Molecular Engineering of Record World Push-Pull Sensitizers for Dye-Sensitized Solar Cells and Bulk-Heterojunction Morphology in Solution Processed Small Molecule Organic Photovoltaics

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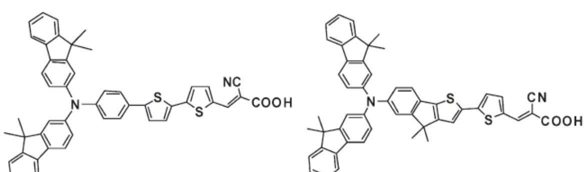
Dye-Sensitized Solar Cells

Dye-sensitized nanocrystalline TiO_2 solar cells (DSSCs) have attracted considerable interest because of their high conversion of sunlight to electricity and easy fabrication. To overcome the prohibitive cost of ruthenium metal complexes, several groups have developed metal free sensitizers and obtained efficiencies in the range of 8~9%. However, a major issue for the low photoconversion efficiency of many organic dyes in dye-sensitized solar cell is due to the formation of dye aggregates on the semiconductor surface. Therefore, for obtaining efficient photoconversion based on organic dyes, aggregation needs to be avoided through the CD(cyclodextrin). An optimal sensitizers, which combine broad visible light absorption with an excited-state directionality for favorable electron-transfer dynamics, is a key issue in the development of DSSC. Recentely, we have synthesized the record-world organic sensitizer having the efficiency of 10.52% using I^-/I_3^- electrolyte. When we used the cobalt electrolyte, the efficiency goes up to 12.52%. In this presentation, we will talk about the basic design of organic dyes and near-IR dyes. We Also present which factors control such high efficiency.



JK-2 JK-225

Figure 1. Molecular structures of JK-2 and JK-225.

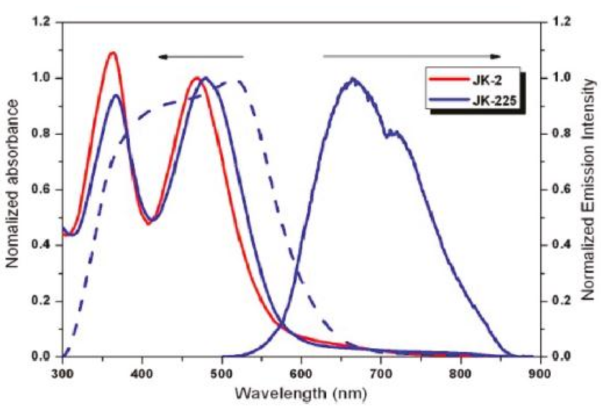


Figure 2. Absorption and emission spectra of JK-2 (red solid line) and JK-225 (blue solid line) in EtOH and absorption spectrum of JK-225 (blue dash line) anchored to TiO_2 film. The emission spectrum of JK-225 was obtained using the same solution at 480 nm at 298 K. The concentration for the solution was 10^{-5} M.

Table 1. Optical, Redox Parameters of Dyes

Dye	$\lambda_{abs}{}^a$/nm (ε/M^{-1} cm^{-1})	$E_{redox}{}^b$/V	$E_{0\text{-}0}{}^c$/V	$E_{LUMO}{}^d$/V
JK-2	**364 (44 000)** **452 (39 000)**	**1.04**	**2.23**	**-1.19**
JK-225	**367 (35 000)** **480 (55 000)**	**0.93**	**2.19**	**-1.26**

[a]Absorption spectra were measured in EtOH solution. [b]Redox potential of dyes on TiO_2 were measured in CH_3CN with 0.1M (n-$C_4H_9)_4NPF_6$ with a scan rate of 50 mV s^{-1} (vs NHE). [c]$E_{0\text{-}0}$ was determined from intersection of absorption and emission spectra in ethanol. [d]E_{LUMO} was calculated by E_{OX}-$E_{0\text{-}0}$.

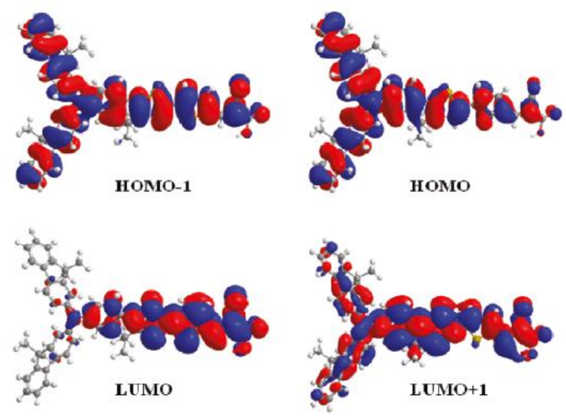


Figure 3. Frontier molecular orbitals of the HOMO_1, HOMO, LUMO, and LUMO+1 with B3LYP/6-31G(d) of JK-225.

