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Fluorescence of 1-anilinonaphthalene-8-sulfonate in solid macrocyclic environments

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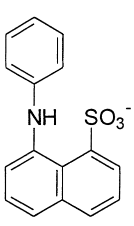
Abstract

Fluorescence spectra, lifetimes and relative quantum yields of ammonium 1-anilinonaphthalene-8-sulfonate (ANS) were measured in solid ANS, in mixtures of ANS with Al_2O_3, SiO_2, $BaSO_4$, talcum and in solid complexes with cyclodextrins, cyclphane CP 66 and cucurbituril. Emission lifetimes ranged from 4.2 in the SiO_2–ANS mixture to 20.0 ns in the β-cyclodextrin complex. The highest relative quantum yields were exhibited by the γ-cyclodextrin and the cucurbituril complex. CP 66 complexed ANS in ethanol solution is protected from oxygen quenching to some extent. In non-polar environments, i.e. in cyclohexane as a solvent as well as in solid paraffin, an unexpectedly short fluorescence lifetime was measured. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: 1,8-ANS; Fluorescence in solids; Fluorescence enhancement; Macrocyclic ligands

1. Introduction

In solution the fluorescence of anilinonaphthalene sulfonates, especially of ammonium 1-anilinonaphthalene-8-sulfonate (ANS), has been studied thoroughly [1]. The influence of solvent polarity on the fluorescence of ANS was investigated in mixtures of dioxane and water [2] and in various alcohols [3]. General features found upon increasing the solvent polarity were (i) a red shift of fluorescence maxima, (ii) a decrease in fluorescence lifetime, and (iii) a drop of fluorescence quantum yield. The emitting state was shown to be an intramolecular charge transfer (ICT) state. More recently it was suggested, that strongly red shifted emissions in such systems may rest on a twisted molecular geometry in the excited state [4–6]. These twisted intramolecular charge transfer (TICT) states are less likely to be formed in systems of high viscosity such as polymer matrices [7] as compared to fluid systems. The observed high sensitivity of ANS to the polarity of the environments has prompted a frequent use of ANS-derivatives as fluorescent probes for micropolarities in biological membrane systems [8]. Also, a strong affinity to certain macrocyclic host molecules was described [9,10] and fluorescence spectra of ANS complexes with β- and γ-CD in aqueous solution can be found in the literature [11–15]. In particular, complexation by modified β-CDs gives rise to enhanced ANS fluorescence in solution [16].



ANS

We will show below that the described properties of the ANS fluorescence in solution are not completely paralleled in solids: we report on the peculiar fluorescence behaviour of ANS in solid supramolecular environments, such as in solid complexes with α-, β-, and γ-cyclodextrin, cyclophane CP 66, and cucurbituril (see Fig. 1). For comparison other (non-complexing) solid systems were included in this investigation, i.e. mixtures of ANS with silica gel, aluminium oxide, barium sulfate and talcum (powdered talc) and a solid matrix of ANS in paraffin as a non-polar reference environment. A few measurements of ANS complexed by macrocycles in solution complete the study.

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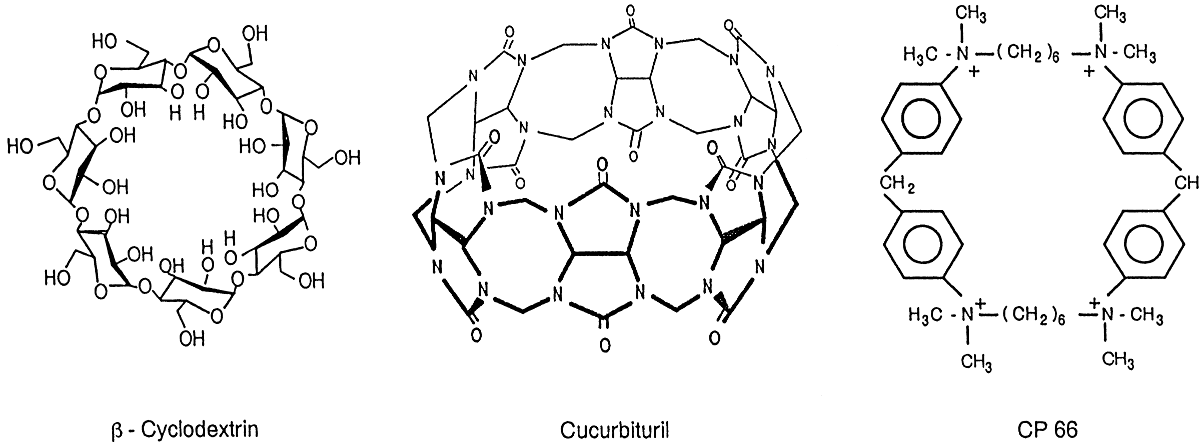
β - Cyclodextrin

