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CYCLIC VOLTAMMETRY FOR ENERGY LEVELS ESTIMATION OF ORGANIC MATERIALS

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In this article we present the cyclic voltammetry investigation and optical properties of some compounds that have been used for the first time in photovoltaic applications. Oxidation and reduction of all compounds were measured under the same experimental conditions to estimate both the energy of the highest occupied molecular orbital (HOMO) and the energy of lowest unoccupied molecular orbital (LUMO). Optical band gap for each compound was measured from the absorption spectra of each organic compound.

Keywords: HOMO, LUMO, cyclic voltametry, bang gap, organic compounds

1. Introduction

Cyclic voltammetry is a very suitable method for a wide range of applications. Moreover, in some areas of research, cyclic voltammetry is one of the standard techniques used for characterization.

Discovering new organic materials with unique properties such as polymers and small molecules, opens up a new approach for fabricating organic photovoltaic devices rather than conventional inorganic, silicon devices. In the past three decades, organic solar cells have become an interesting field of research due to their potential for low-cost, flexibility and lightweight properties. Such devices based on organic semiconductors have also been a dynamic area of research in the past twenty years, and have recently evolved to the stage of commercialization [1].

The focus of our research is to study biodegradable organic semiconductors in order to develop biodegradable organic photovoltaic devices. For this, we chose natural and nature-based dyes that, from our knowledge, have never been tried for this type of application.

The first step in device fabrication is to select the appropriate materials for the active semiconducting layer, the most important component of the entire

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device because it is the place where charge generation, separation and transfer, take place under illumination of light. For a bilayer organic solar cell configuration, efficient exciton dissociation takes place at the donor/acceptor interface [2,3]. In this process, electron transfer from the donor to the acceptor requires that the lowest unoccupied molecular orbital (LUMO) level of the donor is above that of the acceptor, and hole transfer from the acceptor to donor requires that the highest occupied molecular orbital (HOMO) level of the donor is above that of the acceptor, in order to fulfill the energy requirements and thus to generate the photo-current. This is why, when choosing a new material for such applications, it is important to know the energy levels of HOMO, LUMO and the band gap between them.

One of the most useful methods to characterize the organic materials and estimate the energy band diagram is cyclic voltammetry [4,13,14].

For organic semiconductors, HOMO represents the energy required to extract an electron from a molecule, which is an *oxidation* process, and LUMO is the energy necessary to inject an electron to a molecule, thus implying a *reduction* process [5]. These processes can be measured using cyclic voltammetry method by measuring the redox potentials E_{red} and E_{ox}. Ferrocence is used as a known reference to calculate the energy of the HOMO and LUMO levels**,** including the ferrocene value of -4.4 eV**.** The energy levels were calculated using the following empirical Bredas *et all* [6] equations:

$$E\ (HOMO) = -e\ [E_{ox}^{onset} + 4.4], \qquad (1)$$

$$E\ (LUMO) = -e\ [E_{red}^{onset} + 4.4] \qquad (2)$$

In organic molecules, the energy levels of the electronic states correspond to the energy carried by UV or visible radiation. At resonance, the molecules can absorb quantified energy transported by the electromagnetic radiation, and promote an electron from the low-energy molecular orbital to higher energy molecular orbital [7]. These transitions can be measured using a UV-Vis spectrophotometer. E_{opt} corresponds to the energy of the long wavelength edge of the exciton absorption band [8]. The longest absorption wavelength λ_{onset} is used to calculate the optical gap energy, E_g, according to the equation [9]:

$$E_g = 1242/\lambda_{onset} \qquad (3)$$

Coupling these two methods, we can estimate if two materials can work together in the donor-acceptor system.

In this paper, we investigated indigo and one of its derivative cibalackrot and two vat dyes: yellow 1 and orange 3, by cyclic voltammetry and UV-Vis spectroscopy to determine their energy levels.

The chemical structures of the investigated molecules are shown in Fig. 1.

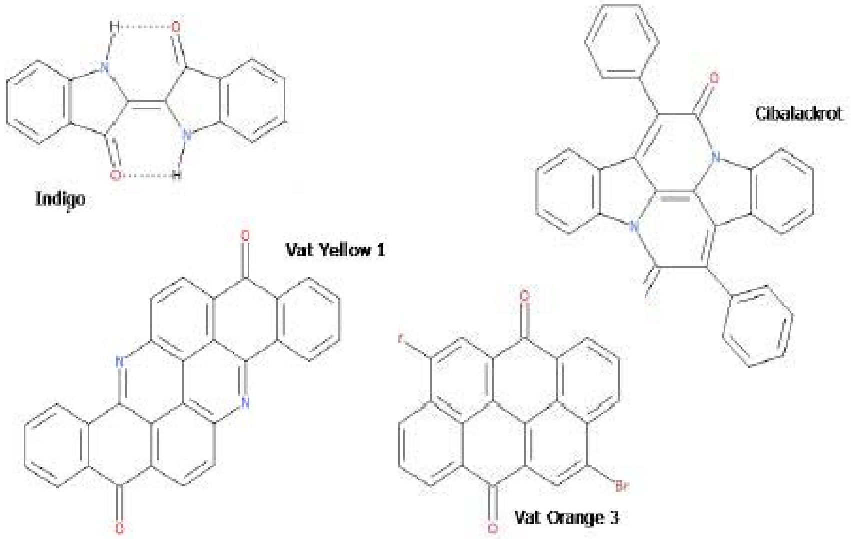

Fig. 1. Molecular structures of the compounds evaluated in this work: indigo, cibalackrot, vat yellow 1 and vat orange 3

