PHOTOVOLTAIC PROPERTIES OF FUNCTIONALIZED INDODICARBOCYANINE DYE

Ibrayev N.Kh.[1*], Seliverstova E.V.[1], Omarova G.S.[1], Ishchenko A.A.[2], Derevyanko N.A.[2], Khamza T.[3]

[1*]Institute of Molecular Nanophotonics, Buketov Karaganda University, Karaganda, Kazakhstan, niazibrayev@mail.ru
[2]Institute of Organic Chemistry, NAS of Ukraine, Kyiv, Ukraine
[3]Nazarbayev Intellectual School of Karaganda, Kazakhstan

The effect of the chemical structure of polymethine dyes on their spectral-luminescent and photovoltaic properties has been studied. It has been shown that the introduction of hydroxyl functional groups into the dye structure leads to a bathochromic shift of the absorption and fluorescence bands. During the adsorption of dyes on the surface of titanium dioxide, a shift of their spectra to the red wavelength region was recorded with a simultaneous broadening of the bands caused by dye aggregation on the semiconductor surface. A decrease in the lifetimes of the excited state of molecules by 64 and 30% was registered for dyes 1 and 2, respectively. Quenching of the fluorescence lifetimes of adsorbed molecules is the result of electron transfer from the dye to the semiconductor. Measurements of the photovoltaic parameters of the studied dye-sensitized solar cells showed a higher efficiency for the functionalized dye, which is associated with better adsorption of this compound on TiO_2.

Keywords: polymethine dyes; functional groups; optical properties; photovoltaics; dye-sensitized solar cells.

Introduction

Currently, the search and active using of new alternative energy sources in many developed countries of the world are accepted as vital, strategically necessary resources. In this regard, active development of photovoltaic cells is carrying out. Solar cells with using of organic dyes, despite their low efficiency, are a good alternative to semiconductor solar panels, since their production is more environmentally friendly and does not require complex technology. The main component of a dye-sensitized solar cell (DSSC) is a semiconductor electrode with adsorbed dye molecules. The most popular and chemically stable sensitizers for DSSC are organometallic chromophores and complexes with rare earth elements [1, 2]. However, their synthesis is a laborious and rather expensive task. In this regard, many groups are developing organic molecules-sensitizers for DSSC.

The aim of the present work is studying if the effect of functional groups in the structure of a polymethine dye on its spectral-luminescent and photovoltaic properties. The choice of these dyes is due to the fact that among organic chromophores they have the largest range of changes in photophysical [3] and nonlinear optical properties, due to which they are widely used in organic photovoltaics [3–6], laser technology [7–10], and nonlinear optics [11-13], information technologies [14, 15], in biology and medicine [16, 17]. Among the important properties of polymethine dyes, their extremely high extinction coefficients having to be highlighted [3]. In this regard, polymethine dyes are a promising class of sensitizers for solar cells. To date, it has been shown that the adsorption of polymethine dyes on TiO_2 leads to an expansion of the efficiency of light harvesting of the cell's working electrode to the red region of the spectrum [18–23]. This increases the conversion efficiency of light into electrical energy. A factor contributing to an increase in the adsorption efficiency of polymethine dyes on the surface of a semiconductor is the "anchor" groups in the structure of the dye.

1. Experiment

Cationic indodicarbocyanine dyes (IPD) were chosen as the objects of study, the structural formulas of which are shown in Fig. 1. IPD 1 with hydroxyl groups is an analog of IPD 2 dye. The main spectral-luminescent and photovoltaic properties of IPD dye are detailed in [5, 24].

