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Pyrene-Naftylamide Bifluorophore for Spectra-Converting Media

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Abstract New bifluorophore containing pyrene as an excitation energy donor and naphtylamide as an acceptor is synthesized and its optical properties are studied. It is founded that excitation spectrum of the bifluorophore is almost the sum of its constituents—pyrene and naftylamide. At the same time, in the luminescence spectrum there only the peak of acceptor luminescence is observed, which indicates the effective radiationless energy transfer from the donor to the acceptor. This is also proved by time resolved measurements of bifluorophore decay. The decay rate was calculated from decay curve and appear to be 0.25 hc^{-1}. The same value obtained from the Förster's theory is almost by an order as high. It indicates that Förster's does not applicable in this particular case. Instead, we have to use the electron excitation density functions approach.

Keywords Photoluminescence · Spectra converting · Bifluorophore

Introduction

Bifluorophore is a substance comprises at least two fluorescent dye moieties covalently linked via a linker group. The dyes are selected so that the emission spectrum of a first (donor) dye overlaps the absorption of a second dye, thereby allowing fluorescent resonance energy transfer (FRET) [1, 2] to occur between the dyes. As the result, bifluorophores absorb at more wide band comparing to their chromophores parts separately and emit at the longest wavelength.

Because of their special properties, bifluorophores are widely used in various applications. Thus, for instance, during recent two decades, there has been a great emergence of interests in the development of fluorescent probes for various metal cations. In the paper [3] a novel bifluorophore bearing one 2,3-naphthocrown-6 and two coumarin amide units is described as a FRET-based fluorometric sensor for F^- and Cs^+ ions. In [4] a new fluorogenic sensor capable of illustrating metal ion-triggered FRET changes has been presented. Based on the FRET changes, this bifliorophore, bearing coumarin-fluorescein moieties, provides a selective sensor for Cu^{2+} and Hg^{2+} ions.

The recently developed tunable dye lasers in the visible are obtained by incorporation of stable laser organic dyes into glasses [5]. It thus becomes necessary to continuously search for new systems and synthesize new laser dyes covering a wide spectral range of excitation. Specific bifluorophores based on laser dyes can solve this problem [6, 7].

Almost the same problem arises in luminescent solar concentrators (LSC) [8] especially when organic photovoltaic cells are used. In [9] an organic cell fabricated of zinc-phtalocyanine and C_{60} is described. This solar cell have its main absorption in the wavelength range between 600 and 800 nm. Below 600 nm, the low absorption limits the quantum efficiency. Luminescent concentrators are used to overcome this limitation by spectrally shifting blue and green light towards the red and waveguiding it to the solar cell.

In luminescent concentrators the broad spectrum of the sunlight is taken up by a material absorbing in as wide as possible spectral range and reemitted in a

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narrow luminescence. Due to the Stokes shift, the luminescence occurs always to higher wavelengths as the absorption, the light can be only redshifted [9, 10]. This luminescence should coincide with the best spectral response of the solar cell.

A promising way to enhance the efficiency of organic solar cells is to use "antenna systems" of absorber materials that donate the energy from photons absorbed in the blue and green spectral ranges to the red absorbing solar cell materials. When multiple dyes are presented in LSC, photons are absorbed and re-emitted by increasingly longer wavelength dyes.

It is commonly assumed that only radiative coupling occurs between the dye molecules [10]. But about a quarter of the energy collected in the first dye is lost in every reemission act. These losses can be reduced if the effective channel of radiationless energy transfer (FRET) between dyes exists. It is to be noted that while FRET between dye molecules can occur with a higher efficiency, the molecular spacing that is required to realize it (less than Förster's radius of energy transfer [1]) could be only achieved in a heavily-doped matrix. But under high concentration of a dye, which is necessary to achieve such small distances, light absorption will be so high that in this case even statement of the considered problem loses its sense.

Therefore the problem is to create cascades of excitation energy migration in which both donor and acceptor are placed at small distances and their concentration can be rather low. Such cascades can be performed in complexes of covalent binding donor and acceptor molecules, that is, in bifluorophores [11, 12].

Present work concerns the synthesis and studies of optical properties of new bifluorophore, based on naphtylamide and pyrene molecules. Our goal was to expand the absorption band of LSC and to provide an effective energy transfer to the long-wave region.

