Photoinduced Electron Transfer in Porphyrin-Quinone Cyclophanes, 7[1]

Porphyrin-Quinone Cyclophanes with Gradually Varied Acceptor Strength: Physical Properties Related to Electron Transfer

Heinz A. Staab*, Guido Voit, Jürgen Weiser, and Michael Futscher

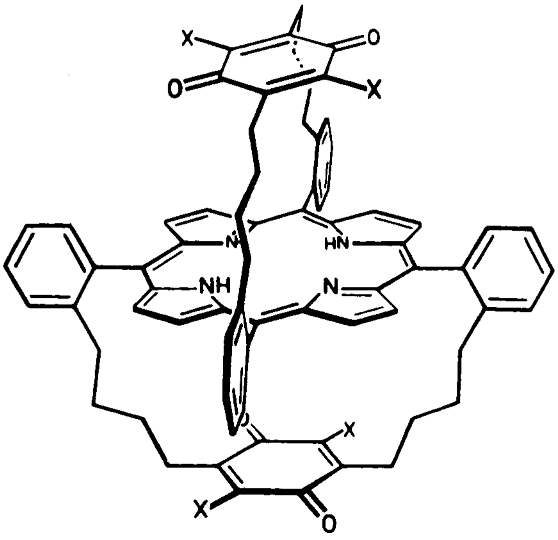
Abteilung Organische Chemie, Max-Planck-Institut für medizinische Forschung,
Jahnstraße 29, W-6900 Heidelberg, F.R.G.

Received April 7, 1992

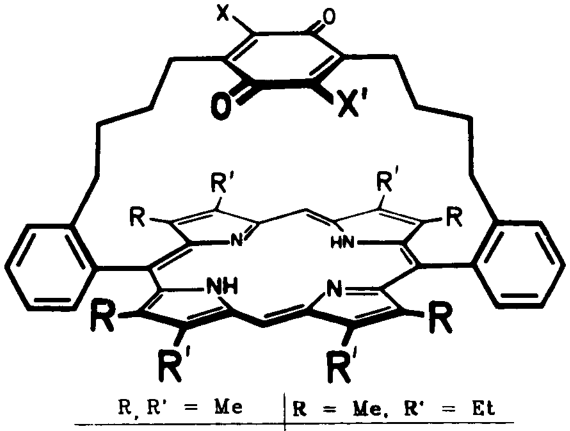
Key Words: Porphyrin-quinone cyclophanes / Photoinduced electron transfer in porphyrin-quinone cyclophanes / Absorption and emission spectra of porphyrin-quinone cyclophanes / Redox potentials and electron transfer in intramolecular porphyrin-quinone systems

Absorption and emission spectra of the doubly quinone-bridged porphyrin cyclophanes **1**–**4** with gradually varied acceptor strength as well as of the single-bridged analogues **5**–**9** and **10**–**13** are reported. Reduction and oxidation potentials of these intramolecular porphyrin-quinone systems have been determined. Based on these data, fluorescence quenching as well as time-resolved fluorescence lifetime measurements are discussed in terms of photoinduced electron transfer to the charge-separated zwitterionic state.

In the context of studies on photoinduced electron transfer in porphyrin-quinone systems[2] we reported in the preceding paper[1] on the syntheses of three series of porphyrin-quinone cyclophanes with gradually varied electron-affinity of the quinone units. The variation of the acceptor strength was achieved by electron-donating and electron-withdrawing substituents X on the quinone rings in the doubly quinone-bridged porphyrin cyclophanes **1**–**4** and in the porphyrin cyclophanes with single quinone bridges linked either to octamethylporphyrins **5**–**9** or to tetraethyltetramethylporphyrins **10**–**13**. The structures of these compounds were conclusively established by the analytical data presented in ref.[1]; they will be discussed in further detail on the basis of X-ray structure analyses and low-temperature ^{1}H-NMR studies in the following publication[3]. In the present paper we wish to report on absorption and emission spectra of these porphyrin-quinone cyclophanes and on reduction and oxidation potentials which are directly related to results on electron-transfer processes obtained from fluorescence quenching measurements and by time-resolved laser spectroscopy[4,5].



1 : X = Me
2 : X = OMe
3 : X = H
4 : X = Cl

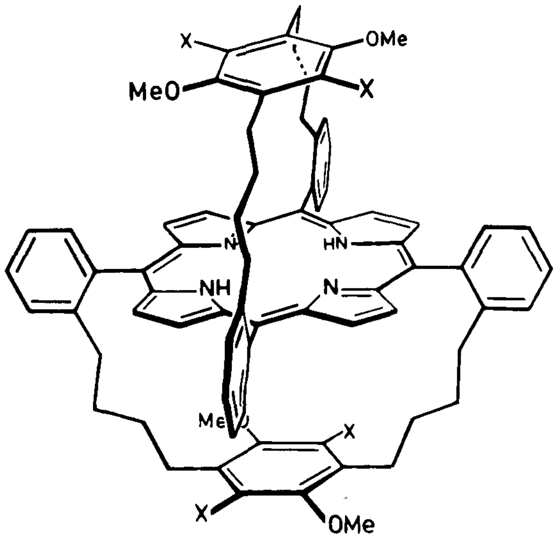


R, R' = Me	R = Me, R' = Et
5 : X, X' = Me	**10** : X, X' = Me
6 : X, X' = OMe	**11** : X, X' = OMe
7 : X, X' = H	**12** : X, X' = H
8 : X=Cl, X'=H	**13** : X, X' = Cl
9 : X, X' = Cl	

These porphyrin-quinone systems will be compared with the porphyrin cyclophanes **14**–**26** which contain the corresponding cyclophane skeleton missing, however, the elec-

