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Communications

Supramolecular Electrode Materials Derived from Pyrrole-Substituted Ruthenium(II) Bipyridyl Calix[4]arenes

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Calixarenes are versatile preorganized building blocks as artificial macrocyclic receptors in supramolecular chemistry. They are readily functionalized at the upper or lower rim, and several groups have succeeded in demonstrating that they can serve as a platform to design host molecules for the specific binding and recognition of guest atoms and molecules.[1] In this context, attachment of metal complexes of the $[Ru(bpy)_3]$ type to calixarene is suitable for the design of redox and photoactive receptor molecules (bpy = 2,2′-bipyridine). For instance, it has been demonstrated that they behave as luminescent pH sensors[2] and can recognize halide,[3,4] hydrogen sulfate, and dihydrogen phosphate[4] guest anions. For application in the field of electrochemical sensor technology, it is necessary to extend these results for mono- and multilayers films of receptors coated onto an electrode surface. Here we report the first example of electropolymerization of calixarenes[5] bearing pendant transition-metal complexes, to produce poly(calixarene−$[Ru(bpy)_3]^{2+}$) modified electrodes.

The monosubstituted bpy-calix[4]arene was prepared by reaction of 5-methyl-5′-(bromomethyl)-2,2′-bipyridine[7] (1 equiv) with *p*-*tert*-butylcalix[4]arene (1 equiv) using $NaHCO_3$ (1 equiv) as base in anhydrous MeCN at 80 °C during one night. Its conformation was inferred from the ^1H NMR spectrum, which exhibits two distinct AB spin systems of equal intensity for the $C_6H_2CH_2C_6H_2$ bridges and two OH signals (intensity 2:1). This pattern, and the chemical shift values of the bridged methylene carbon atoms are in agreement with the compound existing exclusively in a cone conformation at room temperature.[8] The pyrrole-substituted trisbipyridylruthenium(II)-linked calixarenes **1** and **2** were synthesized by heating at 60 °C, in ethanol, the bipyridyl mono- and disubstituted[9] calixarenes with 1 and 2 equiv of $Ru(L)_2Cl_2$ (L ≡ 4-(pyrrol-1-yl)-4′-methyl-2,2′-bipyridine),[10] followed by precipitation as hexafluorophosphate salts on addition of NH_4PF_6, then subsequent purification by flash chromatography on silica with CH_2Cl_2/MeOH (2−10%) as eluant followed by double recrystallization in $CH_2Cl_2/EtOH/Et_2O$.[11] The calixarenes units in both compounds **1** and **2** (Chart 1) also adopt a fixed cone conformation in solution, at room temperature.The two ruthenium subunits in **2** are on the same side of the plane formed by the bridging methylene groups of the macrocycle, as deduced from their ^1H NMR spectrum.

The electrochemical behavior of **1** and **2** (0.5 mM) was investigated by cyclic voltammetry (CV) in tetra-*n*-butylammonium perchlorate (TBAP)−MeCN electrolyte.[12] For complex **1**, reductive scanning produces three waves due to the regular successive reversible one-electron reductions of the bpy ligands ($E_{1/2} = -1.76, -1.97$, and -2.21 V). In contrast, the cyclic voltammogram for complex **2** is severely distorted, due to the strong adsorption of its reduced forms on the electrode. In the positive potential area, for the two complexes the $Ru^{III/II}$ reversible peak system is hidden within the irreversible oxidation wave of pyrrole units, as already observed for other polypyridylruthenium(II) complexes containing pyrrole substituents on their ligands.[13] This behavior indicates the indirect oxidation of pyrrole groups by electrogenerated Ru^{III} species. Thin functionalized polypyrrole films could be grown by repeated

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[1] (a) Ungaro, R.; Pochini, A. In *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H.-J., Dürr, H., Eds.; VCH Publishers: New York, 1991; p 57. (b) Van Loon, J.-D.; Verboom, W.; Reinhoudt, D. N. *Org. Prepr. Proc. Int.* **1992**, *24*, 439.

[2] Grigg, R.; Holmes, J. M.; Jones, S. K.; Amilaprasadh Norbert, W. D. J. *J. Chem. Soc., Chem. Commun.* **1994**, 185.

[3] Beer, P. D.; Dickson, C. A. P.; Fletcher, N.; Goulden, A. J.; Grieve, A.; Hodacova, J.; Wear, T. *J. Chem. Soc., Chem. Commun.* **1993**, 828.

