

A study on the spectroscopy and photophysics of 4'-N,N-dimethylaminoflavone derivatives

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Abstract

The luminescence behavior of 4'-N,N-dimethylaminoflavone derivatives with different structures has been studied in different solvent conditions. Results show that the luminescence depends dramatically on the solvent polarity due to the solvent dependence of the compound conformation. The planar conformation is proved to be favourable for fluorescence emission. In addition, results of viscosity-dependent luminescence show that for compound 3 with the rigidized planar structure the luminescence behavior does not depend on the medium viscosity. In contrast, for compounds 1 and 2 the fluorescence quantum yields increase with increasing medium viscosity, indicating that the rotation relaxation process of the B benzene ring in the molecule is very important in the nonradiative decay process of excited molecules of these compounds.

1. Introduction

Investigations on the photophysics and spectroscopy of compounds with conjugate intramolecular charge transfer character have received considerable attention [1–4]. In particular, after the proposal of the twisted intramolecular charge transfer state by Grabowski, et al. [5–6], the study of this field became very active. This activity occurred because of applications in industry such as fluorescence and laser dyes, nonlinear optical materials, optical recording media, and molecular switching devices, etc. [7–12], and because there arose a series of theoretical problems such as the effect of intramolecular charge transfer process and luminescence properties upon the molecular conformation, formation of TICT state from the self-

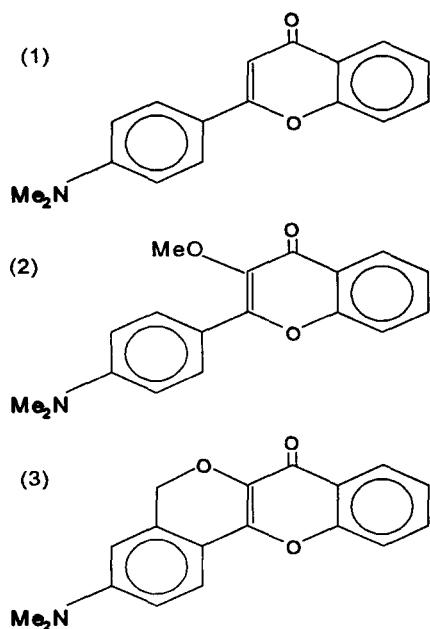
decoupling of orbitals due to the interaction between solute and solvent, etc.

Flavonoids have aroused attention due to their unique photochemical properties [13]. The excited intramolecular proton transfer reaction of their hydroxy substituted derivatives has been discussed extensively [14–16], and 4'-N,N-dimethylaminoflavone which shows very strong ICT character has also been reported in a recent publication [17]. In order to investigate the relaxation process of the excited flavone compounds, we report the photophysical behavior of several flavone derivatives which have the same donor and acceptor groups, but, different structures.

2. Experimental

Compounds 1, 2 and 3 were synthesized by different methods in our laboratory. The detailed

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Scheme 1. The structures: (1) 4'-N,N dimethylaminoflavone; (2) 3-methoxy-4'-N,N-dimethylaminoflavone; (3) 3-N,N-dimethylamino-7-oxo [2]-benzenopyrano [4,3-b][1]benzopyran.

report of preparation will be given elsewhere. The structures were characterized by IR, MS and H^1 NMR and are shown in Scheme 1.

All solvents used in this work were purified by the methods described by Perrin [18].

Absorption and fluorescence spectra were recorded on a Hitachi 330 UV-Vis spectrophotometer and Hitachi MPF-4 Fluorescence spectrophotometer, respectively. The fluorescence quantum yields were determined using the solution of fluorescein in 0.1 M sodium hydroxide as a standard (quantum yield taken as 0.93). The fluorescence lifetimes were recorded on a Horiba NAES-1100 single photon counting apparatus.

3. Results and discussion

Table 1 shows the absorption maxima of these compounds in different solvents. It can be observed that the absorption maxima of these compounds shifted to the red with increasing solvent polarity, indicating that these compounds have intramolecul-

Table 1
The absorption maxima of these compounds in different solvents

Solvents	$(\epsilon - 1/\epsilon + 2)^a$	λ_{ab} [nm]		
		1	2	3
Cyclohexane	0.25	351	361	370
Ethyl acetate	0.63	366	372	388
Acetonitrile	0.92	373	375	396

^a $(\epsilon - 1/\epsilon + 2)$ is the Debye solvent polarizability function [20].

lar charge transfer character in their ground states [19].

