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Symmetric anionic polymethine dyes derived from fluorene and its derivatives with electron-acceptor substituents: synthesis and spectral properties

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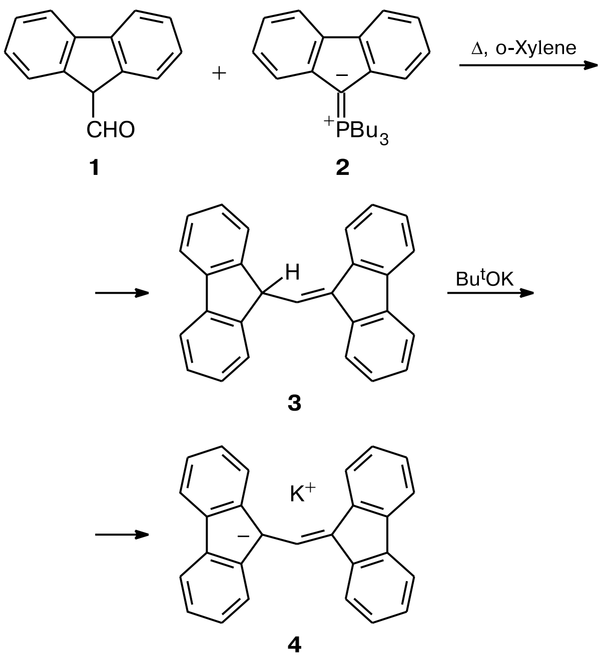
Novel anionic polymethine dyes were synthesized from 2,7-bis(phenoxysulfonyl)-, 2,7-dinitro-, and 2,4,5,7-tetranitrofluorenes. The reasons for the complicated shape of their absorption spectra were analyzed: the formation of contact ion pairs, associates, and conformational isomers and electronic effects of substituents. The quantum chemical calculations by the Pariser—Parr—Pople method and nonempirical DFT and TDDFT methods in the B3LYP/6-31G(d,p) basis set revealed that the orbitals of the nitro groups, unlike the orbitals of the SO_2OPh groups, are efficiently conjugated with the common chromophore system inducing additional electron transitions.

Key words: fluorene derivatives, polymethine dyes, absorption spectra, quantum chemical calculations, molecular orbitals, electron transitions.

Heterocyclic fragments are traditionally used as terminal groups of polymethine (cyanine) dyes.[1] In this work, we described the synthesis of polymethine dyes based on carbocycles and studied specific features of their absorption spectra. Fluorene was chosen as such a carbocycle, since it has a rich π-system and a high electron symmetry and its structure includes the active methylene group that can be involved in cyanine condensation reactions. Unfortunately, unsubstituted fluorene is inactive in these reactions because of its low CH-acidity[2] (pK_a = 20.5) even in the presence of such strong basic condensing agents as DBU, potassium *tert*-butoxide, and 1,8-bis(dimethylamino)naphthalene ("proton sponge"). Hence, indirect routes are used for the synthesis of polymethine dyes from unsubstituted fluorene.[3] Using the approach with phosphorus ylides[4] (Scheme 1), from reactants **1** and **2**, we succeeded to synthesize 9-[(9*H*-fluoren-9-yl)methylidene]-9*H*-fluorene (**3**). Then, monomethinecyanine **4** was obtained by the addition of a strong base, such as potassium *tert*-butoxide or DBU to a solution of **3**. The spectral characteristics of compound **4** in DMSO were as follows: λ_{max} = 558 nm and $\varepsilon = 6.6 \cdot 10^4$ L mol^{-1} cm^{-1}.

Scheme 1



Dye **4** and its higher vinylogs are unstable in air.[3] Instability of these compounds correlates to their high nucleophilicity, which is caused by unfavorable frontier structures with the negative charge on the carbon atoms. These structures can usually be stabilized by the introduction of electron-acceptor substituents into the electron-enriched positions of the chromophore. This substitution also facilitates the activation of the methylene group of the fluorene ring due to an increase in its CH-acidity. Note that substituents in the positions, where the electron density change upon excitation is maximum, exert the most substantial effect on the dye color.[5] Positions 2 and 7 are the such

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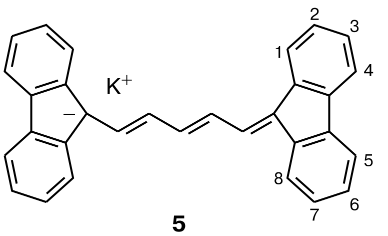
ones, as it follows from the quantum chemical calculation data for dye **5** (Fig. 1). According to the perturbation theory, an increase in the electron density in these positions upon the introduction of electron-acceptor substituents should result in bathochromic shifts of the absorption bands.



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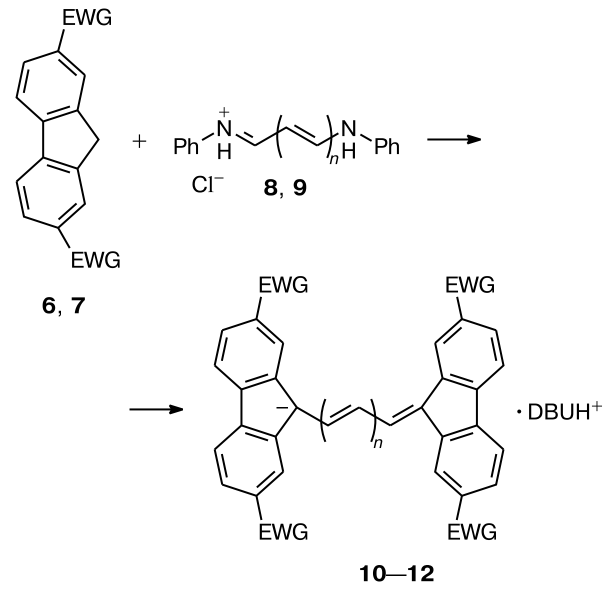
Indeed, the introduction of the electron-acceptor SO_2OPh group into positions 2 and 7 substantially increases the reactivity of the methylene group. Derivatives **6** and **7** react readily with salts **8** and **9** in the presence of DBU to undergo cyanine condensation (Scheme 2). Symmetric anionic dyes **10** and **11**, unlike their analogs (unsubstituted fluorene derivatives), are satisfactorily stable. Compounds **10** and **11** absorb light by nearly 50 nm deeper than the unsubstituted fluorene derivatives (683 and 787 nm; 633 and 740 nm, respectively) (Table 1).

Scheme 2



EWG = SO_2OPh (**6**, **10**, **11**), NO_2 (**7**, **12**)
n = 1 (**8**, **10**), 2 (**9**, **11**, **12**)

Reagents and conditions: DBU, pyridine, heating.

The absorption bands of dyes **10** and **11** have the shape typical of classical polymethine dyes with the pronounced vibration inflection at the short-wavelength edge. The vinylene shift is about 100 nm. The absorption intensity increases with chain elongation (Fig. 2).

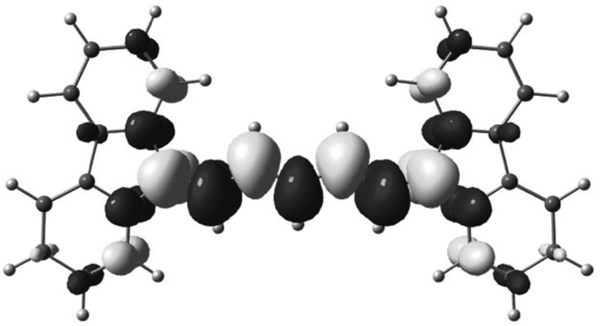


Fig. 1. Change in the electron density induced by excitation in dye **5**. The value of isosurface lines is 0.01. Here and in Fig. 9, the electron density decrease is shown by light and the increase is shown by dark.

