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

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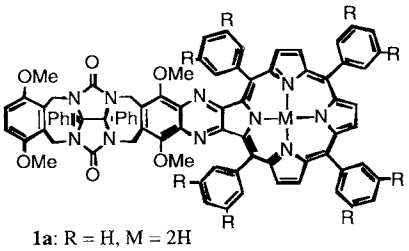
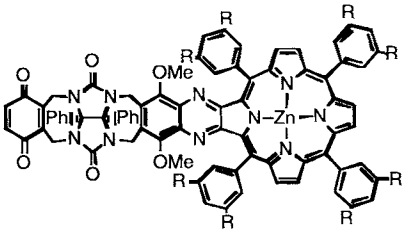
Understanding in detail the mechanism underlying the very efficient conversion of light into chemical energy as displayed by the photosynthetic reaction centers, for example, of the purple photosynthetic bacteria *Rhodopseudomonas viridis* and *Rhodobacter sphaeroides*[1] is of interest with respect to the development of artificial photosynthesis. In recent years the structures of these reaction centers have been elucidated,[1] and in combination with spectroscopic studies on these systems[2] and on model compounds[3] 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.[4] 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.[5, 6] In the photosynthetic reaction centers of *Rhodopseudomonas viridis* and *Rhodobacter sphaeroides*,[1] the aromatic ring of a tryptophan unit is in van der Waals contact with both the primary acceptor (a bateriochlorophyll) 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 phenomemon 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.

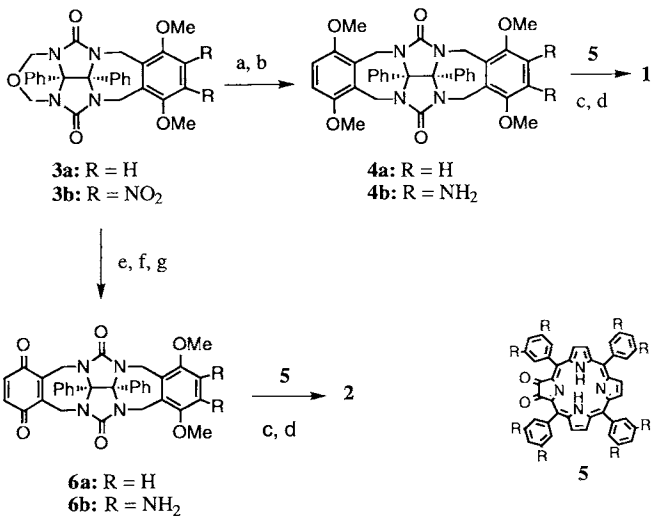


1a: R = H, M = 2H
1b: R = H, M = Zn
1c: R = *t*Bu, M = Zn



2: R = *t*Bu

The synthesis of compound **1a** starts from the diphenylglycoluril derivative **3b**,[7] which was converted in two steps into the diamine functionalized compound **4b** (Scheme 1). First the second *p*-dimethoxybenzene side wall was attached to the molecule. After the reduction of the nitro groups, precursor diamine **4b** was obtained in approximately 50% overall yield. By a simple condensation reaction of **4b** with porphyrin diketone **5**,[8] compound **1a** was prepared in 28% yield (Table 1). Porphyrin **1a** was readily metalated in boiling DMF/toluene by treatment



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), CH_2Cl_2, 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) Cu_2Cl_2, pyridine, DMSO, oxygen; g) triethylammonium formate, Pd/C, THF/MeOH (1/1 v/v), RT, 95% yield.

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[**] We would like to thank Prof. J.-P. Sauvage and Prof. A. Harriman for fruitful discussions.

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

1a: ^{1}H NMR ($CDCl_3$): δ = 8.85 and 8.69 (ABq, 4H, J = 5 Hz, pyrrolic β H atoms), 8.68 (s, 2H, pyrrolic β H atoms), 8.21 (m, 8H, 2,6-ArH, porphyrin), 7.84 (m, 8H, 3,5-ArH, porphyrin), 7.76 (m, 4H, 4-ArH, porphyrin), 7.15 (s, 5H, ArH, diphenylglycoluril), 7.12 (s, 5H, ArH, diphenylglycoluril), 6.62 (s, 2H, ArH), 5.90 and 3.89 (ABq, 4H, J = 15.8 Hz, NC*H*HAr), 5.57 and 3.80 (ABq, 4H, J = 15.8 Hz, NC*H*HAr) 3.86 (s, 6H, OMe), 3.75 (s, 6H, OMe), −2.53 (br. s, 2H, NH); FAB-MS (*m*-nitrobenzyl alcohol matrix): *m/z*: 257 $(M + H)^+$

