CHEMISTRY LETTERS, pp. 1181-1184, 1986.

Magnetic Anisotropy of a Cast Multibilayer Film Containing a Cu(II)/Bilayer Complex[1)]

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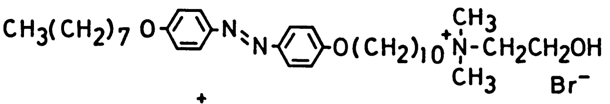
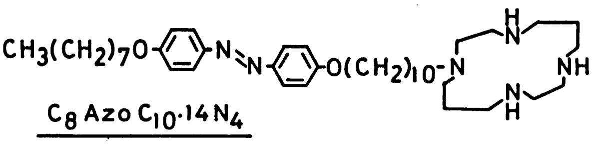
A cast film was prepared from an aqueous mixture of azobenzene-containing, single-chain amphiphiles with the ammonium and Cu(II)-cyclam (1,4,8,11-tetraazacyclotetradecane) head groups. Esr spectra showed the magnetic anisotropy of the film due to the regular orientation of the component amphiphiles.

Bilayer membranes are formed spontaneously by regular, two-dimensional assemblage of component amphiphiles. The regular molecular arrangement of functional units thus obtained has been used to produce unique physicochemical properties such as an efficient energy transfer,[2,3)] efficient charge separation,[4)] and a large magnetic interaction.[5)] The structural features of aqueous bilayer membranes are preserved after immobilization. A bilayer-forming amphiphile, $C_8AzoC_{10}N^+$ was found on the basis of dichroic electronic spectra and X-ray diffraction,[6,7)] to give the parallel azobenzene stacking in an aqueous bilayer as well as in a cast film.



$C_8AzoC_{10}\overset{+}{N}$



$C_8AzoC_{10}\cdot 14N_4$

We prepared an azobenzene amphiphile with the cyclam head group, $C_8AzoC_{10}\cdot 14N_4$,[8)] in order to use the regular molecular packing for controlling the orientation of electron spins. Since its hydrophobic portion is common to that of $C_8AzoC_{10}N^+$, the two compounds are expected to assume the same molecular orientation.

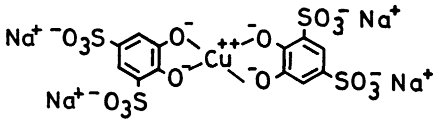
An aqueous dispersion of $[Cu(C_8AzoC_{10}\cdot 14N_4)]SO_4$[9)] was mixed with 27.4 mol/mol of $C_8AzoC_{10}N^+$, and sonicated at ca. 75°C for 3 min (Branson Cell Disruptor 185, 40 W). Larger amounts of the Cu(II) complex were avoided in order to preserve the characteristic esr pattern.[5)] The aqueous mixture was spread on a Teflon sheet and allowed to stand at room temperature for a few days to obtain a yellow, transparent film with thickness of 0.05 - 0.10 mm. Esr spectra were measured by a JEOL JESME 3 X-band spectrometer with 100 KHz magnetic field modulation. The magnetic field was calibrated by the splitting of Mn(II) in MgO.

Figure 1 displays esr spectra of the mixed bilayer. In Fig. 1a, the sample was prepared by quenching of an aqueous mixture by liquid nitrogen. This spectrum is characteristic of a randomly oriented square planar Cu(II) complex. Esr parameters, $g_{\parallel} = 2.18$ and $|A_{\parallel}| = 207 \times 10^{-4}$ cm^{-1}, agree with those of $[Cu(cyclam)_2]Cl_2$ ($g_{\parallel} = 2.186$, $|A_{\parallel}| = 205.0 \times 10^{-4}$ cm^{-1}),10) indicating that the bilayer matrix does not alter the electronic state of the complex. Figures 1b and 1c are esr spectra of the cast film at room temperature. The magnetic field is parallel to the Z-axis of the film in Fig. 1b. The spectrum is mainly composed of the perpendicular components, $g_{\perp}$ and $A_{\perp}$, with small contributions from the parallel components, $g_{\parallel}$ and $A_{\parallel}$. When the film Z axis is set normal to the magnetic field by out-of-plane rotation by 90°, signals due to the parallel components appear and the signal intensity due to the perpendicular components decreases(Fig. 1c). The dependence of the signal intensity of the parallel components on the angle (θ) between the magnetic field and the film Z axis is shown in Fig. 2. The signal intensity increases as the angle approaches 90°. In-plane rotation of the film does not affect the spectrum in all cases. The spectrum is affected by θ alone. These results indicate that the z axis of the Cu(II) complex is perpendicular to the Z axis of the film and its orientation in the X-Y plane is random.

