

## NEW PROBES FOR SURFACTANT SOLUTIONS: PHOSPHORESCENT LABELLED DETERGENTS

JOHN D. BOLT\* and NICHOLAS J. TURRO†

Department of Chemistry, Columbia University, New York, NY 10027, USA

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**Abstract**—A series of alkyltrimethylammonium bromides containing terminal phosphorescent chromophores have been prepared and characterized. 10-(4-bromo, 1-naphthoyl)decyltrimethylammonium bromide (BND-10) has a critical micelle concentration (CMC) of 14 mM and a micellar mean aggregation number ( $\bar{n}$ ) of 105. Analogous detergents, BND-11, -8, and -5 have also been prepared; in each case, the naphthoyl group is located at the terminal carbon of an alkyl chain of the indicated length. The normal behavior of increasing  $\bar{n}$  and decreasing CMC with increasing aliphatic chain length is observed. When compared with unsubstituted alkyltrimethylammonium bromides, the 4-bromo, 1-naphthoyl chromophore is roughly equivalent to 6 methylenes with respect to hydrophobic contribution. A broad phosphorescence maximizing at about 590 nm is readily detected upon photoexcitation of the BND molecules in various solvents. The weak fluorescence of the probes is consistent with efficient intersystem crossing of the BND molecules. BND-10 has a phosphorescence yield of 0.023 and a lifetime of 1 ms in water at 25°C. The probes are useful for the study of micelle-detergent exchange dynamics.

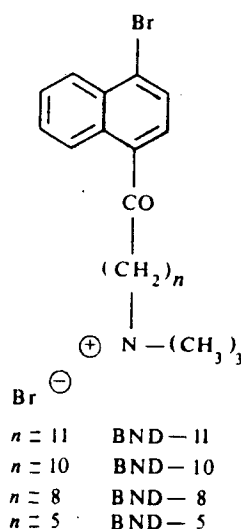
### INTRODUCTION

Fluorescence probes have been extremely useful in the study of micelles and other organized surfactant solutions. Numerous reviews on the use of fluorescence probes are available (Lindig and Rogers, 1980; Turro *et al.*, 1980a; Thomas, 1979; Kalyanasundaram, 1978). One useful approach is the covalent incorporation of luminescent chromophores into surfactant molecules (Almgren, 1972; Nomura *et al.*, 1980; Russell *et al.*, 1980; Schell and Whitten, 1980; Turro and Schore, 1975; Turro *et al.*, 1980b). With the recent discovery of readily detectable phosphorescence in surfactant solutions in mind (Thomas *et al.*, 1977; Turro *et al.*, 1978), we sought to incorporate phosphorescent groups into surfactants. In this paper we describe the synthesis and characterization of  $\omega$ -(4-bromo, 1-naphthoyl)alkyltrimethylammonium bromides (Scheme 1). The primary advantage of phosphorescence is the long lifetime of a typical triplet state in fluid solution, in many cases greater than  $10^{-3}$  s. By contrast, the lifetime of the longest lived singlet (fluorescent) states is commonly less than  $10^{-7}$  s. The increased dynamic range provided by phosphorescent probes has proved useful in studying micelle kinetics (Bolt and Turro, submitted).

\*Present address: Textile Fibers Pioneering Research Laboratory, E.I. duPont de Nemours and Company, Wilmington, DE 19898, USA.

†To whom all correspondence should be addressed.

‡Abbreviations: BND-*n*, bromonaphthoyl detergents containing *n* methylenes; CMC, critical micelle concentration; DDTBr, dodecyltrimethylammonium bromide; HDTBr, hexadecyltrimethylammonium bromide; HDTCl, hexadecyltrimethylammonium chloride;  $\bar{n}$ , mean micelle aggregation numbers; Q, quencher; RuL<sub>3</sub>, anionic ruthenium complex; TLC, thin-layer chromatography.



Scheme 1.

### MATERIALS AND METHODS

**Detergents and solvents.** Hexadecyltrimethylammonium chloride (HCTCl, Eastman)‡, HDTBr (Sigma) and dodecyltrimethylammonium bromide (DDTBr, Eastman) were washed exhaustively with ethyl ether and recrystallized from ethanol-ether mixtures. Water was doubly distilled. Methanol and acetonitrile were spectroquality (Aldrich) and were used as received. All other solvents were reagent grade.

