

- (23) P. J. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).
 (24) C. G. Lee, Ph.D. Thesis, Columbia University, New York, N.Y., 1973.
 (25) (a) N. J. Turro and P. Lechtken, *J. Am. Chem. Soc.*, **94**, 2886 (1972); (b) H.-C. Steinmetzer, A. Yekta, and N. J. Turro, *ibid.*, **96**, 282 (1974); (c) N. J. Turro, N. E. Schore, H.-C. Steinmetzer, and A. Yekta, *ibid.*, **96**, 1936 (1974); (d) P. Lechtken, A. Yekta, and N. J. Turro, *ibid.*, **95**, 3027 (1973).
 (26) (a) T. Higashimura, T. Masuda, S. Okamura, and T. Yonezawa, *J. Polym. Sci., Part A*, **7**, 3129 (1969); (b) T. Fueno, T. Okuyama, and J. Furukawa, *ibid.*, **7**, 3210 (1969).
 (27) It has been found in our laboratories that 1,1-dithoxyethylene is by far the most easily hydrolyzed of all the vinyl ethers we have studied, while its quenching ability is some three times less than that of 15: M. Neimczyk, unpublished results.
 (28) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834 (1969).
 (29) (a) P. J. Wagner and A. E. Kampainen, *J. Am. Chem. Soc.*, **91**, 3085 (1969); (b) P. J. Wagner and R. A. Leavitt, *ibid.*, **95**, 3669 (1973).
 (30) (a) R. S. Davidson and P. F. Lambeth, *Chem. Commun.*, 511 (1968); (b) S. G. Cohen, N. Stein, and N. M. Chao, *J. Am. Chem. Soc.*, **90**, 521 (1968); (c) L. A. Singer, *Tetrahedron Lett.*, 923 (1969); (d) M. T. McCall, G. S. Hammond, O. Yonemitsu, and B. Witkop, *J. Am. Chem. Soc.*, **92**, 6991 (1970); (e) G. N. Taylor and G. S. Hammond, *ibid.*, **94**, 3684 (1972).
 (31) J. F. O'Donnell, J. T. Ayres, and C. K. Mann, *Anal. Chem.*, **37**, 1161 (1965).
 (32) W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, **79**, 2828 (1957).
 (33) C. D. Hurd and M. A. Pollack, *J. Am. Chem. Soc.*, **60**, 1905 (1938).
 (34) H. Post, *J. Org. Chem.*, **5**, 244 (1940).
 (35) S. M. McElvain and C. H. Stammer, *J. Am. Chem. Soc.*, **73**, 915 (1951).
 (36) T. J. Lee, Ph.D. Thesis, Columbia University, New York, N.Y., 1972.
 (37) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969).
 (38) Explosion shields were always used in front of this set-up.

Novel Fluorescent Probe for Micellar Systems. 1,3-Dialkylindoles

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Abstract: The fluorescent properties of several 1,3-dialkylindoles are described in terms of their potential value as fluorescent probes for micellar systems. These compounds display shifts in fluorescence λ_{\max} from 370 to 350 nm and in fluorescence lifetime from 19 to 8 nsec in going from aqueous to micellar environment. One such compound, 11-(3-hexyl-1-indolyl)undecyltrimethylammonium bromide (**5**), forms micelles at concentrations above 10^{-4} M and is readily incorporated into micelles of other cationic surfactants. This indole is useful in determining the critical micelle concentrations (cmc's) of cationic surfactants because of the large shift in its fluorescence spectral distribution upon incorporation into a host surfactant micelle. In addition, use of a wavelength-correlated single photon-counting technique allows resolution of the fluorescence of this compound into aqueous and micellar components in the vicinity of its cmc.

The nature of the intramicellar environment has been the subject of extensive study for decades.¹ Over the years, a simple schematic description of the micelle has evolved based predominantly on measurements of macroscopic solution properties and effects of micelles on chemical reactions.¹ Figure 1 illustrates the typical spherical micelle that is formed in aqueous solutions of roughly 10^{-3} to 10^{-2} M ionic surfactant. The micelle consists of a liquid hydrocarbon-like core surrounded by a highly charged layer (Stern layer) containing ionic head groups of the individual surfactant molecules, oppositely charged counterions, and water. The simplicity of this model raises a number of questions concerning its applicability in detail. For example, how hydrocarbon-like is the micellar core, with respect to polarity (i.e., presence or absence of water), viscosity, or air solubility? Micelles are in dynamic equilibrium with monomeric (i.e., unassociated) surfactant molecules in solution; individual micelles are thought¹ to remain intact no longer than 10^{-4} sec. Thus techniques used to probe the micelle must operate on short enough time scales to provide essentially instantaneous rather than time-averaged information. Measurements of processes such as fluorescence, operating over very short (e.g., nanosecond) time periods, appear to be uniquely adaptable to studies of this nature.

Fluorescent probes have long been employed to provide information on the microenvironments of biological macromolecules and larger structures including membrane systems.² More recently, the use of fluorescent probes in surfactant systems has become popular as interest in the nature of the micellar interior grows.³ In earlier studies, ionic or zwitterionic aromatic molecules were commonly employed due to the extreme sensitivity of their fluorescent

yields to solvent polarity. Recently, however, objections have been raised concerning the validity of using highly polar probes for hydrophobic regions such as micellar interiors,^{4,5} and most recent studies^{3,5} have utilized aromatic hydrocarbons as probes that would be less likely to perturb the properties of the host system under investigation.

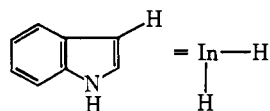
The versatility of the fluorescence technique is illustrated in the varied nature of these studies. Included among the types of measurements involved are excitation and emission spectra,⁶ emission decay rates⁷ and quantum yields,⁸ and static as well as dynamic fluorescence polarization.⁹ Fluorescence spectra and polarization experiments^{3e,1} support the general contention that the core of the micelle is liquid hydrocarbon-like with respect to polarity and viscosity, but other studies based on quantum yields of excimer fluorescence indicate a very high (or perhaps anisotropic) viscosity in the micellar interior.^{3c,8} Fluorescence lifetime and quenching measurements^{3b,f,5} have provided information concerning the general location of solubilized fluorescent molecules in the micelle and their accessibility to quenchers located either in the bulk aqueous medium or deep inside the micelle. With regard to these studies, the question of oxygen solubility in micelles has arisen;^{3c,5} as yet, no clear-cut answer has been forthcoming on this point.

We report here an extension of earlier studies made in these laboratories⁵ using fluorescence-decay techniques^{10,11} to analyze the behavior of small fluorescent molecules in solutions of micelle-forming surfactants. We have evaluated a series of 1,3-dialkylindoles as potentially versatile and powerful fluorescent probes for micelle structure, amenable to both static and dynamic, including time-resolved, fluorescence spectral measurements.

Results and Discussion

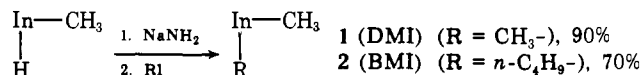
1. Synthesis of Indoles. In view of the favorable fluorescent properties of 1,3-dialkylindoles (vide infra), compounds **1-5** were prepared for use in this survey (Scheme I).

Scheme I

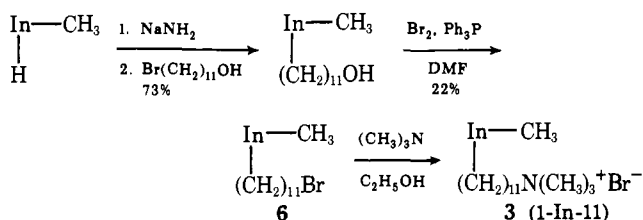


(For brevity, indoles are abbreviated as shown in the equations below.)

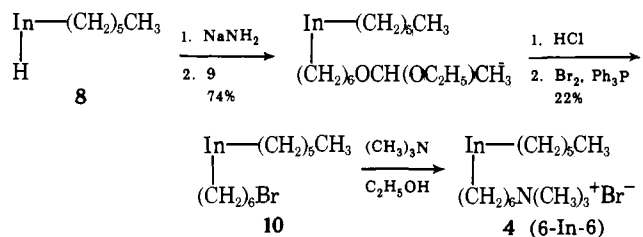
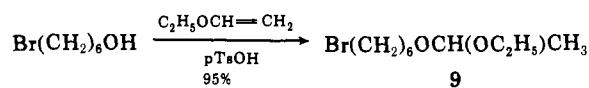
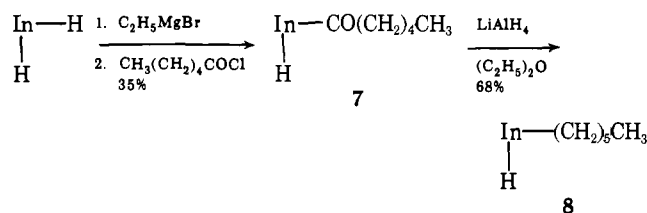
compounds **1** and **2**:



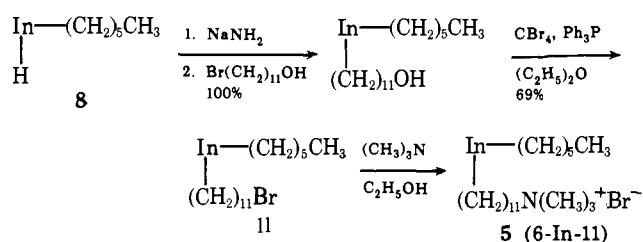
compound **3**:



compound **4**:



compound **5**:



Compounds **1** and **2** were prepared in 90 and 70% yields, respectively, by alkylation of the sodium salt of skatole with either methyl iodide or *n*-butyl iodide in liquid ammonia-diethyl ether.¹² Compound **3** was prepared in three steps from skatole by alkylation of the sodium salt with 11-bromoundecanol, conversion of the alcohol to the bromide **6** with bromine and triphenylphosphine in dimethylformamide (low yield),¹³ and quaternization with trimethylamine in ethanol.¹⁴ For **4** and **5**, indole magnesium bromide was acylated¹⁵ with hexanoyl chloride to yield 3-hexanoylindole (**7**) in 35% yield, and the latter compound was then reduced to 3-hexylindole (**8**) with lithium aluminum hydride in 68%

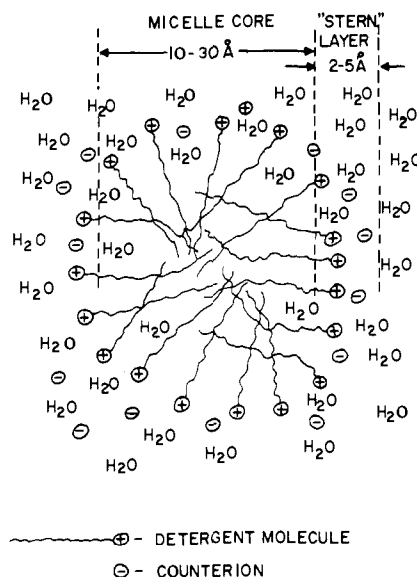


Figure 1. Cross-section of a typical micelle in aqueous solution.

Table I. Fluorescence Properties of Indoles in Cyclohexane and Water Solutions^a

Compd	C ₆ H ₁₂ τ _F , nsec	Water τ _F , nsec	C ₆ H ₁₂ ^b λ _F , nm	Water ^c λ _F , nm
Indole	7.7	4.1	289	344
1-Methyl-	5.5	8.5	295	347
2-Methyl-	3.7	2.0	289	350
3-Methyl-	3.2	9.1	292	362
5-Methyl-	7.9	2.7	296	344
1,3-Dimethyl-	3.8	15.6	304	371
1,2,3-Trimethyl-		8.2	294	382

^a Source: ref 18a and 18d. ^b Wavelength of 0-0 band. ^c Wavelength of fluorescence maximum.

yield. Completion of the synthesis of **5** from **8** was carried out similarly to the synthesis of **3** from skatole, except that the penultimate alcohol-to-bromide conversion was carried out with much greater success in nonacidic media using carbon tetrabromide and triphenylphosphine in ether.¹⁶ Alkylation of 3-hexylindole magnesium bromide with 6-bromohexanol was unsuccessful as a practical route to **4**; however, protection of the alcohol as a ketal (**9**) by treatment with ethyl vinyl ether and *p*-toluenesulfonic acid in ether¹⁷ allowed the alkylation of the indole Grignard reagent to proceed smoothly. Evidently, the unprotected alcohol underwent (intramolecular?) elimination of HBr since evidence for a terminal olefin was obtained by NMR. The synthesis of **4** was completed as for **3**, above, following removal of the alcohol-protecting group with dilute acid.

2. Fluorescent Properties of Indoles. Indoles have been shown to have highly solvent dependent fluorescent properties (Table I).¹⁸ Clearly 1,3-dimethylindole (DMI) best displays properties consistent with a useful fluorescent probe, having both a large lifetime dependence as well as spectral distribution dependence on solvent. In the latter respect, it provides an additional observational parameter that does not exist for the vast majority of simple aromatic probes used in micellar studies. Fluorescence spectra of DMI in hexane and water are compared in Figure 2, emphasizing the potential value of this spectral shift. The causes of this sensitivity of fluorescence to solvent polarity are apparently complex and have been discussed elsewhere;¹⁸ we will not present any novel explanations of our own. The only data that we have that bears on this point come from measurements of fluorescent lifetimes which clearly show that indole fluorescence is *prompt* under all our conditions. In no

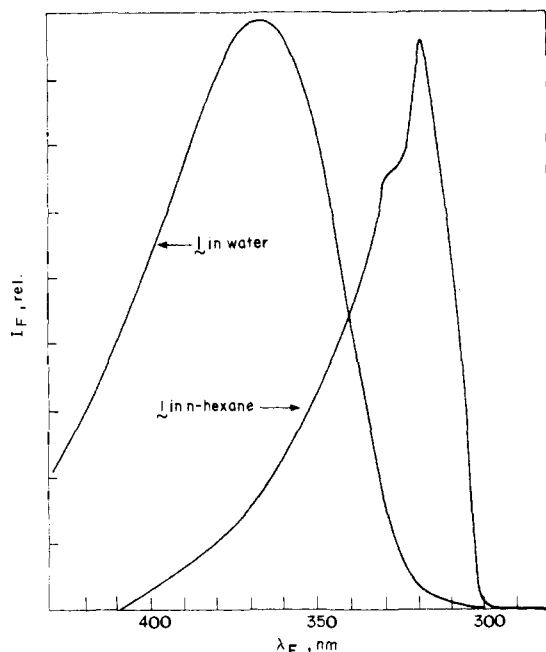


Figure 2. Fluorescence of 1,3-dimethylindole in water and hexane. Excitation wavelength 280 nm.

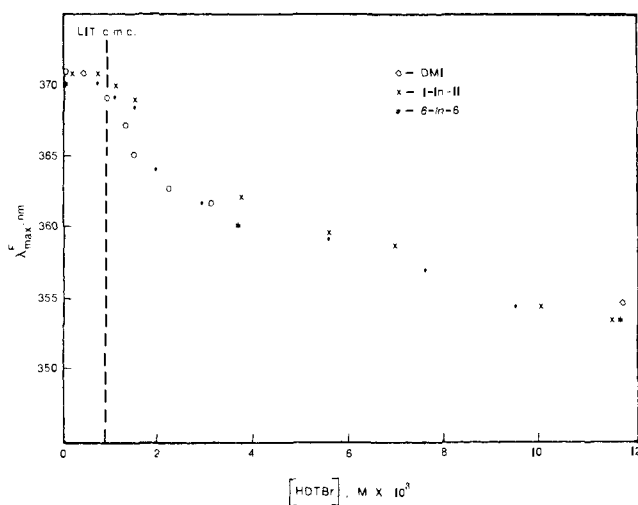


Figure 3. Fluorescence λ_{\max} for compounds 1, 3, and 4 in aqueous solution as a function of added HDTBr.

case do we see a slow build-up of fluorescence that might indicate the presence of any process occurring prior to fluorescence with a rate less than 10^9 sec^{-1} .

3. Fluorescence of Indoles 1–4 in Solutions of Micelle-Forming Surfactants. Compounds 1–4 show essentially identical behavior in dilute aqueous solution, having $\lambda_{\max}^F = 371 \pm 1 \text{ nm}$ and $\tau_F = 18 \pm 2 \text{ nsec}$. Addition of hexadecyltrimethylammonium bromide (HDTBr, $\text{cmc} = 9.2 \times 10^{-4} \text{ M}$)¹⁹ has no effect on the fluorescence spectra of compounds 1–4 until the cmc is reached, at which point a gradual shift of fluorescence to shorter wavelengths is seen (Figure 3). At high [HDTBr], the spectra of all four indole derivatives show a fluorescence $\lambda_{\max} = 354 \pm 1 \text{ nm}$ and $\tau_F = 9\text{--}10 \text{ nsec}$. In none of these cases, do we see anything other than strictly single exponential decay. The intermediate nature of both the lifetime and spectral data leads us to conclude that these compounds are solubilized fairly close to the micelle–water interface, in the presence of a substantial number of water molecules.¹⁹ This conclusion is consistent with studies of naphthalene in HDTBr micelles,⁵ taking

Table II. Fluorescence Data for Aqueous Solutions of Indoles 1–4

Compd ^a	Additive ^b	λ_{\max}^F ^c	τ_F ^d
1		372	16
1	TMABr	371	17
1	HDTCl	358	10
1	HDTBr	355	9
2		371	17
2	TMABr	372	17
2	HDTCl	355	9
2	HDTBr	352	10
3		371	17
3	TMABr	371	16
3	HDTCl	357	10
3	HDTBr	353	10
4		370	18
4	TMABr	370	18
4	HDTCl	355	9
4	HDTBr	353	10

^aIndole concentrations 1.4 to $2.0 \times 10^{-4} \text{ M}$. ^bAdditive concentrations 2.5 to $2.7 \times 10^{-2} \text{ M}$. TMABr = tetramethylammonium bromide. ^cValues in nm, $\pm 1 \text{ nm}$. ^dValues in nsec, $\pm 1 \text{ nsec}$.

into account the increased hydrophilic nature of indole over naphthalene.