The replacement of dichloromethane by more polar solvents results in the hypsochromic shift of the absorption band of dye **11** (λ_{max} = 799 nm (CH_2Cl_2), 796 nm (EtOH), and 791 nm (DMF)) and its broadening. The sign of solvatochromism can correctly be determined in the dichloromethane—DMF solvent pair, since they have similar values of refractive index but strongly differ in polarity. The hypsochromic shift on going from CH_2Cl_2 to DMF unambiguously indicates negative solvatochromism of dyes **10** and **11**. Note that a similar shift upon the replacement of dichloromethane with ethanol cannot serve as a reliable criterion for the estimation of the solvatochromic effect, because a decrease in the refractive index on going to ethanol acts in the direction of this shift. In addition, the solvating ability of ethanol can also be determined by hydrogen bonding.

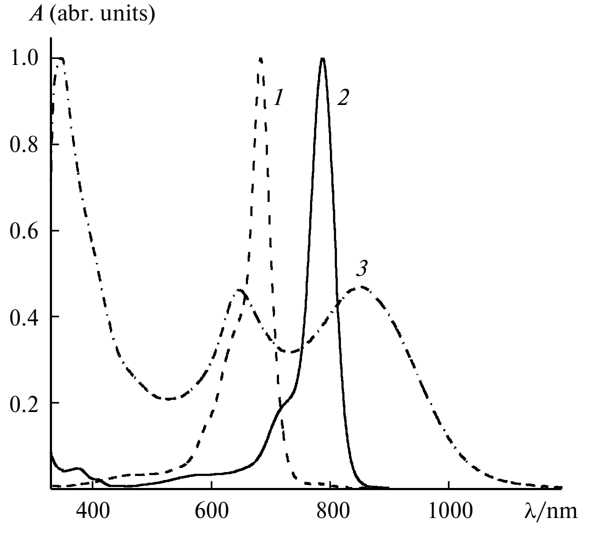


Fig. 2. Normalized absorption spectra of dyes **10** (*1*), **11** (*2*), and **12** (*3*) in acetone.

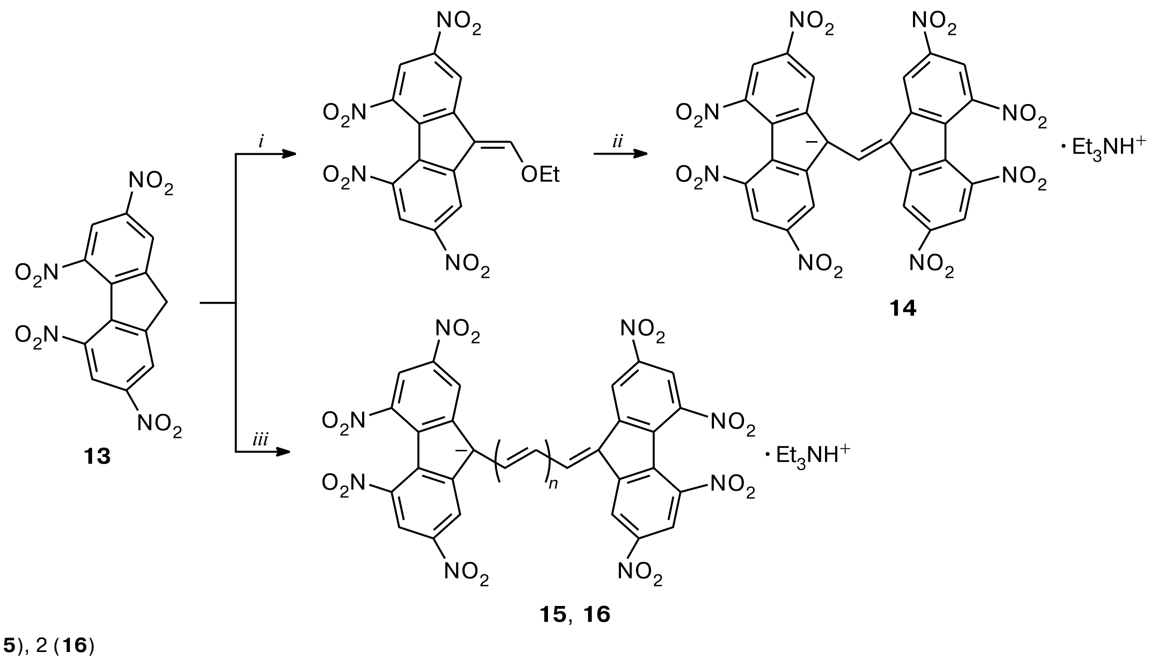
Table 1. Spectral properties of the fluorene-based dyes with electron-acceptor substituents

Compound	Solvent	λ_s/nm	$\varepsilon_s \cdot 10^{-4}$ /L mol^{-1} cm^{-1}	λ_m/nm	$\varepsilon_m \cdot 10^{-4}$ /L mol^{-1} cm^{-1}	λ_l/nm	$\varepsilon_l \cdot 10^{-4}$ /L mol^{-1} cm^{-1}
10	Acetone	—	—	—	—	683	—
11	Acetone	—	—	—	—	787	9.61
12	Acetone	346	—	646	—	851	—
14	CH_2Cl_2	389	4.08	537	1.44	772	1.84
	DMF	390	4.29	540	1.63	758	1.78
	EtOH	382	4.17	532	1.73	751	1.86
15	CH_2Cl_2	390	3.24	606	3.88	813; 892	2.46; 3.06
	DMF	393	3.40	602	4.02	818; 886	2.56; 2.86
	EtOH	385	3.04	596	3.46	806; 870	2.36; 2.65
16	CH_2Cl_2	394	3.00	617; 681	1.62; 4.13	916; 1004	3.88; 4.11
	DMF	396	2.97	611; 679	1.69; 3.74	924; 993	3.59; 3.47
	EtOH	391	2.28	599; 667	2.12; 2.17	889; 982	1.77; 1.48

We succeeded to synthesize nitro-substituted dye **12** from 2,7-dinitrofluorene **7** only under similar drastic conditions with DBU, in spite of stronger electron-acceptor properties of the nitro group compared to the phenoxysulfonyl one ($\sigma_m = 0.36$, $\sigma_p = 0.33$, $\sigma^- = 1.065$ for SO_2OPh (see Refs 6 and 7); $\sigma_m = 0.68$, $\sigma_p = 0.78$, $\sigma^- = 1.27$ for the NO_2 group[8]; which assumed the possibility of making the condensation conditions milder). The spectral properties of dye **12** differ substantially from those of compounds **10** and **11**. The absorption spectrum of compound **12** consists of the band in the UV range and two bands in the visible and near-IR spectral ranges (see Fig. 2, Table 1). It is indicative that the long-wavelength band maximum attains the record value for the anionic dyes (860 nm) at the same polymethine chain length. Unfortunately, the low solubility of dye **12** considerably restricted the possibilities of its investigation.

The presence of four nitro groups in the fluorene ring substantially enhances the acidity: pK_a of 2,4,5,7-tetranitro-9*H*-fluorene (**13**) was approximately 1.2 (see Ref. 9). This allowed us to synthesize (Scheme 3) a series of anionic dyes with tetranitrofluorene terminal groups (**14—16**) under standard conditions of cyanine condensation without using strongly basic condensing agents.

Scheme 3



n = 1 (**15**), 2 (**16**)

Reagents and conditions: *i.* $HC(OEt)_3$, Ac_2O; *ii.* **13**, Et_3N, Ac_2O; *iii.* **8** or **9**, Et_3N, Ac_2O.

The absorption spectra of dyes **14**—**16** likewise compound **12**, have three bands of different shape and intensity (Fig. 3). They strongly differ in shape from the classical cyanine bands and are of fairly low intensity ($\varepsilon = 4.3 \cdot 10^4$ L mol^{-1} cm^{-1}). For such a short polymethine chain length, these dyes are fairly deeply colored (see Table 1). The long-wavelength absorption band maximum of dye **16** in dichloromethane lies at 1004 nm. For classical polymethines based on heterocycles, this absorption range is attained at a significantly longer polymethine chain. For instance, for one of the most popular terminal groups (benzothiazole), the absorption maximum at 1000 nm was obtained at a chain length of 11 methine groups, whereas only 5 methine groups provide the absorption maximum for the tetranitrofluorene derivatives.

