

CW ESR STUDIES OF PORPHYRIN AND PORPHYRIN-QUINONE TRIPLET STATES

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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 centres, may proceed via the triplet state.^{1,2} 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 ESR 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-ESR 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 ESR signals cannot be observed which is ascribed to singlet electron transfer enhanced by folding. The doublet signal of porphyrin or chlorin cation radicals, which is also observed, appears in emission under certain conditions, indicative of the radical triplet pair mechanism. Even without light modulation, the triplet CW ESR spectra of porphyrin free bases may exhibit spin polarization.

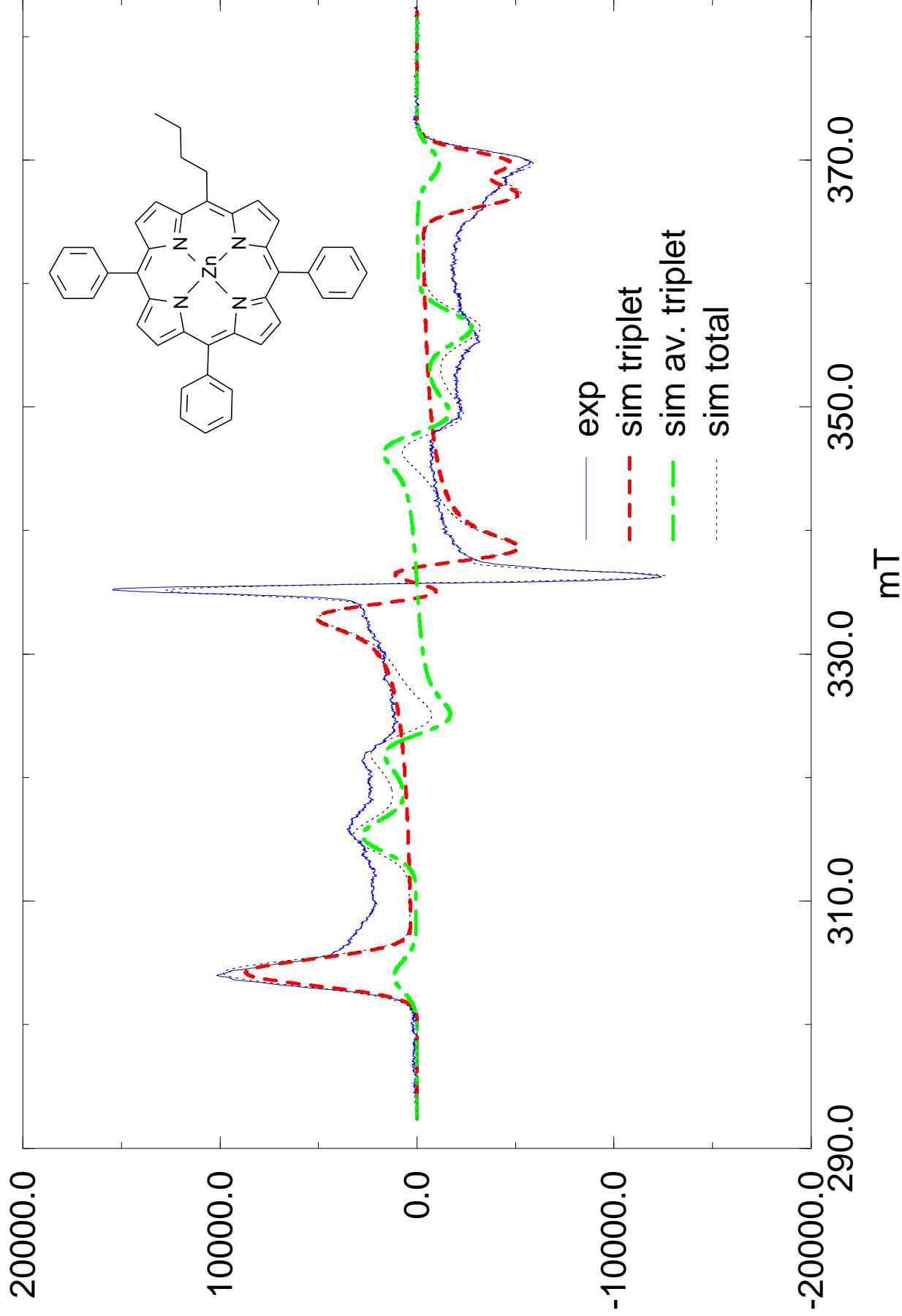
¹ K. Hasharoni, H. Levanon, J. von Gersdorff, H. Kurreck and K. Möbius, *J. Chem. Phys.* **98**, 2916 (1993).

