

## Solution Processable Thin Film Organic Photovoltaic Cells based on Far Red Sensitive Soluble Squaraine Dyes

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### Introduction

Solution processable organic solar cells are potential, versatile and low cost alternative to traditional photovoltaic technology. Amongst polymer based organic photovoltaic cells, regioregular poly (3-hexylthiophene, P3HT) with soluble fullerene derivative PCBM is most studied having conversion efficiency over 5 % which is limited due to photon harvesting up to < 650 nm [1]. Panchromatic photon harvesting is highly desired to further increase the efficiency leading to the development of novel low band gap (LBG) conducting polymers. Efficient LBGs surpassing the efficiency of well studied and robust P3HT/PCBM system are only few [2-3] with tedious multistep synthesis. Controlling the molecular weight and polydispersity index of such LBG conducting polymers is also quite cumbersome. A possible route to bypass the lower performance often observed with such systems, might be the incorporation of low molecular weight sensitizers having absorption in extended wavelength region within the P3HT/fullerene matrix to fabricate the sensitized bulk heterojunction having energy levels intermediate to those of polymer and the fullerene [4].

It has been observed that squaraine dyes have intense and absorption in the NIR wavelength region and they bear the hole transport capability. Planer heterojunction solar cells based squaraine dyes using thermal evaporation squaraine and acceptor moieties has been reported recently [5-6]. In this presentation we are going to discuss about fabrication of completely solution processable planer and bulk heterojunction solar cells using our soluble squaraine dyes as donor/sensitizer and PCBM as acceptor.

### Experimental

For red sensitizing symmetrical squaraine dyes bearing varying alkyl chain length as shown in figure 1 has been synthesized as per method reported by us earlier [7]. Highest occupied molecular orbital (HOMO) energy level of the dyes was measured using photoelectron spectroscopy in air (model AC3) while lowest unoccupied molecular orbital (LUMO) energy level was determined from the edge of optical absorption. Planer heterojunction devices were fabricated in ITO/PEDOT:PSS/Dye/PCBM/LiF/Al device configuration as shown in figure 1. Except top LiF and Al electrodes, all the layers were fabricated by spin coating from their respective solutions. Sensitized bulk heterojunction was also fabricated in the same device architecture where active layer was fabricated using P3HT, PCBM and Dye in 10:8:2 ratios from o-dichlorobenzene solution.

Photovoltaic measurement were conducted under irradiation of 100 mW/cm<sup>2</sup> at global AM 1.5 condition using a solar simulator.

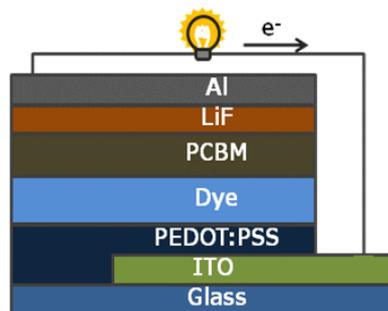
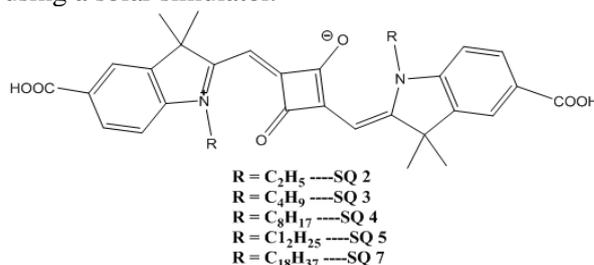


Fig. 1 Structure of squaraine dyes (top) and device configuration of organic planer heterojunction solar cells (bottom).

### Results and discussion

Electronic absorption spectra of thin films of squaraine dyes and P3HT spin coated on glass shown in the figure 2

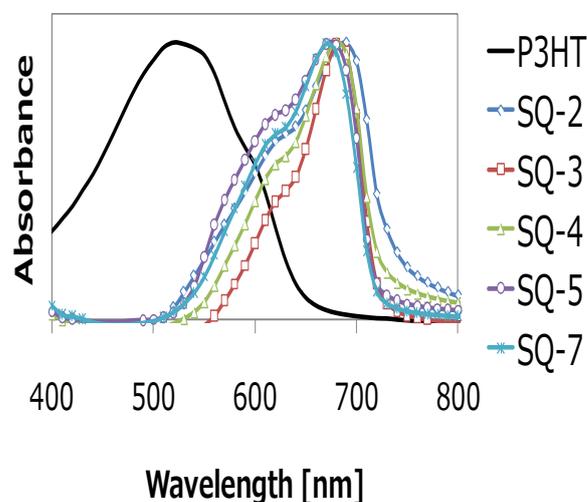


Fig. 2 UV-visible absorption spectra of thin films of P3HT and squaraine dyes spin coated on glass.

clearly indicates that P3HT has no optical absorption beyond 650 nm while squaraine dyes absorb the photon sufficiently. This suggests that incorporation these dyes in P3HT/PCBM bulk heterojunction are expected to extend the photon harvesting window provided that the energetic cascade is maintained. Understanding the minimum driving force for electron injection from the photoexcited dye to acceptor moiety (PCBM) is very much helpful for designing the novel dyes having photon harvesting in extended wavelength region. Figure 3 exhibits the HOMO and LUMO energy levels of dyes along with P3HT donor and PCBM acceptor, which indicates that the dyes under investigation have ability to make energy cascade with P3HT and PCBM. At the same time it also shows that while keeping the nearly same band gap the energy levels of SQ dyes can be tuned by only the alkyl chain length also.