The short-wavelength band of monomethinecyanine **14** is narrow and symmetric. On going from dichloromethane to DMF, this band undergoes the bathochromic shift by 1 nm (66 cm^{-1}), while on going to ethanol the shift is hypsochromic by 7 nm (471 cm^{-1}). The medium band is of low intensity and, similarly to the short-wavelength band, undergoes a bathochromic shift in DMF and a hypsochromic shift in ethanol. The long-wavelength band of dye **14** is broad, less intensive than the short-wavelength one, but more solvent-sensitive. However, it is difficult to unambiguously conclude about the sign of solvatochromism because of considerable diffusing the band contour in the maximum range.

The position, intensity, and shape of the short-wavelength band remain almost unchanged with the polymethine chain elongation. The solvatochromic shifts are small and do not exceed 5 nm. With an increase in the polymethine chain length, the medium band intensity in the spectra of compounds **14**—**16** increases and the band contour approaches that of cyanine. However, the vinylene shifts deviate from the value of 100 nm characteristic of classical cyanines. For example, in dichloromethane the first and second vinylene shifts are 65 and 75 nm, respectively. They insignificantly increase in DMF and decrease in ethanol. Solvatochromism of this band increases with the elongation of the polymethine chain (see Table 1).

The long-wavelength band intensity increases with an increase in the number of methine groups (*n*). The inflection at its short-wavelength edge becomes more pronounced. For dye **11**, the inflection is apart from the maximum by 1100 cm^{-1} in CH_2Cl_2. This numerical value corresponds to the frequency of stretching full-symmetry vibrations of the C—C bonds of the chromophore, indicating the vibrational nature of this "shoulder." [10]

Depending on the polymethine chain length and solvent nature, the vinylene shift of the long-wavelength absorption band varies from 107 to 128 nm (DMF) and from 112 to 120 nm (CH_2Cl_2), which is characteristic of typical polymethines.[10] The solvatochromic effects are enhanced with the increase in *n* (Figs 4 and 5). For pentamethinecyanine **16** on going from dichloromethane to ethanol, the long-wavelength band intensity decreases approximately 2.5-fold and the intensities are redistributed between the main and vibration band maxima (see Fig. 5).

It can be assumed that such complicated absorption spectra are related to the affinity of dyes **14**—**16**, as other anionic polymethines of the fluorene series,[11] to the formation of tight ion pairs, but the replacement of CH_2Cl_2 by more polar and ion-solvating solvents (ethanol, acetonitrile, DMF, and DMSO) only insignificantly changes the shape of the absorption spectra and exerts no effect on the number of bands. Therefore, the presence of several bands in the absorption spectra of dyes **14**—**16** cannot be explained by the formation of various types of ion pairs.

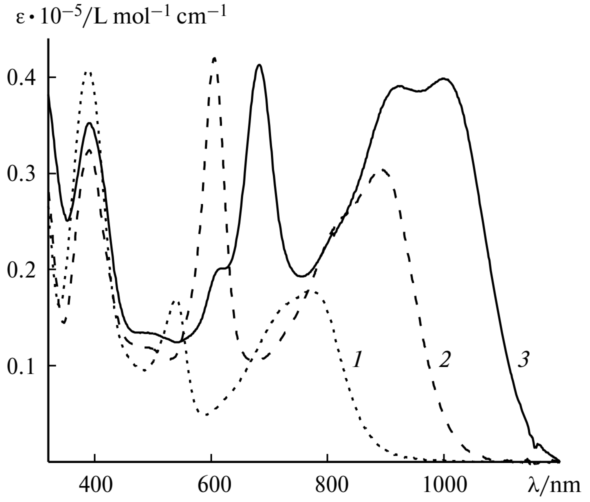


Fig. 3. Absorption spectra of dyes **14** (*1*), **15** (*2*), and **16** (*3*) in CH_2Cl_2.

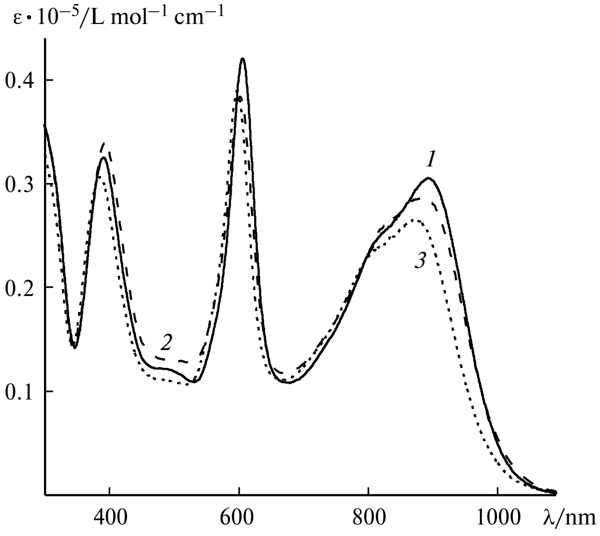


Fig. 4. Absorption spectra of dye **15** in CH_2Cl_2 (*1*), DMF (*2*), and ethanol (*3*).

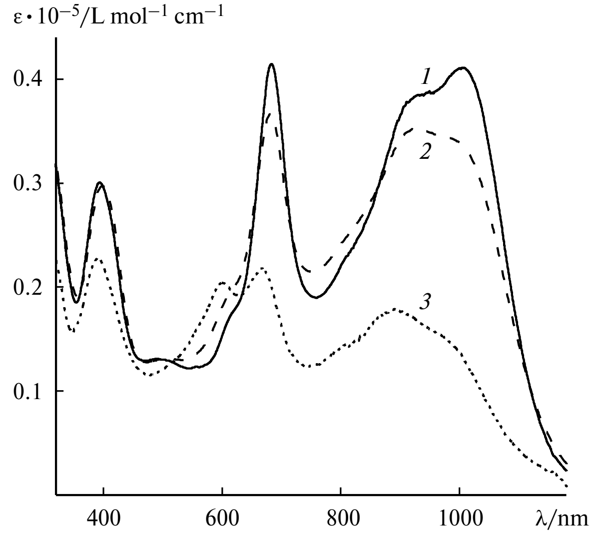


Fig. 5. Absorption spectra of dye **16** in CH_2Cl_2 (*1*), DMF (*2*), and ethanol (*3*).

It is known that additional bands in the spectrum can appear due to molecular aggregation.[10] The Lambert—Beer law was checked for solutions of dyes **14—16**. The absorption spectra do not change in the concentration range from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-4}$ mol L^{-1}. This indicates that dyes **14—16** exist in solutions in the monomeric non-associated state.

The complication of the spectra cannot be explained by the high acceptor ability of nitro groups, since the absorption spectra of fluorene-based polymethines with stronger acceptors in the same positions of the ring[11] contain only one band and the shape of the absorption curve is typical of cyanines.

It is known that the single and double bonds begin to deviate from the polymethine chain center to the edges when the electron-donor ability of the terminal groups of the polymethine dyes deviates from the medium value.[10] Indeed, the calculated bond orders in the ground state of molecules **14—16** increase from the center to edges. This agrees with the spin-spin coupling constants in the ^{1}H NMR spectra, which change in the same direction. Based on this, we can assume that the spectral pattern observed for dyes **14—16** is caused by the formation of conformers due to rotations about the bonds with orders approaching to the ordinary bonds. However, the absorption spectra of dye **16** in the polymer film of polyvinylacetal, where conformational processes are hindered, do not almost differ from its spectrum in a dichloromethane solution. Therefore, the appearance of additional bands in the spectra of the nitrosubstituted dyes compared to their analogs bearing the SO_2OPh group and with unsubstituted polymethines cannot be explained by the formation of conformers. The values of spin-spin coupling constants indicate the full *trans*-conformation of polymethine chain of dyes **14—16**.

