$Ru(bpy)_3^{2+}$ and oxalate in acetonitrile (MeCN)[8] and aqueous[6] solutions, where oxidation of oxalate produces a strong reductant, $CO_2^{-}\cdot$, which ultimately causes reduction of $Ru(bpy)_3^{3+}$ and excited-state production.

The PG/Nafion, $Ru(bpy)_3^{2+}$ electrode shows remarkable stability. The coating did not come off when the electrode was immersed at open circuit in water or aqueous solution for 3 weeks, and occasional cyclic voltammograms taken during this period were perfectly reproducible. The ecl intensity with occasional operation slowly decreased with time, although even after 3 weeks light emission was clearly seen when applying the positive potential steps. When the potential was repetitively cycled between 0.65 and 1.45 V at 100 mV/s, the peak current decreased by ~5% after 350 cycles and by ~16% after 1500 cycles. However, if the electrode was left in the solution overnight at open circuit after this cycling, the peak current recovered to over 90% of its initial value. If the electrode was left to dry in the air and then transferred back to the solution, the ecl intensity decreased sharply or even disappeared.

We have also shown[6] that ecl can be produced by the alternate electrogeneration of $Ru(bpy)_3^{3+}$ and $Ru(bpy)_3^{+}$ in an aqueous solution containing ≥20% MeCN, in a process similar to that found in dry aprotic media.[7] Generation of ecl (in the absence of oxalate) at the PG/Nafion, $Ru(bpy)_3^{2+}$ electrode in aprotic media is complicated by the rapid dissolution of the polymer film in these solutions. However, if the modified electrode is transferred to an aqueous solution containing 20% MeCN and 0.1 M tetrabutylammonium fluoroborate and the potential is repetitively pulsed between the oxidation and the reduction potentials of the adsorbed complex, a very intense luminescence is generated. This ecl rapidly decays upon continued pulsing because of dissolution of the film.[9] This experiment is especially interesting because it provides unique evidence for mobility within the polymer and the possibility of charge transfer and chemical reactions between attached groups, as suggested by Kaufman and Engler.[3c]

Finally, we ran a preliminary experiment to examine the possibility of producing chemiluminescence in membranes. A piece of Nafion membrane (1200 E.W., 10 mil thickness, supplied by duPont de Nemours and Co.) was immersed for 1 h in 5.0 mM $Ru(bpy)_3Cl_2$ in 0.1 M H_2SO_4. The membrane turned orange, indicating that a large amount of $Ru(bpy)_3^{2+}$ was incorporated into it. When this membrane was immersed for ~15 min in an acidic $KMnO_4$ solution, the membrane turned green, signaling production of $Ru(bpy)_3^{3+}$. When the oxidized membrane was transferred to a concentrated aqueous $Na_2C_2O_4$ solution in a dark room and shaken, a weak but definite orange luminescence was observed from the membrane. This preliminary experiment indicates the possibility of electrostatically attaching large amounts of metal complex into Nafion membranes, and carrying out chemical reactions in the membrane or at the interface with the solution.

Because of its stability, Nafion represents a potentially very useful coating at an electrode, and the electrostatic binding technique[4c] offers a simple way of incorporating charged reactants into it. The observation of ecl and its time and potential dependence may be valuable in probing the nature of the charge- and mass-transfer events within polymer layers. Moreover, such electrodes might also be useful for electrocatalytic purposes and in photochemical experiments.[10]

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(10) Support of this research by the Army Research Office is gratefully acknowledged.

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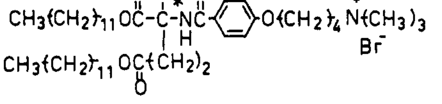
Unique Properties of Chromophore-Containing Bilayer Aggregates: Enhanced Chirality and Photochemically Induced Morphological Change[1]

Sir:

A variety of synthetic single chain[2–4] and double chain (dialkyl)[5–10] amphiphiles produce stable monolayer and bilayer membranes in dilute aqueous solution. These totally synthetic membranes possess structural characteristics which are common to the biolipid membrane, such as molecular alignment and phase transition. These characteristics are readily used for developing unique functional systems. We describe in this communication two examples of the unique property of the chromophore-containing synthetic bilayer membrane.

