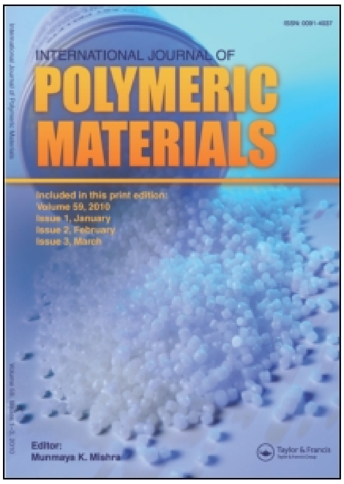

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Poly(Schiff's Bases)-Bifluorophores: Synthesis, Photophysical Properties, Non-radiative Energy Transfer of Electronic Excitation

S. A. Siling; S. V. Shamahin[a]; I. A. Ronova[a]; A. Yu. Kovalevski[a]; A. B. Grachev[b]; O. Yu. Tsiganova[b]; V. I. Yuzhakov[b]
[a] Institute of Organo-Element Compounds, Russian Academy of Sciences, Moscow, Vavilova Street [b] Moscow State University, Physical Faculty, Moscow

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Poly(Schiff's Bases)-Bifluorophores: Synthesis, Photophysical Properties, Non-radiative Energy Transfer of Electronic Excitation

S. A. SILING[a,]*, S. V. SHAMAHIN[a], I. A. RONOVA[a], A. Yu. KOVALEVSKI[a],
A. B. GRACHEV[b], O. Yu. TSIGANOVA[b] and V. I. YUZHAKOV[b]

[a]Institute of Organo-Element Compounds, Russian Academy of Sciences 117813 Moscow, Vavilova Street 28; [b]Moscow State University, Physical Faculty 119899 Moscow

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The method of synthesis of unsymmetrical azomethynes-bifluorophores where one of the fluorescent fragments is a donor of electron excitation energy and the second one is an acceptor was worked out. Photophysical properties of azomethynes-bifluorophores were investigated. It was shown that in these compounds non-radiative energy transfer takes place. It was established that quantum-chemical semiempirical method AM1 may be used for the calculation of spatial structure of amines-fluorophores.

Keywords: Absorption; Fluorescence; Azomethynes-bifluorophores; Transfer of electron excitation energy

Earlier [1] for the first time we have synthesized poly(schiff's bases)-fluorophores by polycondensation of dialdehydes of dicarboxylic acids and diamines-fluorophores. It was shown, that the solutions of this polymers have abnormal high for polymer solutions fluorescence quantum yield reaching 80% at 20°C.

The next purpose of our study is the molecular design of a new class of polymers-bifluorophores – poly(schiff's bases)-bifluorophores, in which non-radiative transfer of energy of electronic excitation in

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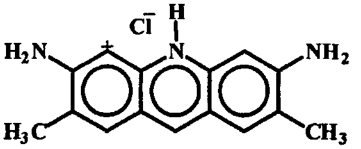
*Corresponding author. Fax: (095) 135 5085, e-mail: siling@ineos.ac.ru polymeric chains is observed, detailed research of photophysical processes occurring in polymers-bifluorophores at absorption of light, establishment of laws and mechanisms of radiative and non-radiative intra- and intermolecular energy transfer as major avenue of the energy dissipation.

The means of non-radiative transfer of energy of electronic excitation in poly(schiff's bases)-bifluorophores are determined by the fluorophores-donors and fluorophores-acceptors being closely spaced about 15 (Å), and by the absence of conjugation between the aldehyde and amine components of polymer [2]. Poly(schiff's bases)-bifluorophores – were not described earlier.

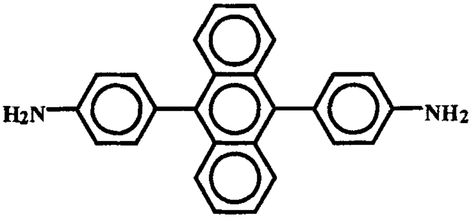
The synthesis of polymers-bifluorophores is complicated, and the study of the mechanism of energy transfer in polymers is associated with large difficulties from the viewpoint of specificity of macromolecules structure. Therefore first of all we developed methods of synthesis of substances modelling elementary units of polymers-bifluorophores – azomethynes-bifluorophores [3]. It was shown, that in the case of azomethynes-bifluorophores non-radiative energy transfer takes place. The mechanism of non-radiative energy transfer was investigated. The obtained data were used as a basis for development of methods of synthesis and research poly(schiff's bases)-bifluorophores.

