Pergamon

Tetrahedron Vol. 51, No. 12, pp. 3535-3548, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4020/95 $9.50+0.00

0040-4020(95)00097-6

Novel Biomimetic Models for Photosynthesis: Porphyrins Covalently Linked to Redox-Active Crown Ether Quinones

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Abstract: The synthesis of biomimetic photosynthetic model compounds, composed of 5,10,15-triphenylporphyrins covalently linked to redox active crown ether quinones *via* different bridges, is described. Using the zinc complex with the flexible *butylene* spacer in non polar solvents backfolding of the crown ether quinone over the porphyrin plane is observed by ^{1}H NMR chemical shift studies. This conformational effect is supported by molecular modelling calculations. The backfolding is induced by complexation of the acceptor with the central atom since it is not observed in the metal free-base porphyrin derivative. Due to steric constraints the zinc porphyrin *cyclohexylene* crown ether quinones lack this backfolding. Cyclic voltammetry measurements show a significant shift of the reduction potential of the quinone crown ether moiety in the presence of alkali metal cations.

INTRODUCTION

The donor and acceptor pigments of the photosynthetic reaction centers are fixed at precise distances and relative orientations by the protein matrix. For studies of photoinduced electron transfer (ET) reactions between these primary reactants porphyrin quinones (P-Q's) have widely been used as biomimetic model compounds.[1-3] P-Q's with flexible spacers are useful for studying conformational preferences in anisotropic media, such as (reversed) micelles, and nematic phases of liquid crystals. In these systems the anisotropic host molecules may dictate energetically favored conformations to be adopted.[4] On the other hand, rigidly linked derivatives with well-defined geometrical arrangements are necessary for studying the dependence of the ET properties on structural and electronic parameters. Previously, we have shown by time-resolved fluorescence spectroscopy that model compounds with a porphyrin donor and a quinone acceptor, linked, e.g., *via* a cyclohexylene bridge, exhibit fast singlet ET on the picosecond time scale at ambient temperature.[5] On cooling, spin selective singlet triplet intersystem crossing (ISC) becomes competitive and triplet ET from the excited porphyrin to the quinone moiety can be observed by time-resolved EPR spectroscopy, allowing unambiguous detection of the charge-separated transient radical pair in the triplet state.[6] In recent years well-defined structures of model systems using other than covalent bonds have been reported. Specifically, the quinone was attached to the porphyrin *via* hydrogen bridges using the Watson-Crick-base pairing concept.[7]

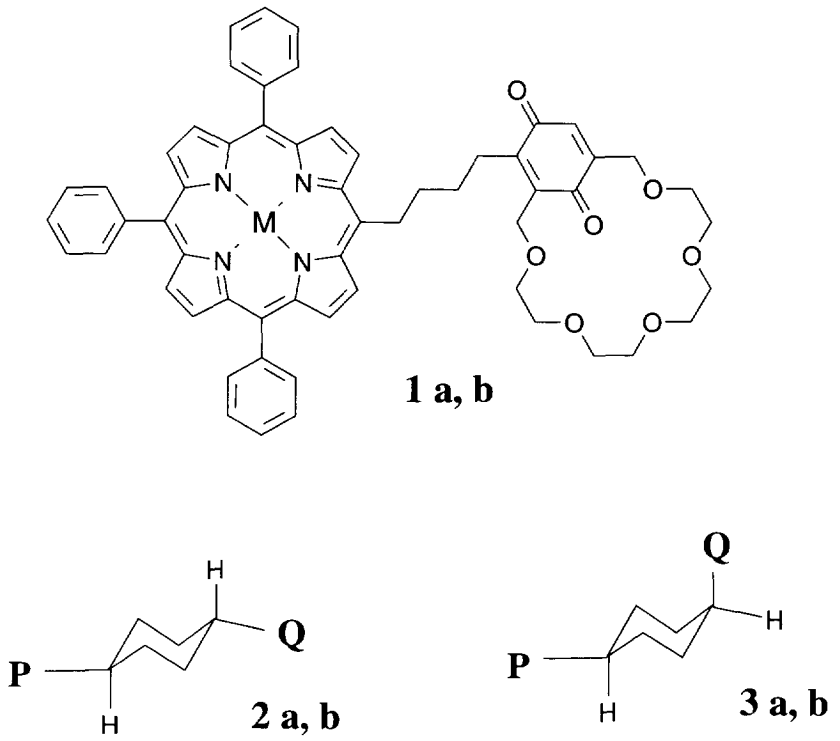
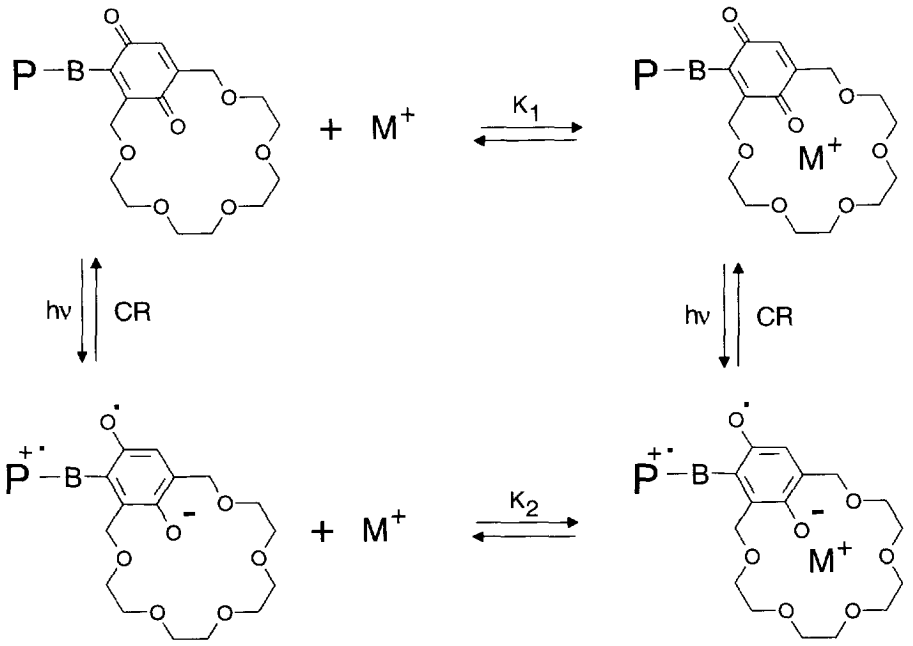


Figure 1. Structures of model compounds (**a**: free base porphyrin, **b**: porphyrin zinc complex, **P**: triphenylporphyrin, **Q**: quinone crown).

