

## A Covalently linked Ruthenium Tris(bipyridine)–Viologen Complex–Polypyrrole Film as a Molecular Photoelectrode

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A modified electrode containing a chromophore linked to an electron acceptor has been prepared by anodic electropolymerization of a new ruthenium tris(bipyridine)–viologen–pyrrole complex; thin films of these polymers act as photoelectrodes when irradiated by visible light in the presence of triethanolamine.

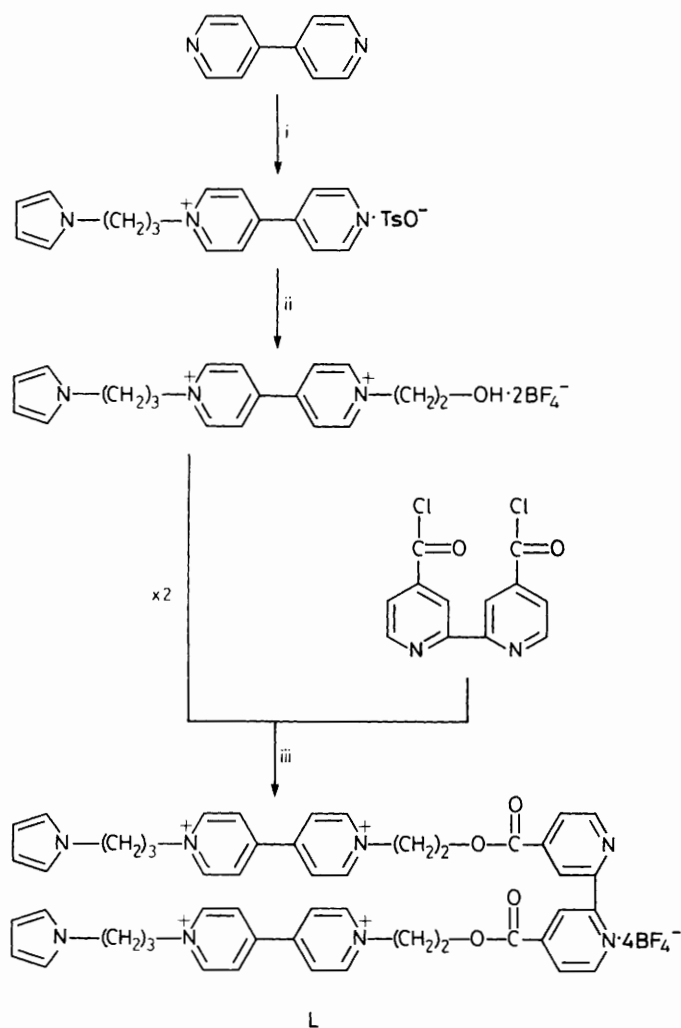
A few examples based on ruthenium tris(bipyridine)–viologen complexes have demonstrated the efficiency of photoinduced electron transfer occurring in an unimolecular photosensitizer–electron acceptor system.<sup>1</sup> However, the recombination by back electron transfer remains the major hindrance of the long-life storage of the redox energy. One eventual solution to that problem is to construct assemblies of chromophores and quenchers as polymeric films on electrode surfaces with the aim of achieving spatial separation of the photogenerated species.<sup>2</sup> In view of the combination of these two effects, we have synthesized a new ruthenium tris(bipyridine)–viologen complex  $[\text{Ru}(\text{bpy})_2(\text{L})]^{6+} \cdot 6\text{BF}_4^-$  (**1**), in which bpy = bipyridine and L denotes a 2,2'-bipyridine linked with two viologen groups bonded to a pyrrole unit. We have recently established that pyrrole is an ideal substituent in preparing, by electropolymerization, electrodes modified with polymeric films containing electroactive and photosensitive centres, especially bulky molecular assemblies.<sup>3</sup> We report here the electrochemical preparation and behaviour of a poly(**1**) modified electrode and its utilization as a molecular photoelectrode.