Thus, so complicated spectra of dyes **14—16** are due to specific features of the electronic structure of the nitro group, which affects the π-system of the dye. The quantum chemical calculations were performed for a more detailed analysis of the electronic structure of the dyes and interpretation of the spectra (Table 2).

For pentamethinecyanine based on unsubstituted fluorene **5**, the maximum coefficients of the HOMO are on the even atoms of the polymethine chain and on the C atoms in positions 1, 3, 6, 8, 4a, 4b, and 9 of the fluorene ring. The electron density is transferred from the even to odd atoms of the polymethine chain and from positions 1, 8, and 9 of the fluorene ring to positions 2 and 7, as well as 8a and 9a, upon excitation (Fig. 6). The $S_0 \rightarrow S_1$ transition occurs from the HOMO to LUMO and results in the long-wavelength band in the calculated absorption spectrum.

In the case of pentamethinecyanine **11** based on fluorene with SO_2OPh groups, the HOMO is concentrated on the even atoms of the polymethine chain and the atoms in positions 1, 3, 6, 8, 4a, 4b, and 9 of the fluorene ring similarly to that of the unsubstituted dye. The $S_0 \rightarrow S_1$ transition is mixed, occurring by 83% from the HOMO to LUMO and by 15% from the HOMO to LUMO+2. Unlike unsubstituted pentamethinecyanine **5**, this transition is accompanied by a smaller shift of the electron density to the odd atoms of the polymethine chain and its noticeable increase on the carbon atoms in positions 2 and 7 of the

Table 2. Quantum chemical calculation data for the anionic polymethine dyes

Compound	λ_{max}^{calc}/nm	*E*/eV	*f*
4	461.1	2.6888	0.615
	417.9	2.9671	0.189
5	541.2	2.2911	2.092
10	587.9	2.1091	0.486
	473.8	2.6169	0.765
11	632.3	1.9608	0.958
	523.4	2.3687	0.784
12	890.8	1.3918	0.3018
	530.0	2.3393	1.5871
	378.2	3.2784	0.2931
14	779.1	1.5915	0.185
	533.3	2.3247	0.070
	412.1	3.0085	0.468
	392.1	3.1624	0.106
15	868.0	1.4284	0.259
	572.9	2.1644	0.220
	458.5	2.7040	0.914
	392.8	3.1562	0.096
16	917.4	1.3515	0.364
	601.4	2.0617	0.516
	500.2	2.4788	1.132
	389.1	3.1865	0.398

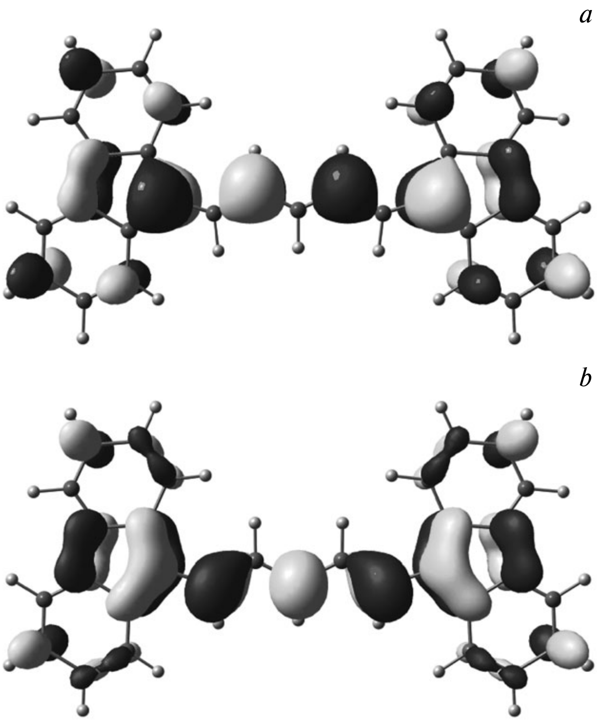


Fig. 6. HOMO (*a*) and LUMO (*b*) of dye **5**. The value of isosurface lines is 0.03.

fluorene ring, which was not observed for dye **5**. This transition is responsible for the long-wavelength absorption band in the calculated spectrum of dye **11**. Another intensive band in the absorption spectrum corresponds to the $S_0 \rightarrow S_3$ transition, which is also mixed (84% from the HOMO to LUMO+2 and 15% from the HOMO to LUMO) (Fig. 7).

The introduction of nitro groups into the fluorene ring induces additional vacant levels compared to a similar substitution by the SO_2OPh group, which results in approaching the HOMO and LUMO, as well as the LUMO and LUMO+1. New levels localized with a significant participation of nitro substituents are inserted between the LUMO+1 and highest vacant levels, which results in the appearance of vacant levels close in energy (quasi-degenerate). Additional electron transitions to these orbitals become probable, which causes the appearance of additional bands in the absorption spectra (Fig. 8).

The principal difference between the electron-acceptor groups NO_2 and SO_2OPh is that the former has the sp^2 hybridization and the latter is sp^3d^2. Therefore, the NO_2 group is capable of complete conjugating with the π-system of the dye and the SO_2OPh group is only partially conjugated, which is a reason for their different effects on the arrangement of the levels of the excited state of dyes **10—12** and **14—16** (Fig. 9).

The calculated absorption spectrum of dye **12** consists of two bands in the visible and near-IR ranges and one band in the near-UV range. The long-wavelength band is caused by the mixed transition $S_0 \rightarrow S_1$ between the HOMO and LUMO (93%) and from the HOMO to LUMO+4 (5%). This transition is accompanied by the electron density transfer from the even atoms of the polymethine chain to the even atoms and from the carbon atoms in position 9 of the fluorene rings to the nitro groups. The $S_0 \rightarrow S_5$ transition is responsible for the second band and is also mixed (67% from the HOMO to LUMO+4, 22% from the HOMO to LUMO+2 and by 6% between the HOMO and LUMO). The electron density is shifted similarly to the $S_0 \rightarrow S_1$ transition but, to a greater extent, to the atoms of the nitro groups (Fig. 10). The short-wavelength band in the calculated spectrum of compound **12** is determined by the mixed transition $S_0 \rightarrow S_9$ that occurs by 89% from the HOMO-3 to LUMO and by 7% from the HOMO to LUMO+7. This transition is characterized by the electron density transfer from the atoms of the fluorene ring to the atoms in the even positions of the polymethine chain and

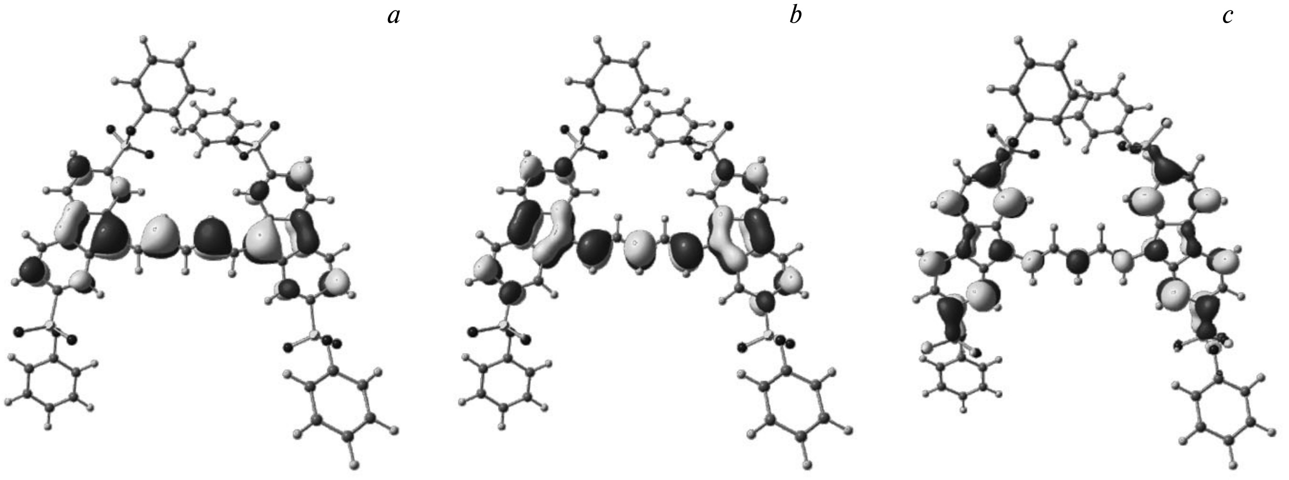


Fig. 7. HOMO (*a*), LUMO (*b*), and LUMO+2 (*c*) of dye **11**.