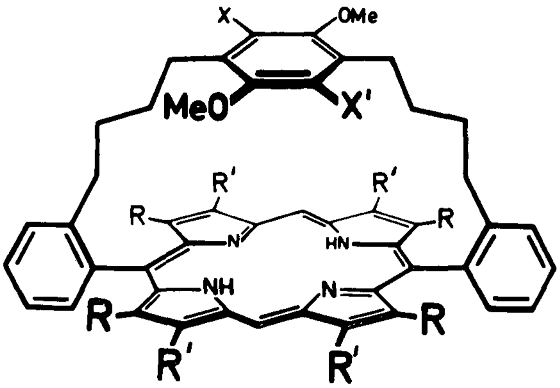
Chem. Ber. **1992**, *125*, 2303–2310 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1992 0009–2940/92/1010–2303 $ 3.50+.25/0

tron-acceptor property. As reference compounds, too, the corresponding simple porphyrins 5,10,15,20-tetraphenylporphyrin (TPP), 2,3,7,8,12,13,17,18-octamethyl-5,15-diphenylporphyrin (**27**)[1] and 2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrin (**28**)[6] will be considered.

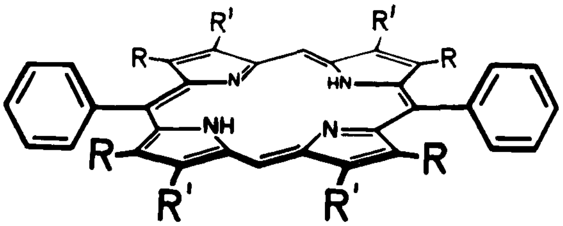


14 : X = Me
15 : X = OMe
16 : X = H
17 : X = Cl

Absorption Spectra: The very characteristic π→π*-electron absorption spectra of porphyrins[7] show in the region of 380 to 420 nm the strong Soret band (ε ≈ 2 to 5 · 10^5 M^{-1} cm^{-1}) of the allowed $S_0 \rightarrow S_2$ transition; between 500 and 650 nm the $S_0 \rightarrow S_1$ transition gives rise to two less intense absorptions Q(0/0) and Q(1/0), the latter being assigned to an excitation to the next higher vibrational state of S_1. Each of these Q-bands is further split into two components for orbital symmetry reasons, thus leading to four Q-bands [$Q_x(0/0)$, $Q_x(1/0)$, $Q_y(0/0)$ and $Q_y(1/0)$]. For example, 5,10,15,20-tetraphenylporphyrin (TPP), the basic porphyrin chromophore present in **1**–**4**, shows the Soret band with a maximum at 418 nm and the four Q-bands with maxima at 515, 551, 590 and 647 nm (Table 1). Increasing the porphyrin symmetry from D_{2h} to D_{4h} by forming metal complexes or by diprotonation on the nitrogen atoms reduces the number of Q-bands from four to two. Partially hydrogenated porphyrins show rather different absorption spectra. Thus, the structure-dependent absorption pattern of porphyrins is an important analytical property which, as the following data prove, is thoroughly applicable to the series of porphyrin cyclophanes, too. As a typical absorption spectrum from the group of porphyrin-quinone cyclophanes the spectrum of **5** is shown in Figure 1 which reveals the predominance of the characteristic porphyrin chromophore (the weak absorption band in the range 250–275 nm is assigned to the quinone unit).



R, R' = Me	R = Me, R' = Et
18 : X, X' = Me	**23** : X, X' = Me
19 : X, X' = OMe	**24** : X, X' = OMe
20 : X, X' = H	**25** : X, X' = H
21 : X=Cl, X'=H	**26** : X, X' = Cl
22 : X; X' = Cl	



27 : R, R' = Me **28** : R=Me, R'=Et

In Table 1 wavelenghts and extinction coefficients of Soret- and Q-band maxima of the doubly quinone-bridged porphyrin cyclophanes **1**–**4** are compared with those of the correspondingly substituted porphyrin cyclophanes **14**–**17** not containing quinone units as electron acceptors. The perfect agreement between these two sets of absorption data indicates that the porphyrin chromophore is not detectably influenced by the neighbouring quinone units; in view of the photoinduced electron transfer occurring in these systems it is noteworthy that the absorption spectra do not reflect

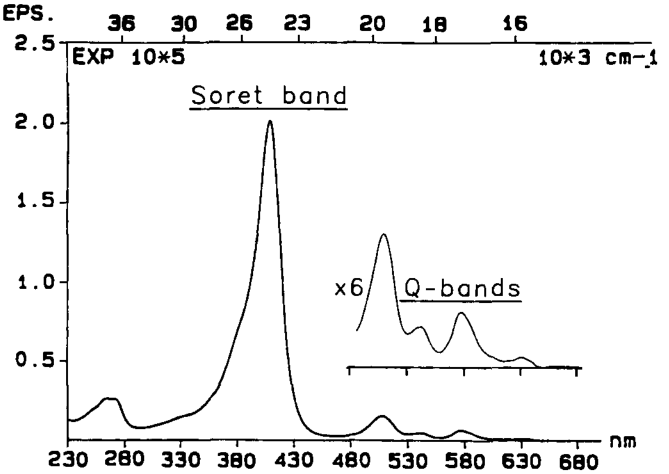


Figure 1. Absorption spectrum of porphyrin-quinone cyclophane **5** (10^{-5} M solution in dichloromethane)

transannular donor-acceptor interactions. Likewise, it is remarkable that the bridging of the porphyrin system in these two groups of porphyrin cyclophanes does not result in a substantial influence on the porphyrin chromophore as a comparison of the data for the cyclophanes **1**–**4** and **14**–**17** with TPP shows. The very small red shifts and reductions of the extinction coefficients with reference to TPP most probably result from the rather slight deviation from planarity of the porphyrin system as discussed on the basis of the X-ray structure analysis of **3**[2].