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

Results and Discussion

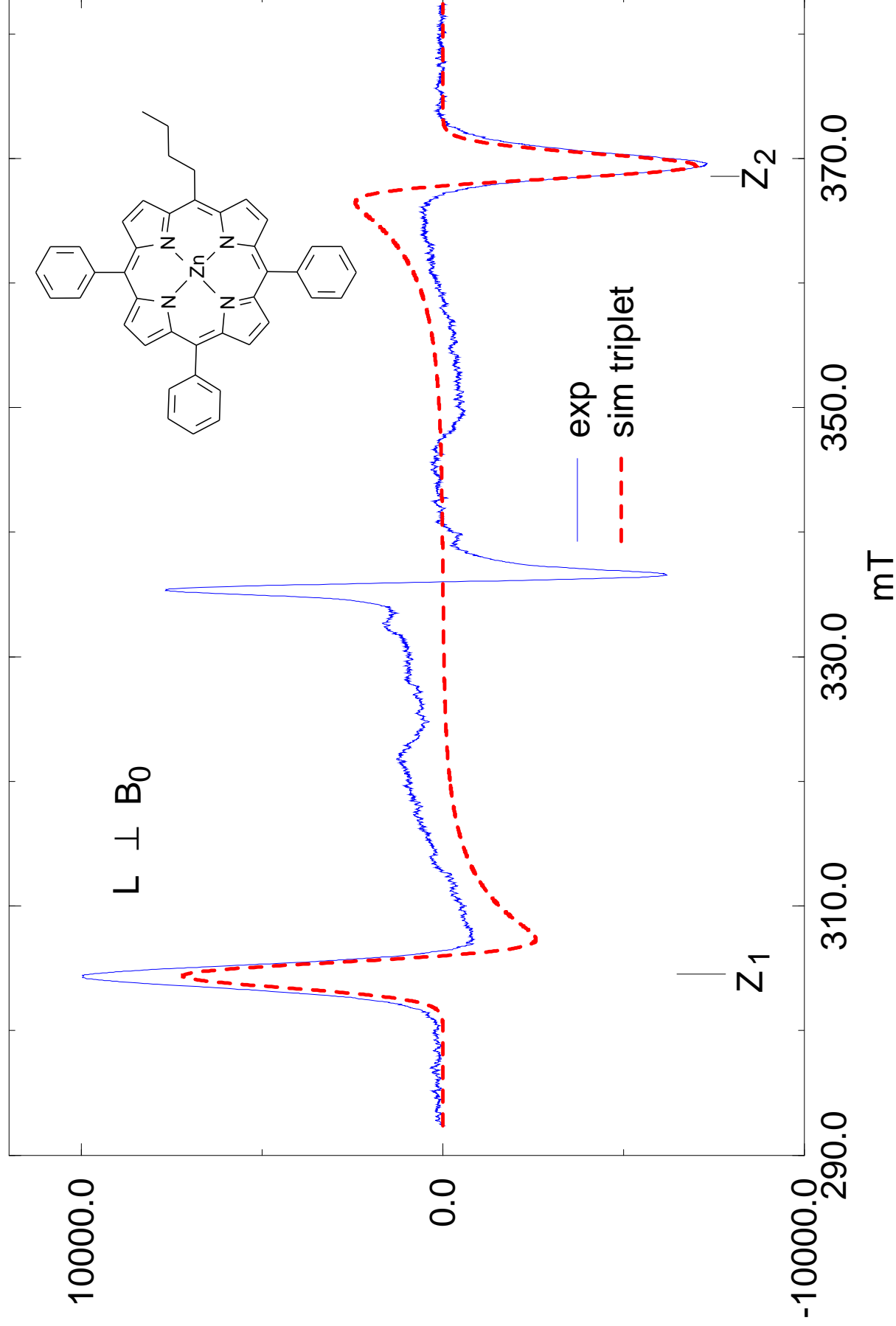
ZnTrPBuP

toluene, 110 K



