

## Synthesis and Photophysical Properties of Porphyrin-Functionalized Molecular Clips

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Different clip-shaped receptor molecules functionalized at one side-wall with a porphyrin unit have been synthesized by a condensation involving a diamino glucoluril derivative and a porphyrin dione. A similar condensation reaction with a porphyrin tetraone resulted in porphyrin molecule with two receptor sites. The binding and photophysical properties of some of these porphyrin-receptor molecules are described.

### Introduction

In light of their special photophysical and catalytic properties, porphyrins have proven to be very interesting building blocks for the construction of functional supra-molecular assemblies. Multiporphyrin systems have been synthesized and studied in order to obtain insight into energy and electron-transfer processes,<sup>1</sup> which are very important with respect to the very efficient solar energy conversion processes observed for photosynthetic bacteria.<sup>2</sup> Understanding of the underlying principles may lead to very efficient artificial solar energy conversion devices. From a catalytic point of view porphyrins are interesting since the different metal complexes are able to mediate different types of reactions such as epoxidation, cyclopropanation, Diels–Alder cycloadditions, cleavage of amides, and alkane hydroxylation.<sup>3</sup>

In the past we have been studying clip-shaped receptor molecules based on diphenylglycoluril, which are able to bind dihydroxybenzene guest molecules by means of hydrogen bonding and  $\pi$ – $\pi$  interactions.<sup>4</sup> In this paper we describe the synthesis and some properties of novel porphyrin molecules (**1–3** see Chart 1) containing a cleft based on diphenylglycoluril. These porphyrin receptor molecules are potentially interesting as supramolecular catalysts.<sup>5</sup> Furthermore, the combination of a binding site for aromatic substrate molecules and the presence of a photoactive component (**1–3**) results in fascinating systems with respect to electron and energy transfer studies. Molecule **2** is of special interest since it contains both a donor (porphyrin) and an acceptor site (quinone) and is able to bind aromatic guest molecules.<sup>6</sup> Using this molecule we have been able to study the role in electron-transfer processes, of aromatic molecules that are situated between the donor and the acceptor.<sup>7</sup> In the photo-synthetic reaction centers aromatic side chains of amino acids are thought to enhance the electron-transfer rate,<sup>8</sup> whereas their role in the lifetime of the charge-separated state is not known.

### Results and Discussion

**Synthesis.** Compounds **1a**, **1e**, and **3a** were synthesized by a condensation reaction of diamino clip **4b**<sup>9</sup> with

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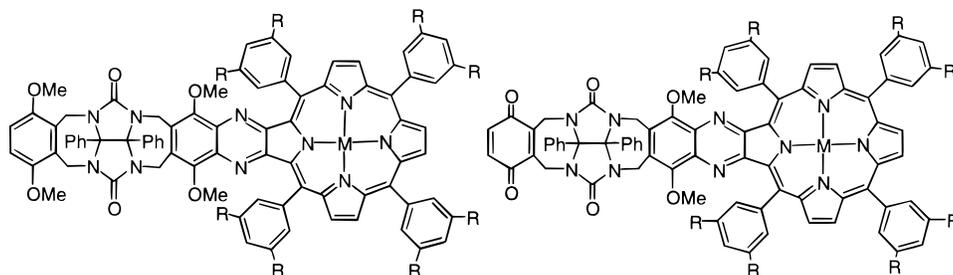
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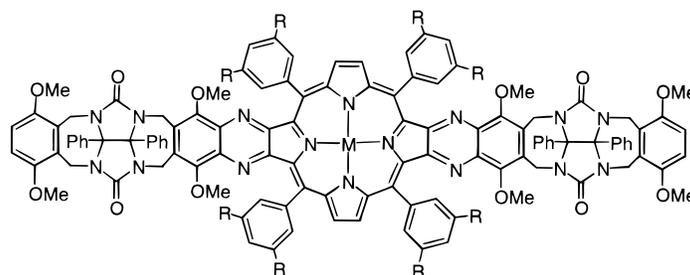
Chart 1



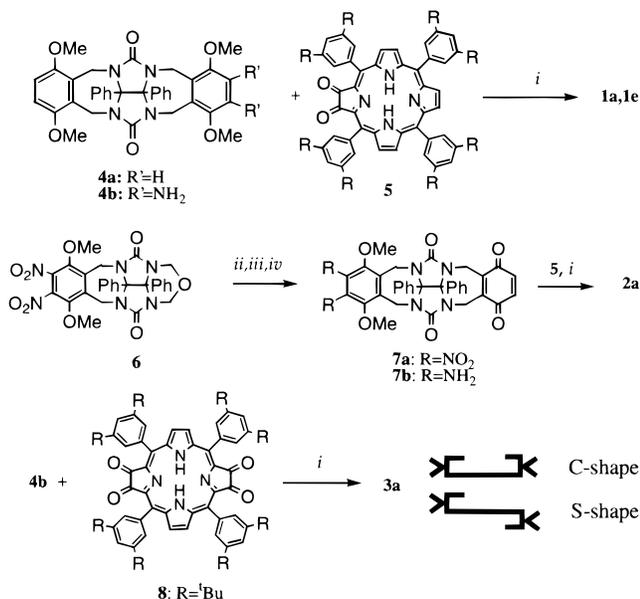
1a: R=H, M=2H  
 1b: R=H, M=Zn  
 1c: R=H, M=Cu  
 1d: R=H, M=Au

1e: R=<sup>t</sup>Bu, M=2H  
 1f: R=<sup>t</sup>Bu, M=Zn

2a: R=<sup>t</sup>Bu, M=2H  
 2b: R=<sup>t</sup>Bu, M=Zn



3a: R=<sup>t</sup>Bu, M=2H  
 3b: R=<sup>t</sup>Bu, M=Zn

Scheme 1<sup>a</sup>

<sup>a</sup> (i) Reflux over mol sieves in CH<sub>2</sub>Cl<sub>2</sub> under N<sub>2</sub>; (ii) hydroquinone, *p*-toluenesulfonic acid, 1,2-dichloroethane, reflux over mol sieves; (iii) Cu<sub>2</sub>Cl<sub>2</sub>, pyridine, DMSO, oxygen; (iv) Pd/C, TEAF, THF/MeOH (1:1, v/v).

porphyrin-2,3-dione **5**<sup>10</sup> and porphyrin 2,3,12,13-tetraone **8**,<sup>11</sup> respectively (Scheme 1). In the latter reaction two isomers were formed, viz., the C-shaped and the S-shaped

isomer, which could not be separated. After metalation to the zinc porphyrin, however, the two isomers were separated by column chromatography.

The synthesis of **2** started from the dinitro half-clip **6**.<sup>9</sup> The second side-wall was attached by treating **6** with hydroquinone in the presence of *p*-toluenesulfonic acid using 1,2-dichloroethane as the solvent. This hydroquinone ring was subsequently oxidized by bubbling air through a solution of the compound in DMSO/pyridine, which contained Cu<sub>2</sub>Cl<sub>2</sub>. After the reduction of the nitro groups with Pd/carbon and triethylammonium formate in THF/MeOH, the condensation reaction with porphyrin-2,3-dione **5** was carried out. The yield of **2a** was 20% with respect to **7a**.

During the sequence of reactions, a new compound (**9**) was obtained as a side product. It had a quinone-like side-wall, and double bonds between the side-wall and the methylene bridges. This same side reaction was observed during the oxidation of the 1,4-dimethoxybenzene/hydroquinone clip **10**, yielding **12** as a side product (Scheme 2). The two AX patterns normally observed in the <sup>1</sup>H NMR spectrum for the CH<sub>2</sub>N protons of a clip molecule with two different side-walls<sup>9</sup> were altered and only one AX pattern and one singlet at low field (8.1 ppm) were visible. The latter signal had the intensity of two protons and is assigned to the doubly bonded bridge between the diphenylglycoluril unit and the side-wall.

