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An Efficient Synthesis of Linear Porphyrin Arrays

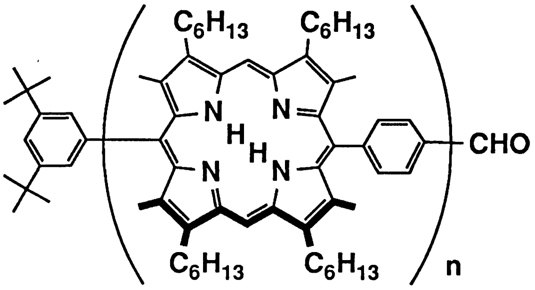
Atsuhiro OSUKA,* Nobuhiro TANABE, Run-Ping ZHANG, and Kazuhiro MARUYAMA
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606

Synthesis of linear porphyrin arrays of unusual length was reported. 1,4-Phenylene-bridged porphyrin oligomers up to a nonamer (ca. 122 Å length) were synthesized by acid catalyzed condensation of formyl-substituted porphyrins with dipyrrylmethane. The absorption and fluorescence spectra of these molecules exhibit systematic changes upon the increase in the number of the porphyrins.

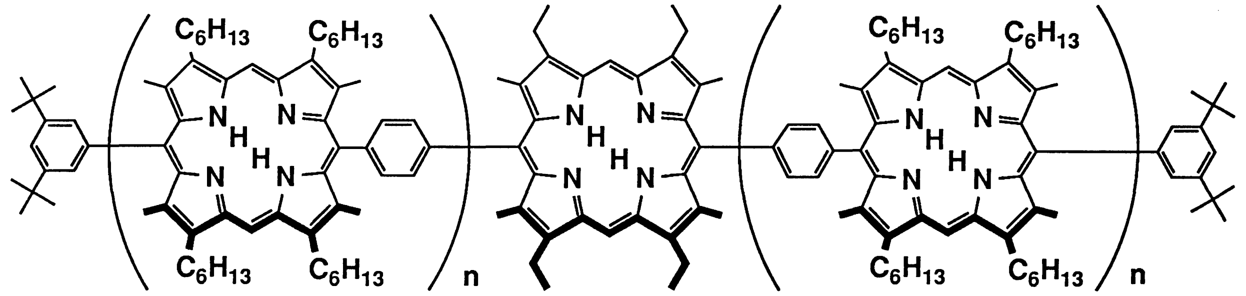
We report here the synthesis of several linear porphyrin arrays of unusual length. In recent years, increasing effort has been devoted to the synthesis and characterization of linear, rigid, and extensively conjugated molecules in relation to the realization of "molecular wire".1,2) Structures with well defined dimensions in the range of 100 Å and defined chemical constitution provide a new field of study with potential applications in areas including molecular electronic devices.

In earlier work, we reported the synthesis of linear and stacked porphyrin trimers and pentamers by the condensation of formyl-substituted porphyrins with dipyrrylmethane **1a**.3) Observed systematic changes in the absorption spectra of these molecules were explained in terms of simple exciton coupling theory. For the linear series , however, serious insolubilities of such porphyrin oligomers precluded a further extension to higher homologues. In the previous system, the substituents at the β-positions were methyl and ethyl groups and that at the terminal meso-positions was 4-methylphenyl group. In this paper, we wish to report a successful extension of our strategy to the synthesis of linear, 1,4-phenylene-bridged porphyrin oligomers with methyl and n-hexyl substituents at the β-positions and 3,5-di-*tert*-butylphenyl group4) at the terminal meso-positions.

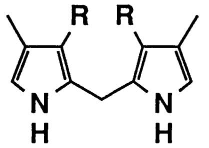
The synthetic strategy is quite simple; 1) first, formyl-substituted porphyrin $\mathbf{A_1}$ was prepared in 37% yield from the condensation of 3,5-di-*tert*-butylbenzaldehyde (**2**) and 4-(5,5-dimethyl-1,3-dioxacyclohexyl)-benzaldehyde (**3**) with bis(3-hexyl-4-methyl-2-pyrrolyl)methane (**1b**)5) followed by acidic hydrolysis (trifluoroacetic acid); 2) homologous formyl-substituted porphyrins $\mathbf{A_2}$ (mass m/e=1772 (M^+)),6) $\mathbf{A_3}$ (mass m/e=2550 (M^+)), and $\mathbf{A_4}$ (mass m/e=3327 (M^+ + 1)) were, respectively, stepwise prepared by the condensation of $\mathbf{A_1}$-$\mathbf{A_3}$ and **3** with **1b** in 39, 42, and 48% yields; 3) the homocondensation7) of $\mathbf{A_1}$, $\mathbf{A_2}$, $\mathbf{A_3}$, and $\mathbf{A_4}$ with **1a** under similar conditions afforded porphyrin arrays $\mathbf{B_1}$(trimer; mass m/e=2409 (M^+); 47%), $\mathbf{B_2}$(pentamer; mass m/e=3967 (M^+ + 3); 37%), $\mathbf{B_3}$(heptamer; mass m/e=5518-5525 (M^+=5521); 16%), and $\mathbf{B_4}$(nonamer; mass m/e=7065-7075 (M^+=7072); 38%), respectively. The porphyrin arrays $\mathbf{B_1}$-$\mathbf{B_4}$ are all quasi-one-dimensional and laterally 44, 70, 96, and 122 Å long, respectively.8) To the best of our knowledge, $\mathbf{B_4}$ is the longest porphyrin oligomer ever prepared. Since the meso-aryl substituents are held nearly perpendicular to the porphyrin plane, it may be pertinent to regard all porphyrins being held at nearly coplanar arrangements.



