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Synthesis, Spectral Properties, and Solvatochromism of Merocyanine Dyes Based on Bis(2,2,3,3,4,4,5,5-octafluoropentyl)-4,5-dinitro-9*H*-fluorene-2,7-disulfonate

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Abstract—Di-, tetra-, and hexamethine merocyanines containing heterocyclic fragments with different electron-donor abilities have been synthesized on the basis of bis(2,2,3,3,4,4,5,5-octafluoropentyl)-4,5-dinitro-9*H*-fluorene-2,7-disulfonate. Their electronic absorption spectra in solvents with different polarities have been studied, and their electronic structure and electronic transitions have been analyzed by DFT and TDDFT quantum chemical calculations using B3LYP functional and 6-31G(*d*,*p*) basis set. The electronic structure of the synthesized merocyanines changes from neutral polyene to polymethine and dipolar polyene, depending on the electron-donor ability of the heterocyclic fragment, length of the polymethine chain, and solvent polarity. Therefore, these merocyanines display positive, negative, and reverse solvatochromism.

Keywords: merocyanines, fluorene, electronic spectroscopy, solvatochromism, quantum chemical calculations

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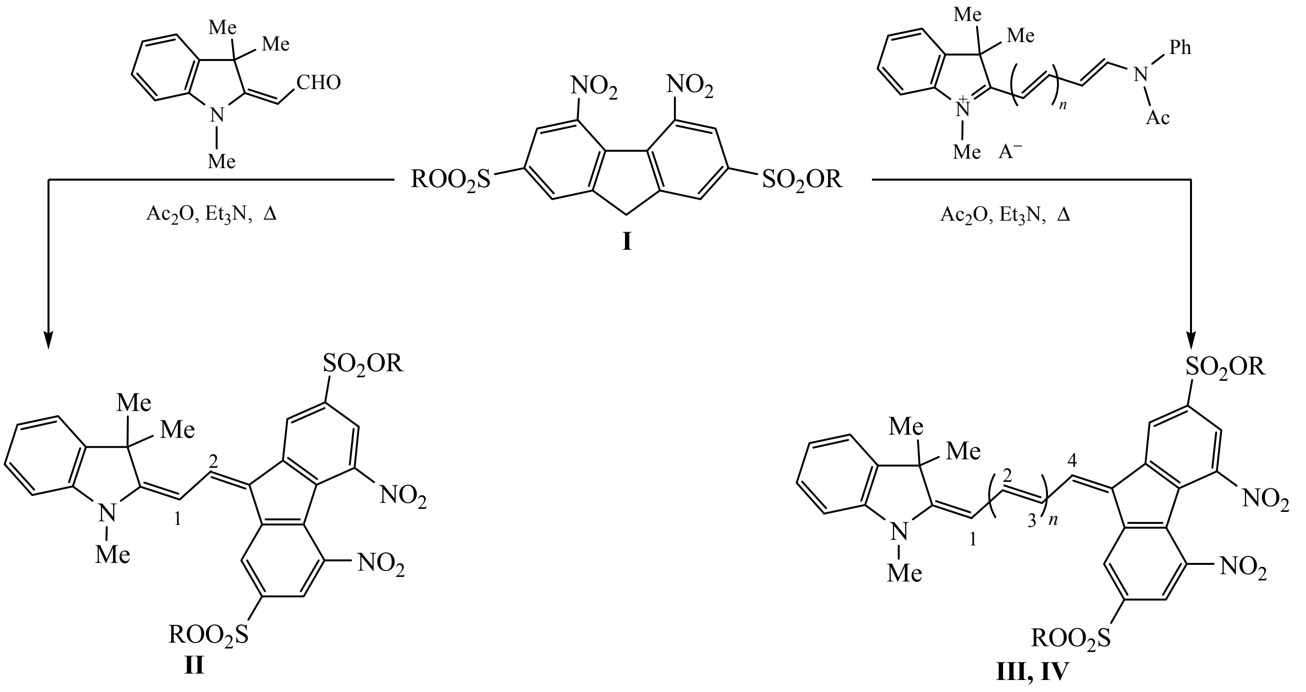
In recent time, increasing attention has been paid to donor–acceptor conjugated systems, in particular to merocyanines [1, 2], containing either a strong electron donor or a strong electron acceptor. Due to intramolecular charge transfer such compounds are quite promising from the viewpoint of the design organic semiconducting materials and sensitizers for photothermoplastic holographic [3–8], photovoltaic [9], and electroluminescent media [10]. Many publications in this field deal with donor–acceptor systems based on tetranitrofluorene [11–13]. However, this compound is more frequently used as a component of mixed complexes with polymers or other donor compounds. Therefore, it seemed reasonable to synthesize intramolecular donor–acceptor merocyanine systems on the basis of fluorenes containing strong electron-acceptor substituents.

We previously described merocyanines based on fluorene containing polyfluoroalkyl sulfonate groups $SO_2OCH_2(CF_2)_3CHF_2$ [14], as well as polynitrofluorene derivatives [15]. Polynitrofluorene-based merocyanines displayed in the electronic absorption spectra several strong bands in the visible and near-IR regions which essentially overlapped each other. The spectra of merocyanines derived from fluorenesulfonates contained only one band. The electron-withdrawing abilities of the NO_2 and $SO_2OCH_2(CF_2)_3CHF_2$ groups are comparable to each other [16]. However, the nitrogen atom in the NO_2 group is sp^2-hybridized, while the sulfur atom in SO_2OR is sp^3-hybridized. Therefore, unlike $SO_2OCH_2(CF_2)_3CHF_2$, the nitro group exerts both inductive and mesomeric effects [17], so that electronic levels of the nitro group and polymethine chromophore overlap each other, and the main electronic transition is split into several constituents [17].

As we showed in [18], the nitro groups in positions 4 and 5 of the fluorene core considerably deviate from the chromophore plane, as compared to those in positions 2 and 7 [18]. Furthermore, the electron-withdrawing effect of the nitro groups in positions 4 and 5 is weakened due to smaller change of electron density in these positions upon excitation [19]. It was interesting to synthesize merocyanines containing

Scheme 1.



I–IV, R = $CHF_2(CF_2)_3CH_2$; *n* = 1 (**III**), 2 (**IV**).

sulfonate groups in positions 2 and 7 and nitro groups in positions 4 and 5 of the fluorene core. We expected smaller overlap of absorption bands originating from different electronic transitions in the spectra of such compounds, which should ensure more accurate analysis of their variation depending on the substrate structure and solvent polarity (Scheme 1).

