Pergamon

Tetrahedron, Vol. 52, No. 25, pp. 8497-8516, 1996
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0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00405-X

Porphyrins Linked to High Acceptor Strength Cyano Quinones as Models for the Photosynthetic Reaction Center.

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Abstract: The synthesis of biomimetic photosynthetic model compounds, composed of 10,15,20-tritolylporphyrins linked to different quinones by cyclohexylene bridges, is described. Cyclic voltammetry measurements show a significant change of the reduction potential of the quinone moiety through introduction of cyano groups as electron withdrawing substituents. EPR and ENDOR spectra of the semiquinone anion radical derivatives reveal a considerable spin density redistribution within the semiquinone moiety caused by the substituents. Lamp irradiation *in situ* of the porphyrin hydroquinones, dissolved in reversed Triton X-100 micelles, through the resonator slits of the EPR spectrometer does not only yield hyperfine resolved absorptive, but also emissive EPR spectra. This is indicative of strong electron spin polarization effects. From the polarization pattern it can be deduced that the radical/triplet pair mechanism between two photoactive species, located in one micelle, gives rise to this effect.
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INTRODUCTION

In order to mimic the charge separation function of the primary processes of photosynthesis that are known to occur in the so-called reaction centers, numerous model compounds have been synthesized in due course, for more recent reviews, see Ref. 1. A significant part of this research has been devoted to the study of the dependencies of electron transfer (ET) rate constants on donor-acceptor distance, on relative orientation of donor and acceptor with respect to one another, on electronic coupling, and, last but not least, on the energetics, that is, on the driving force ΔG_{ET} of the reaction.

In recent years we have synthesized a number of porphyrins linked to quinones via an aliphatic cyclohexylene bridge (porphyrin-quinones).[2] Our rationale for this choice is (a) to get a relatively rigid system with a well-defined geometric arrangement of the constituents, and (b) to keep constant most of the parameters (type and redox potential of the donor, type and geometries of the bridge) except for the type of quinone acceptor that can be varied with respect to its reduction potential, e.g., by different substituents. In this context we have prepared compounds with electron withdrawing and donating substituents at the quinone moiety and measured the changes of the reduction potentials and thereby ΔG_{ET}.[3] According to the famous, bell-shaped curve that results from Marcus' ET theory[4] and describes the so-called Marcus *normal* and *inverted region*, increasing exergonicity results in an increase of the ET

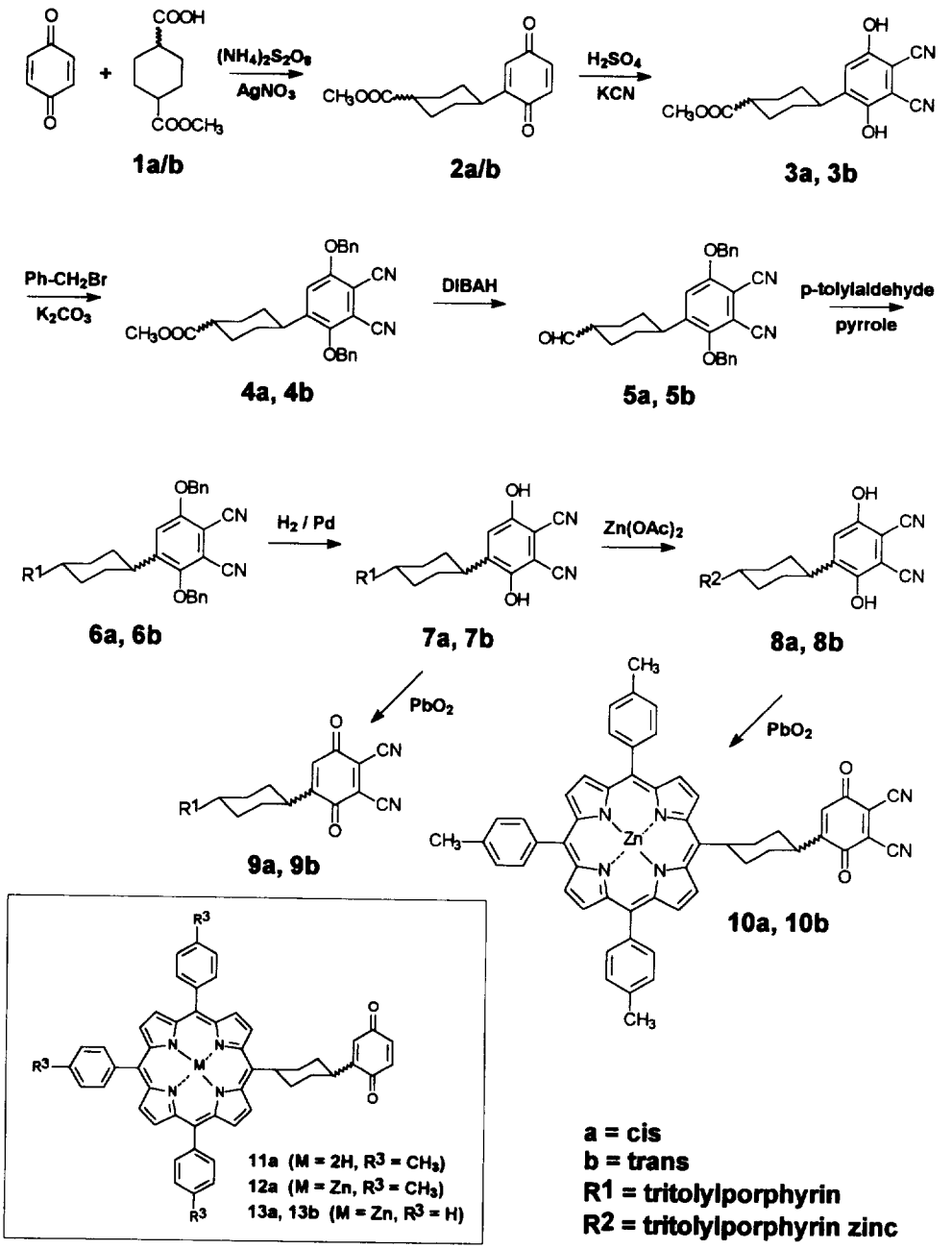
rates; however, for very large (negative) ΔG_{ET} values the ET rates decrease with increasing exergonicity. In order to increase the range of redox potentials and to further study the "Marcus behavior" of the model compounds, we have synthesized novel porpyrin-quinones bearing cyano groups at the quinone which results in exceptionally high acceptor strength. The aliphatic cyclohexylene bridge has the advantages mentioned and, in addition, allows synthesis of two diastereomers *cis* and *trans*, that is, porphyrin-quinones with all molecular parameters almost constant, except for the geometrical arrangement of donor and acceptor. In this paper we present the synthetic details and some characteristics of these systems. In a forthcoming paper we shall report on their time-resolved spectroscopy.

RESULTS AND DISCUSSION

Syntheses: Radical alkylation of *p*-benzoquinone was performed by oxidative decarboxylation of a mixture of **1a/b** (*cis/trans* 3:2)[5] with ammonium peroxodisulfate and $AgNO_3$ as the catalyst, according to the procedure of Jacobsen and Torssell,[6] yielding **2** in a *cis/trans* mixture of 3:2, see Scheme 1. Subsequently the mixture was converted into the dicyano derivative **3a**, 3**b** (*cis:trans* ratio 3:2, separated by chromatography). It is to be noted that under Jacobsen-Torssell conditions all attempts failed to directly oxidize and alkylate the commercially available 2,3 dicyano hydroquinone. Introduction of cyano groups was achieved by the Thiele-Meisenheimer reaction.[7] Since - in contrast to the 100% yield reported in this paper - only poor 10% yield could be obtained (probably due to the formation of very stable quinhydrone complexes, indicated by the tarry black consistency of the reaction mixture that decolourized only after addition of reducing agent), this synthetic procedure could successfully be improved, see Experimental.

Conversion of the carboxylic acid methyl ester group of **3** to the corresponding aldehyde using diisobutylaluminium hydride (DIBAH)[8] requires protection of the hydroxylic groups prior to reduction. However, cleavage of alkyl ethers by various methods led inevitably to decomposition products of unknown structure. Similar problems have already been reported by Staab et al.[9] in their synthesis of dicyano substituted porphyrin quinone cyclophanes.

Introduction of other protective groups such as silylethers failed; finally benzyl ether proved to be the protection group of choice. Condensation of **5a, 5b** with *p*–tolylaldehyde and pyrrole under equilibrium conditions,[10] followed by repetitive chromatography, led to pure **6a, 6b**. Removal of the protecting benzyl groups by hydrogenation of **6a, 6b** with palladium charcoal as the catalyst yielded the free base target compounds **7a, 7b**. Metallation with zinc could easily be performed by stirring a solution of **7** in dichloromethane with methanolic zinc acetate.


