

Solvent-Dependent Radiationless Transitions in Fluorenone: A Probe for Hydrogen Bonding Interactions in the Cyclodextrin Cavity

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Abstract. Fluorescence lifetimes, fluorescence quantum yields and triplet yields were measured for fluorenone in various hydroxylic and non-hydroxylic solvents, and in β -cyclodextrin complexes. The rate of singlet–triplet intersystem crossing, which decreases with increasing polarity, was found to be a good indicator of nonspecific solvent–solute interactions, while the rate of direct internal conversion from the singlet excited state was correlated with hydrogen bonding. The fast internal conversion of singlet excited fluorenone/ β -cyclodextrin complexes shows that the probe molecule, while embedded within the cyclodextrin cavity, still remains hydrogen bonded.

Key words: Fluorescence lifetime, polarity, fluorenone, cyclodextrin.

1. Introduction

Cyclodextrins are water-soluble, torus-shaped cyclic oligosaccharides with a relatively apolar interior [1]. Their remarkable ability to form inclusion complexes with hydrophobic molecules which fit into the central cavity has led to widespread utilization of cyclodextrins in pharmaceutical, food, cosmetic and other chemical industrial areas [1,2]. Hydrophobic effects and van der Waals interactions are considered to be the major forces involved in such complex formation. Estimation of the local polarity of the cyclodextrin cavity helps to predict the kind of guest molecules which can be included in different cyclodextrin derivatives.

Fluorescence techniques have been widely used to examine the microenvironment of encapsulated molecules, since the fluorescence intensities, lifetimes and emission maxima of some fluorophores are very sensitive to, and reflect the nature of their solvation envelopes. Most of these fluorescent probes emit from twisted

* Dedicated to Professor Szejtli.

intramolecular charge transfer (TICT) states [3–7]. Fluorescence lifetime measurements of complexed 2-naphthol [7], or the spectral shifts shown by diphenylamine or exciplexes [8,9], have also been used to evaluate the polarity of the cyclodextrin cavity.

Earlier studies have reported on the solvent and temperature dependence of the rates of various competing photophysical processes depopulating the singlet excited state of fluorenone and its derivatives [10–13]. We now extend these studies to hydroxylic solvents (alcohols). These results are applied to the use of fluorenone as a probe for the investigation of specific hydrogen bonding interactions in the cyclodextrin cavity.

2. Experimental

Fluorenone (FLUKA) was purified by repeated recrystallization from ethanol. HPLC or spectroscopic grade organic solvents (dioxane, ethyl acetate, dichloromethane, acetone, acetonitrile, ethanol, water) were used as received; other solvents (methylcyclohexane, diethylether, tetrahydrofuran, dimethoxyethane, 1-pentanol, 1-octanol) were distilled. Purified β -cyclodextrin (β CD) and heptakis-(2,6-di-*O*-methyl)- β -cyclodextrin (DIMEB) were obtained from CYCLOLAB R&D Lab. Ltd., Hungary.

The inclusion complexes were prepared by adding fluorenone to 0.01M β CD or DIMEB in aqueous solution and warming to 60°C. The absorbances of all solutions were adjusted to 0.080 at the excitation wavelength and the samples were deoxygenated by purging with nitrogen for luminescence or flash photolysis studies.

Fluorescence lifetimes were measured on an Applied Photophysics SP-3 single photon counting apparatus using a hydrogen lamp operated at 30 kHz. Data were analyzed by a nonlinear least-squares deconvolution method.

Corrected fluorescence spectra were recorded on a homemade spectrofluorimeter equipped with a Princeton Applied Research type 1104A/B photon-counting system [14]. Fluorescence quantum yields were determined relative to fluorenone in acetonitrile ($\Phi_F = 0.032$) [10] following the usual procedure described in the literature [15]. 390 nm was chosen as the excitation wavelength, the slit widths of the excitation and emission monochromators were 3 nm and 5 nm, respectively.

Triplet yields were determined by the 'limiting slope' method [16] using fluorenone solution in methylcyclohexane as reference ($\Phi_{ISC}(\text{MCH}) = 1.00$). In this method, values of triplet yields are obtained by flash photolysis measurements of the relative slopes of triplet absorbance vs. flash energy plots, in the linear region. A frequency doubled ruby laser was used for excitation and the triplet-triplet absorption of fluorenone was monitored at 440 nm. The molar extinction coefficient of the triplet was taken to be the same for all solvents and in the cyclodextrin complexes. Further experimental details have been described [12].

