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SYNTHESIS AND SPECTRAL PROPERTIES OF MEROCYANINE DYES DERIVED FROM TETRANITROFLUORENE AND HETEROCYCLES OF VARIOUS ELECTRON-DONATING ABILITY

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Syntheses are reported for di-, tetra-, and hexamethine merocyanines derived from 2,4,5,7-tetranitrofluorene and heterocyclic fragments with various electron-donating ability. The absorption spectra of these compounds were studied in solvents of different polarities. A quantum-chemical analysis was carried out for the electronic structure and types of electronic transitions of these merocyanines by using the DFT and TDDFT methods in the B3LYP/6-31G(d,p) basis set. The electronic structure of these merocyanines varied from neutral polyene to polymethine and bipolar polyene with increasing electron-donating ability of the heterocyclic fragment and with solvent polarity. These differences were strongly reflected in the position, intensity, and shape of the absorption bands, vinylene shifts, and deviations, as well as the sign of solvatochromic effect.

Keywords: merocyanines, 2,4,5,7-tetranitrofluorene, electronic structure, electronic spectra, quantum-chemical calculations, solvatochromism.

There has recently been an increasing interest in donor-acceptor systems containing either a strong electron-donating or a strong electron-withdrawing fragment. These compounds hold considerable promise in light of their characteristic intramolecular charge transfer. This property may be utilized for obtaining organic semiconductors and sensitizers for photothermoplastic holographic [1-6], photovoltaic [7], and electroluminescent media [8]. Extensive work in this field has been devoted to donor-acceptor systems derived from tetranitrofluorene [9-11]. However, tetranitrofluorene is more often used as a component of mixed complexes with polymers or other electron-donor compounds. Thus, we undertook the preparation of intramolecular donor-acceptor systems derived from this fluorene. Individual representatives of such compounds have already been synthesized [2, 4], but they have not yet been subjected to a systematic study.

Merocyanine dyes hold an important position among donor-acceptor systems with intramolecular charge transfer. These dyes have a broad range of useful properties, such as pronounced solvatochromism,

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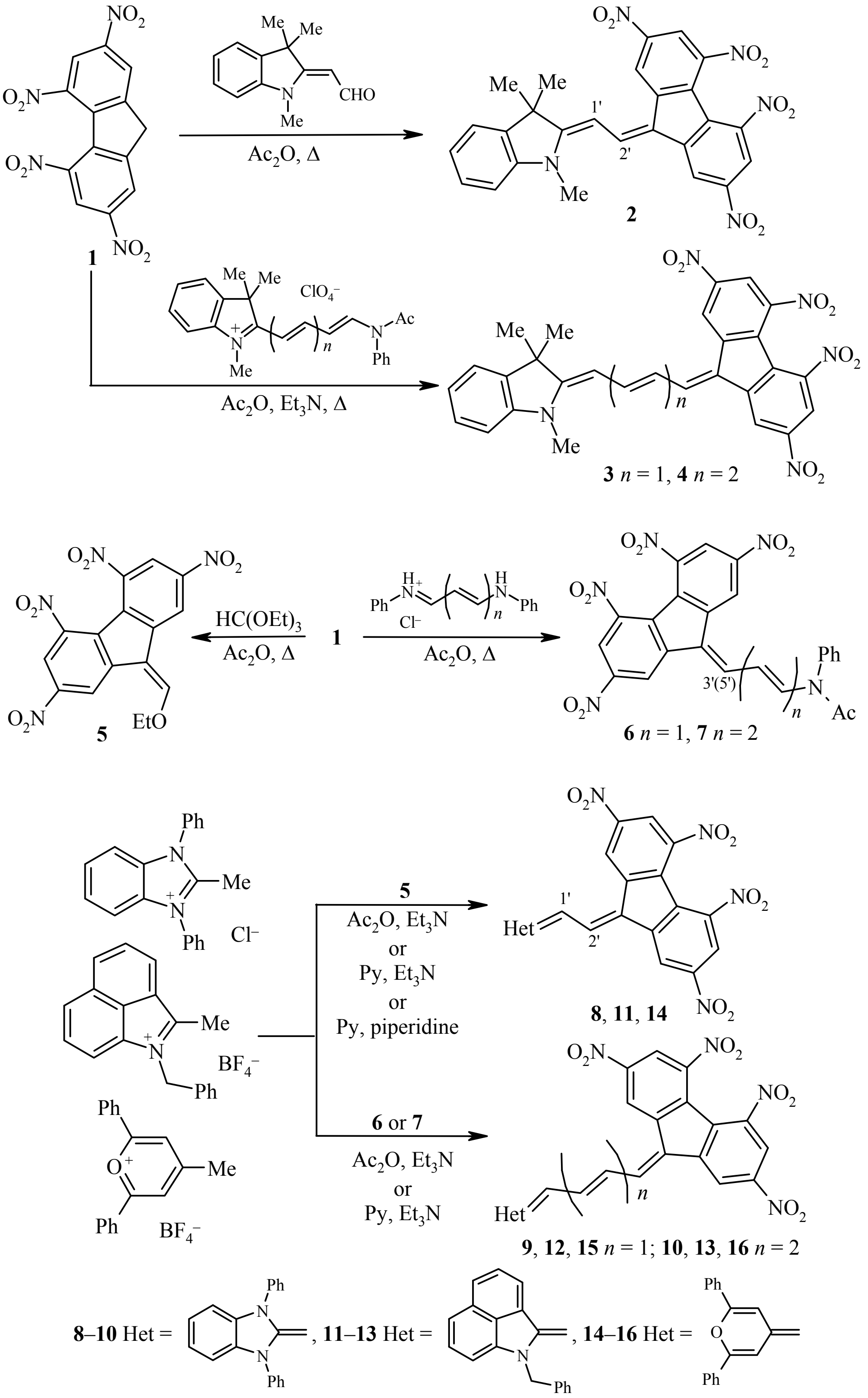
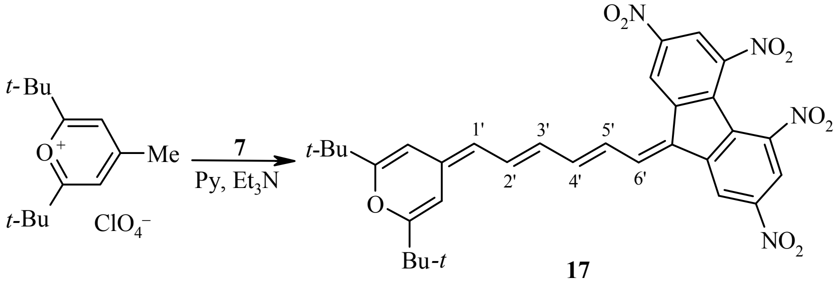
capacity to undergo a significant change in dipole moment upon electronic excitation, and capacity to sensitize various physicochemical processes. They are finding increasing application in optical electronics, nonlinear optics, devices for recording and information processing, medicine, and biology [12, 13].

