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Spectroscopic Study of Solvatochromic Effects in Solution of Amino and Hydroxy Derivatives of Fluorene

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Spectral properties of fluorene and its amino, hydroxyl and phenyl derivatives have been investigated in polar and non-polar solvents at 293 and 77 K as well as in binary mixtures, e.g. McH/EtOH. The hipsochromic shift of the fluorescence spectrum of the two amino derivatives of fluorene observed in polar solvents has been explained on the basis of its zwitterionic form appearing in the ground state only. The radiative k_F and non-radiativer k_{NR} and k_{ISC} rate constants for the compounds under study have been calculated using experimentally determined quantum yields, fluorescence and phosphorescence decay times.

KEY WORDS: Fluorene; aminofluorene derivatives; negative solvatochromism.

INTRODUCTION

The photophysical and photochemical properties of fluorene and its derivatives have been studied extensively in the last decade [1–5]. The reason is the fact that they exhibit several interesting features i.e. they show the twisted intramolecular charge transfer phenomena (TICT) [6], the amino substituents of fluorene form hydrogen bond complexes with protic solvents, or undergo intra/intermolecular complexation and show strong solvatochromaticity [7–11].

The polynitro-9-fluorenol and polynitro-9-fluorenes which have the ability to create charge-transfer tautomers constitute a special groups of fluorene derivatives [12]. They are mostly used to sensitise the photoconductivity of the carbazole molecules dissolved in polymers where they are the most widely known acceptor of the π-electron. Another interesting group of fluorene derivatives are the aromatic amines [8]. They are very good fluorophores and their fluorescence is very sensitive to the environment. Therefor they are often used to probe the characteristics of biomimetic systems and biomembrans [13–16].

In our case hydrogen atoms in the main skeleton of fluorene are substituted by a donor group, e.g. hydroxy (-OH), dimethylamino (-NMe_2), diethylamino (-NEt_2) and phenyl (-Ph). In this work as an extinction of our earlier work [7] we report the results of steady state and time resolved spectroscopic investigation of those substituted fluorenes in various solutions. For the compounds under studies the fluorescence, Φ_F, and phosphorescence, Φ_{Ph}, quantum yields, the decay times, τ_F and τ_{Ph} have been determined and using them the radiative, k_F, and non-radiative, k_{NR} and k_{ISC}, rate constants are calculated.

The fluorescence spectra of the amino derivatives obtained in protic polar solutions confirm that in the ground state an open conformer between alcohol molecules and the amino substituent of fluorene (N̈···H—O) is created. This conformer shows a negative solvatochromic shift and appears as a zwitterionic form of the solute molecules. These findings have been confirmed by quantum chemical calculations.

EXPERIMENTAL

The chemical structures of the fluorene derivatives and their abbreviations are shown in Chart I. The Compounds under study were in part obtained from Aldrich Chemical Co. (FL, 9Ph9FOL, $2NEt_2$9FOL) and one of

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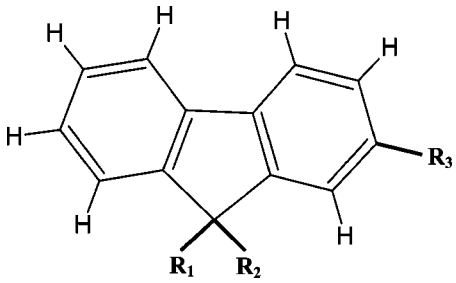

Substituents	R_1	R_2	R_3	Abbreviation
1. Fluorene	H	H	H	FL
2. 9-phenyl-9-fluorenol	OH	$-C_6H_5$	H	9Ph9FOL
3. 2-dimethylamino-9-fluorenol	OH	H	$-N(CH_3)_2$	$2NMe_2FOL$
4. 2-diethylamino-9-fluorenol	OH	H	$-N(C_2H_5)_2$	$2NEt_29FOL$

Chart I

them ($2NMe_29FOL$) is synthesised [7]. They were used without additional purification. The solvents (supplied by E-Merck Ltd.): cyclohexane (CH), methylcyclohexane (McH), chloroform (ChF), ethyl acetate (EtA), tetrahydrofurane (ThF), methanol (MeOH), ethanol (EtOH), acetonitryle (AcN) were spectroscopic grade. All solvents were checked for purity in the wavelength range of interest, by steady-state and time-resolved spectrofluorometer aparatures. The concentration of solutions was maintained at 10^{-4} M through the experiment.

