

Models for Photosynthesis: EPR Studies of Cyclohexylene-Linked Porphyrin Quinones†

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Time-resolved EPR spectra are reported for photoexcited cyclohexylene bridged porphyrin–quinone diads and porphyrin–quinone–quinone triads in isotropic solutions and in the soft glass phase of liquid crystals. Spin-polarized EPR spectra were observed for the charge-separated biradical states. The EPR polarization patterns are discussed in terms of the favored decay channel of the photoexcited singlet state of the porphyrin donor. The decay pathway may either be singlet electron transfer to the quinone(s) followed by singlet–triplet mixing to yield radical pairs (RP) with triplet character or, more likely, triplet electron transfer after spin–orbit intersystem crossing, or a superposition of both pathways. Using liquid crystals, information about the orientation of the guest molecules in the liquid crystal matrix with respect to the long axes of the liquid crystal molecules can be obtained. High field/high frequency (3.4 T, 95 GHz) EPR spectra of the transient porphyrin–quinone RP state are reported for the first time. By comparing the EPR measurements at different Zeeman fields, additional information about the polarization mechanism can be obtained.

Dedicated to Professor Klaus Möbius in honour of his 60th birthday

The search for an understanding of the factors controlling electron transfer (ET) reactions in the primary events of photosynthesis has led to the development of biomimetic model systems, consisting of porphyrins covalently linked to quinones (P-Qs).^{1–5} In these model compounds the porphyrin is photoexcited to the excited singlet state, from which at room temperature intramolecular ET occurs to the quinone, yielding the charge-separated radical pair (RP) in its singlet state. In most of these P-Qs electron back transfer restores the (starting) ground state of the system. Previously it was shown for cyclohexylene bridged P-Qs at low temperatures in highly viscous solutions that spin–orbit intersystem crossing (ISC) can compete with singlet ET. Under these conditions the porphyrin triplet state is created, from which ET may occur to the quinone with spin conservation, yielding the radical pair in its spin-polarized triplet state.^{6–8} Occurrence of the triplet route allows the direct observation of the ET processes by time-resolved EPR spectroscopy. These pronounced spin-polarization effects are generated as a result of spin selective ISC. Shortly after

photoexcitation the EPR spectrum of the spin-polarized triplet state of the porphyrin can be detected. Subsequently, rapid triplet ET occurs prior to polarization decay by T_1 relaxation. Hence, the triplet state of the RP exhibits spin-polarization as well.

In subsequent papers similar experiments on P-Qs were reported using liquid crystals as the 'solvent'.^{9–12} The observed changes of the polarization pattern of the radical pair were attributed, *inter alia*, to simultaneous triplet and singlet ET routes in the nematic and soft glass phase of these media.

In the present paper we review some of our recent results and extend the studies of cyclohexylene bridged P-Qs to triads P-Q_A-Q_B. These are aggregates that contain one porphyrin donor and two quinone acceptors. The photochemical properties of the triads are compared with those of the diads (for structures see formulas in Fig. 1). Steady-state and time-resolved EPR investigations of isotropic solutions and liquid crystals (LC) solutions are reported. In particular ordering effects of the guest molecules in the nematic and soft glass phase of the LC are discussed. Two different ET channels for creating the transient spin-polarized EPR spectra are possible: ET may occur either via the triplet channel involving ISC or, via the singlet channel, provided the

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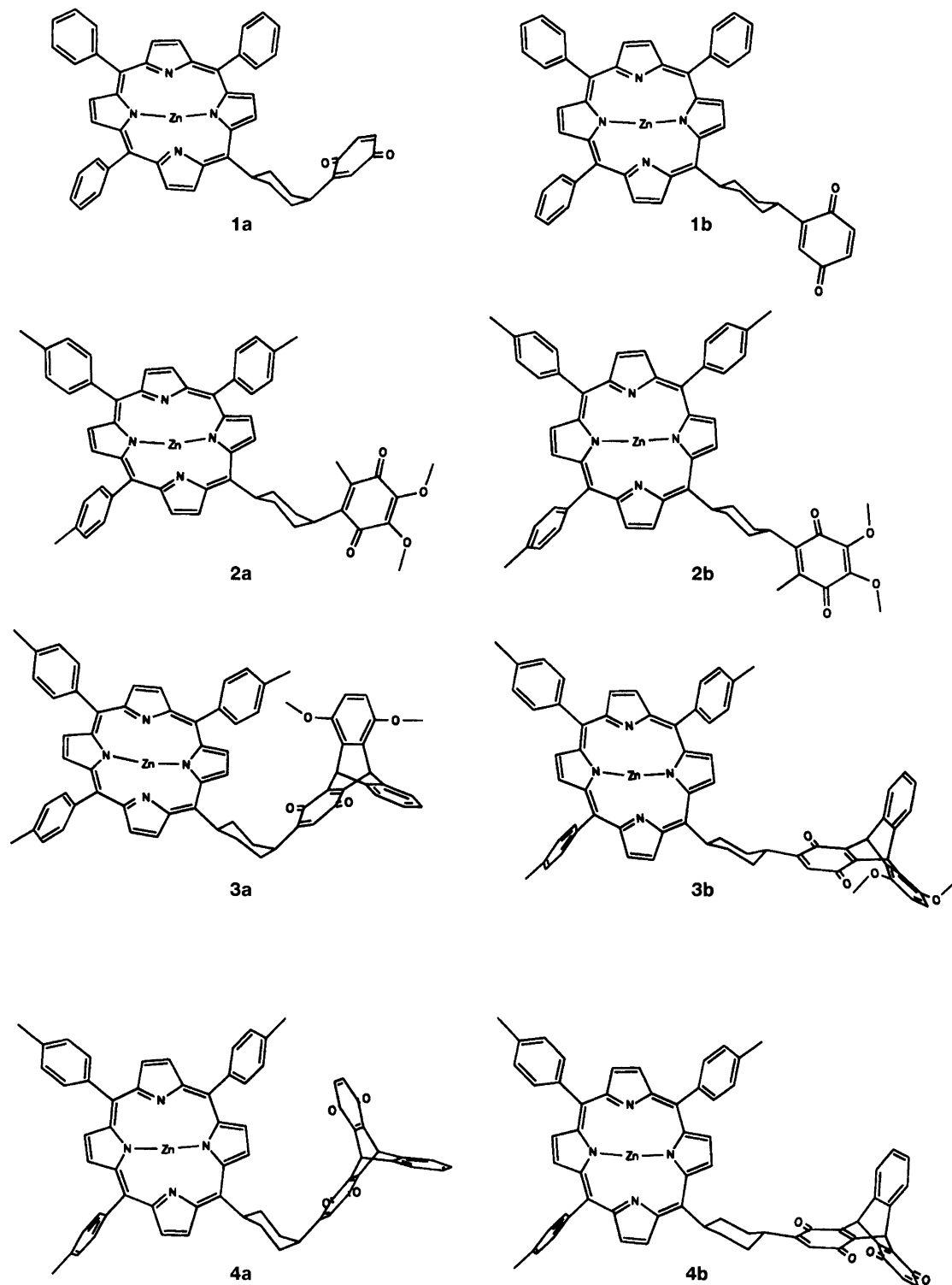