In the present work we synthesized series of merocyanines on the basis of bis(2,2,3,3,4,4,5,5-octafluoropentyl) 4,5-dinitro-9*H*-fluorene-2,7-disulfonate containing medium and strong electron-donating heterocyclic residues and studied their properties.

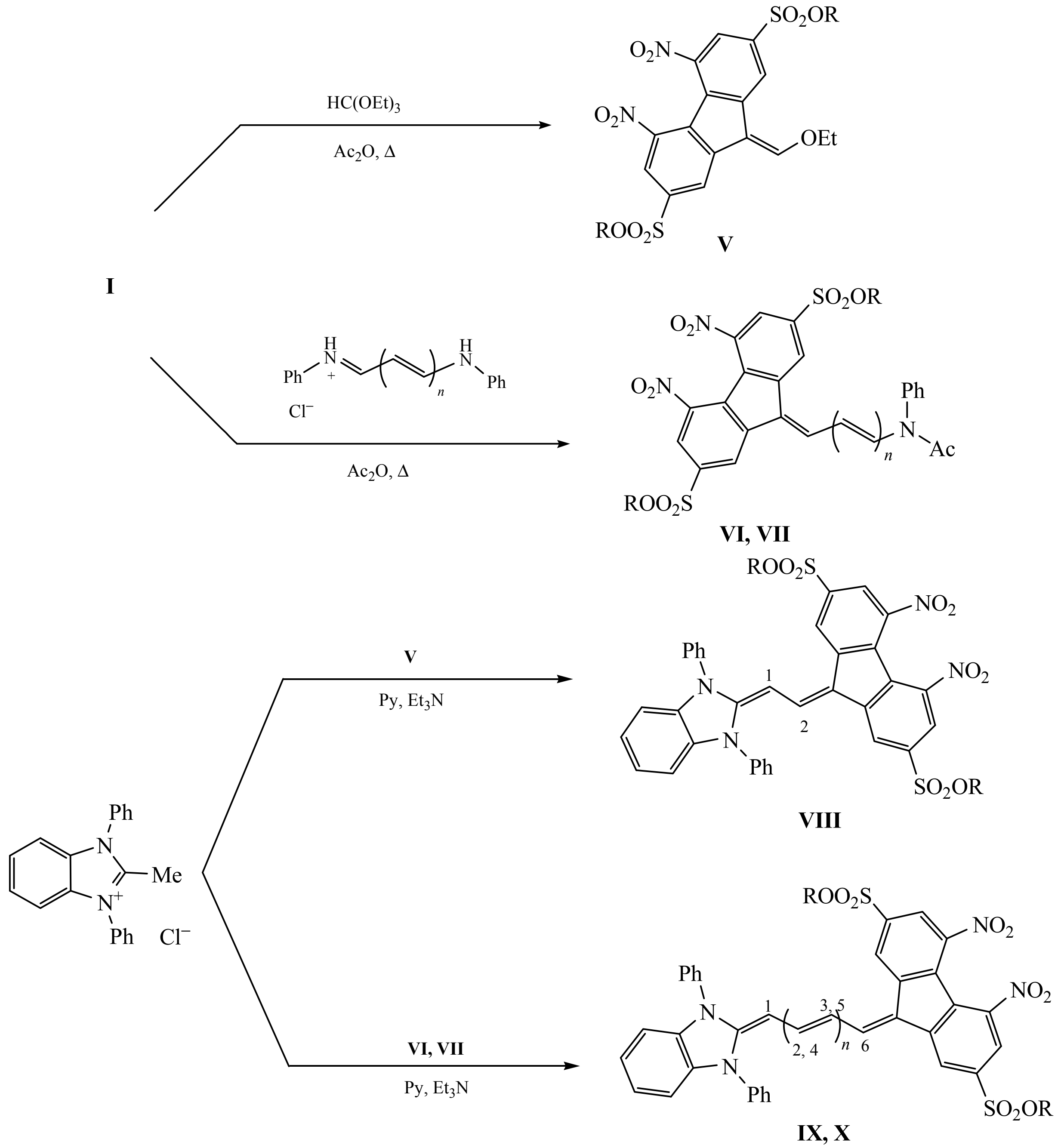
The presence of four electron-withdrawing groups in positions 2, 4, 5, and 7 enhances the CH acidity of the C^9H_2 group and its reactivity in cyanine condensation as compared to unsubstituted fluorene. Therefore, we succeeded in synthesizing merocyanines **II**–**IV**, as well as their analogs **VIII**–**X**, following the standard cyanine condensation procedure. Dyes **II**–**IV** were obtained by reaction of bis(2,2,3,3,4,4,5,5-octafluoropentyl) 4,5-dinitro-9*H*-fluorene-2,7-disulfonate (**I**) [18] with 1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylideneacetaldehyde and hemicyanines derived from 1,3,3-trimethyl-2,3-dihydro-1*H*-indole.

However, we failed to obtain in this way merocyanines containing more electron-donor 2-methyl-1,3-diphenyl-3*H*-benzimidazole fragment. Compounds **VIII**–**X** were synthesized by condensation of 2-methyl-1,3-diphenyl-3*H*-benzimidazol-1-ium chloride with hemicyanines **V**–**VII** derived from substituted fluorene (Scheme 2).

The spectral parameters of merocyanines **II**–**IV** and **VIII**–**X** are given in Table 1. Unlike classical merocyanines [20], compounds **II**–**IV** and **VIII**–**X** displayed several bands in the electronic absorption spectra (Figs. 1, 2), like symmetrical anionic polymethine dyes with analogous terminal groups [18]. The spectra of **II**–**IV** and **VIII**–**X** contained two intense bands in the visible and near-IR regions and weak bands in the region λ 320–380 nm. The electronic spectra were interpreted by quantum chemical calculations (Table 2). The theoretical electronic absorption spectra of **II**–**IV** and **VIII**–**X** were also multiband and were determined by π–π* transitions. As with polynitrofluorene-based merocyanines, the presence of several bands results from additional electronic levels localized on the nitro groups.

The calculated dipole moments of all merocyanines in the S_1 state are higher than in the ground state, which indicates larger contribution of dipolar canonical structure in the first excited state. The dipole moments also increase in going to S_2, but their change

Scheme 2.