The polymers were produced by polycondensation of terephthaldehyde or dialdehyde of 5,5′-methylene-bis-salicylic acid and two diamines-fluorophores where one is the donor of energy and the other is the acceptor. The choice of mono- and diamines-fluorophores was determined by their spectral-fluorescent characteristics, just degree of overlap of radiation field of the amine-donor of energy of electronic excitation by the field of energy absorption of amine-acceptor. On the base of literature and experimental data the following diamines-fluorophores were chosen:



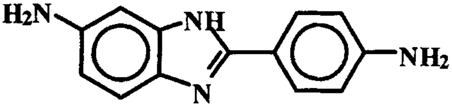
2,8-diamine-3,7-dimethylacrydine hydrochloride

I



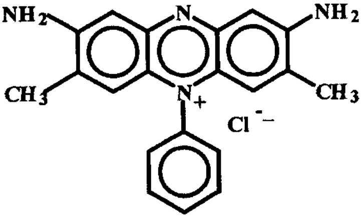
9,9-bis(p-aminophenyl)anthracene

II



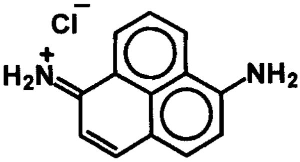
5-amino-2-(4-aminophenyl)benzimidazol

III



Safranine T

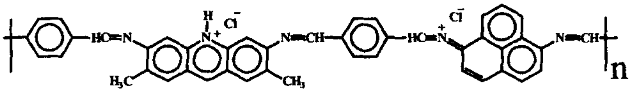
IV



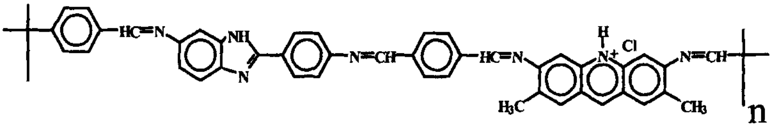
6-amino-1-iminophenalen
hydrochloride

V

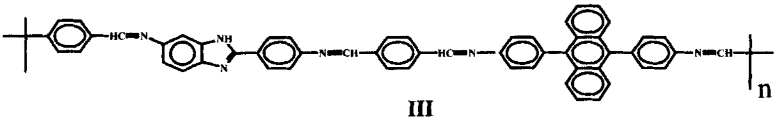
In the initial stage of research, 4 polymers-bifluorophores were synthesized:



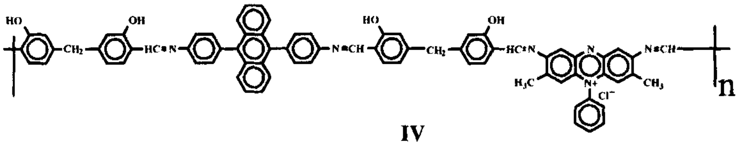
I



II



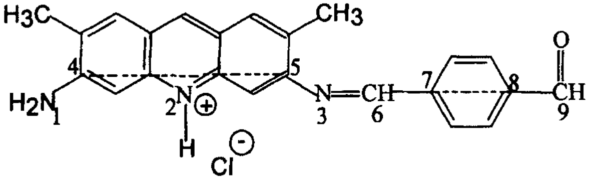
III



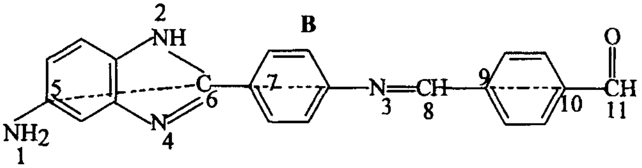
IV

where diamine **III** is the donor of energy, diamines **IV**, **V**-acceptors, and diamines **I** and **II**-donors or acceptors depending on the structure of polymer. For the production of polymers-bifluorophores intermonomer-dialdehyde was gradually added to a solution of eqimolar mixture of two diamines at 120°C, kept for several hours till the disappearance of monomers, then heated to 140°C and kept for 4–5 h. Because of this method of polymers-bifluorophores synthesis – both regular, and the statistical distribution of fluorescent fragments in a polymeric chain are possible. It is largely determined by the basicity of diamines. Below, this aspect of the problem will be considered on the example of polycondensation of terephthaldehyde with 2,8-diamine-3,7-dimethylacrydine hydrochloride and 2-(4-aminophenyl)-6-aminobenzimidazol. Since in the initial stage of reaction there is an interaction of terephthaldehyde with diamines with the formation of the substances of the following structures:

A



B



It is possible to suppose, that diamines can react with terephthaldehyde in various sequences depending on the basicity of amino groups.

For an estimate of reactivity of amino groups the calculation of charges on nitrogen atoms and specification of geometry of both molecules was made by the semi-empirical quantum-chemical method AM1 using a software package MOPAC. The data on the geometry of molecules were used for calculation of the virtual bands inside heterocycles (see structures A and B). The angles, given in the Table I, are additional to valence angles.

