check the planarity and C=O⁺—C nonlinearity, several angle and torsional isomers were reevaluated by PRDDO.

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Supplementary Material Available: Preparation procedures and data for compounds **9**, **36–51**, **53**, **55**, **57–69**, **72–102**, and **104–125**, X-ray crystallographic data and ORTEP structures for compounds **1**, **2a**, **4**, **8–10**, **11a**, **11b**, **70**, **75**, **79**, **87**, **104**, **106**, **110**, and **111a**, and MM2 calculation parameters (Tables III and IV) for **1**, **9**, and **70** (149 pages). Ordering information is given on any current masthead page.

Synthesis and Optical Properties of Conformationally Constrained Trimeric and Pentameric Porphyrin Arrays

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Abstract: Synthesis, UV-visible absorption, and fluorescence emission properties are presented for the trimeric and pentameric porphyrins bridged by rigid aromatic spacers (*m*- or *p*-phenylene, anthracene-1,8-diyl, etc.). The synthetic method utilized here is based on the previously reported synthesis of 5,15-diaryloctaalkylporphyrins, with several important improvements. The new method can be generally utilized for preparation of conformationally constrained oligomeric porphyrins sequentially linked with aromatic spacers. The Soret absorption bands of anthracene-linked series were blue shifted, while those of *p*-phenylene series were split, which can be explained in terms of the exciton coupling theory. The relative fluorescence intensity was observed to decrease for higher oligomers. These porphyrin oligomers will be useful for synthetic model studies on photosynthetic charge separation.

Inspired by the determination of the three-dimensional architecture of bacterial photosynthetic reaction centers,[1] many porphyrin-based synthetic models have been prepared to develop an efficient synthetic catalyst for photosynthetic charge separation. Crucial to this end is an understanding of the importance of distance, orientation, and *number of pigments* in the model aggregates. In recent years, synthetic diporphyrins bridged by rigid aromatic spacers, in which the geometry of the two porphyrin rings is rather restricted, have been shown to be useful and promising for studies on intramolecular energy and/or electron-transfer reactions,[2-6] since these porphyrin models allow examination of the dynamics of energy (electron) transfers without concern for the conformational motions that may complicate analyses of flexible systems. As to higher oligomers, however, there has been reported only one example to date of this type, which is the anthracene-pillared trimeric porphyrin synthesized by Chang in 1985.[2d] Here we report the synthesis and optical properties of conformationally restricted trimeric and pentameric porphyrins.

Table I. Fluorescence Data of Di-, Tri-, and Pentameric Zinc Porphyrins[a,b]

compd	λ_{max}/nm (rel intens[c])	compd	λ_{max}/nm (rel intens[c])
2b	583 (49), 639 (40)	**3e**	578 (61), 633 (33)
3b	584 (23), 638 (26)	**5e**	580 (33), 634 (23)
5b	590 (10), 640 (17)	**1e**	576 (100), 628 (34)
2e	578 (58), 632 (33)		

[a] In 1,2-dichlorobenzene. [b] Excitation at Soret maximum. [c] Normalized for constant optical density at the excitation wavelength.

Results

Synthesis of Trimeric and Pentameric Porphyrins. The synthesis of trimeric porphyrins is shown in Scheme I. Condensation of 5-(3-formyl)dihexylhexamethylporphine[7] (**1a**) and bis(3-ethyl-4-methyl-2-pyrrolyl)methane[8] (**4**) in the presence of 4 equiv of trichloroacetic acid in acetonitrile followed by oxidation with *p*-chloranil gave trimeric porphyrin **3a** in 56% isolated yield. Trimeric porphyrins **3b–e** were prepared in a similar manner. This is a modified procedure of the synthetic method originally reported by Abdalmuhdi and Chang in their synthesis of anthracene-pillared triporphyrin.[2d] However, acid-catalyzed condensation of **1a** with **4** under their conditions (0.25 equiv of *p*-toluenesulfonic acid in methanol) afforded only trace amounts of trimer **3a** with most

(1) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385–398.
(2) (a) Chang, C. K.; Abdalmuhdi, I. *J. Org. Chem.* **1983**, *48*, 5388–5390. (b) Chang, C. K.; Abdalmuhdi, I. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 164–165. (c) Chang, C. K.; Liu, H. Y.; Abdalmuhdi, I. *J. Am. Chem. Soc.* **1984**, *106*, 2725–2726. (d) Abdalmuhdi, I.; Chang, C. K. *J. Org. Chem.* **1985**, *50*, 411–413. (e) Eaton, S. S.; Eaton, G. R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 3177–3184. (f) Fillers, J. P.; Ravichandran, K. G.; Abdalmuhdi, I.; Tulinsky, A.; Chang, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 417–424.
(3) Heiler, D.; McLendon, G.; Rogalskyj, P. *J. Am. Chem. Soc.* **1987**, *109*, 604–606.
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(7) Porphyrin **1a** was prepared from 1,19-dideoxy-biladiene-ac and isophthalaldehyde: (a) Harris, D.; Johnson, A. W.; Gaete-Holmes, R. *Bioorg. Chem.* **1980**, *9*, 63–70. (b) Maruyama, K.; Nagata, T.; Ono, N.; Osuka, A. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3167–3170.
(8) Clezy, P. S.; Nichol, A. W. *Aust. J. Chem.* **1965**, *11*, 1835–1845.

