

# Molecular Design Principles of Organic Dyes and Conjugated Polymers for Solar Cell Applications <sup>[1]</sup>

Bong-Gi Kim<sup>1</sup>, Chang-Gua Zhen<sup>2</sup>, Eun Jeong Jeong<sup>2</sup>, Yutaka Ie<sup>4,5</sup>,  
Xiao Ma<sup>2</sup>, David Bilby<sup>2</sup>, Elizabeth Coir<sup>2</sup>, Yoshio Aso<sup>2</sup>, John Kieffer<sup>2</sup>,  
and Jinsang Kim<sup>1,2,3\*</sup>

<sup>1</sup>Macromolecular Science and Engineering, <sup>2</sup>Materials Science and Engineering, <sup>3</sup>Chemical Engineering

University of Michigan, Ann Arbor 48109

<sup>4</sup>The Institute of Science and Industrial Research, Osaka University,  
8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

<sup>5</sup>JST-REST, Kitakyushu Science and Research Park, 2-5 Hibikino,  
Wakamatsu-ku Kitakyushu City, 808-0135, Japan

## Introduction

Organic dyes, conjugated polymers, and C60 and C70 derivatives play a major role to harvest solar energy and charge generation and transport in solar energy conversion devices such as dye sensitized solar cells (DSSC) and organic photovoltaic cells (OPV). Sun light is absorbed into these molecules and produces exciton, an electron-hole pair. The exciton must be dissociated into an electron and a hole and the charges should be collected to produce useful electric power. Optical and electronic properties of these organic dyes, conjugated polymers, and electron capture molecules are directly related to how efficiently the energy harvesting molecules absorb solar spectrum and how effectively the generated excitons can be dissociated and collected. We have been developing molecular design principles to realize such efficient organic energy harvesting materials with tailored properties through the combination of density functional theory (DFT), chemical synthesis, device fabrication, and performance analysis.

## Experimental

**Molecular geometry calculation.** Electronic structure calculations and spatial relaxation of the molecules were performed using Gaussian03.<sup>[2]</sup> Pre-optimizations of the molecules were carried out using AM1 semi-empirical quantum chemistry model.<sup>[3]</sup> The resulting molecular configurations were then further optimized in the density functional theory (DFT) framework. We used B3LYP as the exchange-correlation functional that is a Hartree-Fock-DFT hybrid where the exchange energy is explicitly calculated using the Hartree-Fock approach.<sup>[4]</sup> The molecular geometries were optimized in the Cartesian coordinate system without any symmetry (maximum degrees of freedom) using 6-31G\* contracted Gaussian basis set with polarization functions.<sup>[5,6]</sup>

**Exciton binding energy calculation.** This quantity is directly related to the charge separation in excitonic solar cells, and hence, it is an important factor for the efficiency of the cells.<sup>[7]</sup> The exciton binding energy can be viewed as the difference between the electronic and optical bandgap energies.<sup>[8]</sup> For small molecules with localized wavefunctions, the electronic bandgap is approximated as the energy difference between HOMO and LUMO, while the optical gap is taken to be the first excitation energy.<sup>[9]</sup> The calculations of the excitation energy are performed using time dependent density functional theory (TDDFT) techniques at the same approximation level as was used for the molecular structure optimizations.<sup>[10]</sup>

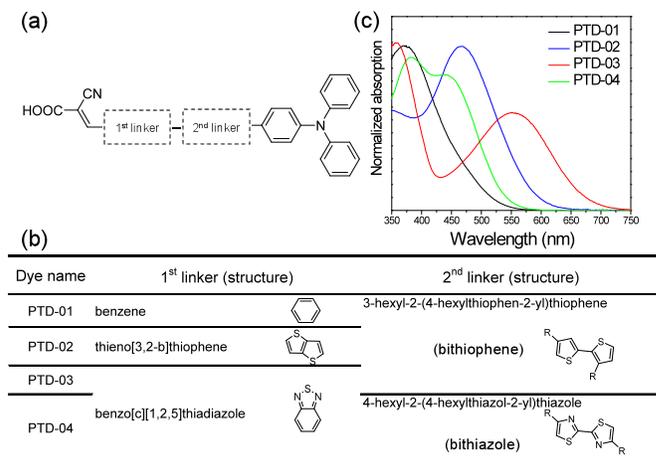
**DSSC device fabrication.** After cleaning, the FTO glass plate was immersed in aqueous 40 mM TiCl<sub>4</sub> at 70 °C for 30min and washed with deionized water and ethanol. Nanocrystalline TiO<sub>2</sub> paste was coated on top of the FTO glass by means of the doctor blade method, followed by sintering at 500 °C for 20 min. The obtained transparent TiO<sub>2</sub> layer was measured with a spectrometer and a surface profiler (haze 35% at 800 nm, 15 μm). The TiO<sub>2</sub> electrodes were immersed into each dye solution (0.5 mM in a mixture of