From the table one can see that the size of the charge on the nitrogen atom of the amino group in substance **B** is higher than the size of the charge on the nitrogen atom of nitrogen of the amino group in substance **A**. Besides this, the nucleophilicy of amino group in substance **A** is reduced because the methyl group in *o*-position to amino

TABLE I Geometrical parameters of molecules A and B and charges on atoms of nitrogen

Molecule	*Charge*	*Bond*	*Length, Å*	*Angle, degree*
A	−0.3341	1−4	1.39	1-4-5−32
		4−5	7.32	4-5-3−32
		5−3	1.39	5-3-6−50.1
		3−6	1.28	3-6-7−48.2
		6−9	5.72	
B	−0.4154	1−5	1.39	1-5-6−20.6
		5−6	4.56	5-6-7−7.8
		6−3	5.70	7-3-8−50.1
		3−8	1.29	3-8-9−48.2
		8−11	5.72	

group creates sterical hinderance to the interaction of aldehyde and amino-groups. As a consequence, the statistical distribution of fluorescent fragments in polymeric chain is the most probable.

In Figure 1 the absorption (1, 3) and fluorescence spectra (2, 4) of solutions of diamine **I** (donor of energy) and **V** (acceptor of energy) in *N*-methylpyrrolidone-2 are shown. From the figure one can see that the field of radiation of diamine **I** is partially overlapped by the field of absorption of diamine **V**, that confirms the opportunity of non-radiative transfer of energy from diamine **I** to diamine **V**.

In Figure 2 the absorption and fluorescence spectra of the solution of polymer **1** in *N*-methylpyrrrolidone-2 are given. From the figure one can see that in the absorption spectrum there are bands of absorption of both initial diamines. In the spectrum of fluorescence of the polymer, obtained by excitation at the band of absorption of diamine **I**, there are intensive peak of fluorescence of diamine **I** and less intensive peak of fluorescence of diamine-acceptor. That is explained by a rather small field of overlap of the radiation field of the donor of energy by the field of absorption of energy acceptor.

In Figure 3 the spectra of absorption (1, 3) and fluorescence (2, 4) of the solutions of diamines **I** and **III** in *N*-methylpyrrolidone-2 are shown. From the figure one can see that the radiation field of diamine

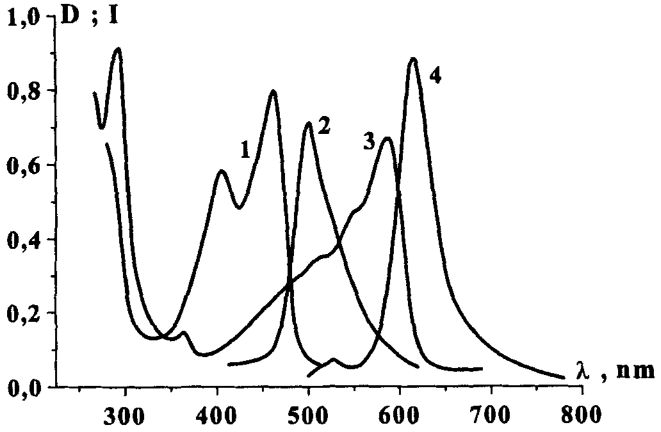


FIGURE 1 Spectral-fluorescent characteristics of solutions of diamines **I** and **V** in *N*-methylpyrrolidone-2: 1 – Spectrum of absorption of diamine **I**, 2 – Spectrum of fluorescence of diamine I (excitation at 410 nm), 3 – Spectrum of absorption of diamine V, 4 – Spectrum of fluorescence of diamine V (excitation at 500 nm).

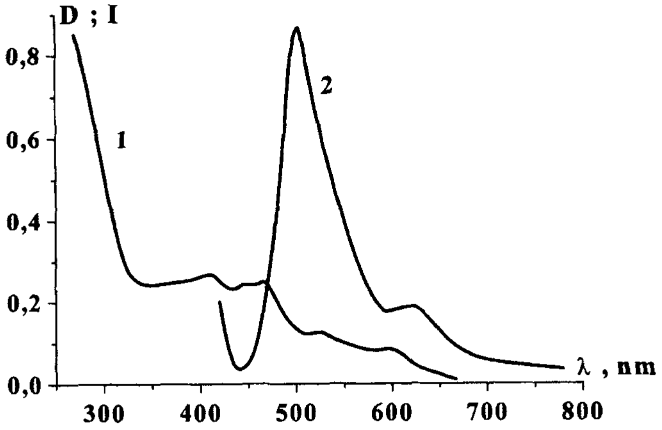


FIGURE 2 Spectral-fluorescent characteristics of a solution of polymer **1** in *N*-methyl-pyrrolidone-2: 1 – Spectrum of absorption, 2 – Spectrum of fluorescence (excitation at 410 nm).