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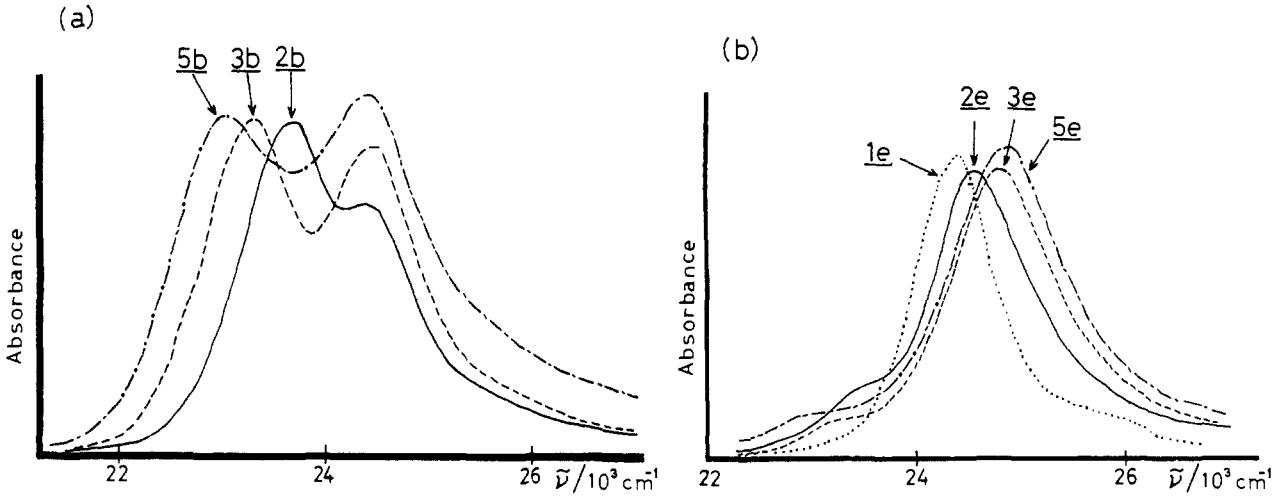
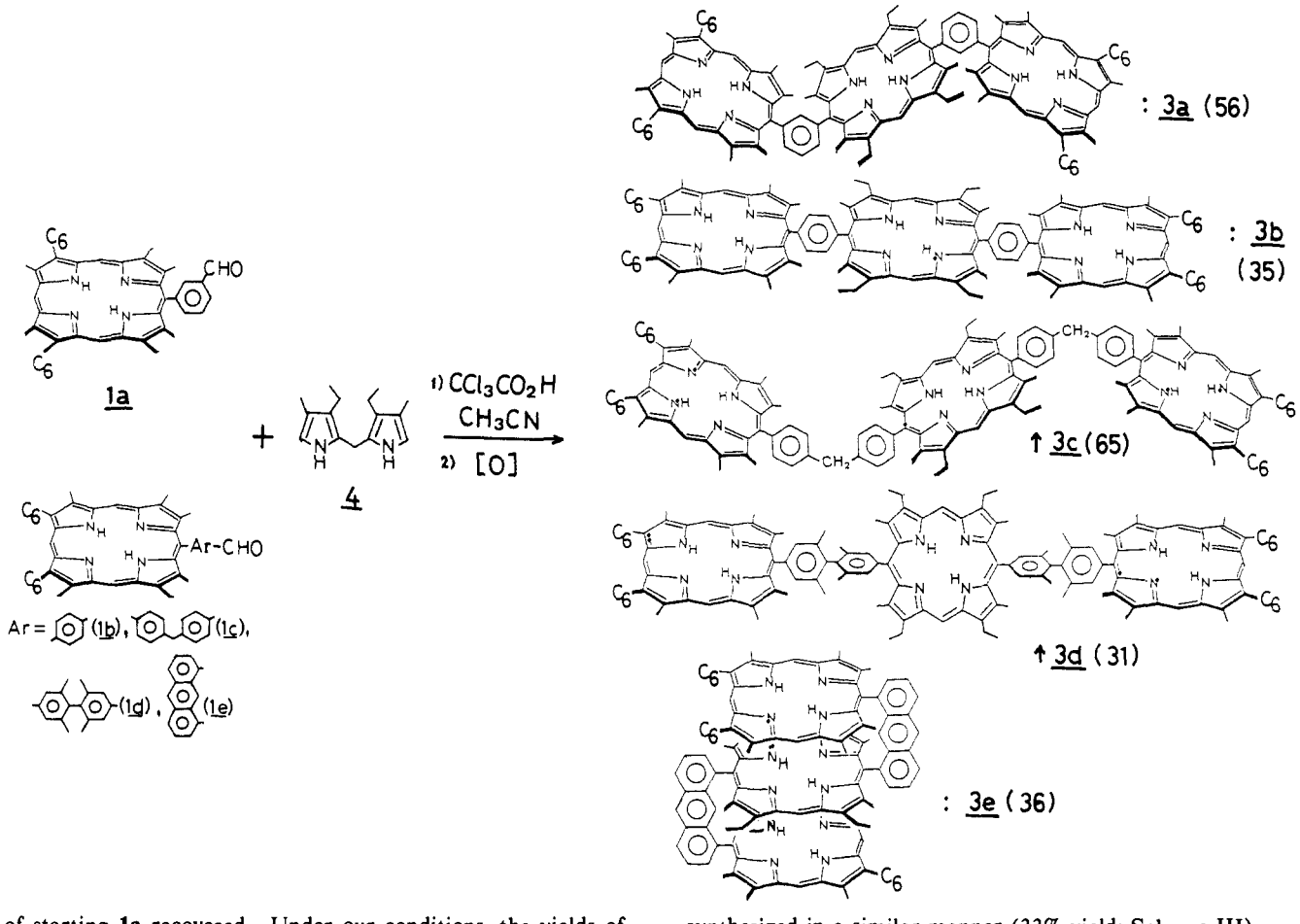


Figure 1. Soret absorption spectra of (a) P series and (b) A series (zinc complexes, in 1,2-dichlorobenzene).

