

## Towards a Synthetic Model of the Structure of the Photosynthetic Reaction Centre

Gene M. Dubowchik and Andrew D. Hamilton\*

Department of Chemistry, Princeton University, Princeton, N.J. 08544, U.S.A.

The synthesis of a new analogue of the structure of the photosynthetic reaction centre containing a dimeric tetrapyrrole covalently linked to two adjacent tetrapyrroles is reported.

The recent X-ray analysis of a bacterial photosynthetic reaction centre from *Rhodospseudomonas viridis*<sup>1</sup> dramatically shows the critical arrangement of six interacting tetrapyrroles at the active site (Figure 1). The hexameric unit has approximately two-fold rotational symmetry and at its centre is a 'special pair' (P) of overlapping bacteriochlorophylls (Bchls) which functions as the primary electron donor. Positioned on either side of the 'special pair,' at a Mg–Mg distance of 13 Å and an interplane angle of 70°, are two monomeric Bchls. These are in turn separated by 11 Å from two bacteriopheophytins (Bphs) (with a 64° angle between the planes).<sup>1</sup> This arrangement suggests two possible electron transfer pathways from P through Bchl to Bph and then on to nearby quinone species (Q). While the role of the bacteriopheophytin in a photoinduced P<sup>+</sup>Bph<sup>-</sup> radical pair is well established,<sup>2</sup> the participation of the monomeric bacteriochlorophyll in an intermediate P<sup>+</sup>Bchl<sup>-</sup> is less clear.<sup>3</sup> In fact recent picosecond kinetics measurements<sup>4</sup> find no evidence for the formation of P<sup>+</sup>Bchl<sup>-</sup> before the formation of P<sup>+</sup>Bph<sup>-</sup>. The role of the Bchl, whether as a direct charge transfer participant or an indirect neighbouring influence (*e.g.* in facilitating electron tunnelling or delocalising charge density<sup>4</sup>), remains to be determined as does the importance of inter-chromophore distance and orientation in the charge separation process.

The preparation and study of synthetic analogues of the photosynthetic mechanism offer an important approach to these problems and in recent years a number of strategies have been reported.<sup>5</sup> As part of a program aimed at the construction of controlled aggregates of multiple tetrapyrroles<sup>6</sup> we are

interested in synthesising accurate models of photosynthetic reaction centres based, as closely as possible, on the arrangement of pigments in Figure 1. Our first synthetic target concerns the primary electron donor–'primary acceptor' complex of P–Bchl<sub>2</sub>. Key features to be incorporated into the analogue should include (i) four interacting tetrapyrrole units

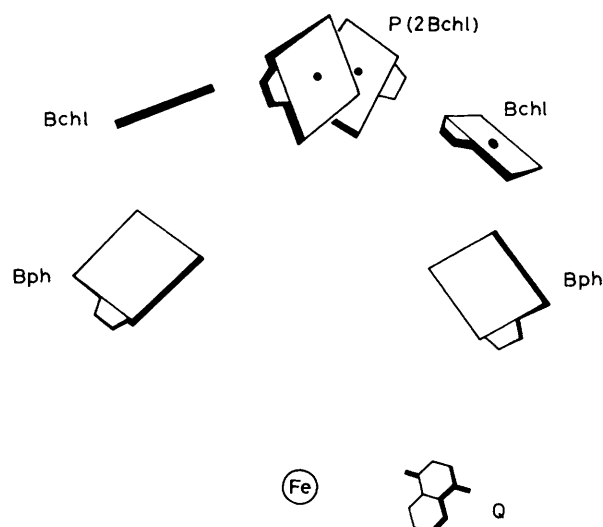
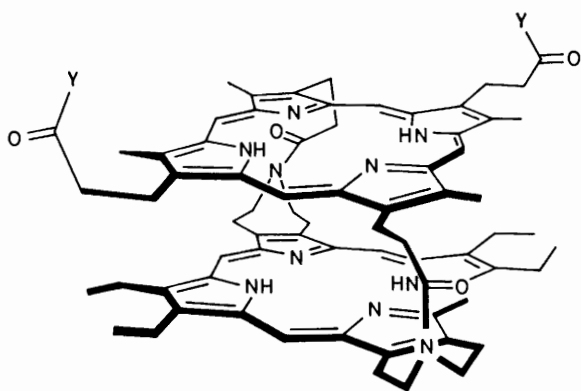
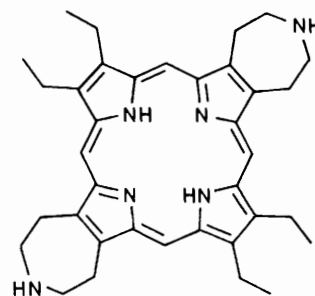


Figure 1. Schematic arrangement of chromophores in bacterial photosynthetic reaction centres from *R. viridis* (redrawn from ref. 1).