In the present work, we synthesized and studied a series of merocyanines derived from 2,4,5,7-tetranitrofluorene containing heterocyclic fragments of various electron-donating ability.



Cyanine condensation at the methylene group proceeded much more readily when the fluorene system had strong electron-withdrawing nitro substituents, in contrast to the case of unsubstituted fluorene [14]. Merocyanines **2-4** were synthesized by the reaction of 2,4,5,7-tetranitrofluorene (**1**) [15] with an aldehyde and hemicyanines derived from 1,3,3-trimethyl-3*H*-indole under the standard conditions for cyanine condensation.

We should note that the merocyanine **16** was sparingly soluble in solvents commonly used for ^{1}H NMR spectroscopy, which complicated the acquisition of a high-quality spectrum. Thus, the di-*tert*-butyl analog **17**, which was more soluble than merocyanine **16**, was synthesized by an analogous procedure in order to confirm the structure of compound **16**.



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The spectral characteristics, namely, absorption maxima (λ_{max}), extinction coefficients (ε), and deviations (D) of merocyanines **2-4** and **8-17** are given in Table 1.

In contrast to common merocyanines [17], derivatives **2-4** and **8-17** have multiple bands in their absorption spectra similar to symmetrical anionic polymethines with terminal tetranitrofluorene groups [16]. The shape of the absorption bands exhibited by merocyanines with heterocyclic fragments possessing moderate (compounds **2-4**) and strong electron-donating properties (compounds **8-10**) differed markedly from the shape exhibited by merocyanines **11-17**, which contain weakly electron-donating heterocyclic fragments (Fig. 1, Table 1).

The absorption spectra showed narrowing and increased intensity of the short-wavelength band and the opposite effect for the long-wavelength band for the series of merocyanines **2-4** and **8-17** with the electron-donating ability of the heterocyclic fragment increasing from pyran and benzo[*cd*]indole to indole and benzimidazole (Fig. 1).

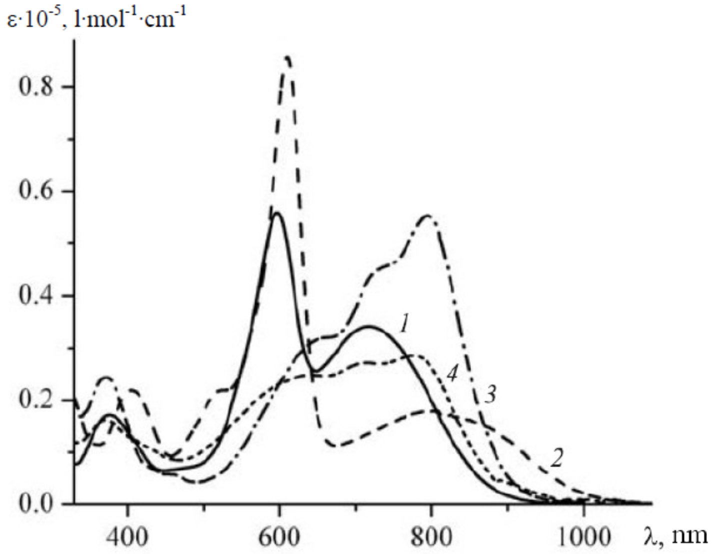

Fig. 1. Electronic absorption spectra of merocyanines **3** (*1*), **9** (*2*), **12** (*3*), and **15** (*4*) in CH_2Cl_2.

TABLE 1. Spectral Properties of Merocyanines **2-4** and **8-17**

Com-pound	Solvent							
	Toluene		CH$_2$Cl$_2$			DMF		
	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$, $l \cdot mol^{-1} \cdot cm^{-1}$	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$, $l \cdot mol^{-1} \cdot cm^{-1}$	*D*, nm	λ_{max}, nm	$\varepsilon \cdot 10^{-4}$, $l \cdot mol^{-1} \cdot cm^{-1}$	*D*, nm
2	640	1.99	655	1.71	30.0	673	1.56	19.5
	612	1.99	515*	5.49		524*	4.85	
	502*	5.23	381	2.24		390	2.25	
	381	2.06						
3	696	4.31	718	3.42	32.0	731	2.76	9.0
	566*	4.43	597*	5.59		613*	6.50	
	369	1.86	376	1.72		392	1.77	
4	773	5.90	805	6.33	44.5	810	5.20	6.5
	627*	3.87	675*	4.99		706*	6.13	
	372	1.57	377	1.66		397	1.71	
			298	2.36		299	2.39	
8	724	1.31	747	1.16	11.0	747	0.85	11.5
	673	1.24	522*	4.82		517*	3.21	
	521*	6.05	455	2.75		450	3.06	
	394	2.13	401	2.66		413	2.96	
	302	1.89	283	3.32		294	2.47	
9	790	2.31	809	1.79	5.5	826	1.09	9.0
	729	2.53	610*	8.57		602*	4.82	
	603*	6.42	405	2.19		521	3.31	
	391	1.44	289	3.07		417	2.41	
						298	2.77	
10	873	5.83	856	2.65	13.5	884	1.16	29.0
	828	6.17	692*	9.12		668*	4.41	
	690*	6.43	408	2.41		417	2.37	
	391	1.82	294	2.77		326	2.53	
11	696	3.87	708	3.70	66.5	720	4.54	—
	642	2.62	588	2.66		601	3.21	
	575*	2.05	365	2.02		369	2.83	
	533	1.26	292	2.80		292	4.20	
	360	1.77						
12	772	5.21	795	5.53	89.0	800	4.98	—
	712	4.67	732	4.52	85.0	739	4.61	
	621*	2.53	656	3.19		670	3.28	
	369	1.95	372	2.44		377	2.11	
			294	3.13		296	2.75	
13	773	—*[2]	865	—*[2]	142.0	802	4.15	—
	655*		809			696*	3.33	
	382		696*			383	2.00	
			376			289	3.33	
			284					
14	684	3.91	687	3.97	47.0	689	3.84	—
	637	3.38	566*	3.67		577*	3.58	
	559*	3.19	363	3.14		366	3.04	
	529	2.72						
	381	2.84						
15	761	3.89	777	—*[2]	69.0	778	4.71	—
	699	4.04	712			720	4.41	
	631*	3.07	637*			658*	3.91	
	362	1.99	370			371	2.33	
16	748	3.66	868	3.19	108.5	871	2.95	—
	697*	3.36	796	4.81		796	3.99	
	352	2.50	693*	4.25		690*	3.86	
			364	2.31		373	2.19	
17	779	4.92	827	6.14		824	5.30	—
	717*	6.03	765*	5.69		748*	5.28	
	369	1.75	374	1.85		376	1.69	

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*Polymethine bands.