Since one of the factors that governs effective ET in these systems are the redox potentials of donor and acceptor (and thereby the driving force ΔG), we have synthesized model compounds with electron donating substituents, e.g., methoxy plus methyl (ubiquinone-type)[8] or electron withdrawing substituents trifluoromethyl plus bromine[9] at the quinone fragment. In this paper we want to present another approach of supramolecular devices, i.e., the synthesis of porphyrins covalently linked to crown ether substituted quinones (molecules **1-3** in Figure 1). Recently, the synthesis and redox properties of empty and alkali metal complexed crown ether quinones were reported.[10] Here we use such a system as the acceptor site of the P-Q's. Whereas compounds **1** represent crown P-Q's with flexible spacers, **2** and **3** are fairly rigid due to the steric constraints introduced by the cyclohexylene bridge.

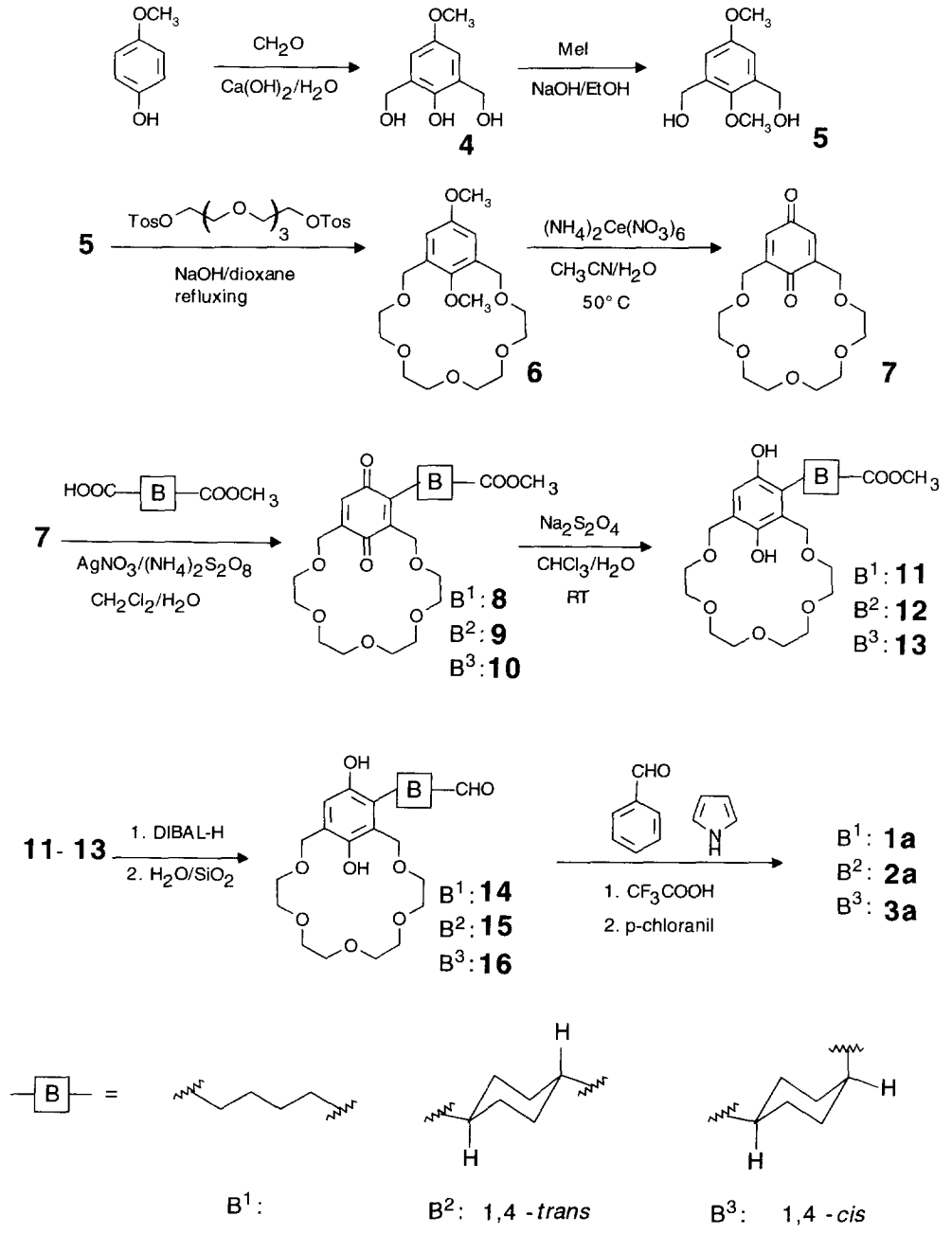
The underlying philosophy is to *load* the crown with different cations, thereby tuning the reduction potential of the quinone and thus the free energy ΔG of the ET. Furthermore, after exciting the porphyrin donor, the stored reducing potential in the charge-separated state may be used to enhance the binding constant of the crown ether with an alkali metal cation (see Scheme 1).[11-13]



Scheme 1. Binding enhancement of the semiquinone radical anion with alkali metal cation. P: porphyrin; B: bridge; M^+: alkali metal cation; CR: charge recombination; K_1: binding constant of the neutral molecule; K_2: binding constant of the charge-separated radical pair state.