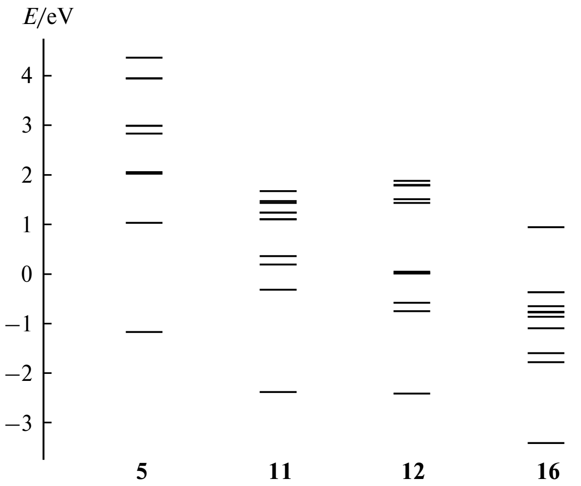


Fig. 8. Energy levels of compounds **5**, **11**, **12**, and **16** calculated by the DFT method.

from the atoms in the even positions of the polymethine chain to the fluorene ring.

It follows from the quantum chemical calculation data that for dyes **14**—**16**, unlike the derivatives with the SO_2OPh groups, three bands caused by the π—π*-transitions should be observed in the visible and near-IR spectral ranges, and the longest-wavelength bands are deeper than those for dyes **10** and **11**.

In dye **16**, as well as in other fluorene pentamethinecyanines, in the S_0 state the electron density is mostly concentrated on the even atoms of the polymethine chain and the atoms of the fluorene rings in positions 1, 8, 4a, 4b, 9, 8a, and 9a, as well as 3 and 6 with an insignificant delocalization on positions 4 and 5 (Fig. 11, *a*).

The longest-wavelength is the $S_0 \rightarrow S_1$ transition between the HOMO and LUMO ($\lambda = 917.4$ nm, $f = 0.364$), upon which the electron density is shifted from the even atoms of the polymethine chain to the odd atoms and from the atoms in positions 3, 6, and 9 of the fluorene ring to the carbon atoms in positions 2 and 7 and the nitro group (see Fig. 11, *b*).

The $S_0 \rightarrow S_3$ transition responsible for the second band in the spectrum ($\lambda = 601.4$ nm, $f = 0.516$) is mixed (85% between the HOMO and LUMO+2, 9% from the HOMO to LUMO+6, and 4% between the HOMO and LUMO) and accompanied by the electron density transfer from the even atoms of the chain to the odd atoms and from the nodal atoms of fluorene (4a, 4b) to the nitro groups in positions 4 and 5. The third band in the visible range ($\lambda = 500.2$ nm, $f = 1.132$) is caused by the transition $S_0 \rightarrow S_7$, which is also mixed: it consists by 82% of the transition from the HOMO to LUMO+6, by 7% of the transition from the HOMO to LUMO+2, and by 5% between the HOMO-1 and LUMO+1. The $S_0 \rightarrow S_7$ transition corresponds to the electron density shift from the even atoms of the polymethine chain to the odd atoms and from the atoms of the fluorene ring to the nitro groups.

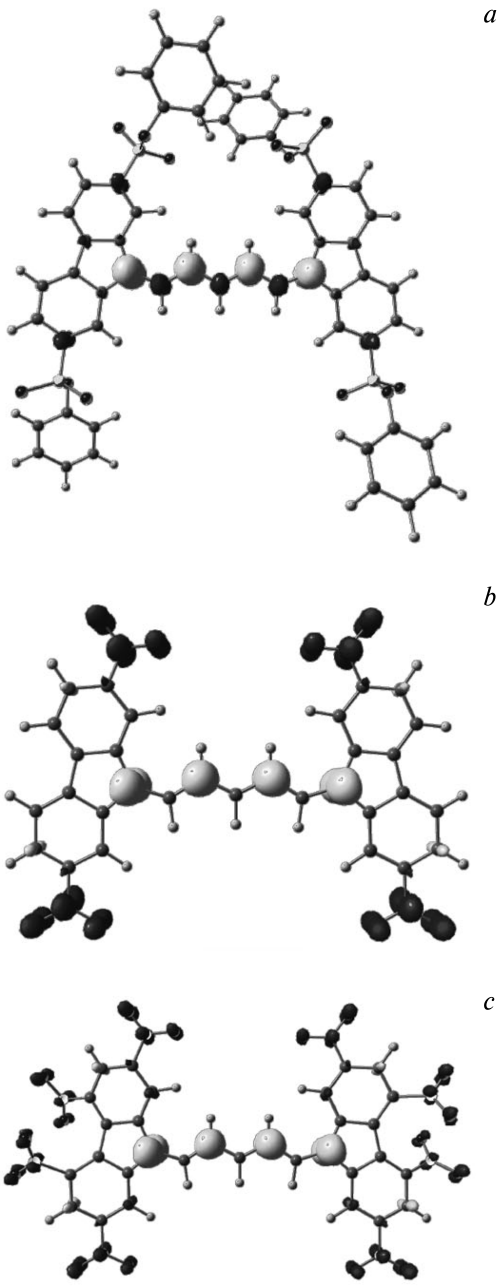


Fig. 9. Change in the electron density of dyes **11** (*a*), **12** (*b*), and **16** (*c*) upon excitation. The value of isosurface lines is 0.003.

The $S_0 \rightarrow S_{12}$ transition is responsible for the shortwavelength band in the spectrum ($\lambda = 389.1$ nm, $f = 0.398$). It is mixed (78% from the HOMO−3 to LUMO, 11% from the HOMO−2 to LUMO+1, and 3% from the HOMO to LUMO+13) and accompanied by the electron density transfer from the carbon atoms of the fluorene ring to the polymethine chain atoms and nitro groups and from the even atoms of the polymethine chain to the nitro groups

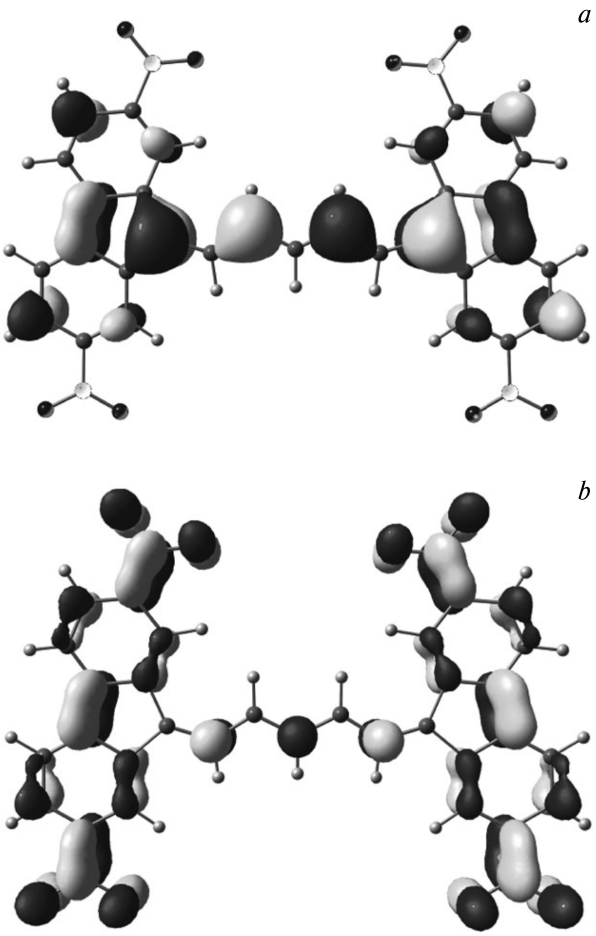


Fig. 10. HOMO (*a*) and LUMO (*b*) of dye **12**.

in positions 4 and 5 of the fluorene ring. The maximum of this band almost coincides with that in the experimental spectrum.

