SHORT PAPER

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Synthesis of 4,4′-di(mercaptomethylthio)-2,2′-bipyridine and *in situ* spectroscopic characterization of its electropolymerized films[†]

Gregoire J.F. Demets,[a] Henrique E. Toma,[a]* Mauricio C.R. de Castro[b] and Claudio L. Donnici[b]

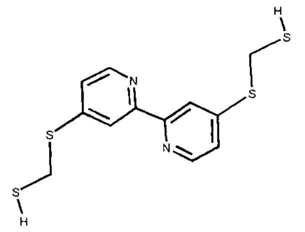
[a]*Instituto de Química, Universidade de São Paulo, Caixa Postal 26077, CEP 05513-970, São Paulo, SP, Brazil*

[b]*Departamento de Química, ICEX, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brazil*

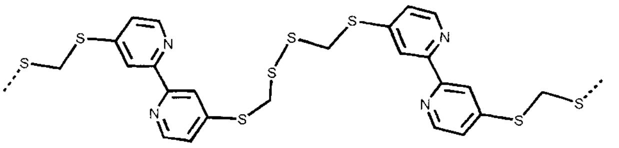
Reported are the synthesis of 4,4′-di(mercaptomethylthio)-2,2′-bipyridine and its electrochemical polymerization in acetonitrile, producing films which are strongly adsorbed onto gold electrodes.

Keywords: electrochemical polymerization, 4,4′-bis[thio(mercaptomethyl)]-2,2′-bipyridine

Bipyridyl based polymers are particularly interesting materials for applications in electronic and optical devices, because of their capability to bind transition metal and lanthanide ions.[1–7] Here we report the synthesis and characterization of a novel 2,2′-bipyridine derivative containing dithiomethylene substituents at the 4,4′-positions (tmbipy). Electropolymerisation of this species has been pursued, in order to generate thin films of bis(2,2′-bipyridin-4-ylthiomethyl)disulfide or poly-tmbipy, adsorbed onto gold electrodes, suitable for interacting with metal complexes.



tmbipy



poly-tmbipy

The monomeric 4,4′-di(mercaptomethylthio)-2,2′-bipyridine species was prepared by starting from 2,2′-bipyridine, and converting sequentially into the corresponding *N*,*N*′-dioxide, 4,4′-dinitro-2,2-bipyridine[8], 4,4′-dichloro-2,2′-bipyridine[9], 4,4′-di(methylthio)-2,2′-bipyridine[10] and finally into the 4,4′-di(methylsulfinyl)-2,2′-bipyridine as described here (see Experimental Section). The Pummerer rearrangement of this disulfoxide with thionyl chloride, to yield the α,α-dichloro derivative, was the key step for the subsequent desired dimercapto functionalization with thiourea. The dimercapto functionalization was confirmed by FTIR spectroscopy, from the characteristic 2550 ($\nu_{S\text{-}H}$), 870 cm^{-1} ($\delta_{S\text{-}H}$) bands, by ^1H NMR and also by the classical test with 5,5′-dithiobis(2-nitrobenzoic) acid (DTNB or Ellman’s reagent).

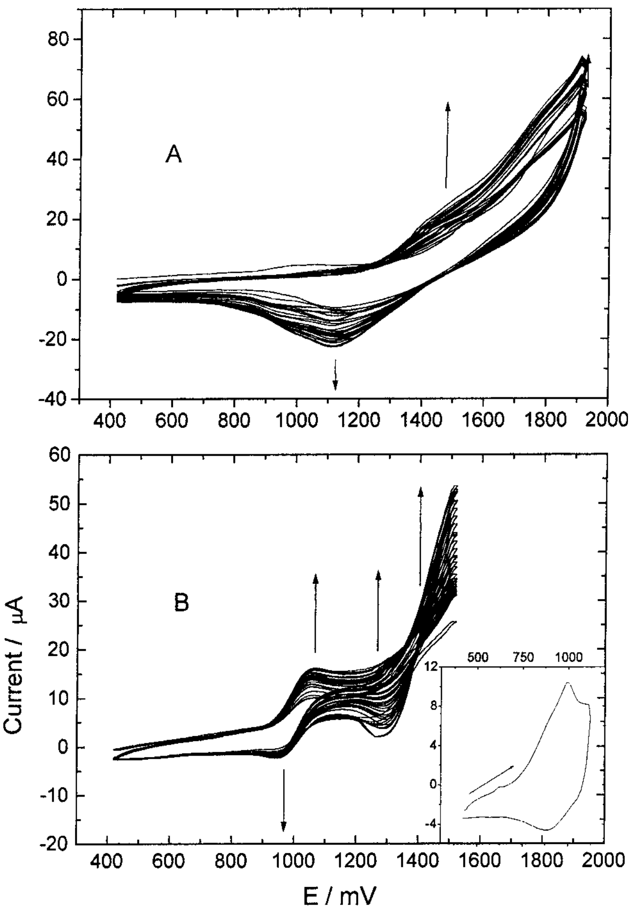


Fig. 1 Electrodeposition by cyclic voltammetry scanning, at 50 mV/s^1, in (0.1 mol/dm^3) $LiClO_4$ acetonitrile solution, of A) tmbipy (3.8 $mmol/dm^3$) over a 3 mm diameter gold disk electrode; B) of the $[Ru(bipy)_2tmbipy]^{2+}$ complex (3 $mmol/dm^3$). Inset: cyclic voltammetry (200 mV/s^1) of the modified electrode B in pure electrolyte solution.