RESULTS AND DISCUSSION

Syntheses: The reaction pathway is shown in Scheme 2. Compound **5** was prepared by hydroxymethylation of *p*-methoxyphenol followed by methylation in aqueous basic solution.[14] After reaction of **5** with tetraethyleneglycol-di-*p*-tosylate in dioxane with NaOH, dimethoxyxylyl crown ether **6** was obtained in 50% yield. Demethylation and subsequent oxidation of **6** with ammonium cerium (IV) nitrate produced the benzoquinone crown ether **7** in 74% yield. Radical alkylation of **7** was performed by oxidative decarboxylation of adipic acid monomethyl ester or 1,4-cyclohexyl dicarboxylic acid monomethyl ester with ammonium peroxodisulfate and silver nitrate as the catalyst,[15] to give the alkylated quinones **8-10** in 25-50% yield. After reduction of the quinones to their hydroquinones (**11-13**) in water/chloroform with $Na_2S_2O_4$, diisobutylammoniumhydride (DIBAL-H) was used to reduce the carboxylic acid methyl esters in diethyl ether at approximately -90°C to the corresponding aldehydes. Alternatively, the ester can be reduced to the corresponding benzylic alcohol followed by oxidation with pyridinium chlorochromate (PCC) to yield the aldehyde.[16] Condensation of (**14-16**) with benzaldehyde and pyrrole in a



Scheme 2. Synthetic procedures of model compounds.

ratio of 1:3:4 in dichloromethane using trifluoroacetic acid as catalyst, followed by oxidation with *p*-chloranil and purification by repetitive chromatography yielded the target compounds **1a-3a** (total yield 4-7%). The zinc complexes were prepared almost quantitatively by reaction of the free bases with zinc acetate in methanol/chloroform.

Table 1. δ_H (ppm) Values of Model Compounds in $CDCl_3$

	1a	**1b**	**2a**	**2b**	**3a**	**3b**
porphyrin N-**H**	-2.78 (br.s)		-2.66 (br.s)		-2.66 (br.s)	
porphyrin-12,13,17,18-**H**	8.79 (br.s)	8.79 (br.s)	8.78 (AB) *J* = 4.56 Hz 8.80 (AB) *J* = 4.68 Hz	8.87 (AB) *J* = 4.54 Hz 8.89 (AB) *J* = 4.56 Hz	8.78 (AB) *J* = 4.72 Hz 8.80 (AB) *J* = 4.73 Hz	8.87 (AB) *J* = 4.67 Hz 8.89 (AB) *J* = 4.68 Hz
porphyrin-2,8-**H**	8.92 (d) *J* = 4.50 Hz	8.97 (d) *J* = 4.59 Hz	8.91 (d) *J* = 4.60 Hz	9.02 (d) *J* = 4.50 Hz	8.91 (d) *J* = 4.80 Hz	9.01 (d) *J* = 4.58 Hz
porphyrin-3,7-**H**	9.48 (d) *J* = 4.71 Hz	9.55 (d) *J* = 4.71 Hz	9.73 (br.s)	9.87 (br.s)	9.65 (d) *J* = 4.85 Hz	9.75 (d) *J* = 4.70 Hz
phenyl *m*-, *p*-**H**	7.77 (m)	7.76 (m)	7.76 (m)	7.78 (m)	7.78 (m)	7.78 (m)
phenyl *o*-**H**	8.20 (m)	8.18 (m)	8.19 (m)	8.21 (m)	8.20 (m)	8.21 (m)
butyl-**H**	1.89 (quint) 2.65 (m) 5.07 (t) *J* = 7.76 Hz	1.54 (quint) 2.29 (t) *J* = 7.61 Hz 2.57 (quint) 5.16 (t) *J* = 6.88 Hz				
cyclohexyl-**H**			2.17 (d) *J* = 11.17 Hz 2.73 (q) 2.88 (d) *J* = 11.92 Hz 3.25 (q) 3.57 (m) 5.41 (t)	2.12 (d) *J* = 12.09 Hz 2.71 (q) 2.91 (d) *J* = 13.07 Hz 3.20 (br.s) 3.52 (m) 5.51 (t)	2.17 (hex) *J* = 6.54 Hz 2.72 (m) 3.52 (m) 3.63 (m) 5.48 (m)	2.09 (hex) *J* = 6.73 Hz 2.62 (m) 2.72 (hex) *J* = 6.90 Hz 3.26 (m) 3.53 (m) 5.57 (m)
quinone-**H**	6.72 (s)	6.42 (s)	6.82 (t)	6.23 (t)	6.86 (t) *J* = 1.81 Hz	6.23 (s)
quinone methyl-**H**	4.24 (s) 4.57 (s)	3.47 (s) 4.03 (s)	4.71 (d) *J* = 1.65 Hz 4.79 (s)	4.04 (s) 4.56 (s)	4.72 (d) *J* = 1.66 Hz 4.74 (s)	3.97 (s) 4.43 (s)
crown ether-**H**	3.25 (t) *J* = 4.27 Hz 3.33 (t) *J* = 4.10 Hz 3.37 (t) *J* = 4.25 Hz 3.48 (m) 3.63 (t) *J* = 3.60 Hz 3.74 (t) *J* = 3.75 Hz	1.15 (t) 1.32 (br.s) 1.41 (t) 1.86 (t) 2.04 (br.s) 2.32 (t) 3.07 (br.s) 3.30 (t)	3.62 (m) 3.72 (m) 3.83 (t) 3.88 (m)	3.28 (m) 3.45 m) 3.62 (m)	3.62 (m) 3.72 (t) *J* = 4.03 Hz 3.83 (t) *J* = 4.04 Hz 3.86 (td) *J*=5.71, 2.00 Hz	3.14 (br.s) 3.20 (m) 3.33 (m) 3.48 (m)

The structures of the target compounds were confirmed by FAB mass spectroscopy and detailed stereochemical analyses using 500 MHz ^{1}H NMR spectroscopy. Comparison of the proton signals of the cyclohexylene moiety with those of the previously published, related *trans* and *cis* cyclohexylene linked P-Q's lacking the crown substituent,[2] yielded the results shown in Table 1.

