# Synthesis and Spectral Properties of Merocyanine Dyes Based on Fluorene and Its Derivatives

I. V. Kurdyukova<sup>a</sup>, N. A. Derevyanko<sup>a</sup>, A. A. Ishchenko<sup>a</sup>, and D. D. Mysyk<sup>b</sup>

<sup>a</sup> Institute of Organic Chemistry, National Academy of Sciences of Ukraine, ul. Murmanskaya 5, Kiev, 02094 Ukraine e-mail: alexish@i.com.ua

<sup>b</sup> Donetsk National Technical University, Donetsk, Ukraine

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Abstract—The di-, tetra- and hexamethine merocyaninyes, the derivatives of fluorene, diphenyl 9*H*-fluorene-2,7-disulfonate, and bis(2,2,3,3,4,4,5,5-octafluoropentyl) 9*H*-fluorene-2,7-disulfonate, as well as the derivatives of the heterocycles of moderate (indolylidene and benzotiazolylidene), weak (benzo[c,d]indolylidene and 2,6-diphenylpyrane) and strong (2,6-diphenylpyridine) electron-donor properties were synthesized and their absorption spectra in solvents of different polarity were studied. The quantum-chemical analysis of electronic structure of the synthesized merocyanines was performed and the types of electronic transitions in them were found by the DFT and TDDFT methods with the B3LYP/6-31G(d,p) basis.

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Merocyanine dyes, due to a wide range of practically important properties, like pronounced solvatochromism, the ability to significantly alter the dipole moment at the electron excitation and sensitize various physical and chemical processes, find an increasingly wide application in optoelectronics, nonlinear optics, recording media and information processing, medicine and biology [1, 2].

Traditionally, the end groups of the merocyanines are the residues of heterocyclic compounds [1, 2]. The search for new heterocycles is the basis for creating the dyes with a deep color, that is, absorbing light at long wavelengths [3]. In this work we aimed at exploring a possibility to synthesize the merocyanines based on aromatic carbocycles. We selected the fluorene framework as the carbocycle. The choice is due to the expanded  $\pi$ -system, the high electronic symmetry and the presence of a methylene group, which can be potentially active in the reactions of cyanine condensation owing to its conjugation with the benzene ring [4].

We synthesized and studied a number of merocyanines based on the unsubstituted fluorene and substituted analogs, diphenyl 9*H*-fluorene-2,7-disulfonate, and bis(2,2,3,3,4,4,5,5-octafluoropentyl) 9*H*-fluorene-2,7-disulfonate, not utilized previously in the synthesis of the merocyanines containing heterocyclic fragments with various electron-donating properties.

We failed to carry out the cyanine condensation at the methylene group of fluorene because of its insufficient C–H acidity ( $pK_a = 20.5$ ) [5] even in the presence of strong bases like 1,8-diazabicycloundec-7ene (DBU) and a "proton sponge" 1,8-bisdimethylaminonaphthalene. The merocyanines based on the unsubstituted fluorene (III–V) were synthesized by Wittig reaction using the fluorene tributylphosphorus ylide I [6] (Scheme 1).

The introduction to the fluorene core of acceptor substituents with the moderate and strong acceptor properties, the phenoxysulfonyl group (for SO<sub>2</sub>OPh  $\sigma_m = 0.36$ ,  $\sigma_p = 0.33$  [7]) and octafluoro-phentyloxysulfonyl group ( $\sigma_m = 0.78$ ,  $\sigma_p = 0.88$  [8]), respectively, facilitated considerably the cyanine condensation at the methylene group of the fluorene frame. The merocyanines based on the fluorene derivatives IX-XVI, XVIII-XIX, XXII-XXIII were synthesized in the reaction of the substituted fluorene with heterocyclic aldehydes and heterocyclic hemicyanines (Scheme 2) under usual conditions of the cyanine condensation. The merocyanines with pyridine ring (XXIV-XXV) were obtained from

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VIa,  $R = SO_2OPh$ ; VIb,  $R = SO_2OCH_2(CF_2)_3CHF_2$ ; VIIa,  $X = C(Me)_2$ ,  $R^1 = Me$ , n = 1,  $A = CIO_4$ ; VIIb,  $X = C(Me)_2$ ,  $R^1 = Me$ , n = 2,  $A = CIO_4$ ; VIIb, X = S,  $R^1 = Et$ , n = 1,  $A = BF_4$ ; VIIb, X = S,  $R^1 = Et$ , n = 2, A = TosO; XVIIa,  $Y = N(Me)_2$ , n = 1,  $A = BF_4$ ; XVIIb, Y = OEt, n = 2,  $A = BF_4$ ; XXI,  $A = BF_4$ ; IX–XIV,  $X = C(Me)_2$ ,  $R^1 = Me$ ; XV–XVI, X = S,  $R^1 = Et$ ; IX–XI, XV–XVI, XVIII–XIX, XXII–XXIII,  $R = SO_2OPh$ ; XII–XIV,  $R = SO_2OCH_2(CF_2)_3CHF_2$ ; IX, XII, XVIII, XXII, n = 0; X, XIII, XV, XIX, XXIII, n = 1; XI, XIV, XVI, n = 2.

pyrilium compounds **XXII**–**XXIII** in the reaction with methylamine (Scheme 3).

Compounds IIa, IIb [9], IIc [10], XVII [11, 12], XX [13], and XXI [14] have been described

previously. The hemicyanines (VII, VIII) were synthesized by the known conventional methods [15].

Merocyanines can be considered as hybrids of two types of symmetric dyes, cationic and anionic, one of



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which has a longer polymethine chain, and another a shorter chain than merocyanine. To calculate the deviations, we used in this work the anionic dyes **XXVI–XXXI** [16–18], and the cationic dyes **XXXII–XXXIX** [16, 17].

The chosen solvents are the almost non-polar hexane ( $n_D = 1,3751$ ,  $\varepsilon_D = 1.890$ , B = 0 cm<sup>-1</sup>, E = 0), which provides the polarity range approaching that in a vacuum, and toluene ( $n_D = 1.4961$ ,  $\varepsilon_D = 2,37$ , B = 58 cm<sup>-1</sup>, E = 1.3), low-polar dichloromethane ( $n_D = 1.4242$ ,  $\varepsilon_D = 8.9$ , B = 23 cm<sup>-1</sup>, E = 2.7), polar acetonitrile ( $n_D =$ 1.3441,  $\varepsilon_D = 36.2$ , B = 160 cm<sup>-1</sup>, E = 5.2) and DMF, ( $n_D = 1.4303$ ,  $\varepsilon_D = 36.7$ , B = 291 cm<sup>-1</sup>, E = 2.6), as well as a typical proton-donor ethanol ( $n_D = 1.3611$ ,  $\varepsilon_D = 24.3$ , B = 235 cm<sup>-1</sup>, E = 11.6) [16]. The latter is regarded primarily as a solvent potentially prone to strong electrophilic solvation, including the formation of hydrogen bonds.

The main parameters describing the electron absorption spectra are the absorption maximum ( $\lambda_{max}$ ) and molar extinction coefficient ( $\epsilon$ ). However, the  $\lambda_{max}$  value does not always reflect objectively the spectral pattern, because it may be affected by various vibronic transitions [16]. In addition, the maximum may be determined with insufficient accuracy in the case of broad, diffuse or highly structured bands. The curves with such shape are characteristic of merocyanines **III–V**, **IX–XVI**, **XVIII–XIX**, and **XXII–XXIII**, in contrast to the corresponding symmetrical ionic dyes.

We performed a mathematical treatment of longwavelength absorption bands of the synthesized dyes by the method of moments [16]. This allowed us a

**Table 1.** Characteristics of long-wavelength absorption bands of merocyanines III–V, IX–XVI, XVIII–XIX, and XXII–XXV in *n*-hexane, toluene, dichloromethane, acetonitrile, DMF, and ethanol.