V–X, R = $CHF_2(CF_2)_3CH_2$; *n* = 1 (**VI, IX**), 2 (**VII, X**).

is smaller than in the transition $S_0 \rightarrow S_1$. This means that the transition to the S_1 state is accompanied by stronger charge separation in the chromophore, and the corresponding absorption band may be charge-transfer band. In fact, the longwave absorption band in the theoretical spectrum originates from electron density transfer along the longitudinal molecular axis from the donor heterocyclic fragment to acceptor fluorene fragment (Fig. 3). The short-wave band corresponds to electron density transfer between neighboring atoms in the polymethine chain and partial increase of the electron density on the nitro groups (polymethine band; Fig. 4). This band assignment is confirmed by the experimental data. The long-wave absorption band

Table 1. Spectral parameters of merocyanines **II**–**IV** and **VIII**–**X**

Comp. no.	CH_2Cl_2		DMF		Toluene	
	λ_{max}, nm	$\varepsilon \times 10^{-5}$, L mol^{-1} cm^{-1}	λ_{max}, nm	$\varepsilon \times 10^{-5}$, L mol^{-1} cm^{-1}	λ_{max}, nm	$\varepsilon \times 10^{-5}$, L mol^{-1} cm^{-1}
II	584	0.2714	579	0.3018	576	0.3112
	516	0.6508	507	0.5014	507	0.5190
	363	0.1602	361	0.0594	359	0.1341
	313	0.2178				
III	675	0.6945	665	0.5644	668	0.7934
	611	0.6629	618	0.8068	584	0.466
	359	0.138	312	0.3388	363	0.145
	323	0.193				
IV	777	1.1105	779	0.992	752	0.9646
	703	0.7119	725	0.815	696	0.727
	331	0.2003	334	0.1607	360	0.1210
VIII	645	0.1128	670	0.084	618	0.1658
	517	1.0763	513	0.8691	518	0.9345
	383	0.1380	390	0.1523	371	0.1434
	328	0.2959	329	0.3030	323	0.2670
IX	696	0.2145	706	0.1171	675	0.4756
	605	0.9822	593	0.7001	611	0.6758
	392	0.0723	400	0.0923	380	0.0830
	339	0.2467	342	0.2713	329	0.2181
X	777	0.4822	775	0.1852	808	1.1096
	693	0.9372	660	0.5827	708	0.5531
	329	0.2181	350	0.3221	338	0.2431

in the spectra of **II**–**IV** and **VIII**–**X** is broader and more diffuse than the short-wave one. Therefore, the fist band is charge-transfer band, and the second is polymethine band.

The intensity of both bands in the spectra of **II**–**IV** increases with extension of the polymethine chain (Fig. 1), and the intensity of the charge-transfer band increases considerably more strongly. Increase in the intensity of

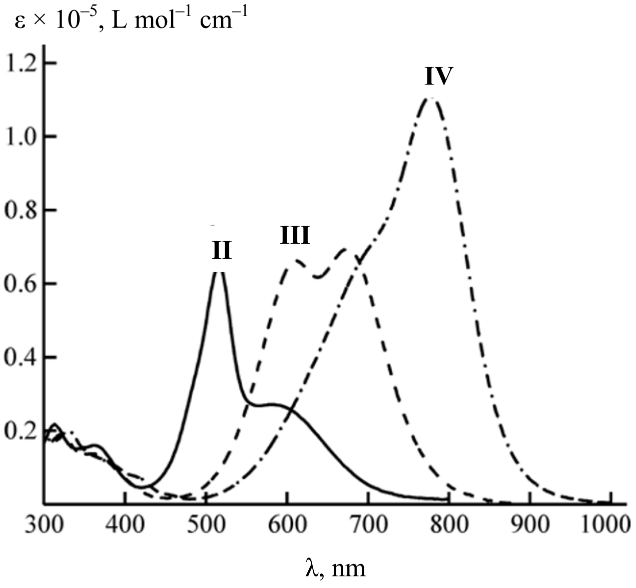


Fig. 1. Electronic absorption spectra of merocyanines **II**–**IV** in methylene chloride.

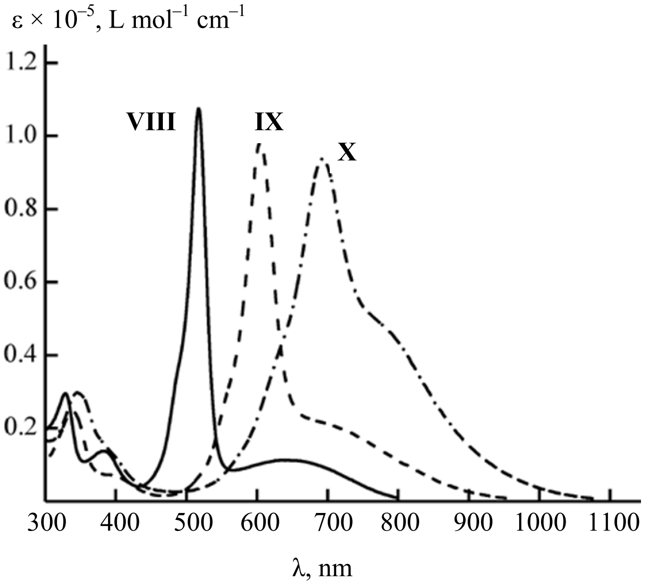


Fig. 2. Electronic absorption spectra of merocyanines **VIII**–**X** in methylene chloride.

Table 2. Calculated [DFT B3LYP/6-31G(*d*,*p*); TDDFT] absorption maxima (λ_{max}^{theor}), oscillator strengths (*f*), and dipole moments in the ground (μ_0) and first (μ_1) and second (μ_2) excited states of merocyanines **II**–**IV** and **VIII**–**X**

Comp. no.	λ_{max}^{theor}, nm	*f*	μ_0, D	μ_1, D	μ_2, D
II	572.94	0.112	14.03	36.57	22.66
	435.87	0.917			
	361.15	0.180			
	339.87	0.114			
III	609.70	0.185	17.02	44.82	27.94
	483.38	1.415			
	364.86	0.166			
IV	647.19	0.297	19.45	52.64	34.39
	530.01	1.799			
	400.89	0.105			
	375.68	0.137			
	369.49	0.129			
VIII	628.72	0.091	16.77	36.55	19.45
	443.31	0.907			
	367.27	0.148			
	358.68	0.130			
IX	663.78	0.141	20.97	45.99	23.94
	494.74	1.525			
	367.42	0.147			
X	705.01	0.217	24.53	55.11	30.15
	546.35	2.041			
	370.14	0.131			

both bands is accompanied by increase of their overlap. Unlike merocyanines **II**–**IV**, extension of the polymethine chain in the series of compounds **VIII**–**X** leads to reduction of the polymethine band intensity, but the intensity of the charge-transfer band increases (Fig. 2).

