Dyes and Pigments 47 (2000) 231–238
www.elsevier.com/locate/dyepig

Influence of the molecular structure and medium on the absorption and emission character of ketocoumarin derivatives and probability of as fluorescence probes

Fang Gao *, Hong-Ru Li, Yong-yuan Yang

Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101, PR China

Received 14 February 2000; received in revised form 18 May 2000; accepted 17 July 2000

Abstract

Three ketocoumarin dyes were synthesized and the influences of their molecular structure and the medium on the absorption and the emission character of the dyes was studied; the probability of as fluorescence probes was valued.

1. Introduction

The photophysical and spectroscopic properties of coumarin and its derivatives have been studied by many authors as a result their commercial importance in the physics, medical and, especially, biological fields. Considerable attention has been paid to the preparation of coumarin derivatives and to the study of their luminescence properties in different media [1–6]. Many aprotic solvents and protic solvents have been used in the study of the spectroscopic analysis of coumarin derivatives [7–10]. For example, the effects of polymer matrix on the spectral properties of some coumarin derivatives were studied by Kaholek et al. [4] who found that the viscosity of the media influenced luminescence efficiency. Elisei and his coworker [8], in a study of the characteristics of both the ground and the excited states of coumarin derivatives in different solvents, found that the decay efficiency of the singlet state depended markedly on the solvents' characteristics. Shim et al. [9] studied the photophysics of pyrazinocoumarin derivatives in different solvents and employed a molecular orbital method to study the excited state properties. A "ULM" (Umbrella Like Model) model has been proposed by Arbeloa and coworkers [10] in a study of the hydrogen bond effect on the photophysics of some coumarin derivatives in protic solvents. However, the mechanism of transportation of coumarins across membranes and the nature of the excited singlet state of ketocoumarin derivatives in microheterogeneous systems, such as in micelles and vesicles, is not understood.

In this work, three ketocoumarin derivatives were synthesized and the photophysical and spectroscopic properties of the compounds were studied in both homogeneous and heterogeneous environments.

---

* Corresponding author. Tel.: +86-10-64888173; fax: +86-10-648797375.

0143-7208/00/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0143-7208(00)00052-8

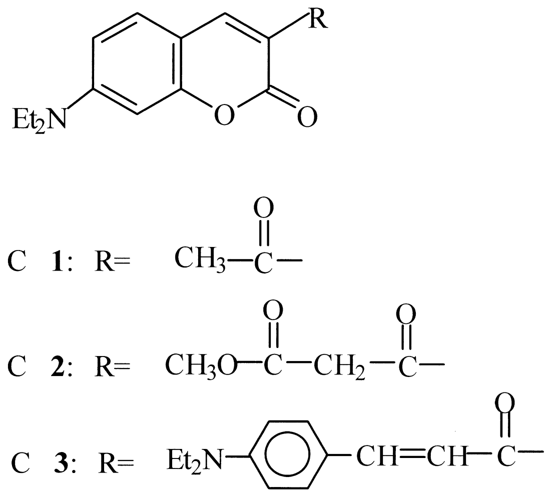
2. Materials and methods

2.1. Materials

The three ketocoumarin derivatives (Scheme 1) were synthesized according to the known procedure [11] and were recrystallized before use four times from a mixture of ethanol and acetonitrile. Sodium dodecyl sulfate (SDS) (Aldrich), cetyltrimethyl ammonium bromide (CTAB) (Aldrich) and polyscyethylene(io)isoctylphenyl ether (TX-100) (Aldrich) were used as received; water was distilled twice. All solvents used were obtained from Beijing Chemical Corp. and were purified before use.