Comp. no.	Solvent	$\lambda_{max}$ , nm	$D_{\lambda}$ , nm	$\epsilon \times 10^{-4}$ , 1 mol <sup>-1</sup> cm <sup>-1</sup>	$M^{-1}$ , nm $D_{\rm M}$ ,		f
Ш	Hexane	429		6.82	422.0		0.93
		452		5.71			
	Toluene	441		4.91	436.1		0.73
		460		4.34			
	$CH_2Cl_2$	447	106.5	6.10	442.0		0.93
	EtOH	439	109.5	6.01	433.7		0.95
	DMF	451	102.5	5.32	444.2	92.9	0.87
IV	Hexane	471		7.80	452.7		1.13
	Toluene	485		5.94	470.5		0.95
	$CH_2Cl_2$	491	151	6.85	480.0		1.15
	EtOH	482	152.5	6.81	433.9		0.94
	DMF	496	141.5	6.30	485.6		1.08
V	Hexane	480		7.53	471.1		1.32
		503		7.80			
	Toluene	509		5.62	492.4		0.98
	$CH_2Cl_2$	516	232.5	7.17	504.5		1.30
	EtOH	504	235.5	7.18	490.7		1.34
	DMF	520	223	6.91	508.7		1.31
IX	Hexane	475		4.09	475.3		0.63
		503		5.80			
	Toluene	518		5.54	488.6		0.67
	$CH_2Cl_2$	519		5.86	495.1		0.73
	EtOH	515		5.67	489.0		0.75
	CH <sub>3</sub> CN	519		5.73	492.4		0.80
	DMF	525		5.85	496.6		0.86

Table 1. (Contd.)

Comp. no.	Solvent	$\lambda_{max}$ , nm	$D_{\lambda}$ , nm	$\epsilon \times 10^{-4}$ , 1 mol <sup>-1</sup> cm <sup>-1</sup>	$M^{-1}$ , nm	$D_{\rm M}$ , nm	f
Х	Hexane	532		6.49	521.5		0.88
		564		5.30			
	Toluene	555		6.13	545.7		0.91
		583	10-	5.61	<b>5</b> 40 0		
	CH <sub>2</sub> Cl <sub>2</sub>	564	107	5.56	549.0		0.90
	EtOH	562	99.5	5.69	544.0	94.1	0.96
	CH <sub>3</sub> CN	567	93.5	5.41	544.6	90.95	0.96
	DMF	580	84	5.13	3 560.9		0.85
XI	Hexane	581		6.47	554.3		1.00
	Toluene	600		6.55	578.7		1.11
	$CH_2Cl_2$	608	170.5	6.57	585.4	168.9	1.21
	EtOH	601	168.5	6.48	583.7	155.8	1.22
	CH <sub>3</sub> CN	600	163.5	6.43	585.2	146.3	1.27
	DMF	614	154.5	6.04	594.7	143.1	1.22
XII	Hexane	480		4.94	478.5		0.83
	T.1	509		7.56	499.4		0.07
	l oluene	521		7.05	488.4		0.87
		523		6.96	490.6		0.93
	EIOH	510		0.41	483.5		0.93
	CH <sub>3</sub> CN	520		6.38	487.3		0.95
VIII	DMF	524		6.35	490.9		0.93
АШ	Hexane	543		0.62 5.06	535.0		0.91
	Talaana	575		5.90	550 1		0.02
	Toluene	587		5.98	332.1		0.95
	CH <sub>2</sub> Cl <sub>2</sub>	570		6 30	557 5		1.01
	0112012	589		6.29	557.5		1.01
	EtOH	563		6.28	547.9		1.05
	CH <sub>3</sub> CN	570		6.24	550.4		1.08
	DMF	578		5.97	557.9		1.02
XIV	Hexane	593		7.97	570.4		1.20
	Toluene	610		7.66	587.7		1.25
	$CH_2Cl_2$	617	158.5	7.49	597.25		1.33
	EtOH	604	162.5	7.42	585.7		1.43
	CH <sub>3</sub> CN	603	156.5	7.04	585.9		1.39
	DMF	613	152.5	6.89	596.0		1.33
XV	Hexane	556			547.5		
	Toluene	612		6.98	569.8		1.08
	$CH_2Cl_2$	620	54	8.03	577.3	73.85	1.22
	EtOH	617	53.5	7.70	574.9	71.15	1.21
	CH <sub>3</sub> CN	621		7.71	577.1		1.24
	DMF	631	40.5	7.80	585.4	61.4	1.20
XVI	Hexane	607			577.1		
	Toluene	627		6.83	604.7		1.10
	$CH_2Cl_2$	637	147.5	7.01	618.1	143.85	1.24
	EtOH	635	146	5.85	614.0	134.35	1.09
	CH <sub>3</sub> CN	634	133	6.43	614.8	120.35	1.25
	DMF	648	130	5.36	626.7	111.3	1.04

Table 1. (Contd.)

Comp. no.	Solvent	$\lambda_{max}, nm$	$D_{\lambda}$ , nm	$\epsilon \times 10^{-4}$ , 1 mol <sup>-1</sup> cm <sup>-1</sup>	$M^{-1}$ , nm	$D_{\rm M}$ , nm	f
XVIII	Hexane	566			551.8		
	Toluene	579		4.73	566.9		0.65
	$CH_2Cl_2$	579		5.49	566.7		0.77
	EtOH	576		5.11	564.3		0.73
	CH <sub>3</sub> CN	576		5.24	564.8		0.77
	DMF	574		7.36	564.0		1.01
XIX	Hexane	606			577.5		
	Toluene	621		5.92	598.5		0.91
	$CH_2Cl_2$	614	168	5.74	598.7	147.05	0.93
	EtOH	609	166.5	6.10	593.9		1.04
	CH <sub>3</sub> CN	604	169.5	5.40	593.7	140.8	0.90
	DMF	618	162	5.34	605.4		0.89
XXII	Hexane	506			502.5		
		537					
	Toluene	521		4.04	520.7		0.83
		550		4.30			
	$CH_2Cl_2$	519		4.20	518.9		0.89
		548		4.47			
	EtOH	517		4.30	515.2		0.93
	CUCN	544		4.49	5164		0.01
	CH <sub>3</sub> CN	522		4.25	510.4		0.91
	DMF	530		4.06	513.8		0.92
	Dim	552		4 34	515.0		0.92
XXIII	Hexane	546			531.4		
	Toluene	566		5.48	556.7		1.07
	CH <sub>2</sub> Cl <sub>2</sub>	567	177.5	5.64	557.2	157.35	1.17
	EtOH	566		4.72	553.4		1.00
	CH <sub>3</sub> CN	562	175.5	5.41	550.2	153.1	1.17
	DMF	573	- / - / -	4.66	560.1		1.00
XXIV	Hexane	571			566.5		
		608					
	Toluene	587		6.36	586.0		0.79
		625					
	$CH_2Cl_2$	624		9.80	584.6		0.93
	EtOH	621		9.46	583.2		0.90
	CH <sub>3</sub> CN	620		9.80	583.4		0.86
	DMF	628		10.34	590.2		0.90
XXV	Hexane	646			619.6		
		699					
	Toluene	668		8.13	654.6		1.19
		724		7.24			
	$CH_2Cl_2$	671	49.5	7.94	668.4	14.1	1.28
		726	-5.5	11.73			
	EtOH	669		7.46	666.3		1.25
	<u></u>	724	<i>i</i> -	11.72			
	CH <sub>3</sub> CN	719	-6.5	14.97	677.9	4.6	1.22
	DMF	726		14.69	682.1		1.18

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reliable estimation of the relevant parameters of the position  $(M^{-1})$  and intensity (*f*) of the bands. The value of  $M^{-1}$ , averaged over all vibronic transitions and corresponding to the average position of the band (in the wavenumber scale, it is the center of gravity of the band:  $\bar{\nu} = 10^7/M^{-1}$ ), makes it possible to compare objectively the curves differing in shape, in contrast to  $\lambda_{\text{max}}$ . Similarly, the integral intensity (oscillator strength *f*) is more advantageous compared with the peak intensity (extinction  $\varepsilon$ ).

Table 1 lists the spectral characteristics of merocyanines III–V, IX–XVI, XVIII–XIX, and XXII–XXV. The data for anionic XXVI, XXX–XXXI and cationic XXXII–XXXIX cyanines are given in [17] and the monograph [16], respectively.

Note that merocyanines III–V, in spite of the fairly well-developed  $\pi$ -system of the core, are colored rather highly (Table 1). Their  $\lambda_{max}$  and  $M^{-1}$  values are in the regoion of much shorter wavelengths than the related values of the classic merocyanines based on the indolylidene [2,11,12]. This indicates in them the more pronounced alternation of bond orders in the chromophore. This conclusion is clearly confirmed by the unusually high values of the deviations compared with the known merocyanines (Table 1, [2]). Thus, the  $D_{\lambda}$  value of dye V reaches 232.5 nm.

The electronic structure of the merocyanine dyes is clearly described as a superposition of three basic boundary structures A1-A3 (Scheme 4) [2], corresponding to the three ideal states: neutral polyene (A1), polymethine (A2) and charged polyene (A3).

The above spectral effects in merocyanines III–V can occur when the electronic structure of the ground state  $S_0$  approaches one of the structures with alternating single and double bonds A1 or A3.

