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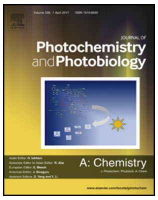

The effect of sulfonate groups on spectral-luminescent and photovoltaic properties of squarylium dyes

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ABSTRACT

Squarylium dye with sulfonate groups has been synthesized and its spectral-luminescent and photovoltaic properties have been studied in comparison with its non-functionalized analogue. It has been demonstrated that the introduction of sulfonate groups in the indolenine heterocycle of squarylium dyes results in the bathochromic shifts of the absorption and fluorescence band. In so doing, the fluorescence quantum efficiency and extinction coefficients of the dyes are virtually independent of the functional groups presence. A fluorescent quantum yield of dyes has been measured on the semiconductor and dielectric surface. It has been shown that the introduction of anchor sulfonate groups in the structure of the dye provides a more intimate contact with TiO_2 nanoparticles which increases the number of charge carriers transferred from the dye to the semiconductor. This phenomenon can be effectively used for the dye-sensitized solar cells (DSSC).

1. Introduction

Nowadays the interest in the dye-sensitized solar cells (DSSC) is growing. The main working component of such solar cell is a dye-sensitizer providing the absorption of solar radiation and the injection of charge carriers in a semiconductor layer. The urgent problem, therefore, the search of low-cost, effective, organic dyes as sensitizer for solar cells.

Squarylium dyes attracted the attention of researchers for their unique spectral-luminescent properties and high photo– and thermal stability [1–4]. They embody the most intense absorption in the visible and near infrared range spectrum among organic dyes [5,6]. Squaraines are promising target for DSSC cells, by virtue of zwitterionic structure ensuring efficient intramolecular charge transfer from the end heterocyclic groups to squarylium fragment. Efficiency of solar cells based on this class of dyes is in the range from 2 to 7% at a current density equal to 21 mA/cm^2 [7]. Where the highest parameters of solar cells possess dyes having the functional groups (SO_3, –COOH, –OH) that promotes more efficient adsorption of the dye on the semiconductor surface [7]. The highest efficiency is equal to 4.5% was obtained for the asymmetric squarylium dye [8].

The aim of present work is to study the spectral-luminescent and photovoltaic properties of new synthesized squarylium dye **1** with sulfonate groups in comparison with the non-functionalized analogue dye **2**.

2. Experiment

Structure of studied dyes **1** and **2** are presented in Fig. 1.

2.1. Synthesis of dye 1

Pyridin-1-ium 1-ethyl-2-((Z)-(3-(((E)-1-ethyl-3,3-dimethyl-5-sulfonatoindolin-2-ylidene)methyl)-2-oxido-4-oxocyclobut-2-en-1-ylidene)methyl)-3,3-dimethyl-3H-indol-1-ium-5-sulfonate (dye **1**).

A mixture of 0.267 g (0.001 mol) of 1-ethyl-2,3,3-trimethyl-*3H*-indol-1-ium-5-sulfonate (inner salt), 0.057 g (0.0005 mol) of squaric acid, 0.079 g (0.16 mL, 0.001 mol) of pyridine in 25 mL of *n*-butanol, and 15 mL of toluene was heated, with water collected in the Dean-Stark trap, for 6 h at 139–140 °C. Then the precipitate was filtered off, transferred into a vessel with acetonitrile and boiled for 5 min, followed by hot filtering and washing with