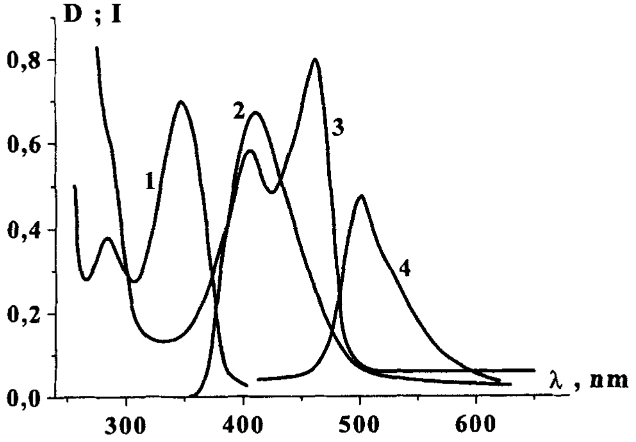


FIGURE 3 Spectral-fluorescent characteristics of the solutions of diamines **III** and **I** in *N*-methylpyrrolidone-2: 1 – Spectrum of absorption of diamine **III**, 2 – Spectrum of fluorescence of diamine **III** (excitation at 348 nm), 3 – Spectrum of absorption of diamine **I**, 4 – Spectrum of fluorescence of diamine **I** (excitation at 410 nm).

III-donor of energy is almost completely overlapped by the field of absorption diamine **I**-acceptor of energy.

The absorption and fluorescence spectra of the solution of polymer **2** in *N*-methylpyrrolidone-2 are given in Figure 4. As follows from

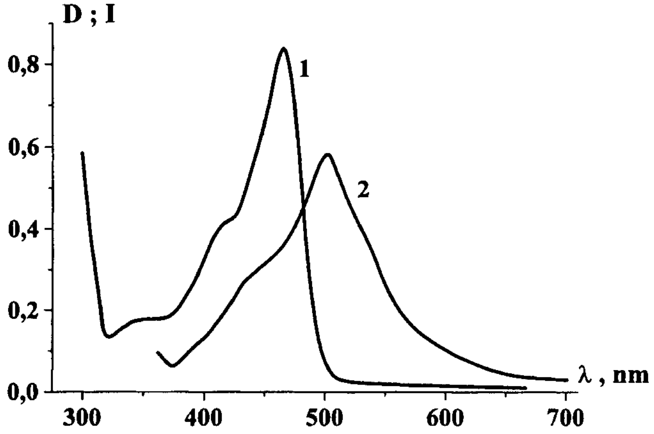


FIGURE 4 Spectral-fluorescent the characteristics of solution of polymer **2** in *N*-methylpyrrolidone-2: 1 – Spectrum of absorption, 2 – Spectrum of fluorescence (excitation at 348 nm).

the figure, in case of excitation in band of absorption of the donor of energy (diamine **III**) – 348 nm in a spectrum of fluorescence of the polymer solution in *N*-methylpyrrolidone-2 an intensive peak of fluorescence of energy acceptor (500 nm) and less intensive peak of fluorescence of the energy donor (420 nm) are observed. It attests to an effective non-radiative energy transfer in polymer **2**.

Spectra of absorption (1, 3) and fluorescence (2, 4) of solutions of diamine **III** (donor of energy) and diamine **II** (acceptor of energy) in *N*-methylpyrrolidone-2 are shown in Figure 5. From the figure one can see that the field of radiation of diamine **III** is largely overlapped by the field of absorption of diamine **II**. That confirms the correct selection of initial diamines-fluorophores for synthesis of polymer **2**.

In Figure 6 the spectra of absorption and fluorescence of the solution of polymer **3** in *N*-methylpyrrolidone-2 are given. From the figure one can see that in the spectrum of absorption of polymer there are bands of the donor and acceptor of energy. That confirms the structure of polymer **3**. The fluorescence spectrum of the solution of polymer **3** in *N*-methylpyrrolidone confirms the presence of non-radiative energy transfer in this polymer.

