86		1.88	3160—3500	2210		1050		760		
$\mathbf{H}_{4a}$	193—195	98	—	7.55	7.51	7.42	7.25—7.28	4.86		c)	3090—3480	2220		1050		760		
$\mathbf{H}_{2b}$	149—151	54	7.53	7.45	—	7.31—7.37		4.69		1.67	3100—3480	2140		1050	1020	790	690	
$\mathbf{H}_{3b}$	130	95	7.54	7.46	—	7.33	7.39	4.69		1.68	3100—3400	2210		1050	1020	790	690	
$\mathbf{H}_{4b}$	120—121	90	7.54	7.46	—	7.33	7.40	4.68		1.73	3120—3440	2220		1050		800	690	
$\mathbf{H}_{2c}$	230(decomp)	60	7.52		7.34		—	4.71		c)	3100—3500	2210,2145		1050	1025	820		
$\mathbf{H}_{3c}$	>290	Quant.	7.52		7.34		—	4.72		1.69	3100—3400	2200		1040	1020	820		
$\mathbf{H}_{4c}$	>300	84	7.55		7.40		—	4.66		c)	3100—3400	2205		1050	1015	800		
								CHO			$\nu_{C≡C}$	$\nu_{C=O}$						
$\mathbf{A}_{2a}$	171—172	62	—	7.68	7.95	7.52	7.60	10.51			2205	1700	1590	1270	1210	760		
$\mathbf{A}_{3a}$	211—213(decomp)	37	—	7.68	7.95	7.53	7.59	10.45			2205	1705	1590	1270	1200	760		
$\mathbf{A}_{4a}$	180(decomp)	58(87)	—	7.68	7.94	7.52—7.61		10.43			2210	1700	1590	1265	1200	760		
$\mathbf{A}_{2b}$	176—177	57(88)	8.03	7.77	—	7.53	7.89	10.00			d)	1710	1580	1250	1160	800	770	680
$\mathbf{A}_{3b}$	162(decomp)	86	8.03	7.77	—	7.53	7.90	9.99			2220	1710	1580	1205	1170	800	745	680
$\mathbf{A}_{4b}$	180(decomp)	51	8.03	7.77	—	7.53	7.91	9.99			2210	1710	1580	1180	1170	800	725	680
$\mathbf{A}_{2c}$	260—261	36(54)	7.68		7.87		—	10.03			2200	1700	1600	1170		825		
$\mathbf{A}_{3c}$	240(decomp)	40	7.69		7.86		—	10.02			2200	1700	1600	1170		830		
$\mathbf{A}_{4c}$	184(decomp)	96	7.68		7.85		—	10.02			2210	1700	1600	1170		830		

a) In parentheses, yields of Jones oxidation. b) Gradually polymerized at lower temperature. c) Not determined. d) Weak, not determined. e) KBr, but in the cases $\mathbf{Y}_{2a}$, $\mathbf{Y}_{2b}$, and $\mathbf{Y}_{3b}$ NaCl.

Table 2. Yields, Melting Points, and Infrared Spectral Data of Polyyne Porphyrins

Compd	Yield/%	Mp/°C	IR/cm^{-1} (KBr)					
$\mathbf{P_{2a}}$	5.8	263—264	2840—3000	a)	1460	1140	1060	770
$\mathbf{P_{3a}}$	1.14	>300	2840—3000	2200	1450	1130	1060	760
$\mathbf{P_{4a}}$	<1	>300	2870—3010	2230	1455	1130	1080	740
$\mathbf{P_{2b}}$	18.5	258	2860—3000	a)	1450	1115	1060	750
$\mathbf{P_{3b}}$	6.1	228—231	2860—3000	2220	1450	1120	1065	750
$\mathbf{P_{4b}}$	6.6	>300	2940	2220	1440	1115	1060	750
$\mathbf{P_{2c}}$	11.5	>300	2820—2950	a)	1440	1110	1060	750
$\mathbf{P_{3c}}$	15.8	>300	2830—2990	2210	1440	1110	1060	750
$\mathbf{P_{4c}}$	16.7	>300	2800—2980	2210	1445	1110	1060	750

a) Weak, not determined.