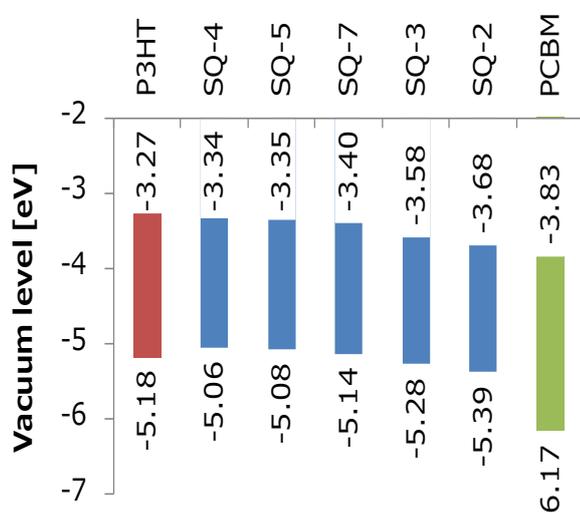


Fig. 3 Energy diagram for squaraine dyes along with P3HT and PCBM used in the present work.

Before the utilization of such dyes to fabricate sensitized bulk heterojunction solar cells, they should work like p-type donor and should be able to form p-n junction with the n-type semiconductor. To test this possibility p-n planer heterojunction solar cells were fabricated utilizing the squaraine dyes with soluble fullerene derivative PCBM as acceptor. The incident photon to electron conversion efficiency (IPCE) as a function of wavelength was measured and shown in the figure 4.

A perusal of this figure indicates that there is drastic increase in photon harvesting when alkyl chain length of dye was increased from ethyl to butyl while further increase in the alkyl chain length led to decrease in the photon harvesting behavior. This can be explained considering the fact that most probably for SQ-2 having energy gap with PCBM about 0.15 eV is not sufficient to inject the electron after photo excitation and SQ-3 with energy gap of 0.25 eV leads to efficient electron injection. Further increase in the alkyl chain length although energetically favorable but most

likely longer alkyl substitution leads to decrease in the hole mobility of the dyes resulting in to decreased photon harvesting.

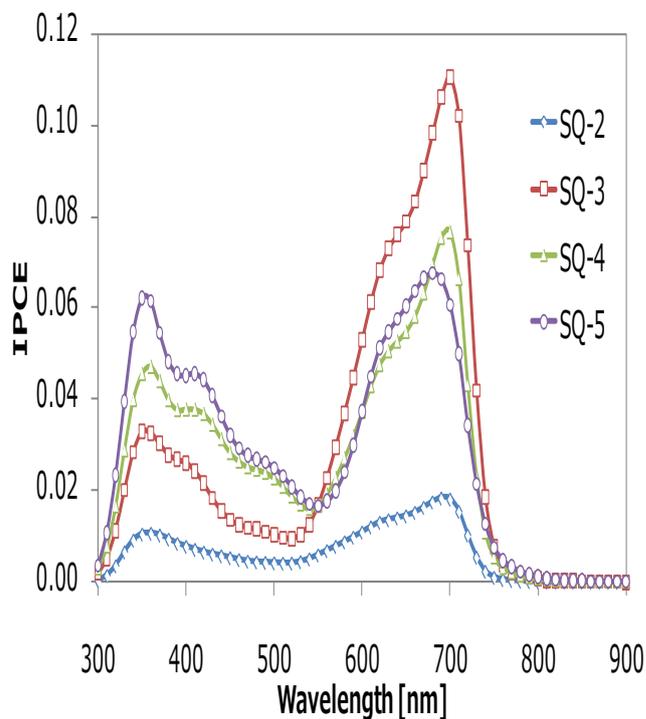


Fig. 4 Photocurrent action spectra for planer heterojunction photovoltaic cells using solution processed squaraine dyes and PCBM.

## Conclusions

Squaraine dyes exhibit the p-type donor behavior with NIR photon harvesting. At least activation energy of 0.25 eV is required for the effective electron injection from LUMO of donor dye to the LUMO of PCBM acceptor. Increase in the alkyl chain length of sensitizer leads to the decrease in the P3HT photon harvesting by suppressing the hole transport.

## References

- [1] J. Y. Kim, S. H. Kim, H. H. Li, K. Li, W. Ma, X. Gong and A. J. Heeger, *Adv. Mater.* **18** (2006) 572.
- [2] J. Hou, H-Y Chen, S. Zhang, R. I. Chen, Y. Yang, Y. Wu and G. Li, *J. Am. Chem. Soc.* **131** (2009) 15586.
- [3] Y. Liang, Z. Xu, J. Xia, S-T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, *Adv. Mater.* **22** (2010) 1.
- [4] J. Peet, A. B. Tamayo, X. D. Dang, J. H. Seo and T. Q. Nguyen, *Appl. Phys. Lett.* **93** (2008) 163306.
- [5] S. Wang, E. I. Mayo, M. D. Perez, L. Griffe, G. Wei, P. I. Djurovich, S. R. Forest and M. E. Thompson, *Appl. Phys. Lett.* **94** (2009) 233304.
- [6] B. Fan, Y. Maniglio, M. Simeunovic, S. Kuster, T. Geiger, R. Hany and F. Nuesch, *Int. J. Photoenergy* (2009)581068.
- [7] S. S. Pandey, T. Inoue, N. Fujikawa, Y. Yamaguchi and S. Hayase, *J. Photochem. Photobiol. A* **214** (2010) 269.