Fig. 1. Structures and numbering of compounds.

charge-separated state is sufficiently long-lived to allow S/T mixing. In principle, both pathways can be described by the correlated coupled radical pair model (CCRP) and discriminated by their different polarization patterns in the time-resolved EPR spectra. When the RP is generated via the singlet route the polarization should be calculated in the same way as reported for photosyn-

thetic reaction centers.¹³ In contrast with photosynthetic reaction centers, however, the polarization patterns of the P-Qs seem to be strongly dependent on relative molecular motion between the porphyrin and the quinone, governed by the flexibility of the cyclohexylene bridge. Rotation of the quinone around the bridge induces a more complex spin dynamic than in the static

case. In addition, the question is addressed of whether a stepwise ET occurs from the photoexcited porphyrin first to Q_A and subsequently to Q_B , or whether a direct ET from the porphyrin to Q_B also takes place. Extension of these experiments to high-field EPR are briefly discussed.

Experimental

The synthesis of the P-Q triads used (**4a**, **4b**, Fig. 1) will be described elsewhere.¹⁴ The liquid crystal used is E7 (Merck: Darmstadt, Germany; Poole, England). Solutions of the P-Qs in LC or isotropic solutions [ethanol, toluene, dimethoxyethane (DME)] were degassed by several freeze-pump-thaw cycles under high vacuum conditions before sealing the sample tube, or by being flushed with argon for at least 30 min. Different solvents and sometimes mixtures had to be used because of the low solubility of the triads and pretriads in ethanol. In the dark, the samples were stable over long periods of time.

Steady-state EPR experiments were performed using a Bruker 200D spectrometer interfaced to a PC computer to allow data averaging. A 1000 W Hg-Xe arc lamp (Oriel) was used as excitation source in conjunction with a water filter and either a 395 nm or a 570 nm cut-off filter. The temperature was controlled by a Bruker VT-1000 temperature control unit.

Time-resolved transient EPR spectra were obtained using an EPR spectrometer described previously.¹⁵ It consists of an X-band microwave bridge (Bruker ER046 XK-T) with two different detection arms, a fast one with a microwave mixer and a video preamplifier (80 Hz to 200 MHz) and a slow one with a microwave diode and a preamplifier (20 Hz to 6.5 MHz). The transient signals were detected directly (without field modulation) with a transient recorder (Tektronix TDS 520A). The time-resolution with the slow detection channel using a standard rectangular TE_{102} (AEG) cavity has a time-resolution of about 200 ns. The fast one, equipped with a home-built loop-gap cavity, has a time-resolution of 20 ns. The molecules were photoexcited by laser pulses from an excimer pumped dye laser (Lambda Physik, excimer laser LPX, dye laser 100 FL2002, 585 nm, 10 ns pulse length, 10–20 mJ pulse⁻¹, 20 Hz repetition rate). Each spectrum is a one-dimensional projection of a two-dimensional data set (time-resolved transients at various external magnetic field positions), which is measured within 15 min (18 000 laser pulses).

The W-band spectrometer (high-field EPR spectrometer) is described elsewhere.¹⁶ The diameter of the sample capillaries was 0.5 mm. The microwave field B_1 was about 0.002 mT and the detection bandwidth was set to 20 MHz.

