

Theoretical investigation of the electron transfer process in water

Kosuke Usui¹, Stephan Irle^{1,2}, Daisuke Yokogawa^{1,2}

¹Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University, Japan

²Department of Chemistry, Graduate School of Science, Nagoya University, Japan

Science & Agricultural Building SA421, Furo-cho, Chikusa-ku, Nagoya, 464-8602, Japan

E-mail : usui.kosuke@f.mbox.nagoya-u.ac.jp

Recently, light emitting molecules in aqueous solution draw a lot of attention and have been synthesized for applications related to bioimaging. Urano and coworkers reported a new class of caged fluorophores which can emit only when photoremovable protecting groups (PRPGs) are removed by UV light irradiation. They found that the acceptor strength of PRPG is correlated to the efficiency of emission quenching [1]. Their fundamental strategy of the molecular design was emission quenching by the efficient intramolecular charge transfer (CT) from BODIPY to PRPG after the excitation (see **Fig. 1a**). Theoretical understanding of this process is necessary to improve the accuracy of molecular design.

In the present study, the importance of solvent fluctuation in the CT process is discussed in terms of the free energy change. The RISM-SCF-SEDD method [2], which combines quantum chemistry and statistical mechanics, is employed to describe the solvent effect. The non-equilibrium treatment of solvation with a hypothetical charge distribution [2] allowed us to compute free energy profiles. As a representative example, we show simulated free energy curves in **Fig. 1b**. As the acceptor strength increases (p -DCB < NB < p -QN), the charge transfer state curve shifts to lower energies, and the activation free energy becomes smaller. These findings compare well to the observed trends in experimentally determined redox potentials. As the charge transfer mostly occurs from a donor molecule in the excited state to an acceptor in the ground state, we also applied our approach to the “true” excited state, which allows us to discuss the energy relaxation path.

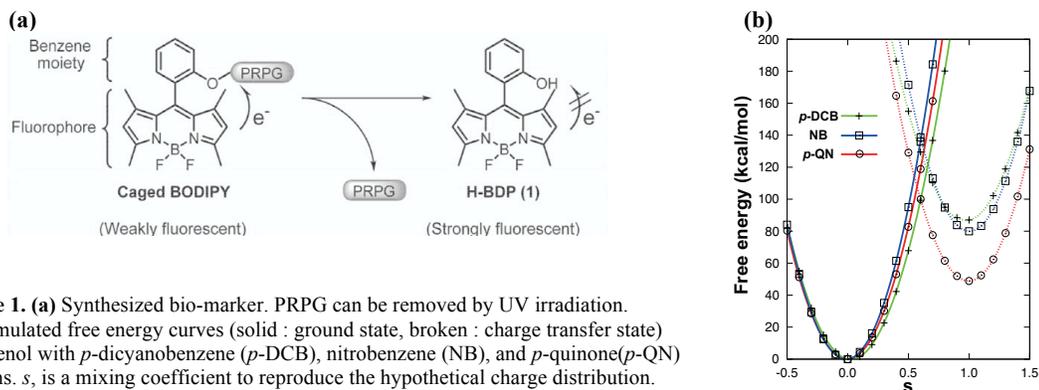


Figure 1. (a) Synthesized bio-marker. PRPG can be removed by UV irradiation.

(b) Simulated free energy curves (solid : ground state, broken : charge transfer state) for phenol with p -dicyanobenzene (p -DCB), nitrobenzene (NB), and p -quinone(p -QN) systems. s , is a mixing coefficient to reproduce the hypothetical charge distribution.

Reference

[1] Urano, Y., *et al.*, *J. Am. Chem. Soc.* **134**, 11153 (2012).

[2] Yokogawa, D., Sato, H., and Sakaki, S., *J. Chem. Phys.* **126**, 244504 (2007).