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A new redox site as an alternative to ferrocene to study electron transfer in self-assembled monolayers†

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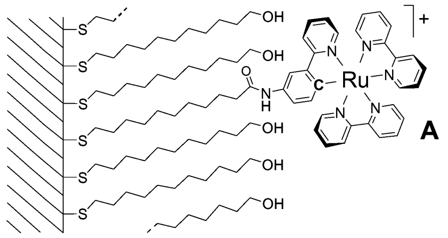
The cyclometallated ruthenium complex [Ru(bpy)$_2$(pp)]$^+$ (bpy: 2,2′-bipyridine; pp: 2-(2′-ylphenyl)pyridine) was easily grafted to a ω-alkanethiol and the resulting compound was coadsorbed with 11-hydroxyundecanethiol on gold yielding a Self-Assembled Monolayer (SAM) in an analogous manner as for a ferrocene derivative, as shown by impedance spectroscopy; the kinetics of the heterogeneous electron transfer were shown to be very fast, compared to ferrocene, which makes this new redox site a promising candidate for further studies about molecular wires.



Scheme 1 Molecule **A** embedded in SAM and fixed at a gold electrode.

The redox active Self-Assembled Monolayer (SAM) is a growing field to study or probe interfacial phenomena from enzymatic catalysis and ion sensoring, to molecular electronics.[1,2] In most of the cases, a SAM is a dense packed layer of suitable thiol derivatives adsorbed on gold prone to thiol exchange and to oxidative processes. If the former is easily limited by the use of an aqueous environment, the latter, however, has to be taken into account, particularly when a redox active component has to be embedded within the layer.[3]

Ferrocene is often used as a redox center, for it has a low oxidation potential (about 0.4 V *vs.* SCE) compatible with the SAM stability, and presents a rich organic chemistry. Its main drawbacks are that its derivatives can be poorly soluble and the redox processes are relatively slow.[4,5] This could be a limitation in the study of interfacial electron transfer reactions. Redox couples faster than ferrocene are known, such as [Ru(bpy)$_3$]$^{3+/2+}$[6,7] but either their chemistry or the value of their redox couple is unadapted to this type of experiment.

Recently, we have shown that the complex [Ru(bpy)$_2$(pp)]$^+$, isosteric of [Ru(bpy)$_3$]$^{2+}$, but by far more easily oxidizable (0.5 V *vs.* SCE against 1.2 V *vs.* SCE), was an easily functionalized synthon for the synthesis of more sophisticated molecules,[8,9]thus we thought of comparing the performances of this new complex to ferrocene. Hence, a molecule **A** of length and backbone similar to a previously described ferrocene analogue[10] was prepared, and we report here our results concerning synthesis, SAM composition and stability and ET rate constant determination.

We have designed our 'molecular wire' as a redox center connected *via* a polar and hydrophilic amide group to a thiol group by an alkyl chain of length identical to the inert coadsorbent thiol. The latter is chosen to be ω-hydroxylated in order to perform electrochemical analysis in water. (Scheme 1).[11]

The general strategy (Fig. 1) developed here is based on a building block approach from the readily available amino derivative **1**[12] taking advantage of the high solubility of all the intermediates.

The complex sensitivity toward acidic or hot protic medium prompted us to change the solvents of the thiol group introduction sequence, classically involving a bromine displacement by thiourea in boiling ethanol followed by an alkaline hydrolysis of the S-alkylthiouronium salt in boiling water. We have found that these two steps could be efficiently performed in a one-pot reaction using DMSO[13] as solvent, the thiol group being liberated by an aminolysis with ethylene diamine.[14] All complexes were purified by column chromatography, and isolated as hexafluorophosphate salts. Their analyses were found to be consistent with the proposed structures and no influence of the amide group was detected on the Ru(III)/Ru(II) redox couple potential .‡