Experimental

The scheme of bifluorophore synthesis is presented in Fig. 1. It can be schematically divided into the following stages:

1. **(a, $C_{19}H_{10}NO_4Cl$). 4-(6-chloro-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-2-yl)benzoic acid**
   8.5 g (0.062 mol) of para-aminobenzoic acid is added to 5.0 g (0.021 mol) 4-chlorinenaphtal anhydride in 40 ml of glacial acetic acid and is heated under boiling temperature during 4 h. After cooling, the precipitate is filtered, washed by hot water and methanol, and dried at about 80 °C temperature. The yield of obtained product is 4.92 g (65%). Melting temperature $T_{melt} > 300$ °C.

2. **(b, $C_{19}H_9NO_3Cl_2$). 4-(6-chloro-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-2-yl)-1-benzenecarbonyl chloride**
   30 ml (0.41 mol) of thionyl chloride are added to 2.0 g (0.0056 mol) of substance "a", boiled during 2 h, then surplus thionyl is distilled off and its residue is removed by azeothrope distillation by dry benzene. Benzene residue is evaporated for dryness in vacuum under room temperature. Yield of obtained product—about 2 g (95%).

3. **(c, $C_{16}H_{11}N$). 3-Aminopyrene**
   is obtained by known technique [13] by means of pyrene nitration by dilute nitric acid in acetic acid with further reduction of resultant 3-nitropyrene by tin chloride in hydrochloric acid.
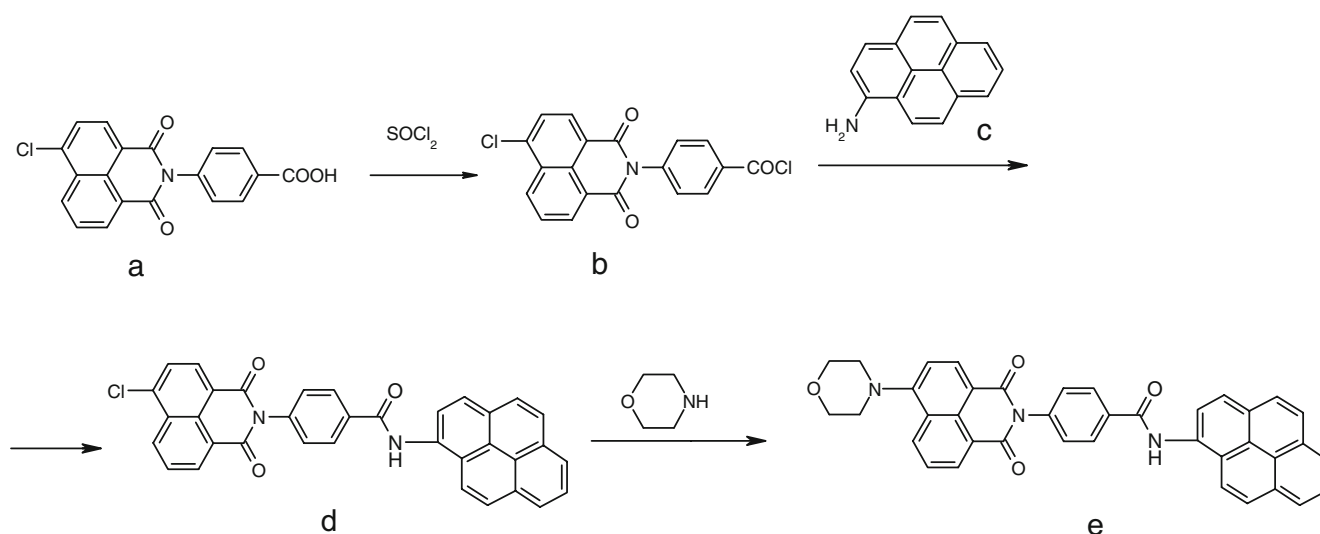

Fig. 1 Synthesis scheme

4. **(d, $C_{35}H_{19}N_2O_3Cl$). 1-[4-(6-chloro-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-2-yl)phenylcarboxamido]pyrene.**

2.2 g (0.0101 mol) of 3-aminopyrene (substance "c") in small discrete portions are added to suspension of 2.0 g (0.0054 mol) of the substance "b" in 30 ml of benzene; then 15 ml of pyridine is dripped and mixed under 60 °C during 6 h. The mass is cooled, the precipitate is washed with methanol and dried. The yield of the product is 2.1 g.