2.2. Equipment

Absorption and fluorescence spectra were recorded using a Hitachi 330 UV–visible spectrophotometer and a Hitachi MPF-4 fluorescence spectrophotometer, equipped with a differential spectrum correction unit, respectively. The fluorescence quantum yield determination was carried out using a Perkin-Elmer LS-5 fluorescence spectrophotometer equipped with a data processing unit for calculating integrated intensities. Fluorescence lifetimes were determined using a Horiba NAES-1100 time-correlated single photon counting unit. Lifetimes were calculated from the decay curves using a least-square method.



Scheme 1.

2.3. Measurements

In homogeneous solution, absorption and emission measurements were carried out at a solute concentration of the order of 10^{-6}–10^{-5} mol dm^{-3}.

Vesicles were prepared from 0.082 M sodium laurate and 0.082 M octyltrimethylammonium bromide at pH 9.2 by sonicating the mixed solution for 0.5 h at 50°C.

Fluorescence quantum yields were determined using 9,10-biphenylanthracene in cyclohexane (ϕ, 0.90) as a standard.

3. Results and discussion

3.1. The maximum wavelengths of absorption and emission

From the molecular structure of the ketocoumarin derivatives, it can be seen that C **1** and C **2** have the same electron-donor group at the 7-position and different electron-acceptor groups at the 3-position. Clearly, the efficiency of electron-acceptance of the latter is slightly higher. The C **3** group characterized by a free double bond, namely, a two electron-donor group (diethylamine group) at both sides and an electron acceptor (cinnamoyl group) in the middle. Table 1 shows that a change in molecular structure influenced the maximum absorption and emission wavelengths in that, for each compound, a bathochromic shift accompanied an increase in red-shift solvent polarity which suggests that each compound is characterized by intramolecular charge transfer. The dramatic red shift in the fluorescence spectra observed shows that the molecules were solvated significantly in the S1 excited state, resulting in a large difference in dipole moment between the S1 excited state and the ground state; also C **3** has the greatest dipole moment difference.

With regards to the Stokes shift as a function of ($\upsilon_{a,max}-\upsilon_{f,max}$, cm^{-1}) the Bilot–Kawski parameter (BK), an excellent linear correlation was obtained (Fig. 1), which suggests that the dipole moment of the compounds increased upon excitation. According to the equation of Bilot and Kawski

Table 1
Spectroscopic constants of the dyes in different media

Medium	$\lambda_{a,max}$ (nm)			$\lambda_{f,max}$ (nm)			Log ε		
	C **1**	C **2**	C **3**	C **1**	C **2**	C **3**	C **1**	C **2**	C **3**
Cyclohexane	418	425	437	430	438	478	4.59	4.55	4.75
Tetrachloro-methane	422	429	455	438	448	508	4.55	4.60	4.73
Toluene	425	434	469	452	457	538	4.54	4.65	4.84
Benzene	427	436	471	455	459	544	4.53	4.59	4.84
1,4-Dioxane	422	432	464	459	459	558	4.54	4.66	4.84
Ethyl acetate	424	434	467	461	471	590	4.60	4.67	4.88
Trichloromethane	432	443	483	464	470	588	4.65	4.73	4.83
1,2-Dichoroethane	432	442	477	466	476	607	4.57	4.57	4.79
Acetone	428	438	471	472	479	626	4.64	4.66	4.88
Acetonitrile	429	440	475	475	487	637	4.65	4.68	4.86
SDS	439	450	487	483	491	621	4.61	4.46	4.84
CTAB	440	451	483	480	485	612	4.61	4.48	4.83
TX-100	439	445	487	475	484	584	4.59	4.68	4.84
Vesicle	433	444	487	475	484	573	4.69	4.71	4.83