Table 1. Absorption bands of doubly quinone-bridged porphyrin cyclophanes **1**–**4** in comparison to non-quinoid porphyrin cyclophanes **14**–**17** and to TPP [λ_{max} in nm; ε (in parentheses): 10^4 M^{-1} cm^{-1}; all data for 10^{-5} M solutions]

	Soret	Q_y (1/0)	Q_y (0/0)	Q_x (1/0)	Q_x (0/0)	Solvent
1	420 (44.7)	515 (1.7)	549 (0.5)	591 (0.5)	648 (0.2)	[a]
	421 (46.2)	515 (1.9)	549 (0.5)	591 (0.6)	648 (0.3)	[b]
2	420 (45.0)	514 (1.7)	547 (0.5)	591 (0.5)	647 (0.2)	[a]
	421 (41.7)	515 (1.7)	547 (0.5)	591 (0.5)	647 (0.2)	[b]
3	421 (38.0)	516 (1.7)	549 (0.44)	593 (0.5)	650 (0.2)	[c]
4	421 (49.6)	515 (1.8)	547 (0.5)	592 (0.5)	648 (0.2)	[b]
14	421 (44.1)	515 (1.8)	548 (0.6)	591 (0.5)	649 (0.3)	[a]
	421 (44.4)	515 (1.9)	549 (0.6)	592 (0.5)	649 (0.3)	[b]
15	421 (44.2)	516 (1.6)	549 (0.5)	592 (0.5)	649 (0.2)	[a]
	422 (42.1)	516 (1.7)	549 (0.5)	592 (0.5)	649 (0.2)	[b]
16	421 (38.0)	516 (1.8)	549 (0.5)	592 (0.5)	649 (0.2)	[c]
17	423 (48.2)	516 (1.8)	550 (0.6)	593 (0.5)	650 (0.2)	[b]
TPP	418 (49.0)	515 (1.9)	551 (0.8)	590 (0.5)	647 (0.4)	[c]
	419 (49.0)	515 (1.9)	551 (0.8)	590 (0.5)	647 (0.4)	[b]

[a] CH_2Cl_2. – [b] $C_6H_5CH_3$. – [c] $CHCl_3$.

For the single-bridged porphyrin cyclophanes the agreement between the spectra of the differently substituted porphyrin-quinone cyclophanes and the spectra of their non-quinoid counterparts is similarly complete. Therefore, instead of presenting a list of nearly identical spectral data for the individual compounds, the very narrow margins of wavelengths and extinction coefficients for the absorption maxima of **5**–**9** and **10**–**13** in comparison with **18**–**22** and **23**–**26**, respectively, are presented in Table 2. These data show the very close coincidence with the respective simple porphyrins **27** [λ_{max} (ε · 10^{-4}) = 408 nm (22.2), 505 (1.9), 538 (0.6), 576 (0.8), 628 (0.1), benzene] and **28** [409 (16.2), 506 (1.3), 537 (0.4), 576 (0.5), 628 (0.1), toluene]. The very small solvent dependence of the absorption bands, listed for the doubly bridged porphyrin systems in Table 1, is also observed for the single-bridged porphyrin cyclophanes as well as for **27** and **28**. All the absorption data thus show the intactness of the porphyrin chromophor in these porphyrin cyclophanes which allows a generalization of the results on electron-transfer reactions discussed in the following.

Although for metalloporphyrin cyclophanes interactions between the oxygen-containing functions in the cyclophane bridges and the metal atom most likely might have been expected, the absorption spectra show a very close similarity of metalloporphyrin cyclophanes with and without quinone units in the bridges to metal complexes of simple porphyrins. As compared to the zinc complex of **27** [λ_{max} (ε · 10^{-4}) = 411 nm (48.4), 538 (2.4), 573 (1.7)], the absorption data for the zinc complexes of **20** and the porphyrin-quinone cyclophane **7** are 416 (47.2), 541 (2.1), 576 (1.0) and 418 (40.0), 544 (2.0), 580 (0.9), respectively. For the magnesium complexes of **27**, **20** and **7** very similar data were obtained [418 (54.0), 552 (2.3), 588 (0.64); 419 (52.4), 552 (2.0), 588 (0.6); 421 (44.0), 554 (2.0), 589 (0.66); all data for benzene solutions][8]. Thus, as in the series of non-metallated porphyrin cyclophanes, for the zinc and magnesium cyclophane complexes besides a reduction in the extinction coefficients only minor redshifts of the Soret- and the two Q-bands are observed in comparison with the corresponding simple metalloporphyrins. These results confirm that here, too, the porphyrin chromophore is not significantly influenced either by the cyclophane bridges or by the variation of the functional groups in these bridges.

Emission Spectra: The fluorescence spectra (excitation in Soret band) of the three groups of porphyrin cyclophanes correspond closely to the two emission bands observed for TPP (λ_{max} = 652 and 719 nm; toluene), **27** (λ_{max} = 635 and 698 nm; benzene) and **28** (λ_{max} = 630 and 697 nm; toluene), respectively. The quinone-bridged porphyrins **1**–**4** and the non-quinoid porphyrin cyclophanes **14**–**17**, containing the TPP chromophore, all show two emission maxima in the narrow range of 650–653 and 716–722 nm. The emission maxima of **5**–**9** as well as **18**–**22**, containing the **27**-chromophore, are observed at 632–636 and 695–703 nm, and those of **10**–**13** and **23**–**26** appear at 628–634 and 694–699 nm in agreement with the fluorescence of **28**. Measurements in *n*-hexane, toluene and dichloromethane show only a very small solvent dependence which actually is covered within the spectral ranges mentioned.