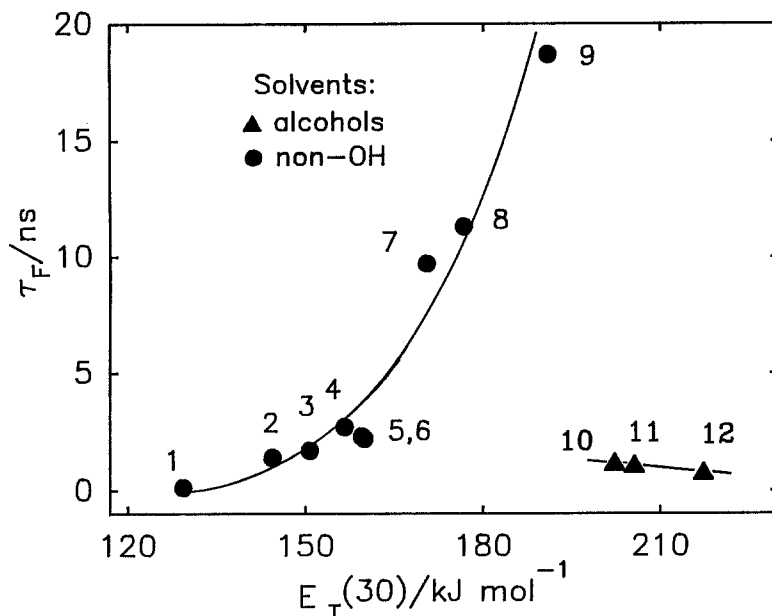


Fig. 1. Fluorescence lifetimes of fluorenone in hydroxylic \blacktriangle and non-hydroxylic \bullet solvents, as a function of $E_T(30)$ solvent polarity parameters. 1 methylcyclohexane, 2 diethylether, 3 dioxane, 4 tetrahydrofuran, 5 ethyl acetate, 6 dimethoxyethane, 7 dichloroethane, 8 acetone, 9 acetonitrile, 10 1-octanol, 11 1-pentanol, 12 ethanol.

3. Results and Discussion

3.1. FLUORESCENCE LIFETIMES AND TRIPLET YIELDS IN ORGANIC SOLVENTS

The fluorescence quantum yield (Φ_F) and fluorescence lifetime (τ_F) of fluorenone showed parallel changes in a series of solvents of different polarity. As the accuracy of the fluorescence lifetimes is better (estimated error $\pm 5\%$), we present here the solvent dependence of τ_F in more detail. Figure 1 gives the fluorescence lifetime of fluorenone as a function of the empirical solvent polarity parameter, $E_T(30)$ [17]. The plotted data clearly show two entirely distinct regions and polarity correlations. In non-hydroxylic (non-OH) solvents, τ_F increases by more than two orders of magnitude in going from methylcyclohexane to acetonitrile. However, in the alcohols, with $E_T(30)$ values higher than any of the non-OH media, the singlet lifetimes are very short, and decrease even further with increasing polarity (octanol \rightarrow ethanol). Taking the dielectric constant as a general measure of polarity, the fluorescence lifetime in ethanol (0.8 ns) is much shorter than in acetone (11.3 ns) although the respective dielectric constants (24.3 and 20.7) are similar. Thus, it appears that a specific interaction between fluorenone and the hydroxylic solvents strongly affects the rate of deactivation of the fluorenone singlet. We take this to be hydrogen bonding.

TABLE I. Photophysical parameters of fluorenone in non-hydroxylic and hydroxylic solvents.

Solvent	$E_T(30)$ kJ/mol	Φ_{ISC}	Φ_F 10^{-3}	τ_F ns	k_{ISC} $10^7 s^{-1}$	k_{IC} $10^7 s^{-1}$
Non-hydroxylic						
Methylcyclohexane ^a	129	1.00	0.5	0.14	710	^b
Diethyl ether	144	0.96	4.9	1.4	69	3
Dioxane	151	0.96	5.8	1.7	56	2
Tetrahydrofuran ^a	157	0.87	6.4	2.7	32	5
Ethyl acetate	160	–	5.5	2.3	–	–
Dimethoxyethane	160	–	5.3	2.2	–	–
Dichloromethane	170	–	20	9.7	–	–
Acetone ^a	177	0.77	21	11.3	6.8	1.8
Acetonitrile ^a	191	0.46	32	18.7	2.5	2.7
Hydroxylic						
1-Octanol	202	0.14	2.5	1.2	12	71
1-Pentanol	206	0.11	2.2	1.1	10	80
Ethanol	217	0.06	1.5	0.8	7	120

^a References 10 and 12.