1a/b
2a/b
3a, 3b
4a, 4b
5a, 5b
6a, 6b
7a, 7b
8a, 8b
9a, 9b
10a, 10b
11a (M = 2H, R3 = CH3)
12a (M = Zn, R3 = CH3)
13a, 13b (M = Zn, R3 = H)
a = cis
b = trans
R1 = tritolylporphyrin
R2 = tritolylporphyrin zinc

Scheme 1.

Unfortunately, the corresponding porphyrin quinones, necessary for ET studies, could not be isolated, because they are immediately reduced to the corresponding hydroquinones. Therefore, the free base porphyrin hydroquinones **7a** and **7b** (and Zn-porphyrin hydroquinones **8a** and **8b**) were oxidized before measurements; the porphyrin-quinones **9a** and **9b**, as well as **10a** and **10b**, exhibited considerable stability in dry solutions, sufficient for ET experiments.

For comparison, the free base and zinc porphyrin cyclohexylene benzoquinone *cis* analogues without cyano groups **11a** and **12a** were also synthesized (see insert in Scheme 1). These porphyrin-quinones are very similar to those previously prepared in our group, **13a** and **13b**, which lack the methyl groups at the porphyrin phenyl rings, cf. Ref. 2. However, this slight modification proved reasonable in order to exclude differences in solvation and electronic effects. For instance, due to the increase of ring electron density produced by the four *p*-methyl groups, the first oxidation potential of tetratolylporphyrin (TTP) is about 50 mV lower than that of tetraphenylporphyrin (TPP).[11]

Cyclic voltammetry: For an understanding of ET properties of these systems knowledge of the energetics, i.e. the energy difference between ground and excited state of the porphyrin moiety and, in particular, the energy difference between the latter and the charge separated state is of greatest importance. The free energy ΔG_{ET} of the ET is described by the Rehm-Weller equation[12] and depends on the first oxidation potential of the porphyrin and the first reduction potential of the quinone units:

$$\Delta G_{ET} = E_{ox}(P/P^+) - E_{red}(Q/Q^-) - e^2/\varepsilon r_{DA} - E(S_0 \rightarrow S_1) \qquad (1)$$

$E(S_0 \rightarrow S_1)$ is the excitation energy accessible from optical spectra; $E_{ox}(P/P^+)$ and $E_{red}(Q/Q^-)$ are the first oxidation and reduction potentials of porphyrin and quinone, respectively, $e^2/\varepsilon \cdot r_{DA}$ is a work term, describing the stabilization of the charge-separated state. The potentials in eq. (1) were determined by cyclic voltammetry, see Table 1. For comparison, the data of the corresponding quinone precursors **3a/b** are as well included as the cyano free benzoquinone analogues and TTP. All measurements were performed in CH_2Cl_2 versus Ag/AgCl with reference to ferrocene as internal standard ($Fc/Fc^+ = 0{,}0$ V), as recommended by IUPAC,[13] supporting electrolyte 0.1 mol/l tetrabutylammonium perchlorate, concentration of porphyrin-quinones 10^{-4} mol/l.

The extremely high electron withdrawing effect of the cyano groups is reflected in the considerable difference of -900 mV between the first reduction potentials $E_{red}(Q/Q^-)$ of the precursors **2a/b** and **3a/b** **quinone**. The cyclic voltammetry data clearly show that this difference is retained in the porphyrin-quinones. Figure 1 depicts the cyclovoltammograms of **10a** and **12a**. The first and second oxidation step of both porphyrins, the first and second reduction step of the quinone of **10a** and the first reduction step of the quinone of **12a** are observed, which are all reversible.

Table 1. Redox Potentials of Porphyrin Quinones and Reference (Precursor) Compounds in V ($Fc/Fc^+ = 0 \pm 0.01$ V).

Compound	$E_{red}(Q^-/Q^{2-})$	$E_{red}(Q/Q^-)$	$E_{ox}(P/P^+)$	$E_{ox}(P^+/P^{2+})$
2a/b		−1.07		
3a/b quinone	−0.99	−0.16		
9a	~ −0.99[b]	−0.16	0.45	irreversible
9b	~ −1.01[b]	−0.16	0.44	irreversible
10a	~ −0.95[b]	−0.16	0.23	0.50
10b	~ −0.92[b]	−0.16	0.23	0.51
11a		−1.04	0.45	irreversible
12a		−0.96	0.23	0.51
TTP[a]			0.46	irreversible
TTP zinc[a]			0.21	0.56

[a] TTP refers to tetratolylporphyrin; [b] Error ± 0.03 V.

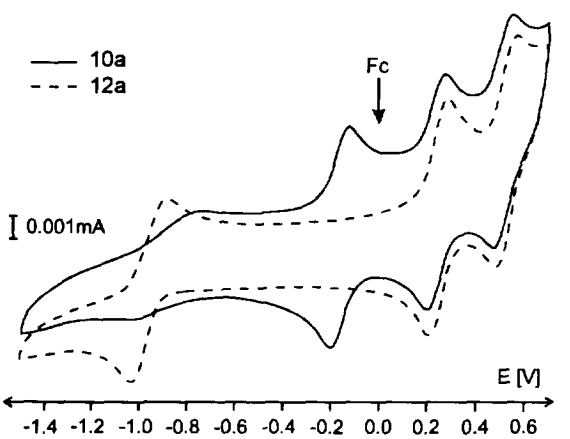


Figure 1. Cyclic voltammograms of **10a** and **12a**. Note the pronounced influence of the cyano groups on the quinone reduction potential; both voltammograms were recorded with and without ferrocene, to assure that the addition of the standard did not cause any shift of peaks.

The first oxidation potentials of the porphyrin-quinones and zinc porphyrin-quinones differ by about 20 mV in comparison with TTP and TTP zinc, respectively, which is a result of the replacement of one aromatic tolyl group by the aliphatic cyclohexylene system. Cyclohexyl, an inductive substituent, shifts the

potential to lower values, i.e., cyclohexyl-tritolyl-porphyrins are easier to be oxidized than the tetratolyl derivatives. The attachment of the quinone fragment does not affect the oxidation potentials $E_{ox}(P/P^+)$. This holds for the metallated compounds as well. Judging from these findings, it stands to reason that no difference is found between the *cis* and *trans* diastereomers, neither in $E_{red}(Q/Q^-)$ nor in $E_{ox}(P/P^+)$. By the way, the data obtained for TTP agree very well with those reported previously, namely, 0.464 V versus ferrocene in CH_2Cl_2.[13]

As expected, the enhanced donor strength of the metallated porphyrin-quinones in comparison with the corresponding free bases is reflected in their $E_{ox}(P/P^+)$ shift to lower potentials of about 200 mV. On the other hand, the $E_{red}(Q/Q^-)$ potential of **12a** is approximately 100 mV less negative than that of the corresponding precursor **2a/b**. Apparently, the semiquinone radical anion is stabilized by the influence of Zn, an effect which has been previously observed.[14] The cyano compounds do not exhibit this, obviously due to the extremely high $E(Q/Q^-)$ potential of the precursor **3a/b quinone** to start with (hinted at by the fact, that the second reduction potentials are indeed shifted).[15]

A similar, but less pronounced stabilization of $E_{red}(Q/Q^-)$ was observed for the free base porphyrin-quinone **11a**, reflected by a shift of about 30 mV between **2a/b** and **11a**. Again, this is not seen in the $E_{red}(Q/Q^-)$ of the cyano compounds.[15]

EPR and ENDOR spectroscopy of chemically generated radicals.

As already mentioned, porphyrin-quinones are well suited biomimetic models for studying photoinduced ET. If an electron is transferred from the porphyrin donor to the quinone acceptor, inherently radical species, that is, porphyrin radical cation and semiquinone radical anion are generated. For theoretical treatment of this reaction knowledge of the electronic structure and its dependence on geometrical parameters is of greatest importance. Therefore we have studied the chemically generated semiquinone derivatives of the porphyrin-quinones by means of steady state EPR and ENDOR (Electron Nuclear DOuble Resonance) spectroscopy, a technique which is known to allow a much better resolution than conventional EPR.[16] Signs of the HFCs were determined by general Electron Nuclear Nuclear TRIPLE resonance.[16] Due to the angular dependence of the β-proton hyperfine coupling constant (HFC)[17] not only the spin density distribution can be elucidated, information about preferred conformation is also accessible. Since the HFCs of the cyclohexyltriphenyl porphyrin radical fragment, with the bulky porphyrin always equatorial, will certainly be quite similar to those of the known cyclohexyltriphenyl porphyrin radical cation and also to those of the tolyl derivatives,[18] we have only studied the radical state of the quinone moiety. Figure 2 shows, as an example, the EPR and ENDOR spectra of the semiquinone radical anions of **10a** and **9b**. The HFCs are collected in Table 2.

