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Synthesis and Photochemical Properties of Anthracene-Polyyne-Porphyrin Assemblies

Shigeki Kawabata,* Iwao Yamazaki,† and Yoshinobu Nishimura†

Department of Liberal Arts and Sciences, Faculty of Engineering, Toyama Prefectural University, Kosugi, Toyama 939-03

†Department of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060

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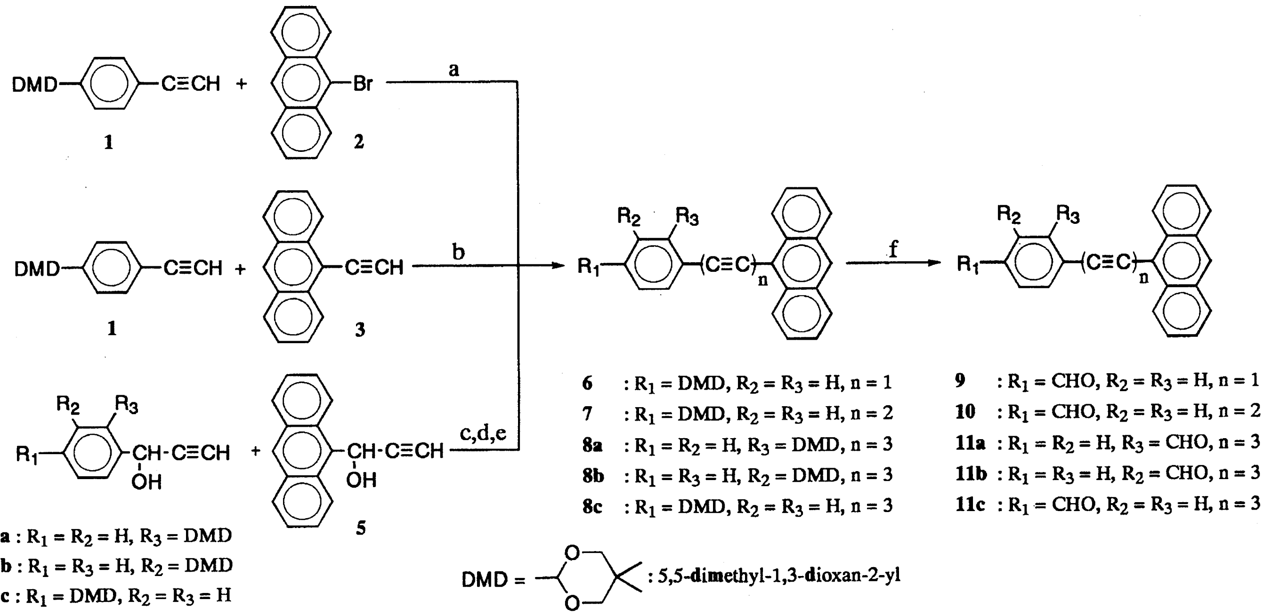
A series of anthrylpolyynes (α-anthryl-ω-(formylphenyl)polyynes) and anthrylpolyynylporphyrins (5-[(anthrylpolyynyl)phenyl]porphyrins) have been synthesized, and their photochemical properties and photoinitiated intramolecular excitation energy transfer from anthracene to porphyrin were studied by picosecond time-resolved fluorescence spectroscopy. Although anthrylpolyynes have strong fluorescence emission and fluorescence high quantum yield, anthrylpolyynylporphyrins, in which porphyrin links to the other side of polyyne, show only typical fluorescence emission of porphyrin and almost no fluorescence emission in the spectral region of anthrylpolyynes. The excitation of anthryl substituent brings about an increase in the fluorescence emission of porphyrin on the picosecond time scale. The mechanism of quantitative energy transfer from the anthryl moiety to the porphyrin is discussed on the basis of the photochemical properties of the component molecules.

The absorption of solar energy by antenna pigments and the efficient transfer of excitation energy to photosynthetic reaction centers are key processes in photosynthesis.[1] Photosynthetic organisms employ light-harvesting complexes to gather dilute sunlight, and to concentrate the energy to the reaction centers. These light-harvesting complexes have an elegant alignment of a pigment-protein complex[2] as well as fine-tuned photophysical and photochemical properties to absorb light in a specific spectral window of the solar emission, and transport it efficiently through energy transfer to the reaction centers. Especially, π-conjugated systems might serve various principal functions in these complexes. In order to elucidate the fundamental mechanism of the energy-transfer process at the molecular level, several synthetic model compounds containing porphyrins and π-conjugated systems have been studied. These studies have indicated that π-conjugated systems could play an important role as an antenna,[3—5] a photoprotector,[6] and an energy-transfer mediator.[7—9] It seems to be more important to determine their medium effects quantitatively. Effenberger et al.[7] have synthesized a series of conjugated 2-(anthrylpolyenyl)porphyrins and 5-(anthrylpolythienyl)porphyrins using the anthryl group as a donor, and have revealed that the intramolecular excitation energy transfer from the anthryl moiety to the porphyrin is appreciably mediated through these linkages. We have also been preparing a series of polyyne- or polyene-bridged diporphyrins[9,10] in order to investigate photonic and electronic interactions between porphyrins through these linkages, and have clarified that linear π-conjugated systems could effectively enhance the through-bond electronic coupling between the donor and the acceptor in energy- and electron-transfer processes. Recent studies have also revealed that the conjugated triple-bond systems effectively mediate photonic interactions between covalently-linked porphyrins.[11—14]

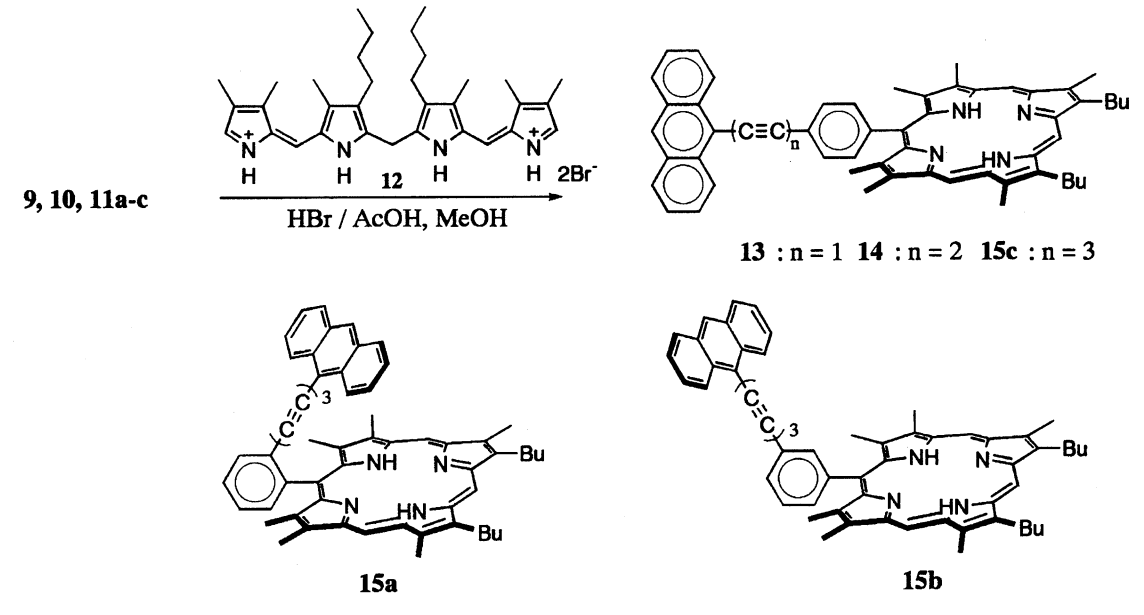
As an approach to investigate the function of linear π-conjugated systems, we have synthesized a series of anthrylpolyynylporphyrins (5-[(anthrylpolyynyl)phenyl]porphyrins), and studied the intramolecular excitation energy transfer from the anthracene to the porphyrin through the polyyne linkage. Moreover, since polyyne linkages have a rigid, linear structure, they can hold both ends of polyyne, anthracene and porphyrin, at a well-defined geometry and at a determined distance, which can be systematically altered. Analogously to Effenberger's work,[7] a selective anthryl excitation and an intramolecular excitation energy transfer from the anthryl moiety to the porphyrin could be performed in these systems. Anthrylpolyynes (α-anthryl-ω-(formylphenyl)polyynes) have appropriate photochemical properties and show high fluorescence quantum yields. Picosecond time-resolved fluorescence spectroscopy would provide us with useful insight for investigating this intramolecular excitation energy-transfer phenomenon. In this paper we report on the synthesis and photochemical properties of anthrylpolyynylporphyrins, and discuss an intramolecular excitation energy transfer through the polyyne linkage.

