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1,3-Bis[4-(*p*-aminostyryl)-pyridinyl]-propane dibromide derivatives: Synthesis and spectroscopic investigation

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Abstract

The synthesis and basic spectroscopic properties of eight dichromophoric solvatochromic styrylpyridinium dyes are presented. The dyes were prepared by the condensation of propane 1,3-bis[4-methylpyridinium] dibromide with *p*-(*N*,*N*-dialkylamino)benzaldehydes. The synthesis of suitable substrates is presented as well. The dyes were characterized by ^{1}H NMR spectroscopy and their purity with the use of thin-layer chromatography. The spectroscopic properties of the prepared dyes were determined in two organic solvents. The electronic absorption spectra of tested dyes demonstrate low sensitivity to the nature of the substituents introduced into the side aromatic rings. In contrast to this, the fluorescence band positions are affected by the structure of an electron donor and solvent polarity.

Keywords: Dichromophoric hemicyanine dye; Synthesis; Spectroscopic properties; The Stokes shift

1. Introduction

Synthesis of new organic molecules and characterization of their photophysical molecular properties in different environments (pure solvents and molecular assemblies) are necessary prerequisites for further research in technological applications.

Monochromophoric aminostyrylpyridinium salts have been thoroughly investigated from the point of view of negative solvatochromism [1] and structure–color relationship [2]. Such dyes have gained increasing interest also because of their applicability in nonlinear optics, physiology, biochemistry areas and as potential sensors. The colorants were found to be useful in studies of the transport mechanisms through cell membranes [3] and voltage-sensitive probes in neurons [4]. These compounds have also found application in the optical sensing of ionic species. Styrylpyridinium salts with significant charge shift between the ground state and excited state [5] have been used as laser dyes [6] and fluorescence probes [7] as well.

Conjugated oligomers have also received great attention during the past few years and have been proved to be one of the most promising candidates for advanced materials due to their unique photo, electro, and magnetic properties [8,9].

Our main task, in the present work, was to synthesize and study the relationship between the chemical structure and spectroscopic properties of the eight representatives of the 1,3-bis[4-(4-aminophenyl-ethenyl)pyridinyl]-propane dibromide that differ by their electron donor properties of substituent present in the aromatic moiety. In this paper, we report the photophysical properties of these dimmers in two organic solvents.

2. Experimental

2.1. Measurements

All starting reagents and solvents (reagent grade) were purchased from Aldrich Chemical Co. and used without further purification. Aldehydes, as substrates for synthesis of dichromophoric dyes, were synthesized according to the procedure given by Gawinecki et al. [10].

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The ^1H NMR spectra were recorded with the use of a Varian spectrometer Gemini 200 operating at 200 MHz. Dimethylsulfoxide (DMSO) was used as the solvent and tetramethylsilane (TMS) as internal standard.

Melting points (uncorrected) were determined on the Boëthius apparatus.

For the measurements of the absorption and emission spectra and the fluorescence quantum yield (Φ) the 1.0×10^{-5} M dye solutions in both acetonitrile (MeCN) and chloroform (TCM) were prepared. At such concentration no aggregation or self-absorption effects of the dyes were observed [11]. Absorption spectra were recorded at room temperature using a Shimadzu UV−vis Multispec-1501 spectrophotometer, and fluorescence spectra were obtained with a Hitachi F-4500 spectrofluorimeter. The fluorescence measurements were performed at an ambient temperature.

The fluorescence quantum yields for the dyes in MeCN and TCM were determined as follows. The fluorescence spectrum of a dilute (<25 μM) dye solution was recorded by excitation at the absorption band maximum of the reference. A dilute Rhodamine B in ethanol ($\Phi = 0.55$ [12]) was used as reference. The fluorescence spectrum of Rhodamine B was obtained by excitation at its absorption peak at 530 nm. The quantum yield of the tested dye (Φ_{dye}) was calculated using equation:

$$\Phi_{\mathrm{dye}} = \Phi_{\mathrm{ref}} \frac{I_{\mathrm{dye}} A_{\mathrm{ref}}}{I_{\mathrm{ref}} A_{\mathrm{dye}}} \tag{1}$$

where Φ_{ref} is the fluorescence quantum yield of reference (Rhodamine B) sample in ethanol, A_{dye} and A_{ref} are the absorbances of the dye and reference samples at the excitation wavelength (530 nm), I_{dye} and I_{ref} are the areas arbitrary units of the corrected fluorescence spectra (plotted in frequency scale) for the dyes and reference samples, respectively.

