Spectroscopic Studies of Dimethylamino Derivatives of Fluorene

J. Heldt[a], J. R. Heldt[a], T. Redzimski[a], H. Diehl[b], and P. Schultz[b]

[a] Institute of Experimental Physics, University of Gdańsk, 80-952 Gdańsk, Poland
[b] Fachbereich Physik und Chemie, Universität Bremen, Bremen, Deutschland

Reprint requests to Dr. Janina H.; Fax: (058) 341-31-75; E-mail: fizjh@paula.univ.gda.pl

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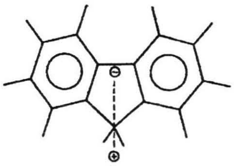
2-dimethylamino-9-fluorenol and 2-dimethylamino-9(4'dimethylamino)phenyl-9-fluorenol in polar solvents in the excited state undergo conformation changes in which two fluorescent isomers are created. The isomers (in the local excited (LE) and charge transfer (CT) configuration) possess separate fluorescence bands, one appearing from the S_1 (LE) state and the second from the intramolecular charge transfer state S_1 (CT) of the neutral, aromatic molecule. Both bands show a solvatochromic effect. Using the method of the solvent induced Stokes shift of the absorption and fluorescence spectra the permanent dipole moment of the excited state of fluorene and its two derivatives have been determined. The dipole moment of the ground state and the Onsager cavity radius of the studied molecules were calculated with the Auestion Model 1 (AM1) program.

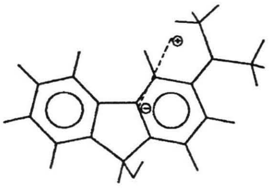
Key words: Isomer; Dual Fluoescence; Solvatochromic Effect; Charge Transfer.

1. Introduction

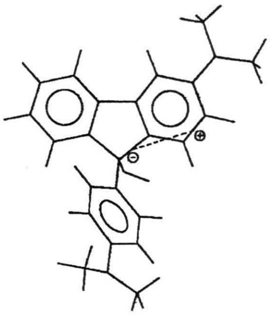
FLUORENE
(1)



2-DIMETHYLAMINO-
9-FLUORENOL
(2)



9-(4'-DIMETHYLAMINO) PHENYL
2-DIMETHYLAMINO-9-FLUORENOL
(3)



Fluorene belongs to organic compounds whose spectroscopic and photophysical properties were often examined [1 - 4]. It has been shown that the compact chemical ring-structure associated with the bridge joining >CH_2 group increases the fluorescence efficiency in comparison to biphenyl. This atomic compactness induces a rigidity and coplanarity of the molecule as whole, which is absent in molecules parts of which may vibrate with respect to each other. A special group of fluorene derivatives are the polynitro-9-fluorenones and polynitro-9-fluorenes whose ability to form charge-transfer complexes is widely used to sensitise the photoconductivity of carbazole-containing polymers [5]. For those systems fluorene is the most widely known acceptor of π-electrons. Derivatives of fluorene in which a hydrogen atom is substituted by a donor group, e. g. dimethylamine (-NMe_2) or hydroxy (-OH), or an acceptor, e. g. amino (-NO_2), show spectroscopic properties which are modified in a complex manner [3, 6]. Up to now, the performed studies concern mainly measurements of absorption spectra. It is known [2] that aromatic molecules which contain both electron donor and acceptor moieties in the excited state often undergo an isomerization in which the donor moiety twists with respect to the acceptor. The fluorescence spectrum of a compound exhibiting these features, named twisted intramolecular charge transfer (TICT), generally exhibits strong solvatochromaticity, which is attributed to the existence of two fluorescent isomers, one being in the locally excited (LE) and the

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Table 1. The absorption and fluorescence band maxima (in nm and cm^{-1}) of the molecules under study, determined in various solvents.

