Self Assembly of Bilayer Membranes from Single-chain Aza Crown Ether

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The synthetic single-chain aza crown ethers containing phenyl group as a rigid segment form self assembly of ordered bilayer membranes as an aqueous dispersion and a cast film.

Since the first report on totally synthetic bilayer membranes by Kunitake and his coworkers in 1977,[1] synthetic bilayer membranes have been investigated widely.[2,3] The structural variety and the ease of molecular design make the synthetic bilayer an attractive vehicle for organizing covalently bound functional units and guest molecules.[4]

Crown ethers containing a suitable lipophilic substituent have attracted some attention recently for their complexing ability with a specific metal cation. They are of interest for energy transport and storage and in organic semiconductors and liquid crystal technology.[5,6] However, the mono- and di-alkyl crown ethers are capable of forming micellar aggregates and are suspected to have difficulty forming well-ordered bilayer membranes in water.[7–10] Monserrat *et al.*[8] found that the silver derivatives of a dialkyldiaza crown ether are capable of vesicle formation. Shinkai *et al.*[9] and Gu *et al.*[10] reported the formation of a bilayer membrane from dialkyl crown ether by introducing an anion-cap as the main hydrophilic group into the crown-ring and by addition of an oligooxyethylene group between the dialkyl group and crown ring, respectively. Here, we report self assembly of ordered bilayer membranes from a series of single-chain aza crown ethers containing the phenyl segment as an aqueous dispersion and as a cast film.

The synthesis of amphiphilic aza crown ethers **2a–e** containing a phenyl rigid segment is illustrated in Fig. 1. **2a–e** were obtained by treating **1**[11] and $C_nH_{2n+1}COCl$ (n = 5, 11, 13, 15, 17) in the presence of potassium hydroxide in benzene. The products were purified and recrystallization in ethanol and their structures were confirmed by MS, ^1H NMR, IR spectroscopy and elemental analyses.

Compounds **2a–e** (10–15 mg) were dispersed in 2 ml water by sonication. **2b–e** form a stable opalescent solution, while **2a** precipitates readily. In the case of **2e**, precipitation did not occur over one month. Stability is lowered for the amphiphiles that have shorter hydrocarbon tails. Transmission electron microscopy (JEOL-200CX) indicates that **2b–e** can form vesicles in aqueous dispersions with diameters of 30–150 nm and layer widths 5–25 nm (Fig. 2). The alkyl tail lengths of the amphiphiles **2b–e** are more than ten carbon atoms, in close agreement with that previously reported by Kunitake.[12]

Differential scanning calorimetry (Micro-DSC, Setaram) of aqueous of **2b–e** displayed sharp endothermic peaks at 74, 80, 89, 93 °C respectively. These peaks may be attributed to the phase transition whose temperature is enhanced progressively with increasing alkyl chain length.[13]

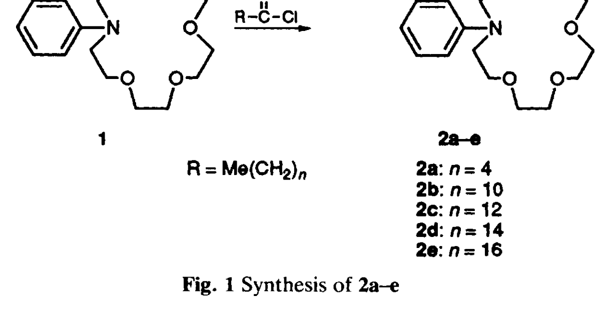

Fig. 1 Synthesis of **2a–e**

Fig. 3 shows the representative absorption spectra of the aza crown ether containing an anilide group in aqueous dispersion and chloroform, respectively. The absorption peaks for the amphiphiles in chloroform occurred at 242, 255 (shoulder peak) and 311 nm, but for aqueous dispersions, the absorption maxima are located at 250 and 272 nm, the split peaks observed at 318 and 325 nm. According to the molecular exciton model,[14] the red shift observed for the bilayer aggregate is derived from stacking the choromophore, called the J-like aggregation, is attributable to the titled chromophore orientation.

A self-supporting film was obtained by casting the aqueous dispersion on a glass plate as described previously.[15] The overall absorption spectra shape of the cast film for **2b–e** is the same as that of the corresponding aqueous dispersions. The long spacings of **2b–e** were obtained from X-ray diffraction (D/Max-RA, Rigaku), X-ray beam was directed towards the

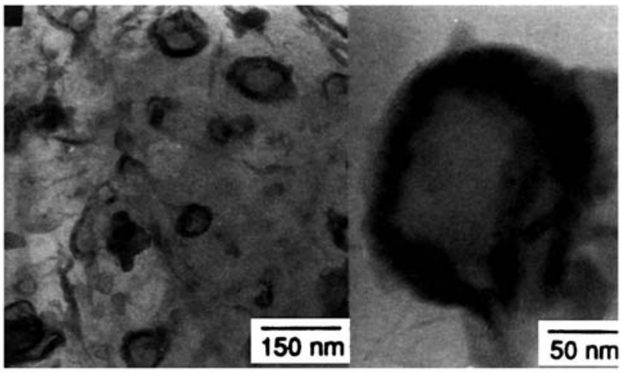

Fig. 2 Transmission electron micrograph of an aqueous dispersion of **2c**

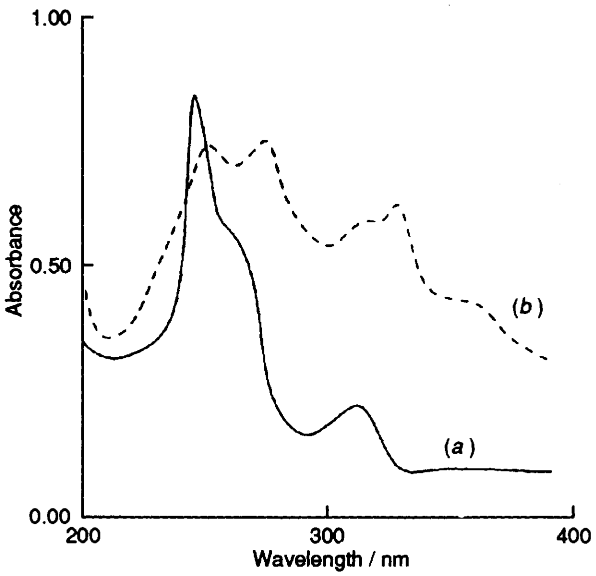

Fig. 3 Absorption spectra of **2c** (*a*) in chloroform solution and (*b*) aqueous dispersion

film edge. The long spacings are 33.4, 36.2, 39.4 and 47.9 Å for **2b–e**, respectively. The absorption spectra and X-ray diffraction indicate that the formation of the titled component arrangement and highly regular structure were obtained in the cast films.

All these results indicate that the synthetic aza crown ethers with single-chain containing more than ten carbons can form stable bilayer membranes when dispersed in water. In comparison with the previous work, it is evident that improved molecular orientation by introducing the phenyl group between the hydrophobic tail and crown-ring is crucial to give an ordered and stable bilayer assembly, and stable bilayer membranes can be produced even from monoalkyl crown ethers whose conformation are restricted by incorporation of rigid segments. It is also confirmed that bilayer formation is a general phenomenon that is observed for a wide variety of synthetic amphiphiles with essential structural elements containing flexible tail, rigid segment and hydrophilic headgroup.

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