The approach of the electronic structure of investigated dyes to one of the ideal structures A1, A2, and A3 can be estimated from the degree of alternation of the bond lengths or orders in the chromophore [19]. To quantify the alternation in merocyanines parameters

BLA (bond length alternation) and BOA (bond order alternation) are most often used [19], which represent a difference between the average lengths (orders) of single and double bonds of the polymethine chain in the resonance structure of uncharged polyene [20]. The BLA parameter takes positive values for the structures A1 and intermediate between A1 and A2, and negative in the case of structures A3 and those in the A2–A3 interval [19]. The BOA parameter has opposite signs in these structures. Both parameters are zero for the structures of type A2.

In addition to the BLA and BOA, we calculated the parameter  $\Delta P_{ch}$  [16]:

$$\Delta P_{\rm ch} = 1/m \sum_{i=1}^{m} |P_{\rm av} - P_i|, \ \Delta P_{\rm av} = 1/m \sum_{i=1}^{m} P_i,$$

where  $P_{av}$  is the average bond order over the chain,  $P_i$  is the bond order of *i*th bond in the chain, *m* is the number of bonds.

The alternation of bonds in the chromophore determines the trends in the change of the vinylene shifts, deviations, and the band shapes, especially their width. The stronger alternation, the less vinylene shifts, larger deviations, and wider bands [16].

The BLA and BOA parameters of the merocyanines III–V are respectively positive and negative (Table 2). Quantum-chemical calculations found in them much greater alternation of bond length in polymethine chains than in the corresponding symmetric cationic and anionic dyes, and close to that in the cyclooctatetraene, which is used as a model of ideal neutral polyene [19] (Table 2). Dipole moments of merocyanines III–V increase at excitation. All this suggests that in merocyanines III–V the  $S_0$  state is most close to the structure A1 in a vacuum.

The unambiguous choice between these structures can be made considering a sign of solvatochromism of the merocyanines. The positive solvatochromism shows the prevalence of structure **A1** in the ground state (dipole moment is higher in the excited than in



D and A are donor and acceptor ends of the chromophore, respectively.

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**Table 2.** The results of quantum-chemical calculations of the parameters of bond orders alternation and dipole moments in the ground and first excited states of merocyanines III–V, IX–XI, anionic (XXVI–XXXI) and cationic (XXXII–XXXIV) dyes, and cyclooctatetraene XL

Comp. no.	BLA	BOA	$\Delta P_{ m ch}$	δ	$\lambda_{max}^{theor}$ nm	$f_{ m theor}$	μ, D	μ*, D
III	0.06	-0.401	0.178	0.4119	405.0	1.104	4.0	9.9
IV	0.061	-0.383	0.1838	0.4350	445.7	1.639	5.2	14.2
V	0.061	-0.376	0.1843	0.4429	485.1	2.107	6.1	18.7
IX	0.044	-0.307	0.1362	0.2946	448.4	0.678	5.3	17.8
					395.1	0.363		
X	0.049	-0.305	0.1466	0.3078	486.1	1.301	7.5	21.4
XI	0.05	-0.31	0.1519	0.3243	528.6	1.821	9.2	26.1
XXVI	0	0	0	0.1623	461.1	0.615	0.2	0.1
					417.9	0.189		
XXVII	0.006	-0.046	0.023	0.1404	492.5	1.395	0.2	0.2
XXVIII	0.006	0.011	0.0249	0.1454	541.2	2.092	0.1	0.7
XXIX	0	0	0	0.1951	546.0	0.289	1.9	3.1
					435.5	0.303		
XXX	0.006	-0.026	0.013	0.2022	587.9	0.486	0.8	0.7
					473.8	0.765		
XXXI	0.0005	-0.021	0.0118	0.1706	632.3	0.958	0.1	0.3
					523.4	0.784		
XXXII	0	0.015	0.0075	0.2717	456.5	1.268	2.9	2.3
XXXIII	0.003	-0.017	0.0078	0.2066	503.1	1.877	2.7	2.6
XXXIV	0.004	-0.028	0.014	0.1526	545.1	2.519	2.5	3.1
XL	0.131	-0.800	0.441	2.02	195.5	0.38	0	0

ground state), while negative sign, on the contrary, corresponds to A3 structure (dipole moment in the ground state is higher than in the excited state) [2]. For the correct determination it is necessary to compare the spectral shifts of the bands in a pair of solvents whose  $n_{\rm D}$  values are similar while macroscopic ( $\varepsilon_{\rm D}$ ) and microscopic (*B* and *E*) parameters of polarity are significantly different. In this study we selected dichloromethane and DMF. The latter is significantly more polar and nucleophilic than the former while their  $n_{\rm D}$  and *E* values are similar. Consequently, the observed red shift of bands of merocyanines III–V in going from CH<sub>2</sub>Cl<sub>2</sub> to DMF is associated with the increased polarity of the medium and demonstrates the positive solvatochromism of these dyes.

By the example of the spectra of merocyanines III– V we can illustrate the above considered often appearing problem of incorrect determination of the sign of solvatochromism. Thus, in the case of merocyanine III the replacement of dichlorometane by a more polar ethanol, unlike the replacement by DMF, causes blue rather than red shift of  $\lambda_{max}$  and  $M^{-1}$ . The same effect was observed with other dyes. It may be concluded that these merocyanines have a negative solvatochromism. However, the reason for this shift is the lower  $n_D$  value of ethanol as compared with CH<sub>2</sub>Cl<sub>2</sub>. It follows from the observed blue shift that this factor dominates over the effect of increasing  $\varepsilon_D$  and *E* parameters at the use of ethanol.

Consequently, the electronic structure of the merocyanines III-V in the ground state approaches the neutral polyene structure A1.

The positive solvatochromism of merocyanines **III–V** is small and varies little with increasing polymethine chain length. The replacement of CH<sub>2</sub>Cl<sub>2</sub> by DMF leads to a red shift of  $\lambda_{max}$  and  $M^{-1}$  by 4 nm 820 cm<sup>-1</sup>) and 2.2 nm (112 cm<sup>-1</sup>) only, respectively, in the case of merocyanine **III** and by 4 nm (149 cm<sup>-1</sup>) and 4.6 nm (180 cm<sup>-1</sup>) in the case of the compound **V** (Fig. 1).

The insignificant positive solvatochromism of merocyanines **III–V** while deviations are significant points to the proximity of their electronic structure in the ground state to that of ideal neutral polyene. This conclusion is confirmed by the numerical values of coupling constants of the polymethine chain protons in the <sup>1</sup>H NMR spectra of the dyes **III–V**. Note that usual <sup>1</sup>H NMR spectra do not allow unambiguous assignment of the signals.



Therefore, we recorded COSY and ROESY spectra of the dye V. Considering the  ${}^{1}H-{}^{1}H$  correlations in the homonuclear COSY spectrum we were able to assign unambiguously all the proton signals of the polymethine chain starting with the proton H<sup>1</sup>. In the ROESY spectrum, at the saturation of the signal of proton  $H^1$  were recorded the responses of both the proton H<sup>3</sup> and the protons of indolenine N-methyl group that indicates the correctness of the initial assignment of the signal of  $H^{1}$ . At the saturation at the frequency of the signal of  $H^2$  proton responses were observed of the protons of isopropylidene group and H<sup>4</sup> proton, as well as the responses of lower intensity of the protons  $H^1$  and  $H^3$ . The proton H<sup>6</sup> interacts with the protons of fluorene framework and a proton H<sup>4</sup>, proton H<sup>3</sup>, with the protons  $H^1$  and  $H^5$ . The values of  $J_{12}$ ,  $J_{23}$ ,  $J_{34}$ ,  $J_{45}$ , and  $J_{56}$  of compound V are 12.0, 14.1, 11.4, 13.2, and 11.7 Hz respectively, indicating that the electronic structure of merocyanines III-V in the ground state is close to A1. We also note that the values of coupling constants indicate all-trans structure of these merocyanines.

The extention of the polymethine chain increases the deviation in the spectra of dyes III–V significantly: it reaches the highest level among all known merocyanines [2]. Thus, in the spectra of compound V the  $D_{\lambda}$  value is 223 nm in DMF and 232.5 nm in CH<sub>2</sub>Cl<sub>2</sub>. As can be seen from Table 1, the replacement of CH<sub>2</sub>Cl<sub>2</sub> by more polar solvents, both strongly nucleophilic DMF and very electrophilic ethanol, reduces the  $D_{\lambda}$  and  $D_{M}$  values. This indicates a slight leveling of bond orders with increasing polarity of the medium, associated with the change of the electronic structure in the merocyanines **III–V** to the **A2** side.



Fig. 1. Absorption spectra of merocyanines III-V in dichloromethane (solid) and DMF (dashed): (1) III, (2) IV, and (3) V.

