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Transient Raman Snapshots of the Twisted Intramolecular Charge Transfer State

Jyotishman Dasgupta

Department of Chemical Sciences, Tata Institute of Fundamental Research, Mumbai, INDIA

E-mail: dasgupta@tifr.res.in

Abstract

Optically triggered twisted intramolecular charge transfer (TICT) states in donor-acceptor chromophores form the molecular basis for designing bio-imaging probes that sense polarity, microviscosity or pH *in vivo*. [1] However, a lack of predictive understanding of the ‘twist’ localization has limited rational structure-function correlations for TICT-based dyes. Time-resolved absorption and emission spectroscopy traditionally used to address this problem, could never unequivocally identify the twist location. [2] Here, using femtosecond stimulated Raman spectroscopy, we reveal distinct Raman signature of the TICT state for stilbazolium-class of mitochondrial staining dye for the first time. [3]

Resonance-selective probing of 4-N,N-diethylamino-4'-N'-methyl-stilbazolium tosylate (DEST) tracks the excited state structure as it relaxes to a TICT state on a picosecond timescale. The remarkably blue-shifted C=C stretching mode at 1650 cm^{-1} in the TICT state is attributed to the ‘twist’ of a single bond adjacent to the ethylenic π -bridge in the DEST backbone through detailed electronic structure and vibrational calculations. Our work demonstrates that the π -bridge connecting the donor and acceptor moiety influences the spatial location of the “twist”, and offers new perspective for designing organelle-specific probes through rational tuning of backbone dynamics.

Fig. 1: TICT state formation caught in the act by time-resolved Raman spectroscopy.

Keywords: Bioimaging probes, TICT state, femtosecond stimulated Raman spectroscopy

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