Results and discussion

Time-resolved EPR in isotropic solution. Fig. 2 shows the reaction scheme valid for a diad-triad aggregate, i.e., consisting of one porphyrin donor, and one or two

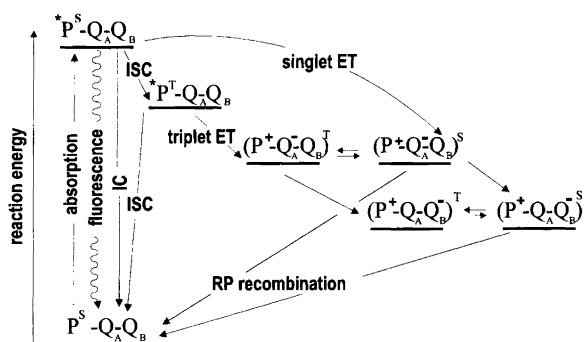


Fig. 2. Energy levels and ET reaction scheme of a triad P- Q_A - Q_B with different ET pathways (P: porphyrin, Q_A : center quinone, Q_B : terminal quinone). After photoexcitation to the excited singlet state of the porphyrin, spin selective intersystem crossing (ISC) competes with singlet ET. If the singlet ET becomes slow enough at low temperatures (140 K in ethanol) the preferred pathway is ISC, followed by triplet ET. Subsequently, ET from the center quinone to the terminal one can occur via both pathways. Singlet-triplet mixing of the spin states is also indicated, for details, see the text.

quinone acceptors. As already mentioned, the excited singlet state of the donor can be quenched by internal conversion, fluorescence, spin-selective spin-orbit intersystem crossing (ISC), and, in addition, by ET processes. The ET processes yield charge-separated transient states where one unpaired electron resides on the porphyrin and the other one on the quinone; in the triad case the other unpaired electron is either on Q_A or Q_B . First the diads P- Q_A (Q_B protected) **3a** and **3b**, here referred to as pretriads, will be considered. An e/a (a: absorption, e: emission) spin-polarized EPR signal was detected for both pretriads **3a** and **3b** (see Fig. 3, **3a/1** and **3b/2**). At 135 K in DME-ethanol the spin polarization decays in a 20 μ s time range. The splitting of the emission and absorption turning points is 5.52 ± 0.1 mT for the *trans* pretriad **3b** and 7.54 ± 0.1 mT for the *cis* pretriad **3a** (see Fig. 3, **3a/1** and **3b/2**). At higher temperatures (160 K) the spectra of both systems appear in emission (see Fig. 3, **3a/2** and **3b/1**). In the temperature range around 145 K in an ethanol-DME mixture the e/a spectrum becomes a full emission spectrum after longer delay times (see Fig. 3, **3b/2** and **3b/3**).

The detection of the emissive spectra and the magnitudes of the splittings of the turning points are in line with those reported previously for cyclohexylene-bridged porphyrin quinones **1a** and **1b** (see Fig. 4, left).^{7,8} The similarities between **1a** and **3a**, **1b** and **3b** are not surprising, because the bridge/acceptor fragments attached to the porphyrin are structurally identical, neglecting the ET inactive (protected) Q_B 'substitution' of the quinone Q_A .

The following interpretation was given for the spin-polarization observed. In isotropic solution at room temperature singlet ET takes place on a short (picosecond) timescale, thereby creating the singlet biradical, which in turn decays to the ground state. In this situation no transient EPR signal can be observed, because the

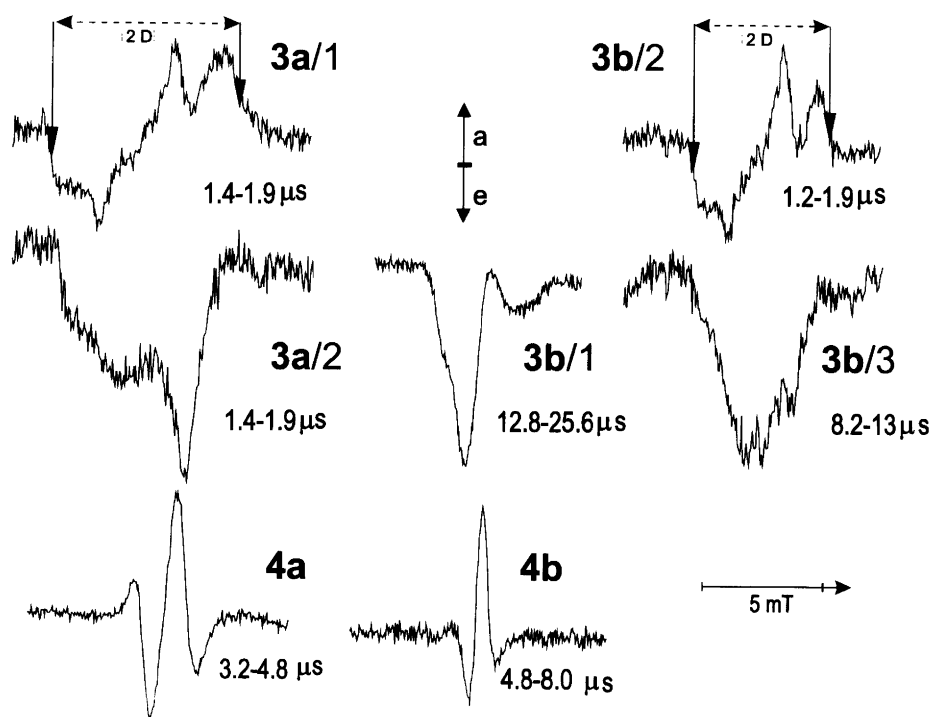


Fig. 3. Spin-polarized transient X-band EPR spectra of the triads and pretriads (Q_B protected) in isotropic solutions. *cis*-Conformer of the pretriad **3a/1** in an ethanol–DME mixture: at 135 K an *e/a* polarization can be observed (left, top); at 160 K the spectrum appears in emission (**3a/2**, left, center). *cis*-Conformer of triad **4a** in an ethanol–DME mixture at 160 K: under the same conditions as the pretriad **3a/2** the triad shows an *a/e/a/e* polarization (left, bottom). *trans*-Conformer of the pretriad **3b/1** in DME at 190 K: the whole spectrum appears in emission (center). *trans*-Conformer of the triad **4b/3** in DME at 190 K: an *a/e/a/e* polarization can be observed (bottom, center). Note that in contrast with the pretriads the EPR spectra of the triads do not become fully emissive – under the same conditions (left: **3a/2** versus **4a**, center: **3b/1** versus **4b**). At a certain temperature (145 K in an ethanol–DME mixture) the *trans* conformer of the pretriad **3b/2** shows the change of the *e/a* polarization to full emission at later delay times (**3b/3**, right). All spectra were accumulated over 50 laser excitations per point, the microwave power for the spectra of **4a** and **4b** was 6.2 mW, and for the other spectra was 19.8 mW.

