

EPR STUDIES OF PORPHYRIN AND PORPHYRIN-QUINONE TRIPLET STATES IN FROZEN NEMATIC SOLUTIONS

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Introduction

Knowledge of the properties of the triplet excited states of porphyrins is important, because light-induced electron transfer between porphyrin donors and quinone acceptors, e.g., in biomimetic model compounds for photosynthetic reaction centers, may proceed via the triplet state.^{1,2} (In native photosynthetic reaction centers, the primary electron transfer process is known to proceed via the singlet excited state of the *special pair*, but formation of the triplet state can be enforced by blocking the electron transfer.) The zero-field splitting parameters, notably the E parameter, depend on the electron distribution and differ in porphyrins and chlorins. In liquid-crystalline solutions, the triplet EPR spectra provide a sensitive probe of the alignment of the molecules. In covalently linked porphyrin-quinones, the distance between donor and acceptor affects the triplet lifetime.

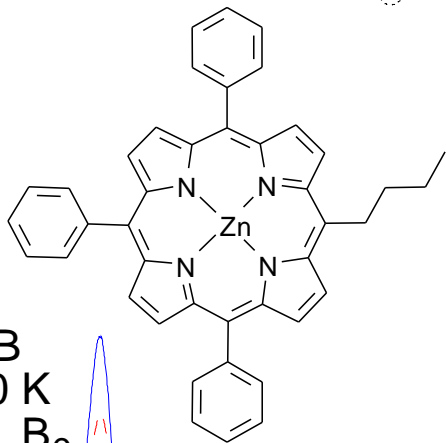
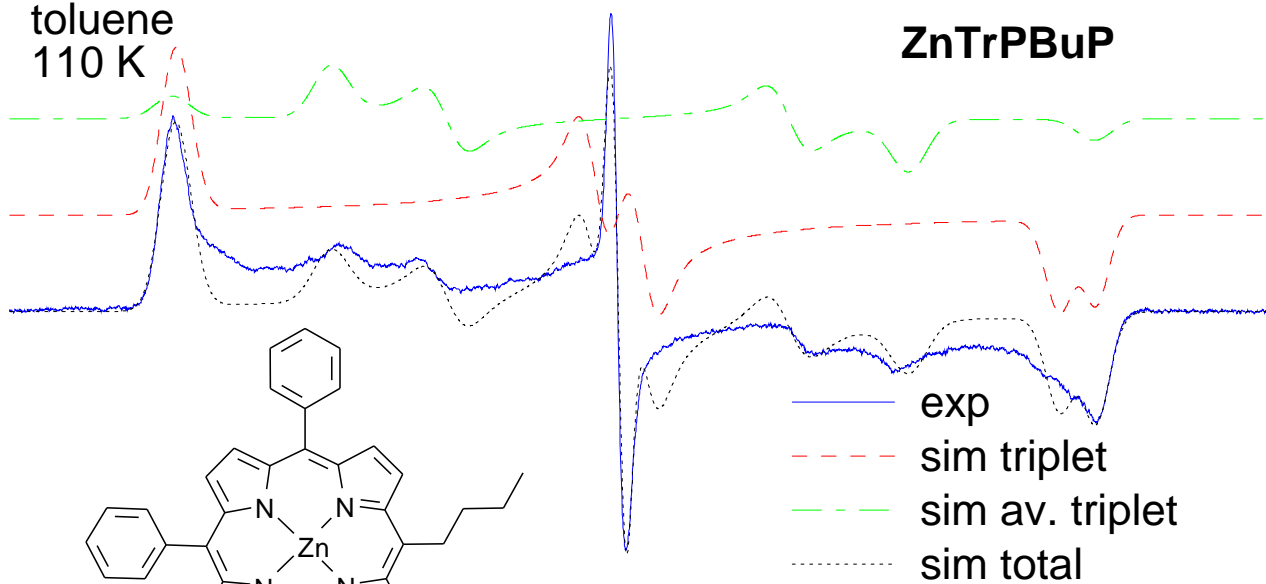
We present the results of CW-EPR studies of the photoexcited triplets of a series of porphyrins and covalently linked porphyrin-quinones in isotropic and anisotropic (liquid-crystalline) frozen solutions. In frozen nematic solutions, the appearance of the spectra is strongly dependent on the orientation of the sample relative to the external magnetic field. This fact allows a differentiation between the z and x, y axes and hence a more accurate determination of the zero-field splitting parameters D and E . In the case of some porphyrin-quinones, steady-state triplet EPR signals cannot be observed which is ascribed to singlet electron transfer enhanced by folding of the quinone acceptor over the porphyrin donor.

¹ K. Hasharoni, H. Levanon, J. von Gersdorff, H. Kurreck and K. Möbius, *J. Chem. Phys.* **98**, 2916 (1993).

