Supramolecular Assembly of Metal Chelates Based on Synthetic Bilayer Membranes

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SUPRAMOLECULAR ASSEMBLY OF METAL CHELATES BASED ON SYNTHETIC BILAYER MEMBRANES

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ABSTRACT

Synthetic bilayer membranes are two-dimensional arrays of am-
phiphilic molecules. A large number of bilayer-forming am-
phiphiles are designed by combinations of the structural elements
(hydrophilic head, hydrophobic tail, connector, rigid segment, etc.).
Metal chelate units have been incorporated into bilayer membranes
as part of the bilayer component or as guest molecules. In the
former example, a positively charged Cu(II)/polyamine complex
and a Cu(II)/diketone unit are used as the hydrophilic head and
rigid segment, respectively. The anisotropic orientation of these
Cu(II) chelates is confirmed on the basis of the anisotropic ESR
patterns observed for cast films of aqueous bilayer dispersions.
Anionic planar Cu(II) complexes are incorporated noncovalently
into cast films of ammonium bilayer membranes. These Cu(II)
complexes are placed either horizontally or vertically, depending on
the distribution of negative charges within each molecule. Strong
antiferromagnetic interaction is observed when Cu(II) chelates are
arranged two-dimensionally on bilayer membranes.

†Contribution No. 917.

INTRODUCTION

A synthetic bilayer membrane was first reported for aqueous disper-
sion of didodecyldimethylammonium bromide in 1977 [1]. During subse-
quent years, a large variety of synthetic amphiphiles was shown to
produce molecular membranes (bilayers and monolayers), and it is now
established that bilayer formation is a general physicochemical phenome-
non. Synthetic bilayer membranes are two-dimensional arrays of am-
phiphilic molecules, as are bilayer membranes of biolipids. Therefore,
they provide an excellent vehicle for the specific orientation of functional
units. In this article we summarize our research on how to organize metal
chelates in bilayer membranes.

BILAYER FORMATION

Phospholipid molecules, the major component of biomembrane bilay-
ers, usually contain two fatty acid chains as the hydrophobic moiety and
a phosphate derivative like phosphocholine as the hydrophilic moiety.
Double-chain ammonium salts are a simple synthetic analog of phospho-
choline lipids. These ammonium salts form bilayer membranes sponta-
neously by dispersion in water when the alkyl chain length is C_{10} to C_{20}
[2]. It has been demonstrated that the alkyl chains and the ammonium
head group can be connected in many ways. The ammonium head group
may be replaced with other hydrophilic units. Anionic double-chain am-
phiphiles (sulfonate, phosphate, carboxylate) have been shown to
produce bilayer membranes [3]. Nonionic (e.g., polyoxyethylene) and
zwitterionic counterparts also form bilayers [4].
    A second class of bilayer-forming compounds is single-chain am-
phiphiles. Monoalkyl surfactants form fluid micelles in dilute solution.
When aromatic units are introduced as rigid segments, surfactant mole-
cules become better oriented in aggregates and can produce bilayer as-
semblies. The rigid aromatic segment includes biphenyl, azobenzene, an-
thracene, etc. [5]. Ammonium salts with three long alkyl chains also
undergo spontaneous bilayer formation. Furthermore, alkyl tails in the
single-chain, double-chain, and triple-chain amphiphiles can be replaced
with perfluorocarbon groups. When the hydrophilic heads are attached
to both ends of appropriate (linear and cyclic) molecules, stable mono-
layer aggregates become available. Polymerization of bilayers or bilayer
formation by polymeric amphiphiles are also possible. The general struc-
tural features of these amphiphiles are summarized in Fig. 1 [6].

More recently, we confirmed the formation of a bilayer assemblage from four-chain ammonium amphiphiles on the basis of electron micrography and thermal measurements [7]. This further enriches the variety of bilayer-forming compounds.

MOLECULAR DESIGN OF BILAYER/METAL CHELATES

Incorporation of metal chelates into bilayer membranes can be accomplished either by using bilayer ligands or by the use of charged metal chelates as counterions of oppositely charged bilayer components.

Covalently bonded ligand units are attached to bilayer components as one of the molecular modules (partial structures) of Fig. 1. The protonated cyclam unit and charged β-diketone unit are attached to single-chain and double-chain hydrophobic portions, respectively, without losing the bilayer assemblage [8]. The cyclam and diketone bilayer ligands form 1 : 1 and 1 : 2 complexes, respectively, with the Cu(II) ion. The resulting complexes are soluble in water and display typical bilayer characteristics.