Table 2. Hyperfine Coupling Constants [MHz] of Porphyrin Semiquinone Radical Anions.

Compound	T [K]	$a_{2\beta}$ [a]	a_3	$a_{2\gamma}$ [b]	a_5	a_6
10a$^{\bullet-}$	280	+2.72	-2.52	0.13	1.77 [c]	1.73 [c]
9b$^{\bullet-}$	280	+1.41	-2.47	0.18	1.79 [c]	1.68 [c]
13a$^{\bullet-}$	270	+7.47	-5.17	0.21	-6.85	-7.14
13b$^{\bullet-}$	270	+3.34	-5.12	0.39	-6.91	-7.05

Error ± 0.005 MHz; 28.06 MHz = 1 mT.
[a] β-Cyclohexylproton (1H); [b] γ-, δ-Cyclohexylprotons[19] (4H), for positions, cf. Fig. 2; [c] ^{14}N HFC, only one ^{14}N-ENDOR line could be detected; values from EPR simulation (2N), accounting for different linewidth effects of the nitrile groups.

The ENDOR spectra not only show different ^1H ENDOR signals, centered around the free proton frequency but in addition ^{14}N high-frequency lines stamming from the cyano groups (B_0= 335.24 mT, Larmor frequency ν_N = 0.96 MHz). From these signals HFCs for a_5(CN) and a_6(CN) can be extracted (1.80 MHz for **10a** and 1.78 MHz for **9b**, the slightly different data given in Tab. 2 are those from EPR spectra simulation). For simulations and iterative least-squares fitting, the program HFFIT described previously[19] was used with the modification to handle M_I dependent linewidths. For the nitril groups different ^{14}N HFCs and linewidths parameters could be determined, see Table 2. Assignments were achieved from the linewidth effects, since the nitrile group in 5-position is on the long molecular axis, cf. Ref. 19 and 23.

Using the Heller-McConnell relation significantly different β cyclohexylene HFCs and thus different twist angles between cyclohexylene and semiquinone could be deduced, namely, 35° for the *cis*-isomer **10a** and 60° for the *trans* compound **9b**. It is noteworthy that these data are consistent with those previously reported for the cyano free analogues.[2a] In comparison with the cyano free porphyrin-quinones the most striking difference is the drastically reduced HFC constant for the semiquinone ring proton HFC, indicating that a considerable delocalization of the unpaired electron occurs to the cyano substituents. This results in a considerable HFC of the cyano nitrogens, allowing - at least the high frequency - ^{14}N-ENDOR line to be detected. It may be assumed that this difference in spin density distribution will be of influence on the acceptor and thereby ET properties of the free bases and zinc complexes of the cyano porphyrin-quinones.

EPR spectroscopy of photochemically generated radicals in reversed micelles.

Anisotropic media like micelles or liquid crystals can be used as solvents for mimicking directionality of ET in the membrane bound pigments of the photosynthetic reaction centers. In reversed micelles an inner water pool is surrounded by the amphiphilic detergent molecules and by the bulk hydrophobic

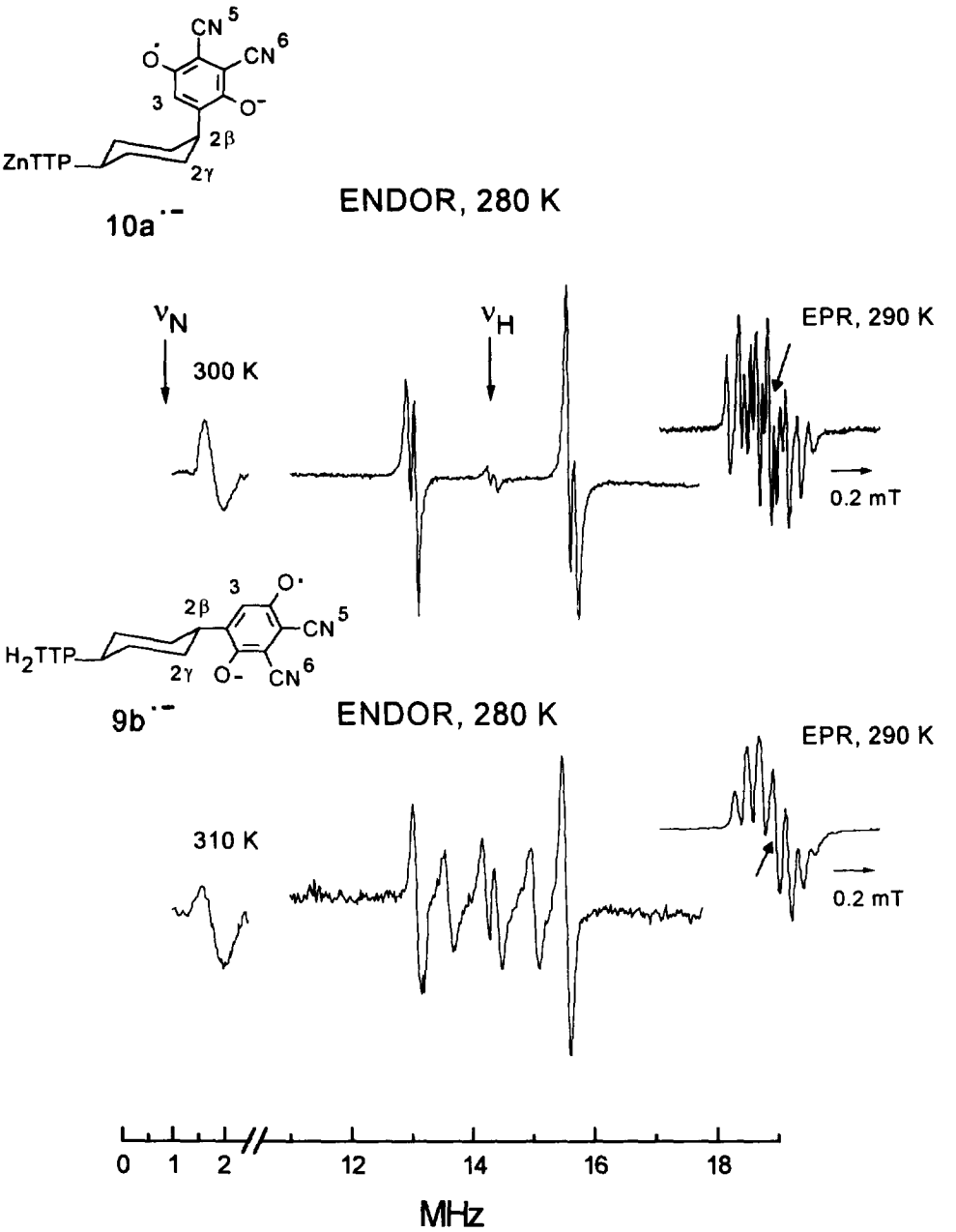


Figure 2. EPR and ENDOR spectra of the semiquinone anion radicals of **10a** and **9b** taken in isopropanol; for details, see Experimental. The signal at about 2 MHz is the high-frequency ^{14}N ENDOR line; ν_N and ν_H are the free nuclear frequencies.

hydrocarbon. It should be noted that, in contrast to water solutions, reversed micelles are suitable for EPR and particularly ENDOR experiments due to their lower microwave absorption (the bulk is hydrocarbon).[20]

Recently we have shown that *in situ* photoexcitation of reversed micellar solutions of porphyrin-quinones (or their hydroquinoid forms) through resonator slits of the EPR spectrometer at ambient temperatures, yielded paramagnetic transient species.[21] They could easily be identified as semiquinone anions since the steady state EPR spectra are almost superimposable with those of the corresponding, chemically generated radicals. On turning off the light, the EPR signals disappear reappearing again under turning on the light. It is particularly interesting that in the case of the cyano substituted compounds different spectral features could be observed in different micelles, see Figure 3.