5. **(e, $C_{39}H_{27}N_3O_4$). 1-[4-(6-morpholino-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-2-yl)phenylcarboxamido]pyrene**

2 ml of morpholine is dripped to 0.4 g of product "d" solution in 20 ml of Dimethylformamide (DMFA) and heated under 90 °C during 3 h. Then the substance is cooled, 30 ml of methanol is added, the yellow precipitate is filtered, washed with methanol and dried under about 80 °C temperature. The obtained product is passed through a chromatograph column of chloroform with silica gel. The yield is 0.23 g (7.09% in terms of 4-(6-chloro-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-2-yl)-1-benzenecarbonyl chloride ("b")). Melting temperature $T_{melt} > 300$ °C.

Molecular mass of obtained substances was measured by Varian 1200 L Quadrupole MS Liquid Chromatograph/Mass Spectrometer chromo-mass-spectrometer (Varian Inc.). It happened to be equal to 610 which is close to the expected value (618, substance "e").

Luminescence spectra of synthesized compounds were measured in chloroform by means of HORIBA JobinYvon "FluoroMax-4" fluorimeter, absorption spectra—by "SPECORD 40" spectrophotometer under 10^{-6} mol·l^{-1} solution concentration. Silica gel 40–100 μm was used for

column chromatography. Purity control of synthesized compounds was made by TCX method on Baker-flex plates "Silica Gel IB-F".

Results

Bifluorophore molecule consists of two luminescent parts (see Fig. 2) one of them (pyrene) being the energy donor and the other (naphtylamide)—its acceptor. To determine optical properties of bifluorophore first of all steady-state spectra of excitation and luminescence of donor and acceptor were studied separately. For this end we used 4-morpholino-N-(4-carboxy)-phenylimide naphthalic acid (substance "f") as the acceptor and 3-acetylamonopyrene (substance "g") as the donor (Fig. 3).

Excitation spectra were registered in a maximum of the luminescent spectrum of the respective dye. They are presented in Fig. 4a. It follows from the figure that the donor emission spectrum with the maximum at 413 nm is well overlapped by excitation spectrum of the acceptor parts of the bifluorophore (maximum at 395 nm). This overlapping makes possible an effective energy transfer between donor and acceptor parts of the bifluorophore molecule.

It is seen in the Fig. 4 that the excitation spectrum of bifluorophore is actually the sum of donor and acceptor maxima at 362 and 395 nm respectively. The width of bifluorophore excitation band is widen up to 110 nm (from 325 to 435 nm), which contains the same values for donor and acceptor parts of bifluorophore molecule. It is to be note that when bifluorophore is excited at 395 nm, there is practically no luminescence of its donor part (Fig. 4b). This

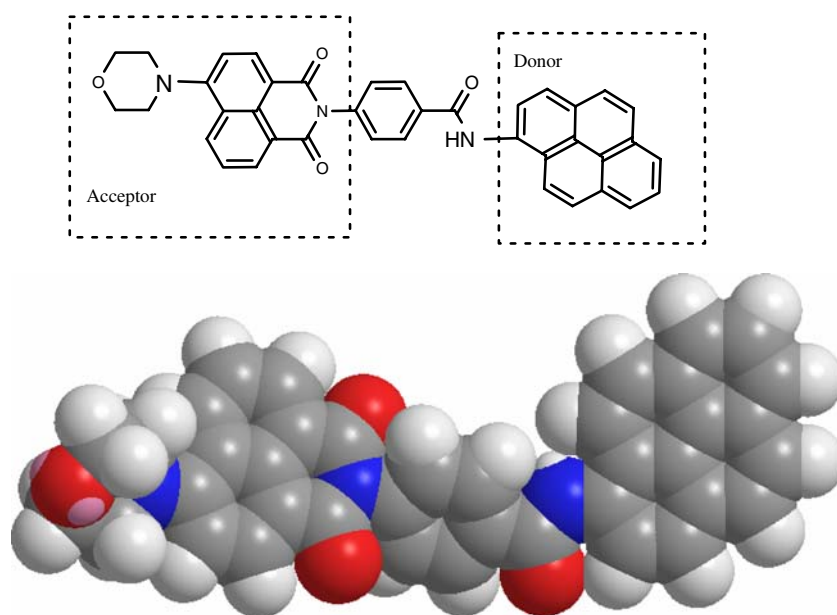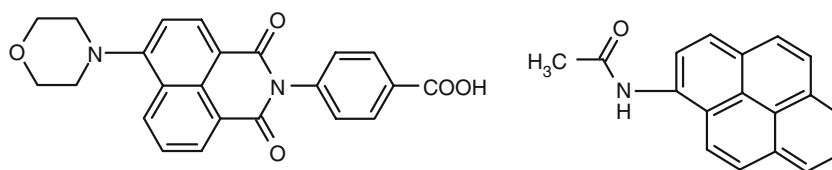**Fig. 2** Scheme of bifluorophore