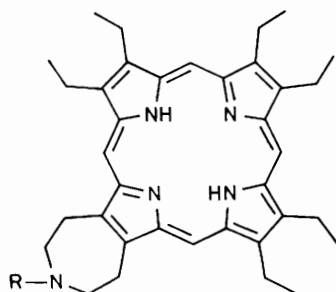


(1) Y = OMe

(6) Y = Cl

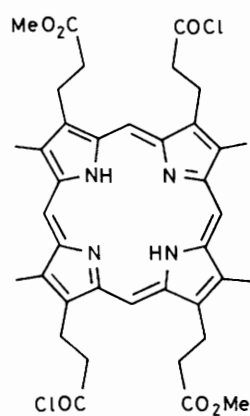


(2)

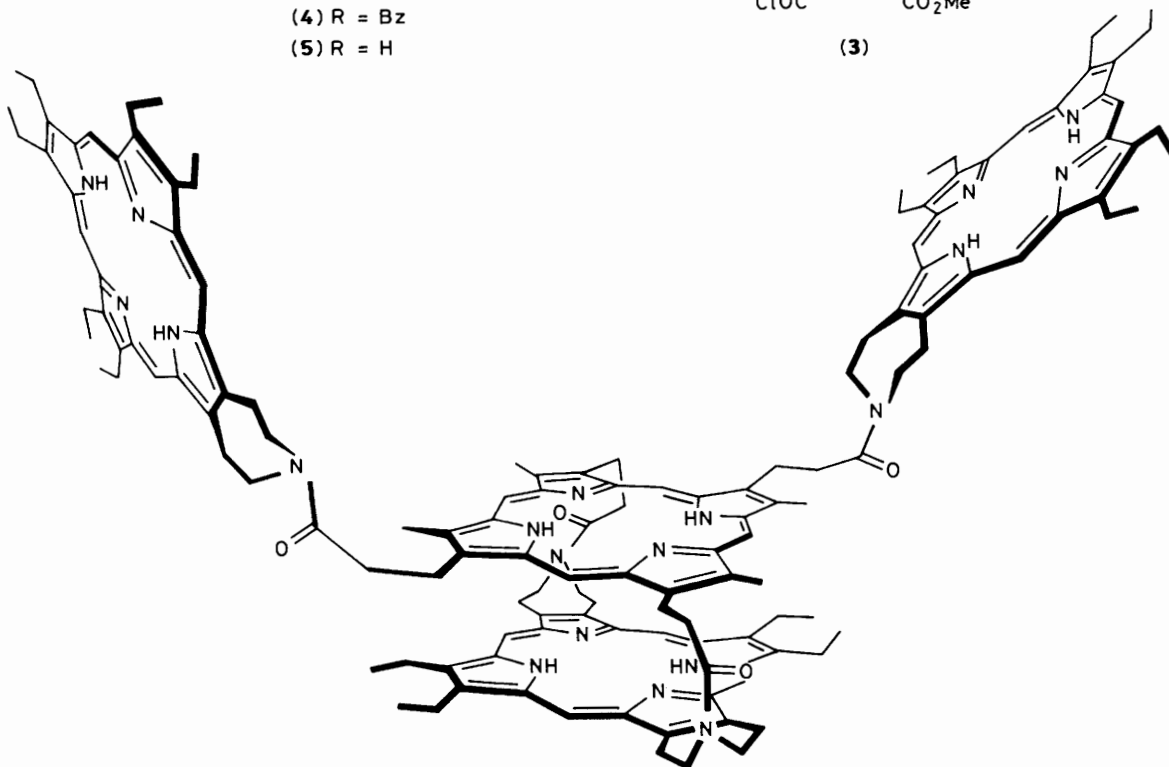


(4) R = Bz

(5) R = H



(3)



(7)