The marked independence of the absorption and emission spectra with regard to the presence or absence of quinone units and to further substitution in the cyclophane bridges contrasts strikingly with the very strong structure dependence of the fluorescence quantum yields. It is true that for the non-quinoid porphyrin cyclophanes **14**–**26** fluorescence quantum yields are still in the same order of magnitude as

Table 2. Ranges of absorption wavelengths (λ_{max} in nm) and extinction coefficients [ε_{max} (in parentheses): 10^4 M^{-1} cm^{-1}] of porphyrin-quinone cyclophanes **5**–**13** and corresponding non-quinoid porphyrin cyclophanes **18**–**26** (10^{-5} M solutions in toluene)

	Soret	Q_y (1/0)	Q_y (0/0)	Q_x (1/0)	Q_x (0/0)
5–**9**	410–412 (18.6–21.7)	507–508 (1.5–1.7)	539–541 (0.4–0.6)	579 (0.6–0.7)	631–632 (0.1–0.2)
18–**22**	411–412 (20.8–21.6)	508 (1.7–1.8)	540–541 (0.5)	578–579 (0.6–0.7)	631–632 (0.1–0.2)
10–**13**	*411 (21.1–21.3)*	508 (1.6–1.7)	539–541 (0.5)	578 (0.6–0.7)	630–631 (0.1–0.3)
23–**26**	409 (16.2)	506 (1.3)	537 (0.4)	576 (0.5)	628 (0.1)

those of TPP, **27** and **28**, but for the porphyrin-quinone cyclophanes a drastic quenching of the fluorescence is observed as in comparison with TPP (Φ_{fl} = 0.13, degassed benzene[9]) was already discussed for **3**[2]. Of special interest in the context of the present work was the dependence of this quenching on the electron affinity of the quinone units in the series of porphyrin-quinone cyclophanes **1**–**13** with gradually varied acceptor strength. Relative quantum yields for these compounds were approximated by integrating the emission bands using as references the respective cyclophanes of the non-quinoid series **14**–**26**; this procedure is especially justified in these cases due to the close coincidence of the emission bands of these groups of porphyrin cyclophanes. For the doubly quinone-bridged porphyrin cyclophanes **1**–**4** such relative quantum yields referred to **14**–**17**, respectively, reveal an increase of the fluorescence quenching by three powers of ten when proceeding within this series from the system with the weakest electron acceptor (**1**: $\Phi_{rel} \approx 0.74$) to its analogue with the quinone unit of the highest electron affinity (**4**: $\Phi_{rel} \approx 0.77 \cdot 10^{-3}$, in toluene). As measurements in toluene (ε = 2.4) and dichloromethane (ε = 9.08) show, the fluorescence quenching is strongly enhanced by increasing the solvent polarity [**1**: $\Phi_{rel} \approx 0.74$ (toluene), $0.9 \cdot 10^{-2}$ (dichloromethane); **2**: $\Phi_{rel} \approx 0.21$ (toluene), $0.4 \cdot 10^{-2}$ (dichloromethane)]. Similar results with regard to the acceptor strength as well as the solvent effect were obtained in the single-bridged porphyrin-quinone cyclophane series, for example for **5** [$\Phi_{rel} \approx 0.71$ (*n*-hexane), $9.7 \cdot 10^{-2}$ (toluene), $1.1 \cdot 10^{-2}$ (dichloromethane)] in comparison with **6** [$\Phi_{rel} \approx 6.7 \cdot 10^{-2}$ (*n*-hexane), $0.5 \cdot 10^{-2}$ (toluene), $0.12 \cdot 10^{-2}$ (dichloromethane)]. These data on relative quantum yields of fluorescence are consistent with results of fluorescence life time measurements obtained for this series of compounds by time-resolved emission spectroscopy on the picosecond time scale (see below and ref.[4]).

The fluorescence behaviour of the porphyrin-quinone cyclophanes (P-Q) dealt with in this study is well understood on the basis of the term scheme of Figure 2 as applied previously to inter- and intramolecular porphyrin-quinone systems: The first excited singlet state of the porphyrin chromophore P*-Q in competition with fluorescence emission is deactivated by an electron transfer from the porphyrin to the quinone unit leading to a charge-separated state $P^{+\bullet}$-$Q^{-\bullet}$. (Deactivation of S_1 by intersystem crossing to the triplet state is considered to be irrelevant in this context because such a process would not explain the decisive influence the quinone units have in comparison with porphyrin cyclophanes without quinone acceptors.) In accordance with the scheme of Figure 2 the fluorescence quenching observed for porphyrin-quinone cyclophanes differing in the electron affinity of the quinone units shows the deactivation route via a charge-separated state to be the more effective, the stronger the acceptor is. The determining factor for this process is the free energy ΔG_{cs} of the charge separation leading to a zwitterionic state composed of porphyrin radical cation and semiquinone radical anion. The observed solvent dependence of fluorescence intensities, is then plausibly understood as the result of the stabilization of the charge-separated state with increasing solvent polarity.