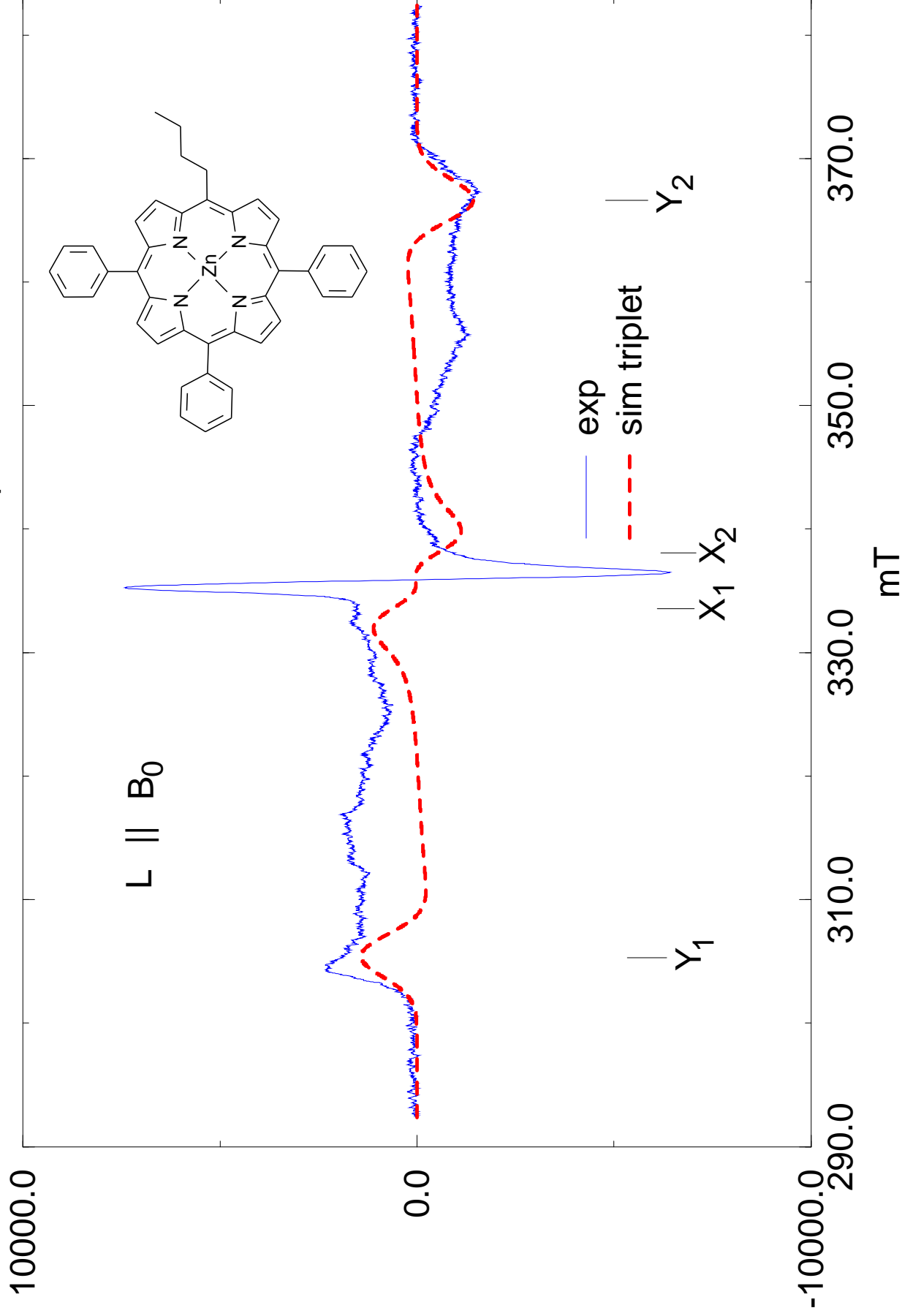
ZnTrPBuP

LC 5CB, 110 K, director perpendicular to field



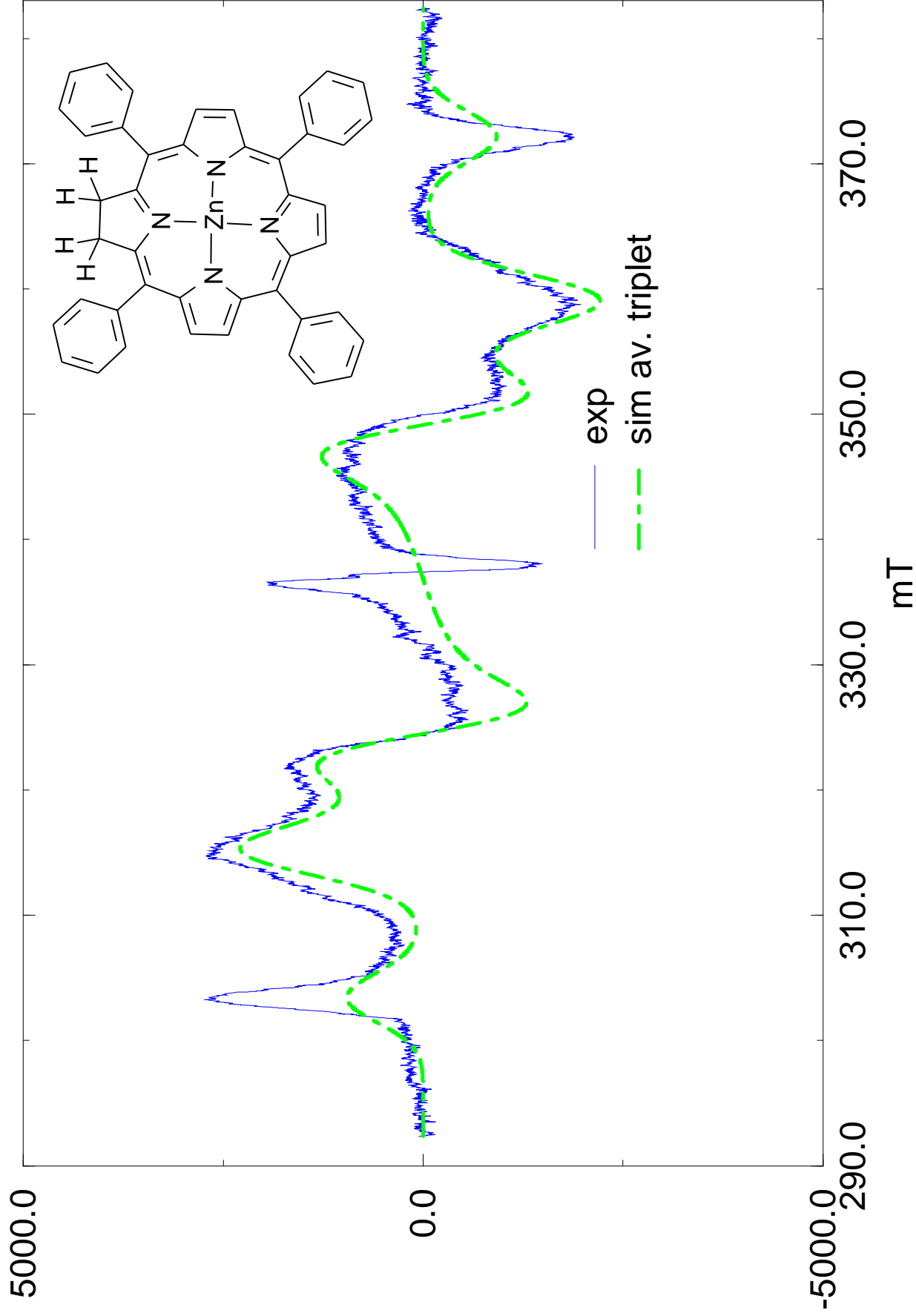
ZnTrPBuP

