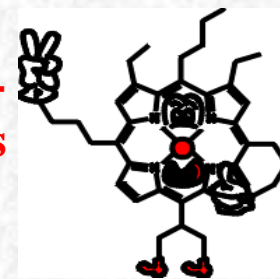


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Synthesis and Characterization of Porphyrin-*o*-Quinones - A New Group of Model Compounds for Photosynthesis



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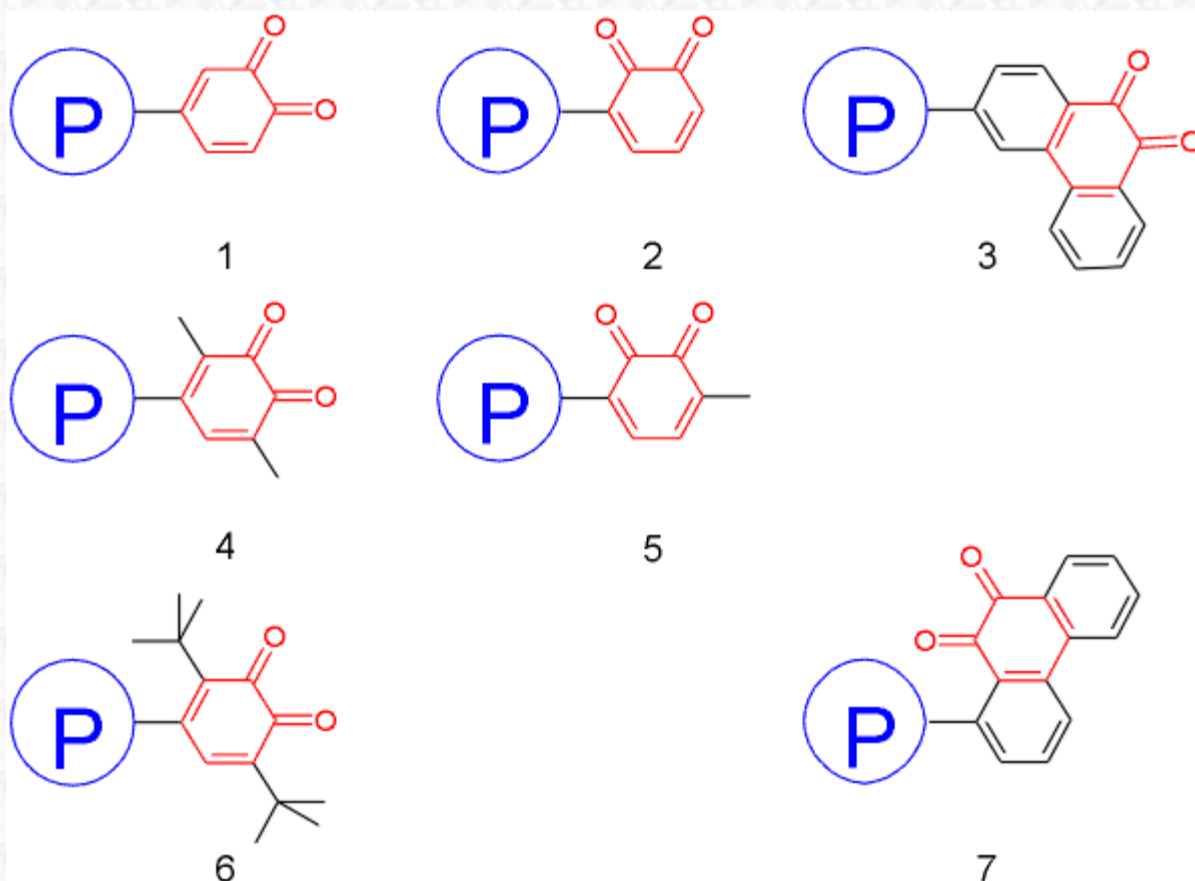
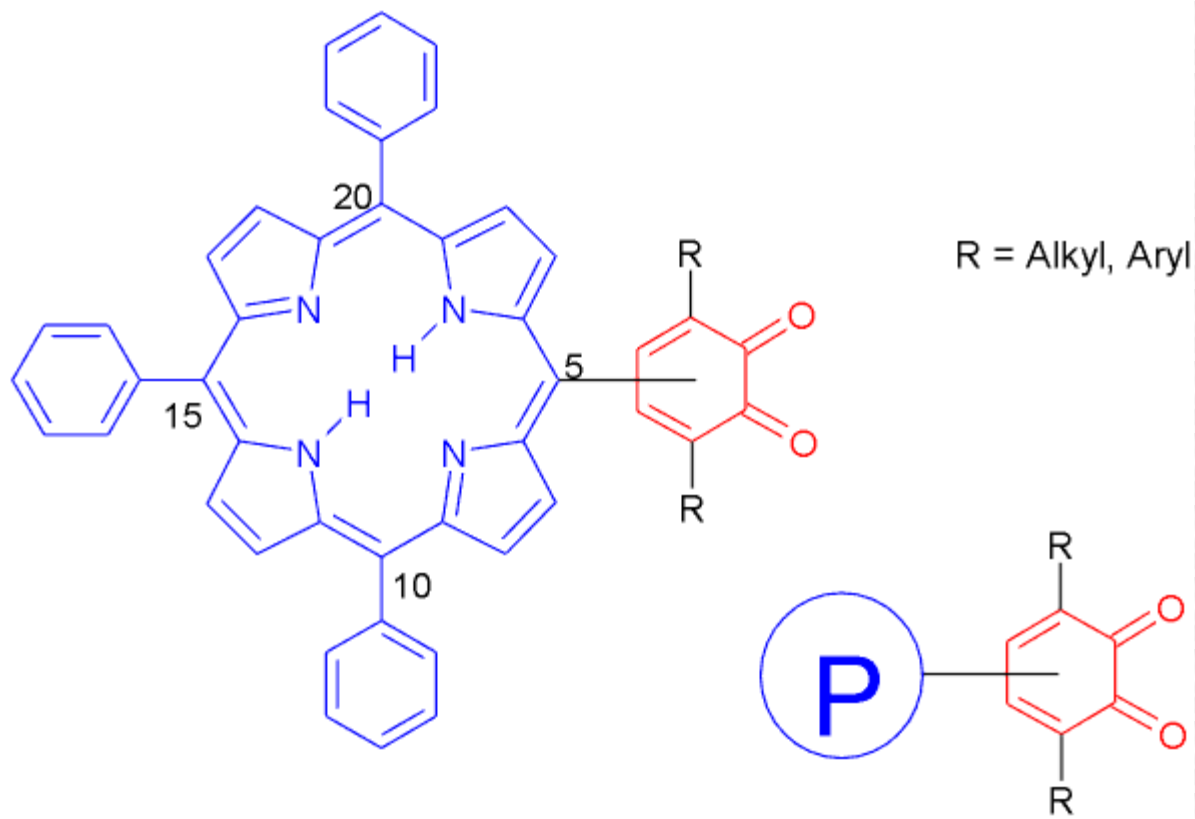
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Introduction