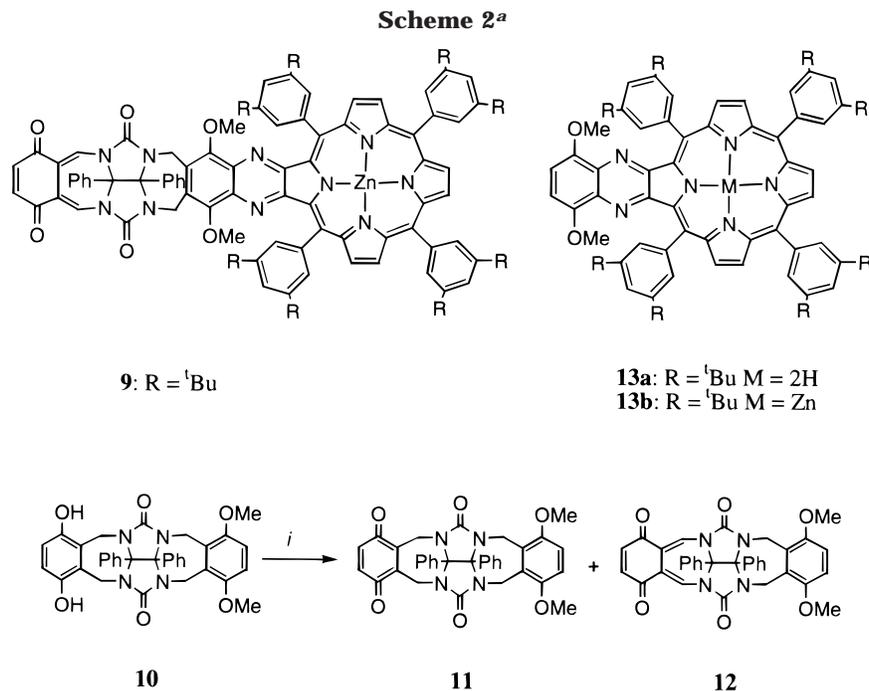
The zinc derivatives of the porphyrins were obtained by treating the free base porphyrins with an excess of Zn(OAc)<sub>2</sub> in DMF/toluene (90% yield). The copper derivative **1c** was synthesized by refluxing **1a** in DMF/toluene with an excess of Cu(OAc)<sub>2</sub>. The gold porphyrin **1d** was obtained by refluxing **1a** for 2 days in acetic acid in the presence of KAuCl<sub>4</sub> and NaOAc.<sup>1c</sup>

Reference compounds **13a** and **13b** were prepared in order to study the influence of the dimethoxyquinoxaline

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unit attached to the porphyrin upon the electronic properties of the latter ring. These derivatives were synthesized by a condensation reaction of 1,4-dimethoxy-2,3-diaminobenzene with **5**, yielding **13a** in 80% yield. The zinc porphyrin **13b** was synthesized from **13a** in the same way as **1b** from **1a**.

**Structures.** Purple crystals of **1a** suitable for a X-ray structure analysis were grown by slow diffusion of diethyl ether into a chloroform solution of this compound.<sup>9</sup> The crystal structure of **1a** is monoclinic and the unit cell contains 4 molecules of **1a**, which are packed in dimeric pairs perpendicular to each other (Figure 1). The diphenylglycoluril unit in the X-ray structure of **1a** is quite similar to that in the X-ray structure of **4a**.<sup>4a</sup> The twist in the diphenylglycoluril framework of molecule **1a** is very small which is clear from the small dihedral angle C21–C9–C9'–C21' (5.5° as compared to 22° in clip **4a**). The methoxy groups of the 1,4-dimethoxybenzene side-wall point upward in the same way as in the crystal structure of **4a**, whereas the methoxy groups of the porphyrin wall point outward. The latter groups are not able to point upward due to steric interactions with the porphyrin unit.

The two dimethoxybenzene groups attached to the diphenylglycoluril unit of **1a** define a tapering cleft, with a center-to-center distance of 6.28 Å. The carbonyl groups make the same angle (37°) as in **4a** (39°), and the distances between the oxygen atoms of the carbonyl groups are almost equal (5.58 Å, as compared to 5.52 Å in **4a**). The porphyrin wall of **1a** is nonplanar and bends toward the cavity with an out of plane angle of 15°, resulting in the porphyrin unit and the opposite dimethoxybenzene wall being parallel. This bending can be attributed to favorable stacking interactions between the two molecules in the dimeric pair (Figure 1). The dimethoxybenzene wall of one molecule occupies the cleft of its dimeric partner, forming a structure which is also found in other clip molecules in both solution and the

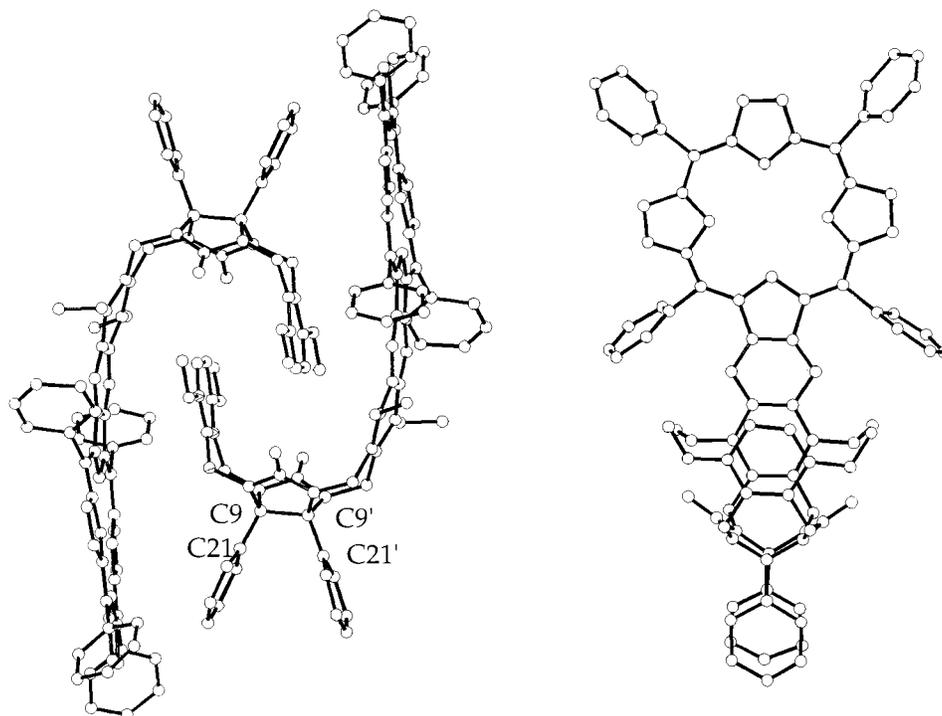
solid state.<sup>12</sup> The large porphyrin wall wraps around the back of the diphenylglycoluril part of its partner, and interacts with a phenyl group on the convex side. Although no crystals suitable for X-ray analysis could be grown from **2**, we expect that a single molecule of **2a** will have approximately the same structure as a single molecule of **1a**, since the X-ray structures of **4a** and **11** were found to be very similar.<sup>4a,12</sup> The edge-to-edge distance between the electron donor (free base and zinc porphyrin) and the electron acceptor (benzoquinone) in **2**, therefore, will be approximately 6.5 Å, with a center-to-center distance of 9 Å.

Molecules **9** and **12** have a geometry that is different from those of **1a** and **2**. The conformations of the free base analogues of **9** and **2a** were calculated with the help of molecular mechanics using the CHARMM force field in the QUANTA modeling package.<sup>13</sup> The structure of **2a** (Figure 2) was found to be very similar to the X-ray structure of **1a**, the main difference being the bent form of the porphyrin in the latter molecule. This bending is the result of the interactions between the two clip molecules in the dimeric structure of **1a**. According to the calculations the doubly bonded connection in **9** results in a side-wall that is perpendicular to the other aromatic side-wall, hence the molecule does not possess a cleft (Figure 2). The center-to-center distance between the porphyrin unit and the quinone-like moiety in **9** is 15 Å, and the planes make an angle of 101°.

As mentioned above the S-shaped and the C-shaped isomers of clip molecule **3b** were separated by column chromatography. Unfortunately we were unable to grow crystals suitable for X-ray diffraction of either the C- or the S-shaped species. All spectroscopic data for the two

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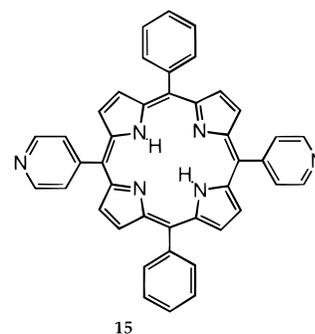
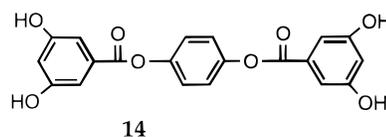


**Figure 1.** X-ray structure of **1a**. A side-view of the dimeric complex (left) and the front-view of the monomer are shown (right). Hydrogen atoms have been omitted for clarity.

structures were very similar. To distinguish between the two species, host–guest binding experiments were carried out and followed by  $^1\text{H}$  NMR spectroscopy.