Results and Discussion

Synthetic schemes of anthrylpolyynes **9**, **10**, **11a—c** and anthrylpolyynylporphyrins **13**, **14**, **15a—c** are shown in Schemes 1 and 2, respectively. Pd(0)-catalyzed coupling reaction of 4-(5,5-dimethyl-1,3-dioxan-2-yl)phenylethyne (**1**) with 9-bromoanthracene (**2**) in triethylamine[15] gave anthrylarylethyne **6** in 40% yield. The reaction of (9-anthryl)-



Scheme 1. Synthetic scheme of anthrylpolyynes. (a) Pd(OAc)$_2$, PPh$_3$, Et$_3$N; (b) Cu(OAc)$_2$, C$_5$H$_5$N, MeOH; (c) CuCl, *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine, air, acetone; (d) SOCl$_2$, C$_5$H$_5$N, THF; (e) EtONa, EtOH; (f) CF$_3$CO$_2$H, H$_2$O, CH$_2$Cl$_2$.



Scheme 2. Synthetic scheme of anthrylpolyynylporphyrins.

ethyne (**3**) with iodobenzene derivatives could not provide the desired compounds in successful yields. A Cu-catalyzed cross-coupling reaction between **1** and (9-anthryl)ethyne (**3**)[16,17] and a separation of the coupling products by column chromatography gave anthrylarylbutadiyne **7** in 19% yield. Anthrylarylhexatriynes **8a**—**c** were synthesized by a Cu-catalyzed cross-coupling reaction between 1-aryl-2-propyn-1-ol **4a**—**c** and 1-(9-anthryl)-2-propyn-1-ol (**5**),[17] halogenation of the hydroxy group with thionyl chloride, and successive dehydrohalogenation with sodium ethoxide in ethanol.[4] Any intermediate which may have existed was not thoroughly isolated, and separation of the final hexatriyne mixture by column chromatography gave the desired anthrylarylhexatriynes **8a**—**c** in 5—19% yields (3 steps). These anthrylarylpolyynes **6**, **7**, **8a**—**c** were hydrolyzed under acidic conditions to give α-anthryl-ω-(formylphenyl)polyynes **9**, **10**, **11a**—**c**, respectively (Scheme 1).

The acid-catalyzed condensation reaction[18] of the corresponding anthrylpolyynes **9**, **10**, **11a**—**c** and biladiene-*ac* **12**[19] in methanol provides the anthrylpolyynylporphyrins **13**, **14**, **15a**—**c** in 6—35% yields, respectively (Scheme 2). The (anthrylpolyynyl)phenyl groups were stable under these reaction conditions. Poor solubility of the aldehydes in methanol decreases these condensation reaction yields significantly. An increase in the number of acetylenic bonds decreases the solubility of anthrylpolyyne, and then lowers the reaction yield. Zinc complexes were also prepared from **13**, **14**, and **15c** by the usual methods.

Figure 1 shows the UV-vis absorption spectra of anthrylpolyynes **9**, **10**, and **11c** in dichloromethane. The main absorption band is found at 264—271 nm, which is characteristic for the anthracene $S_0 \rightarrow S_3$ transition.[7c)] The distinct vibrational fine structure of the long-wavelength maxima and the appearance of a medium-wavelength band are a characteristic of the spectra of the diarylpolyynes.[17)] These long-wavelength absorption maxima are fairly red-shifted with increasing the number of the acetylenic bond. In the hexatriyne compounds **11a**—**c**, the absorption maxima of **11a** and **11c** are more red-shifted than those of **11b** (not shown), which suggests somewhat larger electronic interactions in **11a** and **11c** than those in **11b**. Although the spectra of the anthrylpolyynes are roughly similar to those of di(9-anthryl)polyynes,[17)] the longest wavelength bands of di(9-anthryl)polyynes are more red-shifted than those of the anthrylpolyynes, and the vibrational fine structures of the anthrylpolyynes are more distinctive. Compared with other related molecules, anthrylpolyenes ($n = 1$—3)[7c)] and anthrylpolythiophenes,[7d)] the spectral shape of the anthryl part and the extinction coefficient of the anthracene $S_0 \rightarrow S_3$ transition are not very much different in the anthrylpolyynes. As described in the literature,[7,17)] electronic interactions between anthracene and conjugated systems are relatively weak in these compounds with a linkage in the 9-position of anthracene.

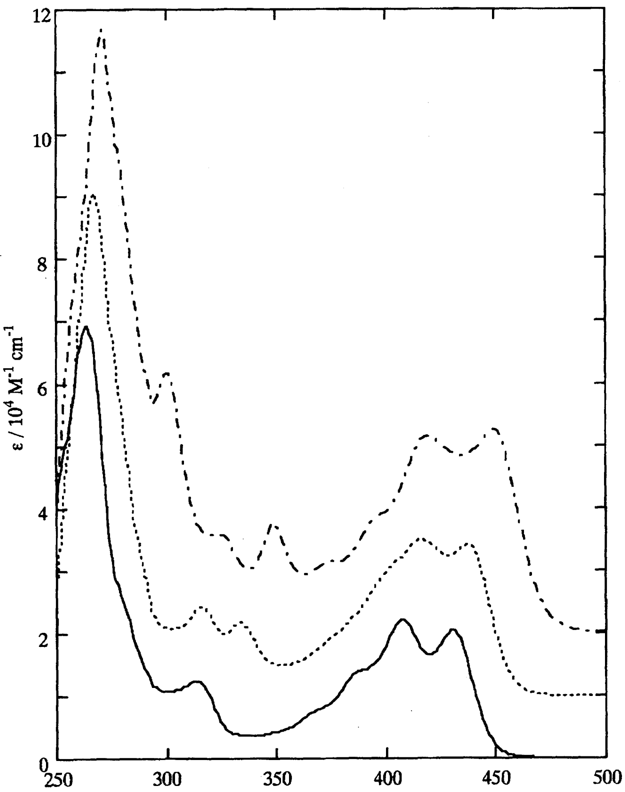


Fig. 1. UV-vis absorption spectra of **9**, **10**, and **11c** in CH_2Cl_2; **9** (solid line), **10** (dotted line, $+10^4$ ε unit), **11c** (dashed-dotted line, $+2\times10^4$ ε unit).