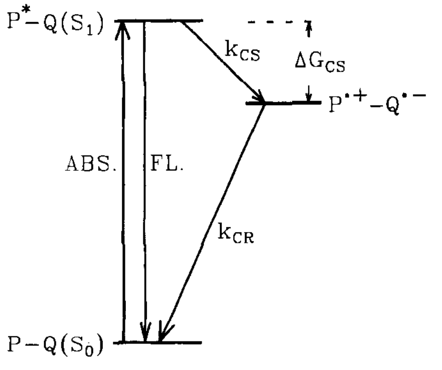
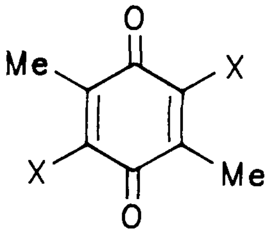


Figure 2. Fluorescence emission vs. photo-induced electron-transfer in porphyrin-quinone cyclophanes

Oxidation and Reduction Potentials of Porphyrin-Quinone Cyclophanes: Since the free energy ΔG_{cs} of the electron transfer depends on the first oxidation potential of the porphyrin and the first reduction potential of the quinone units, redox potentials of the porphyrin-quinone cyclophanes were measured. For comparison, the corresponding porphyrin cyclophanes not containing quinone units as well as simple quinones and porphyrins corresponding to the respective components of the porphyrin-quinone cyclophanes were included in these measurements. All redox potentials listed in Table 3 with reference to ferrocene ($Fc/Fc^+ \equiv 0.0$ V) were measured under equal conditions (dichloromethane, "glassy carbon electrode" vs. Ag/AgCl; for details see Experimental).

For the porphyrin-quinone cyclophanes the redox potentials to be considered are the first and second oxidation potential of the porphyrin systems $E^1_{ox}(P/P^+)$ and $E^2_{ox}(P^+/P^{2+})$, the first and second reduction potentials of the quinone units $E^1_{red}(Q/Q^-)$, and $E^2_{red}(Q^-/Q^{2-})$ and finally, as the most negative potential, the reduction potential of the porphyrin $E^3_{red}(P/P^-)$. The second oxidation potentials of the porphyrin components in some cases (data in parentheses) are not observable as reversible one-electron-steps; the same applies to the higher reduction potentials of the porphyrin-quinone cyclophanes for which E^2_{red} and E^3_{red} correspond to overlapping and/or irreversible steps. In the context of the present study the discussion is focussed on the first oxidation and reduction potentials $E^1_{ox}(P/P^+)$ and $E^1_{red}(Q/Q^-)$ which are relevant for the charge separation in the porphyrin-quinone cyclophanes.

In the first lines of Table 3 the reduction potentials are listed for the simple quinones **29**–**32** representing substitution patterns corresponding to the quinone units in the porphyrin cyclophanes. The different electron affinity is re-



29 : X = Me
30 : X = OMe
31 : X = H
32 : X = Cl

Table 3. Redox potentials of porphyrin-quinone cyclophanes and reference compounds [dichloromethane, potentials quoted with reference to ferrocene E(Fe/Fe$^+$) ≡ 0.0 V; for details see Experimental]

	E^2_{ox} (P^+/P^{2+})	E^1_{ox} (P/P^+)	E^1_{red} (Q/Q^-)	E^2_{red} (Q^-/Q^{2-})	E^3_{red} (P/P^-)
29	–	–	−1.30	−1.86	–
30	–	–	−1.16	−1.82	–
31	–	–	−1.10	−1.75	–
32	–	–	−0.84	−1.57	–
TPP	+0.79	+0.55	–	–	−1.66
14	[irrev.]	+0.51	–	–	−1.86
15	[irrev.]	+0.53	–	–	−1.89
16	[irrev.]	+0.51	–	–	−1.89
17	[irrev.]	+0.49	–	–	−1.85
1	+0.97	+0.54	−1.42(2e)	[≈ −1.86, irrev.]	
2	+0.92	+0.54	−1.27(2e)	[≈ −1.93, irrev.]	
3	+0.87	+0.52	−1.23(2e)	[≈ −1.82, irrev.]	
4	+0.86	+0.53	−0.95(2e)	[≈ −1.91, irrev.]	
18	+.066	+0.31	–	–	−1.99
19	+0.63	+0.34	–	–	−1.99
20	[irrev.]	+0.32	–	–	−2.00
22	+0.64	+0.32	–	–	−1.98
5	+0.64	+0.36	−1.45	[≈ −1.99, 2e]	
6	+0.62	+0.35	−1.30	[≈ −2.04, 2e]	
7	+0.58	+0.33	−1.26	[≈ −1.98, 2e]	
9	+0.64	+0.36	−0.95	−1.72	−2.00
28	+0.58	+0.38	–	–	−1.87
23	+0.64	+0.34	–	–	−2.00
24	+0.63	+0.34	–	–	−2.01
25	[irrev.]	+0.34	–	–	[−2.01]
26	+0.64	+0.36	–	–	[−2.02]
10	+0.63	+0.36	−1.45	[≈ −1.99, 2e]	
11	+0.62	+0.36	−1.31	[≈ −2.04, 2e]	
12	[irrev.]	+0.36	−1.25	[−1.94, 2e, irrev.]	
13	−0.64	+0.36	−0.99	[−2.02, 2e, irrev.]	

flected by the range of about 450 mV between the first reduction potentials of duroquinone (**29**) and 2,5-dichlorodimethyl-*p*-benzoquinone (**32**). As a comparison of these potentials with those of the three groups of porphyrin-quinone cyclophanes **1**−**4**, **5**−**9** and **10**−**13** shows, this range of gradually varied acceptor strength is maintained in the porphyrin-quinone cyclophane systems (the observed shift of 110−150 mV to more negative values is most probably due to sterically hindered solvation of the semiquinone anions).