2.2. Synthetic procedure

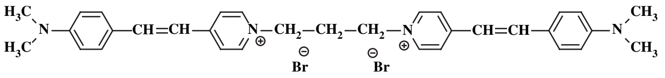
2.2.1. Synthesis of propane 1,3-bis[4-methylpyridinium] dibromide

To a solution of 1,3-dibromopropane (0.1 mol, 20.2 g, 10.2 mL) in anhydrous ethanol (50 mL) γ-picoline (0.2 mol, 22.4 g, 23.4 mL) was added dropwise. The reaction mixture was refluxed for 7 h and then the solution was concentrated in vacuum to give a white solid (yield 60%) [13].

2.2.2. General procedure for synthesis of 1,3-bis[4-(4-dialkylaminophenyl-ethenyl)pyridinyl]-propane dibromide derivatives

1,3-Bis[4-(4-dialkylaminophenyl-ethenyl)pyridinyl]-propane dibromide derivatives were obtained by refluxing (1−2 h) a proper *p*-aminobenzaldehyde (4 mmol) with propane 1,3-bis[4-methylpyridinium bromide] (2 mmol, 0.78 g) in methanol (20 mL) in presence of piperidine (few drops). The precipitate formed after cooling down the reaction mixture was filtered and then crystallized from MeOH/isopropyl alcohol to afford (about 60%) the desired dye, usually red solid [14]. The products were identified by elemental analysis and spectroscopically.

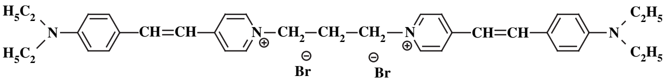
2.2.2.1. Dye **C1** − 1,3-bis[4-(4-(N,N-dimethylamino)phenyl-ethenyl)pyridinyl]-propane dibromide



The dye was prepared by the above described procedure using propane 1,3-bis[4-methylpyridinium bromide] (2 mmol, 0.78 g) and *p*-(*N*,*N*-dimethylamino)benzaldehyde (4 mmol, 0.6 g). The red solid was crystallized from methanol/isopropyl alcohol: yield 57%; $C_{33}H_{38}N_4Br_2$; 650 g/mol; 0.75 g; mp 258−265 °C.

^1H NMR (DMSO) δ (ppm): 2.490−2.609 (m, 2H, $-CH_2-$), 3.013 (s, 12H, $N-CH_3$), 4.513−4.581 (t, 4H, N^+CH_2-), 7.139−7.220 (d, $J = 16.2$ Hz, 2H, $-CH=$), 7.903−7.984 (d, $J = 16.2$ Hz, 2H, $-CH=$), 6.744−6.788 (d, $J = 8.8$ Hz, 4H, Ar), 7.559−7.603 (d, $J = 8.8$ Hz, 4H, Ar), 8.059−8.094 (d, $J = 7.6$ Hz, 4H, Pyr), 8.762−8.795 (d, $J = 6.6$ Hz, 4H, Pyr).

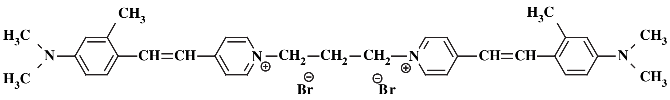
2.2.2.2. Dye **C2** − 1,3-bis[4-(4-(N,N-diethylamino)phenyl-ethenyl)pyridinyl]-propane dibromide



The desired dye was prepared based on the general procedure using propane 1,3-bis[4-methylpyridinium bromide] (2 mmol, 0.78 g) and *p*-(*N*,*N*-diethylamino)benzaldehyde (4 mmol, 0.71 g). The red solid was crystallized from methanol/isopropyl alcohol: yield 83%; $C_{37}H_{46}N_4Br_2$; 706 g/mol; 1.18 g; mp 157−162 °C.

^1H NMR (DMSO) δ (ppm): 1.081−1.149 (m, 20H, $N-C_2H_5$), 2.473−2.563 (m, 2H, $-CH_2-$), 4.480−4.546 (t, 4H, N^+CH_2-), 7.088−7.169 (d, $J = 16.2$ Hz, 2H, $-CH=$), 7.879−7.958 (d, $J = 16.2$ Hz, 2H, $-CH=$), 6.713−6.759 (d, $J = 8$ Hz, 4H, Ar), 7.533−7.579 (d, $J = 8$ Hz, 4H, Ar), 8.035−8.070 (d, $J = 7.6$ Hz, 4H, Pyr), 8.714−8.749 (d, $J = 7$ Hz, 4H, Pyr).