Scheme I



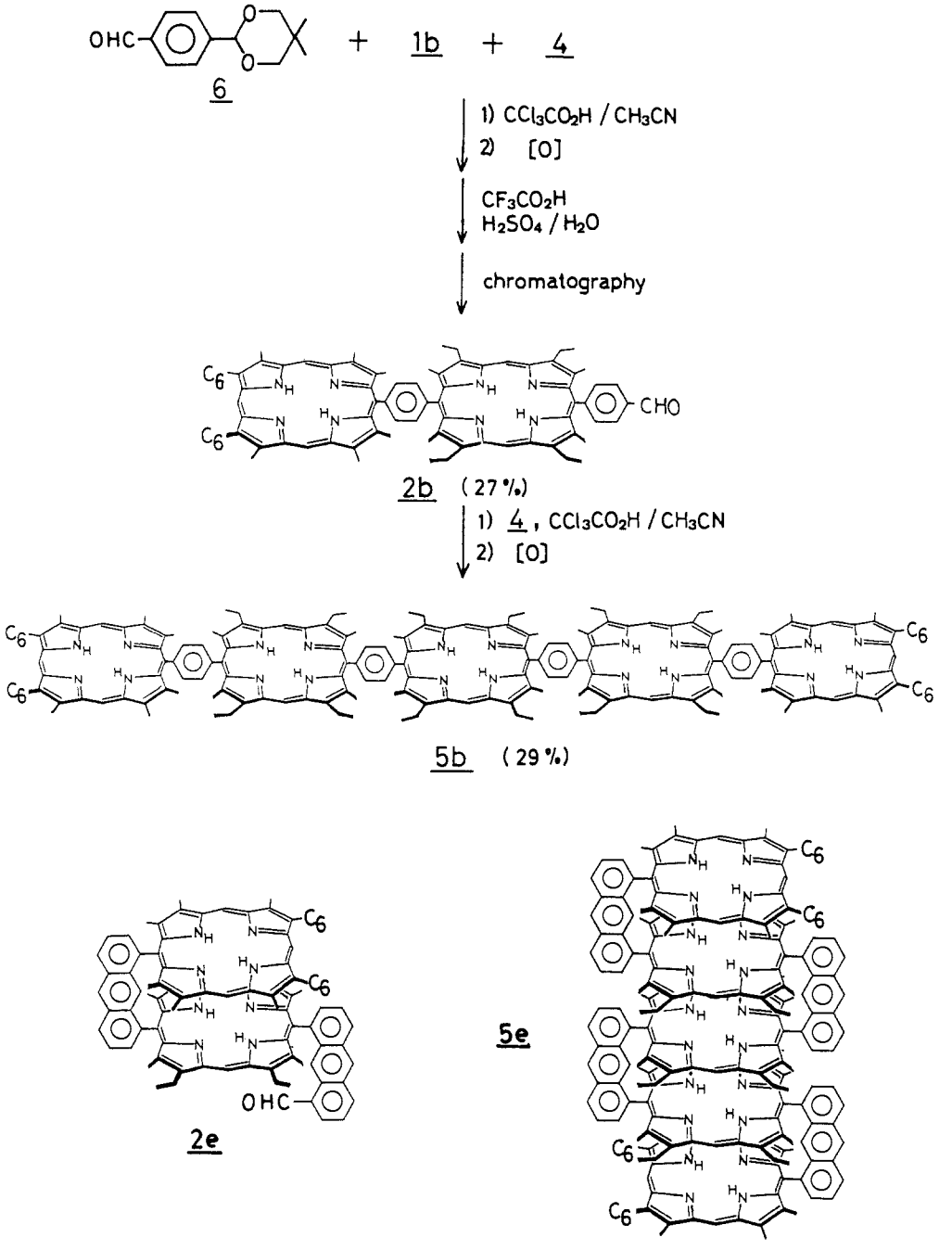
of starting **1a** recovered. Under our conditions, the yields of trimeric porphyrins were dramatically improved. For **3a** and **3c**, the yields were surprisingly high.

As further homologation of this reaction, pentameric porphyrins were prepared by the synthetic sequence shown in Scheme II. Formyl-substituted dimeric porphyrin **2b** was prepared by cross-condensation of **1b** and monoprotected terephthalaldehyde **6** with dipyrromethane (**4**), followed by acidic hydrolysis of acetal protection. Compound **6** was used in 2-fold excess toward **1b**, and the desired product **2b** was obtained in 27% yield (based on **1b**). The obtained **2b** was allowed to condense with **4** in a similar manner to give pentameric porphyrin **5b** in 29% yield. Anthracene-bridged dimeric porphyrin **2e** and pentameric porphyrin **5e** were similarly prepared in 11% and 18% yields, respectively. Bis(2,5-dimethoxyphenyl)-linked pentameric porphyrin **5f** was also synthesized in a similar manner (33% yield; Scheme III).

Optical Spectra of Oligomeric Porphyrins. The two series of di-, tri-, and pentameric porphyrins displayed interesting systematic changes in their UV–visible spectra. The zinc complexes of the *p*-phenylene-linked series (P series; **2b**, **3b**, and **5b**) showed split Soret bands, the splitting width being larger with increasing number of pigments (Figure 1a). On the other hand, the Soret bands of the anthracene-linked series (A series; **2e**, **3e**, and **5e**) were blue shifted without splitting (Figure 1b). The visible Q bands were essentially unchanged for both series.

The fluorescence emission properties of both P and A series also showed systematic changes with the number of pigments (Table I). While the two-peaked spectral profile remained essentially unchanged, the relative emission intensity was notably decreased for higher oligomers. A similar decrease of fluorescence

Scheme II



intensity was reported for stacked porphyrin oligomers linked by amide linkages.[9] The fluorescence decay profiles of Zn-**3e** and -**5e** were essentially single exponential to give lifetimes almost identical with that of the monomeric zinc porphyrin (1.50 ns for both **3e** and **5e**), whereas the decay profile of Zn-**5b** was multiexponential and dependent on the monitoring wavelength. We are currently investigating more detailed emission properties of these compounds.