1b: ^{1}H NMR ($CDCl_3$): δ = 8.89 and 8.54 (ABq, 4H, J = 5 Hz, pyrrolic β H atoms), 8.75 (s, 2H, pyrrolic β H atoms), 8.20–8.0 (m, 8H, 2,6-ArH, porphyrin), 7.81–7.72 (m, 12H, 3,5-Ar, H4-ArH, porphyrin), 7.15 (s, 5H, ArH, diphenylglycoluril), 7.14 (s, 5H, ArH, diphenylglycoluril), 6.62 (s, 2H, ArH), 5.92 and 3.98 (ABq, 4H, J = 15.8 Hz, NC*H*HAr), 5.56 and 3.82 (ABq, 4H, J = 15.8 Hz, NC*H*HAr), 3.86 (s, 6H, OMe) 3.72 (s, 6H, OMe); FAB-MS (*m*-nitrobenzyl alcohol matrix): *m/z*: 1321 $(M + H)^+$

1c: ^{1}H NMR ($CDCl_3$): δ = 8.91 and 8.54 (ABq, 4H, J = 5 Hz, pyrrolic β H atoms), 8.85 (s, 2H, pyrrolic β H atoms), 8.12 (s, 2H, ArH, porphyrin), 8.08 (s, 2H, ArH, porphyrin), 8.01 (s, 2H, ArH, porphyrin), 7.86 (s, 2H, ArH, porphyrin), 7.85 (s, 2H, ArH, porphyrin), 7.77 (s, 2H, ArH, porphyrin), 7.10 (m, 10H, ArH, diphenylglycoluril), 6.46 (s, 2H, ArH), 5.90 and 3.93 (ABq, 4H, J = 15.8 Hz, NC*H*HAr), 5.44 and 3.69 (ABq, 4H, J = 15.8 Hz, NC*H*HAr), 3.73 (s, 6H, OMe), 3.62 (s, 6H, OMe), 1.52, 1.50, 1.41 and 1.26 (4s, 72H, CCH_3); FAB-MS (*m*-nitrobenzyl alcohol matrix): *m/z*: 1768 $(M + H)^+$; HR-MS: calcd for $C_{112}H_{123}N_{10}O_6Zn$: 1767.892; found: 1767.882

2: ^{1}H NMR ($CDCl_3$): δ = 8.92 and 8.57 (ABq, 4H, J = 5 Hz, pyrrolic β H atoms), 8.86 (s, 2H, pyrrolic β H atoms), 8.13 (s, 2H, ArH, porphyrin), 8.08 (s, 2H, ArH, porphyrin), 8.02 (s, 2H, ArH, porphyrin), 7.92 (s, 2H, ArH, porphyrin), 7.87 (s, 2H, ArH, porphyrin), 7.77 (s, 2H, ArH, porphyrin), 7.16 (m, 10H, ArH, diphenylglycoluril), 6.57 (s, 2H, quinone), 5.99 and 3.98 (ABq, 4H, J = 15.8 Hz, NC*H*HAr), 5.49 and 3.72 (ABq, 4H, J = 15.8 Hz, NC*H*HAr) 3.80 (s, 6H, OMe), 1.52, 1.50, 1.41 and 1.26 (4s, 72H, CCH_3); FAB-MS (*m*-nitrobenzyl alcohol matrix): *m/z*: 1738 $(M + H)^+$; HR-MS: calcd for $C_{110}H_{117}N_{10}O_6Zn$: 1737.845; 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 diamine **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.[7]

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**[9] 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

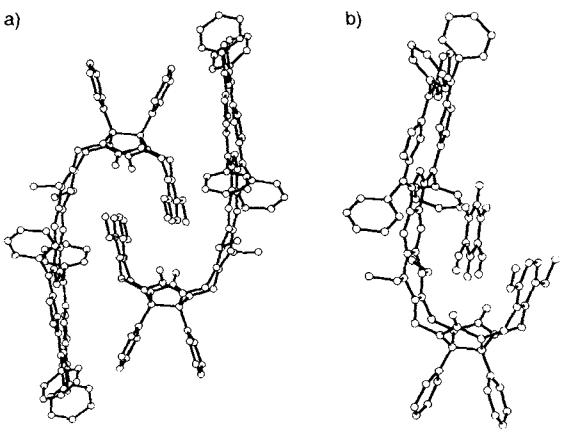

Figure 1. The crystal structure of porphyrin clip **1a** (a) and the structure of the complex between **1a** and a dihydroxybenzene guest molecules as derived from ^{1}H NMR experiments (b). Hydrogen atoms of the clip molecules have been omitted for clarity.

