

Spectral-luminescent properties of new polymer-bifluorophors

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Spectral-luminescent properties of a new class of bifluorophor molecular systems (azometine-bifluorophors and poly Schiff bases-bifluorophors) are presented, as well as some regularities in the intramolecular non-radiative transfer of electronic excitation energy.

The efficient non-radiative intermolecular transfer of electronic excitation energy in solutions usually takes place if the distance between molecules being donors and acceptors of energy is about 50 Å. However, at high concentrations of luminophores¹ in solutions, non-luminescent molecular associates can arise. In actively absorbing the exciting radiation and receiving the electronic excitation from neighboring individual molecules at the radiative transfer, such associates convert this excitation into the energy of oscillations. Thus, the concentration quenching of the luminescence occurs. Therefore, the promising way may be a synthesis of polymer molecules, whose main chain contains fragments among which there are donors and acceptors of the energy of electronic excitation. In contrast to a solution, in which molecules of two types are chaotically distributed over the volume, fragments containing donors and acceptors of the excitation energy in a polymer chain are ordered to a great degree. Changing this order, one can control the efficiency of different ways of exchange of the donor's electronic excitation energy. Besides, photostability of polymers is, as a rule, higher than that of the corresponding binary solutions, what makes the use of the former preferable in many applications.

However, the study of the mechanism of electronic excitation energy transfer in polymers faces some serious problems because of the complex structure of the macromolecules. Therefore, at the first stage we have developed the methods for synthesis of compounds modeling the elementary unit of polymer-bifluorophors, namely, azometine-bifluorophors. It has been shown that non-radiative transfer of the electronic excitation energy takes place in such systems, and the regularities of this transfer have been studied. The data obtained have formed a basis for the development of methods for synthesis and study of poly Schiff bases-bifluorophors.

At the first stage, five azometine-bifluorophors have been synthesized and studied.² The technique of synthesis was the following: condensation of dialdehyde of terephthalic acid with two monoamine-fluorophors.

The individuality and structure of the compounds synthesized are supported by the data of thin-layer chromatography and the methods of chemical analysis and IR spectroscopy. N-methylpyrrolidol was used as a solvent.

The electronic absorption spectra in the UV and visible regions were recorded with a Specord M-40 spectrophotometer, and the spectra of luminescence and excitation of fluorescence were recorded with a Jobin Yvon 3CS spectrofluorometer which provided for automatic correction of spectra. The quantum yield of the luminescence was determined by the relative method. The ethanol solution of coumarin-120 with the quantum yield of fluorescence $\phi = 0.61$ was used as a reference. When we needed to determine the luminescence yield of donor and acceptor fragments in the structure of bifluorophors, their spectra of luminescence were separated into bands by the Alentsev-Fock method.

Figure 1 shows the spectra of absorption, luminescence, and excitation of luminescence of coumarin-120 and 6-aminophenalenon (*a*) and azometine-bifluorophor (*b*) based on them.

The electronic absorption spectra of all the studied azometine-bifluorophors are wide bands with maxima at the wavelengths close to the corresponding absorption maxima of the initial monoamine-fluorophors.

The spectral-luminescent characteristics of the initial monoamines and bifluorophors are summarized in Table 1, which, in particular, gives the values of the quantum yields of luminescence ϕ . The quantum yield of bifluorophor was taken to be the ratio of the number of quanta emitted by the entire bifluorophor molecule, that is, by donor and acceptor fragments, to the number of quanta absorbed at excitation at the wavelength corresponding to the maximum absorption of the donor fragment. Table 2 gives the overlap integrals for the donor luminescence spectrum and acceptor absorption spectrum, the quantum yield of the non-radiative transfer of the electronic excitation energy, and the rate constant of energy transfer of the studied azometine-bifluorophors.

