Evidences of Conformational Fluctuations of 2-methylaminofluorenone and 2-dimethylaminofluorenone in Polar Solvents

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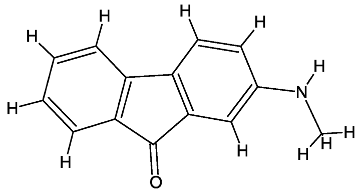
The absorption and fluorescence spectra of 2-methylaminofluorenone (2MAFl) and 2-dimethylaminofluorenone (2DMAFl) were determined at 293 K in a variety of solvents with different polarities. The spectral data were used, in combination with the 2MAFl and 2DMAFl ground state dipole moment (μ_g), to evaluate μ_e of the S_1 state, to determine the outer-sphere solvent reorganization energy λ_{outer}, and the intramolecular reorganization energies: λ_i^* (associated with vibrations for which $h\nu < kT$) and $\lambda_i(h\nu > kT)$. At 77 K the fluorescence spectra in a non-polar solvent are shifted to longer wavelengths. In polar solvents, for both molecules the behavior is opposite. The fluorescence decay data for 2MAFl and 2DMAFl in non-polar solvents are very well fitted by one-exponential functions, while in polar solvents by two-exponential functions. The spectroscopic data distinctly show that both studied molecules in polar solvents form an inhomogeneous emitting system.

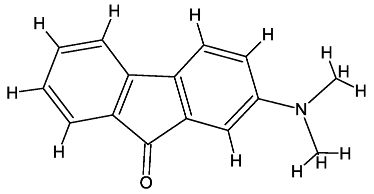
Key words: 2-methylaminofluorenone; 2-dimethylaminofluorenone; Inhomogeneous Broadening; Reorganization Energy.

1. Introduction

Amino substituted derivatives of fluorenone have been studied in several spectroscopic papers [1 – 6]. Particular attention has been paid to their intramolecular charge-transfer capability appearing between the amino group (the electron-donating part) and carbonyl group (the electron-accepting part). Furthermore, it has been shown that the carbonyl group in these molecules behaves as a strong hydrogen-bond acceptor, and that alcohol solutions cause fluorescence quenching. The amino substitutes of fluorenone often increase the probability of radiationless deactivation [3 – 5] and exert a profound influence on the solvatochromic properties. In l-dimethylaminofluorenone, photoinduced charge-transfer (PICT) occurs between the donor (dimethylamino) and acceptor (fluorenone) moieties [1 – 2]. This indicates that these molecules, dissolved in viscous solutions, present an inhomogeneous spectral system where a conformational relaxation phenomenon of the –N(CH_3)$_2$ group takes place. Such peculiarities show that the studied molecules possess interesting photophysical properties [7 – 10].



2-methylaminofluorenone (2MAFl)



2-dimethylaminofluorenone (2DMAFl)

Scheme 1. Chemical structure of molecules under study.

Recently different methyl and dimethylaminofluorenone derivatives have been studied by various authors [1 – 4]. However the photophysical properties of 2-methylaminofluorenone (2MAFl) and 2-dimethyl-

