Scientific Report: Fabrication and Characterization of Tandem-Type Organic Solar Cell Structures Comprising Soluble Perylene Diimide Derivatives

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Introduction

Organic materials are promising candidates for future low cost solar cells. Most of the organic materials can be processed from solution via spin-coating at room temperature, that can enable the manufacture of large area, flexible and lightweight devices. Current progress on organic photovoltaic devices for increasing power conversion efficiency (PCE) is mainly attributed to the bulk heterojunction structure, which enables an efficient charge separation due to the increased photoactive interface area.

As an photovoltaic device, efficiency is very important parameter. In order to increase the PCE of the devices, many aspects should be taken into account, such as the absorption coefficients of the materials, the exciton dissociation rates and the charge-carrier mobilities. Perylene diimides (PDIs) are one of the widely studied classes of organic semiconductors. Their large molar absorption coefficients, high fluorescence quantum yields, photo, thermal and electrochemical stabilities provide them a great potential in application areas of artificial photosynthesis, electrophotography, dye sensitized solar cells, solid state organic solar cells and electroluminescent displays [1–7]. The major problem of PDIs that limits their application areas and increases the costs is their low solubility in regular organic solvents. Most of the applications of perylene derivatives have been performed to dye-sensitized solar cells (DSSC), but their applications to bulk heterojunction photovoltaic devices are very limited.

The major focus of this study is to investigate PDI derivatives that differ in their solubility for solution processable tandem type organic solar cells. Before building tandem type solar cell, they will be applied to the bulk heterojunction solar cell for analyzing the performances of these materials . The two different PDI derivatives are named as N,N-bis-2-(1-hydroxy-4-methylpentyl)-3,4,9,10-perylenebis (dicarboximide) (HMPER) and N,N-bis-2-(1-hydoxyhexyl)-3,4,9,10-perylenebis(dicarboximide) (HHPER) that were introduced in litarature as good candidates for organic solar cell applications [8] was used in this study. Both of them have hydroxyl group that increases their solubility in regular organic solvents and HMPER contains branched methyl group in contrast to HHPER.

Experimental

The organic materials synthesized in Ege University Solar Energy Institute, namely, HHPER and HMPER were used without any further purification. Molecular structures of these materials are shown in figure 1.
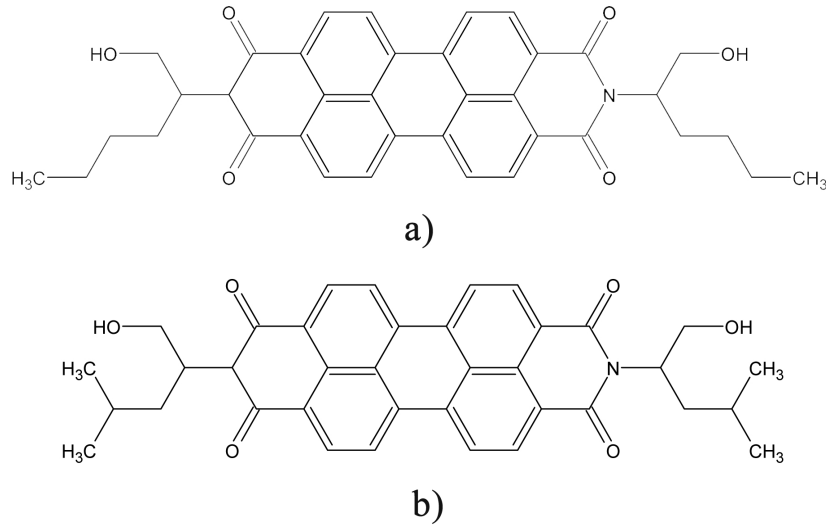

Figure 1: Moleculer structure of a) HHPER and b) HMPER

In the best performing solid state organic solar cells reported, a donor (p-type) conjugated polymer is blended with an electron accepting (n-type) material, to form the bulk-heterojunction structure for efficient exciton dissociation. Of the various types of polymer-based photovoltaic devices with a power conversion efficiency (PCE) of 3-4 %, were fabricated using a blend of poly(3-hexylthiophene) (P3HT) and 6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as the active layer [9]. After these reports P3HT/PCBM based photovoltaic devices were optimized to achieve PCE approaching 5% [10]. In the beginning of our studies, we decided to build bulk heterojunction solar cells with poly[2-methoxy-5-(3,7-dimethyloctyloxy)-p-phenylene vinylene] (MDMO-PPV) as an electron donor material which has more suitable highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels than P3HT (HOMO 5.2 eV., LUMO 3.5 eV.) with PDIs and HHPER/HMPER as an electron acceptor material.