Cucurbituril

CP 66

Fig. 1. Chemical structures of macrocyclic ligands used.

2. Results

The relative fluorescence intensities of ANS as a function of ANS concentration are shown in Fig. 2 (for solid matrices) and Fig. 3 (for solid complexes with macrocyclic ligands). Spectral fluorimetric data and relative quantum yields are collected in Table 1. The latter are expressed as *s*, the slopes of plots of the fluorescence intensity versus the ANS content in ppm. It can be seen that relative quantum yields are highest for cucurbituril and γ-cyclodextrin complexes. The maxima of excitation and emission spectra vary in a series order that was not expected when previous findings in solution are compared: the emission maximum in solid paraffin is among the most red shifted ones, although paraffin provides a non-polar environment; on the contrary, the spectra of ANS on the polar talcum surface are blue shifted.

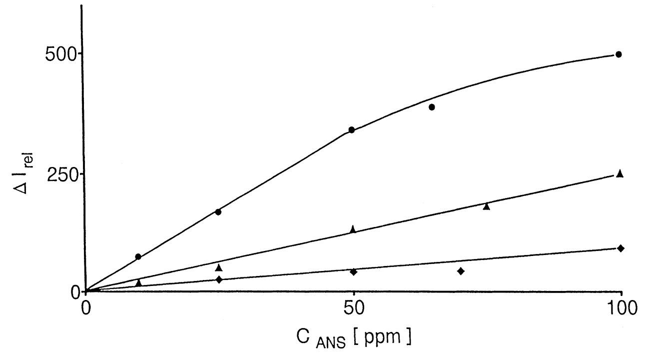

Fig. 2. Relative fluorescence intensity ΔI_{rel} of ANS in solid matrices (◆: $BaSO_4$; ●: Al_2O_3; ▲: SiO_2) as a function of the ANS concentration.

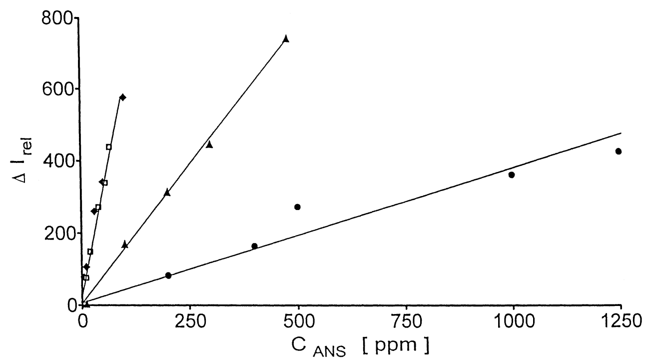

Fig. 3. Relative fluorescence intensity ΔI_{rel} of solid complexes of ANS with different macrocyclic ligands (▲: α-cyclodextrin; ●: β-cyclodextrin; ◆: γ-cyclodextrin; □: cucurbuturil) as a function of the ANS concentration in $BaSO_4$.

Table 1

Maxima of excitation, λ_a, and fluorescence spectra, λ_e lifetimes and relative quantum yields, *s*, (slopes of intensity vs. dye content plots) of 1-anilinonaphthalene-8-sulfonate (ANS) in various solid mixtures and in solid complexes of cyclodextrins (CD) and cucurbituril (CB) and in fluid systems