The vinylene shifts in the spectra of merocyanines **III–V** decrease with increasing chain length to the values close to those characteristic of the carotenoids in both non-polar and polar solvents. For example, the first and second shifts in this series of dyes are respectively 44 and 25 nm in  $CH_2Cl_2$  and 45 and 24 nm in DMF. These values are significantly less than those of traditional merocyanines. For example, in the structural analogs of merocyanines **III–V**, in which the fluorene core is replaced by the residue of malononitrile, the first and second vinylene shifts are 90 and 75 nm respectively [18].

Increase in deviations and decrease in the vinylene shifts at extending the polymethine chain indicate an increase in the contribution of structure A1 in the series of merocyanines III-V. This fact is consistent with the broadening of the absorption bands in all solvents with increasing n (Figs. 1, 2). In the absence of strong intermolecular interactions with environment, this may be due to increased vibronic interactions and increased probability of the photoisomerization processes due to reduced energy barrier for rotation around a formally single bonds. If this mechanism plays a dominant role, then the change in the band width with the length of the polymethine chain would be sharply different in the polymer film and liquid solvents, as photoisomerization in the polymer film is minimized. Inasmuch as the trends in the band width in a liquid solvent and polyvinylethylal polymer film are



Fig. 2. Absorption spectra of merocyanines III–V in n-hexane: (1) III, (2) IV, and (3) V.

similar, we can conclude that they are associated mainly with vibronic interactions. In the structures like A1 and A3 the vibronic interactions reach higher level, because bonds can change order at the excitation, namely, from single to double and vice versa. Therefore, in *n*-hexane and toluene, which are the least polar among the studied solvents and are stabilizing the A1 structure, the largest broadening of the bands occurs.

As a quantitative characteristic of vibronic interactions in dyes [16] the value of the quadratic change of bond order  $\delta$  upon excitation, proportional to the change in the internuclear equilibrium distances upon excitation is used successfully.

$$\delta = \sqrt{\sum_{i=1}^{m} (P^* - P)_i^2},$$

where *i* is the number of the bond, *m* is total number of bonds,  $(P^*-P)$  is the difference between the orders of the *i*th bond in the excited and ground states.

The value of  $\delta$  increases with the extention of the polymethine chain in dyes III–V (Table 2). Therefore, the broadening of the experimental absorption bands in the series of merocyanines III–V (Table 1) is due to the increase in the vibronic interactions. The strengthening of the vibronic interactions at the extention of the polymethine chain is confirmed by the increase in the intensity of the vibrational peak at the short-wave side of absorption and a decrease in the main maximum. As a cosequence, its intensity in the first

maximum of the dye V is higher than in the last maximum, in contrast to compounds IV and I (Fig. 2).

A strong change in bond orders upon excitation, leading to a change in the internuclear equilibrium distances results in the fact that the band maximum is determined by the transition to a higher vibrational sublevel. This defines a symmetrical shape of the band containing vibronic maxima at the short- and long-wavelength sides of the main peak, due to the transition to the higher and lower sublevels, respectively, in relation to the most intense peak. Note that the shape of the absorption bands of merocyanines III–V in *n*-hexane is similar to that of typical neutral polyene carotenoids [2].

Increasing the electron-acceptor properties of fluorene framework by introducing phenoxysulfonyl or 2,2,3,3,4,4,5,5-octafluoropentoxysulfonyl substituents should lead to a decrease in the bond order alternation in the polymethine chain and approaching the merocyanines IX-XIV to the polymethine state. Indeed, according to quantum-chemical calculations, the merocyanines IX-XI have smaller numerical values of alternation of the bond lengths and bond orders, and larger dipole moments than compounds of the III-V series (Table 2). We can conclude that they are somewhat more shifted towards structure A2. The calculated values of BLA and BOA (absolute value),  $\Delta P_{ch}$  and  $\delta$  of the merocyanines IX-XI are considerably less than similar values of the cyclooctatetraene, but higher than those of the corresponding symmetric anionic XXVI-XXXI and cationic XXXII-XXXIV dyes (Table 2). This indicates that in a vacuum the electronic structure of the  $S_0$  state of the former ones corresponds to the range of structures A1-A2. but is shifted markedly to the structure of A1.

This theoretical conclusion is confirmed by experimental data on  $\lambda_{max}$ ,  $M^{-1}$ , red shift of the absorption bands, decrease in deviations, growing first and second vinylene shifts, band narrowing and reduced alternation of proton coupling constants of the polymethine chain relatively the compounds **III–V**. These effects are somewhat greater in the case of derivatives **XII–XIV** than of **IX–XI**, because the 2,2,3,3,4,4,5,5-octafluoropentyloxysulfonyl substituents are stronger electron-acceptors than the phenoxysulfonyl groups.

Similar trends in the spectral effects at the elongation of the polymethine chain in merocyanines **IX–XIV** and **III–V** indicate that in both the former and



Fig. 3. HOMO of dye V (isosurface lines 0.3, in the next figures analogously).



Fig. 5. HOMO of dye XI.

the latter the contribution of structure A1 in the electronic structure of the ground state increases at the chain elongation.

In going from merocyanines III–V to merocyanines IX–XI the energy of both HOMO and LUMO levels decreases, the energy gap also is reduced, which leads to a red shift of  $\lambda_{max. theor}$ . These findings are consistent with large experimental absorption maxima of compounds IX–XI. The energy of the main electronic transition in the merocyanines III–V, IX–XI drops with increasing chain length, and the magnitude of the oscillator strength increases, as might be expected from the calculation.

The HOMO electron density of the dyes III–V, IX–XI comprises the  $\pi$ -system of the entire molecule (in dyes IX–XI the phenoxysulfonyl substituents are not involved), but mostly is concentrated on the polymethine chains, while LUMO is shifted significantly to the fluorene framework (Figs. 3–6). At the



Fig. 4. LUMO of dye V.



Fig. 6. LUMO of dye XI.

excitation, the electron density on the fluorene fragment increases, while on the heterocyclic one decreases (Figs. 7, 8). The orbitals localized on phenoxysulfonyl groups are not involved in the long-wavelength transitions.

The long-wavelength transition in both groups of merocyanines, III–V and IX–XI, are of  $\pi$ – $\pi$ \* type, and 93–97% of them occur between the HOMO and LUMO orbitals. The calculated spectra of compounds III–V, IX–XI include also the low-intensity transitions to higher excited states.

In merocyanines V besides the main transition the most intense is  $S_0 \rightarrow S_3$  transition. It corresponds to a redistribution of electron density from the polymethine chain on the fluorene and heterocyclic fragments.

In the dye IX the  $S_0 \rightarrow S_1$  transition includes 90% of the HOMO to LUMO transition and 9% of the HOMO to LUMO+1 transition, and the  $S_0 \rightarrow S_2$ 



Fig. 7. Change in the electron density at the  $S_0 \rightarrow S_1$  transition of the dye V (*dark* increase, *light* decrease; isosurface lines 0.003).



**Fig. 8.** Change in the electron density at the  $S_0 \rightarrow S_1$  transition of the dye XI.



Fig. 9. Absorption spectra of merocyanines X, XV, XIX, XXIII, XXV in dichloromethane: (1) X, (2) XV, (3) XIX), (4) XXIII, (5) XXV.

transition is a combination of 89% of the HOMO to LUMO+1, and 9% of the HOMO to LUMO transitions. Both transitions correspond to the transfer of electron density from the indolenine framework and polymethine chain on the fluorene fragment.

In the spectrum of merocyanines **X**–**XI** besides the main transition there are intense enough  $S_0 \rightarrow S_2$  transitions from HOMO to LUMO+1. They are characterized by the transfer of electron density from indolenine fragment and the polymethine chain on the fluorene framework and the sulfur and oxygen atoms of the phenoxysulfonyl substituents.

In the series of dyes XV, XVI, XVIII, XIX, XXII– XXV with the same acceptor fragments, the 2,7diphenoxysulfonyl-9*H*-fluorenylidene, and various heterocyclic residues, regular changes are observed in the spectral characteristics depending on the electrondonating property of the heterocycle (Fig. 9).

The benzo[c,d]indolylidene and 2,6-diphenylpyran residues are less electron-donating than indo-lylidene [16]. Hence, we can expect that the electronic structure of dyes **XVIII**, **XIX**, **XXII**, **XXIII** ap-proaches the polyene state closer than merocyanines **IX–XI**. Larger values of deviations, smaller vinylene shifts, broader bandwidth in the former compared with the latter support this assumption (Table 1). Note that the values of  $D_M$  are more sensitive to changes in the electrondonor properties of heterocycles than  $D_{\lambda}$ , due to differences in the shape of the bands of merocyanines **XVIII–XIX**, **XXII–XXIII** (Table 1).