All of the anthrylpolyynes have strong fluorescence emission. The fluorescence-emission spectra of anthrylhexatriynes **11a**—**c** and the date of the excited state of anthrylpolyynes **9**, **10**, **11a**—**c** are shown in Fig. 2 and Table 1. The fluorescence spectra are independent of the excitation wavelength, and the fluorescence lifetimes observed at room temperature can be analyzed by a single exponential. In contrast to the polyenes in the anthrylpolyenes and the polythiophenes in the anthrylpolythiophenes,[7)] polyynes in the anthrylpolyynes are free from a steric hindrance, and no special direction of π-plane would appear at this temperature. In compounds **9**, **10**, **11c** the emission maxima are slightly

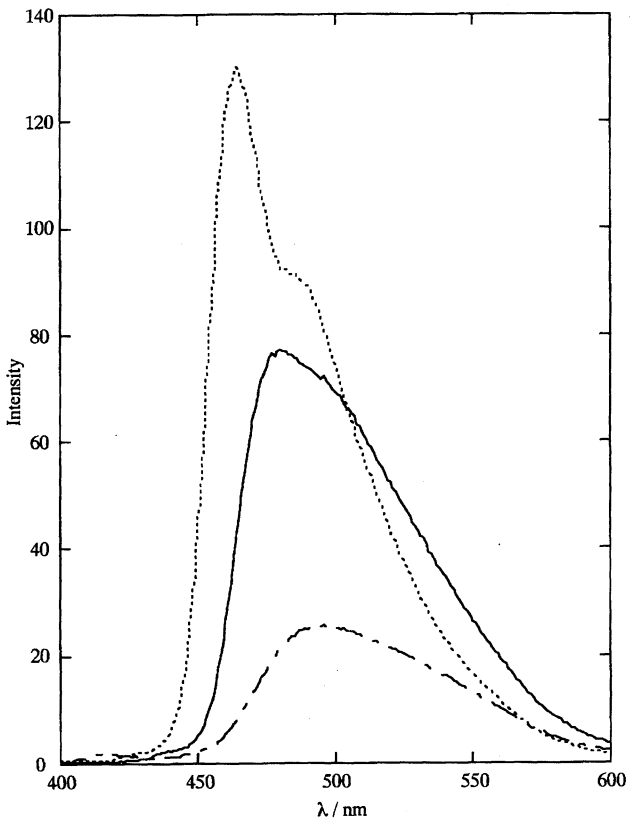


Fig. 2. Fluorescence spectra of **11a**—**c** in CH_2Cl_2; **11a** (solid line), **11b** (dotted line), **11c** (dashed-dotted line).

Table 1. Fluorescence Emission Maxima, Lifetimes, Radiative Rate Constants, and Fluorescence Quantum Yields of **9**, **10**, **11a**—**c** in CH_2Cl_2

Compound	$\lambda_{\mathrm{Em\ max}}/\mathrm{nm}^{a)}$	$\tau_0/\mathrm{ps}^{b)}$	$k_0/10^9\mathrm{s}^{-1}$	$\phi_F{}^{c)}$
9	481	2777	0.36	0.58
10	489	782	1.3	0.14
11a	479	203	4.9	0.050
11b	463, 483sh	260	3.8	0.067
11c	496	184	5.4	0.018

a) $\lambda_{\mathrm{Ex}} = 265$ nm. b) $\lambda_{\mathrm{Ex}} = 265$ nm, $\lambda_{\mathrm{Em}} = 480$ nm. c) Fluorescence quantum yields are determined by integration of fluorescence emission. ϕ_F(anthracene) $= 0.27$ is used as a standard reference. $\lambda_{\mathrm{Ex}} = 377$, Abs $= 0.100$.

red-shifted with increasing the number of acetylenic bonds, which corresponds to the bathochromic shift observed in the absorption spectra. In the same triyne compounds **11a—c** the formyl-substituted position of the phenyl ring somewhat affects their spectral shape due to an alteration of the vibronic coupling, which suggest a slight interaction among π-conjugated systems. More remarkable is the difference in the fluorescence intensities of each compound. Especially, anthrylarylethyne **9** has a notably high fluorescence quantum yield and a relatively long fluorescence lifetime (Table 1). With increasing the number of acetylenic bonds the fluorescence lifetimes and the fluorescence quantum yields become apparently short and low. From these facts, the emitting state of anthrylpolyyne might overlap among the anthryl part, the polyynyl part, and the formylphenyl part to some extent.

Figure 3 shows the UV-vis absorption spectra of anthrylpolyynylporphyrin **15b** together with anthrylpolyyne **11b** in dichloromethane. In all anthrylpolyynylporphyrins **13**, **14**, **15a—c** and the corresponding zinc complexes (**Zinc·13**, **14**, **15c**) the absorption spectra nearly match the sum of the component parts, anthrylpolyyne and porphyrin. As well as the anthrylpolythienylporphyrins,[7d] a direct attachment of the π-systems, anthrylpolyyne and porphyrin, little affect the electronic state of each π-system. The $S_0 \rightarrow S_3$ absorption of the anthracene at 264—270 nm and the Soret band of the porphyrin at 401—405 nm (free-base porphyrin) and 412 nm (zinc porphyrin) are clearly identified. Substitution of polyyne on the aromatic ring at the meso position of porphyrin does not so much perturb the optical spectra of porphyrin, as described in the literature.[4,7—10)]

The fluorescence-emission spectra of anthrylpolyynylporphyrin **15c**, together with anthrylpolyyne **11c**, are shown in Fig. 4. It also shows the intensity of **11c** to be expected when the anthrylpolyynyl part of **15c** absorbs the excitation energy independently (λ_{Ex} = Soret band), and no fluorescence quenching occurs. Anthrylpolyynylporphyrin **15c** shows only typical fluorescence emission of porphyrin and no characteristic emission of anthrylpolyyne at 480 nm. On the other hand, the anthrylpolyynyl group does not quench the porphyrin emission. All other anthrylpolyynylporphyrins show similar fluorescence spectra and almost no fluorescence emission in the spectral region of anthrylpolyyne. The relative fluorescence intensities of anthrylpolyynylporphyrin versus the corresponding anthrylpolyyne at 480 nm are given in Table 2. Fluorescence quenching of the anthrylpolyynyl part is almost complete. Figure 5 shows the fluorescence excitation spectra of **15c** ($\lambda_{\mathrm{Em}} = 627$ nm; not exactly corrected) and its absorption spectra in dichloromethane. The spectra are normalized to the same intensity at 270 nm. In the fluorescence excitation spectrum the anthracene $S_0 \rightarrow S_3$ absorption at 270 nm and the longest wavelength absorption maxima of anthrylpolyyne at 440 nm are clearly identified; the intensities of these bands are rather strong. Within the experimental error the excitation spectrum closely resembles the absorp-

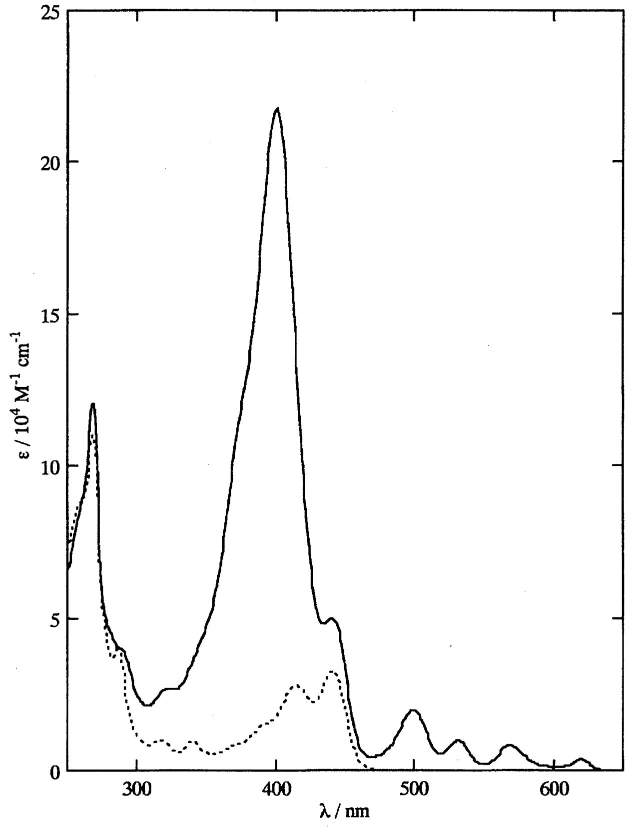


Fig. 3. UV-vis absorption spectra of **15b** (solid line) and **11b** (dotted line).