Device Preparation and measurements

Indium tin oxide (ITO) coated glass substrates (16 mm x 16 mm, Merck, <20 $\Omega/square$) were structured with hydrochloric acid and cleaned with acetone and isopropanol in ultrasonic bath (15 min.). Before device fabrication the cleaned ITO substrates were treated with O_2 plasma for 2 min. After plasma cleaning a 30-40 nm thick layer of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) was spin coated onto the substrate, and the devices were annealed in nitrogen atmosphere for 30 min at 120 ^{0}C. Peumans and Forrest demonstrated the use of PEDOT:PSS on ITO can reduce surface roughness of the substrate and modify the work function of the anode [11]. The active layers were spin coated in glovebox onto the substrates at 1500 rpm. After spin coating process the devices were transferred to vacuum evaporator for the evaporation of Ca (50 nm) and Al (200 nm) contacts. Inficon XTC/2 quartz crystal monitors were used to measure deposition rates and film thicknesses. Figure 2 shows a simplified solar cell structure.
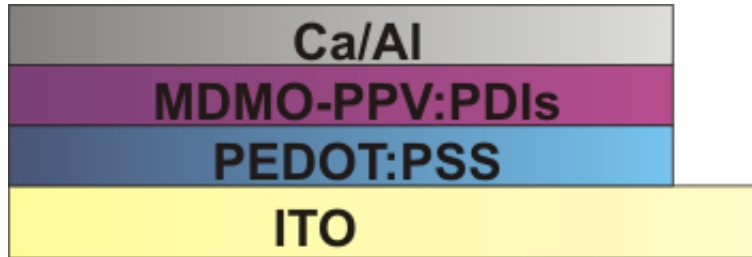

Figure 2: A simplified solar cell structure based on MDMO-PPV:PDIs.

The active layer solutions were prepared in chlorobenzene with an MDMO-PPV concentration of 10 mg/ml, and in different mixing ratios of 1:1, 1:2, 1:4 and 2:1 MDMO-PPV:HMPER and MDMO-PPV:HHPER. HHPER and HMPER were used as electron acceptor in both solar cell. Before spin coating the solutions were stirred for one night.

Device measurements were made in a nitrogen atmosphere, using a Keithley 238 high current source measure unit (SMU). A spectrally monitored Oriel 300 W solar simulator with AM 1.5 filter was used to illuminate the samples with at an irradiance of 850 W/m² (85 mW/cm²) (CIE 85, European standard). Organic layer thicknesses