The NMR data of the bridging cyclohexylene part of the *trans* compound **2a** with both redox active components equatorial reveal, as expected, a chair conformation of the cyclohexane ring and are similar to those of the corresponding P-Q without the crown substituent. On the other hand, the ^{1}H NMR spectrum of the *cis* compound **3a** is different from that of the crown free *cis* analogue. Rather, it is related to that of a previously published *cis* cyclohexylene linked porphyrin-ubiquinone.[8] In these molecules the space-filling triphenylporphyrin moiety is equatorial and thus dictates the quinone to be in the axial position. However, in **3a** the crown ether quinone part is too bulky to adopt the undisturbed axial position. Here, the cyclohexylene is no longer in the chair conformation and a twist-type geometry is favored due to steric effects. The crown ether protons are found between 3.62 ppm and 3.86 ppm; unambiguous assignment of the signals to the different crown positions has not been achieved yet, except for the two α-methylene protons.

Insertion of zinc into the porphyrin parts of the *trans* and *cis* crown P-Q's **2a** and **3a** results only in small signal shifts in the ^{1}H NMR spectra. The NMR spectrum and thereby the resulting structure of the butylene linked free base crown P-Q **1a** is in good agreement with the comparable P-Q compound lacking the crown ether substituent.[2] The signals between 3.25 ppm and 3.74 ppm can be assigned to the crown ether protons. For this part of the spectrum no significant difference is found in comparison with the signals of the corresponding positions of the precursor compound **8**.

In contrast to the data discussed so far, introduction of zinc into the porphyrin moiety of the butylene linked crown P-Q **1a** (to give **1b**) results in a considerable high-field shift (in $CDCl_3$ up to 1.15 ppm) of the crown ether proton signals. The high-field shift of the quinone proton is less pronounced. It is reasonable to consider coordination of the crown ether with the porphyrin center atom through "backfolding" of the flexible butylene crown ether quinone tail. A series of control experiments showed that the observed interaction must be *intramolecular*. For example, the spectrum of a 1:1 mixture of the free base crown P-Q **1a** and ZnTPP is a superposition of the spectra of the constituents. In more polar solvents (DMF) the NMR shifts are smaller, indicating a weaker interaction of crown and zinc due to competition of the solvent molecules in the zinc complexation. Unfortunately, the distances between porphyrin and crown protons are too large to give a significant NOE effect in ^{1}H NMR measurement.

The structure shown in Figure 2 is the result of a force-field calculation using the molecular modelling program (QUANTA/CHARMm 3.3); the backfolded conformation is about 60 kJ/mol more stable than the stretched one. These results are in good agreement with the NMR results.

We also obtained evidence for the backfolding by steady-state and time-resolved EPR experiments (in liquid crystals).[4,17] Without going into the details which are reported in the references cited, these results showed: (a) As already mentioned, the P-Q's show photoexcited singlet ET at ambient temperatures and, on cooling to obtain a highly viscous solution, ISC is observed followed by triplet ET. On cooling further

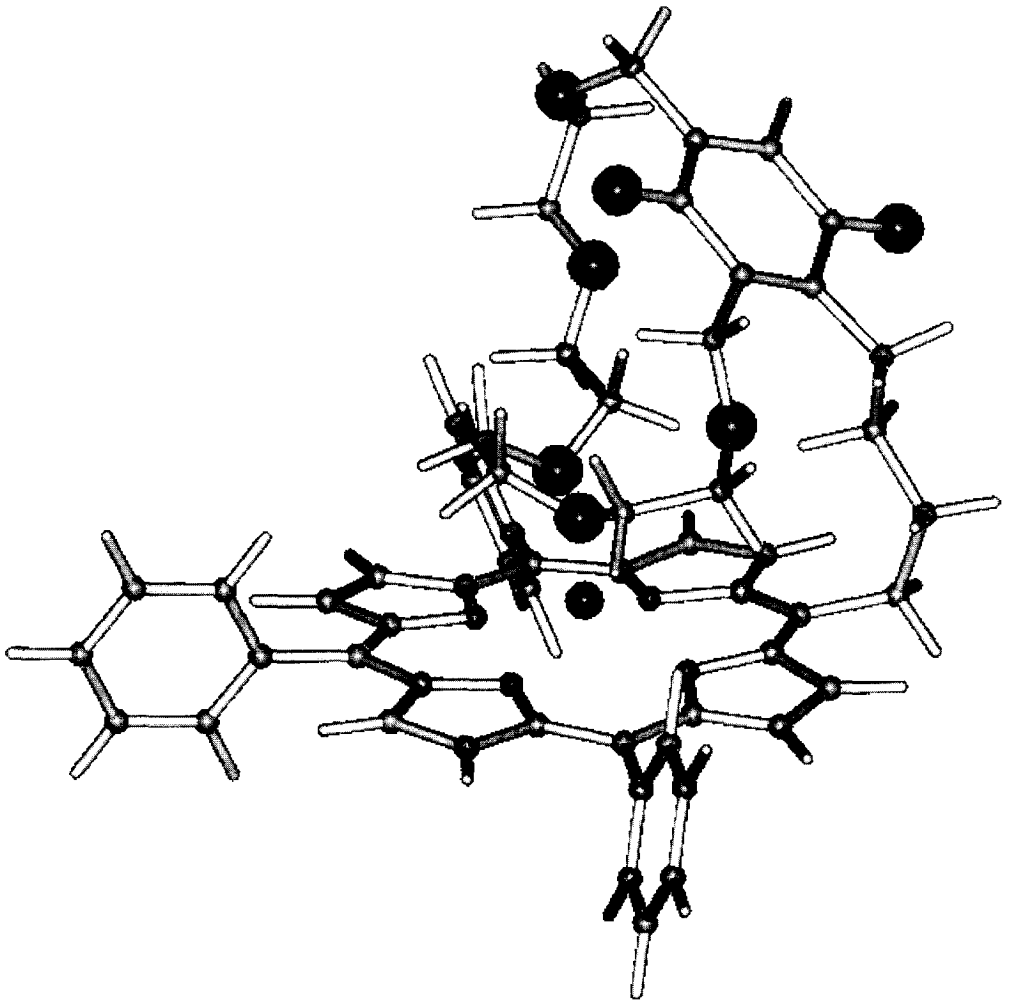


Figure 2. Molecular model of **1b** (QUANTA/CHARMm 3.3). Note the backfolding of the crown ether quinone.