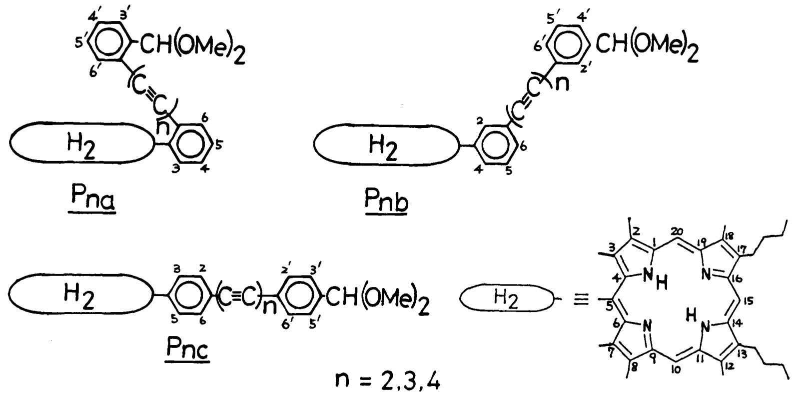


Fig. 1. Directly conjugated polyyne porphyrins.

was so far apart from porphyrin ring that these protons were observed in the lowest field. In the IR spectra a remarkable intensification of the absorption due to $\nu_{C\equiv C}$ with an increase in the number of acetylenic bond was also observed just as in the case of diarylpolyyne.[17)] Significant difference, however, was not observed in each substituted series and the number of acetylenic bond. Relatively high melting points and low solubility in organic solvents are similar in ortho- and para-substituted series. Particularly, melting points are low in meta-substituted series.

Absorption and Fluorescence Spectra. The absorption spectra of diarylpolyynes ($\mathbf{Y_{2c}}$—$\mathbf{Y_{4c}}$) and the spectral data of diarylpolyynes ($\mathbf{Y}_n$) are shown in Fig. 2 and Table 4. Diarylpolyynes have vibrational fine structure in their absorption spectra and the novel linear relation between the longest wavelength maxima (λ_{max}) and the number of the acetylenic bond (n) has been found.[25)] These synthetic methoxymethoxymethyl-substituted diarylpolyynes have the similar relationship to diphenylpolyyne.[16,25)] Absorption maxima and the relationship of each series have not

$\mathbf{Y}_{na}$: $\lambda_{max} = 266.0 + 34.0 \times n$
$\mathbf{Y}_{nb}$: $\lambda_{max} = 262.1 + 34.3 \times n$
$\mathbf{Y}_{nc}$: $\lambda_{max} = 266.8 + 33.8 \times n$[26)]
cf. diphenylpolyyne : $\lambda_{max} = 263.0 + 33.0 \times n$[16,25)]

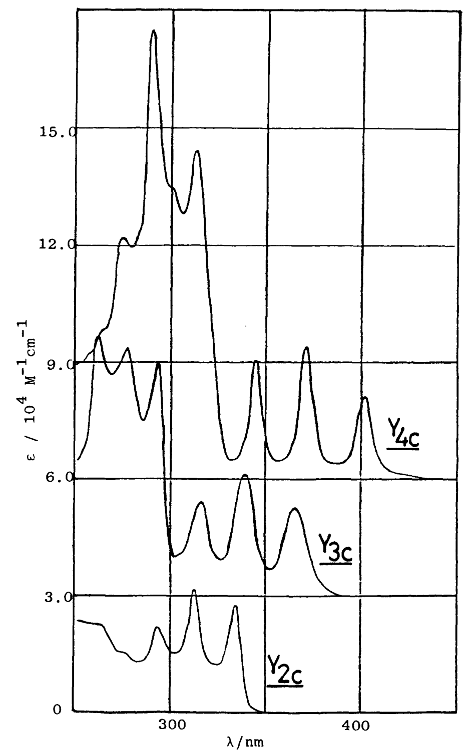


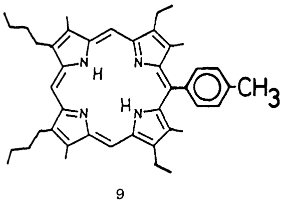
Fig. 2. UV-vis absorption spectra of diarylpolyynes in CH_2Cl_2 solution. Each curve, except for the lowest one, has been displaced upward by 3.0×10^4 ε unit increment from one immediately below it.