For the determination of the influence of the structure of inter-monomer on the process of energy transfer dialdehyde of

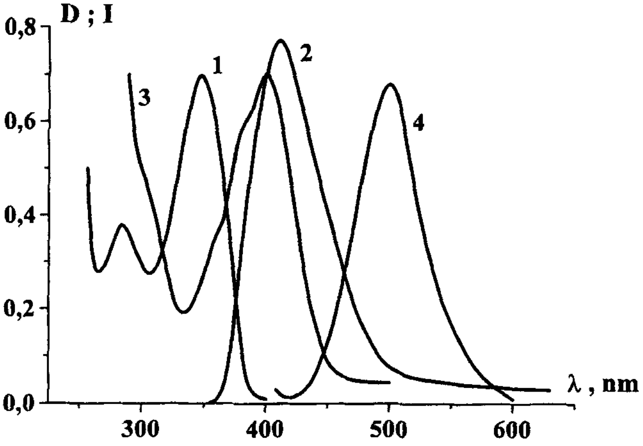


FIGURE 5 Spectral-fluorescent the characteristics of solutions of diamines **III** and **II** in *N*-methylpyrrolidone-2: 1 – Spectrum of absorption of diamine **III**, 2 – Spectrum of fluorescence of diamine **III** (excitation at 348 nm), 3 – Spectrum of absorption of diamine **II**, 4 – Spectrum of fluorescence of diamine **II** (excitation at 410 nm).

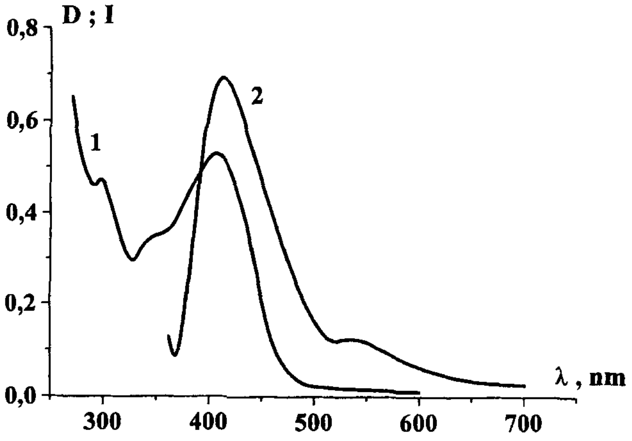


FIGURE 6 Spectral-fluorescent the characteristics of solution of polymer **3** in *N*-methylpyrrolidone-2: 1 – Spectrum of absorption, 2 – Spectrum of fluorescence (excitation at 348 nm).

5,5′-methylene-bis-salicylic acid was used as an intermonomer for the synthesis of polymer **4**.

In Figure 7 the spectra of absorption and fluorescence of 9,9-bis(*p*-aminophenyl)anthracene and cafranine T are given. From the figure

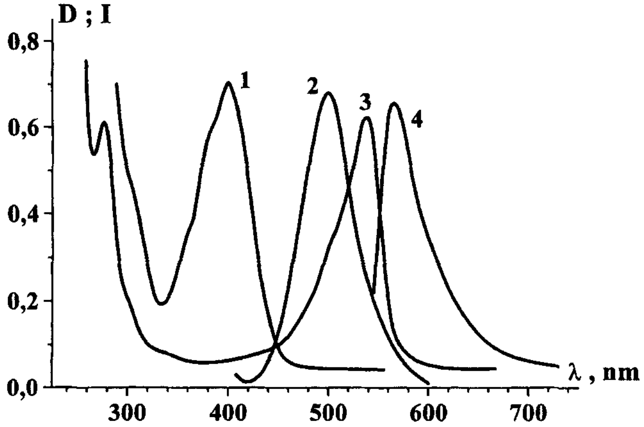
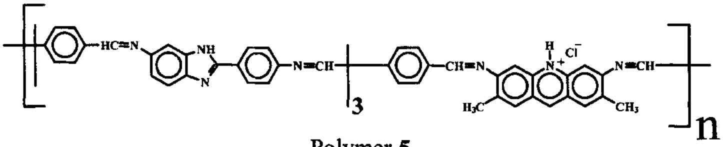


FIGURE 7 Spectral-fluorescent the characteristics of solutions of diamines **II** and **IV** in *N*-methylpyrrolidone-2: 1 – Spectrum of absorption of diamine **II**, 2 – Spectrum of fluorescence of diamine **II** (excitation at 410 nm), 3 – Spectrum of absorption of diamine **IV**, 4 – Spectrum of fluorescence of diamine **IV** (excitation at 535 nm).

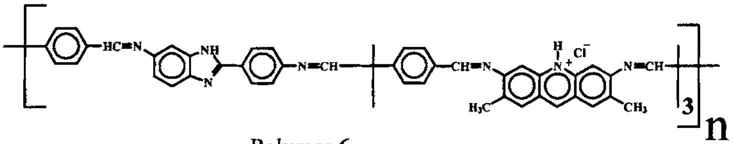
one can see that the overlap of the field of fluorescence of 9,9-bis(*p*-aminophenyl)anthracene by the field of absorption of safranine T is rather great. Because of this it was possible to expect that in a polymer based on these diamines (polymer **4**) non-radiative energy transfer must occur. But it is provided that, in spite of the fact that in the spectrum of absorption of polymer the bands of absorption of both diamine are observed, there is only the band of radiation of the energy donor in spectrum of fluorescence (Fig. 8). Thus, in polymer **4** non-radiative transfer of energy is not observed. It must be associated with large distance between the centers of fluorescence.