Complex (**1**) was obtained in 40% yield by refluxing  $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  (66 mg) with one equivalent of L (150 mg) in a 1 : 1,  $\text{H}_2\text{O}/\text{Bu}^+\text{OH}$  solution for one hour followed by isolation of the  $\text{BF}_4^-$  salt by addition of an aqueous solution of  $\text{NaBF}_4$ . The ligand L was prepared by a procedure summarized in Scheme 1. All new compounds exhibited spectroscopic and analytical data consistent with the assigned structure.†

† Spectroscopic data for (**1**):  $^1\text{NMR}$  ( $\text{CD}_3\text{CN}$ ):  $\delta$  2.58 (q, 4 H,  $J$  7 Hz), 4.14 (t, 4 H,  $J$  7 Hz), 4.68 (t, 4 H,  $J$  7 Hz), 4.91 (m, 4 H), 5.14 (m, 4 H), 6.03 (t, 4 H,  $J$  2 Hz), 6.70 (t, 4 H,  $J$  2 Hz), 7.44 (m, 4 H), 7.72 (m, 4 H), 7.85 (m, 2 H), 7.88–8.18 (m, 6 H), 8.38 (m, 4 H), 8.55 (m, 8 H), 8.84 (m, 4 H), 8.98 (m, 4 H), 9.15 (m, 4 H); FAB MS ( $m/z$ , positive mode):  $\text{C}^{6+} \cdot 5\text{BF}_4^-$ , 1674;  $\text{C}^{6+} \cdot 4\text{BF}_4^-$ , 1587;  $\text{C}^{6+} \cdot 3\text{BF}_4^-$ , 1500;  $\text{C}^{6+} \cdot 2\text{BF}_4^-$ , 1413.

On a platinum or glassy carbon electrode, the cyclic voltammogram of (**1**) in 0.1 M  $\text{Et}_4\text{NClO}_4$ –MeCN exhibits the two reversible waves of the viologen groups ( $E_{1/2} = -0.66$  and  $-1.10$  V vs.  $\text{Ag}/10^{-2}$  mM  $\text{Ag}^+$ ) in the reduction region, followed by the four reversible one-electron waves of the bipyridine ligands ( $E_{1/2} = -1.25$ ,  $-1.73$ ,  $-1.92$ , and  $-2.20$  V). In the anodic region, the  $\text{Ru}^{2+}/\text{Ru}^{3+}$  wave is melted with the irreversible oxidation wave of the pyrrole groups as observed for regular tris(bipyridine) ruthenium(II) complexes containing pyrrole substituents.<sup>5</sup> Repeatedly scanning the potential over the range from 0 to 1.2 V results in a continuous increase in the size of the peaks of the  $\text{Ru}^{2+}/\text{Ru}^{3+}$  system as a consequence of the film formation. Figure 1A shows a typical cyclic voltammogram of a thin film (apparent surface concentration of the complex  $\Gamma = 5.2 \times 10^{-9}$  mol  $\text{cm}^{-2}$ ) of poly(**1**). All the reversible redox couples of the reduction of the molecule are clearly observed ( $E_{1/2} = -0.67$ ,  $-1.09$ ,  $-1.26$ ,  $-1.72$ ,  $-1.96$ , and  $-2.25$  V) as well as that of the  $\text{Ru}^{2+}$  oxidation ( $E_{1/2} = 1.02$  V), associated with a prepeak, which vanished almost entirely on the second scan.<sup>5</sup> For a thicker film ( $\Gamma = 2.1 \times 10^{-8}$  mol  $\text{cm}^{-2}$  for instance), the peak current of the first reduction wave of viologens is markedly less than that for the second one. This phenomenon, also observed with copolymeric films of polypyrrole–viologen and polypyrrole–ruthenium tris(bipyridine)<sup>6</sup> is ascribable to the lower rate of electron transfer for the first process compared to the second one.