Metal chelate units are also introduced into the hydrophobic portion of bilayers. Ammonium amphiphile 3 contains the dibenzoylmethane unit as the rigid segment. Aqueous dispersions of this compound give rodlike aggregates and show the gel-to-liquid-crystal-phase transition typ-
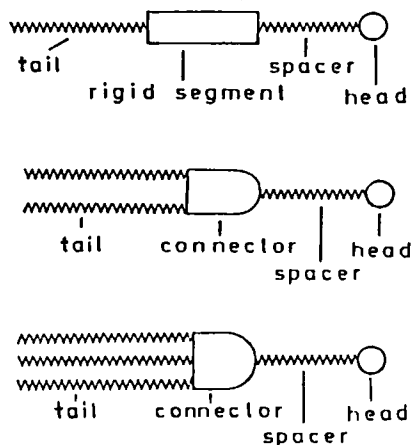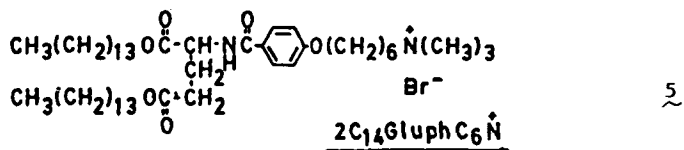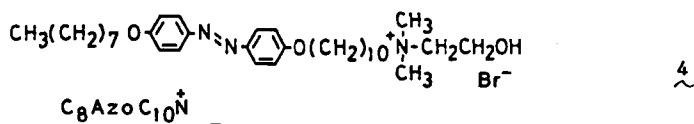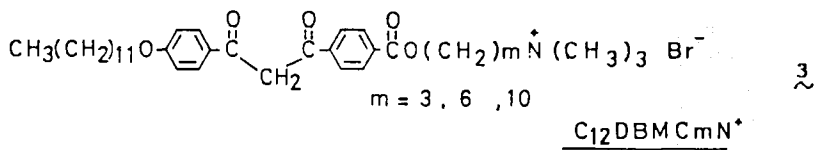

FIG. 1.   Structural modules of bilayer-forming amphiphiles.

$CH_3(CH_2)_7 O$—⟨benzene⟩—$N=N$—⟨benzene⟩—$O(CH_2)_{10}$—N [cyclam macrocycle: H, NH, NH, H]   **1**

$CH_3(CH_2)_{n-1}$ $O\overset{O}{\overset{\|}{C}}$-CH-$N\overset{O}{\overset{\|}{C}}$—⟨benzene⟩—$O(CH_2)_m$-$\overset{+}{N}$ (pyridinium) $\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}} CH_3$

$CH_3(CH_2)_{n-1}$ $O\overset{CH_2}{\underset{O}{\overset{\|}{C}}}$-$CH_2$ Br^- **2**

$CH_3(CH_2)_{11}O$—⟨benzene⟩—$\overset{O}{\overset{\|}{C}}$-$CH_2$-$\overset{O}{\overset{\|}{C}}$—⟨benzene⟩—$\overset{O}{\overset{\|}{C}}O(CH_2)_m\overset{+}{N}(CH_3)_3$ Br^- **3**

$m = 3, 6, 10$

$C_{12}DBMCmN^+$

$CH_3(CH_2)_7 O$—⟨benzene⟩—$N=N$—⟨benzene⟩—$O(CH_2)_{10}$-$\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}$-$CH_2CH_2OH$ **4**

$C_8AzoC_{10}\overset{+}{N}$ Br^-

$CH_3(CH_2)_{13}$ $O\overset{O}{\overset{\|}{C}}$-CH-$N\overset{O}{\overset{\|}{C}}$—⟨benzene⟩—$O(CH_2)_6\overset{+}{N}(CH_3)_3$

$CH_3(CH_2)_{13}$ $O\overset{CH_2}{\underset{O}{\overset{\|}{C}}}$-$CH_2$ Br^- **5**