Analogous results are found using hexadecyltrimethylammonium chloride (HDTCl); of interest is the lack of bromide quenching in going from HDTCl to HDTBr (see τ_F values, Table II). This effect was confirmed by the observation that addition of tetramethylammonium bromide to indole solutions has no effect on any spectral properties (Table II).^{18e} The indoles consistently show smaller fluorescent shifts in HDTCl than in HDTBr; this probably reflects a difference in solubilizing ability between the two surfactants. The same result has been obtained in studies of naphthalene partitioning between bulk aqueous solution and either HDTCl or HDTBr.⁵

The gradual nature of the fluorescent shifts evident from Figure 3 indicates the reluctance with which these indoles are incorporated into micelles. In particular, it is interesting that the two indole-containing surfactants are not solubilized by host surfactants any better than the neutral indoles. In the case of 6-In-6 (4), the indole moiety may simply be too close to the ionic head group to allow for sufficient average micellar penetration. It is striking, therefore, to note that 1-In-11 (3), with an indole separated by 11 carbons from the trimethylammonium ion, is solubilized no better than, and perhaps worse than, the other three compounds in host micelles! The indole clearly has not been forced deeper into the micelles even though it is at the end of a long hydrocarbon chain. Surfactants containing 1,4-dialkoxybenzene moieties at the end of a long chain are similarly poorly solubilized;^{2h} in these cases, attaching a second hydrocarbon chain to the aromatic system improved the micellar incorporation tremendously. This was the philosophy behind the synthesis of 6-In-11 (5).

4. Fluorescence Behavior of 6-In-11 (5) in Aqueous Solution.²⁰ At high dilution (10^{-5} M), the fluorescence spectrum and lifetime of 5 closely resemble the corresponding data for compounds 1–4, i.e., $\lambda_{\max}^F = 370 \text{ nm}$ and $\tau_F = 19 \text{ nsec}$. In the vicinity of 10^{-4} M , the fluorescence spectrum shifts to shorter wavelengths (Figure 4), and the fluorescence-decay curve shows dual exponential character with components $\tau_a = 6 \text{ nsec}$ and $\tau_b = 17 \text{ nsec}$. Comparison of this spectral shift with data obtained from the solubilization of 1–4 in HDTBr lead us to conclude that this reflects micellization of 6-In-11 itself; indeed, we have independently determined²¹ the cmc of 6-In-11 to be approximately $1.5 \times 10^{-4} \text{ M}$, roughly at the inflection point of the curve in Figure 4 ($\lambda_{\max}^F = 360 \text{ nm}$). No significant change occurs in the absorption spectrum throughout this concentration range, as shown in the Beer's law plot, Figure 5.

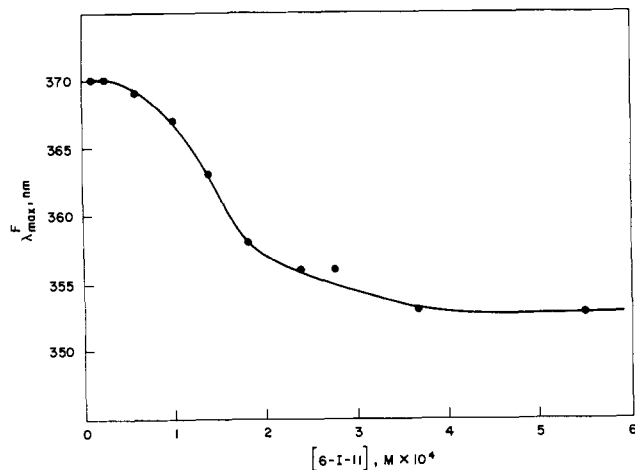


Figure 4. Fluorescence λ_{\max} of aqueous 6-In-11 as a function of concentration.

We have analyzed the fluorescence decay of 6-In-11 at 360 nm at several concentrations in terms of eq 1, which de-

$$I_F(t) = I_F(0)[a \exp(-t/\tau_a) + b \exp(-t/\tau_b)] \quad (1)$$

scribes the fluorescence intensity as a function of time, $I_F(t)$, for a system in which a fraction a of the emission has a lifetime τ_a and a fraction b has a lifetime τ_b . Figure 6 shows a typical dual exponential-decay curve for 6-In-11 in the vicinity of its cmc; the longer lifetime τ_b is determined by the slope of the decay after allowing the shorter-lived emission to decay essentially to zero intensity. The shorter lifetime τ_a is then determined by subtraction of the extrapolated τ_b curve from the total fluorescence decay. It is also possible to determine τ_a directly from the initial slope of the fluorescence-decay curve, but some error is introduced when the initial contribution b of τ_b is relatively large, or when τ_a and τ_b are comparable. The coefficients a and b are obtained by extrapolation of the two resolved decay curves to time $t = 0$.

In Table III, values for the fluorescence lifetimes and coefficients at 360 nm are given for several concentrations of 6-In-11 in water. Qualitatively, the buildup of short-lived fluorescence emission reflected in the a value parallels the shift of the overall fluorescence λ_{\max} (Figure 4), suggesting that time resolution¹¹ of the spectral data might be feasible. This is manifest in the wavelength dependence of a and b at one [6-In-11] as shown in Table IV. In order to apply such data to the generation of time-resolved spectra, it is necessary to convert a and b values to total intensities (integrated over time) in order to compare them with static fluorescence data. For any exponential function, eq 2 may be applied. We have taken static fluorescence spectra at several concentrations of 6-In-11 and resolved the fluorescence intensity at various wavelengths, $I(\lambda)$, into contributions

Table III. Fluorescence Decay of Aqueous Solutions of 6-In-11 as a Function of Concentration^a

[6-In-11], M	a_M	τ_a , nsec	b_W	τ_b , nsec
1.09×10^{-5}			1.00	20
5.45×10^{-5}			1.00	18
1.09×10^{-4}	0.29	6	0.71	18
1.36×10^{-4}	0.43	6	0.57	18
1.82×10^{-4}	0.51	6	0.49	17
2.34×10^{-4}	0.65	7	0.35	17
5.45×10^{-4}	0.71	7	0.29	16
7.03×10^{-4}	0.79	5	0.21	14
1.03×10^{-3}	0.86	6	0.14	15

^a Fluorescence monitored at 360 nm. Error limits in a_M and $b_W \pm 0.05$; in τ values, ± 1 nsec.

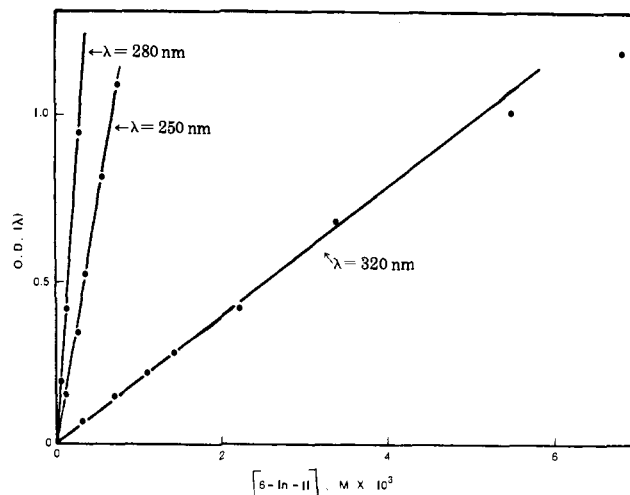


Figure 5. Beer's law plot at several wavelengths for aqueous 6-In-11.

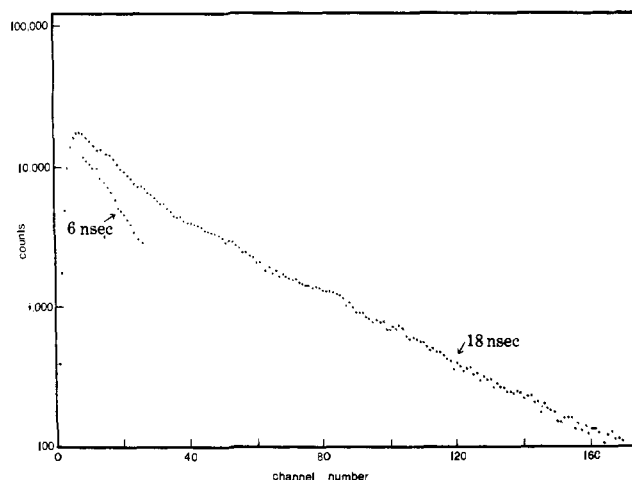


Figure 6. Fluorescence decay of $2.56 \times 10^{-4} M$ aqueous 6-In-11. Monitoring wavelength 360 nm. In this experiment, $a_M = 0.64$, $\tau_a = 6$ nsec, $b_W = 0.36$, and $\tau_b = 18$ nsec. The shorter lived component was resolved by subtraction of the longer lived decay from the total curve as shown.

Table IV. Effect of Wavelength on Fluorescence-Decay Components of Aqueous 6-In-11 at One Concentration^a

Monitoring λ_F , nm	a_M	b_W
440	0.19	0.81
400	0.25	0.75
380	0.32	0.68
360	0.47	0.53
340	0.65	0.35

^a [6-In-11] = $1.36 \times 10^{-4} M$.