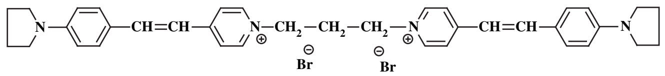
2.2.2.3. Dye **C3** − 1,3-bis[4-(2-methyl-4-(N,N-dimethylamino)phenyl-ethenyl)pyridinyl]-propane dibromide



The dye was prepared applying the methodology given in the general procedure using propane 1,3-bis[4-methylpyridinium bromide] (2 mmol, 0.78 g) and 3-methyl-*p*-(*N*,*N*-dimethylamino)benzaldehyde (4 mmol, 0.65 g). The yielded red solid was crystallized from methanol/isopropyl alcohol: yield 70%; $C_{35}H_{42}N_4Br_2$; 678 g/mol; 0.96 g; mp 223−235 °C.

^{1}H NMR (DMSO) δ (ppm): 2.442−2.585 (m, 2H, $-CH_2-$), 2.720 (s, 6H, $-CH_3$), 2.995 (s, 12H, $N-CH_3$), 4.554−4.587 (t, 4H, N^+CH_2-), 7.103−7.182 (d, $J = 15.8$ Hz, 2H, $-CH{=}$), 7.991−8.070 (d, $J = 16.2$ Hz, 2H, $-CH{=}$), 6.568−6.652 (4H, Ar), 7.682−7.727 (d, $J = 9$ Hz, 4H, Ar), 8.117−8.150 (d, $J = 6.6$ Hz, 4H, Pyr), 8.736−8.771 (d, $J = 7$ Hz, 4H, Pyr).

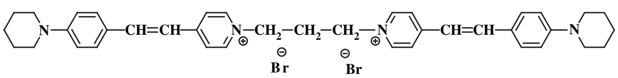
*2.2.2.4. Dye **C5** − 1,3-bis[4-(4-pyrrolidinophenyl-ethenyl) pyridinyl]-propane dibromide*



The dye was prepared based on the general procedure using propane 1,3-bis[4-methylpyridinium bromide] (2 mmol, 0.78 g) and 4-pyrrolidinobenzaldehyde (4 mmol, 0.7 g). The red solid was crystallized from methanol/isopropyl alcohol: yield 56%; $C_{37}H_{42}N_4Br_2$; 702 g/mol; 0.80 g; mp 218−225 °C.

^{1}H NMR (DMSO) δ (ppm): 1.972 (t, 10H, $-CH_2-$), 2.473−2.611 (m, 8H, $N-CH_2-$), 4.477−4.510 (t, 4H, N^+CH_2-), 7.096−7.176 (d, $J = 16$ Hz, 2H, $-CH{=}$), 7.885−7.966 (d, $J = 16.2$ Hz, 2H, $-CH{=}$), 6.591−6.634 (d, $J = 8.6$ Hz, 4H, Ar), 7.549−7.592 (d, $J = 8.6$ Hz, 4H, Ar), 8.023−8.058 (d, $J = 7$ Hz, 4H, Pyr), 8.703−8.738 (d, $J = 7$ Hz, 4H, Pyr).

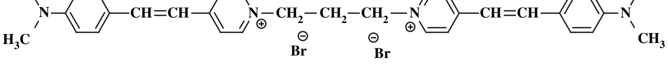
*2.2.2.5. Dye **C6** − 1,3-bis[4-(4-piperidinophenyl-ethenyl)-pyridinyl]-propane dibromide*



The dye was prepared based on the general procedure using propane 1,3-bis[4-methylpyridinium bromide] (2 mmol, 0.78 g) and 4-piperidinobenzaldehyde (4 mmol, 0.76 g). The obtained red solid was crystallized from methanol/isopropyl alcohol: yield 50%; $C_{39}H_{46}N_4Br_2$; 726 g/mol; 0.73 g; mp 214−219 °C.

^{1}H NMR (DMSO) δ (ppm): 1.587 (t, 14H, $-CH_2-$), 2.482−2.596 (m, 4H, $N-CH_2-$), 2.993 (m, 4H, $N-CH_2-$), 4.557−4.592 (t, 4H, N^+CH_2-), 7.178−7.258 (d, $J = 16$ Hz, 2H, $-CH{=}$), 7.894−7.973 (d, $J = 15.8$ Hz, 2H, $-CH{=}$), 6.958−7.004 (d, $J = 9.2$ Hz, 4H, Ar), 7.552−7.595 (d, $J = 8.6$ Hz, 4H, Ar), 8.084−8.119 (d, $J = 7$ Hz, 4H, Pyr), 8.784−8.819 (d, $J = 7$ Hz, 4H, Pyr).

