

Theoretical investigation of the electron transfer process in water

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Until now, light emitting molecules in aqueous solution have been paid attention and been synthesized for the application to bioimaging. Urano and coworkers reported that caged fluorophores which can emit only when photoremovable protecting groups (PRPGs) are removed by the UV light irradiation, and 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 CT process is discussed in terms of the free energy change. RISM-SCF-SEDD method [2], in which the quantum chemical approach and the statistical mechanics are combined, is employed to include solvent effect. Due to the non-equilibrium treatment of solvation with hypothetical charge distribution [2], free energy plots were obtained. As an example, simulated free energy curves are shown in **Fig. 1b**. As the acceptor strength increases (p -DCB < NB < p -QN), the charge transfer state curve shifts to lower energies. This result implies that our approach can be applied to discuss the energetics of the charge transfer process. Specifically speaking, the activation free energy becomes small corresponding to the acceptor strength. The predicted order agrees with the experimentally observed redox potentials. The charge transfer mostly occurs from a donor molecule at excited state to an acceptor at ground state, so our approach was also applied to the “true” excited state, and our method allows us to discuss the energy relaxation path. In the poster session, the discussion for caged BODIPY will be done.

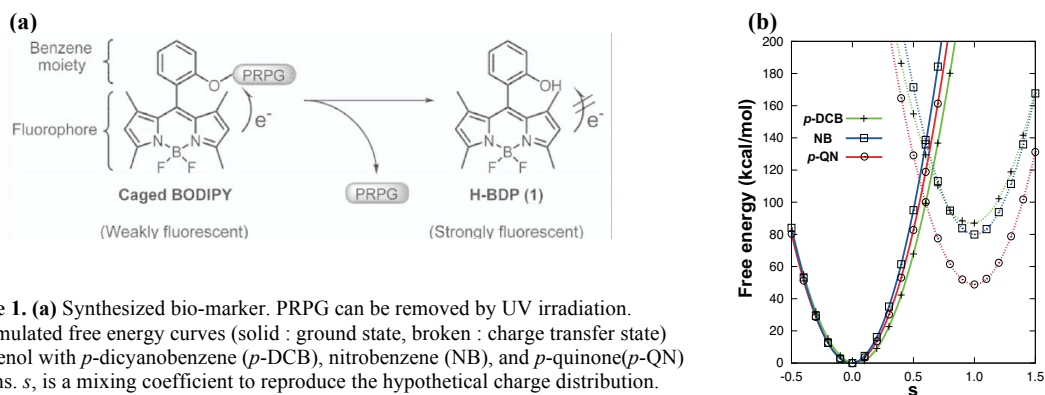


Figure 1. (a) Synthesized bio-marker. PRPG can be removed by UV irradiation. (b) Simulated free energy curves (solid : ground state, broken : charge transfer state) for phenol with p -dicyanobenzene (p -DCB), nitrobenzene (NB), and p -quinone (p -QN) systems. s , is a mixing coefficient to reproduce the hypothetical charge distribution.

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

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