

## Exciton dissociation yields of semiconducting polymer thin film devices doped by various phosphorescent emitters

J. D. An<sup>1,2</sup>, J. Y. Chang<sup>1</sup>, J. W. Han<sup>1</sup>, C. Im<sup>1\*</sup>

<sup>1</sup>Dept. of Chemistry & Research Center for Organic Displays, Seoul, Korea

B. D. Chir<sup>2</sup>

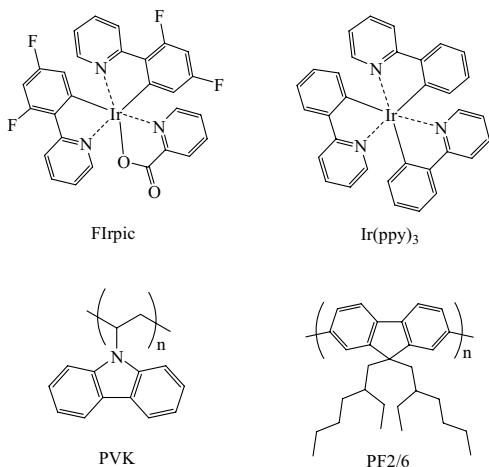
<sup>2</sup> Optoelectronic Materials Research Center, KIST, Seoul, Korea

Phone: +82-2-450-3415, E-mail: chanim@konkuk.ac.kr

### Abstract

To understand the exact charge carrier photogeneration properties of photoactive thin films consisting of a  $\pi$ -conjugated polymer matrix and a triplet dopant, we prepared two types of polymer, poly(9-vinylcarbazole) (PVK) and poly[9,9-bis(2-ethylhexyl)fluorene-2,7-diyl] (PF2/6) doped with triplet emitters for organic light-emitting diodes (OLED), either iridium(III)fac-tris(2-phenylpyridine) ( $\text{Ir}(\text{ppy})_3$ ) or iridium(III)bis[4,6-fluorophenyl-pyridinato- $N, C^2'$ ]picolinate (FIrpic), as thin film devices by using the conventional method. Those doped film devices, as well as pristine film devices, on ITO substrates were characterized by means of steady state photocurrent measurement for a wide spectral range.

### 1. Introduction



**Figure 1 Chemical structures of the materials used in this study.**

Organic  $\pi$ -conjugated polymer materials have recently attracted much interest due to their promising physical and chemical properties for potential

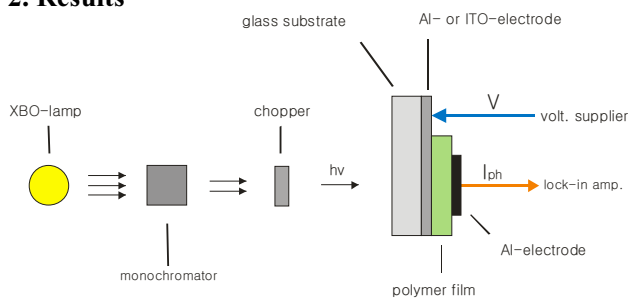
applications as organic light-emitting diodes (OLED) [1]. In spite of some advantages, organic electroluminescent (EL) materials have a crucial fundamental limit correlated with the singlet and the triplet exciton formation probabilities [2]. In order to overcome the limit of the singlet formation rate, believed to be as much as 25% of all recombined excitons due to spinstatistics, many groups have suggested the use of triplet emission as the main radiation source instead of the use of singlet emission [2]. For triplet emission, organometallic complexes having a heavy metal core, such as iridium or platinum, are often used due to their strong spin-orbit coupling by which the triplet population and the subsequent radiation from the triplet dopants are significantly increased.

Expectedly, the triplet-emitter-doped blend systems have more complicated exciton dynamics compared to pristine thin films. Such blend systems are often discussed by means of a binaric donor and acceptor system having, in all probability, various spectral overlaps and different oxidation and/or reduction potentials. One of the most crucial issues concerning these systems is Förster-type resonant energy transfer (RET) [8] from the matrix as the primary exciton donor to the dopants as the exciton acceptor. The other issue, being just as central as the energy transfer issue, is exciton dissociation at microscopic interfaces due to molecular heterojunctions [9]. Exciton dissociation, also known as charge-carrier photogeneration, is important not only for OLEDs but also for photovoltaic devices [5].