$2C_{14}GluphC_6\overset{+}{N}$
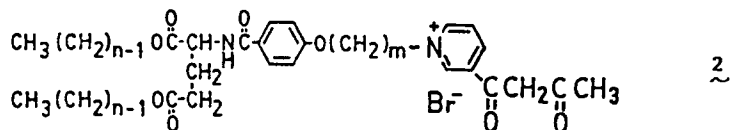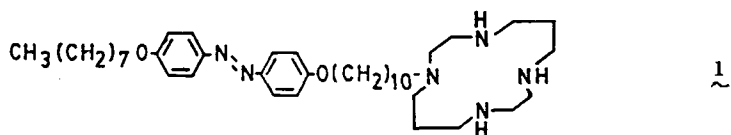
ical of bilayer membranes. They form 2 : 1 complexes with Cu(II) ion as evidenced by absorption spectral changes, and the resulting complexes display characteristic bilayer behavior.

It is clear that the bilayer assembly is quite useful for producing regular arrays of metal chelate units. Schematic illustrations of these situations are given in Fig. 2.

ANISOTROPIC ORIENTATIONS OF METAL CHELATES IN BILAYERS

The illustrations of Fig. 2 suggest that the metal chelates are anisotropically aligned in the bilayer assembly. Molecular anisotropy in these bilayer dispersions is readily transformed into macroscopic anisotropy in multi-bilayer films. When aqueous bilayer dispersions are cast on solid substrates, transparent films in which regular bilayer structures are preserved are formed. Cast films of the Cu(II) complexes of bilayer **1** and **2** give broad ESR signals due to paramagnetic interaction among the Cu(II) chelates. However, when the Cu(II)/bilayer component is imbedded in a large excess (20 times) of an inert bilayer matrix of $C_8AzoC_{10}N^+$ (**4**), the cast film shows a pronounced ESR anisotropy which indicates the Cu(II)/cyclam unit is placed normal to the film plane [9]: see Fig. 3.

Similar anisotropies are attained when metal chelates are incorporated in cast multilayer films as counterions. When $Cu(Tiron)_2$ is incorporated into a powdered cast film of $2C_{12}GluphC_6N^+$, **5**, it produces isotropic
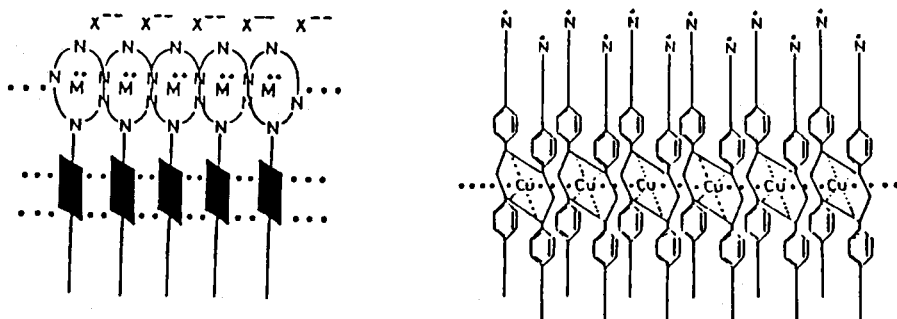