For the study of influence of disposition of fluorescent fragments in a polymeric chain on non-radiative transfer of energy the method of polymers synthesis by polycondensation of oligomer on the basis of the donor of energy (diamine **III**) and diamine-acceptor of energy (diamine **I**) was developed (polymer **5**). Then the method of synthesis of polymer on the basis and diamine-donor of energy (diamine **III**) – and oligomer on a base of diamine-acceptor of energy (diamine **I**) was carried out (polymer **6**). Terephthaldehyde was used as intermonomer.

In Figure 9 the spectra of fluorescence of polymers **5** and **6** (where one of the initial substance is oligomer) and **2** (with statistical



Polymer 5



Polymer 6.

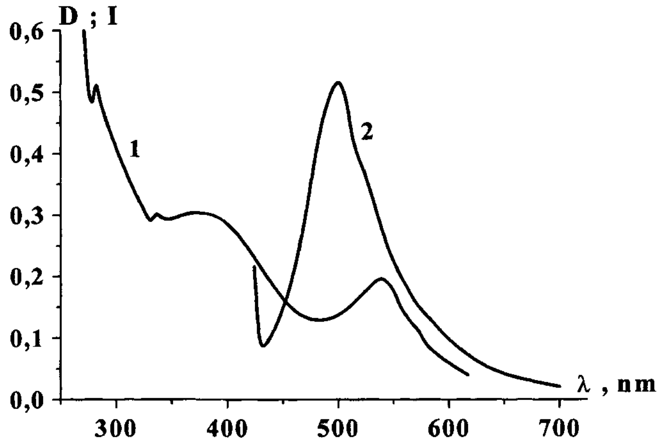


FIGURE 8 Spectral-fluorescent characteristics of solution of polymer **4** in *N*-methyl-pyrrolidone-2: 1 – Spectrum of absorption, 2 – Spectrum of fluorescence by (excitation at 410 nm).

disposition of the diamines-fluorophores in polymer chain) are shown. From the figure one can see that in the spectrum of fluorescence of polymer **5** an intensive band of emission of the donor of energy is present, while a band of emission of energy acceptor is practically absent. In a radiation spectrum of polymer **6** only weak bands of fluorescence of energy acceptor are observed. So the most intensive fluorescence band of energy acceptor at excitation at a band of absorption of energy donor is observed in polymer with statistical distribution of diamines-fluorophores (Fig. 10).

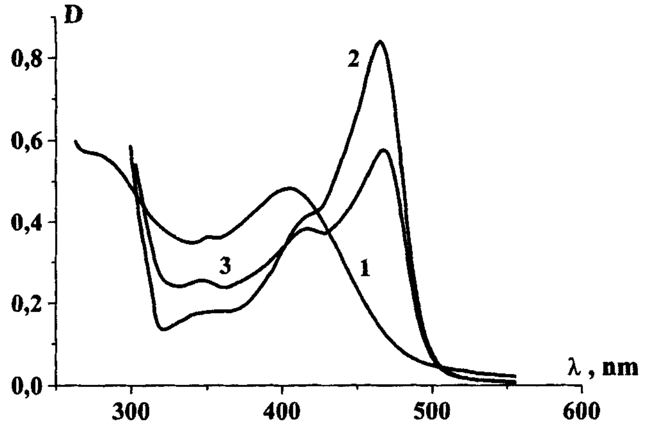


FIGURE 9 Spectrums of absorption of polymer solutions in *N*-methylpyrrolidone-2: 1 – Polymer **5**, 2 – Polymer **2**, 3 – Polymer **6**.

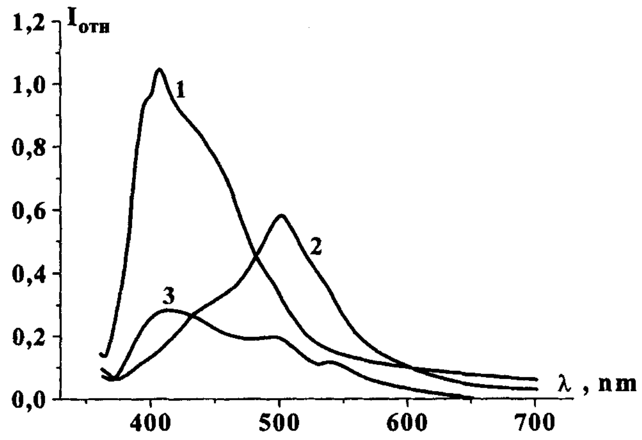


FIGURE 10 Spectra of fluorescence of polymer solutions in *N*-methylpyrrolidone-2 (excitation at 348 nm): 1 – Polymer **5**, 2 – Polymer **2**, 3 – Polymer **6**.