		Fluorene (FL)		2-dimethylamino-9-fluorenol (**2**)			2-dimethylamino-9(4'dimethylamino)-phenyl-9-fluorenol (**3**)		
Solvent	$f(n,\varepsilon)$	$\lambda_A/\tilde{\nu}_A$	$\lambda_F/\tilde{\nu}_F$	$\lambda_A/\tilde{\nu}_A$	$\lambda_F/\tilde{\nu}_F$	$\lambda_{CT}/\tilde{\nu}_{CT}$	$\lambda_A/\tilde{\nu}_A$	$\lambda_F/\tilde{\nu}_F$	$\lambda_{CT}/\tilde{\nu}_{CT}$
1. MCH	–0.001	300.0	315.7	315.0	389.0		335.0	375.0	
		33330	31675	33746	25706		29851	26667	
2. CH	0.001	300.0	315.0	315.0	388.0			380.0	
		33330	31746	31746	25773			26316	
3. 1,3 ClB	0.124	302.0	324.0	325.0	385.0	460	340.0	405.0	512.0
		33112	30864	30769	25974	21740	29412	24691	19531
4. Chf	0.157	301.0	317.5	310.0	380.0	510	340.0	407.0	517.0
		33222	31496	32258	26315	19608	29412	24546	19331
5. 1,2 ClB	0.186	302.0	320.0	324.0	385.0	466	345.0	411.0	518.0
		33112	31250	30864	25974	21740	28986	24331	19305
6. EtA	0.201	300.0	316.0	316.0	375.0	450	326.0	399.0	520.0
		333333	31645	3164	26667	22222	30675	25062	19230
7. ClMt	0.218						346.2	402.6	524.1
							28877	24839	19081
8. EtOH	0.290						338.8	403.6	
							29508	24770	
9. MeOH	0.308	299.0	314.7	310.0	375.0		337.5	420.0	
		33449	31776	32258	26667		29630	23810	
10. AcN	0.305	299.0	313.9	316.0	375.0	490	344.4	420.0	527.0
		33449	31857	31645	26667	20408	29036	23810	18975

second in the charge transfer (CT or TICT) configuration [7, 8].

In this paper we report results of competitive dual fluorescence of two newly synthesised derivatives of fluorene (FL), i. e. 2-dimethylamino-9-fluorenol (**2**) and 2-dimethylamino-9-(4'dimethylamino)phenyl-9-fluorenol (**3**). By steady state spectroscopic measurements we show that in some solvents the fluorescence spectrum consists of two bands which are attributed to the existence of two fluorescent isomers, i. e. one being in the LE and the other in the CT configuration. The spectroscopic data obtained from the solvent induced shift of the absorption and fluorescence bands are used to determine the permanent dipole moments of the parent molecule and derivatives of both isomers in the excited S_1 (LE) and S_1 (CT) states. Chart 1 presents the molecular structures of the compounds under study. The data of the fluorene measurements are used for comparison purposes only.

2. Experimental Details

The compounds under study were recrystallized from methanol before used. Fluorene (FL) was obtained from Aldrich Chemical Co. The compounds **2** and **3**, synthesised by one of us, were used without additional purification. The solvents: cyclohexane (CH), methylcyclohexane (MCH), chloroform (Chf), 1,3-dichlorobenzene (1,3 ClB), 1,2-dichlorobenzene (1,2 ClB), ethyl acetate (EtA), methylene chloride (MlCl) were of spectroscopic grade. They were checked for background emission before use.

The absorption spectra were measured on a Shimadzu UV-2401PC spectrophotometer. Steady-state fluorescence measurements (excitation and emission spectra) were carried out with a Shimadzu RF-5301 spectrofluorometer equipped with a photomultiplier tube Hamamatsu R-928. In the presented fluorescence spectra the spectral sensitivity of the photomultiplier tube has been taken into consideration.