FIG. 2.   Schematic illustrations of bilayers with covalently bonded metal chelates.
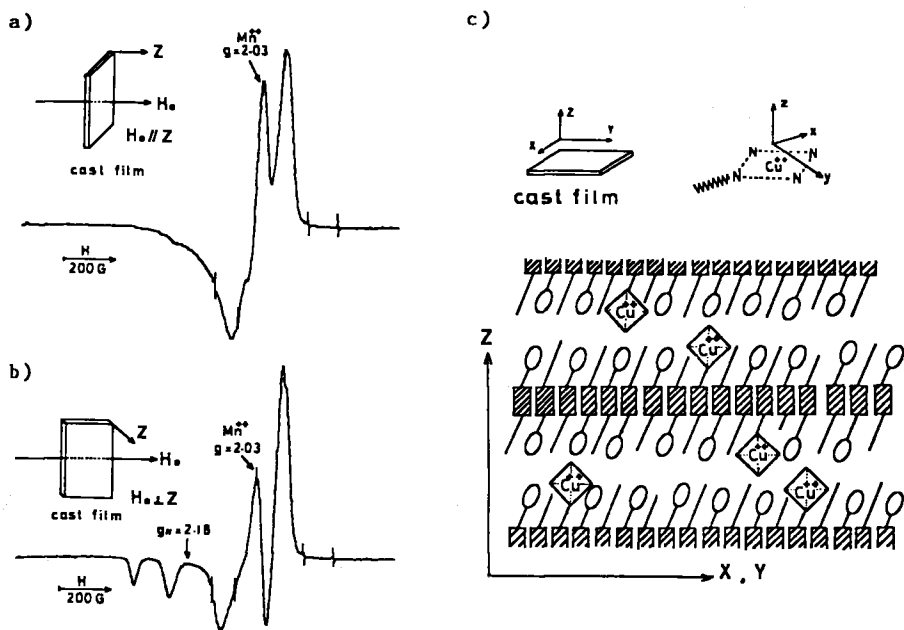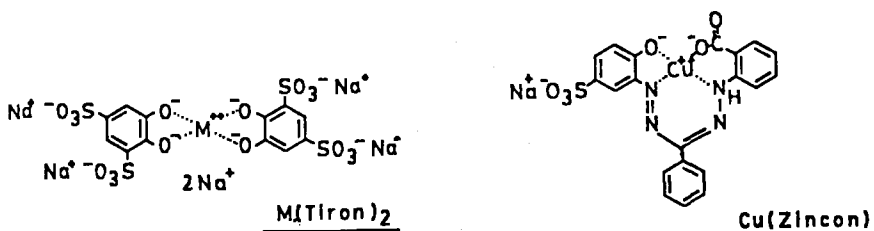
a)

b)

c)

FIG. 3.   ESR spectra of cast films of mixed bilayers (a, b) and a schematic
representation (c).

ESR signals that are typical of a tetracoordinated Cu(II) complex. On the
other hand, anisotropic ESR patterns are found when this Cu(II) com-
plex is incorporated in a planar cast film [10]: see Fig. 4.

M(Tiron)₂

Cu(Zincon)

When the cast film is placed parallel to the magnetic field, the ESR
pattern contains the vertical $(g_\perp)$ component alone, whereas the horizon-
tal $(g_{||})$ component predominates when the film is placed normal to the
magnetic field. These ESR anisotropies are explained by assuming that

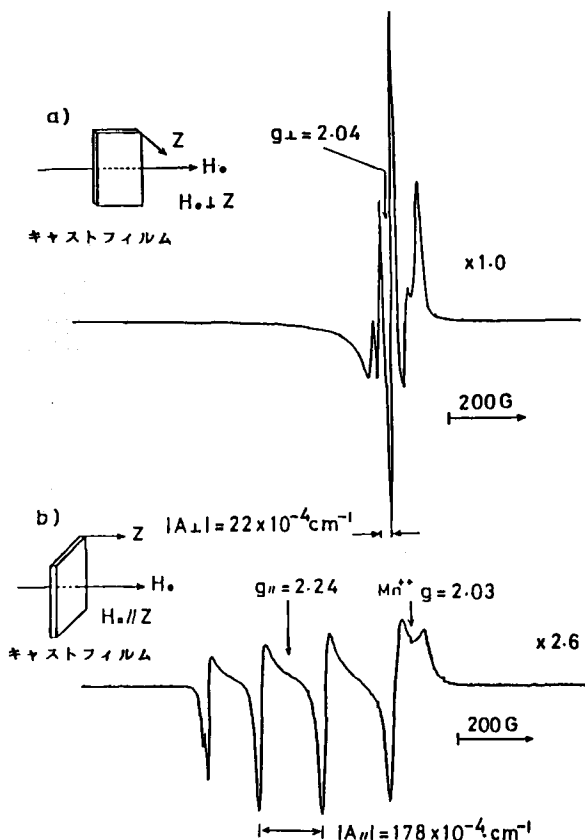FIG. 4.   Anisotropic ESR patterns (a, b) of Cu(Tiron)$_2$ in a cast film of 4 or 5.

planar Cu(Tiron)$_2$ molecules are placed parallel to the film plane in the intrabilayer space. The Cu(Zincon) complex gives reversed anisotropies relative to those of Cu(Tiron)$_2$. This is explained by assuming vertical insertion of this complex into bilayers.

These different modes of incorporation are governed by the distribution of the negative charge on planar Cu(II) complexes. Cu(Tiron)$_2$ is placed flat on the bilayer, so that four negative charges attain maximal ion pairing with the positive charge of the bilayer surface. In contrast,

Cu(Zincon) is composed of the hydrophobic plane and a negative charge at one side of this molecule. Maximal stabilization (both electrostatic and hydrophobic) is attained when this molecule is inserted into the bilayer.