Solid–liquid extraction experiments were performed using a dimeric resorcinol guest molecule (**14**),<sup>14</sup> that was insoluble in chloroform. Only one of the isomers was able to solubilize the substrate by forming a strong complex. Large upfield shifts in the  $^1\text{H}$  NMR spectrum were observed for both the guest molecule and this host molecule, indicating that the former molecule was bound in the cleft of the latter. The other isomer was unable to solubilize **14**, and consequently no complex formation was observed by  $^1\text{H}$  NMR. A similar solid–liquid extraction experiment using **1f** as the receptor showed that this clip is also unable to solubilize **14**. Molecular modeling calculations revealed that **14** fits nicely into the C-shaped structure of **3b**, forming hydrogen bonds with the two diphenylglycoluril parts of the molecule (Figure 3). From this calculation and the fact that clip molecule **1f** is unable to bind guest molecule **14**, we propose that the C-shaped structure of **3b** is the isomer that binds **14**. An experiment to confirm the shapes of the two structures was carried out using the bulky *trans*-pyridylporphyrin **15**. This porphyrin molecule was added stepwise to separate solutions of the S-shaped and the C-shaped isomers of **3b**, and the results were monitored by both  $^1\text{H}$  NMR and UV–vis spectroscopy. Upon the addition of **15** in both cases the Q-bands in the UV–vis spectra of the zinc-porphyrin **3b** shifted to the red, indicating that the pyridine ligands were complexed to the zinc centers.<sup>15</sup>

This complexation was confirmed by  $^1\text{H}$  NMR spectroscopy, which showed that the signals of the zinc-

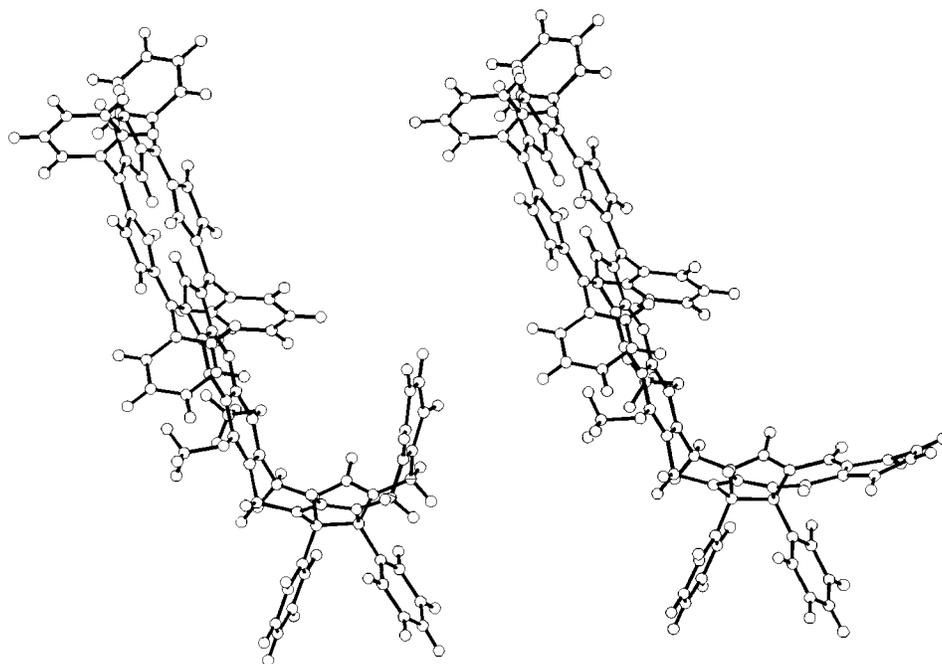


porphyrin shifted to lower field. When **15** was complexed to the S-shaped isomer, a shift of the protons of the *p*-dimethoxybenzene side-walls of the latter molecule was observed, indicating that these protons were in the shielding zone of the complexed porphyrin ligand. In the complex with the C-shaped isomer, no such shifts of the side-wall protons of **3b** were observed. In this case the complexation must have taken place on the outside of the molecule (Figure 4).

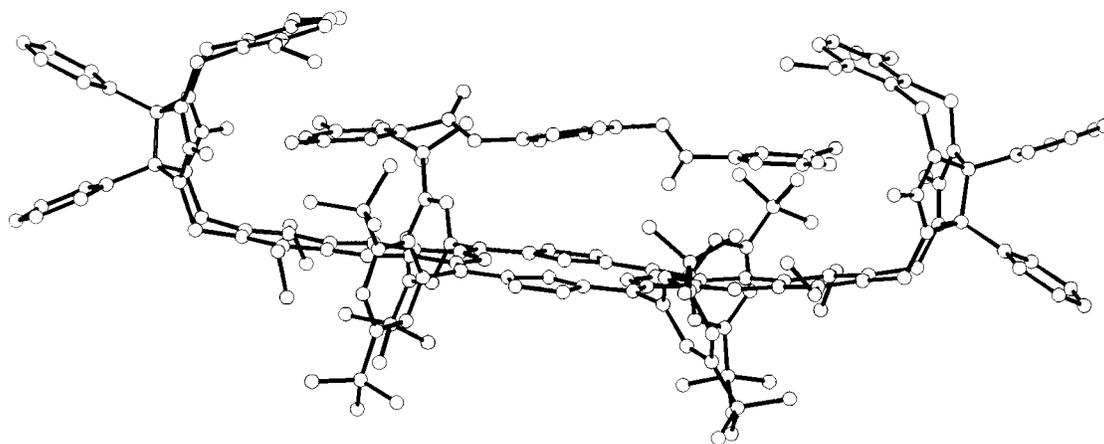
**Binding Properties.** We have shown previously that molecular clips of type **4a** bind dihydroxybenzene guests by hydrogen bonding with its carbonyl functions and  $\pi$ – $\pi$  stacking interactions with its aromatic walls ( $K_a$  resorcinol =  $2600\text{ M}^{-1}$ ).<sup>4</sup>  $^1\text{H}$  NMR titration experiments with **1a** and the guest 5-pentylresorcinol (olivitol) in  $\text{CDCl}_3$  revealed that the latter molecule is bound weakly in the cleft of **1a** ( $K_a = 25\text{ M}^{-1}$ ). The more electron poor guest, hexyl 3,5-dihydroxybenzoate, formed a stronger complex with host molecule **1a** ( $K_a = 120\text{ M}^{-1}$ ). From the calcu-

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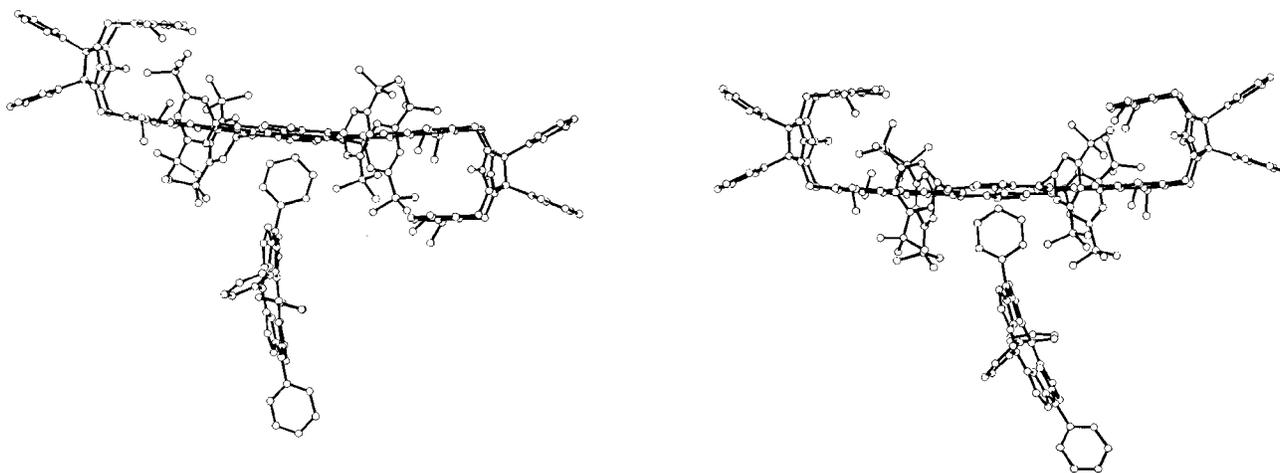
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**Figure 2.** Calculated structures (CHARMm force field) of **2** and **9**. *tert*-Butyl groups have been omitted for clarity.