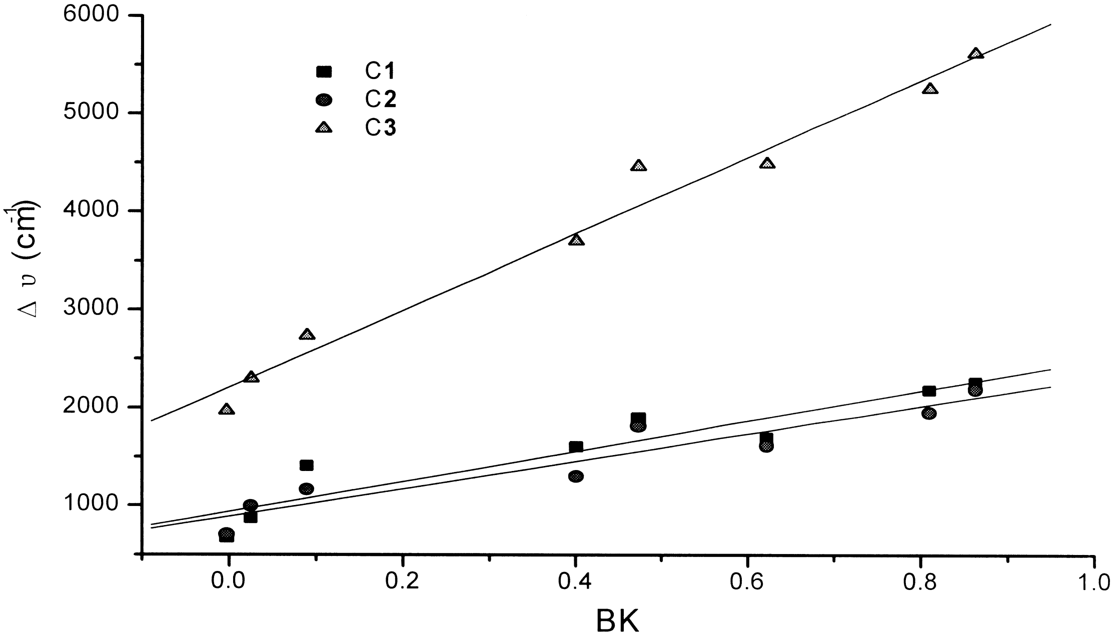


Fig. 1. Plot of Stokes shift of C **1**, C **2** and C **3** vs the BK value.

[12], the differences in the dipole moment between the excited and ground states of a compound can be obtained using Eq. (1).

$$\Delta\mu = \Delta\mu^2 \cdot \mathrm{BK}/hca^3 + \mathrm{constant} \qquad (1)$$

where $\mathrm{BK} = [(\varepsilon-1)/(2\varepsilon+1)]-[(n^2-1)/(2n^2+2)]/[1-\beta(n^2-1)/(2n^2+2)]^2[1-\beta(\varepsilon-1)/(2\varepsilon+1)]$, where h is Planck's constant, c is the velocity of light, a is the Onsager cavity radius, and 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. Thus, the differences in the dipole moments between the excited and ground states can be calculated from the straight line and are listed in Table 2. The calculated results prove that the dipole moment of C **3** is larger than that of C **1** and C **2**, which indicates that there exists greater conformational change, namely, greater charge transfer separation in the excited state in the polar media for C **3**.

3.2. The fluorescence quantum yields

As seen from Table 3, the fluorescence quantum yields of the compounds (ϕ) are dependent on the solvent polarity. The ϕ values increase with solvent polarity over a range of solvent polarity; with further increase in $E_T(30)$ values, the ϕ values decrease with increasing solvent polarity. The observed change in solvent polarity suggests that there exist two mechanisms governing the luminescence of the compounds. One is a so-called "negative solvatokinetic effect", which relates to the increase in the fluorescence quantum yield with suitable enhancement of intramolecular charge transfer. In other words, in non-polar solvents, the non-radiative transition decay of the excited state plays an important role. The other mechanism is a so-called "positive solvatokinetic effect", according to which, fluorescence quantum yields are reduced by the strong intra-molecular charge transfer for the larger polarity of solvents. As compared with C **1** and C **2**, C **3**, which has a free double bond, has a low fluorescence quantum yield in all solvents ($\phi_{f,max} = 0.0416$). For C **3**, the free double bond can undergo conformational change easily [13] and thus a low fluorescence quantum yield is obtained. In all cases, the "negative solvatokinetic effect" can be observed only in slightly polar solvents, indicating that the "positive solvatokinetic effect" plays an important role in the decay process of the excited singlet state.

