

## Supramolecular assembly of a quaterthiophene surfactant†

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**A newly synthesized oligothiophene surfactant self-assembles into unilamellar vesicles in aqueous solution and exhibits semiconductive behavior as a cast film.**

Organic semiconductor materials offer the promise of easily fabricated thin films for a variety of applications, such as backlit displays for LED devices and low end storage materials.<sup>1</sup> Among the many materials that have been prepared and tested, the poly- and oligo-thiophenes offer some of the best semiconductive properties to date.<sup>2</sup> In terms of processability, however, the polythiophenes can be problematic due to low solubility for coating solutions or high temperatures needed for vacuum deposition. Solubility can be improved by the addition of pendent functionality for solution casting<sup>3</sup> or Langmuir–Blodgett deposition,<sup>4</sup> but the electronic performance is often compromised by defects and impurities in the films.

Oligothiophenes offer a number of advantages over their polymeric counterparts.<sup>5</sup> They can be readily synthesized with a variety of functionalities and isolated in pure form to minimize the formation of defects and traps in materials. Furthermore, in spite of their significantly shortened conjugation length, materials prepared with oligothiophenes often exhibit high conductivity.<sup>6</sup> To improve processability, oligothiophenes have been functionalized at their  $\alpha$  and  $\omega$  positions with alkyl groups to improve solubility and aggregational properties during film formation.<sup>7,8</sup> These oligothiophenes form liquid crystalline and crystalline domains that determine the electronic properties of the material.<sup>9</sup> The ability of the oligothiophenes to form ordered structures is thus critical for good electronic performance. However, the ordered phases of these molecules typically develop during solvent evaporation. The rapid dynamics of the evaporation process can lead to entrapped amorphous structures and other defects and impurities that can be difficult to remove through annealing.

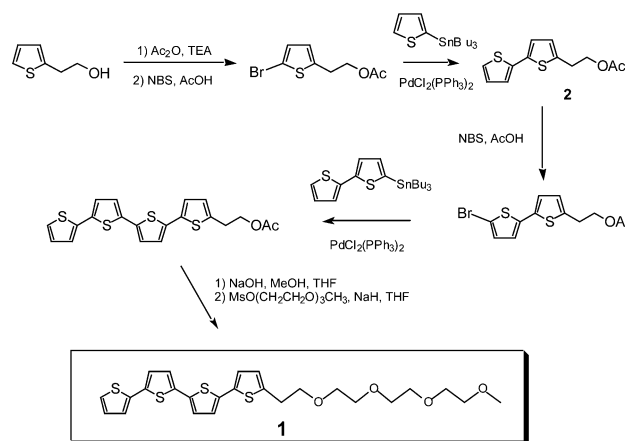
Formation of lyotropic liquid crystalline materials composed of oligothiophene-containing surfactants should provide a desired high supramolecular order in solution leading to highly ordered deposited films. A coated surface could yield multilamellae with contiguous structural order over large areas. The typical design of such a molecule is an amphiphile with a hydrophobic tail of equal cross sectional area to the hydrophilic headgroup.<sup>10</sup> The cylindrical shape of the amphiphile should allow the spontaneous formation of lamellar structures in water.

We designed the quaterthiophene surfactant **1** as our first entry into the development of lyotropic oligothiophene-containing molecules. Coupling an oligoethylene glycol headgroup with an oligothiophene tail, both sections having similar cross sectional area, allows the formation of a cylindrical amphiphile structure. Surfactant **1** was prepared *via* the synthetic route shown in Scheme 1. Commercially available 2-(2-thienyl)ethanol was first acetylated with acetic anhydride (Ac<sub>2</sub>O) and triethylamine (TEA), followed by bromination of the 4-position of the thiophene with *N*-bromosuccinimide (NBS). The brominated compound was then coupled to 2-(tributylstannyl)thiophene under Stille coupling conditions to yield the bithiophene compound **2** in good yield.

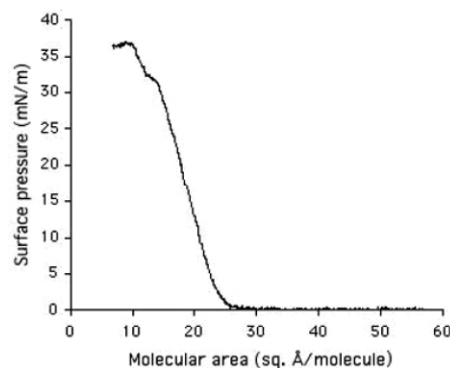
Bromination of **2** with NBS and acetic acid (AcOH), followed by another Stille reaction with 5-(tributylstannyl)-2,2'-(bithiophene), afforded the acetylated quaterthiophene-2-ethanol. The final product was obtained by deprotection of the alcohol under basic conditions and etherification with mesylated methyltriethylene glycol and sodium hydride in tetrahydrofuran (THF). Compound **1** was isolated in high purity as a yellowish, waxy material.<sup>11</sup>

Langmuir monolayers of **1** prepared on pure water exhibited good stability with a phase transition at 32 mN m<sup>-1</sup> and collapse pressure of 36 mN m<sup>-1</sup> (Fig. 1). The film compressed directly to a solid-phase with a molecular area of 24 Å<sup>2</sup>/molecule, as determined by extrapolating the steepest part of the curve to zero pressure. This value is consistent with the largest measured cross sectional area of the molecular model. Isotherms of **1** were reproducible only from freshly prepared spreading solutions with THF (1 mg mL<sup>-1</sup>). Solutions older than several hours exhibited signs of oxidative aging with brownish discoloration. The monolayer films were unstable in air yielding distorted and irreproducible isotherms upon consecutive compressions. The film became discolored within a matter of 30 minutes and increasingly darker thereafter.