From the fluorescence spectra of compounds in different solvents (Figs. 1–3), it is observed that the emission maxima shift dramatically to longer wavelength with increasing solvent polarity, indicating that the molecules are significantly solvated in the excited state, resulting in great differences of dipole moments of the molecules [21]. The peak wave numbers in the fluorescence spectra of compounds can be correlated with the Debye solvent polarizability function $(\epsilon - 1/\epsilon + 2)$, as shown in Fig. 4, and a good linear relationship is obtained. Meanwhile, the solvent-induced shifts of the emission and absorption spectra (Stokes shift) can be linearly correlated with the solvent polarity parameter Bilot-Kawski (BK) values [22].

$$\Delta\tilde{\nu}_s = \tilde{\nu}_a^{\max} - \tilde{\nu}_f^{\max} = \frac{(\mu_e - \mu_g)^2}{hca^3} BK + \text{constant},$$

with

$$BK = \frac{\{(\epsilon - 1)/(2\epsilon + 1)\} - \{(n^2 - 1)/(2n^2 + 2)\}}{\{1 - \beta(n^2 - 1)/(2n^2 + 2)\}^2 \{1 - \beta(\epsilon - 1)/(2\epsilon + 2)\}},$$

where $\Delta\tilde{\nu}_s$ is the Stokes shift, h is Planck's constant, c is the velocity of light, a is the Onsager cavity radius, and where ϵ and n are the static dielectric constant and the refractive index of the solvent, respectively. The β factor approximates to unity in the case of isotropic polarizability. Then, the Stokes shifts obtained for compounds in different solvents are plotted against the BK parameter in Fig. 5. An excellent linear correlation is observed. According to the slopes of the straight line in Fig. 5,

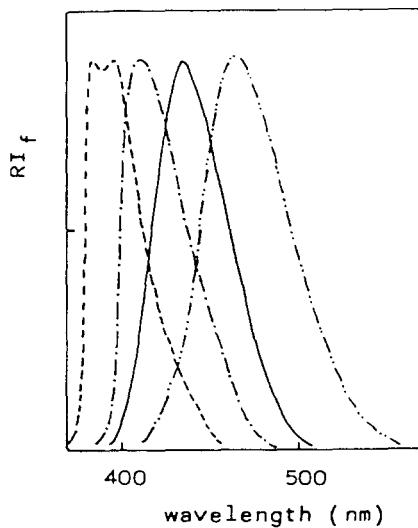


Fig. 1. The fluorescence spectra of compound 1 in different solvents: (---) cyclohexane; (-●-●-●-) benzene; (—) ethyl acetate; (-●●-●●-) acetonitrile.

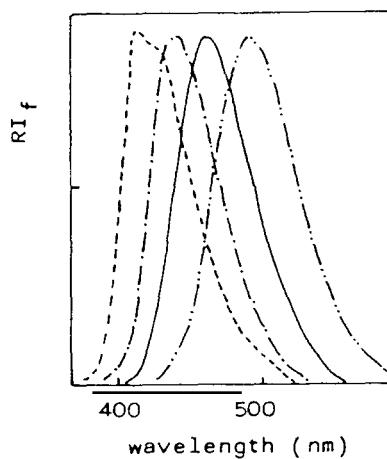


Fig. 2. The fluorescence spectra of compound 2 in different solvents: (---) cyclohexane; (-●-●-●-) benzene; (—) ethyl acetate; (-●●-●●-) acetonitrile.

the differences of dipole moment between excited and ground states were obtained, and are listed in Table 2.

