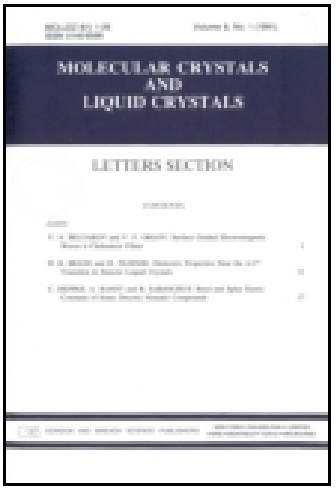

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Role of Energy Transfer in Conversion of Light to Electric Energy

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The role of nonradiative inductive-resonance energy transfer between molecules of Coumarine-7 and rhodamine dyes in the conversion of light into electric energy is studied. It is ascertained that the co-sensitization of a TiO_2 solar cell by donor and acceptor molecules leads to an increase of the efficiency of conversion of light to energy. The measurements show that it is due to a widening of the photosensitivity of a cell into the blue region of the spectrum. The increase of the total energy absorbed promotes increasing the number of generated charge carriers at the interface of TiO_2 and dyes.

Keywords Inductive-resonance energy transfer; organic dyes; solar cell; photovoltaic parameters

Introduction

The process of electronic excitation energy transfer is one of the fundamental problems of physics that has always attracted the attention of researchers [1, 2]. The Förster resonance energy transfer (FRET) was used to create solar concentrators [3], to determine the distance between fluorescent labels in biological molecules, as well as the sensitization of photoactive preparation [4]. At present, this process has become very topical, because the energy transfer is very promising for the use in dye-sensitized solar cells (Grätzel cells).

However, in spite of reports of various authors about the enhancement of a solar cell performance as a result of FRET [5, 6], the works on the study of the energy transfer effect on the photoelectric parameters of TiO_2-based solar cells are practically lacking. The role of the singlet-singlet energy transfer in the efficiency of conversion of light energy into electric energy in dye-sensitized solar cells is studied in this work.

Experiment

Organic dyes Coumarine–7 and Rhodamine 6G myristinate are employed as a donor and an acceptor, respectively. Dyes were purchased from the Institute of Organic Intermediates and Dyes (NIOPIK, Russia). The structural formulae of compounds are shown in Fig. 1.

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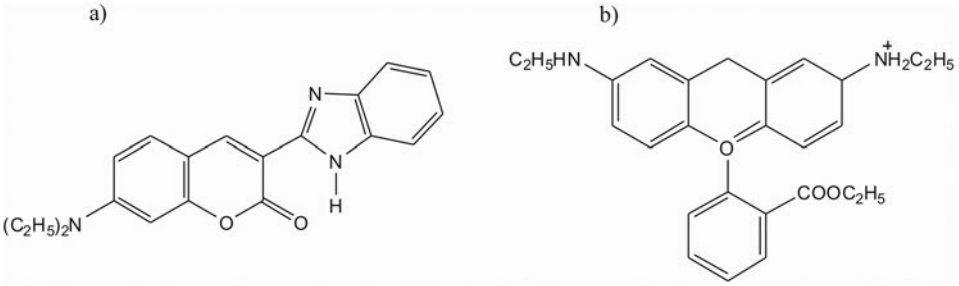

Figure 1. Structure of Coumarine–7 (a) and Rhodamine 6G myristinate (b).

The absorption and fluorescence spectra of donor and acceptor solutions were measured with a spectrometer CM2203. The lifetimes of fluorescence of the donor and the acceptor were measured using a pulse spectrofluorimeter with picosecond resolution with the registration in the time-correlated photon counting mode (Becker & Hickl, Germany).

Solar cells were prepared and assembled according to the procedure described in [7]. Glass substrates coated with a conductive FTO layer were purchased from Sigma-Aldrich. Pastes "Ti-nanoxide HT" and "Ti-nanoxide D" were used for the deposition of transparent and diffusing TiO_2 layers, respectively. Pastes, electrolyte "Iodolyte Z150," Pt catalyst "Platisol," and other components were purchased from Solaronix (Switzerland). The TiO_2 electrode was immersed into an ethanol dye solution and kept at room temperature for 24 h to assure the complete sensitizer uptake.