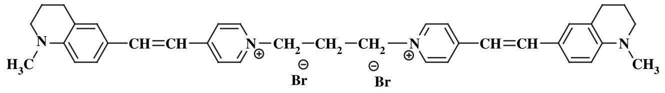
*2.2.2.6. Dye **C7** − 1,3-bis[4-(2-(N-metylo-5,6-dihydroindolino)ethenyl)pyridinyl]-propane dibromide*



The dye was prepared adopting the procedure described above using propane 1,3-bis[4-methylpyridinium bromide] (2 mmol, 0.78 g) and 1-methylindolino-4-aldehyde (4 mmol, 0.64 g). The obtained red solid product was crystallized from methanol/isopropyl alcohol: yield 18%; $C_{35}H_{38}N_4Br_2$; 674 g/mol; 0.25 g; mp 188−196 °C.

^{1}H NMR (DMSO) δ (ppm): 2.484−2.565 (m, 2H, $-CH_2-$), 2.828 (s, 6H, $N-CH_3$), 2.924−3.006 (t, 4H, $-CH_2-$), 3.433−3.515 (t, 4H, $N-CH_2-$), 4.482−4.552 (t, 4H, N^+CH_2-), 7.090−7.169 (d, $J = 15.9$ Hz, 2H, $-CH{=}$), 7.861−7.942 (d, $J = 16.2$ Hz, 2H, $-CH{=}$), 6.493−6.535 (d, $J = 8.4$ Hz, 2H, Ar), 7.359−7.462 (4H, Ar), 8.006−8.039 (d, $J = 6.6$ Hz, 4H, Pyr), 8.709−8.742 (d, $J = 6.6$ Hz, 4H, Pyr).

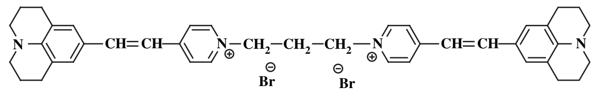
*2.2.2.7. Dye **C8** − 1,3-bis[4-(2-(N-metylo-4,5,6-trihydrochinolino)ethenyl)pyridinyl]-propane dibromide*



The dye-stuff was prepared applying the procedure described above using propane 1,3-bis[4-methylpyridinium bromide] (2 mmol, 0.78 g) and 1-methyl-1,2,3,4-tetrahydrochinolino-4-aldehyde (4 mmol, 0.7 g). The red resulting dye was crystallized from methanol/isopropyl alcohol: yield 75%; $C_{37}H_{42}N_4Br_2$; 702 g/mol; 1.06 g; mp 178−183 °C.

^{1}H NMR (DMSO) δ (ppm): 1.883−1.907 (m, 4H, $-CH_2-$), 2.482−2.565 (m, 2H, $-CH_2-$), 2.682−2.773 (t, 8H, $-CH_2-$), 2.947 (s, 6H, $N-CH_3$), 4.478−4.545 (t, 4H, N^+CH_2-), 7.070−7.149 (d, $J = 15.8$ Hz, 2H, $-CH{=}$), 7.832−7.912 (d, $J = 16$ Hz, 2H, $-CH{=}$), 6.592−6.636 (d, $J = 8.8$ Hz, 2H, Ar), 7.324−7.398 (4H, Ar), 8.004−8.039 (d, $J = 7$ Hz, 4H, Pyr), 8.702−8.735 (d, $J = 6.6$ Hz, 4H, Pyr).

*2.2.2.8. Dye **C9** − 1,3-bis[4-2-(julolidyno))ethenyl) pyridinyl]-propane dibromide*



The dye was prepared using propane 1,3-bis[4-methylpyridinium bromide] (2 mmol, 0.78 g) and julolidyno-4-aldehyde (4 mmol, 0.8 g) as substrates applying the general procedure described earlier. The resulting red solid was crystallized from methanol/isopropyl alcohol: yield 44%; $C_{41}H_{46}N_4Br_2$; 754 g/mol; 0.66 g; mp 200−210 °C.

^{1}H NMR (DMSO) δ (ppm): 1.842−1.871 (m, 8H, $-CH_2-$), 2.483−2.549 (m, 2H, $-CH_2-$), 2.655−2.714 (t, 8H, $-CH_2-$), 3.260−3.329 (t, 8H, $-CH_2-$), 4.461−4.527 (t, 4H, N^+CH_2-), 7.007−7.087 (d, $J = 16$ Hz, 2H, $-CH{=}$), 7.765−7.846 (d, $J = 16$ Hz, 2H, $-CH{=}$), 7.131−7.201 (4H, Ar), 7.956−7.988 (d, $J = 6.4$ Hz, 4H, Pyr), 8.666−8.699 (d, $J = 6.6$ Hz, 4H, Pyr).

3. Results and discussions

3.1. Molecular design and synthetic procedures

The synthetic methodology for tested dichromophoric dyes is analogous to that previously reported by Mishra and Haram [14]. The general route for synthesis of the tested dyes is presented in Scheme 1.