In contrast to the reduction potentials of the quinones, the first oxidation potentials of the porphyrin units in the porphyrin cyclophanes agree rather well with those of the corresponding simple porphyrins. The doubly bridged porphyrin cyclophanes containing 5,10,15,20-tetraphenylporphyrin units show first oxidation potentials in the narrow range of +0.49 to +0.54 V, only slightly reduced in comparison with TPP itself (E^1_{ox} = +0.55 V). The two single-bridged series of porphyrin cyclophanes contain, as stronger donors than TPP, octaalkyldiphenylporphyrins; the oxidation potentials of all porphyrin cyclophanes of these two groups (E^1_{ox} = +0.31 to 0.36 V) correspond very well with that of **28** (E^1_{ox} = +0.38 V) as a suitable reference. Within each of these series the oxidation potentials of porphyrins are nearly constant, and there is neither a significant difference between corresponding non-quinoid and quinoid compounds nor a perceivable influence of the different substitution on the quinone rings. In Figure 3 the cyclovoltammograms of **9**, **7**, **6**, and **5** in the order of decreasing electron affinity of the quinone units demonstrate the constancy of E^1_{ox} of the porphyrins and, on the other hand, the intended variation of the E^1_{red} potentials of the quinone units. Consequently, the difference between these two redox potentials can indeed be used for an assessment of the driving force of the electron transfer in dependence of the acceptor strength of the quinone units.

The zinc porphyrin cyclophanes, as expected, are considerably stronger electron donors (for example, **5** · Zn: E_{ox} = +0.16 V; **7** · Zn: E_{ox} = +0.14 V); in contrast, however, to metal-free porphyrin-quinone cyclophanes the first reduction potentials of the quinone units depend significantly on specific interactions with the porphyrin part. As compared to the zinc-free parent compounds the first reduction potentials of the quinone units are less negative by about 300 mV (**5** · Zn: E_{red} = −1.17 V; **7** · Zn: E_{red} = −0.93); obviously, zinc exerts, due to transannular interaction, a stabilizing effect on the semiquinone radical anion.

In the case of the porphyrin-quinone cyclophanes the dependence of the driving force ΔG_{cs} of the photoinduced electron transfer on the redox potentials E^1_{ox} and E^1_{red} can approximately be described by the following simple equation

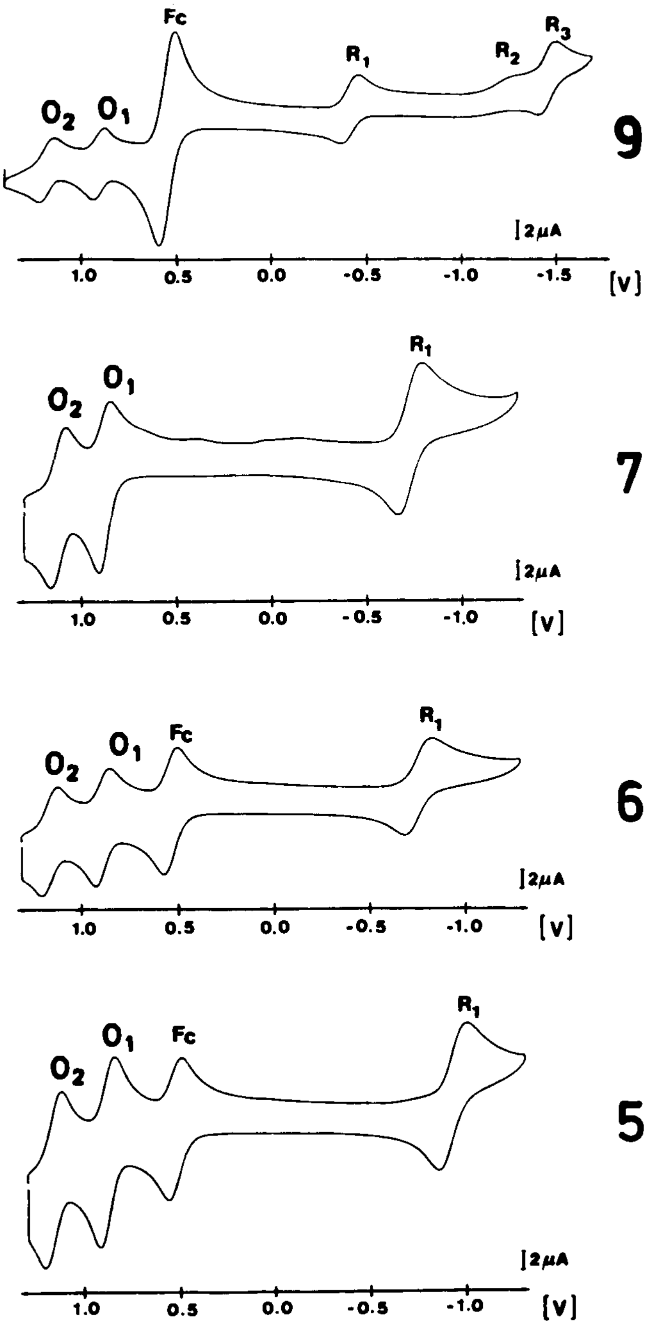


Figure 3. Cyclovoltammetry of **5**, **6**, **7** and **9** in dichloromethane (for details see Experimental)

in which ΔE_{00} is the $S_0 \rightarrow S_1$ excitation energy of the porphyrin chromophore: $\Delta G'_{cs} = (E^1_{ox} - E^1_{red}) - \Delta E_{00}$.

These approximated free energy values ($\Delta G'_{cs}$) are based on the simplifying assumption that for a comparison of the charge-separation processes Coulomb energy and electronic interaction terms can be neglected because of the corresponding geometries within the respective series of porphyrin-quinone cyclophanes. Furthermore, solvent reorganization terms are assumed to be reasonably well taken into account if the redox potentials are measured in the respective solvents. ΔE_{00} was derived from absorption and fluorescence spectra as 1.91 and 1.96 eV for cyclophanes containing tetraphenylporphyrin and octaalkyldiphenylporphyrin chromophores, respectively. With these data and the redox potentials of Table 3 $\Delta G'_{cs}$ values were obtained which for each of the three groups of porphyrin-quinone cyclophanes are listed in Table 4 in the order of increasing electron affinity of the quinone components. For the systems with the weakest electron acceptor this approximation leads to $\Delta G'_{cs}$ values which are close to zero (**5** and **10**) or even positive (for **1** containing, within the horizontal row, the weakest electron donor). Within each of the three columns the increasing acceptor strength leads to more negative $\Delta G'_{cs}$ values in correspondingly similar steps.