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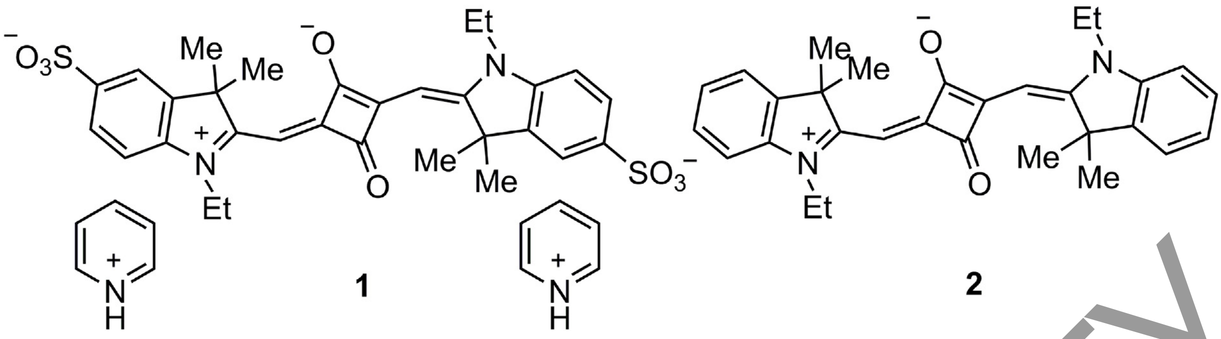

Fig. 1. Structure of dye **1** and **2**.

acetonitrile. The product was dried in a flask at 90 °C in vacuum at a residual pressure of 0.04 mm Hg for 1 h.

Yield 0.210 g (61%).

1-ethyl-2,3,3-trimethyl-*3H*-indol-1-ium-5-sulfonate (inner salt) and dye **2** were synthesized according to the procedure [9] and [10], correspondingly. Squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione, 99%), pyridine (anhydrous, 99.8%), *n*-butanol (ASC reagent ≥ 99.4%), toluene (ASC reagent, ≥ 99.5%), acetonitrile (ASC reagent ≥ 99.5%) were purchased from Sigma-Aldrich.

^{1}H NMR, δ, DMCO-d6: 1.275 (t, *J* = 6.6 Hz, 6H, CH_3-CH_2), 1.675 (s, 12H, (CH_3) 2C), 4.124 (q, *J* = 6.9 Hz, 4H, CH_3-CH_2), 5.812 (s, 2H, H-chain), 7.260 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.617 (d, *J* = 8.4 Hz, 2H, Ar-H), 7.676 (s, 2H, Ar-H), 8.052 (t, *J* = 6.8 Hz, 4H, Py), 8.577 (t, *J* = 7.2 Hz, 2H, Py), 8.916 (d, *J* = 5.1 Hz, 4H, Py).

Molecular Weight: 771.94.

Found% S 8.25; % N 7.44C_{40} $H_{43}N_4O_8S_2$. Calculated% S 8.31; % N 7.26.

2.2. Spectral-luminescent and photovoltaic measurements

The spectral-luminescent properties of dyes have been studied in ethanol, chloroform and dimethyl sulfoxide (DMSO) solutions and on the surface of TiO_2 films since the sensitization of active electrodes of solar cells occurs by adsorption of the dye from solution. Ethanol, chloroform and DMSO were purchased from Sigma-Aldrich. For spectroscopic measurements the concentration of dye in solution was equal to 10^{-5} mol/L. Semiconductor films of TiO_2 (Sigma-Aldrich) with a particle size of 25 nm were deposited onto glass substrates by doctor-blade method. Adsorption of dye was carried out by immersing of TiO_2 films in the ethanol dye solutions for 20 h. The film was placed in an oven at a temperature of 80 °C for at least of 1 h before measurements. The amount of adsorbed dye molecules was monitored by change in the optical density of the solutions before and after the sorption.

Absorption spectra of studied solutions and films were measured on Cary-300 spectrophotometer (Agilent). The fluorescent spectra were obtained on Cary Eclipse spectrofluorimeter (Agilent). The excited-state lifetime of the dyes was measured using a pulsed spectrofluorimeter with picosecond resolution with registration in time-correlated photon counting mode (Becker&-Hickl, Germany). The fluorescence quantum yield (φ_{fl}) of dyes was measured by absolute method with integration sphere (Avantes) as described in [11,12].