*[2] Not determined due to low solubility in the given solvents.

The results of our quantum-chemical calculations indicated that the calculated absorption spectra of merocyanines **2-4** and **8-17**, although possessing multiple peaks, were caused by π-π^* electronic transitions (Table 2). The large number of calculated absorption bands, as in the case of symmetrical polymethine dyes derived from tetranitrofluorene [16], resulted from additional energy levels localized on the nitro groups. The major bands of the theoretical absorption spectra are different in nature.

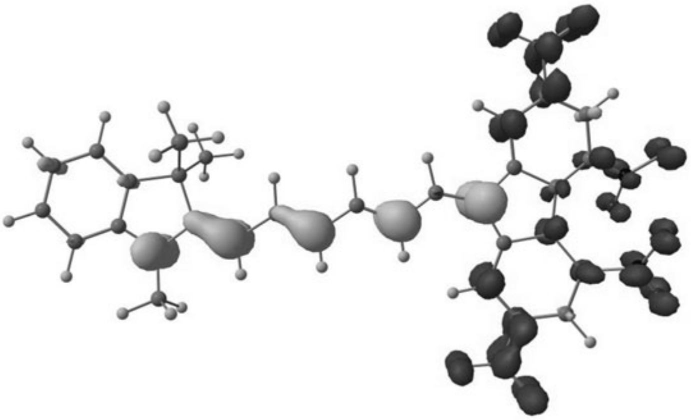

Fig. 2. Change in electron density in merocyanine **4** for the $S_0 \rightarrow S_1$ transition (■ – increase, ▨ – decrease in electron density).

The long-wavelength band in the calculated spectrum of merocyanine **4** was the result of an electron density transfer along the long axis of the molecule from the electron-donating heterocyclic fragment to the electron-withdrawing fluorene moiety (Fig. 2). This band may be considered as a charge transfer band.

The short-wavelength band was accompanied by an electron density transfer between adjacent atoms of the polymethine chain and a partial increase in electron density on the fluorene nitro groups (Fig. 3). This corresponded to the polymethine nature of the absorption band.

The shortest wavelength band due to interaction of fluorene system and nitro group orbitals was found in the calculated spectra of all these merocyanines. This band was caused by one of the higher electronic transitions, such as $S_0 \rightarrow S_7$ in the case of merocyanine **4**, and this calculated band virtually matched the experimental short-wavelength absorption band at 370-400 nm.

The position, intensity, and shape of the shortest wavelength band remained virtually unchanged with increasing the length of the polymethine chain or upon changing from one heterocyclic fragment to another. The solvatochromic shifts were small and did not exceed 5 nm. The same band was found in the spectra of symmetrical anionic dyes derived from tetranitrofluorene. All these findings suggest that this band is a characteristic absorption feature of the tetranitrofluorene system.

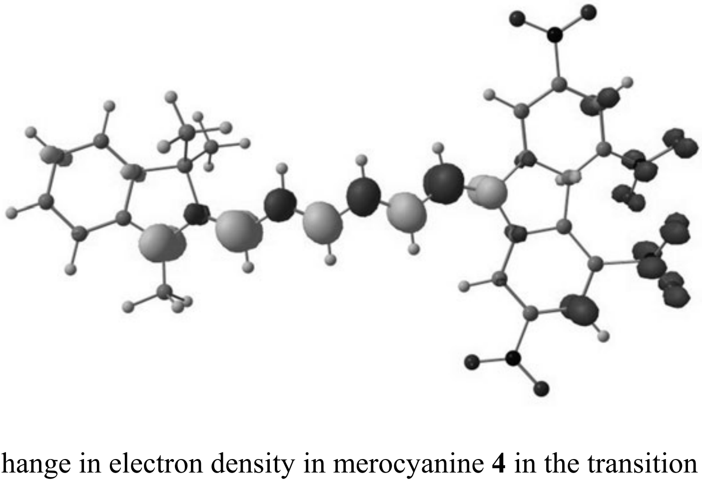

Fig. 3. Change in electron density in merocyanine **4** in the transition $S_0 \rightarrow S_2$.

The conclusion concerning the nature of the transitions is also in accord with the much larger increase in calculated dipole moments of merocyanines upon transition to the S_1 state, compared to a transition to the S_2 state, and suggests that the electronic state of merocyanine in the ground and excited states was considerably more different, compared to the polymethine transition.

TABLE 2. Results of Quantum-chemical Calculations of the Absorption Maxima ($\lambda_{max.theor}$), Oscillator Strength (f_{theor}), and Dipole Moments in the Ground (μ), First (μ^*) and Higher Excited States (μ^{**}) of Merocyanines **2-4** and **8-16**

Compound	$\lambda_{max.theor}$, nm	f_{theor}	μ, D	μ^*, D	μ^{**}[b], D	Compound	$\lambda_{max.theor}$, nm	f_{teop}	μ, D	μ^*, D	μ^{**}[b], D
2	635	0.13	15.18	33.54	33.91	**11**	672	0.19	14.63	35.09	20.07
	455[a]	0.28[a]					517[a]	0.73[a]			
	401	0.70					446	0.10			
	367	0.25					378	0.15			
3	676	0.20	18.27	42.00	36.47	**12**	707	0.30	17.18	43.19	23.81
	489[a]	0.85[a]					551[a]	1.19[a]			
	434	0.63					383	0.13			
	373	0.25					360	0.12			
4	722	0.28	20.97	50.46	39.55	**13**	755	0.41	19.42	51.75	30.57
	529[a]	1.46[a]					590[a]	1.62[a]			
	471	0.15					488	0.14			
	460	0.41					387	0.12			
	378	0.22					375	0.17			
8	701	0.12	17.89	32.68	17.01[c]	**14**	642	0.21	17.67	34.32	19.74
	486	0.12					482[a]	0.97[a]			
	415[a]	0.90[a]					429	0.27			
	376	0.29					375	0.10			
							370	0.16			
							331	0.12			
9	742	0.17	22.22	42.51	28.51[c]	**15**	695	0.29	20.38	43.12	23.19
	514	0.55					525[a]	1.53[a]			
	457[a]	1.05[a]					460	0.13			
	377	0.27					454	0.14			
							382	0.15			
							370	0.16			
							355	0.10			
10	788	0.25	25.96	51.97	40.41	**16**	743	0.40	22.77	51.61	28.71
	552[a]	1.32[a]					567[a]	2.02[a]			
	491	0.72					483	0.18			
	380	0.25					385	0.14			
							372	0.14			
							357	0.11			

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[a] Polymethine bands.