The dimmers, containing various substituents in benzene ring were synthesized, in reasonably good yields, by the condensation reaction between corresponding *p*-substituted benzaldehydes and propane 1,3-bis[4-methylpyridinium bromide] in methanol with a few drops of piperidine as a catalyst. These compounds were purified by recrystallization and characterized on the basis of analytical results and spectral evidences. The purity of the dyes was tested using TLC.

Fig. 1 shows the ^{1}H NMR spectra of **C1**, **C2**, **C5** and **C7** in the region of $\delta = 6.5-9$ ppm. In the region the signals characteristic for the protons in benzene ring, pyridinyl ring, and the central double bond usually are present. All of the peaks are doublets, and each of them is assigned to the corresponding hydrogen atoms in molecule, as presented in Section 2. More details of all the dyes' protons chemical shifts and the coupling constants are also presented in Section 2. The most important common feature of the NMR data is the presence of coupling constants for hydrogens in vinyl group with characteristic spin–spin splitting of about 16 Hz. This value indicates that all dyes are *trans* isomers.

3.2. Electronic absorption and emission properties

Earlier work of Huang et al. on a large number of flexible dichromophoric compounds of the electron donor–acceptor type documented that the visible absorption spectra exhibit an intramolecular charge transfer transition ($S^0 \rightarrow$ CT) [15,16].

The absorption spectra for selected dichromophoric dyes under the study in chloroform are displayed in Fig. 2.

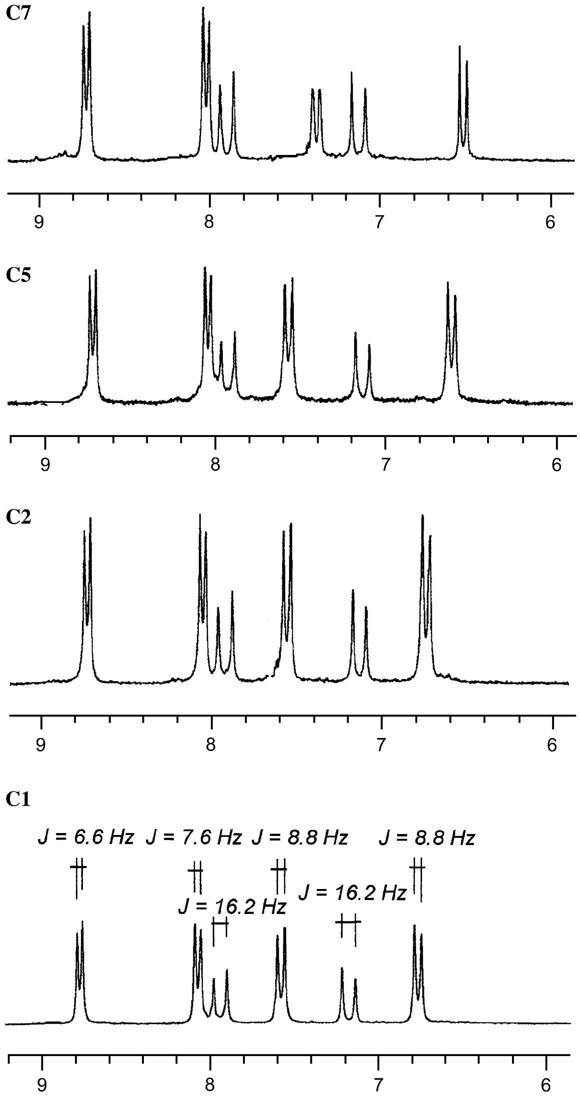
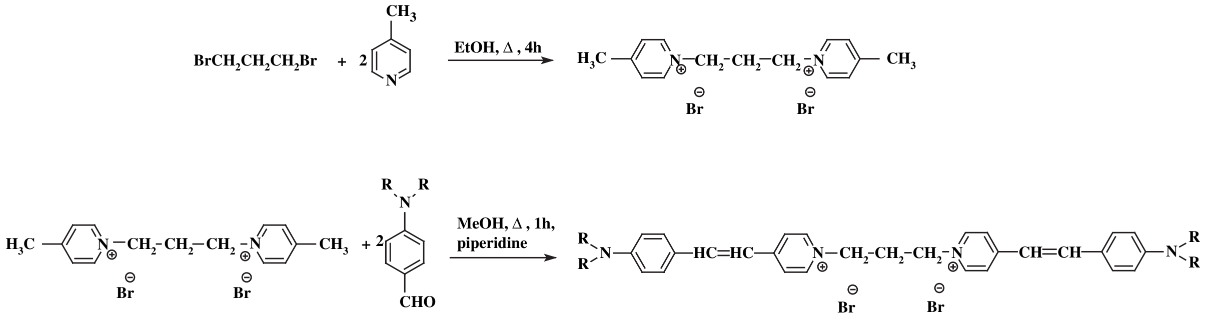


Fig. 1. ^{1}H NMR spectra of **C1**, **C2**, **C5** and **C7** in DMSO.