Solar cells were prepared and assembled according to procedure described in [13–15]. Glass substrates coated with conductive FTO layer were purchased from Sigma-Aldrich. The thickness of TiO_2 films was equal to 10–12 μm as was obtained from SEM (Tescan Mira) measurements. TiO_2 electrode was immersed into ethanol dye solution with concentration of $C = 10^{-4}$ mol/L and kept at room temperature for 24 h. The counter-electrodes were prepared on the FTO surface by electrolytic deposition of Pt from ethanol solution of H_2PtCl_6 (Sigma Aldrcih).

The current-voltage characteristics of DSSC were measured with Solar Cell Tester CT50AAA (Photo Emission Tech. Inc., USA) under illumination of the xenon lamp with light intensity of 100 mW/cm^2. The measurements were performed at room temperature in photovoltaic mode. To analysis the electrical impedance data, obtained on impedance meter Z-500PRO (Elins) was used the equivalent circuit scheme, presented on Fig. 2.

Quantum-chemical calculations of dyes were performed in Gaussian software (Gaussian 09W) by DFT/CAM-B3LYP method in the basis 6–31G(d,p). For an objective comparison of changes in the electron density in dyes **1** and **2** upon excitation, the total charge in the both chromophore was set equal to 0 to reflect their dominant intraionic character. The countercation in dye **2** was not taken into account in the calculations. Its role in neutralizing the negative charge on SO_3^-groups was compensated by setting them in the form of a neutral group – SO_3H.

3. Results and discussion

Analyze the energy of HOMO-LUMO orbitals was performed with the aim of to study the formation of electronically excited states of the dye molecules. The calculations have shown that for dye **1** HOMO orbital is located about −5 eV, and the energy of LUMO orbitals is equal to −2.98 eV. Energy of these orbitals is respectively equal to −4.98 eV and −2.80 eV for dye **2**. From the obtained data it is obvious squarylium dyes may act as an electron donor respect to TiO_2.

As measurements have shown, the absorption band of dyes **1** and **2** are located in the wavelengths range of 500–700 nm (Fig. 3) for ethanol solution. Absorption spectrum of the dye **1** exhibits the

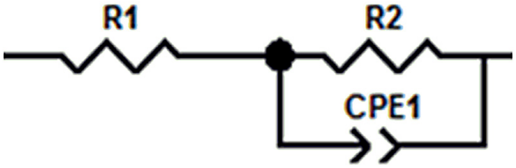

Fig. 2. Equivalent circuit scheme of solar cell used for estimation of timing parameters of charge carriers in TiO_2 films.

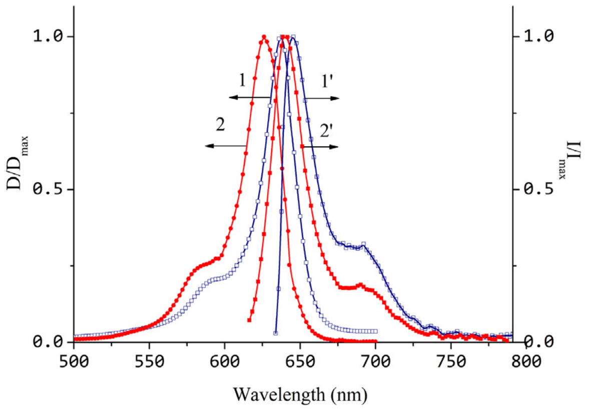

Fig. 3. Absorption (1,2) and fluorescence (1′,2′) spectra of ethanol solutions of dye **1** (1,1′) and **2** (2,2′).