were measured with a Dektak 8000 profiler. Active area of the devices was 24 mm^2.
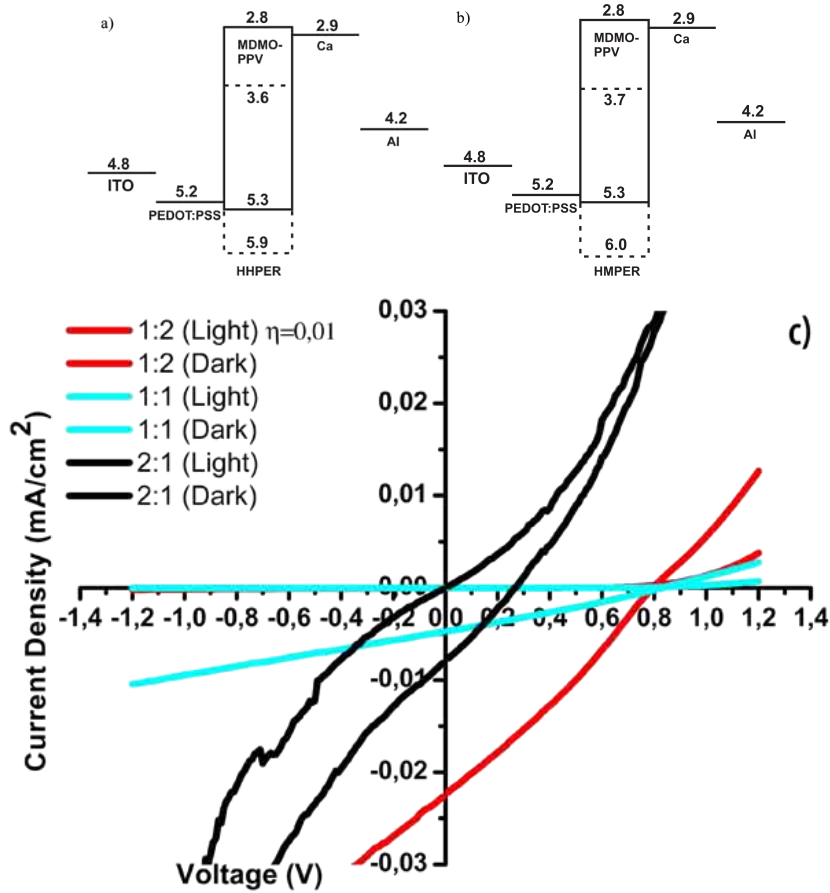

Figure 3: HOMO-LUMO energy diagram of a) MDMO-PPV:HHPER and b) MDMO-PPV:HMPER based devices and c) I-V curve of the MDMO-PPV:HHPER device

Maximum current density and voltage of MDMO-PPV:HMPER based solar cell obtained at 1:2 blend ratio are 0.012 mA/cm^2 and 0.795 mV, and the efficiency and fill factor values of the solar cell are 0.01 % and 28.9 % respectively. The active layer in a typical solar cell should absorb a significant fraction of the suns light. Therefore the thickness of any organic semiconductors, generally must only be 100-500 nm thick to absorb most of the light at their peak absorption wavelength. The thickness of the active layers with different blend ratio 1:1, 1:2, and 2:1 w / w are 220 nm, 130 nm and 88 nm, respectively. In our solar cell configuration, 130 nm thickness and 1:3 blend ratio are the best values for the modarate power conversion efficiency of MDMO-PPV:HMPER based solar cell.

4

In the case of bulk heterojunction solar cells, both blend morphology and charge mobility are influenced by thermal treatment. Padinger et al. reported postproduction treatment of P3HT:PCBM bulk heterojunction solar cells [12]. After a combined heat and applied DC voltage postproduction treatment, the power conversion efficiency could be raised to 3.5 % [13].

After the first measurement, only thermal annealing was applied to MDMO-PPV:HMPER based solar cells. In figure 4 the effect of thermal annealing treatments on the IV characteristics are presented. After the thermal annealing, the short circuit current density (I_{sc}) and open circuit voltage (V_{oc}) decreased with increasing annealing temperature and I_{sc} values decreased more than V_{oc} values. This is consistent with the fact that V_{oc} mainly depends on material properties, namely the ionization potential of the donor polymer and electron affinity of the acceptor PDI molecule.
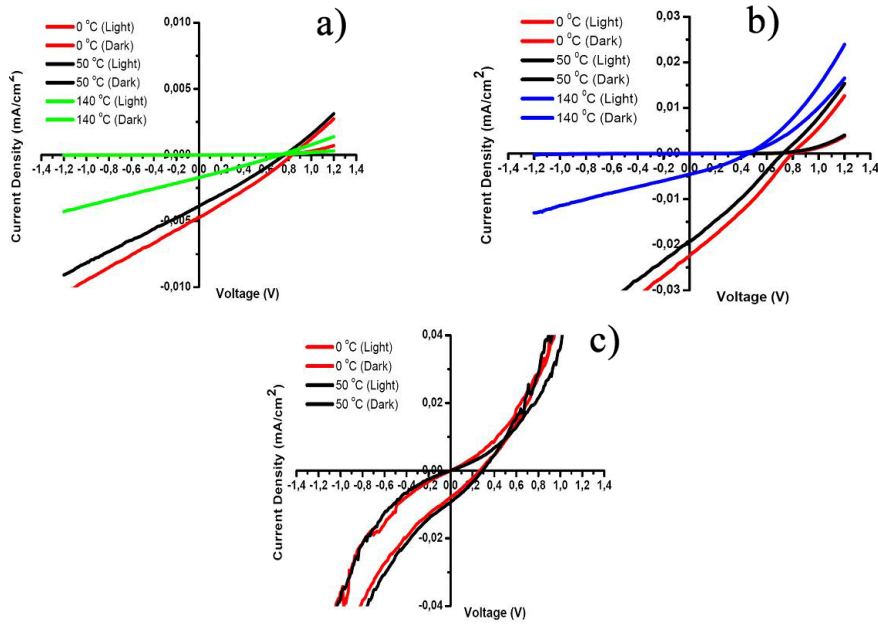