In both micelles, i.e., CTAB or Triton X-100, before irradiation the (dark) EPR signal of the semiquinone radical anion is detected. In the former micelles the signal intensity increases under irradiation, decreasing after longer irradiation. In contrast, in Triton X-100 micelles - shortly after irradiation - the EPR signals turn into full emission. Moreover, the spectrum is a superposition of a broad (porphyrin type) radical cation and the narrow, hyperfine resolved semiquinone. This finding is indicative of a strong electron spin polarization mechanism. Previously, we were able to give an interpretation of this altogether puzzling situation during our studies of other porphyrin-quinones,[21] using the so-called radical/triplet pair mechanism, introduced by Paul and coworkers.[22]

Undoubtedly, the main reaction proceeding on a very fast time scale (under the experimental conditions used), is the photoinduced cycling ET process *via* the singlet channel and thus EPR blind. Species detectable by steady state EPR can only be generated through *intermolecular* reactions. This reaction requires two porphyrin-quinone molecules to be in the same micelle and a prerequisite for a pronounced radical triplet pair mechanism is the formation of the porphyrin triplet *via* spin orbit intersystem crossing (ISC) from the singlet excited state and a sufficiently long lifetime of the triplet. Only in the hydroquinoid form singlet ET is blocked and the adjacent singlet excited porphyrin will undergo ISC and generate long-lived triplet states.

In fact, after freezing a Triton X-100 micellar solution of hydroquinones **8a, 8b** respectively, and *in situ* irradiation, the photoexcited triplet state of the porphyrin could be detected (not reproduced in the Figure). The finding that only in Triton X-100 micelles emissive EPR signals are observed, whereas in CTAB micelles the signals remain absorptive, cannot yet be explained. It may be assumed that the different properties of the detergent molecules, that is, neutral amphiphilic Triton X-100 and positively charged ammonium headgroups in CTAB, differently affect either the location of the photoreactive aggregates in the interface of the micelle or the ET dynamics between the triplet state and the doublet state species. Further studies of the polarization processes are in progress.

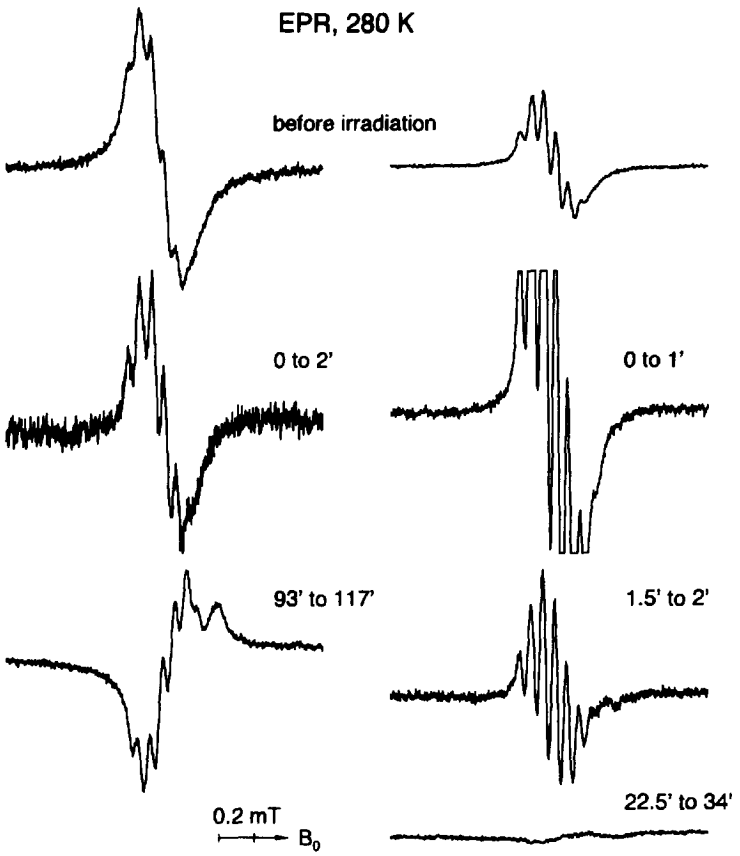


Figure 3. EPR spectra of **8b** in Triton X-100 (left) and CTAB (right) reversed micelles, observed under *in situ* irradiation (light cut-off filter 395 nm) in the EPR cavity,observation time in minutes, for details see Experimental. In both micelles a (dark) signal is already observed before irradiation, increasing under light in CTAB, then decreasing. In Triton X-100 micelles the signal turns into emission shortly after turning on the light. Note that the emissive signal is a superposition of two paramagnetic species, see text.

In summary, it can be stated that the energy gap between the photoexcited singlet state of the porphyrin and the charge-separated state, i.e., the driving force ΔG_{ET} for the dicyano porphyrin-quinones, is more than twice as large as the gap of the benzoquinone analogues. In this respect the novel porphyri-quinones are no doubt interesting candidates for further time-resolved optical and magnetic resonance spectroscopies, specifically, time-resolved picosecond fluorescence and time-resolved EPR. Work along this line is already proceeding.

EXPERIMENTAL

Cyclic voltammetry: Potentiostat: Heka Elektronic PG28; output: Siemens Kompensograph C1020; Cell: Metrohm; reference electrode Ag/AgCl (LiCl/ethanol/saturated); 0,1 M solution of tetrabutylammonium perchlorate (TBAP) in dry dichloromethane; all measurements were performed at 20 °C; concentration of compounds $1 \cdot 10^{-4}$ M; voltage increase rate 50 mV/s, reference ferrocene [$E(Fc/Fc^{+}) = +0{,}499 \pm 0{,}01$ V]. The solvent system was calibrated prior to addition of electroactive agent by determining the CV potential limits, defined by background current < 20 μA.

EPR and ENDOR spectra: Steady state EPR experiments were performed using a Bruker ER 200D spectrometer, interfaced to a PC computer to allow data averaging. A 1000 W Hg-Xe lamp (Oriel) was used as an excitation source in conjunction with a water filter and either a 395 or a 570 nm cut-off filter. Experiments were carried out at 295 K, the temperature being controlled with a Bruker VT-1000 temperature control unit. For ENDOR measurements laboratory-built NMR supplements were used, described elsewhere.[16a] Typical experimental conditions for ENDOR experiments: microwave power 10 mW, radiofrequency power 100 W (corresponding to a field strength of B_{RF} ca. 0.3 mT in the rotating frame) and radio frequency modulation ±25 kHz at 10 kHz in ENDOR, for details, see Ref. 23.

For EPR and ENDOR studies of chemically generated semiquinone derivatives, solutions of **13a, 13b** were treated in 2-propanol with benzyltrimethylammonium hydroxyde as base, and, if necessary, with a trace of benzoin as reductant; solutions of cyano porphyrin-quinones **8a**, **9b** in 2-propanol were oxidized by addition of Ag_2O and treated with tetrabutylammonium hydroxide. Reversed micellar solutions were prepared with isooctane/hexan-1-ol (5:1 v/v) as the organic solvent. Cetyltrimethylammonium bromide (CTAB, 0.2 mol dm^{-3}) was used as cationic and Triton X-100 (0.1 mol dm^{-3}), a polyethylene derivative, as neutral detergent. Aqueous solution ($5 \cdot 10^{-2}$ mol dm^{-3} sodium phosphate buffer, pH ca. 7) was added to give a W_0 (molar ratio of water to surfactant) of approximately 10. The porphyrin-quinones were dissolved in methylene chloride and transferred to the sample tube where the solvent was removed by flushing with argon. The micellar solution was added and the solution flushed with argon to remove oxygen. Ethanol solutions were prepared in a similar manner. The concentration of the porphyrin-quinones was approximately $5 \cdot 10^{-4}$ mol dm^{-3}. The samples were closed using a ground glass stopper. No significant differences in results were obtained when samples were degassed by freeze-pump-thaw cycles and then sealed under high vacuum.

Syntheses: The synthesis of **11a** is analogue to that published previously for the cyclohexylene bridged triphenylporphyrin quinones[2], therefore no experimental details will be given here.

5-(4(a)-[p-Benzoquinonyl]-cyclohex-(e)-ylene)-10,15,20-tri-*p*-tolyl-porphyrin (11a):
m.p. = 241°C. MS (EI, 350°C): m/z = 770 (9%, $[M+2H]^+$), 768 (4%, M^+), 580 (86%, tritolylporphyrin$^+$). IR (KBr): ν = 3309 (s, N-H), 3019 (m, aryl-H), 2916, 2865 (s, C-H), 1655 (s, C=O), 1596 (m, quinone C=O), 1557 and 1510 cm^{-1} (m, C=C). ^1H NMR (500 MHz, $CDCl_3$): δ = -2.64 (s, 2H; -NH), 2.5 (m, 4H; cyclohexane-$H_{a,e}$-3, -5), 2.6-2.75 (s, 3H; 15-tolyl-CH_3; s, 6H; 10, 20-tolyl-CH_3 and 2H; cyclohexane-H_e-2, -6), 3.25 (m, 2H; cyclohexane-H_a-2, -6), 3.6 (s, 1H; cyclohexane-H_e-4), 5.32 (t, 1H; cyclohexane-H_a-1), 6.93 (s, 2H;quinone-H-5, -6) 7.39 (s, 1H; quinone-H-3), 7.54 (two d, 6H; tolyl-H_{meta}), 8.05 (two d, 6H; tolyl-H_{ortho}), 8.79 (AB, 4H; porphyrin-H-12, -13, -17, -18), 8.87 (d, 2H; porphyrin-H-2, -8), 9.5 ppm (d, 2H; porphyrin-H-3, -7). Anal. calcd. for $C_{53}H_{44}N_2O_2$ (768.9): C 82.79, H 5.77, N 7.20, found: C 82.69, H 5.72, N 7.07.

