Novel Cleft-Containing Porphyrins as Models for Studying Electron Transfer Processes**

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Understanding in detail the mechanism underlying the very efficient conversion of light into chemical energy as displayed by the photosynthetic reaction centers, for example, of the purple photysynthetic bacteria *Rhodopseudomonas viridis* and *Rhodobacter sphaeroides* is of interest with respect to the development of artificial photosynthesis. In recent years the structures of these reaction centers have been elucidated, and in combination with spectroscopic studies on these systems this has led to deeper insight into their working and the importance of specific variables. Until now most model systems described in the literature consist of covalently linked chromophores. Only a few examples have appeared in which a supramolecular approach was followed. Even fewer model systems have been reported that can be used to study the role of intervening aromatic amino acid residues as bridging molecules to enhance the electron transfer over large distances. In the photosynthetic reaction centers of *Rhodopseudomonas viridis* and *Rhodobacter sphaeroides* the aromatic ring of a tryptophan unit is in van der Waals contact with both the primary acceptor (a bacteriochlorophyll) and the quinone and is therefore expected to play an important role in the electron transfer process. To date the model systems designed to study this phenomenon consist of covalently linked chromophores separated by an aromatic spacer. These model systems, however, have several limitations, the most serious one being that electron transfer can and predominantly does occur through the bonds. In this communication we describe novel porphyrin molecules derived from the building block diphenylglycoluril, which contain a substrate binding site and either a donor (1) or an acceptor group (2). These systems have been developed in order to study the role in the electron transfer process of intervening aromatic molecules that are complexed between the donor and the acceptor.

![Diagram](image-url)

**Scheme 1.** a) 3b, p-dimethoxybenzene (1.2 equiv), acetic acid, trifluoroacetic acid, 96% yield; b) triethylammonium formate, Pd/C, THF/MeOH (1/1 v/v), room temperature (RT), 95% yield; c) compound 4b (or 6b) and 5 (1 equiv), CH₂Cl₂, molecular sieves, reflux, 45% yield; d) excess Zn(OAc)₂, DMF/toluene (1/1 v/v), reflux, 90% yield; e) 3b, hydroquinone (1.1 equiv), p-toluenesulfonic acid, dichloromethane; f) CuCl₂, pyridine, DMSO, oxygen; g) triethylammonium formate, Pd/C, THF/MeOH (1/1 v/v), RT, 95% yield.

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**References**


[20] The electrochemical investigations were performed in dichloromethane in the presence of 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (TBAPF₆). The potentials given were measured with a Ag/AgCl electrode. Ferrocene, which is oxidized at +0.48 V against Ag/AgCl, served as internal standard.


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Table 1. Spectroscopic data of 1a – 1c and 2.

1a: ¹H NMR (CDCl₃): δ = 8.85 and 8.69 (ABq, 4 H, pyrrolic β H atoms), 8.86 (s, 2 H, pyrrolic β H atoms), 8.21 (m, 8 H, 2,6- Ar H, porphyrin), 7.84 (m, 8 H, 3,5- Ar H, porphyrin), 7.76 (m, 4 H, 4-Ar H, porphyrin), 7.15 (s, 5 H, ArH, diphenylglycoluril), 7.12 (s, 5 H, ArH, diphenylglycoluril), 6.62 (s, 2 H, ArH), 5.90 and 3.89 (ABq, 4 H, J = 15.8 Hz, NCH₂Ar), 5.57 and 3.80 (ABq, 4 H, J = 15.8 Hz, NCH₂HAr), 3.86 (s, 6 H, OMe), 3.75 (s, 6 H, OMe), —2.53 (br s, 2 H, NH); FAB-MS (m-nitrobenzyl alcohol matrix): m/z: 257 (M + H⁺).

1b: ¹H NMR (CDCl₃): δ = 8.89 and 8.54 (ABq, 4 H, J = 5 Hz, pyrrolic β H atoms), 8.75 (s, 2 H, pyrrolic β H atoms), 8.20 – 8.00 (m, 8 H, 2,6- Ar H, porphyrin), 7.81 – 7.72 (m, 12 H, 3,5-Ar, H₄-ArH, porphyrin), 7.15 (s, 5 H, ArH, diphenylglycoluril), 7.14 (s, 5 H, ArH, diphenylglycoluril), 6.62 (s, 2 H, ArH), 5.92 and 3.98 (ABq, 4 H, J = 15.8 Hz, NCH₂Ar), 5.56 and 3.82 (ABq, 4 H, J = 15.8 Hz, NCH₂HAr), 3.86 (s, 6 H, OMe) 3.72 (s, 6 H, OMe); FAB-MS (m-nitrobenzyl alcohol matrix): m/z: 1321 (M + H⁺); HR-MS: calcld for C₁₁₂H₁₁₂N₆O₆Zn: 1767.892; found: 1767.882.