The influence of the viscosity of the media on the fluorence quantum yield was also determined in binary solvents (*n*-hexane/paraffin liquid) which had similar polarity but very different viscosity. The results show that fluorescence quantum yields are sensitive to viscosity. Table 4 shows that the ϕ values increased with increasing viscosity of the binary solvents, indicating that the compounds can be used as fluorescence probes to determine the viscosity of the microenvironment. The above findings suggest that torsion of a substituent at the 3-position has an effect on the decay of the excited singlet state of the ketocoumarin derivatives.

Table 2
Calculated difference in dipole moment between the ground state and the excited state

Compounds	C **1**	C **2**	C **3**
$\Delta\mu$ (Debye)	5.349	9.451	12.552

Table 3
The fluorescence quantum yields and lifetimes of compounds

Medium	ϕ			τ (ns)		
	C **1**	C **2**	C **3**	C **1**	C **2**	C **3**
Cyclohexane	0.0627	0.450	0.0130	0.504	1.66	0.488
Tetrachloro-methane	0.479	0.350	0.0270	1.70	2.36	0.515
Benzene	0.621	0.613	0.0416	2.35	2.61	0.520
1,4-Dioxane	0.758	0.483	0.0285	2.55	2.75	0.568
Ethyl acetate	0.51	0.371	0.00636	0.94	1.90	0.502
Acetone	0.0624	0.093	0.00125	0.517	1.196	0.406
Acetonitrile	0.033	0.0633	0.00051	0.264	1.738	0.463
SDS	0.0479	0.0526	0.00246	0.681	2.413	0.410
CTAB	0.0647	0.0826	0.00868	1.118	2.309	0.472
TX-100	0.241	0.210	0.0355	0.964	1.109	0.549
Vesicle	0.031	0.044	0.00708	0.377	0.305	0.697

3.3. The radiative transition constant and non-radiative transition constant

The non-radiative constant (K_{nr}) and radiative constant (K_{r}) can be calculated according to formula below and are listed in Table 5:

$$K_{\mathrm{r}} = \phi/\tau \qquad (2)$$

$$K_{\mathrm{nr}} = 1 - \phi/\tau \qquad (3)$$

Table 5 reveals that the non-radiative rate constants of C **1** and C **2** were small in different solvents (except for C **1** in acetonitrile), indicating that radiative decay plays an important role in the decay of the excited state. For C **3**, the non-radiative rate constants were large in different solvents, suggesting that non-radiative decay predominates in the excited singlet state. The non-radiative decay plays an important role during the decay of the excited states when ketocoumarin dyes are solubilized in micelles and vesicle. This also suggests that for, C **1** and C **2**, the electron-acceptor strength of the substituent at the 3-position does not strongly influence the radiative decay process of the excited singlet states. A free double bond and surfactants influence the decay of the excited state of the ketocoumarin dyes.

Table 4
The influence of viscosity of media on the fluorescence quantum yields of compounds

n-Hexane/paraffin liquid	ϕ	
	C **1**	C **3**
5/0	0.0954	0.0194
4/1	0.118	0.0237
3/2	0.134	0.0254
5/5	0.164	0.0281
2/3	0.234	0.0300
1/4	0.33	0.0311

3.4. The potential as a fluorescence probe

The correlation of the emission maxima of compounds with the solvent polarity parameter $E_{\mathrm{T}}(30)$ value [14] is well represented by an excellent line (Fig. 2), from which the values of $E_{\mathrm{T}}(30)$ of micelles can be estimated. The correlation can be expressed as follows [Eq. (1)].

