ChemComm
www.rsc.org/chemcomm

Potential-controlled switching of 2-(2′-thienyl)pyridine adsorbed on Au(111)

Emily Chung, Dan Bizzotto* and Michael O. Wolf*

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, Canada V6T 1Z1. E-mail: mwolf@chem.ubc.ca; bizzotto@chem.ubc.ca; Fax: +1-604-822-2847; Tel: +1-604-822-6816 (Bizzotto) and 1-604-822-1702 (Wolf)

Received (in Cambridge, UK) 12th September 2002, Accepted 24th October 2002
First published as an Advance Article on the web 15th November 2002

Switching between three different adsorbed states was achieved using potential control to separately induce electrochemical behaviour associated with changes in binding and orientation of the thiophene and pyridine moieties of 2-(2′-thienyl)pyridine adsorbed to Au(111) in neutral and basic solution.

Molecules that contain multiple donor groups may bind as ligands to transition metal centres in a number of ways, depending on both the nature of the metal and the binding groups. These ligands have been widely used in coordination chemistry, and it has been shown that changes in the redox state of the metal may result in switching between different coordination modes.[1] For example, in $Ru(NH_3)_5$(acetone) complexes, η^1 coordination of O is favoured by Ru(III), while η^2 coordination of the carbonyl group is favoured by Ru(II).

In metal complexes, only integral redox states (1+, 2+ *etc.*) are accessible, and so bifunctional ligands can only bind in the specific coordination modes that stabilise these states. By assembling such bifunctional molecules on metal electrode surfaces, the electronic environment can be continuously tuned *via* the applied potential. Thus, a more detailed understanding of the electronic factors governing the switching behaviour may be attained.

There have been only a few investigations of the surface chemistry and electrochemistry of molecules with two different surface active functional groups, most involving molecules bearing a thiol such as 2-mercaptopyridine.[2] Here we report the first attempt to control the orientation and binding of two functionally different donor groups on a gold electrode.

The bifunctional molecule 2-(2′-thienyl)pyridine (TP) is known to form complexes with many transition metals including gold, in several different binding modes.[3] Like thiols, thiophene has been shown to self-assemble on gold from ethanolic solution in the absence of an applied potential, initially adsorbing parallel to the surface and subsequently forming a close-packed, pi-stacked layer normal to the surface.[4] Pyridine is physisorbed in the absence of an applied potential, but under potential control, it either physisorbs in a parallel, aromatic pi-bonded state or chemisorbs in an N-bonded perpendicular configuration on Au(111), depending on the applied potential.[5] The differences in binding behaviour of thiophene and pyridine to gold surfaces make TP ideal for this study.

TP was synthesized *via* a Kumada coupling[6] and purified by sublimation. Cyclic voltammetry (CV) and differential capacity experiments were performed on deaerated solutions of TP in 0.05 M $KClO_4$ electrolyte using a single crystal Au(111) working electrode, a gold counter electrode and a saturated calomel electrode (SCE) reference. The electrochemical interface was characterised in both neutral and basic pH solutions. The pH was increased by addition of 0.1 M NaOH solution.

Some of the typical features associated with TP at a concentration of 10^{-3} M and at pH 10.7 are shown in Fig. 1 (data in basic solution are shown for clarity, as the two sets of peaks are better separated). A slight depression in the capacitance and preliminary chronocoulometry data suggest that adsorption occurs near −0.8 V. Two main peaks are visible in the positive scan of both the CV and capacitance curves. A very sharp peak **A1**, appears near −0.4 V and a broader peak **B** appears at 0.1 V in the capacitance curves. Peak **A1** is reversible, giving a very similar peak **A2** on the negative scan, provided the positive potential limit is kept negative of the onset of **B**. However, after scanning past **B** on the positive scan, significant hysteresis is observed. This is particularly noticeable in the capacitance plot. Here **A2** disappears, and a single broad peak **C** appears at −0.6 V.

Cycling the electrode repeatedly over the full potential range also leads to the splitting of **A1** and **A2** into two peaks. The process related to the small peak **D** near −0.9 V occurs even in the restricted potential range, but the peak is less pronounced. However, by varying the negative potential limit, we have determined that the molecules are completely desorbed negative of peak **D**.

A comparison of the behaviour of surface-confined TP at different pHs shows that peak **A** is pH independent. This is consistent with other evidence that **A** is due to changes in the interfacial capacitance. Peak **B** shifts 60 mV negative per unit pH increase, suggesting that it is due to a faradaic process involving one proton. The apparent pH shift of peak **C** is greater than 60 mV, increasing with decreasing concentration and increasing scan rate.