Table 3. ^{1}H NMR Chemical Shift of Polyyne Porphyrins in $CDCl_3$ Solution

Compd	CH$_3$(pyrrole)			H meso		NH		Meso aryl					Aryl					Dimethyl acetal	
	3,7	2,8	12,18	15	10,20			H2	H6	H3	H5	H4	H2′	H6′	H3′	H5′	H4′	CH	CH$_3$O
P$_{2a}$	2.50	3.54	3.61	9.94	10.14	−3.15	−3.32	—	7.97—8.00		7.73	7.80	—	6.75—6.78		6.93—6.99		4.13	1.86
P$_{3a}$	2.47	3.54	3.62	9.96	10.16	−3.16	−3.31	—	7.93	7.99	7.73	7.79	—	7.02	7.07	7.16	7.30	5.02	2.97
P$_{4a}$	2.45	3.54	3.63	9.96	10.16	−3.17	−3.31	—	7.94	7.99	7.71—7.81		—	7.43	7.21—7.33		7.12	5.27	3.16
P$_{2b}$	2.48	3.52	3.63	9.95	10.15	−3.21	−3.34	8.26	7.96	—	7.71	8.07	7.62	7.47	—	7.31	7.43	5.34	3.29
P$_{3b}$	2.46	3.52	3.62	9.95	10.15	−3.22	−3.35	8.26	7.97	—	7.71	8.09	7.62	7.44 —7.48	—	7.32	7.44 —7.48	5.34	3.29
P$_{4b}$	2.45	3.52	3.62	9.95	10.15	−3.22	−3.35	8.27	7.98	—	7.72	8.11	7.62	7.47	—	7.32	7.47	5.34	3.29
P$_{2c}$	2.46	3.52	3.62	9.94	10.14	−3.20	−3.32	7.90		8.03		—	7.62		7.49		—	5.43	3.35
P$_{3c}$	2.46	3.52	3.62	9.95	10.15	−3.21	−3.33	7.92		8.05		—	7.59		7.46		—	5.42	3.33
P$_{4c}$	2.45	3.52	3.62	9.95	10.15	−3.21	−3.34	7.92		8.06		—	7.57		7.45		—	5.40	3.32

marked difference. Substitution upon aromatic ring by alkyl group showed little perturbation for the electronic state of diphenylpolyyne. In meta-substituted series (b series), however, slightly blue shift relative to other series was observed.

The absorption curves and electronic spectral data of polyyne porphyrins are shown in Figs. 3 and 4 and Table 5. The absorption spectra in the region above 450 nm were similar to those of reference porphyrin (**9**). Therefore, direct conjugation with polyyne have little effect upon porphyrin S_1 state. The absorption maxima (λ_{max}) of porphyrin Soret band are slightly red shifted with increasing the number of conjugated acetylenic bond. Especially in para-substituted series (c series) this tendency is remarkable. On the other hand, significant broadening of the vibrational fine structure of diarylpolyyne was observed. Conjugated large porphyrin macrocycle on one end and unsymmetric structure are presumably responsible for these broadening. The absorption maxima were also red shifted. In ortho-substituted series (a series), however, the extinction coefficient of polyyne was greater relative to other series and the vibrational fine structure was somewhat distinguishable. Similar trend was recognized in the case of indirect conjugated compound. Consequently, it is apparent that not only direct conjugation through bond but also close proximity of each component through space have influenced the electronic absorption spectra.



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These synthetic directly conjugated polyyne porphyrin have usual fluorescence emission spectra compared to reference porphyrin **9**. Fluorescence emission maxima and total emission intensity were not significantly perturbed by direct conjugation of polyyne. On one hand, it was found that diarylpolyyne could not quench at all the fluorescence of porphyrins in solution. From Table 6 relative emission intensities (I_b/I_a) are different in each series, respectively. Difference in substituted position was presumed to alter the overlap of 0–0 and 0–1 band.