decay of the singlet state is too fast. At low temperatures when solvent viscosity is increased, however, singlet ET is slower and ISC to the triplet state of the porphyrin, followed by triplet ET to the quinone, can successfully compete. Transient optical absorption measurements revealed that – after ISC – triplet ET occurs in the 100 ns time range.¹⁷ Following this route, the spin-polarized triplet state of the RP is generated with an *a/e* polarization indicative of the triplet mechanism. These *a/e* polarized spectra show a very low signal intensity. This might be due to relaxation and recombination processes being fast compared with ET and causing the later *e/a* and *e* polarization, which are discussed now.

For the P-Qs **1a** and **1b** the whole EPR spectrum occurs in emission after a 1 μ s delay, and no *e/a* polarization is observed (Fig. 4, left). Based on a static radical pair model it was concluded that the change of the starting *a/e* polarization pattern arises from an effective S/T_0 and S/T_- mixing and subsequent electron back transfer from the singlet level to the ground state.⁸ It should be noted that below 140 K the P-Qs **1a** and **1b** also show an *e/a* polarization (unpublished results). This *e/a* polarization is difficult to explain by the radical pair mechanism used in Ref. 8.

We would like to emphasize that the characteristic spectral features (polarization: *e/a* or *e*, and the splitting of the turning points in the *e/a* spectrum) are obtained in all the isotropic solvents and solvent mixtures used (ethanol, ethanol–DME, ethanol–toluene, DME). It is not surprising that, owing to differences in viscosity and polarity of the media, the corresponding polarization patterns are observed at different temperatures.

The *e/a* polarization is also observed at higher temperatures for the specific class of cyclohexylene linked P-Qs where a methyl substituent at the quinone *ortho* to the cyclohexylene bridge is introduced (see Fig. 4, right). Therefore, we assume that the different molecular flexibility, i.e., more or less free or severely hindered rotation about the single bond between quinone and cyclohexylene bridge, accounts for the different polarization signature. It is currently under investigation how a more pronounced molecular dynamic process modulates, via relative orientation and separation between donor and acceptor, the important parameters for the spin dynamics, such as the exchange interaction J , the dipole–dipole interaction D and Δg - and hyperfine-induced state mixing. Whereas the rotation within the substituted system is hampered by the methyl group, in the case of

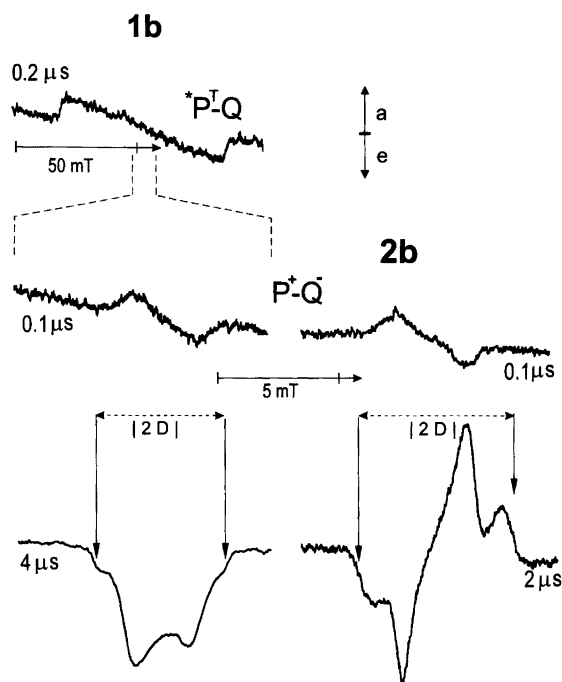


Fig. 4. Time-resolved EPR X-band spectra of cyclohexylene-linked P-Qs with a benzoquinone (left) and a ubiquinone acceptor (right). Note the different spin polarization pattern after longer delay times. Whereas the unsubstituted P-Q finally exhibits a fully emissive spectrum, that of the porphyrin ubiquinone remains in *e/a* (for details, see the text). The integration window for every spectrum was 500 ns. All spectra were measured with 19.8 mW microwave power. 24 laser excitations were accumulated per point. For details of the emissive spectra of the diads **1a** and **1b** see Ref. 8.

the non-substituted quinone acceptor system lower temperatures are needed in order to 'freeze out' librations. This finding seems to be quite general since it was also detected for other P-Q systems with different quinone substituents (unpublished results). In the context of this interpretation it should be noted that previous ENDOR and ENDOR-induced EPR (EIE) studies on semiquinone derivatives of P-Qs, bearing a methyl group at the quinone next to the cyclohexylene bridge, indicated the presence of two different conformer species in the solvent used.¹⁸ Fig. 5 shows EPR, ENDOR and EIE spectra of the radical anion of the *trans* linked P-Q **2b** with a ubiquinone acceptor. The EIE spectra clearly indicate different *g*-factors of the two species. Note the different positions of the methyl groups in the energetically favored conformations, obtained from molecular modeling calculations. It stands to reason that the EIE spectra I and II cannot be assigned to their specific conformer.

