Preface

When I first came into contact with EPR spectroscopy during my diploma thesis, I was skeptical. How should radicals be of any help in the structural determination of complex materials? After all, I was merely interested in the radicals themselves but in the environment surrounding them. I forgot that unlike nuclear spins, electrons experience a large spatial distribution enabling them to 'see' and 'sense' far into their neighborhood. Although other characterization methods I used at that time also provided quite insightful results, it was EPR spectroscopy that delivered an insight into the nanoscopic structural and dynamic arrangement of molecules. This triggered my decision to solely focus on EPR spectroscopy as a tool to probe complex macromolecular systems in my PhD research.

The unique sensing capabilities of electron spins have been known for a long time and led many researchers to exploit radicals as spectral sensors. The concept of spin probing and spin labeling has come of age and has been applied to many biological and synthetic systems. Yet, the recent advent and continuing development of pulse techniques keep expanding the potential and applicability of EPR spectroscopy. Although still a scientific niche, it is a fast growing field that nicely complements established scattering and spectroscopic techniques. Particularly, the possibility to reliably infer distances in the range of several nanometers between two spin labels fueled the expansion of EPR spectroscopy in the field of structural and molecular biology. Such distance constraints can be used to determine the 3D structure and assembly of macromolecular systems like proteins and nucleic acids. However, the synthetic effort for obtaining and labeling specific protein mutants is high and tedious. Moreover, only one distance constraint can be obtained by one spin labeled mutant and distance measurement in most cases. Focusing on transporting materials this triggered the idea to approach the problem differently. Instead of labeling the fatty acid transporter human serum albumin itself, I simply replaced the transported guests by EPR-active fatty acids. The insights into the functional structure of albumin from the viewpoint of the transported guest molecules and the implications of such self-assembled systems for the respective EPR method are presented in Chap. 3. Yet, one does not always require state-of-the-art

technology to obtain novel and exciting findings. This is demonstrated in Chaps. 5 and 7, where the thermal collapse of thermoresponsive polymeric systems is studied by one of the most elementary nitroxide spin probes and simple continuous wave EPR spectroscopy.

The broad applicability of modern EPR spectroscopy in structural biology and materials science is emphasized by the examined systems: With a transport protein, a biomimetic host system, and responsive hydrogels and dendronized polymers, three substantially different transporting agents were examined by a variety of EPR spectroscopic methods and probes. In either case, EPR spectroscopy delivered illuminating and sometimes surprising insights into the molecular transporters, leading to a detailed molecular understanding of the materials' functions.

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