Fig. 3 Substances used to study acceptor (substance "f", left) and donor (substance "e", right) separately

behavior of bifluorophore molecules luminescence can be observed even in very small concentration. In such a way, any influence of reabsorption effects on donor luminescence is eliminated.

Observed spectrum of bifluorophore fluorescence shows the existence of an effective channel of radiationless energy transfer between its donor and acceptor parts. The existence of such a channel is also proved by time-resolved measurements of bifluorophore decay.

First of all we measured decay curves of a donor and acceptor separately (see Fig. 5). The measurements were done for solutions of these substances in dichlorethane, the concentration being 10^{-6} M·l^{-1}. The figure shows that

decay curves as donor and acceptor are strictly single-exponentials (10 ns–40 ns and 10 ns–60 ns regions) which indicates the absence of additional quenching channels. The lifetime of the exited states of donor and acceptor appear to be equal to 4.3 ns and 8.2 ns, respectively.

In accordance with Förster theory [14], the radiationless channel of relaxation in a donor-acceptor system must cause the change in a donor's luminescence decay law. Instead of simple exponent, the following decay dependence on time must be observed:

$$F(t) = \exp\left(-t/\tau_0 - c_D \cdot \int g(r)(1 - \exp(w(r) \cdot t))dr\right) \quad (1)$$

where C_D concentration of donor molecules in a sample
$g(r)$ pair correlation function of donor-acceptor mutual spatial distribution
$w(r)$ rate of radiationless energy transfer between donor and acceptor located at r distance:

$$w(r) = 1/\tau_0(R_0/R)^s \quad (2)$$

τ_0 lifetime of the donor in the absence of the acceptor
s power, determined by the degree of multipolarity of interaction. For dipole-dipole interaction $s=6$
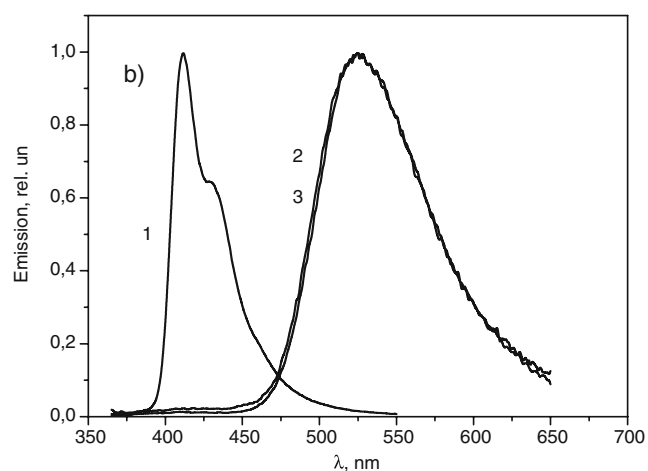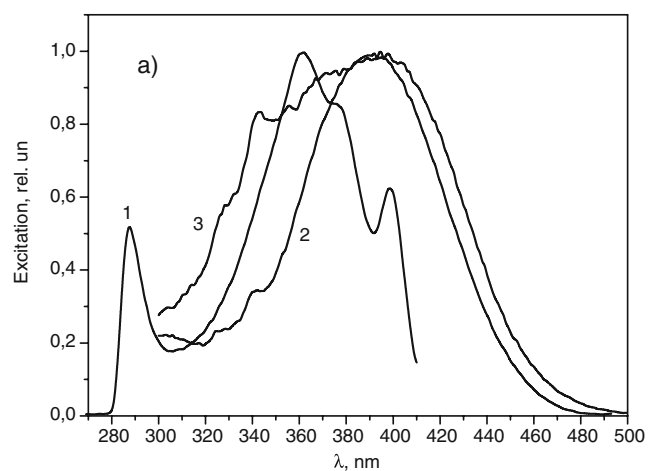