Energy Transfer. Figure 5 shows the uncorrected fluorescence excitation spectra of directly conjugated polyyne porphyrins (**P$_4$**). Assuming that the difference between the absorption spectra of polyyne porphyrin and those of reference porphyrin **9** was the excitation energy absorbed by polyyne, energy transfer efficiency from polyyne to porphyrin could be evaluated from the difference between absorption spectra and fluorescence excitation spectra. These values are shown in

Table 4. UV Vis Spectral Data of Diarylpolyynes

Compd	λ_{max}/nm ($\varepsilon/10^3$ M^{-1} cm^{-1})$^{a)}$				
$\mathbf{Y}_{2a}$			296.0(23)	313.5(31)	335.0(27)
$\mathbf{Y}_{2b}$			292.0(22)	310.0(31)	331.5(28)
$\mathbf{Y}_{2c}$			294.5(22)	313.0(31)	335.0(27.8)
$\mathbf{Y}_{3a}$	275.0(63)	290.5(52)	317.5(25)	340.0(31)	366.0(21)
$\mathbf{Y}_{3b}$	270.5(62)	287.0(52)	314.5(24)	337.0(31)	363.0(22)
$\mathbf{Y}_{3c}$	277.0(62)	293.5(59)	317.0(23.9)	340.0(31.2)	366.5(21.9)
$\mathbf{Y}_{4a}$	290.5(115)	313.5(82)	346.0(30)	372.5(34)	403.0(21)
$\mathbf{Y}_{4b}$	288.5(121)	310.5(88)	344.0(31)	370.0(34)	400.0(20)
$\mathbf{Y}_{4c}$	290.0(115)	314.0(85.9)	346.0(30.0)	372.0(34.2)	402.5(22.4)

a) 1 M=1 mol dm^{-3}.

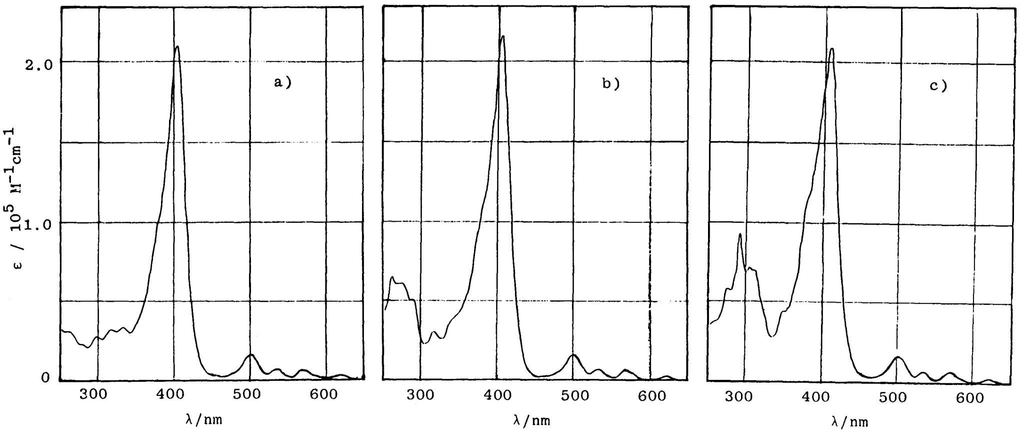

Fig. 3. UV-vis absorption spectra of directly conjugated polyyne porphyrins. a) $\mathbf{P}_{2c}$, b) $\mathbf{P}_{3c}$, c) $\mathbf{P}_{4c}$.

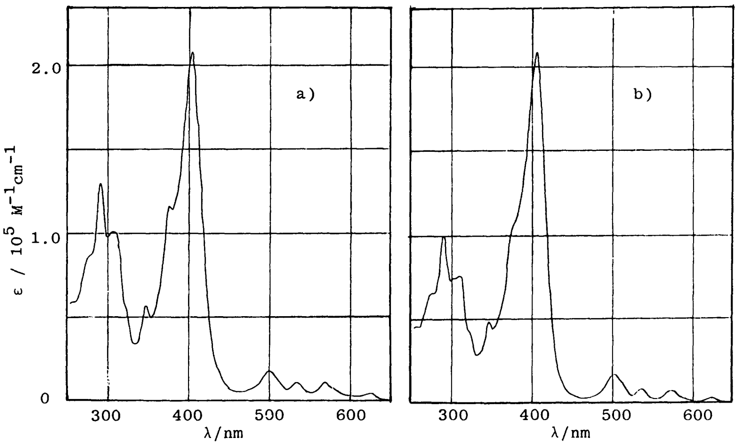

Fig. 4. UV-vis absorption spectra of directly conjugated polyyne porphyrins. a) $\mathbf{P}_{4a}$, b) $\mathbf{P}_{4b}$.