All electronic absorption spectra clearly present two bands whose maxima are located at about 300 and 500 nm regions. The shortest wavelength bands are attributed to the $\pi \rightarrow \pi^*$ transitions whereas the long wavelength bands, generally characterized by higher molar absorption coefficients, are attributed to the $S^0 \rightarrow$ CT transition. Inspection of the illustrative absorption spectra, presented in Fig. 2, shows that the position and intensity of CT absorption band, to some extent, depend on the dye molecule structure. This finding can be summarized as follows: (i) the planar conformation of dialkylamino group with respect to the benzene ring (**C9**) increases the probability of the radiative transitions in comparison to the other



Scheme 1. A general route for the synthesis of the 1,3-bis[4-(4-aminophenyl)ethenyl)pyridinyl]-propane dibromide derivatives.

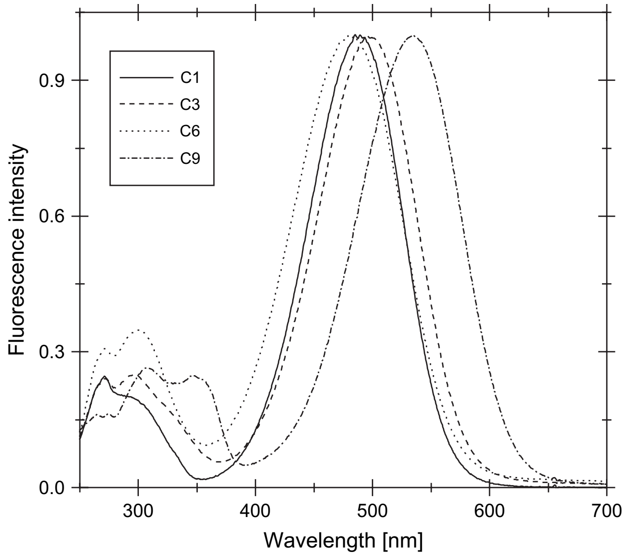


Fig. 2. Electronic absorption spectra of selected dichromophoric dyes in acetonitrile at 293 K. The chromophores possess different donor groups (dye marked in the figure).

molecules; (ii) the coplanar conformation of this group with respect to benzene ring decreases this probability which is demonstrated by a significant blue shift of CT absorption band. This specific irregularity can be additionally illustrated by the data obtained by Gawinecki et al. during the study on the resonance substituent constants of *p*-substituted benzaldoximes [17]. CT character of the long-wavelength absorption band is additionally reflected by the values of the ground state dipole moments of the dyes.

The influence of the solvent polarity on the electronic absorption and emission spectra is illustrated in Fig. 3.

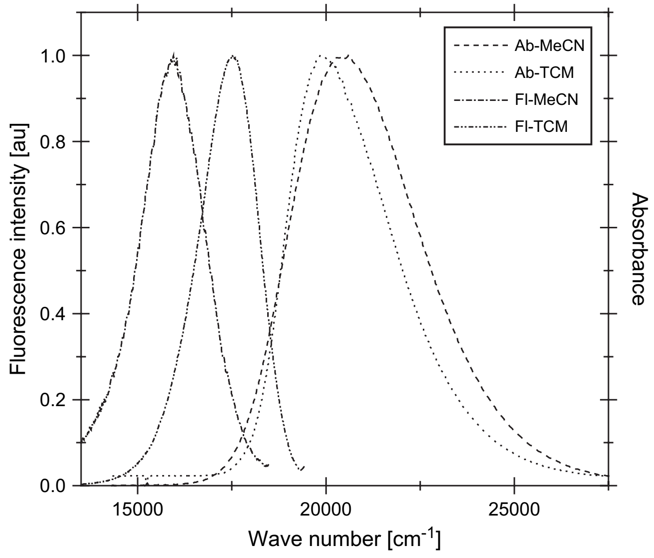


Fig. 3. Representative electronic absorption and fluorescence emission spectra of the **C1** dye. Spectra recorded in acetonitrile (MeCN) and chloroform (TCM) at 293 K.

It has been established experimentally that the molecules with π-electrons, for which the charge distribution in the electronic ground state is considerably different from that in the excited state exhibit pronounced solvatochromism. Thus, for the tested organic compounds only a comparatively small solvent dependence of their UV–vis absorption spectra is observed. A solvent change from chloroform to acetonitrile causes a hypsochromic shift of only ca. 300 cm^{-1} (17 nm) for its longest wavelength absorption band, e.g., the maximum absorption peak for **C1** is at 503.5 nm in chloroform and 485 nm in acetonitrile. Table 1 reveals that the long wavelength absorption band undergoes a hypsochromic shift (absorption peak position blue-shifts) as the solvent polarity increases (negative solvatochromism), if the ground state is more dipolar than the excited state ($\mu_g > \mu_e$). This relation allows concluding that the dipole moments of the excited states reached directly after excitation are rather small.