The electronic structure of merocyanines may be represented by three canonical structures: neutral polyene (**A1**), polymethine (**A2**), and dipolar polyene (**A3**) [2]. The contributions of structures **A1**–**A3** can be estimated by analysis of solvatochromism. Increase of solvent polarity favors charge separation and hence stabilizes more polar structure (**A3** > **A2** > **A1**) [2]. Structure **A2** is responsible for the maximum red shift, intensity, and sharpness of the polymethine band. By contrast, blue shift, reduced intensity, and broadening of absorption band in going to more polar solvent indicates increased contribution of dipolar polyene **A3** as compared to **A2** [2] (Scheme 3).

Replacement of weakly polar toluene by methylene chloride leads to red shift, increase of intensity, and narrowing of the short-wave (polymethine) absorption band of merocyanine **II** (Table 1); i.e., compound **II** shows positive solvatochromism. Therefore, the electronic structure of **II** in these solvents can be represented by structures **A1** to **A2**. Further increase of solvent polarity in going from methylene chloride to dimethylformamide is accompanied by spectral changes typical of negative solvatochromism due to increase of the contribution of structure **A3**. Thus, compound **II** displays reverse solvatochromism.

Merocyanines **III** and **IV** in the solvent series PhMe–CH_2Cl_2–DMF revealed positive solvatochromism of the polymethine band (Table 1, Fig. 5). Presumably, their electronic structure conforms to **A1** to **A2** range. Judging by the second vinylene shift

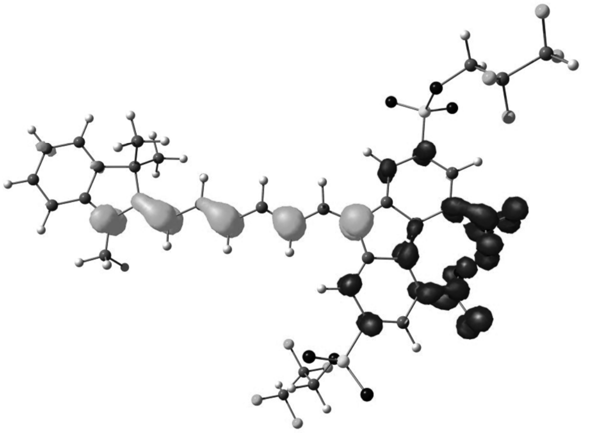


Fig. 3. Change of the electron density in merocyanine **IV** molecule upon $S_0 \rightarrow S_1$ excitation; isosurface value 0.003; light and dark shadings denote, respectively, decrease and increase of electron density.

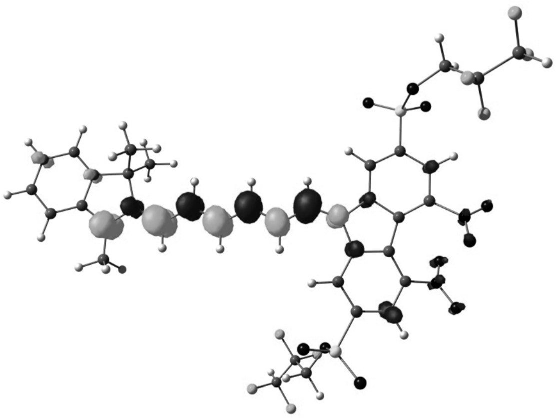
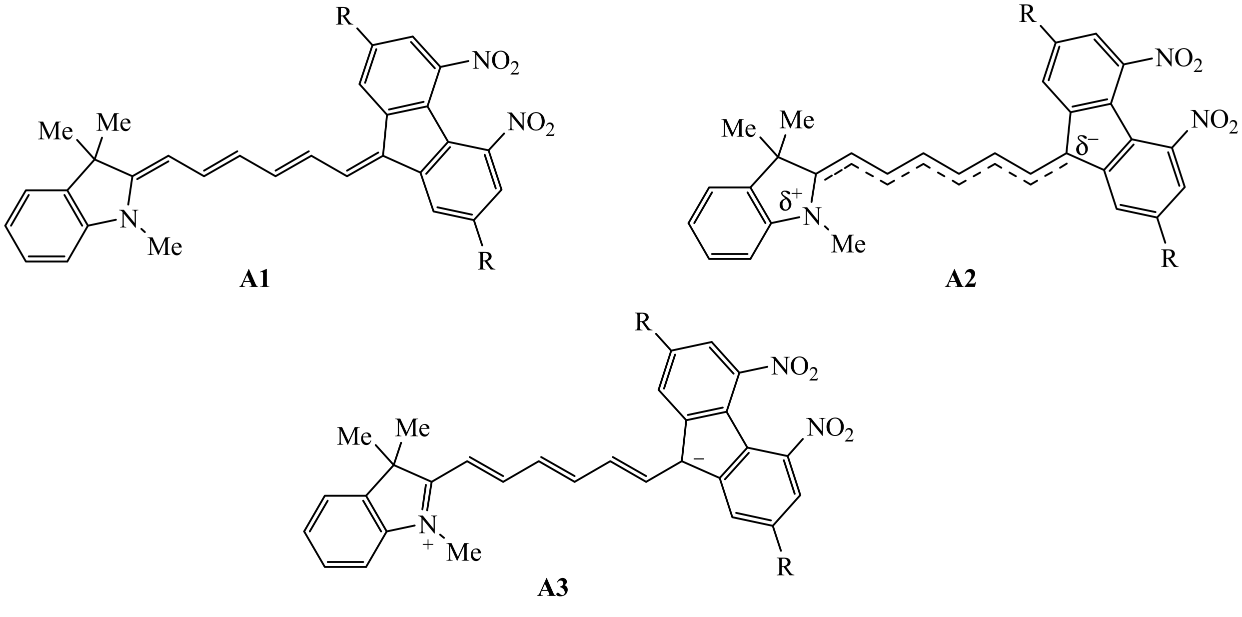


Fig. 4. Change of the electron density in merocyanine **IV** molecule upon $S_0 \rightarrow S_2$ excitation; light and dark shadings denote, respectively, decrease and increase of electron density.