The replacement of the indolylidene residue in the merocyanines IX, X by a more electron-donor benzothiazolylidene should change the electronic structure of the ground state of dyes XV, XVI, in contrast to compounds XVIII, XIX, XXII, and XXIII, to the side of the boundary structure A2, that is, bring them closer to the polymethine state. This is reflected by virtually all above spectral parameters. However, large deviations, small vinylene shifts, low intensity, and broad bands indicate the dominance of the polyene structure A1 in merocyanines XV, XVI.

The nucleus of 2,6-diphenylpyridine is much more electron-donating than the benzothiazolidene nucleus. Consequently, for merocyanines **XXIV**, **XXV** even greater approach to the ideal polymethine state is expectable. Indeed, even in the nonpolar *n*-hexane a significant increase occurs in vinylene shifts and narrowing of the bands in the spectra of these compounds compared with merocyanines **XV**, **XVI**. With increasing solvent polarity these effects are even more contrasting. Already in dichorometane the vinylene shifts increase up to 100 nm: this value is typical of symmetrical polymethine dyes (Table 1). The deviations virtually disappear (they are small negative and positive in value for  $\lambda_{max}$  and  $M^{-1}$ , respectively). The values of the proton coupling constants in CDCl<sub>3</sub> in the polymethine chain of the merocyanine **XXV** are leveled compared with those of compounds **III–V**, **XV**, **XVI**, **XVIII**, **XIX**, **XXII**, **XXIII**:  $J_{12} = J_{23} = J_{34} = 13.2$  Hz.

The growth of the solvent polarity facilitates the displacement of electron density from the donor to the acceptor fragment in the molecule of merocyanine, that is, its bipolarity increases. This leads to an increase in the order of the single bonds and a decrease in the order of the double bonds in the chromophore, that is, equalizes the bonds (making them closer to sesquialteral). As a result, the electronic structure of merocyanines in  $S_0$  state at increasing polarity of the solvent withdraws from structure A1 and approaches structure A2.

The maximal approach by merocyanines **XXIV**, **XXV** to the ideal polymethine state is also seen from the fact that their absorption bands have a universal form with a pronounced vibration maximum at the short-wavelength edge, characteristic of symmetric polymethine dyes [16] (Fig. 9). In addition, the narrowness of their spectra led to the highest values of molar extinction coefficient among the studied merocyanines. For merocyanines **XXV** in DMF  $\varepsilon \times 10^{-4} = 14.69 \text{ 1 mol}^{-1} \text{ cm}^{-1}$ , which is close to that of the corresponding symmetrical dyes.

The approach of the electronic structure of dyes (XXIV, XXV) to the ideal polymethine state is also reflected in the maximum deepening of their color among the studied merocyanines, characteristic of this state (Table 1). This effect is especially spectacular in a seriesr of dyes of the same structural type XXII-XXV. The merocyanines on the basis of pyridine XXIV, XXV absorb by 76 and 159 nm more to the red side, respectively, than their pyrilium counterparts XXII, **XXIII**, whereas the pairs of related cationic symmetric pyrido- and pyrilium-cyanines show reverse pattern [16]. Note that reacing the ideal polymethine state is difficult even in the case of symmetric dyes, since the deviation in electron-donating (electron-withdrawing) properties of end groups from the average values to one or the other side leads to the alternation of bond orders from the heterocyclic residues to the center of the chain.

Decrease in  $D_M$ , growth of  $\varepsilon$  and f, and narrowing of the bands at the elongation of the polymethine chain in merocyanines **XXIV**, **XXV** in contrast to compounds **III–V**, **XV**, **XVI**, **XVIII**, **XIX**, **XXII**, **XXIII** points to the decrease in polyene and increase in polymethine character of the electronic structure of the ground state.

Thus, the use of fluorene and its derivatives in the cyanine condensation made it possible to obtain the merocyanines with the structure maximally approaching that of the ideal neutral polyene. They are characterized by the maximum deviations, minimum vinylene shifts, the large width of the vibrational structure at the short- and long-wavelength edges of the bands and a slight positive solvatochromism. Therewith, by introducing electron-withdrawing substituents in 2,7 positions of the fluorene framework and using strong electron-donor heterocycles as the end groups it is possible to create merocyanines with the structure of at least ideal polymethines.

## EXPERIMENTAL

The absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer with 1 cm cells at a concentration of solute 10<sup>-5</sup> M. Solvents were purified by known methods [21]. CH<sub>2</sub>Cl<sub>2</sub> was stabilized by adding 1% of anhydrous ethanol. Moments of the absorption bands are determined by previously described [12, 16] method. For merocyanines XV, XVI, XVIII, XIX, XXII-XXIV the  $\varepsilon$  and f values were not determined because of insufficient solubility in n-hexane. For chromatography silica gel 60 (Fluka) and aluminum oxide-90 (Merck) were used. The purity of dyes was monitored by TLC (Silufol UV-254), eluent acetonitrile). The <sup>1</sup>H NMR spectra were recorded on a Varian VXR-300 spectrometer (299.945 MHz), internal reference TMS. Twodimensional correlation spectra were recorded on a Bruker-600 spectrometer (600.133 MHz). Melting points were measured in open capillaries and were not corrected.

The quantum-chemical calculations were carried out using the PC Gamess/Fierfly software package by the non-empirical DFT method with a B3LYP/6-31G(d,p) basis, with a preliminary geometry optimization of the ground state in the same basis. Electronic transitions were calculated by the TDDFT method.

(2Z)-2-[2-(9H-Fluoren-9-ylidene)ethylidene]-1,3,3-trimethyl-2,3-dihydro-1*H*-indole (III) 183 mg of tri-*n*-butylphosphoniumfluorenylide I and 101 mg

(2E)-(1,3,3-trimethyl-1,3-dihydro-2H-indol-2of vlidene)-acetaldehvde IIa was heated in 7 ml of oxylene for 4 h. The reaction process was monitored spectrophotometrically. At the end of reaction the solvent was removed at a reduced pressure, to the residue ethanol was added and the mixture was filtered. The precipitate was chromatographed on Al<sub>2</sub>O<sub>3</sub>, using dichloromethane as eluent. Yield 120 mg (69%), mp 166°C. <sup>1</sup>H NMR spectrum, δ, ppm: 1.774 s  $[6H, C(CH_3)_2], 3.355 \text{ s} (3H, NCH_3), 6.377 \text{ d} (1H, J =$ 12.9 Hz, H<sup>1</sup>), 6,751 d (1H, J = 7.5 Hz, ArH), 6.939 t (1H, J = 7.5 Hz, ArH), 7.193-7.409 m (6H, ArH),7.900 d (1H, J = 12.9 Hz, H<sup>2</sup>), 7.728 d (1H, J = 6.9 Hz, ArH), 7.792 d (1H, J = 6.9 Hz, ArH), 7.852 d (1H, J = 6.9 Hz, (ArH), 7.991 d (1H, J = 6.9 Hz, ArH).

(2Z)-2-[(2E)-4-(9H-Fluoren-9-ylidene)but-2-enylidene]-1,3,3-trimethyl-2,3-dihydro-1H-indole (IV). 110 mg of compound (I) and 68 mg of (2E,4E)-4-(1,3,3-trimethyl-1,3-dihydro-2H-indol-2-ylidene)but-2-enal (IIb) was heated in 3 ml of *o*-xylene for 2 h. The solvent was distilled off at a reduced pressure, and the residue was chromatographed on Al<sub>2</sub>O<sub>3</sub> using dichloromethane as eluent. The solid was recrystallized from ethanol. Yield 80 mg (71%), mp 193°C. <sup>1</sup>H NMR spectrum: 1.669 s [6H, C(CH<sub>3</sub>)<sub>2</sub>], 3.215 s (3H, NCH<sub>3</sub>), 5.637 d (1H, J = 11.7 Hz, H<sup>1</sup>), 6.6.70 d (1H, J = 7.8 Hz, ArH), 6.888 t (1H, J = 7.8 Hz, ArH), 7.150–7.410 m (9H, ArH), 7.714-7.816 m (3H, ArH), 7.370 d (1H, J =12.0 Hz, H<sup>4</sup>), 8.039-8.092 m (1H, ArH).