It has been shown that chiral dialkylammonium amphiphiles as synthesized from alanine and glutamic acid produce well-developed bilayer membranes in water.[11] We subsequently prepared chiral membranes with the aromatic chromophore.

Dialkyl amphiphile L-**1**[12] similarly produces bilayer vesicles in water as probed by electron microscopy. The layer width inferred from an electron micrograph of a negatively stained sample was ca. 50 Å. Interestingly, the magnitude of the optical activity was sensitive to the temperature of measurement. Figure 1 shows the temperature dependence of the CD spectrum of L-**1** in dilute aqueous solution (1.0×10^{-4} M).[13] At temperatures above 31–32 °C, which is the phase-transition temperature (T_c), the CD spectrum possesses a maximum at 245 nm with $[\theta]_{245} = +6000$. This spectrum is identical with that observed in methanol. At temperatures below T_c, there are observed extremely large maxima at 220 and 260 nm with a shoulder extending beyond 700 nm; $[\theta]_{220} = +360\,000$ and $[\theta]_{260} = -400\,000$. The temperature dependence of $[\theta]_{max}$ near 260 nm is shown in Figure 2. The $[\theta]_{max}$ value changes at T_c drastically. These spectral changes are reversible; however, when the temperature is lowered, aging is required to fully regain the low-temperature spectrum. Similar spectral changes are observed for D-**1** in the mirror image.



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The CD enhancement is highly dependent on the amphiphile concentration. When the concentration is lowered from 1.0×10^{-4} M to 5.0×10^{-6} M, $[\theta]_{260}$ decreases from −400 000 to −22 000. The $[\theta]_{260}$ value is not sensitive to the amphiphile concentration

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(1) Contribution No. 569 from the Department of Organic Synthesis.

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(12) This compound was prepared by condensation of didodecyl L-glutamate and *p*-(4-bromobutoxy)benzoic acid and the subsequent quaternization with trimethylamine; mp 45–220 °C (the liquid crystalline behavior was observed in this temperature range), $[\alpha]^{20}_{D}$ +7.46° (*c* 2.00, $CHCl_3$). D-**1** and DL-**1** were similarly prepared. The purity was confirmed by elemental analysis, thin-layer chromatography, and ^1H NMR spectroscopy.

(13) Sonication of an aqueous suspension of **1** was carried out by using a Branson ultrasonic cleaner 12 (bath type) for 3–5 min. The aggregate weight was 6×10^9. When L-**1** was sonicated with the cell disruptor for 5–10 min, the low-temperature CD spectrum could not be observed even after aging for 10 h at 0 °C.

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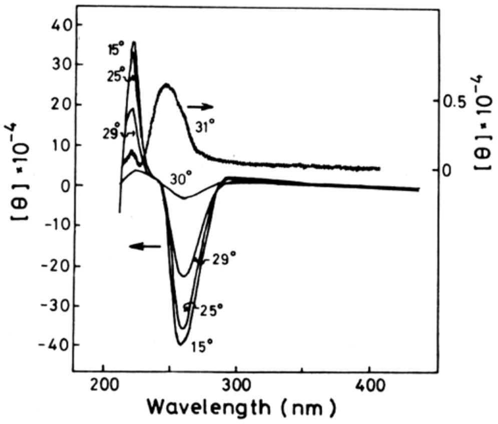


Figure 1. CD spectra of chiral bilayers in water. [L-**1**] = 1.0×10^{-4} M.