to the solid state, ET is suppressed and the porphyrin triplet state is detected by EPR spectroscopy under *in situ* illumination. However, crown P-Q **1b** does not show any porphyrin triplet signal under these conditions, indicating that singlet ET is still the dominant decay channel due to the small distance between porphyrin donor and quinone acceptor.[17] (b) The charge-separated state of **1b**, generated in liquid crystals under *in situ* laser irradiation, could be observed by time-resolved EPR techniques. The zero field splitting parameters, deduced from the EPR spectra, show not only a stretched but a folded conformation as well.[4]

Cyclic Voltammetry. In ET studies, knowledge of the energetics of the reaction is of utmost importance, e.g., for determining theoretical ET rates. The free reaction enthalpy ΔG_{ET} is given by the difference of the energies of the initial and terminal states of the reaction. We have determined the one-electron redox potentials of the oxidation of the porphyrin [P-Q]/[$P^{\bullet+}$-Q] and the reduction of the quinone [P-Q]/[$P\text{-}Q^{\bullet-}$].

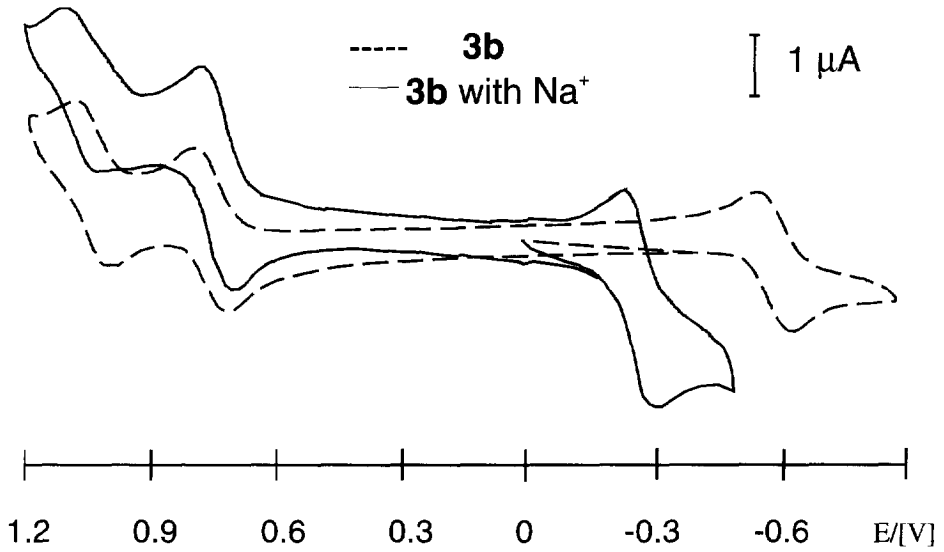


Figure 3. Cyclic voltammograms of crown P-Q **3b**. Note the influence of sodium insertion on the reduction potential of the quinone fragment.

Table 2: First Redox Potentials (± 20 mV) of the Porphyrin and Quinone Moieties of the Compounds in Dichloromethane/Acetonitrile (90:10).

Compound	E^{ox}(P)/mV	E^{red}(Q)/mV	ΔG_{ET}/eV
1b	731	-577	0.75
1b with $NaClO_4$	727	-265	1.09
2b	755	-588	0.72
2b with $NaClO_4$	740	-290	1.05
3b	760	-598	0.72
3b with $NaClO_4$	732	-278	1.05

ΔG_{ET} is the free enthalpy for the charge separation. ΔG_{ET} was calculated using Equation $\Delta G_{ET} = E^{ox} - E^{red} - E\,(S_0 \rightarrow S_1)$ neglecting solvent correction, E^{ox} is the one-electron oxidation potential of the donor, E^{red} is the one-electron reduction potential of the acceptor; $E\,(S_0 \rightarrow S_1)$ is the excited state energy.

From these measurements it turned out that the redox steps of porphyrin and quinone are reversible. As an example, in Figure 3 the cyclovoltammograms of crown P-Q **3b** with and without sodium ion are compared. Whereas the porphyrin waves are similar, reduction of the quinones occurs at significantly different potentials, i.e., complexation with sodium cation results in a lower (smaller negative) reduction potential. The smaller the reduction potential of the quinone, the lower the energy of the charge-separated state and the larger the free enthalpy ΔG_{ET} of the reaction (Table 2). This result establishes the assumption that introduction of the crown substituent with its potential to complex metal ions offers an alternative way to vary the acceptor strength and concomitant the ET properties.

EXPERIMENTAL

Instrumentation. ^{1}H NMR spectra were recorded on a Bruker AM 500 or AM 270 NMR spectrometer; absorption spectra (UV/VIS) were recorded on a Perkin-Elmer λ9 spectrometer. Mass spectrometric measurements were carried out on Varian MAT 711 spectrometer. Equipment and conditions for HPLC separation: Knauer Modulsystem, Pump 64, MPLC, UV-Detector at 420 nm, Column Schreiber, Absorbance Nucleosil (Macherey-Nagel). Analytical HPLC: 5 µm Nucleosil 50, 4x250 mm; Preparative HPLC: 5 µm Nucleosil 50, 32x250 mm. Eluent: n-hexane/ethyl acetate (50:50). Cyclic voltammetric measurements were conducted in a mixture of dichloromethane and acetonitrile (90:10) at a platinum electrode, ferrocene as internal standard, reference electrode SCE.

Chemicals. DIBAL-H (1.0 M solution in n-hexane or in dichloromethane), adipic acid monomethyl ester (99%) and tetraethylene glycol-di-*p*-tosylate (97%) were obtained from Aldrich Chemical Co. and used without further purification. Alkali metal tosylate salts were prepared by reaction of the alkali metal carbonates with *p*-toluenesulfonic acid. After recrystallization from ethanol/water (90:10) tosylates were dried in vacuum at 50°C over silica gel.

Solvents. All solvents were distilled and stored under argon. Dichloromethane was distilled over P_2O_5. Pyrrole was distilled from calcium hydride and stored over argon. N,N-Dimethylformamide (DMF) was stirred over BaO, decanted, and distilled under reduced pressure.

