Theoretical Studies on Photoinduced Charge Separation of Molecular Hetero-Junction and Dye-Sensitized Solar Cells

Koichi Yamashita
Department of Chemical System Engineering, The University of Tokyo, 113-8656 Tokyo, Japan

I will discuss our theoretical studies on the optical and electronic process that take place in organic solar cells. First, in order to obtain the design rules of conjugated polymer required for improved molecular electronics, the charge transport properties at different organic-organic semiconductor interfaces (TFB/F8BT) are studied based on *ab initio* quantum master equations. The results suggest a mechanism of exciton-migration followed by a hole back transfer addition to a simple charge-transfer, which leads to a red-shifted and longer-lived emission of F8BT. Secondary, I will discuss about several new transitions due to the interfacial charge transfer found for the TCNE/TiO_2 dye-sensitized solar cells. The surface complex of TiO_2 nanoparticles and TCNQ are studied based on DFT calculations and the structure of the surface complex optimized shows an IR spectrum analogous to the experimental spectrum. From TDDFT calculations based on this optimized structure, we show that the interfacial charge transfer transitions from the HOMO of the surface-bound TCNQ molecules to the unoccupied levels of the TiO_2 nanoclusters occur in the visible to near IR region. Finally, recombination in dye-sensitized solar cells with direct injection which is cast as internal conversion will be discussed. For catechol-thiophene dyes with 1, 2, or 3 thiophene units, the complex reproduces the previously observed dye-to-semiconductor bands. Based on *ab initio* calculations, we compare the decomposition of the internal conversion rate by vibrational mode and predict a trend in recombination with the extension of conjugation, which offers an explanation for the trend in DSSC efficiency. We also analyze derivative coupling constants in dyes NK1 (2E,4E-2-cyano-5-(4-dimethylaminophenyl) penta-2,4-dienoic acid) and NK7 (2E,4E-2-cyano-5-(4-diphenylaminophelyl) penta-2,4-dienoic acid) and relate them to the different dynamics that was observed for these dyes on TiO_2.

References

[1] ”Theoretical Study of the Surface Complex of TiO_2 and TCNQ: Interfacial Charge Transfer Transitions”, Ryota Jono, Jun-ichi Fujisawa, Hiroshi Segawa, Koichi Yamashita, *J. Phys. Chem. Lett.*, **2,** 1167-1170 (2011).
[2] “Derivative coupling constants of NK1, NK7 dyes and their relation to excited state dynamics in solar cell applications”, Sergei Manzhos, Hiroshi Segawa, and Koichi Yamashita, *Chem. Phys. Lett*, **501**, 580-586 (2011).
[3] “A model for recombination in Type II dye-sensitized solar cells: catechol-thiophene dyes”, Sergei Manzhos, Hiroshi Segawa, Koichi Yamashita, *Chem. Phys. Lett.* **504**, 230-235 (2011).