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Formation and electrochemical desorption of stable and electroactive self-assembled monolayers (SAMs) of oligothiophene–fulleropyrrolidine dyads

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Stable, electroactive SAMs of oligothiophene–fulleropyrrolidine dyads have been prepared by spontaneous adsorption; electro-oxidation of the oligomeric system results in desorption.

Self-assembled monolayers (SAMs) provide unique opportunities to develop chemically tailored surfaces with specific chemical and physical properties.[1,2] Besides the considerable amount of work devoted to the development of selective electrochemical sensors,[1,2] SAMs have attracted increasing interest due to potential use in molecular electronics.[3]

In this context, there have been several reports concerning the preparation and characterization of SAMs derived from various kinds of linear π-conjugated oligomers on gold surfaces.[3–5] However, until now, all of these monolayers were prepared from oligomeric systems possessing one or two terminal alkanethiol groups eventually connected to the conjugated system *via* a flexible alkyl spacer. Recently, this approach has been successfully applied to the preparation of SAMs of C_{60}-derivatized oligothiophenes.[5] On the other hand, despite some theoretical controversy, the adsorption of thiophene onto Au(111) was recently demonstrated.[6]

Here, we show for the first time that stable SAMs can be produced on Au(111) surfaces by spontaneous adsorption of C_{60}-derivatized, π-conjugated oligomers of the thiophene and thienylenevinylene[7] series. Although the fulleropyrrolidine group represents a very convenient electroactive probe, its role in the process of SAM formation is not clearly elucidated at the present time.

Compounds **1**–**6** (Chart 1) were newly synthesized by reacting the appropriate carbaldehyde with C_{60} in the presence of *N*-methylglycine according to the methodology of Prato and coworkers[8] with a slight modification as reported for the synthesis of C_{60}–thiophene dyads by ourselves.[9] All new compounds were fully characterized by the usual spectroscopic and analytical techniques giving satisfactory results.†

SAMs were prepared by dipping ultra-clean, spherical, gold (99.9999%) bead electrodes‡ for 24–72 h in 1 mM *o*-dichlorobenzene (ODCB) solutions of compounds **1**–**6**. The electrodes were then thoroughly rinsed with ODCB and CH_2Cl_2, dried under an argon flow and immersed in 0.05 M Bu_4NPF_6–ODCB for electrochemical characterization. Sonication in ODCB did not remove the SAMs, indicating that the compounds are chemically adsorbed and not simply physisorbed.

The cyclic voltammogram (CV) of a SAM of **3** (Fig. 1) shows two well-resolved reversible cathodic waves with $E^0{}_1 = -0.65$ V and $E^0{}_2 = -1.04$ V corresponding to the first two one-electron reductions of the C_{60} fragment.[10] Scanning the potential to -1.8 V (*vs.* Ag/AgCl) allowed the observation of the reversible third reduction at -1.57 V (not shown in Fig. 1 due to an impurity present in OBCD at around -1.2 V). Within