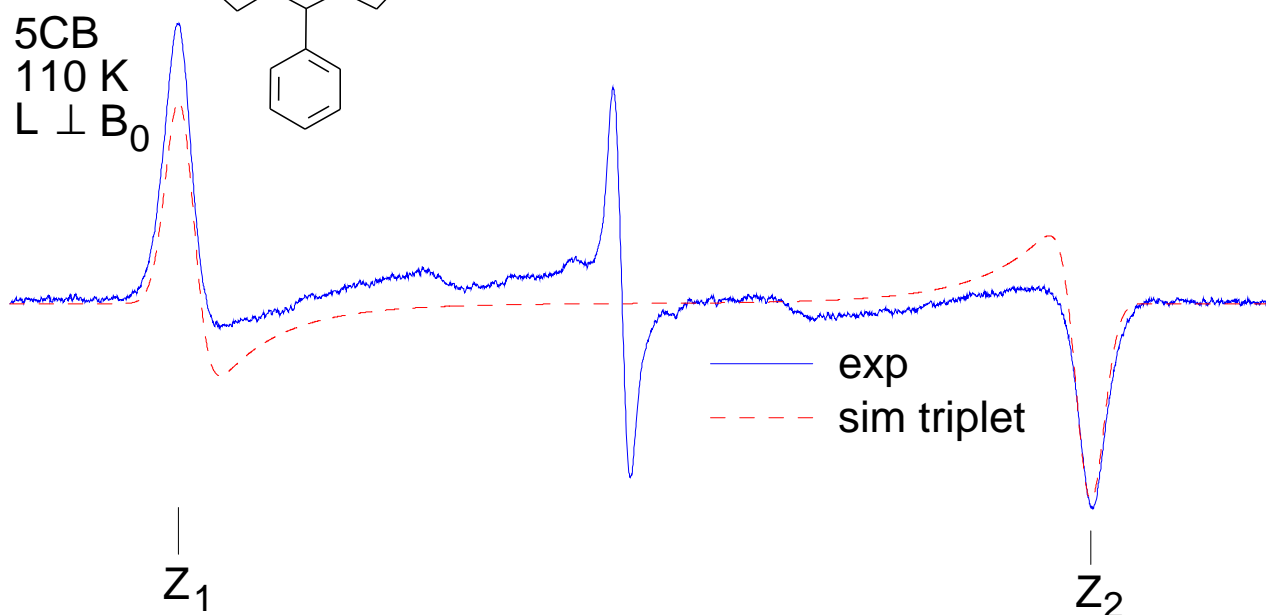
² L. Sun, J. von Gersdorff, D. Niethammer, P. Tian and H. Kurreck, *Angew. Chem. Int. Ed. Engl.* **33**, 2318 (1994).

ZnTrPBuP

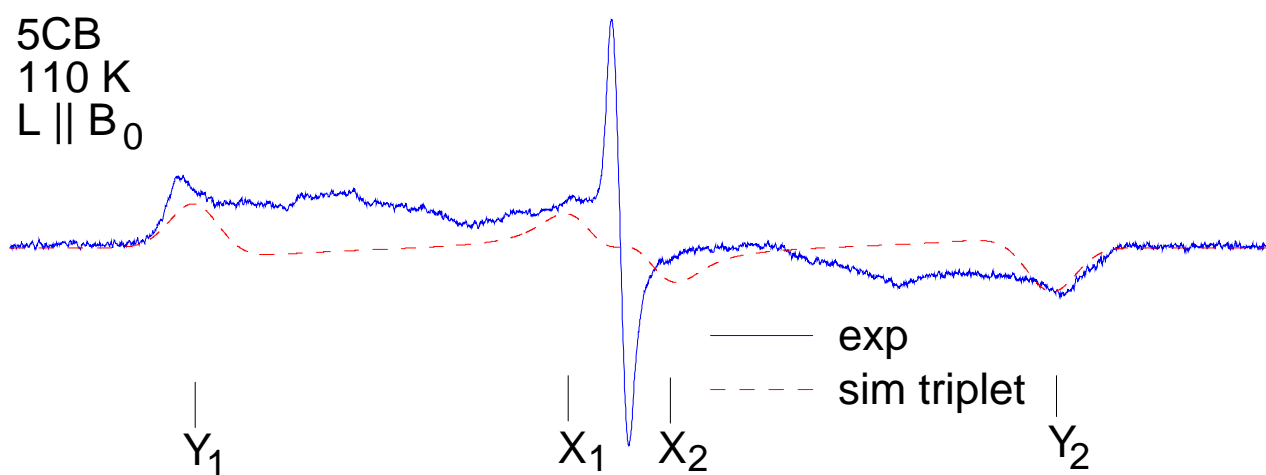
toluene
110 K



5CB
110 K
 $L \perp B_0$



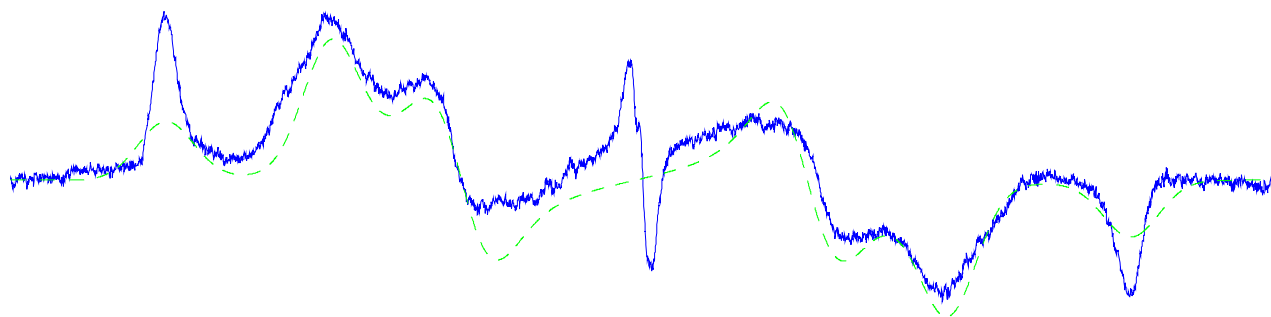
5CB
110 K
 $L \parallel B_0$



290.0 310.0 330.0 350.0 370.0
mT

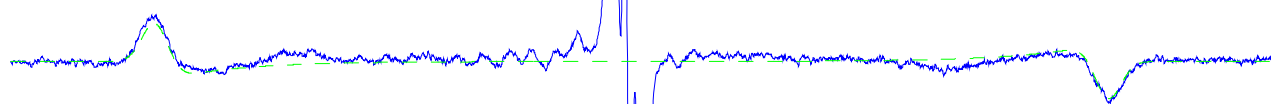
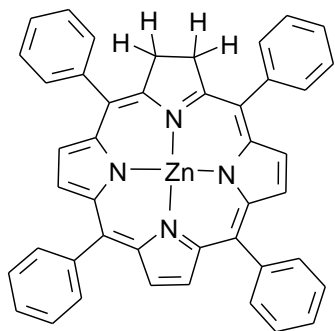
toluene
120 K