The absorption and the stationary fluorescence spectra at room temperature and 77 K were carried out on Shimadzu UV-2401 PC and RF-5301 spectrofluorometer equipped with a Hamamatsu R-928 photomultiplier and special attachment to obtain phosphorescence spectrum only. Additionally to the neat solution measurement the absorption and emission spectra in the binary mixed solvent at various concentration of EtOH (from 10^{-3}–10^{-5} M) in McH were carried out. The quantum yields were determined using relative methods [17], where as reference quantum yields ($\Phi_{FL} = 0, 80$) fluorene [18] and 9-phenyl-fluorene ($\Phi_{FL} = 0.19$, $\Phi_{Ph} = 0.09$) were used as a standard [19].

The fluorescence decay times, at room temperature, were determined using the experimental set-up described in [20]. In these measurements the probes were excited with polarised light form a Spectra Physics picosecond laser system consisting of an argon laser-pumped Ti-Sapphire 720–850 nm laser Tsunami. The third harmonic of the Ti—sapphire laser generates picosecond pulses in the region (240–333 nm) at a repetition rate in the range from 4 MHz to a single shot. The fluorescence light was polarised and observed under the "magic" angle with respect to the polarised exciting beam. The whole light detection system was equipped with a cooled light detector MCP-PMT R3809U-05 coupled with a biased TAC model TC 864 (Tennelec) amplituner. The data points of the fluorescence decays were fitted by the reference function consisting of the sum of the exponentials:

$$I(t) = \sum_{i} \alpha_i \exp\left(\frac{-t}{\tau_i}\right), \qquad (1)$$

where α_i and τ_i are the pre-exponential coefficient and the decay time of the i-th fluorescence component, respectively. Decay curves were both individually and globally analysed by using single, double and triple exponentials. The goodness of the individual fits was judged by the magnitude of $\chi^2_R \approx 1$ and the shape of the autocorrelations function and the weighted residuals. The fluorescence decay measurements were carried out at the temperature of 293 K. The phosphorescence decay time was measured on the home made aparature.

RESULTS AND DISCUSSION

Steady State Measurements—Absorption and Emission Spectra

The absorption and emission spectra of fluorene are very precisely described in literature [5,7,18]. Generally the absorption spectrum of fluorene (Fig. 1A) in polar and non-polar solvents consists of three bands in the region 200–310 nm. The first (the strongest) band is in the region 200–230 nm, the second (weaker) in 230–290 nm, the third the weakest possessing vibrational structured is situated in 290–310 nm region. The position and shape of the absorption spectra do not depend on the solvent polarity. A similar absorption spectrum shows the first derivative of fluorene 9Ph9FOL (Fig. 1B) where the three bands appear in the 200–320 nm region. They show a small red shift being determined in different solvents.

For the $2NMe_29FOL$ and $2NEt_29FOL$ compounds the absorption spectra shows big difference in the band position and shape in comparison to that of fluorene (see Fig. 2). They possess in 200–375 nm region only two well resolved bands. The two band, short wavelength with $\lambda_{max} = 224$ nm and the long wavelength with $\lambda_{max} = 315$ nm posses comparable molar coefficients with $\varepsilon_M \cong 25,000\ M^{-1}\ cm^{-1}$ in EtOH.

Figures 1 and 2 display the emission spectra of the respective compounds under study in non-polar (McH), polar non-protic (ThF) and protic (EtOH) solvents. All