Photosynthesis is the most important energy conversion process for life on earth. Thus, many research groups attempt the synthesis of covalently linked porphyrin quinones to mimic the underlying electron transfer processes occurring in the primary step of photosynthesis.

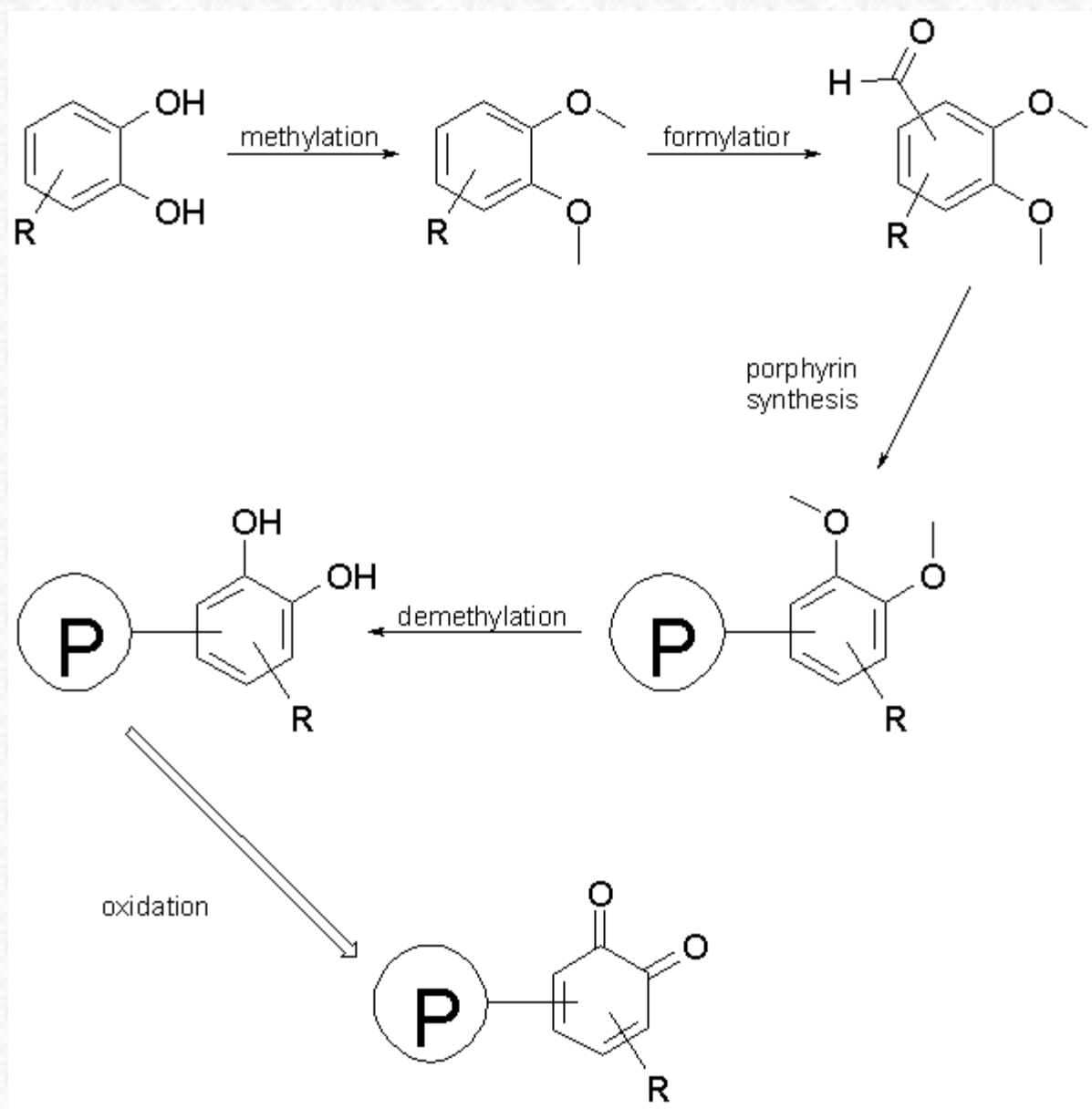
In order to study the influence of different acceptor strengths and geometrical parameters on the electron transfer properties a few hundred porphyrin-*p*-quinones with different bridging and acceptor units were synthesized.^[1] In this context we became interested in the synthesis of stabilized porphyrin-*o*-quinones, which have not been described by other groups.