[b] Dipole moments in the second excited state (S_2).

[c] Dipole moments in the fourth excited state (S_4).

According to the Franck-Condon principle, the intensity of light absorption in the charge transfer transition should be lower than in the polymethine transition. This conclusion is also supported by the theoretical oscillator strengths f_{theor} (Table 2) obtained in quantum-chemical calculations. Indeed, the experimental long-wavelength absorption bands are less intense than the analogous short-wavelength bands (Table 1).

The increase in the calculated dipole moments upon excitation indicates positive solvatochromism for the $S_0 \rightarrow S_2$ transition in all the merocyanines studied (Table 2). Indeed, any increase in the solvent polarity in the merocyanine series **2-4** and **11-17** containing medium and weakly electron-donating fragments, and in going from toluene to dichloromethane for merocyanines **8-10** caused bathochromic shifts of the short-wavelength absorption bands. A positive solvatochromism sign indicated that for these dyes a neutral polyene ground state structure predominated among the three possible limiting structures (neutral polyene, ideal polymethine, and dipolar polyene).

The shift of electron density from the heterocycle to the polymethine chain increased with higher electron-donating ability of the heterocycle in the series from pyran and benzo[*cd*]indole to indole and benzimidazole, which led to enhanced alternation of the positive and negative charges on the chain atoms and leveling of the bond orders in the chain. In other words, the electronic structure of the merocyanines approached an ideal polymethine structure [13]. This conclusion was supported not only by the above-mentioned intensity increase and narrowing of the short-wavelength bands, but also by the increase in the vinylene shifts of these bands with higher electron-donating ability of the heterocyclic fragments. The vinylene shifts in the spectrum of merocyanine **9** reached 88 nm, which was comparable to the values of these shifts for common merocyanines, such as malononitrile derivatives (90 nm) and symmetrical dyes (~100 nm). Still further evidence for the increasing contribution of polymethine structure in going from pyran and benzo[*cd*]indole to indole and benzimidazole was found in the deviation change calculated for the short-wavelength bands. These values dropped with increasing electron-donating ability of the heterocyclic fragment from 108.5 nm in the spectrum of merocyanine **16** to 13.5 nm in the spectrum of derivative **10**.

The vinylene shifts, deviations, band intensity, band shape, and especially the width of bands determined the trends for polyene-polymethine electronic relaxation variations in donor-acceptor systems, since these factors reflected the extent of bond order alternation in the chromophore. An increase in bond order alternation led to decreasing vinylene shifts and band intensity, but greater deviation and wider bands [18].

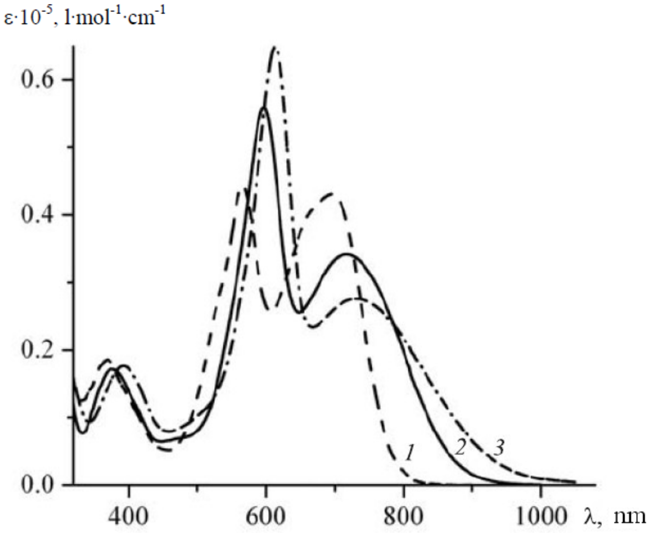

Fig. 4. Electronic absorption spectra of merocyanine **3** in toluene (*1*), CH_2Cl_2 (*2*), and DMF (*3*).

Increased solvent polarity had an effect on the absorption spectra of merocyanines **2-4** that was similar to increased electron-donating ability of the heterocycles, as illustrated by the short- and long-wavelength band intensity redistribution in the case of dye **3** (Fig. 4). This effect was related to the stabilization of charge separation in the chromophore by polar solvents, and was especially pronounced for merocyanines **8-10**, which had the strongest electron-donating heterocycle (1,3-diphenylbenzimidazole). The slight increase in polarity upon replacing toluene with dichloromethane was accompanied by a bathochromic shift of the absorption band (positive solvatochromism), while the further increase in polarity to DMF led to a hypsochromic shift (negative solvatochromism). Hence, merocyanines **8-10** have reversible solvatochromism. Such behavior suggests that dyes **8-10** are closest to an ideal polymethine structure in a specific solvent, in this case, dichloromethane. This is supported by the maximum extinction coefficient values (Table 1). Higher polarity of the medium favored a dipolar polyene structure, while a decrease in polarity led to a neutral polyene structure, resulting in reversible solvatochromism.

We note that the long-wavelength band for all the merocyanines studied underwent only bathochromic shifts upon any increase in solvent polarity. This served as an additional proof that this band was due to charge transfer, since charge transfer in all neutral compounds always causes a greater dipolarity of the excited state than the ground state, thus the excited state energy was decreased more strongly than the ground state energy upon solvation by a polar solvent.

A decrease in the vinylene shifts and increase in deviations of the short-wavelength band upon increasing the length of the polymethine chain provided evidence for an increased contribution of the neutral polyene structure in merocyanines **2-4** and **11-16** (Fig. 5, Table 1). The redistribution of short- and long-wavelength band intensities with increasing value of *n* was also in accord with this conclusion.

On the other hand, an increase of the polymethine chain length in merocyanines **8-10** was accompanied by an increased contribution of polymethine structure in toluene and dichloromethane (Fig. 6, Table 1). Similar behavior was apparent in DMF, when going from dimethinemerocyanine **8** to the tetramethinemerocyanine **9**. However, a further increase in chain length, judging from the drop in the extinction coefficient and broadening of the short-wavelength band of dye **10**, was linked with an increased contribution of a dipolar polyene structure.