The surface coverage of TP after scanning positive of **B** was estimated by assuming that **C** is due to a one electron reduction. Integrating under **C** at equilibrium and accounting for the capacitive charge gave a coverage of 4.6 (±0.4) × 10^{-10} mol cm^{-2}, consistent with a full monolayer of TP molecules oriented on average with the plane of both rings normal or near

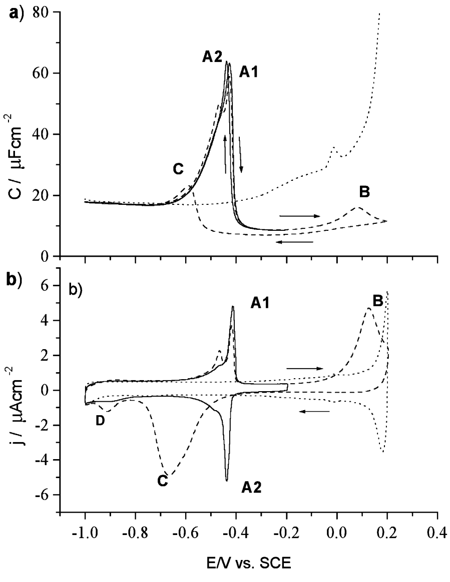

Fig. 1 (a) Differential capacity (25 Hz, 5 mV rms, 5 mV s^{-1} scan rate) and (b) cyclic voltammetry curves (20 mV s^{-1} scan rate, direction indicated by arrows) in the presence of 0.05 M $KClO_4$ (···) and 10^{-3} M 2-(2′-thienyl)pyridine + 0.05 M $KClO_4$ (— and ----), at pH 10.7. Note the effect of varying the positive potential limit.

DOI: 10.1039/b208912b

normal to the long axis parallel to the surface. This is comparable to the 5 × 10^{-10} mol cm^{-2} surface coverage reported for the structurally similar 2,2′-bipyridine at positive potentials.[7]

Insight into the origin of the various peaks in the CV and capacity curves can be gained by comparing the electrochemical data for TP with that of pyridine and thiophene.† The aqueous electrochemistry of pyridine on Au(111) has been well-characterised previously.[5] A differential capacitance plot of 10^{-3} M pyridine at neutral pH shows two sets of reversible peaks. A peak at −0.55 V is associated with adsorption and a very sharp peak at 0.10 V is attributed to a two-dimensional phase transition in which the orientation of the pyridine molecules changes from parallel to perpendicular relative to the surface. This latter peak closely resembles peak **A** in TP as shown in Fig. 2. Typical of capacitive peaks, they are sharp and reversible, with minimal charge beneath the peak, and they broaden dramatically as the concentration of surfactant decreases. They also both result in a similar drop in the capacitance positive of the peak. In the case of pyridine, this lower capacitance is due to the lower dielectric constant of the perpendicular pyridine monolayer relative to the parallel oriented pyridine monolayer. We propose that peak **A** is due to the pyridine half of TP and that it is the result of a phase transition similar to that seen in pyridine from an initial flat-lying state to a perpendicular N-bonded state. The fact that the peak is shifted to more negative potentials in TP relative to pyridine is consistent with the large negative shift of this transition relative to pyridine seen in 2,2′-bipyridine.[7] It is interesting to note that this type of reorientation would increase the dihedral angle between the rings, and therefore the stabilising change in the TP–gold interaction on reorientation would need to be greater than the increase in pi orbital energy due to reduced conjugation between the rings.

There are no reports of significant surface activity for thiophene in aqueous electrolyte within the potential range examined. Cyclic voltammetry and differential capacitance curves of thiophene show two major broad peaks (Fig. 3). At a thiophene concentration of 10^{-3} M at neutral pH, the first peak occurs at 0.25 V on the positive scan in the differential capacitance curve. The second peak occurs in the negative scan at −0.35 V and is more prominent in the CV than in the differential capacitance plot. The peak at 0.25 V is quite similar to TP peak **B** in its irreversible behaviour, the low capacitance that appears after scanning past it and reversing the scan direction, and the 60 mV shift negative per unit increase in the pH. The peak at −0.35 V also shifts negative as the pH is raised.