^b Cannot be determined (see text).

In all media studied, the fluorescence quantum yield of fluorenone is low (Table I), so that deactivation proceeds mainly by radiationless processes. This may occur either by direct internal conversion of the singlet to the ground state, or by intersystem crossing to the triplet state. Proton transfer reactions of the singlet excited fluorenone leading rapidly to the ground state would be included in our k_{IC} , but there is no specific evidence for this pathway. Figure 2 (filled points) gives results of triplet yield measurements in various solvents. It is evident that, again, sharp differences appear between the alcohols and the non-OH solvents, the former showing very low values of Φ_{ISC} .

Table I summarizes experimental values of triplet yields (Φ_{ISC}) and singlet lifetimes (τ_F) for several solvents. Also listed are rate constants for singlet–triplet transitions (k_{ISC}) and direct internal conversion to the ground state (k_{IC}) derived from the relations:

$$k_{ISC} = \Phi_{ISC}/\tau_F$$

$$k_{IC} = (1 - \Phi_F - \Phi_{ISC})/\tau_F$$

The values of k_{ISC} , derived from the measured Φ_{ISC} and τ_F , are conservatively estimated to be reliable to $\pm 15\%$. However, the uncertainty in k_{IC} becomes quite large if Φ_{ISC} approaches unity. Thus, the differences in k_{IC} among the first three entries of Table I are within experimental error. For the opposite situation of

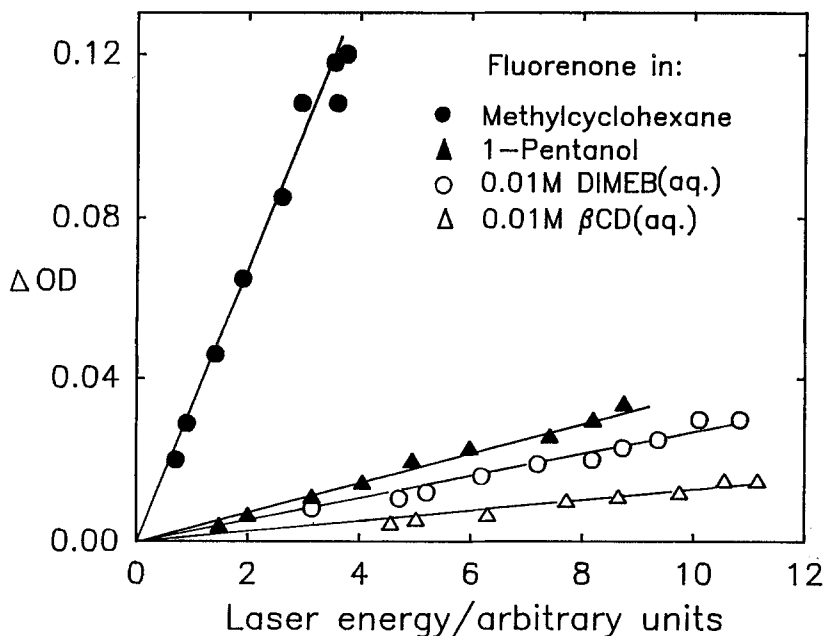


Fig. 2. Determination of triplet yields: triplet-triplet absorbance of fluorenone at 440 nm vs. laser energy in methylcyclohexane ●, in 1-pentanol ▲, in 0.01 M aqueous DIMEB ○, in 0.01 M aqueous β CD △.

low Φ_{ISC} , k_{IC} is determined primarily by τ_F . We judge the uncertainty in k_{IC} in hydroxylic solvents and in cyclodextrin complexes to be about $\pm 10\%$.

The data of Table I indicate that:

1. For the non-OH solvents, k_{IC} is relatively small, and is essentially independent of polarity; k_{ISC} is much larger, and decreases with polarity. It is mainly this process, singlet-triplet transition, which controls the solvent dependency of τ_F in these media.
2. For the alcohols, k_{ISC} is close to that of the non-OH solvents of comparable polarity, while k_{IC} is much greater. It is the OH-enhanced rate of internal conversion which results in a low triplet yield and a short singlet lifetime in this case. The rate decreases slightly with increasing chain length, as expected for a weakening hydrogen bonding interaction [17].