**Figure 3.** Computer-modeled structure of the complex between the C-shaped structure of **3b** and the guest **14**.



**Figure 4.** Complexation of *trans*-bipyridyl-porphyrin **15** to the S-shaped isomer (left) and the C-shaped isomer (right) of **3b**.

lated complex-induced shift values it followed that the guest was bound in an slightly off-center position between the xylene walls of **1a**, as was found for complexes with

other clip molecules.<sup>4</sup> The complexation of dihydroxybenzenes in zinc porphyrin clip **1f** was somewhat stronger (hexyl 3,5-dihydroxybenzoate:  $K_a = 540 \text{ M}^{-1}$ ). This

feature was also observed for other metal-functionalized clip molecules.<sup>9</sup> It is known that the incorporation of metals into porphyrins increases the  $\pi$ - $\pi$  stacking interactions of the latter molecules.<sup>15a</sup> Binding studies in  $\text{CCl}_4$  using an external solvent as the lock signal and the reference revealed that the association constant between hexyl 3,5-dihydroxybenzoate and **1f** is much stronger ( $K_a = 2 \times 10^3 \text{ M}^{-1}$ ) in this solvent. The binding affinities of **2** are expected to be lower than those of **1**: on the basis of measurements carried out with **4a** and **12** we estimate that the difference is about 3 kJ/mol.<sup>4,9</sup> The geometry of the complex with **2** will be similar to that of the complex with **1f**, i.e., the guest will be located between the zinc porphyrin and the quinone function. This host-guest complex, therefore, was felt to be an interesting model for studying the influence of an intervening aromatic molecule upon the electron-transfer process between a porphyrin donor and a quinone acceptor (vide infra).<sup>7</sup>

**Self-Association.** Some clip molecules are able to dimerize not only in the solid state but also in solution. Water-soluble clip molecules were shown to have a very strong self-association which is driven by hydrophobic effects.<sup>16</sup> The porphyrin-functionalized molecules were also found to form dimers in solution, with a geometry similar to that observed in the X-ray structure of **1a** (see below). Upon diluting a concentrated solution of **1a** in  $\text{CDCl}_3$ , the signals of the aromatic walls in the  $^1\text{H}$  NMR spectrum shifted downfield, indicating that the dimeric complex of **1a** dissociated. The shifts were not large enough for a self-association constant to be calculated. The metal-functionalized porphyrin clip molecules showed a stronger self-association behavior, probably due to a decrease in electron density on the porphyrin side-wall. As was found for the binding of dihydroxybenzene guest molecules, a decrease in electron density and hence a decrease in electrostatic repulsion between aromatic rings leads to higher association constants. In the case of molecular clips **1b**, **1d**, and **1f** the shifts were large enough to calculate the self-association constant:  $K_{as} = 18 \text{ M}^{-1}$  for **1b** and **1f**, and  $K_{as} = 12 \text{ M}^{-1}$  for **1d**. (For **1c** no measurements were carried out).

The *p*-dimethoxybenzene side-wall and the methylene bridges to which the porphyrin ring is attached, showed together with the methoxy groups—the largest shifts upon dilution, indicating that the dimeric complex had a geometry similar to that in the crystal structure (Figure 1). The self-association of **1f** was measured at various temperatures. At lower temperatures the dimeric complex was found to be more stable, indicating that the process of dimerization is enthalpy driven (a similar observation was made for clip molecules which were monofunctionalized with a phenanthroline ring).<sup>12</sup> At very low temperatures larger aggregates were formed in  $\text{CCl}_4$ . For instance, the UV-vis spectra broadened upon cooling the solution to  $-200^\circ\text{C}$ , to such an extent that Q-bands could no longer be distinguished. At room temperature the spectrum very slowly ( $\pm 15$  min) returned to the normal spectrum. The fluorescence intensity also decreased at lower temperature, supporting the idea that larger aggregates were formed.

$^1\text{H}$  NMR dilution studies on the S-shaped isomer of **3b** revealed that this molecule forms dimers as well. The

observed shifts were rather small suggesting that the strength of the dimeric complex was weak. This is probably due to the steric hindrance caused by the phenyl groups on the porphyrin ring. The  $^1\text{H}$  NMR signals of the C-shaped isomer of **3b** not only shifted upon an increase in concentration, but also broadened. This suggests that the rate of exchange between the monomeric and the dimeric species is slow. The higher energy barrier for dimerization of the C-shaped isomer of **3b** is not unexpected since in the dimer the molecules fit tightly together, and two large surfaces have to be solvated upon breaking the complex. In Figure 5 the calculated structures of the dimeric species of both the S- and C-shaped isomers of **3b** are shown. The dimer of S-shaped **3b** is of interest because it has two clefts which can further interact with other molecules of **3b** to form a long chain of organized porphyrins.<sup>17</sup> The propensity of our porphyrin-containing clip molecules to self-associate makes them interesting building blocks for constructing organized multiporphyrin arrays in order to study tandem electron transfer and tandem energy transfer processes.

**Electrochemistry.** The redox properties of porphyrin clip molecules **1**, **2**, **9**, and those of the model compounds **13** were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). In Table 1 the reduction potentials of the different porphyrins are given. All first reductions of the porphyrin  $\pi$ -systems were reversible or nearly reversible, except the reduction of the  $\pi$ -system of porphyrin clip **2**. This, however, is due to the quasireversible reduction of the quinone unit of this molecule, which leads to adsorption on the electrode.<sup>18</sup> As expected, metalation of the porphyrin resulted in a change in the reduction potential. The second reduction of **1b** and **1c** is shifted approximately 200 mV to lower potential. The charged Au(III) porphyrin clip **1d** displayed a reduction at higher potential ( $-0.91 \text{ V}$  vs  $F_c/F_c^+$ ), which is similar to the reduction potential of quinone ( $-0.93 \text{ V}$ ). This Au(III) porphyrin, therefore, can be used as an electron acceptor in electron-transfer processes.<sup>1c</sup>

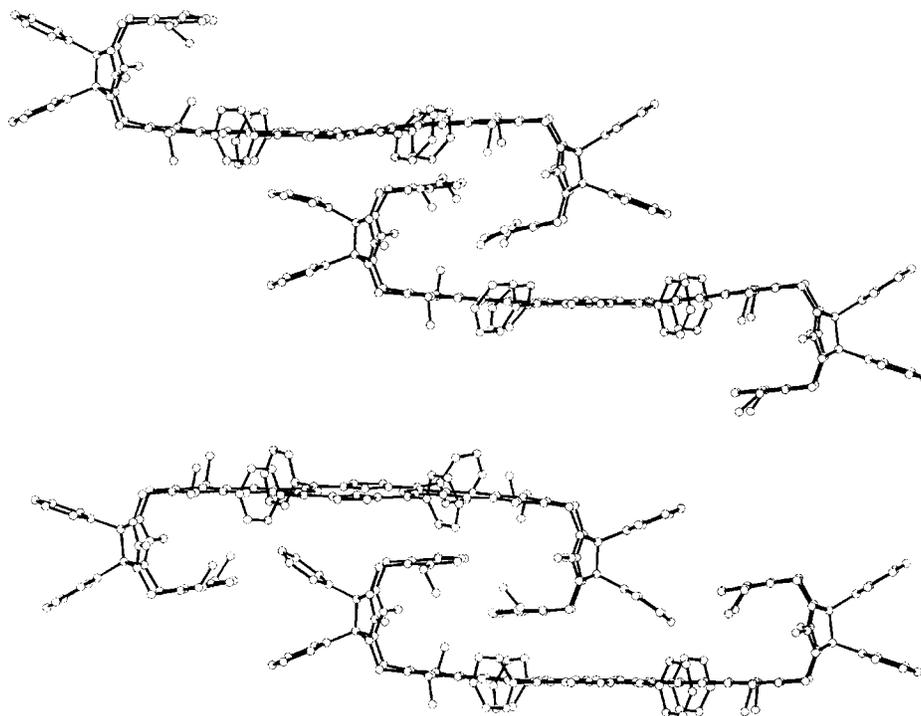
Important with respect to possible photoinduced electron-transfer processes are the oxidation potentials of the electron-donating group (zinc porphyrin) and the reduction potential of the electron-accepting group (quinone) (see Table 1). The first oxidation potentials of the zinc porphyrins in **1b**, **1f**, **2b**, and **9** were all reversible and at approximately 0.3 V vs  $F_c/F_c^+$ , which is similar to potentials found for comparable systems in the literature.<sup>15</sup> The free base and the copper porphyrins were somewhat harder to oxidize than the zinc porphyrin molecules (0.4 and 0.5 V, respectively). No oxidation of the gold porphyrin **1d** was observed. The reduction of the quinone group of clip **2b** occurred at  $-0.93 \text{ V}$  and was quasireversible. The latter was confirmed by scan rate studies. It is known that quinone groups can polymerize and interact with the electrode.<sup>18</sup>

The presence of an excess of hexyl 3,5-dihydroxybenzoate guest had a small influence on the oxidation potential of **1f** and **2b**. The reduction of the quinone group of **2b**, was found to be shifted 0.2 V to higher potential.