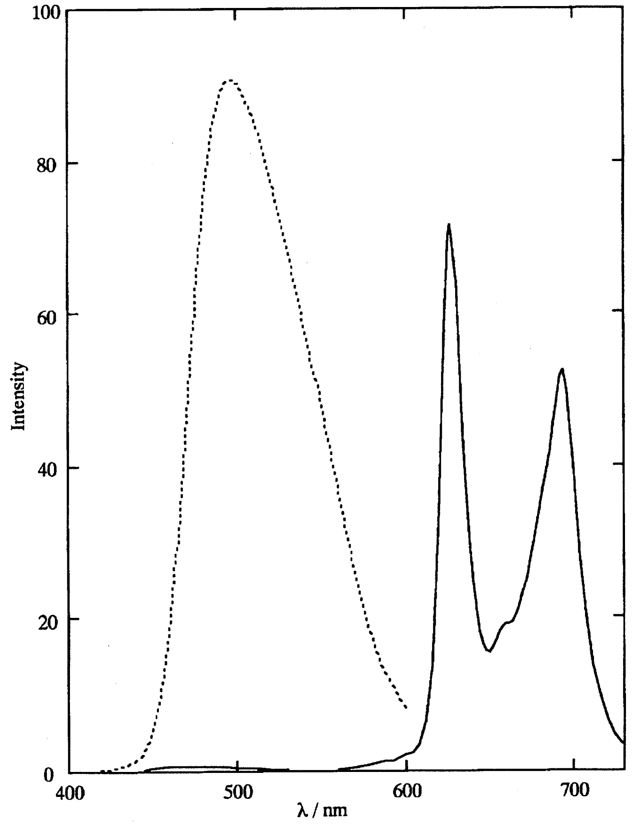


Fig. 4. Fluorescence emission spectra of **11c** (dotted line) and **15c** (solid line) in CH_2Cl_2; $\lambda_{\mathrm{Ex}} = 405$ nm.

Table 2. Relative Fluorescence Intensities of Anthrylpolyynylporphyrin versus Anthrylpolyyne (**9**,**10**, **11a**—**c**) at 480 nm

Compound	Relative fluorescence intensity
13/9	0.001 >
14/10	0.001
15a/11a	0.001 >
15b/11b	0.001 >
15c/11c	0.007
Zn·13/9	0
Zn·14/10	0.0001 >
Zn·15c/11c	0

λ_{Ex} = Soret region.

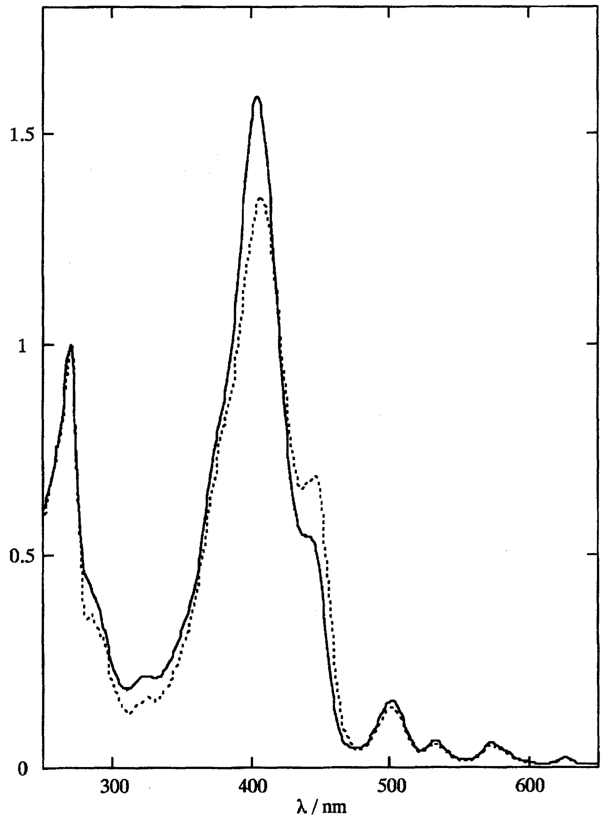


Fig. 5. UV-vis absorption (solid line) and fluorescence excitation spectra (dotted line, $\lambda_{Em} = 627$ nm) of **15c** in CH_2Cl_2; each spectrum is normalized at 270 nm.

tion spectrum. Therefore, it is evident that the excitation energy absorbed by the anthryl part at 270 nm is entirely transferred to the emitting state of the porphyrin. Under our dilute conditions (ca. 10^{-7} M, M = mol dm^{-3}), intermolecular excitation energy transfer can be excluded. Consequently, these fluorescence spectroscopic findings have indicated almost a quantitative intramolecular excitation energy transfer from the anthryl moiety to the porphyrin in all anthrylpolyynylporphyrins. The number of acetylenic bonds and the substituted position of anthrylpolyyne in the aromatic ring at the *meso* position of porphyrin are independent of this energy-transfer efficiency.

In order to elucidate more the detailed mechanism of these intramolecular excitation energy-transfer reactions in anthrylpolyynylporphyrins, we further performed spectroscopic measurements by picosecond time-resolved fluorescence spectroscopy. The excitation wavelength was 265 nm, which could selectively excite the anthryl part of the anthrylpolyynylporphyrins. Table 3 gives the fluorescence main decay times observed at 480 nm and the fluorescence increase times of the porphyrin observed at 626 nm for free-base porphyrins and at 576 nm for zinc porphyrins. The fluorescence lifetimes observed at 480 nm in the spectral region of the anthrylpolyynyl part consist of the main component with a very short time constant (< 17 ps), and residuals with a relatively long time constant (160—3300 ps), which would be derived from the presence of fluorescent impurities. The main decay times of all the compounds are extremely short (almost the same as the pulse response of the apparatus), which is roughly in agreement with the steady-state fluorescence spectra, that almost no emission in the spectral region of anthrylpolyynyl part could be detected. A rapid increase in the porphyrin fluorescence at 626 nm or at 576 nm was observed with the nearly the same time constant, which was also almost the detection limit of the apparatus. The fluorescence decay at 626 nm or at 576 nm is monoexponential with a time constant of 10—11 ns for free-base porphyrins and 1.1—1.4 ns for zinc porphyrins. The detection of the increase in the porphyrin emission on the picosecond time scale might suggest that the excitation energy of the anthrylpolyynyl part is stepwise, but rapidly migrated to the porphyrin part. The rate constants of the intramolecular excitation energy transfer, which are also given in Table 3, were estimated using

$$k_{EN} = \tau_d^{-1} - \tau_0^{-1}, \tag{1}$$

$$k_{EN} = \tau_r^{-1} - \tau_0^{-1}, \tag{2}$$

where τ_d is the fluorescence lifetime of the anthrylpolyynylporphyrin observed at 480 nm, τ_0 is the fluorescence lifetime of the corresponding anthrylpolyyne, and τ_r is the fluorescence increase time of the anthrylpolyynylporphyrin observed at 626 nm or at 576 nm. The calculated k_{EN} values

Table 3. Fluorescence Lifetimes and Energy Transfer Data of Anthrylpolyynylporphyrins in CH_2Cl_2 ($\lambda_{Ex} = 265$ nm)