The conclusion about the localization of this transition on the fluorene residues is also confirmed by a comparison of the absorption spectra of dyes **14**—**16** and the tetranitrofluorenide anion. The $S_0 \to S_1$ transition in the latter is symmetry-forbidden. The transitions with the highest forces of the oscillator correspond to the absorption in the near-UV range and are determined, similarly to dyes **14**—**16**, by the electron density transfer from the carbon atoms of the fluorene ring to the nitro groups. The bands caused by the $S_0 \to S_5$ and $S_0 \to S_6$ transitions lie in the same range as the short-wavelength bands in absorption spectra of dyes **14**—**16**. The experimental values of maxima in these bands are also rather close (Fig. 12). It is clear from this why the position of the short-wavelength band in the spectra of dyes **14**—**16** is independent of the polymethine chain length.

For mono- and trimethinecyanines **14** and **15**, the transitions are similar to those in compound **16**. However, in dye **14** the $S_0 \to S_1$ transition is symmetry-forbidden, as in

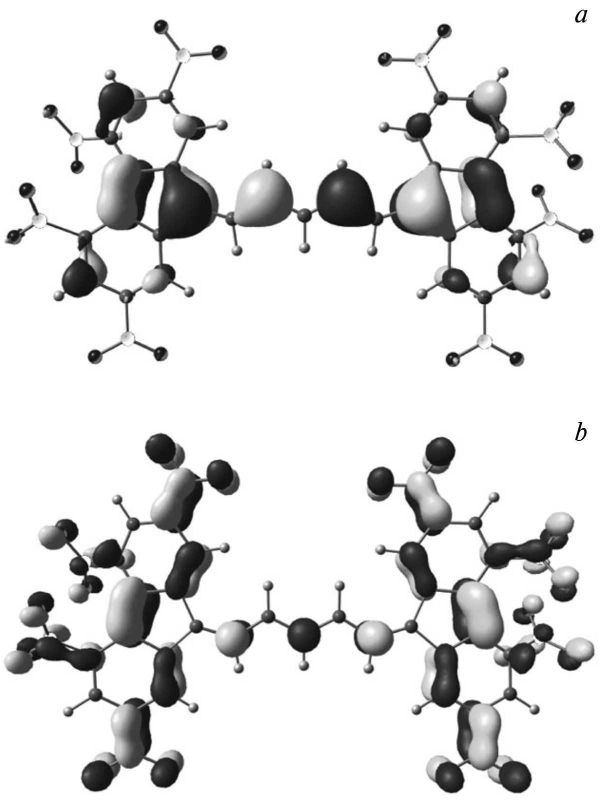


Fig. 11. HOMO (*a*) and LUMO (*b*) of dye **16**.

the tetranitrofluorenide anion. The longest-wavelength transition of the allowed transitions ($S_0 \to S_2$) occurs between the HOMO and LUMO and is accompanied by the electron density shift from the fluorene rings to the nitro groups and from the center of the molecule to the edges.

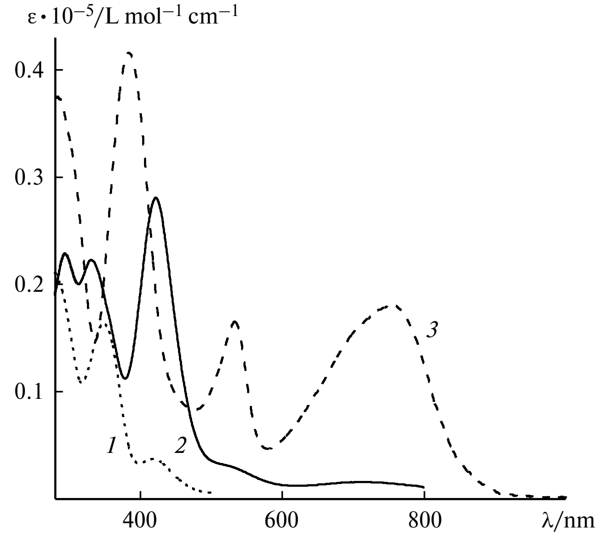


Fig. 12. Absorption spectra of compound **13** (*1*), the anion of compound **13** (*2*), and dye **14** (*3*) in ethanol.

It is known that nonempirical calculation methods often substantially underestimate the values of absorption maxima.[12] One of the reasons for this is the stock-taking into account the contribution of σ-electrons that are not involved in conjugation to the energy of transitions. Therefore, we decided to check whether the σ-electrons distorted at least the tendency in changing π—π* transitions in the case of the studied dyes. For this purpose, we calculated these dyes by the Pariser—Parr—Pople method, which operates with π electrons only.

The calculations by this method using the known parameters[13] showed that the nitro groups in positions 2 and 7 of the fluorene ring result in the bathochromic shifts of the maxima in the calculated absorption spectra of the anionic dyes (λ_{max} = 691 nm for compound **5** and 740 nm for dye **12**). The number of bands increases compared to the spectrum of the unsubstituted dye. However, the known parameters[13] for the nitro group do not adequately describe its interaction with the main π-system of the dye, because they were selected for cationic and neutral compounds. A small correction of the nitro group parameters, reflecting only the tendency of going from cationic to anionic dyes, gives good results. For example, a decrease in the parameter β modulus for the N—O bond from 3.05 to 2.5 corresponding to an increase in the conjugation of the oxygen atoms of the nitro group with the main chromophore induces the bathochromic shift of the absorption maxima in the calculated spectrum from 740 and 487 to 881 and 577 nm, a decrease in the oscillator force (*f*) of the long-wavelength band, and its increase for other bands. A similar tendency is observed for the regular increase in parameter β for the C—N bond and ionization potential for the N and O atoms in the nitro groups. At $\beta_{N-O} = -2.4$, the long-wavelength absorption maxima in the calculated and experimental spectra coincide.

In all the Pariser—Parr—Pople calculations, the long-wavelength in the spectrum, as in the DFT calculations, corresponds to the $S_0 \to S_1$ transition and is determined by the electron density transfer from the even atoms of the polymethine chain to the odd atoms and from the fluorene rings to the nitro groups.

The consecutive change in the parameters, at first two bands corresponding to the transitions $S_0 \to S_1$ and $S_0 \to S_3$ are observed in the calculated spectra, and then the short-wavelength transition $S_0 \to S_7$ localized at the terminal groups is added. The further change induces a decrease in the intensity of the $S_0 \to S_3$ and $S_0 \to S_7$ transitions and an increase in the intensity of the band corresponding to the transition $S_0 \to S_5$. In this case, the levels LUMO+1, LUMO+2, and LUMO+3 are approached with the LUMO.

An increase in the number of configurations in calculation results in the bathochromic shift of the absorption maximum and a decrease in the oscillator force of the long-wavelength transition but does not change the number of bands.