Figure 4: IV measurements of MDMO-PPV:HMPER solar cells with different mixing ratio a) 1:1, b) 1:2, c) 2:1 after thermal annealing.

HMPER was also used as an electron donor material in a PCBM based solar cell as there are report on the electron donor properties of PDIs in literature. The concentration and blend ratio were the same with the MDMO-PPV:HMPER based solar cell. Unfortunately, HMPER:PCBM based devices didn't show any solar cell behavior. From this results we can conclude that HMPER has only electron accepting properties.

HHPER were also used as an electron acceptor material with electron donor MDMO-PPV. When compared to HMPER, HHPER has a lower solubility in organic solvents, therefore 4 mg/ml HHPER could be used. Unfortunately, we could not get a solar cell response from this cell. Many of alternative ways were tested such as tuning the thickness, but no results was found for this type of solar cells. For the efficient absorption of light the active layer thickness is very important. The comparatively lower solubility of HHPER, hence the low thickness might be responsible for the results.

Because of these unpromising results and limited time of the visit, we decided not to go on building tandem type organic solar cells. However we believe that very high efficiencies may be achieved by using spin coating technique for more soluble PDI derivatives or by using vacuum evaporation technique in bulk heterojunction organic solar cells.

Organic Light Emitting Diode (OLED)

Recently, many researchers and companies have become interested in white organic light emitting diodes due to usability as a solid state lighting. There are many ways for achieving white light in an OLED system, such as combining three or two emission material inside the OLED structure, using single emission material that has an emission covers all visible spectrum or combining three color layer by layer or as a blend inside the device. Exciplex emission is another method for the achieving white OLED.

An exciplex is formed by intermolecular interaction between a molecule in the ground state and another different molecule in an excited state. Electroluminescence and photoluminescence emission wavelength from such devices reflected the energy difference

between the highest occupied molecular orbital (HOMO) level of donors and the lowest unoccupied molecular orbital (LUMO) level of acceptors [14]

In the second part of the studies in Light Technology Institute (LTI) an imidazolium PF$_6$ salt (SO6) and a PDI derivative N,N-di-(1-dehydroabietyl)perylene -3,4,9,10-bis(dicarboximide)(ABIPER) were used in an OLED device. Molecular structures of the materials are shown in figure 5.
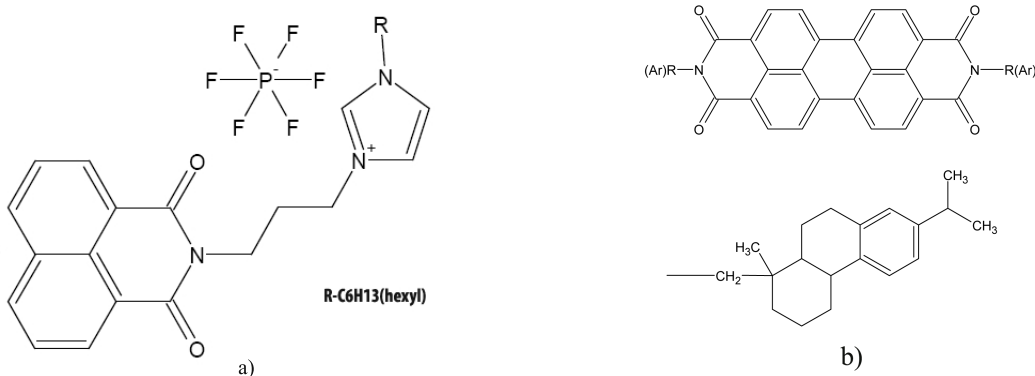

Figure 5: Moleculer structures of the a) SO6 and b) ABIPER.