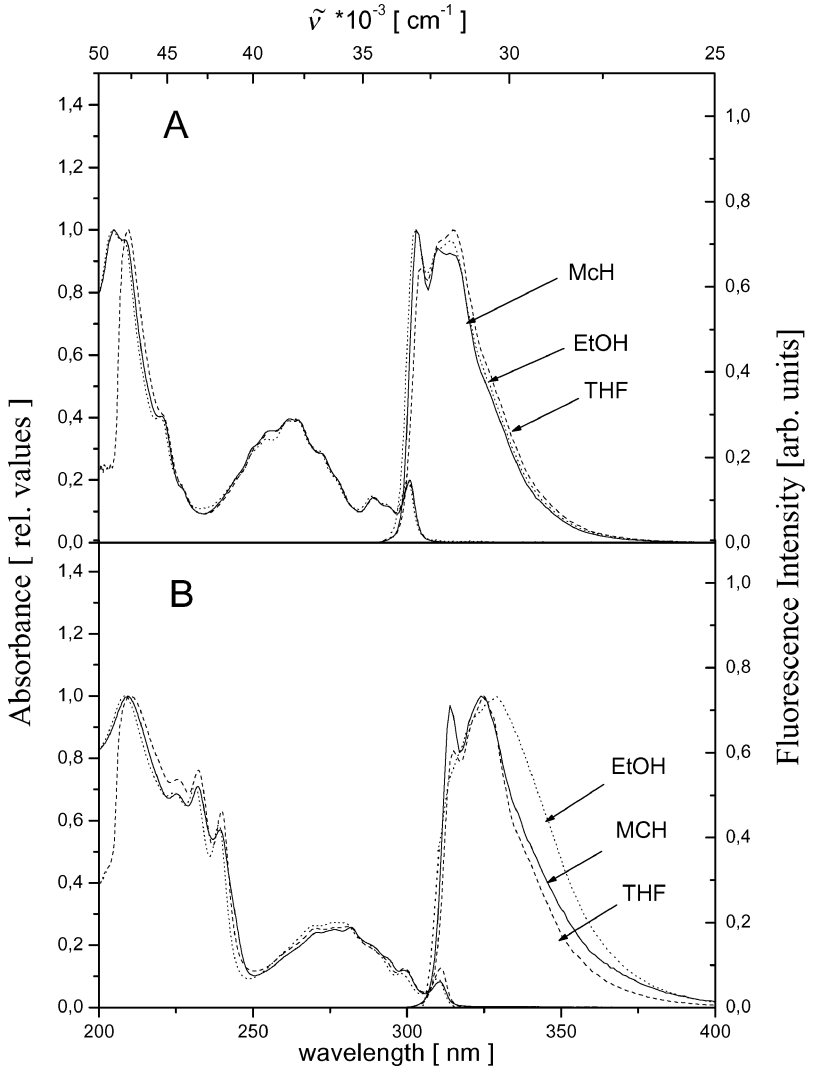

Fig. 1. Absorption and emission spectra of fluorene (A) and 9-phenyl-9-fluorenol (B) in different solvents at 293 K.

compounds in the representative solvents possess one fluorescence band only. The emission spectrum of 9Ph9FOL is very similar to that of fluorene and is red shifted about 10 nm in comparison to the parent molecule. Its λ_{max} depends on the solvent polarity. The half width values of the fluorescence spectra, $\Delta\tilde{\nu}_{1/2}^{FL}$, of FL and 9Ph9FOL are the same and amount to about 2600 cm^{-1}. The fluorescence spectra of the $2NMe_2$9FOL and $2NEt_2$9FOL are broader and are sensitive to the nature of solvents. They are all shifted to the longer wavelength. The fluorescence band maximum, λ_{max}, amounts 389 nm and 392 nm for $2NMe_2$9FOL and for $2NEt_2$9FOL respectively.

Table I contains the spectroscopic parameters determined from the absorption and fluorescence spectra of molecules under study. On analysing the collected data, it follows that the Stokes shift $\Delta\tilde{\nu}_{ST}$ (determined as the $\Delta\tilde{\nu}_{ST} = \tilde{\nu}_{max}^{A} - \tilde{\nu}_{max}^{FL}$) has different values, for 9Ph9FOL it is comparable with that of fluorene (230 cm^{-1} *versus* 320 cm^{-1}) but about 14 times larger value is noted for dimethylamino and diethylamino derivative of fluorene, i.e. (**3** and **4** molecules).

Substituents and Solvents Effect

When analysing the absorption spectrum of the 9Ph9FOL (Fig. 1B) it can be seen that hydroxyl and phenyl substituent change the short-wavelength band of fluorene at 200–250 nm more than the two longer wavelength bands which are red-shifted by about 1050 cm^{-1} in McH [5]. In the short wavelength band the oscillation structure is more

