

Excited State Relaxation in Vacuum Deposited and Solution Processed Films of Merocyanine/Fullerene Blends

D. Peckus^{1,*}, A. Devižis¹, D. Hertel², V. Gulbinas^{1,†}

¹ Center for Physical Sciences and Technology, Savanoriu 231, LT-02300 Vilnius, Lithuania

² Department of Chemistry, Physical Chemistry, University of Cologne, Luxemburgerstr. 116, 50939 Cologne, Germany

(Received 22 June 2012; published online 14 August 2012)

Exciton dynamics in merocyanine/fullerene blend films made by vacuum deposition and solution processing techniques were investigated by means of steady-state and time resolved fluorescence and absorption spectroscopy. Intermolecular charge transfer states are formed during several ps in neat merocyanine films, which determine their fluorescence properties. Fullerene additives cause formation of new heterogeneous charge transfer states. Even a small fullerene concentration significantly influences the exciton dynamics by quenching inherent merocyanine fluorescent states and causing appearance of new fluorescence bands caused by the charge transfer states between merocyanine and fullerene molecules. All fluorescence bands are quenched in films with high fullerene concentration due to the charge carrier generation, and the quenching effect is stronger in vacuum deposited films.

Keywords: Merocyanine, Heterojunction, Exciton dynamics, Electron donor, Electron acceptor, Organic solar cells.

PACS numbers: 78.40.Me, 78.47.J –

1. INTRODUCTION

The growing need for energy stimulates scientific research directed to creation of efficient, low-cost energy sources, one of them may be photovoltaic devices. Organic semiconductors have emerged as a new class of materials, which promise development low-cost and large-area solar cells. The bulk heterojunction (blend) concept has turned out to be the most promising approach to highly efficient organic solar cells, since it features an extended interface between the phases of the electron donor compound and the electron acceptor compound and leads to an enhanced generation of free charge carriers [1,2].

Two main processing techniques are possible for fabrication of blend devices: vacuum deposition and solution processing. A broad variety of organic conjugated polymers and small molecules can be used as electron donors and fullerene as an electron acceptor. Small molecules may be deposited under high vacuum conditions by thermal evaporation. On the other hand, soluble materials like polymers can be spin coated from solution. Many semiconducting polymers have been successfully applied in solution processed solar cells devices [3, 4].

Solution processing is a relatively fast and low-priced method for fabricating thin layers. However, the stacking of several layers on top of each other becomes a great problem, because new layer dissolve older one. Nevertheless, the highest solar cells made from organic polymers by solution processing technique shows efficiencies more than 9 % while small molecules shows efficiencies up to 6 % [3].

Polymer blends have been widely investigated, while investigations of blends of small polar molecules are less intensive. It is reliable that organic small mol-

ecules have some unused potential, because of that more detail investigation of organic small molecules is necessary. Perhaps some technological improvement of vacuum deposition or solution processing methods may increase solar cells of small molecules efficiency dramatically.

Recently, low-molecular-weight merocyanine dyes have been introduced as new absorbers and electron-donating compounds in blend solar cells [3-5]. It was found that small merocyanine molecules can be either thermally evaporated in vacuum or processed from solution. Here we address the excited state dynamics in blend films fabricated by the two processing methods.

MD376 molecules, which belong to the family of merocyanine dyes, were used as samples in our measurements [3, 4].

Pure MD376 films and blends with fullerene derivatives at various concentration ratios have been investigated. MD376 solutions in dichloromethane and toluene were also studied.

The main goal of our investigation was to compare ultrafast excitonic processes in different films and solutions. The charge transfer exciton formation features in films of MD376 were very interesting for us, because charge transfer exciton can be much more easily divided into free charge carriers.

2. EXPERIMENTAL

Steady-state and time resolved fluorescence spectroscopy techniques were used for merocyanine sample investigations. The fluorescence spectra and fluorescence decay kinetics were measured with an Edinburgh Instruments Fluorescence Spectrometer F900. A diode laser EPL-375 emitting 50 ps pulses at 375 nm with a repetition rate of 20 MHz were used.

* domantas@ar.fi.lt

† vidgulb@ktl.mii.lt

3. RESULTS AND DISCUSSION

Steady-state fluorescence spectra of neat films reveal the presence of several molecular species, with relative concentrations strongly dependent on the film preparation. Even low concentrations of fullerene or its derivatives cause a clear decrease of the merocyanine fluorescence intensity, while new fluorescence bands attributed to the charge transfer between merocyanine and fullerene appear in the long wavelength region. Fluorescence intensity is quenched more significantly in vacuum deposited blend samples (Fig. 1). This correlates with the fact that solar power conversion efficiency of merocyanine cells prepared by vacuum deposition method is higher than of cells processes from solutions [3].