(2Z)-2-[(2E,4E)-4-(9H-fluoren-9-vlidene)hexa-2,4dienylidene]-1,3,3-trimethyl-2,3-dihydro-1H-indole (V). 100 mg of compound I and 69 mg of (2E, 4E, 6E)-6-(1,3,3-trimethyl-1,3-dihydro-2*H*-indol-2-ylidene) hexa-2,4-dienal (IIc) was heated in 3 ml of o-xylene for 1 h. During the cooling of the solution a precipitate formed. It was chromatographed on Al<sub>2</sub>O<sub>3</sub> using dichloromethane as eluent and recrystallized from ethanol. Yield 75 mg (69%), mp 183°C. <sup>1</sup>H NMR spectrum: 1.614 s [6H, C(CH<sub>3</sub>)<sub>2</sub>], 3.157 s (3H, NCH<sub>3</sub>), 5.439 d  $(1H, J = 12.0 \text{ Hz}, \text{H}^1)$ , 6.335 d.d  $(1H, J_1 = 14.1 \text{ Hz},$  $J_2 = 11.4$  Hz, H<sup>3</sup>), 6.639 d (1H, J = 7.8 Hz, ArH), 6.853 t (1H, J = 13.2 Hz, H<sup>5</sup>), 6.877 d (1H, J = 7.8 Hz, ArH), 7.035 d.d (1H,  $J_1 = 12.0$  Hz,  $J_2 = 14.1$  Hz,  $H^2$ ), 7.148 d (1H, J = 6.0 Hz, ArH), 7.178 t (1H, J = 7.8 Hz, ArH), 7.248–7.363 m (6H, ArH), 7.671–7.813 m (3H, ArH), 7.972-8.048 m (1H, ArH).

**Diphenyl 9-[(2E)-2-(1,3,3-trimethyl-1,3-dihydro-2H-indol-2-ylidene)ethylidene]-9H-fluorene-2,7-disulfonate (IX).** 119 mg of diphenyl 9H-fluorene-2,7disulfonate (VIa) and 50 mg of compound IIa was heated in 1 ml of acetic anhydride until they dissolved. To the solution was added 5 drops of triethylamine and the mixture was heated for 5 min. The reaction mixture was treated with water. The precipitate formed was isolated and recrystallized from chloroform. Yield 156 mg (94%), mp 217°C. <sup>1</sup>H NMR spectrum: 1.700 s [6H, C(CH<sub>3</sub>)<sub>2</sub>], 3.32 s (3H, NCH<sub>3</sub>), 6.190 d (1H, J = 13.2 Hz, H<sup>1</sup>), 7.06–7.15 m (5H, ArH), 7.175 d (1H, J = 8.4 Hz, ArH), 7.24–7.42 m (7H, ArH), 7.498 d (1H, J = 7.2 Hz, ArH), 7.718 d (1H, J = 8.4 Hz, ArH), 7.860 d (1H, J = 8.1 Hz, ArH), 8.113 d (1H, J = 14.1 Hz, H<sup>2</sup>), 8.32–8.34 m (3H, ArH), 8.452 d (1H, J = 8.1 Hz, ArH).

9-[(2E,4E)-2-(1,3,3-trimethyl-1,3-di-Diphenyl hydro-2H-indol-2-ylidene)but-2-enylidene]-9H-fluorene-2,7-disulfonate (X). 48 mg of compound (VIa) and 44 mg of  $2-\{(1E,3E)-4-[acetyl(phenyl)amino]\}$ buta-1,3-dienyl}-1,3,3-trimethyl-3H-indolium perchlorate (VIIa) was heated to dissolution in 1 ml of acetic anhydride. 5 drops of triethylamine was added and the mixture was heated for 5 min. The reaction mixture was treated with water. The resulting residue was chromatographed on silica gel, and then again on Al<sub>2</sub>O<sub>3</sub> with dry chloroform as eluent. Yield 41 mg (59%), mp 181°C. <sup>1</sup>H NMR spectrum: 1.617 s [6H,  $C(CH_3)_2$ ], 3.335 s (3H, NCH 3), 5.925 d (1H, J = 12.9 Hz, H<sup>1</sup>), 6.890–6.960 m (2H, ArH), 6.956–7.115 m (5H, ArH), 7.164–7.358 m (9H, ArH), 7.672 d.d (1H, J<sub>1</sub> = 4.3 Hz,  $J_2 = 1.5$  Hz, ArH), 7.767 d.d (1H,  $J_1 = 3.9$  Hz,  $J_2 = 1.2$  Hz, ArH), 7.880 t (1H, J = 12.9 Hz, H<sup>2</sup>), 8.106 d (1H, J = 12.6 Hz, H<sup>4</sup>), 8.204 d (1H, J = 8.4 Hz, ArH), 8.271 d (1H, J = 8.4 Hz, ArH), 8.301 s (1H, ArH). 8.426 s (1, r–H). 8.426 s (1H, ArH).

Diphenyl 9-[(2E,4E,6E)-2-(1,3,3-trimethyl-1,3-dihvdro-2H-indol-2-ylidene)hexa-2,4-dienylidene]-9Hfluorene-2,7-disulfonate (XI). 48 mg of compound VIa and 48 mg of  $2-\{(1E,3E,5E)-6-[acetyl(phenyl)$ amino]hexa-1,3,5-trienyl}-1,3,3-trimethyl-3H-indolium perchlorate (VIIb) was heated to dissolution in 1 ml of acetic anhydride. 3 drops of triethylamine was added and the mixture was heated for 5 min. The reaction mixture was treated with water. The resulting residue was chromatographed on Al<sub>2</sub>O<sub>3</sub>, using dry chloroform an eluent. Yield 70 mg (98%), mp 120°C. <sup>1</sup>H NMR spectrum: 1.576 s [6H, C(CH<sub>3</sub>)<sub>2</sub>], 3.234 s (3H, NCH<sub>3</sub>), 5.667 d (1H, J = 12.3 Hz, H<sup>1</sup>), 6.362 t (1H, J = 13.5 Hz, H<sup>3</sup>), 6.809–6.877 m (2H, ArH), 6.959–7.166 m (6H, ArH), 7.209-7.378 m (9H, ArH), 7.702-7.744 m (2H, ArH), 7.812 d (1H, J = 8.4 Hz, ArH), 8.165 d (1H, J = 8.1 Hz, ArH), 8.241 d (1H, J = 8.4 Hz, ArH), 8.255 s (1H, ArH), 8.359 s (1H, ArH).

Bis(2,2,3,3,4,4,5,5-octafluoropentyl) 9-[(2 Z)-2-(1,3,3-trimethyl-1,3-dihydro-2H-indol-2-ylidene)ethylidene]-9H-fluorene-2,7-disulfonate (XII). 75 mg of bis(2,2,3,3,4,4,5,5-octafluoropentyl) 9H-fluorene-2,7disulfonate (VIb) and 20 mg of compound IIa was heated in a minimal amount of acetic anhydride in the presence of triethylamine, monitoring the reaction course spectrophotometrically. The precipitate was washed with alcohol. Yield 90 mg (98%), mp 165°C. <sup>1</sup>H NMR spectrum: 1.815 s [6H,  $C(CH_3)_2$ ], 3.481 s (3H, NCH<sub>3</sub>), 4.558 t (4H, J 13.5 Hz,OCH<sub>2</sub>), 6,021 min  $(2H, J_1 52.2 Hz, J_2 5.4 Hz, CF_2 H), 6.450 d (1H, J =$ 13.5,  $H^1$ ), 6.926 d (1H, J = 8.1 Hz, ArH), 7.094 t (1H, J = 6.9 Hz, ArH), 7.323 t (1H, J = 7.2 Hz, ArH), 7.335 d (1H, J = 7.2 Hz, ArH), 7.854 d (1H, J = 7.8 Hz, ArH), 7.912 d (1H, J = 8.1 Hz, ArH), 8.111 d (1H, J = 8.1 Hz, ArH), 8.174 d (1H, J = 7.8 Hz, ArH), 8.191 d  $(1H, J = 14.1 \text{ Hz}, \text{H}^2)$ , 8.291 s (1H, ArH), 8.642 s (1H, ArH).

