

Fluorescence Quenching of the S₁ and S₂ States of Zinc meso-Tetrakis(4-sulfonatophenyl)porphyrin by Halide Ions

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The excited state quenching of zinc meso-tetrakis(4-sulfonatophenyl)porphyrin, ZnTPPS, by halide ions (*i.e.*, Cl⁻, Br⁻ and I⁻) has been studied in water and various aqueous micellar solutions using both steady-state and time-resolved fluorescence techniques. The quenching efficiencies of the S₁ state of ZnTPPS ($\tau \sim 1.7$ ns) by halide ions in water increase in the order Cl⁻ < Br⁻ < I⁻. The Stern-Volmer plots for Br⁻ and I⁻ quenchers are described in terms of dynamic and static quenching processes. The various possible mechanisms involved (*i.e.*, electron transfer, heavy atom effect and Watkin's mechanism) will be discussed. On the other hand, quenching of the short-lived S₂ state ($\tau \sim 1.3$ ps) of ZnTPPS is achieved only when I⁻ is used as a quencher, and the quenching mechanism proceeds *via* electron transfer between fluorophore and I⁻ within the quenching sphere of action. The results are consistent with the Gibbs free energy change (ΔG^0) involved in the charge-separation process. Finally, the fluorescence quenching of ZnTPPS by the halide ions is examined in both cationic (*i.e.*, DTAB and CTAC) and neutral (*i.e.*, TX-100) micelles.