This simple binding mechanism is readily extended to other planar Cu(II) complexes, and anisotropic incorporation of charged porphyrins and phthalocyanines has been accomplished: $Cu(TPPS_4)$ and $Cu(PhCS_4)$ are placed horizontally on the bilayer plane, and Cu(PP) and Cu(ChP) are inserted into the bilayer. The representative modes of incorporation are summarized in Fig. 5.
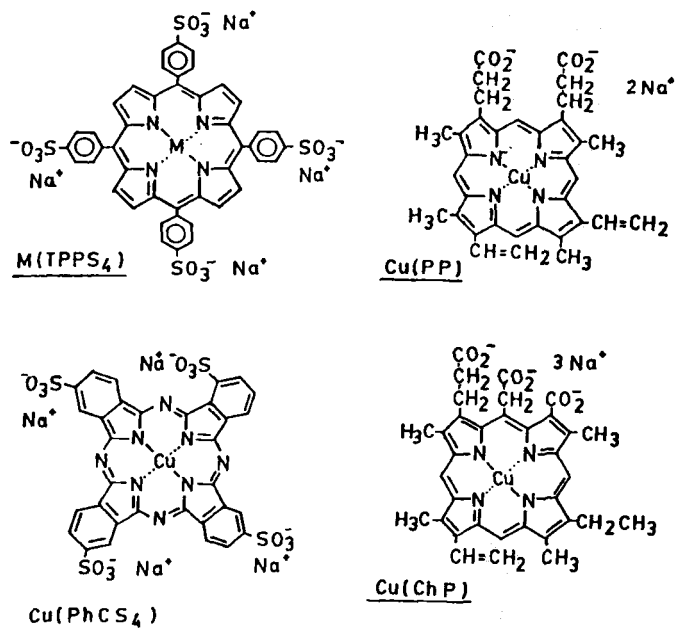
MAGNETIC INTERACTION OF METAL CHELATES IN BILAYERS

When a bilayer component that contains the cyclam/Cu(II) unit (4) is imbedded in an inert matrix bilayer of $2C_{16}N^+2C_1$, it displays the ESR spectrum of a typical tetracoordinated Cu(II) complex. The spectrum is broadened in the absence of the matrix bilayer due to the spin-spin inter-action of the ordered Cu(II) ions. The magnetic susceptibility of the powdered sample obeys the Curie-Weiss law at 80 to 300 K. The Weiss
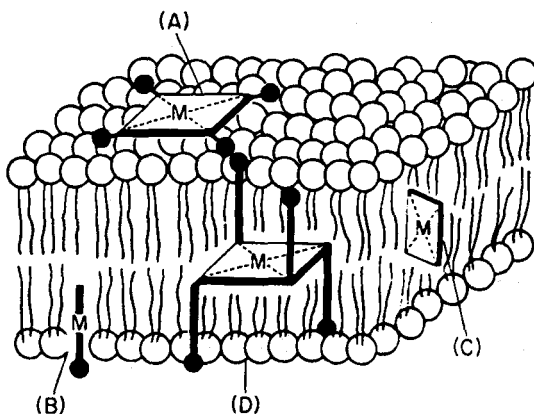
FIG. 5.   Four modes of anisotropic incorporation of planar metal chelates into bilayer.

constants which are estimated from the susceptibility data are large and negative: -44 K for [Cu[II] · 1]lCl$_2$ and -154 K for [Cu[II] · 1]SO$_4$. The θ values for ordinary Cu(II) complexes are 0 ± 10 K and, therefore, the values obtained for the bilayers indicate strong antiferromagnetic interactions among Cu(II) ions [11].

Similarly strong, antiferromagnetic interactions are found for other bilayers which contain metal chelate units. Therefore, the bilayer assembly is a convenient medium for producing regular arrays of magnetically coupled metal ions.

CONCLUSION

We have discussed how metal chelate units can be assembled regularly by using synthetic bilayer membranes. Metal chelate units may be bound to synthetic bilayers either covalently or noncovalently. The rich structural variety of synthetic bilayers and the facile formation of regular cast films are advantageous in designing novel assemblies of metal chelates.

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