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Photoinduced electron transfer from aromatic amino acids to the excited isoalloxazine in flavin mononucleotide binding protein. Is the rate in the inverted region of donor–acceptor distance not real?

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ABSTRACT

Mechanisms of photoinduced electron transfer (ET) from tryptophanes 32 and 106 in subunits A and B (Trp32A, Trp32B, Trp106A and Trp106B) of wild type flavin mononucleotide binding protein (FBP) dimer were studied through relations of the logarithmic ET rate (ln Rate) vs the donor-acceptor distance (Rc). The sum (GT) of standard free energy gap (SFEG) between the products and reactants, electrostatic energy (ESDA) between the photo-products and solvation reorganization energy (SROE) and electrostatic energy (NetES) between the photo-products and ionic groups inside the protein were numerically determined for the all donors with atomic coordinates obtained by molecular dynamic simulation. The GT values of Trp32A and Trp32B displayed always negative in the entire Rc range, which predicts that ET rate becomes slower as the Rc shorter. The reason of negative GT values in Trp32A and Trp32B were numerically elucidated with the mean values of SFEG, ESDA, SROE, and NetES.

1. Introduction

Photoinduced electron transfer (ET) has been central field in photochemistry and photobiology [1–3]. The ET in flavoproteins plays an important role on photobiology, since many new flavin photoreceptors have been found in the last decade [4,5]. In some of them ET from tyrosine to the excited flavins is considered to be the first step of their biological functions.

The ET from aromatic amino acids to the excited isoalloxazine (Iso*) easily takes place in many flavoproteins other than the photoreceptors, so that fluorescence lifetimes of isoalloxazine (Iso) in the flavoproteins become ultrashort [6–8]. The fluorescence lifetimes [7–9] and decays [10–13] of flavoproteins have been analyzed to obtain the ET rates and related physical quantities with atomic coordinates of the flavoproteins obtained by means of molecular dynamics simulation (MDS) and a theoretical ET rate.

Flavin mononucleotide binding protein from *Desulfovibrio vulgaris* (Miyazaki F) (FBP) is a small flavoprotein (Mw 13 kDa with 122 amino acids) that contains flavin mononucleotide (FMN) as a cofactor [14]. The protein structure of FBP was initially determined by means of NMR spectroscopy in solution as monomeric form [15] and X-ray diffraction method in crystal as dimeric form [16]. Now it is recognized that FBP is also dimer in solution [17].

The logarithmic ET rates (ln Rate) in some flavoproteins display a bell-shape behavior against the donor-acceptor distances (Rc) [10,13,18], which was predicted to occur in some conditions among

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the physical quantities contained in theoretical ET rate [18]. It was pointed out that the theoretical ET rates in the Rc range shorter than the distances at a peak of ln Rate is not valid anymore, because the ET rate becomes slower with the Rc being shorter, despite that the interaction between the donor and acceptor should increase with decreasing Rc. Here we call this region of Rc to be a Rc-inverted region. The bell shape behavior of ln Rate against Rc is originated from square term in the exponential function of the ET theory, which should be essential for any ET theories as Marcus theory [19,20], Marcus-Hush theory [2] and Kakitani-Mataga (KM) theory [21,22], and others. In the present work the ET rates in the Rc-inverted region have been numerically studied with wild type FBP dimer, using the atomic coordinates obtained with a method of MDS in the preceding work [23].

2. Methods of analysis

In the present work KM rate [21,22] was used, because it is applicable for non-adiabatic ET processes in addition to adiabatic processes, and has been found to provide satisfactory results for both static [7–9] and dynamic ET analyses [10–13]. FBP contains two tryptophans (Trp32 and Trp106) and one tyrosine (Tyr35) in each subunit. Here only Trp32 and Trp106 were taken into account as ET donor, because ET rates from Tyr35 were negligibly slow compared to Trps [10,11]. Explicit form of KM rate is described in SI, and expressed by Eq. (S1). The ln Rate may be decomposed into three terms as in Eq. (1).

$$\ln \text{Rate} = \ln \text{EC} + \ln \text{SQ} - \text{GTLAM} \tag{1}$$

Here,

$$\ln \text{Rate} = \ln k_M^{jk} \tag{2}$$

$$\ln \text{EC} = \ln \frac{\nu_0}{1 + \exp\left\{\beta(R_{jk}^M - R_0)\right\}} \tag{3}$$

$$\ln \text{SQ} = \ln \sqrt{\frac{k_B T}{4\pi\lambda_{jk}^M}} \tag{4}$$

$$\text{GTLAM} = -\frac{\{GT\}^2}{4\lambda_{jk}^M k_B T} \tag{5}$$

The GT in Eq. (5) is expressed as Eq. (6).