From Table 2, it can be seen that the change of dipole moment of compound 3 with rigidized structure is less than those of compounds 1 and 2. The

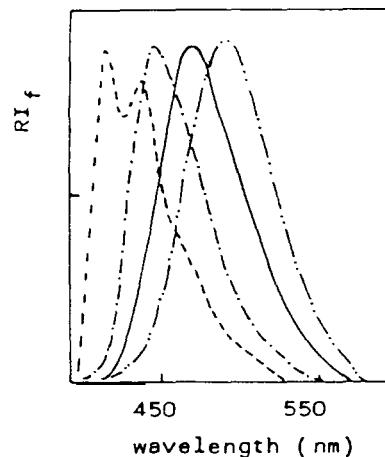


Fig. 3. The fluorescence spectra of compound 3 in different solvents: (---) cyclohexane; (-●-●-●-) benzene; (—) ethyl acetate; (-●●-●●-) acetonitrile.

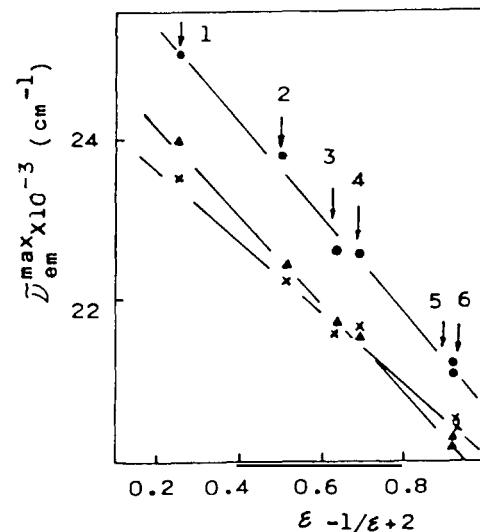


Fig. 4. The change of maximum emission wave numbers of compounds 1 (●), 2 (▲), 2 (X) with the Debye solvent polarizability function: 1:cyclohexane; 2: ethyl ether; 3: ethyl acetate; 4: THF; 5; acetonitrile; 6: DMF.

reason can be attributed to both the greater polarization in the ground state and the smaller molecular conformation change for compound 3 than that of compounds 1 and 2.

Table 3 indicates the fluorescence quantum yields of the compounds in different solvents.

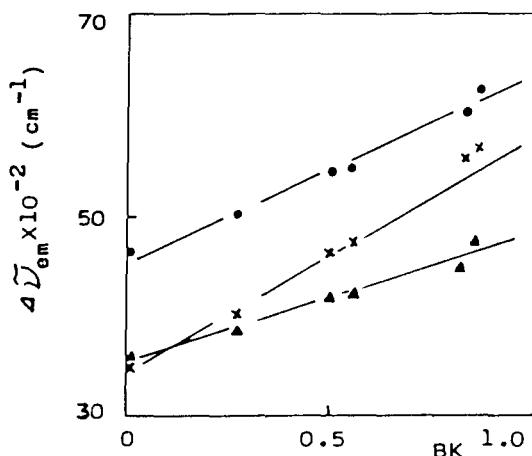


Fig. 5. The plot of Stokes shifts of the compounds 1 (X), 2 (●), 3 (▲) with BK values.

Table 2
The differences of dipole moment between the excited and ground states ($\Delta\mu$) of these compounds

Compound	1	2	3
$\Delta\mu$ [D]	8.2	7.3	5.8

Table 3
The fluorescence quantum yields of these compounds in different solvents

Solvents	ϕ_f		
	1	2	3
Cyclohexane	0.007	0.048	0.5
THF	~1	0.88	0.91
Acetonitrile	0.96	0.69	0.86
Methanol	0.095	0.021	0.68

From this table, it can be observed that in polar solvents all compounds have high fluorescence quantum yields. In contrast, in nonpolar solvents only compound 3 exhibits a high fluorescence quantum yield, indicating that the coplanar structure is favorable to fluorescence emission. The fluorescence quantum yields of the compounds are plotted against the Debye solvent polarizability function in Fig. 6. It can be seen that the flu-

