The structure of **2** is also unique in several respects. The most outstanding feature is the μ-oxo structure in which an oxygen atom bridges two titanium(IV) atoms. Although a few similar complexes are known,[7] **2** has by far the lowest Ti–O–Ti angle, 152.0 (2)°. The low angle suggests reduced Ti–O π-bonding, and this view is supported by the greater Ti–O bond lengths (average 1.84 Å), which are about midway between the predicted Ti–O single-bond length, 1.9 Å, and the values (ca. 1.79 Å) in most of the linear Ti–O–Ti moieties.[7] The geometry at titanium is close to trigonal bipyramidal, and the titanium amido nitrogen distances average 1.94 Å as in **1**. The Ti(1)–N(4) and Ti(2)–N(8) distances are unique, having the fairly long values of 2.283 (4) and 2.300 (4) Å. The hydrogen atoms on N(4) and N(8) are illustrated in Figure 2. They both display a weak interaction with the central oxygen atom; O···H(4) = 2.37 (2) Å and O···H(8) = 2.33 (2) Å.

The ^1H NMR (90 MHz) spectra of both **1** and **2** in C_6H_6 (27 °C) are complex. For **1**, the spectrum consists of two multiplets at δ 3.3 ($N-CH_2$) and 2.0 ($C-CH_2-C$) in a 2:1 ratio; for **2** the multiplets are centered at δ 3.4, 3.1, ($N-CH_2$) and 1.95 ($C-CH_2-C$). In the IR spectrum (Nujol) of **2**, the band at 720 cm^{-1} has been assigned to the Ti–O stretch. The lower position[7] of the band is consistent with the weaker nature of the Ti–O bond.

Studies of related systems involving vanadium and molybdenum with macrocycles of various ring sizes and their reactions are in progress.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support.

Supplementary Material Available: List of atom coordinates, temperature factors, bond distances and angles, and experimental details (4 pages). Ordering information is given on any current masthead page.

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Absorption and Emission Characteristics of Merocyanine 540 in Microemulsions

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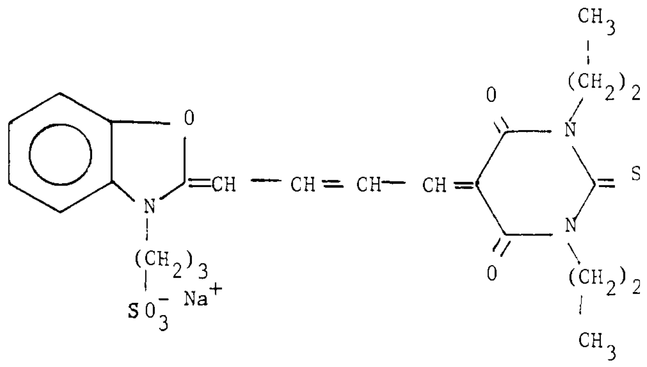
Cyanine dyes are heterocyclic chromophores that are extensively used in a number of areas. For example, they are used as photographic sensitizers, in photographic filter layers, for textiles, and in chemotherapy.[1] Recently they have also been examined as possible candidates for solar energy conversion in the form of monolayers and thin films on glass substrates.[2-4] The efficiency of the cyanine dyes as photosensitizers depends upon their emission properties and also on their photostability. Unfortunately, it is commonly observed that the cyanine dyes with a polymethine chain in the molecular framework degrade in light. In a recent communication, Humphrey-Baker et al.[5] have shown that both the fluorescence yield and photostability of a cyanine dye are significantly enhanced in anionic micellar solution, and they have attributed it to a microviscosity effect. We report here on the absorption and fluorescence properties of merocyanine 540 in anionic and cationic microemulsion. Measurements have also been performed in water, ethanol, 1-pentanol, and aqueous micellar solutions to serve as a basis of comparison.