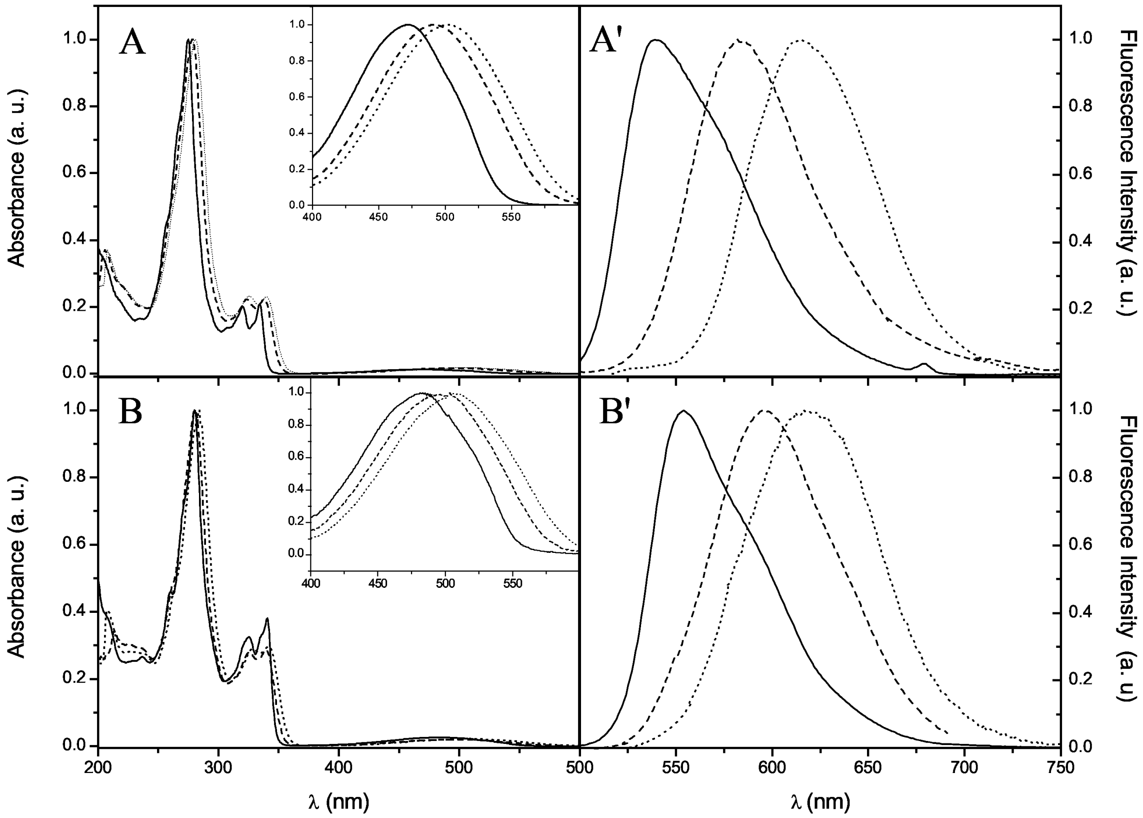


Fig. 1. Absorption (A and B) and fluorescence (A' and B') spectra of 2MAFl (A and A') amd 2DMAFl (B and B') in MCH (——), DE (- - - - -) and THF (· · · · · ·).

aminofluorenone (2DMAFl) (see Scheme 1) are only known for non-polar solutions. The lack of these and other spectroscopic data inspirited us to perform the measurements and theoretical calculations reported in this paper.

2. Experimental

2-methylaminofluorenone and 2-dimethylaminofluorenone were purchased from Aldrich Chemical Co. and purified by recrystallization from toluene. Their purity was checked chromatographically. All solvents used were highest grade commercially available. Methylcyclohexane was distilled before use from a sodium potassium amalgam to ensure that it is pure and free of water.

The absorption and fluorescence spectra were recorded using a Shimadzu UV-2401 PC spectrophotometer and Shimadzu RF-5301 spectrofluorometer with 5.0 nm band-width for excitation and emission. The radiation was observed transversally to the direction of the exciting beam. The samples for fluorescence measurements were prepared using a 0.2 cm high sensitivity micro quartz cell. For the measurements at 77 K, suprasil tubes (3 mm in diameter) inserted into liquid nitrogen in the finger of the quartz dewar were applied. The concentration of the solutions was about $5 \cdot 10^{-4}$ M. The luminescence spectra were corrected for the spectral response of the photomultiplier (Hamamatsu R-928), but not for reabsorption.

The fluorescence decay data were collected by a time-correlated photon counting apparatus (the pico/femto second laser system, thermoelectrically cooled MCP-PTM R3809U-05) in the Laboratory of Ultrafast Laser Spectroscopy at A. Mickiewicz University in Poznań [11]. The samples were excited with a Spectraphysics picosecond laser system: argon-pumped Ti-Sapphire-Tsunami 720 – 850 nm laser. The second harmonic (360 – 500 nm) of the Ti-Sapphire laser generated picosecond pulses with a repetition rate in the range from 4 MHz to single shot. The fluorescence light was monitored at the magic angle

Tab. 1. Absorption and fluorescence spectra characteristics of 2MAFl and 2DMAFl in different solvents.