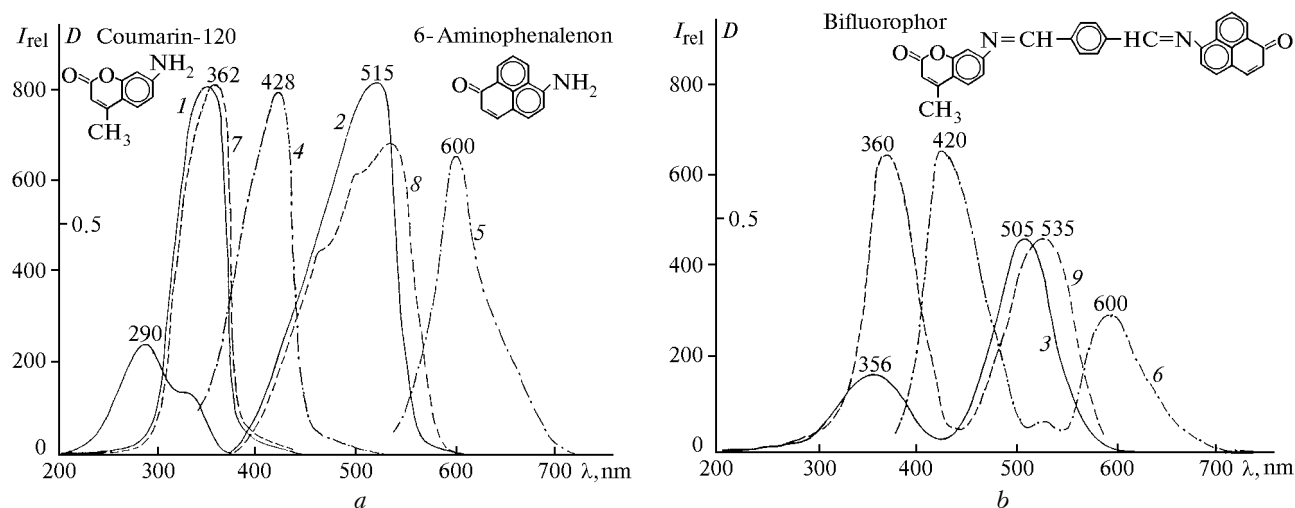


Fig. 1. Spectra of absorption (1, 2, 3), fluorescence (4, 5, 6) ($\lambda_{exc} = 360$ nm), and excitation of fluorescence (7, 8, 9) of the initial fluorophors of coumarin-120 (1, 4, 7) and 6-aminophenalenon (2, 5, 8) (a) and azometine-bifluorophor synthesized from them (3, 6, 9) (b).

Table 1

| Compound | λ_{max}^{abs} | λ_{max}^{lum} | λ_{max}^{exc} | Extinction coefficient $\frac{1}{\epsilon}$, (mol-cm) | Φ_q | $\Delta\lambda_{D-A}^{abs}$, nm | $\Delta\lambda_{D-A}^{lum}$, nm | $\frac{\epsilon_{max}^1}{\epsilon_{max}^a}$ |
|-------------------------------------------|-----------------------|-----------------------|-----------------------|-----------------------------------------------------------|----------|----------------------------------|----------------------------------|---------------------------------------------|
| Coumarin-120 | 355 | 428 | 362 | 41600 | 0.42 | | | |
| N-aminoimid- 4-aminonaphthalic acid | 445 | 520 | 450 | 15360 | 0.30 | 90 | 92 | 2.70 |
| Bifluorophor I C-120+NI | 343 | 420 | 350 | 19965 | 0.178 | 101 | 110 | 0.91 |
| Coumarin-120 Nile blue | 355 | 428 | 362 | 41600 | 0.42 | 155 | 182 | 2.45 |
| Bifluorophor II C-120+NB | 355 | 418 | 360 | 24940 | 0.23 | 200 | 197 | 0.86 |
| Coumarin-120 6-aminophenalenon | 355 | 428 | 362 | 41600 | 0.42 | 160 | 172 | 0.81 |
| Bifluorophor III C-120+6APh | 356 | 420 | 360 | 36120 | 0.54 | 179 | 180 | 1.68 |
| Acridine yellow (AY) 6-aminophenalenon | 410 | 505 | 415 | 15600 | 0.69 | 105 | 95 | 0.30 |
| Bifluorophor IV AY+6APh | 416 | 500 | 420 | 90000 | 0.36 | 94 | 90 | 2.50 |
| AY 3-Aminobenzantron | 410 | 505 | 415 | 15600 | 0.69 | 116 | 125 | 0.84 |
| Bifluorophor V AY+3AB | 416 | 499 | 420 | 62980 | 0.37 | 99 | 111 | 1.34 |
| | 515 | 610 | 520 | 47000 | | | | |