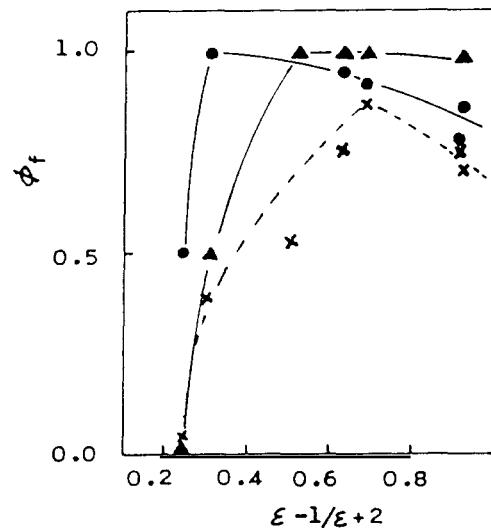


Fig. 6. The change of fluorescence quantum yields of the compounds 1 (▲), 2 (X), 3 (●) with the Debye solvent polarizability function.

rescence quantum yields of the compounds increase with solvent polarity just in the primary region. With a further increase of the solvent polarity the fluorescence quantum yields decreases, producing a distinct maximum, shown in Fig. 6. These results indicate that the luminescence behavior of these compounds depends not only on the molecular structures, but also on the surrounding solvents, indicating that there are two competing mechanisms of excited state relaxation which occur with an increase in the solvent polarity. The first one, which is concerned with the presence of the enone structure in the molecule, produces an increase in the fluorescence quantum yields with the suitable enhancement of intramolecular charge transfer, the so-called “negative solvato kinetic effect”. Some suggestions such as “biradicaloid formation” [23], “proximity effect” [24], and “conformation change” [17], have been proposed to explain the behavior of “negative solvato kinetic effect”. For compounds studied in this work, the mechanism of “biradicaloid formation” is not suitable due to the fact that the double bond of the enone compound is rigidized in the ring. Therefore, the other two mechanisms may play some role. The “proximity effect” will be reduced owing to the enhancement of intramolecular charge transfer, which causes the ϕ_f

value to increase with increasing solvent polarity. The second, which is usually observed in molecules with ICT character, is the reduction of fluorescence quantum yield from the strong intramolecular charge transfer, the so-called "positive solvatochemical effect". The two competing mechanisms may result in the observed maxima Fig. 6 also shows that for compound 1 the fluorescence quantum yield increases with increasing solvent polarity within a wide span of solvents; only in the very strong polar solvent (acetonitrile, $(\epsilon - 1/\epsilon + 2) = 0.92$) does the ϕ_f value decrease. For compound 2 the ϕ_f values increase from nonpolar solvents to moderate polar solvents (THF, $(\epsilon - 1/\epsilon + 2) = 0.69$), then they decrease when the solvent polarity increases further. For compound 3 the ϕ_f values increase only in slightly polar solvent (toluene, $(\epsilon - 1/\epsilon + 2) = 0.30$), then decrease gradually. These results indicate that for compound 3, with a rigidized structure, the second mechanism plays a predominant role even in slightly polar solvents, whereas, for compound 1 and 2 the second mechanism plays the most important role only in moderate and strongly polar solvents.

Table 4 shows the radiation decay rate constants, which are calculated from fluorescence quantum yields and lifetimes of these compounds.

From this table, it can be seen that for compounds 1 and 2, the maxima of the radiative decay rate constants can be observed in the middle part of the whole span of solvent polarity, but, for compound 3 the radiative decay rate constants decrease with increasing solvent polarity, inferring that the bridging of the B benzene ring affects the nonradiative process of the excited states significantly.

Table 4
The photophysical constants of compounds in different solvents

Solvent	1		2		3	
	$k_r [\times 10^{-8}]$	$\tau [ns]$	$k_r [\times 10^{-8}]$	$\tau [ns]$	$k_r [\times 10^{-8}]$	$\tau [ns]$
Cyclohexane	0.1	0.65	0.7	0.67	5	0.99
Ethyl ether	4.1	0.78	4.3	0.88	4.2	2.39
THF	5.3	2.01	4.3	2.05	3.7	2.33
Ethyl acetate	4.3	2.29	4.5	1.67	3.7	2.54
Acetonitrile	3.9	2.54	2.5	2.71	3	2.87

The radiative decay rate constants of compound 3 with a rigidized structure are larger than those of compounds 1 and 2 with flexible substituents, and decrease with increasing solvent polarity due to the fact that the conformation change from the pretwisted to the coplanar structure does not occur. In contrast, the conformation change will play important role for compounds 1 and 2. Thus, the enhancement of radiative decay rate constants can be observed.