The absorption and fluorescence spectra of the dyes were measured on a Cary-300 and Eclipse spectrometer (Agilent Techn.). The lifetimes of the excited state of the dye molecules were measured with using of a pulsed spectrofluorimeter with picosecond resolution and recording in the time-correlated photon counting mode (Becker&Hickl, Germany) [25, 26].
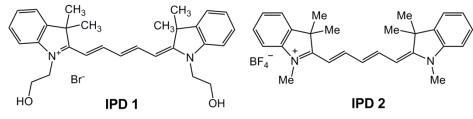

Fig. 1. Structure of IPD 1 and 2

Glass plates coated with FTO (surface resistivity ~7 Ω/sq, Sigma Aldrich) were used to prepare and assemble solar cells. A nanometer blocking layer of TiO_2 was deposited on the FTO surface. Pastes from TiO_2 nanoparticles (Sigma-Aldrich, d~21 nm) were prepared according to the procedures of [4–6, 27]. TiO_2 pastes were deposited onto the surface of a conductive glass by the doctor-blading method. The films were left to relax in air for 3 minutes, dried at 125 ºC for 6 minutes, and annealed stepwise (with a step of 175 ºC) in the temperature range from 175 to 500 ºC.

Ethanol solutions with dye concentration equal to 10^{-4} mol/L were used for the sorption. For this purpose, porous semiconductor films were placed into dye solution for the 24 h. After that, the films were dried in an oven (T=70°C) for 30 minutes. The sorption of the dye into the pores and the estimation of its concentration were controlled by the methods of absorption spectroscopy. The platinum electrodes were prepared separately on the FTO surface. Platinum was deposited with electrochemical method from an ethanol solution of H_2PtCl_6 (Sigma Aldrcih). At the final stage, the cells were assembled according to the standard procedure [27].

The current-voltage characteristics (CVC) of solar cells were measured under illumination by Xe lamp with a light power of 100 mW/cm^2 on a CT50AAA Cell Tester measuring complex (Photo Emission Tech.). The measurements were carried out in the photovoltaic mode at room temperature. The parameters of the DSSC as the open circuit voltage (V_{oc}), the short circuit current density (J_{sc}), the fill factor (FF), and the efficiency (η) of the cell were determined from the CVCs.

2. Results and discussion

The absorption and fluorescence spectra of IPD 1 dye measured in ethanol solution are shown in the Fig. 2a. The absorption bands of IPD 1 and 2 are located in the wavelength range of 500–700 nm. The absorption spectrum maximum of the IPD 1 dye exhibits at 645 nm (Table 1) with a shoulder at ~600 nm. For the parent dye IPD2, the band maximum is hypsochromically shifted by 10 nm and exhibits at 635 nm with a shoulder at $^a\lambda_{2\,max}$=595 nm. At the same time, it should be noted that the extinction coefficient of IPD 1 dye have the close values as for IPD 2 dye [5].

Table 1. Spectral and luminescent properties of IPD 1 and 2 in ethanol solutions (C=10^{-5} mol/L)

Dye	$^a\lambda_{1\,max}$ (nm)	$^a\lambda_{2\,max}$ (nm)	$\Delta^a\lambda_{1/2}$ (nm)	$^f\lambda_{1max}$ (nm)	$^f\lambda_{2max}$ (nm)	$\Delta\lambda^f_{1/2}$ (nm)
IPD 1	645	600	45	670	720	35
IPD 2	635	595	45	655	715	31

Photoexcitation of the emission spectra of dye solutions was carried out both from the short-wavelength (λ_{exc}=590 nm) and long-wavelength side (λ_{exc}=630 nm) of the absorption spectrum of luminophores. The highest dye fluorescence intensity was recorded upon excitation at 630 nm. As in the absorption spectra, the short-wavelength shoulder in the region of 715 – 720 nm is mirrored in the fluorescence spectra. The maximum of the fluorescence spectrum of the dyes IPD 1 and IPD 2 was registered at 670 and 655 nm, respectively. Thus, it has been established that functional groups have practically no effect on the spectral and luminescent characteristics of the IPD 1 dye. However, they play an important role in the adsorption of dyes on semiconductor films.
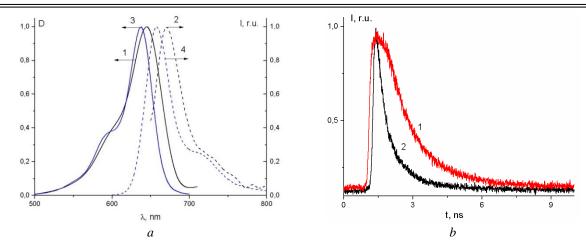
Fig.2. (a) Absorption (1, 3) and fluorescence (2, 4) spectra of dyes 1 (1, 2) and 2 (3, 4) in ethanol (C=10^{-5} mol/L); (b) fluorescence decay kinetics of dye 1 in ethanol solution (1) and on TiO$_2$ film (2), λ_{exc}=488 nm

Since the sensitization of the active electrodes of the Grätzel cells occurs by the adsorption of dyes from solutions, it was interesting to find out what spectral changes would occur in the absorption and fluorescence spectra of the dyes on the surface semiconductor films.

