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**Host Institute: Linz Institute for Organic Solar Cells (LIOS)**

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**CARBAZOLE-BASED DYES FOR DYE-SENSITIZED SOLAR CELLS**

**INTRODUCTION**

Solar energy has a great importance among the renewable energy sources. Since sunlight can be transformed into electricity using solar cells, many researchers have been focused on this subject. First of all, conventional solar cells were built from inorganic materials such as silicon. The efficiency of this kind of solar cells reached up to %24. However, their fabrication process is quite expensive. In addition silicon based solar cell show low efficiency at high temperatures. Hybrid and photoelectrochemical (dye sensitized) solar cells have been the alternative for conventional silicon solar cells. Dye-sensitized solar cells (DSSCs) have attracted great attention over the last 15 years owing to their prospect of high energy conversion efficiency and low production cost [1]. Until now, however, only few photosensitizers based on ruthenium metal complexes have achieved solar-to-electric power conversion over 10% under AM 1.5 [2]. Recently, several groups have developed metal free organic sensitizers to overcome the prohibitive cost of ruthenium metal complexes, and the impressive photovoltaic performance has been obtained with some organic coumarin,[3] indoline,[4] oligoene,[5] merocyanine,[6] and hemicyanine [7] dyes having efficiencies in the range of 5-8%. However, many organic dyes have often presented the low conversion efficiency and low operation stability compared to metal complexes. The major factor for the low conversion efficiency of many organic dyes in the DSSCs is due to the formation of dye aggregates on the semiconductor surface. Another issue of organic dyes is the stability due to the formation of unstable radical species during redox reaction cycles.

Donor–acceptor  $\pi$ -conjugated organic dyes possessing broad and intense spectral features are especially useful as sensitizers. Furthermore, the charge recombination of the injected electron in to metal oxide with donor–acceptor  $\pi$ -conjugated dyes was an order of magnitude slower than for comparable dyes that lacked the electron donor groups, because spatial separation of the positive charge density on donor moiety of the oxidized dye (excited dye) and the injected electrons has the crucial effect of retarding the rate of charge recombination between the injected electrons and the oxidized dye. The charge recombination with the oxidized dye is a key loss mechanism of DSSCs [8-13]. Many donor–acceptor  $\pi$ -conjugated dyes with carboxyl group, acting as not only anchoring group for attachment on metal oxide but also the electron acceptor, have been synthesized and used as sensitizers of DSSCs [14-17]. A number of studies have suggested that a carboxyl group can form an ester linkage with  $\text{TiO}_2$  surface to provide a strongly bound dye and a good electron communication between them. However, development of new donor–acceptor  $\pi$ -conjugated dyes for DSSCs is limited because a carboxyl group is required to combine with  $\pi$ -conjugation system or electron acceptor moiety of dyes for the above reasons.

## THE AIM OF STUDY

The aim of this project is to fabricate and characterize different kinds of dye-sensitized solar cells and also to understand the limiting factors for the efficiency of these solar cells and to find solutions meeting all these limiting factors.

In this study  $\text{TiO}_2$  based dye-sensitized solar cells will be fabricated with donor–acceptor  $\pi$ -conjugated dyes. The project will mainly focus on the donor–acceptor  $\pi$ -conjugated dyes which will be experimented in this project were synthesized by Özlem Usluer and co. workers using different synthetic pathways. Two novel donor–acceptor  $\pi$ -conjugated dyes, (2*E*)-2-cyano-3-{5-[7-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9,9'-spirobi[fluoren]-2-yl]-2-thienyl} acrylic acid dyes with one (**OU-01**) and two thiophene (**OU-02**) rings, carrying carbazole donor groups were designed and synthesized. They are fully original materials and they have not been used in solar cells before. With this project we will firstly determine solar cell efficiencies and characteristics of these dyes.

## EXPERIMENTAL

The organic materials used in this study were synthesized and characterized by Özlem USLUER and co.workers in Ege University Solar Energy Institute.