ZnTPC

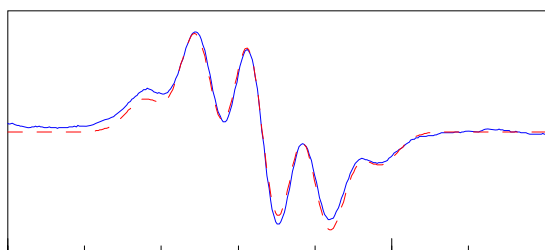


— exp
- - - sim av. triplet

5CB
110 K
 $L \perp B_0$

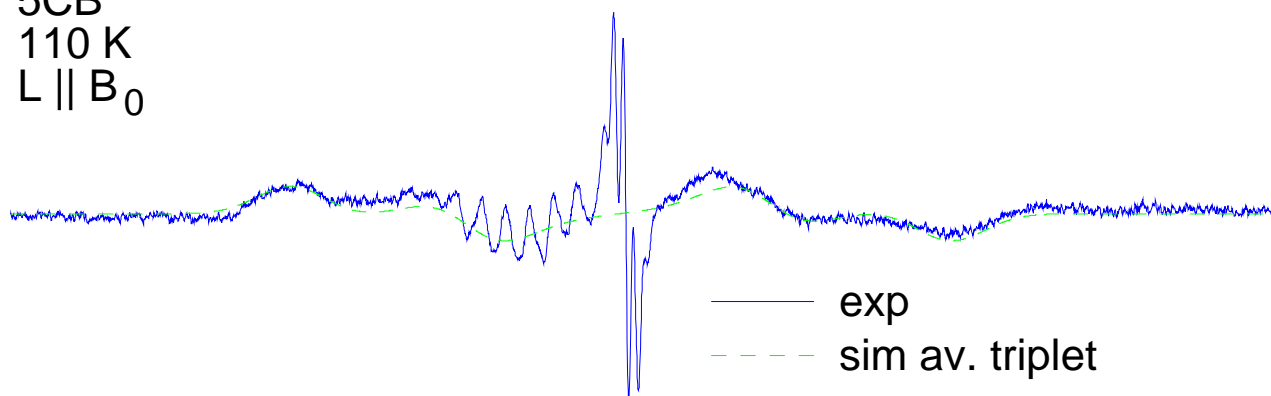


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333.0 338.0

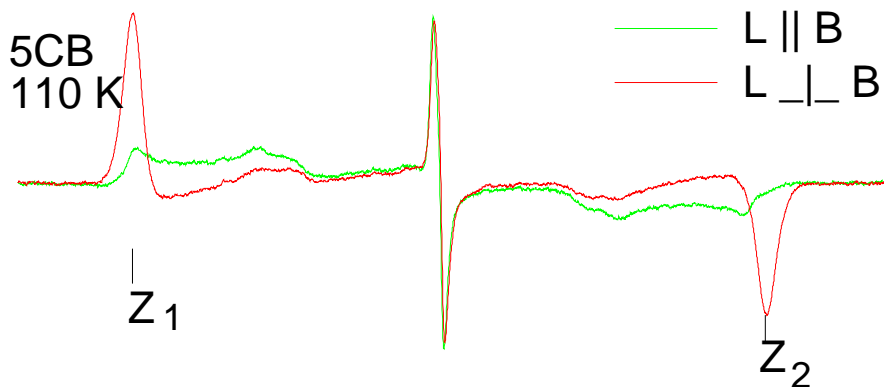
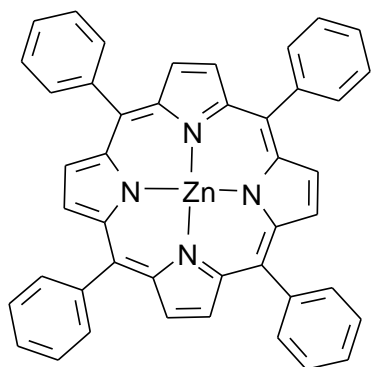
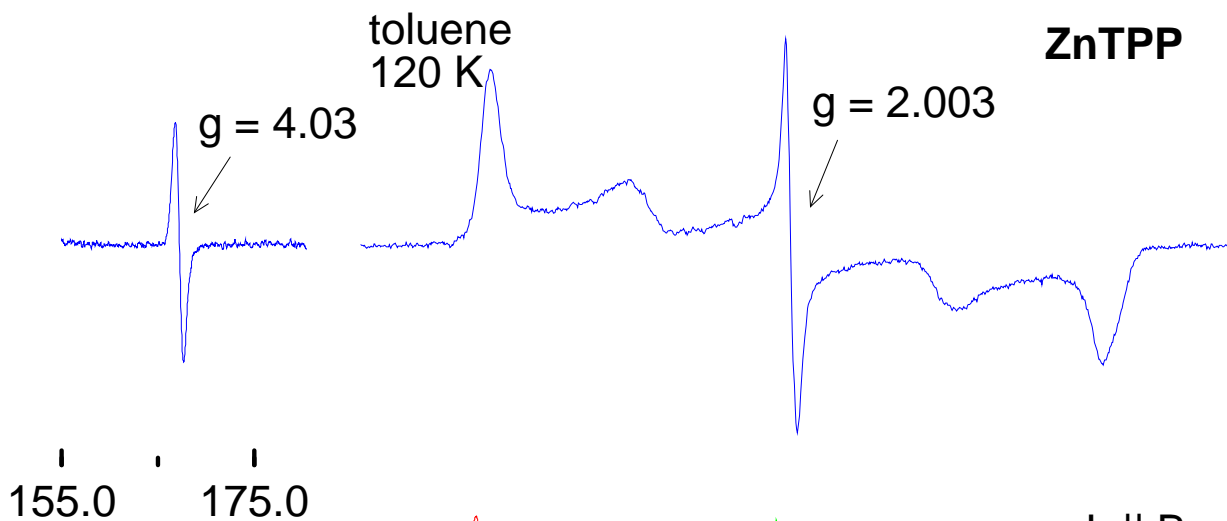
5CB
110 K
 $L \parallel B_0$



