

The influence of the distance between the donor-acceptor groups of polymethine dyes on their photovoltaic properties

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Abstract. Spectral-luminescent and photovoltaic properties of polymethine dyes of various structures are studied. It is shown that an increase in the length of the methylene chain between the active chromophores leads to a red-wave shift of the absorption and fluorescence spectra. Significant changes in the absorptivity and lifetime of fluorescence do not occur in this case. The best photovoltaic parameters have cells sensitized with shorter dye molecules. It is shown, that for a longer dye the resistance associated with electron recombination on the TiO₂/electrolyte surface is much higher than the electron transfer resistance in the semiconductor, which reduces the efficiency of electron transfer in the solar cell, sensitized with longer dye molecules.

1. Introduction

About solar cells sensitized with organic dyes (DSSC) usually mentioned as an alternative to solar batteries based on inorganic semiconductors. DSSCs are less expensive and harmless than inorganic semiconductors. Despite the potentially high quantum efficiency, solar cells based on organic dyes have a number of drawbacks that prevent the commencement of large-scale industrial production of such solar cells. Their main drawback is the low efficiency of conversion of solar energy, which, usually, does not exceed of 7 – 13% [1, 2]. For effective operation of an organic solar cell, a strong absorption of light by the working layer, an optimal difference in the energy levels of the donor and acceptor of the charge carriers, sufficient mobility of electrons (holes) in the acceptor (donor) phase and ohmic contacts of the acceptor (donor) with the cathode (anode) are necessary. As was shown in [3, 4], polymethine dyes have extremely high extinction coefficients. The possibility of reconstructing the absorption spectra in the entire visible and near infrared region makes polymethine dyes a perspective object for use in solar cells.

Because of their unique optical properties, polymethines are used in nonlinear optics, in recording and storage devices, like fluorescent probes in biomolecules or as contrast agents in optical images of tissues. Oxidation-reduction properties of polymethine dyes have also been studied from the point of view of their role as a sensitizer or desensitizer for silver halides. A wide spectrum of oxidation-reduction potentials allows polymethines to act both as electron donors and as electron acceptors in photoinduced electron transfer processes [4]. A literary review in the field of cells based on polymethine dyes shows that the efficiency of dyes of this class varies in a wide range from 2 to 7% with a current density more than 21 mA/cm² [5]. The dyes with functional groups (SO₃, -COOH, -



OH), which promote more effective adsorption of the dye on the semiconductor surface, have the highest photovoltaic parameters [6].

In this paper, the results of a study on the influence of the structure of polymethine dyes on their spectral-luminescent and photovoltaic properties are presented.

2. Experiment

The dyes with different lengths of polymethine chain between the terminal donor-acceptor groups were chosen as the object of the study and shown in Figure 1. Dye absorption and fluorescence spectra were measured on a Cary-300 (Agilent) spectrophotometer. The lifetimes of the excited state of the dye molecules were measured using a pulsed spectrofluorimeter with a picosecond resolution and registration in a time-correlated photon count mode (Becker&Hickl, Germany). The fluorescence quantum yields (ϕ_f) of the dyes were measured relative to the standards – ethanol solutions of methylene blue ($\phi_f = 0.01$) and oxazine 17 ($\phi_f = 0.70$).



Figure 1. Structure of dyes.

The preparation and assembling of solar cells was carried out according to the procedure detailed in [7, 8]. To prepare of solar cells, glass substrates coated with a FTO layer (Sigma-Aldrich, surface resistance of $\sim 10 \text{ Ohm/sq}$) were used. Blocking layer of TiO_2 was deposited on the surface of the FTO. Semiconductor films were prepared by the doctor-blading method. To prepare the films, TiO_2 with a nanoparticle size of 25 nm was used (Sigma-Aldrich). The thickness of the resulting films was measured by the SEM (Tescan Mira-3) and was equal to 10 – 12 microns. Sensitization of semiconductor electrodes with polymethine dye K1 or K2 was carried out by immersion of TiO_2 films in an ethanol dye solution with concentration equal to $4 \times 10^{-4} \text{ mol/l}$ for 20 hours. Before measurement, the films were kept in an oven at a temperature of 80°C for at least of 1 hour. The number of adsorbed dye molecules in all samples was controlled by the change in the optical density of the solutions before and after sorption.

The current-voltage characteristics of DSSC were measured with Solar Cell Tester CT50AAA (Photo Emission Tech. Inc., USA) under illumination of the Xe lamp with light intensity of 100 mW/cm^2 . The measurements were performed at room temperature in photovoltaic mode. From the obtained values of the open circuit voltage, short-circuit current, fill factor, efficiency of the cells were determined. Electric transport properties of solar cells were studied by measuring the impedance of an electrochemical cell. The measurements were carried out on an Z-500PRO impedance meter (Elins, Russia) under irradiation of cells with standard simulated solar radiation (Air Mass (AM) 1.5). For the analysis of the data obtained, the ZView 3.2b program and the equivalent solar cell circuitry (Figure 2), presented below, were used.

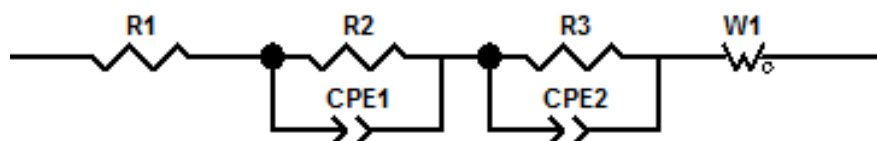


Figure 2. Equivalent solar cell circuitry.

3. Results

Measured absorption and fluorescence spectra and spectral-luminescent parameters of dyes in ethanol solutions are presented in Figure 3 and Table 1.