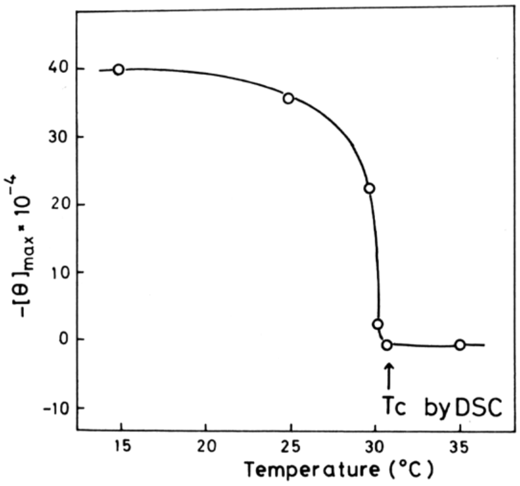


Figure 2. Temperature dependence of $[\theta]_{max}$ for aqueous bilayers of L-**1**. [L-**1**] = 1.0×10^{-4} M.

outside this concentration range. This concentration dependence appears to be related to the critical micelle concentration of **1**, since the cmc value of other membrane-forming dialkylammoniums is 10^{-5}–10^{-6} M.[14–16] The enhanced optical activity is destroyed by the addition of surfactants. For instance, when cetyltrimethylammonium bromide (CTAB) is added in portions to an aqueous solution of L-**1** (1.0×10^{-4} M) at temperatures below 30 °C, $[\theta]_{max}$ decreases gradually and reaches a constant value of +6000 at [CTAB] ≥ 1.0 mM. All of these data indicate that the enormously enhanced circular dichroism is derived from the molecular fixation of chiral surfactants in the rigid bilayer assembly.[17]

The synthetic membrane imbedded with chromophores which undergo the cis–trans isomerization should be interesting as models of photoreceptor cell membranes.[20] In this study, the azobenzene moiety was selected as the photoresponsive unit since its photoisomerization behavior has been studied in detail in various systems.[21]

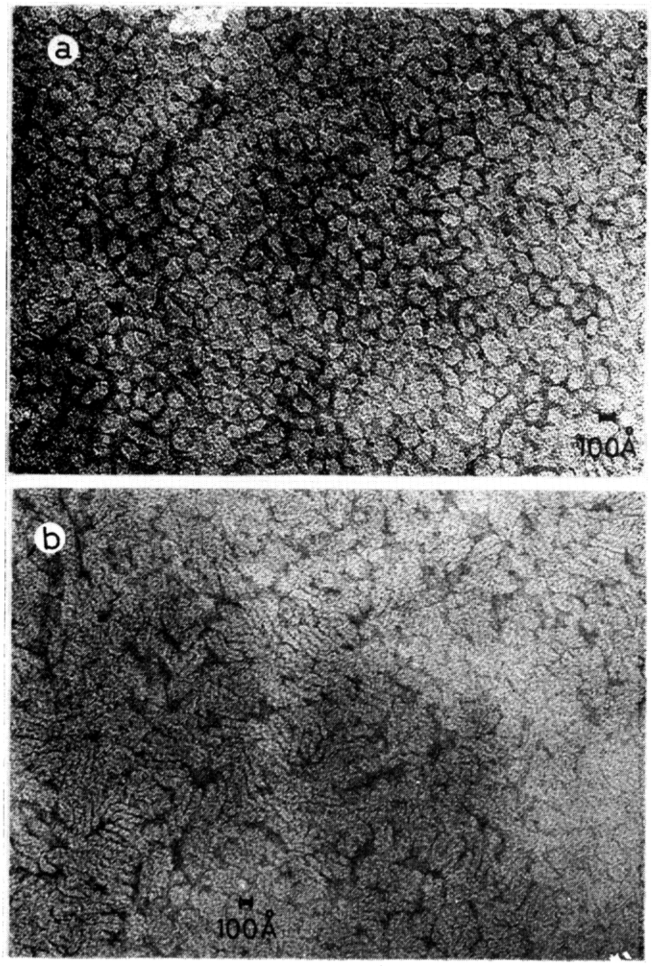
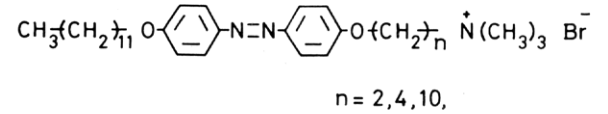


Figure 3. Electron micrographs of the ammonium bilayer with the azobenzene unit. Stained by uranyl acetate (pH 4), magnification 300 000×. (a) **2**, *n* = 4: 100% trans isomer, 10 mM. (b) **2**, *n* = 4: 45% cis isomer, 5 mM.