$I_a(\lambda)$ and $I_b(\lambda)$, corresponding to lifetimes τ_a and τ_b , respectively, using eq 3 and 4.

$$I_a^{\text{total}} = \int_0^{\infty} I_a(t) dt = \int_0^{\infty} I_a(0) \exp(-t/\tau_a) dt = I_a(0)\tau_a \quad (2)$$

$$I_a(\lambda) = \frac{a(\lambda)\tau_a}{a(\lambda)\tau_a + b(\lambda)\tau_b} I(\lambda) = X_a^F I(\lambda) \quad (3)$$

$$I_b(\lambda) = \frac{b(\lambda)\tau_b}{a(\lambda)\tau_a + b(\lambda)\tau_b} I(\lambda) = X_b^F I(\lambda) \quad (4)$$

Figures 7-10 show the total and component fluorescence spectra obtained in this manner for four concentrations of 6-In-11. In each spectrum, we note the presence of two

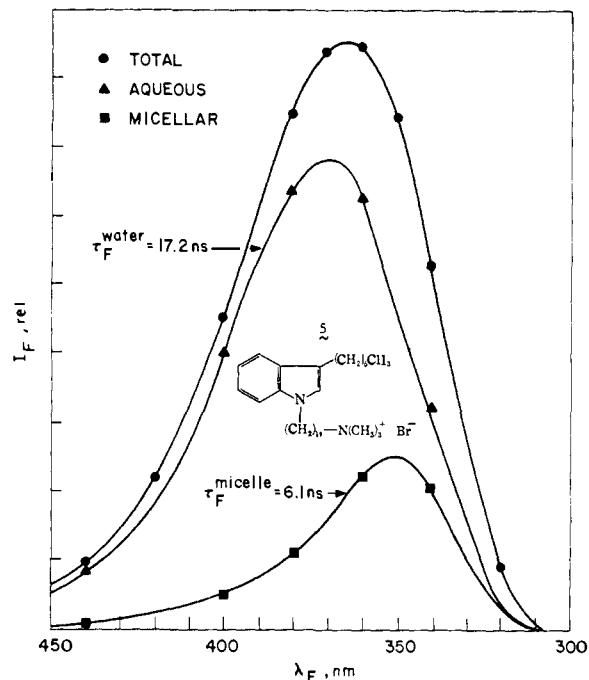


Figure 7. Time-resolved fluorescence spectra of aqueous 6-In-11 at $1.36 \times 10^{-4} M$.

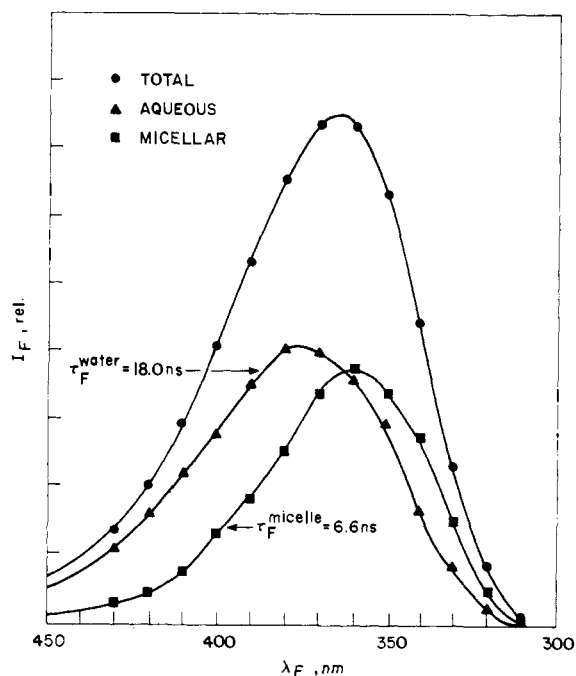


Figure 8. Time-resolved fluorescence spectra of aqueous 6-In-11 at $1.56 \times 10^{-4} M$.

components with $\lambda_{F_{max}}$ values, τ_F values, and relative contributions consistent with the data in Figure 4 and Table III. These spectra provide direct evidence supporting the premise that indole emission takes place at a much more rapid rate than does exchange between micellar and aqueous environment. Thus the observed fluorescence shift is due solely to the overlap of different contributions of two distinct fluorescence emissions, one due to essentially aqueous indole, and the other due to indole incorporated into a micelle. We have not determined relative fluorescence quantum yields for aqueous vs. micellar indole surfactant and therefore do not know the absolute partitioning of the surfactant between the two environments from the above data.

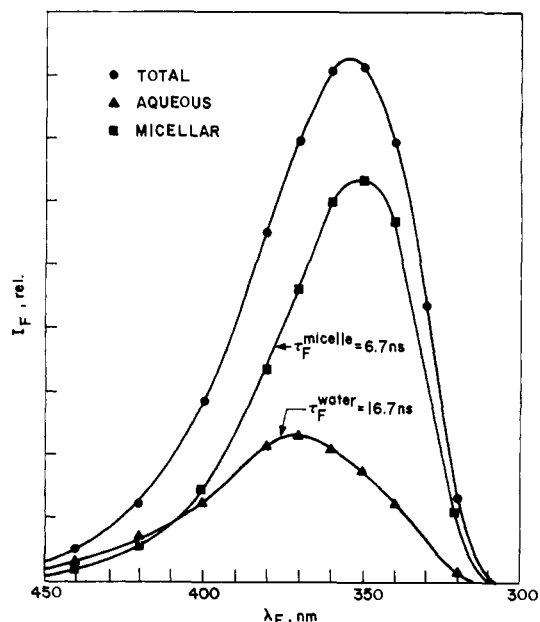


Figure 9. Time-resolved fluorescence spectra of aqueous 6-In-11 at $4.15 \times 10^{-4} M$.

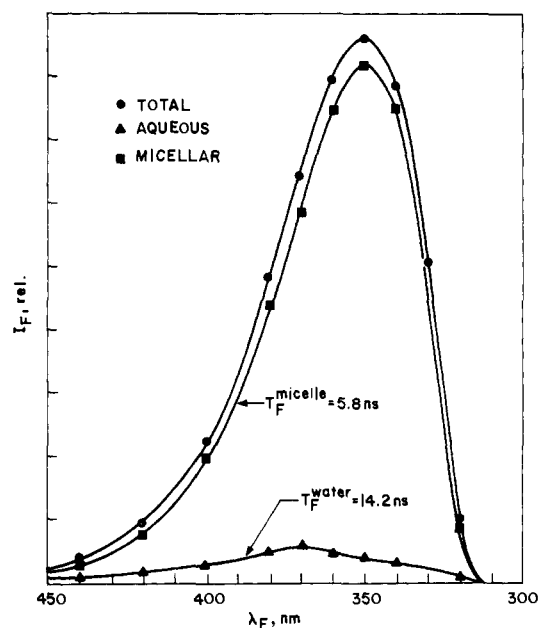


Figure 10. Time-resolved fluorescence spectra of aqueous 6-In-11 at $1.28 \times 10^{-3} M$.

5. Fluorescence of 6-In-11 in Solutions of Micelle-Forming Host Surfactants. Addition of hexadecyltrimethylammonium bromide to dilute ($10^{-5} M$) 6-In-11 solutions causes a sudden and dramatic shift in the fluorescence λ_{max} of the indole when the concentration of the host surfactant approaches its cmc (Figure 11). Indeed, the inflection point of this curve occurs at a concentration of HDTBr ($8.8 \times 10^{-4} M$) very close to the known¹⁹ cmc of HDTBr ($9.2 \times 10^{-4} M$). The fluorescence lifetime of the indole as a function of [HDTBr] is shown in Table V. In general, as with indoles 1-4, single exponential decay is observed.¹¹ At the cmc of HDTBr, however, the decay is neither strictly exponential nor readily resolvable into two components. The wavelength dependence of the "best-guess" single τ_F is evidence for the same type of time-resolved spectral overlap seen for 6-In-11 alone. In the case of the host surfactant, however, the values of τ_F for micellar and aqueous indole appear to be too similar to allow resolution simply by visual inspection of the decay curve.

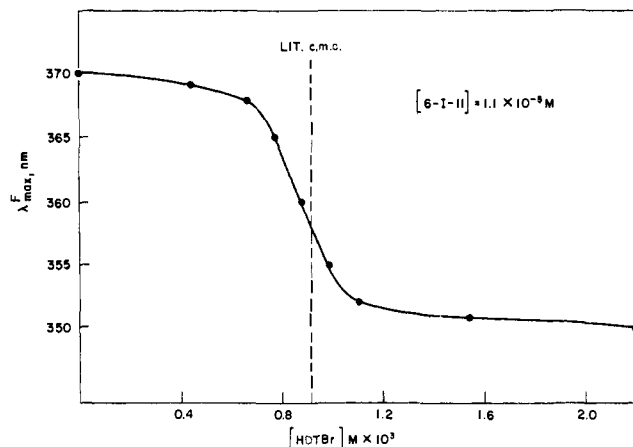


Figure 11. Fluorescence λ_{\max} of aqueous 6-In-11 as a function of added HDTBr.

Table V. Dependence of 6-In-11 τ_F upon HDTBr Concentration^a

[HDTBr], <i>M</i>	τ^{400}	τ^{380}	τ^{360}	τ^{340}
0			17	
5.0×10^{-4}			18	
9.2×10^{-4}	13	12	10	10
1.4×10^{-3}			9	
2.7×10^{-3}			9	

^a [6-In-11] = 2×10^{-5} *M* or less; values ± 1 nsec.