3. Results and Discussion

3.1. Absorption and Fluorescence Spectra

Figure 1a shows the absorption spectra of the molecules under study dissolved in CH at room temperature. The spectrum of FL in the region of 200 - 310 nm has three distinct bands: a strong band around, 200 - 230 nm ($\varepsilon_{max} \cong 40\,000$ $M^{-1}cm^{-1}$), a weaker one in the region 230 - 290 nm ($\varepsilon_{max} \cong 20\,000$ $M^{-1}cm^{-1}$) and a weak vibrational structured band in the region 270 - 310 nm ($\varepsilon_{max} \cong 10\,000$ $M^{-1}cm^{-1}$). The shape is similar to that given in the literature [7, 8]. The λ_{max}

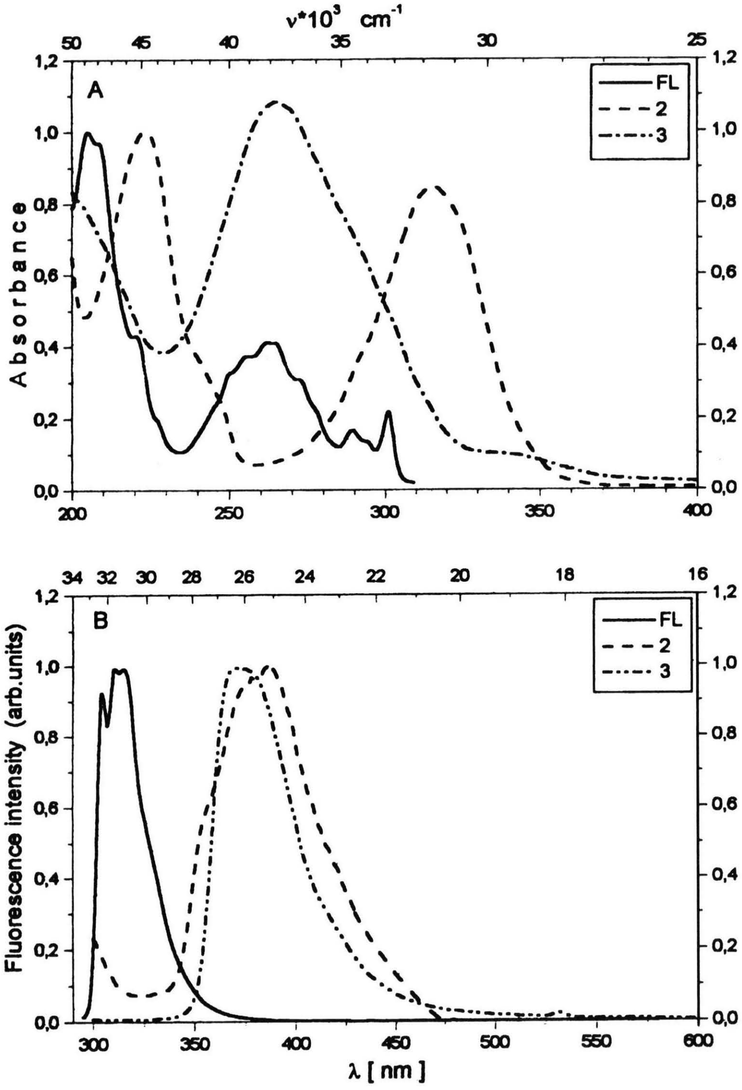

Fig. 1. Absorption (A) and fluorescence (B) spectra of studied molecules in CH, $c = 5 \cdot 10^{-4}$ M.