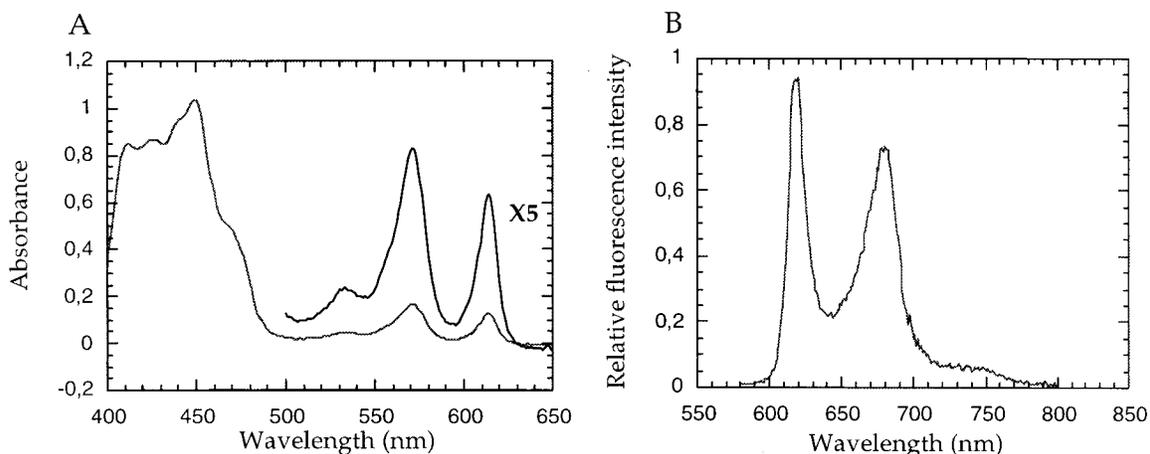
(17) Upon diluting a concentrated solution of the reference compound **13b**, no  $^1\text{H}$  NMR shifts were observed, indicating that this compound does not self-associate, besides the normal aggregation behavior known for porphyrin molecules.<sup>15</sup>

(18) Lindsey, A. S. In *Polymeric Quinones, The Chemistry of Quinoid Compounds*; Patai, S., Ed.; John Wiley and Sons: New York, 1974.

(16) Reek, J. N. H.; Kros, A.; Nolte, R. J. M. *Chem. Commun.* **1996**, 245.



**Figure 5.** Calculated structures of the dimers of the C-shaped (under) and S-shaped (above) isomers of **3b**.



**Figure 6.** Typical absorption (A) and emission spectra (B) of zinc-porphyrins to which the conjugated quinoxaline unit is attached.

The reduction was now chemically irreversible, resulting in a small reoxidation current. The reduction of the quinone like side-wall in **9** was observed at  $-1.45$  V (vs  $F_c/F_c^+$ ) and found to be quasireversible as well. This group is harder to reduce than to the quinone unit in **2b** and hence is not a good electron acceptor compared to the quinone side-wall.

**Steady-State Absorption Spectroscopy.** The conjugated quinoxaline group attached to the porphyrin units induces a symmetry element which is different from normal tetraphenyl porphyrin (TPP), resulting in somewhat deviating absorption spectra. In the case of the free base porphyrins **1a**, **1e**, **2a**, and **13a** a large Soret band at approximately 440 nm was observed, as well as two Q-bands at 530 and 600 nm, and two very small Q-bands at 568 and 650 nm. The zinc-porphyrin molecules **1b**, **1f**, **2b**, **9**, and **13b** showed a broad solvent dependent Soret band with one or two maxima between 420 and the 450 nm, two larger Q-bands at 570 and 612 nm, and a small Q-band at 530 nm (see Figure 6A). The porphyrin unit

in **3** has a different symmetry and hence a different absorption spectrum. For the free base porphyrin **3a**, the Soret band was observed at 463 nm, and the Q-bands (in decreasing intensities) at 540, 619 and 673 nm. The zinc-porphyrin in **3b** gave absorption bands at 475 nm (Soret band) and at 661 nm and in addition to this some small bands at 560, 586, 610, and 630 nm (Q-bands), similar to the pattern seen for chlorins.<sup>15</sup>

**Steady-State Fluorescence Spectroscopy.** A typical emission spectrum of a zinc porphyrin with an attached conjugated quinoxaline unit, is shown in Figure 6B. Two maxima are observed at 620 and 680 nm. Comparison of the fluorescence quantum yields of the different zinc-porphyrin molecules can provide information about additional processes involved in the decay of the excited state, i.e., photoinduced electron transfer.

In  $CCl_4$  the quantum yields of **1b**, **1f**, **2b**, and **13b** were comparable to those observed for Zn(TTP) (Table 2). In the more polar solvents  $CH_2Cl_2$  and  $CHCl_3$ , the fluorescence quantum yield of **2b** was approximately 10 times

**Table 1. Halfwave Potentials (from CV and DPV) for the Reduction and Oxidation of Different Porphyrin Clip Molecules<sup>a</sup>**

porphyrin	reduction potentials		oxidation potentials	
	$E_{1/2}$ (V)	$\Delta E_p$ (mV)	$E_{1/2}$ (V)	$\Delta E_p$ (mV)
<b>1a</b>	-1.61	60	0.40	62
	-1.79	63		
<b>1b</b>	-1.69	42	0.30	70
<b>1c</b>	-2.02	69	0.52	70
	-1.62	52		
	-2.00	54		
<b>1d</b>	-0.91	66	–	–
<b>1e</b>	-1.44	57	0.42	56
	-1.67	70		
	-1.86	80		
<b>1f</b>	-1.78	70	0.30	76
	-2.04	90	0.56	80
<b>1f</b> + guest			0.29	80
			0.58	125
<b>2b</b>	-0.93 <sup>b</sup>	74	0.30	68
<b>2b</b> + guest	-1.77	70	0.56	98
<b>9</b>	-2.06	–	0.28	69
<b>13a</b>	-0.78 <sup>b</sup>	55	0.32	73
<b>13b</b>	-1.45 <sup>b</sup>	70	0.57	107
	-1.67	80		
	-1.86	65		
	-1.75	70		
	-2.04			

<sup>a</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte. A Pt working electrode, a Pt auxiliary electrode, and a Ag/AgI (0.1 M<sup>-1</sup> TBAH, 0.02 TBAI) electrode were used. Potentials are reported vs  $F_c/F_c^+$  in CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> These values are for the quinone side-wall.

**Table 2. Fluorescence Quantum Yields of Different Porphyrins Measured in Various Chlorinated Solvents<sup>a</sup>**

porphyrin	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>	CCl <sub>4</sub>
<b>1b</b>	0.016	0.016	0.022
<b>1f</b>	0.016	0.016	0.020
<b>2b</b>	0.002	0.002	0.020
<b>13b</b>	0.024	–	0.024
Zn(TPP)	0.025	–	0.025

<sup>a</sup> Excitation wavelength 572 nm.

**Table 3. Fluorescence Quantum Yields of Porphyrins 1f and 2b Measured in Various Nonchlorinated Solvents<sup>a</sup>**

solvent	$\epsilon$	<b>1f</b>		<b>2b</b>	
		$\Phi_f$	$\lambda_{em}$ (max)	$\Phi_f$	$\lambda_{em}$ (max)
c-hexane	2.03	0.020	615 nm	0.018	616 nm
hexane	2.05	0.018	615 nm	0.013	616 nm
diethyl ether	4.20	0.012	624 nm	0.004	624 nm
THF	7.58	0.018	625 nm	0.004	625 nm
dibutyl ether	3.10	0.016	626 nm	0.004	625 nm
acetonitrile	37.50	0.0052	635 nm	0.001	633 nm

<sup>a</sup> Excitation wavelength 572 nm.

lower than that of the other molecules, e.g., reference compound **13b**. This suggests that in these more polar solvents electron transfer can occur from the excited state of the zinc porphyrin to the quinone side-wall.

The quantum yields of **1f** and **2b** were also measured in a series of non-chlorinated solvents (Table 3). Again the quantum yields were very dependent upon the dielectric constant of the solvent, suggesting that in the more polar solvents the fluorescence of **2b** is quenched by a photoinduced electron-transfer process. For both molecules, the maxima of the emission wavelengths changed to longer wavelength as the solvent polarity increased. The excited states of these molecules are stabilized by more polar solvents, which suggests that

this state has a larger dipole moment than the ground state.