The value of τ_F for 6-In-11 incorporated into HDTBr micelles (9 nsec) is similar to the τ_F values obtained for indoles 1–4 in HDTBr and significantly longer than the value for 6-In-11 incorporated into its own micelle (6 nsec). We suspect that this reflects a self-quenching process, i.e., the quenching of an excited-state indole by a neighboring ground-state indole. In support of this explanation, we have found that the lifetime of 1 in water is somewhat concentration dependent, dropping from a value of 20 nsec at 10^{-5} *M* to 16 nsec at 4×10^{-4} *M*, indicating a diffusion-controlled rate for self-quenching ($\sim 3 \times 10^{10}$ *M*⁻¹ *sec*⁻¹). An energy-transfer process has been observed in micelles containing a tryptophan-derived surfactant.^{2d} The τ_F in this case was found to be 4.7 nsec for, formally, a 3-methylindole located relatively close to the micelle-water interface. Our τ_F data seem to indicate that we are seeing a similar quenching phenomenon in the 6-In-11 micelles.

The sensitivity of the 6-In-11 λ_{\max}^F to the cmc of a cationic host is a general and potentially useful phenomenon. As a second example, we have observed the fluorescence shift of 6-In-11 in solutions of decyltrimethylammonium bromide (DTABr, lit.²² cmc = 6.4×10^{-2} *M*; our sample had a cmc = 5.7×10^{-2} *M* as determined by color change of added eosin dye).²² As in the case of HDTBr, a plot of λ_{\max}^F vs. host-surfactant concentration displays a steep slope in the vicinity of the independently measured cmc; for DTABr, the inflection point occurs roughly at 5.7×10^{-2} *M* (Figure 12). In the above determination, [6-In-11] $\sim 10^{-6}$ *M*. Above the DTABr cmc, 6-In-11 possesses a $\tau_F \sim 10$ nsec, indicative of solubilization near the micelle-water interface as we have already shown for HDTBr and HDTCl. The λ_{\max}^F of 6-In-11 at high [DTABr] is about 347 nm, blue shifted with respect to that seen in HDTBr (351 nm). This may reflect a slightly lower water content in the smaller and more compact micelle derived from the ten-carbon surfactant. Otherwise, there appear to be no other significant differences between the DTABr and HDTBr micelle systems with regard to their effect on 6-In-11 fluorescence.

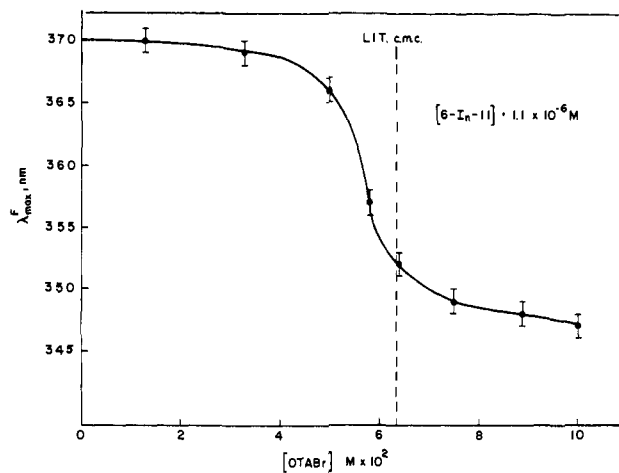


Figure 12. Fluorescence λ_{\max} of aqueous 6-In-11 as a function of added DTABr.

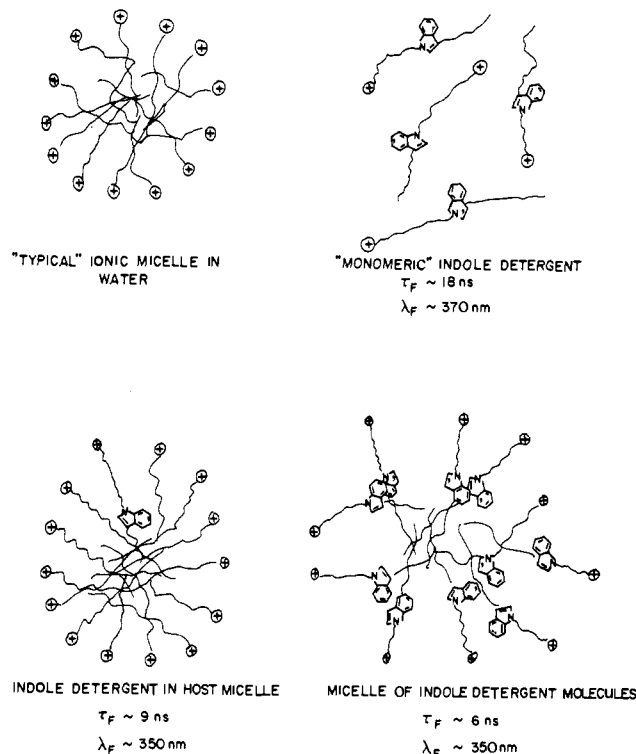


Figure 13. Outline of the fluorescence properties of 6-In-11 as a function of environment.

Summary

The 1,3-dialkylindole fluorophore has been evaluated as a fluorescent probe in micellar systems. Four such systems show limited applicability as useful probes, being too polar to be readily incorporated into micelles. A fifth, 11-(3-hexyl-1-indolyl)undecyltrimethylammonium bromide (6-In-11), forms micelles itself with a cmc of about 10^{-4} *M*. In addition, it is readily incorporated into micelles of other cationic surfactants, showing a striking and easily observable change in both fluorescence spectral distribution and lifetime which is quantitatively useful in determining cmc values for host surfactants. This is summarized in Figure 13.

Analysis of the wavelength-dependent fluorescence decay of 6-In-11 enables resolution of the fluorescence spectrum of the surfactant into an emission due to micellar indole and an emission due to aqueous indole. The relative intensities of these emissions correlate qualitatively with the increasing

proportion of micellized surfactant as the surfactant concentration is increased beyond the cmc.

Having established the general structural characteristics required for an indole moiety to be useful as a micelle probe, it is possible to design indole-containing molecules that might be useful as probes for other systems as well. Preparation of a 6-In-11 with the trimethylammonium group replaced by sulfate would lead to a potential probe for anionic micelles which could serve as a cmc indicator and provide information concerning the similarities and differences between the interiors of cationic and anionic surfactant. Similarly, appropriate indole-containing molecules may be prepared for use in membrane systems. Fluorescence polarization is an attractive technique that may be applied in membrane studies, perhaps in comparison with micelle work. The fluorescence lifetime range of the 1,3-dialkylindole makes it very suitable for nanosecond polarization, further illustrating the potential versatility of the system as a fluorescence probe.

Experimental Section

Reagents. All inorganics were reagent grade and used without further purification. Either tap distilled or doubly distilled (all glass apparatus) water was used without any observed difference. Tetramethylammonium bromide (Eastman) was used as received. Hexadecyltrimethylammonium bromide (Matheson Coleman and Bell) and chloride (Eastman) were washed with ether and recrystallized from ethanol-ether mixtures.

Preparation of 1,3-Dimethylindole (1).¹² Ammonia (200 ml) was condensed in a three-necked flask flushed with nitrogen and fitted with a Dry Ice-acetone condenser. Several small crystals of ferric nitrate nonahydrate (Baker) were added with stirring (Teflon-coated magnetic stirring bar). Cut-up sodium metal (2.0 g, 0.09 mol) was added over a period of 30 min, and the solution allowed to stir for an hour. A solution of 10.0 g (0.08 mol) of skatole (Aldrich) in 50 ml of dry ether was added rapidly and the solution stirred for another hour. Methyl iodide (Baker) (15.0 g, 0.10 mol) was added dropwise over a 15-min period, and the solution was stirred for several hours, during which time the Dry Ice in the condenser evaporated, allowing the ammonia solvent to evaporate. The solid residue was treated with 50 ml of water and 75 ml of ether and stirred. The ether was separated and the water layer extracted with an additional 75 ml of ether. The combined ether extracts were washed with water, dried over Na₂SO₄, and evaporated to give 9.0 g (90% yield) of crude **1** as a red-brown liquid. The product was flash distilled twice, collected by VPC (2 ft × 4 in. 10% SE-30 on Chromosorb P) and redistilled for spectral use: NMR (CCl₄) δ 2.28 (d, *J* = 1 Hz, 3 H), 3.64 (s, 3 H), 6.61 (m, 1 H), 6.75–7.17 (m, 3 H), 7.25–7.55 (m, 1 H).

Preparation of 1-*n*-Butyl-3-methylindole (2). The procedure for **1** was followed exactly but scaled down by a factor of 1/5 using 0.4 g (0.017 mol) of sodium, 2.0 g (0.015 mol) of skatole, and 4.0 g (0.22 mol) of *n*-butyl iodide (Matheson Coleman and Bell). Crude yield of 1.7 g (70% yield) was purified as for **1**, above: NMR (CCl₄) δ 0.75–2.05 (m, 7 H), 2.29 (s, 3 H), 4.00 (t, *J* = 6.5 Hz, 2 H), 6.70 (br s, 1 H, indole H-2), 6.90–7.50 (m, 4 H); MS *m/e* (%) 188 (14, M + 1, calcd for C₁₃H₁₇N, 14), 187 (95), 145 (30), 144 (100, C₁₀H₁₀N).