It is clear that the photophysical properties of fluorenone are sharply different in alcohols, where internal conversion is the main dissipative channel from the singlet, and in non-OH solvents, (particularly those of low polarity), where transition to the triplet is the dominant pathway. It is striking that hydrogen bonding interactions markedly increase the rate of internal conversion, while intersystem crossing is scarcely affected. Conversely, non-specific polarity-dependent interac-

TABLE II. Photophysical properties of fluorenone inclusion complexes.

Complex	τ_F ns	Φ_F 10^{-3}	Φ_{ISC}	k_{ISC} $10^7 s^{-1}$	k_{IC} $10^7 s^{-1}$
Fluorenone/ β CD	1.2	2.4	0.04	3.3	79
Fluorenone/DIMEB	2.2	4.8	0.08	3.6	41

tions between singlet excited fluorenone and solvent do not influence the rate of internal conversion but do decrease intersystem crossing.

On the basis of its characteristic responses to different solvents, we may expect that fluorenone will provide a useful probe to study separately specific hydrogen bonding and non-specific dielectric interactions in the cyclodextrin cavity.

3.2. PHOTOPHYSICAL PROPERTIES OF FLUORENONE INCLUSION COMPLEXES

The formation of complexes between fluorenone and β CD or DIMEB is demonstrated unambiguously by cyclodextrin-enhanced solubility and very directly by the appearance of circular dichroism of fluorenone in the presence of β CD [19].

Table II presents photophysical properties of fluorenone embedded in β CD or DIMEB cavities. In both cases, fluorescence decays fit single exponential functions and lifetimes (1–2 ns) are quite short. In these measurements, interference from emission of uncomplexed fluorenone is negligible because of its low concentration and quantum yield. The results of triplet yield measurements are given in Figure 2 (open points). It is immediately evident that the yields for both complexes are low and close to those observed for alcohols. In accord with this, the derived rate constants k_{ISC} and k_{IC} (Table II) establish that direct internal conversion to the ground state is the dominant decay process in these complexes, and is mainly responsible for the short singlet lifetimes. This indicates that hydrogen bonding interactions with the fluorenone guest are significant.

In interpreting this result, we may exclude, on the basis of molecular dimensions and cavity geometry, the possibility that fluorenone is complexed equatorially, with the carbonyl group oriented toward water [19]. Indeed, an axially-bound complex is clearly demonstrated by the circular dichroism spectrum, which, assuming axial geometry, leads to the same spectroscopic assignments as are derived from crystal absorption and fluorescence polarization data [19]. Moreover, the qualitative similarity of the photophysical properties of β CD and DIMEB complexes indicates that no hydrogen bonds are formed between the fluorenone carbonyl and the OH groups of β CD. This agrees also with the expectation, based on the circular dichroism results, that fluorenone is probably symmetrically incorporated in β CD. Thus, we conclude that fluorenone while embedded in the cyclodextrin cavity still retains H-bonded water. This itself may be outside the cyclodextrin cavity. Additional sites for bonding water within the cavity may be provided by the cylindrically disposed,

central glycosidic oxygens, but the precise extent to which any such originally bound water is displaced, or stabilized, by complexed fluorenone is, of course, still uncertain.

As noted above, since both Φ_F and Φ_{ISC} are small, the derived values of k_{IC} in Table II depend primarily on the fluorescence lifetimes, which are measured with fairly good accuracy ($\pm 5\%$). We estimate that the uncertainty in the k_{IC} s are not greater than $\pm 10\%$. Thus, the twofold difference observed in k_{IC} between the β CD and DIMEB complexes is well beyond the experimental error. This difference is matched by a corresponding reverse change in k_{ISC} , suggesting that the DIMEB cavity provides an environment somewhat closer to that of the non-OH solvents than does β CD. This may be related to a smaller content of internally bound water in the methylated case.

The values of both k_{ISC} and k_{IC} given in Table I and Table II support the following conclusions:

- (i) If we take k_{ISC} values as indicators of the dielectric polarity (Table I), it is apparent that the cyclodextrin cavity is much more polar than dioxane or tetrahydrofuran and its polarity is close to that of ethanol.
- (ii) However, the rates of internal conversion (k_{IC}) show that the strength of hydrogen bonding with the fluorenone is lower in the cavity of cyclodextrins than in ethanol and it is more similar to that found in 1-octanol.