1c: ¹H NMR (CDCl₃): δ = 8.91 and 8.54 (ABq, 4 H, J = 5 Hz, pyrrolic β H atoms), 8.85 (s, 2 H, pyrrolic β H atoms), 8.12 (s, 2 H, ArH, porphyrin), 8.08 (s, 2 H, ArH, porphyrin), 8.01 (s, 2 H, ArH, porphyrin), 7.86 (s, 2 H, ArH, porphyrin), 7.85 (s, 2 H, ArH, porphyrin), 7.77 (s, 2 H, ArH, porphyrin), 7.10 (m, 10 H, ArH, diphenylglycoluril), 6.46 (s, 2 H, ArH), 5.90 and 3.93 (ABq, 4H, J = 15.8 Hz, NCH₂Ar), 5.44 and 3.69 (ABq, 4 H, J = 15.8 Hz, NCH₂HAr), 3.73 (s, 6 H, OMe), 3.62 (s, 6 H, OMe), 3.52, 1.50, 1.41 and 1.26 (4s, 72 H, C₂H₅); FAB-MS (M₁ n-nitrobenzyl alcohol matrix): m/z: 1768 (M + H⁺); HR-MS: calcld for C₁₁₂H₁₁₂N₆O₆Zn: 1767.845; found: 1737.840.

with an excess of zinc acetate to yield 1b in 90% yield. Compound 1c was obtained analogously. Compound 2 was synthesized by a condensation of diaminobenzene 6b with porphyrin diketone 5. The former compound was obtained by treating hydroquinone with 3b. Subsequently the hydroquinone was oxidized to benzoquinone, and the nitro groups reduced to amine functions. Full synthetic details will be described in a forthcoming full paper.[¹⁷]

Purple crystals of 1a suitable for an X-ray structure analysis were grown by slow diffusion of diethyl ether into a chloroform solution of 1a. The crystal structure of 1a'[¹⁰] is monoclinic. The unit cell contains four clip-shaped molecules, which are packed as two dimers (Figure 1a) that are perpendicular to each other. As expected the diphenylglycoluril unit in the X-ray structure of 1a is quite similar to that in the X-ray structure of 4a[¹⁰] (which was synthesized in an identical manner to 4b, but from 3a). The two dimethoxybenzene groups attached to the diphenylglycoluril unit define a tapering cleft with a center-to-center distance of 6.28 Å, which is ideal for forming sandwich complexes with aromatic guest molecules. The twist in the diphenylglycoluril framework of molecule 1a is somewhat smaller than observed for molecular clip 4a[¹⁰]. The porphyrin wall of 1a is nonplanar and bends towards the cavity with an out-of-plane angle of 15°, with the result that the porphyrin unit is arranged parallel to the opposite dimethoxybenzene wall. This bending can be attributed to stacking interactions between two molecules in the solid state (Figure 1a). The large porphyrin wall wraps around the back of the diphenylglycoluril part of the molecule and interacts with a phenyl group on the convex side. The dimethoxybenzene wall of one molecule occupies the cleft of its dimeric partner. Although no crystals suitable for X-ray analysis could be grown from 2, a single molecule of 2 is expected to have approximately the same structure as a single molecule of 1a[¹¹]. The edge-to-edge distance between the electron donor (zinc porphyrin) and the electron acceptor (benzoquinone) in 2 will be approximately 6.5 Å, and the center-to-center distance 9 Å. This is somewhat smaller than the distance between the bacteriopheophytin and the quinone observed in the X-ray structure of the reaction center of Rps. viridis (9.7 Å edge-to-edge and 14.3 Å center-to-center).[¹¹]