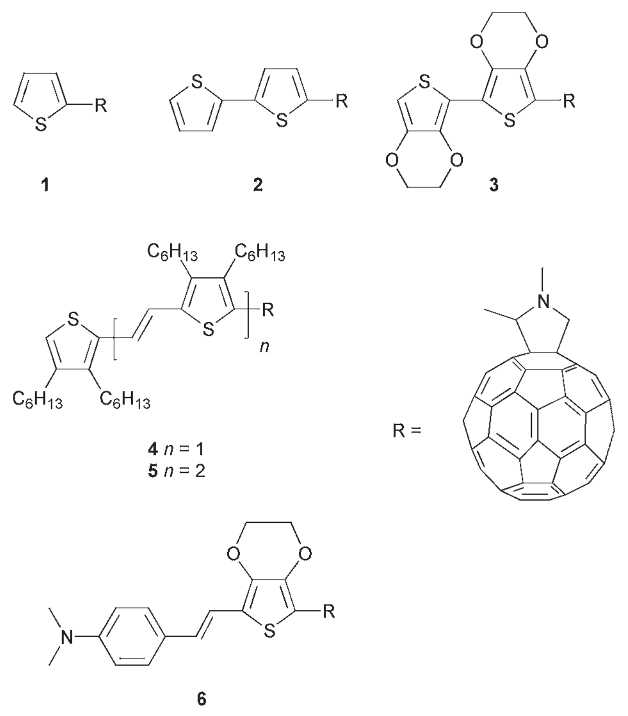

Chart 1

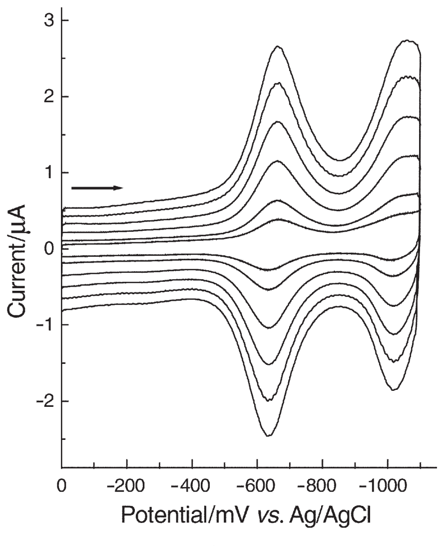

Fig. 1 CVs of a SAM of **3** in 0.05 M Bu_4NPF_6–ODCB system, scan rates between 100 (smallest current) and 1000 (largest current) mV s^{-1}.

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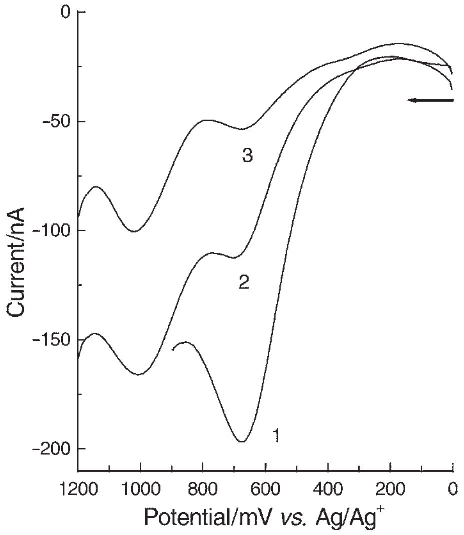

Fig. 2 Repetitive oxidation of a SAM of **3** by Osteryoung square-wave voltammetry in 0.05 M Bu_4NPF_6–ODCB system using a sweep width of 25 mV, frequency of 15 Hz, step potential of 4 mV, and a quiet time of 2 s.

the range of scan rates investigated (100–1000 mV s^{-1}), peak currents increased linearly with the scan rate while the peak potentials and peak-to-peak separations (ΔE_p) (19 and 27 mV for the first and the second reductions, respectively) were independent of scan rate. These characteristics together with the Gaussian shape of the CV waves are typical for surface-confined electroactive species.

Further confirmation of the formation of a surface-attached monolayer on the gold surface was obtained by analyzing the CV response of the $Ru(NH_3)_6{}^{3+/2+}$ couple at a bare gold electrode and at an electrode modified by a SAM of **3**. The CV recorded in the first case exhibits a reversible redox couple with $E^0 = -0.16$ V and $\Delta E_p = 63$ mV at 100 mV s^{-1}. In contrast, the CV recorded at the modified electrode reveals a drastic decrease of the intensity of the cathodic peak currents together with a *ca.* 50 mV negative shift of the E_{pc} and almost disappearance of the corresponding anodic wave. These results indicate that electron transfer at the interface between the modified gold surface and the solution redox species is severely hindered by the presence of the insulating monolayer.