**Photoinduced Charge Separation.** Within the framework of the Marcus theory,<sup>19</sup> the energy barrier  $\Delta G^\ddagger$  for electron transfer can be expressed by eq 1:

$$\Delta G^\ddagger = (\Delta G^\circ + \lambda)^2/4\lambda \quad (1)$$

where  $-\Delta G^\circ$  is the driving force and  $\lambda$  is the overall reorganization energy. The driving force for photoinduced electron transfer  $\Delta G^\circ$  can be calculated using eq 2:

$$\Delta G^\circ = e[E_{OX} - E_{RED}] - E_S - (e^2/4\pi\epsilon_S\epsilon_0 R_{CC}) = e[E_{OX} - E_{RED}] - E_S - (14.4/\epsilon_S R_{CC}) \quad (2)$$

where  $E_{OX}$  refers to the redox potential for one-electron oxidation of the Zn porphyrin (0.30 V vs  $F_c/F_c^+$  for **2b**),  $E_{RED}$  refers to the redox potential for one-electron reduction of the quinone (-0.93 V vs  $F_c/F_c^+$  for **2b**),  $E_S$  is the singlet excitation energy of the porphyrin unit (2.18 eV for **2b**), and  $R_{CC}$  is the center-to-center distance between the porphyrin and the quinone. When the distance is large and/or the solvent is polar, the last term of eq 2 equals zero. In the case of **2b** the distance is approximately 9 Å, indicating that the last term of eq 2 is significant. From eq 2 we can calculate that for **2b** the driving force ( $-\Delta G^\circ$ ) in dichloromethane is 1.13 eV. The reorganization energy  $\lambda$  for similar systems has been estimated to be 0.9–1 eV in polar solvents.<sup>20</sup> Assuming that the reorganization energy is comparable in our system we can calculate that the energy barrier for electron transfer in **2b** in dichloromethane is very low. To calculate the energy barrier in other solvents the electrochemical data of eq 2 should be corrected for the solvation energy of the ions in these solvents, since the electrochemistry was only performed in dichloromethane. This correction can be made using the Born equation (eq 3),

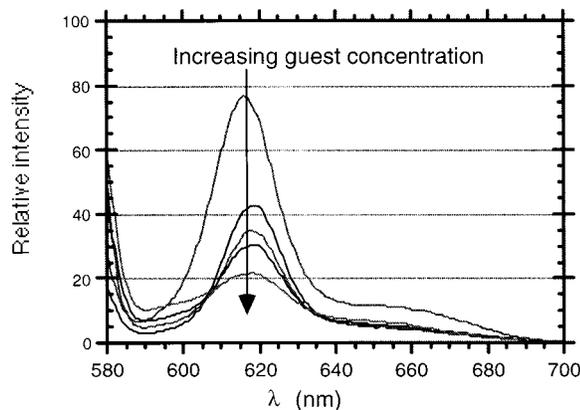
$$\Delta G^\circ_{solv} = -(e^2/2)\{(1/r_{d+}) + (1/r_{a-})\}(1 - 1/\epsilon) \quad (3)$$

where  $r_{d+}$  and  $r_{a-}$  are effective radii of the cation and the anion radical. Assuming radical distances of 5 Å, one can calculate that there is still a positive driving force (0.70 for CCl<sub>4</sub> and 0.59 for hexane) in apolar solvents. Furthermore, the corrected  $\Delta G$  values in the different solvents are all within the Marcus normal region. It is clear from the fluorescence data, however, that there is a significant barrier to the electron-transfer process in the apolar solvents CCl<sub>4</sub> and hexane.

**Influence of Guest Molecules on the Electron Transfer.** We showed that dihydroxybenzene guest molecules can be bound in the cleft of molecules **1** and **2**. The addition of hexyl 3,5-dihydroxybenzoate or olivetol to a solution of **2b** in CCl<sub>4</sub> resulted in a decrease in fluorescence intensity (Figure 7). This decrease in fluorescence intensity was not observed for either Zn(TPP), **1f**, or **13b** (Table 4), and hence is likely to be the result of a photoinduced electron-transfer process.<sup>21</sup> The addition of hexyl 3,5-dihydroxybenzoate to a CCl<sub>4</sub> solution of

(19) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

(20) Antolovich, M.; Keyte, P. T.; Oliver, A. M.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W.; Jonker, S. A.; Warman, J. M. *J. Chem. Phys.* **1991**, *95*, 1933.



**Figure 7.** Fluorescence intensity of **2b** as a function of the guest concentration measured in  $\text{CCl}_4$ . Excitation wavelength 570 nm.

**Table 4. Fluorescence Quantum Yields of Different Porphyrins Measured in  $\text{CCl}_4$  in the Presence of a Guest Molecule<sup>a</sup>**

porphyrin	$\text{CCl}_4$	$\text{CCl}_4$ + guest <sup>b</sup>
<b>1f</b>	0.020	red-shift <sup>c</sup>
<b>2b</b>	0.020	0.004
<b>13b</b>	0.024	0.024
Zn(TPP)	0.025	0.025

<sup>a</sup> Excitation wavelength 572 nm. <sup>b</sup> Addition of an excess of hexyl 3,5-dihydroxybenzoate. <sup>c</sup> An additional emission band appeared at 680 nm.

**1f** resulted in the appearance of an extra emission band, indicating that the emission process was altered by the binding of the guest molecule. This emission is ascribed to an exciplex (excited complex) between the bound guest molecule and the porphyrin in **1f**.

The significant enhancement of the electron transfer upon complexation of a guest molecule is of great interest since in the photosynthetic reaction center intervening aromatic residues are thought to play a role in the electron-transfer process.<sup>8</sup> Studies on a variety of covalently linked donor acceptor systems, which were shown to have through bond electron transfer, have supported this suggestion of aromatic mediation.<sup>19</sup> It was suggested that a super exchange mechanism was responsible for the enhancement in electron transfer. Recently, a super exchange pathway was also suggested for the solvent-mediated electron transfer in a donor-acceptor system.<sup>6</sup> This solvent-mediated transfer can be seen as a noncovalent way of coupling the two components. In our case the aromatic guest is selectively bound between the donor and the acceptor. It is, of course, of interest to know the precise mechanism of the electron transfer process when the guest molecule is bound between the porphyrin and the quinone. The electron transfer occurs either via an exchange mechanism or a change in the local polarity due to the bound guest molecule, or a combination of both effects. From our CV measurements, it is clear that the guest molecule changes the redox potentials of both the donor and the acceptor species, and hence the driving force is also modified. The changes in

the local polarity cannot, however, account fully for the electron-transfer enhancement, and we feel that an exchange mechanism also plays a role. More-detailed photophysical studies on this host-guest system and the design of new host-guest systems displaying photo-induced electron transfer which is independent of the solvent polarity are planned in the future in order to obtain a more-detailed insight into the mechanism.

## Conclusions

A series of novel porphyrin containing clip molecules has been synthesized and characterized. These molecules contain a binding site for dihydroxybenzene guest molecules that are bound nearby a porphyrin ring. Besides the binding of guests, these molecules are able to form dimers in solution and in the solid state. Although the self-association constants of these molecules are low, the observed type of dimeric complex is of interest for the study of tandem electron and energy transfer processes. Clip molecule **2** is very useful for studying electron transfer reactions, since in this molecule the binding site for dihydroxybenzene guests is located exactly between a donor and an acceptor group. The photoinduced electron transfer from the zinc porphyrin in **2** to the quinone site appears to be dependent on the solvent polarity. In  $\text{CCl}_4$  and hexane no photoinduced electron transfer is observed, but upon binding a dihydroxybenzene guest molecule between the donor and the acceptor the fluorescence of the porphyrin was quenched.

## Experimental Section

**General.** Triethylammonium formate was distilled prior to use. THF and diethyl ether were distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane and chloroform were distilled from  $\text{CaCl}_2$ . All other solvents and chemicals were commercial materials and used as received. For column chromatography Merck Silica Gel (60H) was used, and for thin-layer chromatography Merck Silica Gel F<sub>254</sub> plates were used.

**Physical Measurements.** Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed using a conventional three-electrode cell, with Pt working and auxiliary electrodes, and 0.1 M TBAH electrolyte was used. A Ag/AgI reference electrode was employed.