## DEVICE PREPARATION

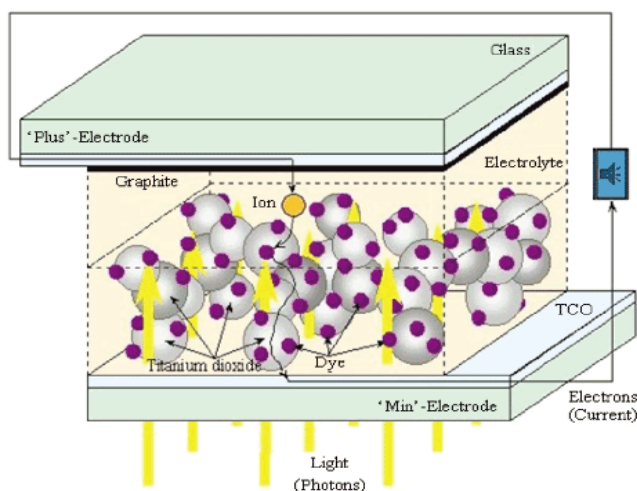


Figure 1. The structure of DSSC device

### *Preparation of electrolytes*

1-Butyl-3-methylimidazolium iodide (BMII) was synthesized to prepare the reference IL electrolyte. The reference electrolyte consists of 0.6M 1-butyl-3-methylimidazolium iodide (BMII), 0.1M lithium iodide (LiI), 0.05M iodine (I<sub>2</sub>) and 0,5 M *tert*-butyl pyridine (TBP) dissolved in 3-methoxy propionitrile (MPN).

### *Synthesis of TiO<sub>2</sub> nanoparticles and electrode preparation*

TiO<sub>2</sub> nanoparticles were synthesized by sol-gel method and growth to the 20–25 nm by Ostwald ripening in autoclave. The preparation of TiO<sub>2</sub> electrodes was done by modification of procedure previously reported by Graetzel and coworkers [18]. The TiO<sub>2</sub> paste was coated on transparent conductive oxide coated glass electrodes (SnO<sub>2</sub>:F, TEC15,

Rsheets:  $15\Omega/\square$ ) by doctor blade technique.  $\text{TiO}_2$  coated electrodes first dried at room temperature and then sintered at  $450\text{ }^\circ\text{C}$  for 1h with  $10\text{ }^\circ\text{C}/\text{min}$  heating rate. The thickness of the electrodes was measured as  $10\text{ }\mu\text{m}$  and the particle size was determined as  $25\text{ nm}$  by AFM.

### *Sensitization with dye and DSSC assembly*

Sintered electrodes were allowed cool down slowly. While electrode temperature is around  $100\text{ }^\circ\text{C}$ ,  $\text{TiO}_2$  electrodes were immersed in dye solution containing  $0.3\text{ mM}$  **OU-01** and **OU-02** in chloroform and Z-907 dye that was used for comparison with novel dyes in acetonitrile: *tert*butanol (1:1) for 3 h. Sensitized  $\text{TiO}_2$  electrodes were rinsed with acetonitrile and kept in desiccators. Counter electrode was prepared by thermal reduction of hexachloroplatinic acid to the platinum. 1% (v/v) solution in 2-propanol was used for platinization of FTO coated electrode. Drop casted electrodes annealed at  $400\text{ }^\circ\text{C}$  for 20 min. The DSSCs were prepared by placing the electrodes in sandwich geometry top of each other and in the middle  $50\text{ }\mu\text{m}$  thick thermoplastic polymer frame Surlyn® 1702 (DuPont). The electrodes were sealed by heating around  $100\text{ }^\circ\text{C}$  and pressing slightly. Prepared electrodes were filled into cell via pre-drilled small hole by vacuum. Finally the small hole was sealed with piece of Surlyn and cover glass. The active areas of the prepared solar cells were  $1.0\text{ cm}^2$ . The photovoltaic characterizations of the DSSCs were done under the dark and standard conditions by illumination of AM1.5 global radiation with  $100\text{ mW}/\text{cm}^2$  light intensity.