Bz = benzyl

**Table 1.** Electronic and fluorescence spectral data.

Porphyrin	$\lambda_{\max}/\text{nm}$	$Q(00)^a/\text{nm}$	$\Phi_F$
OEP <sup>b</sup>	397,497,532,566,619	622	0.09
ZnOEP	400,531,568	573	0.06
(7)	397,378(sh),502,535,569,621	625	0.012
(8)	385,402,534,570	582,596	0.002
(9)	391,501,535,573,620	624	0.0005

<sup>a</sup> In degassed methylene chloride at 25 °C. <sup>b</sup> Octaethylporphyrin.

arranged as a dimeric 'special pair' with two monomers positioned on either side, (ii) two distinct absorptions in its optical spectrum corresponding to the dimer and monomer environments,<sup>†</sup> (iii) effective interaction between dimer and monomer which may lead to electron transfer. In this paper we report the first synthesis of a covalently linked analogue of the P-Bchl<sub>2</sub> complex which possesses the above features and thus represents a preliminary step towards the assembly of an artificial photosynthetic reaction centre.

The dimer component (1) was prepared by the high dilution coupling of diamine (2)<sup>6a</sup> with diester diacid chloride porphyrin (3).<sup>6b</sup> The monomeric component was derived from benzylaminoporphyrin (4)<sup>‡§</sup> ( $M^+ + H$  638.4222, C<sub>43</sub>H<sub>52</sub>N<sub>5</sub> requires 638.4201) which was formed *via* the pyrromethene route by previously reported methods.<sup>6a,8</sup> Transfer hydrogenation of (4) (formic acid, Pd-C) gave amine (5)<sup>‡</sup> which was purified as its hydrochloride salt (5a). Reaction of (5a) with diacid chloride (6) [formed from (1) by base hydrolysis (KOH, tetrahydrofuran-MeOH) followed by treatment with oxalyl chloride<sup>6b</sup>] in CH<sub>2</sub>Cl<sub>2</sub> and triethylamine afforded, after alumina chromatography and recrystallisation from methanol, the tetrameric porphyrin derivative (7)<sup>‡¶</sup> ( $M^+ + H$  2238.3, C<sub>144</sub>H<sub>165</sub>N<sub>20</sub>O<sub>4</sub> requires 2238.3<sup>¶</sup>) in 89% yield.

The <sup>1</sup>H n.m.r. spectrum of (7) shows two sets of NH protons each integrating for 4H at  $\delta$  -3.9 and -8.0, corresponding to monomer and dimer components respectively. The absence of an upfield shift in the monomer signals suggests a conformation for (7) approximately as shown in which the two monomers are held away from the dimer and its ring current effects.<sup>||</sup> Any intramolecular stacking interaction between monomer and dimer would be reflected in strong ring current induced shifts.<sup>9</sup> Similarly the simplified *meso* proton region shows four singlets at  $\delta$  9.8-10.2 from the unaffected monomers and four singlets between  $\delta$  7.6 and 9.1 from the dimer in a predominantly parallel conformation.<sup>6a</sup> Reaction of (7) with zinc acetate (CH<sub>2</sub>Cl<sub>2</sub>-methanol) leads to the tetra-zinc complex (8) in 98% yield. We anticipated that the rates of demetallation of the various rings in (8) would be different and