Thus for the first time poly(schiff's bases)-bifluorophores are synthesized. It is shown, that in this polymers non-radiative transfer of energy of electron excitation is realized.

The results of the study will be used for developing of scientific bases of synthesis of polymers-bifluorophores, where the selective process of exchange of energy of electronic excitation in solid and liquid states of polymers is possible. So the new approach will be thus carried out to the decision of one of the fundamental problems in photophysics – development of methods of management of processes of energy conversation.

The polymers-fluorophores and bifluorophores are perspective for use as active components for liquid and solid lasers, scintillators, especially for indication of hard radiation, for transformation of short-wave radiation to long-wave one for transfer of information in optical fiber communication lines, for capacity increase of solar batteries, for protection of valuable papers, for manufacturing publicity boards, *etc.*

1. EXPERIMENTAL

1.1. Synthesis of Polymer I

Solutions of 6-amino-1-iminophenalen hydrochloride (0,4594 g, 0,002 mol) in 8 cm^3 of *N*-methylpyrrolidone and of 2,8-diamine-3,7-dimethylacrydine hydrochloride (0.5471 g, 0.02 mol) in 10 cm^3 of *N*-methylpyrrolidone were placed in four-necked flask fitted with a condenser, capillary for argon supply, thermometer and drop funnel, and heated to 130°C under argon. The solution of terephthaldehyde (0.5364 g, 0.004 mol) in 4 cm^2 of the mixture *N*-methylpyrrolidone : *p*-xylene = 3 : 1 vol was placed in dropfunnel and added dropwise for 3 h to the mixture of diamines solution, kept at this temperature for 5 hours, heated to 180°C for *N*-methylpyrrolidone distillation, cooled to room temperature. The solids were filtered off, washed with methanol, extracted by ethanol for 24 h, dried in vacuum for 24 h.

The mass of solids was 1.24 g (91.2%).

1.2. Synthesis of Polymer II

Solutions of 5-amino-2-(4-aminophenyl)benzimidazol (0.4256 g, 0.0019 mol) in 1.5 cm^2 of *N*-methylpyrrolidone and of 2, 8-diamine 3,7-dimethylacrydine hydrochloride (0.4503 g, 0.0019 mol) in 10 cm^3 of *N*-methylpyrrolidone were placed in four-necked flask fitted with a condenser, capillary for argon supply, thermometer and dropfunnel and heated to 130°C under argon. The solution of terephthaldehyde (0.5092 g, 0.0038 mol) in 4 cm^2 of the mixture *N*-methylpyrrolidone : *p*-xylene = 3 : 1 vol was placed in dropfunnel and added dropwise for 5 h to the mixture of diamines solution, kept at this temperature for 5 hours, heated to 180°C for *N*-methylpyrrolidone distillation, cooled to 50°C and poured into 50 cm^3 of methanol. The solids were filtered off, washed with methanol, reprecipitated from *N*-methylpyrrolidone to methanol, dried in vacuum for 24 h.

The mass of solids was 0.51 g (40.86%).

1.3. Synthesis of Polymer III

Solutions of 5-amino-2-(4-aminophenyl)benzimidazol (0.202 g, 0.009 mol) in 1.5 cm^2 of *N*-methylpyrrolidone and of 9,9-bis(*p*-aminophenyl)anthracene (0.325 g, 0.009 mol) in 5 cm^3 of *N*-methylpyrrolidone were placed in four-necked flask fitted with a condenser, capillary for argon supply, thermometer and dropfunnel and heated to 130°C. The solution of terephthaldehyde (0.242 g, 0.0018 mol) in 4 cm^2 of the mixture *N*-methylpyrrolidone : *p*-xylene = 3 : 1 vol was placed in dropfunnel and added dropwise for 3 h to the mixture of diamines solution, kept at this temperature for 5 hours, heated to 180°C for distillation of 5 cm^3 of *N*-methylpyrrolidone, cooled to 50°C and poured into 50 cm^3 of methanol. The solids were filtered off, washed with methanol, reprecipitated from *N*-methylpyrrolidone to methanol, dried in vacuum for 24 h.

The mass of solids was 0.52 g (74.07%).