Sonication of **1** in pure water produced clear dispersions of small unilamellar vesicles. Dynamic light scattering (DLS) measurements (Protein Solutions DynaPro LSR, Lakewood, NJ) found that



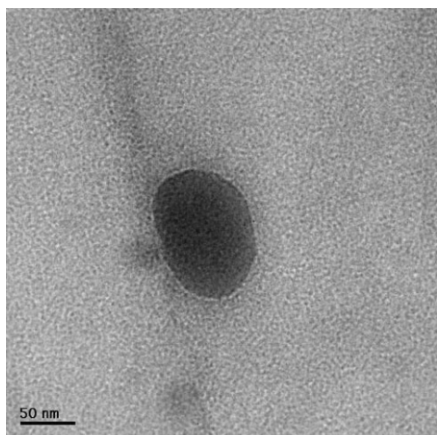
Scheme 1

Fig. 1 Langmuir isotherm of **1** on pure water at 20 °C.

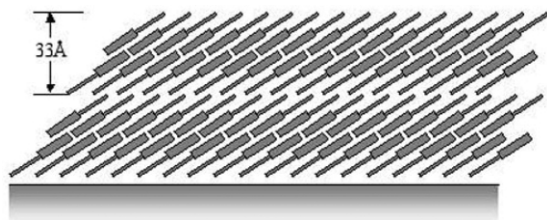
† Electronic supplementary information (ESI) available: synthetic procedures and spectral characterization of **1** and precursors of Scheme 1. See <http://www.rsc.org/suppdata/cc/b3/b316657k/>

the dispersed surfactant formed a narrow distribution of  $78 \pm 15$  nm diameter particles. The size and distribution were independent of the concentration of surfactant in solution within the range of 0.10 mM to 16 mM. Cryo-transmission electron micrographs (TEM) of the particles found unilamellar vesicles with elliptical shape (Fig. 2). It is unclear why the elliptical shape predominates as compared to the spherical structure of vesicles composed of natural or synthetic lipids<sup>12</sup> and at that specific size. One possibility is that the rigid tetrathiophene segment may prefer a particular packing order to maximize  $\pi$ - $\pi$  overlap of adjacent surfactants. The UV-vis spectrum of the water-borne vesicles indicates high aggregational order of the oligothiophene chromophores with a blue-shifted absorption of  $\lambda_{\max} = 342$  nm, compared to the isotropic absorption of **1** in THF ( $10 \mu\text{M}$ ) where  $\lambda_{\max} = 394$  nm.<sup>13</sup>

Films of **1** cast from water (sonicated dispersion) or organic solvents (ethanol, tetrahydrofuran) formed ordered lamellar structures as determined by X-ray diffraction (XRD). The films were prepared by casting solutions of the surfactant (1–10 mM) onto glass slides followed by solvent evaporation under ambient conditions. The XRD measurements of all films indicate a stacked structure with a  $d$ -spacing of 33 Å. Assuming a bilayer structure and an extended conformation of the surfactant (31 Å), a surfactant tilt angle of  $58^\circ$  was determined. Figure 3 shows a schematic of the tilted structure in multilamellae. This structure is distinct from the perpendicular stacking of  $\alpha,\omega$ -dihexylquaterthiophene (DH6T) films produced by vacuum deposition.<sup>14</sup> UV-vis spectra of the films prepared from aqueous solution show a  $\lambda_{\max} = 350$  nm with a weak shoulder at 450 nm, whereas a film prepared from THF gave a  $\lambda_{\max} = 381$  nm and a prominent shoulder at 459 nm. The hypsochromic



**Fig. 2** Vesicle of surfactant **1** formed by sonication in water (1% ammonium molybdate stain).



**Fig. 3** Bilayer lamellar structure of **1** in cast film with tilt angle of  $58^\circ$ .

$\lambda_{\max}$  shift of **1** in the films and the emergence of shoulders and fine structure at longer wavelength (believed to be frozen conformers) are similar to the absorption behavior of vapor deposited oligothiophenes.<sup>6</sup>

A preliminary bulk conductivity study was performed on a cast film coated upon 10 micron spaced interdigitated electrodes. A film cast from 60% THF–ethanol solution showed complex non-ohmic and time dependent conductivities when excited by a 10 Hz sawtooth voltage of several volts. The bulk conductivity of the undoped cast films was on the order of  $10^{-7}$  S  $\text{cm}^{-1}$ . The material exhibited photoconductive behavior as well as an inverse relationship between conductivity and atmospheric humidity. No electrical degradation or discoloration of the material was observed over several days of study in air under ambient conditions. The cast film's improved stability to oxidation and its low conductivity, compared respectively to that of the Langmuir film of **1** and to previous oligothiophene films prepared by vapor deposition, may be related to the highly tilted orientation of the oligothiophene units in the bilayer structure leading to poor charge injection and transport.

These results demonstrate that oligothiophene surfactants can readily form self-organized structures in solution resulting in ordered thin films by simple casting methods from green solvents. To improve surfactant self-assembly for enhanced semiconductor properties, we are currently investigating new molecular structures and functionalities in an effort to generate improved packing order and orientation in the supramolecular architecture.

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