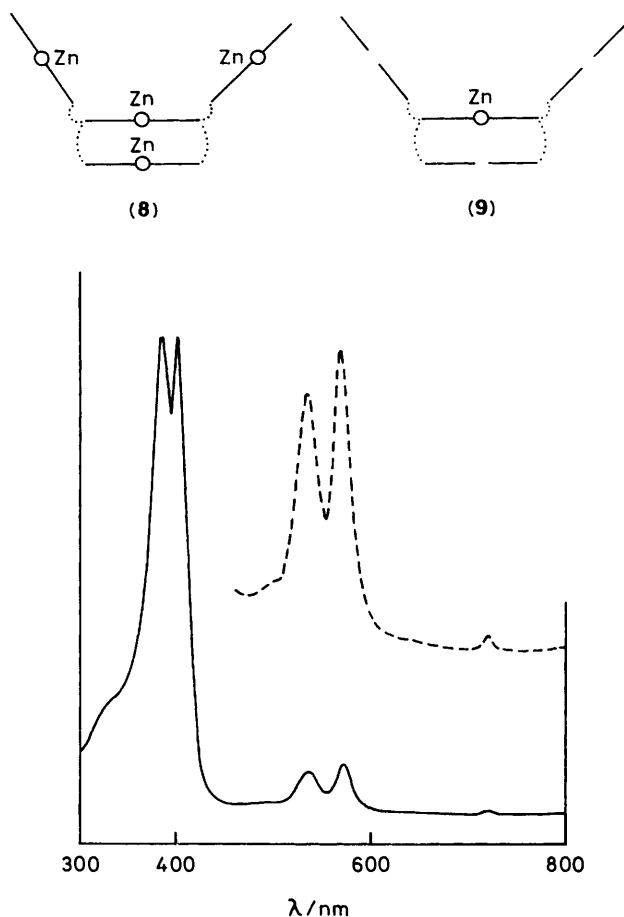
<sup>†</sup> For example as seen in the absorption spectrum of reaction centres from *R. sphaeroides*<sup>7</sup> which has bands at 865 nm and 800 nm due to the Bchl 'special pair' and its associated Bchls, respectively.

<sup>‡</sup> All new compounds gave satisfactory spectroscopic, analytical, and/or mass spectral data.

<sup>§</sup> (4), <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>) -3.78(2H, s, NH), 1.90(18H, t, CH<sub>3</sub>), 3.52(4H, m, NCH<sub>2</sub>CH<sub>2</sub>), 4.10(12H, q, CH<sub>2</sub>CH<sub>3</sub>), 4.29(2H, s, PhCH<sub>2</sub>), 4.35(4H, m, NCH<sub>2</sub>CH<sub>2</sub>), 7.46(5H, m, PhH), 9.99 and 10.10 (each 2H, s, *meso*-H).

<sup>¶</sup> Fast atom bombardment spectrum at 8 keV accelerating voltage using a dithioerythritol matrix.

<sup>||</sup> While the aza-cycloheptyl group forms a fairly rigid connection to (5), the propionate substituents on (1) will cause some flexibility between monomer and dimer in (7).



**Figure 2.** U.v.-visible spectrum of the tetra-zinc complex of tetramer (8) in CH<sub>2</sub>Cl<sub>2</sub>.

that careful acid treatment would allow us to prepare non-symmetrically metallated tetramers. Indeed reaction of (8) with formic acid (25 °C, 1 min) leads to the mono-zinc derivative (9). This has n.m.r. signals at  $\delta$  -8.5 (integrating for 2H) and -4 (integrating for 4H), confirming that the single metal is in the dimer.<sup>\*\*</sup>

Table 1 contains optical spectroscopy data for (7), (8), and (9) and compares them with those for related monomer and dimer species. Free base (7) and tetra-zinc (8) show two Soret bands corresponding to the two porphyrin environments. This is most clearly seen in (8) (Figure 2) which has a distinct separation of 17 nm between the monomer Soret band at 402 nm and the blue-shifted (as a result of exciton coupling<sup>6a,b</sup>) dimer Soret band at 385 nm. Fluorescence emission spectroscopy provides evidence for interaction between the chromophores (Table 1). The quantum yield for fluorescence emission is reduced eight-fold in tetramer (7) relative to octaethylporphyrin, confirming the existence of a pathway, either *via* energy or electron transfer, for fluorescence quenching between the monomer and dimer components. This effect increases to eighteen-fold in mono-zinc (9) and thirty-fold in tetra-zinc (8) (compared with Zn octaethylporphyrin). Preliminary fluorescence lifetime measurements, which show a decrease from 15 ns for a free base monomeric porphyrin to 6 ns for (7) and 4 ns for (9), are consistent with this interpretation.

<sup>\*\*</sup> At this stage it is not possible to state which of the two porphyrins in the dimer contains the zinc.

In summary we have prepared a synthetic analogue of the photosynthetic apparatus which contains key features of the reaction centre structure. These include a dimer-bis(monomer) arrangement of four tetrapyrrole pigments, two distinct optical absorptions due to the two environments, and evidence for electron or energy transfer interactions between dimer and monomer. We are currently using fast optical techniques to probe further the nature and extent of dimer-monomer interactions. We are also modifying our synthetic design to increase the rigidity of the dimer-monomer link and to extend the number of potential electron acceptors beyond the Bchl analogues.

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