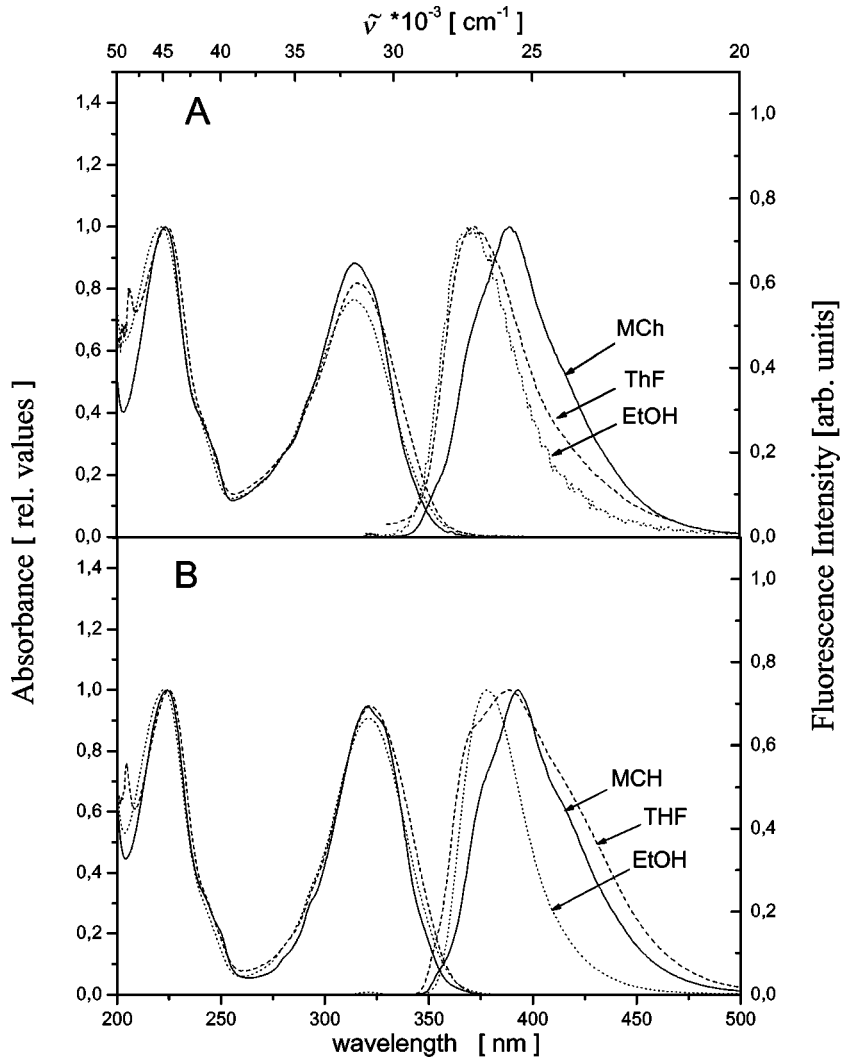

Fig. 2. Absorption and emission spectra of 2-dimethylamino-9-fluorenol (A) nad 2-diethylamino-9-fluorenol (B) in different solvents at 293 K.

pronounced and the band is broadened in comparison to fluorene. It is obvious that the amino group -N(Me)$_2$ and -N(Et)$_2$ at position 2 of the parent molecule (along the long axis of the molecule), perturb the long axis transitions of fluorene more than the short axis in the case of molecules **3** and **4**. Fig. 2 demonstrated this behaviour, e.g., in the absorption spectrum of these molecules instead of two bands we observe only one structurless, broad and red shifted band in the longwave part of absorption spectrum of fluorene. The half width of this red shifted band equals to about 3500 and 3400 cm^{-1} for 2NMe$_2$9FOL, 2NEt$_2$9FOL in McH, respectively (Table I). Due to that interaction the long wavelength absorption band of the fluorene derivatives is red-shifted in comparison to the parent molecule (see Table I and [8]).

It is worth noticing that the emission spectra of the two derivatives, by changing the solvent from non-polar to polar and polar-protic solvents, changes the λ_{max} and $\Delta\tilde{\nu}^{FL}_{1/2}$ value. Also, the Stokes shift $\Delta\tilde{\nu}_{ST}$ and the destabilisation energy, E_{dest} (defined as $E_{dest} \cong h\tilde{\nu}^{A}_{max} - h\tilde{\nu}^{F}_{max}$ [21]) are changed. Analysing respective the data collected in Table I it follows that: for the amino substituted derivatives (**3** and **4**) significantly increase of the $\Delta\tilde{\nu}^{FL}_{1/2}$, $\Delta\tilde{\nu}_{ST}$ and E_{dest} values, in comparison to that of fluorene is noted. Changing the solvents from non-polar to polar-protic one, in the case of molecules **3** and **4** the negative solvatochromic effect is observed. This finding can be explained by the fact that the amino substituent in the studied derivatives acts as the proton acceptor for the alcohol molecules.

Table I. Values of the Long Wavelength Absorption, λ_{max}^{Ab}[cm^{-1}] and Fluorescence λ_{max}^{FL} [cm^{-1}] Band Maxima, Destabilization Energy, E_{dest} (eV), Stokes Shift $\Delta\tilde{\nu}_{ST}$ [cm^{-1}] and Full Width at Half Maximum $\Delta\tilde{\nu}_{1/2}^{FL}$ [cm^{-1}] of Fluorene and Studied Derivatives in Various Solvent