For these reasons, we decided to study various doped blend systems to depict how the underlying mechanisms correlated with each other and how they affected each other's emission properties. For our purpose, two  $\pi$ -conjugated, PVK and PF2/6, polymers were chosen. For the triplet-doping materials, we

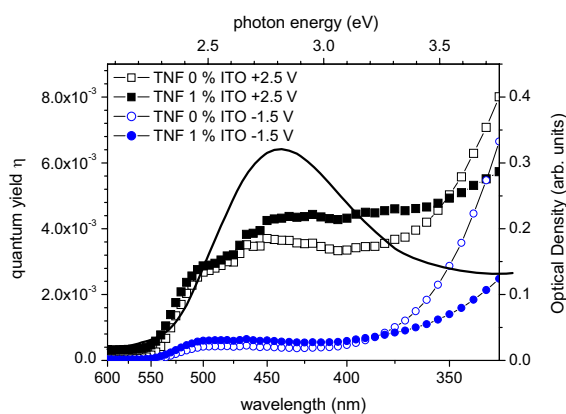
selected two well-known organometallic compounds, Ir(ppy)<sub>3</sub> and FIrpic. In order to verify the exact doping effect on the spectral, field, and temperature dependences of steady-state photoconductivity.

## 2. Results



**Figure 2** Used experimental set-up.

Photocurrent measurements were performed in a temperature-controlled cryostat with a combination of monochromator and a xenon lamp as a light source. Photocurrent signals were detected with a lock-in amplifier (EG&G 7620) which was connected to a chopper with a chopping rate of either 10 Hz or 400 Hz positioned between the cryostat and the light source.

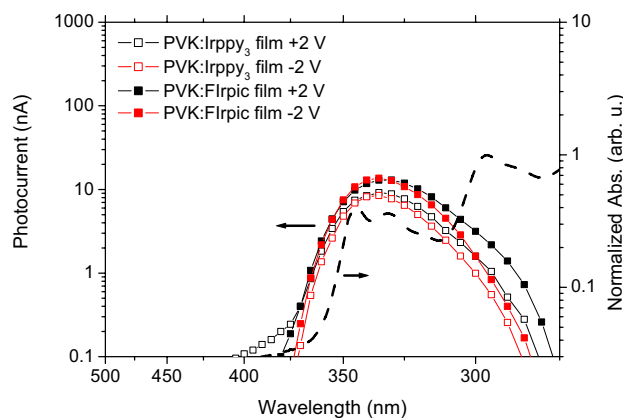


**Figure 3** Spectral dependences of the charge carrier photogeneration quantum yield  $\eta$  in ITO/PhPPV/Al configuration at 293 K. The electric fields for both bias directions were approximately  $2.5 \times 10^5$  V/cm.

The benefit of the lock-in technique is that it automatically subtracts the dark current from the measured signal. The quantum yield was calculated

from the measured photocurrents taking into account corrections for the light source performance and the light absorption in the glass substrates, contacts and in the active areas of the films. Spectral dependencies of the corresponding optical densities were measured with Varian Cary 100 UV-Vis spectrometer.

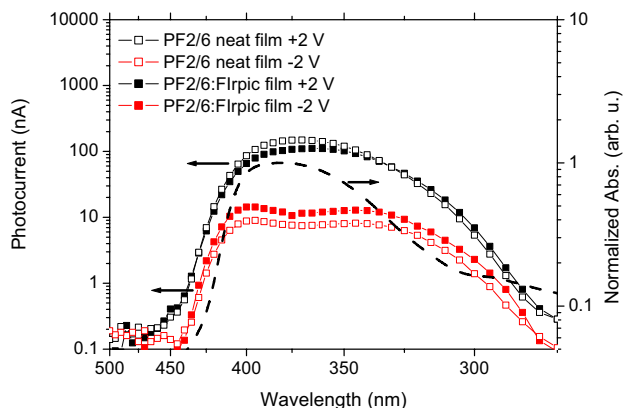
Figure 3 shows spectral dependences of the charge carrier photogeneration quantum yield  $\eta$  in ITO/PhPPV/Al configuration at 293 K and the electric fields for both bias directions were approximately  $2.5 \times 10^5$  V/cm. In case of forward bias quantum yield curve have shown that there is significant extrinsic contribution at the interface while in case of reverse bias quantum yield curve have shown virtually no extrinsic contribution. Additional feature of the result in figure 3 is clear effect of electron accepting dopant, TNF, below 1 eV from absorption edge range where there is no sufficient excess photon energy for dissociation.[5]



**Figure 4** Spectral dependences of the photocurrent in ITO/PVK/Al configuration at 293 K. The applied voltage for both bias directions were 2.0 V.