$$GT = SFEG + ESDA + SROE + NetES \tag{6}$$

Here SFEG = ΔG_M^0, ESDA = $-e^2/\varepsilon_0^k R_{jk}^M$, SROE = λ_{jk}^M, and NetES = $E_{Net}^{Mk}(j)$ [see below Eq. (S1) for notations (SI)]. Likewise a quantity GP is defined by Eq. (7), eliminating NetES term from GT.

$$GP = SFEG + ESDA + SROE \tag{7}$$

3. Results

3.1. ET parameters in WT FBP dimer

Details of the protein structure of wild type (WT) FBP dimer are described elsewhere,[1] and is shown in Fig. 1. It was demonstrated

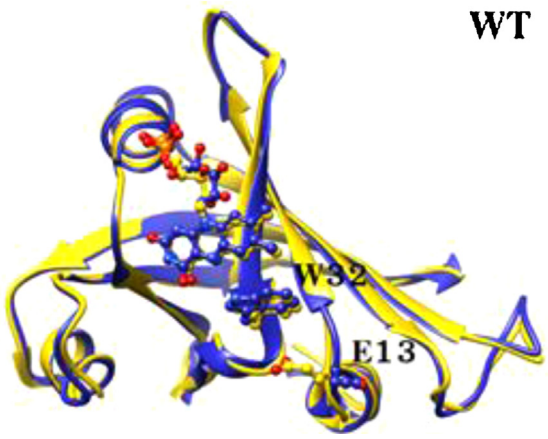

Fig. 1. Comparison of MDS structures between Sub A and Sub B in WT FBP dimer. The structures of the peptide back bones, FMN, Trp32 and amino acids at Glu13 of the WT FBP dimer is super imposed between Sub A and Sub B. The amino acids are indicated with one letter notation.

that MDS structures of subunit A (Sub A) is quite different from Sub B.[1] The mean donor-acceptor distances over 10,000 snapshots are 0.71 nm in Trp32A (Trp32 in Sub A), 0.68 nm in Trp32B, 0.86 nm in Tyr35A, 1.03 nm in Tyr35B, 1.03 nm in Trp106A and 0.94 nm in Trp106B.[1] Fluorescence lifetimes of WT FBP are 0.167 ps (96% of component fraction) and 1.5 ps (4%) [8]. The ultrashort lifetimes are ascribed to fast ET from Trp32 and Trp106 to Iso*. The ultrafast fluorescence dynamics of five FBP dimers (WT, E13 K; Glu13 is replaced by Lys, E13R; Glu13 replaced by Arg, E13T; Glu13 replaced by Thr, E13Q; Glu13 replaced by Gln) were analyzed together to obtain the ET rates from Trp32 and Trp106 to Iso* and related physical quantities in the both subunits, according to the method described in SI. Agreements between the experimental and calculated decays were excellent as shown in Fig. 2.

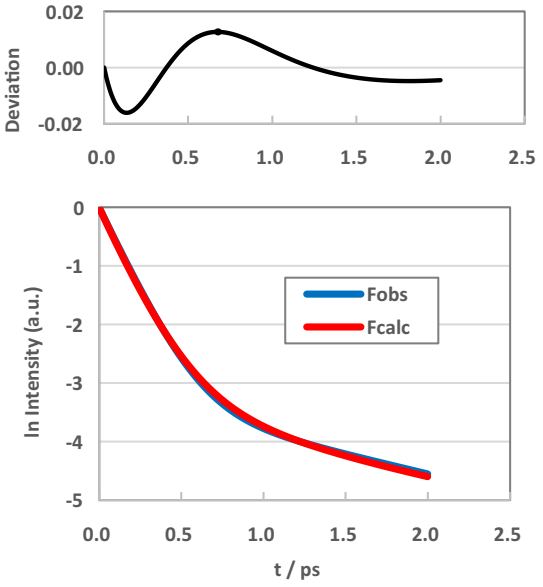

Fig. 2. Fluorescence decays of WT FBP dimer.
Fobs in inserts denotes the experimental fluorescence decay [8], and Fcalc the calculated decay given by Eq. (S7) in SI, obtained by the ET rate with the best-fit ET parameters described in text.

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