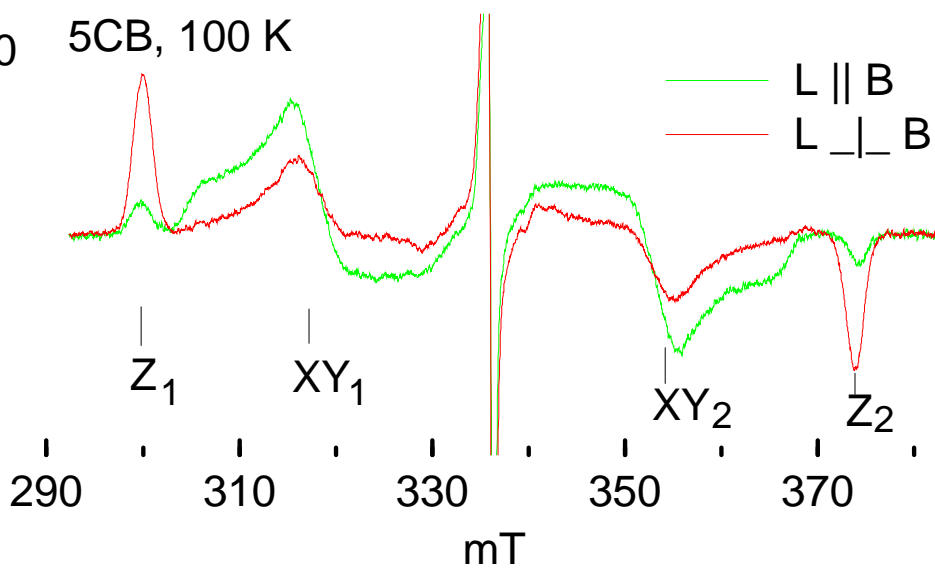
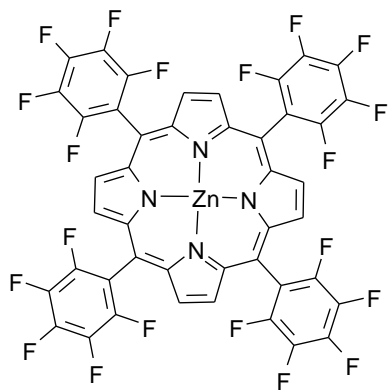
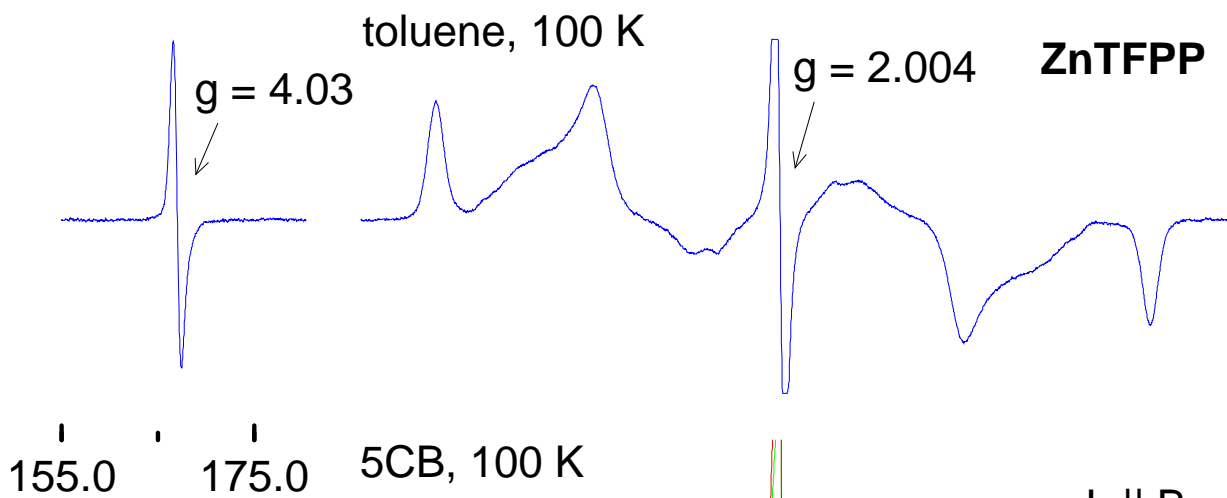
— exp
- - - sim av. triplet