Experimental

Indium tin oxide (ITO) coated glass substrates (Merck, <20 $\Omega/square$) were patterned with photolithograpy technique by using UV light and cleaned with acetone and isopropanol in ultrasonic bath (15 min.). Before device fabrication the cleaned ITO substrates were treated with O$_2$ plasma for 2 min. After plasma cleaning a 30-40 nm thick layer of poly(3,4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS) was spin coated onto the substrate, and the samples were annealed in nitrogen atmosphere for 30 min at 120 ^{0}C. The organic materials were spin coated in glovebox onto the substrates at 2000 rpm. After spin coating the samples were transferred to vacuum evaporator for the evaporation of Ca (50 nm), BPhen (20 nm) and Al (200 nm) contacts. Inficon XTC/2 quartz crystal monitors were used to measure deposition rates and film thicknesses. The characterization was carried out under inert nitrogen environment inside a glove box system. A Keithley 236 source meter was used to investigate I-V charateristics and OLED Characterization System

(OCS) box was used for the determination of Luminance and Electroluminescence characteristics of OLEDs.
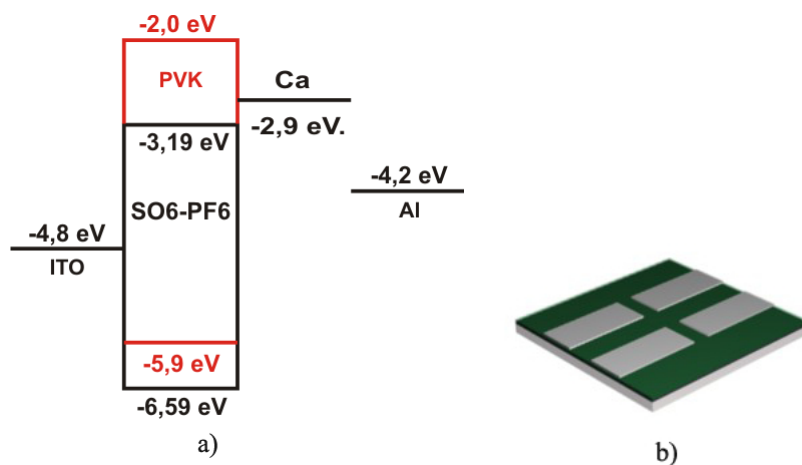

Figure 6: a) HOMO LUMO levels of ITO/PEDOT:PSS/PVK:SO6/Ca/Al and b) a simplified OLED device.