Previous work in our group has showed that molecular clips of type 4a and 6a[¹⁷] bind dihydroxybenzenes and related compounds by hydrogen bonding with the carbonyl functions of the diphenylglycoluril unit and π – π stacking interactions with the aromatic walls of the clip (4a + resorcinol, Kₛₛ = 2600 M⁻¹).[¹⁰] It was also shown that a clip with two functionalized aromatic walls is not capable of binding dihydroxybenzenes.[¹⁰, ¹²] NMR titration experiments[¹³] with 1a and the guest hexyl 3,5-dihydroxybenzoate in CDCl₃ revealed that the latter molecule is bound in the cleft of the former molecule (Kₛₛ = 120 M⁻¹), but the exchange between the bound and the free guest is fast on the NMR time scale. This guest formed stronger complexes with the host molecules 1b and 1c (Kₛₛ = 540 M⁻¹), since the metatation of the porphyrins results in more favorable π–π interactions. The binding constants were even larger in CCl₄—which is the solvent used for the fluorescence studies (see below)—because of the larger contribution of the hydrogen bonds to the binding process (Kₛₛ = 2 × 10¹³ M⁻¹ for the binding of hexyl 3,5-dihydroxybenzoate in 1c). Calculations with the Johnson and Bovey tables[¹⁴] and the obtained complex-induced shift (CIS) values from the ¹H NMR spectra indicated that the guest is complexed in a slightly off-center position between the dimethoxybenzene walls of 1a (Figure 1b). ¹H NMR showed that in the case of 2 the guest molecule is bound in a similar way and hence located between the zinc porphyrin and the quinone function. This host–guest complex was therefore an interesting model for studying the influence of an intervening aromatic guest molecule on the electron transfer process between a porphyrin donor and a quinone acceptor. Cyclic voltammetric studies of 2 in CH₂Cl₂ revealed that the first oxidation potential of the porphyrin was at 0.30 V and the first reduction potential of the quinone at 0.93 V (potentials vs. an internal ferrocene reference system. According to Marcus theory,[¹⁵] the electron transfer process for the donor–acceptor system of molecule 2 should have a low energy barrier in polar solvents and a relatively high energy barrier in apolar solvents. Fluorescence studies with compounds 1 and 2 carried out in different solvents revealed that this was indeed the case (Table 2). In the apolar solvent CC₁₄ the fluorescence quantum yields of 1b, 1c, and 2 were comparable to that observed for [Zn(tpp)] (TPP = tetraphenylporphyrin)
almost no electron transfer occurred. In the more polar solvents CH₂Cl₂ and CHCl₃, the fluorescence quantum yield of 2 was much lower than those of 1b and 1c, which can be explained by a fast electron transfer from the excited porphyrin (570 nm) to the quinone.¹⁶ In line with these experiments, time-resolved single-photon-counting fluorescence (SPC) studies in CHCl₃ showed that the decay profiles of 1c and 2 were virtually the same. The decay profile of 2 in CH₂Cl₂ was different and showed an additional rapid process (52 ps), which was the major contribution (90%) to the fluorescence decay. In CHCl₃, almost no quenching of the fluorescence of 2 due to electron transfer processes was observed. After the addition of hexyl 3,5-dihydroxybenzoate, however, 75% of the intensity showed that the decay profile of 2 in CH₂Cl₂. This is in contrast to a recent measurement in which a covalently linked phenyl moiety is positioned between the two chromophores, in which a covalent linkage for the host-guest complex. This is in contrast to a recent experiment in which a covalently linked phenyl moiety is positioned between the two chromophores. The latter effect is partly due to a superexchange mechanism. The latter effect results from a local polarity effect and buttressing or contact effects of the latter effect results from a local polarity effect and buttressing or contact effects.

**Table 2.** Fluorescence quantum yields (Φₚ, nm = 620 nm) of 1b, 1c, 2, and [Zn(TPP)] in various solvents and in the presence of hexyl 3,5-dihydroxybenzoate 7 [a].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>1b</th>
<th>1c</th>
<th>2</th>
<th>[Zn(TPP)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂Cl₂</td>
<td>0.016</td>
<td>0.016</td>
<td>0.020</td>
<td>0.025</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>0.016</td>
<td>0.016</td>
<td>0.020</td>
<td>0.025</td>
</tr>
<tr>
<td>CCl₄</td>
<td>0.002</td>
<td>0.002</td>
<td>0.020</td>
<td>0.004</td>
</tr>
<tr>
<td>CCl₄ + 7</td>
<td>0.025</td>
<td>–</td>
<td>0.025</td>
<td>0.025</td>
</tr>
</tbody>
</table>

[a] Excitation wavelength 572 nm. [b] An excess (100-fold) of 7 was added. [c] An extra emission band appeared at 680 nm.

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**The Dependence of the Fluorescence Quantum Yield of 2 on Solvent and Published Data on Other Zincporphyrins**

The dependence of the fluorescence quantum yield of 2 on solvent and published data on other zincporphyrins—quinone systems (see ref. [3]) suggests that the fluorescence is quenched by electron transfer from the zincporphyrin to the quinone, although other mechanisms (energy transfer) cannot yet be ruled out. The concentrations of host and guest were approximately 0.02 mmol and 1 mmol, respectively. This means that in the experiments approximately 75% of the host molecules bind a guest, and 25% are free.


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**Reversible Dimerization of Diphenylpolyene Radical Cations: An Alternative to the Bipolaron Model**

Andreas Smie and Jürgen Heinze*

The bipolaron model is the classical model for characterizing the special properties of conducting polymers. Based on the principles of solid-state physics, this model postulates that, on account of lattice distortions, bipolarons will be more stable.

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