Solvent	2MAFl $\tilde{\nu}^{A}_{max}$ (cm^{-1})	$\tilde{\nu}^{F}_{max}$ (cm^{-1})	$\Delta\tilde{\nu}^{A}_{1/2}$ (cm^{-1})	$\Delta\tilde{\nu}^{F}_{1/2}$ (cm^{-1})	$\Delta\tilde{\nu}^{ST}$ (cm^{-1})	2DMAFl $\tilde{\nu}^{A}_{max}$ (cm^{-1})	$\tilde{\nu}^{F}_{max}$ (cm^{-1})	$\Delta\tilde{\nu}^{A}_{1/2}$ (cm^{-1})	$\Delta\tilde{\nu}^{F}_{1/2}$ (cm^{-1})	$\Delta\tilde{\nu}^{ST}$ (cm^{-1})
Pentane	21276	18416	4175	2300	889	20768	18148	4300	2070	702
Hexane	21276	18382	4200	2250	904	20725	18083	4580	2025	731
Heptane	21208	18281	4150	2200	949	20746	18050	4360	2035	746
MCH	21208	18264	4300	2250	893	20639	17953	4170	1975	773
Toluen	20470	16891	4375	1950	1127	19880	16556	4200	1860	1285
DE	20325	16750	4335	2030	1365	20000	16778	4380	2080	1207
BA	20100	16447	4225	2175	1272	19880	16207	4340	2055	1523
THF	20040	16286	4325	2000	1196	19841	16194	4300	2150	1396
MeChl	19880	16129	4350	1950	1399	19494	—	4350	—	—
Ac	19841	15723	4335	2090	1759	19607	—	4370	—	—
AcN	19762	—	4350	—	—	19596	—	4300	—	—

MCH: methylcyclohexane, DE: diethylether, BA: buthylacetate, THF: tetrahydrofuran, MeChl: methylencloride, Ac: acetone, AcN: acetonitril

with respect to the plane of polarisation of the exciting beam. The pulse timing and data processing systems employed a biased TAC model TC 864 (Tennelec) and the thermoelectrically cooled detector MCP-PMT R3809U-05, equipped with an preamplifier. The photon count rate was limited to 20 kHz when the repetition rate of the exciting pulses was 4 MHz. The time period between exciting pulses was at least 5-times longer than the measured fluorescence decay time, ensuring excitation of a fully re-equilibrated sample with each laser pulse.

The recorded decay data were theoretically analyzed by fitting the decay curves to the sum of exponents

$$I(t) = \sum_{i} \alpha_i \exp(-t/\tau_i) \tag{1}$$

where α_i and τ_i are the pre-exponential coefficient and the decay time of the i-th fluorescence component, respectively, by the use of the interactive convolution method. All of the time-resolved measurements were performed at room temperature.

3. Result and Discussion

3.1. Steady State Spectroscopic Studies

The absorption spectra of 2MAFl and 2DMAFl obtained in methylcyclohexane (MCH), diethyl ether (DE) and tetrahydrofuran (THF) are shown in Figs. 1A and 1B. The spectra possess three absorption bands in the observed 200 – 600 nm region. The long-wavelength absorption band shows red shift with increasing solvent polarity (see insert of Figs. 1A and 1B and Tab. 1). In addition, the separation of the first and second absorption bands becomes more pronounced in 2MAFl, and 2DMAFl than in fluorenone. The fluorescence spectra of 2MAFl and 2DMAFl show a significant solvent sensitivity. In non-polar solvents, fluorescence maxima appear at around $\lambda = 545$ nm for 2MAFl and $\lambda = 555$ nm for 2DMAFl. The long-wavelength absorption band and the fluorescence spectrum show mirror image symmetry. On the other hand, in polar solvents the mirror image symmetry is broken – the shape of the fluorescence band becomes gaussian like. The maximum is shifted to long-wavelengths in comparison with that in MCH. The emission spectra obtained at room temperature upon excitation at 475 nm consist of a broad structuraless band (Figs. 1A' and 1B') for all used solutions. There is no excitation wavelength dependence in the fluorescence spectrum. Using a solvent of higher polarity, a bathochromic shift in the emission maximum and an insignificant increase (2DMAFl) and decrease (2MAFl) in full width at half maximum (FWHM) is observed (see Tab. 1). It can be seen in Tab. 1 that the $\Delta\tilde{\nu}^{A}_{1/2}$ value depends on the solvent. It varies from 2300 cm^{-1} to 1950 cm^{-1} and 2150 cm^{-1} to 1975 cm^{-1} for 2MAFl and 2DMAFl. The width at half maximum of the long-wavelength absorption band and the fluorescence spectrum, $\Delta\tilde{\nu}^{A}_{1/2}$ and $\Delta\tilde{\nu}^{F}_{1/2}$, differ twofold for both molecules under study in non-polar and polar solvents (see Table 1). Furthermore, the fluorescence intensity decreases with increasing solvent polarity. For both studied molecules, at room temperature no fluorescence emission can be detected in more polar solvents than $\varepsilon > 15$; i. e., ethanol, acetonitrile. This suggests that in more polar media ($\varepsilon > 15$) the interaction of solute-solvent molecules enhances fluorescence quenching.