tetrahydrofuran and tert-butyl alcohol (v/v. 8/2), and kept at room temperature for 24 hours under dark condition. Counter electrodes were prepared by coating with a drop of H<sub>2</sub>PtCl<sub>6</sub> solution on an FTO glass and heated at 400 °C for 15 min. The dye-adsorbed TiO<sub>2</sub> electrode and Pt counter electrode were assembled and sealed with an ionomer film under hot-press. A drop of the electrolyte was filled by means of vacuum backfilling and finally, the hole was sealed with ionomer film. The electrolyte was made with l-propyl-3-methylimidazolium iodide (PMII, 0.7 M), iodine (I<sub>2</sub>, 0.03 M), Guanidiumthiocyanate (GSCN, 0.05 M) and 4-tert-butylpyridine (TBP, 0.5 M) in 3-methoxypropionitrile (MPN) solvent.

**OPV device fabrication:** PCBM[70] was purchased from SES research and used without further purification. After dissolving obtained CPs (10 mg) and PCBM[70] (10 mg) into *o*-dichlorobenzene (2.0 ml) and 1,8-octanedithiol (26 μl), the mixture was filtered with a syringe filter having 0.45 μm pore and used to form the active layer by means of spin casting. In case of PBT8PT, 1.5 ml of *o*-dichlorobenzene and 20 μl of 1,8-octanedithiol were used for the blend solution. ITO-coated glass was cleaned with acetone and IPA followed by UV ozone treatment for 10 minutes. PEDOT:PSS (Baytron PH 500) was spin cast on the substrate and baked at 140°C for 15 minutes. Different polymer/PCBM[70] blend solutions were spin cast at 700 rpm for 30 seconds and used for metal electrode evaporation without further treatment. Final devices were fabricated by depositing a 1 nm thick LiF and a 70 nm Al layer (9.6 mm<sup>2</sup>) sequentially under 5 × 10<sup>-7</sup> torr. All devices were characterized under the nitrogen condition and the typical illumination intensity was 100 mW/cm<sup>2</sup> (AM 1.5G Oriel solar simulator).

## Results and Discussion

To analyze the relationship between the dyes' chemical structures and their exciton binding energy (EBE), we divided each dye's frame into four sections, as shown in Figure 1(a). Since the characteristic properties, such as aggregation behavior, absorption range, and molar extinction coefficient,<sup>[11,12]</sup> strongly depend on the chemical structure, we fixed triphenyl amine as an electron donor and cyanoacrylic acid to anchor the dyes to the semiconducting TiO<sub>2</sub> in this study. The EBE of each dye was varied by changing the 1st and 2nd linkers (Figure 1(b)), and the calculated EBEs are summarized in Table 1.



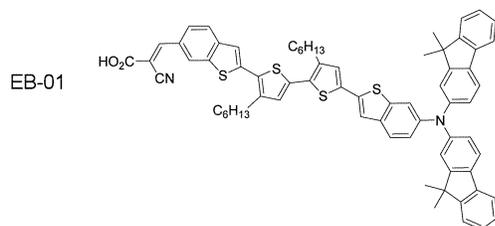
**Figure 1.** (a) Prototype dye structure, (b) specific dye structures (R; hexyl), and (c) absorption spectra in THF.

**Table 1. Summaries of DSSC device performance and optical/electrical properties of PTD series**

Sample	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF (%)	PCE (%)	photon full absorption	EBE [eV]	$E_{redox}^{[a]}$ [V]	$E_{D0}^{[b]}$ [V]	$E_{LUMO}^{[c]}$ [V]
PTD-01	7.56	0.79	70.2	4.17	13.20%	0.224	1.06	2.54	-1.48
PTD-02	8.97	0.73	63.9	4.10	18.40%	0.302	1.07	2.43	-1.36
PTD-03	0.87	0.60	71.9	0.37	24.90%	0.297	1.08	2.58	-1.50
PTD-04	didn't work				15.70%	0.400	1.14	2.36	-1.22

The results showed that the photocurrent generation efficiency of the synthesized dyes strongly depends on their EBEs. Dyes with lower EBE exhibit better efficiency in generating current from the absorbed light, which demonstrates an inverse relationship between EBE and maximum IPCE of the dyes in DSSC devices. When the electron withdrawing moiety, benzo[c][1,2,5]-thiadiazole, is introduced into the dye structure it significantly impairs the photocurrent generation because the electron-withdrawing moiety pulls the electron strongly, weakening electron coupling between the dyes and the TiO<sub>2</sub>, causing an adverse effect on charge transport.