The rate constants of the electronic excitation energy transfer given in Table 2 were calculated assuming that $\Phi^2 = 0.9$ for all bifluorophors (Φ is the orientation factor). This value was obtained from quantum-chemistry calculations of all possible *cis*- and *trans*-isomers of the bifluorophor II and probabilities that its molecule is in each of these form. For other bifluorophors the value of the orientation factor was not calculated and was taken to be equal to 0.9, what is in agreement with the literature data. Thus, for bifluorophor based on 3-

aminophthalimide (donor) and stilbene (acceptor) this value was $3.5 \cdot 10^{12} \text{ s}^{-1}$; for bifluorophor based on 2,6-diphenyloxazole (donor) and rhodamine B (acceptor) this value, which was determined from the kinetics of reconstruction of absorption by the fragment that is being the energy donor, is 10^4 s^{-1} (Ref. 3).

The second stage of this work was synthesis of poly Schiff bases-bifluorophors (polymers) and study of photoprocesses taking place in them. The general formula of the elementary unit is given in the bottom of Table 3.

Table 2

| Compound | I_A/I_D | Integral of the overlap $\int_0^\infty F_D(v)\epsilon_A(v)\frac{dv}{v^4}$ | Rate constant of energy transfer K_{D-A}, s^{-1} | Quantum yield of transfer |
|------------------|-----------|------------------------------------------------------------------------------|-------------------------------------------------------|---------------------------|
| Bifluorophor I | 0.50 | 0.296 | $1.14 \cdot 10^{12}$ | 0.12 |
| Bifluorophor II | 0.38 | 0.214 | $1.05 \cdot 10^{12}$ | 0.15 |
| Bifluorophor III | 0.30 | 0.215 | $1.09 \cdot 10^{12}$ | 0.39 |
| Bifluorophor IV | 0.67 | 0.711 | $0.43 \cdot 10^{12}$ | 0.36 |
| Bifluorophor V | 0.61 | 0.742 | $1.46 \cdot 10^{12}$ | 0.37 |

The polymer-fluorophors, bifluorophors, and poly Schiff bases-bifluorophors are much promising for use

as active media of liquid and solid-state lasers and scintillators, especially to indicate the presence of hard radiation, transform shortwave radiation into longwave one at information transfer through fiber-optics communication lines, increase the power of solar batteries, securities purposes, advertising, and so on. Poly Schiff bases-bifluorophors were not earlier described in the literature.

Polymers were produced by polycondensation of terephthalic aldehyde and two diamine-fluorophors, one of which is a donor and the other one an acceptor of the energy of electronic excitation. Figure 2 shows the structure formulas of the diamine-fluorophors used, whereas Figure 3 shows the formulas of the polymer-bifluorophors studied.

Table 3. Spectral-luminescent characteristics of new polymer-bifluorophors

| Polymer | Donor | Acceptor | $\lambda_{\max}^{\text{abs}}, \text{nm}$ | $\lambda_{\max}^{\text{lum}}, \text{nm}$ | B_q | $K_{\text{transfer}}, s^{-1}$ |
|---------|------------------------------------------------------------|-----------------------------------------------------|------------------------------------------|------------------------------------------|-------|-------------------------------|
| 1 | AY | 6-amino-1-imino-phenalene hydrochloride [PhH] | 410, 460, 600 | 502, 630 | 0.19 | $1.02 \cdot 10^9$ |
| 2 | 5-amino-2-(<i>n</i> -aminophenyl) benzimidazol (softener) | AY | 348 | 420, 500 | 0.32 | $1.73 \cdot 10^9$ |
| 3 | softener (S) | 9,10-bis(<i>n</i> -aminophenyl) anthracene (BAPhA) | 310, 420 | 415, 543 | 0.34 | $1.76 \cdot 10^9$ |
| 4 | BAPhA | safranin T | 290, 380, 545 | 334, 498, 570 | 0.15 | $0.85 \cdot 10^9$ |
| 5 | 3S | 1AY | 280, 405 | 410, 505 | 0.26 | $1.43 \cdot 10^9$ |
| 6 | 1S | 3AY | 348, 410, 470 | 415, 500, 536 | 0.16 | $1.22 \cdot 10^9$ |

General formula of new polymer-bifluorophors:

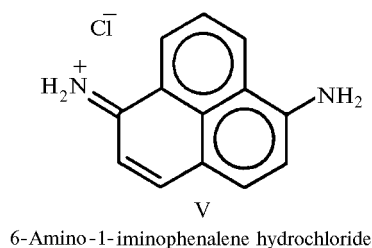
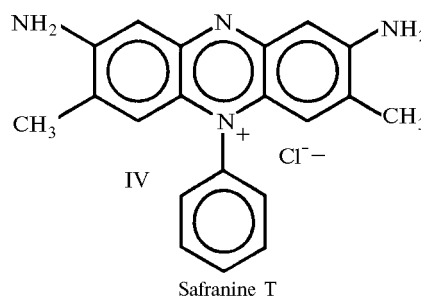
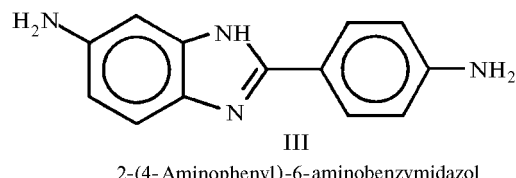
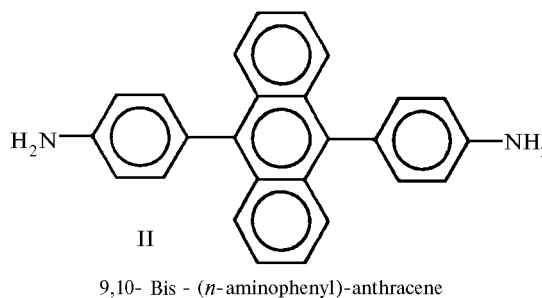
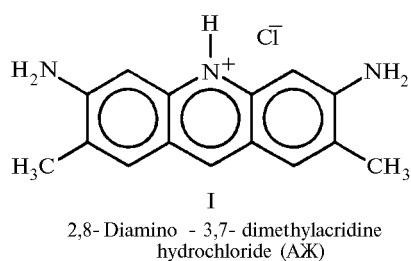


Fig. 2. Structure formulas of the diamine-fluorophors used.