Fig. 4 Excitation **a** and emission **b** spectra of donor (1), acceptor (2) and bifluorophore (3) molecules
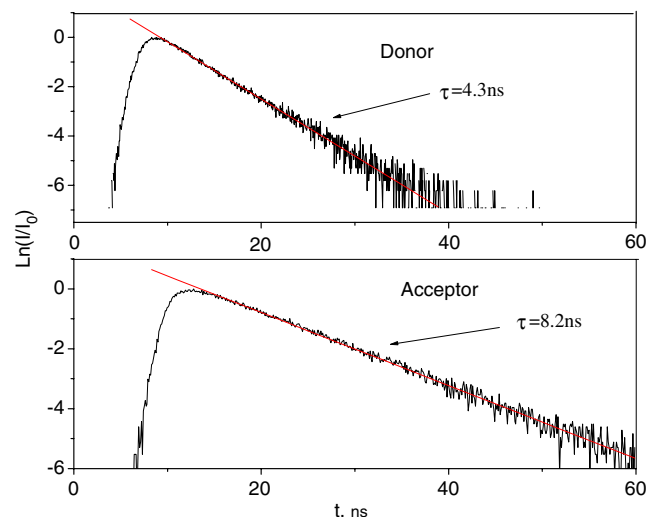

Fig. 5 Decay curves of the donor and acceptor

R_0 critical (Förster) transfer radius, which is determined from known expression of spectra overlapping [14]:

$$R_0^6 = \left[(9000 \ln 10) k^2 \varphi_d \big/ (128 \pi^5 N n^4) \right]$$
$$\cdot \int \varepsilon_a(\nu) I_d(\nu) \nu^{-4} d\nu, \qquad (3)$$

where $\varepsilon_a(\nu)$ molar extinction of the acceptor

$I_d(\nu)$ normalized fluorescence spectrum of the donor

φ_d quantum yield of the donor in the absence of acceptor

N   Avogadro's number

n   refractive index of the medium

k^2 orientation factor, related to mutual orientation of two interacting dipoles (as a rule, it is chosen as 2/3).

Decay curve of donor part of bifluorophore is presented in Fig. 6. It is seen in the figure that decay curve of donor part of bifluorophore obviously deviate from a single exponential. It can be fitted by two exponents with 2 ns and 7 ns lifetimes (10 ns–40 ns region).

It is to be noted that two-exponent fitting is not so correct when there is a channel of radiationless energy transfer. Let us consider the bifluorophore solution. Energy transfer from its donor part can be either to an acceptor, which is a part of the same molecule (intramolecular transfer) or to an acceptor part of another molecule in the solution (intermolecular transfer). Therefore, the donor-acceptor correlation function must consist of a regular part $g_c(r) \sim \delta(r - R_{da})$, which is determined by covalently linked donor and acceptor, and a random part $g_r(r) = 4\pi c_a r^2$, which is determined by chaotically distributed bifluorophore molecules in a solution. It means that observed donor decay dependence on time must be a two-component one (taking no account to donor's spontaneous decay with 4 ns life-time). The first, (regular) component which relates to energy transfer to the acceptor part of the same molecule at the distance R_{da}^0, is determined by exponent with linear power $t \big/ \tau_0 (R_0/R_{da}^0)^6$, and the second, (irregular), component, related with energy transfer to the acceptor parts of another molecules, must be characterized by root dependence of power on time $\sim c_d \sqrt{t}$. Therefore the observed decay dependence on time must have the following form:

$$I(t) \sim \exp\left(-t \big/ \tau_0 - t \big/ \tau_0 \left(R_0/R_{da}^0 \right)^6 - \gamma c_d \sqrt{t} \right), \qquad (4)$$