Discussion

Synthesis. The synthetic method described here has several advantages over earlier methods for preparation of conformationally constrained oligomeric arrays of porphyrins. Oligomeric porphyrins bridged by rigid aromatic spacers have been prepared by several groups, and the synthetic methods utilized were the modified MacDonald synthesis,[2a-c,3,5,6] The Rosemund reaction,[3,10] and Chang's synthesis of 5,15-diarylporphyrins.[2d,11] Although the MacDonald method (acid-catalyzed condensation of 5,5′-diformyl- and 5,5′-unsubstituted dipyrromethanes) has been widely utilized for synthesis of diporphyrins,[2a-c,3,5,6] it is not suitable for the synthesis of an array of porphyrins, because of the terminal nature of the MacDonald method (i.e., it fails when the starting materials have other porphyrin rings). The Rosemund reaction was utilized for synthesis of tetrakis[(triphenylporphyrinyl)-phenyl]porphyrin,[9] which is a highly symmetric pentameric porphyrin. However, synthesis of more sophisticated oligomeric porphyrins by the Rosemund reaction may be inexpressibly tedious.

Our method is a modification of Abdalmuhdi and Chang's, who used as an acid catalyst 0.25 equiv of *p*-toluenesulfonic acid in

(9) Dubowchik, G. M.; Hamilton, A. D. *J. Chem. Soc., Chem. Commun.* **1986**, 665-666.

(10) Wennerstroem, O.; Ericsson, H.; Raston, I.; Svensson, S.; Pimlott, W. *Tetrahedron Lett.* **1989**, *30*, 1129-1132.

(11) Synthesis of 5,15-diaryloctaalkylporphyrins via acid-catalyzed condensation of aromatic aldehyde and 5,5′-unsubstituted dipyrromethane was first reported by Ogoshi et al. and later improved by Gunter and Mander and by Young and Chang: (a) Ogoshi, H.; Sugimoto, H.; Nishiguchi, T.; Watanabe, T.; Matsuda, Y.; Yoshida, Z. *Chem. Lett.* **1978**, 29-32. (b) Gunter, M. J.; Mander, L. N. *J. Org. Chem.* **1981**, *46*, 4792-4795. (c) Young, R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 898-909.

Scheme III

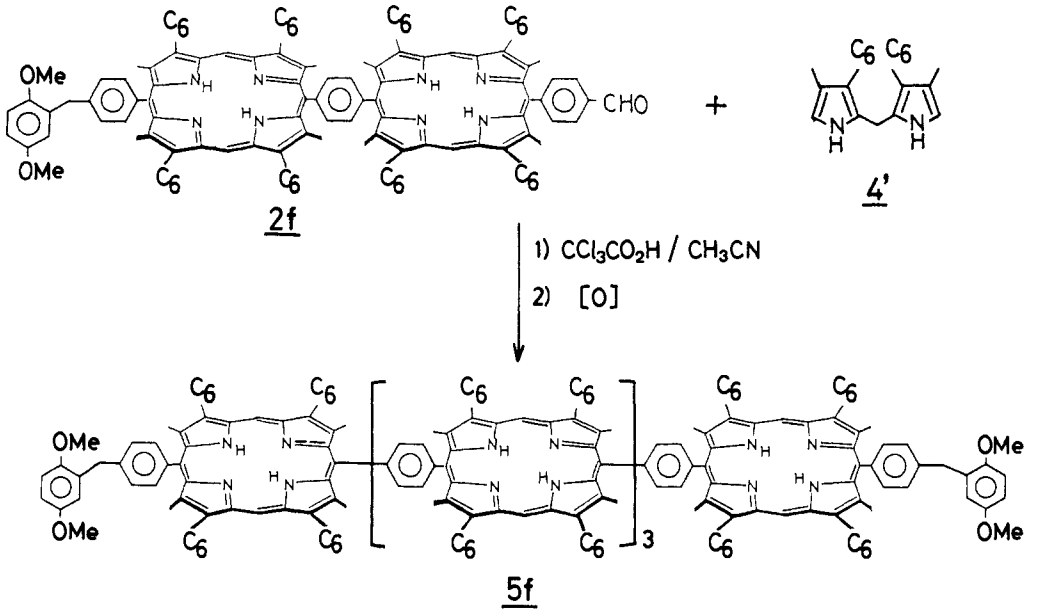


Table II. Soret Absorption Maxima and Exciton Splitting/Shift Energies of P and A Series Oligomers

compd[a]	Soret: λ_{max}/nm	ΔE/cm^{-1}
	P Series (Splitting Energy)	
2b	410.3, 423.0	930
3b	409.0, 428.8	1200
5b	410.2, 434.2	1450
	A Series (Shift Energy[b])	
2e	407.0	250
3e	403.2	430
5e	402.7	560

[a] Zinc complexes. [b] Shift width from the imaginary "reference" spectra. See text.

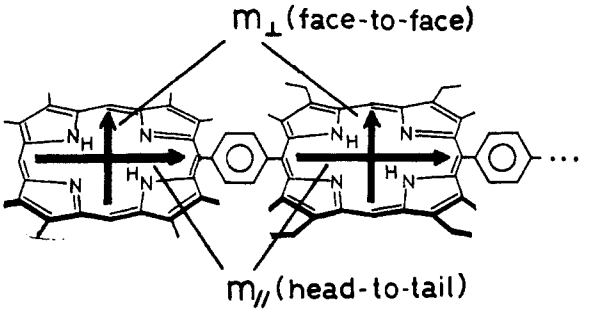


Figure 2. Two Soret transition dipole moments of the P series porphyrin oligomers.

methanol for their synthesis of triple-decker triporphyrin.[2d] However, in our hands, condensation of **1a** and **4** under their conditions afforded only trace amounts of **3a**. Clearly the amount of acid catalyst is of great importance. As a free base, porphyrin is bibasic; up to 2 equiv of acid may be consumed by protonation to porphyrin. We used 4 equiv of acid catalyst for successful synthesis of trimeric porphyrins. In this way, the porphyrin ring forming reaction can proceed smoothly even in the case that the starting aldehydes have other porphyrin rings.

The use of trichloroacetic acid as an acid catalyst has another advantage in constructing higher oligomeric arrays of porphyrins. The porphyrin-forming reaction conditions are, although acidic, mild enough for the 5,5-dimethyl-1,3-dioxacyclohex-2-yl group (a cyclic acetal protecting group of an aldehyde) to be unaffected. After the porphyrin ring is constructed, the acetal can be hydrolyzed to the corresponding aldehyde, which can be used for construction of the next porphyrin ring. Subsequent homologation of oligomeric porphyrins is thus possible.