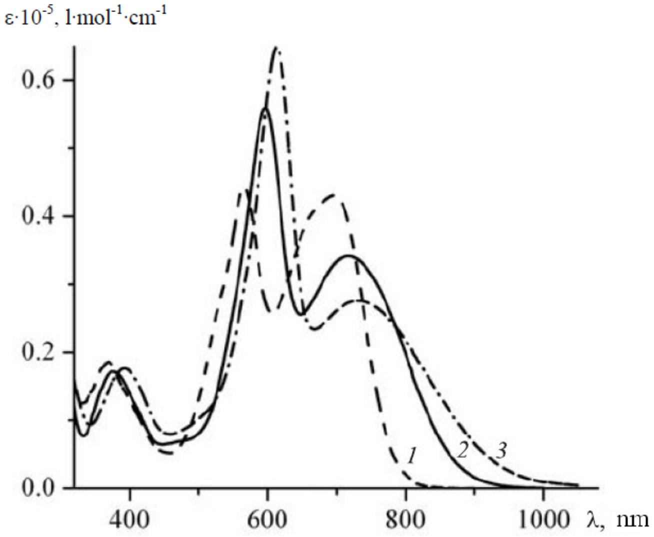

Fig. 5. Electronic absorption spectra of merocyanines **2** (*1*), **3** (*2*), and **4** (*3*) in CH_2Cl_2.

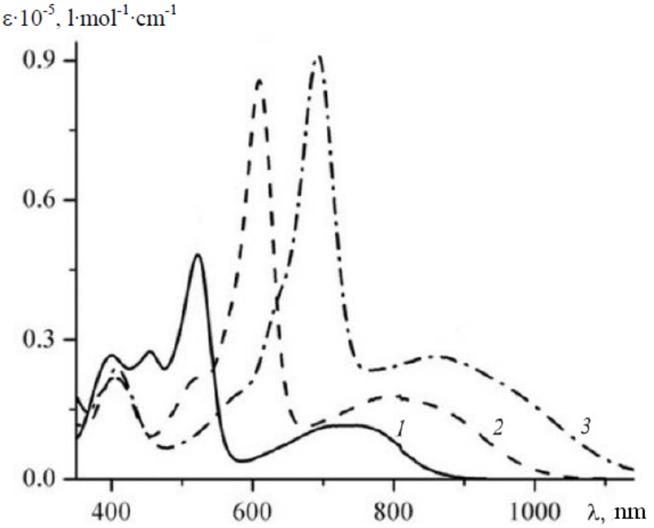

Fig. 6. Electronic absorption spectra of merocyanines **8** (*1*), **9** (*2*), and **10** (*3*) in CH_2Cl_2.

Thus, we were able to predictably control the electronic structure of merocyanines based on 2,4,5,7-tetranitrofluorene in the range of limiting ideal structures (neutral polyene, polymethine, and dipolar polyene) by changing the electron-donating ability of the heterocyclic fragment and solvent polarity. The position, intensity, and shape of the absorption bands, as well as the sign of solvatochromic effect were altered correspondingly.

EXPERIMENTAL

The absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer in 1-cm cells. The concentration of the dissolved samples was 10^{-5} mol/l. The ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 MHz for merocyanines **6, 7,** and **11-17** and a Jeol Eclipse-400 spectrometer at 400 MHz for compounds **2-4** and **8-10**, with TMS as internal standard. The elemental analysis was carried out on a Carlo Erba Strumentazione Elemental Analyzer 1106. The melting points were determined in an open capillary and not corrected. The purity of the dyes was checked by thin-layer chromatography on Silufol UV-254 plates with acetonitrile as the eluent. The solvents were purified by reported methods [19]. Dichloromethane was stabilized by adding 1% of absolute ethanol.

The *ab-initio* DFT quantum-chemical calculations were carried out using the PC Gamess/Firefly software package in the B3LYP/6-31G(d,p) basis with prior optimization of the ground state geometry in the same basis set. The TDDFT method was used to calculate the electronic transitions. In describing the calculated spectra, electronic transitions with oscillator strength greater than 5% of the transition intensity at the greatest osccilator strength were taken into account.

(2*E*)-1,3,3-Trimethyl-2-[2-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)ethylidene]indoline (2). A solution of (2*E*)-(1,3,3)-trimethyl-1,3-dihydro-2*H*-indol-2-ylidene)acetaldehyde (20 mg, 0.1 mmol) and 2,4,5,7-tetranitrofluorene (**1**) (35 mg, 0.1 mmol) in acetic anhydride (2 ml) was heated at reflux for 3-4 min. The precipitate was filtered off, washed with acetic anhydride and then with acetone (3×10 ml) to give indoline **2**. Yield 52 mg (99%). Dark-green powder; mp >270°C (acetic acid). R_f 0.40. ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm (*J*, Hz): 1.86 (6H, s, C(CH$_3$)$_2$); 3.83 (3H, s, NCH$_3$); 6.91 (1H, d, *J* = 14.4, H-1'); 7.28 (1H, t, *J* = 6.8, H Ar); 7.42 (1H, d, *J* = 6.8, H Ar); 7.43 (1H, s, H Ar); 7.45 (1H, t, *J* = 7.2, H Ar); 7.62 (1H, d, *J* = 7.6, H Ar); 8.57 (1H, d, *J* = 1.6, H Ar); 8.74 (1H, d, *J* = 14.4, H-2'); 9.34 (2H, d, *J* = 1.6, H Ar). Found, %: C 58.73; H 3.36; N 13.01. $C_{26}H_{19}N_5O_8$. Calculated, %: C 58.98; H 3.62; N 13.23.

(2*E*)-1,3,3-Trimethyl-2-[(2*E*)-4-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)but-2-enylidene]indoline (3). A mixture of 2-{(1*E*,3*E*)-4-[acetyl(phenyl)amino]buta-1,3-dienyl}-1,3,3-trimethyl-3*H*-indolium perchlorate (45 mg, 0.1 mmol) and 2,4,5,7-tetranitrofluorene (**1**) (35 mg, 0.1 mmol) was dissolved with heating at reflux in acetic anhydride (2 ml) over 3-4 min, and then Et$_3$N (1 ml) was added. A precipitate formed immediately. The reaction mixture was cooled. The precipitate was filtered off and washed with acetic anhydride, then with acetone (3×10 ml) to give indoline **3**. Yield 55 mg (99%). Dark-green powder with a bronze sheen; mp >270°C (acetic acid). R_f 0.43. ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm (*J*, Hz): 1.76 (6H, s, C(CH$_3$)$_2$); 3.64 (3H, s, NCH$_3$); 6.52 (1H, d, *J* = 13.6, H-1'); 7.22 (1H, t, *J* = 7.6, H Ar); 7.31 (1H, d, *J* = 7.6, H Ar); 7.39 (1H, t, *J* = 14.4, H-3'); 7.39 (1H, t, *J* = 7.6, H Ar); 7.56 (1H, d, *J* = 7.6, H Ar); 8.31 (1H, t, *J* = 12.8, H-2'); 8.53 (2H, s, H Ar); 8.70 (1H, d, *J* = 13.2, H-4'); 9.32 (2H, s, H Ar). Found, %: C 60.40; H 3.68; N 12.89. $C_{28}H_{21}N_5O_8$. Calculated, %: C 60.54; H 3.81; N 12.61.