Table 7. Although a little error originating from correction of the fluorescence excitation spectra could not be excluded, energy transfer efficiencies were estimated to be almost unity. Substituted position, distance, and orientation did not affect energy transfer efficiency. Considering the facts that energy transfer had not been observed in a mixed dichloromethane solution of diarylpolyyne and porphyrin and that diarylpolyyne did not fluoresce, this energy transfer mechanism might be intramolecular singlet–singlet energy transfer or internal conversion from polyyne to porphyrin S_1 state through direct conjugation.

For comparison, indirectly conjugated polyyne porphyrins with ester linkage were synthesized (Fig.

Table 5. UV Vis Absorption Spectral Data of Directly Conjugated Polyyne Porphyrins

Compd	λ_{max}/nm (log[ε/M^{-1} cm^{-1}])							
9				403.0(5.32)	502(4.25)	535(3.90)	570(3.87)	623(3.39)
$\mathbf{P_{2a}}$		318(4.6)	337(4.7)	405.7(5.3)	502(4.3)	537(4.0)	572(3.9)	625(3.6)
$\mathbf{P_{2b}}$		313(4.6)	332(4.6)	403.7(5.3)	502(4.3)	537(3.9)	572(3.9)	625(3.5)
$\mathbf{P_{2c}}$		317(4.5)	334(4.5)	404.3(5.3)	502(4.3)	536(3.9)	572(3.9)	624(3.4)
$\mathbf{P_{3a}}$	262(4.9)	319(4.6)	344(4.7)	406.4(5.3)	502(4.3)	537(4.0)	573(3.9)	624(3.6)
$\mathbf{P_{3b}}$	260(4.9)	316(4.5)	340(4.7)	404.6(5.3)	502(4.3)	537(3.9)	571(3.9)	623(3.3)
$\mathbf{P_{3c}}$	263(4.8)	318(4.5)	sh.[a]	405.4(5.3)	502(4.3)	537(3.9)	571(3.9)	624(3.4)
$\mathbf{P_{4a}}$	291(5.1)	348(4.7)	375(5.0)	405.0(5.3)	502(4.3)	537(4.0)	571(4.0)	625(3.6)
$\mathbf{P_{4b}}$	289(5.0)	345(4.7)	sh.	405.9(5.3)	502(4.3)	537(3.9)	571(3.9)	624(3.5)
$\mathbf{P_{4c}}$	291(5.0)	sh.	sh.	407.0(5.3)	503(4.3)	536(3.9)	570(3.9)	624(3.4)

a) sh.; shoulder,

Table 6. Fluorescence Emission Spectral Data of Directly Conjugated Polyyne Porphyrins

Compd	$\lambda_{Em\ max}$/nm a; Q (0–0)	b; Q (0–1)	I_b/I_a
9	625	689	0.72
$\mathbf{P_{2a}}$	626	692	0.53
$\mathbf{P_{2b}}$	625	691	0.64
$\mathbf{P_{2c}}$	625	692	0.70
$\mathbf{P_{3a}}$	625	691	0.53
$\mathbf{P_{3b}}$	624	691	0.61
$\mathbf{P_{3c}}$	624	691	0.72
$\mathbf{P_{4a}}$	625	692	0.54
$\mathbf{P_{4b}}$	625	691	0.62
$\mathbf{P_{4c}}$	625	690	0.72