LC 5CB, 110 K, director parallel to field



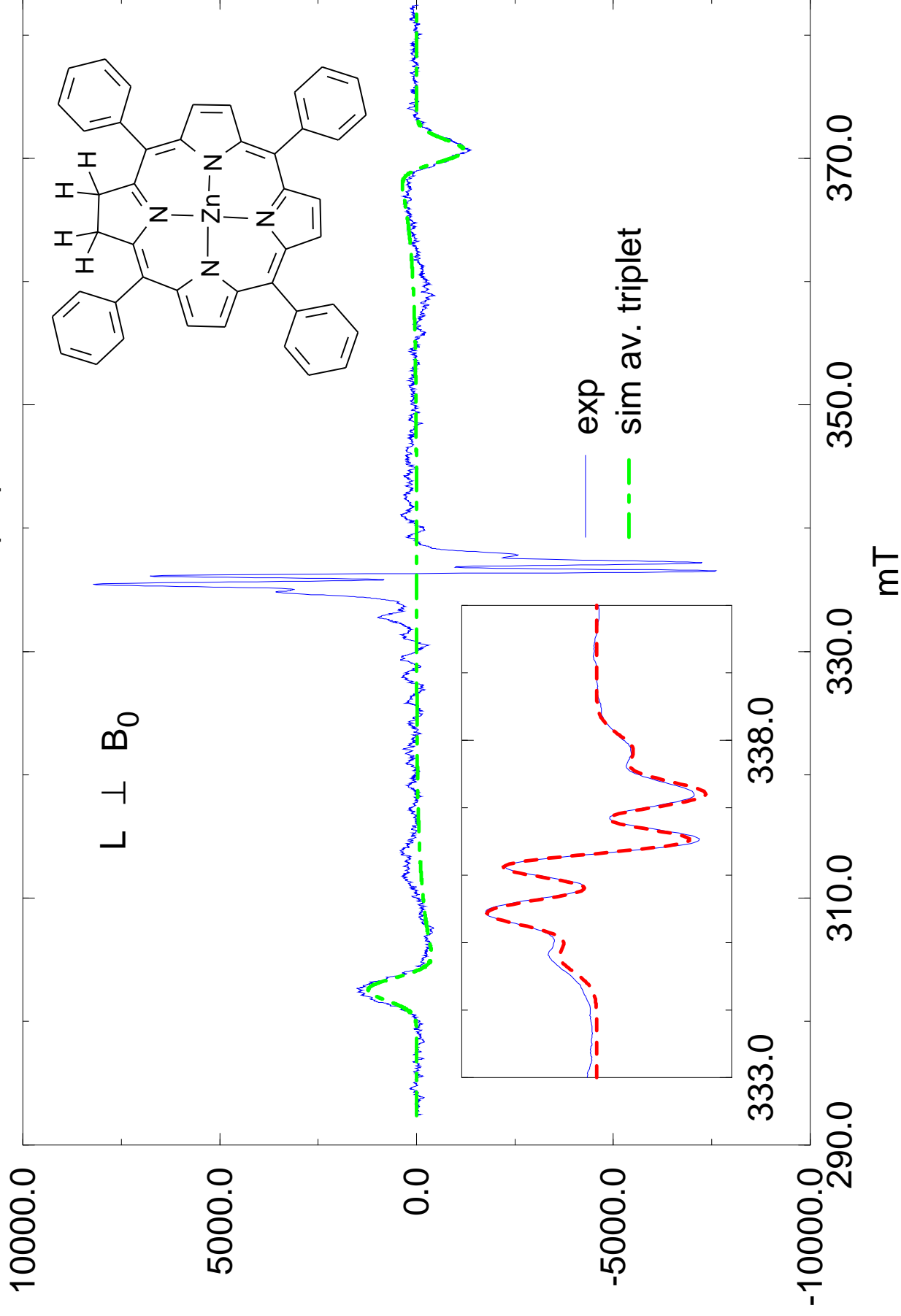
ZnTPC

toluene, 120 K



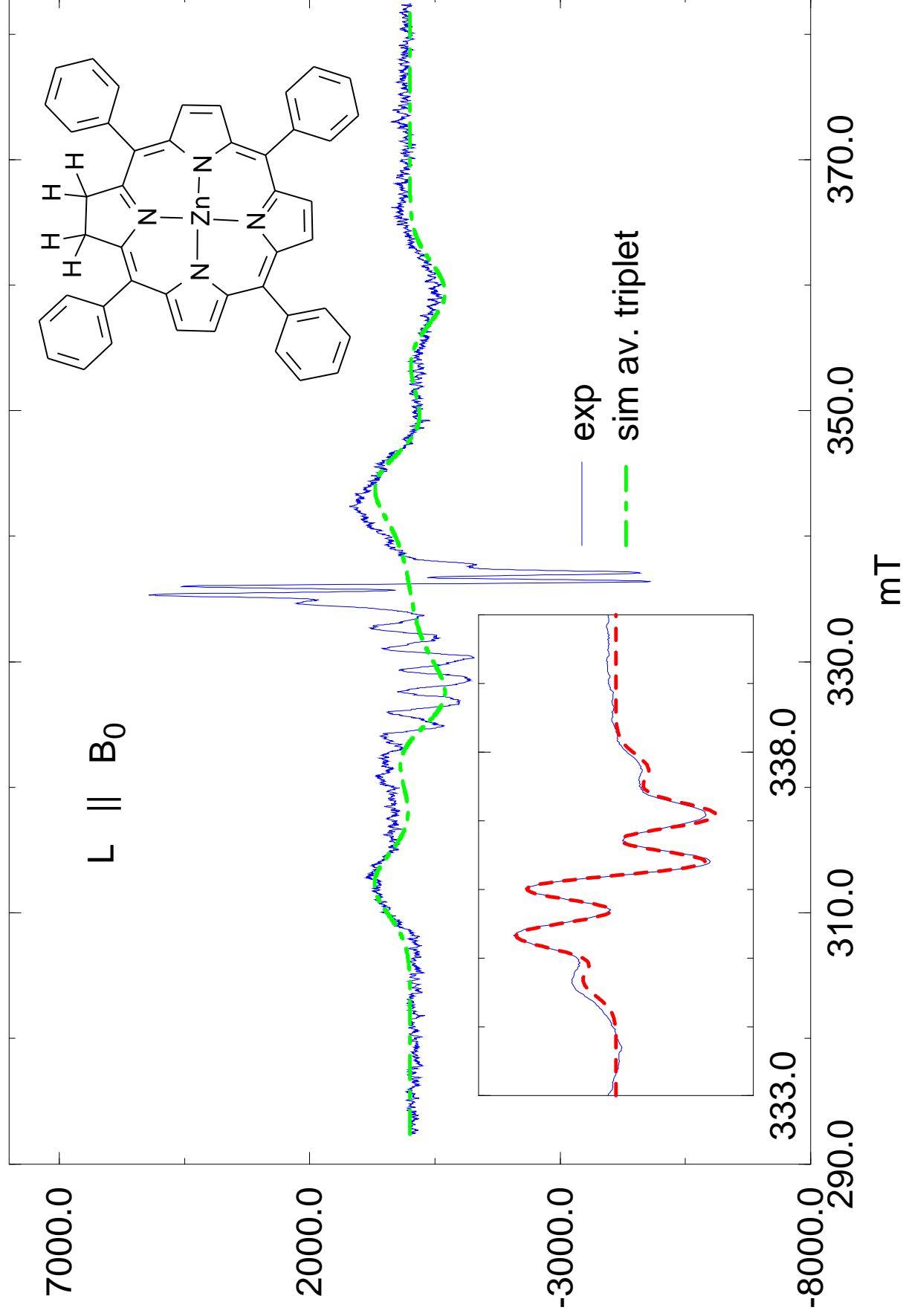