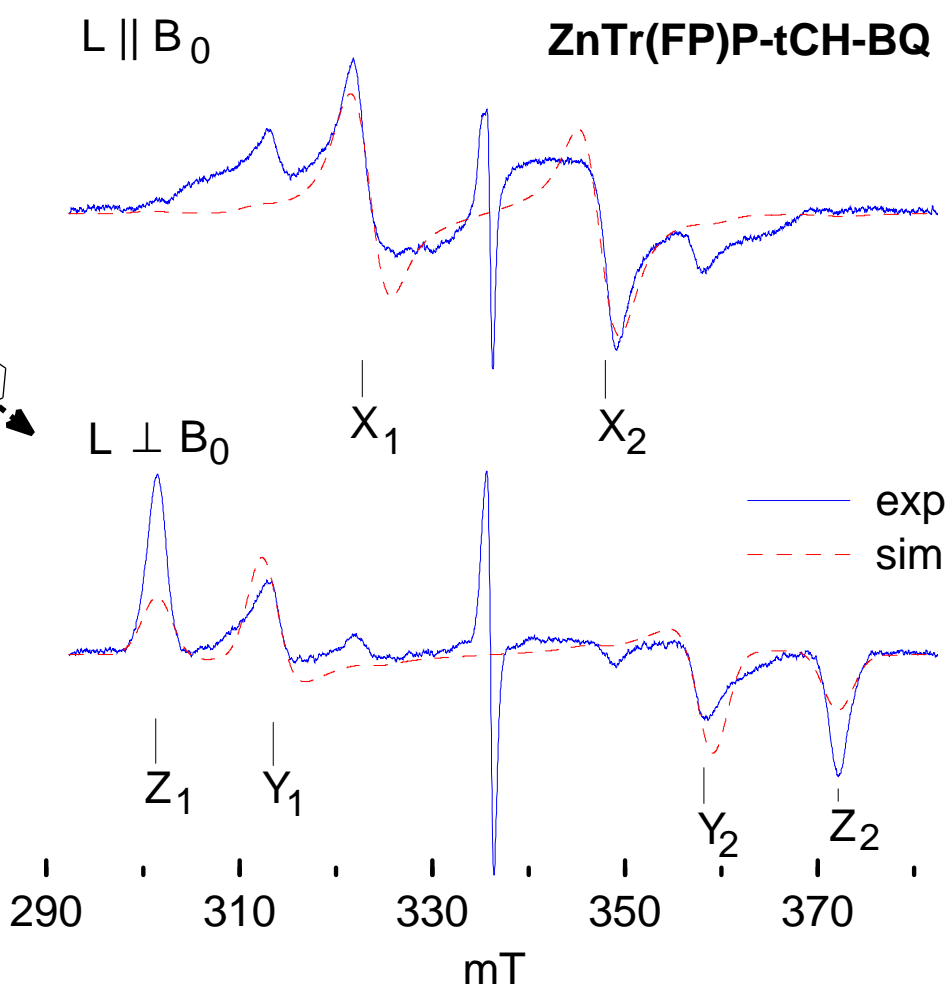
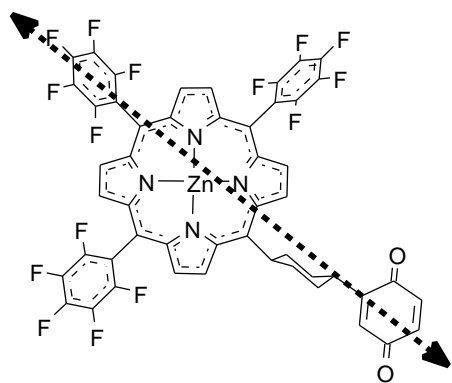
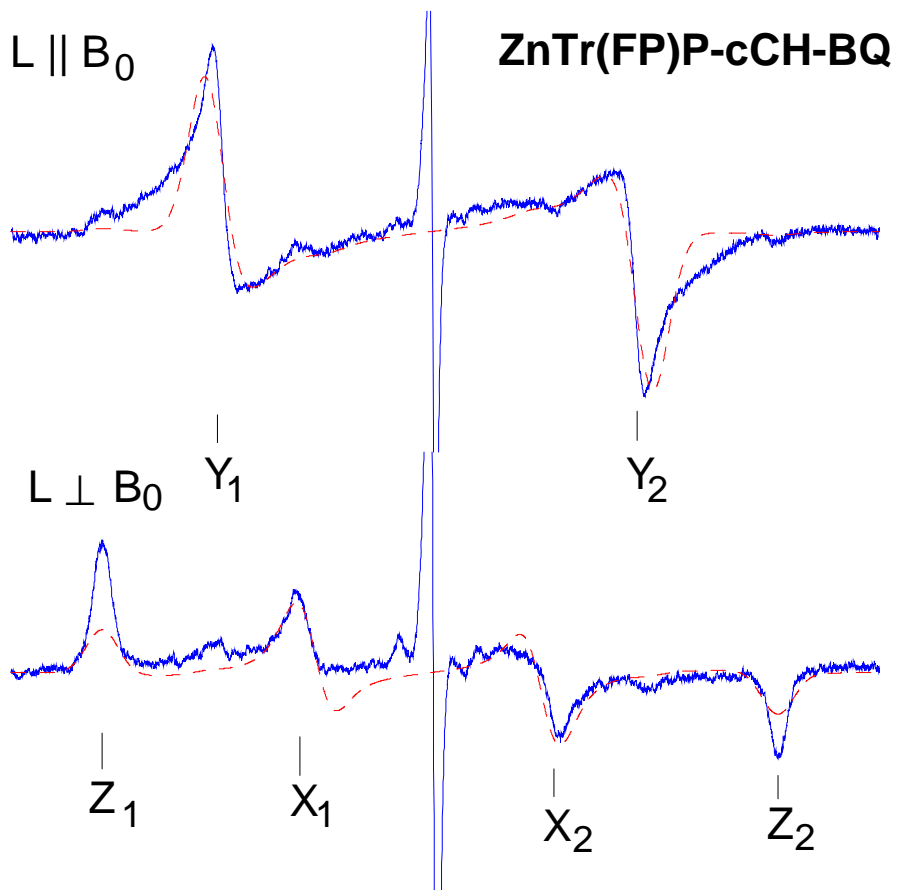
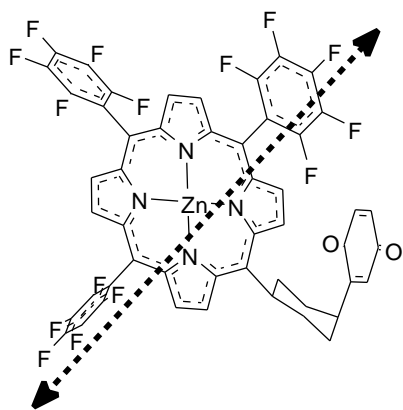
290.0 310.0 330.0 350.0 370.0
mT