Mixture or complex	λ_a (nm)	λ_e (nm)	*s* (ppm^{-1})
Solid mixtures			
ANS pure	414	486	–
SiO_2/ANS	416	471	2.5
Al_2O_3/ANS	411	467	3.4[a]
$BaSO_4$/ANS	415	483	0.9
Talcum/ANS	404	458	–
Paraffin/ANS	413	478	–
Solid complexes			
α-CD/ANS	402	481	1.56
β-CD/ANS	395	465	0.43
γ-CD/ANS	394	461	6.47
CP 66/ANS	438	480	–
CB/ANS	386	470	6.47
Fluid solutions			
ANS in ethanol	402	468	–
ANS in H_2O (pH 6.8)	–	535[b]	–
α-CD/ANS in H_2O	–	509[b]	–
β-CD/ANS in H_2O	–	495[b]	–
CP 66/ANS in ethanol	400	500	–
ANS in cyclohexane	403	460	–

[a] Initial slope.

[b] From ref. [11].

Table 2
Lifetimes τ (aerated) and τ_0 (evacuated solid samples or argon saturated solutions, respectively), and oxygen quenching constant k_q of ANS in solid mixtures and complexes and in fluid systems

Mixture, complex, solution	Sample no.	τ/ns	τ_0/ns	k_q (10^{10} dm^3 mol^{-1} s^{-1})
Solid mixtures				
ANS pure		4.5 ± 0.4	5.1 ± 0.4	–
SiO_2/ANS		4.2 ± 0.4	5.6 ± 0.5	–
Al_2O_3/ANS		4.5 ± 0.4	6.1 ± 0.5	–
$BaSO_4$/ANS		4.4 ± 0.4	–	–
Talkum/ANS		4.4 ± 0.4	–	–
Paraffin/ANS		4.2 ± 0.4	–	–
Solid complexes				
α-CD/ANS	1	10.6 ± 0.8	–	–
	2	8.6 ± 0.8	8.0 ± 0.7	–
β-CD/ANS	1	8.2 ± 0.7	–	–
	2	20.0 ± 1.2	14.9 ± 1.1	–
γ-CD/ANS	1	9.6 ± 1.0	–	–
	2	12.1 ± 1.1	14.3 ± 1.2	–
CP 66/ANS	1	12.9 ± 1.0	–	–
	2	10.6 ± 0.9	9.6 ± 0.9	–
CB/ANS	1	14.5 ± 1.4	–	–
	2	10.9 ± 0.8	10.3 ± 0.8	–
Solutions				
ANS in ethanol		12.5±0.5	16.8 ± 0.5	1.0 ± 0.2
ANS/CP 66 in ethanol		12.9±0.7	14.6 ± 0.6	0.5 ± 0.2
ANS in cyclohexane		7.1±0.4	10.0 ± 0.5	2.0 ± 0.2

Standard deviations for 3–6 repeated measurements of identical samples are given.

Due to these discrepancies we became interested in the fluorescence lifetimes which are comprised in Table 2. Again, the value in paraffin is unexpectedly among the shortest ones and does not deviate much from those of the solid mixtures and of pure solid ANS. The solid complexes show considerably longer lifetimes throughout, which, in contrast to the mixtures, turned out to depend on the individual sample. In order to prove possible protection of ANS from oxygen quenching by the macrocyclic complex ligands we measured evacuated complexes, too. However, the lifetimes shortened rather than increased after removing the air (in contrast to the solid mixtures). Therefore, protection from oxygen quenching cannot be the only reason for the observed prolonged lifetimes in the solid complexes.

For comparison, we performed a few analogous measurements in fluid solutions which are included in the tables. Dye concentrations did not exceed 10^{-5} M in these experiments. The lifetime in argon saturated ethanol (16.8 ns) agrees fairly well with the published value (18.1 ns [3]). Comparing values in aerated and argon saturated solvents we can obtain oxygen quenching constants k_q according to

$$k = k_0 + k_q[O_2] \tag{1}$$

where $k = 1/\tau$ and $k_0 = 1/\tau_0$; the index 0 refers to oxygen-free solutions. Values for k_q are in the range of 10^{10} dm^3 mol^{-1} s^{-1} as expected for nearly diffusion controlled oxygen quenching [17].