The current-voltage characteristics of dye-sensitized solar cells were measured with an amperemeter UNI-T UT 803 and a voltmeter FLUKE 8846A under irradiation with white light from a Xenon arc lamp with the power equal to 2.1 W/cm^2. The fill factor (FF) and

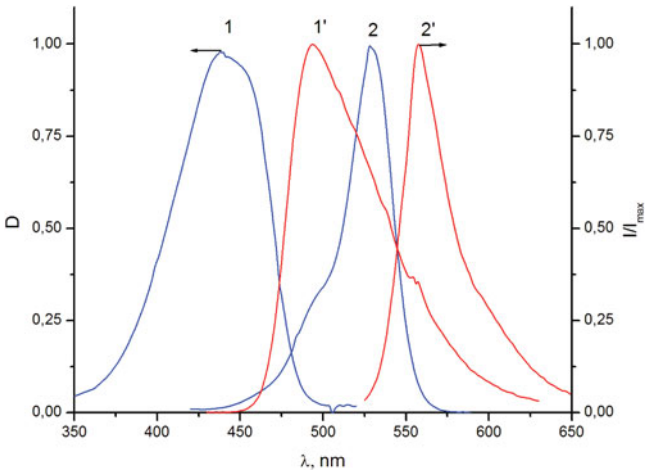

Figure 2. Normalized absorption (1,2) and fluorescence (1′,2′) spectra of donor (1,1′) and acceptor (2,2′) solutions at the concentration C = 10^{-5} mol/l.

Table 1. Calculated values of critical parameters of energy transfer

Solution	Overlap integral, M^{-1} cm^3	R_0, Å	C_0, mol/l
Donor	$5.8 \cdot 10^{-12}$	94.2	$4 \cdot 10^{-3}$
Acceptor	$7.4 \cdot 10^{-14}$	48	$8 \cdot 10^{-3}$
Donor-acceptor	$2.4 \cdot 10^{-13}$	55.3	$7 \cdot 10^{-3}$

the energy conversion efficiency (η) were calculated according to the equations

$$FF = \frac{(I_{\max} * U_{\max})}{I_{sc} * U_{oc}}, \tag{1}$$

$$\eta = \frac{FF * I_{sc} * U_{oc}}{P_{in}} * 100\%, \tag{2}$$

where: I_{max}, U_{max} – values of maximal current and voltage, respectively; I_{sc}, U_{oc} – values of short-circuit current and open-circuit voltage; P_{in} – power of the incident light.

Results and Discussion

The electron excitation energy transfer between Coumarine–7 and Rhodamine 6G myristinate was studied in ethanol solutions. The donor concentration was equal to 10^{-5} mol/l and was constant. The acceptor concentration was varied from 10^{-7} to 10^{-4} mol/l. Photoexcitation of donor and donor-acceptor solutions was carried out with radiation from a laser with the wavelength $\lambda_{gen} = 375$ nm. Photoexcitation of neat acceptor solution was carried by a laser with $\lambda_{gen} = 488$ nm. The registration of the donor and acceptor fluorescence was carried out at 480 and 555 nm, respectively.

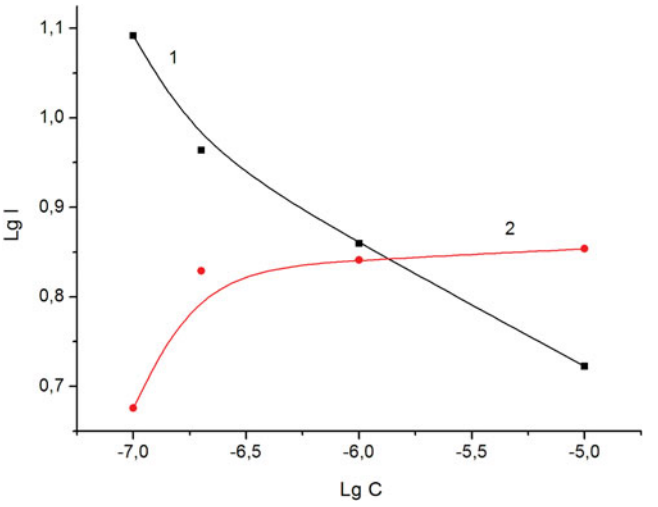

Figure 3. Fluorescence intensity of the donor (1, $C_D = 10^{-5}$ mol/l, $\lambda_{reg} = 480$ nm) and the acceptor (2, $\lambda_{reg} = 555$ nm) depending on the concentration of the latter.