To gain better insight into the spin-polarization properties, the results of the isotropic solution studies are compared with those obtained in liquid crystals. For all P-Qs in the LC media the spectra are *e/a* polarized. Unexpectedly no full emission is observed. The occurrence of *e/a* polarization is apparently not caused by a unique property of the LC medium. The high viscosity of this solvent reduces the libration dynamics of the P-Q.

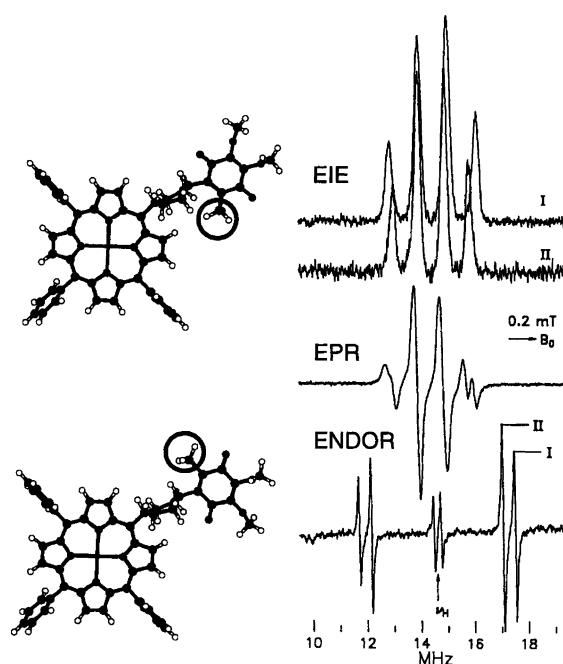


Fig. 5. EPR (290 K), ENDOR (290 K), and EIE spectra (270 K) of the chemically generated semiquinone radical anion of a cyclohexylene-linked porphyrin ubiquinone (**2a**). The energetically favored conformations (derived from Alchemy III and MNDO calculations) are also given. It can be seen that the spectra, in particular the EIE spectra, indicate two species with different *g* factors. The Roman numerals in the ENDOR spectrum characterize the field positioning used in measuring the spectra I and II, respectively. In the P-Q used here the porphyrin moiety was substituted with tolyl fragments. The *para* methyl groups on the phenyl rings of the porphyrin are omitted (for details see Ref. 18).

This is very similar to the effect observed on cooling the isotropic solution, or alternatively, when introducing a steric restraint, that is, a methyl substituent *ortho* to the bridging cyclohexylene group. Obviously, two classes of the present types of P-Q can be discriminated: (a) P-Qs with some freedom of rotation between bridge and quinone acceptor (**1a**, **1b**, **3a**, **3b**), and (b) P-Qs with sterically hindered rotational motion of the bridge/acceptor fragments, such as the ubiquinone linked system (**2a**, **2b**).

Different EPR spectra are obtained for the triads **4a** and **4b** (Fig. 3, **4a** and **4b** bottom). For both triads in isotropic solution the biradical EPR spectra show after photoexcitation an antiphase *a/e/a/e* pattern which decays like that of the pretriads within 20 μ s. (Note that, although these spectra exhibit a first-derivative lineshape, they are recorded in the direct detection mode without field modulation). The absorptive peak on the low field side of **4b** is very weak (Fig. 3, bottom, compare **4a** and **4b**). The width of the spectrum of the *cis* triad **4a** is 3.0 mT, whereas the spectral width of the *cis* pretriad **3a** amounts to 7.5 mT. Obviously the dipole-dipole splitting of the triads is smaller than that of the diad and different spin dynamics are operative compared with the pretriads and diads. It is an open question as to whether this

polarization sequence is caused by the triplet pathway or, alternatively, by singlet ET, followed by triplet generation via the radical pair mechanism (for details of this mechanism, see Refs. 19, 20). A prerequisite for effective singlet–triplet mixing is a small exchange integral J and a long lifetime of the charge-separated state that allows successful competition of the singlet–triplet mixing with back ET to the ground state.

Previously, Wasielewski *et al.* reported time-resolved EPR investigations of porphyrin- and chlorin-based diads and triads in which, *inter alia*, triptycyl-type quinone acceptors were used.^{21–24} They observed long-lived charge-separated states on the millisecond timescale at low temperatures in frozen solutions. The difference in the temperature dependence, state of aggregation (fluid or solid), and the lifetimes might be due to the direct linkage of the acceptor to the porphyrin-type donors, whereas in our compounds the constituents are separated by the extended aliphatic cyclohexylene bridge.