ZnTPP

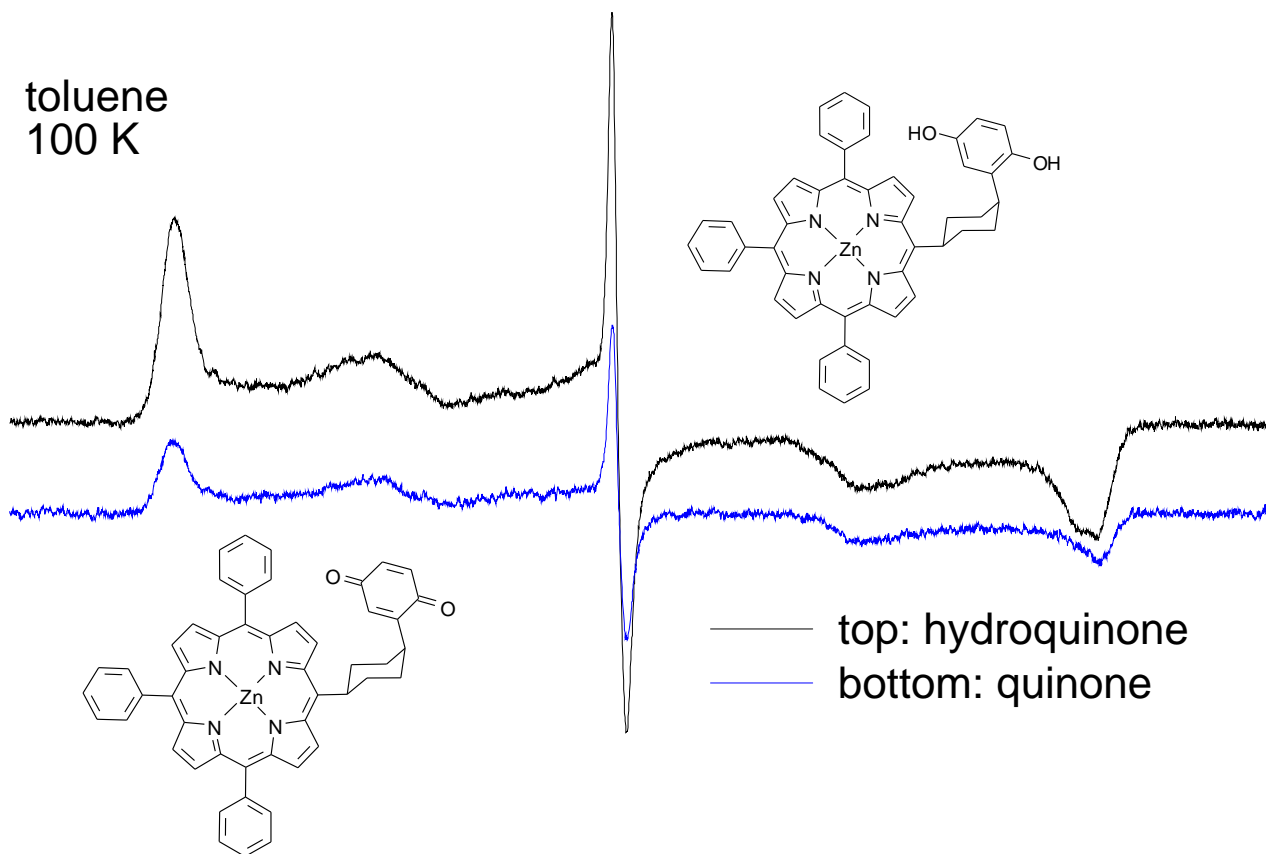


ZnTFPP

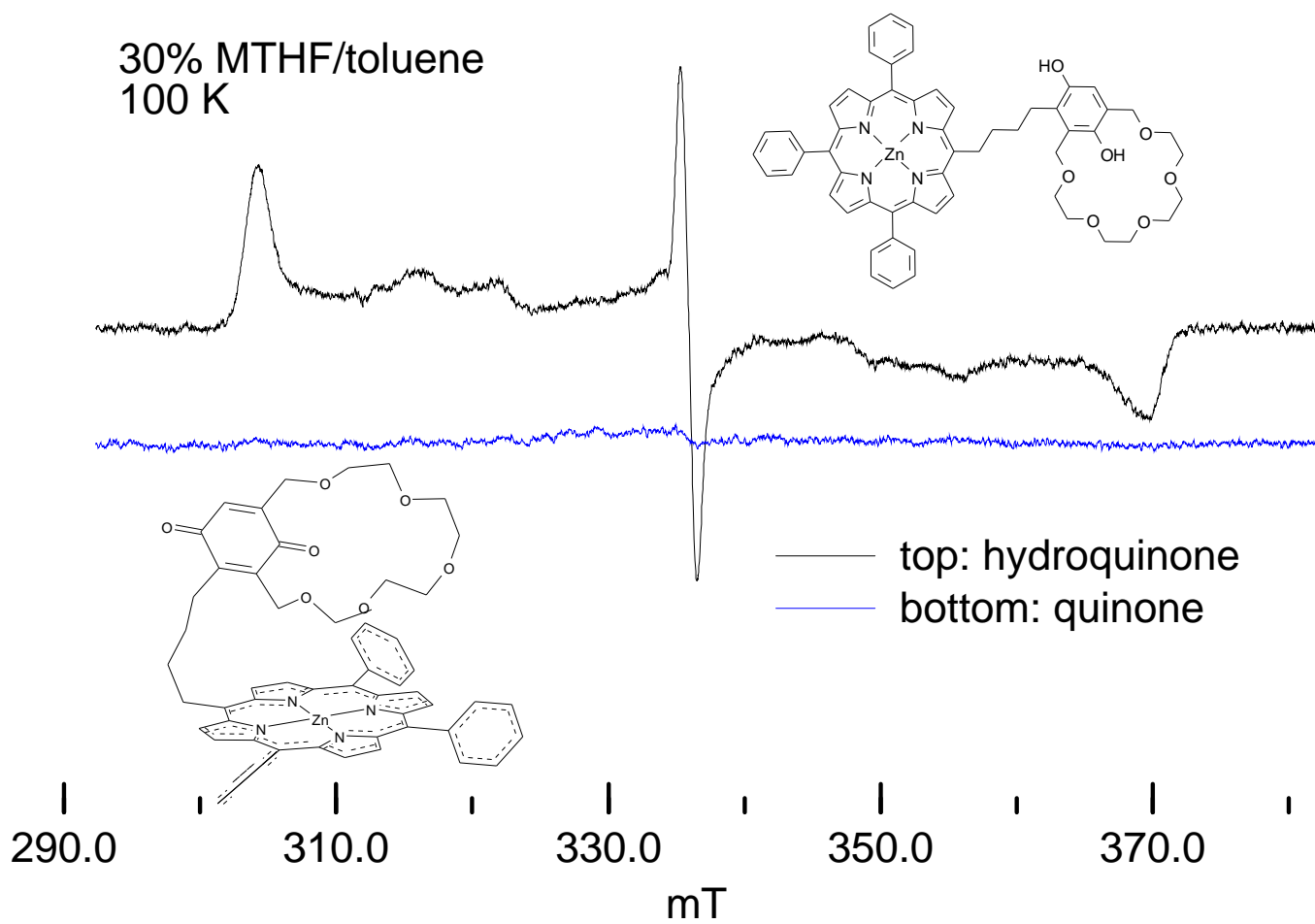


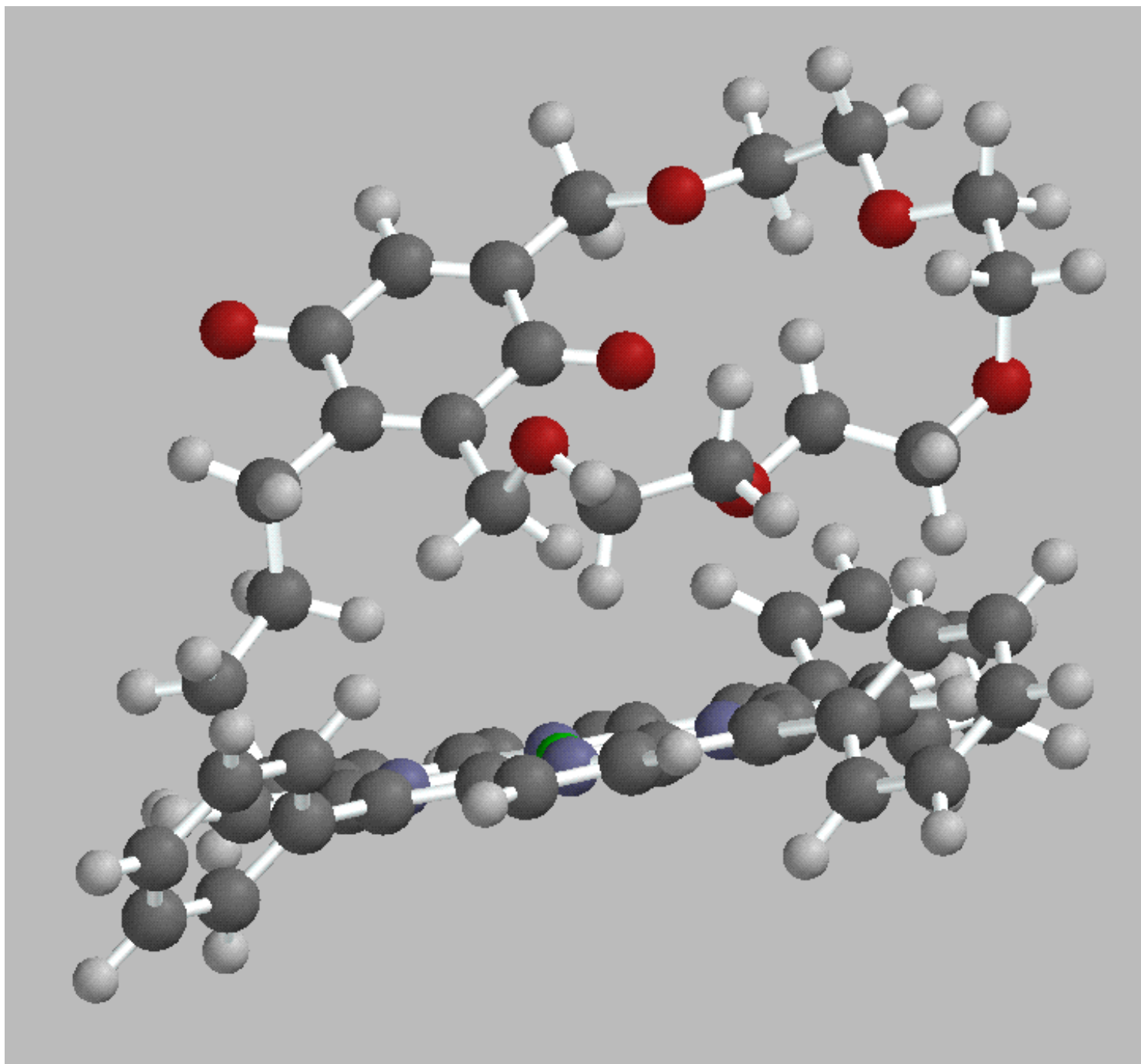


toluene
100 K



30% MTHF/toluene
100 K





Results and Discussion

Both ZnTPP ($D = 32$ mT) and the fluorinated compound ZnTFPP ($D = 37$ mT) exhibit tetragonal symmetry, at least on the dynamic average. However, the xy peaks are weaker than expected, due to rhombic distortion (Jahn-Teller effect). In liquid-crystalline solution, either the xy (director $L \parallel \mathbf{B}$) or the z peaks ($L \perp \mathbf{B}$) are enhanced.

In the *cis* or *trans* cyclohexylene linked porphyrin quinones (ZnTr(FP)P-cCH-BQ and ZnTr(FP)P-tCH-BQ), the tetragonal symmetry is lifted, affecting both the molecular shape and the orbitals LUMO and NLUMO, which are degenerate in the symmetric porphyrins, but not in the porphyrin quinones. Experimentally, distinct x and y peaks are observed. Although the EPR spectra of the photoexcited triplets of the *cis* and the *trans* compound in toluene are very similar, a complementary behavior is observed in liquid-crystalline solution. Thus, in the case of the *cis* compound, the y peaks are enhanced when $L \parallel \mathbf{B}$, and the x