Such compounds offer the intriguing possibility to modulate the redox potential of the porphyrin-quinones via chelation of the *o*-quinone with various cations. In addition, *t*-butylated *o*-quinones are also of interest as model compounds for catecholase reactions.^[2]



Scheme 1

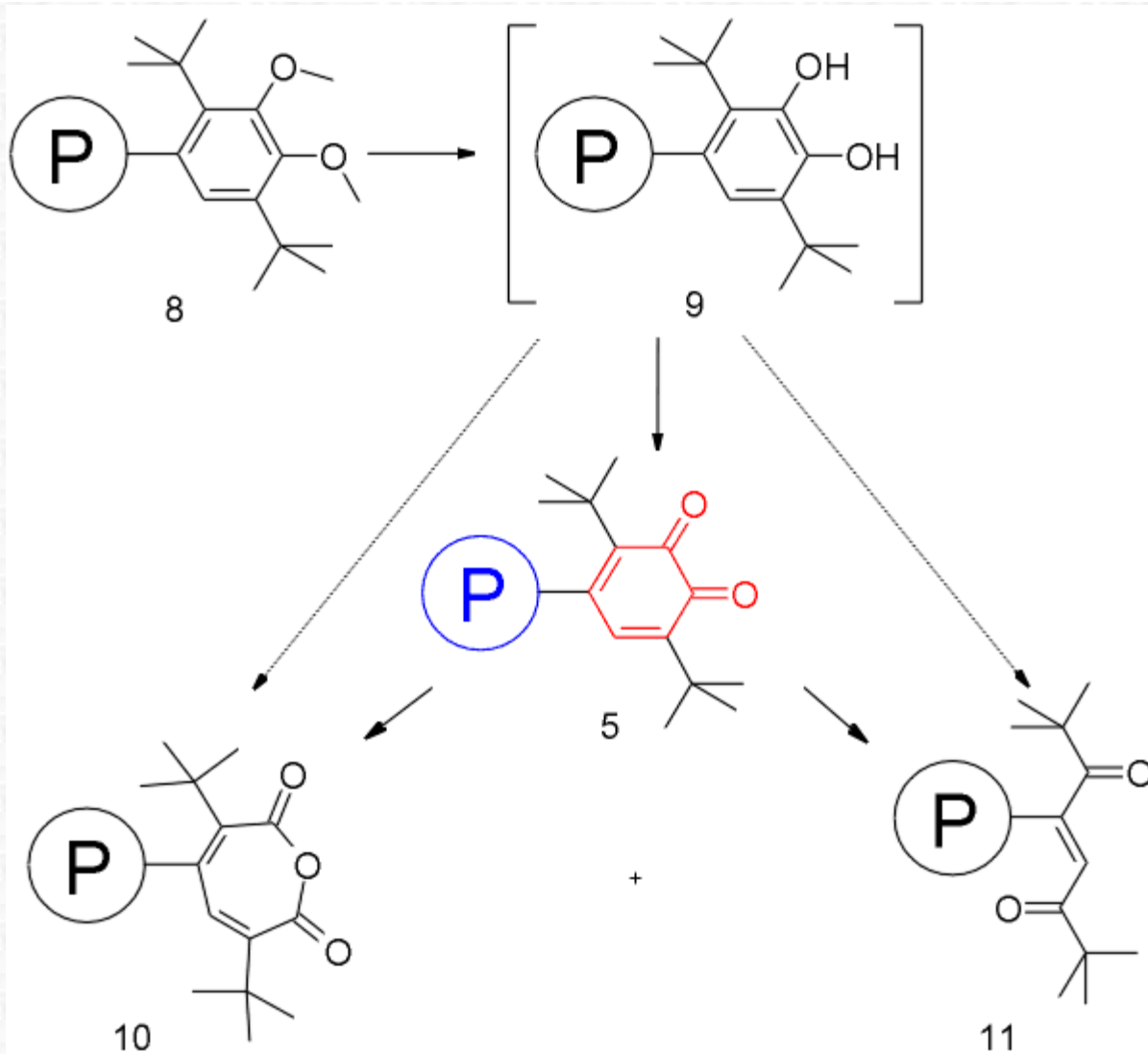
The synthesis of the porphyrins follows the Lindsey procedure. Pyrrole, benzaldehyde and another protected *o*-quinone aldehyde were condensed in dichloromethane under acidic conditions. The reactions are described in Scheme 2.