Electropolymerizations were also accomplished by potentiostatting the electrode at 0.75 V (electropolymerization yield, 53%). Then the modified electrode exhibits the regular electroactivity of *N*-substituted polypyrroles<sup>3b</sup> with a quasi-reversible redox system at 0.2 V as seen in Figure 1B, curve (a). By cycling the electrode up to 1.8 V, apart from the  $\text{Ru}^{2+}/\text{Ru}^{3+}$  peak systems, a large irreversible peak appears ( $E_{\text{pa}} \sim 1.5$  V) due to the over-oxidation of the polypyrrole corresponding to an ill-defined chemical transformation of the polymer<sup>7</sup> [Figure 1B, curve (b)]. As a consequence, on the

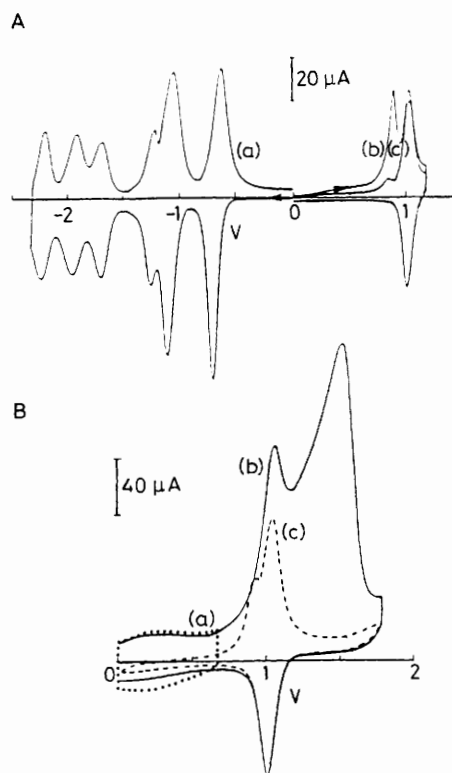


**Scheme 1.** Synthetic route for the preparation of the ligand L. i, monoquaternization with 3-(pyrrol-1-yl) propyl tosylate; ii, quaternization with 2-bromoethanol followed by an anion exchange; iii, reflux in MeCN + collidine followed by an anion exchange. (Ts =  $\text{OSO}_2\text{C}_6\text{H}_4\text{Me-p}$ ).

reverse scan the electrochemical response of the polypyrrole is lost while the complete electroactivity of complex (1) is unchanged on further scans [Figure 1B, curve (c)] and the film stays remarkably adherent. The latter modified electrode has the same features as the former one, obtained by repetitive cyclic voltammetry.

Electropolymerization is also easily performed on an optically transparent doped indium oxide electrode (ITO). An ITO/poly(1) modified electrode, in which the electroactivity of the polypyrrole is missing, acts as an efficient photoelectrode when irradiated by visible light $\ddagger$  in the presence of an irreversible electron donor like triethanolamine (TEOA) in MeCN solution. An intense steady-state photocurrent is obtained when the electrode is potentiostatted at 0 V. By analogy with related solution systems involving  $\text{Ru}(\text{bpy})_3^{2+}$ ,  $\text{V}^{2+}$  (methyl viologen), and TEOA,<sup>8</sup> the origin of the photocurrent is due to the electrochemical oxidation of  $\text{V}^{2+}$

$\ddagger$  Film preparation and photoelectrochemical measurements were made using a sandwich-type cell.<sup>2f</sup> The ITO film was irradiated with a 250 W Hg lamp through UV and IR cut-off filters with a surface light intensity of  $150 \text{ mW cm}^{-2}$ .



**Figure 1.** Cyclic voltammograms in MeCN containing  $0.1 \text{ M Et}_4\text{N-ClO}_4$ . A, C(diameter 5 mm)/poly(1) modified electrode ( $\Gamma = 5.2 \times 10^{-9} \text{ mol cm}^{-2}$ ) prepared by cycling voltammetry, sweep rate  $\nu = 100 \text{ mV s}^{-1}$ ; curve (a) between 0 and  $-2.3 \text{ V}$ ; curve (b) between 0 and  $1.2 \text{ V}$ , first scan; curve (c), second scan. B, C/poly(1) modified electrode ( $\Gamma = 1.1 \times 10^{-8} \text{ mol cm}^{-2}$ ) prepared by potentiostating the potential at  $0.75 \text{ V}$ , sweep rate  $\nu = 100 \text{ mV s}^{-1}$ ; curve (a) (---) between 0 and  $0.6 \text{ V}$ ; curve (b) (—) between 0 and  $1.8 \text{ V}$ , first scan; curve (c) (- - -) second scan.