The fluorescence intensity distribution in polar solvents (DE, THF) is described by a gaussian shape, as can be expected for a dynamic interaction case of the solute-solvent molecules [7 – 9, 12]. Such a shape is characteristic for fluorescence spectra when the mo-

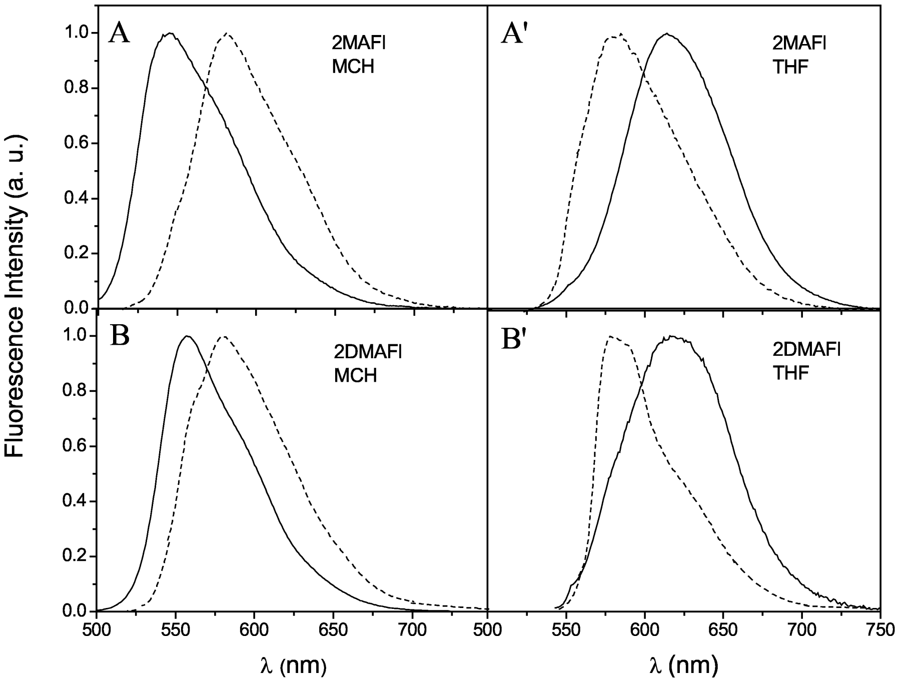


Fig. 2. Fluorescence spectra of 2MAFl and 2DMAFl in MCH and THF determined at 293 K (——) and 77 K (······).

tions in the fluorophore environment occur simultaneously or faster than the emission $\tau_R \leq \tau_F$. For these cases a very large number of different solute-environment space configurations is possible. They possess a large variation of interaction energies, forming an ensemble of sub-states. Each sub-state can possess a sharp maximum, but their joined contributions give a broad band emission spectrum of gaussian shape. It has been shown that the solvate sub-state distribution function at thermal equilibrium is Boltzman's [12–16]. These conformational broadening factors cause fluorescence band broadening at its short wavelength slope (see Figs. 1A' and 1B').