**Compounds.** The syntheses of compounds **1a**, **1e**, **4**, **6**, porphyrin-2,3-dione **5** and porphyrin-2,3,12,13-tetraone **8** have been described elsewhere.<sup>9-11</sup> All reactions with porphyrins were carried out under nitrogen atmosphere and with the reactions flasks covered with aluminum foil. The pyridine-containing porphyrins used to determine the structure of **3b** were synthesized as described in the literature.<sup>15b</sup>

**Zn-Porphyrin Clip 1b.** A mixture of 47 mg (0.037 mmol) of **1a** and an excess of  $\text{Zn}(\text{OAc})_2$  (50 mg) in 2 mL of toluene was refluxed for 16 h. After cooling, 15 mL of toluene was added and the solution was washed with water (3×), with 5%  $\text{Na}_2\text{CO}_3$  solution (2×) and again with water. The organic solution was evaporated to dryness and the green solid was purified by column chromatography ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 98:2 v/v), yielding 40 mg of **1b** (80%); mp: > 310 °C; <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  8.89, 8.54 (ABq, 4H,  $J = 5$  Hz), 8.75 (s, 2H), 8.20–8.0 (m, 8H), 7.81–7.72 (m, 12H), 7.15 (s, 5 H), 7.14 (s, 5H), 6.62 (s, 2H), 5.92 and 3.98 (ABq, 4H,  $J = 15.8$  Hz), 5.56 and 3.82 (ABq, 4H,  $J = 15.8$  Hz) 3.86 (s, 6H) 3.72 (s, 6H); UV-vis ( $\text{CHCl}_3$ )  $\lambda/\text{nm}$ : 408, 447, 530, 570, 612; FAB-MS (*m*-nitrobenzyl alcohol)  $m/z$  1321 (M + H)<sup>+</sup>.

**Cu-Porphyrin Clip 1c.** A mixture of 40 mg (0.032 mmol) of **1a** and an excess of  $\text{Cu}(\text{OAc})_2$  (50 mg) in 2 mL of toluene and 1 mL of DMF was refluxed for 16 h. After cooling, 25 mL of toluene was added and the solution was washed with water (3×), with 5%  $\text{Na}_2\text{CO}_3$  solution (2×), and again with water.

(21) SPC time-resolved fluorescence measurements performed on the complex of **2b** with dihydroxybenzene showed no additional decay, suggesting that the electron transfer between the porphyrin and the quinone became faster than the detection limit. This indicates that the photoinduced electron transfer is faster when an aromatic guest is bound between the donor and the acceptor.

The organic solution was evaporated to dryness, and the green solid was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 99:1 v/v) yielding 38 mg of **1c** (90%); mp: >310 °C; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda$ /nm: 411, 446, 532, 564, 608; FAB-MS (*m*-nitrobenzyl alcohol)  $m/z$  1318 (M + H)<sup>+</sup>.

**Au-Porphyrin Clip 1d.** A mixture of 40 mg (0.032 mmol) of **1a**, 30 mg (0.080 mmol) of KAuCl<sub>4</sub>, and 10 mg (0.13 mmol) of NaOAc in 15 mL of acetic acid was refluxed for 48 h. After cooling, the solvent was evaporated and the solid dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The resulting solution was washed with water (3x), with 5% Na<sub>2</sub>CO<sub>3</sub> solution (2x) and again with water. Anion exchange was carried out by stirring the organic phase with saturated KPF<sub>6</sub> solution. The organic solution was washed with water and evaporated to dryness. The brown solid was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 98:2 v/v) yielding 38 mg of **1d** (90%); Mp: >310 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  9.13 and 8.90 (ABq, 4H,  $J$  = 5 Hz), 9.08 (s, 2H), 8.20–8.05 (m, 8H), 7.93–7.81 (m, 12H), 7.15 (s, 5 H), 7.15 (s, 5H), 6.63 (s, 2H), 5.92 and 3.96 (ABq, 4H,  $J$  = 15.8 Hz), 5.58 and 3.81 (ABq, 4H,  $J$  = 15.8 Hz), 3.84 (s, 6H), 3.74 (s, 6H); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda$ /nm: 438, 549, 593; FAB-MS (*m*-nitrobenzyl alcohol)  $m/z$  1451 (M-PF<sub>6</sub>)<sup>+</sup>.

**Zn-Porphyrin Clip 1f.** The same procedure was used as for **1b**. Purification was carried out by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>), yield 90%; Mp: >310 °C; <sup>1</sup>H NMR (diluted solution) (CDCl<sub>3</sub>)  $\delta$  8.91 and 8.54 (ABq, 4H,  $J$  = 5 Hz), 8.85 (s, 2H), 8.12, 8.07, 8.01, 7.86, 7.85, 7.77 (6s, 12H), 7.15 (m, 10 H), 6.46 (s, 2H), 5.90 and 4.01 (ABq, 4H,  $J$  = 15.8 Hz), 5.44 and 3.69 (ABq, 4H,  $J$  = 15.8 Hz) 3.89 (s, 6H) 3.61 (s, 6H), 1.52, 1.50, 1.48 and 1.41 (4s, 72 H); UV-vis (CHCl<sub>3</sub>)  $\lambda$ /nm: 412, 447, 530, 572, 615; FAB-MS (*m*-nitrobenzyl alcohol)  $m/z$  1769 (M + H)<sup>+</sup>. HRMS Calcd for C<sub>111</sub>H<sub>132</sub>N<sub>10</sub>O<sub>6</sub>Zn: 1767.887; C<sub>112</sub>H<sub>123</sub>N<sub>10</sub>O<sub>6</sub><sup>-</sup>Zn: 1767.892; Found: 1767.882.

**Quinone Porphyrin Clip 2a.** Compound **7b** was obtained after reduction of 220 mg (0.32 mmol) of dinitro derivative **7a** by stirring the latter in 10 mL of THF and 10 mL of MeOH in the presence of TEAF and Pd/C.<sup>9</sup> The Pd/C was filtered off under nitrogen, 10 mL of CH<sub>2</sub>Cl<sub>2</sub> and 350 mg of porphyrindione **5b** were added, and the mixture was refluxed for 18 h over molecular sieves (3 Å). After cooling, the solution was washed with water (3x) and the organic solvents were removed in vacuo. After column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/EtOH, 99:1 v/v), 107 mg (20%) of pure **2a** was obtained; mp >310 °C; <sup>1</sup>H NMR (diluted solution) (CDCl<sub>3</sub>)  $\delta$  8.90 and 8.56 (ABq, 4H,  $J$  = 5 Hz), 8.73 (s, 2H), 8.20, 8.08, 8.04, 7.92, 7.88, 7.87 (6s, 12H), 7.15 (m, 10 H), 6.59 (s, 2H), 5.97 and 3.95 (ABq, 4H,  $J$  = 15.8 Hz), 5.50 and 3.72 (ABq, 4H,  $J$  = 15.8 Hz), 3.79 (s, 6H), 1.54, 1.52, 1.50 and 1.48 (4s, 72 H), -2.50 (s, 2H, NH); UV-vis (CHCl<sub>3</sub>)  $\lambda$ /nm: 441, 531, 568, 601, 650; FAB-MS (*m*-nitrobenzyl alcohol)  $m/z$  1678 (M + 2H)<sup>+</sup>.

**Quinone Porphyrin Clip 2b.** The same procedure was used as for **1b**. Purification was carried by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>), yield 90%; mp: >310 °C; <sup>1</sup>H NMR (diluted solution) (CDCl<sub>3</sub>)  $\delta$  8.92 and 8.57 (ABq, 4 H,  $J$  = 5 Hz), 8.86 (s, 2 H), 8.13 (s, 2 H), 8.08 (s, 2 H), 8.02 (s, 2 H), 7.92 (s, 2 H), 7.87 (s, 2 H), 7.77 (s, 2 H), 7.16 (m, 10 H), 6.57 (s, 2 H), 5.99 and 3.98 (ABq, 4 H,  $J$  = 15.8 Hz), 5.49 and 3.72 (ABq, 4 H,  $J$  = 15.8 Hz), 3.80 (s, 6 H), 1.52, 1.50, 1.48 and 1.41 (4s, 72 H); UV-vis (CHCl<sub>3</sub>)  $\lambda$ /nm: 421, 449, 530, 571, 615; FAB-MS (*m*-nitrobenzyl alcohol)  $m/z$  1738 (M + H)<sup>+</sup>; HRMS Calcd for C<sub>110</sub>H<sub>117</sub>N<sub>10</sub>O<sub>6</sub>Zn: 1737.845; Found: 1737.840.