The PVK:SO6 solutions were prepared in tetrahydrofuran (THF) solvent with an PVK concentration of 10 mg/ml, and in different mixing ratios of 0, 2.5, 5, 10 and 15 % PVK:SO6. Before spin coating the solutions were stirred for one night. Figure 7 shows the absorbance and PL spectra of the materials. it is clearly seen that SO6 has an emission maximum wavelength at 463 nm and PVK has an emission maximum wavelength at 410 nm.
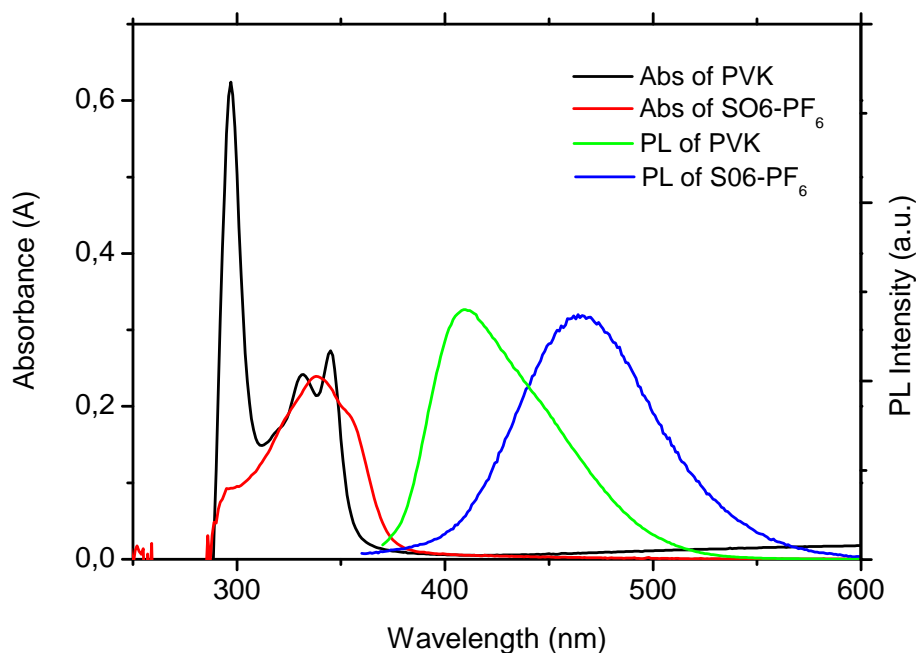
Figure 7: Absorbance and PL spectra of the materials.

White emission was obtained from ITO/PEDOT:PSS/PVK:SO6/Ca/Al device, although it was comprising two blue emission materials as an emission layer. Fig. 6 shows the HOMO-LUMO energy diagram and a simplified OLED device.

The exciplex emission process can be schematized as $D^* + A \rightarrow D^+ / A^- \rightarrow D + A + h\nu$. For the understanding the white emission where it came from, photoluminescence measurement was taken for the different blend ratio of PVK:SO6. The energy difference between the LUMO level of SO6 and the HOMO level of PVK is 2.7 eV., therefore an exciplex emission was expected at around 490-500 nm. Figure 8 shows the PL spectrum of the PVK:SO6 (blue curve 5% and red curve 10% doping ratio) film. Two peak can be seen from the PL sepctrum of PVK:SO6 at 415 nm and 508 nm. The peak at 508 nm might be an exciplex emission between PVK and SO6.

Figure 9 a) shows the I-V curves of ITO/PEDOT:PSS/PVK:SO6/Ca/Al device with different doping ratio of SO6. Current density values of this device was very high and therefore luminance measurement couldn't be done because of the very low light output.
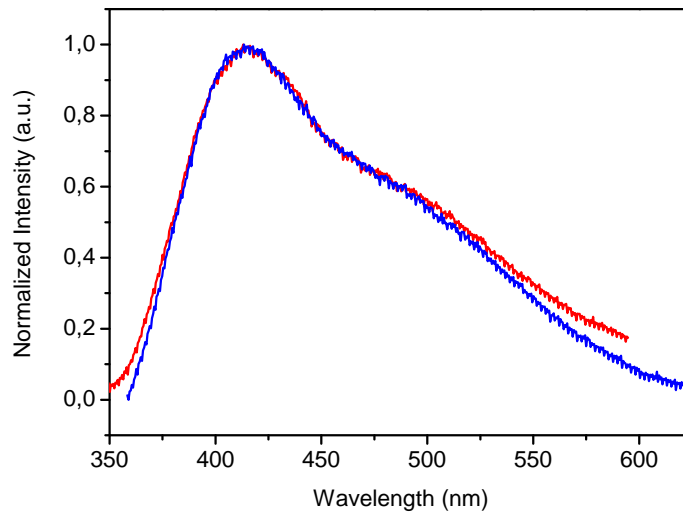
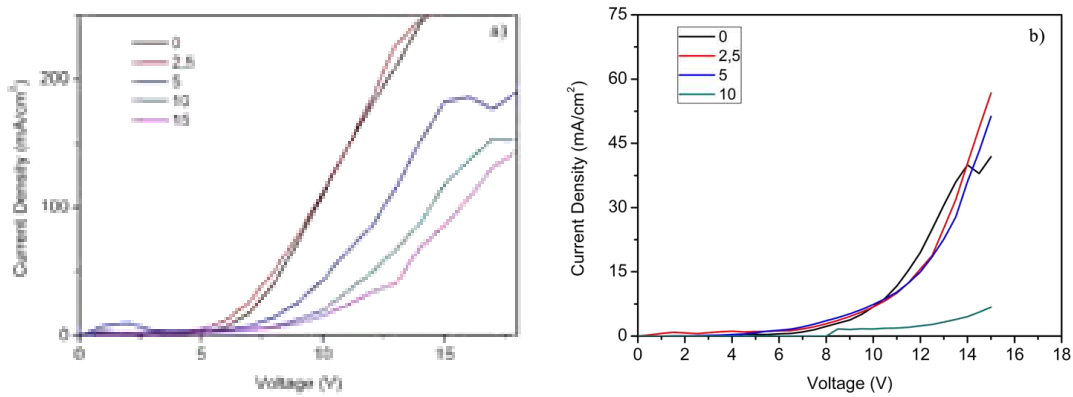Figure 8: Normalized PL spectrum of PVK:SO6