**Spectroscopic measurements.** Absorption measurements were made on Cary 15 and Cary 17 recording spectrophotometers. Steady state luminescence measurements were made on a Perkin-Elmer Hitachi MPF-3L spectrofluorimeter. The quantum yield of BND-10 in H<sub>2</sub>O was determined from the corrected emission spectrum compared to that of quinine sulfate according to Parker (1968). A standard tungsten lamp from Optronics Inc. was used to

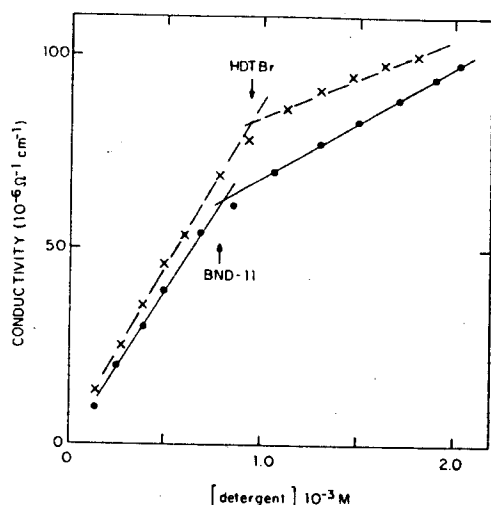
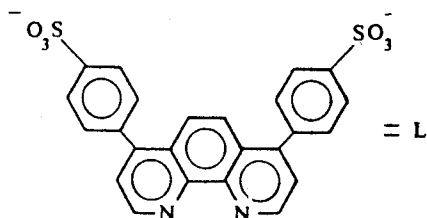


Figure 1. CMC behavior of HDTBr (x) and BND-11 (●). Plots of the specific conductance vs. detergent concentration, 25°C in H<sub>2</sub>O.

calibrate the wavelength dependence of the relative sensitivity of the fluorimeter.

Phosphorescence lifetimes were measured as described previously (Turro and Aikawa, 1980) using the multi-channel analyzer-photon counting technique. Samples were purged with nitrogen (Linde, O<sub>2</sub> free grade) for approx. 30 min. An airgap arc lamp, Xenon Corp. model 437A nanopulser, was used for excitation light. Time dependent fluorescence decays were measured using single photon counting as described by Turro *et al.* (1980b). All measurements were made at 25°C unless otherwise indicated.

**Mean aggregation number,  $\bar{n}$ .** (a) *Pyrene decay.* For HDTCl, HDTBr and DDTBr,  $\bar{n}$  was determined from the decay of pyrene monomer fluorescence based on Poisson distribution of pyrenes in the micelle population (Atik *et al.*, 1979; Lianos and Zana, 1980). (b) *RuL<sub>3</sub> quenching.* UV absorption and fluorescence quenching by the phosphorescent probe detergents precluded analysis of  $\bar{n}$  using the pyrene method. Instead, we used a modification of the luminescence quenching method of Turro and Yekta (1978): for the cationic micelles an anionic ruthenium complex, RuL<sub>3</sub><sup>-</sup> was employed. The structure of the ligand L is shown.

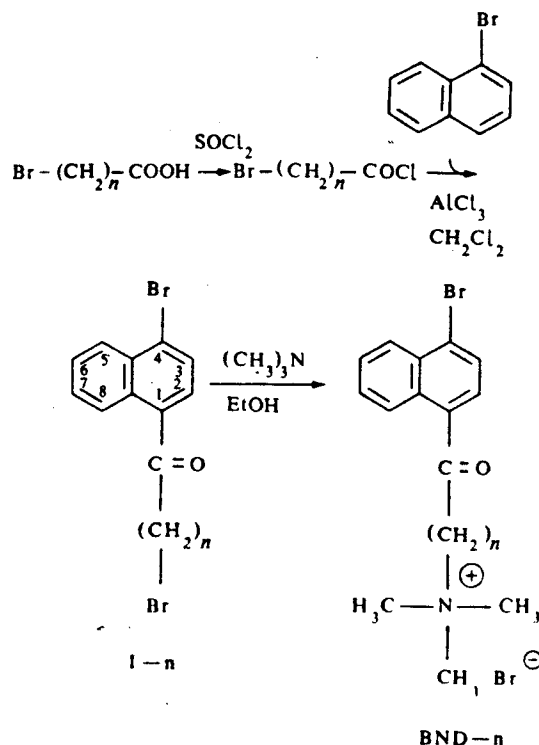


Scheme 2.