Zinc Insertion. About 30 mg of the free base crown P-Q were dissolved in 100 ml chloroform and mixed with 5 ml of a saturated methanolic solution of $Zn(OAc)_2$. The metallation was completed (TLC control) after warming the solution for 5 minutes to 60°C. After cooling, the solution was diluted with 100 ml chloroform and washed several times with water. Subsequently the solvent was removed under reduced pressure. The zinc crown P-Q's were crystallized from n-hexane/dichloromethane in almost quantitative yield.

1,4-Dimethoxy-2,6-xylyl-18crown5 (6). 10.00 g (50.51 mmol) of compound **5**[14] and 25.70 g (50.51 mmol) tetraglycol-di-tosylate were dissolved in 500 ml dioxane; 16.00 g (392.00 mmol) sodium hydroxide powder were added under stirring and the solution was refluxed for eight h. After cooling to room temperature, the solution was filtered. The filtrate was concentrated under reduced pressure yielding a yellow oil. The residue was dissolved in 300 ml dichloromethane and after shaking with 300 ml water, the organic phase was separated and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a yellow oil. Further purification of the crude product was achieved by flash chromatography on silica gel 60

with dichloromethane/ethanol (50:1) as eluent. Crystallization of the colorless viscous oil obtained from n-hexane/dichloromethane (10:1) yielded 8.9 g (50%) colorless crystals, m.p. 93°C. ^{1}H NMR (250 MHz, $CDCl_3$), δ(ppm) = 3.50 (m, 8H, crown-CH_2), 3.64 (m, 8H, crown-CH_2), 3.81 (s, 3H, CH_3), 4.08 (s, 3H, CH_3), 4.59 (s, 4H, α-CH_2), 6.80 (s, 2H, quinone-H). Anal. Calcd. for $C_{18}H_{28}O_7$: C 60.0, H 7.86; found C 60.33, H 7.68.

1,4-Benzoquinone-2,6-18crown5 (7). A solution of 5.00 g (14.04 mmol) of **6** in 60 ml acetonitrile and a solution of 19.20 g (34.65 mmol) ceric ammonium nitrate in 60 ml water were mixed and stirred at 50°C for 40 min. After cooling to room temperature, the mixture was diluted with 200 ml dichloromethane and 100 ml water. The organic phase was separated, washed with water, dried over anhydrous sodium sulfate and evaporated. The residue (yellow oil) was purified by column chromatography on silica gel 60 with ethyl acetate as eluent. Crystallization from n-hexane gave 3.2 g (70%) of yellow crystals, m.p. 76.5°C. ^{1}H NMR (250 MHz, $CDCl_3$), δ(ppm) = 3.54 (m, 8H, crown-CH_2), 3.62 (m, 4H, crown-CH_2), 3.75 (m, 4H, crown-CH_2), 4.53 (s, 4H, α-CH_2), 6.72 (s, 2H, quinone-H). Anal. Calcd. for $C_{16}H_{22}O_7$: C 58.88, H 6.74; found: C 58.50, H 6.61.

2-[4-(Methoxycarbonyl)butyl]-1,4-benzoquinone-3,5-18crown5 (8). 3.70 g (11.35 mmol) benzoquinone crown **7** and 3.69 g (22.65 mmol) adipic acid monomethyl ester, dissolved in 50 ml dichloromethane, were mixed with a solution of 1 g $AgNO_3$ in 20 ml water and refluxed. Under vigorous stirring a solution of 5.20 g (22.60 mmol) ammonium peroxodisulfate in 20 ml water was added dropwise into the reaction mixture during 90 min. After completion of the addition the mixture was refluxed for an additional 20 min. The reaction mixture was cooled to room temperature and the organic phase was diluted with dichloromethane, separated, neutralized by washing several times with water and dried over anhydrous sodium sulfate. After evaporating the solvent under reduced pressure, a yellow oil of the desired monosubstituted product was obtained which contained starting compound **7** and bisubstituted products. After column chromatography on silica gel 60 (0.040-0.063 mm) with dichloromethane/acetone (70:30) as the eluent, 1.2 g of the monosubstituted product **8** could be separated as a yellow oil (yield 25%).
^{1}H NMR (250 MHz, $CDCl_3$), δ(ppm) = 1.46 (quint, 2H, butylene-CH_2), 1.68 (quint, 2H, butylene-CH_2), 2.32 (t, 2H, butylene-CH_2), 2.56 (t, 2H, butylene-CH_2), 3.56 (m, 8H, crown-CH_2), 3.62 (m, 4H, crown-CH_2), 3.68 (s, 3H, ester-CH_3), 3.76 (m, 4H, crown-CH_2), 4.44 (s, 2H, α-CH_2), 4.63 (d, 2H, α-CH_2), 6.74 (t, 1H, quinone-H); MS (EI, 70 eV): *m/z* = 440 (14%, M^+); 246 (96%), 89 (85%), 45 (100%). Anal. Calcd. for $C_{22}H_{32}O_9$: C 60.00, H 7.27; found: C 59.72, H 7.18.

4-(3,6-Dihydroxy-2,4-xylyl-18crown5)pentaneacid methylester (11). A solution of 3.00 g (6.82 mmol) of **8** in 200 ml chloroform was shaken with 200 ml of a 5% aqueous sodium hyposulfite solution until the organic phase became colorless. The organic phase was washed several times with water, dried over anhydrous sodium sulfate and evaporated. Purification by column chromatography on silica gel using dichloromethane/methanol (98:2) as eluent yielded 2.4 g (80%) colorless viscous oil of **11**.
^{1}H NMR (250 MHz, $CDCl_3$), δ(ppm) = 1.52 (quint, 2H, butylene-CH_2), 1.68 (quint, 2H, butylene-CH_2), 2.36 (t, 2H, butylene-CH_2), 2.67 (t, 2H, butylene-CH_2), 3.67 (m, 16H, crown-CH_2), 4.57 (s, 2H, α-CH_2),

4.69 (s, 2H, α-CH_2), 6.62 (s, 1H, hydroquinone-H); MS (EI, 70 eV): *m/z* = 442 (72%, M^+); 250 (17%), 89 (61%), 45 (100%). Anal. Calcd for $C_{22}H_{34}O_9$: C 59.69, H7.69; found: C 59.44, H 7.59.