## **RESULTS**

The current density–voltage ( $I$ – $V$ ) characteristics of the DSSCs with BMII electrolyte under dark and  $100\text{ mW}/\text{cm}^2$  light intensity of AM1.5 global radiation are shown in Fig. 2. The dark  $I$ – $V$  characteristics of the DSSCs show a sharp rectifying behaviour. The photovoltaic parameters of DSSC solar cells can be obtained from the following equations [19].

$$FF = \frac{V_m I_m}{V_{oc} I_{sc}} \quad (1)$$

$$\eta = \frac{I_{sc} V_{oc} FF}{P_{in} A} \quad (2)$$

where FF is filling factor,  $V_{oc}$  is the open circuit voltage,  $I_{sc}$  is the short current.  $I_m$  and  $V_m$  are current and potential maximum power point,  $P_{in}$  is the intensity of incident light  $A$  is the cell area. The FF and  $\eta$  values of the DSSCs were calculated using Eqs. (1) and (2) and are given in Table 1.

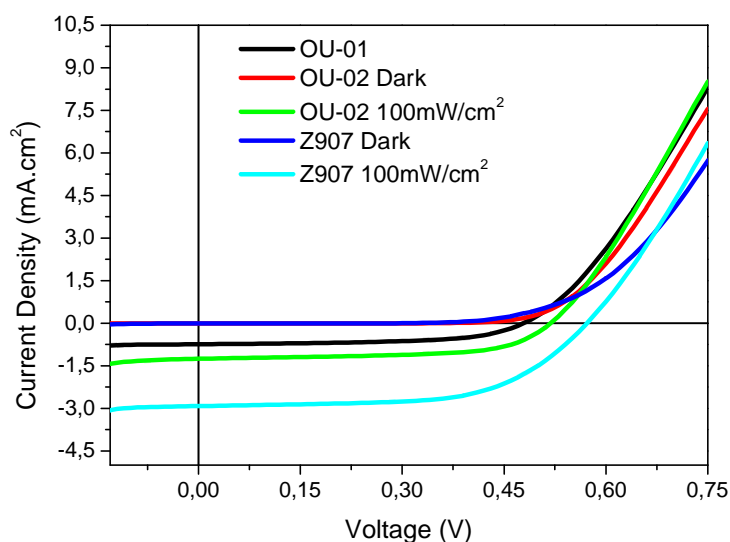


Figure 2. I-V curve of dyes under dark and illumination

**Table 1.** The current-voltage characteristics of novel dyes with reference Z907 under dark and illumination at AM 1.5 condition.

Dye	$J_{sc}(\text{mA.cm}^{-2})$	$V_{oc}(\text{mV})$	FF	Max. Power ( $\text{mW.cm}^{-2}$ )	$J_{mmp}(\text{mA.cm}^{-2})$	$V_{mmp}(\text{mV})$	Efficiency (%)
<b>OU-01</b>	0,73	480	0,57	0,20	0,56	360	0,20
<b>OU-02</b>	1,24	520	0,61	0,39	0,97	410	0,40
<b>Z907</b>	2,99	560	0,59	0,99	2,49	400	1

## **ORGANIC LIGHT EMITTING DIODE (OLED)**

Organic light-emitting diodes (OLEDs) have attracted much attention owing to their advantages of low-power consumption, high contrast, high brightness and potential applications to full color flat panel displays [20].

During last decade, the intensive research has been carried out to generate the material with high light emitting efficiencies, high thermal stability, and good amorphous film formation property [21, 22]. The electro-luminescence (EL) characteristic of OLED materials depend on the appropriate HOMO and LUMO energy levels and the electron and hole motilities.

Carbazole-based compounds have been extensively studied in many applications such as electrochromic devices, organic light-emitting diodes, organic field-effect transistors and photovoltaic cells, exploiting their intrinsic photophysical and redox properties [23-26]. These compounds demonstrate high thermal, morphological and photochemical stability [27]. Polyfluorene and its derivatives are also important materials for light-emitting materials because of their high photoluminescence (PL) and electroluminescence (EL) efficiencies and high thermal stabilities [28].