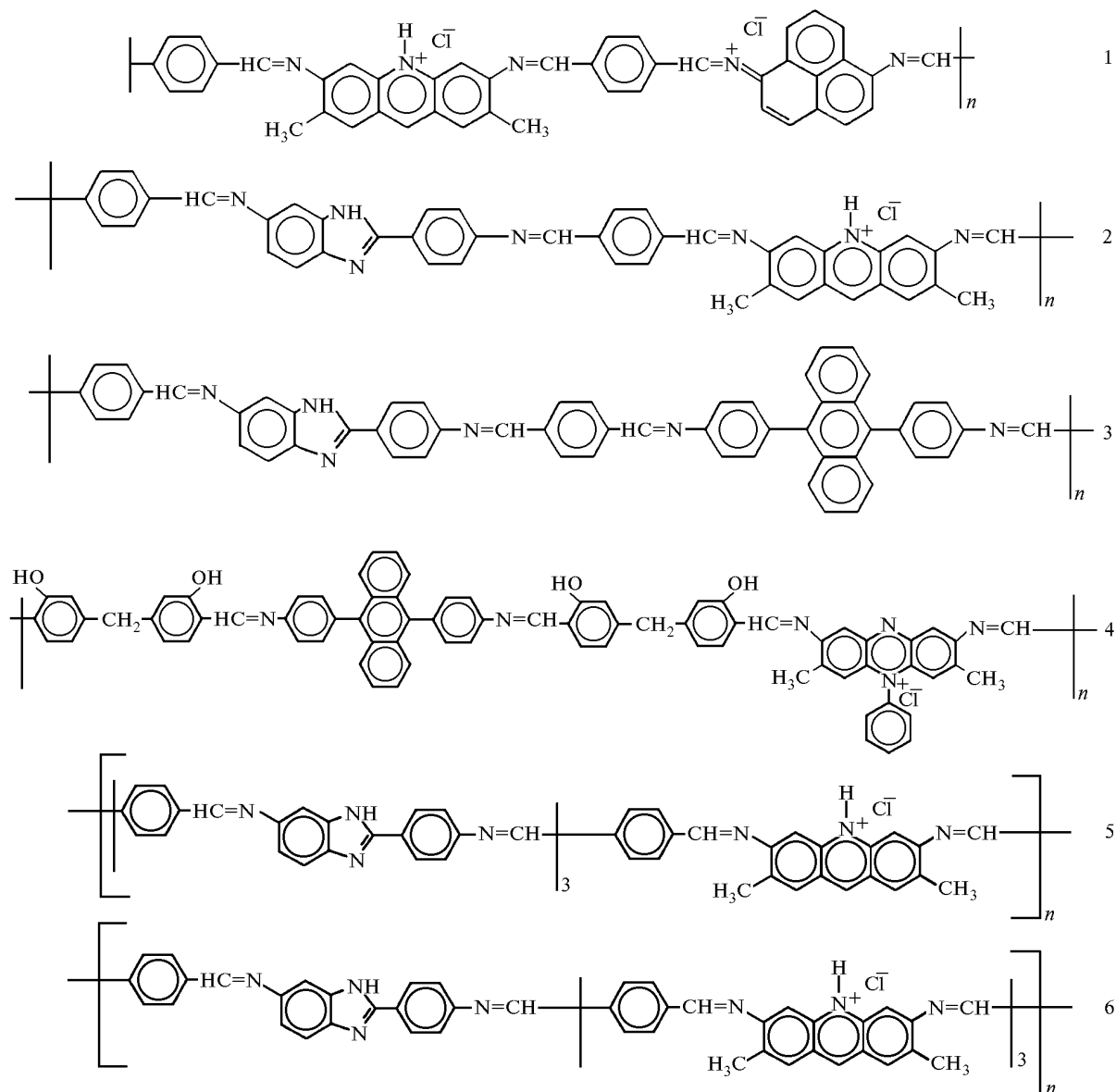


Fig. 3. Structure formulas of the elementary unit of polymer-bifluorophors with the statistical (1-4) and non-statistical (5, 6) distribution of the fluorescent elements over the polymer chain: AY+PhH (1), S+AY (2), S+BAPhA (3), BAPhA+safranin T (4), 3S+1AY (5), and 1S+3AY (6).

Figure 4a shows the absorption (1, 3) and luminescence (2, 4) spectra of respectively acridine yellow (AY) and diamine 6-amino-1-imino-phenalaline hydrochloride (PhH), while Fig. 4b shows the absorption (1) and luminescence (2) spectra of the polymer 1 produced from them. In the latter spectra we can see the bands corresponding to the absorption bands of both of the initial diamines. Note that similar pattern was observed in other polymers as well, that is, the absorption spectra of the initial components and the polymer-bifluorophors were close enough. This allowed us to assume that as all the studied polymers are excited at the wavelength corresponding to the excitation of the donor of electronic excitation energy, at which the acceptor excitation was minimal (the value of the wavelength was selected experimentally

from the absorption and excitation spectra of the solutions of the diamines which were acceptors of the electronic excitation energy). The emission from an acceptor in the polymer is possible only after transfer of the excitation energy from the donor. In the experiments we used low concentration solutions (10^{-6} – 10^{-5} mol/l), that allowed us to exclude the efficient radiative transfer of energy. In the fluorescence spectrum of the polymer 1 at excitation at the wavelength corresponding to excitation of the donor, an intense peak of its fluorescence was observed, as well as a low-intensity fluorescence band of the acceptor. Consequently, for this polymer the efficiency of intramolecular non-radiative energy transfer was proved to be low, what can be explained by a small area of overlapping of the donor's emission spectrum

with the absorption spectrum of the acceptor of the electronic excitation energy.