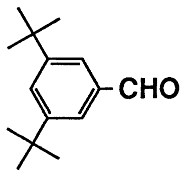
A_n : n = 1,2,3,4



B_n : n = 1,2,3,4



1a; R = Et
1b; R = C_6H_{13}



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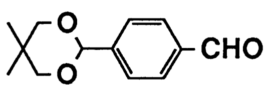

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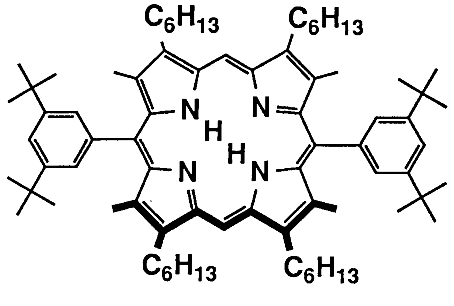

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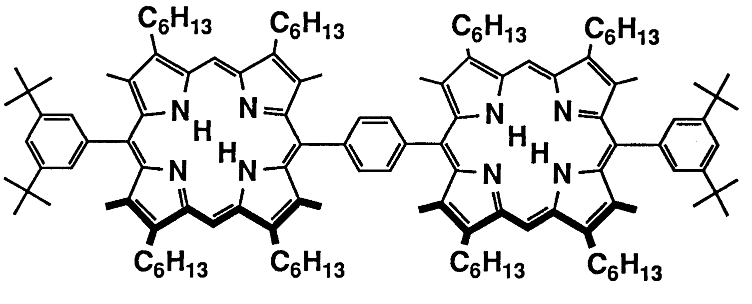

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In the Fig. 1, the absorption and fluorescence spectra of the zinc complexes of **B_1-B_4** are presented together with those of the related monomer **4** and dimer **5**. Other than **4**, all the zinc porphyrin oligomers display split Soret bands owing to exciton coupling. The Soret bands at shorter wavelength are observed at nearly the same wavelength (ca. 416 nm), while those at longer wavelength shift steadily to longer wavelength