5-(4(a)-[*p*-benzoquinonyl]-cyclohex-(e)-ylene)-10,15,20-tri-*p*-tolyl-porphyrin zinc (12a):
m.p. = 296°C. MS (EI, 350°C): m/z = 832 (23%, $[M+2H]^+$), 830 (8%, M^+), 642 (100%, tritolylporphyrin zinc$^+$). IR (KBr): ν = 3020 (w, aryl-H), 2920, 2851 (s, C-H), 1655 (s, C=O), 1595 (m, quinone C=C), 1524 cm^{-1} (m, C=C). ^1H NMR (500 MHz, $CDCl_3$): δ = 2.49 (m, 4H; cyclohexane-$H_{a,e}$-3, -5), 2.62-2.76 (s, 3H; 15-tolyl-CH_3; s, 6H; 10, 20-tolyl-CH_3 and 2H; cyclohexane-H_e-2, -6), 3.32 (m, 2H; cyclohexane-H_a-2, -6), 3.6 (s, 1H; cyclohexane-H_e-4), 5.46 (t, 1H; cyclohexane-H_a-1), 6.91 (s, 2H; quinone-H5, -6), 7.4 (s, 1H; quinone-H-3), 7.55 (two d, 6H; tolyl-H_{meta}), 8.07 (two d, 6H; tolyl-H_{ortho}), 8.9 (AB, 4H; porphyrin-H-12, -13, -17, -18), 9.02 (d, 2H; porphyrin-H-2, -8), 9.66 (d, 2H; porphyrin-H-3, -7). Anal. Calcd. for $C_{53}H_{42}N_4O_2Zn$.: 830.25992 Found: 830.25903 (MS: $[C_{53}H_{42}N_4O_2{}^{64}Zn]^+$), and 832.27535 (MS: $[C_{53}H_{44}N_4O_2{}^{64}Zn]^+$)

3a, 3b: To a stirred solution of 7.5 g (0.03 mol) of **2a/b** in isopropanol (1000 ml) are added 98% sulfuric acid (1.7 ml, 0.03 mol) in isopropanol (15 ml) and 11.7 g (0.18 mol) of KCN in 35 ml water in this order (Caution! HCN), while the temperature is kept between 20 and 30°C. After stirring for 10 h, a freshly prepared, saturated solution of $Na_2S_2O_4$ in water is added in portions of 10 ml to the black solution (pH=7) until precipitation is complete. The now orange solution is filtered and condensed to near dryness to remove isopropanol. After addition of 400 ml of water and 100 ml of ether, the mixture is acidified by sulfuric acid to pH=1 and extracted with 4 portions (100 ml) of ether. The etheric solution is dried (Na_2SO_4) and the solvent evaporated. Repetitive chromatography (SiO_2 , ether) yielded the hydroquinones of **2a/b** (2.58 g, 12.8 mmol, 85%), and the target compounds **3a** (2.58 g, 8.6 mmol, m.p. 220°C, decomp.)

and 3b (1.72 g, 5.7 mmol, m.p. 230°C, decomp.) as colourless crystals (total yield of **3a** and **3b** both 95%).

Methyl-4(e)-(3,4-dicyano-2,5-dihydroxy-phenyl)-cyclohexane-(a)-carboxylate (3a):
MS (EI, 180°C): m/z = 300 (37%, M^+), 268 (42%, $[M-CH_3OH]^+$), 240 (100%, $[M-CH_3OH-CO]^+$). IR (KBr): ν = 3276-3379 (s, OH), 2945 (s, C-H), 2240 (s, C≡N), 1732, 1699 (s, C=O), 1605 cm^{-1} (m, C=C). ^1H NMR (250 MHz, [D_6] DMSO): δ = 1.38 (q, 2H; cyclohexane-H_a-3, -5), 1.63 (m, 4H; cyclohexane-H_a-2, -6; -H_e-3, -5), 2.11 (d, 2H; cyclohexane-H_e-2, -6), 2.78 (s, 1H; cyclohexane-H_e-1), 2.95 (t, 1H; cyclohexane-H_a-4), 3.65 (s, 3H; CH_3), 7.05 (s, 1H; phenyl-H-6) and 10.28 and 11.07 ppm (two s, 2H; OH). Anal. Calcd. for $C_{16}H_{16}O_4N_2$ (300.3): C 63.99, H 5.37, N 9.33, found: C 64.04, H 5.64, N 9.32.

Methyl-4(e)-(3,4-dicyano-2,5-dihydroxy-phenyl)-cyclohexane-(e)-carboxylate (3b):
MS (EI, 180°C): m/z = 300 (22%, M^+), 268 (35%, $[M-CH_3OH]^+$); 240 (100%, $[M-CH_3OH-CO]^+$). IR (KBr): ν = 3280-3365 (s, OH), 2954, 2938 (s, C-H), 2242 (s, C≡N), 1709 (s, C=O), 1609 cm^{-1} (m, C=C). ^1H NMR (250 MHz, [D_6] DMSO): δ = 1.24-1.59 (m, 4H; cyclohexane-H_a-2, -3, -5, -6), 1.8 (d, 2H; cyclohexane-H_e-3, -5), 2.0 (d, 2H; cyclohexane-H_e-2, -6), 2.42 (t, 1H; cyclohexane-H_a-1), 2.89 (t, 1H; cyclohexane-H_a-4), 3.6 (s, 3H; CH_3), 7.07 (s, 1H; benzene-H-6), 10.28 and 11.15 ppm (two$? s, 2H; OH). Anal. Calcd for $C_{16}H_{16}O_4N_2$ (300.3): C 63.99, H 5.37, N 9.33, found: C 63.95, H 5.41, N 8.88.

4: 0.60 g (2.0 mmol) of **3** and 3.0 g solid K_2CO_3 in 80 ml dry acetone are stirred under argon and heated under reflux. After addition of 0.47 ml (4.0 mmol) of benzyl bromide and refluxing for another hour, the mixture is allowed to cool, filtrated and the solvent evaporated. Recrystallization from ethanol yields 0.93 g (1.90 mmol, 97-99 %) of **4** in white needles (**4a** m.p. 146°C, **4b** m.p. 132°C).

Methyl-4(e)-(2,5-bis-benzyloxy-3,4-dicyano-phenyl)-cyclohexane-(a)-carboxylate (4a):
MS (EI, 180°C): m/z = 480 (39%, M^+), 449 (3%, $[M-CH_3O]^+$), 91 (100%, $[C_7H_7]^+$). IR (KBr): ν = 3032 (w, aryl-H), 2947 (s, C-H), 2227 (s, C≡N), 1730 (s, C=O), 1588 cm^{-1} (s, C=C). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.34-1.56 (m, 6H; cyclohexane-H_a-2, -6, -3, -5; -H_e-3, -5), 2.19 (d, 2H; cyclohexane-H_e-2, -6), 2.71 (s, 1H; cyclohexane-H_e-1), 2.8 (t, 1H; cyclohexane-H_a-4), 3.73 (s, 3H; -CH_3), 5.1 and 5.2 (two s, 4H; -CH_2-), 7.03 (s, 1H; phenyl-H-6) and 7.35-7.47 ppm (m, 10H; benzyl-H). Anal. Calcd. for $C_{30}H_{28}O_4N_2$ 480.20491, found 480.20480 (MS: M^+).