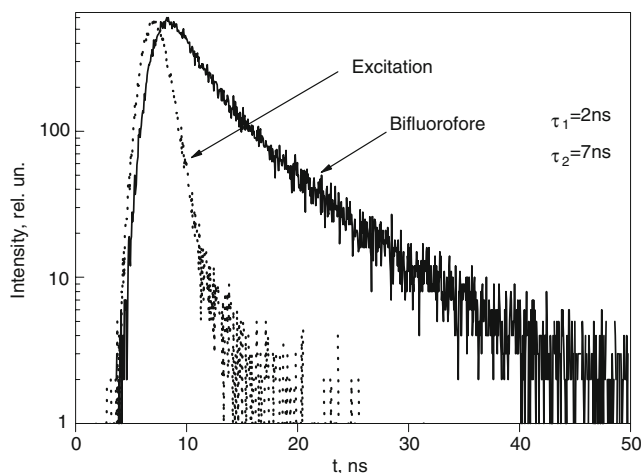where γ - a numerical coefficient.

Fig. 6 Fluorescence decay of the donor part of bifluorophore

The contribution of the intermolecular component can be minimized by decreasing the concentration of bifluorophore in the sample. As it follows from (4), under low concentration of the bifluorophore, the rate of energy transfer on the adjacent molecule tends to zero. But it is impossible to ignore absolutely the intermolecular energy transfer. Therefore, the observed decay law must have a two-component character with different decay laws. The first exponent with 2 ns lifetime can be related with the quenching of the donor part of bifluorophore molecule by acceptor parts of the same molecule as well as by the rate of spontaneous decay. It appears impossible to select the irregular component from the decay curves because it is superimposed by "parasitic" luminescence of the acceptor with 8 ns lifetime. It is the component that provides the second, "long", exponent. It is to be noted that the luminescence of donor part of bifluorophore molecules is very weak, so to register it we have to use rather long time to store.

From the "short" part of the donor's decay curve (Fig. 6) we can estimate the rate of energy transfer from the donor to the acceptor, about 0.25 нс$^{-1}$. The same value can be obtained in another way. To do so we must know the Förster radius of transfer which is easily calculated from absorption and fluorescence spectra according to Eq. (3) (R_0=34 Å in our case) and the distance between donor and acceptor part which is determined from structural formula of the bifluorophore molecule (R=10–15 Å). Resulting quenching rate is greater than observed one almost by an order. It is possible that instrumentation used for decay time measurement (apparatus half-width of excitation pulse is ~1 ns) does not resolve such a transfer rate, or suggested approach does not take into account peculiarities of closely placed chromophores. In the latter case we must use the electron excitation density functions approach [15].

The quantum yield of our bifluorophore was determined by means of relative measurements. They include the measurement of the integral of luminescence curves I and absorption coefficients on the same wavelength for unknown and reference media. Then the quantum yield φ is determined according to:

$$\varphi = \varphi_r \left(\frac{I}{I_r}\right) \left(\frac{n}{n_r}\right)^2 \left(\frac{\varepsilon_r}{\varepsilon}\right) \qquad (5)$$

where n, I, φ, ε are the respective refraction coefficient, integral intensity of luminescence, quantum yield and absorbance of studied solutions, and n_r, I_r, φ_r, ε_r are the same quantities of reference medium. As the reference medium we select 2,5-Diphenyloxazole (PPO) solution in cyclohexane with quantum yield φ_r–0.99 [16]. Measurement shows that the bifluorophore quantum yield is $\varphi = 0.47$.

Conclusions

Synthesized bifluorophore consists of pyrene molecules as the donor and naphtylamide molecules as the acceptor of excitation energy. It is shown in the paper that the resulting absorption spectrum of the bifluorophore is the sum of donor and acceptor respective spectra. So the total absorption is increased allowing to utilize more wide part of the Sun spectrum in a luminescent concentrator (LSC). Donor emission in a 380–450 nm band (UF—blue) almost disappears in the bifluorophore being shifted to green-red band about 500–600 nm. This in turn allows more effective coupling with the organic photovoltaic cell.

Quantum yield of obtained bifluorophore is rather low now, about 0.47 and is increasing is the subject of further investigations.

It is shown in the present work that observed effective radiationless energy transfer cannot be explained by Förster's theory. It can be relate with small distance between the donor and the acceptor in the bifluorophore. This problem requires more detailed separate study.

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