Preparation of Methyl 11-Bromoundecanoate. The general esterification procedure of Kadaba²³ was used. 11-Bromoundecanoic acid [10.3 g (0.039 mol)] (Aldrich) was dissolved in 100 ml of methanol and 10 ml of boron trifluoride etherate (Matheson Coleman and Bell) added. The mixture was refluxed 18 hr, cooled mixed with saturated aqueous Na₂CO₃, and extracted with ether. The ether was washed with water, dried over MgSO₄, and evaporated leaving 10.8 g (97% yield) of crude ester which was used without purification: NMR (CCl₄) δ 1.10–2.10 (m, 16 H), 2.22 (br t, *J* = 6.5 Hz, 2 H), 3.34 (t, *J* = 6.5 Hz, 2 H), 3.60 (s, 3 H).

Preparation of 11-Bromoundecanol.²⁴ Methyl 11-bromoundecanoate [10.8 g (0.038 mol)] was dissolved in 100 ml of dry ether and cooled to 0°. A suspension of 1.0 g (0.024 mol) of lithium aluminum hydride (Alfa-Ventron) in 20 ml of ether was added over a 10-min period and the mixture stirred at 0° for 45 min. Then 1 ml of water, 1 ml of 15% aqueous NaOH, and 3 ml of water were

added successively. The ether solution was filtered through MgSO₄ and evaporated, leaving 9.5 g (100% yield) of solid alcohol [mp 44.0–47.5° (lit.²⁵ mp 46.0–46.5°)], which was used without purification: NMR (CCl₄) δ 1.00–2.00 (m, 18 H), 2.64 (br, s, 1 H, -OH), 3.20–3.70 (m, 4 H).

Preparation of 1-(11-Bromoundecyl)-3-methylindole (6). The procedure for **1** was followed in a modified form. A sodamide solution was prepared as before using ferric nitrate and 0.67 g (0.029 mol) of sodium in 100 ml of ammonia. Skatole [1.3 g (0.010 mol)] dissolved in 20 ml of dry tetrahydrofuran (freshly distilled from LiAlH₄) was added and the solution stirred for an hour. A solution of 4.0 g (0.017 mol) of 11-bromoundecanol in 20 ml of dry THF was added dropwise and the solution stirred under a Dry Ice-acetone condenser for 20 hr. The solvent was allowed to evaporate and the residue treated with dilute aqueous HCl and ether. The ether extract was washed with several portions of water, dried over MgSO₄, and evaporated, leaving a mixture of 1.0 g of unreacted 11-bromoundecanol and 2.2 g (73% yield) of 1-(11-hydroxyundecyl)-3-methylindole (by NMR) which was used directly in the next step: NMR (CCl₄) δ 1.10–2.00 (m, 18 H), 1.77 (s, 1 H, -OH), 2.29 (s, 3 H), 3.50 (t, *J* = 7.0 Hz, 2 H), 4.00 (t, *J* = 6.5 Hz, 2 H), 6.70 (br s, 1 H), 6.90–7.50 (m, 4 H).

The mixture of alcohols (3.0 g, 0.010 mol of total alcohol) was brominated¹³ by dissolution in 100 ml of dimethylformamide (dried over molecular sieve and distilled) containing 2.8 g (0.011 mol) of triphenylphosphine (Aldrich), followed by dropwise addition of 1.7 g (0.011 mol) of bromine (Fisher), keeping the solution temperature below 55°. After 5 min of stirring, the mixture was poured into 300 ml of cold water which was then extracted with ether. The ether was washed with dilute aqueous Na₂CO₃ and then water, dried over MgSO₄, and evaporated leaving a semisolid. Trituration with pentane and filtration gave a solution which was evaporated, leaving 3.8 g of an oil which was chromatographed on silica gel (Merck) using pentane as eluent. Initial fractions contained 1,11-dibromoundecane,²⁶ an unidentified indole,²⁷ and triphenylphosphine. A total of 0.6 g (22% yield) of **6** was then collected as a nearly colorless oil: NMR (CCl₄) δ 1.10–2.10 (m, 18 H), 2.30 (d, *J* = 1 Hz, 1 H); 3.33 (t, *J* = 6.5 Hz, 2 H), 4.01 (t, *J* = 6.5 Hz, 2 H), 6.71 (m, 1 H), 6.85–7.55 (m, 4 H); MS *m/e* (%) 366 (4, M + 1, calcd for C₂₀H₃₀N, 4), 365 (17), 364 (4), 363 (17), 145 (30), 144 (100, C₁₀H₁₀N).

Preparation of 11-(3-Methyl-1-indolyl)undecyltrimethylammonium Bromide (3).¹⁴ **6** (0.3 g) was dissolved in 30 ml of absolute ethanol (Commercial Solvents Corp.), and 5 ml of anhydrous trimethylamine (Eastman) was distilled in using a Dry Ice-acetone condenser. The stirred solution was refluxed 6 hr and cooled and the solvent evaporated. Addition of 25 ml of ether created an emulsion which yielded a gummy solid upon scratching and cooling. The extremely hygroscopic product was collected but not weighed. A sample was prepared for spectral use by recrystallization from benzene, removal of solvent by decantation followed by drying under vacuum, and lyophilization of a filtered aqueous solution: NMR (D₂O) δ (approx) 0.9–1.8 (m, 18 H), 2.28 (s, 3 H), 3.0 (br, 2 H), 3.08 (s, 9 H), 3.75 (br, 2 H), 6.65 (s, 1 H), 6.8–7.5 (m, 4 H). Anal. Calcd for C₂₃H₃₉N₂Br·H₂O: C, 62.59; H, 9.30; N, 6.35. Found: C, 62.98; H, 9.16; N, 6.08.

Preparation of 3-Hexanoylindole (7). This procedure was adopted from that of Jackson, Naidoo, and Smith.¹⁵ To a solution of 21 g (0.18 mol) of hexanoic acid (Aldrich) in 25 ml of dry benzene (distilled from CaH₂) was carefully added 75 g (0.60 mol) of oxalyl chloride (Matheson Coleman and Bell). The mixture was refluxed for 30 min and allowed to stir at room temperature under nitrogen until used as below.

A flask containing 3.6 g (0.15 mol) of magnesium turnings (Mallinckrodt) was flame dried under nitrogen, cooled, and charged with 150 ml of dry ether. Ethyl bromide [21 g (0.20 mol)] (Matheson Coleman and Bell) was added dropwise, and the mixture stirred (overhead mechanical stirrer) and refluxed until all the Mg had reacted. Then, 150 ml of dry benzene was added and the mixture warmed under a stream of nitrogen to evaporate the ether and excess ethyl bromide. A solution of 17.4 g (0.15 mol) of indole (Aldrich Gold Label) in 60 ml of dry benzene was added slowly and the mixture refluxed for 30 min. Excess oxalyl chloride was evaporated from the hexanoyl chloride solution prepared previously, and this solution was then added dropwise to the well-cooled and vigorously stirred indole magnesium bromide mixture.

A dark-red solid formed which was thoroughly mixed with 150 ml of 2 *N* HCl and 500 ml of warm ethyl acetate. The ethyl acetate solution was washed with 150 ml of water, 2 × 150 ml of saturated aqueous NaHCO₃, 150 ml of water, and 100 ml of saturated aqueous NaCl. The solution was dried over MgSO₄, the solvent removed, and the residue recrystallized from acetone to yield 10.0 g (35% yield) of **7** as a tan powder, mp 147.0–150.5°. Four additional recrystallizations from acetone yielded white crystals: mp 153.0–154.5°; NMR (DMSO-*d*₆) δ 0.70–1.80 (m, 9 H), 2.80 (t, *J* = 6.5 Hz, 2 H), 6.95–7.60 (m, 4 H), 8.00–8.20 (m, 2 H); ir (KBr) 3130 (NH), 1630 (C=O), 748 cm⁻¹ (indole H-2). Anal. Calcd for C₁₄H₁₇NO: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.35; H, 8.08; N, 6.40.

Preparation of 3-Hexylindole (8). To a suspension of 5.0 g (0.025 mol) of **7** in 400 ml of dry ether was added dropwise a suspension of 2.5 g (0.60 mol) of LiAlH₄ in 150 ml of dry ether. The solution was refluxed under nitrogen for 15 hr, cooled, and treated with 2.5 ml of water, 2.5 ml of 15% NaOH, and 7.5 ml of water. The ether was filtered through MgSO₄ and evaporated leaving 4.7 g of an orange oil which was flash distilled at 120° (1 mmHg) to give 3.4 g (68% yield) of a pale-yellow oil which was suitable for use without further purification: NMR (CCl₄) δ 0.70–2.20 (m, 11 H), 2.70 (t, *J* = 7.0 Hz, 2 H), 6.72 (m, 1 H), 6.80–7.70 (m, 5 H); ir (neat) 3330 (NH), 740 cm⁻¹ (indole H-2); MS *m/e* (%) 202 (2.3, M + 1, calcd for C₁₄H₁₉N, 2.3), 201 (15), 131 (13), 130 (100, C₉H₈N).

Preparation of Methyl 6-Bromohexanoate. 6-Bromohexanoic acid [5.0 g (0.025 mol)] (Aldrich) was dissolved in 50 ml of methanol and 3.5 g (0.025 mol) of boron trifluoride etherate added. The reaction was carried out and worked up as for methyl 11-bromoundecanoate, yielding 4.7 g (87% yield) of ester, used without purification: NMR (CCl₄) δ 1.40–2.10 (m, 6 H), 2.28 (br t, *J* = 6.5 Hz, 2 H), 3.40 (t, *J* = 6.5 Hz, 2 H), 3.63 (s, 3 H); ir (neat) 1740 cm⁻¹ (C=O).