Methyl-4(e)-(2,5-bis-benzyloxy-3,4-dicyano-phenyl)-cyclohexane-(e)-carboxylate (4b):
MS (EI, 130°C): m/z = 480 (8%, M^+), 91 (100%, $[C_7H_7]^+$). IR (KBr): ν = 3032 (w, aryl-H), 2942 (s, C-H), 2232 (s, C≡N), 1730 (s, C=O), 1586 cm^{-1} (s, C=C). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.19 (q, 2H; cyclohexane-H_a-3, -5), 1.42 (q, 2H; cyclohexane-H_a-2, -6), 1.6 (d, 2H; cyclohexane-H_e-3, -5), 2.03 (d, 2H; cyclohexane-H_e-2, -6), 2.26 (t, 1H; cyclohexane-H_a-1), 2.76 (t, 1H; cyclohexane-H_a-4), 3.67 (s, 3H; CH_3), 5.09 and 5.2 (two s, 4H; -CH_2-), 6.96 (s, 1H; phenyl-H-6) and 7.4 ppm (m, 10H; benzyl-H). Anal. Calcd. for $C_{30}H_{28}O_4N_2$ (480.6): C 74.98, H 5.87, N 5.83, found: C 74.84, H 5.95, N 5.48.

5: A solution of 0.90 g (1.90 mmol) of 4 in a mixture of 100 ml of dry ether and 50 ml of dry dichloromethane is vigorously stirred under argon and cooled to -95°C. 5.60 ml (5.60 mmol) of DIBAH (diisobutylaluminium hydride in 1 M solution in dichloromethane) are added and the mixture kept at -95°C for one h. Then 20 ml of 12% HCl are added and after warming up the solution is washed with aqueous $NaHCO_3$ and water. After evaporation of the solvent 0.8 g (1.77 mmol, 94-95%) of **5** precipitate in white crystals (**5a** m.p. 153°C, **5b** m.p. 125°C).

4(e)-(2,5-Bis-benzyloxy-3,4-dicyano-phenyl)-cyclohexane-(a)-carbaldehyde (5a):
MS (EI, 150°C): m/z = 450 (6%, M^+), 422 (1%, $[M\text{-}CO]^+$), 91 (100%, $[C_7H_7]^+$). IR (KBr): ν = 3034 (w, aryl-H), 2936, 2916 (s, C-H), 2228 (s, C≡N), 1716 (s, C=O), 1587 cm^{-1} (s, C=C). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.15 (q, 2H; cyclohexane-H_a-3, -5), 1.45 (d, 2H; cyclohexane-H_e-3, -5), 1.53 (q, 2H; cyclohexane-H_a-2, -6), 2.28 (d, 2H; cyclohexane-H_e-2, -6), 2.53 (s, 1H; cyclohexane-H_e-1), 2.76 (t, 1H; cyclohexane-H_a-4), 5.11 and 5.19 (two s, 4H; -CH_2-), 6.92 (s, 1H; phenyl-H-6), 7.42 (m, 10H; aryl-H) and 9.72 ppm (s, 1H; -CHO). Anal. Calcd. for $C_{29}H_{26}O_3N_2$: 450.19434, found: 450.19422 (MS: M^+).

4(e)-(2,5-Bis-benzyloxy-3,4-dicyano-phenyl)-cyclohexane-(e)-carbaldehyde (5b):
MS (EI, 250°C): m/z = 450 (3%, M^+), 91 (100%, $[C_7H_7]^+$). IR (KBr): ν = 3032 (w, aryl-H), 2931, 2855 (s, C-H), 2228 (s, C≡N), 1721 (s, C=O), 1587 cm^{-1} (s, C=C). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.23 (m, 4H; cyclohexane-H_a-2, -3, -5, -6), 1.66 (d, 2H; cyclohexane-H_e-3, -5), 2.06 (d, 2H; cyclohexane-H_e-2, -6), 2.21 (t, 1H; cyclohexane-H_a-1), 2.74 (t, 1H; cyclohexane-H_a-4), 5.12 and 5.22 (two s, 4H; -CH_2-), 7.0 (s, 1H; phenyl-H-6), 7.39 (m, 10H; aryl-H) and 9.62 ppm (s, 1H; -CHO). Anal. Calcd for $C_{29}H_{26}O_3N_2$: 450.19434, found: 450.19428 (MS: M^+).

6: To 500 ml dry dichloromethane 530 mg (1.20 mmol) of **5**, 0.4 ml (3.5 mmol) of freshly distillated *p*-tolylaldehyde, 0.32 ml (4.7 mmol) of freshly distillated pyrrole and 0.36 ml (4.7 mmol) trifluoroacetic acid are added in this order under argon and exclusion of light. The mixture is stirred for two h., then 0.8 g (3.51 mmol) of DDQ in 100 ml dichloromethane are added and after stirring for another 30 min. the

mixture is shaken with 100 ml saturated aequous K_2CO_3 solution. 400 ml of water are added and the mixture is allowed to stand for 5 min. Subsequently it is transferred to a column and the organic phase filtered over silicagel (d 5 cm, h 15 cm) by adding two times dichloromethane (1000 ml) until the porphyrins are completely washed off. Chromatography (silicagel, dichloromethane) and recrystallization from dichloromethane/n-hexane yields 250 mg (0.25 mmol, 20-22%) violet crystals of **6** (**6a** m.p. 308°C, **6b** m.p. 291°C, decomp.).

5-(4(a)-[2,5-Bis-benzyloxy-3,4-dicyano-phenyl]-cyclohex-(e)-ylene)-10,15,20-tri-*p*-tolyl-porphyrin (**6a**): MS (FAB^+): m/z = 1002 (5%, $[M+H]^+$), 1001 (4%, M^+), 819 (2%, $[M-2C_7H_7]^+$). IR (KBr): ν = 3302 (m, N-H), 3023 (m, aryl-H), 2919, 2861 (s, C-H), 2227 (s, C≡N), 1583 and 1559 cm^{-1} (s, C=C). ^1H NMR (500 MHz, $CDCl_3$): δ = -2.64 (s, 2H; -NH), 2.35 (q, 2H; cyclohexane-H_a-3, -5), 2.41 (d, 2H; cyclohexane-H_e-3, -5), 2.62 (s, 3H; 15-tolyl-CH_3; and 2H; cyclohexane-H_e-2, -6), 2.69 (s, 6H; 10, 20-tolyl-CH_3), 3.17 (q, 2H; cyclohexane-H_a-2, -6), 3.57 (s, 1H; cyclohexane-H_e-4), 5.28 (t, 1H; cyclohexane-H_a-1), 5.21 and 5.5 (two s, 4H; -CH_2-), 7.4-7.58 (m, 16H; aryl-H and tolyl-H_{meta}), 7.88 (s, 1H; phenyl-H-6), 8.03 (d, 6H; tolyl-H_{ortho}), 8.79 (AB, 4H; porphyrine-H-12, -13, -17, -18), 8.88 (d, 2H; porphyrine-H-2, -8) and 9.42 ppm (d, 2H; porphyrine-H-3, -7). Anal. Calcd. for $C_{69}H_{56}N_6O_2$ (1001.2): C 82.77, H 5.64, N 8.39, found: C 82.84, H 5.62, N 8.27.

5-(4(e)-[2,5-Bis-benzyloxy-3,4-dicyano-phenyl]-cyclohex-(e)-ylene)-10,15,20-tri-*p*-tolyl-porphyrin (**6b**): MS (FAB^+): m/z = 1002 (23%, $[M+H]^+$), 819 (10%, $[M-2C_7H_7]^+$), 580 (26%, tritolylporphyrin$^+$), 91 (100%, $[C_7H_7]^+$). IR (KBr): ν = 3308 (m, N-H), 3022 (m, aryl-H), 2919, 2863 (s, C-H), 2228 (s, C≡N), 1584 and 1557 cm^{-1} (s, C=C). ^1H NMR (500 MHz, $CDCl_3$): δ = -2.65 (s, 2H; -NH), 1.82 (q, 2H; cyclohexane-H_a-3, -5), 1.98 (d, 2H; cyclohexane-H_e-3, -5), 2.65 (s, 3H; 15-tolyl-CH_3), 2.71 (s, 6H; 10-, 20-tolyl-CH_3 and 2H; cyclohexane-H_e-2, -6), 3.07 (q, 2H; cyclohexane-H_a-2, -6), 3.35 (t, 1H; cyclohexane-H_a-4), 5.19 (t, 1H; cyclohexane-H_a-1), 5.26 and 5.35 (two s, 4H; -CH_2-), 7.3 (s, 1H; phenyl-H-6), 7.4-7.64 (m, 16H; aryl-H and tolyl-H_{meta}), 8.08 (two d, 6H; tolyl-H_{ortho}), 8.78 (AB, 4H; porphyrine-H-12, -13, -17, -18), 8.92 (d, 2H; porphyrine-H-2, -8) and 9.5 ppm (d, 2H; porphyrine-H-3, -7). Anal. Calcd. for $C_{69}H_{56}N_6O_2 \cdot 0.5\ H_2O$ (1010.2): C 82.35, H 5.68, N 8.32, found: C 82.12, H 5.61, N 8.21.