The emission spectra of 2MAFl and 2DMAFl in methylocyclohexane and tetrahydrofuran at 77 K are presented in Figure 2. It follows from the figure that in MCH glass the fluorescence spectrum preserves the shape observed at 293K but its maximum is shifted to longer wavelengths. In THF glass, for both molecules, an opposite behaviour is noted, i.e., the fluorescence maximum is shifted to shorter wavelengths and its shape is similar to that observed in MCH solution at 77 K. Furthermore, the λ-onsets of the fluorescence spectra in THF obtained at 293 K and 77 K are equal (see Figs. 1A' and 1B'). It has been found that the steady-state fluorescence spectra of 2MAFl and 2DMAFl do not depend on the excitation energy at room temperature. This suggests that there exists an energy relaxation with a time scale shorter than the lifetime of the electronic excited state of the solute molecule. These results distinctly indicate that in polar solvents the molecules under study form an inhomogeneous spectroscopic medium consisting of two kinds of emitting centres (cells).

3.2. Permanent Dielectric Dipole Moments of the S_0 and S_1 States

The interaction between the solvent and the fluorophore affects the energy difference, $\Delta\tilde{\nu}_{AF} = \Delta\tilde{\nu}_A - \tilde{\nu}_F$, between the ground and excited state. The energy difference is a property of the refractive index (n) and dielectric constant (ε) of the solvent, and is described by [17–18]

$$\Delta\tilde{\nu}_{AF} = \tilde{\nu}_A - \tilde{\nu}_F = \frac{(\Delta\mu)^2}{2\pi\varepsilon_0 hca^3}\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{n^2+2}\right)$$
$$= \frac{(\Delta\mu)^2}{2\pi\varepsilon_0 hca^3} f(\varepsilon,n), \qquad (2)$$

where μ_g, μ_e are the dipole moments of the molecule in the S_0 and S_1 states, and $\tilde{\nu}_A$ and $\tilde{\nu}_F$ are the maximal wave numbers of the absorption and emission

	2MAFl				2DMAFl			
Solvent	τ(ns)	α [%]	τ(ns)	α [%]	τ(ns)	α [%]	τ(ns)	α [%]
MCH	λ_{obs} = 546 nm		λ_{obs} = 590 nm		λ_{obs} = 555 nm		λ_{obs} = 610 nm	
	2.71	100	2.67	100	2.98	100	3.00	100
DE	λ_{obs} = 596 nm		λ_{obs} = 650 nm		λ_{obs} = 596 nm		λ_{obs} = 640 nm	
	3.84	58.7	3.70	46.7	3.65	54.0	3.70	47.7
	0.39	41.3	0.39	55.3	0.41	46.0	0.41	52.3
THF	λ_{obs} = 600 nm		λ_{obs} = 640 nm		λ_{obs} = 620 nm		λ_{obs} = 640 nm	
	3.86	76.6	3.77	62.1	3.80	59.9	3.81	51.2
	0.39	23.4	0.35	37.9	0.41	40.1	0.42	48.2

Tab. 2. Fluorescence decay times of 2MAFl and 2DMAFl in MCH, DE, and THF solvents.

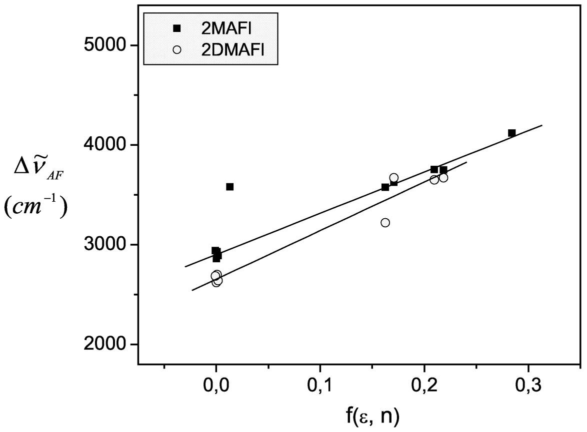


Fig. 3. Spectral shifts, $\Delta\tilde{\nu}_{\text{AF}}$, of 2MAFl and 2DMAFl *versus* the solvent polarity function $f(\varepsilon, n)$.

spectra, respectively. The constants ε_0, h, c, and a are the permittivity of vacuum ($8.85 \cdot 10^{-12}$ C V^{-1} m.$^{-1}$), Planck's constant ($6.626 \cdot 10^{-34}$ J s.), the velocity of the light in vacuum ($3.0 \cdot 10^{8}$ m. s.$^{-1}$), and the radius of the solvent cavity (in nm). For 2MAFl and 2DMAFl the spherical radii, a, were estimated to be 0.35 nm and 0.36 nm, respectively. $\Delta\mu = \mu_{\text{e}} - \mu_{\text{g}}$, the dipole moment of the electronic excited states can be determined only if μ_{g} is known. In the absence of experimental results, μ_{g} of the ground-state has been calculated using the CAChe WS 5.04 computer program and the PM3 method. These calculations give 3.2 D and 3.1 D for 2MAFl and 2DMAFl, respectively.