Subsequently, the orientation of the azobenzene chromophore was examined by absorption spectroscopy, as shown in Fig. 3. The spectrum of the mixed bilayer in ehtanol (λ_{max} 360 nm) is attributed to monomeric (non-interacting) azobenzenes and that in water (λ_{max} 303 nm) is associated with the parallel stacking of azobenzene.6) In the case of the cast film placed normal to the incident light, the spectral shape is similar to that of the aqueous dispersion, implying that the mode of the chromophore stacking is identical in both systems. However, the intensity at 303 nm is much lessened relative to that at 250 nm. Since these peaks are ascribed to the transition dipoles along the long and short axes of the molecule, respectively,7) the spectrum of the cast film indicates that the long axis of the azobenzene unit is parallel to the Z axis of the film. Similar results have been obtained for a single-component cast film and a polyion-complexed Langmuir-Blodgett film of $C_8AzoC_{10}N^+$.7,11)

The esr and absorption spectroscopic data are consistent with a schematic illustration of the cast film shown in Fig. 4. Both the azobenzene unit and the Cu(II)/cyclam plane are aligned normal to the film plane. Partial incorporation of the chelate head group does not perturb the molecular packing of $C_8AzoC_{10}N^+$.

In conclusion, fixed orientation of a metal chelate was achieved by taking advantage of the regular, two-dimensional structure of cast multibilayer films. We have separately shown that $Cu(Tiron)_2$ and other chelates incorporated into cast films as counterions are macroscopically oriented.12) Therefore, magnetically anisotropic thin films in which metal chelates are either covalently or non-covalently bound to the component amphiphiles can be readily prepared.



$Cu(Tiron)_2$

The magnetic anisotropy of planar metal chelates has been studied by doping in

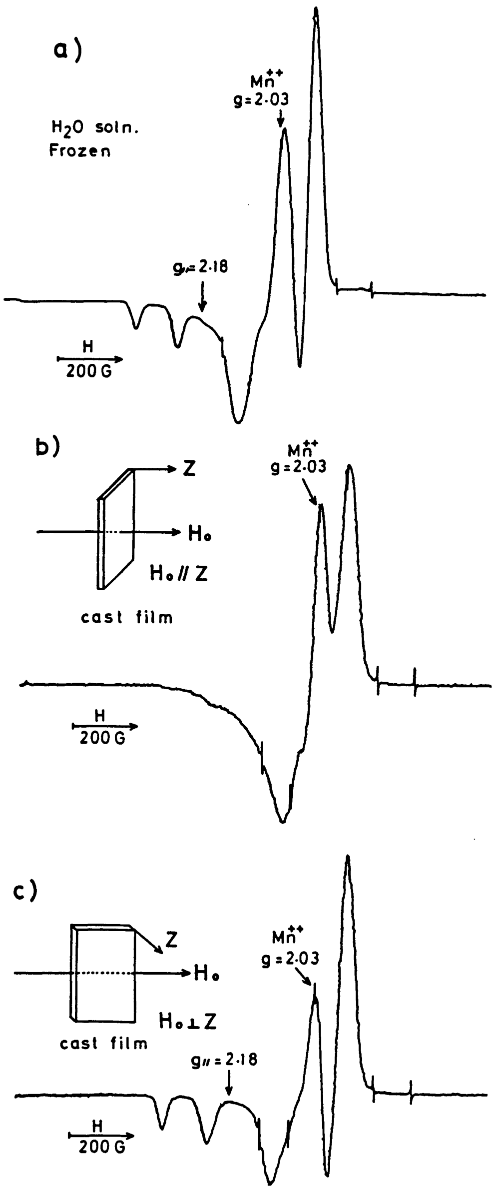


Fig. 1. Esr spectra of mixed bilayers.

a) sample, a quenched aqueous dispersion. $[C_8AzoC_{10} \cdot 14N_4]$ = $[CuSO_4]$ = 2 mM; $[C_8AzoC_{10}N^+]$ = 40 mM; modulation amplitude, 12.5 G; microwave frequency, 9.20 GHz.

b) c) sample, a cast film. $[Cu(C_8AzoC_{10} \cdot 14N_4)]SO_4/[C_8AzoC_{10}N^+]$ = 1/27.4; room temperature; modulation amplitude, 12.5 G; microwave frequency, 9.73 GHz.