Table 1
Spectral-luminescent parameters of dyes **1** and **2**.[a]

Medium	$^a\lambda_{max}$ (nm)	$^a\lambda_{shmax}$ (nm)	$\Delta\lambda^a_{1/2}$ (nm)	ε^a 10^{-4}. (L/M cm)	$^f\lambda_{max}$. (nm)	$^f\lambda_{shmax}$ (nm)	$\Delta\lambda^f_{1/2}$ (nm)	τ_f. (ns)	φ_f
Dye **1**									
Ethanol	638	590	24	15.5	648	703	25	1.4	0.08
Chloroform	650	600	26	26	658	705	29	2.0	0.08
DMSO	652	604	26	26	665	710	29	1.8	0.13
TiO_2	643	592	126	–	654	–	62	0.53	0.003
Dye **2**									
Ethanol	628	584	28	28.7	643	690	26	1.4	0.1
Chloroform	634	587	26	35	649	700	30	1.4	0.3
DMSO	642	595	27	12	651	700	29	1.3	0.2
TiO_2	635	590	124	–	650	–	75	1.2	0.09

[a] where: $^a\lambda_{max}$, $^f\lambda_{max}$ – maximum of the absorption and fluorescence spectra of dyes, correspondingly; $^a\lambda_{shmax}$, $^f\lambda_{shmax}$. – position of the shoulders of the absorption and fluorescence spectra of dyes; $\Delta\lambda^a_{1/2}$, $\Delta\lambda^f_{1/2}$ – half-width of the absorption and fluorescence spectra of dyes, correspondingly; τ_f. – the fluorescence life time; φ_f – quantum yield of dye.

maximum at 638 nm. This band is red shifted in comparison with the absorption spectrum of dye **2** (Table 1). The shortwave maximum at 590 nm exhibits as a shoulder of absorption spectrum of dye.

The registration of dyes fluorescence spectra was carried out under photoexcitation of solutions both at the maximum (λ_{ex} = 620 nm) and the short-wavelength shoulder (λ_{ex} = 570 nm) of the absorption band (Fig. 3). The highest intensity of dyes fluorescence was recorded under excitation at 620 nm. Measurements have shown that the fluorescence spectra of functionalized dye are shifted bathochromically relative to the fluorescence band of the original dye (Fig. 3). Thus, the maximum of fluorescence of dye **1** is located at wavelength equal to 645 nm, and for dye **2** – at 643 nm (Table 2) in ethanol solution. The fluorescence spectra are mirror symmetric relative to the absorption spectra.

The Table 2 shows the results of the vertical transitions energies, oscillator strengths and the corresponding transitions in dyes. As could be seen from obtained data the main absorption band of dye **1** at 529 nm is formed by transition between HOMO → LUMO molecular orbitals with the contribution of 70%. The contribution of electronic transitions between other molecular orbitals is less than 10%. Absorption of dye **2** in the visible region of spectrum occurs at 518 nm. It can be seen that the absorption of dye **1** is red-shifted compared to dye **2**, which is in agreement with experiment. The higher singlet states are weakly allowed. Molecular orbitals involved in the formation of the main optical transition are depicted in Fig. 4.

Referring to Fig. 4 it is observed that the both electron density of **1** and **2** molecules are distributed along the long axis of the chromophore enclosed between the nitrogen atoms. The excitation of the molecule is maintained with a change in this distribution (Fig. 5). The electron density increases on the odd carbon atoms of this chromophore (the first is the joint carbon atom of the heterocycle and chain). And electron density decreases on the even carbon atoms, as well as on the atoms of the squaraine fragment (on the C=O groups) and the nitrogen atoms of the heterocycles. It

Table 2
Calculated spectral and energy parameters of dyes **1** and **2**.

State	The wavelength of transition, nm	Energy of transition (eV)	Oscillator strength	Occupied molecular orbitals	Unoccupied molecular orbitals	% of contribution
Dye **1**						
1	529	2.34	1.57	HOMO	LUMO	70
Dye **2**						
1	518	2.39	1.46	HOMO	LUMO	69

