

Self-Assembly of Organic Semiconducting Films from Oligothiophene Surfactants

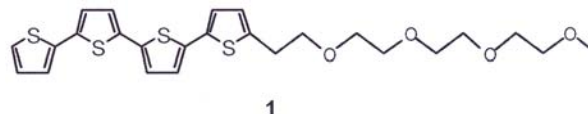
by *D. Y. Sasaki*

Motivation—Conductive organic materials offer the promise of easily fabricated thin films for a variety of applications, such as backlit displays for light emitting diode (LED) devices and low-end storage materials. Among the many materials that have been prepared and tested, the poly- and oligo-thiophenes offer some of the best ion mobilities and on/off rates to date. In terms of processability, however, the polythiophenes are problematic with their low solubility in most solvents and high temperatures needed for vacuum deposition. Alternative routes for film preparation use oligothiophenes with pendent functionality to improve solubility, but environmentally harmful solvents must typically be used. Through proper design of the headgroup and oligothiophene dimensions we hoped to develop a surfactant that disperses and self-organizes in water.

Accomplishment—We designed molecule **1** as our first entry into the development of aqueous phase lyotropic oligothiophene surfactants. By connecting a short oligoethylene glycol on one end of a tetrathiophene unit a surfactant of cylindrical dimensions could be prepared that should have the tendency to form lamellar bilayer assemblies in water. Surfactant **1** was prepared synthetically through Stille coupling to form the tetrathiophene moiety and Williamson ether synthesis to attach the hydrophilic triethylene glycol headgroup.

Sonication of **1** in pure water produced clear dispersions of small vesicles. Dynamic light scattering (DLS) measurements of the solutions found that the dispersed surfactant formed a narrow distribution of 83 ± 5 nm diameter particles.

Interestingly, the size and distribution were independent of surfactant concentration. Transmission electron microscopy (TEM) of the particles found them as unilamellar vesicles with elliptical shape (Fig. 1).



Films cast from water, organic solvent, and from tetraethylorthosilicate sol spontaneously formed ordered lamellar structures on glass substrates. X-ray diffraction (XRD) measurements of the sol-gel films found that the surfactants formed stacked lamellae with a perpendicular orientation of the surfactants to the glass surface (Fig. 2).

In a preliminary study, we performed a bulk conductivity measurement of these cast films. The undoped films exhibited conductivity on the order of $10^{-7} \Omega^{-1}\text{cm}^{-1}$, which is of similar range for typical undoped organic semiconductor materials. Signs of photoconductivity were also observed as well as a negative effect of electrical conductivity towards humidity.

Significance—The ability of π -conjugated materials to form ordered and oriented supramolecular structures is essential for the electronic performance of these materials. The oligothiophene-containing molecule **1** forms bilayer structures in water and as cast films on solid substrates. This molecule provides a route towards the preparation of highly oriented and packed superstructures of organic conductors via an environmentally safe deposition solvent.

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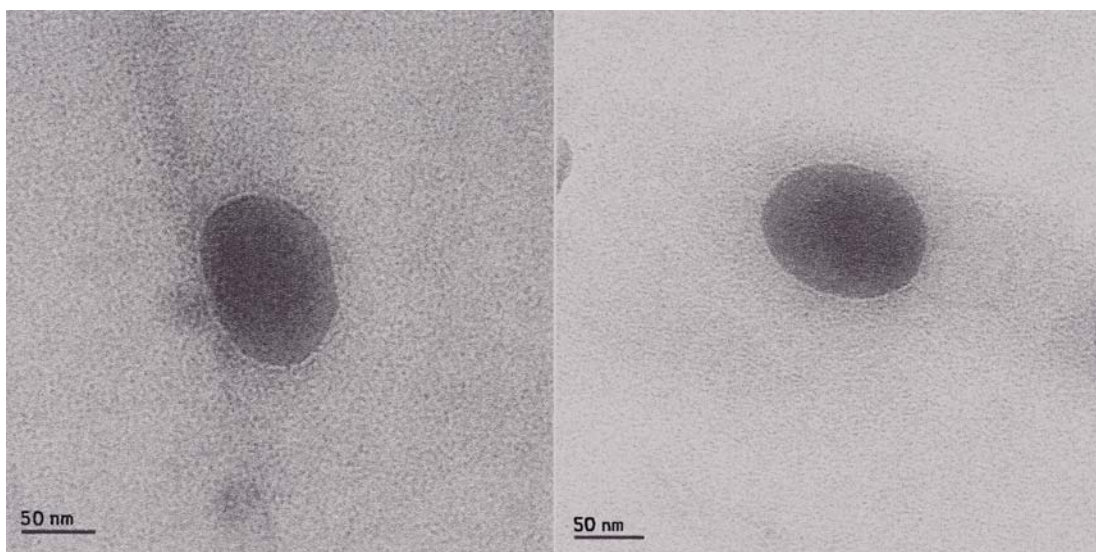


Figure 1. Cryo-TEM images of vesicles of surfactant **1** prepared in water and stained with ammonium molybdate. These images are representative of the structures visible in the sample revealing their ellipsoidal shape and narrow size distribution.

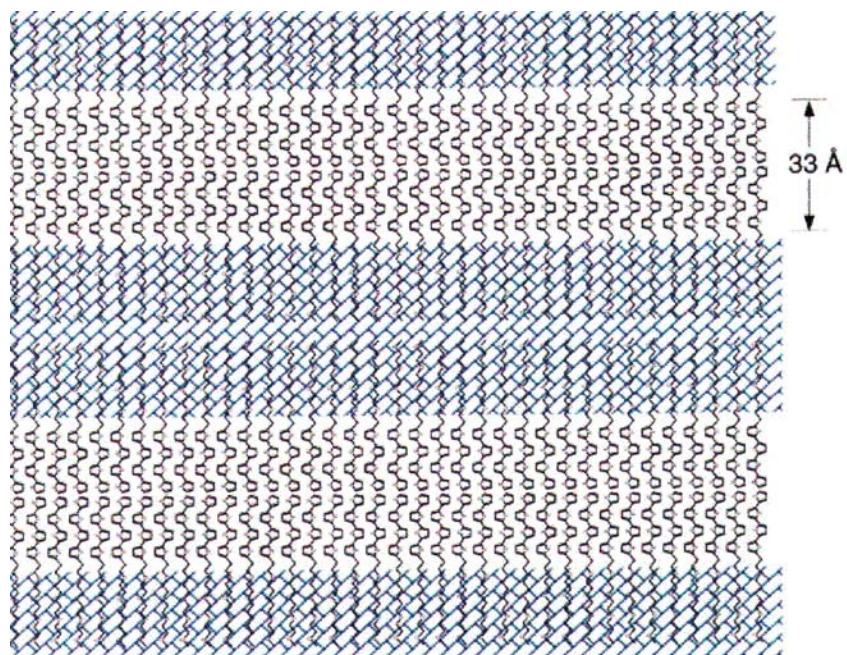


Figure 2. Illustration of the lamellar structure formed from TEOS sol-gel dip-cast film with **1**. XRD measurement of the film showed a spacing of 33\AA , consistent with the hydrophobic core segment of the **1** bilayer in a perpendicular orientation.