3. Discussion

3.1. Fluid systems

In previous work on ANS fluorescence non-polar solvents like cyclohexane were not investigated, probably for reasons of solubility. The decrease of lifetime as compared to ethanol observed here is unexpected on the basis of the rule that lifetimes increase with decreasing polarity of the solvent [1–3]. Possibly, the non-dissociated ANS is solubilized in cyclohexane giving rise to a molecular geometry differing from that of the anion in ethanol and other protic solvents. Also, an aggregation of ANS in non-polar solvents may occur. In other systems uncommon fluorescence properties ascribed to the formation of aggregates were already reported [18], particularly in two TICT-state forming systems [19,20]. The reduced oxygen quenching constant for ANS in ethanol in the presence of CP 66 (Table 2) indicates complexation and some protection of excited ANS from oxygen.

3.2. Solid systems

Upon evacuation a decrease of lifetimes was observed in the solid CP 66 complex as well as in most of the other solid complexes. This counterintuitive observation can be rationalized when the evacuation process is considered in detail. Obviously, the evacuation of cells containing the solid complexes seems to remove not only air (i.e oxygen and nitrogen) but also remnants of solvent molecules (left from preparation procedures) and adsorbed water (from air humidity) from the solids investigated. Since by that the nearest environments of the dye change, lifetimes can be affected. From a previous investigation it is already known that removing coadsorbed molecules may give rise to quantum yield variations: the fluorescence of anthracene adsorbed on SiO_2 is quenched not only by photochemical quenchers like oxygen but also in the presence of coadsorbed argon which does not quench in homogeneous systems [21]. A sensitivity of ANS lifetimes to slightly different sites of the dye molecules is also indicated by the fact that lifetimes differ for individual aerated samples (while results from identical samples are satisfactorily reproducible). These differences may result from two distinct origins: (i) it is known that different charges of cucurbituril, although prepared in the same way, may contain various amounts of water [22–24]; (ii) although all complexes were prepared in a 1 : 1 stoichiometry, the amount of actually complexed ANS in cyclodextrins or cucurbituril may be distinct for individual preparations. Future investigations, therefore, will concentrate on the preparation of more uniform solid complex samples.

3.3. Solution versus solid systems

In solution (except for cyclohexane, see above) short lifetimes and red shifted emissions prevailed in polar solvents and could be ascribed to a TICT emission state. Twisting of the aniline moiety of ANS can be expected to be restricted in the solid. In solution the absorption maxima do not depend much on solvent polarity (see Table 1 and [1–3]) indicating that twisting of the anilino group occurs in the excited state, while in some of the solids the observed shifts of excitation spectra indicate differing geometries already in the ground state, depending on the adsorption or complexation site.

4. Experimental

The following chemicals were of the highest purity commercially available. They were used without further purification: ammonium 8-anilinonaphthalene-1-sulfonate (ANS, Fluka), Al_2O_3 (ICN), SiO_2 (Kieselgel 60, Merck), $BaSO_4$ (Merck), tetramethylammonium hydroxide (Fluka), talcum (Fluka), ethanol (Merck), cyclohexane (Merck), α-cyclodextrin (α-CD, Merck), β-cyclodextrin (β-CD, Wacker), and γ-cyclodextrin (γ-CD, Merck). The macrocyclic ligand cucurbituril (CB) was synthesized and purified as described in the literature [22]. The cyclophane CP 66 was a gift from Prof. H.-J. Schneider, Saarbrücken; its preparation has been described elsewhere [10].

4.1. Preparation of solid samples

The desired mixtures of ANS and SiO_2, Al_2O_3, $BaSO_4$ and talcum were weighed and mortared to a fine powder. Solutions of ANS in molten paraffin were prepared at 60°C and allowed to cool to room temperature. They form a waxy solid thereafter. Solid complexes of ANS with different ligands were prepared from solutions containing ligand and ANS (1 : 1 ratio) by slow evaporation of the solvent. Due to the fact that the ligand cucurbituril is only soluble in acidic aqueous solution the complex formed in this solution was precipitated by changing the pH value using tetramethylammonium hydroxide.

Fluorescence and excitation spectra taken from the front surfaces of the samples were recorded using a fluorescence spectrometer (LS-3B, Perkin-Elmer). The relative fluorescence intensities of solid samples with all macrocyclic ligands were too high to be measured directly. Therefore, the concentration of the ANS-complexes was reduced to the 100 ppm-level by mixing with $BaSO_4$ (see figures).