A study of the fluorescence of all tested dyes has been performed in chloroform and acetonitrile at room temperature. Fig. 4 shows fluorescence spectra for selected dimmers.

All dimmers show similar fluorescence characteristic with one broad emission band. The illustrative fluorescence spectra, presented in Fig. 4, suggest that the structure of the donor groups in the molecule is affecting the position of the emission band and its intensity. The elimination of the freedom of rotation of the dialkylamino group leads to the red shift in the fluorescence, which is illustrated by the fluorescence maximum shift from 570.8 nm for dye **C1** to 610 nm for dye **C9** (see Table 1).

As is shown in Fig. 3 and documented by the data represented in Table 1, a pronounced red shift of about 1300 cm^{-1} (50 nm) is observed on going from chloroform to acetonitrile. This shift is accompanied by a decrease in the fluorescence quantum yield (*Φ*). The fluorescence quantum yield (*Φ*) changes from 0.15 for dye **C3** to 0.31 for dye **C5**

Table 1
Spectroscopic properties of the dichromophoric hemicyanine dyes tested in both chloroform and acetonitrile as a solvent

Dye	$\lambda_{\max}^{\mathrm{Ab}}$(nm), $\varepsilon(\mathrm{M}^{-1}\ \mathrm{cm}^{-1})$	$\lambda_{\max}^{\mathrm{Fl}}$(nm)	Φ_{Fl}
Acetonitrile ($\varepsilon = 35.94$, $n_D^{20} = 1.34411$)			
C1	485, 101,000	627	0.0020
C2	502.5, 88,700	625.6	0.0031
C3	495, 59,000	629.4	0.0012
C5	501.5, 75,500	629	0.0021
C6	479.5, 37,000	633.4	0.0022
C7	500, 59,500	649.2	0.0010
C8	508.5, 55,500	639.8	0.0018
C9	534, 43,500	657.8	0.0013
Chloroform ($\varepsilon = 4.806$, $n_D^{20} = 1.4459$)			
C1	503.5, 126,000	570.8	0.25
C2	514, 105,500	577.4	0.29
C3	511, 69,600	581.6	0.15
C5	514.5, 85,800	581	0.31
C6	496.5, 39,100	586.2	0.22
C7	519.5, 72,000	602.6	0.17
C8	523, 85,500	591	0.28
C9	545, 77,000	610	0.16

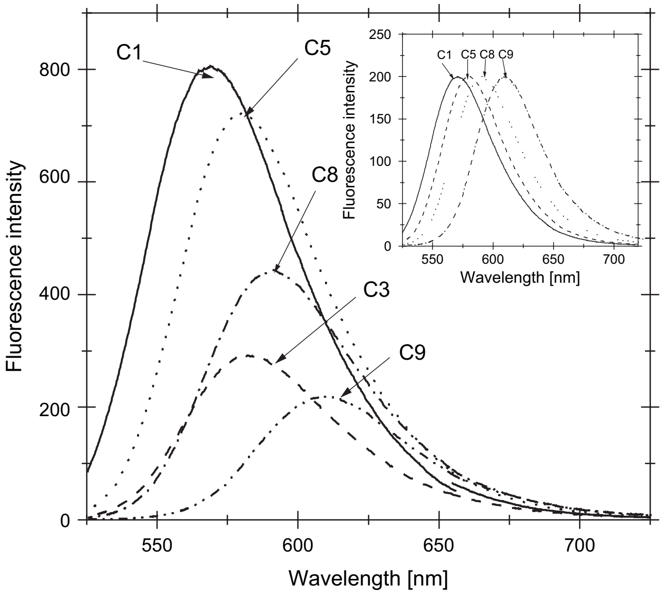


Fig. 4. Fluorescence emission spectra of the selected dyes. Spectra recorded in chloroform at 293 K at the dye concentration equal 1.5 × 10^{-6} M. Inset: Normalized fluorescence spectra of selected dyes illustrating the influence of the dye structure on the position of the emission maximum.

in chloroform or from 0.001 for dye **C7** to 0.0031 for dye **C2** in acetonitrile (see Table 1). The fluorescence quantum yields are dependent on both structure pattern of the studied dimmers and the solvent polarity. The fluorescence emission spectra bands are somewhat narrower than the absorption spectra (see Table 2). If the broadening of the spectra is understood as deriving from the population of the thermally available conformers, then according to Rettig [18], the observed results can be taken as the evidence that some of these conformers are nonemissive (reduction of fluorescence band width). The twisting of the olefinic double bonds gives this type of a conformer. The deactivation of this state should occur mainly by radiationless processes because the energy gap between its excited state and the ground state is very small [19].