Scheme 2

To purify the model compounds for electron transfer investigations and NMR spectroscopy multiple steps of column chromatography and finally preparative HPLC were used.

The "stable" porphyrin-*o*-quinone **6** with two *tert*-butyl groups undergoes a decomposition under light and oxygen. The decomposition products **10** and **11** were obtained in high purity (Scheme 3).



Scheme 3

The unsubstituted porphyrin-*o*-quinone isomers **1** and **2** were also synthesized and characterized. The spectroscopic measurements were performed at $-20\text{ }^{\circ}\text{C}$.

Spectroscopy

NMR spectroscopy is an important method for characterization of the porphyrin-*o*-quinones. ^1H and ^{13}C NMR investigations and additional homo- and heteronuclear 2D experiments allowed us to completely assign the different signals in both types of spectra for all porphyrin-*o*-quinones.

The importance of the ^{13}C NMR spectroscopy is shown in the case of the decomposition products of the free base **6** (Figure 2). Proton NMR spectra alone do not allow a complete assignment (Figure 1).

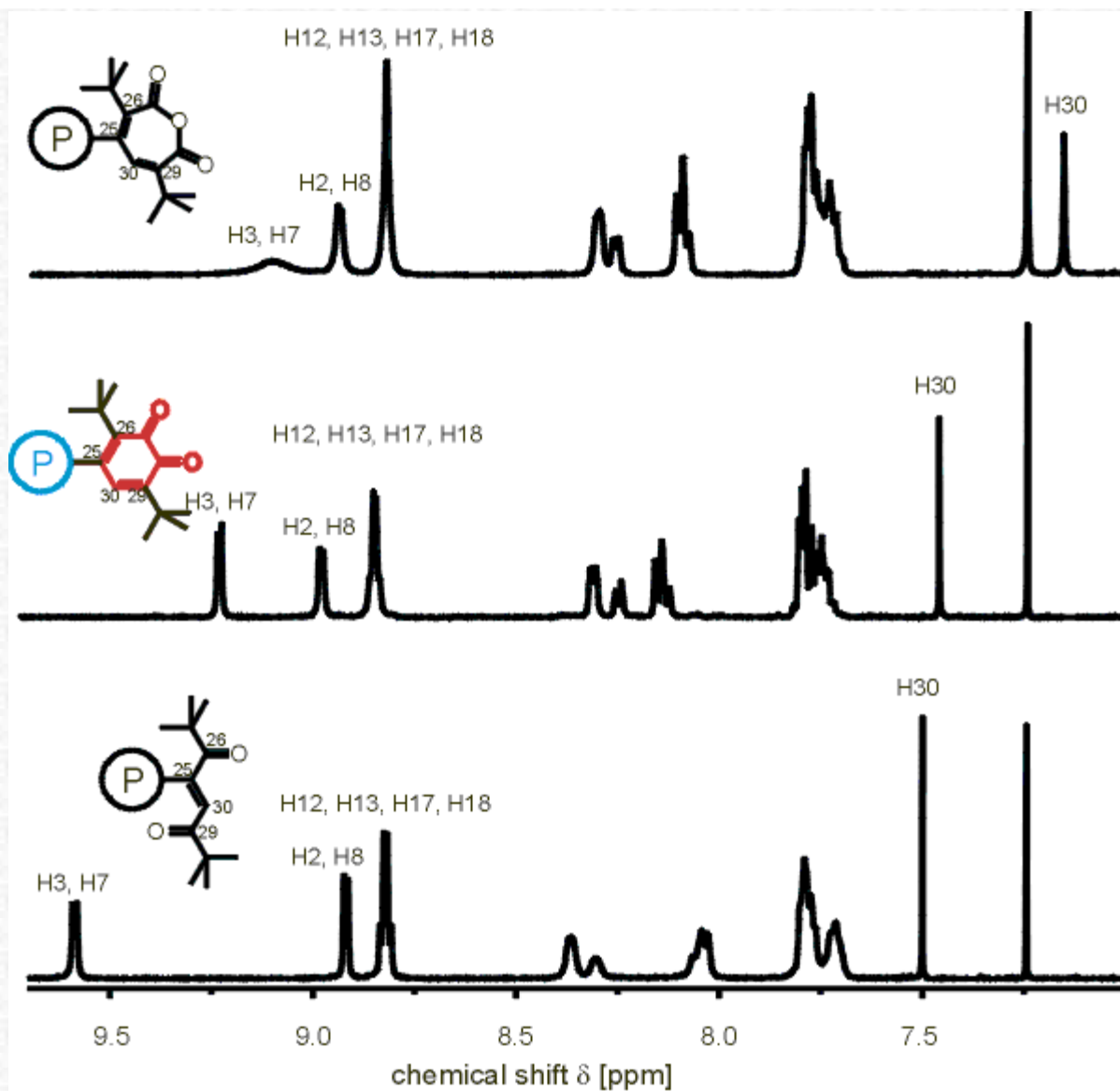


Figure 1: ^1H NMR spectra of different *tert*-butylated porphyrins (range of aromatic protons)