SAM formation was investigated for the other compounds. Similar results were obtained for compounds **2**, **4** and **5**, but the surface coverage (Γ) decreased from 2.1×10^{-10} mol cm^{-2} for **3** to about 1.1×10^{-10}, 0.4×10^{-10} and 0.3×10^{-10} mol cm^{-2} for **2**, **4** and **5**, respectively.§ It is noteworthy that these Γ values are significantly larger than those reported for SAMs of C_{60}-derivatized oligothiophenes prepared *via* thiol attachment.[5] On the other hand, and despite many attempts using many different conditions (solvent, concentration, time of immersion), no SAM formation could be detected for compounds **1** and **6**.

SAMs derived from compounds **2–5** were stable under repetitive cycling in the negative potential region (up to -1.8 V *vs.* Ag/AgCl) and no modification of the CV response was observed after several weeks of storing the modified electrodes under ambient conditions. However, application of a positive potential corresponding to the first oxidation of the oligomeric π-conjugated system produces the rapid desorption of the SAMs (Fig. 2). Desorption was confirmed by the simultaneous disappearance of the fullerene-based reduction peaks. This behavior, which contrasts strikingly with the oxidative stability of SAMs derived from oligothiophenes attached *via* an alkanethiol,[4] suggests that the electron density of the sulfur atom, which depends on the redox state of the π-conjugated oligomer, could play an important role in the adsorption–desorption process.

To summarize, we have demonstrated that stable, electroactive SAMs of dyads involving fulleropyrrolidine and thiophene-based, π-conjugated oligomers can be readily formed on a gold surface and that these SAMs can be easily desorbed by electro-oxidation of the π-conjugated system. Although these preliminary results pose intriguing questions regarding the relationships between the process of SAM formation and the structural variables of the molecules (C_{60} group, substitution of the thiophene ring, presence of a free α-position at the terminal thiophene ring, chain length of the oligomeric system, *etc.*), the unique combination of properties exhibited by this new class of SAMs can open interesting perspectives in the field of thiophene-based molecular electrochemical and electronic devices.

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Notes and references

† *Selected data* for **2**: Mp. > 250 °C. ^{1}H NMR (CS_2/C_6D_6): δ 7.12 (d, ^3J 3.7 Hz, 1H), 6.97 (dd, ^3J 5.0 Hz, ^3J 1 Hz, 1H), 6.96 (dd, ^3J 3.5 Hz, ^3J 1 Hz, 1H), 6.90 (d, ^3J 3.5 Hz, 1H), 6.79 (dd, ^3J 5.0 Hz, ^3J 3.7 Hz, 1H), 5.06 (s, 1H), 4.78 (d, ^3J 9.5 Hz, 1H), 4.09 (d, ^3J 9.5 Hz, 1H), 2.78 (s, 3H). MALDI-TOF mass spectrum: calc. for $C_{71}H_{11}NS_2$: *m/z* 941.03; found: 940.0 (M − H$^+$). Anal. calc. for $C_{71}H_{11}NS_2$: C 90.53, H 1.18, N 1.49, S 6.81. Found: C 90.19, H 1.54, N 1.53, S 6.56%.

‡ The geometric area (*A*) of the gold bead electrodes was determined from the slopes of the linear plot of the cathodic peak current *versus* the square root of the scan rate obtained for the diffusion-controlled reduction of $Ru(NH_3)_6{}^{3+}$, *i.e.*, $A = \text{slope}/((2.69 \times 10^5) \times 1 \times D_0)^{1/2} \times C_0))$. A diffusion coefficient (D_0) of 7.5×10^{-6} cm^2 s^{-1} (at 25 °C in 0.1 M NaCl) was used (see: C. M. Yip and M. D. Ward, *Langmuir,* 1994, **10**, 549). Typical values for the geometric area of the electrode varied between 0.02 and 0.03 cm^2.

§ Surface coverage (Γ) of the SAMs was calculated by integration of the cathodic current during the first CV scan.

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