Table 4. Approximated $\Delta G'_{cs}$ values for photo-induced electron-transfer in porphyrin-quinone cyclophanes (solvent: dichloromethane)

$\Delta G'_{cs}$	$\Delta G'_{cs}$	$\Delta G'_{cs}$
1: +0.06	**5**: −0.15	**10**: −0.15
2: −0.10	**6**: −0.31	**11**: −0.29
3: −0.16	**7**: −0.37	**12**: −0.35
4: −0.43	**9**: −0.65	**13**: −0.61

Table 5. Fluorescence lifetime (in ps) of porphyrin-quinone cyclophanes **5**–**9** and their solvent-dependence (two figures for lifetimes indicate biexponential fluorescence decay for which the relative amplitudes in percent are quoted in parentheses; for experimental details and the evaluation of these measurements see ref.[4])

Solvent (ε)	**5**	**6**	**7**	**8**	**9**
n-Hexane (1.88)	9200	432 (82) 19 (18)			
Toluene (2.38)	1360 (82) 120 (13)	32 (25) 8 (73)	31 (10) 3 (89)	1 (99)	1 (98)
Dichloromethane (8.93)	20 (28) 3 (71)	18 (5) 2 (95)	1 (99)	1 (97)	1 (97)
Acetone (20.7)	30 (30) 5 (67)	30 (7) 4 (89)	2 (99)	1 (98)	2 (94)
Dimethylformamide (36.7)	21 (29) 4 (65)	18 (7) 3 (92)			

For the zinc porphyrin-quinone cyclophanes with the oxidation and reduction potentials mentioned above and with E_{00} = 2.14 eV (for **27** · **Zn**) approximated $\Delta G'_{cs}$ values of −0.81 and −1.07 were obtained for **5** · **Zn** and **7** · **Zn**, resp., showing in comparison with **5** and **7** the stronger driving force for the electron transfer occurring in zinc porphyrin-quinone cyclophanes.

Certainly, the significance of these $\Delta G'_{cs}$ values as a measure of the free energies of the electron-transfer processes remains questionable, at least as far as the quantitative meaning of the figures are concerned. On the other hand, these data, easily obtainable from redox potentials, are reasonably well suited to interpret *relative* trends of the structure dependence of photoinduced electron transfer reactions, as will be shown by a discussion of some results of time-resolved fluorescence decay measurements details of which were reported recently in a separate publication[4].

In Table 5 fluorescence lifetimes (in picoseconds) of the porphyrin-quinone cyclophanes **5**–**9** for solvents of different polarities are listed. Under the conditions of these measurements the fluorescence lifetime of the non-quinoid reference compound **20** was determined to be 11–13 nanoseconds not showing a significant dependence on solvent polarity. The porphyrin-quinone cyclophanes **8** and **9** with monochloro- and dichloro-substituted quinone units as strong electron acceptors show a monoexponential fluorescence decay with lifetimes of 1–2 ps within the experimental limits of measurement independent of solvent polarity. For **7** virtually the same fluorescence lifetimes (of order of 1–2 ps, monoexponential decay) are observed in the polar solvents acetone and dichloromethane whereas in toluene a second component with a considerably longer lifetime (31 ps) shows up with about 10% amplitude. This trend is also perceivable for **6** which in polar solvents still shows a strong predominance of the fluorescence component with short lifetimes whereas in toluene the contribution of the slower process is increased, and in *n*-hexane the amplitude ratio is even reversed with the slow component (432 ps), now accounting for an amplitude of 82%. The porphyrin-quinone cyclophane **5** containing the weakest electron acceptor in this series shows in *n*-hexane as well as in isooctane monoexponential fluorescence decays with lifetimes in the order of 10 nanoseconds as found for porphyrins not containing quinone components as acceptors; in toluene the slow fluorescence component with a lifetime >1 ns still prevails, and only in solvents of higher polarity predominant contributions of the picosecond process are observed.

For the fluorescence behaviour of **5**–**9** and especially its dependence on acceptor strength and solvent polarity the following interpretation is suggested which is supported by the approximated free energy values $\Delta G'_{cs}$ for the electron transfer: The missing fluorescence quenching of **5** in non-polar solvents is attributed to a positive free energy of the charge separation; thus, the electron transfer from P*-Q to $P^{+\bullet}$-$Q^{-\bullet}$ cannot compete with the normal fluorescence emission from the excited porphyrin chromophore. The increasing stabilization of the charge-separated state with rising solvent polarity, however, makes the charge separation increasingly competitive. Stronger electron acceptors, too, like higher solvent polarity shift the charge separation to more negative free energies (see Table 4). In an intermediate range, i.e. for **6** and **7** in non-polar solvents, the charge-separated state will energetically be close to the P*-Q state. This is the range for which biexponential decays with slow and fast components are observed; as a plausible explanation for this effect it is suggested that in these cases the charge separation is followed by a thermally activated back reaction from the charge-separated state, to the P*-Q state, thus leading to a fast and a delayed fluorescent component. For **7** in polar solvents, however, the charge separation process is sufficiently favoured so that the deactivation of P*-Q by electron transfer leads to only one very short decay time in the order of 1–2 ps. For **8** and **9**, containing the strongest electron acceptors in this series, such short decay times are observed even for solutions in non-polar solvents. The electron transfer rates k_{cs} for these systems are higher than $5 \cdot 10^{11}\ s^{-1}$. On the basis of time-resolved emission and absorption spectroscopy the lifetimes of the charge-separated states were estimated to be in the order of 10 to 100 ps[4,5,10].