Solvent	FL	9Ph9FOL	2NMe$_2$9FOL	2NEt$_2$9FOL
McH				
λ_{max}^{Ab}	33,230	32,180	31,780	30,950
λ_{max}^{FL}	33,000	31,860	25,700	25,510
$\Delta\tilde{\nu}_{ST}$	230	320	6080	5440
E_{dest}	0.03	0.05	0.76	0.72
$\Delta\tilde{\nu}_{1/2}^{FL}$	2600	2650	3500	3400
ThF				
λ_{max}^{Ab}	33,290	32,180	31,670	31,030
λ_{max}^{FL}	32,820	31,650	26,850	25,830
$\Delta\tilde{\nu}_{ST}$	470	530	4820	5200
E_{dest}	0.04	0.05	0.59	0.66
$\Delta\tilde{\nu}_{1/2}^{FL}$	2730	2510	3090	3920
EtOH				
λ_{max}^{Ab}	33,330	32,360	31,830	31,150
λ_{max}^{FL}	33,020	31,640	26,960	26,450
$\Delta\tilde{\nu}_{ST}$	310	720	4870	4700
E_{dest}	0.04	0.09	0.60	0.58
$\Delta\tilde{\nu}_{1/2}^{FL}$	2700	4270	2640	2500

Unlike of the rest of the fluorene derivatives for 2NMe$_2$9FOL and 2NEt$_2$9FOL in EtOH, MeOH and ThF the fluorescence band maximum is blue shifted according to McH and the other non polar solvents (not shown on Fig. 2). Also, the $\Delta\tilde{\nu}_{ST}$, E_{dest} and $\Delta\tilde{\nu}_{1/2}^{FL}$ values (see Table I) are smaller for these derivatives in EtOH than in McH. This unusual fluorescence behaviour has been studied in detail performing additional measurements; e.g., fluorescence spectra measurement in binary mixed solvents, McH/EtOH and EtOH/McH and total emission (fluorescence and phosphorescence) in McH and EtOH obtained at 77 K.

The Fig. 3 shows the emission spectrum of 2NEt$_2$9FOL in McH/EtOH mixtures for different molar fraction χ_p of EtOH under excitation at $\lambda_{exc} = 325$ nm. As we can see, the contents of EtOH in McH increase the fluorescence band position and shape changes. Increasing the EtOH concentration in McH the $\Delta\tilde{\nu}_{1/2}^{FL}$ value, first increases the reading of the maximum value and then decreases to the value given for the neat solvent EtOH (see the insert in Fig. 3). This behaviour indicates that the fluorescence spectrum of binary solution consists of two different luminescence centres, e.g., solvates preserving different stechiometric composition of EtOH and McH in the surrounding of the luminescence molecule. The second obvious observed feature is the hipsochrmic shift of the fluorescence band whose value depends on the molar fraction of EtOH. This anomalous shift in protic solvents (MeOH and EtOH) shows that in the S_0 state a specific association is dominated by the weak hydrogen bond. Similar to other amines, the short-wavelength band of the

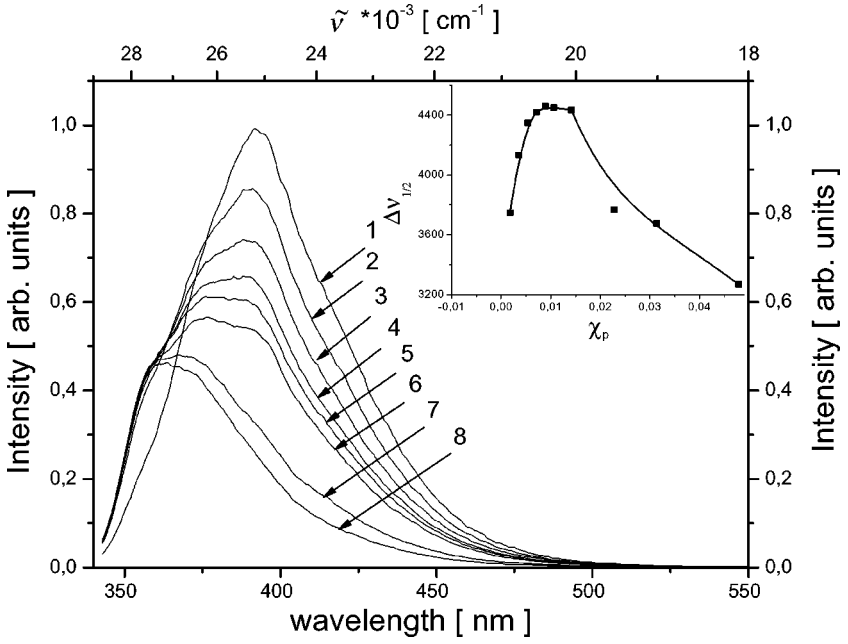

Fig. 3. Fluorescence spectrum of 2-diethlamino-9-fluorenol in binary mixed solvents (McH/EtOH) at 293 K obtained for different molar fraction $\chi_p = 0{,}002$ (1), $\chi_p = 0{,}004$ (2), $\chi_p = 0{,}005$ (3), $\chi_p = 0{,}007$ (4), $\chi_p = 0{,}009$ (5), $\chi_p = 0{,}02$ (6), $\chi_p = 0{,}05$ (7), EtOH(8).