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).[1]

Previous work in our group has shown that molecular clips of type **4a** and **6a**[7] 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, $K_{ass} = 2600\,M^{-1}$).[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 $CDCl_3$ revealed that the latter molecule is bound in the cleft of the former molecule ($K_{ass} = 120\,M^{-1}$) and that 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** ($K_{ass} = 540\,M^{-1}$), since the metalation of the porphyrins results in more favorable π–π interactions. The binding constants were even larger in CCl_4—which is the solvent used for the fluorescence studies (see below)—because of the larger contribution of the hydrogen bonds to the binding process ($K_{ass} = 2 \times 10^3\,M^{-1}$ 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 ^{1}H NMR spectra indicated that the guest is complexed in a slightly off-center position between the dimethoxybenzene walls of **1a** (Figure 1b). ^{1}H 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 CH_2Cl_2 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 CCl_4 the fluorescence quantum yields of **1b**, **1c**, and **2** were comparable to that observed for [Zn(tpp)] (TPP = tetraphenylporphyrin), which suggests that

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

Porphyrin	CH_2Cl_2	$CHCl_3$	CCl_4	CCl_4 + 7 [b]
1b	0.016	0.016	0.022	[c]
1c	0.016	0.016	0.020	[c]
2	0.002	0.002	0.020	0.004
[Zn(tpp)]	0.025	–	0.025	0.025

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

almost no electron transfer occurred. In the more polar solvents CH_2Cl_2 and $CHCl_3$ 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 CCl_4 showed that the decay profiles of **1c** and **2** were virtually the same. The decay profile of **2** in CH_2Cl_2 was different and showed an additional rapid process (52 ps), which was the major contribution (90%) to the fluorescence decay.

In CCl_4 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 was quenched. (A similar effect is expected in CH_2Cl_2; however the binding constant is much lower in this solvent, and the effect cannot be observed). Under the same conditions this quenching was not observed for either [Zn(TPP)], **1b**, or **1c**, and hence this process is likely to be the result of the guest molecule's presence between the donor and acceptor functions of **2**. Further confirmation comes from the quenching of **2**, which is highly dependent upon the guest concentration. The lack of fluorescence quenching for **1b** and **1c** also indicates that the quenching process for **2** is not due to a proton transfer mechanism from the guest to the host, since the most basic sites (the quinoxaline nitrogen atoms) are present in all three molecules. Preliminary SPC measurements indicate that the electron transfer between the porphyrin and the quinone in **2**, responsible for the multiexponential decay of the fluorescence intensity, is substantially faster for the host–guest complex. This is in contrast to a recently constructed porphyrin–quinone system, in which a covalently linked phenyl moiety is positioned between the two chromophores. In this covalently linked system no rate enhancement occurred by through-space electron transfer across the interspaced aromatic moiety.[5] The enhanced electron transfer by the aromatic guest molecule in our system is probably partly a result of a local polarity effect and buttressing or contact effects and partly due to a superexchange mechanism. The latter effect has previously been observed for porphyrin quinone model systems that have aromatic units linking the two chromophores[6] and in solvent-mediated donor–acceptor systems.[17] The addition of hexyl 3,5-dihydroxybenzoate to a solution of **1b** or **1c** in CCl_4 resulted in the appearance of an extra emission band, indicating that the emission process was affected by specific interactions between the host and guest (Table 2). More time-resolved fluorescence studies and transient absorption measurements are in progress to provide a better insight into the mechanisms involved in these new model systems. These results will be presented in a full paper.

Received: July 31, 1996 [Z9405IE]
German version: *Angew. Chem.* **1997**, *109*, 396–399

Keywords: electron transfer · host–guest chemistry · porphyrinoids · supramolecular chemistry

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

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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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[**] The Volkswagen Foundation and the Fonds der Chemischen Industrie provided financial support for this paper. We thank Professor H.-D. Martin's group, Heinrich Heine University, Düsseldorf, for providing the diphenylpolyenes.