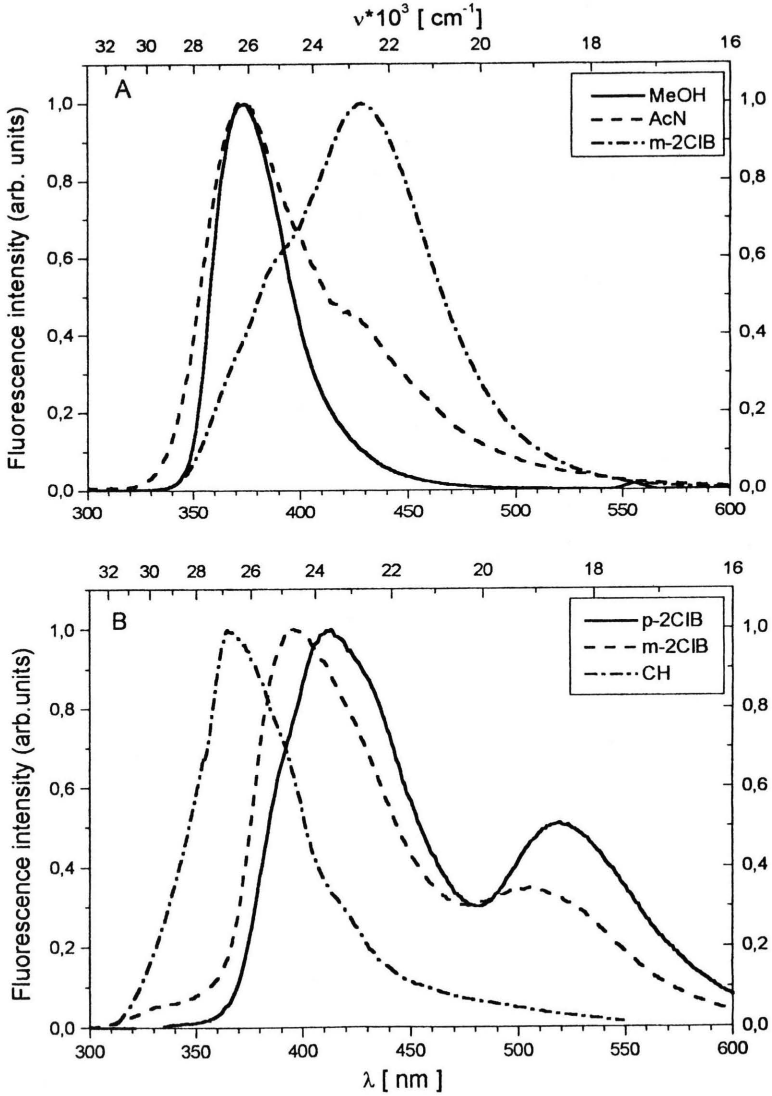

Fig. 2. The fluorescence spectra of molecule **2** (A) and **3** (B) in various solvents.