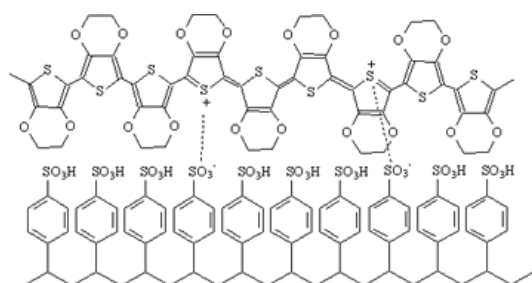
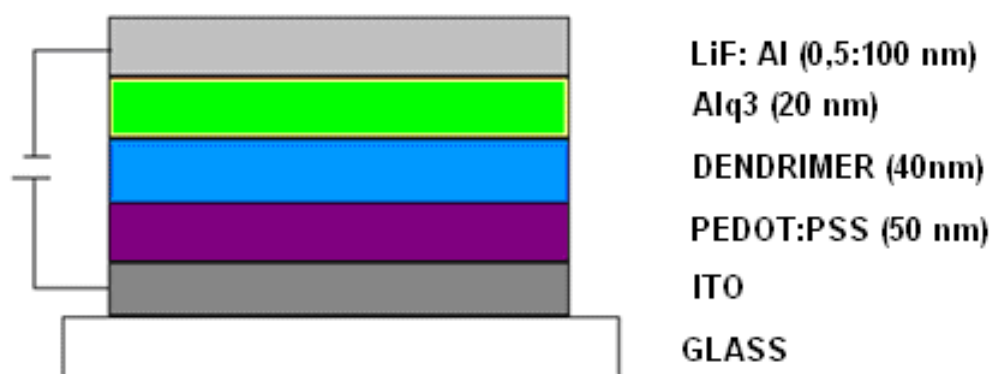
In this study OLED devices were fabricated with novel second generation carbazol dendrimers. The hole-transporting properties of dendrimers were investigated by preparing a double-layer device with the light-emitting material, Alq3.

### **EXPERIMENTAL**

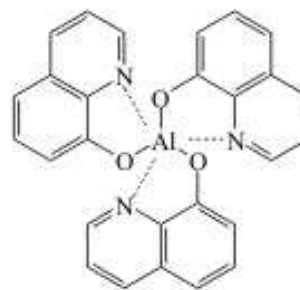
The second generation carbazol derivatives with different fluorene core **OU-17** and **OU-25**, used in OLED devices were synthesized and characterized by Özlem USLUER in Ege University Solar Energy Institute.

## DEVICE PREPARATION

Indium tin oxide (ITO) glass substrate with a sheet resistance  $15\Omega/\square$  was used. Oxygen plasma cleaning was performed before used. After plasma cleaning a 50 nm thick layer of poly(3,4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS) was spin coated onto the substrate at a spin speed of 4000 rpm for 30 s. The samples were annealed in nitrogen atmosphere for 30 min at  $150^\circ\text{C}$ . Chlorobenzene solutions of OU-017 and OU-025 (1.5%, w/v) were spin-coated on ITO glass substrates at a spin speed of 3000 rpm for 30 s to get a 40 nm thick of hole-transporting layers (HTL). Then  $\text{Alq}_3$  was deposited onto the surface of the OU-017 and OU-025 films as emissive (EML) and electron-transporting layer (ETL) with a thickness of 20 nm. Finally the Al cathode (100 nm) with an ultra thin LiF layer (0.5 nm) was vapor deposited. 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 characteristics. The electroluminescence (EL) and luminance properties were measured using Spectrascan PR-655 spectroradiometer.