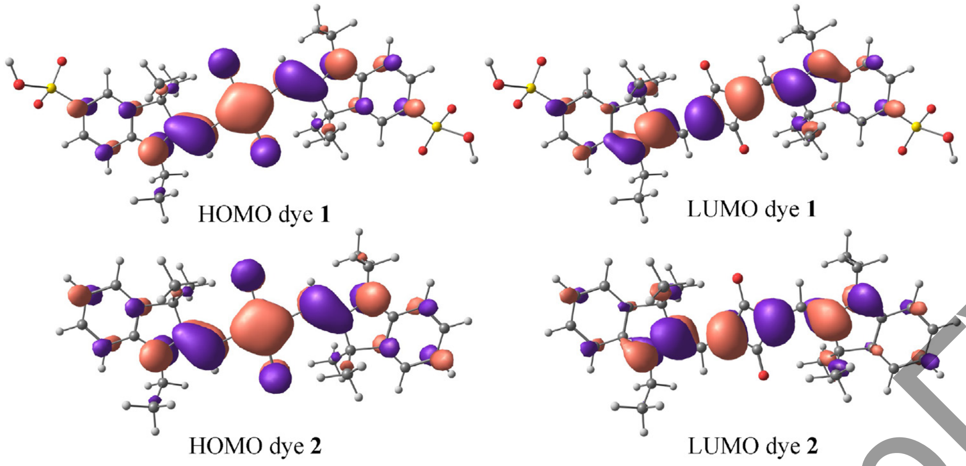

Fig. 4. Calculated distribution of electron density on molecular orbitals of dye **1** and **2.**

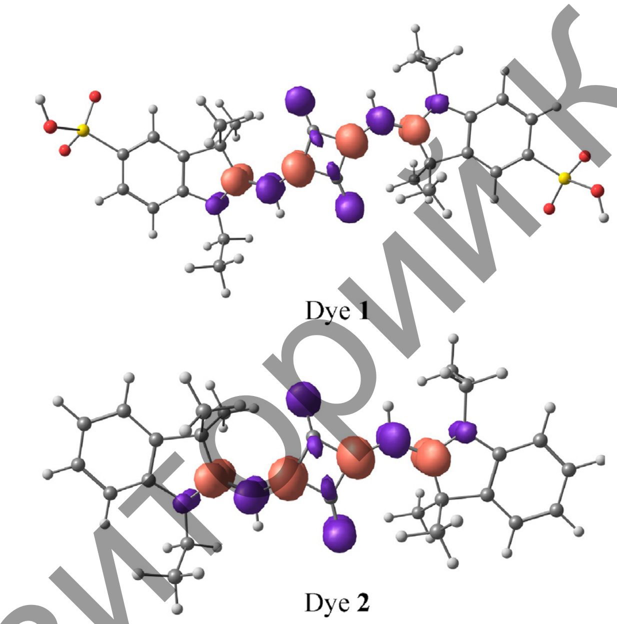

Fig. 5. Calculated change of electron density (blue color – decreasing, orange – increasing of electron density) of dye **1** and **2** upon excitation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

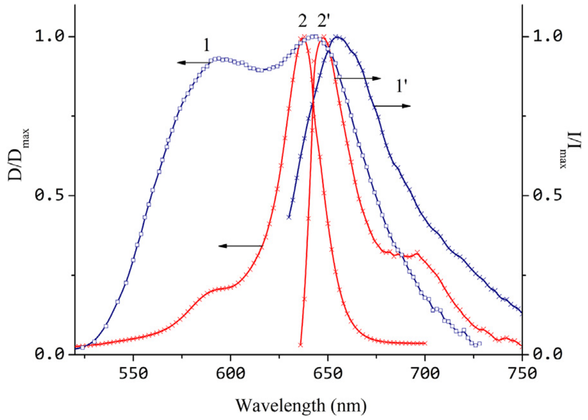

Fig. 6. Absorption (1, 2) and fluorescence (1′, 2′) spectra of adsorbed (1, 1′) and ethanol solution (2, 2′) of dye **1.**

is seen from Fig. 5 that the change in the electron density of dyes **1** and **2** upon excitation is not only similar, but also close in magnitude for the first electronic transition.

The data of calculations indicate that the experimental solvatochromic effects in both dyes should be practically identical upon a change in the polarity of the medium. Therefore we measure the absorption and fluorescence of dye **1** and **2** in a weakly polar (chloroform) and strongly polar solvent (DMSO). The choice of a low-polar solvent was limited by the solubility of the dye. The results are shown in Table 1.