Figure 3 shows a graphical presentation of the spectral shifts $\Delta\tilde{\nu}_{\text{AF}}$ *versus* the solvent polarity function $f(\varepsilon, n)$ of both molecules. Using a linear regression to fit the data collected in Tab. 1, a good linearity for the majority of the solvents is noted. The permanent dipole moment changes $\Delta\mu$ of 2MAFl and 2DMAFl have been calculated and equaled about (4.2 ± 0.2) D and (4.8 ± 0.4) D, respectively. The correlation coefficients of the fits are larger than 0.95, but taking into consideration the earlier determined $\Delta\mu$ and μ_{g} values it is evident that the dipole moment of the excited state of both molecules enlarges more than twofold.

We calculated the most stable structure of 2MAFl and 2DMAFl in the ground and excited states using the CAChe WS 5.04 computer program (PM3). The optimized structures of 2MAFl and 2DMAFl in the ground and excited states are coplanar. Inoue and co-workers [2] showed that 4DMAFl and 1DMAFl could not be coplanar due to the steric hindrance between the dimethylamino group and the hydrogen atom at the 5-position (4DMAFl) or the carbonyl group (1DMAFl). As discussed above, 2MAFl and 2DMAFl are not able to form a TICT state.

3.3. Time-resolved Spectroscopy

Figure 4 shows typical examples of the fluorescence decay curves of 2MAFl and 2DMAFl obtained in nonpolar (MCH) and polar (DE, THF) solvents. The decay curves have been detected at two emission wavelengths. Table 2 collects the calculated fluorescence decay time data, τ_{F}, and the preexponential factors, α_i, describing the contribution of the i-th fluorescence decay component to the total emission. The average value of χ^2, describing the goodness of the fitting procedure for all decay curves, i.e., one- and two-exponentials fitting, equals $\chi^2 = 1.15 \pm 0.05$.

By analyzing the fluorescence decay data collected in Table 2, it follows that:

- the fluorescence decays of both molecules in nonpolar solvent (MCH) are very well fitted by a one-exponential function for both selected wavelengths of the emission band (see also Figs. 3A and 3B). Its values do not depend on the detection wavelength. The differences comprise the error limit of the τ determination,
- in polar solvents (DE or THF) the two-exponential function is used to fit the fluorescence decay data of both molecules for both selected wavelenghts. The fast fluorescence decay component (observed in po-