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[*] To receive any correspondence. E-mail henetoma@iq.usp.br

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Electropolymerization of tmbipy was carried out in acetonitrile solutions, using gold electrodes, by cycling the potentials in the 400–1900 mV range. Thiol groups are known to form very strong chemical adsorbates onto gold surfaces. As shown in Fig. 1A, there is a gradual current increase above 1400 mV, associated with the oxidation of thiol groups in the adsorbed monomeric species.

In general,[11] polymerization of thiols proceeds *via* the combination of the adsorbed radical species, as represented by Eqns (1) and (2).

$$\text{HS-R-SH} \rightarrow \text{HS-R-S}^{\bullet} + \text{H}^{+} + \text{e} \qquad (1)$$

$$2\ \text{HS-R-S}^{\bullet} \rightarrow \text{HS-R-S-S-R-SH} \qquad (2)$$

and/or *via* the propagation of the electron transfer steps, leading to extended chains (Eqn (3)):

$$\text{HS-R-S}^{\bullet} + \text{HS-R-SH} \rightarrow \quad \text{HS-R-S-S-R-S}^{\bullet} + \text{H}^{+} + \text{e} \qquad (3)$$

The anodic potential was kept below 1900 mV, in order to minimize the oxidation of the thiol radicals to -SO_3^- groups (Eqn (4)), as previously reported for a number of organic thiol species.[11]

$$\text{R-S}^{\bullet} + 3\text{H}_2\text{O} \rightarrow \text{...R-SO}_3^- + 6\text{H}^{+} + 5\text{e} \qquad (4)$$

This step will block the propagation of the polymerization process, and is probably responsible for the saturation of current response observed after *ca* 50 voltammetric cycles.

In the reverse scan, a broad cathodic wave was observed around 1100 mV, involving the reduction of the redox sites responsible for the electronic transport above 1400 mV.

The growth of the polymeric film was successfully monitored by *in situ* electronic spectroscopy, using fibre optics, as well as by means of FTIR spectroscopy using Ge-ATR probes. Typical successive electronic spectra recorded during the polymerisation process can be seen in Fig. 2. A strong band is observed around 540 nm, reaching a maximum intensity above 50 voltammetric cycles. Considering that the several isolated components of the polymer do not absorb in the visible region, the observed bands should be ascribed to $\pi \rightarrow \pi^*$ transitions involving the chromophore sites generated during the oxidation process, as usually observed for conducting polymers.

The FTIR (Ge-ATR) spectra of the films recorded during the electropolymerization process are shown in Fig. 3. In addition to the H_2O bands at 3400 (νOH) and 1647 cm^1 (δOH_2), one can see the νCH peak at 2907 cm^{-1}, and the 2,2′-bipyridine vibrational peaks[12] at 1593 (νCC + νCN), 1508, 1458, 1423 (δCCH + νCC + νCN), 1369, 1319 (δCCH + νCC) 1265 (νCC + νCN), 1161, 898 (δCCH + νCC + αCCC) and 810 cm^{-1} (αCCC + δCCH + νCC). A strong, broad peak can be observed at 1053 cm^{-1}, corresponding to the stretching vibrations of the $-\ SO_3^-$ groups generated at the end of the polymerization process. The νSS peak usually occurs[13] below the working limit (700 cm^{-1}) of the Ge-ATR probe, and, in addition, it is expected to be infrared-inactive and not detected by FTIR.

In order to exploit the formation of polymeric metal complexes, the tmbipy compound (0.065 g, 0.21 mmol) was treated with an equivalent amount of $[Ru(bipy)_2Cl_2]$ (0.10 g, 0.211 mmol) in 10 cm^3 of 3:2 ethanol:water solution, and kept under reflux for 5 h in the presence of fivefold excess of ascorbic acid. After solvent evaporation to about 1/4 of the initial volume, a small amount of an orange-brown solid precipitated on adding NH_4PF_6 in excess. This material was characterized spectroscopically from its characteristic absorption band at 450 nm, ascribed to ruthenium-to-bipy MLCT transitions, as for the $[Ru(bipy)_3]^{2+}$ analogue.[14] Its electropolymerization onto gold electrodes was carried out by cycling the potentials from 400 to 1500 mV, as illustrated in Fig 1B. The increase of the $Ru^{III/II}$ redox wave at 1.00 V indicated the presence of the $[Ru(bipy)_2(tmbipy)]$ centres in the polymeric films. *In situ* optical and electrochemical measurements for the thin films