Recently, some intramolecular charge transfer compounds which contain the dimethylanilino ring as an electronic donor have been studied [25–27]. Results indicated that the dimethylanilino ring has a certain freedom of rotation in the molecule at room temperature, this motion representing an important deactivation pathway of the S_1 excited singlet state. As the solvent viscosity increases in the n-alkane series, the rotation amplitude of the dimethylanilino ring moiety is reduced, resulting in a marked decrease of the nonradiative decay rate constant and consequently in an increase in the fluorescence yield. In order to investigate the effect of internal rotation of compounds on the relaxation process of the excited states, we determined the change of fluorescence quantum yields in the media with different viscosities and with almost constant polarity, as shown in Table 5 and Fig. 7.

From Table 5, it can be found that the ϕ_f of compound 3 is independent of the viscosity, but, the ϕ_f of compounds 1 and 2 increase with increasing viscosity of the medium about 3 times, indicating that the rotation process of the B benzene ring has a great influence on the nonradiative process of the excited states. Fig. 7 shows the fluorescence quantum yields in a series of methanol-glycerol

Table 5
The fluorescence quantum yields in nonpolar media with different viscosities

Media	Viscosity [CP]	ϕ_f			
			1	2	3
Cyclohexane	0.98	0.007	0.048	0.50	
Liquid paraffin	23.6 ^a	0.021	0.128	0.50	

^a Measured in this work.

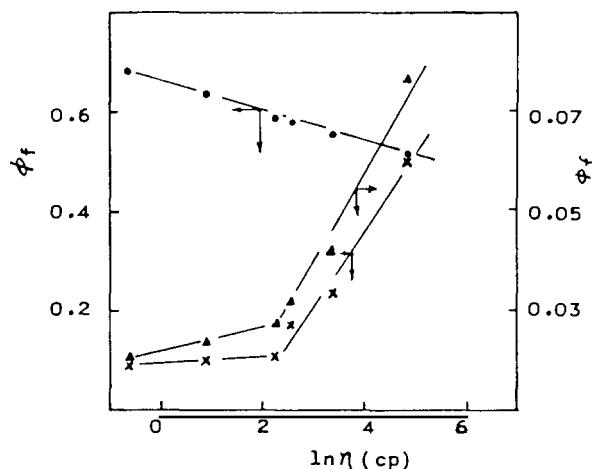


Fig. 7. The change of fluorescence quantum yields of the compounds 1 (X), 2 (▲), 3 (●) with the medium viscosity: methanol-glycerol mixtures.

mixtures (among which the polarizability function varied only trivially (from 0.919 to 0.936)) [28]. These mixtures show very great viscosity change but only a trivial variation of the polarity. The fluorescence quantum yields of these compounds in protic solvents are lower than those in polar aprotic solvents (see Table 3), indicating that there is a special interaction between solute and protic solvents. From Fig. 7, the fluorescence quantum yields of compounds 1 and 2 increase with viscosity of the medium when the viscosity is higher than about 10 CP, which is consistent with our previous work [29]. Interestingly, the fluorescence quantum yields of compound 3 decrease slightly with increasing viscosity of the medium. This effect can be attributed to the trivial enhancement of the medium polarity which causes the slight decrease of fluorescence quantum yield. It can also be seen in Fig. 7 that the change of the fluorescence quantum yields of compound 2 with methoxy group at the 3-position is smaller than that of compound 1, inferring that the relatively non-coplanar structure of compound 2 is responsible for this result. From the viscosity dependent results, it is suggested that the rotation of the B ring possesses great influence on the nonradiation decay process of the excited states.

4. Conclusion

According to the discussion above, it is suggested that these compounds have different conformations in solvents with different polarities, resulting in the different luminescence behaviors. Results show the coplanar conformation is favorable for fluorescence emission. Therefore, for compound 3 with a rigidized structure the high fluorescence quantum yields were observed under different conditions. Results also show that the luminescence properties of these compounds are related to the solvent polarity and medium viscosity due to the strong solute and solvent interaction and the viscosity dependent nonradiative decay process for these compounds.

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