Design of a Novel Bilayer System responsive to Chemical Signals; Selective Discrimination of Na^+ by a Spectroscopic Method

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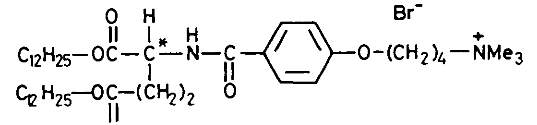
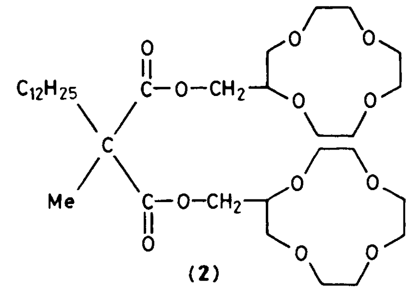
Mixed bilayers composed of chromophore-containing chiral amphiphile–crown ether chains can discriminate ionic signals with high selectivity through transduction to spectroscopic information.

Bilayer formation has been observed for a number of synthetic amphiphiles.[1] These 'synthetic bilayer membranes' possess physicochemical properties fundamentally similar to those of biological membranes. One of the most important and interesting functions of biological membranes is molecular (or ion) recognition, but studies in this field with synthetic bilayer membranes are limited.[2—6] Host–guest[7] and synthetic bilayer membrane[8] chemistry have both made remarkable progress in recent years. Combination of these two systems would be very useful for the development of molecular assembly systems responsive to chemical signals.

As previously reported,[9] the chromophore-containing



(1)



(2)

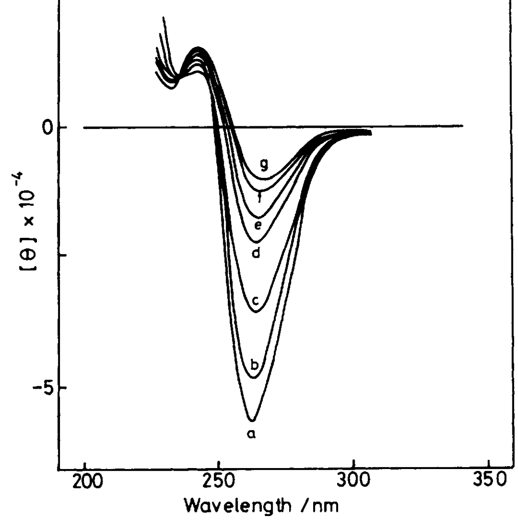


Figure 1. C.d. spectral change induced by the addition of Na^+ to a bilayer of composition (**1**) 1.0×10^{-4} M, (**2**) 5.0×10^{-5} M, Me_4NCl 0.1 M, 20 °C. Na^+ concentrations (a) 0 M, (b) 1×10^{-5} M, (c) 5×10^{-5} M, (d) 1×10^{-4} M, (e) 1×10^{-3} M, (f) 5×10^{-3} M, (g) 1×10^{-2} M.

double-chain amphiphile (**1**) shows marked enhancements of circular dichroism in chiral bilayers due to strong exciton coupling of the chromophores $\{[\theta]_{260}$ −400 000 at temperatures below phase transition$\}$. Chloroform solutions of amphiphile (**1**) and bis(12-crown-4) derivative (**2**)[10] (purchased from Dojindo Laboratories) were mixed and, after evaporation of the solvent, dispersed by warming or by sonication (Branson ultrasonic cleaner 12) in 0.1 M aqueous tetramethylammonium chloride solution to give transparent solutions, which were used for measuring c.d. spectra. The enhanced c.d. gradually decreased with increasing molar ratios of (**2**) to (**1**). Ion addition experiments were conducted in aqueous solutions containing 1.0×10^{-4} M (**1**) and 5.0×10^{-5} M (**2**).

Figure 1 shows the suppression of c.d. spectra by Na^+ addition. It is interesting that a very small amount of Na^+ (1.0×10^{-5} M) produced a considerable lowering of the c.d. intensity. The intensity showed a gradual decrease as the Na^+ concentration was increased. Figure 2 shows the decrease in $[\theta]_{260}$ with alkali metal concentrations. Li^+, K^+, and Rb^+ all affect the c.d. intensity, but only slightly. On the other hand, the bilayer is apparently highly sensitive to the Na^+ ion. These differences may be attributed to the specific binding of Na^+ to the crown moiety of (**2**).