The method described here can be generally utilized for preparation of oligomeric array of porphyrins.[12] Compound **5f** is particularly interesting since it can be converted into a bis(quinone)-linked pentameric porphyrin, which is an interesting model compound of the photosynthetic system. We are currently investigating synthesis of more sophisticated supramolecular systems as models for the photosynthetic reaction centers.

Optical Properties. The Soret absorption maxima of P series (zinc complexes of **2b**, **3b**, and **5b**) and A series (**2e**, **3e**, and **5e**, also zinc complexes) are compiled in Table II. Since there is substantial difference between the Soret absorption of (5-aryloctaalkylporphinato)zinc and that of (5,15-diaryloctaalkylporphinato)zinc (the absorption maxima are at 410 and 419 nm, respectively), we used as "reference" spectra appropriately weighted averages of the Soret absorptions of Zn-**1e** and [5,15-bis(4-formylphenyl)-3,7,13,17-tetraethyl-2,8,12,18-tetramethylporphinato]zinc. Each split Soret band of the P series was fitted to the sum of the two reference bands, from which the splitting width was estimated, whereas the shift widths of the A series were obtained by comparison of absorption maxima of the observed and reference spectra. Table II shows that both the splitting widths of the P series and the shift widths of the A series are increased for higher oligomers.

These systematic changes can be explained in terms of exciton coupling theory.[13,14] We must consider two degenerated Soret transitions $B_{\parallel}$ and $B_{\perp}$ ($m_{\parallel}$ and $m_{\perp}$ being the corresponding transition dipoles).[15,16] In the case of the P series (Figure 2), $B_{\parallel}$ will be red shifted and $B_{\perp}$ blue shifted, due to the head-to-tail and face-to-face orientations of $m_{\parallel}$ and $m_{\perp}$, respectively, resulting in the split Soret band. On the other hand, both $m_{\parallel}$ and $m_{\perp}$ of the A series are in face-to-face orientation, leading to the blue-shifted (not split) Soret band. According to the theory, the exciton

(12) This method was also utilized successfully for synthesis of monomeric 5,15-diaryloctaalkylporphyrins: Osuka, A.; Nagata, T.; Kobayashi, F.; Maruyama, K., submitted for publication.

(13) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371–392.

(14) For an application of exciton theory to porphyrin aggregates see ref 6b and: (a) Sharp, J. H.; Lardon, M. *J. Phys. Chem.* **1968**, *72*, 3230–3235. (b) Schick, G. A.; Schreiman, I. C.; Wagner, R. W.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 1344–1350. (c) Maltzan, B. v. *Z. Naturforsch. A: Phys., Phys. Chem., Kosmophys.* **1985**, *40*, 389–420.

(15) Gouterman, M. *The Porphyrins*; Academic Press: New York, 1978; Vol. III, pp 1–165.

(16) In our cases of 5,15-diarylporphyrins, it may be appropriate to place the transition dipoles along the 5,15- and 10,20-axis because the porphyrin has the roughly D_{2h} symmetry.

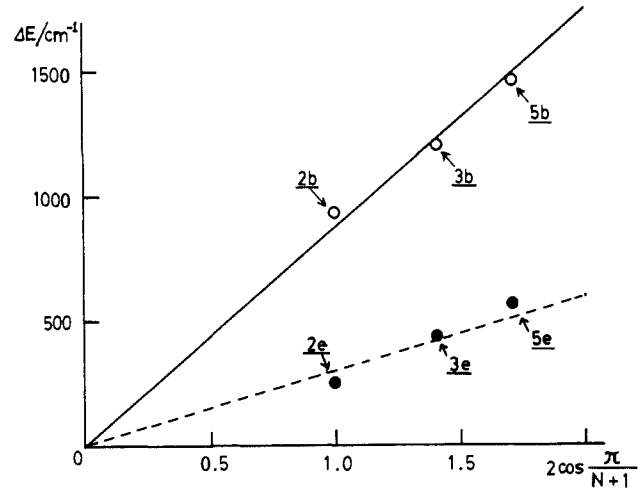


Figure 3. Plot of exciton splitting (P series) and shift (A series) energy ΔE versus 2 cos $(\pi/(N + 1))$.

splitting energy ΔE for the P series is expected to be $2(|J_\parallel| + |J_\perp|)$ cos $(\pi/(N + 1))$,[17] where J's are the exciton coupling integrals and N is the number of pigments. A plot of the observed splitting energy versus 2 cos $(\pi/(N + 1))$ for the P series gave a roughly straight line (Figure 3, solid line). In the case of the A series, the exciton *shift* energy ΔE will be $(|J_\parallel| + |J_\perp|)$ cos $(\pi/(N + 1))$, assuming similarity and symmetry of spectral line shapes of $B_\parallel$ and $B_\perp$. A plot of observed shift energy versus 2 cos $(\pi/(N + 1))$ also gave a roughly straight line (Figure 3, broken line). We must be prudent in giving interpretations to the plot of the A series, since the "observed" shift widths depend upon the rather arbitrary definition of the reference spectra. Nevertheless, the linearity of the two plots in Figure 3 strongly suggests that the absorption spectral change is actually effected by the increasing number of pigments in the aggregate systems and that the component pigments are aligned in regular arrangement, as we may expect from the paper-drawn structures on Schemes I–III.

Concluding Remarks

Conformationally constrained trimeric and pentameric porphyrin arrays were prepared according to the synthetic sequences outlined in Schemes I–III. The method described here greatly improved the yield and opens the door to highly structured oligomeric porphyrins as models for the photosynthetic reaction centers.

The synthesized trimeric and pentameric porphyrins showed characteristic shifts or splittings in their UV absorption spectra, which were explained in terms of exciton coupling. The exciton splitting (or shift) energies estimated from the observed spectra had a good correlation with the number of component pigments. This strongly suggests that the component pigments in these compounds are regularly arranged even in solutions.