Scheme 3.



R = $SO_2OCH_2(CF_2)_3CHF_2$.

approaching 100 nm (Δλ = 112, 94, and 102 nm in toluene, methylene chloride, and DMF, respectively), i.e., the value typical of symmetrical polymethines, the contribution of structure **A2** predominates.

Replacement of the dihydroindole fragment in **II**–**IV** by more electron-donor benzimidazole (**VIII**–**X**) changes the sign of solvatochromism of the short-wave band. All dyes **VIII**–**X** are negatively solvatochromic, which corresponds to structures **A2**–**A3**. It should be noted that these compounds are first negatively solvatochromic merocyanine dyes based on fluorene.

The solvatochromic shifts of dyes **VIII**–**X** regularly increase with extension of the polymethine chain and are 37, 162, and 306 cm^{-1} in going from toluene to methylene chloride and 151, 335, and 722 cm^{-1}, respectively, in going from methylene chloride to dimethylformamide. These findings suggest increase of the contribution of zwitterionic structure **A3**, which also follows from reduction of the intensity and broadening of the short-wave band as the polymethine chain becomes longer (Fig. 6). Increased contribution of structure **A3** in more polar solvents is also reflected in the decrease of the first and second vinylene shifts in the series PhMe–CH_2Cl_2–DMF: Δλ 93, 88, and 80 nm (first shifts) and 97, 88, and 67 nm (second shifts), respectively.

Our conclusions that the electronic structure of merocyanines **II**–**IV** is given by structures **A1** to **A2**, and of **VIII**–**X**, by structures **A2** to **A3** are also supported by the vicinal coupling constants of CH protons in the polymethine chain in the ^{1}H NMR spectra. In keeping with the ^3J values, the C^1–C^2 bond in **II**–**IV** is close to single (J = 13.2 Hz), while the corresponding bond in **VIII**–**X** approaches a double bond (J = 15.0 Hz). Replacement of $CDCl_3$ as solvent by DMSO-d_6 reduces alternation of the coupling constants of **II**–**IV**, indicating leveling of bond orders,

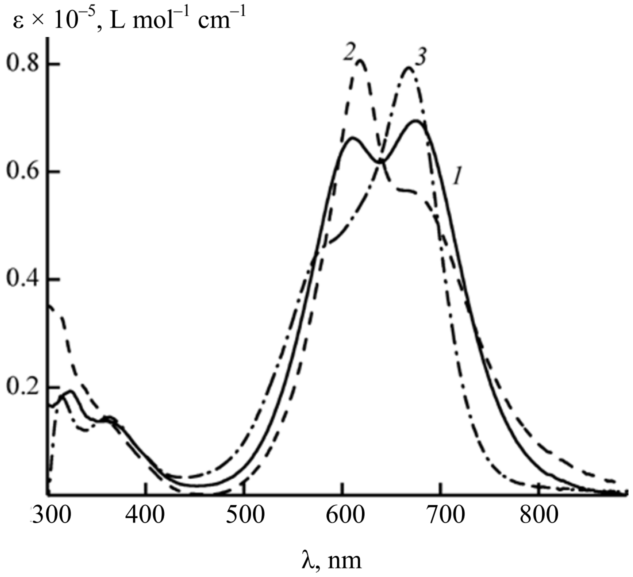


Fig. 5. Electronic absorption spectra of merocyanine **III** in (*1*) methylene chloride, (*2*), DMF, and (*3*) toluene.

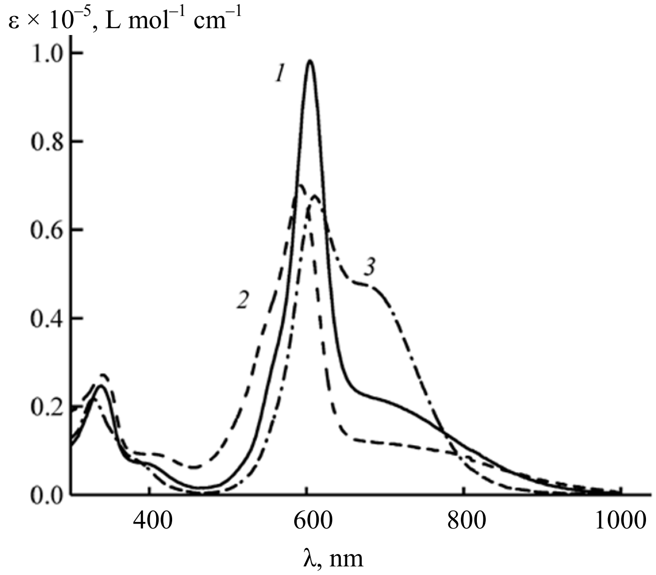


Fig. 6. Electronic absorption spectra of merocyanine **IX** in (*1*) methylene chloride, (*2*), DMF, and (*3*) toluene.

i.e., increase of the contribution of the ideal polymethine structure. By contrast, alternation of the coupling constants in the spectra of merocyanines **VIII**–**X** increases in going from $CDCl_3$ to DMSO-d_6, which may be interpreted as increase of the contribution of the dipolar polyene structure. For instance, the coupling constants for compound **IX** in $CDCl_3$ are 13.5, 12.0, 11.7, and 13.5 Hz, and in DMSO-d_6, 15.3, 11.4, 10.5, and 14.7 Hz.

Charge-transfer electronic transition in donor–acceptor systems enhances charge separation in the excited state. Therefore, polar solvents should reduce the energy of the excited state to a stronger extent than the energy of the ground state. As a result, the charge-transfer band should display positive solvatochromism. In fact, unlike the short-wave polymethine band, the long-wave absorption band of merocyanines **VIII** and **IX** shifts red as the solvent polarity increases (Table 1, Fig. 6). It was difficult to determine the type of solvatochromism of the charge-transfer band of compound **X**, as well as of **II**–**IV**, due to its considerable overlap by the polymethine band.