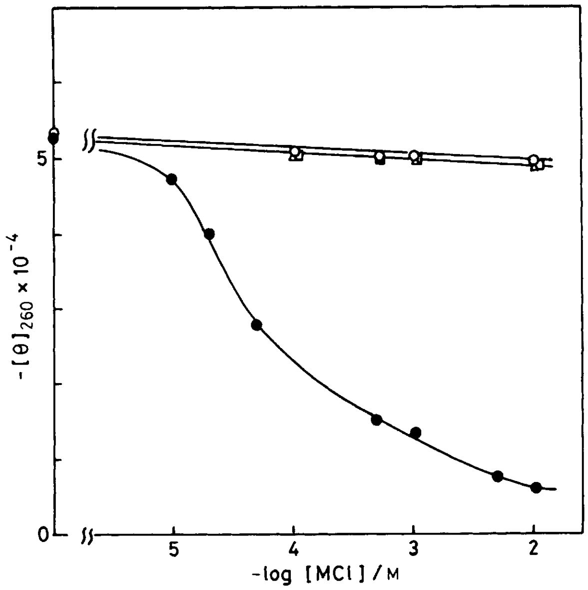


Figure 2. $[\theta]_{260}$ c.d. value *vs.* concentration of Na^+ (●), K^+ (△), Li^+ (□), and Rb^+ (○). Bilayer composition as for Figure 1.

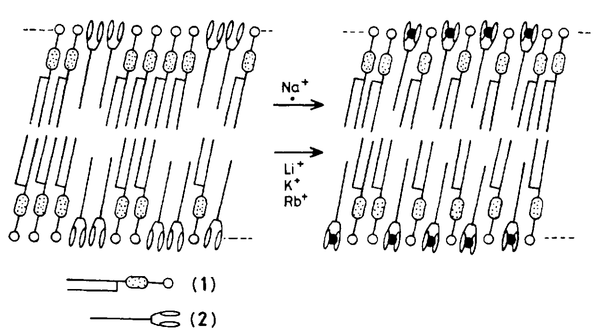


Figure 3. Schematic illustration of the suppression of c.d. intensity in an amphiphile–crown ether bilayer.

The reduction of c.d. intensity on Na^+ addition was most probably caused by changes in the membrane component distribution in the bilayers and/or changes in membrane fluidity. It was confirmed by differential scanning calorimetry (d.s.c.) that the latter is a minor factor, *i.e.*, phase transition temperatures do not change in the presence of Na^+; T_c is 28 °C for bilayers of both compositions [(**1**) 20 mM, (**2**) 10 mM, Me_4NCl 100 mM] and [(**1**) 20 mM, (**2**) 10 mM, NaCl 100 mM]. Thus compound (**2**) perturbs the ordered chromophore orientation of bilayer (**1**) through its binding to Na^+ and leads to the suppression of c.d. intensity. The situation is illustrated in Figure 3.

The crown compound (**2**) used here was developed as a Na^+ ion-selective neutral carrier.[10] The selectivity ratio (Na^+–K^+)

is reported to be about 100:1 in a polyvinyl chloride (PVC) membrane electrode system. On the other hand, in the bilayer system, the selectivity is obviously higher (Figure 2), *i.e.*, 10^{-5} M Na^+ affects the c.d. intensity more than 10^{-2} M K^+. The higher selectivity presumably results from (i), the enhancement of the Na^+ selectivity of (**2**) in the 'bilayer extraction' system and/or (ii), the amplification of the chemical signal through the transduction to spectroscopic information.

To the best of our knowledge, this is the first example of the selective discrimination of ions by a spectroscopic method in an aqueous bilayer system. The system should be applicable to a variety of synthetic and biological ionophores making the evaluation of their ability as 'ion receptors' in bilayers quite easy, and it should also be important in the development of artificial sensory systems to mimic biological membranes.

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