Table 2 Photovoltaic Data Measured under the 100 mW cm^{-2} AM1.5 Sunlight

Dye	J_{sc} [mA cm^{-2}]	V_{oc} [mV]	*FF*	η^a [%]
JK-2	**12.34**	**750**	**0.75**	**6.9**
JK-225	**13.84**	**790**	**0.75**	**8.2**

[a]Performances of DSSCs were measured with 0.158 cm^2 working area. Electrolyte: 1 M 1,3-dimethylimidazolium iodide, 0.02 M iodine, 0.05 mM lithium iodide, 1 M 4-tert-butylpyridine, and 0.1 M guanidinium thiocyanate in acetonitrile**.**

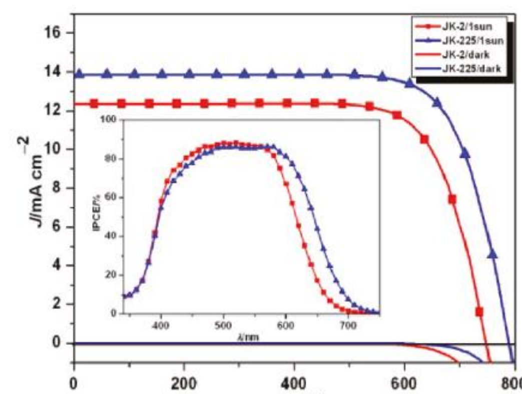


Figure 4. *J-V* curve and IPCE spectra (inset) of JK-2 (■) and JK-225 (▲). Cell area tested with a metal mask: 0.158 cm^2. Dark current-bias potential relationship is shown as a solid line.

Organic Photovoltaics

Solution processed organic solar cells based on bulk-heterojunction (BHJ) materials comprising of small molecule chromophores and fullerene derivatives have offered special opportunities showing their promising power-conversion efficiencies (PCE) of above 4% as attractive alternatives to π-conjugated (semiconducting) polymers. Although the BHJ devices fabricated by small molecule chromophore present lower efficiency than ~7% of that by polymer, these approaches by small molecule seem to fascinate more than polymer from the viewpoint of mass production for commercial application due to their low reproducibility for characteristics such as average molecular weight (M_w) and polydispersity index (PDI) as well as difficulty in purification. We have also focused on the development of new chromophores for small molecule BHJ solar cell, which are motivated by organic dyes in dye-sensitized solar cell (DSSC) and push-pull chromophores in nonlinear optics (NLO) due to a strong structural similarity with small molecule chromophores reported in BHJ solar cell.

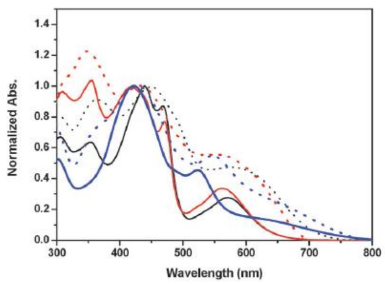
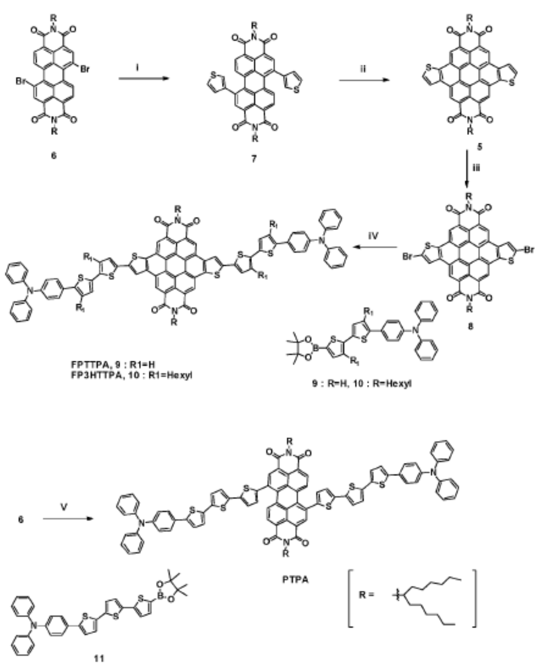


Figure 5. Absorption spectra of FPTTPA (black line), FP3HTTPA (red line), and PTPA (blue line) in CH_2Cl_2 (solid line) and thin film (dotted line).



Scheme 1 Reagents: (i) thiophene-3-ylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, THF; (ii) I_2, *hv*, dichloromethane; (iii) Br_2, CH_2Cl_2; (iv) for R = H, compound 9; for R = hexyl, compound 10, $Pd(PPh_3)_4$, K_2CO_3, THF; (v) compound 11, $Pd(PPh_3)_4$, K_2CO_3, THF.

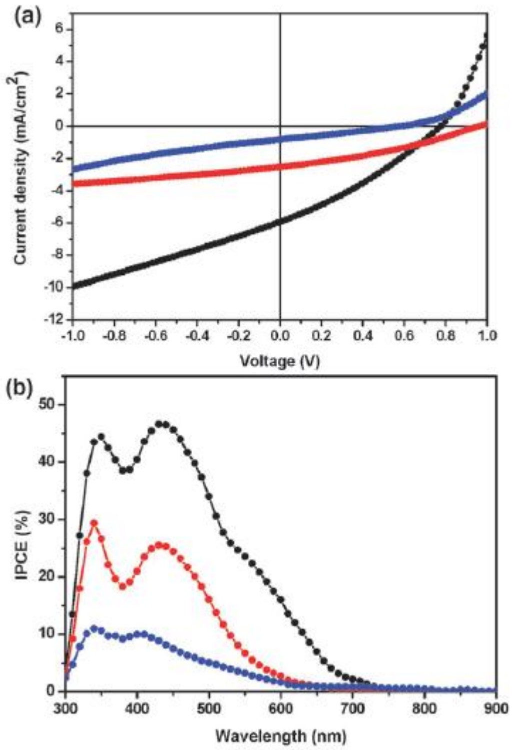


Figure 6. J－V curves (a) and IPCE (b) spectra of BHJ solar cells based on the FPTPA:C_{61}-PCBM (black line), FP3HTTPA:C_{61}-PCBM (red line), and PTPA:C_{61}-PCBM (blue line).

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References

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