It was found that increase in the solvent polarity from chloroform to DMSO results in the red shift of the absorption and fluorescence bands of dyes **1** and **2**. This effect is practically equal for the both dyes. This indicates that for the substituted dye **1**, as well as for the unsubstituted **2,** zwitterion structure dominates that is characteristic for the squaraine. This structure determines the proximity of their spectral-luminescent properties, including the changes in the solvent polarity. Such statement is in the agreement with the fact that the first electronic transition of both dyes is contributed by the transition from HOMO to LUMO orbitals (for dye **1** contribution is equal to 70% and for dye **2** – 69%).

Table 1 shows that the values of the fluorescence quantum yields (φ_f) and extinction coefficients (ε) of dyes **1** and **2** are close to each other.

Bathochromic shift of absorption band maximum is observed in the case of dyes adsorption on the porous surface of the semiconductor (Table 1, Fig. 6). The fluorescence spectra of dyes **1** and **2** on the surface of TiO_2 represent broad bands and red shifted by 5–7 nm relative to the emission spectrum in the ethanol solution. Both dyes in comparison to the absorption and fluorescence bands in ethanol solution have a considerable broadening.

The observed changes in the position of the absorption and fluorescent bands of dyes on the semiconductor surface are the result of strong dye-dye intermolecular interactions on the TiO_2 surface. As it was shown in [16] a change in dipole moment of dye molecule occurs under electronic excitation, which creates an imaginary dipole in a semiconductor. This dipole leads to the lowering of electron-excited state energy of the luminophore that is manifested as a red shift of the absorption band of the dye.

The formation of the charge transfer state [17] may be another explanation of the changes of adsorbed dyes absorption and fluorescence. During the deposition of dye molecules on semiconductor, dye molecules are adsorbed by the nanoparticles surface. Some of molecules that anchored via sulfonate groups to the semiconductor generate a charge transfer complexes. The formation of such band is known process for complex of organic dye – nanoparticles TiO_2 [18–21]. However, as it was shown by the results of spectral measurements and calculations, the formation of such a band for dye **1** is unlikely.

For estimating the efficiency of electron transfer from dyes **1** and **2** to the semiconductor surface have been taken the lifetime and the fluorescence quantum yield of dyes (φ_f) measurement in comparing with the values of these parameters for dielectric surface. To accomplish this, the solutions of dyes of equal volume and concentration (10^{-4} mol/L) were deposited onto surface of TiO_2 and silica (SiO_2, Silufol UV-254) films with equal area.

Table 4
Photovoltaic parameters of DSSC based on dye **1** and **2**.

Dye	J_{sc} (A/cm^2)	U_{oc} (mV)	FF	η (%)	$\tau = R_2{*}C_1$ (s)
1	0.62	270	0.47	1.030	0.034
2	0.03	300	0.10	0.008	0.055

According to the results (Table 3), the values of φ_f of dyes slightly increases on the silica surface in comparison the values for solutions owing to the increase in rigidity of molecular structure thus reduction of nonradiative losses of absorbed energy. For both dyes the reduction of φ_f values were registered for TiO_2 films, and whereas for dye **2** this reduction is about 10%, for dye **1** value of φ_f was decreased by almost in 20 times.

It was demonstrated by measurements of fluorescence decay kinetics of dyes on the TiO_2 surface the lifetimes of dyes excited states are also decreased (Table 3). It has to be emphasized that the lifetime of the excited state of the dye **1** with sulfonate groups undergoes to a stronger reduction on semiconductor films.

Thus, measurements have shown the adsorption of dye molecules on the surface of titanium dioxide leads to shift and broadening of the absorption bands, and to quenching of the excited state of dye. The efficiency of fluorescence quenching of molecules with functionalized groups is significantly higher than in the case of the parent dye. This can be explained by the fact that molecules of dye **1** are in closer contact with the titanium dioxide nanoparticles due to the presence of anchor sulfonate groups in the structure of molecule that increases the amount of charge carriers transferred from the dye to the semiconductor.