Table 7. Energy Transfer Efficiency of Directly Conjugated Polyyne Porphyrins

Porphyrins	Energy transfer efficiency
$\mathbf{P_{2a}}$	1.04±0.15
$\mathbf{P_{2b}}$	1.01±0.07
$\mathbf{P_{2c}}$	1.06±0.11
$\mathbf{P_{3a}}$	0.99±0.10
$\mathbf{P_{3b}}$	0.97±0.10
$\mathbf{P_{3c}}$	1.12±0.14
$\mathbf{P_{4a}}$	1.08±0.20
$\mathbf{P_{4b}}$	1.11±0.22
$\mathbf{P_{4c}}$	1.11±0.11

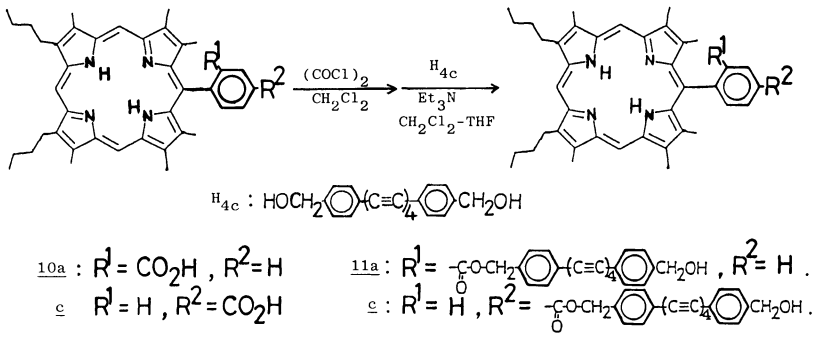

Fig. 6. Indirectly conjugated polyyne porphyrins.

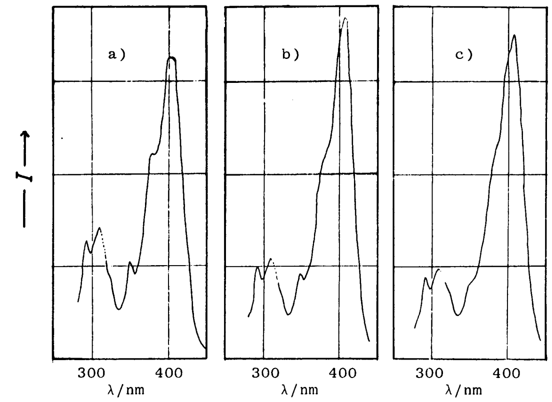

Fig. 5. Fluorescence excitation spectra of directly conjugated polyyne porphyrins. a) $\mathbf{P_{4a}}$, b) $\mathbf{P_{4b}}$, c) $\mathbf{P_{4c}}$. Em. 625 nm, solvent; CH_2Cl_2.

6). The UV-vis absorption spectra and the fluorescence excitation spectra of **11a** and **11c** are shown in Figs. 7 and 8. The absorption spectra of indirectly conjugated polyyne porphyrins are approximately identical to the sum of those of the two components, indicating absence of interaction between them. Energy transfer efficiencies from polyyne moiety to porphyrin moiety calculated similarly as described above are shown in Table 8. Characteristic in these porphyrins is that distance and orientation play a crucial role in energy transfer process. That is, close proximity of the concerned chromophores is quite important for the effective energy transfer. In the mixture of each component, however, energy transfer was not observed and energy transfer efficiency was concentration-independent. Therefore, in this case

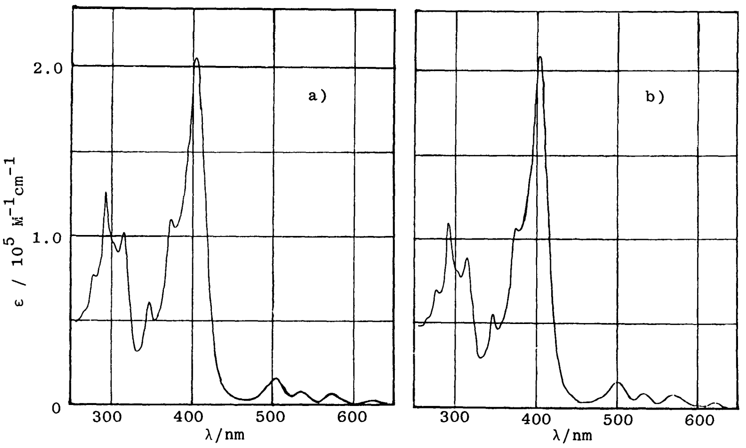

Fig. 7. UV-vis absorption spectra of indirectly conjugated polyyne porphyrins. a) **11a**, b) **11c**. Solvent; CH_2Cl_2.