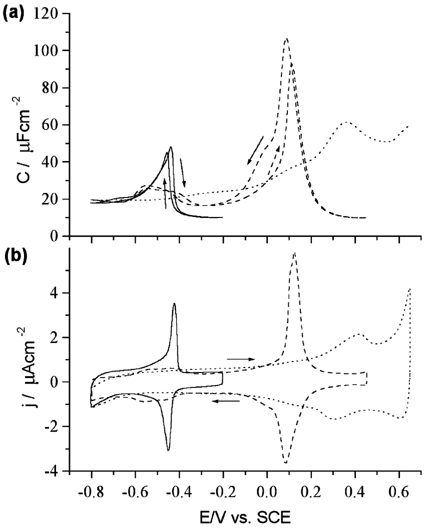

Fig. 2 (a) Differential capacity (25 Hz, 5 mV rms, 5 mV s^{-1} scan rate) and (b) CV (20 mV s^{-1} scan rate) curves of 0.05 M $KClO_4$ (···), 10^{-3} M 2-(2′-thienyl)pyridine + 0.05 M $KClO_4$ (—) and 10^{-3} M pyridine + 0.05 M $KClO_4$ (----) at pH 7; scan direction indicated by arrows.

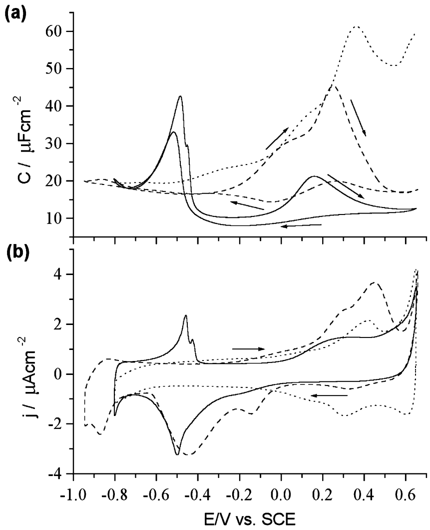

Fig. 3 (a) Differential capacity (25 Hz, 5 mV rms, 5 mV s^{-1} scan rate) and (b) CV (20 mV s^{-1} scan rate) curves of 0.05 M $KClO_4$ (···), 10^{-3} M 2-(2′-thienyl)pyridine + 0.05 M $KClO_4$ (—) and 10^{-3} M thiophene + 0.05 M $KClO_4$ (----) at pH 7; scan direction indicated by arrows.

Thiophene also shows a peak similar to **D** near −0.9 V. The similarities between TP peaks **B**, **C** and **D** and features of thiophene suggest these peaks are due to the thiophene half of the molecule, and are caused by similar processes in both TP and thiophene.

In summary, thiophene and pyridine adsorbed on Au(111) respond differently to changes in the applied potential. When they are linked in 2-(2′-thienyl)pyridine, two separate sets of features are observed, giving rise to three states. Scanning positively from the state initially adsorbed at negative potentials, we observe features similar to those associated with changes in the orientation and binding of pyridine, giving a second state. At even more positive potentials, a separate set of features similar to those seen in thiophene arise and are believed to correspond to changes in the orientation and binding of the thiophene half of the molecule, giving a third state. Thus, by controlling the potential of the metal surface, it is possible to separately influence the orientation and binding of each moiety in a bifunctional ligand bearing two donor groups.

Chronocoulometry, *in situ* STM and *in situ* IR studies are being conducted to confirm these initial findings and to further our understanding of the potential-induced changes in orientation and binding that are occurring.

We thank the Natural Sciences and Engineering Research Council of Canada for their support.

Notes and references

† Thiophene and pyridine were used as received from the manufacturer (Aldrich, 99+%).

1 D. W. Powell and P. A. Lay, *Inorg. Chem.*, 1992, **31**, 3542; A. Livoreil, C. O. Dietrich-Buchecker and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1994, **116**, 9399.
2 T. Sawaguchi, F. Mizutani, S. Yoshimoto and I. Taniguchi, *Electrochim. Acta*, 2000, **45**, 2861.
3 Y. Fuchita, H. Ieda, S. Wada, S. Kameda and M. Mikuriya, *J. Chem. Soc., Dalton Trans.*, 1999, 4431; K. P. Balashev, M. V. Puzyk, V. S. Kotlyar and M. V. Kulikova, *Coord. Chem. Rev.*, 1997, **159**, 109; H. Sigel, H. Wynberg, T. J. van Bergen and K. Kahmann, *Helv. Chim. Acta*, 1972, **55**, 610.
4 T. Matsuura, M. Nakajima and Y. Shimoyama, *Jpn. J. Appl. Phys.*, 2001, **40**, 6945; M. H. Dishner, J. C. Hemminger and F. J. Feher, *Langmuir*, 1996, **12**, 6176.
5 L. Stolberg, S. Morin, J. Lipkowski and D. E. Irish, *J. Electroanal. Chem.*, 1991, **307**, 241.
6 K. Tamao, S. Kodama, I. Nakajima and M. Kumada, *Tetrahedron*, 1982, **38**, 3347.
7 D. Yang, D. Bizzotto, J. Lipkowski, B. Pettinger and S. Mirwald, *J. Phys. Chem.*, 1994, **98**, 7083.