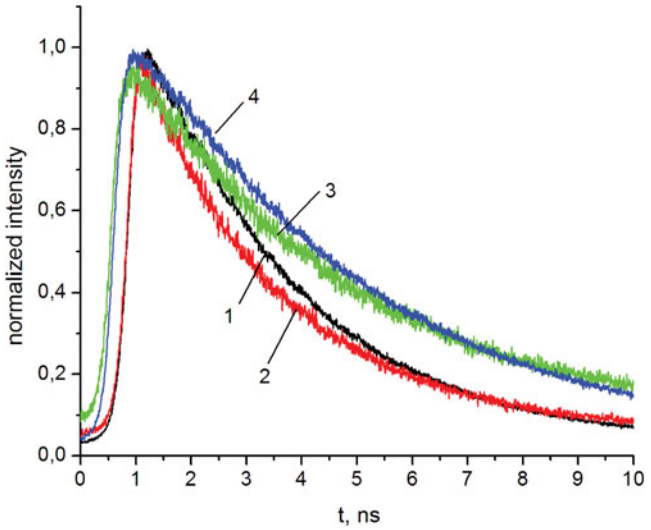

Figure 4. Fluorescence decay kinetics of the donor and the acceptor registration at $\lambda = 480$ nm (curves 1 and 2) and at $\lambda = 555$ nm (curves 3 and 4). The dye concentrations (mol/l): 1 – $C_D = 10^{-5}$; 2,3 – $C_D = 10^{-5}$, $C_A = 10^{-5}$; 4 – $C_A = 10^{-5}$. Excitation wavelengths are: $\lambda_{ex} = 375$ nm (curves 17–3), $\lambda_{ex} = 488$ nm (curves 4).

Figure 2 shows the normalized absorption and fluorescence spectra of the donor and the acceptor. The fluorescence spectrum of the donor and the absorption spectrum of the acceptor overlaps, which is a prerequisite for the effective electronic excitation energy transfer.

The Förster distance and critical concentrations were calculated in order to prepare samples with proper concentrations of donor and acceptor molecules. Critical parameters were determined from the well-known Förster formula based on the spectral measurements [1, 8]. Calculated values of critical parameters are presented in Table 1.

The data shows that the selected concentrations of the donor and the acceptor are lower than the critical concentration, which means that most of the excitation energy will be transferred to acceptor molecules.

Figure 3 illustrates the dependence of the fluorescence intensity of the donor and the acceptor depending on the concentration of rhodamine dye. As can be seen from Fig. 3, the

Table 2. Parameters of energy transfer at various acceptor concentrations, donor concentration was constant and equal to $C_D = 10^{-5}$ mol/l

Acceptor concentration, mol/l	k_{ET}, s^{-1}	τ_{fl}, ns	
		$\lambda = 480$ nm	$\lambda = 542$ nm
0	–	3	—
10^{-6}	$3.1 \cdot 10^5$	2.6	3.9
10^{-5}	$2.4 \cdot 10^5$	2.6	3.9
10^{-4}	$1.5 \cdot 10^2$	2.6	4

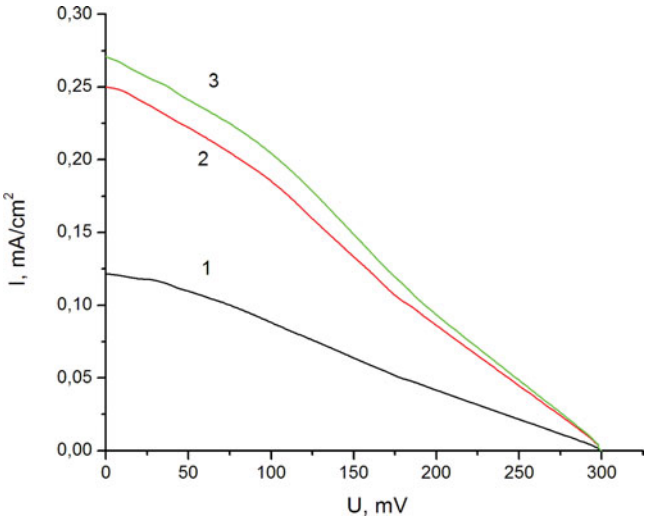

Figure 5. Current-voltage characteristics of solar cells sensitized by acceptor molecules (curve 1) and by the donor-acceptor system (curves 2,3) at different donor concentrations (mol/l): 2 – 10^{-5}; 3 – 10^{-2}.

presence of acceptor molecules leads to quenching the fluorescence intensity of the donor. The appearance of fluorescence coinciding in the spectrum with the fluorescence band of the acceptor was registered in the long-wave part of the spectrum. Fluorescence of the acceptor was not recorded upon the direct excitation at $\lambda = 375$ nm. Thus, the appearance of a long-wave emission, whose spectrum coincides with the acceptor fluorescence spectrum, indicates that the singlet levels of Rhodamine 6G myristinate are occupied as a result of the non-radiative energy transfer from Coumarin-7 to Rhodamine 6G myristinate molecules.