Preparation of 6-Bromohexanol. Methyl 6-bromohexanoate [4.7 g (0.022 mol)] was dissolved in 25 ml of dry ether and treated with 0.5 g (0.013 mol) of LiAlH₄ in the manner described for 11-bromoundecanol. Crude yield was 3.5 g (87% yield), used without purification: NMR (CCl₄) δ 1.35–2.15 (m, 8 H), 2.50 (br s, 1 H, -OH), 3.25–3.75 (m, 4 H); ir (neat) 3350 cm⁻¹ (OH).

Attempted Alkylation of 3-Hexylindole Sodium Salt with 6-Bromohexanol. The procedure for **6** was repeated starting with 0.40 g (0.017 mol) of sodium to form the sodamide followed by addition of **8** (0.90 g, 0.005 mol) in 15 ml of THF, and finally 1.9 g (0.011 mol) of 6-bromohexanol in 10 ml of THF. NMR of the crude product mixture showed unreacted 3-hexylindole, evidence for a terminal olefin (δ 4.70–6.20, perhaps 5-hexen-1-ol), and only a minute amount (<5% yield) of desired product.

Preparation of 6-Bromohexyl 1-Ethoxyethyl Ether (9).¹⁷ 6-Bromohexanol [1.5 g (0.008 mol)] was dissolved in a mixture of 10 ml of ethyl vinyl ether (Aldrich) and 40 ml of dry ether. *p*-Toluenesulfonic acid monohydrate [0.05 g (0.0003 mol)] was added and the solution stirred at room temperature for an hour. Then 10 ml of 1 *N* NaOH was added and the mixture stirred for several min. The ether layer was separated and washed several times with water made slightly basic with NaOH solution. The ether was dried over K₂CO₃ and evaporated leaving an orange liquid, 2.0 g (95% yield), which was used without purification: NMR (CCl₄) δ 1.13 (t, *J* = 6.5 Hz, 3 H), 1.22 (d, *J* = 5.0 Hz, 3 H), 1.31–2.10 (m, 8 H), 3.20–3.75 (m, 6 H), 4.58 (q, *J* = 5.0 Hz, 1 H); MS *m/e* (%) 253 (0.5, M - H), 251 (0.5), 239 (16), 237 (16), 209 (16), 207 (16), 165 (41), 163 (40), 73 (100, C₄H₉O).

Preparation of 1-(6-Bromohexyl)-3-hexylindole (10). The procedure for **6** was repeated starting with 0.06 g (0.0026 mol) of sodium in 50 ml of ammonia to form sodamide followed by addition of **8** (0.46 g, 0.0023 mol) in 10 ml of THF, and finally 1.71 g (0.0067 mol) of **9** in 5 ml of THF. In the work-up, dilute acetic acid was used in place of dilute HCl. The isolated product contained 0.68 g of unreacted **9** and 0.63 g (74% yield) of 6-(3-hexyl-1-indolyl)hexyl 1-ethoxyethyl ether: NMR (CCl₄) δ 0.85–2.10 (m, 25 H), 2.65 (br t, *J* = 7.0 Hz, 2 H), 3.15–3.65 (m, 4 H), 4.00 (t, *J* = 6.5 Hz, 2 H), 4.55 (q, *J* = 5.5 Hz, 1 H), 6.72 (br s, 1 H), 6.80–7.50 (m, 4 H).

The alkylation product mixture was dissolved in 50 ml of methanol and treated with 3 drops of concentrated HCl. After 90 sec of stirring, 50 ml of saturated aqueous NaHCO₃ was added, followed after another minute by 200 ml of water. The mixture was extract-

ed with 2 × 100 ml of ether which was washed with aqueous NaHCO₃, water, and aqueous NaCl and dried over MgSO₄. Evaporation left the crude alcohol, 1-(6-hydroxyhexyl)-3-hexylindole: NMR (CCl₄) δ 0.80–2.20 (m, 19 H), 2.00 (s, 1 H, OH), 2.75 (br t, *J* = 7.0 Hz, 2 H), 3.50 (t, *J* = 7.0 Hz, 2 H), 4.00 (t, *J* = 7.0 Hz, 2 H), 6.68 (s, 1 H), 6.80–7.50 (m, 4 H).

Bromination was carried out as for **6**. The mixture of alcohols (0.95 g, 0.004 mol total alcohol), 1.15 g (0.004 mol) of triphenylphosphine, and 0.60 g (0.004 mol) of bromine were reacted in 35 ml of dry DMF. Work-up and silica gel chromatography yielded 1,6-dibromohexane,²⁶ an unidentified indole,²⁷ and 0.15 g (24% yield) of **10** as a yellow oil: NMR (CCl₄) δ 0.70–2.05 (m, 19 H), 2.70 (br t, *J* = 7.0 Hz, 2 H), 3.28 (t, *J* = 6.5 Hz, 2 H), 4.03 (t, *J* = 6.5 Hz, 2 H), 6.70 (br s, 1 H), 6.78–7.55 (m, 4 H).

Preparation of 6-(3-Hexyl-1-indolyl)hexyltrimethylammonium Bromide (4). The procedure used for **3** was repeated, using 0.1 g of **10** and 2 ml of anhydrous trimethylamine in 15 ml of absolute ethanol. This product also proved to be highly hygroscopic so no weight was taken; small samples were prepared for spectral use by recrystallization and lyophilization: NMR (D₂O) δ (approx) 0.9–1.9 (m, 19 H), 2.83 (br, 2 H), 2.9 (br, 2 H), 2.94 (s, 9 H), 3.93 (br, 2 H), 6.71 (br s, 1 H), 6.7–7.6 (m, 4 H). Anal. Calcd for C₂₃H₃₉N₂Br·½H₂O: C, 63.89; H, 9.26; N, 6.48. Found: C, 63.84; H, 9.20; N, 6.28.

Preparation of 1-(11-Bromoundecyl)-3-hexylindole (11). The procedure for **6** was followed starting with 0.70 g (0.030 mol) of sodium in 250 ml of ammonia to form sodamide followed by addition of **8** (2.00 g, 0.010 mol), in this case, neat, and finally 4.70 g (0.019 mol) of 11-bromoundecanol in 80 ml of dry THF. The product contained 2.4 g of unreacted bromoalcohol and 3.6 g (100% yield) of 1-(11-hydroxyundecyl)-3-hexylindole: NMR (CCl₄) δ 0.80–2.00 (m, 29 H), 2.10 (br s, 1 H, -OH), 2.68 (br t, *J* = 7.0 Hz, 2 H), 3.50 (m, 2 H), 3.97 (t, *J* = 7.0 Hz, 2 H), 6.70 (br s, 1 H), 6.80–7.50 (m, 4 H).

Four grams (0.0133 mol total alcohol) of the above mixture was dissolved in 75 ml of dry ether containing 8.84 g (0.0267 mol) of carbon tetrabromide (Matheson Coleman and Bell). According to the method of Hooz and Gilani,¹⁶ a solution of 7.00 g (0.0267 mol) of triphenylphosphine in 125 ml of dry ether was added dropwise under nitrogen at room temperature and the solution stirred for an hour. The mixture was filtered and the solids washed with 2 × 50 ml of ether. Evaporation of the combined filtrates left material that was triturated with pentane followed by filtration and evaporation of solvent. The oily residue was chromatographed on silica gel using pentane, as for **6** and **10**. This time, no anomalous indole was detected. Essentially pure **11** was isolated as a colorless oil, 1.91 g (69% yield): NMR (CCl₄) δ 0.88 (t, *J* = 5.0 Hz, 3 H), 1.05–2.10 (m, 26 H), 2.68 (br t, *J* = 6.5 Hz, 2 H), 3.30 (t, *J* = 6.5 Hz, 2 H), 3.98 (t, *J* = 6.5 Hz, 2 H), 6.68 (s, 1 H), 6.70–7.55 (m, 4 H); MS *m/e* (%) 436 (28, M + 1, calcd for C₂₅H₄₀N, 28), 435 (100), 434 (28), 433 (100), 365 (25), 364 (98), 363 (25), 362 (98), 284 (7), 282 (11), 240 (6), 226 (5), 214 (38), 144 (42), 130 (45).

Preparation of 11-(3-Hexyl-1-indolyl)undecyltrimethylammonium Bromide (5). The procedure used for **3** was followed using 1.0 g of **11** and 10 ml of anhydrous trimethylamine in 100 ml of absolute ethanol. Again, the hygroscopic product was collected but not weighed, and small samples were prepared for spectral purposes: NMR (D₂O) δ (approx) 0.65–2.00 (m, 29 H), 2.60 (br, 2 H), 3.0 (br, 2 H), 3.09 (s, 9 H), 3.75 (br, 2 H), 6.63 (br s, 1 H), 6.75–7.65 (m, 4 H). At 100 MHz and 50°, the signals at δ 2.60 and 3.75 are resolved as triplets, *J* = 6.5 Hz. Anal. Calcd for C₂₈H₄₉N₂Br: C, 68.13; H, 10.01; N, 5.77; Br, 16.19. Found: C, 67.94; H, 10.06; N, 5.77; Br, 16.15.

Spectroscopy. Fluorescence spectra were recorded on a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter using 280 nm as the wavelength of excitation. Fluorescence λ_{max} values are precise to ±1 nm. Absorption data were obtained at individual wavelengths using a Gilford uv-visible spectrometer.