In summary, we have synthesized several series of merocyanine dyes on the basis of bis(2,2,3,3,4,4,5,5-octafluoropentyl) 4,5-dinitro-9*H*-fluorene-2,7-disulfonate and heterocycles possessing different electron-donor abilities. Like polynitrofluorenes and unlike fluorene-based dyes containing only sulfonate groups in the fluorene fragment, the electronic absorption spectra of the synthesized compounds contain three bands. Their color is determined by the short-wave polymethine and long-wave charge-transfer bands. Variation of the donor ability of the heterocyclic fragment, length of the polymethine chain, and solvent polarity changes the electronic structure of merocyanine dyes from neutral polyene to polymethine and dipolar polyene. The examined compounds showed all types of solvatechromism: positive, negative, and reverse.

EXPERIMENTAL

The electronic absorption spectra were measured on a Shimadzu UV-3100 spectrophotometer using 1-cm cells at concentrations of 10^{-5} M. The ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 MHz using tetramethylsilane as internal reference. The melting points were determined in open capillaries and are uncorrected. The purity of the dyes was checked by TLC on Silufol UV-254 plates with acetonitrile as eluent. The solvents were purified by standard procedures [21]. Methylene chloride was stabilized by addition of anhydrous ethanol (1%).

Quantum chemical calculations were performed at the DFT B3LYP/6-31G(*d*,*p*) level of theory with preliminary optimization of geometric parameters of the ground states at the same level (Firefly 8.0 [22]). The electronic transitions were simulated in terms of the TDDFT approximation. Electronic transitions with an oscillator strength higher than 7% (of the maximum value) were taken into account.

(*E*)-Bis(2,2,3,3,4,4,5,5-octafluoropentyl) 4,5-dinitro-9-[2-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)ethylidene]-9*H*-fluorene-2,7-disulfonate (II). A mixture of 22 mg (0.11 mmol) of (2*E*)-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)acetaldehyde and 84 mg (0.1 mmol) of bis(2,2,3,3,4,4,5,5-octafluoropentyl) 4,5-dinitro-9*H*-fluorene-2,7-disulfonate in 1 mL of acetic anhydride was heated until complete dissolution, 0.1 mL of triethylamine was added, and the mixture was heated for 2 min under reflux, allowed to cool down, treated with water, and left to stand for 24 h. The green–blue lustrous precipitate was filtered off, washed with water, dried, and recrystallized from chloroform. Yield 55 mg (53%), mp 251–252°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.83 s (6H, CCH_3), 3.81 s (3H, NCH_3), 4.91–5.15 m (4H, OCH_2), 6.69 t. t (2H, CF_2H, J = 51.0, 5.4 Hz), 6.91 d (1H, 1-H, J = 14.7 Hz), 7.23 t (1H, H_{arom}, J = 7.2 Hz), 7.36 d (1H, H_{arom}, J = 7.2 Hz), 7.40 t (1H, H_{arom}, J =

7.2), 7.56 d (1H, $\mathrm{H_{arom}}$, *J* = 7.2), 8.28 br. s (1H, $\mathrm{H_{fluor}}$), 8.34 br. s (1H, $\mathrm{H_{fluor}}$), 8.82 d (1H, 2-H, *J* = 15.0 Hz), 8.94 br.s (1H, $\mathrm{H_{fluor}}$), 9.14 br.s (1H, $\mathrm{H_{fluor}}$). Found, %: C 41.97; H 2.43; N 4.12; S 6.18. $\mathrm{C_{36}H_{25}F_{16}N_3O_{10}S_2}$. Calculated, %: C 42.07; H 2.45; N 4.09; S 6.24.

Bis(2,2,3,3,4,4,5,5-octafluoropentyl) 4,5-dinitro-9-[(2*E*,4*E*)-4-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)but-2-en-1-ylidene]-9*H*-fluorene-2,7-disulfonate (III). A mixture of 132 mg (0.3 mmol) of 2-{(1*E*,3*E*)-4-[acetyl(phenyl)amino]buta-1,3-dien-1-yl}-1,3,3-trimethyl-3*H*-indol-1-ium perchlorate and 252 mg (0.3 mmol) of bis(2,2,3,3,4,4,5,5-octafluoropentyl) 4,5-dinitro-9*H*-fluorene-2,7-disulfonate in 4 mL of acetic anhydride was heated until complete dissolution, 0.4 mL of triethylamine was added, and the mixture was heated for 3 min under reflux and treated with water. The precipitate was filtered off, washed with water, dried, and recrystallized from chloroform. Yield 140 mg (44%), mp 228–229°C. ^{1}H NMR spectrum (acetone-*d*$_6$), δ, ppm: 1.70 s (6H, $\mathrm{CCH_3}$), 3.59 s (3H, $\mathrm{NCH_3}$), 5.00 t (4H, $\mathrm{OCH_2}$ *J* = 13.8 Hz), 6.42 d (1H, 1-H, *J* = 13.2 Hz), 6.694 t.t (2H, $\mathrm{CF_2H}$, *J* = 51.3, 5.1 Hz) 7.14 t (1H, $\mathrm{H_{arom}}$, *J* = 7.8 Hz), 7.20 d (1H, $\mathrm{H_{arom}}$, *J* = 8.1 Hz), 7.32 t (1H, $\mathrm{H_{arom}}$, *J* = 7.8 Hz), 7.36 pseudo t (1H, 3-H, *J* = 13.2 Hz), 7.47 d (1H, $\mathrm{H_{arom}}$, *J* = 7.2 Hz), 8.29 br. s (2H, $\mathrm{H_{fluor}}$), 8.31 pseudo t (1H, 2-H, *J* = 12.9 Hz), 8.64 d (1H, 4-H, *J* = 13.5 Hz), 8.88 br.s (1H, $\mathrm{H_{fluor}}$), 8.97 br.s (1H, $\mathrm{H_{fluor}}$). Found, %: C 43.17; H 2.51; N 3.87; S 5.99. $\mathrm{C_{38}H_{27}F_{16}N_3O_{10}S_2}$. Calculated, %: C 43.31; H 2.58; N 3.99; S 6.09.