Porphyrin	τ_d/ps[a]	$k_{EN}/10^{10}s^{-1}$[b]	τ_r/ps[c]	$k_{EN}/10^{-10}s^{-1}$[d]
13	15>	6.6<	18	5.5
14	15>	6.5<	20	4.9
15a	5.5	18	23	3.9
15b	17>	5.5<	19	4.9
15c	15	6.1	24	3.6
Zn·13	8.3	12	16	6.2
Zn·14	9.0	11	16	6.1
Zn·15c	7.0	14	19	4.7

a) Fluorescence main decay times observed at 480 nm. b) Rates of singlet excitation energy transfer calculated on the basis of τ_d according to the Eq. 1. c) Fluorescence increase times of the porphyrin observed at 626 nm for **13**, **14**, **15a**—**c** and 576 nm for zinc porphyrin. d) Rates of singlet excitation energy transfer calculated on the basis of τ_r according to the Eq. 2.

are one-to-two orders of magnitude larger than the radiative lifetimes of the anthrylpolyynes. Therefore, these spectroscopic findings indicate that almost a complete energy transfer occurs, not by a delocalization interaction through the whole molecule, but by a rapid intramolecular excitation energy-transfer from the anthryl moiety to the porphyrin in all anthrylpolyynylporphyrins.

The mechanism of intramolecular excitation energy-transfer is briefly discussed. Table 4 gives the distances between the porphyrin center and the anthracene estimated from the CPK model, the spectral overlap integrals between the anthrylpolyyne emission and the porphyrin absorption, and the critical transfer distances of Förster theory.[20] Because of difficulties in determining the anthrylpolyyne center, the distances between the porphyrin center and the anthracene were given in Table 4. The orientation factors were roughly calculated by assuming that the direction of the transition dipole moment of the anthrylpolyyne is parallel to the direction of polyyne, and that the aromatic ring at the meso position is perpendicular to the porphyrin plane. In all compounds, the distances between the porphyrin center and the anthracene are considerably shorter than the calculated critical transfer distances (distance at 50% energy transfer). The distances between the porphyrin center and the anthrylpolyyne center should be shorter. The fluorescence high quantum yield of anthrylpolyyne and the available spectral matching between the anthrylpolyyne emission and the porphyrin absorption lead to the prediction of higher excitation energy transfer efficiencies. Another mechanism, a through-bond interaction by the polyyne linkage, as previously reported,[8,9] may open an additional pathway for energy transfer. Actually, in the excited state there are suitable interactions between the anthryl part and the aromatic ring at the other side of polyyne. If the emitting state of anthrylpolyyne is availably delocalized in the whole (anthrylpolyynyl)phenyl group, the energy donor and the energy acceptor are in close contact and might have a sufficient electronic interaction (Dexter mechanism[21]). However, further discrimination cannot be given at present. In any case, these anthrylpolyyne components have favorable photochemical properties, and could act as an excellent constituent for energy-gathering systems by combining them with the porphyrin moiety.

Table 4. Data for Anthrylpolyynylporphyrins in CH_2Cl_2

Porphyrin	$R/10^{-10}\mathrm{m}$[a]	$J/10^{-14}\mathrm{cm}^6\,\mathrm{mmol}^{-1}$[b]	$R_0/10^{-10}\mathrm{m}$[c]
13	13.1	5.0	48
14	15.6	5.6	39
15a	10.1	6.2	28
15b	15.9	6.2	33
15c	18.1	7.1	29
Zn·13	13.1	3.4	45
Zn·14	15.6	4.3	37
Zn·15c	18.1	6.4	28

a) Distances between the porphyrin center and the anthracene estimated from CPK model. b) Spectral overlap integrals between anthrylpolyyne emission and porphyrin absorption. c) Critical transfer distances of Förster theory.

Although there are few significant electronic interactions between anthrylpolyyne and porphyrin in the absorption spectra, the efficiencies of intramolecular excitation energy transfers from the anthryl moiety to the porphyrin are almost unity. Analogously to the anthrylpolythienylporphyrin[7d] and multiporphyrin compounds connected with the ethyne linkage,[8,9,11—13] the polyynediyl group and polyyne linkage could construct efficient photonic systems.

Experimental

^{1}H NMR spectra were determined on a JEOL JNM-EX 400 spectrometer with TMS as an internal standard. The mass spectra were obtained on a JEOL JMS-AX 500 spectrometer. IR spectra were obtained on a Shimadzu FTIR-8100 spectrometer. NMR, Mass, and IR measurements are performed at Toyama Prefectural University, Biotechnology Research Center. UV-vis spectra were recorded with a Hitachi 150-20 spectrometer and steady-state fluorescence spectra were taken on a Shimadzu RF-5300PC spectrofluorometer. The fluorescence lifetimes were measured on 10^{-7} M air-saturated solutions with a picosecond time-correlated single-photon counting system.[22] The solvents and reagents were purified by standard methods before use.

1-(9-Anthryl)-2-[4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]ethyne (6). 4-(5,5-dimethyl-1,3-dioxan-2-yl)phenylethyne (**1**)[23] (1.08 g, 5 mmol) and 9-bromoanthracene (**2**) (1.29 g, 5 mmol) were dissolved in dry triethylamine (30 ml).[15] $Pd(OAc)_2$ (28 mg), triphenylphosphine (66 mg), and a small amount of $[PdCl_2(PPh_3)_2]$ were added, and the mixture was refluxed under Ar for 2 h, then stirred for 1 h at room temperature. The mixture was poured into 2 M HCl and extracted with benzene, washed with aqueous $NaHCO_3$, and dried over anhydrous Na_2SO_4. The product was purified by silica-gel column chromatography with benzene, and recrystallized from CH_2Cl_2–MeOH. Yield 799 mg, 40%; yellow powder; mp 212 °C; ^{1}H NMR ($CDCl_3$) $\delta=8.65$ (2H, d, $J=8.8$ Hz, 1,8-An), 8.44 (1H, s, 10-An), 8.02 (2H, d, $J=8.3$ Hz, 4,5-An), 7.78 (2H, d, $J=8.3$ Hz, ArH), 7.60 (2H, t, $J=8.4$ Hz, 2,7-An), 7.59 (2H, d, $J=8.3$ Hz, ArH), 7.52 (2H, t, $J=8.3$ Hz, 3,6-An), 5.46 (1H, s, CH), 3.82 (2H, d, $J=11.2$ Hz, CH_2), 3.69 (2H, d, $J=10.7$ Hz, CH_2), 1.33 (3H, s, CH_3), 0.83 (3H, s, CH_3); IR (KBr) 2955, 1509, 1387, 1102s, 1022, 818, 737 cm^{-1}. HRMS (EI) Found : m/z 392.1766. Calcd for $C_{28}H_{24}O_2$: M, 392.1776. Found: C, 85.45; H, 6.20%. Calcd for $C_{28}H_{24}O_2$: C, 85.68; H, 6.16%.