(2*E*)-1,3,3-Trimethyl-2-[(2*E*,4*E*)-6-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)hexa-2,4-dienylidene]-indoline (4). A mixture of 2-{(1*E*,3*E*,5*E*)-6-[acetyl(phenyl)amino]hexa-1,3,5-trienyl}-1,3,3-trimethyl-3*H*-indolium perchlorate (47 mg, 0.1 mmol) and 2,4,5,7-tetranitrofluorene (**1**) (35 mg, 0.1 mmol) was dissolved with heating at reflux in acetic anhydride (2 ml), and Et$_3$N (1 ml) was added. The mixture was heated at reflux for an additional 2-3 min. The precipitate was filtered off, washed with acetic anhydride and then with acetone (4×10 ml) to give indoline **4**. Yield 44 mg (75%). Dark-green powder, mp >270°C (acetic acid). R_f 0.48. ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm (*J*, Hz): 1.67 (6H, s, C(CH$_3$)$_2$); 3.53 (3H, s, NCH$_3$); 6.17 (1H, d, *J* = 13.2, H-1'); 6.78 (1H, t, *J* = 12.4, H-2'); 7.14 (1H, t, *J* = 7.2, H Ar); 7.19 (1H, d, *J* = 7.6, H Ar); 7.34 (1H, t, *J* = 7.2, H Ar); 7.39 (1H, t, *J* = 12.8, H-4'); 7.46 (1H, d, *J* = 7.2, H Ar); 7.70-7.89 (2H, m, H-3',5'); 8.41 (1H, d, *J* =14.0, H-6'); 8.55 (2H, s, H Ar); 9.27 (2H, s, H Ar). Found, %: C 61.75; H 3.73; N 11.90. $C_{30}H_{23}N_5O_8$. Calculated, %: C 61.96; H 3.99; N 12.04.

***N*-Phenyl-*N*-[(1*E*)-3-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)prop-1-enyl]acetamide (6).** A solution of 2,4,5,7-tetranitrofluorene (**1**) (173 mg, 0.5 mmol) and *N*-[3-anilinoprop-2-enylidene]anilinium chloride (130 mg, 0.5 mmol) in acetic anhydride (3 ml) was heated at reflux for 2-3 min. The product precipitated immediately. The precipitate was filtered off and washed with acetic anhydride and ethanol to give acetamide **6**. Yield 255 mg (99%). Brown powder; mp 265-266°C (acetic acid). ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 2.06 (3H, s, $COCH_3$); 6.20 (1H, t, *J* = 12.6, H-2'); 7.58 (2H, d, *J* = 8.1, H Ar); 7.73 (3H, t, *J* = 7.5, H Ar); 8.37 (1H, d, *J* = 1.8, H Ar); 8.59 (1H, d, *J* = 1.8, H Ar); 8.61 (1H, d, *J* = 12.3, H-1); 8.62 (1H, d, *J* = 1.8, H Ar); 8.72 (1H, d, *J* = 13.2, H-3); 9.14 (1H, d, *J* = 1.8, H Ar). Found, %: C 55.45; H 2.81; N 13.39. $C_{24}H_{15}N_5O_9$. Calculated, %: C 55.71; H 2.92; N 13.54.

***N*-Phenyl-*N*-[(1*E*,3*E*)-5-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)penta-1,3-dienyl]acetamide (7).** A solution of 2,4,5,7-tetranitrofluorene (**1**) (173 mg, 0.5 mmol) and *N*-[5-anilinopenta-2,4-dienylidene]anilinium chloride (143 mg, 0.5 mmol) in acetic anhydride (3 ml) was heated at reflux for 2-3 min. The product precipitated immediately. The precipitate was filtered off and washed with acetic anhydride and ethanol, to give acetamide **7**. Yield 260 mg (96%). Shiny black powder; mp 270-271°C (acetic acid). ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 2.14 (3H, s, CH_3); 5.63 (1H, t, *J* = 12.6, H-2); 7.40 (2H, d, *J* = 7.2, H Ar); 7.49-7.68 (5H, m, H-3,4, H Ar); 8.15 (1H, d, *J* = 13.8, H-1); 8.72 (1H, d, *J* = 10.5, H-5); 8.64 (1H, s, H Ar); 8.67 (1H, s, H Ar); 9.09 (1H, s, H Ar); 9.15 (1H, s, H Ar). Found, %: C 57.28; H 3.19; N 13.00. $C_{26}H_{17}N_5O_9$. Calculated, %: C 57.46; H 3.15; N 12.89.

1,3-Diphenyl-2-[2-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)ethylidene]-2,3-dihydro-1*H*-benzimidazole (8). A solution of 2-methyl-1,3-diphenyl-3*H*-benzimidazol-1-ium chloride (32 mg, 0.1 mmol) and 9-(ethoxymethylene)-2,4,5,7-tetranitro-9*H*-fluorene (**5**) (40 mg, 0.1 mmol) in pyridine (3 ml) with Et_3N (1 ml) was heated at reflux for 2-3 min. The precipitate was filtered off and washed with cold pyridine and acetone to give benzimidazole **8**. Yield 42 mg (66%). Gray powder with a blue sheen; mp >270°C (pyridine). R_f 0.42. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 6.22 (1H, d, *J* = 14.6, H-1'); 7.11 (1H, d, *J* = 15.2, H-2'); 7.11 (2H, dd, *J* = 6.4, *J* = 2.6, H Ar); 7.51 (2H, dd, *J* = 6.4, *J* = 2.6, H Ar); 7.71-7.82 (10H, m, H Ar); 8.28 (2H, d, *J* = 2.0, H Ar); 8.81 (2H, d, *J* = 2.0, H Ar). Found, %: C 63.43; H 3.08; N 12.97. $C_{34}H_{20}N_6O_8$. Calculated, %: C 63.75; H 3.15; N 13.12.