Time-resolved EPR in liquid crystals. A certain family of LCs forms domains of nematic phases with the long molecular axes parallel to each other. These solutions are macroscopically isotropic. In an external magnetic field, however, macroscopic ordering occurs. For E7 the long molecular axes of the molecules are oriented parallel to the field axis of the external field. If a P-Q guest molecule is dissolved in such a liquid crystal, this alignment is carried over from the host to the guest: specifically, the bulky porphyrin dictates the orientation such that the species will be aligned with the porphyrin plane parallel to the external magnetic field (porphyrin z -axis perpendicular to the magnetic field).^{9,25–27} In Fig. 6 (left) the orientation dependence of the spectral features of the triplet state of zinc-tetraphenylporphyrin is shown. The triplet state was generated by *in situ* irradiation with a 1000 W lamp through slits in the EPR cavity. Before excitation the porphyrin was aligned at a magnetic field of about 1 T, and at higher temperature in the fluid nematic phase of the liquid crystal E7, and subsequently cooled to the solid state. Under these conditions the liquid crystal molecules will not realign when the sample tube is rotated. The spectral features unambiguously indicate that the porphyrin z -axis is parallel to the direction of the magnetic field only if the sample tube is rotated by 90°, resulting in the appearance of pronounced z components in the EPR spectrum (for a description and interpretation of triplet EPR spectra, see Refs. 28–31). From Fig. 6 (right) it can be deduced that a similar anisotropic orientation of the porphyrin unit is achieved for the triad P-Q_A-Q_B. It should be noted that in the solid state, both ETs from the excited state of the porphyrin are (almost) completely blocked. Therefore ISC is the dominant decay channel, thus creating a high yield of the long-lived triplet state of the porphyrin moiety.

The relaxation properties of the liquid crystal E7 makes it, in addition to the alignment, suited for time-resolved EPR studies of photochemically generated paramagnetic transients in a large temperature range, as

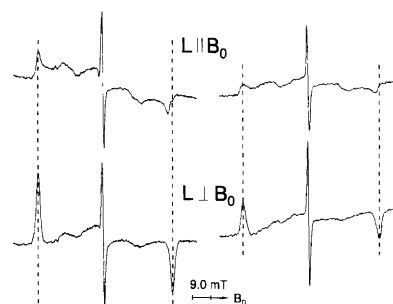


Fig. 6. Steady-state X-band EPR spectra of the photoexcited triplet state of zinc-tetraphenylporphyrin (left) and of the porphyrin donor of the triad **4b** in the frozen nematic phase of the liquid crystal E7. The upper spectra with the director parallel to the external magnetic field were obtained after freezing the solution (110 K), the bottom spectra after rotation of the sample tube by 90° with the solution still frozen. Note that in the model compound the triplet state is also observed, indicating that ISC is the favored decay pathway and that a pronounced orientation is achieved – similar to that of zinc-tetraphenylporphyrin.

previously shown by Levanon *et al.*³² *In situ* laser excitation of both the *trans* pretriad **3b** (Q_B protected) and the *trans* triad **4b** (Q_B deprotected) in the liquid crystal E7 yield the spin-polarized transient EPR spectra depicted in Fig. 7. For the pretriad **3b**, over a time range up to 100 μs after the laser pulse (at 235 K), an *e/a* spin-polarized EPR spectrum is detected (Fig. 7, top). In contrast with the results in isotropic solution at higher temperatures (Fig. 3, bottom) the polarization does not change to full emission. This indicates the importance of the solvent for the time evolution of the polarization. In the case of the triads the time-resolved EPR spectrum under identical conditions (liquid crystal, temperature, and delay time after laser excitation) also shows an *e/a* polarization, but in contrast with the pretriad, two more lines in the center of the spectrum are observed. The spectrum of the *trans* triad **4b** is explained as being a superposition of the spectra of two species, both exhibiting an *e/a* pattern with different line splittings, for the following reasons. The splitting and feature of the outer signals (2.62 ± 0.05 mT) are almost superimposable with those of the pretriad **3b** spectrum (2.62 ± 0.05 mT). In other words, these signals indicate the presence of one biradical with one electron on the porphyrin and another one on the acceptor Q_A. Accordingly, we assign the inner lines (1.22 ± 0.05 mT) as arising from the ‘true triad’ species, that is, one electron residing on the porphyrin and the other one on Q_B. The separation of the unpaired electrons is obviously larger than in the pretriad case, resulting in a smaller dipolar coupling. With the assumption that solely the x', y' components parallel to the director of the LC are detected (see below), the zero field splitting parameter $D = 1.22$ mT for the *trans* triad **4b** splitting can be extracted out of the inner lines of the spectrum (Fig. 7, center). This value corresponds to a center-to-center distance of 13.2 Å between the porphyrin and Q_B. It may be assumed that a stepwise ET from P to Q_A, then to Q_B, occurs. This interpretation is supported

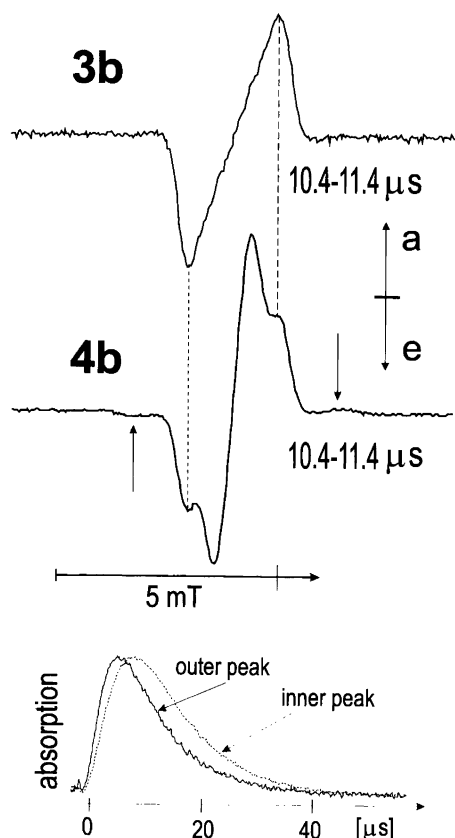


Fig. 7. Time-resolved EPR spectra of the charge-separated states of the triad with Q_B protected (**3b**, top) and the triad $P-Q_A-Q_B$ (**4b**, bottom) in the liquid crystal E7 at 240 K. It is assumed that the triad spectrum is a superposition of the spectra of the biradicals $P^{+\cdot}Q_A^{\cdot-}Q_B$ and $P^{+\cdot}Q_A^{\cdot-}Q_B^{\cdot-}$, because the outer e/a line pair of the triad spectrum (bottom) has splitting and spectral features identical with the pretriad spectrum (top). The arrows point at the broad outer resonance signals, discussed in the text, see also Fig. 8. All spectra were measured with 6.2 mW microwave power. 60 laser excitations were accumulated per point.

by the finding that the outer lines show up at earlier delay times than the inner signals (Fig. 7, bottom). However, an additional direct ET from P to Q_B cannot be excluded.