Fluorescence lifetimes were derived from fluorescence decay curves (not spectrally resolved) measured after excitation by 337 nm 0.5 ns pulses of a N_2-Laser (Lambda Physik, Model K50 PS). Decay curves were recorded on a Hewlett Packard Model 54502A digital oscilloscope employing an Avalanche photodiode (Opto Electronics, Model PD 30). This apparatus was successfully employed in the investigation of other solid systems [25,26]. The fluorescence decay followed first-order kinetics throughout (a few percent deviation from first-order kinetics cannot be detected within the accuracy limits) indicating a quite narrow site distribution of absorbed ANS in the individual samples. Oxygen free samples were prepared by evacuating the solids at 0.05 mbar for 0.5 h at room temperature or by saturating fluid samples with argon.

5. Conclusions

Fluorescence spectra and lifetimes of ANS in solid environments vary in a way reflecting the spatial situation of the dye and its immediate surrounding rather than the polarity of the environment. For possible applications exploiting fluorescence of solids it may be important that quantum yields can be significantly enhanced in the presence of γ-cyclodextrin and of cucurbituril as compared to other solid systems.

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References

[1] E.M. Kosower, Acc. Chem. Res. 15 (1982) 259.
[2] E.M. Kosower, H. Dodiuk, H. Kanety, J. Am. Chem. Soc. 100 (1978) 4179.
[3] K. Chakraborti, W.R. Ware, J. Chem. Phys. 55 (1971) 5494.
[4] W. Rettig, Angew. Chem. 98 (1986) 969.
[5] W. Rettig, Nachr. Chem. Techn. Lab. 39 (1991) 398.
[6] W. Rettig, EPA Newsletter 41 (1991) 3.
[7] K.A. Al-Hassan, T. Azumi, Chem. Phys. Lett. 146 (1986) 121.
[8] L. Brand, J.R. Gohlke, Ann. Rev. Biochem. 41 (1972) 843.
[9] Y. Murakami, J. Kikuchi, T. Hirayama, Chem. Lett. (1987) 161.
[10] H.-J. Schneider, R. Kramer, S. Simova, U. Schneider, J. Am. Chem. Soc. 110 (1988) 6442.
[11] F. Cramer, W. Saenger, H.-C. Spatz, J. Am. Chem. Soc. 89 (1967) 14.
[12] I. Tabushi, K. Shimokawa, N. Shimizu, H. Shirakata, K. Fujita, J. Am. Chem. Soc. 98 (1976) 7855.
[13] G.C. Catena, F.V. Bright, Anal. Chem. 61 (1989) 905.
[14] J.W. Park, H.J. Song, J. Phys. Chem. 93 (1989) 6454.
[15] H.-J. Schneider, T. Blatter, S. Simova, J. Am. Chem. Soc. 113 (1991) 1996.
[16] B.D. Wagner, P.J. MacDonald, J. Photochem. Photobiol. A: Chem. 115 (1998) 151.
[17] W.R. Ware, J. Chem. Phys. 66 (1961) 455.
[18] T. Wolff, K. Pfanner, C. Springob, J. Photochem. Photobiol. A: Chem. 74 (1993) 247.

[19] K. Rotkiewicz, H. Leismann, W. Rettig, J. Photochem. Photobiol. A: Chem. 49 (1989) 347.
[20] E. Gilabert, R. Lapouyade, C. Rullière, Chem. Phys. Lett. 185 (1991) 82.
[21] T. Wolff, F. Akbarian, G. von Bünau, Ber. Bunsenges. Phys. Chem. 94 (1990) 833.
[22] R. Behrend, E. Meyer, F. Rusche, Justus Liebigs Ann. Chem. 339 (1905) 1.
[23] W.A. Freeman, W.L. Mock, N.-Y. Shih, J. Am. Chem. Soc. 103 (1981) 7367.
[24] N.-Y. Shih, Host–Guest Chemistry of Cucurbituril, Dissertation, University of Illionis, USA, 1981.
[25] C. Springob, G. von Bünau, T. Wolff, F. Schüth, Ber. Bunsenges. Phys. Chem. 100 (1996) 1206.
[26] C. Springob, T. Wolff, J. Photochem. Photobiol. A: Chem. 101 (1996) 75.