Table 2
The half-width of absorption and emission spectra, Stokes shift, $\lambda_0 + \lambda_i$ and ΔG_{CT} for tested dyes

Dye	FWHM$_A$ (cm^{-1})	FWHM$_{Fl}$ (cm^{-1})	$\bar{\nu}$(cm^{-1})	$\lambda_0 + \lambda_i$ (kJ/mol)	$-\Delta G_{CT}$ (kJ/mol)
Chloroform ($\varepsilon = 4.806$, $n_D^{20} = 1.4459$)					
C1	1324	802	2342	14.0	223.5
C2	1216	763	2136	12.8	219.9
C3	1372	778	2376	14.2	219.8
C5	1257	764	2225	13.3	219.1
C6	1696	799	3082	18.4	222.4
C7	1559	762	2655	15.9	214.3
C8	1257	768	2200	13.2	215.5
C9	1181	722	1955	11.7	207.7
Acetonitrile ($\varepsilon = 35.94$, $n_D^{20} = 1.34411$)					
C1	1672	820	4670	27.9	218.6
C2	1537	793	3916	23.4	214.5
C3	1700	809	4314	25.8	215.8
C5	1582	808	4042	24.2	214.3
C6	2002	821	5067	30.3	219.1
C7	2026	846	4596	27.5	211.7
C8	1618	817	4036	24.1	211.0
C9	1504	784	3524	21.1	202.9

Tested dyes represent dichromophoric non-conjugated molecules that show large Stokes shift (see Table 2). This indicates that an emitting state is not the Franck–Condon S_1 state reached in the absorption transition but different, the solvent relaxed state, from which the fluorescence originates. It cannot be also assumed that the excited state dipole moment remains unchanged during transition from Franck–Condon state to the emitting state. The nature of emitting state in tested molecules may change with the solvent (see Tables 1 and 2) or can be changed with the dye structure that is forcing or precluding the excited state relaxation via selected channels (see Table 2 and Ref. [20]) or may be controlled by the viscosity of the medium [21].

The quantitative explanation of this specific behaviour of tested dyes may come from the estimation of a reorganization energy λ_0 related to the solvent and solute motions and reorganization energy λ_i corresponding to the changes in the solute bond lengths and angles accompanying the excited-state electron transfer [22–24]. The following approximate expressions for the maxima of CT absorption and emission spectra can describe the dependence of both organization energies, as well as the value of ΔG_{CT}.

$$\mathrm{h}c\nu_{abs} = -\Delta G_{CT} + \lambda_0 + \lambda_i \quad (2)$$

$$\mathrm{h}c\nu_{Fl} = -\Delta G_{CT} - \lambda_0 - \lambda_i \quad (3)$$

Thus, the sum of the frequency of CT absorption and fluorescence maxima is connected with ΔG_{CT} (Eq. (3)) and their difference with the sum of the reorganization energies, respectively.

$$-\Delta G_{CT} = 1/2(\mathrm{h}c\nu_{abs} + \mathrm{h}c\nu_{Fl}) \quad (4)$$

$$\lambda_0 + \lambda_i = 1/2(\mathrm{h}c\nu_{abs} - hc\nu_{Fl}) \quad (5)$$

The data calculated from the electronic absorption and emission spectra, characterizing $-\Delta G_{CT}$ and $\lambda_0 + \lambda_i$ values are also summarized in Table 2. Comparison of the data shows that the lowest values of $-\Delta G_{CT}$ and $\lambda_0 + \lambda_i$ is mostly observed for molecules with freedom-less dialkylamino group. Elimination of the free rotation of dialkylamino group by the bridging with benzene ring causes a bathochromic shift in fluorescence band (**C9**) and a decrease in its intensity.

4. Conclusions

A series of hemicyanine dimmers, in which two identical chromophores are linked via three methylene groups, have been synthesized and their electronic absorption and steady-state fluorescence spectra have been investigated. The dyes were obtained by condensation of *p*-aminobenzaldehyde and propane 1,3-bis[4-methylpyridinium] dibromide. The UV–vis and steady-state fluorescence spectroscopic investigations show a solvent dependent absorption and emission, which result from the intramolecular charge transfer (ICT) nature of the chromophores present in the dendritic structure. In high polar solvent (acetonitrile), all of the dyes indicate low fluorescence quantum yields, whereas in a medium polarity solvent such as chloroform, the fluorescence quantum yield increases significantly.

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