Table I. Absorption Maxima and Solubility of Merocyanine 540 in Various Media at Room Temperature[a]

medium	λ_{max}, nm	10^{-5}, M^{-1} cm^{-1}	solubility, mM (±3%)
H_2O	533	0.47	0.08
ethanol	559	1.38	4.00
SDS (84 mM)	558	1.02	6.20
60% SCS microemulsion	560	1.21	>10.00
1-pentanol	562	1.28	0.20
50% 1-pentanol + 50% mineral oil	564	0.40	
80% mineral oil + 20% 1-pentanol	566	0.22	
benzene	567	0.32	

[a] All spectra were recorded at 1.76 μM dye concentration.



merocyanine 540

Merocyanine 540 (Eastman) was recrystallized twice from anhydrous ethanol. Aqueous (60% water) sodium cetyl sulfate (SCS) and cetyltrimethylammonium bromide (CTAB) microemulsions were prepared as previously described.[6] Sodium dodecyl sulfate (SDS, Sigma) was used as received. Absorption spectra were recorded on a Perkin-Elmer 320 spectrophotometer. Steady-state fluorescence and polarization measurements were carried out on a SLM instrument equipped with a corrected spectra unit. The details of the instrument are published elsewhere.[7]

The absorption maxima (λ_{max}) along with the molar extinction coefficients (ϵ) of the dye in various solvents are summarized in Table I. Two points are immediately evident from these results. First, λ_{max} is considerably red shifted (ca. 30 nm) in microemulsion, ethanol, and SDS micellar solution. Second, the band intensities are higher by a factor of 2 in these media compared to water. The large shift in λ_{max} to longer wavelength in organized media may be attributed to the decrease in the polarity experienced by the dye molecules, comparable to that of ethanol.

The spectrum in water changes with the dye's concentration. The absorption ratio (A_{533}/A_{501}) decreases as the dye concentration increases. This is common behavior of dyes undergoing aggregation.[8] The low- and high-energy bands are assignable respectively to electronic transitions of monomeric and dimeric dye. Thus, the lower value of the extinction coefficient at λ 533 nm in water is due to dye aggregation, which is extensive even at 1 μM. At this concentration, little if any aggregation is occurring in the other media. For example, the dye obeys Beer's law at

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Table II. Emission Maxima (λ_{em}), Relative Fluorescence Quantum Yields (ϕ_{rel}), Fluorescence Lifetimes (τ_f), Rotational Correlation Times (τ_r), and Polarization (p) for Merocyanine 540[a] in Various Media

medium	λ_{em}, nm	ϕ_{rel}[b]	τ_f (±0.2), ns	τ_r (±0.2), ns	$\langle p \rangle$[c] (±0.01)
H_2O	572	1.0	1.3	16.7	0.36
1-pentanol	582	4.5			
SDS (84 mM)	585	7.8	3.0	19.1	0.28
60% SCS microemulsion	584	8.0	2.8	19.3	0.29
CTAB (7.27 mM)	586	12.3			
60% CTAB microemulsion	584	12.0			
ethanol	583	7.8	2.4	15.3	0.28

[a] Optical density of the solution at the excitation wavelength is about 0.06 in all the media. [b] ϕ_{rel} = quantum yield in medium/quantum yield in H_2O; absolute quantum yield of dye in H_2O is 0.05. [c] $\langle p \rangle$ is the average value in the range 530–610 nm. The value of p_0 determined in glycerol is 0.50 ± 0.01.

concentrations below 0.45 mM in 60% SCS.

