Nano-ions as Superchaotropic Fluorescence Quenchers: A Model for Protein-Surface Interactions.

Sanyukta Bhattacharjee [1], Fayçal Hadj Sadok [1], Coralie Pasquier [1], Olivier Diat [1], Pierre Bauduin [1]

[1] ICSM, CEA, CNRS, ENSCM, Univ. Montpellier, Marcoule, France, Centre de Marcoule, 30207 Bagnols-sur-Cèze, France.

sanyukta.BHATTACHARJEE@cea.fr

The low charge density of superchaotropic anions like polyoxometalates (POMs), giant POMs (Mo_{154}, Mo_{132}), and inorganic boron clusters ($B_{12}X_{12}^{2-}$; X=H, Br, I) renders them distinct hydration properties. [1] Despite a growing interest, its effect on optical properties [2,3] and peptide dynamics remains poorly understood. Herein, we report a systematic investigation of the effect of structurally diverse nanometric-sized inorganic clusters on the fluorescence properties of N-acetyl-L-tryptophanamide (NATA). [4] Initially, tryptophan was chosen as the fluorophore; however, certain POMs, most notably ammonium metatungstate hydrate (AMTH), at higher concentrations produce anomalous distortions in its excitation spectra rather than the expected fluorescence quenching. Such a distortion was indicative of a direct chemical interaction between the POM and the fluorophore rather than a purely photophysical mechanism. To overcome this complication, we have chosen NATA, the protected analogue of tryptophan. Steady-state, time-resolved fluorescence measurements, coupled with SAXS, reveal a novel quenching mechanism that cannot be attributed solely to energy transfer. The quenching efficiency was found to be a complex interplay of the size and charge density of the nano-ions, with Mo_{154} and Mo_{132} exhibiting the strongest quenching behaviour consistent with their giant size [5] and surface charge distributions while, smaller POMs (HPW, HSiW, AMTH, $K_8SiW_{11}O_{39}$) at equimolar concentrations acted as comparatively mild quenchers. Strikingly, rather than quenching, boron clusters at equivalent concentrations to other nano-ions were found to support the fluorescence enhancement of NATA. Our results thus demonstrate a contrasting effect on the photophysics of NATA, subject to nano-ions, which is yet to be rationalized.

Keywords:
Superchaotropic, Giant POMs, Boron Clusters, Fluorescence, SAXS.

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