Journal of Luminescence 220 (2020) 116953

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: http://www.elsevier.com/locate/jlumin

Interaction of proflavin with tryptophan in reverse micellar microenvironment of AOT: Photoinduced electron transfer probed by magnetic field effect

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ARTICLE INFO

Keywords:
Laser flash photolysis
Magnetic field effect
Reverse micelle
Hyperfine interactions
$B_{1/2}$ value

ABSTRACT

Photoinduced electron transfer (PET) from a biological amine, tryptophan to a well-known acridine-derivative, proflavin has been investigated employing laser flash photolysis technique in heterogeneous AOT reverse micelles (RMs). In AOT RMs a significant magnetic field effect (MFF) on PET has been observed which authenticates the triplet spin states of the precursors of PET. The measurement of $B_{1/2}$ value gives an indication of the extent of hyperfine interactions present in the system in AOT medium. The cause of discrepancy between calculated and experimental $B_{1/2}$ values is explained. Further, it is observed that MFE decreases with increase in pool size of the RMs which highlights the importance of optimum separation between the corresponding radical ions pairs to maximize MFE.

1. Introduction

Electron transfer (ET) is one of the most fundamental reactions that occur in biological systems [1]. The study of the crucial role of ET in different proteins ranging from photosynthetic proteins to protein containing copper, iron-sulfur or heme group, becomes imperative day by day [2–7]. Generally in proteins, ET is a long distance phenomenon (>10 Å) which occurs through hopping between different protein residues in order to reduce the time that would be required for a single step tunneling from donor to acceptor [8–10]. Among the amino acid residues of proteins, Tryptophan (TrpH) in particular acts as a relay in such processes [11–16]. Among the four aromatic amino acids (i.e. phenylalanine, tyrosine, histidine, and tryptophan), TrpH is the only one which can donate and forms an ET-complex, as observed with riboflavin, serotonin (5-hydroxytryptamine), tryptamine derivatives, lysergic acid etc [17,18]. This kind of ET occurs from the π-electron pool of the indole system of residue to the acceptor [19]. TrpH also acts as a photo-triggered electron donor as observed in cryptochromes [20], DNA repairing by photolyase [21] etc. Further, when there is no electron acceptor nearby, TrpH undergoes ET with the backbone of the protein as observed in case of apo-myoglobin mutants, small cyclic peptides, and human γ–D-crystallin etc [22]. Recently, it has been observed that a "Tryprtophan triad" is able to make an ET channel during photoreduction of FAD in various protein families [23–26]. Therefore, the versatility of TrpH-mediated ET in proteins and its widespread occurrence in proteins, make TrpH a routine as well as pivotal probe in investigation of the dynamics of protein.

Proflavin (PF^+), an acridine derivative is well known for its antibacterial and antifungal properties against many gram-positive bacteria and is extensively used as an extrinsic probe to reveal biological intricacies as it is able to bind with DNA and proteins [27,28]. Further, its intrinsic fluorescence and triplet absorption properties make PF^+ an efficient probe for the investigations of ground and excited state phenomena [29]. It remains positively charged in a long range of pH (0.2–9.5) including biological pH [30]. Thus, it may act as a good electron acceptor which was confirmed by previous studies from our laboratory [31,32]. The interaction of PF^+ with aliphatic amine (e.g. triethylamine) [31] or aromatic amines (e.g. *N, N′*-dimethylaniline and 4,4′–bis (dimethylamino) diphenylmethane) [32] indicates the dependence of photoinduced electron transfer (PET) on the nature of acceptor

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https://doi.org/10.1016/j.jlumin.2019.116953
Received 11 October 2019; Received in revised form 30 November 2019; Accepted 5 December 2019
Available online 6 December 2019
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