species built up into the film resulting from the regeneration of the  $\text{Ru}^{\text{II}}$  species by irreversible oxidation of TEOA. The magnitude of the anodic photocurrent depends on both TEOA concentration and  $\Gamma$ . For  $[\text{TEOA}] = 0.3 \text{ M}$  the photoresponse of the system reaches a saturation. Figure 2 shows the evolution on the steady state photocurrent  $I_s$  vs.  $\Gamma$  at constant concentration. After a limiting value is reached,  $I_s$  decreases slowly as  $\Gamma$  increases as a consequence of the slower electron transfer of the  $\text{V}^{2+} \rightleftharpoons \text{V}^{\cdot+}$  process involved in the propagation of electrons into the film.

Under optimum conditions a photocurrent intensity up to  $12 \mu\text{A cm}^{-2}$  is obtained which is fifteen times larger than that observed with a copolymer polypyrrole-viologen or polypyrrole-ruthenium tris(bipyridine) photolysed in the same experimental conditions.<sup>9</sup> The photoresponse is remarkably stable, since after two hours of irradiation, no loss of photocurrent is detected while the electroactivity of the modified electrode remains identical. Irradiation in the absence of TEOA produces only a very small cathodic photocurrent ( $<0.04 \mu\text{A cm}^{-2}$ ). Another experiment was performed with an ITO/poly(1) exhibiting the electrochemical response of the polypyrrole.  $I_s$  is lowered by one-half in comparison to the previous value, probably because of the capability of the polypyrrole to act as a p-type semiconductor.<sup>10</sup> The latter process competes with the anodic photocurrent resulting from the photoinduced charge separation.

Finally, our preliminary results demonstrate that films based on an unimolecular design act as significantly more

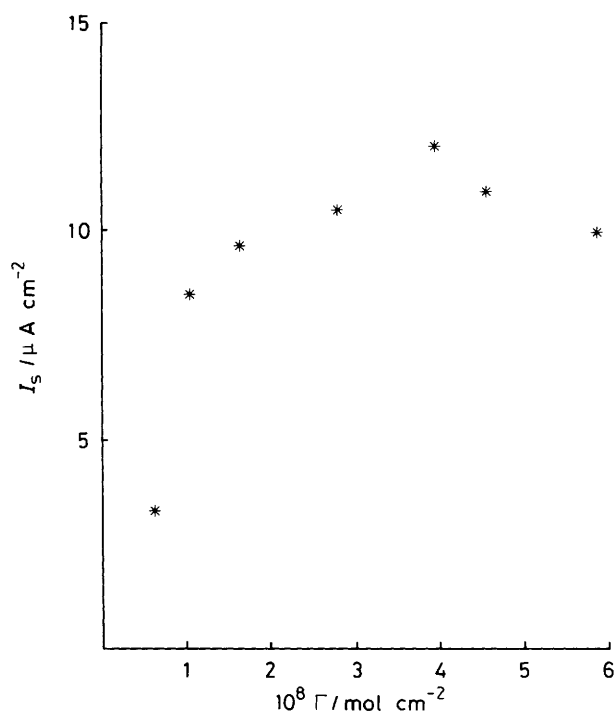


Figure 2. Plots of the steady-state photocurrents  $I_s$  vs.  $\Gamma$ ; [TEOA] = 0.3 M in MeCN containing 0.1 M  $\text{Et}_4\text{NClO}_4$ .

efficient photoelectrodes than those based on copolymers of the two independent components. Photophysical studies are currently underway to evaluate the efficiency of the intramolecular quenching process and the quantum yield of the photoreduction of the viologen units in the film.

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