

Ultrafast Spectroscopic Studies on the Interaction of a Potential Food Carcinogen with Biologically Relevant Macromolecules

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Abstract – Benzo[a]pyrene (BP), a potential carcinogen in a class of pyrene derivatives shows interesting photophysics including very sharp vibronic structures in the emission spectrum. A detail spectroscopic study on the close interaction of the carcinogenic molecule with other biologically relevant macromolecules through ultrafast energy/charge transfer reactions is the motive of the present review. Firstly, we present our picosecond resolved studies on the Förster resonance energy transfer (FRET) from various vibronic bands in BP, showing strong dependency on the spectral overlap of an energy acceptor in a confined environment. Our study on the dipolar interactions between BP and different acceptors ethidium (Et), acridine orange (AO) and crystal violet (CV) at the surface of a model anionic micelle reveals the Förster distance (R_0) and the rate of energy transfer to be dependent on the individual spectral overlap of the vibronic bands of BP with the absorption spectra of different energy acceptors. The differential behaviour of the vibronic bands is compared with that of different dyes (quantum dots; QDs) in a 'dye-blend' (mixture) under FRET to an energy acceptor. Such comparison of the FRET of QDs with that of BP, not only confirms independent nature of dipolar interaction of the vibronic bands with other organic molecules, the use of deconvolution technique in the interpretation of the donor-acceptor (D-A) distance has also been justified. We have also shown that consideration of differential FRET from vibronic bands of BP and from the QDs in the 'dye-blend' is equally acceptable in the theoretical frameworks including 'Infelta-Tachiya' model and D-A distribution analysis in the nano-environments. While such energy transfer reactions act as "spectroscopic ruler" to measure the distance between two sites on a macromolecule, reactions involving electron transfer (ET)/charge transfer (CT) and reactive oxygen species (ROS) play a pivotal role in carcinogenesis and cancer biochemistry. The review further emphasizes our studies on UVA radiation induced ET reaction as one of the key aspects of BP in the presence of a wide variety of molecules covering organic para-benzoquinone (BQ), biological macromolecules like calf-thymus DNA (CT-DNA), human serum albumin (HSA) protein and inorganic zinc oxide (ZnO) nanorods (NRs). Steady-state and picosecond-resolved fluorescence spectroscopy have been used to monitor such ET reactions. Physical consequences of BP association with CT-DNA have been investigated through temperature-dependent circular dichroism (CD) spectroscopy. The temperature-dependent steady-state, picosecond-resolved fluorescence lifetime and anisotropy studies reveal the effect of temperature on the perturbation of such ET reactions from BP to biological macromolecules, highlighting their temperature-dependent association. Furthermore, the electron donating property of BP has been corroborated by measuring wavelength-dependent photocurrent in a BP-anchored ZnO NR-based photodevice, offering new physical insights for the carcinogenic study of BP.

Keywords: Benzo[A]Pyrene (BP), Vibronic Fine Structures, Förster Resonance Energy Transfer (FRET), Nanoscopic Micelle, Quantum Dots Blend, Femtosecond Resolved Vibrational Cooling, UVA Radiation Induced Electron Transfer (ET) Reaction, Temperature-Dependent Picosecond-Resolved Fluorescence of BP, Temperature-Dependent Binding of BP to DNA and Protein, Zinc Oxide Nanorod (Zno NR) Fabricated Photodevice

Nomenclature

R_0	Förster distance	$J(\lambda)$	Overlap integral
κ^2	Orientation factor	E	Energy transfer efficiency
n	Refractive index	r	Distance between donor and acceptor
Q_D	Quantum yield	P_n^*	Micelle containing n quencher molecules and one excited probe
		P_n	Micelle containing n quencher molecules