ZnTPC

LC 5CB, 110 K, director perpendicular to field

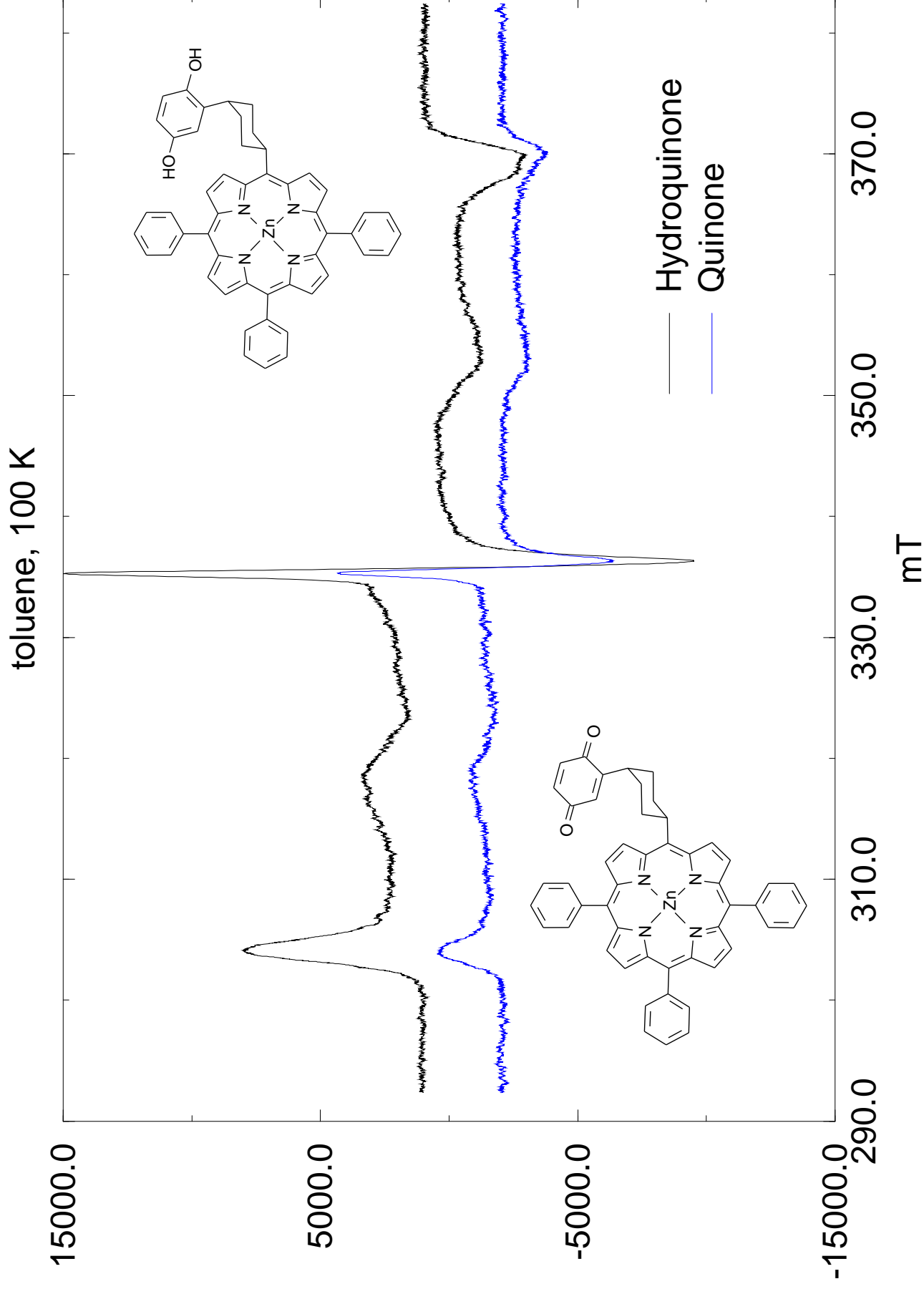


ZnTPC

LC 5CB, 110 K, director parallel to field