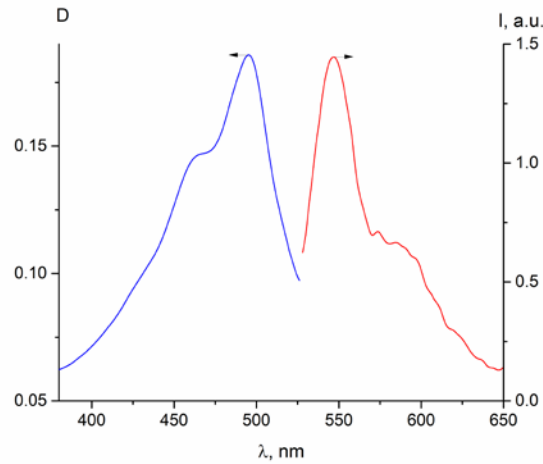


Figure 3. Absorption (a left) and fluorescence (at right) spectra of K1 dye in ethanol solution, $C_{\text{dye}}=10^{-5}$ mol/l

Table 1. Spectral parameters of K1 and K2 dyes.

Dye	K1	K2
$\lambda_{1 \text{ max}}^a$, nm	550	646
$\lambda_{2 \text{ max}}^a$, nm	520	598
$\Delta\lambda_{1/2}^a$, nm	54	42
$\epsilon \cdot 10^4$, l/mol cm	0,8	1,4
λ_{max}^f , nm	568	670
λ_{max}^f , nm	—	724
$\Delta\lambda_{1/2}^f$, nm	26	40
τ_f , ns	2.6	2.45
Φ_f	0.05	0.25

It can be seen from the Figure and the data that as the length of the polymethine chain increases, the absorption spectrum shifts to the red region of the spectrum. The extinction coefficient (ϵ) of the K2 dye is higher than that of K1, as the quantum yield of fluorescence.

The results of measurements of the I-V characteristics of the dyes are presented in Table 2.

Table 2. Photovoltaic parameters of solar cells sensitized with K1 and K2

Dye	J_{sc} , mA/cm ²	U_{oc} , mV	FF	η , %
K1	0.4575	378.5	0.264	0.11
K2	0.36	272.0	0.300	0.02

It can be seen that the dye K1 has better photovoltaic parameters, in comparison with K2, in spite of that the fill factor of the K2 dye is higher. This can be explained by the fact that the absorption spectrum of K2 is shifted to the region of red wavelengths. As is known, in this area the intensity of sunlight is lower than in the shorter-wave region (at green region of spectrum).

The electrotransport and amplitude-frequency characteristics of the prepared solar cells were investigated (Figure 4).

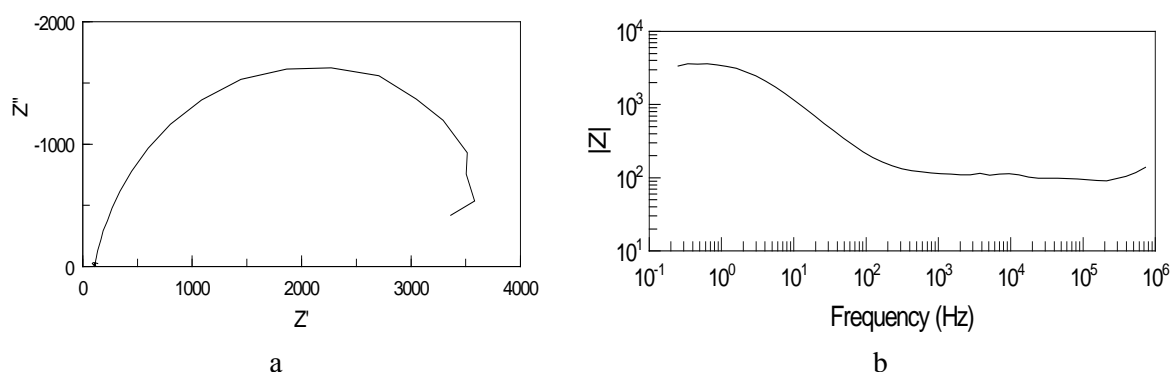


Figure 4. Impedance (a) and amplitude-frequency characteristics (b) of a solar cell sensitized by K1.

Table 3. The value of the elements of the DSSC circuit.

Dye	R_1 , mOhm	R_2 , Ohm	C_1 , μF	$\tau = R_2 \cdot C_1$, s
K1	106	3955	22.4	0.093
K2	392	4740	13.7	0.072

From Table 3 it is seen that the diffusion time of the charge carrier for the dye K2 is less than for K1. This, in turn, reduces the probability of electron transfer to a semiconductor film, which affects the magnitude of the current generated by the cell [9]. In addition, this parameter is affected by the value of the active resistance R_2 (in Figure 3 – parameter Z') and it is have the value of the order of several thousand Ohms. Hence, the resistance associated with the recombination of electrons on the TiO_2 /electrolyte surface is much higher than the resistance of electron transfer in a semiconductor [10]. This is the result of the fact that the lifetime of an electron is much higher than the time of electron transfer, and the diffusion length is greater than the thickness of the cell [11].

4. Summary

Thus, when studying the influence of the length of a polymethine chain between chromophores in a dye molecule, it was shown that the cells sensitized with dye molecules K1 possess the best photovoltaic parameters. This can be explained by the fact that the efficiency of absorption of sunlight in a dye with a long chain decreases, due to a shift in the absorption spectrum of the dye to the region of red wavelengths. In studying the electrophysical parameters of solar cells, it was shown that for K2 dye the resistance associated with electron recombination on the TiO_2 /electrolyte surface is much higher than the electron transfer resistance in the semiconductor, which reduces the electron transfer efficiency within the solar cell.

Acknowledgments

This work was performed at financial support of Ministry of Education and Science of the Republic of Kazakhstan.

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