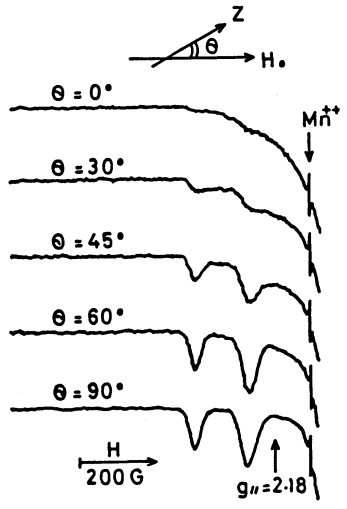


Fig. 2. Changes of the esr pattern of the cast film with angle θ between the magnetic field and the film Z axis. The sample is the same as in Fig. 1 b, c.

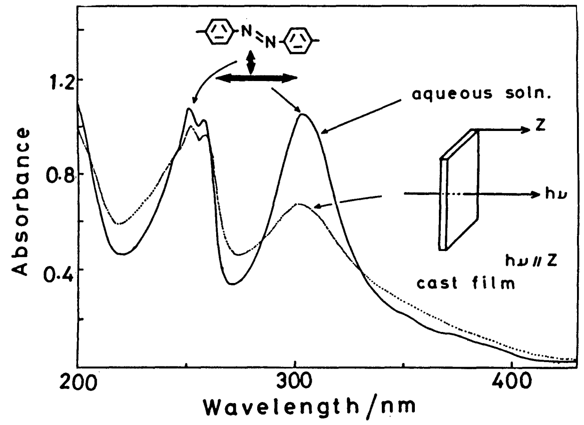


Fig. 3. Absorption spectra of mixed bilayers. solid line: 15°C; pH 8.5 (0.02 M borate buffer, μ(KCl) 0.02); $[C_8AzoC_{10} \cdot 14N_4]$ = $[CuSO_4]$ = 2.6 x 10^{-6}M; $[C_8AzoC_{10}N^+]$ = 7.0 x 10^{-5}M. dotted line; the cast film placed normal to the incident light; room temp.

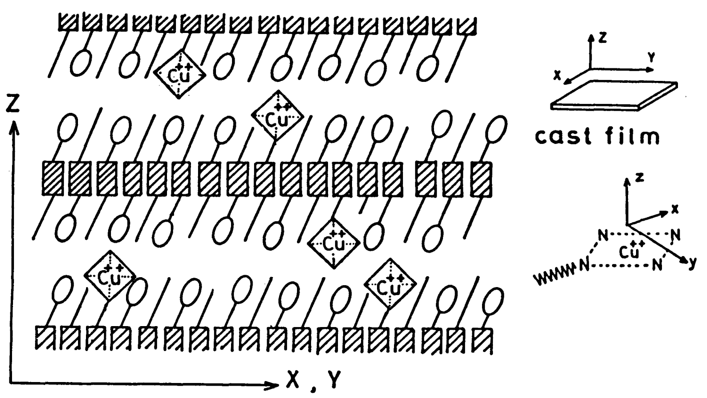


Fig. 4. Schematic representation of the cast film.

single crystals13) and in nematic liquid crystals.14) Difficulties in these systems include the preparation of doped single crystals, solubility control of metal chelates in matrix single crystals, and limited orientations in the liquid crystal matrix. The present method has advantages over these systems in the structural flexibility of metal chelates and in the use of film formation. Doped multibilayer films should be interesting as a new methodology in metal complex chemistry and as new magnetic materials.

We are grateful to Dr. H. Okawa, Faculty of Science, Kyushu University, for his helpful discussion.

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8) $C_8AzoC_{10}\cdot 14N_4$ was prepared from the azobenzene-containing precurser6) and cyclam; NMR ($CDCl_3$); 0.89 (t, 3H, $C-CH_3$), 1.31 (m, 28H, CH_2 in the alkyl chain), 1.69 (m, 4H, $C-CH_2-C$ in cyclam), 2.60 (m, 21H, $N-CH_2$ + N-H), 3.98 (t, 4H, OCH_2), 6.90 (d, 4H, aromatic), 7.69 (d, 4H, aromatic). Anal Calcd for $C_{40}H_{64}N_6O_2\cdot H_2O$: C, 70.76; H, 9.80; N, 12.38. Found: C, 70.99; H, 10.28; N, 11.90.

9) Aqueous $[Cu(C_8AzoC_{10}\ 14N_4)_2]SO_4$ was obtained by mixing stoichiometic amounts of aqueous $C_8AzoC_{10}\ 14N_4$ and $CuSO_4$, and was shown to give rod-like aggregates (diameter, 35-45 A) by transmission electron microscopy.

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(Received April 23, 1986)