**PEDOT:PSS**



**Alq<sub>3</sub>**

Figure 3. The structure of OLED device

## RESULTS

In order to investigate their hole-transporting property, OLED devices of ITO/PEDOT:PSS/HTL/Alq<sub>3</sub>/LiF:Al were fabricated using OU-017 and OU-025 as the hole-transporting layer (HTL), Alq<sub>3</sub> as the light-emitting and electron-transporting layers, indium tin oxide (ITO) as the anode and LiF:Al as the cathode. Fig.6 shows voltage-current ( $I$ - $V$ ) characteristics of the the ITO/PEDOT:PSS(50 nm)/OU-017(40 nm)/Alq<sub>3</sub> (20 nm)/LiF:Al (0,5 nm:100 nm) and ITO/PEDOT:PSS(50 nm)/OU-025 (40 nm)/Alq<sub>3</sub> (20 nm)/LiF:Al (0,5 nm:100 nm) devices.

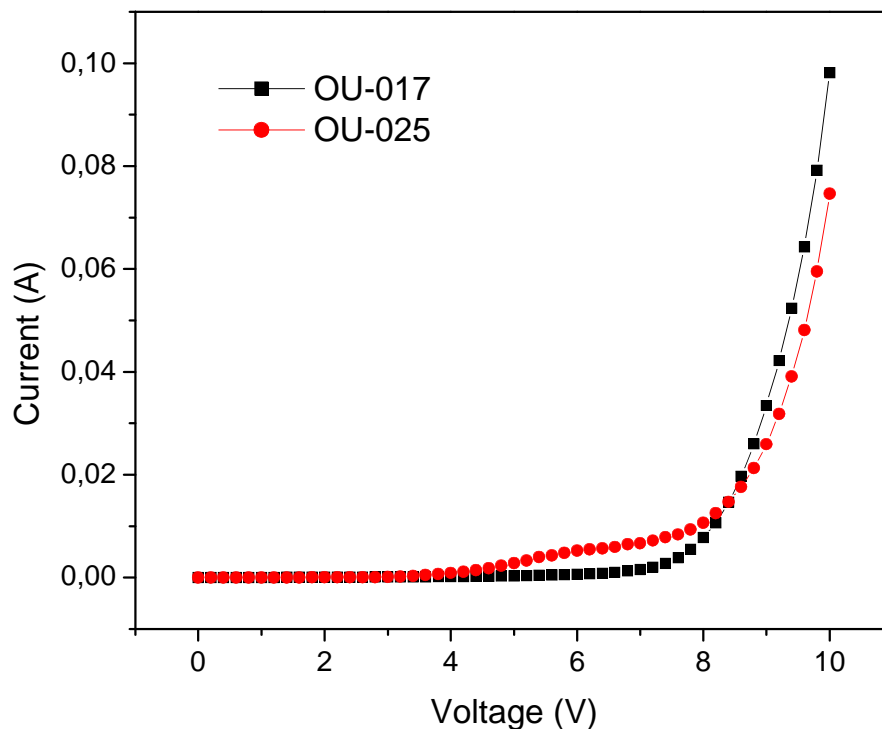


Figure 4.  $I$ - $V$  characteristics of the ITO/PEDOT:PSS(50 nm)/OU-017(40 nm)/Alq<sub>3</sub> (20 nm)/LiF:Al (0,5 nm:100 nm) and ITO/PEDOT:PSS(50 nm)/OU-025 (40 nm)/Alq<sub>3</sub> (20 nm)/LiF:Al (0,5 nm:100 nm) devices.

When a bias potential was applied to the electrodes, the ITO/ PEDOT:PSS(50 nm)/ OU-017(40 nm)/Alq<sub>3</sub> (20 nm)/LiF (0.5 nm)/Al (100 nm) and ITO/ PEDOT:PSS(50 nm)/ OU-025(40 nm)/Alq<sub>3</sub> (20 nm)/LiF (0.5 nm)/Al (100 nm) devices emitted a bright green luminescence with emission maxima at 516 nm, . The electroluminescence (EL) spectrum of the devices are shown in Fig.7.