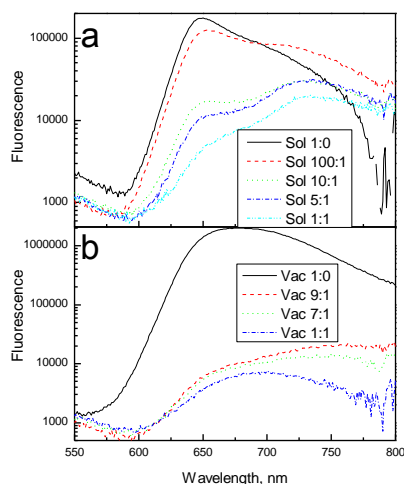


Fig. 1 – Fluorescence spectra of MD376 molecules (a) of film processed from solution (Sol) with various PCBM concentrations and (b) of vacuum deposited (Vac) film with various fullerene derivatives concentrations

Fluorescence spectra of films strongly depend on the film preparation conditions and aging. The spectra are composed of two main bands. Fluorescence band at about 650 nm shall be attributed to Frenkel excitons. The long wavelength fluorescence band at about 720 nm has very large Stokes shift, therefore it evidently belongs to some impurity or exciplex states. Both fluorescence bands of neat films decay almost exponentially with the identical lifetime of about 1 ns independently of the detection wavelength. That is for both solution processed and vacuum deposition technique made films (Fig. 2, 3).

PCBM additives cause strong quenching of the inherent MD376 fluorescence and cause appearance of the band with maximum at about 730 nm (Fig. 1a). Even 1% of PCBM causes quenching of the inherent fluorescence by about 30% and appearance of the new fluorescence band with comparable intensity. Surprisingly intensities of both fluorescence bands drop down in films with high PCBM concentration. This is attributed to the free charge carrier generation, which becomes efficient at high fullerene concentrations when its droplets are formed.

Fluorescence decay in solution processed blend films strongly depends on the detection wavelength (Fig. 2). Fluorescence at 650 nm decays nonexponentially and much faster than in neat films, while fluorescence at 725 nm attributed at CT states between MD376 and fullerene decays almost exponentially with about 3 ns time constant independently of the fullerene concentration.

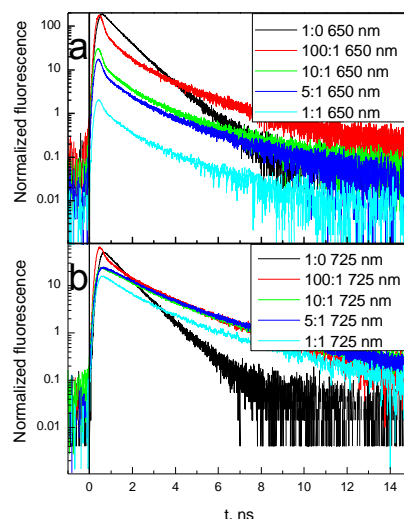


Fig. 2 – Fluorescence decay kinetics at 650 nm (a) and 725 nm (b) of MD376 films processed from solution with various PCBM concentrations

Fluorescence of vacuum deposited films decays non-exponentially at both detection wavelengths and its intensity decays more significantly with increase in fullerene concentration. (Fig. 3). It correlates with the higher solar energy conversion efficiency of the vacuum deposited films. Morphology of the vacuum deposited films is evidently more favorable for the free carrier generation quenching fluorescent states.

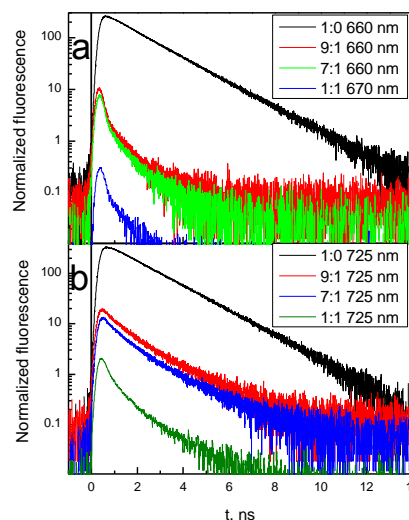


Fig. 3 – Fluorescence decay kinetics at 650 nm (a) and 725 nm (b) of MD376 films made by vacuum deposition technique with various fullerene concentrations

4. CONCLUSIONS

Absorption and fluorescence spectra reveal different aspects of properties neat MD376 films. The spectra show different sensitivity to the material structure. Energy migration and excitation localization at low energy states makes fluorescence spectra very sensitive to minor molecular species and to formation of new low energy excited electronic states. Charge transfer states formed between merocyanine molecules and those formed between merocyanine and fullerene molecules

determine fluorescence properties of neat films and blends. Generation of free charge carriers cause additional fluorescence quenching at high fullerene concentrations.

REFERENCES

1. J.J.M. Halls, C.A. Walsh, N.C. Greenham, E.A. Marseglia, R.H. Friend, S.C. Moratti, A.B. Holmes, *Nature* **376**, 498 (1995).
2. G.Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* **270**, 1789 (1995).
3. N.M. Kronenberg, V. Steinmann, H. Bürckstümmer, J. Hwang, D. Hertel, F. Würthner and K. Meerholz, *Adv. Mater.* **22**, 4193 (2010).
4. V. Steinmann, N. M. Kronenberg, M.R. Lenze, S.M. Graf, D. Hertel, K. Meerholz, H. Bürckstümmer, E.V. Tulyakova, F. Würthner, *Adv. Energy Mater.* **1**, 888 (2011).
5. Frank Würthner, Theo E. Kaiser, and Chantu R. Saha-Möller, *Angew. Chem. Int. Ed.* **50**, 3376 (2011).

ACKNOWLEDGEMENT

This research was funded by the European Social Fund under the Global Grant measure.