Figure 9: I-V curve of ITO/PEDOT:PSS/PVK:SO6/Ca/Al and ITO/PEDOT:PSS/PVK:SO6/Bphen/Al devices.

Therefore, an electron transport/hole blocking material was used for the increasing the electron density and brightness of the devices. Figure 9 b) shows the I-V curve of ITO/PEDOT:PSS/PVK:SO6 /BPhen/Al device. Though the current density decreased, the light output still very low for this device. Therefore Luminance, luminous efficiency (Cd/A), quantum efficiency or current efficiency (lm/W) couldn't be measured for OLED devices.

ABIPER was also used as a dopant in ITO/PEDOT:PSS/4,4'-di (N-carbazolyl) bi-phenyl (CBP):ABIPER/Ca/Al. ITO cleaning and the device preparation procedure were the same as previous. CBP:ABIPER solution was prepared in 1,2- dichloroben-zene solvent with an CBP concentration of 5 mg/ml, and in different mixing ratios of 0, 2, 5, 10 and 15 % CBP:ABIPER.
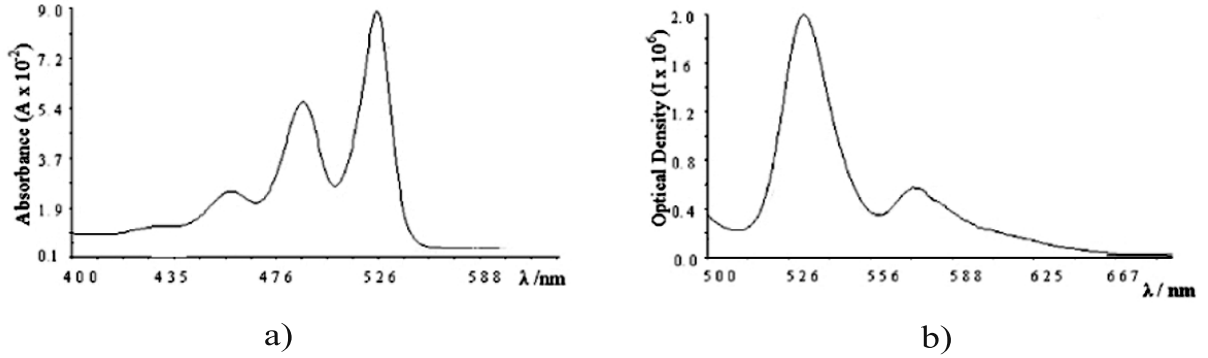

Figure 10: a) Absorbance and b) PL spectrum of ABIPER

After the PEDOT:PSS coating and thermal annealing the CBP:ABIPER solution was spin coated at 1000 rpm on the PEDOT:PSS and the samples were transferred to vacuum evaporator for the evaporation of Ca (50 nm), Al (200 nm) . ABIPER has an emission at 510-600 nm (Fig. 10). Therefore, red light was obtained from this device, but the brightness of this device was too low, therefore, luminance and electroluminescence (EL) measurement could not performed.

Acknowledgments

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