We are currently investigating synthesis and optical properties of more sophisticated oligomeric porphyrins. We hope that these molecules can shed light on new aspects of photochemistry and photophysics of porphyrin aggregates.

Experimental Section

Unless otherwise stated, all commercially available solvents and reagents were used without further purification. Acetonitrile was stored over molecular sieves for several days before use. UV–Visible spectra were obtained with a Shimadzu UV-3000 spectrometer. Steady-state fluorescence spectra were taken on a Shimadzu RF-502A spectrofluorimeter. ^{1}H NMR spectra were recorded on a JEOL GX-400 spectrometer, chemical shifts being reported in the δ scale relative to Me_4Si. Mass spectra of porphyrins were recorded on JEOL DX-300 and HX-110 spectrometers, with the positive FAB (fast-atom bombardment) method (accelating voltages 1.5 and 10 kV, Xe atom as the primary ion source). The FAB matrix was 3-nitrobenzyl alcohol/chloroform unless otherwise stated.

Synthesis of Trimeric Porphyrins. 5,15-Bis[3-(12,18-dihexyl-2,3,7,8,13,17-hexamethylporphin-5-yl)phenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphine (3a). The 5-(3-formylphenyl)porphyrin **1a**[7b] (30 mg, 0.045 mmol) was dissolved in acetonitrile (5 mL) containing trichloroacetic acid (30 mg, 0.184 mmol; anhydrous). Dipyrromethane (**4**;[8] 10 mg, 0.045 mmol) was added, and the mixture was stirred overnight at room temperature (dark, under nitrogen). *p*-Chloranil (18 mg) dissolved in THF was added, and stirring was continued for 2.5 h. The solvent was evaporated, and the residual solids were dissolved in methylene chloride and washed with aqueous sodium bicarbonate several times. In the course of this process, red-violet crystals precipitated from the CH_2Cl_2 layer. The organic layer was separated, a small amount of methanol was added, and the solid material was collected by filtration: yield 22 mg (0.013 mmol, 56%); ^{1}H NMR ($CDCl_3$) δ 10.03 (2 H, s, meso), 10.01 (4 H, s, meso), 9.82 (2 H, s, meso), 3.96–3.90 (16 H, t + q, Et and hex-1), 3.50 (12 H, s, Me), 3.44 (12 H, s, Me), 3.01–2.99 (24 H, 2 s, 2 Me), 2.19 (8 H, quint, hex-2), 1.66 (20 H, m, hex-3 and Et), 1.42 (8 H, quint, hex-4), 1.28 (m, hex-5), 0.83 (12 H, t, hex-6), –1.82 (2 H, br, NH), –2.97 (2 H, br, NH), –3.14 (2 H, br, NH); MS (FAB) *m/e* 1753 (M + H$^+$), 877 (M + 2 H$^+$); UV–vis (CH_2Cl_2) λ_{max} 405, 422 (sh), 508, 540, 576, 637 nm. Compound **3a** was probably a mixture of the two atropisomers (U-shaped syn and Z-shaped anti), although we have been unsuccessful to separate them.

Other trimeric porphyrins were prepared in a similar manner.[20] Only compound data are listed below.

3b: ^{1}H NMR (HCl salt, $CDCl_3$) δ 10.41 (4 H, s, meso), 10.38 (2 H, s, meso), 10.21 (2 H, s, meso), 8.96 (8 H, s, phenyl), 3.93 (8 H, t, hex-1), 3.81 (8 H, br, Et), 3.58 (12 H, s, Me), 3.80 (12 H, s, Me), 2.71–2.70 (24 H, 2 s, 2 Me), 2.43 (8 H, quint, hex-2), 1.92 (8 H, quint, hex-3), 1.85 (12 H, t, Et), 1.64 (m, hex-4), 1.5 (m, hex-5), 1.03 (12 H, t, hex-6), –0.37 (4 H, s, NH), –0.42 (4 H, s, NH), –1.73 (4 H, s, NH); MS (FAB) *m/e* 1753 (M + H$^+$), 877 (M + 2 H$^+$); UV–vis (ODCB = 1,2-dichlorobenzene) λ_{max} 421, 507, 537, 575, 626 nm.

3c: ^{1}H NMR ($CDCl_3/CF_3CO_2D$, v/v, 100/1) δ 10.42 (4 H, s, meso), 10.28 (2 H, s, meso), 10.25 (2 H, s, meso), 8.38 (8 H, 2 d, Ph), 8.03 (8 H, 2 d, Ph), 4.82 (4 H, s, PhCH_2Ph), 4.00 (8 H, t, hex-1), 3.78 (8 H, m, Et), 3.58 (12 H, s, Me), 3.30 (12 H, s, Me), 2.38 (12 H, s, Me), 2.36 (12 H, s, Me), 2.14 (8 H, quint, hex-2), 1.67 (8 H, quint, hex-3), 1.47 (8 H, quint, hex-4), 1.41 (12 H, t, Et), 1.35 (8 H, m, hex-5), 0.90 (12 H, t, hex-6), –2.24 (2 H, s, NH), –2.30 (2 H, s, NH), –3.52 (2 H, s, NH); MS (FAB) *m/e* 1932 (M + H$^+$), 966 (M + 2 H$^+$); UV–vis (ODCB) λ_{max} 410, 504, 535, 573, 635 nm.

3d: ^{1}H NMR (HCl salt, $CDCl_3$) δ 10.39 (8 H, s, 2 meso), 10.20 (2 H, s, meso), 8.29 (8 H, s, phenyl), 3.92 (8 H, t, hex-1), 3.84 (8 H, q, Et), 3.58 (12 H, s, Me), 3.42 (12 H, s, Me), 2.59 (24 H, s, 2 Me), 2.57 (12 H, s, Me), 2.43 (8 H, quint(?), hex-2), 1.92 (12 H, t, Et), 1.7–1.4 (m, hex-3,4,5), 1.03 (12 H, t, hex-6), –0.76 (4 H, s, NH), –0.90 (4 H, s, NH), –1.86 (4 H, s, NH); MS (FAB) *m/e* 2018 (M + H$^+$), 1009 (M + 2 H$^+$); UV–vis (ODCB) λ_{max} 411, 504, 535, 572, 625 nm.