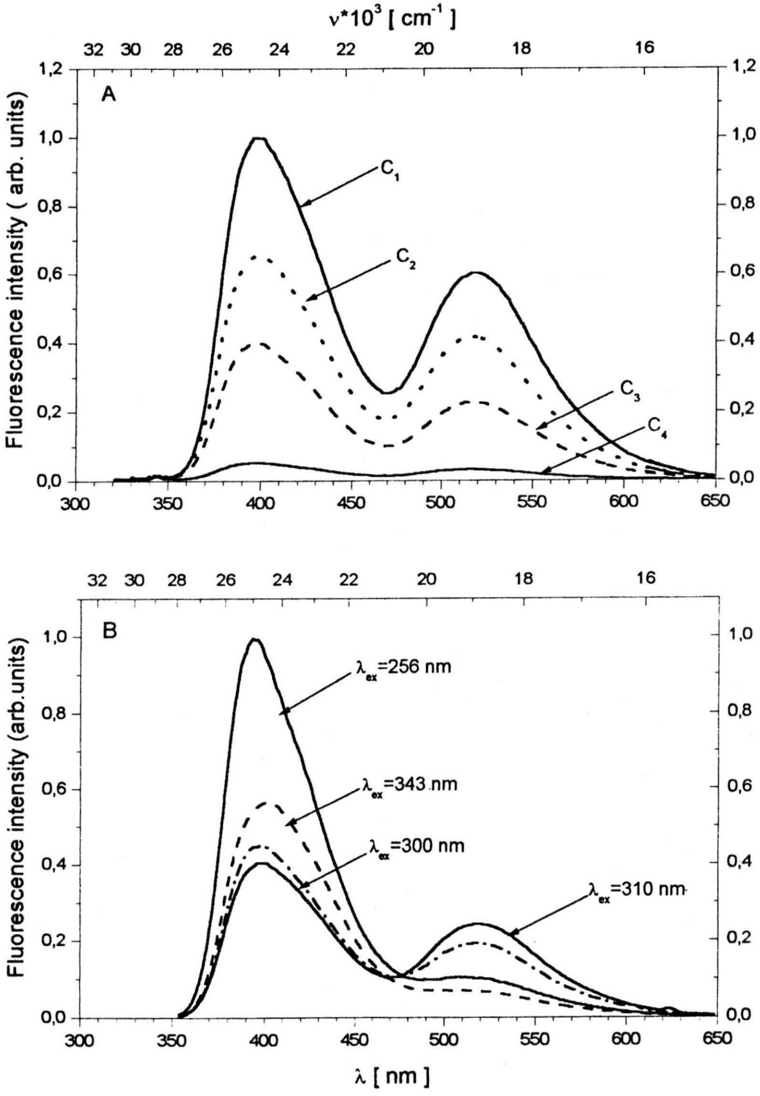

Fig. 3. The fluorescence spectra of molecule **3** obtained in ethyl acetate for different concentrations (A) ($c_1 > c_2 > c_3 > c_4$) and for different excitation wave lengths (B).

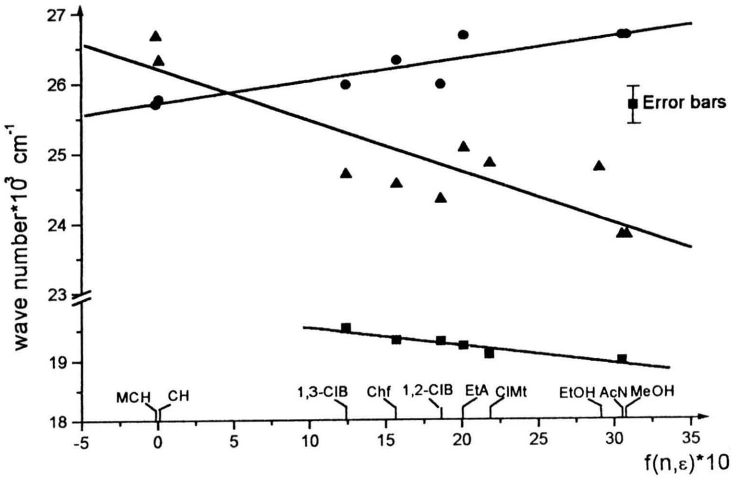

Fig. 4. The $\tilde{\nu}$ [cm^{-1}] values of the fluorescence band maxima of molecules **2** (●: $\tilde{\nu}_{2F}$) and **3** (■: $\tilde{\nu}_{3CT}$; ▲:$\tilde{\nu}_{3F}$) *versus* the Lippert polarizability function $f(n, \varepsilon)$ of the solvents used.

Table 2. The Onsager cavity radius $a$dw0 and the permanent dipole moment of the ground, μ_g and excited, μ_{S_1} states of the studied molecules.

Compound	a_0 / 10^{-8} cm	μ_{S_0} / D	$\mu_{S_1(LE)}$ / D
Fluorene (FL)	1.88	0.37	0.61
		0.62[a]	0.86*
2-dimethylamino-9-fluorenol (**2**)	2.50	3.00	> 3.00
2-dimethylamino-9(4'dimethylamino)-phenyl-9-fluorenol (**3**)	3.86	3.15	9.21

[a] experimental value obtained by V. Baliah and M. K. Pillay [14].

* calculated using μ_g = 0.62 D [14].

values of the bands depend on the solvent, whereas their shape remains generally unchanged.

The absorption spectrum of the molecule **2** and **3** shows big differences in the shape as well as in the band positions in comparison to that of fluorene (see Fig. 1a). Molecule **2** possesses two bands only: one in the short wave length region (200 - 255 nm) with $\lambda_{max} \cong 225$ nm and the second in the region 250 - 360 nm with $\lambda_{max} \cong 315$ nm. Its molar extinction coefficients are comparable and are in the 30 000 $M^{-1}cm^{-1}$ range.

The absorption spectrum of **3** differs from those of FL and **2**. It shows a very intensive band at $\lambda_{max} \cong 265$ nm ($\varepsilon_{max} \cong 40000\ M^{-1}cm^{-1}$) and very weak, broad and displaced of vibrational band in the region 290 - 370 nm. In comparison to the absorption spectrum of fluorene the weak broad band reflects the longer wave length part only. The bands at $\lambda_{max} = 265$ nm and about 350 nm correspond to respective bands of the parent molecule, being shifted to the red by 15 nm and 60 nm, respectively. Its smooth shape, composed of vibrational peaks, results from the appearance of low frequency vibrational motions of the -NMe_2 and -phenyl substituents.