Amphiphiles **2**[22] produce clear aqueous solutions (ca. 10 mg/2 mL) upon sonication (Bransonic sonifier 185) in water for several minutes. Large aggregates are formed as can be estimated by the small angle light scattering experiment: the molecular weight of *trans*-**2** (*n* = 4) is 6.8×10^5. The gel filtration experiment (Sephadex G-50) showed that the aggregate can entrap a water-soluble probe (methylene blue). These aqeuous solutions



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(17) One of the referees pointed out that the observed CD spectra might actually be derived from linear dichroism (LD). The LD is derived from the anisotropic absorption (*A*) of aggregates (or microcrystallites) of achiral compounds: LD = $A_{\parallel} - A_{\perp}$.[18,19] Although minor involvement of LD cannot be denied, the observed CD spectra must be real for the following reasons. (a) The bilayer solutions used for the CD measurement are clear, consistent with the presence of vesicles (diameter ca. 4000 Å or less) as inferred by electron microscopy. Therefore, there is no macroscopic anisotropy. (b) There is no CD spectrum observed for DL-**1**, and the CD spectra of L-**1** and D-1 are mirror images with each other. This suggests that the extrinsic CD is derived from true chirality of the aggregates. (c) The high sensitivity of the observed CD spectrum to T_c and the CD reversibility are inconceivable for anisotropic microcrystallites, if they exist.

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were placed in a quartz cell and irradiated at 366 nm with a 500-W Hg lamp. The absorption peaks at 247 and 343 nm due to the *trans*-azobenzene unit disappeared, and a new peak of the cis isomer appeared at ca. 450 nm, consistent with the literature data.[21a] The reverse (cis-to-trans) isomerization could be induced thermally or by irradiation at 450 nm. Therefore, clean, reversible cis–trans isomerization is induced by photochemical and thermal means. The photostationary state with the 366-nm light was attained in less than 10 min under the conditions used.

The isomerization is accompanied by the change in the aggregate morphology. The trans isomers of **2** are shown by electron microscopy to assemble in water to globular aggregates with diameters of ca. 200 Å (see Figure 3a).[23] The fine structure of these aggregates cannot be seen clearly; however, the observation of the phase transition[24] strongly suggests the presence of local molecular ordering (bilayers). Upon irradiation, the globular aggregate is transformed to the short rods (diameter 50–70 Å) of Figure 3b. The isomer ratio (trans/cis) of the latter was 55:45. The aggregate weight was 5.3×10^5 after irradiation, and, therefore, the aggregate size does not change essentially in spite of the morphology change. Further irradiation at 450 nm (cis-to-trans isomerization) produced the original globular morphology. Similar, reversible isomerization and morphology change were observed with the other azobenzene-containing amphiphiles (**2**, $n = 2$, 10).

The isomerization process is influenced by the physical state of the bilayer aggregate. The cis fraction at the photostationary state increased from 0.2 to 0.5 abruptly at 40–50 °C in the case of **2** ($n = 10$), corresponding to its phase transition ($T_c = 46$ °C). Its thermal (cis-to-trans) isomerization showed similarly peculiar behavior, and the Arrhenius plots of the initial rate were composed of two lines with an inflection near T_c:$E_a = 21$ and 27 kcal/mol and $\Delta S = -4$ and 11 eu in the temperature range below 35 °C and above 45 °C, respectively.

In conclusion, the present study establishes that the bilayer characteristics can be used for designing novel functions. The chromophore-containing bilayer should find many applications in fundamental and practical research.

Acknowledgment. We are grateful to Professors M. Takayanagi and K. Yamafuji for the use of an electron microscope and a spectropolarimeter, respectively.

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(23) The amphiphile solution as prepared by sonication (and the subsequent aging in an ice bath for 30 min) was mixed with an equal volume of 2% aqueous uranyl acetate, sonicated for 10–20 s, and applied to carbon-coated Cu grids for electron microscopy (Hitachi Model H-500). The photoisomerization was performed with and without uranyl acetate. The resulting morphologies were the same.