absorption spectrum becomes blue-shifted in EtOH, indicating that the amino group is acting as a proton acceptor in the S_0 state [22]. In the excited state S_1, the hydrogen bond breaks down and the emission appears from the non-associated molecule. It means that in the ground state we have a highly dipolar complex, alcohol-solute molecule, with almost whole negative charge on the oxygen atom in position 9 of the fluorene skeleton. The non-bonding *n* electrons of the nitrogen atom in the amino group take weighing part in the formation of a hydrogen bond. In the S_1 state this weak hydrogen bond is broken and as a result we get a smaller dipole moment in the excited state. In the literature [23] this effect is known as the negative solvatochromism caused by a highly dipolar zwitterionic form of the solute molecule in the ground state and a less dipolar one in the S_1 state.

To confirm the above assumption we calculated the steady dipole moments of the ground S_0 state of **3** and **4** molecules using the standard PM3 and AM1 method (Cache WS 5.04 Program). In order to calculated the μ values the necessary optimisation of the geometrical structure for the zwitterionic ($2NMe_2 9FOL \cdots EtOH$ or $2NEt_2 9FOL \cdots EtOH$) and for the free molecule ($2NMe_2 9FOL$ and $2NEt_2 9FOL$) has been employed. Table II shows the computed dipole moments for this two system in vacuum and in a solvent. On analysing data collected in Table II for which the dielectric constant $\varepsilon \approx 24$ (for EtOH) it is evident that for $2NEt_2 9FOL \cdots EtOH$ solute possesses μ_{zw} value which is almost doubly higher than for free molecule μ_f. Such clear evidence is not shown for 3 molecule for which only PM3 calculation gives satisfied results $\mu_{zw} > \mu_f$. On the other hand we find out that the partial charge on key atoms is changing. The calculation made with PM3 method shows that on the nitrogen atom the charge decreases after creating hydrogen bond about 25 procent and on the oxygen atom we noted a slight increase of the negative charge. The above results confirm our suspicion that the **3** and **4** molecules in protic solvents form zwitterionic form in the ground state.

Table II. Dipole Moments of the Zwitterionic Form μ_{zw} and Free Molecule μ_f (in Debye) for **3** and **4**

	2NMe$_2$9FOL		2NEt$_2$9FOL	
Method	μ_{zw}	μ_f	μ_{zw}	μ_f
AM1				
Vacuum	2.20	2.30	4.10	2.30
EtOH	2.70	2.70	4.60	2.70
PM3				
Vacuum	1.90	1.80	3.40	1.90
EtOH	2.30	2.00	3.90	2.20

Emission at 77 K

Fig. 4 shows the total luminescence spectra (fluorescence and phosphorescence) for 2NMe$_2$9FOL and 2NEt$_2$9FOL in McH and EtOH at 293 and 77 K. Comparing those obtained at 77 K we see that the fluorescence spectra are similar and follow that obtained in McH at room temperature. A hipsochromic shift and decrease of the $\Delta\tilde{\nu}_{1/2}^{FL}$ value is noted for alcohol solvents only. This indicates that a zwitterionic form of the two molecules exist only at room temperature (EtOH) in the ground state giving the negative solvatochromic shift. At 77 K the band position of the luminescence spectrum, λ_{max} and $\Delta\tilde{\nu}_{1/2}^{FL}$ values are the same for these two amino derivatives. These two molecules exhibits structured phosphorescence (see the insert in Fig. 4). The experimentally obtained energy of triplet state T_1 equals 21,110 and 21,270 cm^{-1} for **3** and **4** molecule respectively. When changing the solvent from non-polar McH to polar EtOH there is no drastic changed in position and shape of the posphorescence spectra. In Table III we placed the determined phosphorescence decay time τ_{Ph} and calculated phosphorescence quantum yields Φ_{Ph}. As it follows analysing the data of Table III τ_{Ph}value equals about 1-s for both molecule amino derivatives indicates that the lowest triplet state has ($\pi\pi^*$) nature. Also, determined quantum yields of phosphorescence show that their values are smaller than for fluorene.