The fluorescence spectra of the compounds under study obtained in non-polar solvents consist of one band which corresponds to the fluorescence of the isomer being in the S_1 (LE) state (see Fig. 1b). The half width of the $S_1(LE) \rightarrow S_0$ band equals to $\sim 4400\ cm^{-1}$ and $3100\ cm^{-1}$ for **2** and **3**, respectively. The $\Delta\tilde{\nu}_{1/2}$ values are larger from those of fluorene $\Delta\tilde{\nu}_{1/2} \cong 2600\ cm^{-1}$). The fluorescence spectrum of both molecules are shifted to larger wavelength in comparison to fluorene by the same amount, i. e. $\tilde{\nu}_{FL} - \tilde{\nu}_2 = \tilde{\nu}_{FL} - \tilde{\nu}_3 \cong 5400\ cm^{-1}$. In the calculations the center gravity the of gravity of the fluorescence band is take into consideration. Additionally, the emission spectrum of **2** shows some characteristics of a more complex spectrum, e. g. bending in the short wavelength wing pointing to a vibrational structure. Taking into consideration the above findings, we can state that the steric hindrances of the 9(4'-dimethylamino)phenyl substituent with the main skeleton minimise mutual conjugation, indicating that the 2-dimethylaminofluorene moiety is responsible for the LE emission.

The fluorescence spectra of **2** and **3** in polar non protic solvents distinctly differ from those described above (see Figure 2 and 3). In most solvents they possess two fluorescence bands: one attributed to the emission from the S_1(LE) state and the second ascribed to the emission of an isomer in which the charge transfer phenomenon took place [9, 10]. The wave length maxima of the two bands are given in Table 1.

Analysing the assembled data and the spectra shown in Figs. 2 and 3 it results, that:

- the fluorescence spectra of **2** and **3** in weak polar non protic solvents possess two emission bands assigned to the transitions $S_1(LE) \rightarrow S_0$ and $S_1(CT) \rightarrow S_0(FC)$, which belong to the two isomers,
- the difference of the fluorescence band maxima $\Delta\tilde{\nu} = \tilde{\nu}_{max}(LE) - \tilde{\nu}_{max}(CT)$ for the molecule **3** is by about $1000\ cm^{-1}$ larger than that noticed for **2**. The $\tilde{\nu}_{max}(LE)$ and $\tilde{\nu}_{max}(CT)$ values depend on the solvent.
- the fluorescence band maxima $\tilde{\nu}_{max}(LE)$ and $\tilde{\nu}_{max}(CT)$ show a linear dependence on the Lippert solvent function $f(n, \varepsilon)$ (see Figure 4),
- the intensity ratio of the two emission bands, e. g $J_F(LE) / J_F(CT)$ depends on the solvent and excitation wave length and does not depend on the solute concentration if c is changed in the range $5 \cdot 10^{-3}$ - $5 \cdot 10^{-5}$ M (see Figure 3).

4. Solvent Effects

Generally, the solvents influence the properties of fluorescent compounds in two ways: firstly they cause solvent induced shifts of the absorption and normal fluorescence spectra, secondly they create a new emission band which is attributed to a fluorescent isomer of the compound being in CT configuration. Thus, the fluorescence spectrum of both derivatives in polar solvents exhibit a second band which is attributed to the emission of the CT isomer. The intensity of the CT band depends on the solvent and excitation wave length (see Figure 3). In polar solvents the CT state of the molecule is stabilised via dipole-dipole interactions between the solute and solvent molecules [11]. The stabilisation energy depends on the dipole moment μ_{CT} of the CT-state and the solvent polarity. Usually the dipole moment μ_{LE} of the molecule in the S_1(LE) state is smaller than that of μ_{CT}. As can be deducted from Table 1, the difference of the fluorescence band maxima $\Delta\tilde{\nu} = \tilde{\nu}_{max}(LE) - \tilde{\nu}_{max}(CT)$ is a constant (within the error bar of its determination) and equals $4300\ cm^{-1}$ and $5300\ cm^{-1}$ for **2** and **3**, respectively. The band maximum, $\tilde{\nu}_{max}(CT)$, depends only weakly on the solvent polarity function $f(n, \varepsilon)$. This shows that the permanent dipole moment of the

CT isomer in the excited state differs not much from that of the equilibrated ground state value.