The RuL<sub>3</sub>Cs<sub>4</sub> complex was a generous gift from Dr. Norman Sutin of the Brookhaven National Laboratory. 9-Methylanthracene (Aldrich 99%) was used as the micellized quencher.

**CMC measurements.** Critical micelle concentrations were determined from plots of specific conductance against concentration using a Type CDM3 conductivity meter from Radiometer-Copenhagen. In three cases it was possible to confirm the CMC from the intercept of the RuL<sub>3</sub> quenching experiments (*vide supra*). However, in most cases the CMC was too low to be determined within the precision of RuL<sub>3</sub> quenching measurements.

**Probe synthesis.** The phosphorescent labelled detergents were prepared according to the steps shown in Scheme 3



Scheme 3.

**Synthesis of BND-8.** 4.7 g (0.02 mol) of 9-bromononanoic acid (ICN Pharmaceuticals) was combined with 1.7 ml (0.024 mol) SOCl<sub>2</sub> and heated to 70°C for 1 h. After removal of excess SOCl<sub>2</sub> under vacuum, 4 ml of dry CH<sub>2</sub>Cl<sub>2</sub> was added, the solution was cooled to 0°C, and 2.7 g (0.02 mol) of AlCl<sub>3</sub> was added. A solution of 4 ml CH<sub>2</sub>Cl<sub>2</sub> and 3.1 g (0.02 mol) of 1-bromonaphthalene (Aldrich) was then added dropwise. The solution was warmed to 20°C and stirred for 30 min. The reaction mixture was poured onto ice-HCl, combined with ether and extracted with aqueous bicarbonate. After purification on silica, 5.1 g (60% yield) of 1-bromo, 10-(4-bromo, 1-naphthoyl)decane, I-8 was isolated as a yellow oil. The proton NMR in CDCl<sub>3</sub> was consistent with 1,4 substitution: δ1.26 (broad envelope 12H, -CH<sub>2</sub>-), δ2.95 (t 2H, -CH<sub>2</sub>-CO), δ3.33 (t 2H, -CH<sub>2</sub>-Br), δ7.58 (m 4H, ArH 2,3,6,7), δ8.24 (doublet of doublets, 1H, ArH 5 or 8) δ8.43 (doublet of doublets, 1H, ArH). IR (CHCl<sub>3</sub>) 1677 cm<sup>-1</sup> (C=O).

1-Acetyl, 4-bromonaphthalene was prepared by the same procedure; mp 50°C, lit. 47°C. The aromatic region of the proton NMR was essentially identical to that of compound I-8.

BND-8 was prepared from 2.8 g (6.6 mmol) of I-8 by refluxing with a 40-fold excess of (CH<sub>3</sub>)<sub>3</sub>N in absolute ethanol for 2 h. The product was washed by refluxing in ether several times and crystallized from an ethanol-ether mixture to give 2.3 g (72%) BND-8. TLC on silica eluted with 10% acetic acid in methanol gave one spot. The <sup>1</sup>H NMR of BND-8 in D<sub>2</sub>O was essentially identical to that of I-8 except for a decrease of resolution, the loss of resonance associated with the -CH<sub>2</sub>Br protons and the appearance of a singlet at δ3.46 and a multiplet δ3.54 (CH<sub>3</sub>-N and -CH<sub>2</sub>-N, respectively, 11H total). The <sup>13</sup>C NMR of BND-8 in D<sub>2</sub>O was consistent with the assigned structure: δ in ppm with respect to TMS at 0 ppm using CH<sub>3</sub>-N- at 55.5 ppm as an internal standard, 207.5 (C=O), 138 to 128.6 (aromatic C's, 10 peaks), 69 (-CH<sub>2</sub>-N), 55.5

Table 1. Critical micelle concentrations and mean aggregation numbers at 25°C in H<sub>2</sub>O

Detergent	CMC* (mM)	$\bar{n}^\ddagger$	
		Pyrene decay	RuL <sub>3</sub> quenching
HDTBr	0.94 (0.92)	87	86
HDTCl	1.4 (1.3, 1.5)	95	89
DDTBr	15† (15)	56	39
BND-11	0.78	—	—
BND-10	1.4	—	105
BND-8	3.7, 3.4†	—	72
BND-5	13.5, 12†	—	38

\*CMC values from specific conductance graphs unless otherwise noted; error limits  $\pm 3\%$ . Literature values in parentheses from Mukerjee and Mysels (1970).