Fluorescence Decay Time

The fluorescence decay time determined for the molecules under study in EtOH, ThF and McH solvents detecting the fluorescence light at the band maximum. The data obtained are compiled in Table III. The fluorescence decays of compounds **1**–**4** are well characterised by a single exponential fit with a good $\chi^2 \approx 0,96$–$1,17$ and autocorrelation function values. We see that the τ_F data depends on the substituent. In all solvents the fluorescence decay time of the fluorene derivatives are shorter from that of the parent molecule. The fluorescence decay time of fluorene obtained by us is in good agreement with the literature value [18]. In the case of 9-hydroxyl-9-phenylfluorene a drasting decrease of τ_F value (in comparison) is noted (see Table III) in contrary to that of 9-phenylfluorene ($\tau_F = 5{,}1$ ns) [19]. This result suggests that the OH substituent is mainly responsible for the τ_F decrease of 9Ph9FOL fluorescence. The amino substituents of 9-hydroxy-9-fluorenol increase the τ_F value by about 3 ns according to FL. The data collected in Table III show

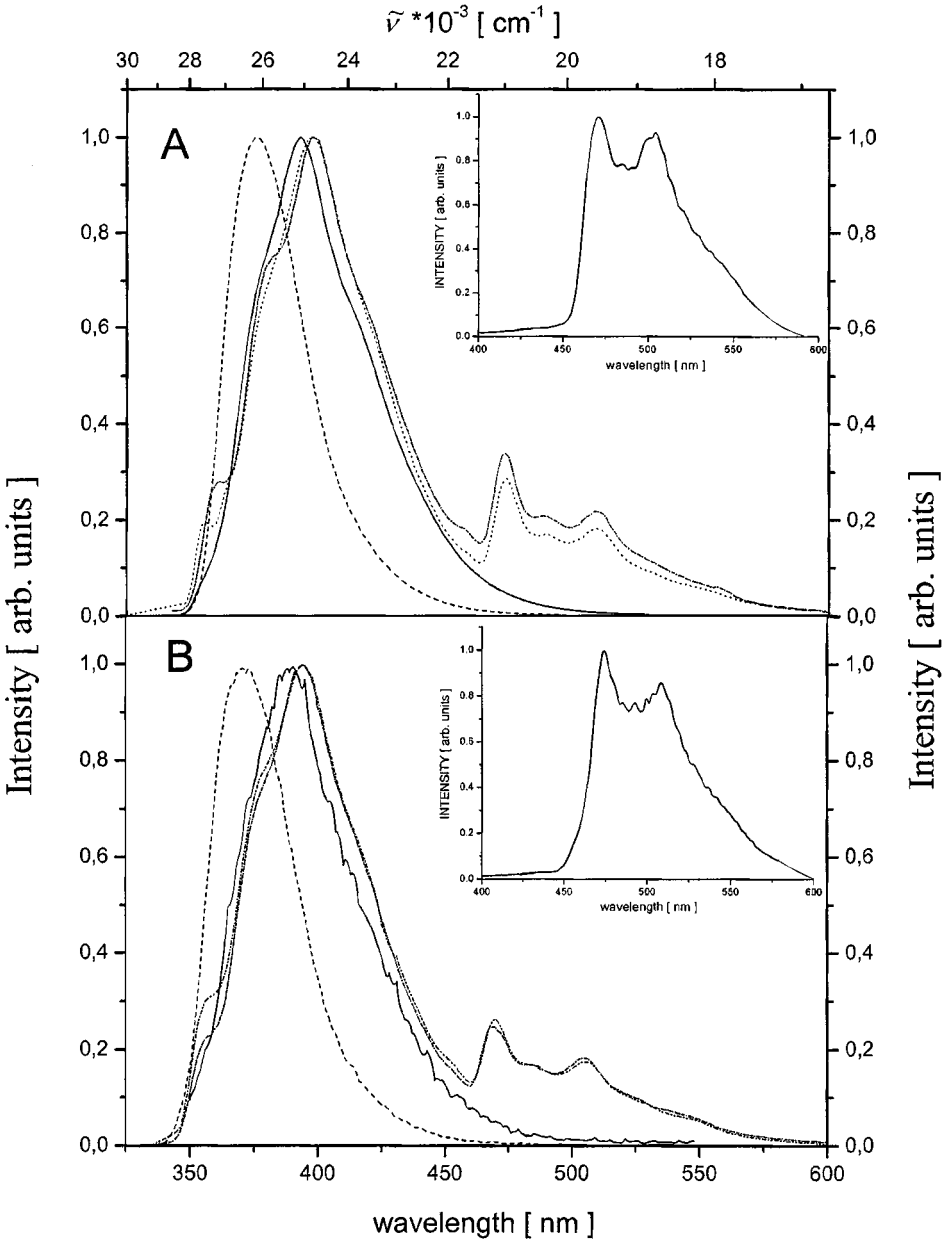

Fig. 4. Luminescence spectrum of 2-diethylamino-9-fluorenol (A) and 2-dimethylamino-9-fluorenol (B) in McH at 293 K (——) and 77 K (.....) and in EtOH at 293 K (-----) and at 77 K (------). The insert consist the pure phosphorescence spectrum obtained on McH.

that the fluorescence decay time for **1**, **3** and **4** molecules increase as the solvent polarity increases whereas the τ_F of 9Ph9FOL decreases.

