

Light Induced and FRET based Photoisomerization Inhibition and Fluorescence Enhancement of Azobenzene by Al³⁺ ion coordinated rhodamine derivative

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Azobenzene is one of the most studied photochromic molecule that shows reversible cis↔trans isomerism by thermal and photochemical pathways,^[1,2] which enables them to be useful in phototriggered biological systems.^[3] Since the photochemical azobenzene isomerization is the dominant excited state deactivation pathway, an another, competitive, photophysical property, i.e. fluorescence becomes negligible and in fact, has not experimentally been observed many cases. The fluorescence properties of azobenzene are highly desirable, which would be promising skeleton in the fields of light-emitting devices, fluorescent probes, and fluorescent sensors etc. Hence, making fluorescent azobenzene derivatives are quite challenging in the current scenario. Though few examples of fluorescent azobenzene are available, the quantum yield is quite low.^[4] Here we have designed and synthesized a novel azobenzene appended rhodamine derivative (Azo-Rho) and their photochemical and photophysical properties were studied. Though, Azo-Rho undergoes photoisomerization similar to unsubstituted azobenzene, presence of Al³⁺ ion induces the rhodamine ring opening rather than the trans↔cis photoisomerization. As a consequence, fluorescence enhancement of both azobenzene and rhodamine unit was observed. The enhanced fluorescence would have originated by restricting the excited state photochemical pathways and also the energy transfer from azobenzene to rhodamine via Chelation Enhancement Fluorescence (CHEF) assisted Fluorescence Resonance Energy Transfer (FRET) was observed as shown in Figure 1.

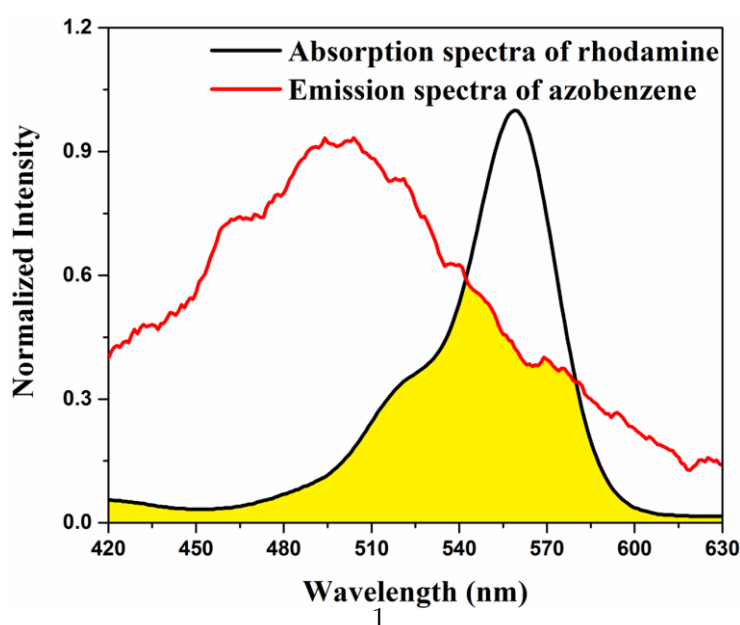


Figure 1. The spectral overlap of azobenzene (donor) and rhodamine (acceptor)

The mechanism involved in this process was monitored by both fluorescence and ^1H NMR spectroscopy. The selectivity of Al^{3+} towards the Azo-Rho over various metal ions were examined after irradiation with $\lambda=365$ nm (Cu^{2+} , Fe^{2+} , Fe^{3+} , Pb^{2+} , Zn^{2+} , Ni^{2+} as perchlorate salts). Only Al^{3+} was found to show significant enhancement in fluorescence, however, a slight enhancement is also observed for Hg^{2+} and Fe^{3+} ions. The stoichiometric ratio of AZO-Rho to the Al^{3+} was found to be 1:1 by Job's plot and the binding constant calculated using Benesi-Hildebrand plot corresponds to $5.2 \times 10^3 \text{M}^{-1}$. The competitive ring opening of Rho resulted in fluorescent azobenzene and subsequent energy transfer by CHEF assisted FRET pathway.

Funding: This work was supported by XIIth plan suprainstitutional project "STRAIT". A. Raman is recipient of DST-INSPIRE fellowship

Acknowledgement: We thank The Director, CSIR-Central Leather Research Institute, for his support.

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