The position of the LE fluorescence band maximum of both compounds in various solvents shows small wavelength differences. This shows that for the LE emission in **2** and **3** the same molecular moiety is responsible, i. e. the 2-dimethylaminofluorene. This means that the 9-substituents interact only weakly with the main skeleton of the molecules.

According to Ooshika, McRae, Lippert, and Mataga [11], and Bilot and Kawski [12] the solvatochromic shift of the absorption and fluorescence band maxima is given by the expression

$$\tilde{\nu}_{\max}(\mathrm{A}) - \tilde{\nu}_{\max}(\mathrm{LE}) = \frac{2(\mu_{\mathrm{ex}} - \mu_{\mathrm{g}})^2}{cha_0^3} f(n, \varepsilon), \qquad (1)$$

$$f(n, \varepsilon) = \frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{2n^2 + 1},$$

where μ_{ex}, μ_{g} are the permanent dipole moments of the LE fluorescent and ground states of the solute, $\tilde{\nu}_{\max}(\mathrm{A})$ and $\tilde{\nu}_{\max}(\mathrm{LE})$ are the absorption and LE fluorescence band maxima, a_0 is the effective radius of the Onsager cavity [13] and ε and n are the static dielectric constant and the refractive index of the solvent, respectively. For fluorene and the two new molecules the respective data of $f(n, \varepsilon)$, $\tilde{\nu}_{\max}(\mathrm{A})$, and $\tilde{\nu}_{\max}(\mathrm{LE})$ are collected in Table 1. They show a satisfying linear correlation between the $\tilde{\nu}_{\max}(\mathrm{A}) - \tilde{\nu}_{\max}(\mathrm{LE})$ values and the solvent polarity function $f(n, \varepsilon)$ (see Fig. 4, correlation coefficient $0.80 \leq r \leq 0.92$). Using the slope value of the $\tilde{\nu}_{\max}(\mathrm{A}) - \tilde{\nu}_{\max}(\mathrm{LE})$ *vs.* $f(n, \varepsilon)$ dependence and the a_0 and μ_{g} data of these molecules, the excited state S_1(LE) dipole moments, calculated with the AM1 method and the Hyperchem program, have been determined. The obtained data are listed in Table 2. For fluorene the μ_{g} value calculated by us differs from that experimentally determined [14]. Thus, for the S_1(LE) state of fluorene two μ_{ex} values are given in the last column of Table 2 respective to the ground state data. The uncertainty of the determined μ_{ex} data is large (± 1 D). The error is mainly caused by the approximations made in the calculations of the a_0, μ_{g} data and in the uncertainties of the $\tilde{\nu}_{\max}(\mathrm{A}) - \tilde{\nu}_{\max}(\mathrm{LE})$ determination. Further studies of the solvent effects are needed in order to determine the μ_{ex}(LE) and μ_{ex}(CT) values of the molecules with better accuracy.

5. Conclusions

The results of the steady state spectroscopic measurement of the new synthesised derivatives of fluorene allow to confirm that, due to the electron donating substitutents, -$\mathrm{NMe_2}$ and -OH, the lowest energy excited state of **3** shows a considerable charge-transfer character. Its dipole moment increases by about 6 D. Such large change in the dipole moment is not noticed for molecule **2**. We suppose that it is caused by a difference in the interaction of the -9-hydroxy substituent with the π electrons of fluorene skeleton of both derivatives. In **3** the steric hindrances of the 9(4'-dimethylamino)phenyl-9-hydroxy substituent eliminate any interaction between the two moieties whereas in **2** the fluorescence spectra point its presence.

Fluorescence quantum yield and decay time measurements of these molecules will give a better knowledge of the radiation and excited state electron transfer processes.

Acknowledgement

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