Fluorescence-decay curves were obtained using a single photon-counting technique.¹¹ An air-spark flash lamp gave an excitation pulse with a half-width of 2 nsec. The fluorescence was monitored at several wavelengths using a Jarrell-Ash 82-410 monochromator. The multichannel pulse-height analyzer was generally calibrated at 0.238 nsec/channel using a time-to-amplitude converter range of 0.3 μsec. The number of counts in the peak channel was generally 10⁴ to 10⁵.

Table VI. Data for 1.36×10^{-4} M 6-In-11 as Plotted in Figure 7; τ_b 17.2 nsec

λ^F , nm	X_b^F	$I_F^{\text{total}}(\lambda)$	$I_b(\lambda)$
440	0.92	0.096	0.088
400	0.89	0.450	0.400
380	0.85	0.746	0.635
360	0.74	0.847	0.626
340	0.61	0.528	0.322

Table VII. Data for 1.56×10^{-4} M 6-In-11 as Plotted in Figure 8; $\tau_a = 6.1$ nsec; $\tau_b = 18.0$ nsec

λ^F , nm	X_a^F	$I_F^{\text{total}}(\lambda)$	$I_a(\lambda)$
430	0.20	0.133	0.027
420	0.21	0.200	0.042
410	0.25	0.293	0.074
400	0.32	0.407	0.130
390	0.34	0.533	0.183
380	0.38	0.655	0.252
370	0.46	0.737	0.340
360	0.51	0.737	0.374
350	0.54	0.635	0.340
340	0.62	0.444	0.277
330	0.65	0.233	0.152
320	0.69	0.071	0.049

Table VIII. Data for 4.15×10^{-4} M 6-In-11 as Plotted in Figure 9; $\tau_a = 6.7$ nsec; $\tau_b = 16.7$ nsec

λ^F , nm	X_b^F	$I_F^{\text{total}}(\lambda)$	$I_b(\lambda)$
440	0.58	0.050	0.029
420	0.54	0.123	0.067
400	0.45	0.283	0.127
380	0.39	0.550	0.214
370	0.34	0.695	0.236
360	0.26	0.809	0.210
350	0.22	0.814	0.179
340	0.18	0.694	0.125
320	0.12	0.132	0.016

Table IX. Data for 1.28×10^{-3} M 6-In-11 as Plotted in Figure 10; $\tau_a = 5.8$ nsec; $\tau_b = 14.2$ nsec

λ^F , nm	X_b^F	$I_F^{\text{total}}(\lambda)$	$I_b(\lambda)$
460	0.33	0.018	0.006
440	0.25	0.037	0.009
420	0.17	0.092	0.016
400	0.12	0.223	0.027
380	0.10	0.483	0.048
370	0.09	0.643	0.058
360	0.06	0.792	0.047
350	0.05	0.860	0.043
340	0.04	0.786	0.035

The decay curves were analyzed as described in the Results and Discussion. It was found that the elimination of scatter by the use of polarization filters greatly simplified the visual analysis of the dual-component decay curves without affecting the values of τ_F or a and b to any significant extent.

The data used for the generation of time-resolved spectra, Figures 7-10, are listed in Tables VI-IX. In these tables, λ^F is the monitoring wavelength; X_a^F and X_b^F are the coefficients defined in eq 3 and 4; I_F^{total} as a function of wavelength was taken directly from static fluorescence spectra.

$$I_a(\lambda) + I_b(\lambda) \equiv I_F^{\text{total}}(\lambda)$$

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References and Notes

- (1) Review: E. J. Fendler and J. H. Fendler, *Adv. Phys. Org. Chem.*, **8**, 271 (1970).
- (2) Reviews: G. M. Edelman and W. O. McClure, *Acc. Chem. Res.*, **1**, 65 (1968); L. Brand and J. R. Gohlke, *Annu. Rev. Biochem.*, **41**, 843 (1972).
- (3) (a) S. C. Wallace and J. K. Thomas, *Radiat. Res.*, **54**, 49 (1973); (b) L. K. Patterson and E. Viell, *J. Phys. Chem.*, **77**, 1191 (1973); (c) R. C. Dorrance and T. F. Hunter, *Trans. Faraday Soc.*, **68**, 1313 (1972); (d) M. Shinitzky, *Chem. Phys. Lett.*, **18**, 247 (1973); (e) M. Shinitzky, A. C. Dianoux, C. Gitler, and G. Weber, *Biochem.*, **10**, 2106 (1971); (f) A. Alm-gren, *Photochem. Photobiol.*, **15**, 297 (1972); (g) H. J. Pownall and L. C. Smith, *J. Am. Chem. Soc.*, **95**, 3136 (1973); (h) R. R. Hautala and R. L. Letsinger, *J. Org. Chem.*, **36**, 3762 (1971); (i) M. Hauser and U. Klein, *Z. Phys. Chem. (Frankfurt am Main)*, **78**, 32 (1972); (j) T. Forster and B. Selinger, *Z. Naturforsch.*, **19a**, 39 (1964); (k) T. Forster and H. P. Seidel, *Z. Physik. Chem. (Frankfurt am Main)*, **45**, 58 (1965); S. J. Rehfeld, *J. Colloid Interface Sci.*, **34**, 518 (1970).
- (4) G. A. Davis, *J. Am. Chem. Soc.*, **94**, 5089 (1972).
- (5) (a) R. R. Hautala and N. J. Turro, *Mol. Photochem.*, **4**, 545 (1972); (b) R. R. Hautala, N. E. Schore, and N. J. Turro, *J. Am. Chem. Soc.*, **95**, 5508 (1973).
- (6) (a) C. A. Parker, "Photoluminescence of Solutions", Elsevier, New York, N.Y., 1968; (b) L. Stryer, *Science*, **168**, 526 (1968).
- (7) R. D. Spencer and G. Weber, *J. Chem. Phys.*, **52**, 1654 (1970).
- (8) G. Gluibrault, "Practical Fluorescence", Marcel Dekker, New York, N.Y., 1973.
- (9) (a) Y. Kubota, M. Kodama, and N. Nriura, *Bull. Chem. Soc. Jpn.*, **46**, 100 (1973); (b) J. Yguerabide, H. F. Epstein, and L. Stryer, *J. Mol. Biol.*, **51**, 573 (1970).
- (10) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley, New York, N.Y., 1970.
- (11) See W. A. Ware in "Creation and Detection of the Excited State", A. A. Lamola, Ed., Marcel Dekker, New York, N.Y., 1971.
- (12) K. Ishizumi, T. Shioiri, and S. Yamada, *Chem. Pharm. Bull.*, **15**, 863 (1967).
- (13) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964). The low yields may have been due to acid-catalyzed rearrangement of the indole. Cf. A. N. Kost, V. A. Budylin, E. D. Matveeva, and D. O. Sterligov, *J. Org. Chem. USSR*, **6**, 1516 (1970).
- (14) The procedure was suggested by Professor Richard Hautala, University of Georgia, Athens, Ga.
- (15) A. Jackson, B. Naidoo, and P. Smith, *Tetrahedron*, **24**, 6119 (1968).
- (16) J. Hooz and S. S. H. Gilani, *Can. J. Chem.*, **46**, 86 (1968).
- (17) (a) E. J. Corey, K. Achiwa, and J. A. Katzenellenbogen, *J. Am. Chem. Soc.*, **91**, 4318 (1969); (b) C. B. Reese, R. Saffhill, and J. E. Sulston, *Tetrahedron*, **26**, 1023 (1970).
- (18) (a) M. S. Walker, T. W. Bednar, and R. Lumry in "Molecular Luminescence", E. C. Lim, Ed., W. A. Benjamin, New York, N.Y., 1969; (b) M. Walker, T. Bednar, and R. Lumry, *J. Chem. Phys.*, **47**, 1020 (1967); (c) R. W. Ricci, *Photochem. Photobiol.*, **12**, 67 (1970); (d) M. S. Walker, T. W. Bednar, and F. Humphries, *ibid.*, **14**, 147 (1971); (e) E. P. Busel, T. L. Bushueva, and E. A. Burshtein, *Opt. Spectrosc. (USSR)*, **32**, 158 (1972); (f) T. R. Hopkins and R. Lumry, *Photochem. Photobiol.*, **15**, 555 (1972).
- (19) E. J. Fendler and J. H. Fendler, *Adv. Phys. Org. Chem.*, **8**, 271 (1970).
- (20) N. E. Schore and N. J. Turro, *J. Am. Chem. Soc.*, **96**, 306 (1974).
- (21) The cmc was estimated using the technique of laser-light scattering. Some scattering was seen at 1.1×10^{-4} M, and the intensity was found to rise, becoming roughly constant above 1.6×10^{-4} M. We thank Mr. John Gethner for making this measurement.
- (22) For a discussion of methods of cmc determination, see P. Mukerjee and K. J. Mysels, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **36**, 5 (1971).
- (23) P. K. Kadaba, *Synthesis*, 316 (1971).
- (24) This procedure was suggested by Professor Kathlyn Parker, Brown University, Providence, R.I.
- (25) N. G. Kulkarni, N. Krishnamurti, P. C. Chatterjee, and J. S. Aggarwal, *J. Chromatogr.*, **42**, 267 (1969).
- (26) Identified by NMR.
- (27) Compound lacked the indole H-2 signal at δ 6.7. See note, ref 13.