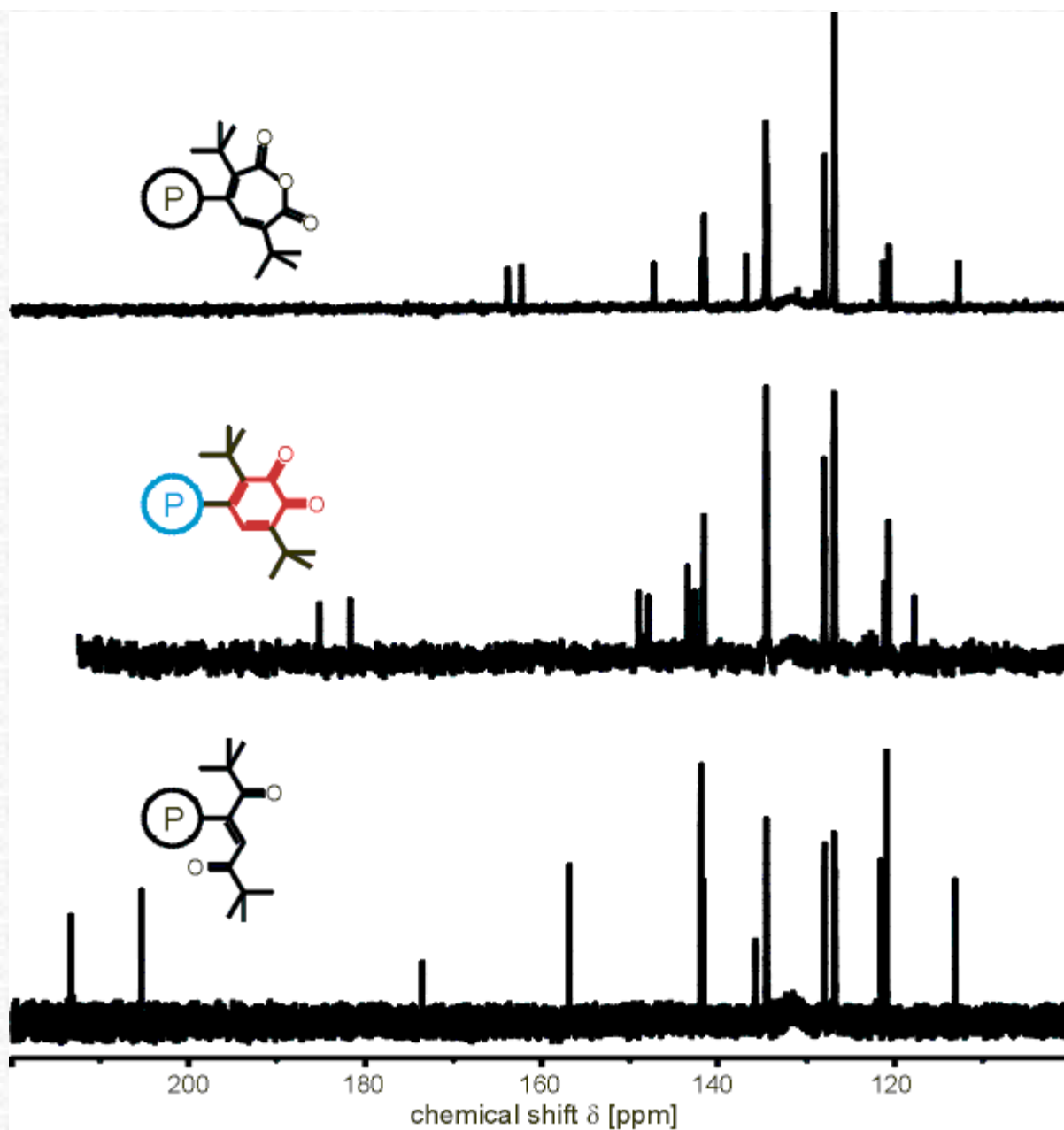


Figure 2: ^{13}C NMR spectra of the decomposition products (range of the C=O and aromatic carbons)

In contrast to other groups, we obtained the proton spectra of the unsubstituted porphyrin-*o*-quinones **1** and **2**. The coupling constants and the different multiplicity are the result of the connecting position between porphyrin moiety and the *o*-quinone.