Redox active species embedded in the SAM are very sensitive to their environment, and molecules located at defects, mostly grain boundaries in the SAM itself or in the metallic substrate, are expected to give a different kinetic response compared to the one in crystalline homogeneous domains.[15] To improve the quality of the surface we have used a gold ball electrode known to exhibit less defects, on which the SAM is prepared by coadsorption of **A** and 11-mercaptoundecanol. After being dipped in an ethanolic solution of the two thiols, the substrate is immersed for several hours in an ethanolic 11-mercaptoundecanol solution to remove defective thiols *i.e.* those adsorbed at grain boundaries. Among the various electrochemical techniques, such as cyclic voltammetry[16,17] or chronoamperometry,[18,19] used to probe SAM, few can cope with a SAM prepared this way containing few redox sites. Impedance spectroscopy, one of these few, is an ac technique relying on the study of the faradaic response of an electrode as a function of the frequency of a small-amplitude, oscillating-superimposed potential with a rather high signal-to-noise ratio. It has been adapted to such studies during the past decade.[11,20–22]

Variable frequency ac voltammograms were acquired§ in a range of potential around the oxidation potential of the molecule (0.3 V) over typically one hour. These measurements can be repeated many times with the same monolayer which is in sharp

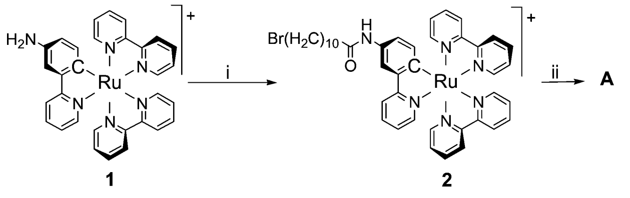


Fig. 1 Reagents and conditions: (i) 11-bromoundecanoylchloride, Et$_3$N (1 equiv.), CH$_2$Cl$_2$, 20 min, RT, 70%; (ii) thiourea (10 equiv.), DMSO, 5 h, 45 °C, then ethylene diamine (7 equiv.), 3 h, 45 °C, 61%.

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† Electronic supplementary information (ESI) available: ac voltammograms, amount of redox active molecules determination, fitting law and SAM preparation protocol. See http://www.rsc.org/suppdata/cc/b2/b205073k/

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contrast to some ferrocene-containing SAM, irreversibly destroyed after only one measurement.

The amount of redox active molecules, estimated to be 2.2×10^{-11} mol cm^{-2} from the low frequency voltammograms, applying a model based on the perturbation of a Nerstian distribution of states by a superimposed potential oscillation,[20,21,23] is of the same order of magnitude as available data for SAM prepared by the same procedure but with ferrocene-terminated alkanethiols.[10] We can conclude from this result that solubilities of those redox active molecules in the supporting hydroxyalkane thiol are comparable despite the obvious charge difference. This is explained by the similarity between the molecular wires structures and the inert thiols, both being basically alkanes.

Observed at the standard potential, the evolution of the faradaic current I_{peak} with the frequency can be used to determine the average heterogeneous ET rate constant k_o. Indeed, the I_{peak} vanishes for the high frequencies when the redox reaction is no longer able to keep up with the rapid change of the potential. Recently, Creager and Wooster have shown that the ratio of I_{peak} to the background current is a sigmoid curve of the log (frequency) depending on only two independent parameters, one of them being the rate constant.[11]

The quality of the fit to this theoretical model, related to the rate constant dispersion thus to the SAM heterogeneities, can be used to optimize the 'chemical annealing' time: in our case a very good fit is obtained after only 5 hours compared to 15 for ferrocene.[10] Once this stage is reached, a reproducible value of 45000 ± 9000 s^{-1} for the rate constant is obtained (Fig. 2). The 20% uncertainty is arbitrarily chosen to take into account the multiple data processing.