1,3-Diphenyl-2-[(2*E*)-4-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)but-2-enylidene]-2,3-dihydro-1*H*-benzimidazole (9). A solution of 2-methyl-1,3-diphenyl-3*H*-benzimidazol-1-ium chloride (32 mg, 0.1 mmol) and acetamide **6** (52 mg, 0.1 mmol) in pyridine (3 ml) with Et_3N (1 ml) was heated at reflux for 3-4 min. The precipitate formed was filtered off and washed with pyridine and acetone to give benzimidazole **9**. Yield 36 mg (54%). Gray-green powder; mp >270°C (pyridine). R_f 0.45. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 6.17 (1H, d, *J* = 15.2, H-1'); 6.75 (1H, dd, *J* = 15.2, *J* =11.6, H-2'); 6.99 (1H, dd, *J* = 14.8, *J* =11.6, H-3'); 7.29 (2H, dd, *J* = 6.4, *J* = 2.6, H Ar); 7.34 (1H, d, *J* = 14.8, H-4'); 7.54 (2H, dd, *J* = 6.4, *J* = 2.6, H Ar); 7.83-7.95 (10H, m, H Ar); 8.27 (2H, d, *J* = 2.0, H Ar); 8.99 (2H, d, *J* = 2.0, H Ar). Found, %: C 64.53; H 3.09; N 12.42. $C_{36}H_{22}N_6O_8$. Calculated, %: C 64.87; H 3.33; N 12.61.

1,3-Diphenyl-2-[(2*E*,4*E*)-6-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)hexa-2,4-dienylidene]-2,3-dihydro-1*H*-benzimidazole (10). A solution of 2-methyl-1,3-diphenyl-3*H*-benzimidazol-1-ium chloride (32 mg, 0.1 mmol) and acetamide **7** (55 mg, 0.1 mmol) in pyridine (3 ml) was heated at reflux for 3-4 min. The precipitate formed was filtered off and washed with acetone to give benzimidazole **10**. Yield 30 mg (43%). Dark-green powder; mp >270°C (pyridine). R_f 0.51. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 6.05 (1H, d, *J* = 14.4, H-1'); 6.44 (1H, t, *J* = 11.2, H-3'); 6.51 (1H, t, *J* = 11.6, H-2'); 6.68 (1H, t, *J* = 13.2, H-4'); 6.92 (1H, dd, *J* = 15.2, *J* = 11.2, H-5'); 7.32 (2H, dd, *J* = 6.4, *J* = 3.2, H Ar); 7.60 (2H, dd, *J* = 6.0, *J* = 3.2, H Ar); 7.82–7.91 (10H, m, H Ar); 7.93 (1H, d, *J* = 15.2, H-6'); 8.26 (2H, d, *J* = 2.0, H Ar); 9.18 (2H, d, *J* = 2.0, H Ar). Found, %: C 65.61; H 3.24; N 11.98. $C_{38}H_{24}N_6O_8$. Calculated, %: C 65.90; H 3.49; N 12.13.

(2*E*)-1-Benzyl-2-[2-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)ethylidene]-1,2-dihydrobenzo[*cd*]indole (11). A mixture of 1-benzyl-2-methylbenzo[*cd*]indolium tetrafluoroborate (35 mg, 0.1 mmol) and 9-(ethoxymethylidene)-2,4,5,7-tetranitro-9*H*-fluorene (**5**) (40 mg, 0.1 mmol) in acetic anhydride (2 ml) was heated at reflux until the starting compounds were completely dissolved (2-3 min). Then Et_3N (1 ml) was added. The precipitate formed was filtered off and washed with acetic anhydride, hot ethanol, and acetone to give dihydrobenzoindole **11**. The pure compound is readily soluble in polar aprotic solvents. Yield 50 mg (80%). Dark-green powder; mp >270°C (acetic acid), R_f 0.25. ^1H NMR spectrum (pyridine-d$_5$), δ, ppm (*J*, Hz): 5.73 (2H, s, NC$\underline{H}_2$Ph); 7.25-7.32 (3H, m, H Ar); 7.34 (1H, d, *J* = 13.6, H-1'); 7.37-7.48 (2H, m, H Ar); 7.49-7.56 (1H, m, H Ar); 7.64-7.75 (2H, m, H Ar); 7.78-7.85 (1H, m, H Ar); 8.15 (1H, d, *J* = 8.0, H Ar); 8.84 (1H, s, H Ar); 8.91 (1H, s, H Ar); 8.95 (1H, d, *J* = 8.0, H Ar); 9.15 (1H, s, H Ar); 9.23 (1H, d, *J* = 14.0, H-2'); 9.54 (1H, s, H Ar). Found, %: C 64.33; H 3.01; N 11.14. $C_{33}H_{19}N_5O_8$. Calculated, %: C 64.60; H 3.12; N 11.41.

(2*E*)-1-Benzyl-2-[(2*E*)-4-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)but-2-enylidene]-1,2-dihydrobenzo[*cd*]indole (12). A mixture of 1-benzyl-2-methylbenzo[*cd*]indolium tetrafluoroborate (35 mg, 0.1 mmol) and acetamide **6** (52 mg, 0.1 mmol) in acetic anhydride (2 ml) was heated at reflux until the starting compounds completely dissolved (3-4 min). Then Et_3N (1 ml) was added. The precipitate formed was filtered off, washed with ethanol, and dried. The crude product was transferred to a flask and heated at reflux in chloroform (10 ml). The precipitate was filtered off and dried to give dihydrobenzoindole **12**. Yield 43 mg (67%). Green powder with a bronze sheen; mp >270°C (acetic acid). R_f 0.27. ^1H NMR spectrum (pyridine-d$_5$), δ, ppm (*J*, Hz): 5.34 (2H, s, NC$\underline{H}_2$Ph); 6.96 (1H, d, *J* = 13.5, H-1'); 7.02 (1H, d, *J* = 6.9, H Ar); 7.27-7.41 (6H, m, H-2', H Ar); 7.41-7.67 (3H, m, H Ar); 7.87 (1H, t, *J* = 12.6, H-3'); 7.97 (1H, d, *J* = 7.2, H Ar); 8.28 (1H, d, *J* = 7.2, H Ar); 8.64 (1H, t, *J* = 13.5, H-4'); 8.81 (1H, s, H Ar); 8.86 (1H, s, H Ar); 9.28 (1H, s, H Ar); 9.33 (1H, s, H Ar). Found, %: C 65.58; H 3.14; N 10.77. $C_{35}H_{21}N_5O_8$. Calculated, %: C 65.73; H 3.31; N 10.95.