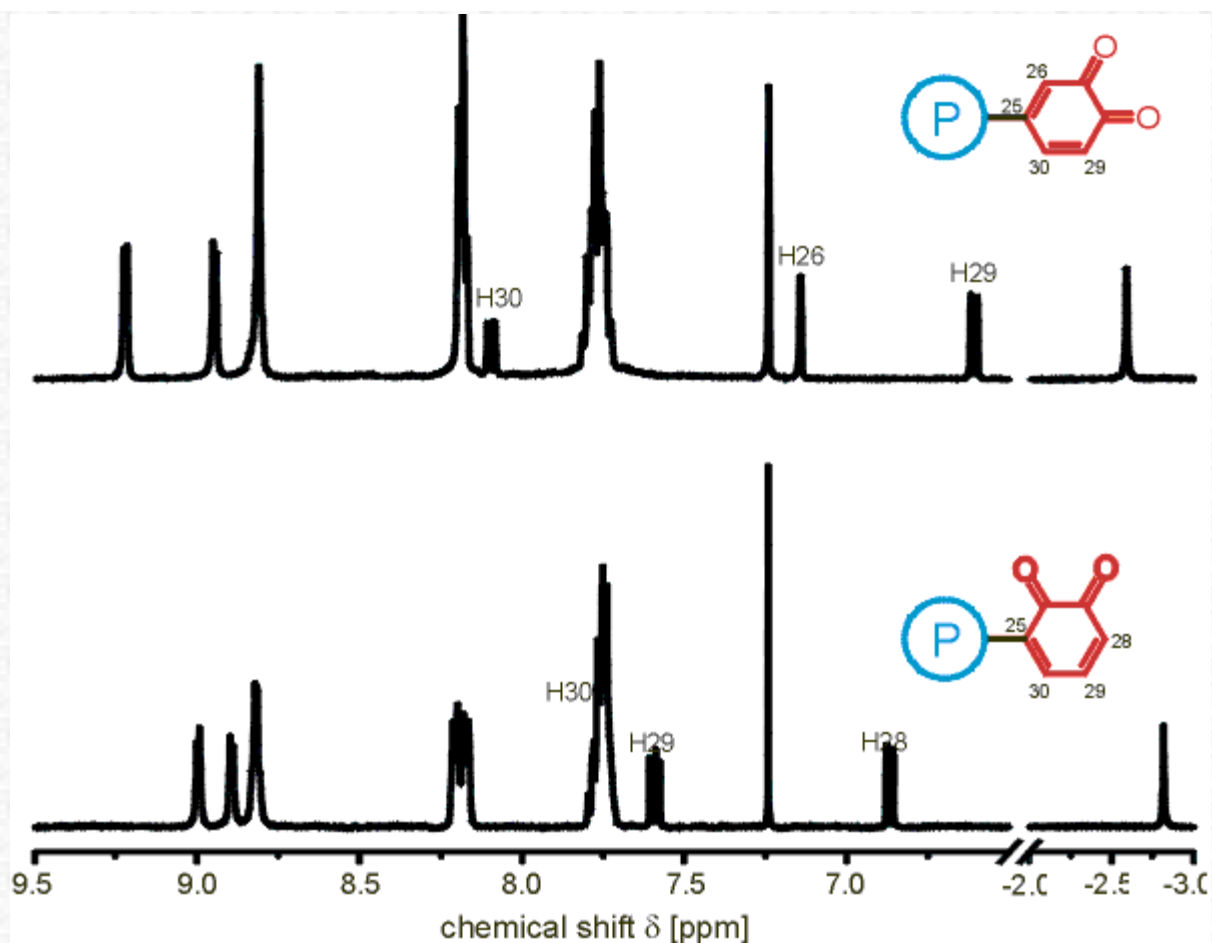


Figure 3: Proton NMR spectra of the unsubstituted Porphyrin-*o*-quinones **1** and **2**

In accordance with the strong electronic coupling, the porphyrin-*o*-quinones show a broadening of the Q-bands. In the case of the unsubstituted compound **1**, we get an additional broad charge transfer band (see below). The lineshape of the Q-bands depends on the dihedral angle between porphyrin donor