Emission maxima (λ_{em}), relative fluorescence quantum yields (ϕ_{rel}), fluorescence lifetimes, (τ_f), rotational correlation times (τ_r), and polarization (p) for the dye are summarized in Table II. Parallel to the shift in absorption maxima, λ_{em} are also red-shifted (ca. 10 nm) in organized media. In addition, the fluorescence quantum yields are considerably higher in microemulsion than in water. Normal micellar solutions also produced similar results. The yields are somewhat higher in cationic aggregates compared to those of the anionic ones. It should also be noted that the solubility of the dye in the microemulsion is much greater than in any of the components of the microemulsion. This is consistent with the solubilization of dye in the interfacial region of the microdroplet, in accord with the spectral data.[9,10] The solubility in ethanol is somewhat less than that in the microemulsion. If the actual volume of the interphase is taken into account (35% of the total volume), then the solubility becomes 30 mM in this region.

The enhancement of fluorescence yield in organized assemblies is normally due to either a microviscosity or a micropolarity[11,12] effect. A direct means to investigate these effects is to measure polarizations (p) and rotational correlation times (τ_r). If the increase in the fluorescence quantum yield is due to a microviscosity effect, then both p and τ_r are expected to be significantly higher in organized media than in water. However, the data presented in Table II indicate that both p and τ_r values in microemulsions are comparable to those in water. Therefore, it may be concluded that the high quantum yields in organized media are due to an effect of micropolarity and not of microviscosity. The dye experiences a micropolarity in microemulsions comparable to that in ethanol. This is corroborated by the fact that λ_{em}, p, and τ_r in ethanol are almost the same as those in microemulsion.

Irradiation of an aqueous solution of dye (1.74 μM) with white light from a 450-W Xe lamp fitted with a Corning 360-nm cutoff filter resulted in a colorless solution in about 20 min. Under identical conditions, photobleaching of the dye was negligible (<3%) in alcohols and micellar solutions, and no photobleaching was observed in microemulsion. However, the photostability of dye to unfiltered white light depended on the medium. In water and 1-pentanol the dye degraded completely in less than 5 min and in about 20% ethanol and SDS solution, over a period of 70 min. In contrast, there was no detectable degradation of the dye in microemulsion. Therefore, unlike the other media, microemulsion is unique in maintaining the photostability of the dye under the experimental conditions employed in this study. The reasons for the enhanced photostability of the dye in microemulsion are not clear.

In summary, the increased fluorescence quantum yield of merocyanine 540 in microemulsion and aqueous SDS micelles is due to the micropolarity rather than the microviscosity. Microemulsion is superior to ethanol or aqueous micellar solution in terms of dye solubility and photostability. Similar behavior has been noted for the cyanine dye 3,3′-dihexyloxacarbocyanine iodide.

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Registry No. Merocyanine 540, 62796-23-0; sodium cetyl sulfate, 1120-01-0; cetyltrimethylammonium bromide, 57-09-0; sodium dodecyl sulfate, 151-21-3.

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gem-Alkylcyclopentadienes. 2. Secondary Deuterium Kinetic Isotope Effect Study of the Cycloaddition of Diphenylketene and 5,5-Dimethylcyclopentadiene[1,2]

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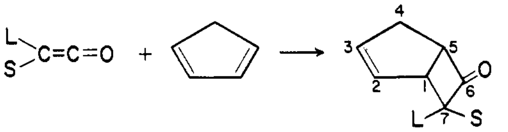
Ketenes[3] react with alkenes to yield cyclobutanones;[4-6] with cyclopentadiene synthetically useful[4] bicyclo[3.2.0]hept-2-en-6-ones are formed (eq 1) with remarkable stereoselectivity.[6] These



(1)

cycloadditions are always highly periselective[3,7] (only (2 + 2) and no (4 + 2) for all-carbon ketenophiles), supraselective[8] on the diene (only cis-fused products), regioselective[8,9] (no bicyclo[3.2.0]-hept-2-en-7-ones), and somewhat less highly spatioselective[10-12] (when L $\neq$ S the larger ketene substituent L prefers the more hindered endo position). These unusual stereochemical features are consistent with an allowed ($_{\pi}2_s + {}_{\pi}2_a$) process in which the ketene acts antarafacially, and the reaction has been widely interpreted as concerted.[13-15]

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