†Obtained from intercept of RuL<sub>3</sub> quenching,  $\pm 10\%$ .

‡Reproducibility  $\pm 3$  for RuL<sub>3</sub> quenching,  $\pm 4$  for pyrene decay.

(CH<sub>3</sub>-N), 44.5 (CH<sub>2</sub>-CO), 31.5 to 25.0 (aliphatic 6 peaks).

BND-11, -10, and -5 were prepared in a manner analogous to that described for BND-8 from 12-bromododecanoic acid (ICN), 11-bromoundecanoic acid and 6-bromohexanoic acid (Aldrich), respectively.

## RESULTS

### Critical micelle concentrations

Measurements of CMC values and  $\bar{n}$  for HDTCl, HDTBr, DDTBr and the BND probes were made both for comparison and for checks of the reliability of the methods. Figure 1 shows the specific conductivity of HDTBr and BND-11 as a function of concentration. For both detergents, the clearly discernible breaks in the plots indicate the occurrence of critical concentration behavior typical of micelle formation (McBain *et al.*, 1939). The CMC value of HDTBr determined by this method was found to be 0.94 mM and is in good agreement with the literature value of 0.92 mM (Table 1). The CMC values of HDTCl and DDTCl, Table 1, are also in excellent agreement with the literature. From the CMC of BND-11 is determined to be 0.78 mM. For the probe detergents decreasing aliphatic chain size results in increasing CMC, Table 1. This behavior is typical of both conventional cationic and conventional anionic detergents (McBain *et al.*, 1939; Scott and Tartar, 1943).

### Mean aggregation numbers, $\bar{n}$

When pyrene is solubilized in micellar solutions, a nonexponential decay of monomer fluorescence is observed if some micelles contain two or more pyrenes (Atik *et al.*, 1979). A fast decay due to pyrene in multiply occupied micelles and a slower decay due to pyrene in singly occupied micelles is observed under these conditions. On the basis of Poisson statistical distribution of pyrene in the micelle population, it is possible to determine the ratio of the molar concentrations of pyrene [P] and micelle [M] (Atik *et al.*,

1979; Lianos and Zana, 1980). If the ratio of the amplitudes of the longer lived decay to the total decay at time zero is  $p$ , then

$$\ln p = [P]/[M] \quad (1)$$

The mean aggregation number,  $\bar{n}$ , is equal to  $([\text{detergent} - \text{CMC}])/[M]$ . From the CMC, the observed fluorescence decay, and the concentrations of pyrene and detergent,  $\bar{n}$  was determined for HDTBr, HDTCl and DDTCl, and the resulting values are listed in Table 1.

Also using an approach based on the Poisson distribution of a static luminescence quencher, Q, Turro and Yekta (1978) deduced an expression for steady state luminescence intensity. When  $I^0$  and  $I$  are the intensities of RuL<sub>3</sub> luminescence in the absence and presence of Q (9-methylanthracene), then

$$\ln \frac{I^0}{I} = \frac{[Q]\bar{n}}{[\text{detergent}] - \text{CMC}} \quad (2)$$

A plot of  $(\ln I^0/I)^{-1}$  vs. detergent concentration is given in Fig. 2 for HDTBr and BND-8. The luminescence lifetime of RuL<sub>3</sub> was constant for each series of detergent solutions, confirming the assumption of static quenching. From the slope of Fig. 2, we calculate  $\bar{n} = 86$  for HDTBr, in excellent agreement with  $\bar{n} = 87$  from the pyrene method. Similar good agreement is found for HDTCl, Table 1. For DDTBr the value of  $\bar{n}$  from the RuL<sub>3</sub> method is 39, and from the pyrene method  $\bar{n}$  is 56. This discrepancy in  $\bar{n}$  could be attributed to a perturbation of micelle structure due to the relatively large sizes of the ruthenium complex and 9-methylanthracene compared to the smaller micelles. Despite this discrepancy, the usual trend of