(2*E*)-1-Benzyl-2-[(2*E*,4*E*)-6-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)hexa-2,4-dienylidene]-1,2-dihydrobenzo[*cd*]indole (13). A mixture of 1-benzyl-2-methylbenzo[*cd*]indolium tetrafluoroborate (52 mg, 0.15 mmol) and acetamide **7** (81 mg, 0.15 mmol) in pyridine (3 ml) was heated at reflux for 2-3 min, then Et_3N (1 ml) was added. Heating at reflux was continued until a precipitate began to form (2-3 min). The precipitate was filtered off and washed with acetone (3×5 ml) to give dihydrobenzoindole **13**. Yield 50 mg (75%). Black powder with a green sheen; mp >270°C (pyridine). R_f 0.31. ^1H NMR spectrum (DMSO-d$_6$), δ, ppm (*J*, Hz): 5.35 (2H, s, NC$\underline{H}_2$Ph); 6.54 (1H, d, *J* = 12.0, H-1'); 6.99 (1H, t, *J* = 12.3, H-3'); 7.03 (1H, d, *J* = 6.4, H Ar); 7.22-7.55 (6H, m, H-2', H Ar); 7.62 (1H, t, *J* = 12.0, H-4'); 7.72-7.89 (2H, m, H Ar); 7.93-8.05 (3H, m, H-5', H Ar); 8.28 (1H, d, *J* = 6.4, H Ar); 8.49 (1H, d, *J* = 12.0, H-6'); 8.65 (2H, s, H Ar); 9.30 (2H, s, H Ar). Found, %: C 66.43; H 3.28; N 10.19. $C_{37}H_{23}N_5O_8$. Calculated, %: C 66.77; H 3.48; N 10.52.

2,6-Diphenyl-4-[2-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)ethylidene]-4*H*-pyran (14). A solution of 4-methyl-2,6-diphenylpyrilium tetrafluoroborate (33 mg, 0.1 mmol) and 9-(ethoxymethylidene)-2,4,5,7-tetranitro-9*H*-fluorene (**5**) (42 mg, 0.1 mmol) in pyridine (3 ml) with piperidine (0.5 ml) was heated at reflux for 2-3 min. A precipitate formed upon cooling, which was filtered off and washed with ethanol and hot acetone to give pyran **14**. Yield 30 mg (50%). Green powder with a bronze sheen; mp >270°C (pyridine). R_f 0.39. ^1H NMR spectrum (D_2SO_4), δ, ppm (*J*, Hz): 4.11 (1H, s, H-1'); 6.86-7.11 (6H, m, H Ar); 7.38-7.59 (4H, m, H Ar); 7.62 (2H, s, H Ar); 8.21 (1H, s, H Ar); 8.29 (1H, s, H Ar); 8.44 (1H, d, *J* = 12.9, H-2'); 9.92 (2H, s, H Ar). Found, %: C 63.53; H 2.88; N 9.01. $C_{32}H_{18}N_4O_9$. Calculated, %: C 63.79; H 3.01; N 9.30.

2,6-Diphenyl-4-[(2*E*)-4-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)but-2-enylidene]-4*H*-pyran (15). A mixture of 4-methyl-2,6-diphenylpyrilium tetrafluoroborate (33 mg, 0.1 mmol) and acetamide **6** (52 mg, 0.1 mmol) in pyridine (2-3 ml) with Et_3N (1 ml) was heated at reflux for 3-4 min. The precipitate formed was filtered off and washed with acetone (3×5 ml) to give pyran **15**. Yield 40 mg (63%). Black powder with a green sheen; mp >270°C (pyridine). R_f 0.44. ^1H NMR spectrum (DMSO-d$_6$), δ, ppm (*J*, Hz): 6.58 (1H, d, *J* = 12.8, H-1'); 7.53 (1H, t, *J* = 13.2, H-2'); 7.55-7.71 (6H, m, H Ar); 7.95-8.14 (6H, m, H Ar); 8.32 (1H, t, *J* = 12.2, H-3'); 8.51 (1H, d, *J* = 12.8, H-4'); 8.62 (2H, s, H Ar); 9.27 (2H, s, H Ar). Found, %: C 64.73; H 3.04; N 8.77. $C_{34}H_{20}N_4O_9$. Calculated, %: C 64.97; H 3.21; N 8.91.

2,6-Diphenyl-4-[(2*E*,4*E*)-6-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)hexa-2,4-dienylidene]-4*H*-pyran (16). A solution of 4-methyl-2,6-diphenylpyrilium tetrafluoroborate (34 mg, 0.1 mmol) and acetamide **7** (54 mg, 0.1 mmol) in pyridine (3 ml) was heated at reflux for 3 min, then Et_3N (1 ml) was added. The precipitate formed was filtered off and washed with pyridine and acetone to give pyran **16**. Yield 12 mg (18%). Black powder with a green sheen; mp >270°C (pyridine). R_f 0.41. Found, %: C 65.83; H 3.12; N 8.41. $C_{36}H_{22}N_4O_9$. Calculated, %: C 66.06; H 3.39; N 8.56.

2,6-Di-*tert*-butyl-4-[(2*E*,4*E*)-6-(2,4,5,7-tetranitro-9*H*-fluoren-9-ylidene)hexa-2,4-dienylidene]-4*H*-pyran (17). A solution of 4-methyl-2,6-di-*tert*-butylpyrilium perchlorate (31 mg, 0.1 mmol) and acetamide **7** (54 mg, 0.1 mmol) in pyridine (3 ml) was heated at reflux for 3 min, then Et_3N (1 ml) was added. The precipitate formed was filtered off and washed with pyridine and acetone to give pyran **17**. Yield 50 mg (81%). Black powder with a bronze sheen; mp >270°C (pyridine). R_f 0.56. ^1H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.25 (9H, s, $C(CH_3)_3$); 1.31 (9H, s, $C(CH_3)_3$); 5.82 (1H, d, $J = 12.6$, H-1'); 5.98 (1H, d, $J = 1.5$, H Ar); 6.39 (1H, d, $J = 1.5$, H Ar); 6.59 (1H, t, $J = 12.3$, H-2'); 7.28-7.35 (2H, m, H-3',4'); 7.89 (1H, t, $J = 12.6$, H-5'); 8.72 (1H, d, $J = 1.5$, H Ar) Found, %: C 62.17; H 4.48; N 8.99. $C_{32}H_{30}N_4O_9$. Calculated, %: C 62.54; H 4.92; N 9.12.

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