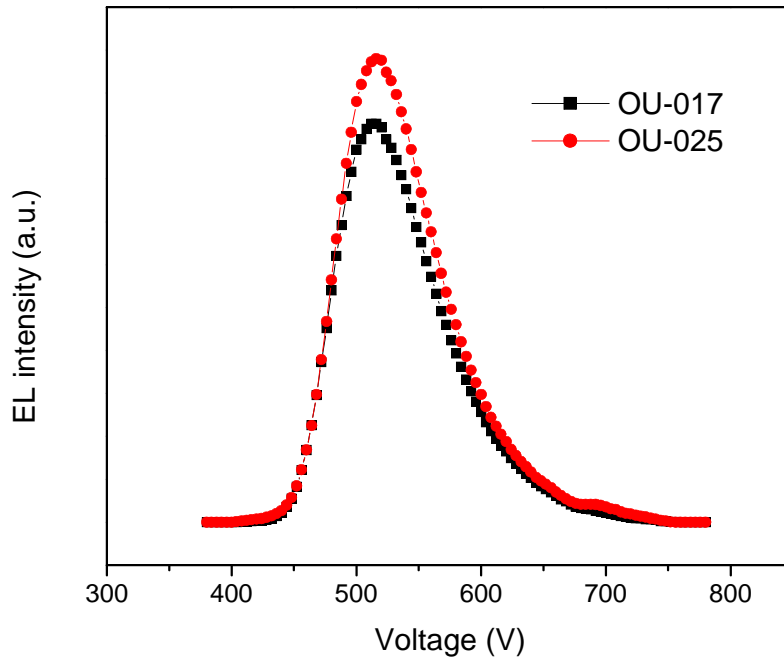


Figure 5. EL spectrum of the ITO/PEDOT:PSS(50 nm)/OU-017 (40 nm)/Alq<sub>3</sub> (20 nm)/LiF:Al (0,5 nm:100 nm) and ITO/PEDOT:PSS(50 nm)/OU-025 (40 nm)/Alq<sub>3</sub> (20 nm)/LiF:Al (0,5 nm:100 nm) devices.

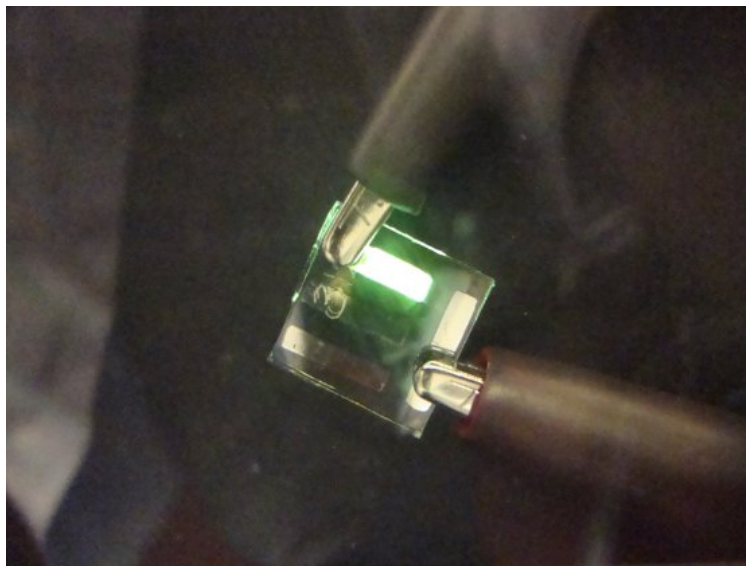


Figure 6. The picture of ITO/PEDOT(50 nm)/OU-025 (40 nm)/Alq<sub>3</sub> (20 nm)/LiF:Al (0,5 nm:100 nm) device

## CONCLUSION

We investigated the EL properties of OU-017 and OU-025 as a hole-transporting layer. The ITO/PEDOT(50 nm)/OU-017(40 nm)/Alq<sub>3</sub> (20 nm)/LiF:Al (0,5 nm:100 nm) device showed a bright green emission of 19820 cd/m<sup>2</sup> at 10V, the device ITO/PEDOT(50 nm)/OU-025(40 nm)/Alq<sub>3</sub> (20 nm)/LiF:Al (0,5 nm:100 nm) also showed green emission of 23120 cd/m<sup>2</sup> at 10V.

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