Even so, this value remains higher than the one reported for the analogous ferrocene derivative (1200 s^{-1}).[10] It is admitted that ET rate constant depends mostly on two parameters, a matrix element $|V|$ describing the electronic coupling between the sites and the reorganisation energy λ,[24] which can be reasonably approximated for large molecules to its outer sphere component (λ_{os}). [25] For $[\text{Ru(bpy)}_2\text{(pp)}]^+$, a calculated radius value of 7 Å gives a λ value of 0.55 eV which is less than the one already measured for ferrocene derivatives (0.85 eV).[10] This rather small change has in fact a dramatic effect on the observed process: we have found that it accounts for about 70% of the rate constant enhancement. Furthermore, since an error of 20% is commonly admitted on the coupling parameter value determined by this technique, one can conclude that there is no significant change of the matrix element which is easily understood since both molecules exhibit the same length alkylthiol chain.

The present study shows that the complex $[\text{Ru(bpy)}_2\text{(pp)}]^+$ compares favorably to ferrocene. Firstly a large range of modifications is available *via* electrophilic functionalization, offering different ways for the synthesis of various molecular skeletons. Secondly, the positive charge does not affect the solubility of a saturated wire in the neutral SAM of 11-mercaptoundecanol. Finally, due to the smaller reorganisation energy of the ruthenium moiety, the ET rate constant is greatly enhanced compared to ferrocene for a wire of the same length and same structure. All these properties tend to show that this complex is a convenient redox site for the electrochemical screening of several molecular wires of various skeleton and length in order to feed molecular electronics.[26,27] Extension to other types of structures such as conjugated molecules is now in progress.

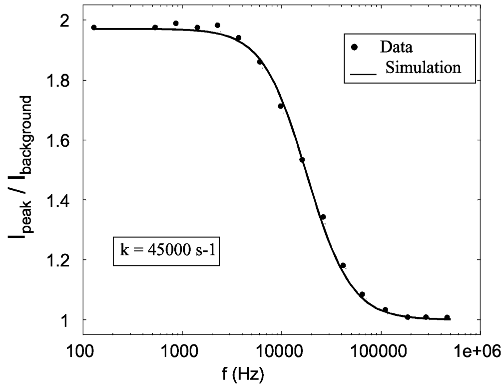

Fig. 2 Plot of $|I|_{\text{peak}}/|I|_{\text{background}}$ *vs.* f in log scale.

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Notes and references

‡ *Selected analytical data* for **3**: ^{1}H NMR [CD_2Cl_2, 250 MHz, $SiMe_4$] δ: 2.30 (t, 2 H, 7.0 Hz), 2.49 (q, 2 H, 7.0 Hz), 6.39 (d, 1 H, 8.0 Hz), 6.88 (m, 2 H), 7.18 (m, 2 H), 7.43 (m, 4 H), 7.57 (d, 1 H, 5.0 Hz), 7.73 (m, 5 H), 7.90 (d, 1 H, 7.0 Hz), 7.98 (d, 1 H, 7.0 Hz), 8.19 (m, 4 H), 8.27 (d, 1 H, 8.0 Hz), 8.37 (d, 1 H, 8.0 Hz). ESMS *m/z*: 783.2 (M-PF_6)$^+$. $E°_{\text{Ru(III)}}/\text{Ru(II)} = 0.41$ V / SCE (Pt, MeCN, nBu_4PF_6 0.1 M).

§ Electrochemical experiments were performed using a single compartment cell (~ 4 mL electrolyte solution volume). The electrolyte solution was 1 M $NaClO_4$. The cell was housed in a homemade Faraday cage to reduce stray electrical noise. Measurements were performed in three-electrode mode with a Ag/AgCl/KCl reference electrode (Radiometer-Sodimel S.A.) and a Pt wire auxiliary electrode. The working electrode was positioned such that the gold ball was immersed just below the surface of the electrolyte and very close to the reference electrode. SAM coated gold electrodes were prepared by melting the end of a clean gold wire (125 μm in diameter) into a small spherical ball (500 μm in diameter) in an O_2–C_2H_2 flame, that was then immediately immersed in the ethanolic thiol solution. Electrochemical measurements were made using an AUTOLAB PGSTAT 100 potentiostat/ frequency response analyser system, under computer control by FRA2 software package (ECO CHEMIE BV). ac voltammograms were acquired in stepped mode using a rms amplitude of 10 mV with one point being acquired every 10 mV.

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