$$\Delta\upsilon = -1680.95 + 85.5E_T$$

$$(R = 0.9734, N = 8, P < 0.0001, \text{for C}\,\mathbf{1}$$

$$\Delta\upsilon = -2913.13 + 114.12E_T$$

$$(R = 0.98290, N = 8, P < 0.0001, \text{for C}\,\mathbf{2}$$

$$\Delta\upsilon == -6496.13 + 265.00E_T$$

$$(R = 98247, N = 8, P < 0.0001, \text{for C}\,\mathbf{3}$$

Table 5
The values of K_{r} and K_{r} of compounds in different media

Medium	K_{r} (10^8·S^{-1})			K_{nr} (10^8·S^{-1})		
	C1	C2	C3	C1	C2	C3
Cyclohexane	1.24	2.71	0.290	18.5	3.31	22.03
Tetrachloro-methane	2.82	1.48	0.520	3.06	2.75	18.90
Benzene	2.64	2.35	0.800	1.62	1.48	18.4
1,4-Dioxane	2.97	1.76	0.500	0.949	1.88	17.1
Ethyl acetate	1.80	1.95	0.127	1.60	3.31	19.8
Acetone	1.20	0.778	0.030	1.81	7.58	24.60
Aceonitrile	1.25	0.364	0.0111	36.6	5.39	21.59
SDS	0.703	0.218	0.060	14.0	3.93	24.33
CTAB	0.579	0.405	0.184	8.37	4.50	21.0
TX-100	2.5	1.89	0.610	7.87	7.12	17.60
Vesicle	0.822	1.44	0.100	25.7	31.34	14.25

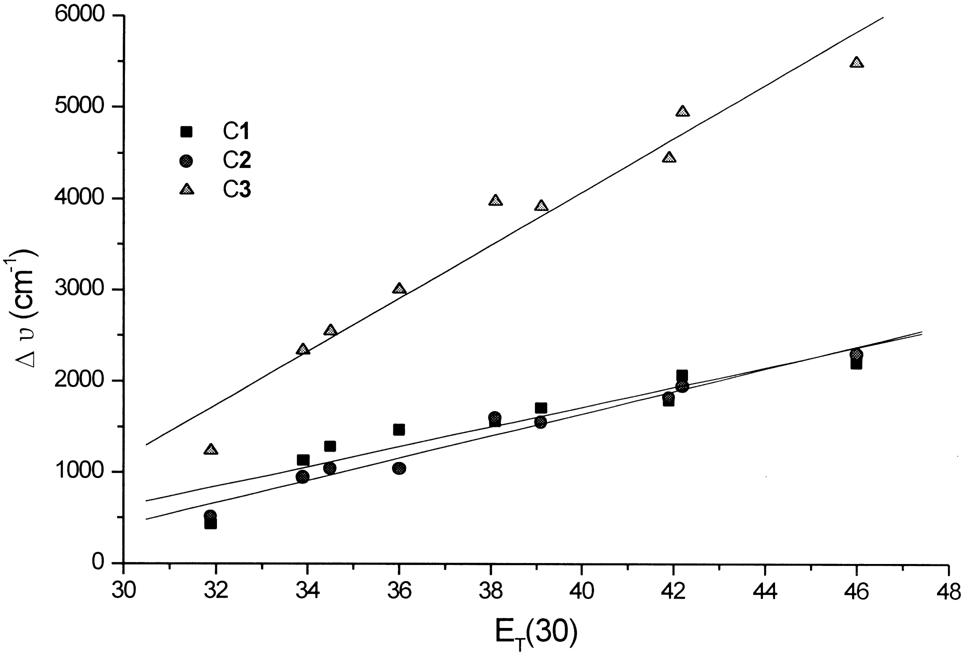


Fig. 2. Fluorescence maxima of C **1**, C **2** and C **3** in various aprotic solvents plotted as a function of the $E_T(30)$ value of solvents. Fluorescence maximum in cyclohexane as the reference point.