Bis(2,2,3,3,4,4,5,5-octafluoropentyl) 9-[(2E,4Z)-2-(1,3,3-trimethyl-1,3-dihydro-2H-indol-2-ylidene)but-2-enylidene]-9H-fluorene-2,7-disulfonate (XIII). 75 mg of compound VIb and 46 mg of compound VIIa was heated in a minimum amount of pyridine in the presence of piperidine, monitoring the reaction course spectrophotometrically. Aqueous methanol was added and the precipitate formed was separated and chromatographed on silica gel, eluent dichloromethane with the addition of triethylamine. The solvent was removed at a reduced pressure. The precipitate was recrystallized from methanol. Yield 92 mg (96%), mp 203–204°C. <sup>1</sup>H NMR spectrum: 1.715 s [6H, C(CH<sub>3</sub>)<sub>2</sub>], 3.347 s (3H, NCH<sub>3</sub>), 4.538 t.d (4H,  $J_1 = 13.5$  Hz,  $J_2 =$  $3.9 \text{ Hz}, \text{ OCH}_2$ ),  $5.855 \text{ d} (1\text{H}, J = 12.6 \text{ Hz}, \text{H}^1)$ , 5,993 t.t $(J_1 = 52.2 \text{ Hz}, J_2 = 5.4 \text{ Hz}, \text{ CF}_2\text{H}), 6.803 \text{ d} (1\text{H}, J = 5.4 \text{ Hz})$ 7.8 Hz, ArH), 7.002 t (1H, J = 9.6 Hz, ArH), 7.082 t  $(1H, J = 12.6 \text{ Hz}, \text{H}^3)$ , 7.272 d (1H, J = 7.5 Hz, ArH), 7.598 t (1H, J = 12.6 Hz, H<sup>3</sup>), 7.689 t (1H, J = 12.6 Hz,  $H^{2}$ ), 7.841 d (1H, J = 7.8 Hz, ArH), 7.909 d (1H, J = 8.1 Hz, ArH), 8.059 d (1H, J = 8.4 Hz, ArH), 8.114 ppm (1H, J = 8.1 Hz, ArH), 8.394 s (1H, ArH), 8.625 s (1H, ArH)

Bis(2,2,3,3,4,4,5,5-octafluoropentyl) 9-[(2E,4E,6Z)-2-(1,3,3-trimethyl-1,3-dihydro-2H-indol-2-ylidene)hexa-2,4-dienylidene]-9H-fluorene-2,7-disulfonate (XIV). 94 mg of compound VIb and 57 mg of compound VIIb was heated in a minimal amount of pyridine in the presence of piperidine, monitoring the reaction course spectrophotometrically. The solvent was removed at a reduced pressure. The residue was chromatographed on Al<sub>2</sub>O<sub>3</sub>, using as eluent chloroform, and recrystallized from methanol. Yield 70 mg (71%). mp <sup>1</sup>H NMR spectrum: 1.578 s [6H, C(CH<sub>3</sub>)<sub>2</sub>], 3.166 s (3H, NCH<sub>3</sub>), 4,482 t.d (4H,  $J_1 = 13.5$  Hz,  $J_2 =$ 9.6 Hz), 5.507 d (1H, J = 12.6 Hz, H<sup>1</sup>), 5.937 t.t (2H,  $J_1 = 52.2$  Hz,  $J_2 = 5.4$  Hz, CF<sub>2</sub>H), 6.384 d.d (1H,  $J_1 =$ 13.5 Hz.  $J_2 = 10.5$  Hz, ArH), 6.663 d (1H, J = 8.4 Hz, ArH), 6.875 t (1H, J = 7.2 Hz, ArH), 6.997–7.158 m (5H, ArH), 7.527 d (1H, J = 11.4 Hz, ArH), 7.804 d (1H, J = 8.1 Hz, ArH), 7.867 d (1H, J = 8.1 Hz, ArH), 7.971 d (1H, J = 7.8 Hz, ArH), 8.025 d (1H, J =8.1 Hz, ArH), 8.249 s (1H, ArH), 8.522 s (1H, ArH).

Diphenyl 9-[(2E,4E,6Z)-6-(3-methyl-1,3-benzothiazol-2(3H)-ylidene)hexa-2,4-dienylidene]-9H-fluorene-2,7-disulfonate (XV). 48 mg of compound VIa and 105 mg of 2-{(1E,3E)-4-[acetyl(phenyl)amino]buta-1,3-dienyl}-3-ethyl-1,3-benzothiazol-3-ium tetrafluoroborate (VIIIa) was heated in acetic anhydride in the presence of triethylamine. The reaction mixture was quenched with water. The resulting precipitate was filtered off and chromatographed on silica gel with the toluene-chloroform (95:5 to 92:8) as eluent. The merocyanine was crystallized from acetone- $d_6$ . Yield 55 mg (79%), mp 230°C. <sup>1</sup>H NMR spectrum: 1.314 t  $(3H, J = 7.2 \text{ Hz}, \text{NCH}_2\text{CH}_3), 4.124 \text{ g} (2H, J = 7.2 \text{ Hz},$ NCH<sub>2</sub>CH<sub>3</sub>), 6.144 d (1H, J = 11.4 Hz, H<sup>1</sup>), 6.990 t (1H, J 12.6 Hz, H<sup>3</sup>), 6.979–7.165 m (7H, ArH), 7.204– 7.487 m (12H, ArH), 7.552 d (1H, J = 7.8 Hz, ArH), 7.660 d.d (1H,  $J_1 = 8.1$  Hz,  $J_2 = 1.5$  Hz, ArH), 7.744 d.d (1H,  $J_1 = 8.1$  Hz,  $J_2 = 1.5$  Hz, ArH), 7.869 d (1H, J = 8.1 Hz, ArH), 7.938 d (1H, J = 12.9 Hz, H<sup>4</sup>), 8.116 s (1H, ArH), 8.183 d (1H, J = 7.8 Hz, ArH), 8.231 d (1H, J = 7.8 Hz, ArH), 8.254 d (1H, J = 7.8 Hz, ArH),8.329 s (1H, ArH), 8.425 s (1H, ArH).

Diphenyl 9-[(2E,4Z)-2-(1-benzylbenzo[cd]indol-2 (1H)-ylidene)ethylidene]-9H-fluorene-2,7-disulfonate (XVI). 48 mg of compound VIa and VIa and 110 mg of  $2-\{(1E,3E,5E)-6-[acetyl(phenyl)amino]hexa-1,3,5$ trienyl}-3-ethyl-1,3-benzothiazol-4-ium methylbenzenesulfonate (VIIIb) was heated in 2.5 ml of pyridine. The reaction mixture was diluted with water. The resulting precipitate was filtered off and chromatographed on silica gel with toluene-chloroform (95:5) as eluent. The resulting merocyanine was recrystallized from ethanol. Yield 36 mg (50%), mp 206°C. <sup>1</sup>H NMR spectrum: 1.354 t (3H, J = 7.2 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 3,916 q (2H, J = 7.2 Hz, NCH<sub>2</sub>CH<sub>3</sub>), 5.629 d (1H, J =11.4 Hz, H<sup>1</sup>), 6.363 d.d (1H,  $J_1 = 13.5$  Hz,  $J_2 = 11.4$  Hz, chain protons), 6.727 t (1H, J = 13.5 Hz, H<sup>3</sup>), 6.885 d (1H, J = 8.1 Hz, ArH), 6.944-7.102 m (8H, ArH),

7.187–7.322 m (6H, ArH), 7.367 d (1H, J = 7.2 Hz, ArH), 7.442 d (1H, J = 11.4 Hz, H<sup>6</sup>), 7.721 d.d (1H,  $J_1 = 8.1$  Hz,  $J_2 = 1.5$  Hz, ArH), 7.754 d.d (1H,  $J_1 =$ 8.4 Hz,  $J_2 = 1.5$  Hz, ArH), 7.908 d (1H, J = 8.1 Hz, ArH), 7.955 d (1H, J = 7.8 Hz, ArH), 8.207 s (1H, ArH), 8.452 s (1H, ArH).

Diphenyl 9-[(2Z)-2-(1-benzylbenzo[cd]indol-2(1H)ylidene)ethylidene]-9H-fluoren-2,7-disulfonate (XVIII) 166 mg of compound VIa and 140 mg of 1-benzyl-2-[(E)-2-(dimethylamino)vinyl]benzo[cd]indolium tetrafluoroborate XVIIa was heated in acetic anhydride, and a few drops of DBU was added. To the reaction mixture was added ethanol and the precipitate formed was filtered off. The merocyanine was chromatorgaphed on silica gel with toluene-chloroform (3:1) as eluent. Yield 30 mg (40%), mp 242°C. <sup>1</sup>H NMR spectrum: 5.201 (NCH<sub>2</sub>), 6.733 d (1H, J = 13.5 Hz,  $H^{1}$ ), 6.927 d (1H, J = 6.6 Hz, ArH), 7.032 t (4H, J = 7.8 Hz, ArH), 7.154–7.231 m (2H, ArH), 7.271–7.360 m (6H, ArH), 7.383-7.546 m (5H, ArH), 7.701-7.830 m (3H, ArH), 7.951 d.d (3H,  $J_1 = 7.8$  Hz,  $J_2 = 10.8$  Hz, ArH), 8.126 d (1H, J = 7.2 Hz, ArH), 8.235 s (1H, ArH ), 8.235 d (1H, J = 12.9 Hz, H<sup>2</sup>), 8.444 s (1H, ArH).