Radiative and Radiativelesse Rate Constants

Making use of the experimentally determined τ_F, τ_{Ph} and Φ_F, Φ_{Ph} values of the compounds under study the radiative (k_F) and non-radiative (k_{NR} and k_{ISC}) decay rate constants are calculated using the following forms [19] :

$$k_F = \Phi_F/\tau_F \quad (2)$$

$$k_{NR} = \frac{1}{\tau_F} - k_F \quad (3)$$

Table III. Values of Quantum Yields (Φ_F and Φ_{Ph}), Fluorescence, and Phosphorescence Decay Time (τ_F and τ_{Ph}), the Radiative, (k_F and k_{Ph}), Nonradiative (k_{NR} and k_{ISC}), Rate Constants of the Molecules Under Study in McH and EtOH

Compounds	Φ_F	Φ_{Ph}	τ_F (ns)	τ_{Ph} (s)	k_F (10^8 s^{-1})	k_{Ph} (s^{-1})	k_{NR} (10^8 s^{-1})	k_{ISC} (10^8 s^{-1})
FL								
McH	0.58	0.31	4.48	5.47	1.29	0.13	0.94	0.69
EtOH	0.51	0.15	4.96	5.0*	1.03	0.06	0.99	0.30
9Ph9FOL								
McH	0.08	0.44	0.77	0.69	1.09	0.69	11.89	5.71
EtOH	0.05	0.01	0.10	0.95	1.5	0.01	98.54	0.30
$2NMe_2$9FOL								
McH	0.11	0.05	3.31	1.08	0.32	0.05	2.70	0.15
EtOH	0.03	0.03	3.85	0.89	0.06	0.03	2.53	0.08
$2NEt_2$9FOL								
McH	0.11	0.03	3.34	1.00	0.32	0.03	2.68	0.09
EtOH	0.07	0.06	3.67	1.29	0.18	0.05	2.54	0.16

*[25]

$$k_{ISC} = k_F \frac{(1 - \Phi_F)}{\Phi_{Ph}} \quad (4)$$

In Table III calculated rate constants are collected which reveal how the environment and molecular structure affect the competition between the various energy dissipation channels. It is obvious that changing solvents from polar EtOH to non polar McH there is no drastic changed in the rate constant values noted an except constitute molecule **2**. As it follows when analysing the assembled data the non-radiative rate constants follow the inequality $k_{NR} > k_F$ for all derivatives except fluorene for which k_F and k_{NR} are comparable. For amino derivatives of fluorene the k_{NR} is two order of magnitude higher than for k_F in EtOH and one order in McH. An explanation of these findings is due to the fact that the flexibility of molecules in the excited states increases the non-radiative decay process. On the other hand the amino substituents of fluorene increase the $S_1 \rightarrow T_n$ energy gap decreasing the intersystem crossing k_{ISC} constant. An addition the electron donating dimethylamino group makes $S_1 \rightarrow T_n$ transition more endothermic which cause the deceleration of the triplet formation [24]. It is interesting to note that for molecule **2** we observed a particular increase of k_{ISC} in McH in accordance with EtOH and it is followed by connecting with an increase of non-radiative constant k_{NR} in both solutions in opposition to other molecule.

CONCLUSIONS

The performed spectroscopic studies of compounds under study confirm that:

- In binary mixed solvents, e.g., McH/EtOH the $2NMe_2$9FOL and $2NEt_2$9FOL molecules show a negative solvatochromic shift of the fluorescence spectrum. Its appearance is understandable under the assumption that these molecules in alcoholic solvents appear in the zwitterionic form in the ground state S_0 in which they possess a large dipole moment.
- The amino substituents of fluorene cause the batochromic shift of the absorption and emission spectra and large broadening of the both spectra.
- The hydroxy substituent at 9 position of fluorene (molecule **2**) causes a strong decrease of the quantum yields and fluorescence decay time (about 7 times).
- In all cases except the fluorene, non-radiative process k_{NR} dominates over the radiative process k_F.
- Because of the fact that amino derivatives of fluorene exhibit a negative solvatochromism, they can be used as a probe to characterise biological system.

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