Thus, the fluorene derivatives containing the electron-acceptor groups SO_2OPh or NO_2 in positions 2 and 7 and especially 2,4,5,7-tetranitrofluorene easily undergo cyanine condensation at the methylene group. Thus synthesized dyes are more deeply colored than the compounds with a similar polymethine chain length with heterocyclic terminal groups. The ability of the nitro group to be completely conjugated with the π-system of the dye allows its excited states to efficiently insert into the general chromophore system. The electron transitions to these levels result in the appearance of additional bands in the absorption spectra of the nitrosubstituted dyes compared to their analogs with the SO_2OPh group in the same positions of the fluorene ring.

Experimental

Absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in cells with an optical path length of 1 cm at the concentrations of the solute 10^{-5} mol L^{-1}. Solvents were purified by known methods.[14] Dichloromethane was stabilized by the addition of 1% absolute ethanol. Silica gel 60 (Fluka) and alumina-90 (Merck) were used for chromatography. The purity of the dyes was monitored by TLC (Silufol UV-254, eluent acetonitrile). ^1H NMR spectra were measured on a Varian VXR-300 spectrometer (299.945 MHz) using Me_4Si as an internal standard. Melting points were measured in an open capillary and were not corrected.

Quantum chemical calculations were performed in the PC Gamess/Firefly program package by the nonempirical DFT method in the B3LYP/6-31G(d,p) basis set with preliminary geometry optimization of the ground state in the same basis set. The electron transitions were calculated by the TDDFT method. When describing the calculated spectra, the electron transitions with the oscillator force higher than one-tenth of the intensity of the transition with the highest oscillation force were taken into account. Pentamethinecyanines are most appropriate for description, since their rather long chain makes it possible to avoid effect associated with the close arrangement of fluorene rings and the planar structure allows one to evaluate the transition polarized along the main axis of the chromophore.

9-(9*H*-Fluoren-9-ylidenemethyl)-9*H*-fluorene (3). A mixture of 9-(tributylphosphonio)fluoren-9-ide[4] (0.2 g, 0.546 mmol) and 9*H*-fluorene-9-carboxaldehyde[15] (106 mg, 0.546 mmol) in *o*-xylene (6 mL) was refluxed for 3 h. The cooled reaction mixture was concentrated *in vacuo* and chromatographed on silica gel (eluent benzene). The appropriate fraction was evaporated and treated with *n*-hexane to form a powdered pale yellow precipitate, which was filtered off and dried. The yield was 120 mg (64%), m.p. 201 °C. Found (%): C, 94.38; H, 5.12. $C_{27}H_{18}$. Calculated (%): C, 94.70; H, 5.30. ^1H NMR ($CDCl_3$), δ: 5.87 (d, 1 H, H(9) of fluorene, *J* = 10.2 Hz); 6.51 (d, 1 H, =CH, *J* = 10.2 Hz); 7.19—7.62 (m, 11 H, ArH); 7.76 (d, 1 H, H(4) of fluorene, *J* = 7.8 Hz); 7.84 (d, 2 H, H(8), H(8´) of fluorene, *J* = 7.8 Hz); 7.85 (d, 1 H, H(1´) of fluorene, *J* = 7.8 Hz); 8.33 (d, 1 H, H(1) of fluorene, *J* = 7.8 Hz).

Potassium 9-[(9*H*-fluoren-9-ylidene)methyl]-9*H*-fluoren-9-ide (4). Several droplets of a solution of potassium *tert*-butoxide in DMSO were added to a solution of compound **3** with a concentration of $1 \cdot 10^{-5}$ mol L^{-1} in DMSO. The crimson color of the solution indicates the formation of the anionic dye. The compound is stable in DMSO in a closed vessel under argon for 1 h.

2,7-Bis(phenoxysulfonyl)-9*H*-fluorene (6). A mixture of fluorene-2,7-disulfochloride[16] (1.8 g, 4.95 mmol), phenol (2.35 g, 0.025 mol), and pyridine (2 mL) was heated for 30 min at 110—120 °C. Propan-2-ol (15 mL) and water (5 mL) were added, and the mixture was refluxed for several minutes. After cooling, the precipitate was filtered off and treated with hot water. A substance with m.p. 200—202 °C was obtained in a yield of 1.75 g (73%). The obtained precipitate was dissolved in boiling dioxane (8 mL), and the solution was diluted with propan-2-ol (8 mL). Compound **6** was obtained as lustrous white lamellae with m.p. 202—203 °C in a yield of 1.6 g (68%). ^{1}H NMR (DMSO-d$_6$), δ: 4.22 (s, 2 H, CH_2); 7.07 (d, 4 H, phenoxyl protons, *J* = 8.4 Hz); 7.28—7.43 (m, 6 H, phenoxyl protons); 7.91 (d, 2 H, H(4), H(5), *J* = 8.4 Hz); 8.22 (s, 2 H, H(1), H(8)); 8.34 (d, 2 H, H(3), H(6), *J* = 8.4 Hz).

2,3,4,6,7,8,9,10-Octahydropyrimido[1,2-*a*]azepin-1-ium (*E*)-9-[3-(2,7-bis(phenoxysulfonyl)-9*H*-fluoren-9-ylidene)prop-1-enyl]-2,7-bis(phenoxylsulfonyl)-9*H*-fluoren-9-ide (10). A mixture of compound **6** (100 mg, 0.21 mmol), *N*-(3-anilinoprop-2-enylidene)anilinium chloride (**8**) (26 mg, 0.1 mmol), and pyridine (3.2 mL) was heated to complete dissolution, 3 droplets of DBU were added, and the mixture was heated for 2 h in a water bath (125 °C) (spectrophotometric monitoring*). The reaction mixture was cooled and the solvent was evaporated under reduced pressure. The residue was triturated in water and filtered off. The yield was 60 mg (52%), m.p. 126 °C. Found (%): C, 64.89; H, 4.40; S, 11.02. $C_{62}H_{52}N_2O_{12}S_4$. Calculated (%): C, 65.07; H, 4.49; S, 11.21. ^{1}H NMR (acetone-d$_6$), δ: 1.58—1.73 (m, 6 H, CH_2 groups of cation); 2.72—2.80 (m, 2 H, CH_2 group of cation); 3.19—3.27 (m, 2 H, CH_2 group of cation); 3.27—3.39 (m, 2 H, CH_2 group of cation); 3.52—3.61 (m, 4 H, CH_2 groups of cation); 6.81 (t, 1 H, β-proton of chain, *J* = 12.0 Hz); 7.01—7.19 (m, 8 H, phenoxyl protons); 7.24—7.46 (m, 12 H, phenoxyl protons); 7.91 (d, 2 H, α-protons of chain, *J* = 13.2 Hz); 8.07 (d, 8 H, Ar—H, *J* = 8.0 Hz); 8.27 (br.s, 4 H, Ar—H).

2,3,4,6,7,8,9,10-Octahydropyrimido[1,2-*a*]azepin-1-ium 9-[(1*E*,3*E*)-5-(2,7-bis(phenoxysulfonyl)-9*H*-fluoren-9-ylidene)-penta-1,3-dienyl]-2,7-bis(phenoxysulfonyl)-9*H*-fluoren-9-ide (11). A mixture of compound **6** (128 mg, 0.27 mmol), *N*-(5-anilinopenta-2,4-dienylidene)anilinium chloride (**9**) (40 mg, 0.14 mmol), and pyridine (2.5 mL) was heated to complete dissolution, and 3 droplets of DBU were added. The reaction mixture was heated for 40 min in an oil bath (125 °C) (spectrophotometric monitoring). The solvent was evaporated under reduced pressure, and the residue was triturated in ethanol, filtered off, and washed with anhydrous diethyl ether (3×10 mL). The yield was 120 mg (83%), m.p. 111 °C. Found (%): C, 65.35; H, 4.50; S, 10.78. $C_{64}H_{54}N_2O_{12}S_4$. Calculated (%): C, 65.68; H, 4.56; S, 10.96. ^{1}H NMR (CD_3CN), δ: 1.71—1.73 (m, 4 H, CH_2 groups of cation); 2.81—2.83 (m, 4 H, CH_2 groups of cation); 3.39 (t, 2 H, CH_2 group of cation, *J* = 6.0 Hz); 3.61 (t, 2 H, CH_2 group of cation, *J* = 6.0 Hz); 3.64—3.66 (m, 4 H, CH_2 groups of cation); 6.13 (d, 2 H, α-protons of chain, *J* = 14.4 Hz); 6.82 (t, 2 H, β-protons of chain, *J* = 12.0 Hz); 6.95—7.20 (m, 8 H, phenoxyl protons); 7.23—7.45 (m, 1 H, proton of chain, 12 H, Ar—H phenoxyl protons); 8.18 (d, 4 H, Ar—H, *J* = 8.0 Hz); 8.28 (d, 4 H, Ar—H, *J* = 8.0 Hz); 9.16 (s, 4 H, Ar—H).