4-(3,6-Dihydroxy-2,4-xylyl-18crown5)pentanealdehyde (14). 2.80 g (6.33 mmol) of **11** were dissolved in 500 ml anhydrous diethyl ether. The solution, protected by argon gas, was cooled to -90°C (acetone/liquid nitrogen). Under vigorous stirring 22 ml (22 mmol) diisobutyl aluminium hydride (1M solution in n-hexane) was dropped into the solution *via* a syringe while the temperature was kept below -80°C. After 30 min. stirring, 30 g silica gel loaded before with 15 ml water was added to the reaction mixture under vigorous stirring. The temperature of the reaction mixture was allowed to rise to room temperature. The reaction mixture was filtered through a short silica gel column (2 cm) and the silica gel was eluted with a mixture of dichloromethane and acetone (70:30). After evaporating the solvent the crude product was purified by column chromatography on silica gel using dichloromethane and acetone (70:30) as eluent; 2.2 g (85% yield) of a pale viscous oil were obtained.
^{1}H NMR (250 MHz, $CDCl_3$), δ(ppm) = 1.53 (quint, 2H, butylene-CH_2), 1.71 (quint, 2H, butylene-CH_2), 2.47 (t, 2H, butylene-CH_2), 2.68 (t, 2H, butylene-CH_2), 3.67 (m, 16H, crown-CH_2), 4.57 (s, 2H, α-CH_2), 4.68 (s, 2H, α-CH_2), 6.55 (s, 1H, quinone-H), 9.76 (s, 1H, aldehyde-H); MS (EI, 70 eV): *m/z* = 412 (87%, M^+), 328 (16%), 218 (19%), 89 (76%), 45 (100%). Anal. Calcd for $C_{21}H_{32}O_8$: C 61.13, H 7.76; found: C 61.09, H 7.67.

2-[4-(Methoxycarbonyl)cyclohexyl]-1,4-benzoquinone-3,5-18crown5 (*trans/cis* mixture) (9 + 10). 6.00 g (18.40 mmol) benzoquinone crown ether **7** and 8.40 g (45.16 mmol) 1,4-cyclohexane dicarboxylic acid monomethyl ester (*trans/cis* mixture ca 1:1) were dissolved in 40 ml dichloromethane and mixed with 1.2 g $AgNO_3$ dissolved in 30 ml water. Under vigorous stirring at room temperature, a solution of 10.20 g (44.47 mmol) ammonium peroxodisulfate in 30 ml water was dropped into the reaction mixture in about 60 min. When the addition was completed, the reaction mixture was gently refluxed for 45 min. After cooling to room temperature the separated organic phase was washed with water four times and dried over anhydrous sodium sulfate. A column chromatographic separation (silica gel, eluent ethyl acetate, R_f = 0.75) gave 5.5 g (65% yield) of a yellow oil (*trans* and *cis* mixture).
^{1}H NMR (250 MHz, $CDCl_3$), δ(ppm) = 1.54-1.71 (m, 4H, cyclohexane-H), 2.05-2.24 (m, 4H, cyclohexane-H), 2.43 (m, 1H, cyclohexane-H), 2.92 (m, 1H, cyclohexane-H), 3.56-3.66 (m, 16H, crown-CH_2), 3.68 [s, 1.5H, CH_3 (*trans*)], 3.77 [s, 1.5H, CH_3 (*cis*)], 4.49 (d, *J*=3.39Hz, 2H, α-CH_2), 4.61 (s, 2H, α-CH_2), 6.66 (d, *J*=2.0Hz, 1H, quinone-H); MS (EI, 70 eV): m/z = 466 (14%, M^+), 435 (4%), 380 (7%), 272 (100%), 212 (45%). Anal. Calcd for $C_{24}H_{34}O_9$: C 61.72, H 7.28; found C 61.60, H 7.23.

4-(3,6-Dihydroxy-2,4-xylyl-18crown5)cyclohexane carboxylic acid methylester (*trans/cis* mixture) (12 + 13). The yellow oil mixture (**9** + **10**) obtained in the previous procedure was dissolved in 200 ml dichloromethane and shaken with 200 ml 10% aqueous sodium hyposulfite solution until the yellow color of the organic phase has disappeared. The separated organic phase was washed with water several times, dried over anhydrous sodium sulfate and evaporated to dryness. A colorless viscous oil was obtained which was used without further purification.

4-(3,6-Dihydroxy-2,4-xylyl-18crown5)cyclohexanealdehyde (*trans/cis* mixture) (15 + 16). 5.50 g (11.75 mmol) (**12 + 13**) were dissolved in 500 ml absolute ether under argon gas protection; the solution was cooled to -95°C (acetone/liquid nitrogen). Under vigorous stirring 42 ml of a DIBAL-H solution (1.0 M in methylene chloride) were carefully dropped into the cold solution with a syringe. The temperature of the reaction mixture was kept below -95°C. Stirring was continued for 30 minutes at -95°C, then the reaction was quenched with 30 g wet silica gel (shaken before use with 15 ml water) at -95°C. The reaction mixture was warmed to room temperature and filtered through a short silica gel column (2 cm). Subsequently the silica gel was eluted with a mixture of dichloromethane and acetone (70:30). After evaporating the solvent the crude product was purified by column chromatography on silica gel, using the same eluent. 4.0 g (78% yield) of a colorless viscous oil (**15 + 16**) were obtained consisting of 50% *trans* and 50% *cis* isomers (^{1}H NMR analysis).