1-(9-Anthryl)-4-[4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]butadiyne (7). Compound **1** (0.61 g, 3 mmol) and 9-anthrylethyne (**3**) (0.65 g, 3 mmol) were dissolved in pyridine (8 ml) and MeOH (8 ml).[16] Copper(II) acetate monohydrate was added, and the mixture was stirred overnight at room temperature. Benzene was added, and an insoluble material was removed by filtration, and washed with benzene. 6 M HCl was added to the filtrate, and extracted with benzene, washed with aqueous $NaHCO_3$, and dried over anhydrous Na_2SO_4. The product was purified by silica-gel column chromatography with benzene (2nd fraction), and recrystallized from CH_2Cl_2–MeOH. Yield 233 mg, 19%; orange needles; mp 194 °C; ^{1}H NMR ($CDCl_3$) $\delta=8.58$ (2H, d, $J=7.8$ Hz, 1,8-An), 8.46 (1H, s, 10-An), 8.02 (2H, d, $J=8.3$ Hz, 4,5-An), 7.63 (2H, d, $J=8.3$ Hz, ArH), 7.61 (2H, t, $J=6.8$ Hz, 2,7-An), 7.53 (2H, d, $J=8.3$ Hz, ArH), 7.52 (2H, t, $J=7.6$ Hz, 3,6-An), 5.42 (1H, s, CH), 3.79 (2H, d, $J=11.2$ Hz, CH_2), 3.67 (2H, d, $J=10.8$ Hz, CH_2), 1.30 (3H, s, CH_3), 0.82 (3H, s, CH_3); IR (KBr) 2955, 1509, 1387s, 1102s, 1021, 822, 735 cm^{-1}. HRMS (EI) Found : m/z 416.1783. Calcd for $C_{30}H_{24}O_2$: M, 416.1776. Found: C, 86.64; H, 5.86%. Calcd for

$C_{30}H_{24}O_2$: C, 86.51; H, 5.81%.

1-(9-Anthryl)-6-[2-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]hexatriyne (8a). [2-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]-2-propyn-1-ol (**4a**) (2.95 g, 12 mmol) and 1-(9-anthryl)-2-propyn-1-ol (**5**) (2.78 g, 12 mmol) were dissolved in acetone (70 ml). Copper(I) chloride (0.40 g, 4 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (0.48 g, 4 mmol) were added, and stirred overnight in the open air at room temperature.[17] After the mixture was concentrated at reduced pressure, 0.2 M HCl was added. This was extracted with ether, washed with brine, and dried over anhydrous Na_2SO_4. The solvent was removed at reduced pressure, and the residue was dissolved in dry THF (60 ml). After thionyl chloride (4.3 g, 36 mmol) and pyridine (3.1 g, 39 mmol) in dry THF (18 ml) were added in dropwise, the mixture was stirred for 5 h at 0 °C. The resulting mixture was directly added to a solution of sodium (2.76 g, 120 mmol) in EtOH (150 ml) at 0 °C, and stirred for 1 h. An ammonium chloride solution was added to the mixture, and extracted with benzene, washed with brine, and dried over anhydrous Na_2SO_4. The product was purified by silica-gel column chromatography with benzene (2nd fraction), and recrystallized from CH_2Cl_2–hexane. Yield 441 g, 8.3% (3 steps); brownish yellow powder; mp 124 °C; ^{1}H NMR ($CDCl_3$) δ=8.54 (2H, d, *J*=8.8 Hz, 1,8-An), 8.49 (1H, s, 10-An), 8.03 (2H, d, *J*=8.3 Hz, 4,5-An), 7.75 (1H, d, *J*=7.3 Hz, ArH), 7.63 (2H, t, *J*=7.8 Hz, ArH), 7.59 (1H, d, *J*=6.3 Hz, ArH), 7.53 (2H, t, *J*=7.1 Hz, 3,6-An), 7.46 (1H, t, *J*=7.6 Hz, ArH), 7.34 (1H, t, *J*=7.34, ArH), 5.80 (1H, s, CH), 3.82 (2H, d, *J*=10.7 Hz, CH_2), 3.77 (2H, d, *J*=10.8 Hz, CH_2), 1.35 (3H, s, CH_3), 0.85 (3H, s, CH_3); IR (KBr) 2957, 2363, 1508s, 1113s, 1092s, 1019, 760, 737 cm^{-1}. HRMS (EI) Found: *m/z* 440.1781. Calcd for $C_{32}H_{24}O_2$: M, 440.1776. Found: C, 86.92; H, 5.58%. Calcd for $C_{32}H_{24}O_2$: C, 87.25; H, 5.49%.

1-(9-Anthryl)-6-[3-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]hexatriyne (8b). The synthetic procedure was the same as for **8a**. Yield 261 mg, 4.9% (3 steps); brownish yellow powder; mp 175 °C; ^{1}H NMR ($CDCl_3$) δ=8.53 (2H, d, *J*=8.8 Hz, 1,8-An), 8.52 (1H, s, 10-An), 8.03 (2H, d, *J*=8.3 Hz, 4,5-An), 7.74 (1H, s, ArH), 7.63 (2H, t, *J*=7.6 Hz, 2,7-An), 7.56 (2H, d, *J*=7.8 Hz, ArH), 7.53 (2H, t, *J*=7.6 Hz, 3,6-An), 7.37 (1H, t, *J*=7.8 Hz, ArH), 5.39 (1H, s, CH), 3.79 (2H, d, *J*=11.2 Hz, CH_2), 3.66 (2H, d, *J*=10.7 Hz, CH_2), 1.30 (3H, s, CH_3), 0.82 (3H, s, CH_3); IR (KBr) 2955, 2359s, 1509, 1107s, 1019, 737 cm^{-1}. HRMS (EI) Found: *m/z* 440.1779. Calcd for $C_{32}H_{24}O_2$: M, 440.1776. Found: C, 87.00; H, 5.42%. Calcd for $C_{32}H_{24}O_2$: C, 87.25; H, 5.49%.

1-(9-Anthryl)-6-[4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl]hexatriyne (8c). The synthetic procedure was the same as for **8a**. Yield 819 mg, 18.6% (3 steps); deep yellow powder; mp 199 °C; ^{1}H NMR ($CDCl_3$) δ=8.53 (2H, d, *J*=7.8 Hz, 1,8-An), 8.48 (1H, s, 10-An), 8.03 (2H, d, *J*=8.3 Hz, 4,5-An), 7.63 (2H, t, *J*=7.6 Hz, 2,7-An), 7.59 (2H, d, *J*=8.3 Hz, ArH), 7.52 (2H, t, *J*=7.1 Hz, 3,6-An), 7.51 (2H, d, *J*=8.3 Hz, ArH), 5.40 (1H, s, CH), 3.78 (2H, d, *J*=11.2 Hz, CH_2), 3.66 (2H, d, *J*=10.3 Hz, CH_2), 1.29 (3H, s, CH_3), 0.81 (3H, s, CH_3); IR (KBr) 2953, 2350, 2193, 1509, 1103s, 1019, 820, 735 cm^{-1}. HRMS (EI) Found: *m/z* 440.1761. Calcd for $C_{32}H_{24}O_2$: M, 440.1776. Found: C, 87.11; H, 5.32%. Calcd for $C_{32}H_{24}O_2$: C, 87.25; H, 5.49%.

Hydrolysis of 2,2-Dimethyl-1,3-propanediyl Acetal as the Protecting Group. A solution of **6**, **7**, **8a**—**c** (0.5 mmol) in CH_2Cl_2 (16 ml) was stirred overnight with 50% trifluoroacetic acid (16 ml) at 0 °C, respectively. The solution was extracted with CH_2Cl_2, washed with saturated $NaHCO_3$ solution, and dried over Na_2SO_4. The product was recrystallized from CH_2Cl_2–hexane.