2. Experimental

Indigo, vat yellow 1, vat orange 3 were purchased from Aldrich and purified several times by vacuum gradient sublimation. Cibalackrot was obtained from the Department of Biochemistry, University of Bayreuth, Germany. For each compound, slides of 3 x 1 cm were prepared. Each compound was deposited as a thin layer of approximately 40 nm by vacuum thermal evaporation at slow rates, less than 1 nm/sec, on glass/ITO substrates. The glass/ITO slides were cleaned with detergent, rinsed with distilled water, followed by base piranha solution at 70^oC for 15 min and then rinsed again in pure water. These slides containing the thin layer of organic compound were used as the working electrode; Ag/AgCl couple and platinium plate were reference electrode and auxiliary electrode, respectively. CV experiments were performed at a scan rate of 20 mV/s at room temperature under nitrogen. The setup is computer controlled consisting of a potentiostat VoltaLab 40. As electrolite a solution of 0.1M of tetrabutylammonium phosphorus hexafluoride (*TBAPF6*) in anhydrous acetonitrile (CH_3CN) solution was used.

As for obtaining UV-Vis absorption data, we prepared clean glass substratets on which the compound was thermally evaporated as a thin layer of approximately 40 nm. Absorption spectra were acquired at room temperature using a UV-Vis Cary (Agilent Technologies) spectrophotometer.

2. Results and discussions

On cyclo voltammograms regarding indigo behaviour, a reversible two-electron reduction is observed, with an onset of approx. –1.1 V and 0.6 V followed by a large increase after 1 V with respect to Ag/AgCl (Fig. 2).

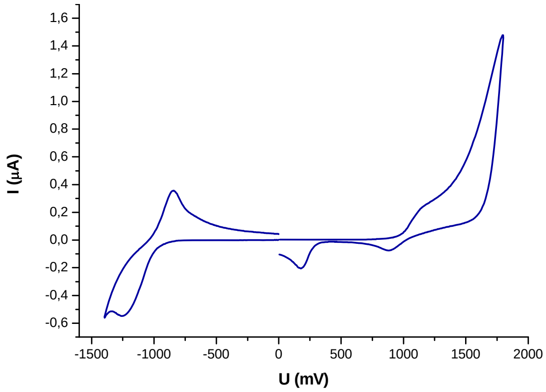

Fig 2. Cyclic voltammetry curve for indigo

From the CV curve, we estimated the bandgap to be 1.7 eV, in agreement with the bandgap estimated from the onset of optical absorption, 1.7 eV. The reversible oxidation and reduction of indigo suggest ambipolar charge transport, while the low bandgap implies the possibility of efficient injection of both carriers from the same metal electrode.

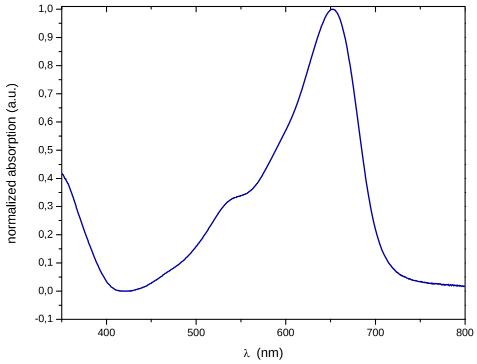

Fig 3. Optical absorption curve for indigo

The shape of CV curve of Cibalackrot (Fig. 4) is very similar to that of indigo, except with a wider band gap, which was calculated at 2.5 eV. The onset of reduction appeared at 0.9 V, which means a LUMO level at -3.5 eV, and the oxidation onset at -1.2 V, leading to a HOMO level calculated at -5.6 eV.

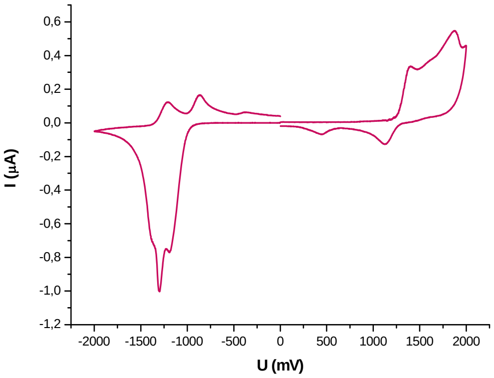

Fig 4. Cyclic voltammetry curve for cibalackrot

Indigoids have common the reversible electrochemical behavior due to reduction of ketone groups and oxidation of amines [10-12].