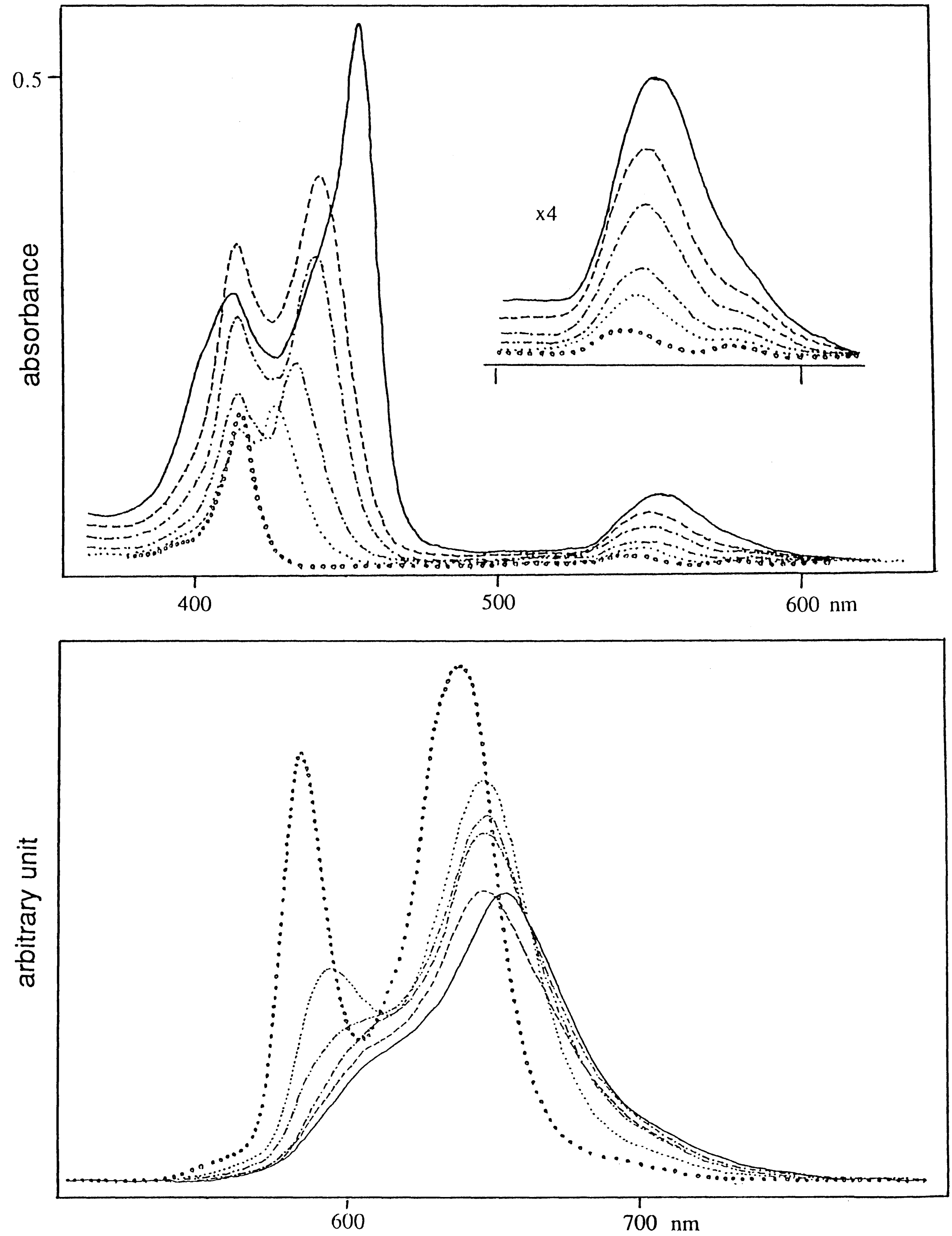

Fig. 1. Absorption (a, upper) and fluorescence (b, lower) spectra of the zinc complexes of **4**, **5**, and **B$_1$**-**B$_4$** in THF at room temperature; **4** (○○○○), **5** (·····), **B$_1$** (— · ·), **B$_2$** (— · —), **B$_3$** (— — —), and **B$_4$** (——). Concentrations for the former measurement were 3 x 10^{-7} M. The latter were taken for excitation at 416 nm, at which the absorbances were adjusted ca. 0.2.

upon the increase in the number of the porphyrins. Notably, a remarkably strong absorption is observed at 457 nm for **B**$_4$. The relative intensities of the split Soret bands are also dependent upon the number of the porphyrins; the intensities of the bands at the longer wavelength become increasingly stronger relative to those at the shorter wavelength. The fluorescence spectra also exhibit rather systematic changes: the fluorescence peak maxima are shifted to longer wavelength and the spectral bands become increasingly broader (characteristic vibrational bands observed for **4** change to a broad, nearly one-peaked band in **B**$_4$). These changes are consistent with those in the Q-bands of the absorption spectra. These results indicate that both S_1- and S_2-states of the porphyrin arrays become more stabilized upon the increase in the number of the porphyrins. These stabilizations are more prominent in the S_2-states.

In summary, our synthetic method for oligomeric porphyrin arrays has been extended to porphyrin heptamer and nonamer by introducing appropriate peripheral substituents. Now a study directing toward examination of long-range electron- and/or energy-transfer reactions across these extended porphyrin arrays are in progress by preparing models in which electron and/or energy donor and acceptor are covalently attached to these linear porphyrin arrays at the both ends.

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3) T. Nagata, A. Osuka, and K. Maruyama, *J. Am. Chem. Soc.*, **112**, 3054 (1990).
4) 3,5-Di-*tert*-butylphenyl substituent has been often employed in artificial models, since its introduction provides porphyrins good solubility in a number of solvents by retarding π-π-stacking of porphyrins. See, Ref. 2); S. Noblat, C. O. Dietrich-Buchecker, and J.-P. Sauvage, *Tetrahedron Lett.*, **28**, 5829 (1987); A. Osuka, B. Liu, and K. Maruyama, *J. Org. Chem.*, **58**, 3582 (1993); A. Osuka, B. Liu, and K. Maruyama, *Chem. Lett.*, **1993**, 949; H. Tamiaki, S. Suzuki, and K. Maruyama, *Bull. Chem. Soc. Jpn.*, **66** (1993) in press.
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6) All new compounds described in this paper gave satisfactory spectral data consistent with the assigned structures. The mass spectra were measured by a JEOL HX-100 spectrometer; the positive-FAB ionization method, accelerating voltage 10 kV, *m*-nitrobenzyl alcohol matrix.
7) The condensation reaction with **1b** gave low yields; the isolated yields for the corresponding trimer and pentamer were 17 and 19% yields, respectively.
8) Estimated from Corey-Pauling-Koltum models.

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