(24) The phase-transition temperature, T_c, was determined by differential scanning calorimetry (Daini Seikosha Model SSC/560) for 30 mM aqueous solutions; T_c = 16, 25, and 46 °C for **2** (n = 2, 4, and 10), respectively.

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Successful Isolation of a Reduced Tetrathiometallate Complex. Synthesis and Structural Characterization of the $[(MoS_4)_2Fe]^{3-}$ Trianion

Sir:

The extended X-ray absorption fine structures (EXAFS) of the Mo centers in the Fe–Mo protein component of certain nitrogenases[1] and in the Fe–Mo cofactor[1,2] have been obtained and analyzed. The results of these analyses indicate that the Mo atom is situated at close proximity to four or five sulfur atoms at 2.36 Å and to two or three iron atoms at ~2.7 Å.

Recent attempts toward the synthesis of Fe–Mo–S analogue complexes have resulted in the isolation of two types of multinuclear aggregates which appear to be in relative compliance with the structural constraints imposed by EXAFS studies. These two types of Fe–Mo–S complexes are the Mo_2Fe_6 "double cubanes" and certain Fe complexes with MoS_4^{2-} as a ligand. In the double-cubane cluster complexes $[Mo_2Fe_6S_9(SEt)_8]^{3-3}$ and $[Mo_2Fe_6S_8(SR)_9]^{3-}$ (R = Et,[3] Ph,[4] and SCH_2CH_2OH[5]), the Mo atoms are coordinated to six sulfur atoms with Mo–S bond lengths ranging from 2.35 to 2.57 Å.[3] At a close proximity to the Mo atoms also are found three iron atoms at ~2.7 Å. From the recently reported Fe–MoS_4 complexes,[6] the $[Cl_2FeS_2MoS_2FeCl_2]^{2-}$ anion[6b] contains a central MoS_4^{2-} unit (Mo–S ~2.20 Å) bridging two $FeCl_2$ fragments with a Mo–Fe distance of ~2.8 Å. The presence of MoS_4^{2-} in the latter complex may be a relevant structural feature, to the extent that MoS_4^{2-} also may be present in nitrogenase. This contention finds support in a recent study of the Fe–Mo protein component from *Clostridium pasteurianum* The results of this study indicate that MoS_4^{2-} is released following acid hydrolysis of the Fe–Mo protein. The possibility that a MoS_4 unit may be involved in coordination to Fe atoms in the active site of nitrogenase prompted us to examine further the coordination properties of the MoS_4^{2-} ligand.

The tetrathiometallate anions, MS_4^{2-} (M = Mo, W), as "ligands"[8] are unique to the extent that in addition to the sulfur donor atoms they contain metal atoms with vacant d orbitals. Upon chelation, the MS_4 units bridge the Mo or W ions (formally in the 6+ oxidation state) within a relatively short distance (2.7–2.9 Å) from the chelated metal ion (M′). As expected, and suggested previously,[9] overlap between the d functions of the M′ ions and those of the Mo or W ions could result in M′ → M(VI) charge delocalization. The ability of the MS_4^{2-} anions to facilitate a delocalization of electrons is aptly illustrated in the remarkable redox properties of the $[(MS_4)_2M']^{2-}$ complexes (M = Mo, W; M′ = Ni, Pd)[10] and more recently of the $[(WS_4)_2Co]^{2-}$ complex.[11] In all of these complexes, two one-electron reversible reductions are observed.

As an extension of our studies on the MoS_4–Fe complexes, we proceeded with a reinvestigation of the synthesis and properties of the $[(MoS_4)_2Fe]^{2-}$ complex anion. This compound was reported previously[9] as an X-ray-amorphous material and was not characterized extensively because of its assumed questionable purity.

In this communication, we report on the synthesis and structural characterization of the new $[(MoS_4)_2Fe]^{3-}$ complex. We obtained this complex in microcrystalline form, in good yields and analytically pure, as the tris(tetraethylammonium) and tris(tetramethylammonium) salts. Specifically, the reaction of a concen-

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