In conclusion, the following results can be summarized for the series of porphyrin-quinone cyclophanes with gradually varied electron-acceptor strength: Wavelengths and intensities of absorption bands show porphyrin and quinone chromophores in these systems not to be significantly influenced by transannular interactions. The fluorescence behaviour of these compounds, on the other hand, is characterized by the potentiality of a deactivation of the porphyrin S_1 state by an electron transfer from P* to the quinone component. The extent to which this charge separation can compete successfully with the deactivation by the regular fluorescence emission strongly depends on the acceptor strength of the quinone unit and on solvent polarity. The simple relation to the difference between E^1_{ox} and E^1_{red} and to the approximated free energies $\Delta G'_{cs}$ derived therefrom surprisingly well describes the photoinduced electron transfer occuring in these systems, considering the fact that any specific electrostatic and electronic coupling terms as well as reorganization energy terms are neglected. These simplifications are obviously justified by the specific and within the series unchanged structural features of these porphyrin-quinone cyclophanes as discussed before[2]. It may be of interest that these porphyrin-quinone cyclophanes simulate some aspects of the primary charge separation step in biological photosynthesis due to the accidental fact that relevant electron transfer parameters are similar to those in biological systems[4].

We gratefully appreciate an excellent cooperation and many stimulating discussions with *M. E. Michel-Beyerle*, *H. Heitele*, *F. Pöllinger*, and coworkers (Technische Universität München).

Experimental

UV/Vis absorption spectra: Cary 2300 (Varian). – Fluorescence spectra: Fluorolog F 112 XE (Spex, Grassbrunn); 10^{-5} M solutions in toluene and dichloromethane, $\approx 10^{-6}$ M solutions in *n*-hexane; emission correction. – Cyclic voltammetry: Potentiostat PAR 362 (EG & G Princeton Applied Research); "glassy carbon electrode", reference electrode Ag/AgCl (3.5 M KCl/water); 0.2 M solution of tetrabutylammonium perchlorate (puriss., Fa. Fluka) in dichloromethane (purified by washing with conc. sulfuric acid, dried with calcium hydride, fractional distillation under argon); concentration of measured compounds 10^{-3}–10^{-4} M; voltage increase rate 200 mV s^{-1}; all measurements performed at 20°C; reference ferrocene [E_{ox} (Fc/Fc$^+$) = +0.54 ± 0.01 V].

---

[1] Part 6: H. A. Staab, J. Weiser, M. Futscher, G. Voit, A. Rückemann, C. Anders, *Chem. Ber.* **1992**, *125*, 2285–2301; preceding paper.

[2] H. A. Staab, J. Weiser, E. Baumann, *Chem. Ber.* **1992**, *125*, 2275–2283.

[3] C. Krieger, G. Voit, M. Dernbach, A. Döhling, T. Carell, H. A. Staab, *Chem. Ber.*, to be submitted.

[4] H. Heitele, F. Pöllinger, K. Kremer, M. E. Michel-Beyerle, M. Futscher, G. Voit, J. Weiser, H. A. Staab, *Chem. Phys. Lett.* **1992**, *188*, 270–278.

[5] W. Frey, R. Klann, F. Laermer, T. Elsaesser, E. Baumann, M. Futscher, H. A. Staab, *Chem. Phys. Lett.* **1992**, *190*, 567–573; see also P. O. J. Scherer, S. F. Fischer, *Chem. Phys. Lett.* **1992**, *190*, 574–580.

[6] H. K. Hombrecher, G. Horter, *Liebigs Ann. Chem.* **1991**, 219–227.

[7] Review: M. Gouterman, in *The Porphyrins* (Ed.: D. Dolphin), vol. III, Academic Press, New-York, San Francisco, London **1978**, p. 1.

[8] For these compounds an additional, less intensive absorption with $\lambda_{max} \approx 510$ nm is observed which is assigned to a Q(2/0) transition (see ref.[7]).

[9] D. J. Quimby, F. R. Longo, *J. Am. Chem. Soc.* **1975**, *97*, 5111–5117.

[10] For comparable results on less rigid porphyrin-quinone systems see M. P. Irvine, R. J. Harrison, G. S. Beddard, P. Leighton, J. K. M. Sanders, *Chem. Phys.* **1986**, *104*, 315.

[160/92]

CAS Registry Numbers

1: 142294-23-3 / **2**: 142294-24-4 / **3**: 91295-89-5 / **4**: 142294-25-5 / **5**: 140188-24-5 / **6**: 140188-25-6 / **7**: 103548-74-9 / **8**: 140188-26-7 / **9**: 140208-85-1 / **10**: 142294-26-6 / **11**: 142294-27-7 / **12**: 142294-28-8 / **13**: 142294-29-9 / **14**: 142294-30-2 / **15**: 142294-31-3 / **16**: 104182-02-7 / **17**: 142294-32-4 / **18**: 142319-21-9 / **19**: 142294-33-5 / **20**: 103548-73-8 / **21**: 142294-34-6 / **22**: 142294-35-7 / **23**: 142294-36-8 / **24**: 142319-22-0 / **25**: 142294-37-9 / **26**: 142294-38-0 / **28**: 101325-63-7 / **29**: 527-17-3 / **30**: 5691-54-3 / **31**: 137-18-8 / **32**: 46010-98-4