3e: ^{1}H NMR ($CDCl_3$) δ 9.29 (2 H, s, meso), 9.20 (4 H, s, meso), 9.01 (2 H, s, meso), 3.66 (8 H, m, hex-1), 3.26 (8 H, m, Et), 3.14 (12 H, s, Me), 2.94 (12 H, s, Me), 1.92 (8 H, quint, hex-2), 1.81 (12 H, s, Me), 1.72 (12 H, s, Me), 1.46 (8 H, quint, hex-3), 1.31 (8 H, quint, hex-4), 1.23 (8 H, sext, hex-5), 1.01 (12 H, t, Et), 0.82 (12 H, t, hex-6), –4.51 and –4.64 (6 H, br, NH); anthryl 8.71 (2 H, br), 8.48 (4 H, d), 8.01 (2 H, br), 7.63 (2 H, dd), 7.60 (2 H, br), 7.28 (d?), 6.96 (2 H, br); MS (FAB) *m/e* 1953 (M + H$^+$); UV–vis (ODCB) λ_{max} 401, 506, 538, 577, 629, 655 nm.

Synthesis of Pentameric Porphyrins. 5-(4-Formylphenyl)-15-[4-(13,17-dihexyl-2,3,7,8,12,18-hexamethyl-5-porphinyl)phenyl]-2,8,12,18-

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(18) The exciton coupling integral J's depend on the distance and relative orientation between chromophores. Simple dipole approximation[13] with interchromophore distances of 11.4 Å (P series) and 4.8 Å (A series, both estimated from CPK molecular models) gave $J_P/J_A = 0.11$, whereas experimental values from Figure 3 gave 1.43 ($J = |J_\parallel| + |J_\perp|$). This large deviation suggests that dipole approximation may be no longer valid in these systems with large transition dipoles and small interchromophore distances. Maltzan's extended dipole treatment with $l = 4.05$ Å[14c] gave 0.18 of this ratio, whereas direct calculation of the exciton interaction integral with the PPP molecular orbitals of porphyrins[19] and the CNDO approximations gave 0.32; there are still large deviations from the experimental value. One possible explanation for these deviations is that, in solutions, the porphyrin rings in the A series oligomers may move away from each other in order to release the steric hindrance, resulting in larger interchromophore distances than our estimation. Another is the "reference" problem described in text.

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(20) Compounds **1b–1e** were prepared in a manner similar to that for **1a**[7]. The compound data of these compounds can be found in the supplementary material.

tetraethyl-3,7,13,17-tetramethylporphine (2b). 5-(4-Formylphenyl)-porphyrin **1b** (700 mg, 1.05 mmol), 4-(5,5-dimethyl-1,3-dioxacyclohex-2-yl)benzaldehyde (**6**;[21] 462 mg, 2.10 mmol), **4** (727 mg, 3.15 mmol), and trichloroacetic acid (1.0 g, 6.12 mmol) were dissolved in acetonitrile, and the resulting solution was stirred for 5.5 h (room temperature, under N_2, dark). *p*-Chloranil (1.2 g, 4.73 mmol) in 50 mL of THF was added, and stirring was continued overnight. The reaction mixture was evaporated, dissolved in chloroform, washed with saturated aqueous $NaHCO_3$ and water, dried over $NaSO_4$, and evaporated. The residue was dissolved in trifluoroacetic acid (40 mL) and 5% H_2SO_4, heated under reflux for 2 h, poured into water, extracted repeatedly by chloroform, dried, and evaporated. The residue was separated by column chromatography (silica gel, chloroform). The second porphyrinic fraction was the desired product **2b** (27% based on **1b**). Data: ^{1}H NMR ($CDCl_3$) δ 10.35, 10.27, 9.94 (3 H, 2 H, 1 H; 3 s; meso and CHO), 4.18 (4 H, q, Et), 4.08–4.02 (8 H, m, Et + hex-1), 3.69 (12 H, s, 2 Me), 3.14 (6 H, s, Me), 3.11 (6 H, s, Me), 2.46 (6 H, s, Me), 2.32 (4 H, quint, hex-2), 1.90 (6 H, t, Et), 1.83 (6 H, t, Et), 1.78 (4 H, m, hex-3), 1.6 (m, hex-4), 1.40 (sext, hex-5), 0.93 (6 H, t, hex-6), −1.89 (1 H, s, NH), −2.02 (1 H, s, NH), −2.72 (1 H, s, NH), −2.97 (1 H, s, NH); phenyl 8.43 (4 H, s), 8.22 (4 H, AB quartet); MS (FAB) *m/e* 1220 (M + H$^+$); UV–vis (ODCB) λ_{max} 417, 507, 538, 575, 626, 657 nm.

5,15-Bis[4-[15-[4-(13,17-dihexyl-2,3,7,8,12,18-hexamethyl-5-porphinyl)phenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5-porphinyl]-phenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphine (5b, Para Pentamer). Compound **2b** (68 mg, 0.056 mmol), dipyrromethane (**4**; 13 mg, 0.056 mmol), and trichloroacetic acid (70 mg, 0.43 mmol) were dissolved in acetonitrile (10 mL), and the solution was stirred overnight (room temperature, N_2, dark). *p*-Chloranil (24 mg) in THF was added, and after 1.5 h the reaction mixture was evaporated, dissolved in chloroform, and washed with aqueous $NaHCO_3$. At this stage insoluble porphyrinic precipitates appeared. Chloroform was evaporated, and the solids were collected by filtration and washed with methanol and chloroform. Recrystallization from CF_3CO_2H–$CHCl_3$/Et_3N–MeOH gave violet crystals, yield 12 mg (0.004 mmol, 15%). Concentration of the filtrates gave a second crop, total yield being 29%. Data: ^{1}H NMR (HCl salt, $CDCl_3$) δ 10.42–10.20 (12 H, 4 s, meso), 8.99–8.96 (16 H, s and AB quartet, phenyl), 3.93 and 3.84 (8 H and 24 H, br, Et and hex-1), 3.58 (12 H, s, Me), 3.42 (12 H, s, Me), 2.75–2.72 (48 H, 4 s, Me), 2.43 (8 H, quint, hex-2), 1.90–1.86 (48 H, m, Et and hex-3), 1.64 (m, hex-4), 1.5 (m, hex-5), 1.04 (12 H, t, hex-6), −0.34 (12 H, s, NH), −0.41 (4 H, s, NH), −1.72 (4 H, s, NH); MS (FAB) *m/e* 2859 (M + H$^+$), 1429 (M + 2 H$^+$); UV–vis (ODCB) λ_{max} 410, 508, 535, 574, 628 nm.