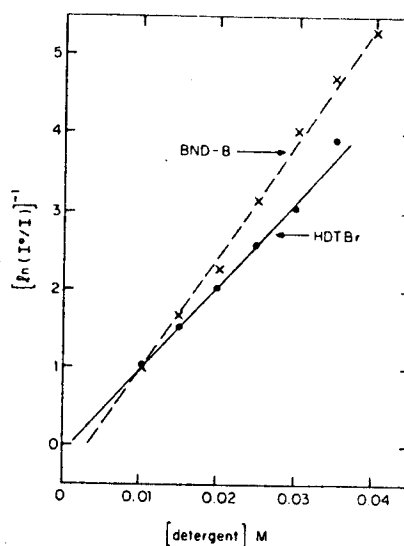


Figure 2. Detergent concentration dependence of RuL<sub>3</sub> luminescence intensity in the presence of Q, 9-methylanthracene. [RuL<sub>3</sub>] = 25  $\mu$ M. For HDTBr (●), [Q] = 0.108 mM. For BND-8 (×), [Q] = 95  $\mu$ M. Excitation and emission wavelengths were 490 and 620 nm, respectively, at 25°C.

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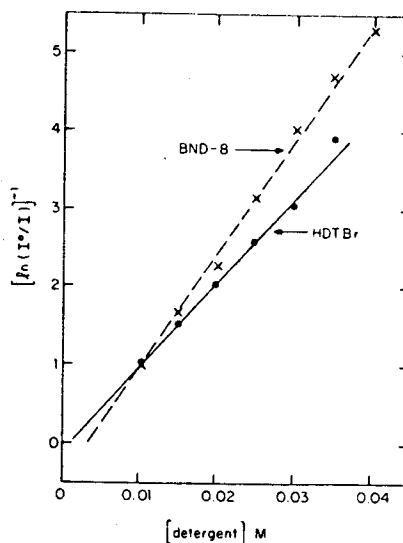


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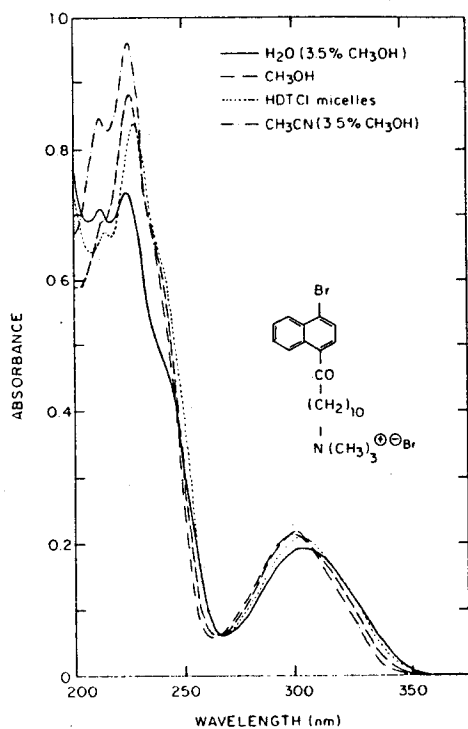


Figure 3. Absorption spectra of  $25.5 \mu\text{M}$  BND-10 in various solvents. (—) In water containing 3.5% methanol; (---) in methanol; (···) in aqueous micelles of HDTCl at 0.02 M; (-·-·) in acetonitrile containing 3.5% methanol.

decreasing  $\bar{n}$  with decreasing hydrocarbon chain (Mukerjee and Mysels, 1970) was maintained. For the BND probes the same trend is observed. The range of aggregation numbers for the probes is similar to the alkyltrimethylammonium salts, from  $\bar{n} = 105$  for BND-10 to  $\bar{n} = 38$  for BND-5.

The RuL<sub>3</sub> quenching method also gives the CMC from the intercept of plots such as Fig. 2. For detergents with low CMC's, the precision of the measurements is not sufficient for reliable estimation of the CMC. However, for DDTBr, BND-5 and BND-8 the CMC's agree well with the CMC's determined by conductance, Table 1.

#### Absorption properties of BND probes.

The absorption of BND-10 in water, methanol, acetonitrile and in HDTCl micelle solution is shown in Fig. 3. In water, three absorption maxima are observed at 303 nm ( $\epsilon = 7.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ), 223 ( $\epsilon = 2.9 \times 10^4$ ) and 213 ( $\epsilon = 2.8 \times 10^4$ ). A fourth band exhibits a shoulder at about 240 nm. In polar organic solvents the 303 nm band shifts slightly to longer wavelength and the extinction coefficients at the maxima increase roughly 10%. The shorter wavelength bands increase in intensity (particularly the shoulder at 240 nm) and shift slightly to longer wavelength. The 223 nm band increases relative to the 213 nm band. In micellar solution the absorption due to the detergent probes closely resembles the absorption in methanol. The absorption band shapes and extinction coefficients of BND-11, -8, and -5 are the same as for BND-10 within our experimental reproducibility.