[4] Beer, P. D.; Chen, Z.; Goulden, A. J.; Grieve, A.; Hesek, D.; Szemes, F.; Wear, T. *J. Chem. Soc., Chem. Commun.* **1994**, 1269.

[5] Electrochemical copolymerization of a pyrrole-substituted calix[4]arene with regular pyrrole[6] has been very recently reported.

[6] Chen, Z.; Gale, P. A.; Beer, P. D. *J. Electroanal. Chem*, **1995**, *393*, 113.

[7] Rodriguez-Ubi, J.-C.; Alpha, B.; Plancherel, D.; Lehn, J.-M. *Helv. Chim. Acta* **1984**, *64*, 2264.

[8] Jaime, J.; De Mendoza, C.; Prados, P.; Nieto, P. M.; Sanchez, C. *J. Org. Chem.* **1991**, *56*, 3372.

[9] Ulrich, G.; Ziessel, R. *Tetrahedron Lett.* **1994**, *35*, 6299.

[10] Collomb Dunand-Sauthier, M.-N.; Deronzier, A.; Le Bozec, H.; Navarro, M. *J. Electroanal. Chem.* **1996**, *410*, 21.

[11] All new compounds gave spectroscopic and analytical data in accordance with the assigned structures. Selected data are for calix[4]arene-monobpy: yield 33%, FAB mass spectrum 831.4 (calc. 830); IR ν_{OH} 3329 cm^{-1}, ^1H NMR (200.1 MHz, $CDCl_3$, 20 °C) δ 9.55 (s, 2H, OH), 8.90 (s, 1H, OH), 8.59 (s, 1H bpy), 8.55 (s, 1H bpy), 8.38 (d, 1H bpy, $^3J = 8.2$ Hz), 8.33 (d, 1H bpy, $^3J = 8.8$ Hz), 7.68 (d, 2H bpy, $^3J = 8.2$ Hz), 7.06 and 6.99 (AB system, 4H m-C_6H_2, $^4J = 1.8$ Hz), 7.04 (s, 4H m-C_6H_2), 5.25 (s, 2H, OCH_2 bpy), 4.36 and 3.46 (AB system, 4H, $^2J = 13.0$ Hz), 4.23 and 3.41 (AB system, 4H, $^2J = 13.0$ Hz), 2.43 (s, 3H, CH_3), 1.23 (s, 9H, ^tBu), 1.22 (s, 18H, ^tBu), $^{13}C\{^1H\}$ (50.1 MHz, $CDCl_3$, 20 °C) δ 156.89−120.87 (aromatic quaternary C + aromatic CH), 76.11 (CH_2 bpy), 34.25, 33.92, 33.85 (3s, $C(CH_3)_3$), 32.86 and 32.38 (2s, $C_6H_2CH_2C_6H_2$), 31.46 (s, $C(CH_3)_3$), 31.20 (s, $C(CH_3)_3$). For **1**: λ_{max} = 451 nm (ϵ 10 800 dm^{-3} mol cm^{-1}), 283 (62 700). For **2**: λ_{max} = 452 nm (23 400), 283 (143 500).

[12] Electrochemical experiments were conducted in a conventional three-electrode cell under an argon atmosphere. The Ag/10 mM $AgNO_3$ + 0.1 M TBAP in MeCN system was used as a reference electrode. The potential of the ferrocene/ferricinium couple was 0.07 V under our experimental conditions. The working electrode was a vitreous carbon disk (0.07 cm^2).

[13] Cosnier, S.; Deronzier, A.; Moutet, J.-C. *J. Electroanal. Chem.* **1985**, *193*, 193.