The results of measurements of the donor and acceptor fluorescence decay kinetics indicate the presence of energy transfer between coumarin and rhodamine dye molecules (Fig. 4, Table 2).

The role of non-radiative energy transfer in the conversion of light energy into electric energy with solar cells was studied at the next stage. For this aim, the TiO_2 films sensitized with neat rhodamine dye and TiO_2 films sensitized with the donor-acceptor compound were prepared. The concentration of rhodamine dye in these films was constant and equal to C = 10^{-2} mol/l, and the donor concentration was varied from 10^{-5} to 10^{-2} mol/l.

Table 3. Phototelectric parameters of solar cells sensitized by acceptor molecules and the donor-acceptor compound

Donor concentration	I_{sc}, mA/cm2	U_{oc}, mV	FF	η, %	η/η_0
0	0.125	300	0.25	0.45	
10^{-5}	0.261	300	0.25	0.93	2
10^{-4}	0.268	300	0.25	0.96	2.1
10^{-3}	0.277	300	0.25	0.99	2.2
10^{-2}	0.284	300	0.25	1.0	2.2

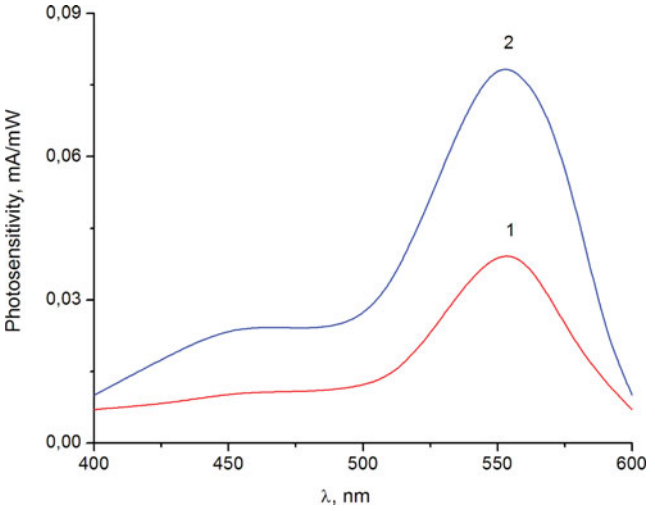

Figure 6. Spectral photosensitivity of a solar cell based on the acceptor (curve 1) and the donor-acceptor compound (curve 2).

Figure 5 shows the current-voltage characteristics of solar cells sensitized by Rhodamine 6G myristinate molecules.

I_{sc} of solar cells with neat rhodamine dye was equal to 0.125 mA/cm^{-2}, $U_{oc} = 300$ mV. For the co-sensitization of a solar cell with the donor and the acceptor, the increase of the current (Fig. 5, curves 2 and 3) was recorded. The power conversion efficiency of a TiO_2 solar cell containing the donor-acceptor compound increased by 2 times over that of a pristine cell (Table 3).

The curves of the spectral photosensitivity of a solar cell based on the acceptor and the donor-acceptor compound are shown in Fig. 6.

We note that the photosensitivity of a cell by the FRET was increased in the range of 400–500 nm, where Coumarine-7 absorbs light, but the rhodamine dye does not. The increase of the total energy absorbed promotes increasing the number of generated charge carriers at the interface of TiO_2 and dyes.

Conclusion

In the present paper, the role of the nonradiative inductive-resonance energy transfer between molecules of Coumarine-7 and rhodamine dyes has been studied. It is ascertained that the co-sensitization of a solar cell by donor and acceptor molecules leads to increasing the conversion efficiency of light into energy. It is shown that increasing the conversion efficiency occurs as a result of widening the photosensitivity of cells into the blue region of the spectrum. The increase of the total energy absorbed promotes increasing the number of generated charge carriers at the interface of TiO_2 and dyes.

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