and quinone acceptor. The protected porphyrin-*o*-quinones have similar absorption spectra with a habitus like the spectra of TPP.

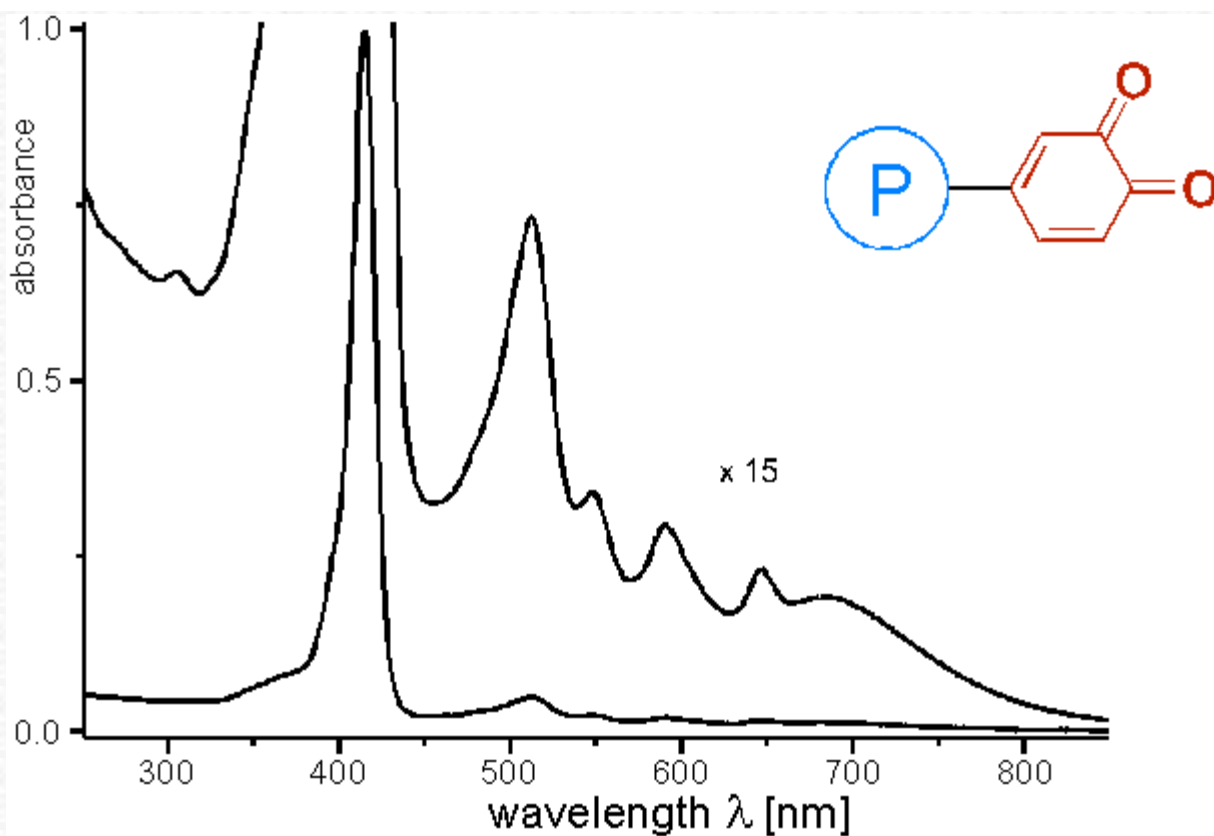


Figure 4: Absorption spectrum of the unsubstituted Porphyrin-*o*-quinone **1**

With all model compounds static EPR/ENDOR measurements were performed. Different counter ions allowed detailed informations about spin density of various semi-*o*-quinone anions.