^{1}H NMR (250 MHz, $CDCl_3$), δ(ppm) = 1.40-1.72 (m, 4H, cyclohexane-H), 2.17-2.50 (m, 5H, cyclohexane-H), 2.90 (m, 1H, cyclohexane-H), 3.68 (m, 16H, crown-CH_2), 4.55 (d, *J*=3.26 Hz, 2H, α-CH_2), 4.74 (s, 2H, α-CH_2), 6.45 (s, 0.5H, *cis* quinone-H), 6.47 (s, 0.5H, *trans* quinone-H), 9.65 (s, 0.5H, *cis* CHO), 9.84 (s, 0.5H, *trans* CHO); MS (EI, 70 eV): *m/z* = 438 (100%, M^+), 244 (65%), 195 (26%), 89 (67%), 45 (95%). Anal. Calcd. for $C_{23}H_{34}O_8$: C 62.97, H7.75; found: C 62.68, H 7.44.

5-[4-(3,6-Benzoquinonyl-2,4-18crown5)butyl]-10,15,20-triphenylporphyrin (1a). 1.03 g (2.50 mmol) of the aldehyde **14**, 0.80 g (7.50 mmol) benzaldehyde and 0.67 g (10.00 mmol) pyrrole were dissolved in 1000 ml anhydrous dichloromethane under argon protection. The solution was purged with argon for 20 min. Subsequently 0.77 ml (10 mmol) trifluoroacetic acid were added and the reaction mixture was stirred for 2 h. at room temperature. During this period the color of the solution changed from yellow to purple. 2.56 g (10.00 mmol) *p*-chloranil were added to the solution all at once; the color of the solution immediately changed to black. The oxidation was completed by refluxing for 2 h. and allowing the solution to stand overnight at room temperature. The reaction mixture was stirred together with 30 g basic aluminium oxide for several minutes and filtered over a short silica gel column. The adsorbance was thoroughly washed with dichloromethane until porphyrin was no longer detectable in the filtrate (TLC). Evaporation of the solvent gave a black solid, containing mainly TPP, the desired product and non characterized byproducts. **1a** was isolated by repetitive column chromatography on silica gel using a mixture (97:3) of dichloromethane/methanol as eluent. Crystallization from n-hexane/dichloromethane (95:5) yielded 92 mg (4%) violet crystals, m.p.= 226°C; ^{1}H NMR (500MHz, in $CDCl_3$) see Table 1. MS (FAB): m/z = 921 (87%, $[M+3H]^+$), 920 (65%, $[M+2H]^+$), 918 (10%, M^+), 579 (43%), 552 (100%), 539 (39%), 727 (13%).

Zinc complex (1b): m.p.>210°C (decomposition); ^{1}H NMR (500MHz, in $CDCl_3$) see Table 1. MS (FAB): *m/z* = 983(64%, $[M+3H]^+$), 981(25%, $[M+H]^+$), 789 (20%), 613 (100%), 600 (41%), $C_{58}H_{52}O_7N_4Zn$ requires 980.

5-[4-(3,6-Benzoquinonyl-2,4-18crown5)cyclohexyl]-10,15,20-triphenylporphyrin (*trans/cis* mixture) (2a + 3a). Reaction of 1.10 g (2.50 mmol) *trans/cis* mixture (**15 + 16**) and 0.80 g (7.50 mmol) benzaldehyde with 0.67 g (10.00 mmol) pyrrole, followed by oxidation with 2.56 g (10.00 mmol) *p*-chloranil and repetetive column chromatography (according to the procedure described above) gave

150 mg (7% yield) of the *trans/cis* mixture **(2a +3a)**. The ratio of the two diastereomers in the mixture is about 1 : 1 (500 MHz, ^{1}H NMR analysis). The mass spectrum (FAB) showed the molecular ion $(M+2H)^+$= 946, in accordance with the proposed structure ($C_{60}H_{56}O_7N_4$ requires 944).

Separation of the *trans* (2a) and *cis* (3a) isomers. The *trans* **2a** and *cis* **3a** isomers of the cyclohexylene linked porphyrin quinone crown ether were separated by preparative HPLC, using a *Nucleosil* column and n-hexane/ethyl acetate (50:50) as eluent .

5-[4(e)-(3,6-Benzoquinonyl-2,4-18crown5)cyclohex-(e)-yl]-10,15,20-triphenylporphyrin (2a). m.p.=168-170°C, ^{1}H NMR (500 MHz, $CDCl_3$) see Table 1. MS (FAB): m/z = 947 (100%, $[M+3H]^+$), 946 (98%, $[M+2H]^+$), 944 (24%, M^+), 577 (70%), 565 (55%), 539 (98%).
Zinc complex (2b): m.p.>230°C (decomposition); ^{1}H NMR (500 MHz, $CDCl_3$) see Table 1. MS(FAB): *m/z* = 1009 (67%, $[M+3H]^+$); 639 (51%), 626 (60%), 601 (100%), 561 (60%), $C_{60}H_{54}O_7N_4Zn$ requires 1006.

5-[4(a)-(3,6-Benzoquinonyl-2,4-18crown5)cyclohex-(e)-yl]-10,15,20-triphenylporphyrin (3a). m.p. = 269-270°C, ^{1}H NMR (500 MHz, $CDCl_3$) see Table 1. MS (FAB): *m/z* = 947 (100%, $[M+3H]^+$), 946 (68%, $[M+2H]^+$), 577 (42%), 565 (44%), 539 (46%), $C_{60}H_{56}O_7N_4$ requires 944.

Zinc complex (3b): m.p.>202°C (decomposition); ^{1}H NMR (500 MHz, $CDCl_3$) see Table 1. MS (FAB): *m/z* = 1009 (100%; $[M+3H]^+$), 1007 (33%, $[M+H]^+$), 639 (52%), 626 (63%), 602 (91%), 600 (99%), 549 (58%), $C_{60}H_{54}O_7N_4Zn$ requires 1006.

ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 337 and Normalverfahren) and the Fonds der Chemischen Industrie (H. K.). L. Sun wishes to thank the Alexander von Humboldt foundation for a postdoc research fellowship. We thank Dr. B. Kirste for helpful discussions of the NMR spectra, Ms. E. Franzus for her assistance in the HPLC separation, Dipl.-Chem. B. Roelfs for helpful support of assistance during the cyclic voltammetry measurements.

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(*Received in Germany* 9 *November* 1994; *revised* 30 *January* 1995; *accepted* 2 *February* 1995)