



Solvent effects on excited-state electron-transfer rate of pyrene-labeled deoxyuridine: A theoretical study



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ABSTRACT

Solvent effects on the quenching process from the first excited state of 5-(1-pyrenyl)-2'-deoxyuridine (Py-dU) were theoretically examined. Our results suggest that the excited-state electron transfer occurs without the so-called proton-coupled electron transfer process, which supports experimental results. Although there are no remarkable differences observed in the structure and the corresponding S_1 excitation energy between the solutions of MeOH and MeCN within a polarizable continuum model, we report here that hydrogen bonds between the explicit MeOH molecule with the dU moiety, whose structure was frequently found in molecular dynamics simulations, result in an enhancement of the electron-transfer rate constant.

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1. Introduction

Fluorescence sensing technology is widely used to recognize the specific bases labeled by fluorophores [1]. In polynucleotide sensing, fluorescence methods have been used for DNA sequencing [2,3], DNA-staining dyes [4], DNA hybridization [5–7], and molecular beacons for DNA [8,9] and mRNA [10], etc. Various types of fluorescent probes for nucleotides and polynucleotides have been explored [11,12]. Pyrene (Py), known as a useful organic fluorophore because of its long lifetimes [1,11] has been introduced to nucleic acid [1,6,11–15]. Netzel et al. systematically synthesized Py-labeled deoxyuridines (dUs), in which the 1-position of Py was directly linked to the 5-position of 2'-dU [16] (Py-dU: see Fig. 1) and via amide or ketone linkages [17]. Structural and solvent effects on emission quantum yields and electron-transfer reactivity have been discussed [16–18]. As reported in [19–21], the 2-position of Py is also joined to the 5-position of 2'-dU (2Py-dU), and both Py-dU and 2Py-dU are incorporated into oligonucleotides.

For Py-dU in methanol (MeOH), the S_1 state of Py is quenched and the charge transfer (CT) emission occurs, and so does the

π - π^* emission from Py-dU in acetonitrile (MeCN) and tetrahydrofuran (THF). That demonstrates that the electron transfer from the photoexcited Py to dU preferably occurs in MeOH [16,18]. It is proposed that the CT emission in MeOH occurs because of the proton-coupled electron transfer (PCET) through the formation of energetically favorable $\text{Py}^{*\bullet}/\text{dU}(\text{H})^{\bullet}$, where a proton is provided from MeOH [16]. However, Amann et al. showed that charge-separated $\text{Py}^{*\bullet}/\text{dU}^{\bullet-}$ is first produced upon photoexcitation of Py, being independent of the pH value ranging between 2 and 12, and concluded that proton transfer to dU occurs after electron transfer [22]. The Py^* absorption band decay and the alternative $\text{Py}^{*\bullet}$ absorption band rise within 35 ps after excitation were observed in MeOH by fs-broadband pump-probe spectroscopy [23]. Trifonov et al. suggested electron transfer from Py to dU being activated in MeOH because of enhanced π -electron overlap at a more planar geometry between Py and dU, which is affected by the hydrogen bonding interaction with MeOH (Scheme 1) [23].

It is important to clarify the mechanism of solvent effects on the electron-transfer reactivity of Py-dU to design more sophisticated fluorophores for deoxyuridine and other nucleotides. To the best of our knowledge, the electron-transfer activation mechanism between Py and dU in a protic solvent such as MeOH has not been theoretically elucidated. Although some computational studies have been investigated on the mechanism of absorbance and fluorescence spectral shifts of 5-(N-carboxyl-1-aminopyrenyl)-2'-deoxyuridine and 2-(1-ethynylpyrene)-adenosine, which have structures similar to Py-dU [24,25], the electron-transfer reaction rate from Py to dU has not been discussed yet.

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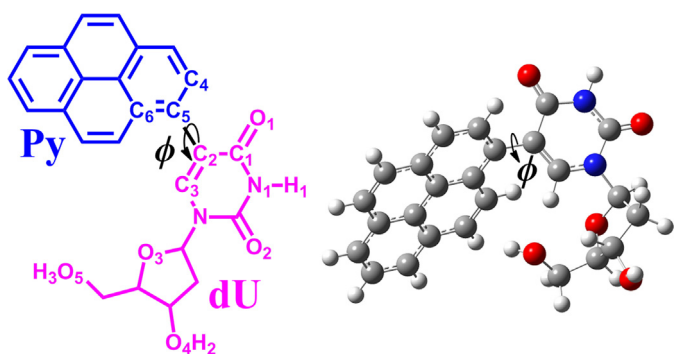
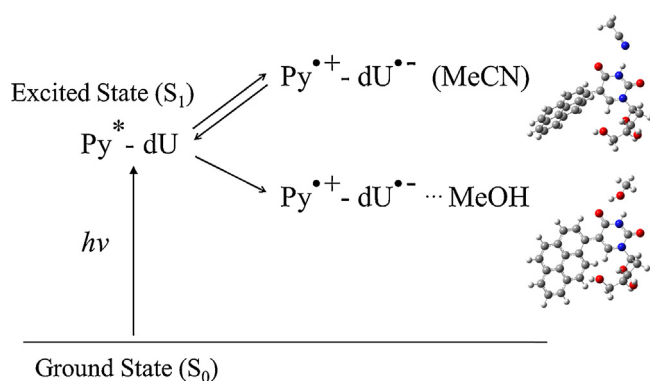


Figure 1. Chemical and geometrical structures of 5-(1-pyrenyl)-2'-deoxyuridine (Py-dU), where ϕ indicates the dihedral angle between the Py and dU moieties.



Scheme 1. A hydrogen bond-assisted electron transfer from Py^* to dU suggested by Trifonov et al. [23].