7: 40 mg (0.04 mmol) of **6** in 200 ml acetic acid ethylester are hydrogenated (p H_2 1 atm) using 10 mg palladium charcoal (Pd 10%) as the catalyst for 24 h. 200 ml of dichloromethane are added and the mixture is washed with aqueous $NaHCO_3$ until UV-spectra no longer show the dication band at λ = 450 nm. After washing with water the organic layer is separated, dried with Na_2SO_4, filtered off (the catalyst is also removed at this step) and the solvent is evaporated. Chromatography (silicagel, dichloro-

methane/methanol: 10/1) yields 32 mg (0.04 mmol, 97-98%) of 7, precipitating after concentration of the solution as violet crystals (**7a** m.p. ›230°C decomp.; **7b** m.p. 340°C).

5-(4(a)-[3,4-Dicyano-2,5-dihydroxy-phenyl]-cyclohex-(e)-ylene)-10,15,20-tri-*p*-tolyl-porphyrin (7a): MS (FAB$^+$): m/z = 821 (4%, $[M+H]^+$), 820 (3%, M^+), 581 (1%, [tritolylporphyrin+H]$^+$), 580 (0.5%, tritolylporphyrin$^+$). IR (KBr): ν = 3500-3200 (s, OH), 3308 (s, N-H), 3021 (m, aryl-H), 2920, 2854 (s, C-H), 2230 (s, C≡N), 1608 and 1559 cm^{-1} (s, C=C). ^{1}H NMR (500 MHz, [D$_6$] DMSO): δ = -2.83 (s, 2H; -NH), 2.51 (m, 4H; cyclohexane-H$_{a,e}$-3, -5), 2.6-2.65 (s, 3H; 15-tolyl-CH$_3$; s, 6H; 10, 20-tolyl-CH$_3$ and 2H; cyclohexane-H$_e$-2, -6), 3.16 (q, 2H; cyclohexane-H$_a$-2, -6), 3.78 (s, 1H; cyclohexane-H$_e$-4), 5.42 (t, 1H; cyclohexane-H$_a$-1), 7.57 (two d, 6H; tolyl-H$_{meta}$), 8.01 (two d, 6H; tolyl-H$_{ortho}$), 8.05 (s, 1H; phenyl-H-6), 8.75 (AB, 4H; porphyrin-H-12, -13, -17, -18), 8.79 (d, 2H; porphyrin-H-2, -8), 9.72 (s, 2H; porphyrin-H-3, -7) and 10.55 and 11.53 ppm (two s, 2H; OH). Anal. Calcd. for $C_{55}H_{44}N_6O_2 \cdot CH_3OH$ (853.0): C 78.85, H 5.67, N 9.85, found: C 79.15, H 5.89, N 9.24.

5-(4(e)-[3,4-Dicyano-2,5-dihydroxy-phenyl]-cyclohex-(e)-ylene)-10,15,20-tri-*p*-tolyl-porphyrin (7b): MS (EI, 300°C): m/z = 820 (0.07%, M^+), 580 (2%, tritolylporphyrin$^+$). IR (KBr): ν = 3600-3200 (s, OH), 3314 (s, N-H), 3022 (m, aryl-H), 2923, 2853 (s, C-H), 2227 (s, C≡N), 1607 and 1557 cm^{-1} (m, C=C). ^{1}H NMR (500 MHz, [D$_6$] DMSO): δ = -2.85 (s, 2H; -NH), 2.1 (q, 2H; cyclohexane-H$_a$-3, -5), 2.2 (d, 2H; cyclohexane-H$_e$-3, -5), 2.59 (s, 3H; 15-tolyl-CH$_3$), 2.63 (s, 6H; 10, 20-tolyl-CH$_3$), 2.71 (d, 2H; cyclohexane-H$_e$-2, -6), 3.3 (q, 2H; cyclohexane-H$_a$-2, -6), 3.71 (t, 1H; cyclohexane-H$_a$-4), 5.42 (t, 1H; cyclohexane-H$_a$-1), 7.42 (s, 1H; phenyl-H-6), 7.52 and 7.55 (two d, 6H; tolyl-H$_{meta}$), 8.0 (two d, 6H; tolyl-H$_{ortho}$), 8.72 (AB, 4H; porphyrin-H-12, -13, -17, -18), 8.84 (d, 2H; porphyrin-H-2, -8), 9.94 (d, 2H; porphyrin-H-3, -7) and 10.6 and 11.35 ppm (two s, 2H; -OH). Anal. Calcd. for $C_{55}H_{44}N_6O_2$: 820.35257, found: 820.35288 (MS: M^+).

Zn-7: To a solution of 30 mg (0.0036 mmol) of 7 in 10 ml of dichloromethane/methanol (10/1) 1 ml of a saturated methanolic zinc acetate solution is added and stirred for 15 min. Chromatography (silicagel, dichloromethane/methanol 10/1) yields 30 mg (0.034 mmol, 94%) of **Zn-7** which crystallizes upon evaporation of the solvent (**Zn-7a** m.p. ›330°C, **Zn-7b** m.p. ›330°C).

5-(4(a)-[3,4-Dicyano-2,5-dihydroxy-phenyl]-cyclohex-(e)-ylene)-10,15,20-tri-*p*-tolyl-porphyrin zinc (8a): MS (FAB$^+$): m/z = 883 (3%, $[M+H]^+$). MS (EI, 350°C): m/z =.642 (100%, tritolylporphyrin zinc$^+$). IR (KBr): ν = 3500-3200 (s, OH), 3019 (m, aryl-H), 2919, 2860 (s, C-H), 2242 (s, C≡N), 1606 and 1530 cm^{-1} (m, C=C). ^{1}H NMR (500 MHz, [D$_6$] DMSO): δ = 2.55 (m, 4H; cyclohexane-H$_{a,e}$-3, -5), 2.6-2.9

(s, 3H; 15-tolyl-CH_3; s, 6H; 10, 20-tolyl-CH_3 and 2H; cyclohexane-H_e-2, -6), 3.25 (q, 2H; cyclohexane-H_a-2, -6), 3.78 (s, 1H; cyclohexane-H_e-4), 5.5 (t, 1H; cyclohexane-H_a-1), 7.56 (two d, 6H; tolyl-H_{meta}), 8.0 (two d, 6H; tolyl-H_{ortho}), 8.08 (s, 1H; phenyl-H-6), 8.70 (AB, 4H; porphyrin-H-12, -13, -17, -18), 8.76 (d, 2H; porphyrin-H-2, -8), 9.68 (s br., 2H; porphyrin-H-3, -7) and 10.52 and 11.52 ppm (two s, 2H; OH). Anal. Calcd. for $C_{55}H_{42}N_6O_2Zn \cdot H_2O$ (902.4): C 73.21, H 4.91, N 9.31, found: C 73.28, H 4.95, N 9.62.

5-(4(e)-[3,4-Dicyano-2,5-dihydroxy-phenyl]-cyclohex-(e)-ylene)-10,15,20-tri-*p*-tolyl-porphyrin zinc (8b): MS (EI, 350°C): m/z = 882 (7%, M^+), 642 (100%, tritolylporphyrin $zinc^+$). IR (KBr): ν = 3580-3200 (s, OH), 3020 (m, aryl-H), 2920, 2859 (s, C-H), 2240 (s, C≡N), 1608 and 1523 cm^{-1} (m, C=C). ^1H NMR (500 MHz, [D_6] DMSO): δ = 2.12 (q, 2H; cyclohexane-H_a-3, -5), 2.28 (d, 2H; cyclohexane-H_e-3, -5), 2.63 (s, 3H; 15-tolyl-CH_3), 2.66 (s, 6H; 10, 20-tolyl-CH_3), 2.76 (d, 2H; cyclohexane-H_e-2, -6), 3.33 (q, 2H; cyclohexane-H_a-2, -6), 3.76 (t, 1H; cyclohexane-H_a-4), 5.0 (t, 1H; cyclohexane-H_a-1), 7.44 (s, 1H; phenyl-H-6), 7.57 (two d, 6H; tolyl-H_{meta}), 8.1 (two d, 6H; tolyl-H_{ortho}), 8.7 (AB, 4H; porphyrin-H-12, -13, -17, -18), 8.82 (d, 2H; porphyrin-H-2, -8), 9.89 (d, 2H; porphyrin-H-3, -7) and 10.58 and 11.33 ppm (two s, 2H; -OH). Anal. Calcd. for $C_{55}H_{42}N_6O_2Zn \cdot H_2O$ (902.4): C 73.21, H 4.91, N 9.31, found: C 73.48, H 4.78, N 9.54.