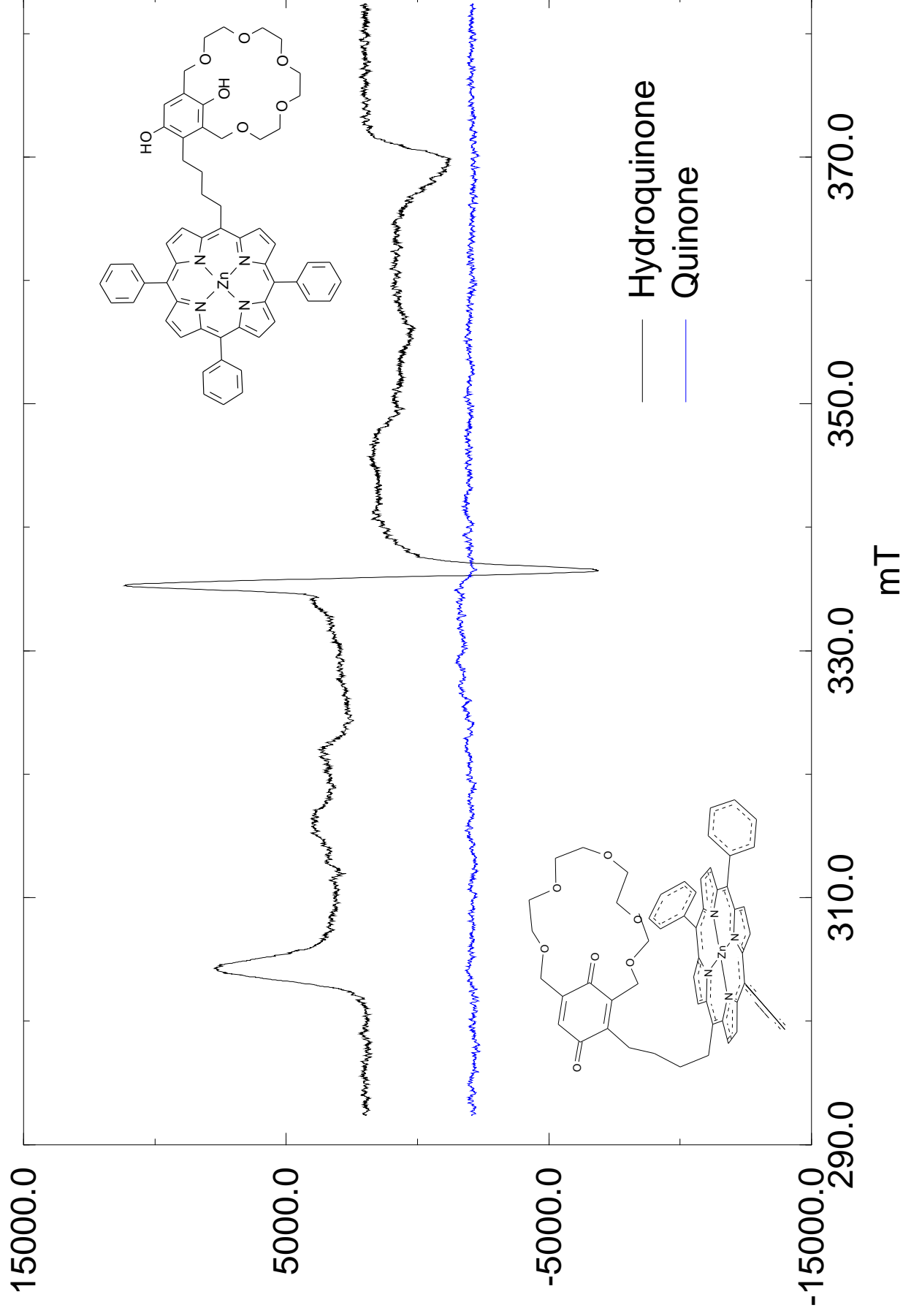


ZnTrPP-cCH-BQ / ZnTrPP-cCH-HQ

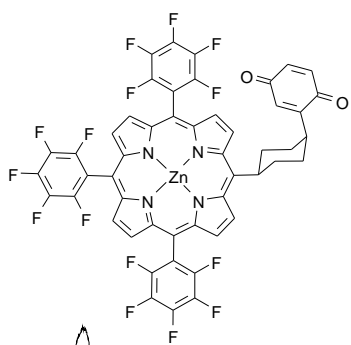
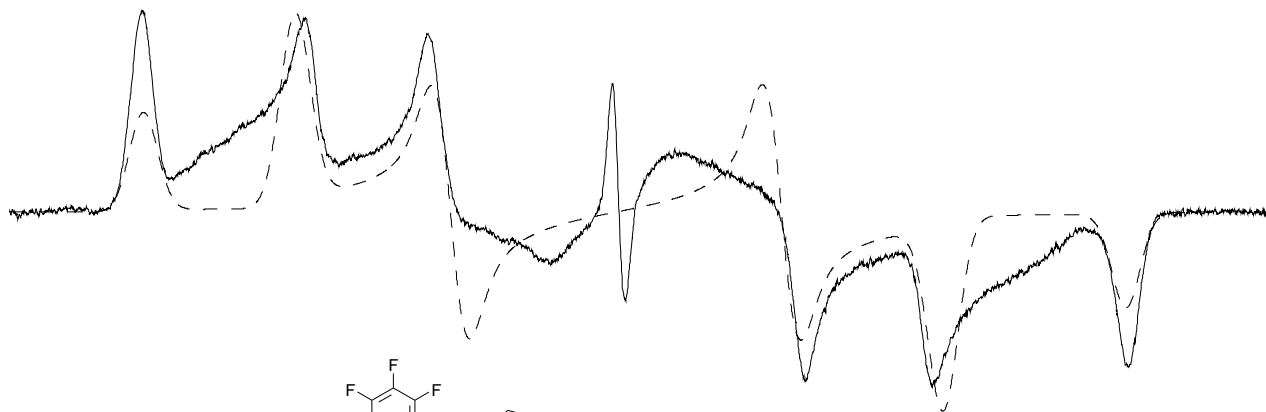