In the present letter, we theoretically investigate the difference between the protic and aprotic solvent effects on the excited-state electron transfer reactivity of Py-dU by directly evaluating the electron-transfer reaction rate. In the following sections, let us summarize the computational details and models used here, provide the results and discussion, and present our conclusions.

2. Materials and methods

2.1. Electron transfer reaction rate

The electron transfer reaction rate, k_{ET} , is calculated via the following Marcus equation [26–28] as

$$k_{\text{ET}} = \frac{\kappa k_{\text{B}} T}{h} \exp \left[-\frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_{\text{B}} T} \right] \quad (1)$$

where κ is the electronic transmission coefficient, i.e., $\kappa = 1$ for adiabatic electron transfer and $\kappa \propto |H_{ij}|^2$ for nonadiabatic electron transfer, h the Planck constant, λ the reorganization energy, k_{B} the Boltzmann constant, T the temperature, ΔG° the Gibbs free energy change of the reaction. H_{ij} is the electronic coupling matrix from the initial state (i) to the final state (j). We assumed $T = 298$ K. Generally, the nonadiabatic electron transfer rate is expressed [28] as

$$k_{\text{ET}} = \frac{2\pi}{h} |H_{ij}|^2 (4\pi\lambda k_{\text{B}} T)^{-1/2} \exp \left[-\frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_{\text{B}} T} \right], \quad (2)$$

The adiabatic and nonadiabatic limits were determined by the Landau–Zener parameter, γ_{LZ} [28]:

$$\gamma_{\text{LZ}} = |H_{ij}|^2 (4\hbar\nu)^{-1} (\pi\lambda k_{\text{B}} T)^{-1/2}, \quad (3)$$

where ν is the frequency of an effective nuclear vibrational mode. We assumed the wavenumber of the effective mode is 200 cm^{-1} .

The adiabatic limit is realized for $2\pi\gamma_{\text{LZ}} \gg 1$. On the other hand, the weak coupling nonadiabatic limit is set to $2\pi\gamma_{\text{LZ}} < 1$.

We evaluated H_{ij} using the generalized Mulliken–Hush (GMH) method, developed by Cave and Newton [29], as

$$H_{ij} = p_{ij} \Delta E_{ij} [(\Delta p_{ij})^2 + 4(p_{ij})^2]^{-1/2}, \quad (4)$$

where Δp_{ij} , p_{ij} , and ΔE_{ij} denote the differences between the value of the donor and acceptor states: the dipole moment, the transition dipole moment, and the energy gap. To evaluate H_{ij} among the excited states, we adopted Tamm–Dancoff approximation for simplicity [30], while the optimized equilibrium structures were obtained by time-dependent density functional theory (TD-DFT) calculation within the random-phase approximation.

The reorganization energy was calculated using the four-point method [31]. λ in the CT was expressed as

$$\lambda = E_+^*(D) - E_+^*(D) + E_-^0(A) - E_-^0(A), \quad (5)$$

According to Pinto's work [32], we estimated free energy changes, ΔG° , for the CT processes from the energy difference of the constituents in its initial and final states as follows:

$$\Delta G^\circ = E_+^*(D) + E_-^-(A) - E_+^*(D) - E_-^0(A) + \Delta E_q, \quad (6)$$

with

$$\Delta E_q = (4\pi\epsilon_0\epsilon_s)^{-1/2} \left(\frac{q_{D^+}q_{A^-}}{r_{D^+A^-}} - \frac{q_{D^0}q_{A^0}}{r_{D^0A^0}} \right), \quad (7)$$

where $E_Y^X(Z)$ ($X, Y = 0, *, +, -$ and $Z = D, A$) is the X state energy of the isolated Z monomer at the optimized structure of the Y state, and $0, *, +, -$ represent the ground, the first excited, the cationic, and anionic states. The donor (Py) and acceptor (dU) are denoted as D and A . q_D and q_A are the total charges of each state denoted again by $0, *, +, -$. ϵ_0 and ϵ_s are the static dielectric constants of the vacuum and the solvents (33.10 for MeOH [33] and 35.99 for MeCN [34] at 298 K). The centroid distance between the Py and dU moieties at the first excited state equilibrium structure of Py-dU is denoted as r_{DA} . Note here that for computations of λ and ΔG° values Py-dU is approximated as isolated models, i.e., Py and dU capped with a hydrogen atom, because it is difficult to find the charge-transfer state equilibrium structure of the whole Py-dU and to evaluate its electronic structure and energy accurately. This approximation has the advantage of wide applicability to large molecules such as Py-dU and has been shown to be reliable for the evaluation of these physical quantities in Pinto's work [32], though the isolated model approximation might neglect the effect of mutual polarization between Py and dU.

2.2. Calculations of the electronic structure

The conventional DFT is well known to have the problem of underestimating both charge-transfer and Rydberg excitation energies in the TD-DFT calculations [35]. Tawada et al. reported that a long-range correction (LC) scheme for the generalized gradient approximation (GGA) exchange–correlation functional (LC-DFT) [36] could solve this problem [37]. We started a benchmark test to determine which exchange–correlation functional could provide the best results for the experimental excitation energy. Since the CAM-B3LYP functional [38] well reproduced the S_0 – S_1 excitation energy (see Section 3.1 for details), we adopted it for further analyses. To take van der Waals dispersion interactions into account, Grimme's D3 damping function was included [39] and the cc-pVDZ basis sets [40] were employed for all atoms. The implicit solvent effects of MeOH and MeCN were considered using the conductor-like polarizable continuum model (C-PCM) [41], and all electronic structure calculations were performed using GAUSSIAN 09, Revision D.01 [42].

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