3a/b quinone, 9a, 9b, 10a, and 10b: Oxidation of dicyano hydroquinones was achieved by addition of an access of at least five equivalents of freshly activated PbO_2[23] to the hydroquinone solution, followed by ultrasonofication for three min. and removal of the oxidant by pressure filtration over Celite 535 (FLUKA). Completeness of oxidation was controlled by UV spectra, i.e., disappearance of the absorption at λ = 337 nm. All procedures were carried out under dried argon and with exclusion of light.

ACKNOWLEDGEMENTS

This work was supported by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 337 and Normalverfahren), by the Volkswagen-Stiftung and by the Fonds der Chemischen Industrie.

REFERENCES AND NOTES

1 Comprehensive, more recent reviews are, e.g., Bixon, M., Fajer, J., Feher, G., Freed, J. H., Gamliel, D., Hoff, A. J., Levanon, H., Möbius, K. Nechushtai, R., Norris, J. R., Scherz, A., Sessler, J. L., Stehlik, D. *Isr. J. Chem.* **1992**, *24*, 369-518; Gust, D., Moore, T. A. *Adv. Photochem.* **1991**, *16*, 1f; Gust, D., Moore, T. A. *Top. Curr. Chem.* **1991**, *159*, 103-151; Wasielewski, M. R. *Chem. Rev.* 1992, *92*, 435-461; Kurreck, H., Huber, M. *Angew. Chemie*, **1995**, *107*, 929-947; *Angew. Chem. Int. Ed. Engl.*, **1995**, *34*, 849-866; Gust, D., Moore, T. A. In *The Photosynthetic Reaction Center* Deisenhofer, J., Norris, J. R. Eds. (Vol. II) 1993, Academic Press, p. 419-464; Wasielewski, M. R. In *The Photosynthetic Reaction Center*, Deisenhofer, J., Norris, J. R. Eds., Vol. II, 1993, Academic Press, p. 465-511.

2 Examples of cyclohexylene bridged porphyrin quinones are described in:
(a) Lendzian, F., Schlüpmann, J., von Gersdorff, J., Möbius, K., Kurreck, H. *Angew. Chem.* **1991**, *103*, 1536-1539; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1461-1463;
(b) Kurreck, H., von Gersdorff, J., Kirste, B., Lendzian, F., Schlüpmann, J., Möbius, K., Willig, F., Kietzmann, R. In *Proceedings of the International Workshop of Disordered Systems, EMARDIS-1991*, Yordanov, N. D. Ed.) World Scientific 1991, p. 158-174; Schlüpmann, J., Lendzian, F., Plato, M., Möbius, K. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 2853-2862; Hasharoni, K., Levanon, H., von Gersdorff, J., Kurreck, H., Möbius, K. *J. Chem. Phys.*, **1993**, *98*, 2916-2926; Batchelor, S. N., Sun, L., Möbius, K., Kurreck, H. *Magn. Reson. Chem.*, **1995**, in press; Fuchs, M., von Gersdorff, J., Dieks, H., Kurreck, H., Möbius, K., Prisner, T. *J. Chem. Soc. Faraday Trans.*, **1995**, in press.

3 Dieks, H., Sobek, J., Tian, P., Kurreck, H. *Tetrahedron Lett.* **1992**, *33*, 5951-5954.

4 See, e.g., Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966-679, Marcus, R. A. *Discuss. Faraday Soc.* **1960**, *29*, 21-31; Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679-701; Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891-899.

5 Yale, H. L. *J. Am. Chem. Soc.* **1957**, *79*, 4762-4765.

6 Jacobsen, N., Torssell, K. *Liebigs Ann. Chem.* **1972**, *763*, 135-147; N. Jacobsen, N., Sharman, S. C., Torssell, K. *Acta Chem. Scand.* 33 Ser.B,**1979**, 499-502.

7 Thiele, J., Meisenheimer, J. *Ber. Dtsch. Chem. Ges.* **1900**, *33*, 675-676; Wallenfels, K., Bachmann, G., Hofmann, D., and Kern, R. *Tetrahedron* **1965**, *21*, 2239-2256.

8 Winterfeldt, E. *Synthesis* **1975**, 617-630.

9 Staab, H. A., Weiser, J., Futscher, M., Voit, G., Rückemann, A., Anders, C. *Chem. Ber.* B125, **1992**, 2285-2301.

10 Lindsey, J. S., Schreiman, I. C., Hsu, H. C., Kearney, P. C., Marguerettaz, A. M. J. Org. Chem. 1987, 52, 827-836.

11 Wilford, J. H., Archer, M. D., Bolton, J. R., Ho, T.-F., Schmidtand, J. A., Weedon, A. C. *J. Phys. Chem.* **1985**, *89*, 5395-5398.

12 A. Weller, *Z. Phys. Chem. N.F.* **1982,** 133, 93-98, and Refs. cited.

13 Gritzner, G., Kuta, J. *Electrochim. Acta* **1984**, *29*, 869-873.

14 Staab, H. A., Voit, G., Weiser, J., Futscher, M. *Chem. Ber.* B125, **1992**, 2303-2310.

15 The second reduction step of the cyano quinones could be observed, but the peaks are very weak (except for **3a/b**), and therefore only rough estimates can be given. It is remarkable, however, that the second reduction potentials $E_{red}(Q^{-}/Q^{2-})$ of the cyano compounds experience the stabilization by the metallated porphyrin, for they are, as expected, shifted to higher potentials by 40, 70 mV respectively. Surprising is in this context, that the $E_{red}(Q^{-}/Q^{2-})$ in case of free base porphyrins **7a/b** are not shifted to positive potentials, but on the contrary, seem to be shifted to more negative potentials. This effect is probably due to poor solvation of the corresponding hydroquinone dianion. The difference in solvation of the diastereomeres will also account for the difference in shifts of the second potentials $E_{red}(Q^{-}/Q^{2-})$ found for the diastereomeric hydroquinone dianions.

16 (a) Kurreck, H., Kirste, B., Lubitz, W. *Methods in Stereochemical Analysis*, ed. A. P. Marchand VCH Publishers, Inc. New York, **1988**;
(b) Möbius, K., Plato, M., Lubitz, W. *Phys. Rep.* **1982**, *87*, 171-208.

17 Heller, H. C., McConnell, H. M. *J. Chem. Phys.* **1960**, *32*, 1535-1539.

18 Huber, M. *Ph. D. Thesis*, **1989**, FU Berlin.

19 Kirste, B. *J. Magn. Reson.* **1987**, *73*, 213-224; Niethammer, D., Kirste, B., Kurreck, H. *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 3191-3196; Kirste, B., Niethammer, D., Tian, P., Kurreck, H. *Appl. Magn. Reson.* **1992**, *3*, 1-18.

20 Janzen, E. G., Kotake, Y., Coulter, G. A., Oehler, U. M. *Chem. Phys. Lett.* **1986**, *126*, 205-208; Bretz, N., Mastalsky, I., Elsner, M., Kurreck, H. *Angew. Chem.* **1987**, *99*, 357-359; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 345-347.

21 Kurreck, H., Tian, P., Dieks, H., von Gersdorff, J., Newman, H., Schubert, H., Stabingis, T., Wiehe, A., Sobek, J. *Appl. Magn. Reson.* **1994**, *6*, 17-27; Kurreck, H., Aguirre, S., Batchelor, S. N., Dieks, H, von Gersdorff, J., Kay, C. W. M., Mößler, H., Newman, H, Niethammer, D., Schlüpmann, J., Sobek, J., Speck, M., Stabingis, T., Sun, L., Tian, P., Wiehe, A., Möbius, K. *Sol. Energy Mat.* **1995**, *38*, 91-110; Kay, C. W. M., Kurreck, H., Batchelor, S. N., Tian, P., Schlüpmann, J., Möbius, K. *Appl. Magn. Reson.* **1995**, *9*, 459-480.

22 Blättler, C., Jent, F., Paul, H. *Chem. Phys. Lett.* **1990**, *166*, 375-380; Blättler,C., Paul, H. *Res. Chem. Intermed.* **1991**, *16*, 201-207; Goudsmit, G.-H., Paul, H., Shushin, A. I. *J. Phys. Chem.* **1993**, *97*, 13243-13249.

23 Kuhn, R., Hammer, J. *Chem. Ber.* **1950**, *4*, 413-414.

(*Received in Germany* 15 *January* 1996; *revised* 24 *April* 1996; *accepted* 25 *April* 1996)