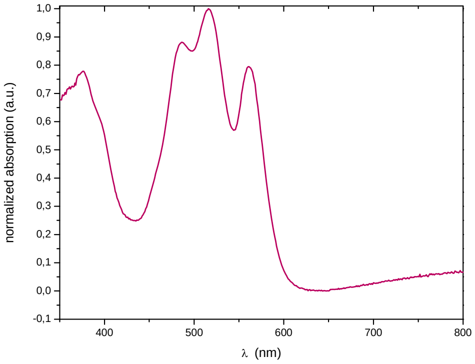

Fig 5. Optical absorption curve for cibalackrot

Vat yellow 1 cyclic voltammetry measurements, show a LUMO level of -3.6 eV and a HOMO energy level of -6.3 eV, which indicates a high potential for oxidation. Vat orange 3 revealed a HOMO energy level of -6.2 eV and a LUMO energy level of -3.8 eV, similar to vat yellow 1.

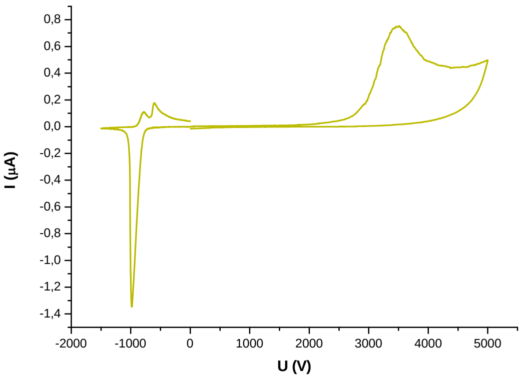

Fig 6. Cyclic voltammetry curve for vat yellow 1

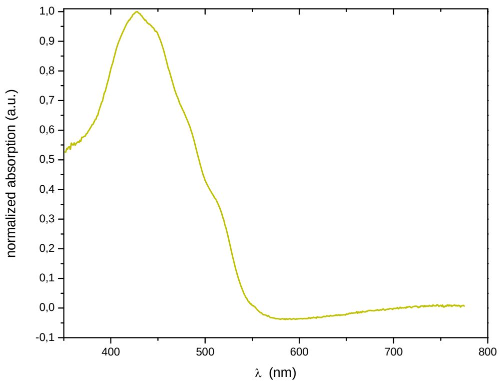

Fig 7. Optical absorption curve for vat yellow 1

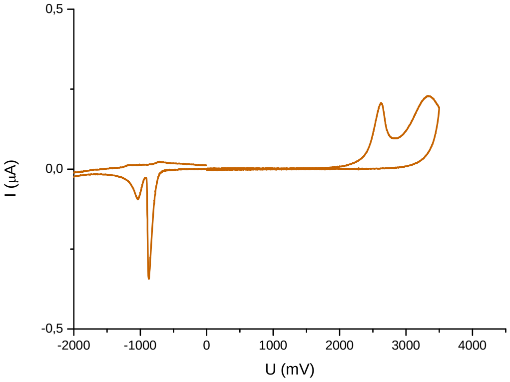

Fig 8. Cyclic voltammetry curve for vat orange 3

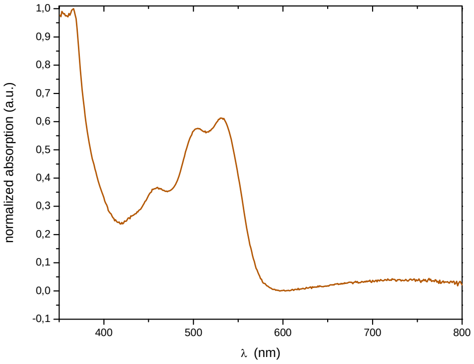

Fig 9. Optical absorption curve for orange 3

Optical absorption and cyclic voltammetry measurements revealed that both yellow 1 and orange 3 compounds are wide-band gap semiconductors with high electron affinity (LUMO level ~ -3.6 to -3.8 eV) and high positive oxidation potential. These properties indicate these two compounds as good candidates as acceptor materials for organic heterojunction solar cells.

The HOMO and LUMO levels approximated from CV as well as the band gap (optical and the one obtained from CV) are shown in table 1.

Table 1

Energy levels for indigo, cibalackrot, vat yellow 1 and vat orange 3

Compound	**E_{ox}^{onset} vs. Ag/AgCl (V)**	**HOMO level (eV)**	**E_{red}^{onset} vs. Ag/AgCl (V)**	**LUMO level (eV)**	**E_g [from CV (eV)]**	**Optical E_g (eV)**
Indigo	-1.1	-5.5	0.6	-3.8	1.7	1.7
Cibalackrot	-1.2	-5.6	0.9	-3.5	2.5	2.0
Vat yellow 1	-1.9	-6.3	0.8	-3.6	2.7	2.3
Vat orange 3	-1.8	-6.2	0.6	-3.8	2.4	2.1

4. Conclusions

Four organic dyes were studied, for photovoltaic applications. Cyclic voltammetry measurements were performed for each of these compounds to estimate their energy levels. Indigo and cibalackrot compounds revealed ambipolar behavior, which indicated their ability to transport both type of charge, positive and negative. Yellow 1 and orange 3 compounds present high electron affinity, which suggest they are good candidates as acceptor compounds for organic heterojunction solar cells.

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