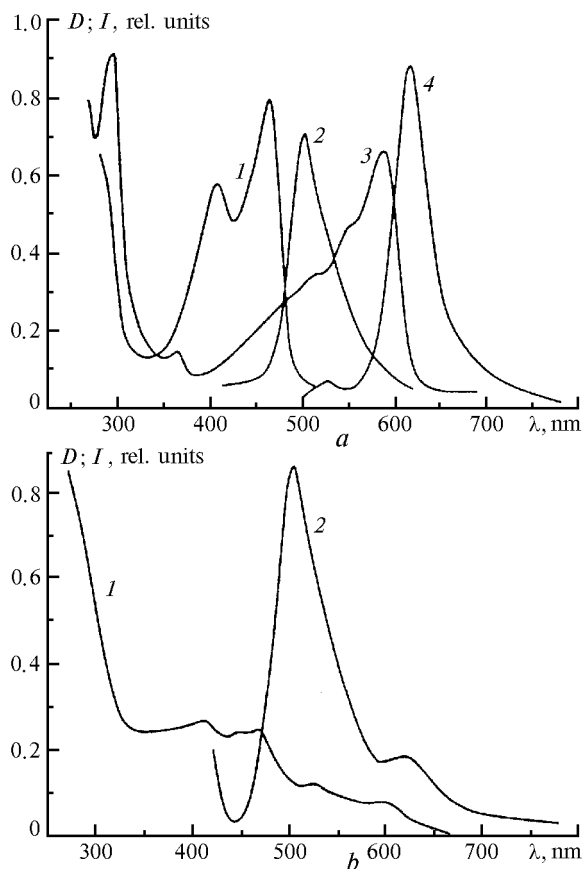


Fig. 4. Spectra of the solutions of AY and PhH diamines (*a*) and polymer 1 (AY+PhH) (*b*) in N-methylpyrrolidone: absorption spectra of AY and PhH diamines (1, 3), luminescence spectra of S and AY diamines (2, 4) when excited at $\lambda = 348$ and 410 nm; absorption spectrum of polymer 1 (1), and luminescence spectrum of polymer 1 (2) when excited at $\lambda = 410$ nm.

From Fig. 5 one can see that as the polymer 2 is excited by radiation at the wavelength of 348 nm, which excites mostly the donor component, intense fluorescence of the acceptor (500 nm) and weak fluorescence of the donor (420 nm) are observed in the fluorescence spectrum of the polymer. One can also note a good overlap of the luminescence spectrum of the donor and the absorption spectrum of the acceptor. Taking into account the above notes, we can judge on the possibility of the efficient non-radiative transfer of the electronic excitation energy to occur in the polymer 2. Quite different pattern was observed for the spectral-luminescent characteristics of the polymer 3 and the initial diamines. The emission spectrum of the donor diamine strongly overlaps the absorption spectrum of the acceptor diamine. However, as the donor component in the polymer is excited, fluorescence of the acceptor is low-efficient and, consequently, the efficiency of the non-radiative transfer of the electronic excitation energy is low. That

means that the conformation structure of the polymer (distance between the donor and acceptor components and their mutual orientation) affects significantly the efficiency of the energy transfer. (In the case considered, the conformation is likely to be unfavorable.) In particular, if the distance between the emission centers is large (polymer 4), then the non-radiative transfer of the electronic excitation energy is not observed experimentally.

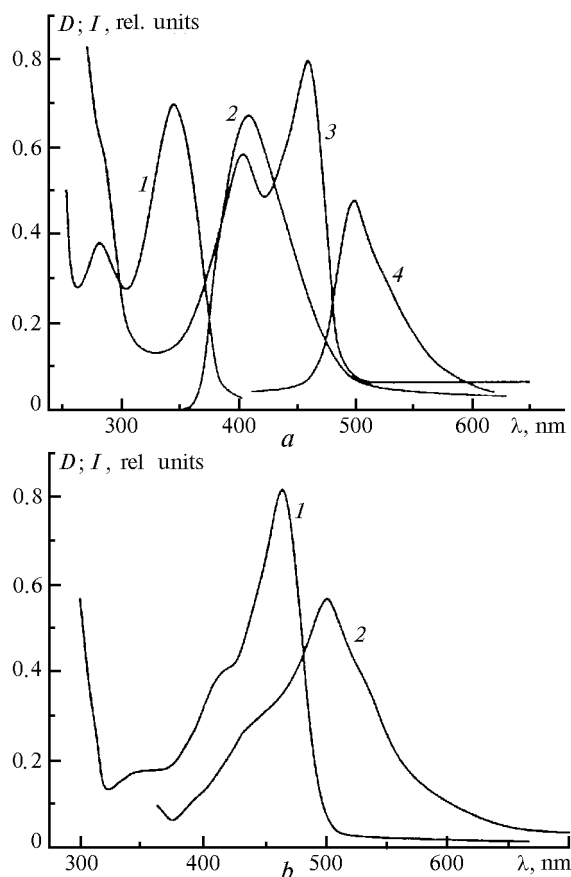


Fig. 5. Spectra of the solutions of the softener (S) and AY diamines (*a*) and the polymer 2 (S+AY) (*b*) in N-methylpyrrolidone: absorption spectra of S and AY diamines (1, 3) and luminescence spectra of S and AY diamines (2, 4) when excited at $\lambda = 348$ and 410 nm; absorption spectrum of polymer 2 (1) and luminescence spectrum of polymer 2 excited by radiation at $\lambda = 348$ nm (2).