An unexpected finding, regarding the orientation of the triptycyl quinone aggregates within the LC matrix, will now be discussed. As shown in Fig. 6, the bulky porphyrin is oriented within the nematic phase such that the plane is parallel to the external magnetic field, the main z -axis being perpendicular. As a consequence, for the porphyrin triplet state the z components are observed if the sample tube is rotated by 90° (see Fig. 6). Reference to the literature indicates that P-Qs with a *trans* bridge, **1b**, **2b**, additionally align with their long molecular axis parallel to the external field.^{9,10} This is the dipolar axis (z' -axis) of the charge-separated biradical species. Therefore the z' components of the biradical species, giving rise to the largest splitting of the spectrum, should be observed without sample rotation. In contrast, the triptycyl type P-Qs show different behavior. Closer

inspection of Fig. 7 (center) reveals that on both sides of the EPR spectrum [low field (e) and high field (a)] broad bumps can be seen (in Fig. 7 indicated by arrows) which have not been discussed so far. If the sample is cooled to just above the freezing point of the LC, the charge-separated state is still generated and the viscosity of the solution is increased. Owing to the high viscosity, reorientation of the liquid crystal molecules is somewhat hampered and makes it possible to record the time-resolved EPR spectra of the perpendicularly oriented molecules by rotating the sample tube by 90° , see Fig. 8. Surprisingly, for the triptycyl P-Qs **3a**, **3b**, **4b** the tube rotation results in the disappearance of the strong signals detected at 0° rotation, and a build-up in intensity of the broad outer signals showing the largest splitting of the spectrum. The magnitude of the splitting is identical with the splitting in isotropic solution and is twice as large as the splitting at 0° rotation. This effect holds for the (protected) *trans*- and *cis*-diads and for the *trans* triad.

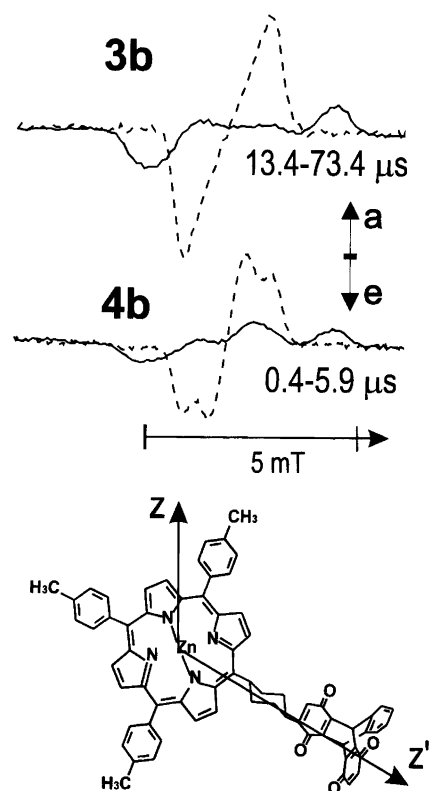


Fig. 8. Time-resolved EPR spectra of the transient biradicals of the pretriad (**3b**, top) and the triad $P-Q_A-Q_B$ (**4b**, bottom) in the liquid crystal E7 at 235 K before (dashed line) and after rotation of the sample tube by 90° (full line). It is clearly seen that the larger splitting is observed after rotation of the tube (for details, see the text). The z -axis of the zero-field splitting (ZFS) tensor of the porphyrin triplet is perpendicular to the porphyrin plane. The x, y -axes are in the porphyrin plane. The z' -axis of the ZFS tensor of the RP lies along the line joining the centers of the porphyrin and quinone moieties. The ZFS tensor of the RP has approximate cylindrical symmetry. All spectra were measured with 6.2 mW microwave power. 60 laser excitations were accumulated per point.

The *cis* triad **4a** shows at 0° rotation the same splitting as the *cis* pretriad **3a**, but because of the weak signal no rotational dependence was measured. The line splitting of the spectra and the rotation dependence are in obvious contrast with the behavior of the P-Qs with benzoquinone and ubiquinone acceptors (**1a**, **1b**, **2a**, **2b**), *vide supra*.⁹ Without rotation of the sample tube the P-Q diads (**1a**, **1b**) show a splitting of the same magnitude as the pretriads (**3a**, **3b**) after 90° rotation. The corresponding splittings of the *trans* and *cis* pretriads in E7 after 90° rotation and the splittings in isotropic solutions have the same magnitude.

A reasonable interpretation of the rotational dependence of the EPR spectra of **3a**, **3b**, and **4b** in the LC is a preferred orientation of the P-Qs in the nematic and soft glass phase in such a way that both the porphyrin *z*-axis and the *z'*-axis of the RP are perpendicular to the director. In other words, without rotation of the sample tube the charge-separated transient exhibits the smaller split *x'*, *y'* components, whereas the larger splitting of the *z'* components is observed after 90° tube rotation.