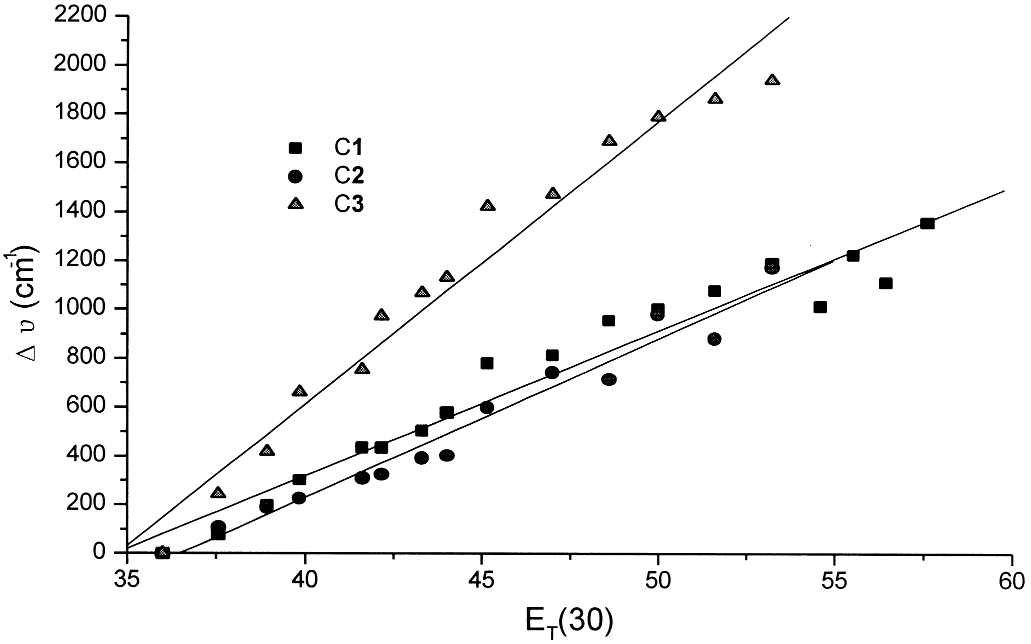


Fig. 3. Fluorescence maxima of C **1**, C **2** and C **3** in 1,4-dioxane–water mixed solvents plotted as a function of the $E_T(30)$ value of media. Fluorescence maximum in 1,4-dioxane as the reference point.

Table 6
The estimated $E_T(30)$ values of micelles and vesicle

Medium	C **1**	C **2**	C **3**
SDS	54.4	57.7	52.7
CTAB	52.5	53.5	50.3
TX-100	49.1	52.8	42.5
Vesicle	49.1	52.8	39.2

It is interesting to note that the maximum emission of C **1**, C **2**, C **3** in 1,4-dioxane–water mixed solvents can be correlated with the solvent polarity parameter $E_T(30)$ as shown in Fig. 3 and, a good linear relationship is obtained [Eq. (2)].

$$\Delta\upsilon = -2315.77 + 65.58E_T$$

$$(R = 0.99214, N = 18, P < 0.0001, \text{for C } \mathbf{1}$$

$$\Delta\upsilon = -2196.69 + 60.81E_T$$

$$(R = 0.09843, N = 8, P < 0.0001, \text{for C } \mathbf{2}$$

$$\Delta\upsilon = -3333.84 + 99.57E_T$$

$$(R = 98247, N = 8, P < 0.0001, \text{for C } \mathbf{3}$$

The polarity of micelles and vesicles, can be estimated from these relationships. It is obvious that the values deduced from Eqs. (1) and (2) differ. The values obtained from Eq. (1) are lower than those reported [15,16] because aprotic solvents do not mimic well micelles and vesicles. 1,4-Dioxane–water mixed solvents mimic vesicles and micelles because water and alkyl chains contribute to the surface polarity of the aqueous micelle and 1,4-dioxane–water mixed solvents provided a wide range of $E_T(30)$ values. The values of the microenvironment parameters deduced from Eq. (2) agree well with those reported [15,16] (Table 6).