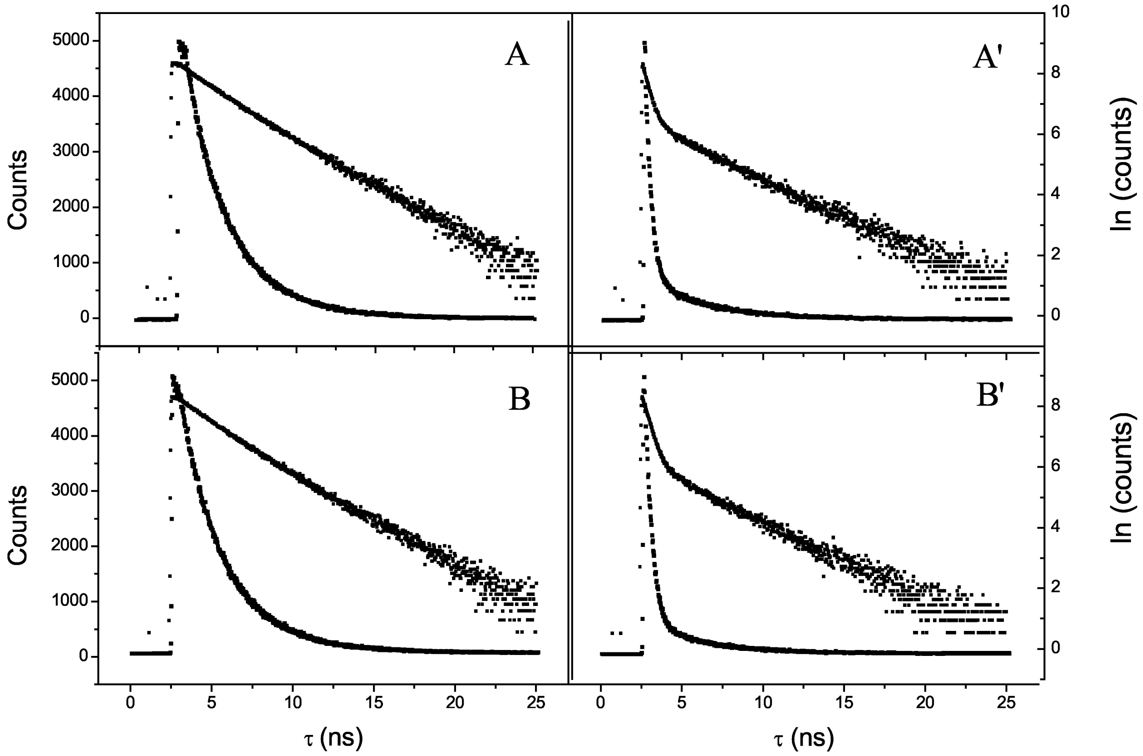


Fig. 4. Fluorescence decay curves (and its ln presentation) of 2MAFl (A and A') and 2DMAFl (B and B') in MCH (A and B) and THF (A' and B') solvents.

lar solvents only) is about one order shorter than the main component and does not depend on the solvent molecule as well as its polarity,

- the decay constants of the fluorescence decay component possess similar values for both molecules under study if determined in a polar solvent. In nonpolar ones (MCH) the decay time of 2DMAFl is bigger than of the 2MAFl molecule (2.67 *versus* 3.00 ns).

3.4. Determination of the Outer-sphere and Intramolecular Reorganization Energy

As it has been mentioned earlier, in polar solvents the mirror image symmetry is broken, the fluorescence spectrum possesses a gaussian shape and its halfwidth (FWHM) is about twofold smaller than the long-wavelength absorption band, its value decreases with increasing solvent polarity. The fluorescence decay data also indicate that in polar solutions the molecules under study form two types of emitting centres: decaying fast ($\tau_1 \approx 0.4$ ns and $\alpha \approx 40\%$) and slowly ($\tau_2 \approx 3.7-3.9$ ns). These findings indicate that in nonpolar and polar solvents the compounds possess significantly different surroundings established from the solvent molecules. In the first case (MCH) the solute molecule is surrounded by solvent molecules which only weakly influence in the radiation process. In the case of polar solvents, reorientation processes are involved in the fluorescence emission, especially in its decay.

Brunschwig et al. [19] have shown that the full width at half maximum of the fluorescence band ($\Delta\tilde{\nu}^{F}_{1/2}$) is related to the coupling of the outer-sphere solvent reorganization energy λ_{outer}, and to the intramolecular reorganization energies λ_i^*, and λ_i, by the formula

$$\frac{(\Delta\tilde{\nu}^{F}_{1/2}hc)^2}{8\ln 2} = 2\lambda_{\text{outer}} + 2\lambda_i^* kT + \lambda_i h\nu_i, \qquad (3)$$

where λ_i^* is the intramolecular reorganization energy associated with vibrations for which $h\nu < kT$, and λ_i is the intramolecular reorganization energy associated with vibrations for which $h\nu > kT$. For a molecule with permanent dipole moments μ_g, μ_e in S_0 and S_1 states, respectively, the outer-sphere reorganization en-

Tab. 3. Determined outer-sphere, λ_{outer}, and intramolecular reorganization ernergies, λ_i^*, λ_i (in eV), of 2MAFl and 2DMAFl in various solvents.