1-(9-Anthryl)-2-(4-formylphenyl)ethyne (9). Yield 117 mg, 76%; brownish yellow needles; mp 148 °C; ^{1}H NMR ($CDCl_3$) δ=10.08 (1H, s, CHO), 8.63 (2H, d, *J*=8.8 Hz, 1,8-An), 8.50 (1H, s, 10-An), 8.05 (2H, d, *J*=8.3 Hz, 4,5-An), 7.97 (2H, d, *J*=8.3 Hz, ArH), 7.92 (2H, d, *J*=8.3 Hz, ArH), 7.64 (2H, t, *J*=7.6 Hz, 2,7-An), 7.54 (2H, t, *J*=6.8 Hz, 3,6-An); IR (KBr) 2191, 1696s (C=O), 1597, 1208, 826, 739 cm^{-1}; UV-vis (CH_2Cl_2) $\lambda_{\max}$/nm (ε/10^4 M^{-1} cm^{-1}) 264 (6.9), 314 (1.2), 408 (2.2), 431 (2.0). HRMS (EI) Found: *m/z* 306.1050. Calcd for $C_{23}H_{14}O$: M, 306.1045. Found: C, 90.13; H, 4.53%. Calcd for $C_{23}H_{14}O$: C, 90.17; H, 4.61%.

1-(9-Anthryl)-4-(4-formylphenyl)butadiyne (10). Yield 132 mg, 80%; brownish yellow powder; mp 197 °C; ^{1}H NMR ($CDCl_3$) δ=10.05 (1H, s, CHO), 8.57 (2H, d, *J*=8.8 Hz, 1,8-An), 8.50 (1H, s, 10-An), 8.04 (2H, d, *J*=8.8 Hz, 4,5-An), 7.90 (2H, d, *J*=7.8 Hz, ArH), 7.76 (2H, d, *J*=8.3 Hz, ArH), 7.63 (2H, t, *J*=7.6 Hz, 2,7-An), 7.53 (2H, t, *J*=6.8 Hz, 3,6-An); IR (KBr) 2190, 1698s (C=O), 1601, 1206, 824, 737 cm^{-1}; UV-vis (CH_2Cl_2) $\lambda_{\max}$/nm (ε/10^4 M^{-1} cm^{-1}) 267 (8.1), 316 (1.4), 333 (1.2), 415 (2.5), 438 (2.4). HRMS (EI) Found: *m/z* 330.1033. Calcd for $C_{25}H_{14}O$: M, 330.1045. Found: C, 90.69; H, 4.40%. Calcd for $C_{25}H_{14}O$: C, 90.89; H, 4.27%.

1-(9-Anthryl)-6-(2-formylphenyl)hexatriyne (11a). Yield 96 mg, 54%; orange yellow powder; mp 215 °C (decomp); ^{1}H NMR ($CDCl_3$) δ=10.53 (1H, s, CHO), 8.53 (2H, d, *J*=8.3 Hz, 1,8-An), 8.51 (1H, s, 10-An), 8.04 (2H, d, *J*=8.3 Hz, 4,5-An), 7.97 (1H, d, *J*=8.8 Hz, ArH), 7.72 (1H, d, *J*=6.8 Hz, ArH), 7.64 (2H, t, *J*=8.3 Hz, 2,7-An), 7.62 (1H, t, *J*=7.8 Hz, ArH), 7.54 (3H, t+t, *J*=7.6 Hz, 3,6-An+ArH); IR (KBr) 2159, 1698s (C=O), 1541, 1509, 731 cm^{-1}; UV-vis (CH_2Cl_2) $\lambda_{\max}$/nm (ε/10^4 M^{-1} cm^{-1}) 268 (10.4), 286 (3.6), 350 (1.1), 418 (3.0), 447 (3.3). HRMS (EI) Found: *m/z* 354.1049. Calcd for $C_{27}H_{14}O$: M, 354.1045. Found: C, 89.26; H, 4.03%. Calcd for $C_{27}H_{14}O$: C, 91.50; H, 3.98%.

1-(9-Anthryl)-6-(3-formylphenyl)hexatriyne (11b). Yield 160 mg, 90%; brownish yellow powder; mp 172 °C (decomp); ^{1}H NMR ($CDCl_3$) δ=10.02 (1H, s, CHO), 8.53 (2H, d, *J*=8.3 Hz, 1,8-An), 8.50 (1H, s, 10-An), 8.06 (2H, d, *J*=8.3 Hz, 4,5-An), 8.03 (1H, s, ArH), 7.92 (1H, d, *J*=7.8 Hz, ArH), 7.82 (1H, d, *J*=7.8 Hz, ArH), 7.64 (2H, t, *J*=7.1 Hz, 2,7-An), 7.56 (1H, t, *J*=7.8 Hz, ArH), 7.54 (2H, t, *J*=7.6 Hz, 3,6-An); IR (KBr) 2159, 1695s (C=O), 1541, 1509, 731 cm^{-1}; UV-vis (CH_2Cl_2) $\lambda_{\max}$/nm (ε/10^4 M^{-1} cm^{-1}) 268 (11.0), 287 (4.1), 317 (0.99), 341 (0.96), 415 (2.8), 441 (3.3). HRMS (EI) Found: *m/z* 354.1039. Calcd for $C_{27}H_{14}O$: M, 354.1045. Found: C, 90.21; H, 4.22%. Calcd for $C_{27}H_{14}O$: C, 91.50; H, 3.98%.

1-(9-Anthryl)-6-(4-formylphenyl)hexatriyne (11c). Yield 123 mg, 69%; brownish yellow powder; mp 235 °C (decomp); ^{1}H NMR ($CDCl_3$) δ=10.04 (1H, s, CHO), 8.53—8.51 (3H, d+s, *J*=8.8 Hz, 1,8-An+10-An), 8.04 (2H, d, *J*=8.3 Hz, 4,5-An), 7.88 (2H, d, *J*=8.3 Hz, ArH), 7.72 (2H, d, *J*=8.3 Hz, ArH), 7.64 (2H, t, *J*=8.3 Hz, 2,7-An), 7.54 (2H, t, *J*=7.1 Hz, 3,6-An); IR (KBr) 2159, 1701s (C=O), 1559, 1509, 731 cm^{-1}; UV-vis (CH_2Cl_2) $\lambda_{\max}$/nm (ε/10^4 M^{-1} cm^{-1}) 271 (9.7), 301 (4.2), 325 (1.6), 349 (1.8), 419 (3.1), 449 (3.3). HRMS (EI) Found: *m/z* 354.1062. Calcd for $C_{27}H_{14}O$: M, 354.1045. Found: C, 91.19; H, 4.10%. Calcd for $C_{27}H_{14}O$: C, 91.50; H, 3.98%.

Reaction of Acid-Catalyzed Porphyrin Cyclization. Aldehyde **9**, **10**, **11a**—**c** (0.25 mmol) and 8,12-dibutyl-2,3,7,13,17,18-hexamethylbiladiene-*ac*-1,19-diium dibromide (**12**)[19] (165 mg, 0.25 mmol) were suspended in MeOH, and heated, respectively. After a few ml of anhydrous 25% HBr in AcOH was added, the mixture was refluxed for 3 d under Ar in the dark.[18] After cooling, the mixture was stirred in the open air for 12 h, and poured into water. This solution was extracted with CH_2Cl_2, washed with brine, and dried over Na_2SO_4. The product was purified by silica-

Table 5. UV-vis Absorption and Fluorescence Spectral Data of **13**, **14**, **15a**—**c** and **Zn·13**, **Zn·14**, **Zn·15c** in CH_2Cl_2