Compounds **2b** and **2e** were prepared in a similar manner. The compound data are listed below.

2e: ^{1}H NMR ($CDCl_3$) meso, CHO, and anthryl-9,10 δ 9.34 (2 H, s), 9.33 (1 H, s), 9.25 (2 H, s), 9.17 (1 H, s), 9.12 (1 H, s), 8.71 (1 H, s), 8.53 (1 H, s), 8.15 (1 H, s); anthryl ^{1}H NMR ($CDCl_3$) 8.592 (1 H, d), 8.584 (1 H, d), 7.769 (1 H, dd), 7.765 (1 H, dd), 7.525 (1 H, d), 7.515 (1 H, d), 8.422 (1 H, d), 7.88 (1 H, ABX), 8.211 (1 H, d), 7.360 (1 H, dd), 7.590 (1 H, d); alkyl ^{1}H NMR ($CDCl_3$) 3.74 (4 H, ABX_2, hex-1), 3.58 (4 H, q, Et), 3.58–3.49 (4 H, ABX_3, Et), 3.21 (6 H, s, Me), 3.09 (6 H, s, Me), 1.99 (10 H, s + m, Me and hex-2), 1.84 (6 H, s, Me), 1.5 (m, hex-3), 1.39 (4 H, m, hex-4), 1.36 and 1.33 (12 H, 2 t, Et), 1.27 (4 H, m, hex-5), 0.86 (6 H, t, hex-6), −3.35 (1 H, s, NH), −3.73 (1 H, s, NH), −4.51 (1 H, s, NH), −4.58 (1 H, s, NH); MS (FAB) *m/e* 1420 (M + H$^+$); UV–vis (ODCB) λ_{max} 404, 507, 538, 576, 629, 655 nm.

5e: ^{1}H NMR ($CDCl_3$) meso δ 9.24 (2 H, s), 9.20 (4 H, s), 8.99 (2 H, s), 8.61 (4 H, s); anthryl ^{1}H NMR ($CDCl_3$) 8.90, 8.52, 8.00, 7.74 (each 2 H, s), 8.46, 7.61, 7.26 (2 H, d; 2 H, dd; d?), 8.42, 7.52, 6.72 (2 H, d; 2 H, dd; 2 H, d), 8.36, 7.46, 6.66 (2 H, d; 2 H, m; 2 H, d), 8.35, 7.46, 6.75 (2 H, d; 2 H, m; 2 H, d); alkyl ^{1}H NMR ($CDCl_3$) 3.59 (8 H, m, hex-1), 3.2–3.0 (24 H, m, Et), 3.09 (12 H, s, Me), 2.93 (12 H, s, Me), 1.86 (8 H, quint, hex-2), 1.79 (12 H, s, Me), 1.63 (12 H, s, Me), 1.53 (12 H, s, Me), 1.51 (12 H, s, Me), 1.41 (8 H, quint, hex-3), 1.26 (8 H, quint, hex-4), 1.19 (8 H, sext?, hex-5), 0.90, 0.84, 0.77 (48 H, 3 t, Et and hex-6), −4.53 (br, NH); MS (FAB *m/e* 3260 (M + H$^+$); UV–vis (ODCB) λ_{max} 401, 509, 540, 578, 630, 656 nm.

Bis(dimethoxyphenyl)-Linked Pentameric Porphyrin 5f. Compound **5f** was prepared in a similar procedure as **5b** from the formyl-substituted dimer **2f**[22] (100 mg, 0.053 mmol), bis(3-hexyl-4-methylpyrrol-2-yl)-methane (**4**;[22] 19 mg, 0.053 mmol), and trichloroacetic acid (30 mg) in acetonitrile (12 mL). In this case, 20 mg of the starting **2f** was recovered. Yield of **5f**: 32 mg (34% based on consumed amount of **2f**). Data: ^{1}H NMR (HCl salt, $CDCl_3$) δ 10.39, 10.38, 10.31 (10 H, 3 s, meso), 8.99, 8.95 (16 H, 2 s, Ph), 8.19 (4 H, d, Ph), 7.74 (4 H, d, Ph), 6.96 (4 H, m, Ph), 6.91 (2 H, dd, Ph), 4.36 (2 H, s, benzylic CH_2), 3.93, 3.87 (12 H, 2 s, OMe), 3.6–3.8 (40 H, m, hex-1), 2.72, 2.69, 2.68 (48 H, s, Me), 2.31 (s, Me) + 2.27 (m, hex-2) = 52 H, 1.9–1.4 (m, hex-3, 4, 5), 1.9 (m, hex-6), −0.31 (12 H, s, NH), −0.53 (4 H, s, NH), −0.77 (4 H, s, NH); MS (FAB) *m/e* 4263 (M + H$^+$), 2131 (M + 2 H$^+$); UV–vis (CH_2Cl_2) λ_{max} 410 (sh), 435, 510, 541, 575, 627 nm.

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Supplementary Material Available: Spectroscopic data for compounds **1b**, **1c**, **1d**, and **1e** (2 pages). Ordering information is given on any current masthead page.

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(22) Synthetic details of these compounds will be described elsewhere.