Bis(2,2,3,3,4,4,5,5-octafluoropentyl) 4,5-dinitro-9-[(2*E*,4*E*,6*E*)-6-(1,3,3-trimethyl-2,3-dihydro-1*H*-indol-2-ylidene)hexa-2,4-dien-1-ylidene]-9*H*-fluorene-2,7-disulfonate (IV). A mixture of 118 mg (0.25 mmol) of 2-{(1*E*,3*E*,5*E*)-6-[acetyl(phenyl)amino]hexa-1,3,5-trien-1-yl}-1,3,3-trimethyl-3*H*-indol-1-ium perchlorate and 211 mg (0.25 mmol) of bis(2,2,3,3,4,4,5,5-octafluoropentyl) 4,5-dinitro-9*H*-fluorene-2,7-disulfonate in 4 mL of acetic anhydride was heated until complete dissolution, 0.4 mL of triethylamine was added, and the mixture was heated for 3 min under reflux and treated with water. The precipitate was filtered off, washed with water, dried, and recrystallized twice from chloroform (4 mL). Yield 100 mg (37%), fine green crystals, mp 179–180°C. ^{1}H NMR spectrum (acetone-*d*$_6$), δ, ppm: 1.64 s (6H, $\mathrm{CCH_3}$), 3.49 s (3H, $\mathrm{NCH_3}$), 5.01 t (4H, $\mathrm{OCH_2}$, *J* = 13.8 Hz), 6.08 d (1H, 1-H, *J* = 13.5 Hz), 6.61 pseudo t (1H, 2-H, *J* = 11.7 Hz), 6.71 t.t (2H, $\mathrm{CF_2H}$, *J* = 51.0, 5.1 Hz), 7.06 t (1H, $\mathrm{H_{arom}}$, *J* = 7.5 Hz), 7.10 d (1H, $\mathrm{H_{arom}}$, *J* = 8.1 Hz), 7.28 t (1H, $\mathrm{H_{arom}}$, *J* = 7.2 Hz), 7.31 pseudo t (1H, 4-H, *J* = 14.7 Hz), 7.41 d (1H, $\mathrm{H_{arom}}$, *J* = 7.2 Hz), 7.65 pseudo t (1H, 3-H, *J* = 12.9 Hz), 7.81 pseudo t (1H, 5-H, *J* = 13.2 Hz), 8.30 d (1H, 6-H, *J* = 13.2 Hz), 8.31 s (2H, $\mathrm{H_{fluor}}$), 8.95 s (2H, $\mathrm{H_{fluor}}$). Found, %: C 44.32; H 2.73; N 3.77; S 5.86. $\mathrm{C_{40}H_{29}F_{16}N_3O_{10}S_2}$. Calculated, %: C 44.49; H 2.71; N 3.89; S 5.94.

Bis(2,2,3,3,4,4,5,5-octafluoropentyl) 4,5-dinitro-9-[(*E*)-3-(N-phenylacetamido)prop-2-en-1-ylidene]-9*H*-fluorene-2,7-disulfonate (VI). A mixture of 190 mg (0.225 mmol) of bis(2,2,3,3,4,4,5,5-octafluoropentyl)-4,5-dinitro-9*H*-fluorene-2,7-disulfonate (**I**) and 59 mg (0.228 mmol) of *N*-[3-anilinoprop-2-en-1-ylidene] anilinium chloride in 2.5 mL of acetic anhydride was heated until complete dissolution, 0.4 mL of triethylamine was added, and the mixture was heated for 2 min under reflux. The mixture turned green–yellow and was treated with water and left overnight. The precipitate was filtered off, washed with water, dried, and subjected to column chromatography on silica gel using methylene chloride as eluent. A bright orange fraction was collected and evaporated under reduced pressure. Yield 120 mg (52%), fine red–orange highly electrifiable powder, mp 143–144°C. ^{1}H NMR spectrum (acetone-*d*$_6$), δ, ppm: 2.13 s (3H, $\mathrm{COCH_3}$), 4.97 t (2H, $\mathrm{OCH_2}$, *J* = 13.2 Hz,), 5.08 t (2H, $\mathrm{OCH_2}$, *J* = 13.2 Hz), 6.29 pseudo t (1H, 2-H, *J* = 12.9 Hz), 6.76 t.t (1H, $\mathrm{CF_2H}$, *J* = 50.7, 5.4 Hz), 6.80 t. t (1H, $\mathrm{CF_2H}$, *J* = 50.7, 5.4 Hz), 7.62 d (2H, $\mathrm{H_{arom}}$, *J* = 7.5 Hz), 7.75 t (3H, $\mathrm{H_{arom}}$, *J* = 7.5 Hz), 8.25 s (1H, $\mathrm{H_{fluor}}$), 8.49 s (2H, $\mathrm{H_{fluor}}$), 8.80 pseudo t (1H, 3-H, *J* = 12.9 Hz), 8.81 d (1H, $\mathrm{H_{arom}}$, *J* = 12.3 Hz), 8.32 d (1H, 1-H, *J* = 13.2 Hz), 9.13 s (1H, $\mathrm{H_{fluor}}$). Found, %: C 40.02; H 2.01; N 4.02; S 6.33. $\mathrm{C_{34}H_{21}F_{16}N_3O_{11}S_2}$. Calculated, %: C 40.21; H 2.08; N 4.14; S 6.31.

Bis(2,2,3,3,4,4,5,5-octafluoropentyl) 4,5-dinitro-9-[(2*E*,4*E*)-5-(*N*-phenylacetamido)penta-2,4-dien-1-ylidene]-9*H*-fluorene-2,7-disulfonate (VII). A mixture of 422 mg (0.5 mmol) of bis(2,2,3,3,4,4,5,5-octafluoropentyl) 4,5-dinitro-9*H*-fluorene-2,7-disulfonate (**I**) and 143 mg (0.5 mmol) of *N*-(5-anilinopenta-2,4-dien-1-ylidene)anilinium chloride in 4.5 mL of acetic anhydride was heated under stirring until complete dissolution (2 min), 0.1 mL of triethylamin was added, and the mixture was heated for 5 min under reflux, cooled, and diluted with a threefold volume of diethyl ether. The fine turquoise solid was filtered off to isolate 70 mg of symmetrical anionic pentamethine dye. The mother liquor was evaporated, the residue was treated with water,and the precipitate was filtered off, dried, and dissolved in chloroform. The undissolved material (symmetrical dye) was filtered off, and the filtrate was evaporated. Yield 370 mg (71%), mp 136–137°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.95 s (3H, $COCH_3$), 4.94 t (2H, OCH_2, J = 13.8 Hz), 5.00 t (2H, OCH_2, J = 13.8 Hz), 5.60 d.d (1H, 4-H, J = 13.8, 11.1 Hz), 6.67 t.t (1H, CF_2H, J = 51.0, 5.1 Hz), 6.69 t.t (1H, CF_2H, J = 51.0, 5.1 Hz), 7.33–7.42 m (2H, H_{arom}); 7.50–7.65 m (5H, H_{arom}, 2-H, 3-H), 8.15 d (1H, 5-H, J = 13.8 Hz), 8.42 d (1H, H_{fluor}, J = 1.2 Hz), 8.44 d (2H, 1-H, J = 11.7 Hz), 8.46 d (1H, H_{fluor}, J = 1.2 Hz), 8.89 d (1H, H_{fluor}, J = 1.2 Hz), 8.98 d (1H, H_{fluor}, J = 1.2 Hz). Found, %: C 41.37; H 2.14; N 3.97; S 6.04. $C_{36}H_{23}F_{16}N_3O_{11}S_2$. Calculated, %: C 41.51; H 2.23; N 4.03; S 6.16.

