

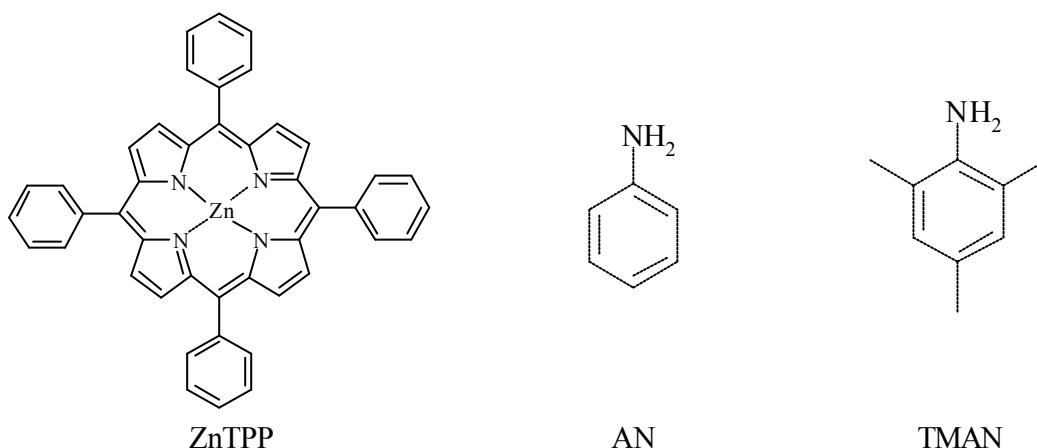
Spectroscopy and Photophysics of Metalloporphyrin Excited State Quenching

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Metalloporphyrins are widely present in nature and are key components in various biological processes, including photosynthesis. To gain further insight into the photon-induced quenching processes occurring in metalloporphyrins, the S_1 and S_2 emission quenching dynamics of zinc tetraphenylporphyrin (ZnTPP) by various quenchers (*i.e.*, 2,4,6-trimethylaniline (TMAN), aniline (AN) and carbon tetrabromide) in toluene and dichloromethane solvents were investigated.



The ZnTPP absorption spectrum is perturbed (*i.e.*, formation of new bands) upon the addition of the quenchers, indicating the formation of ground-state complexes. Association constants have been measured. In the fluorescence spectrum, a decrease in the ZnTPP emission intensity (quenching) is observed. The excited ZnTPP-CBr₄ complex does not fluoresce from either S_1 or S_2 , but ZnTPP-AN and ZnTPP-TMAN complexes do. The S_1 fluorescence lifetime of ZnTPP (~2.2 ns) remains unchanged with the addition of either AN or CBr₄ in toluene, and the excited ZnTPP-AN complex has a lifetime similar to ZnTPP. We propose that electron transfer occurs between ZnTPP and CBr₄ in the S_2 excited state of the ZnTPP-CBr₄ complex.

The larger association constants found for the one-to-one complex formation of ZnTPP-AN and ZnTPP-TMAN in dichloromethane suggest a more efficient quenching in this solvent compared to toluene. This is also reflected in the higher apparent rates of S_1 and S_2 fluorescence quenching of ZnTPP by CBr₄ in dichloromethane.