For this purpose, TiO$_2$ films were prepared on nonluminescent quartz substrates by the doctor-blading method. The measurements showed (Table 2) that a bathochromic shift of the absorption and fluorescence bands of both dyes occurs on the surface of the porous films. At the same time, the absorption and fluorescence band of the dyes were deformed, which is expressed in the broadening of the spectra, as well as the virtual absence of a shoulder in both the absorption and fluorescence spectra of the dye.

Table 2. Spectral-luminescent parameters of IPD 1 and 2 adsorbed on the surface of TiO$_2$ films

Dye	$^a\lambda_{1\,max}$ (nm)	$\Delta^a\lambda_{1/2}$ (nm)	$^f\lambda_{1max}$(nm)	$\Delta\lambda^f_{1/2}$ (nm)	τ_f (ns)	$\tau_f/\tau_f^{solution}$
IPD 1	648	128	672	132	0.40	0.36
IPD 2	646	125	663	130	0.65	0.70

Measurements of the fluorescence decay kinetics of dyes on TiO$_2$ films have shown that the lifetime of the excited state of the dye was reduced by 64 and 30% for IPD 1 and 2, respectively (Fig. 2b). The quenching of the fluorescence lifetime of adsorbed dyes is the result of the electron transfer from the dye to semiconductor when colored films were irradiated with visible light [22, 25]. This effect is more pronounced for IPD 1.

The higher efficiency of electron transfer was confirmed by data on the photovoltaic characteristics of solar cells, sensitized with dye 1 or 2 (Table 3).

Table 3. Photovoltaic parameters of DSSC, sensitized with IPD 1 and 2

Dye	J_{sc} (mA/cm^2)	V_{oc}(mV)	FF	η(%)
IPD 1	0.46	272.0	0.30	0.037
IPD 2	0.11	375.0	0.15	0.006

It can be seen that the cell with the IPD 1 has better photovoltaic parameters compared to the IPD 2, despite the fact that the open-circuit voltage Voc for the IPD 2 is higher. This can be explained by the fact that the presence of functional groups in the IPD 1 dye molecule leads to an almost 4-fold increase in the J_{sc} value compared to IPD 2. This parameter directly depends on the number of charge carriers transferred from the dye to the semiconductor [28, 29]. That is, the process of charge-carriers generation in the cell is more efficient due to the presence of anchor groups in the structure of the dye 1. In addition, this assumption was confirmed by the change in the optical density of dye solutions before and after their adsorption on the surface of the TiO$_2$ films. As the estimation of the number of adsorbed molecules (N) on the cell surface showed, N=2.5·10^{16} for IPD 1 and N=1.7·10^{16} for IPD 2.

Conclusion

Thus, the measurements showed that the introduction of functional groups into the structure of the indodicarbocyanine dye molecule leads to a bathochromic shift of its absorption and fluorescence bands. During the adsorption of the studied dyes, a shift of their spectra towards red wavelengths was recorded. At the same time, the absorption and fluorescence bands of the dyes were broaded, as well as the shoulder in both the absorption and fluorescence bands of the dye the virtual was absent. This is accompanied by a decrease in the lifetime of the excited state of the dye by 64 and 30% for IPD 1 and 2, correspondingly. The quenching of the fluorescence lifetimes of adsorbed dyes is the result of electron transfer from the lower unoccupied molecular orbital of the dye to the conduction band of the semiconductor upon irradiation of the films with visible light. On the basis of the photovoltaic parameters, it can be concluded that the presence of functional groups in the dye molecule leads to an increase in the efficiency of the photovoltaic characteristics of solar cells sensitized with organic dyes.

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