2,3,4,6,7,8,9,10-Octahydropyrimido[1,2-*a*]azepin-1-ium 2,7-dinitro-9-[(1*E*,3*E*)-5-(2,7-dinitro-9*H*-fluoren-9-ylidene)-penta-1,3-dienyl]-9*H*-fluoren-9-ide (12). A mixture of 2,7-dinitro-9*H*-fluorene (**7**) (256 mg, 1 mmol) (see Ref. 17) and compound **9** (150 mg, 0.52 mmol, 10% excess) was dissolved in DMF (5 mL) and heated to boiling, and DBU (200 mg, 1.32 mmol) was added (spectrophotometric monitoring). The reaction mixture was cooled to ambient temperature and treated with anhydrous diethyl ether. The precipitate that formed was filtered off after sedimentation. The yield was 450 mg (96%), m.p. 132 °C. Found (%): C, 65.92; H, 4.44; N, 11.27. $C_{40}H_{34}N_6O_8$. Calculated (%): C, 66.20; H, 4.58; N, 11.58. ^{1}H NMR (DMSO-d$_6$), δ: 1.53—1.62 (m, 6 H, CH_2 groups of cation); 1.94—2.02 (m, 2 H, CH_2 group of cation); 2.58—2.63 (m, 4 H, CH_2 groups of cation); 3.46—3.51 (m, 2 H, CH_2 group of cation); 3.53—3.57 (m, 2 H, CH_2 group of cation); 7.61 (t, 1 H, γ-proton of chain, *J* = 12.0 Hz); 7.98 (t, 2 H, β-protons of chain, *J* = 12.9 Hz); 8.29 (d, 2 H, α-protons of chain, *J* = 13.5 Hz); 8.88 (s, 8 H, H(3), H(4) of fluorene); 8.96 (br.s, 4 H, H(1), H(8) of fluorene).

9-(Ethoxymethylidene)-2,4,5,7-tetranitro-9*H*-fluorene. A mixture of 2,4,5,7-tetranitro-9*H*-fluorene (**13**) (105 mg, 0.3 mmol) (see Ref. 18) and triethyl orthoformate (~0.7 mL) in acetic anhydride (1.5 mL) was refluxed for several minutes, while the product precipitated from the hot reaction mixture. The precipitate was filtered off, washed with acetic anhydride and ethanol, and recrystallized from acetone. The yield was 90 mg (75%), m.p. >250 °C. Found (%): C, 47.32; H, 2.44; N, 13.78. $C_{16}H_{10}N_4O_9$. Calculated (%): C, 47.77; H, 2.51; N, 13.93. ^{1}H NMR (DMSO-d$_6$), δ: 1.06 (t, 3 H, O—$CH_2C\underline{H}_3$, *J* = 6.9 Hz); 3.44 (q, 2 H, O—$C\underline{H}_2CH_3$, *J* = 6.9 Hz); 8.41 (s, 2 H, H(3), H(6)); 9.57 (br.s, 2 H, H(1), H(8)); 10.25 (s, 1 H, methinic proton).

Triethylammonium 2,4,5,7-tetranitro-9-[(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)methyl]-9*H*-fluoren-9-ide (14). A mixture of 9-(ethoxymethylidene)-2,4,5,7-tetranitro-9*H*-fluorene (80 mg, 0.2 mmol) and compound **13** (70 mg, 0.2 mmol) was heated in a minimum amount of acetic anhydride until dissolution, several droplets of triethylamine were added, and the mixture was heated for several minutes more. A precipitate of the product formed was filtered off and washed with Ac_2O and EtOH. The yield was 150 mg (93%), m.p. >270 °C. Found (%): C, 49.03; H, 3.01; N,15.27. $C_{33}H_{25}N_9O_{16}$. Calculated (%): C, 49.32; H, 3.14; N, 15.69. ^{1}H NMR (DMSO-d$_6$), δ: 1.17 (t, 9 H, $NCH_2C\underline{H}_3$, *J* = 7.2 Hz); 3.06—3.14 (m, 6 H, $NC\underline{H}_2CH_3$); 8.52 (d, 4 H, Ar—H of fluorene, *J* = 2.1 Hz); 8.96 (br.s, 4 H, Ar—H of fluorene); 9.75 (s, 1 H, proton of chain).

Triethylammonium (*E*)-2,4,5,7-tetranitro-9-[3-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)prop-1-enyl]-9*H*-fluoren-9-ide (15). A mixture of compound **13** (138 mg, 0.4 mmol), compound **8** (52 mg, 0.2 mmol), acetic anhydride (1.5 mL), and several droplets of triethylamine was refluxed for 3 min, and the product precipitated from the reaction mixture. The precipitate was filtered off and washed with a minimum amount of acetic anhydride and ethanol. The yield was 150 mg (90%), m.p. >270 °C. Found (%): C, 50.42; H, 3.16; N, 14.93. $C_{35}H_{27}N_9O_{16}$. Calculated (%): C, 50.67; H, 3.28; N, 15.19. ^{1}H NMR (DMSO-d$_6$), δ: 1.20 (t, 9 H, $NCH_2C\underline{H}_3$, *J* = 7.2 Hz); 3.05—3.13 (m, 6 H, $NC\underline{H}_2CH_3$); 7.71 (t, 1 H, β-proton of chain, *J* = 13.2 Hz); 8.28 (s, 4 H, Ar—H of fluorene); 8.50 (d, 2 H, α-proton of chain, *J* = 13.2 Hz); 9.04 (s, 4 H, Ar—H of fluorene).

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* The reaction was spectrophotometrically monitored at the longest-wavelength absorption band of the product formed.

Triethylammonium 2,4,5,7-tetranitro-9-[(1*E*,3*E*)-5-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)penta-1,3-dienyl]-9*H*-fluoren-9-ide (16). A mixture of compound **13** (138 mg, 0.4 mmol), compound **9** (58 mg, 0.2 mmol), acetic anhydride (2 mL), and several droplets of triethylamine was refluxed for 3 min, and the product precipitated from the reaction mixture. The precipitate was filtered off and washed with a minimum amount of acetic anhydride and ethanol. The yield was 160 mg (94%), m.p. >270 °C. Found (%): C, 51.81; H, 3.33; N, 14.53. $C_{37}H_{29}N_9O_{16}$. Calculated (%): C, 51.99; H, 3.42; N, 14.73. ^{1}H NMR (DMSO-d_6), δ: 1.16 (t, 9 H, $NCH_2C\underline{H}_3$, J = 6.8 Hz); 2.90—3.11 (m, 6 H, $NC\underline{H}_2CH_3$); 7.63 (t, 2 H, β-protons of chain, J = 13.2 Hz); 7.93 (t, 1 H, γ-proton of chain, J = 12.4 Hz); 8.27 (d, 2 H, α-protons of chain, J = 14.0 Hz); 8.34 (s, 4 H, Ar—H of fluorene); 9.15 (s, 4 H, Ar—H of fluorene).

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