Figure 4 shows photocurrent curves as a function photon energy (wavelength of excitation) using ITO/PVK:FIrpic/Al and ITO/PVK:Ir(ppy)<sub>3</sub>/Al doped devices. PVK blend systems have shown relatively lower photocurrent response compare to PF2/6 blend systems shown in figure 5. Very weak bias polarity dependence of PVK systems was significantly different than PF2/6 as well as PPV systems. This might be explained with the effective conjugation length of polymer main chain because PPV and PF polymers have  $\pi$ -conjugated main chain while PVK have no  $\pi$ -conjugation along main chain.

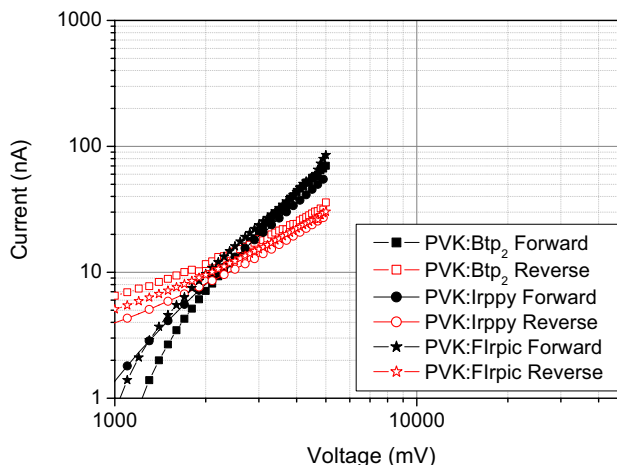
Figure 5 shows photocurrent curves measured with ITO/PF2/6/Al and ITO/PF2/6:Flrpic/Al devices. PF blend systems have shown clear bias polarity dependence being comparable to PPV systems. One of most important results shown here is that PF systems have shown dramatically increased photocurrent values, to be more precisely, the amount of exciton dissociation compare to PVK blends systems.



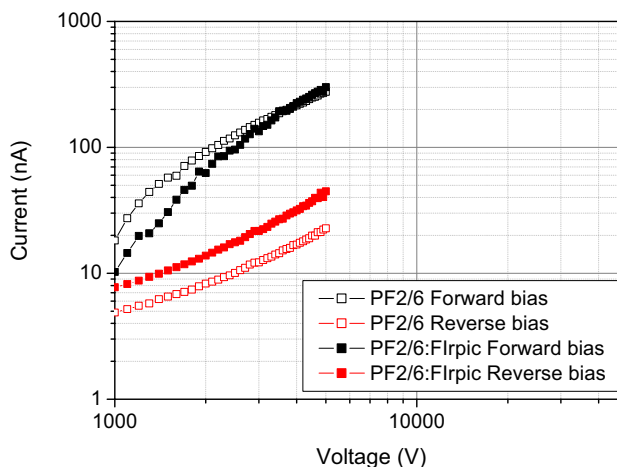
**Figure 5 Spectral dependences of the photocurrent in ITO/PF2/6/Al configuration at 293 K. The applied voltage for both bias directions were 2.0 V.**

From figure 5 one can recognize an additional doping effects which is bias polarity dependent. In case of reverse bias, doping of Flrpic triplet emitters have caused enhancing of photocurrent yield. This might explained with bulk sensitization of exciton dissociation and subsequent increasing of photocurrent under reverse bias. But under forward bias situation one can observe magical reduction of photocurrent yield which might be explained by means of trapping and subsequent non-radiative relaxation of generated charge carriers.

Figure 6 and 7 show photocurrent characteristics as a function of applied bias voltage. Both cases of PVK and PF2/6 have shown typical voltage-photocurrent characteristics with which one can describe forward cases as extrinsic interface enhanced charge carrier photogeneration and their photocurrent while reverse cases let explain by means of intrinsic bulk charge carrier photogeneration having sublinear shape of curve. This type of curve can be fitted within the frame work of Onsager 3D charge carrier photogeneration model being developed by Arkhipov et. al.



