

Synthesis of Novel Porphyrin Dimers with Twisted Orientations: Models for Biological Excitation Energy and Electron Transfer Reactions

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Three novel dimeric porphyrins bridged by spirobi-indan spacers have been synthesized; for these monozinc mixed porphyrins (Zn-*P*-H₂-*P*), the rates of intramolecular singlet excitation energy transfer from Zn-*P* to H₂-*P* were determined by picosecond time-resolved fluorescence spectroscopy.

Green plants and bacterial photosynthetic organisms employ closely associated tetrapyrrole pigments as carriers of photons and electrons. The recent *X*-ray analysis of the photosynthetic reaction centre from two photosynthetic bacteria has shown that photoactive pigments are held in twisted and carefully controlled arrangements that optimize the efficiency of photon or electron transfers.¹ A useful approach to a study of the primary events of natural photosynthesis is to synthesize model compounds with known distances and orientations.²

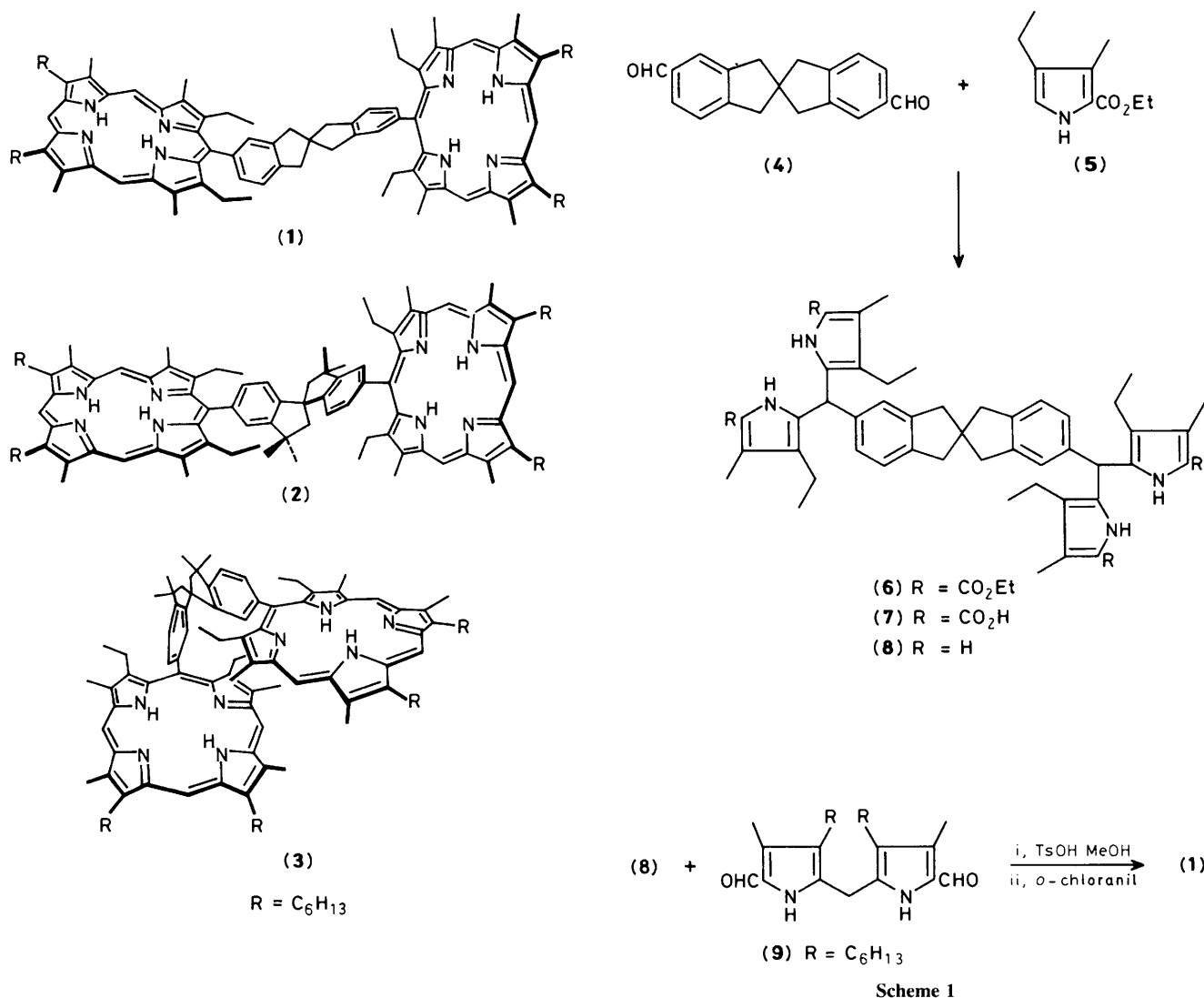
We report here the synthesis of three covalently linked

porphyrin dimers (**1**)–(**3**) as models for biological excitation energy and electron transfer reactions. The linkages of these models consist of rigid spirobi-indan structures which ensure that the two porphyrin rings are fixed in twisted orientations. Space-filling molecular models show unique, twisted stereochemical features of these model diporphyrins, which are well characterized by the geometrical parameters listed in Table 1. Interestingly, the centre-to-centre separations of the models (**1**) and (**2**) are similar to those of hemes in the cyt *c*/cyt *c* peroxidase complex and in the cyt *c*/cyt *b*₅ complex, respec-

Table 1. Geometry and fluorescence characteristics of the model compounds (1)–(3).