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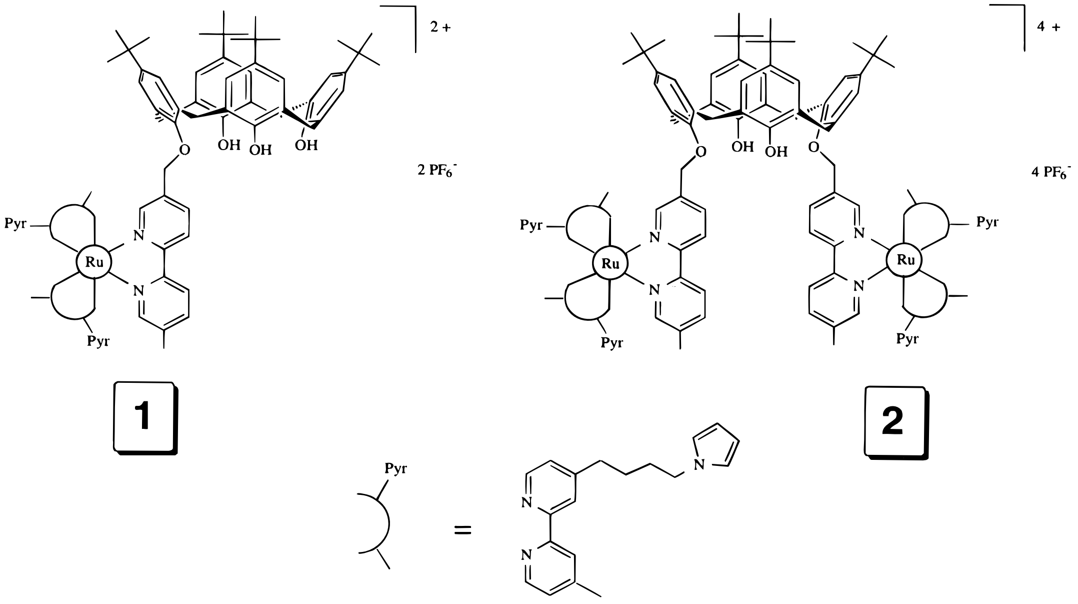
Chart 1



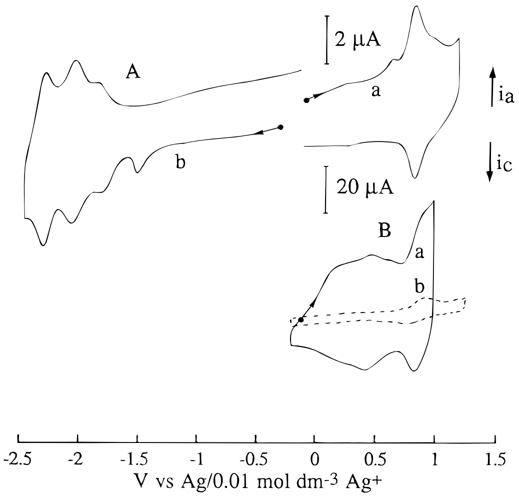


Figure 1. CV curves in MeCN + 0.1 M TBAP, $\nu = 0.1$ V s^{-1}. (A) C/poly-**1** modified electrode (diameter 3 mm; $\Gamma_{Ru} = 3 \times 10^{-10}$ mol cm^{-2}). (B) Electrode modified with a poly-(*N*-methylpyrrole-**1**) copolymer film (4 mC passed at 0.8 V) before (curve a) and after (curve b) cycling the film up to 1.7 V.

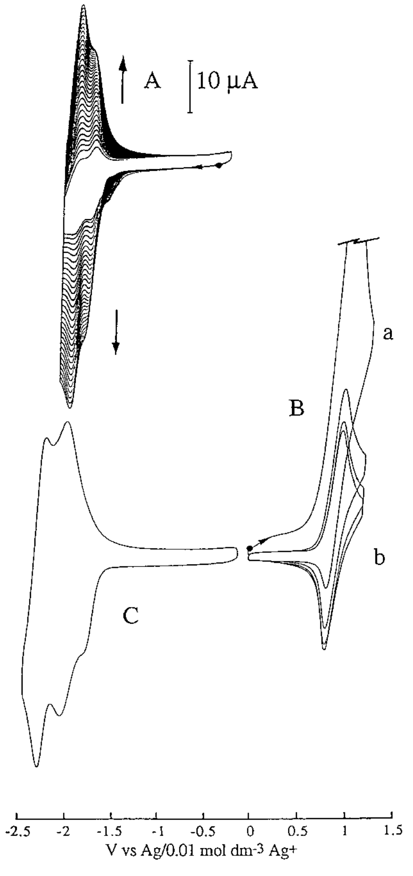


Figure 2. (A) Growth of an adsorbed film of **2** on a C electrode upon repeated cycles (31 cycles) in 0.5 mM **2** in MeCN electrolyte. (B) Oxidative electropolymerization of this adsorbed layer of **2** ($\Gamma_{Ru} = 10^{-8}$ mol cm^{-2}): first to fourth cycles. (C) Cyclic voltammetry curve (2nd cycle) for the resulting C/poly-**2** modified electrode over the -0.1 to -2.5 V range; $\nu = 0.1$ V s^{-1}.

