

SPECTROSCOPY AND PHOTOPROCESSES IN LASER DYES EMITTING IN THE BLUE-GREEN SPECTRAL REGION

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Spectral and photophysical properties of a number of amino- and hydroxycoumarins have been studied experimentally and theoretically using the methods of quantum chemistry. The probability of different pathways of the photoprocesses is shown to be dependent on substituents and a position and a nature of molecular orbitals. It is shown that fluorination most strongly influences the properties of the $\pi\pi^$ excited states because of unique electronic effect of fluorine atoms and due to significant charge transfer at these excited electronic states.*

In many fields of science and engineering (spectroscopy, photochemistry, nonlinear optics, atmospheric and ocean sensing, biology, etc.), it is important to have efficient and stable fluorophores in the visible and, especially, in the blue-green spectral regions. Moreover, different practical and scientific applications need for different properties of luminophores.

In quantum electronics, high emissivity is important in addition to the smooth wavelength tuning, whereas in the case of fluorescent sounds or biological marks most important is high responsiveness of fluorophores to changes in the environment. Coumarin derivatives well meet these requirements. The compounds from this class are among most efficient laser dyes emitting in the blue-green spectral region.

Molecules of the coumarin series are distinguished for their strong polarity, significant charge transfer (CT), and large values of the dipole moments.^{1,2} From the above-said and from the nature of the objects under study it is clear that intermolecular interactions (IMI), both universal and specific, play an important role in the spectroscopy, photophysics, and photochemistry of coumarin molecules. Molecular structure and IMI of coumarins cause high emissivity of solvated molecules and their different forms (ionic, tautomeric) resulting from the processes of proton transfer (PT), especially in the excited states.^{3,4}

Parent molecule, nonsubstituted coumarin (NC), at room temperature shows only weak fluorescence in polar solvents, with the fluorescence lifetime in the subnanosecond range.⁵ Only temperature lowering causes notable fluorescence of coumarin in both polar and nonpolar solvents, and emission is different in the media of different polarity.⁶ Experimental investigations and quantum-chemical computations

allows us to explain the extraordinary luminescent properties of the coumarin molecule, first of all, by a very close positions of the singlet electronic levels, $\pi\pi^*$ and $n\pi^*$, from different orbitals in this system⁷ (see Fig. 1). This results in high probability of the process of internal conversion $S_1 \rightsquigarrow S_0$. Temperature lowering decreases the efficiency of deactivation processes and initiates the fluorescence of $n\pi^*$ type in the nonpolar solutions and $\pi\pi^*$ type in the polar ones. Increase in solvent polarity results in hypsochromic shift of the triplet $n\pi^*$ level toward $S_{\pi\pi^*}$ level and, consequently, in an increase in the intercombination conversion and initiation of an intense phosphorescence of $\pi\pi^*$ type.

Even after our publication⁷ there have appeared papers where the $\pi\pi^*$ state is still considered to be the lower singlet state of NC⁸ or quantum mechanical calculations ignore the orbital character of the lower singlet state at all.⁹ Only recently the paper¹⁰ was published, in which, in accordance with our conclusions based on the fluorescent measurements, the $n\pi^*$ nature of the lower singlet state of NC has been proved. The main argument in favor of such an assignment was the measured value of NC radiation lifetime in cyclohexane and dioxane (330 and 250 ns, respectively). It is clear that the lifetime of fluorescent state can be so long only if the state is, to a great extent, symmetry forbidden. And only an increase in solvent polarity (addition of water) shortens the lifetime, making $n\pi^*$ and $\pi\pi^*$ states closer.

Analysis of wave functions obtained for NC has shown that the main contribution to formation of the first $\pi\pi^*$ transition, polarized along the molecular long axis, comes from carbon atoms in positions 7, 4, and 3 (see Fig. 1). Electron-donor substitution of OH, NH₂, N(CH₃)₂, etc. in the position 7 results in an efficient fluorescence, and often even in lasing.¹¹

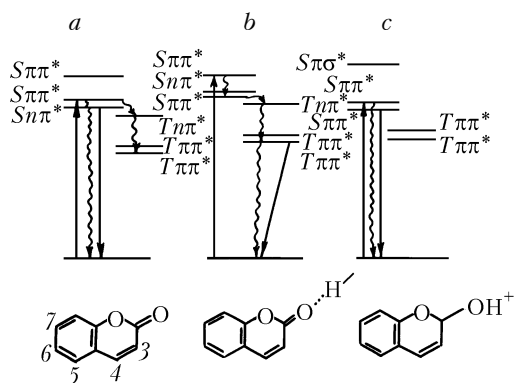


FIG. 1. Scheme of electronic terms: coumarin molecule in a nonpolar solvent (a), coumarin molecule in a polar solvent (b), and coumarin cation (c).