#### Emission properties of BND probes

Figure 4 shows the luminescence of BND-10 in H<sub>2</sub>O at 25 C. The emission is dominated by a broad band of maximal intensity at 575 nm. In the corrected spectrum used for quantum yield determination, the  $\lambda_{\text{max}}$  is 595 nm. The sensitivity of the emission in Fig. 4 to quenching by oxygen suggests a long-lived readily quenched excited state, i.e. the triplet state of

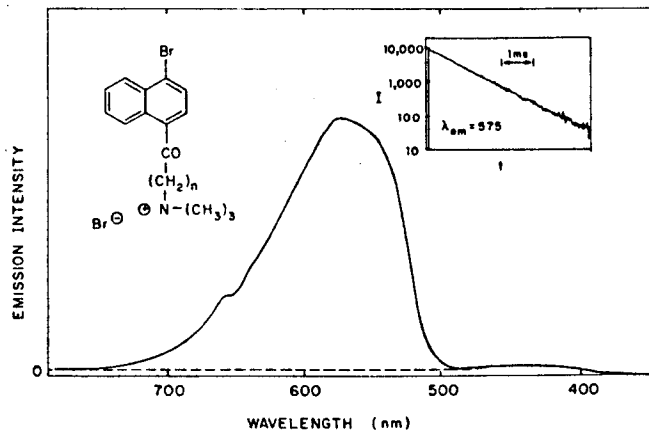


Figure 4. Typical luminescence spectrum of the 4-bromo-1-naphthoyl phosphorescence probe for concentrations of  $25 \mu\text{M}$  in water. Solid line, N<sub>2</sub> purged; dashed line, aerated. Uncorrected for detection response. Inset: semilog plot of the phosphorescence decay. Excitation wavelength = 318 nm. The very weak emission at 430 nm is found in all of the probes studied. This indicates that either a ubiquitous impurity is present or the emission is a true molecule fluorescence. Control experiments (oxygen purging to quench the phosphorescence completely) demonstrate that scattered light and other artifacts do not contribute to the shape of the phosphorescence emission.

Table 2. Quantum yields and lifetimes of phosphorescence of substituted naphthalenes at 77 K

	$\phi_p$	$\tau$ (ms)
Naphthalene*	0.04-0.10	2250
1-Acetylnaphthalene*	0.08-0.10	860
1-Bromonaphthalene*	0.14	18
1-Acetyl, 4-bromonaphthalene†	0.15	8.9
BND-10‡	0.14	6.5

\*In EPA (Murov, 1973).

†In methylcyclohexane, the error limits in the measurement of  $\phi$  are  $\pm 0.02$ .

‡In 50% glycerol-water, the error limits in the measurement of  $\phi$  are  $\pm 0.02$ .

the 1-bromo-4-naphthoyl probe. Typical lifetimes of 1 ms were measured for emission at 575 nm, Fig. 4.

The fluorescence of BND-10 and the other BND probes is extremely weak suggesting a highly efficient intersystem crossing as would be expected to be induced by both the bromine and the carbonyl moieties. In preparations of the BND probes a broad weak emission, possibly fluorescence, is observed to maximize at 430 nm (Fig. 4). However, 1-acetylnaphthalene and 1-acetyl, 4-bromonaphthalene exhibit broad weak fluorescence at about 360 nm. Thus, the observed emission at 430 nm may reflect trace impurities in the BND probes. However, since we have not been able to eliminate this emission through several recrystallizations, we feel that it may be assigned to probe fluorescence.

The quantum yield of phosphorescence of 14  $\mu$ M, BND-10 in water was found to be 0.023 at 25 C. The lifetime of this sample was 1.1 ms. If the quantum yield of intersystem crossing from the first excited singlet state approaches unity (as suggested by the weak fluorescence), then the inherent radiative lifetime ( $\tau_r$ ) of the triplet state can be calculated from Eq. 3 where  $\tau$  is the observed lifetime, and  $\phi_p$  is the phosphorescence quantum

$$\tau_r = \frac{\tau}{\phi_p} \quad (3)$$

yield.  $\tau_r$  is thus calculated to be 48 ms.