scans over the -0.2 to 1.3 V potential range or by potentiostating the electrode at the potential range 0.8–0.9 V. The resulting modified electrodes transferred to fresh MeCN electrolyte clearly exhibit the regular electroactivity of the ruthenium complex, with four reversible peak systems located at 0.84, -1.82, -2.07, and -2.26 V (Figure 1A). As expected, the film-forming ability increases with the number of pyrrole groups contained in the monomer. However, film accumulation under potentiostatic or potentiometric conditions remained limited to ca. 3×10^{-10} and 10^{-9} mol cm^{-2} with **1** and **2**, respectively.[14] This is possibly due to the solubility of the polymers formed upon oxidation.

Thicker conducting films could be grown from controlled potential oxidation at 0.8 V of an MeCN solution containing a mixture of **1** and *N*-methylpyrrole (0.5 mM each). The CV of these films in the positive potential region (Figure 1B, curve a) reveals two different redox processes corresponding to the polypyrrole moiety ($E_{1/2} = 0.5$ V) and the ruthenium complex (Ru$^{III/II}$; $E_{1/2} = 0.85$ V). Estimation of the $[Ru(bpy)_3]^{2+}$ content in the film from the integrated charge under a CV wave leads to an approximate value of 1 metal center/20 pyrrole groups of the polymer matrix. It is worth noting that

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(14) The apparent surface concentration of immobilized ruthenium species, Γ_{Ru}, was calculated from the integrated charge under the Ru^{III}/Ru^{II} oxidation wave.

the conductivity of the film is mainly due to the polypyrrole moiety. As a matter of fact, destruction of its conductivity following its overoxidation by cycling the modified electrode up to 1.7 V[15] leads to a film characterized by a very poor $Ru^{III/II}$ response (Figure 1B, curve b). Evidently, the $[Ru(bpy)_3]^{2+}$ sites are largely isolated from one another and cannot ensure a viable redox conductivity in the film.

On the other hand, the low solubility in acetonitrile electrolyte of the reduced forms of complex **2** allows the coating of carbon surfaces with thick films of homopolymer. Repeated cycles through the first, or the second ligand reduction waves results in the steady growth of films of monomer **2** and the built up of well-behaved waves of increasing intensity (Figure 2A), due to the strong adsorption and the precipitation on the electrode surface of the reduced complex.[16] The same behavior was observed with complex **1**, but the film growth was slower. These adsorption−precipitation phenomena in MeCN/TBAP electrolyte are very similar to that already reported for other hydrophobic ruthenium(II) complexes.[17] Electrodes modified in this way and transferred to fresh MeCN/TBAP electrolyte are not very stable. Repeated scans in the negative potential region resulted in a slow and continuous decrease in the size of the voltammetry waves. However, a very fast electropolymerization takes place by scanning in the positive potential area. The first anodic cycle is characterized by a large wave due to the polymerization of almost the whole of the pyrrole subunits contains in the monomeric film (Figure 2B, curve a). After a few scans, the $Ru^{III/II}$ wave appears fully reversible (Figure 2B, curve b). By using this technique, stable poly-**1** and poly-**2** films with Γ_{Ru} as high as 2×10^{-8} mol cm^{-2} could be easily obtained. Fair electrochemical responses were obtained with these polymerized films, even by scanning down to the third ligand-based reduction (Figure 2C). However, CV curves are characterized by peaks broadening and by a strong decrease in the size of the first reduction peak system. A similar behavior has already been observed with films synthesized by electropolymerization of other pyrrole-substituted polypyridyl ruthenium complexes.[17] One can reasonably ascribe such voltammetric features to the difficult incorporation and release of counterions from the electrolyte associated with the redox processes in the film, due to the poor permeability of these cross-linked polymers.

In conclusion, novel pyrrole-substituted metal complexes containing calixarene have been prepared and shown to form thin polymer films on electrode surface upon electropolymerization. Currently, experiments are performed to test these modified surfaces as electrochemical and luminescent sensors.

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(15) Cosnier, S.; Deronzier, A.; Roland, J.-F. *J. Electroanal. Chem.* **1990**, *285*, 133.

(16) No film accumulation occurred by scanning down the third bpy reduction, due to the solubility in this medium of the triply reduced form of the complex.

(17) Deronzier, A.; Moutet, J.-C.; Zsoldos, D. *J. Phys. Chem.* **1994**, *98*, 3086.