peaks when $L \perp \mathbf{B}$. For the *trans* compound, it is the other way round. This behavior may be explained by assuming a preferential alignment along the respective “long” molecular axes, see the dashed arrows depicted in the formulas.

Conclusions

- Photoexcited triplets of zinc porphyrins in isotropic and anisotropic glasses generally exhibit a superposition of EPR spectra due to the rhombic (Jahn-Teller) triplet states ($D = 31.7 \dots 33.0$ mT, $E = 9.5 \dots 10.1$ mT) and to dynamically averaged triplets (D unchanged, $E = 0 \dots 2.8$ mT). Dynamic averaging, which may occur intramolecularly over the two orbital components of the nearly degenerate triplet state or intermolecularly in the case of aggregation, is indicated by line broadening of the x, y components. In the case of the chlorin ZnTPC, only the dynamically averaged triplet was observed ($D = 33.9$ mT, $E = 4.3$ mT).
- Use of nematic glasses allows differentiation between the in-plane (x, y) ZFS components (director parallel to the static external field) and the out-of-plane (z) component (director perpendicular to the field). In the spectrum simulations, constant linewidths are assumed. The simulations refer to a fairly high degree of ordering (exponential parameter $a = -10$ corresponding to order parameters $\bar{P}_2 = O_{zz} = -0.425$). Note that in the case of the porphyrin-quinone ZnTr(FP)P-cCH-BQ (“*cis*”) pronounced alignment along the y axis is observed, $O_{yy} \approx 0.5$, whereas in ZnTr(FP)P-tCH-BQ (“*trans*”) alignment along the x axis is preferred. Deviations in intensities may be attributed to residual spin polarization.

- In covalently linked porphyrin-quinones, basically the same triplet EPR patterns are observed as in the constituent triplet porphyrins or the respective porphyrin-hydroquinones. However, singlet electron transfer from the porphyrin to the quinone reduces the signal intensities and may even prevent detection of the triplet spectrum. Thus, no triplet signal was observed in the case of the butylene linked crown compound (ZnTrPP-Bu-CrownQ) which we ascribe to back folding.

Acknowledgment

Most of the compounds were prepared by Dr. Jörg von Gersdorff, Hans Mößler, Hans Newman and Dr. Licheng Sun which is gratefully acknowledged. We thank the Deutsche Forschungsgemeinschaft (SFB project 337 and normal funding), the Fonds der Chemischen Industrie and the Volkswagen-Stiftung for financial support.