1.4. Synthesis of Polymer IV

Solutions of safranine T (0.3505 g, 0.001 mol) in 10 cm^2 of *N*-methylpyrrolidone and of 9,9-bis(*p*-aminophenyl)anthracene (0.36 g, 0.001 mol) in 5 cm^3 of *N*-methylpyrrolidone were placed in four-necked flask fitted with a condenser, capillary for argon supply, thermometer and dropfunnel and heated to 130°C. The solution of 5,5′-methylene-bis-salicylic dialdehyde (0.512 g, 0.002 mol) in 8 cm^2 of the mixture *N*-methylpyrrolidone : *p*-xylene = 3 : 1 vol was placed in dropfunnel and added dropwise for 3 h to the mixture of diamines solution, kept at this temperature for 5 hours, heated to 180°C for distillation of 15 cm^3 of *N*-methylpyrrolidone, cooled to 50°C and poured into 50 cm^3 of methanol. The solids were filtered off, washed with methanol, reprecipitated from *N*-methylpyrrolidone to methanol for 2 times, dried in vacuum for 24 h.

The mass of solids was 0.71 g (79.3%).

1.5. Synthesis of Polymer V

1.5.1. Synthesis of Oligomer with Dialdehyde End Groups on the Base of 5-amino-2-(4-aminophenyl)benzimidazol

A solution of terephthaldehyde (0.536 g, 0.04 mol) in 50 cm^3 of ethanol and a solution of 5-amino-2-(4-aminophenyl)benzimidazol (2.37 g, 0.01 mol) in 50 cm^3 of ethanol placed in three-necked flask fitted with a condenser, capillary for argon supply and thermometer, heated to 78°C, kept at this temperature for 3 hours and cooled to 20°C. The solids were filtered off, washed with methanol, dried in vacuum for 24 h.

The mass of solids was 1.81 g (49.41%).
Found, % : C – 72.59; H – 4.47; N – 14.39
Calc. for $C_{71}H_{12}N_{48}O_2 \cdot 4\ H_2O$, % C – 72.70; H – 4.78; N – 14.33.

1.5.2. Synthesis of Polymer

A solution of oligomer (0.7032 g, 0.0006 mol) in 6 cm^3 of *N*-methylpyrrolidone-2 and a solution of 2,8-diamine-3,7-dimethylacrydine hydrochloride (0.1641 g, 0.0006 mol) in a mixture of 3 cm^3 of *N*-methylpyrrolidone-2 and 2 cm^3 of *p*-xylene were placed in three-necked flask fitted with a condenser, capillary for argon supply and thermometer, heated to 160°C, kept at this temperature for 6 hours, cooled to 20°C and poured into 50 cm^3 of methanol. The solids were filtered off, washed with methanol, reprecipitated from *N*-methylpyrrolidone to methanol for 2 times, dried in vacuum for 24 h.

The mass of solids was 0.21 g (24.83%).

1.6. Synthesis of Polymer VI

1.6.1. Synthesis of Oligomer with Dialdehyde End Groups on the Base of 2,8-diamine-3,7-dimethylacrydine hydrochloride

A solution of terephthaldehyde (2.68 g, 0.02 mol) in 50 cm^3 of DMF and a solution of 2,8-diamine-3,7-dimethylacrydine hydrochloride (1.275 g, 0.0047 mol) in 100 cm^3 of DMF were placed in a three-necked flask fitted with a condenser, capillary for argon supply and thermometer, heated to 50°C, kept at this temperature for 8 hours, distilled 120 cm^3 of DMF, cooled to 20°C and poured into acetone. The solids were filtered off washed with acetone, dried in vacuum for 24 h.

The mass of solids was 0.86 g. (44.01%).
Found, % : C – 75.26; H – 5.25; N – 10.18
Calc. for $C_{77}H_{57}N_9O_2 \cdot 5\ H_2O$, % C – 75.18; H – 5.45; N – 10.25.

1.6.2. Synthesis of Polymer

A solution of oligomer (0.3687 g, 0.0003 mol) in 4 cm^3 of *N*-methylpyrrolidone-2 and a solution of 5-amino-2-(4-aminophenyl)-benzimidazol (0.0672 g, 0.0003 mol) in a mixture of 1 cm^3 of *N*-methylpyrrolidone-2 and 0.5 cm^3 of *p*-xylene were placed in three-necked flask fitted with a condenser, capillary for argon supply and thermometer, heated to 150°C, kept at this temperature for 6 hours, cooled to 20°C and poured into 50 cm^3 of methanol. The solids were filtered off, washed with methanol, reprecipitated from *N*-methylpyrrolidone to methanol for 2 times, dried in vacuum for 24 h. The mass of solids was 0.15 g (35.29%).

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