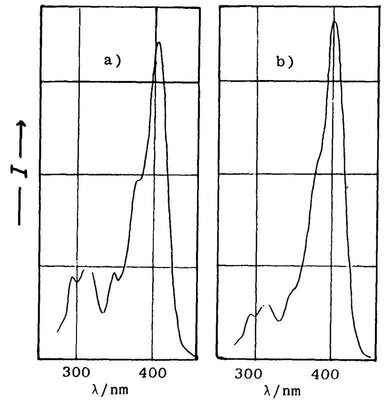

Fig. 8. Fluorescence excitation spectra of indirectly conjugated polyyne porphyrins. a) **11a**, b) **11c**. Em. 625 nm, solvent; CH_2Cl_2.

Table 8. Energy Transfer Efficiency of Indirectly Conjugated Polyyne Porphyrins

Porphyrins	Energy transfer efficiency
11a	0.81±0.16
11c	0.57±0.22

intramolecular singlet-singlet energy transfer had occurred.

Recently, Kobayashi et al. investigated the absorption spectra of diphenylpolyyne in detail.[27] Excited state of diphenylpolyyne has charge-transfer character, from polyyne to aromatic ring or the opposite direction. Two perpendicular π-conjugated systems interact significantly. As in our case one aromatic ring was directly conjugated with large porphyrin macrocycle system, charge-transfer character was presumed to be eminent. In unsymmetric long linear π-conjugated system, vectorial charge-transfer character might play a role of molecular wire from one end to the other.

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 and 100 MHz JEOL-PS-100 instruments, with tetramethylsilane as an internal reference. Infrared spectra were measured with a JASCO IRA-1 spectrometer. Mass spectra were recorded with a JEOL DX-300 spectrometer. UV-vis spectra were measured with Shimadzu UV-3000 and UV-160 spectrometer. Fluorescence spectra were taken on a Shimadzu RF-502A spectrofluorometer. Dichloromethane was freshly distilled and passed through alumina column. The elemental analysis were performed at the Microanalysis Center of Kyoto University.

Preparation of the Polyyne Porphyrins. Melting points, ^{1}H NMR spectral data in $CDCl_3$ solution, and IR spectral data are given in Tables 1—3. Measurement of mass spectra gave satisfactory values. Synthetic methods of nine kinds of compounds ($\mathbf{H}_{2a-4c}$, $\mathbf{A}_{2a-4c}$, $\mathbf{P}_{2a-4c}$) were similar.

Synthesis of Diarylpolyynediols ($\mathbf{H}_{2a-4c}$). To a solution of the corresponding diarylpolyyne ($\mathbf{Y}_n$) (3 mmol) in 30 ml of acetone was added a 12 ml of 6 mol dm^{-3} HCl solution, and resulting solution was refluxed for 2—4 h under nitrogen in the dark. After cooling, the mixture was extracted with tetrahydrofuran–ether, washed with aqueous $NaHCO_3$ solution, and dried over Na_2SO_4. After evaporation and recrystallization from tetrahydrofuran–hexane, corresponding diols were obtained.

Synthesis of Diarylpolyyne Dicarbaldehydes ($\mathbf{A}_{2a-4c}$). Method A. To a solution of the corresponding diarylpolyynediol ($\mathbf{H}_n$) (1 mmol) in 30—60 ml of tetrahydrofuran was added a 3.0 g of active MnO_2,[20] and resulting solution was stirred overnight at room temperature in the dark. Manganese oxide was filtered off, and the residue obtained from the filtrate by evaporation of the solvent was purified by chromatography over silica gel, using benzene as an eluent with gradual addition of $CHCl_3$.