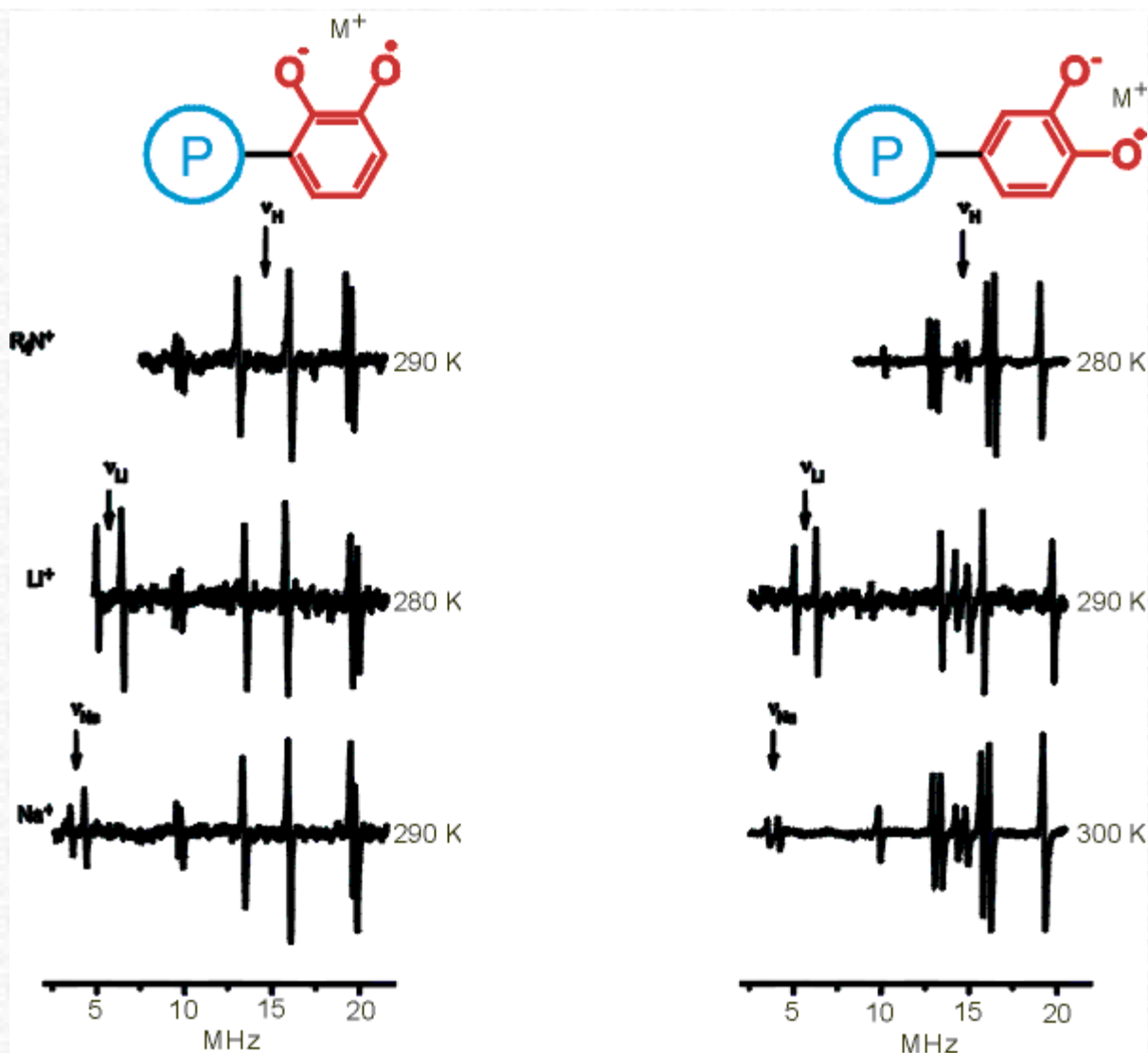


Figure 5: ENDOR spectra of the unsubstituted Porphyrin-*o*-semiquinones with different counter ions

Conclusion

As we have shown, porphyrin-*o*-quinones can be synthesized as stable model systems for photoinduced electron transfer and characterized with analytical methods. They are better electron acceptors than their analogous *p*-isomers. The dimethyl compound has the same stability as "normal" porphyrin-*p*-quinones. The EPR/ENDOR investigations show the difference in electronic properties with or without additional cations. First investigations of the ET properties show a strong electronic coupling of donor and acceptor, connected with a high rate of electron transfer. The ET is the main process of relaxation in these systems. Additional processes like ISC, IC and fluorescence play a minor role.

The importance of the *tert*-butylated compound **6** as a model system for catecholase reactions is currently under detailed investigations.

Acknowledgment

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