At 77 K in a 50% glycerol-water glass, the lifetime of BND-10 increases to 6.5 ms, giving a calculated quantum yield at low temperature of 0.14 if a radiative lifetime of 48 ms is assumed. These values are consistent with a trend of increasing quantum yield and decreasing lifetime upon substitution of carbonyl and bromine functions into naphthalene as listed in Table 2.

Phosphorescence from BND-10 has been observed in a wide variety of solvents and surfactant systems including organic solvents, micelles, microemulsions, lipids and polyelectrolyte solutions, Table 3. In other solvents the shape of the phosphorescence spectrum is essentially unchanged. However, the relative quantum yield and lifetime of BND-10 phosphorescence decreased somewhat. From Table 3 there is a linear dependence of  $\tau$  on  $\phi_p^{rel}$  supporting Eq. 3. The phosphorescence spectra, lifetimes, and quantum yields of BND-5, -8, and -11 consistently parallel that of BND-10.

The probes are quite stable photochemically. A typical sample solution lost less than 3% of its UV absorption after emission spectra and lifetime measurements.

#### DISCUSSION

The micellar properties of the BND probes closely parallel those of conventional ionic detergents. For example, the CMC's of the BND probes decrease and the mean aggregation numbers increase with increasing aliphatic content. The CMC's of BND-11, -10, -8, and -5 are very similar to the CMC's of alkyltrimethylammonium bromides containing 5 or 6 additional aliphatic carbons. The mean aggregation numbers of the BND probes correspond to aggregation numbers of alkyltrimethylammonium bromides with about 7 additional methylenes. Thus, we may assign an 'equivalent hydrophobic contribution' of roughly 6 methylenes to the 4-bromo, 1-naphthoyl moiety. Other work suggests that this empirical correlation also extends to the kinetics of micelle detergent exchange (Bolt and Turro, submitted for publication). Our results are consistent with the conclusion that with the exception of increasing hydrophobic content, the addition of an aromatic chromophore group does not significantly alter the surfactant properties of the BND series.

Similarly, we conclude that the incorporation of a detergent side chain does not greatly change the spectroscopic properties of the chromophore. The absorption and emission spectra are essentially identical to those of 1-acetyl, 4-bromonaphthalene in  $\text{CH}_3\text{CN}$ , in  $\text{H}_2\text{O}$  and micelles. The changes in absorption spectra from polar to non-polar solvents and the extinction coefficients support the assignment of the singlet

Table 3. Relative quantum yield and lifetime of BDN-10 phosphorescence\*

	$\phi_p^{rel}$	$\tau$ (ms)
$\text{H}_2\text{O}$	100	0.93
0.03 M HDTBr in $\text{H}_2\text{O}$	65	0.67
SDS microemulsion†	67	0.51
$\text{CH}_3\text{OH}$	50	0.39
$\text{CH}_3\text{CN}$	25	0.21
Lipid vesicles‡	—	0.93

\*20 C, 20  $\mu$ M.

†5.5% Sodium dodecylsulfate, 10.3% pentanol, 5.1% dodecane.

‡1.5 mM Dimyristoylphosphatidyl choline in  $\text{H}_2\text{O}$  containing 3% ethanol.

Scattered light is too great for an accurate measurement of  $\phi$ .

states to  $\pi, \pi^*$  states (Turro, 1978). Phosphorescence is readily detected from the BND probes in fluid solution, a result of the relatively large quantum yield. The differences in phosphorescence yield and lifetime in various solutions (Table 3) are probably a result of several factors, including the presence of trace impurity quenchers, the efficiency of removing oxygen from different solvents and the possibility of self-quenching.

The usefulness of the BND probes lies in the long-lived triplet state which is readily detected by phosphorescence. A lifetime of 1 ms includes a dynamic range 3-4 orders of magnitude greater than that of the longest lived singlet states. In particular, we have probed detergent-micelle exchange dynamics (Bolt and Turro, submitted) and polyelectrolyte-detergent association (Okubo and Turro, submitted) using these phosphorescent labelled detergents. The detection of phosphorescence in many different systems (Table 3) suggests additional areas of application.

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