The estimated $E_T(30)$ values can be used to probe what region of micelles and vesicles interact with molecules. Table 6 shows that C **1** and C **2** are located around the micelle–water and vesicle–water interface (close to polar head). As compared with C **1** and C **2**, C **3** lies in the hydrophobic region in the TX-100 micelle and in the vesicle, while it is close to the polar head and surface in ionic micelles. The hydrophobic interaction of C **3** with a surfactant is stronger than that of C **1** and C **2** due to its greater hydrophobicity. Although the absolute $E_T(30)$ values show dependence on the structure of the probes, the order of increasing $E_T(30)$ values (TX-100 < CTAB < SDS) is in agreement with each other. The reproducibility of the relative magnitude of the $E_T(30)$ values was found earlier [15], the main reason being that the polarity of the solubilization site is mainly determined by the degree at penetration into the micelles.

4. Conclusion

It can be conclude that the absorption and fluorescence characteristics of the ketocoumarin dyes are significantly dependent on molecular structure and medium. The three compounds can all be used as fluorescence probes to determine the polarity of micelles and vesicles. The results show that increasing the electron acceptor strength at the 3-position does not strongly influence the radiative decay process of the excited singlet state. A free double bond plays an important role in increasing the nonradiative decay rate of the excited singlet state of the ketocoumarin dyes.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (Project number: 59973023).

References

[1] Raju BB, Varadarajan TSJ. Photochem Photobiol A: Chem 1985;85:263.

[2] Heldt JR, Heldt J, Stoñ M, Diehl HA. Spectrochim Acta Part A 1995;51:1549.

[3] Marques ADS, Marques GSS. Photochem Photobiol 1994;59:153.

[4] Kaholek M, Hrdlouic PJ. Photochem Photobiol A: Chem 1997;108:283.

[5] Wenska G, Paszyc S. Can J Chem 1998;66:513.

[6] Datta A, Pal SK, Mandal D, Bhattacharyya K. J Phys Chem B 1998;102:6114.

[7] (a) Jones II G, Bergmark WRJ. Photochem. 1984;26:179. (b) Jones II G, Jackson WR, Choi C, Bergmark WR. J Phys Chem 1985;89:294. (c) Abdel-Mottaleb MSA, Loutfy RO, Lapougade RJ. Photochem Photobiol A: Chem 1989: 48:87.

[8] Ellisel F, Aloisi GG, Lattarini C, Latterini L, Dallacqua F, Gaiotto A. Photochem Photobiol 1996;64:67.

[9] (a) Shim SC. Kang HK, Park SK, Shin El. I. Photochem. 1987;37:125. (b) Shim SC, Han GS. Photochem. Photobiol 1997;66:156

[10] (a) Arbeloa TL. Arbeloa F. Tapia MJ. Arbeloa IL. J Phys Chem 1993;97:4704. (b) Arbeloa TL, Arbeloa FL, Estévez MJT, Arbeloa TL. J Lumin 1994;59:369. (c) Arbeloa TL, Arbeloa FL, Arbeloa IL. J Lumin 1996;68:149

[11] Specht DP, Martic PA, Farid S. Tetrahedron 1982;38:1203.

[12] Bilot L, Kawaki A. Z Naturforsh Tell A 1962;17:621.

[13] Wang P, Wu S. Acta Chim Sinica 1994;52:341.

[14] Riechardt C. Angew Chem int Ed Engl 1979;18:98.

[15] Ortica F, Favaro G. J Lumin 1996;68:137.

[16] Banerjee D, Das P, Mondal S, Ghosh S, Bagchi S. J Photochem Photobio A: Chem 1996;98:183.