There are extremely large discrepancies in the literature among the data on the polarity of the cyclodextrin cavity with 'effective equivalent dielectric constants' ranging from 2.2 to 55 [18,26]. From the fluorescence spectrum of exciplexes [20,21] or from the absorption spectrum of *p*-tert-butylphenol [22], it has been concluded that the polarity of the cyclodextrin cavity resembles that of dioxane. However, using pyrene-3-carboxaldehyde as a fluorescent probe, $\epsilon = 55$ and $\epsilon = 48$ has been derived for the dielectric constant of the γ -CD and β -CD cavity, respectively [23]. Other authors have found that the polarity of the cyclodextrin interior is like that of methanol [24], ethanol [7-9], 1-propanol [25], tert-butanol, ethylene glycol [5], 1-pentanol [26] or 1-octanol [27]. The discrepancies probably arise from any or all of the following factors: (a) some probes are not entirely encapsulated in the cyclodextrin, or are held in different configurations relative to the cavity wall [5]. (b) The number of water molecules inside the different cyclodextrin complexes may differ because of steric or energetic reasons. (c) The probes which have been used are able to respond primarily to the bulk polarity of the region; their sensitivity to the nonspecific solvent-solute interactions relative to their sensitivity to hydrogen bonding interactions varies considerably. The utilization of fluorenone as a molecular probe facilitates the study of nonspecific and hydrogen bonding interactions separately.

In connection with the above situation, the effect of complexation on the absorption spectrum of fluorenone is of interest. Figure 3 shows that the low energy band of fluorenone in β CD is red-shifted, broadened and loses fine-structure, compared

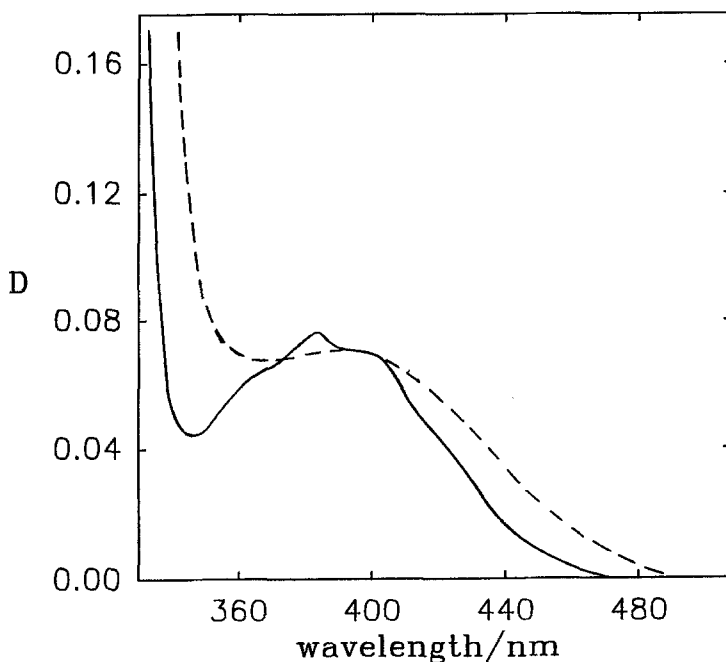


Fig. 3. Absorption spectrum of fluorenone in ethanol — and in 0.01 M aqueous β CD solution - - -.

to the spectrum in ethanol. The lowest energy transition of fluorenone is $\pi - \pi^*$ [13], which is characteristically red-shifted in polar media. While the observed effect may indeed indicate a highly polar cavity environment, other mechanisms may account for the effect. In particular, we suggest that especially strong van der Waals interactions with the cavity couple the $\pi - \pi^*$ transition more closely to the surroundings than is the case in the less structured geometry of liquid solutions. This would both lower the energy of the excited state and smear out vibrational structure.

4. Conclusions

Fluorescence decays fit single exponential functions and lifetimes (1–2 ns) are quite short when fluorenone is embedded in β CD or DIMEB cavities. The triplet yields for both complexes are low and close to those observed for alcohols. Excluding the possibility that fluorenone is complexed equatorially, with the carbonyl group oriented toward water, an axially-bound complex is clearly demonstrated as derived from crystal absorption and fluorescence polarization data. The fast internal conversion of singlet excited fluorenone/ β -cyclodextrin complexes shows that the probe molecule embedded within the cyclodextrin cavity still remains hydrogen

bonded. Water within the cavity may be provided by the cylindrically disposed, central glycosidic oxygens.

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