Bis(2,2,3,3,4,4,5,5-octafluoropentyl) 9-[2-(1,3-diphenyl-2,3-dihydro-1*H*-benzimidazol-2-ylidene)ethylidene]-4,5-dinitro-9*H*-fluorene-2,7-disulfonate (VIII). A mixture of 90 mg (0.1 mmol) of disulfonate **V** and 32 mg (0.1 mmol) of 2-methyl-1,3-diphenyl-3*H*-benzimidazol-1-ium chloride in 1.5 mL of pyridine was heated under reflux until complete dissolution, 0.1 mL of triethylamine was added, and the mixture was heated under reflux 2 min more. The mixture was cooled, diluted with 15 mL of water, and allowed to settle down, and 5 drops of glacial acetic acid in 1 mL of water were added for crystallization. The precipitate was filtered off, dried, and recrystallized from chloroform. Yield 46 mg (61%), mp 283–284°C. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 4.86 t (4H, OCH_2, J = 13.2 Hz), 6.41 d (1H, 1-H, J = 15.9 Hz), 6.72 t.t (2H, CF_2H, J = 51.3, 5.4 Hz), 7.25–7.33 m (2H, H_{arom}), 7.44–7.51 m (2H, H_{arom}), 7.50 d (1H, 2-H, J = 15.9 Hz), 7.84–7.96 m (12H, $10H_{arom}$, $2H_{fluor}$), 8.03 d (2H, H_{fluor}, J = 1.2 Hz). Found, %: C 46.23; H 2.22; N 4.95; S 5.49. $C_{44}H_{26}F_{16}N_4O_{10}S_2$. Calculated, %: C 46.41; H 2.30; N 4.92; S 5.63.

Bis(2,2,3,3,4,4,5,5-octafluoropentyl) 9-[(2*E*)-4-(1,3-diphenyl-2,3-dihydro-1*H*-benzimidazol-2-ylidene)but-2-en-1-ylidene]-4,5-dinitro-9*H*-fluorene-2,7-disulfonate (IX). A mixture of 203 mg (0.2 mmol) of compound **VI** and 64 mg (0.2 mmol) of 2-methyl-1,3-diphenyl-3*H*-benzimidazol-1-ium chloride in 2 mL of pyridine was heated under stirring until complete dissolution, 0.1 mL of triethylamine was added, and the mixture was heated for 5 min under reflux, cooled, and treated with water. The precipitate was filtered off, dried, and purified by chromatography on silica gel 100 using chloroform as eluent. Yield 120 mg (52%), mp 256–257°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.49 t (4H, OCH_2, J = 13.2 Hz), 5.81 d (1H, 1-H, J = 15.6 Hz), 6.01 t.t (2H, CF_2H, J = 52.5, 5.4 Hz), 6.43 pseudo t (1H, 3-H, J = 11.4 Hz), 6.64 pseudo t (1H, 2-H, J = 12.0 Hz), 6.89 d (1H, 4-H, J = 15.3 Hz), 7.12–7.23 m (2H, H_{arom}), 7.36–7.48 m (2H, H_{arom}), 7.67–7.77 m (4H, H_{arom}), 7.81–7.93 m (6H, H_{arom}), 8.00 s (2H, H_{fluor}), 8.23 s (2H, H_{fluor}). Found, %: C 47.30; H 2.31; N 4.74; S 5.55. $C_{46}H_{28}F_{16}N_4O_{10}S_2$. Calculated, %: C 47.43; H 2.42; N 4.81; S 5.51.

Bis(2,2,3,3,4,4,5,5-octafluoropentyl) 9-[(2*E*,4*E*)-6-(1,3-diphenyl-2,3-dihydro-1*H*-benzimidazol-2-ylidene)hexa-2,4-dien-1-ylidene]-4,5-dinitro-9*H*-fluorene-2,7-disulfonate (X). A mixture of 208 mg (0.2 mmol) of compound **VII** and 64 mg (0.2 mmol) of 2-methyl-1,3-diphenyl-3*H*-benzimidazol-1-ium chloride in 2 mL of pyridine was heated under stirring until complete dissolution, 0.1 mL of triethylamine was added, and the mixture was heated for 5 min under reflux, cooled, and treated with water. The precipitate was filtered off, dried, and purified by chromatography on silica gel 100 using chloroform as eluent. Yield 110 mg (46%), mp 210–211°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.52 t (4H, OCH_2, J = 13.2 Hz), 5.63 d (1H, 1-H, J = 14.7 Hz), 5.83 pseudo t (1H, 4-H, J = 12.9 Hz), 6.01 t.t (2H, CF_2H, J = 52.5, 5.4 Hz), 6.19 pseudo t (1H, 3-H, J = 12.9 Hz), 6.34 pseudo t (1H, 2-H, J = 14.4 Hz), 6.35 pseudo t (1H, 5-H, J = 13.2 Hz), 7.15 d (1H, 6-H, J = 14.7 Hz), 7.13–7.21 m (2H, H_{arom}), 7.39–7.47 m (2H, H_{arom}), 7.62–7.70 m (4H, H_{arom}), 7.81–7.90 m (6H, H_{arom}), 8.02 s (2H, H_{fluor}), 8.44 s (2H, H_{fluor}). Found, %: C 48.29; H 2.46; N 4.55; S 5.46. $C_{48}H_{30}F_{16}N_4O_{10}S_2$. Calculated, %: C 48.41; H 2.54; N 4.70; S 5.39.

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