For testing this assumption, we measured the photovoltaic characteristics of DSSC based on the dyes **1** and **2**. The results of the measurements of the current-voltage characteristics and parameters measurements of solar cells are presented in Table 4 and on Fig. 7 (J_{sc} – short-circuit current, U_{oc} – open circuit voltage, FF – the fill-factor of the solar cell, η – the efficiency of the cell). The charge carrier diffusion lifetime τ in the cell was determined from measurements of solar cell impedance using the scheme shown in Fig. 2.

The low value of the short-circuit current density (0.03 mA/cm^2) was recorded for DSSC with dye **2.** However the voltage has the value typical for this class of dyes. The values of the fill-factor and cell efficiency have been also low. At the same time, nearly all parameters recorded for DSSC based on dye **1** have had higher values than for dye **2**. Thus the functional groups presence in one dye molecule increases of I_{sc} values in 20 times in comparison with the dye **2**. As is customary [22], this parameter depends on the amount of charge carriers transferred from the dye to the semiconductor. The process of electrons generation in the cell occurs more effectively by reason of the sulfonate groups presence in molecule **1** structure. This fact was confirmed by the values of the charge carriers diffusion lifetime (τ in Table 4). In addition, this assumption was confirmed by a change in the optical density of dye solutions before and after sensitization of TiO_2 films. It was found that the optical density of dye **1** solution decreased after sorption by more than 10 times (from 3.13 to 0.3). For dye **2** the optical density was changed in 2.4 times (D before sorption was equal to 3.04, after –1.28).

Table 3
Quantum yields and fluorescence lifetimes of dyes **1** and **2** in various media.

Dye	φ_f, ethanol	φ_f, SiO_2	φ_f, TiO_2	$\varphi_{ethanol}/\varphi_{SiO2}$	$\varphi_{ethanol}/\varphi_{TiO2}$	τ_f, ethanol (ns)	τ_f, SiO_2 (ns)	τ_f, TiO_2 (ns)
1	0.06	0.09	0.003	0.067	20	1.6	1.1	0.5
2	0.1	0.15	0.09	0.67	1.11	1.7	1.4	0.73

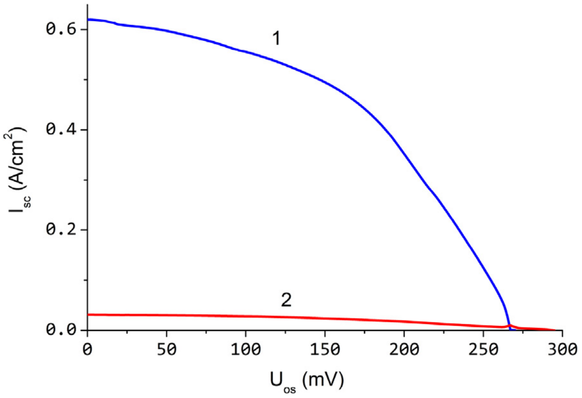

Fig. 7. Current-voltage characteristics of DSSC, based on dye **1** (curve 1) and **2** (curve 2).

4. Conclusions

The measurements have shown, thus the introduction of sulfonate groups in the indolenine heterocycle of squarylium dyes leads to bathochromic shifts of the absorption and fluorescence band. In this case, the fluorescence quantum efficiency and extinction coefficients of the dyes are virtually independent of the functional groups presence. The calculations have shown that the presence of sulfonate groups in molecule of dye **1** do not results in considerable changes in electron density of molecule in ground and excited state. However it leads to improved adsorptive capacity of dye with respect to the semiconductor surface due to electrostatic interaction between the anchor group and the TiO_2 surface.

On the basis of the measurements of photovoltaic parameters, estimation of the absolute quantum yield and the fluorescence lifetime of dyes it be concluded the presence of functional groups in the dye molecules leads to improved photovoltaic efficiency of solar cells sensitized with squarilium dyes.

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