ZnTrPP-Bu-CrownQ / ZnTrPP-Bu-CrownHQ

30% MTHF/toluene, 100 K

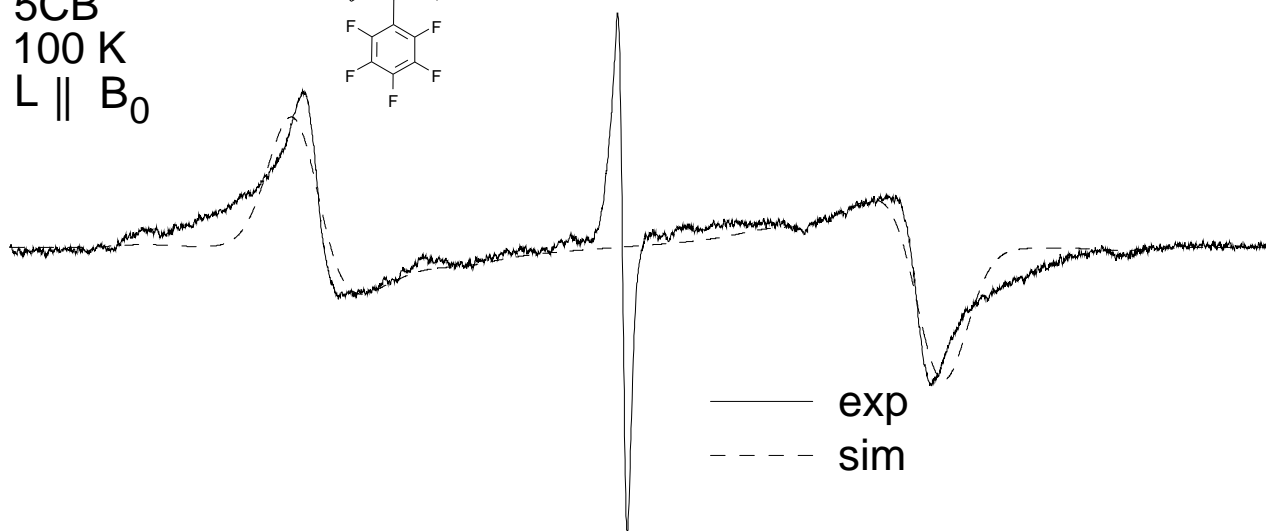


toluene
100 K



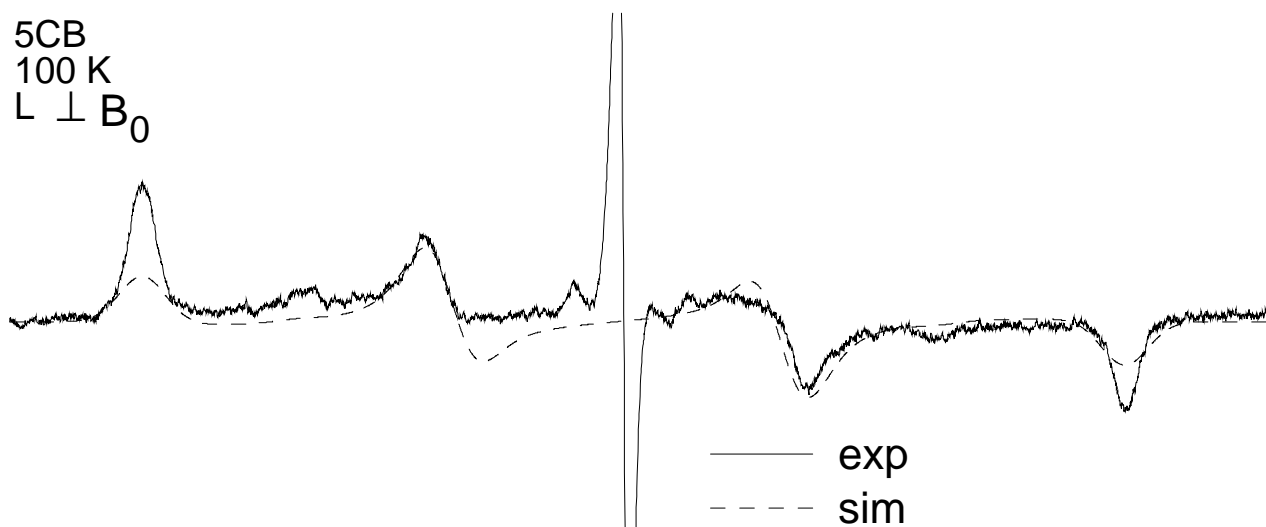
— exp
- - - sim

5CB
100 K
 $L \parallel B_0$



— exp
- - - sim

5CB
100 K
 $L \perp B_0$

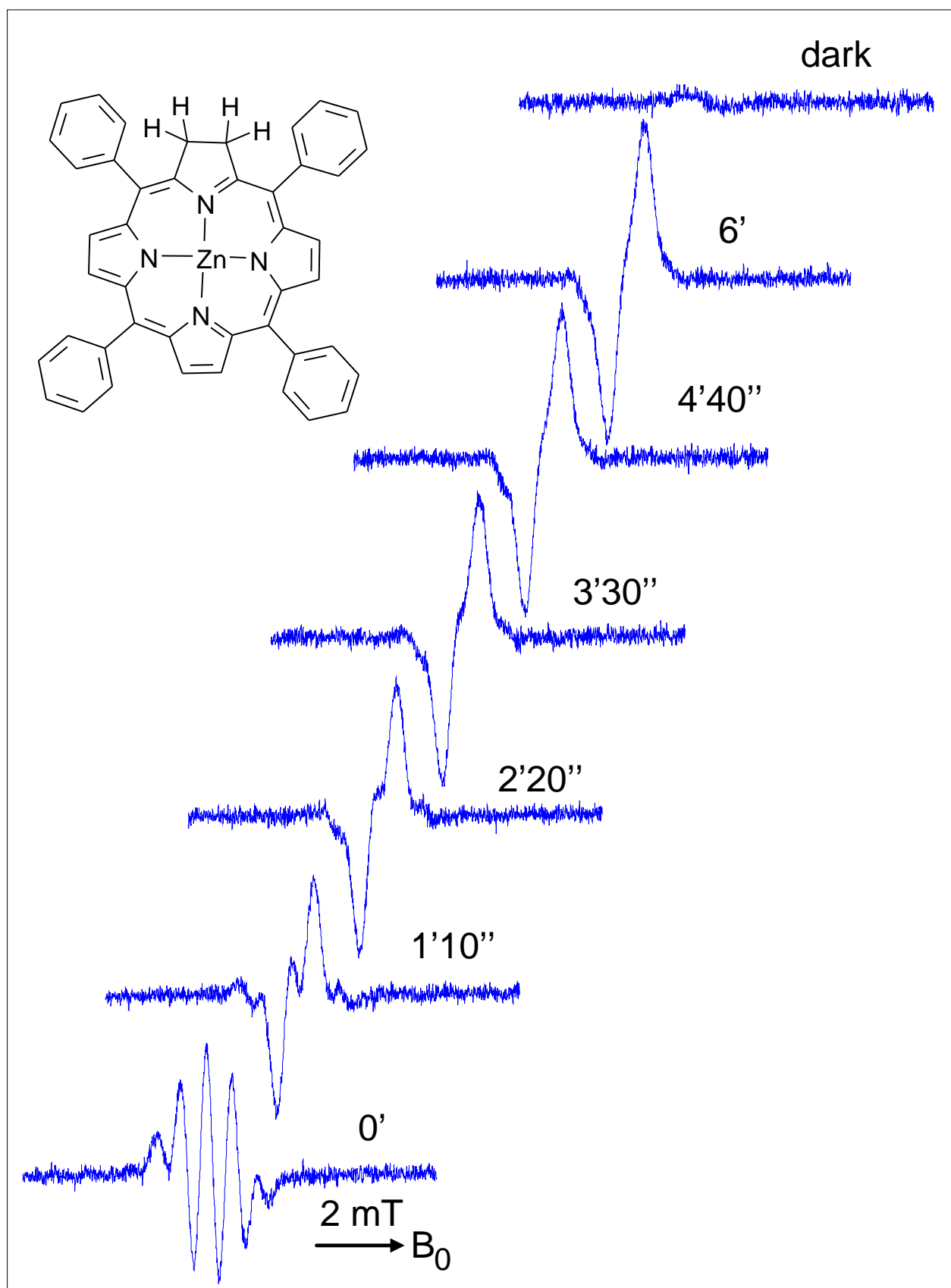


— exp
- - - sim

290.0 310.0 330.0 350.0 370.0
mT

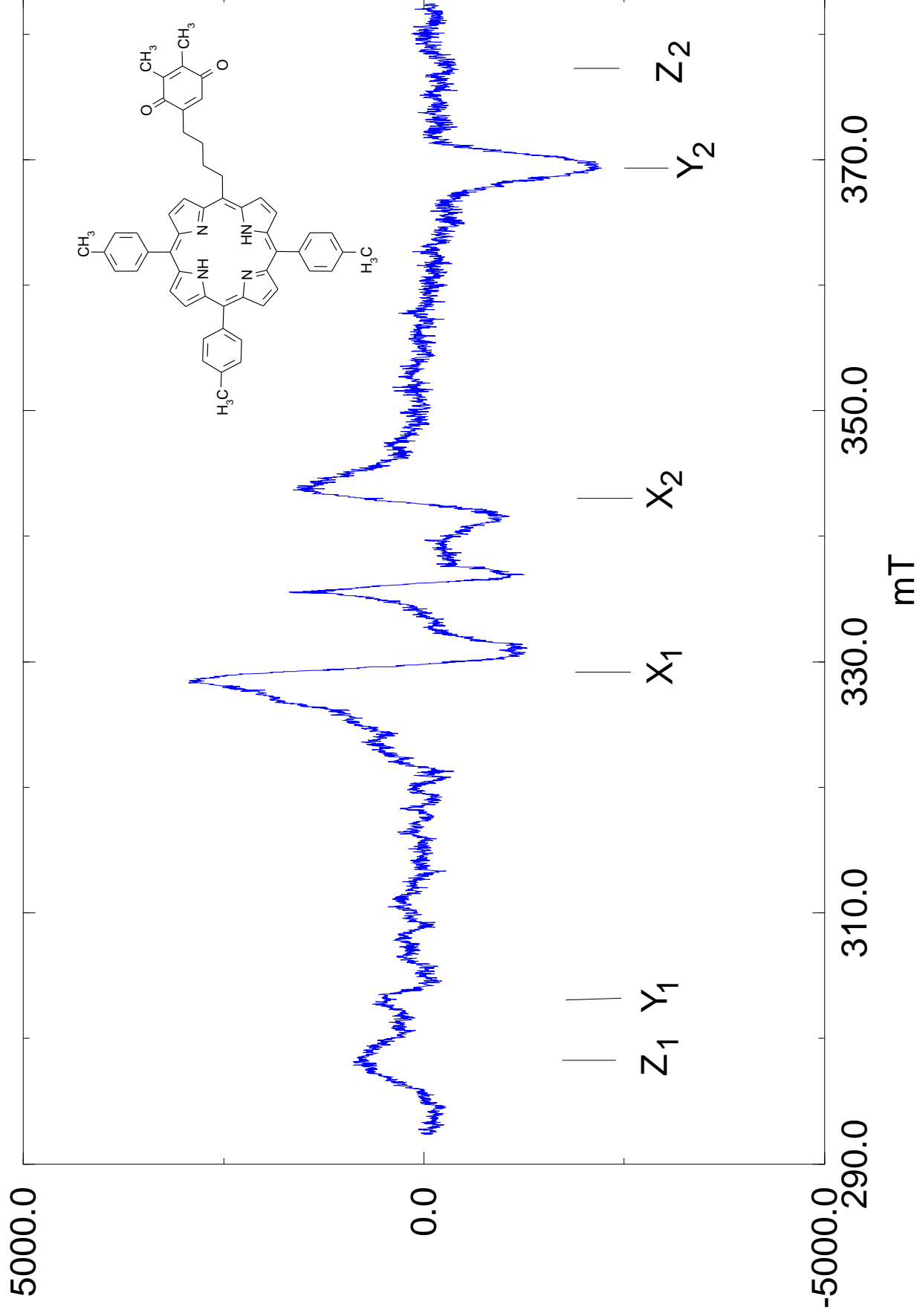
ZnTPC Radical Cation: Spin Polarization

Ethanol 190 K, light cut-off 395 nm



TrTP-Bu-diMeBQ

toluene, 110 K



Conclusions

- Photoexcited triplets of zinc porphyrins in isotropic and anisotropic glasses generally exhibit a superposition of ESR 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 pronounced alignment along the y axis is observed, $O_{yy} \approx 0.5$. Deviations in intensities may be attributed to residual spin polarization.
- In covalently linked porphyrin-quinones, basically the same triplet ESR 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.
- In the case of ZnTPC in fluid solution (ethanol, 190 K), the doublet signal of the ZnTPC radical cation (generated by irradiation at 110 K) occurs in *emission* on irradiation. We ascribe that to interaction with ZnTPC triplets according to the radical triplet pair mechanism.

Acknowledgment

Compounds were prepared by Dr. Jörg von Gersdorff, Werner Kalisch, 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.