Among other examples of changing coumarin structure (second substituent), most important could be the so-called "fluorination" of coumarins, i.e., introduction of trifluoromethyl group into the position 4 (Ref. 12). This group, possessing good electron-acceptor properties, intensifies CT along the molecular long axis,¹³ thus causing increase in emissivity and bathochromic shift of spectra. Note that introduction of trifluoromethyl groups in the part of a molecule where aminogroup is located, on the contrary, depresses CT along the molecular long axis and thus causes a great hypsochromic shift, ~50 nm, and reduces the emissivity.¹⁴

Analysis of the properties of 7-OH-4CF₃-coumarin allows us to conclude that fluorination of the methyl group in oxycoumarins not only increases their photostability due to high strength of the C-F bond, but also markedly changes the acid-basic properties of these compounds. In response to unique electronic effects from fluorine atoms, CT in the system sharply increases, and acid properties in $S_1 \pi\pi^*$ state increase also. As a result, photoanion becomes the most probable emitting form of F4MU and 7OH-4CH₃-3CN-coumarin synthesized for the first time.

The experimentally discovered difficulties in formation of the phototautomeric forms of these compounds, as compared to their nonfluorinated analogs,¹⁵ has been first predicted earlier by calculations using the method of molecular electrostatic potential (MESP). Fluorination increases fluorescence efficiency of neutral and anion forms. Consequently, it can be applied to compounds of this class in order to increase not only their photostability but also their emissivity.

Studying the lasing properties of F4MU excited with a XeCl* laser³ we have revealed the following peculiar features in contrast to the case of flash-lamp excitation, where only the anion form generates radiation.¹² In the former case we have observed stimulated emission from the four protolytic forms, namely, neutral (N), cationic (C⁺), anionic (A⁻), and phototautomeric (PhT). We explain this by selectivity of

radiation used for excitation and its short duration (drop in losses in the triplet channel). Our computations of the scheme of electronic levels of F4MU protolytic forms as well as the probability of absorption from the excited states ($S_1 \rightarrow S_i$, $T_1 \rightarrow T_i$) confirmed the assumption on an essential overabsorption of radiation in the system of triplet levels.

Aminocoumarins being the polar molecules are, as a rule, good solvatochromatic and solvatofluorochromatic molecules. Varying solvents one can obtain fluorescence and lasing in a wide wavelength range. However, intermolecular interactions, both specific and universal, influence not only the position of spectral maxima but the emissivity as well. There is no uniformity in the aminocoumarin series. Thus, an increase in solvent polarity leads to a growth of the fluorescence quantum yield ϕ_{f1} in some compounds, whereas a decrease in this value occurs in some others (see Fig. 2).

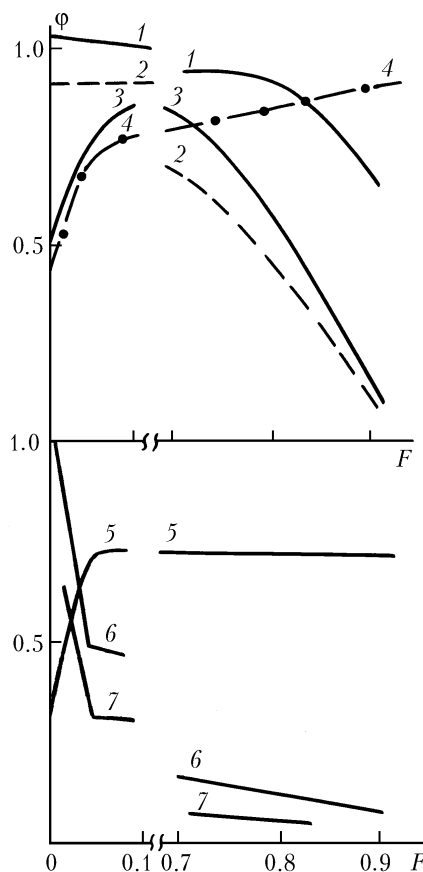


FIG. 2. Fluorescence quantum yield as a function of medium polarity (F) for the following coumarins (C): C102 (1), C153 (2), C1 (3), C120 (4), FC120 (5), FC1 (6), FC1CN (7). Solvents: pentane ($F = 0.001$), cyclohexane (0.002), benzene (0.013), CCl₄ (0.035), dioxane (0.042), diethyl ether (0.367), ethyl acetate (0.386), butanol (0.753), acetone (0.791), ethanol (0.823), acetonitril (0.863), methanol (0.869), water (0.913).

TABLE I. Spectral and lasing properties of aminocoumarins in ethanol ($C = 8$ mmole/liter).

Molecule	λ_{abs} , nm	λ_{fl} , nm	Φ_{fl}	λ_{las} , nm	Efficiency, %	$E(50\%)^1$, J/cm ³	MESP, kcal/mole	
							S_0	S_1^*
UC4	379	445	0.75	462	32	320	- 132	- 149
UC15	377	443	0.75	460	36	250		
UC17	411	518	0.40	525	30	890	- 120	- 141
UC1	416	520	0.20	530	25	700		
UC3	424	470	0.40	477	24	200 ²	- 118	- 123
UC16	421	468	0.50	475	24	220 ²		
AC3F	396	478	0.60	497	32	890	- 115	- 138
C1	370	457	0.50	460	27	370	- 129	- 141
C1N	372	461	0.30	465	30	600	- 124	- 144
3-phenyl C1	375	461	0,86	462	24	120	- 127	- 144
3-(2-pyridyl) C1	383	473	0.67	483	24	800	- 120	- 134
3-(3- pyridyl) C1	390	475	0.65	486	24	900	- 128	- 141
3-(4- pyridyl) C1	394	485	1.00	501	17	1500	- 121	- 139

¹⁾ E is the total excitation energy "pumped" into a unit volume of a lasing solution that halves the initial energy of radiation.