	2MAFl		2DMAFl	
Solvent	$\lambda_{\text{outer}} \cdot 10^{-2}$	$\lambda_i^* + \lambda_i h\nu_i/2kT$	$\lambda_{\text{outer}} \cdot 10^{-2}$	$\lambda_i^* + \lambda_i h\nu_i/2kT$
Pentane	0.015	0.290	0.016	0.235
Hexane	0.013	0.276	0.014	0.224
Heptane	0.059	0.265	0.062	0.227
MCH	0.073	0.277	0.076	0.213
Toluen	1.054	0.198	1.090	0.179
DE	12.96	0.097	13.58	0.102
BA	13.62	0.123	14.27	0.089
THF	16.71	0.052	17.50	0.078
MeChl	17.41	0.035	18.24	—
Ac	22.66	0.013	23.73	—
AcN	24.35	—	25.50	—

ergy, λ_{outer}, is given by [12]

$$\lambda_{\text{outer}} = \frac{\Delta\mu^2}{4\pi\varepsilon_0 a^3} f(\varepsilon, n), \quad (4)$$

where $f(\varepsilon, n)$ is the Lippert polarizability function

$$f(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}. \quad (5)$$

Combining (3) – (5), the outer-sphere solvent reorganization energy, λ_{outer}, can be calculated. Its value allows us to determine the total intramolecular reorganization energies, λ_i^* and λ_i, in different solvents using the formula

$$\lambda_i^* + \frac{\lambda_i h\tilde{\nu}_i}{2kT} = \frac{(\Delta\tilde{\nu}^{\text{F}}_{1/2} h\tilde{\nu})}{16kT \ln 2} - \frac{\mu_e^2}{4\pi\varepsilon_0 a^3} f(\varepsilon, n). \quad (6)$$

Table 3 compiles the data of the outer-sphere reorganization, and the intramolecular vibrational and torsional reorganization energies of both molecules studied in different solvents. For non-polar solvents the refraction index n^2 is very close to the static dielectric constant ε, and λ_{outer} is only slightly higher than zero (see Tab. 3). The average intramolecular reorganization energy, obtained by the use of (6), for a non-polar solvent equals 0.28 eV and 0.23 eV for 2MAFl and 2DMAFl, respectively. This means that the inner sphere, i. e., the intramolecular reorganization energy is dominant for both studied molecules in non-polar solvents. By analysis of the data collected in Table 3 it can be seen that the intramolecular reorganization energy decreases along with the increasing solvent polarity, and for more polar solvents the outer sphere reorganization energy (λ_{outer}) becomes dominant.

The performed calculations confirm the earlier findings concerning the influence of the solvation shells of non-polar and polar solvent molecules in the radiation process of 2MAFl and 2DMAFl. The above differences corroborate with the Stokes shift data $\Delta\tilde{\nu}^{\text{ST}}$ (defined as $\Delta\tilde{\nu}^{\text{ST}} = \tilde{\nu}^{\text{A}}_{\text{max}} - \tilde{\nu}^{\text{F}}_{\text{max}}$) determined for both molecules dissolved in various solvents (see Table 1). It is obvious from the data that the $\Delta\tilde{\nu}^{\text{ST}}$ values are bigger in polar solvents than in non-polar ones. In THF about 25% for 2MAFl and 50% for 2DMAFl in comparison with that obtained in pentane. Furthermore, it is necessary to note that the fluorescence efficiency (quantum yield) is much lower in polar solvents than in non-polar ones. The strong polar and all protic solvents quench completely the radiative deactivation processes of the S_1 state.

4. Summary

Results of steady state and time-resolved spectroscopic studies of 2MAFl and 2DMAFl in non-polar and polar aprotic solvents point out that:

- the above compounds dissolved in non-polar solvents establish a homogeneous solute-solvent distribution for which the photophysical properties depend only on the intramolecular reorganization energy, λ_i^* and λ_i, including torsion vibrations,
- dissolved in polar solvents, the compounds form an inhomogeneous emitting system at room as well as at lower temperatures. In this medium they establish space conformational forms – micro-phases. Its composition, molecular order and internal dynamics are different from those of the surrounding macro-phase. The multi-mode luminescent processes occurring in such a medium depend on the solvate outer-sphere, λ_{outer}, as well as on the intramolecular reorganization energies λ_i^* and λ_i. These radiation differences are observed in the fluorophore emission which can be modulated by the kind of environment molecules and especially by its temperature [19].

Fluorescence emission anisotropy measurements in connection with time-resolved spectroscopy should be very efficient in studies of the multi-mode fluorescence dynamics of such inhomogeneous media.

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