Diporphyrin model	Distance ^a <i>r</i> /Å	Angle ^b (°)		Fluorescence ^c decay at 580 nm		Fluorescence ^c increase at 690 nm	
		α	θ	<i>d</i> ^d /ps	$10^{-9} k_E/s^{-1}$	<i>r</i> ^e /ps	$10^{-9} k_E/s^{-1}$
(1)	23	70	55	197	4.4	215	4.0
(2)	18	110	70	148	6.1	150	6.0
(3)	10	15	70	21	47	25	39

^a Centre-to-centre distances. ^b α = angle between the porphyrin normals; θ = angle between the ring normal and the centre-to-centre vector. ^c Excitation at 570 nm, where *ca.* 73% of the incident light was absorbed by Zn-*P* and *ca.* 27% by H₂-*P*. Measured in air-saturated CH₂Cl₂ at 295 K by single-photon counting technique. ^d Fluorescence decay times of Zn-*P*. ^e Fluorescence increase times of H₂-*P*.

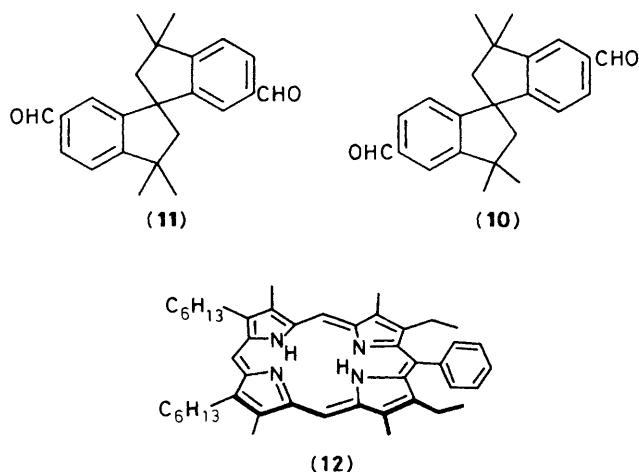


tively,³ while the model (3) well duplicates the twisted and partially overlapping structure of the pair in the bacterial photosynthetic reaction centre.^{1,2c}

The synthesis of the 2,2'-spirobi-indan-bridged dimeric porphyrin (1) is outlined in Scheme 1. Condensation of ethyl 4-ethyl-3-methylpyrrole-2-carboxylate (5)⁴ with the dialdehyde (4)⁵ in ethanol-HCl gave the bis(dipyrrolyl)methane (6) in 82% yield. Hydrolysis and decarboxylation by Chang's

procedure^{2a} gave the α -unsubstituted bis(dipyrrolyl)methane (8) in 85% yield. The final cyclization was carried out by treating (8) and 2 equiv. of (9) with toluene-*p*-sulphonic acid for 48 h, giving (1) in 5% yield.† Similarly, compounds (2) and

† All new compounds described in this paper gave satisfactory spectral data consistent with the assigned structure.



(3) were prepared from the corresponding aryl dialdehydes (10) and (11), respectively.‡

The absorption and fluorescence spectra of (1) and (2), and their bis-zinc complexes (1 Zn) and (2 Zn) are almost identical with those of the corresponding monomers (12) and (12 Zn), respectively. In contrast, the Soret band of (3 Zn₂) is split, owing to exciton coupling, indicating a close association of the two porphyrin rings.^{2c} As was reported for zinc porphyrins (Zn-P) covalently bound to metal-free porphyrins (H₂-P) with more flexible linkages,⁷ intramolecular singlet excitation energy transfer from Zn-P to H₂-P was observed in all the models (1)–(3).§ The rates of energy transfer were determined by measuring fluorescence decays (λ_{em} 580 nm) of the Zn-P as well as the fluorescence increases (λ_{em} 690 nm) of the H₂-P, using picosecond time-resolved fluorescence spectroscopy (Table 1).⁸ Notably, fluorescence decays of the Zn-P in

‡ The dialdehydes (10) and (11) were prepared from the corresponding dimethylspirobi-indans.⁶ Yields in the final cyclisation step were 7% for (2) and 6% for (3), respectively.

§ The mono-Zn complexes of (1)–(3) were prepared by reaction with zinc acetate in CH₂Cl₂ and purified by flash column chromatography (silica gel; CH₂Cl₂/Et₂O).

(1)–(3) exhibited singly decaying components; 197 ps for (1), 148 ps for (2), and 21 ps for (3), indicating that the singlet excited state of the Zn-P is quenched by the H₂-P through a single conformation. Taking the radiative lifetime of (12 Zn) (1.5 ns, τ_0), we can calculate the rate of energy transfer, k_E , from the equation $k_E = 1/\tau_d - 1/\tau_0$. These rates were in good agreement with the values calculated from the fluorescence increase of the H₂-P as shown in Table 1. Clearly, these geometry-defined dimeric porphyrins will very useful for the quantitative evaluation of the geometry dependence of energy and electron transfer processes and will give a clue to the meanings of the twisted orientations found in biological systems.

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