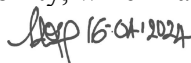## Abstract (Eng.)

Porphycenes are at the heart of 2nd generation photosensitization in Photodynamic Therapy (PDT) due to their intrinsic spectral, photophysical, and photobiological properties. Regarding fundamental studies of hydrogen transfer processes involving single or double proton transfer, porphycenes are known as models for such investigations. Here, a series of porphycene derivatives, substituted either with nitro, amino, or mixed nitro and amino groups, were studied. In order to ascertain their suitability in the above-mentioned applications, spectral, photophysical, and photostability characterization were performed using steady-state electronic absorption, emission, Magnetic Circular Dichroism (MCD) spectroscopy, and quantum chemical calculations. In addition, time-resolved studies were employed to characterize the excited state dynamics of these porphycenes. The specific influence of electron-donating and withdrawing groups and bulky *tert*-butyl groups, as well as the position of the substituent, were investigated.

In our studies, we found that substitution with the amino group results in red-shifted absorption bands in the spectra of aminoporphycenes. Nitroporphycenes (with the exception of the *meso*-tetraphenyl derivatives), on the other hand, showed marginal changes in absorption compared to parent unsubstituted porphycenes. Single emission is observed for both the amino and nitro series. The previous interpretation of dual emission in aminoporphycenes has to be abandoned. All nitro derivatives (except *tert*-butyl nitroporphycene) were better emitters than their amino counterparts. The introduction of bulky tertiary butyl groups results in a significant influence on the photophysics: loss of fluorescence and lack of population of the triplet state is evident in the *tert*-butyl derivatives, indicating the dominance of non-radiative processes. *Meso*-tetraphenyl substitution of porphycene, while varying the position of the nitro group to β or β' results in interesting chemistry. In the β' derivative, we observe a moderate yield of fluorescence, ~30% singlet oxygen (SO) generation, and a triplet state that lived up to 200 ns. The β counterpart is a weak emitter with ~1% yield of SO, and the triplet signal was too weak to be accurately determined, given the resolution of our instrument. Photodegradation studies revealed three orders of magnitude differences in photostability between the nitro and aminoporphycenes, with nitroporphycenes being more stable. All compounds showed a solvent effect in the obtained results. We conclude that several nitroporphycenes qualify as candidates for sensitization in PDT due to their photophysics and photostability, which have been established from this study.

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