Compound	UV-vis absorption λ_{max}/nm (rel intensity[a])								Fluorescence emission λ_{max}/nm[b] (rel intensity[c])	
13	264	301	405		501	533	572	626	626	692
	(56)	(14)	(1000)		(9.2)	(3.8)	(3.5)	(1.6)	(72)	(51)
14	266		405		501	533	573	626	626	692
	(63)		(1000)		(9.2)	(3.7)	(3.4)	(1.5)	(75)	(54)
15a	269		402	444	502	536	570	623	627	694
	(72)		(1000)	(22)	(8.7)	(4.4)	(3.9)	(1.8)	(100)	(52)
15b	268		401	440	500	533	569	620	628	692
	(56)		(1000)	(23)	(9.2)	(4.5)	(3.8)	(1.7)	(83)	(53)
15c	270		405	440	502	533	573	627	627	694
	(63)		(1000)	(34)	(9.6)	(3.9)	(3.7)	(1.6)	(72)	(52)
Zn·13	263	302	412			542	575		576	628
	(329)	(76)	(1000)			(61)	(37)		(76)	(31)
Zn·14	266		412			541	576		576	628
	(371)		(1000)			(61)	(37)		(75)	(31)
Zn·15c	270		412			541	576		576	627
	(356)		(1000)			(66)	(39)		(71)	(30)

a) Relative absorption intensity vs. Soret absorption (ε: nearly 2.18×10^5 M^{-1} cm^{-1} for free-base porphyrin and nearly 4.1×10^5 M^{-1} cm^{-1} for zinc porphyrin). b) λ_{Ex}=Soret region. c) Relative fluorescence intensity vs. **15a** fluorescence intensity; *I* (**15a**, 627 nm) is set to 100.

gel column chromatography with CH_2Cl_2 as an eluent (**15a**, **b**; 10% hexane–CH_2Cl_2), and recrystallized from CH_2Cl_2–MeOH. The UV-vis spectral data and steady-state fluorescence spectral data of anthrylpolyynylporphyrins are shown in Table 5.

Anthrylpolyynylporphyrin (13). Yield 68 mg, 35%; red purple crystals; ^{1}H NMR ($CDCl_3$) δ=10.16 (2H, s, *meso*-H), 9.95 (1H, s, *meso*-H), 8.88 (2H, d, *J*=8.3 Hz, 1,8-An), 8.50 (1H, s, 10-An), 8.14 (4H, ABq, ArH), 8.08 (2H, d, *J*=8.8 Hz, 4,5-An), 7.72 (2H, t, *J*=7.1 Hz, 2,7-An) 7.58 (2H, t, *J*=7.1 Hz, 3,6-An), 4.03 (4H, t, *J*=7.6 Hz, Bu-1), 3.63 (6H, s, CH_3), 3.55 (6H, s, CH_3), 2.58 (6H, s, CH_3), 2.28 (4H, p, *J*=7.3 Hz, Bu-2), 1.77 (4H, m, *J*=7.3 Hz, Bu-3), 1.13 (6H, t, *J*=7.3 Hz, Bu-4), −3.17 (2H, br, NH); MS (FAB) *m*/*z* 783 (M^++1).

Anthrylpolyynylporphyrin (14). Yield 26 mg, 13%; red purple crystals; ^{1}H NMR ($CDCl_3$) δ=10.16 (2H, s, *meso*-H), 9.96 (1H, s, *meso*-H), 8.69 (2H, d, *J*=8.8 Hz, 1,8-An), 8.51 (1H, s, 10-An), 8.11 (2H, d, *J*=8.3 Hz, ArH), 8.07 (2H, d, *J*=8.8 Hz, 4,5-An), 8.01 (2H, d, *J*=7.8 Hz, ArH), 7.68 (2H, t, *J*=7.3 Hz, 2,7-An), 7.57 (2H, t, *J*=7.6 Hz, 3,6-An), 4.05 (4H, t, *J*=7.6 Hz, Bu-1), 3.64 (6H, s, CH_3), 3.55 (6H, s, CH_3), 2.52 (6H, s, CH_3), 2.29 (4H, p, *J*=7.6 Hz, Bu-2), 1.77 (4H, m, *J*=7.5 Hz, Bu-3), 1.13 (6H, t, *J*=7.3 Hz, Bu-4), −3.19 (1H, br, NH), −3.33 (1H, br, NH); MS (FAB) *m*/*z* 807 (M^++1).

Anthrylpolyynylporphyrin (15a). Yield 13 mg, 6.3%; red purple crystals; ^{1}H NMR ($CDCl_3$) δ=10.19 (2H, s, *meso*-H), 9.97 (1H, s, *meso*-H), 8.21 (1H, s, 10-An), 8.03 (1H, d, *J*=6.8 Hz, ArH), 7.96 (1H, d, *J*=6.3 Hz, ArH), 7.92 (2H, d, *J*=7.8 Hz, 1,8-An), 7.82 (1H, t, *J*=7.5 Hz, ArH), 7.78 (2H, d, *J*=8.3 Hz, 4,5-An), 7.75 (1H, t, *J*=7.6 Hz, ArH), 7.26 (2H, t, *J*=7.3 Hz, 3,6-An), 7.19 (2H, t, *J*=7.8 Hz, 2,7-An), 4.05 (4H, t, *J*=7.6 Hz, Bu-1), 3.63 (6H, s, CH_3), 3.57 (6H, s, CH_3), 2.51 (6H, s, CH_3), 2.27 (4H, p, *J*=7.6 Hz, Bu-2), 1.75 (4H, m, *J*=7.0 Hz, Bu-3), 1.11 (6H, t, *J*=7.3 Hz, Bu-4), −3.12 (1H, br, NH), −3.29 (1H, br, NH); MS (FAB) *m*/*z* 831 (M^++1).

Anthrylpolyynylporphyrin (15b). Yield 25 mg, 12%; red purple crystals; ^{1}H NMR ($CDCl_3$) δ=10.16 (2H, s, *meso*-H), 9.96 (1H, s, *meso*-H), 8.50 (2H, d, *J*=8.8 Hz, 1,8-An), 8.43 (1H, s, 10-An), 8.31 (1H, s, ArH), 8.11 (1H, d, *J*=7.8 Hz, ArH), 8.02 (1H, d, *J*=7.8 Hz, ArH), 7.98 (2H, d, *J*=8.3 Hz, 4,5-An), 7.74 (1H, t, *J*=7.6 Hz, ArH), 7.59 (2H, t, *J*=7.3 Hz, 2,7-An), 7.49 (2H, t, *J*=7.1 Hz, 3,6-An), 4.04 (4H, t, *J*=7.6 Hz, Bu-1), 3.63 (6H, s, CH_3), 3.54 (6H, s, CH_3), 2.50 (6H, s, CH_3), 2.28 (4H, p, *J*=7.6 Hz, Bu-2), 1.77 (4H, m, *J*=7.5 Hz, Bu-3), 1.13 (6H, t, *J*=7.3 Hz, Bu-4), −3.21 (1H, br, NH), −3.34 (1H, br, NH); MS (FAB) *m*/*z* 831 (M^++1).

Anthrylpolyynylporphyrin (15c). Yield 16 mg, 7.8%; red purple crystals; ^{1}H NMR ($CDCl_3$) δ=10.16 (2H, s, *meso*-H), 9.96 (1H, s, *meso*-H), 8.59 (2H, d, *J*=8.3 Hz, 1,8-An), 8.50 (1H, s, 10-An), 8.09 (2H, d, *J*=7.8 Hz, ArH), 8.05 (2H, d, *J*=7.8 Hz, 4,5-An), 7.97 (2H, d, *J*=8.3 Hz, ArH), 7.67 (2H, t, *J*=7.1 Hz, 2,7-An), 7.55 (2H, t, *J*=7.6 Hz, 3,6-An), 4.04 (4H, m, Bu-1), 3.64 (6H, s, CH_3), 3.54 (6H, s, CH_3), 2.49 (6H, s, CH_3), 2.28 (4H, m, Bu-2), 1.77 (4H, m, *J*=7.3 Hz, Bu-3), 1.13 (6H, t, *J*=7.3 Hz, Bu-4), −3.23 (1H, br, NH), −3.35 (1H, br, NH); MS (FAB) *m*/*z* 831 (M^++1).

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