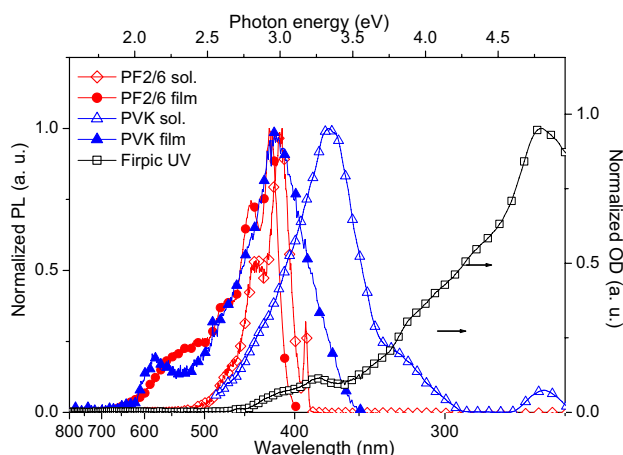
**Figure 6 Bias polarity dependence and bias voltage dependences of the photocurrent in ITO/PVK/Al configuration at 293 K.**



**Figure 7 Bias polarity dependence and bias voltage dependences of the photocurrent in ITO/PF2/6/Al configuration at 293 K.**

### 3. Discussion

In earlier study[9], PVK blend systems have shown significantly enhanced energy transfer and subsequent radiative decay from the doped triplet emitters while PF2/6 system as well as PPV system have shown virtually no efficient energy transfer and emission from those triplet dopant molecules. Therefore we had proposed that additional electron transfer (exciton dissociation) and triplet back-transfer from triplet dopant to matrix triplet sites should take into account to explain those different emitting behavior between PVK and PF2/6 blend systems.



**Figure 8 Spectral dependences of the photocurrent in ITO/PF2/6/Al configuration at 293 K. The applied voltage for both bias directions were 2.0 V.**

From figure 4 and figure 5 one can see dramatically different charge carrier photogeneration behavior between PVK systems and PF2/6 systems. PF2/6 systems have shown almost one order of magnitude higher photocurrent generation than that of PVK systems. And this fact strongly supports that electron transfer mechanism is one of the most important competitive way of exciton relaxation to energy transfer[10],[11] and subsequent emission from those triplet dopants. As one can see from figure 8 PVK system has much pronounced energy transfer facility due to its intrinsically higher lying absorption band which can accelerate exciton migration from PVK matrix to doped acceptors while PF2/6 system has significantly less overlapping with dopant, here Firpic. On the other hand, diverse HOMO and LUMO values[12],[13] from, for instance, cyclic voltametry has shown that there is a potential differences which can cause effective electron transfer not only energy transfer for such molecularly heterojunctioned systems.

#### 4. Conclusion

As a concluding remark, it is noteworthy to mention that the electron transfer and subsequent forming of electron and hole pairs at molecularly heterojunctioned interfaces due to their different electrochemical potentials and also the back-transfer of triplet excitons from the dopant to the matrix should be taken into account. This and the exciton migration due to RET are both important to consider

in order to better understand and achieve a highly efficient donor-acceptor doping system.

#### 5. Acknowledgements

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#### 5. References

- [1] C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* **51**, 913 (1987)
- [2] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, and W. R. Salaneck, *Nature*. **397**, 121 (1999)
- [3] C. Adachi, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *J. Appl. Phys.* **90**, 15 (2001)
- [4] C. Im, J.M. Lupton, P. Schouwink, S. Heun, H. Becker, and H. Bässler, *J. Chem. Phys.* **117**, 1395 (2002)
- [5] C. Im, E. V. Emelianova, and H. Bässler, *J. Chem. Phys.*, **117**, 2961 (2002)
- [6] F. Laquai, C. Im, A. Kadashchuck, and H. Bässler, *Chem. Phys. Lett.* **375**, 286 (2003)
- [7] C. Im, W. Tian, H. Bässler, A. Fechtenkötter, M.D. Watson and K. Müllen, *J. Chem. Phys.*, **119**, 3952 (2003)
- [8] S.A. Bagnich, C. Im, H. Bässler, D. Neher, U. Scherf, *Chemical Physics*, **299**, 11 (2004)
- [9] J. Chang, J. An, C. Im and Y.K. Kim, *J. Kor. Phys. Soc.*, **47**, 1028, (2005) [11] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy* (Plenum Press, New York, 1983).
- [10] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy* (Plenum Press, New York, 1983).
- [11] T. Förster, *Disc. Faraday Soc.* **27**, 7 (1957).
- [12] C. Adachi, R.C. Kwong, P. Djurovich, V. Adamovich, M.A. Baldo, M.E. Thompson, and S.R. Forrest, *Appl. Phys. Lett.* **79**, 2082 (2001).
- [13] S. Tokito, T. Iijima, Y. Suzuri, H. Kita, T. Tsuzuki, and F. Sato, *Appl. Phys. Lett.* **83**, 569 (2003).