**Bisclip-Porphyrin 3a.** In situ prepared compound **4b** (0.29 mmol) was refluxed with 100 mg (0.1 mmol) of porphyrin-tetraone **8** in CH<sub>2</sub>Cl<sub>2</sub> for 36 h. After cooling, the mixture was washed with water (3x), and the organic solvent was removed in vacuo. After column chromatography (CH<sub>2</sub>Cl<sub>2</sub>), monoreacted porphyrin and directed porphyrin **3a** were isolated. It was not possible to separate the S-shaped isomer from the C-shaped one (see text), leaving a mixture of the two isomers (56% yield); mp > 310 °C; <sup>1</sup>H NMR (diluted solution) (CDCl<sub>3</sub>)  $\delta$  8.57 and 8.54 (2s, 4H), 8.18 (m, 4H), 7.87 (m, 8H), 7.16 (m, 20H), 6.62 and 6.58 (2s, 4H), 5.90 and 3.93 (ABq, 8H,  $J$  = 15.8 Hz), 5.56, 5.54, and 3.90, 3.88 (2 ABq, 8H,  $J$  = 15.8 Hz), 3.75, 3.71 (2s, 24H), 1.52, 1.50, 1.48, and 1.41 (4s, 72 H), -2.50 (s, 2H, NH); UV-vis (CHCl<sub>3</sub>)  $\lambda$ /nm: 463, 540, 619, 673; FAB-MS

(*m*-nitrobenzyl alcohol)  $m/z$  2348 (M + H)<sup>+</sup>. HRMS Calcd for C<sub>148</sub>H<sub>155</sub>N<sub>16</sub>O<sub>12</sub>: 2348.201, Found: 2348.207.

**Bisclip-Zn-porphyrin 3b.** The same procedure was used as for **1b**. Purification was carried out by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>), total yield 60% after purification. The S-shaped and C-shaped isomers could be separated by column chromatography; Mp (both fractions): >310 °C; <sup>1</sup>H NMR (fraction 1, S-shape, dilute CDCl<sub>3</sub> solution)  $\delta$  8.57 (s, 4H), 8.14 (s, 4H), 7.87, 7.84, 7.83 (3s, 8H), 7.16 (m, 20H), 6.52 (s, 4H), 5.92 and 3.94 (ABq, 8H,  $J$  = 16 Hz), 5.50 and 3.75 (ABq, 8H,  $J$  = 16 Hz) 3.74, 3.66 (2s, 24H), 1.52, 1.50, 1.48 and 1.41 (4s, 72 H); <sup>1</sup>H NMR (fraction 2, C-shape, dilute CDCl<sub>3</sub> solution)  $\delta$  8.56 (s, 4H), 8.14 (s, 4H), 7.86 (s, 8H), 7.16 (m, 20H), 6.52 (s, 4H), 5.91 and 3.93 (ABq, 8H,  $J$  = 16 Hz), 5.50 and 3.78 (ABq, 8H,  $J$  = 16 Hz), 3.74, 3.68 (2s, 24H), 1.52, 1.50, 1.48, and 1.41 (4s, 72 H) (peaks at 6.52, 5.50 and 3.68 are slightly broadened). UV-vis (CHCl<sub>3</sub>)  $\lambda$ /nm: 473, 560, 586, 610, 630, 660; FAB-MS (*m*-nitrobenzyl alcohol)  $m/z$  2410 (M + H)<sup>+</sup>. HRMS Calcd for C<sub>148</sub>H<sub>153</sub>N<sub>16</sub>O<sub>12</sub>Zn: 2410.115; Found: 2410.120.

**Dinitro Compound 7a.** A mixture of 420 mg (0.714 mmol) of **6** and 300 mg (1.57 mmol) of *p*-toluenesulfonic acid in 10 mL of 1,2-dichloroethane was refluxed under nitrogen over molecular sieves for 10 min. To this solution was added 155 mg (1.4 mmol) of 1,4-dihydroxybenzene, and refluxing was continued for 16 h. The solvent was removed in vacuo, and the solid was dissolved, in 10 mL of DMSO. To this solution were added 50 mg Cu<sub>2</sub>Cl<sub>2</sub> and 0.6 mL of pyridine and air was bubbled through the solution for 2 h. The suspension was poured into 50 mL of aqueous 1 N HCl and the product was extracted with 50 mL of CHCl<sub>3</sub>. The organic layer was washed with aqueous 1N HCl, aqueous 5% NH<sub>3</sub> (2x) and with water, and concentrated in vacuo. After purification, 260 mg (54%) of pure **7a** was obtained. Mp: >310 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.95–7.20 (m, 10H), 6.75 (s, 2H), 5.52 and 3.85 (ABq, 4H,  $J$  = 16 Hz), 5.50 and 3.70 (ABq, 4H,  $J$  = 16 Hz), 4.15 (s, 6H). This compound was directly used for further synthesis.

**Dimethoxyquinoxaline Porphyrin 13a.** 2,3-Diamino-1,4-dimethoxybenzene was obtained after reduction of 40 mg (0.175 mmol) of 2,3-dinitro-1,4-dimethoxybenzene by stirring the latter compound in 5 mL of THF and 5 mL of MeOH in the presence of TEAF and Pd/C.<sup>9</sup> The Pd/C was filtered off under nitrogen, and the solvent was evaporated in vacuo. Subsequently 10 mL of CH<sub>2</sub>Cl<sub>2</sub> and 80 mg of porphyrin-dione **5b** were added, and the mixture was refluxed for 3 h. over molecular sieves (3 Å). After cooling, the solution was washed with water (3x) and the organic solvents were removed in vacuo. After column chromatography (CHCl<sub>3</sub>/hexane, 1:1 v/v), 31 mg (35%) of pure **13a** was obtained; mp >310 °C; <sup>1</sup>H NMR (diluted) (CDCl<sub>3</sub>)  $\delta$  8.96 and 8.93 (ABq, 4H,  $J$  = 5 Hz), 8.77 (s, 2H), 8.04, 8.01, 7.87, 7.80 (4s, 12H), 7.01 (s, 2H), 3.82 (s, 6H), 1.54, 1.52, 1.50, and 1.48 (4s, 72 H), -2.47 (s, 2H, NH); UV-vis (CHCl<sub>3</sub>)  $\lambda$ /nm: 438, 531, 568, 600, 650; FAB-MS (*m*-nitrobenzyl alcohol)  $m/z$  1226 (M + H)<sup>+</sup>.

**Dimethoxyquinoxaline Zn-Porphyrin 13b.** The same procedure was used as for **1b**. Purification was carried out by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>), yield 90%; mp >310 °C; <sup>1</sup>H NMR (diluted) (CDCl<sub>3</sub>)  $\delta$  8.98 and 8.82 (ABq, 4H,  $J$  = 5 Hz), 8.81 (s, 2H), 8.05 (d, 4H,  $J$  = 2 Hz) 7.97 (d, 4H,  $J$  = 2 Hz), 7.66 (t, 2H,  $J$  = 2 Hz), 7.50 (t, 2H,  $J$  = 2 Hz), 7.56 (s, 2H), 3.82 (s, 6H), 1.54, 1.52, 1.50 and 1.48 (4s, 72 H); UV-vis (CHCl<sub>3</sub>)  $\lambda$ /nm: 412, 447, 530, 572, 615; FAB-MS (*m*-nitrobenzyl alcohol)  $m/z$  1289 (M)<sup>+</sup>. Anal. Calcd for C<sub>84</sub>H<sub>100</sub>N<sub>6</sub>O<sub>2</sub>: C, 82.31; H, 8.22; N, 6.86. Found: C, 82.45; H, 8.29; N, 6.65.

The two side products with a double bond as connection between the side-wall of the clip and the diphenylglycoluril framework had the following physical properties:

**Zn-porphyrin clip 9:** mp: >310 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.93 and 8.58 (ABq, 4H,  $J$  = 5 Hz), 8.87 (s, 2H), 8.16 (s, 2H), 8.13 (s, 2H), 8.09 (s, 2H), 8.02 (s, 2H), 7.92 (s, 2H), 7.87 (s, 2H), 7.78 (s, 2H), 7.16 (m, 5H), 7.05 (m, 5H), 6.67 (s, 2H), 6.16 and 3.98 (ABq, 4 H,  $J$  = 15.8 Hz), 4.07 (s, 6 H), 1.52, 1.50, 1.48 and 1.41 (4s, 72 H); UV-vis (CHCl<sub>3</sub>)  $\lambda$ /nm: 421, 449, 530, 571, 615; Field Desorption  $m/z$  1736 (M + H)<sup>+</sup>; HRMS Calcd for C<sub>110</sub>H<sub>115</sub>N<sub>10</sub>O<sub>6</sub>Zn: 1735.829; Found: 1735.820.

**Clip 12:** mp: >310 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.12 (s, 2H), 7.16 (m, 5H), 6.90–7.10 (m, 5H), 6.87 (s, 2H, ArH), 6.69 (s, 2H), 5.78 and 3.84 (ABq, 4H, *J* = 16 Hz), 3.89 (s, 6H). FAB-MS (*m*-nitrobenzyl alcohol) *m/z* 587 (M + H)<sup>+</sup>.

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**Supporting Information Available:** <sup>1</sup>H NMR peak assignments for all compounds. This material is available free of charge on the Internet at <http://pubs.acs.org>.

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