The separations of the EPR lines in isotropic solutions for the P-Qs **1a**, **1b**, **2a**, **2b**, **3a**, **3b** are in good agreement with the corresponding calculated *D* values. This agreement lends strong support to the interpretation of the angular dependence of the spectral features with respect to the relative orientation of the P-Q guest molecules within the liquid crystalline hosts. In the point dipolar approximation, where one electron is assumed to be localized in the center of the porphyrin and the other in the center of the quinone, the center-to-center distance between the porphyrin and the quinone can be calculated from the line separation of the transient EPR spectrum. From the line splittings of the protected *trans* pretriad **3b** (electron on acceptor Q_A) a zero-field splitting parameter *D* of 2.62 mT can be extracted that indicates a separation of the unpaired electrons of about 10.2 Å. This value is in satisfactory agreement with the center-to-center distance between porphyrin and Q_A evaluated from crystallographic data (10.9 Å, obtained for **1b**) and the result of vacuum AM1 calculations (10.65 Å).³³

Time-resolved EPR spectroscopy at high magnetic field (W-band). EPR spectroscopy is usually performed at X-band frequencies. In analogy to modern NMR spectroscopy, spectral resolution can be increased if higher Zeeman fields and microwave frequencies are applied. Presently, there are only a few high frequency spectrometers working at frequencies above 90 GHz; commercial machines are now becoming available. In the laboratory of K. Möbius in Berlin, a high-field EPR spectrometer (3.4 T, 95 GHz) is being used to record many paramagnetic species, in particular, in photosynthetic reaction centers. Currently, the model compounds discussed here are being studied by this technique. Using these modern techniques additional information about the ET properties and spin dynamics can be obtained. Because of the different field dependences of the various terms of the

spin Hamiltonian, S/T mixing is affected by the higher field and different polarization patterns are expected for the W-band spectra compared with those of the X-band spectra. Also the widths of the spectra should increase at higher magnetic field due to the difference between the *g* values of the porphyrin and quinone radical. Recently we have performed time-resolved W-band EPR experiments on several P-Q diads and triads described in this paper. In order to give an example of the experimental success, two high-field EPR spectra of charge-separated transient states are reproduced in Fig. 9. The spectrum of the *trans* diad **1b** (Fig. 9, bottom) in an ethanol-toluene mixture at 160 K corresponds to the X-band spectrum in Fig. 4 (left). The surprising result is that neither the linewidth nor the polarization pattern exhibit pronounced changes. Also unexpected is the fact that the W-band spectrum is again completely emissive. Actually, this finding contradicts the interpretation of the X-band spectra given in Ref. 8, using static radical pair models and S/T₋ mixing. As a matter of fact, in this model the ten times larger Zeeman energies should drastically alter the polarization pattern. It is obviously demanding to improve the present models, and attempts have been made recently.³⁴ An interpretation in terms of a model including dynamic effects of the radical pair on the timescale of the experiment is in progress.

Fig. 9 (top) shows the EPR spectrum of the biradical of the *trans* triad **4b** in the liquid crystal E7; it corresponds to the X-band EPR spectrum in Fig. 7 (center). Again, this spectrum is narrower (ca. 6.0 mT) than expected from the differences of the *g*-values of porphyrin and quinone (within the frame of a static coupled radical pair model).

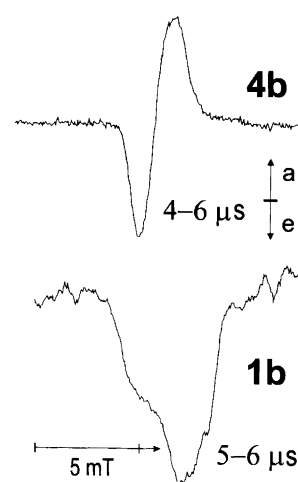


Fig. 9. Time-resolved high field/high frequency (3.4 T/95 GHz) cw EPR spectra of the charge-separated radical pairs of the triad **4b** in the liquid crystal E7 at 250 K (top) and the cyclohexylene-linked P-Q **1b** in ethanol-toluene at 166 K (bottom). The polarization patterns are very similar to those obtained at lower X-band field/frequencies (see Fig. 4, left, after 4 μ s and Fig. 7, center). The laser excitation energy was 10 mJ pulse⁻¹; the repetition rate was 10 Hz; the B_1 field was about 0.002 mT, the acquisition time was 40 min.

With the results from the W-band experiments – in addition to the X-band results – current theoretical models of the spin dynamics in P-Qs which may explain the X-band spectra can be excluded. We expect that a dynamic model that describes the W- and X-band measurements satisfactorily will provide us with more unambiguous information about the dynamics of the spin relaxation, charge separation and recombination and the relative energy levels. However, a final interpretation of the spectra cannot yet be given and is the subject of intense discussion.

Conclusions. Time-resolved EPR techniques are well suited to studies of photochemically generated transient paramagnetic species. From the spectral features the triplet type states of the biradicals can be identified and the distance of the unpaired electrons can be extracted within the frame of the point-dipolar approximation. The polarization pattern of the transient spectra and their time evolution yield information about the electron transfer channels, that is, singlet or triplet route, and about the spin dynamics, e.g., decay mechanisms of the polarization. This paper has demonstrated that the use of biomimetic model compounds does not *a priori* facilitate the interpretation of the complex processes occurring in native photosynthetic reaction centers. This statement holds, even if it contradicts the rationale for studying model compounds, namely, to make the properties of the systems less complex. Nevertheless, previous and the present investigations on biomimetic model compounds have proved that valuable information can be obtained about interesting features of ET characteristics.

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