²⁾ Obtained for concentration $C = 2$ mmole/liter.

The Neporent-Bakhshiev function F of universal interactions¹⁶ truncated at the first term related to the dipole-dipole orientation interaction is taken as a measure of solvent polarity.

The drop of Φ_{fl} in aminocoumarins with increasing medium polarity is connected with the formation of nonplane H -bonded complexes with the solvent through coupling with 7-alkylaminogroups and results in intensification of radiationless deactivation. Introduction of strong electron-acceptor groups CF_3 and $\text{C}\equiv\text{N}$ into positions 4 and 3 results in a further decrease in Φ_{fl} with the increasing medium polarity. As calculations have shown, such a substitution results in maximum CT along the molecular long axis what in turn weakens C-N bond and makes the rotation about it easier. We have found that in pentane, where aminocoumarin molecules can be considered to be isolated systems and Φ_{fl} is only determined by the molecular structure, radiative properties correlate with the calculated value of contribution coming from the electron density into the $S_0 \rightarrow S_i$ transition of the electron-donor substituent.

The value of coumarin I fluorescence Quantum yield as a function of solvent polarity is described by a curve with an extreme point, and its maximum emissivity corresponds to solvents with small polarity, but sufficient viscosity. For other coumarins only a portion of this curve is realized depending on the charge-transfer character of the first transition.

By special synthesis it is possible to lock the alkylaminogroup by embedding it with nonaromatic cycle that causes a great increase in the fluorescence Quantum yield in polar solvents.

Experimental and theoretical researches in this area allowed Vasil'eva¹⁷ to develop new aminocoumarins using other ways of locking. These aminocoumarins possess high emissivity (see Table I).

One more important transformation of the coumarin structure could be the introduction of a heterocyclic nitrogen atom that can markedly influence both the spectral properties and the course of photoprocesses.

In azacoumarin AC3F, the ring nitrogen (see Fig. 3) does not take part in formation of the first absorption band, while, showing the inductive properties, it results in hypsochromic shift of the first absorption band by 20 nm as compared to the analog containing no heterocyclic nitrogen. The presence of nitrogen atom in AC3F structure slows down the processes of proton phototransfer (PPT) in a fluorescent state, thus leading to an increase in photostability (see the table). Introduction of a pyridyl fragment into position 3 of coumarin C1 causes a change in the sequence of generation of protonated forms: the first protonation proceeds through nitrogen of the pyridyl ring, and the second one does through the nitrogen of alkylaminogroup. Appearance of the basic centers in these structures slows down the reaction of protonation in the C=O group (both electron and steric factors), thus increasing photostability. As a consequence, we can conclude that there are certain relations between the change of acid-

basic properties due to introduction of heterocyclic nitrogen and the photostability of molecules exposed to XeCl*-laser radiation ($\lambda = 308$ nm, pulse power density 15–20 MW/cm², pulse duration 10 ns, pulse repetition frequency 1.7 and 5 Hz).

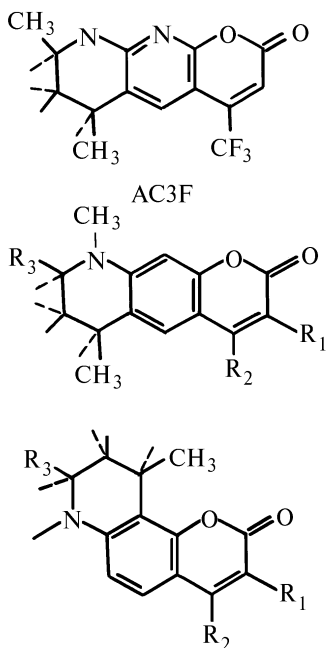


FIG. 3. Structure formulas of new aminocoumarins: UC4: R₁-H, R₂-CH₃, R₃-CH₃; UC15: R₁-H, R₂-CH₃, R₃-H; UC1: R₁-H, R₂-CF₃, R₃-CH₃; UC17: R₁-H, R₂-CF₃, R₃-H; UC3: R₁-CN, R₂-CH₃, R₃-CH₃; UC16: R₁-CN, R₂-CH₃, R₃-H.

Thus, the electronic structure and stereoeffects of proton-acceptor substituents (nitrogen heteroatom in AC3F, CF₃, pyridyl rings) are responsible for a lower probability for the oxygen of carbonyl group to take part in the processes of intermolecular interaction and the transformation of electronic structure in $n\pi^*$ states. These, in their turn, result in slowing down phototransformations of such structures excited by UV radiation and a 2–3-fold increase in the photostability of laser-active media developed on the basis of substituted coumarins and azacoumarins.

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