

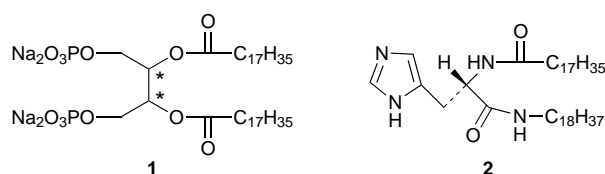
# Supramolecular expression of chirality in assemblies of gemini surfactants

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**Supramolecular expression of chirality occurs in mixtures of an L-histidine derivative and the (S,S) isomer of a phosphatidic acid-based gemini surfactant, but not in mixtures of this histidine derivative and the (R,R)- or (R,S)-gemini surfactant.**

Gemini surfactants are amphiphilic molecules containing two hydrophilic head groups and two long aliphatic chains, which are linked by a rigid<sup>1,2</sup> or flexible spacer,<sup>3,4</sup> and as such have potentially interesting properties.<sup>1</sup> Theoretical calculations<sup>5</sup> and recent experimental results<sup>6,7</sup> indeed indicate that ‘geminis’ behave differently from normal surfactants, which opens the way for new applications.



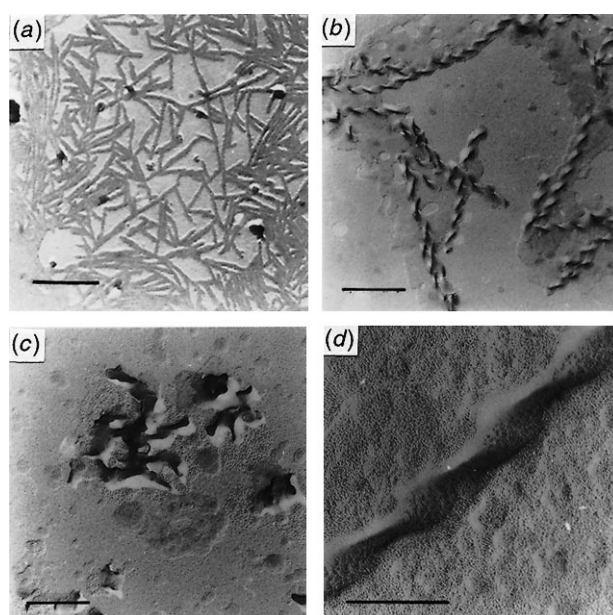
In a previous paper we showed that gemini surfactants based on phosphatidic acid (see **1**) can undergo stereodependent fission or fusion in the presence of calcium ions.<sup>8</sup> Here we report that these surfactants are capable of recognising a long chain L-histidine derivative, leading to a stereodependent expression of molecular chirality at the supramolecular level.

The (R,R), (S,S) and (R,S) forms of compound **1** were synthesised as described elsewhere.<sup>8</sup> All three stereoisomers of **1** formed bilayer aggregates when they were dispersed in water. Histidine surfactant **2** alone could not be dispersed in water to form distinct aggregates due to its low solubility.‡ When **2** (25 or 50 mol%) was mixed with the (R,S) isomer of **1** and dispersed in water at pH 6.5, vesicles with diameters ranging from 150 to 750 nm were generated. Increasing the concentration of **2** to 75 mol% led to the formation of extended bilayers and multilayer structures. In contrast, at all concentrations aqueous dispersions of **2** and the (R,R) isomer of **1** yielded irregularly shaped, rod-like structures with an average diameter of 30 nm and a length of 0.2–2.0 μm [Fig. 1(a)]. When **2** and the (S,S) isomer of **1** were mixed, helical structures together with planar bilayer aggregates were found in samples containing 25 mol% of **2** [Fig. 1(b)]. In samples containing 50 and 75 mol% of **2**, the aggregates tended to form twisted structures [Fig. 1(c)], but no distinct morphologies could be detected in the bulk of the material.

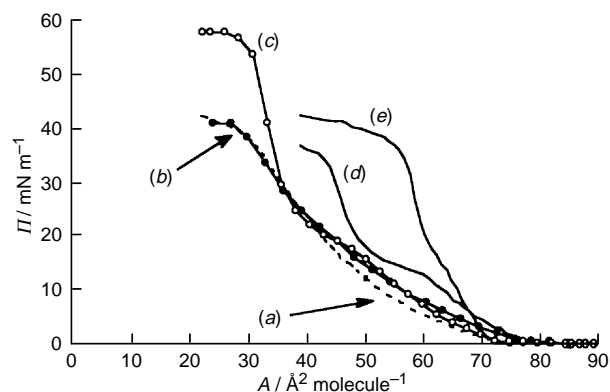
Further experiments revealed that the helical structures were only generated when the concentration of **2** was between 25 and 35 mol%, with the optimum lying at 30 mol%. Right-handed helices with a pitch of approximately 90 nm and a thickness of ca. 40 nm were observed exclusively [Fig. 1(d)].§ When the concentration of **1** deviated from 30 mol%, the observed helices were shorter and many of them contained defects [Fig. 1(c)]. The fact that the pitch and the thickness of the helices were similar in all cases suggests that their formation occurred in a precise manner, requiring a distinct ratio of the two surfactants, rather than a variable one. Since a concentration of 30 mol% of **2** appeared to be optimal, 1 : 2 complexes of **2** and (S,S)-**1** are

probably the building blocks from which the helices are constructed.

Monolayer experiments revealed that **2** forms stable monolayers at the air–water interface. The surface area–surface pressure isotherms displayed a transition to a non-compressible state at relatively low surface pressure (Fig. 2). This suggests



**Fig. 1** Transmission electron micrographs [Pt shadowing, (a)–(c) bars represent 400 nm, (d) bar represents 100 nm] of mixtures of (a) (R,R)-**1** and **2** (75 mol%), (b) (S,S)-**1** and **2** (25 mol%), (c) (S,S)-**1** and **2** (50 mol%) and (d) (S,S)-**1** and **2** (30 mol%)



**Fig. 2** Monolayer isotherms recorded at 20 °C of mixtures of (S,S)-**1** and **2** on a sub-phase of pH 6.5: (a) 25, (b) 33, (c) 50, (d) 75 and (e) 100 mol% **2**