To study the influence of arrangement and number of fluorescent fragments in the polymer chain on the efficiency of the process of non-radiative energy transfer, we have developed the method for producing polymers by polycondensation of donor-based oligomer (three parts of the softener diamine in the elementary unit) and acceptor diamine, as well as acceptor-based oligomer (3 parts of AY diamine) and donor diamine. Thus we obtained the polymer 5 with prevalence of the donor molecules in the chain and the polymer 6 with prevalence of the acceptor molecules (see Fig. 3). Figure 6 shows the absorption and fluorescence spectra

of the polymers 5 and 6, and for comparison the fluorescence spectrum of the polymer 2. The polymer 2 is based on the same diamine-fluorophors, but with the statistical distribution of them over the polymer chain.

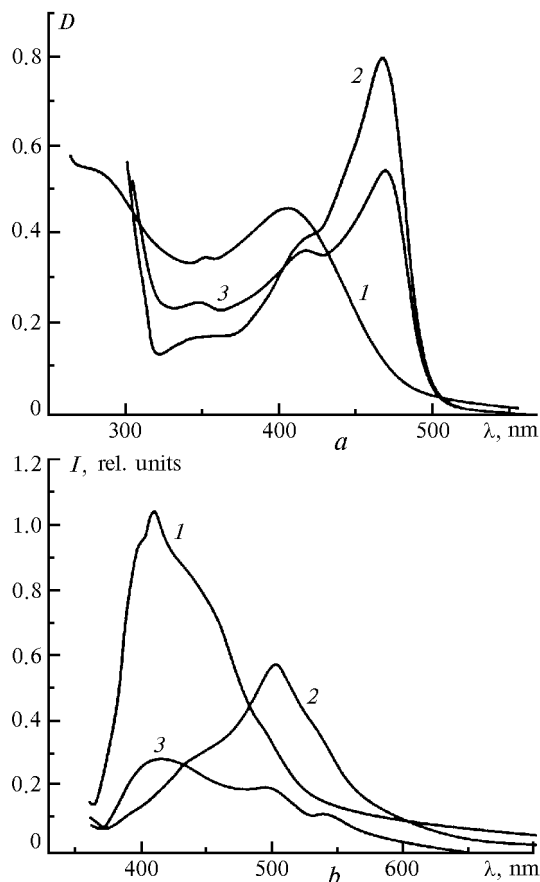


Fig. 6. Absorption (a) and fluorescence (b) spectra of the polymer 5 (1), polymer 6 (3), and, for a comparison, of polymer 2 (2) excited by radiation at $\lambda = 348$ nm.

One can see from the figure that the polymer 5 is characterized by an intense luminescence of the donor,

while luminescence of the acceptor is absent. In the polymer 6 the acceptor is weakly fluorescing. The fluorescence maximum of the acceptor when excited at the wavelength corresponding to the donor absorption is observed in the polymer 2. Table 3 gives the principal spectral-fluorescent characteristics of the polymers studied. (Note that the given values of the transfer rate constant were calculated under the condition that $\Phi^2 = 0.9$ for all polymers.) This comparison allows the conclusion to be drawn that synthesis of polymers with the statistical distribution of fluorophor fragments is preferable for the development of the systems with efficient intramolecular migration of the electronic excitation energy, and the polymers are promising for use as active media in both liquid and solid-state lasers.

Thus, for the first time we have synthesized poly Schiff bases-bifluorophors and studied the influence of the composition and structure of such systems on the possibility of non-radiative transfer of the electronic excitation energy in them.

The results obtained will be used to form the scientific basis for the directed synthesis of polymer-bifluorophors which would allow the selective process of electronic excitation energy exchange in solid and liquid media. Thus the new approach will be obtained to solution of one of the fundamental problems in photophysics – development of the methods for performing control over the processes of energy transformation.

References

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