From the results for our prototype dyes, we derived dye design principles for highly efficient photo-sensitizer in DSSC. As a proof of concept, a novel organic dye, EB-01, shown in Figure 2, was designed based on the developed design principles, and its photosensitizing property was investigated. The two peripheral phenyl rings of the triphenyl amine of prototype dyes were replaced with the larger fluorine and the inner phenyl groups in PTD-01 were substituted with the longer benzene derivative (benzothiophene). These modifications give the dye a longer conjugation and more spatial distance for electron distribution between the LUMO and HOMO, lowering the EBE. The EBE of EB-01 is 0.180 eV, which produces a dramatically enhanced maximum IPCE (over 81%). In order to entrap the incident light more efficiently for a high performance DSSC, a scattering TiO<sub>2</sub> layer (~4 μm) was applied and the device showed a largely improved 9.18 % power conversion efficiency (PCE) mostly due to the enhanced  $J_{sc}$  (16.86 mA/cm<sup>2</sup>). Over 9.0 % PCE is rarely reported from pure organic photosensitizers in DSSC devices. This outstanding performance of EB-01 can be ascribed to its lower EBE for an efficient light-to-electric energy conversion and to its somewhat broadened absorption characteristic for better harvesting of solar spectrum.



**Figure 2.** Chemical Structure of EB-01.

Conjugated polymers also have been used for organic photovoltaic cells (OPVs). To harvest sunlight efficiently the band gap of conjugated polymers for OPV should be matched the high photon flux region of the solar spectrum. In this regards donor-acceptor co-polymer structures have been widely utilized to reduce the band gap of conjugated polymers. However, in a bulk heterojunction solar cell the LUMO of a conjugated polymer should be a certain eV higher than the LUMO of an electron acceptor molecule for efficient excitation dissociation. Therefore, there is a limit for conjugated polymer's LUMO to be lowered. The HOMO of a conjugated polymer also cannot be moved up freely because the gap between the conjugated polymer's HOMO and the LUMO of electron acceptor molecules is directly related to the open circuit voltage of

bulk heterojunction solar cells. Therefore, a capability to precisely control HOMO and LUMO of conjugated polymer is very important to develop efficient conjugated polymers for OPVs. We have designed and synthesized series of conjugated polymers having alternating donor-acceptor monomer units. By fixing the donor unit and gradually changing the electron withdrawing power of the acceptor unit we have systematically investigated the correlation between the monomers' HOMO and LUMO levels and the resulting conjugated polymers' HOMO and LUMO. From the experimental results combined with DFT calculation we recently could develop an effective rule to precisely predict HOMO and LUMO of conjugated polymers from the HOMO and LUMO of their constituent monomers. Applying this rule to a novel conjugated polymer we could achieve the predicted HOMO and LUMO and over 7% power conversion efficiency before device and morphological structure optimization of the device made out of the novel polymer.

## Conclusions

Molecular design assisted by density functional theory is an important and powerful tool to design organic dyes and conjugated polymers having predictable optical and electronic properties. By combining DFT, chemical synthesis, device fabrication, and performance analysis related to chemical structures, we developed a pure organic dye showing 9.18% PCE in a DSSC. We also developed series of conjugated polymers having tailored HOMO and LUMO levels and achieved over 7% PCE. The developed molecular design principle can be readily applicable to other organics for optoelectronic applications.

**Acknowledgement.** This research was supported as part of the Center for Solar and Thermal Energy Conversion in Complex Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number (DE-SC0000957).

## References

- Parts of the work presented in this preprint were submitted for journal publications.
- Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, Jr. J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, h. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
- J. J. P. Stewart, *J. Comput. Chem.* **1989**, *10*, 209.
- A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
- M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654.
- W. J. Hehre, R. Ditchfie, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257.
- R. A. Marcus, N. Sutin, *Biochim. Biophys. Acta* **1985**, *811*, 265.
- B. A. Gregg, *J. Phys. Chem. B* **2003**, *107*, 4688.
- G. D. Scholes, G. Rumbles, *Nature Mater.* **2006**, *5*, 683.
- C. -G. Zhen, U. Becker, J. Kieffer, *J. Phys. Chem. A* **2009**, *113*, 9707–9714.
- M. Pastore, F. D. Angelis, *ACS Nano*, **2010**, *4*, 556.
- H. Chen, H. Huang, X. Huang, J. N. Clifford, A. Forneli, E. Palomares, X. Zheng, L. Zheng, X. Wang, P. Shen, B. Zhao, S. Tan, *J. Phys. Chem. C* **2010**, *114*, 3280–3286.