Diphenvl 9-[(2E,4Z)-4-(1-benzylbenzo[cd]indol-2(1H)-ylidene)but-2-enylidene]-9H-fluorene-2,7-disulfonate (XIX). 108 mg of VIa and 96 mg of 1benzyl-2-[(1E,3E)-4-(N-phenylacetamido)buta-1,3dienyl]benzo[cd]indolium tetrafluoroborate XVIIb was heated in acetic anhydride with a few drops of triethylamine. The reaction mixture was diluted with ethanol. The precipitate formed was filtered off and chromatographed on silica gel, washing out the merocyanine with toluene. Yield 30 mg (37%), mp 260°C. <sup>1</sup>H NMR spectrum: 5.214 s (2H, NCH<sub>2</sub>), 6.221 d (1H, J 13.5 Hz, H<sup>1</sup>), 6.666 d (1H, J = 6.5 Hz, ArH), 7.038 t (5H, J = 7.0 Hz, ArH), 7.138 t (1H, J = 7.0 Hz, ArH), 7.200 t (2H, J = 7.0 Hz, ArH), 7.275–7.433 m (11H, ArH), 7.598 d (1H, J = 12.5 Hz, H<sup>3</sup>), 7.713–7.845 m (4H, ArH), 7.879 t (1H, J = 12.5 Hz, H<sup>2</sup>), 7.923 d (1H, J = 7.5 Hz, ArH), 7.962 d (1H, J = 7.5 Hz, ArH), 8.168 d (1H, J = 7.0 Hz, ArH), 8.316 s (1H, ArH), 8.366 s (1H, ArH).

**Diphenyl 9-[2-(2,6-diphenyl-4***H***-pyran-4-yliden)ethylidene]-9***H***-fluorene-2,7-disulfonate (XXII). 84 mg of compound VIa and 79 mg of (2,6-diphenyl-4***H***pyran-4-ylidene)acetaldehyde XX was heated in a minimal amount of acetic anhydride in the presence of a few drops of triethylamine. The merocyanine separated at cooling the reaction mixture. It was chromatographed on silica gel, washing out with di-** chloromethane containing triethylamine. Yield 92 mg (72%), mp 273°C. <sup>1</sup>H NMR spectrum: 6.585 d (1H, J = 13.2 Hz, H<sup>1</sup>), 6.772 d (1H, J = 1.5 Hz,  $\beta$ -H), 7.060 d (2H, J = 7.8 Hz, ArH), 7.052 t (1H, J = 7.8 Hz, ArH), 7.166 d (1H, J = 1.5 Hz,  $\beta$ -H), 7.202–7.352 m (6H, ArH), 7.485–7.604 m (5H, ArH), 7.710 d.d (1H,  $J_1 = 8.1$ Hz,  $J_2 = 1.5$  Hz, ArH), 7.773 d.d (1H,  $J_1 = 8.1$  Hz,  $J_2 = 1.5$  Hz, ArH), 7.872 d (1H, J = 13.5 Hz, H<sup>2</sup>), 7.880 d.d (2H,  $J_1 = 8.1$  Hz,  $J_2 = 1.5$  Hz, ArH), 7.952 d.d (2H,  $J_1 = 8.1$  Hz,  $J_2 = 1.5$  Hz, ArH), 7.952 d.d (2H,  $J_1 = 8.1$  Hz,  $J_2 = 1.5$  Hz, ArH), 7.952 d.d (2H,  $J_1 = 8.1$  Hz,  $J_2 = 1.5$  Hz, ArH), 7.988 d (1H, J = 7.8 Hz, ArH), 8.345 s (1H, ArH), 8.532 s (1H, ArH).

9-[(2E)-4-(2,6-diphenyl-4H-pyran-4-Diphenvl vlidene)but-2-envlidene]-9H-fluorene-2,7-disulfonate (XXIII). 96 mg of compound VIa and 110 mg of 4-[(1E,3E)-4-ethoxybuta-1,3-dienyl]-2,6-diphenylpyrilium tetrafluoroborate XXI was heated in a minimal amount of pyridine, containing piperidine as a base. The reaction mixture was treated with water. The resulting precipitate was chromatographed on silica gel and then on Al<sub>2</sub>O<sub>3</sub> with dry chloroform as eluent. Yield 80 mg (53%), mp 237°C. <sup>1</sup>H NMR spectrum: 6.038 d  $(1H, J = 12.0 \text{ Hz}, \text{H}^1)$ , 6.566 d  $(1H, J = 1.5 \text{ Hz}, \beta\text{-H})$ , 6.986–7.103 m (6H, ArH), 7.080 t (1H, J = 12.0 Hz, H<sup>3</sup>), 7.241–7.349 m (8H, ArH), 7.446–7.595 m (10H, ArH), 7.743 d.d (2H,  $J_1 = 8.4$  Hz,  $J_2 = 1.5$  Hz, ArH), 7.713 d (2H, J = 7.5 Hz, ArH), 7.798 d.d (1H,  $J_1 =$ 8.1 Hz.  $J_2 = 1.5$  Hz, ArH), 7.887 d.d (2H,  $J_1 = 7.8$  Hz,  $J_2 = 1.5$  Hz, ArH), 7.918 d (2H, J = 8.4 Hz, ArH), 7.966 d (2H, J = 8.4 Hz, ArH), 8.249 s (1H, ArH), 8.467 s (1H, ArH).

Diphenvl 9-[2-(1-methyl-2,6-diphenvlpyridine-4 (1H)-ylidene)ethylidene]-9H-fluorene-2,7-disulfonate (XXIV). 60 mg of merocyanine XXII was dissolved in DMSO containing 1.5 ml of 25% solution of methylamine and heated on a silicone bath at a temperature of 95°C for 10 min. The reaction mixture was treated with a weak solution of sodium chloride. The resulting precipitate was filtered off and chromatographed on Al<sub>2</sub>O<sub>3</sub>, washing out the merocyanine with dichloromethane containing triethylamine. The compound obtained was crystallized from acetoneitrile. Yield 50 mg (82%), mp 251°C. <sup>1</sup>H NMR spectrum: 3.157 s (3H, NCH<sub>3</sub>), 6.357 d (1H, J = 14.1 Hz, H<sup>1</sup>), 6.542 d (1H, J = 2.7 Hz,  $\beta$ -H), 6.942–7.031 m (5H, ArH), 7.133– 7.290 (m, 5H, ArH), 7.465-7.665 m (13H, ArH), 7.923 d (1H, J = 14.1 Hz, H<sup>2</sup>), 7.969 d (1H, J = 8.4 Hz, ArH), 8.032 d (1H, J = 8.1 Hz, ArH), 8.237 s (1H, ArH), 8.534 s (1H, ArH).

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Diphenyl 9-[(2E)-4-(1-methyl-2,6-diphenylpyridine-4(1H)-vlidene)but-2-envlidene]-9H-fluorene-2,7-disulfonate (XXV). 50 mg of merocyanine XXIII was dissolved in DMSO containing 1.5 ml of 25% solution of methylamine, and heated on a silicone bath at a temperature of 95°C for 10 min. The reaction mixture was treated with a weak solution of sodium chloride. The resulting precipitate was filtered off and chromatographed on Al<sub>2</sub>O<sub>3</sub> washing out merocyanine with the dichloromethane containing triethylamine. The compound obtained was crystallized from acetonitrile. Yield 32 mg (63%), mp 228°C. <sup>1</sup>H NMR spectrum: 3.075 s (3H, NCH<sub>3</sub>), 5.810 d (1H, J = 13.2 Hz, H<sup>1</sup>), 6.282 s (1H, β-H), 6.741 s (1H, β-H), 6.870 t (1H, J =13.2 Hz, H<sup>3</sup>), 6.940–7.074 m (4H, ArH), 7.192–7.314 m (6H, ArH), 7.378 t (1H, J = 13.2 Hz, H<sup>2</sup>), 7.420– 7.568 m (12H, ArH), 7.564 d (1H, J = 13.2 Hz, H<sup>4</sup>), 7.617 dd (1H,  $J_1 = 8.4$  Hz,  $J_2 = 1.5$  Hz, ArH), 7.673 d.d  $(1H, J_1 = 8.4 \text{ Hz}, J_2 = 1.5 \text{ Hz}, \text{ArH}), 7.954 \text{ d} (1H, J =$ 8.1 Hz, ArH), 8.001 d (1H, J = 8.1 Hz, ArH), 8.206 s (1H, ArH), 8.492 s (1H, ArH).

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