Method B (Jones Oxidation).[21] One mmol of diarylpolyynediol ($\mathbf{H}_n$) were dissolved in acetone (150—200 ml). To an ice-cooled solution 2 mol dm^{-3} Jones reagent was added dropwise until an orange tint persisted in the reaction mixture. Then, isopropyl alcohol was added dropwise to destroy excess Jones reagent, as indicated by the reappearance of a deep green color. After removal of the solvent in vacuo and aqueous treatment, the mixture was extracted with tetrahydrofuran–ether and dried over Na_2SO_4. The solvent was evaporated and the solid was purified by chromatography as described above.

Synthesis of Directly Conjugated Polyyne Porphyrins (P_{2a-4c}). A quarter mmol of diarylpolyyne dicarbaldehyde (A_n) and 0.25 mmol of ac-biladiene (**8**) were dissolved in 40 ml of dry methanol with stirring. Anhydrous 25% HBr–acetic acid solution was added and the mixture was refluxed for 2—5 d under nitrogen in the dark. After cooling, the mixture was poured into water and extracted with $CHCl_3$, and dried over Na_2SO_4. After evaporation, the residue was purified by flash-column chromatography, with an eluent CH_2Cl_2. The second fraction was collected and evaporated in vacuo. Recrystallization from CH_2Cl_2–MeOH gave the desired corresponding polyyne porphyrin conjugated directly.

Synthesis of Indirectly Conjugated Polyyne Porphyrin (11a). 28 mg of porphyrin monoacid **10a** was dissolved in 5 ml of CH_2Cl_2. To this solution 0.1 ml of oxalyl dichloride was added, and the mixture was stirred for 8 h at room temperature in the dark. The excess oxalyl dichloride and CH_2Cl_2 were removed in vacuo quickly, then residue, porphyrin acid chloride, was dissolved in dry CH_2Cl_2 (5 ml) again under N_2. This was added to a solution of diarylpolyynediol (H_{4c}) (12.4 mg) and triethylamine (0.01 ml) in 3 ml of THF, and stirred overnight at room temperature in the dark. The reaction mixture was poured into water, then extracted with $CHCl_3$, washed with aqueous $NaHCO_3$ solution, and dried over Na_2SO_4. The solvent was evaporated and the residue was purified with column chromatography on silica gel, using $CHCl_3$ as an eluent. The second colored fraction gave **11a**: ^{1}H NMR ($CDCl_3$) δ=−3.28 (2H, s, NH), 1.17 (6H, t, ^{n}Bu-Me), 1.79—1.85 (4H, m, ^{n}Bu), 2.30—2.40 (4H, m, ^{n}Bu), 2.32 (6H, s, 3,7-Me), 3.44 (6H, s, 2,8-Me), 3.66 (6H, s, 12,18-Me), 4.03—4.13 (4H, m, ^{n}Bu), 4.54 (2H, d, polyyne close phenyl), 4.71 (2H, s, $C\underline{H}_2OH$), 4.83 (2H, d, polyyne close phenyl), 7.35 (2H, d, polyyne far phenyl), 7.58 (2H, d, polyyne far phenyl), 7.81—7.91 (2H, m, meso-phenyl), 7.99 (1H, d, meso-phenyl), 8.35 (1H, d, meso-phenyl), 9.99 (1H, s, H15), and 10.09 (2H, s, H10,20).

Synthesis of Indirectly Conjugated Polyyne Porphyrin (11c). This was synthesized by the same method as described for the synthesis **11a**: ^{1}H NMR ($CDCl_3$) δ=−3.33 (1H, s, NH), −3.20 (1H, s, NH), 1.12 (6H, t, ^{n}Bu-Me), 1.71—1.81 (4H, m, ^{n}Bu), 2.23—2.31 (4H, m, ^{n}Bu), 2.41 (6H, s, 3,7-Me), 3.51 (6H, s, 2,8-Me), 3.62 (6H, s, 12,18-Me), 4.03 (4H, t, ^{n}Bu), 4.70 (2H, s, $C\underline{H}_2OH$), 7.33 (2H, d, polyyne far phenyl), 7.53 (2H, d, polyyne far phenyl), 7.59 (2H, d, polyyne close phenyl), 7.65 (2H, d, polyyne close phenyl), 8.17 (2H, d, meso-phenyl), 8.44 (2H, d, meso-phenyl), 9.93 (1H, s, H15), and 10.15 (2H, s, H10,20).

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