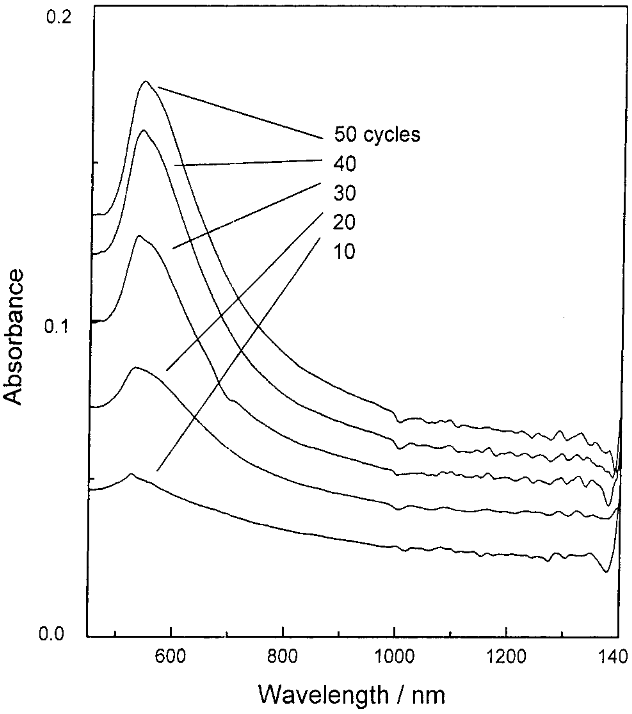

Fig. 2 *In situ* electronic spectra of electrodeposited films of tmbipy onto gold electrode after 10, 20, 30, 40 and 50 voltammetric cycles.

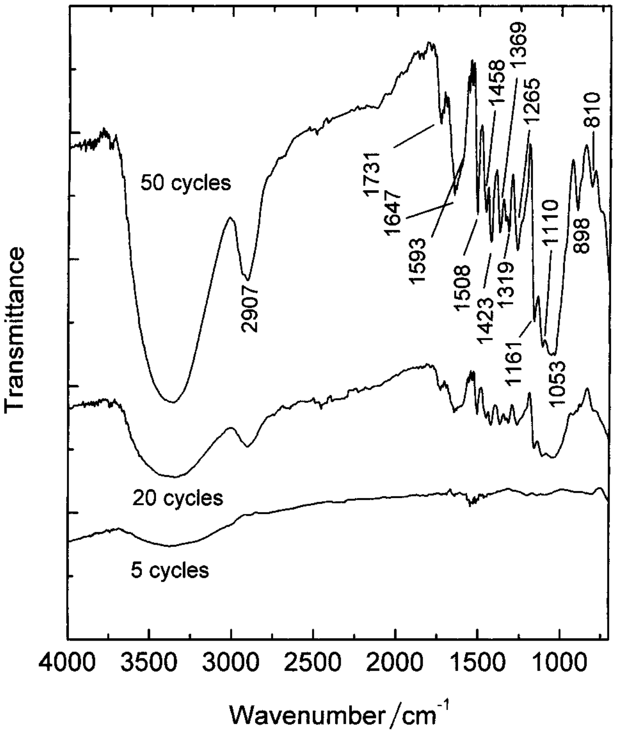

Fig. 3 FTIR spectra of the electrodeposited films of tmbipy onto gold electrode, recorded using a Ge-ATR microscopy probe, after 5, 20 and 50 voltammetric cycles.

also confirmed the presence of the ruthenium(II) complex, from the detection of the characteristic strong band at 450 nm, and the reversible redox wave at 1.0 V (Fig. 1B, inset), in pure electrolyte solutions.

Experimental

4,4′-Di(methylsulfinyl)-2,2’-bipyridine: To a solution of 0.20 g (0.81 mmol) of 4,4’-dimethylthio-2,2′-bipyridine in glacial acetic acid (8 cm^3) in a flask equipped with magnetic stirring and reflux condenser, was slowly added 0.25 cm^3 (2.05 mmol) of hydrogen peroxide (30%) solution and 2 cm^3 of glacial acetic acid. The mixture was stirred at room temperature for 24 h and after filtration and crystallization, 0.17 g (71%) of a pinkish solid (m.p. = 193–201^{o}C) was obtained. The presence of diastereoisomers in this material was evidenced by the splittings of the NMR signals: ^{1}H (d, $CDCl_3$): 8.89–8.63 (2H, dd, H6H6′ *J* = 4.8 Hz), 8.67–8.64 and 8.63–8.52 (2H, m, H3H3′ *J* = 1.9 Hz); 7.76–7.53 (2H, m, H5H5″) and 3.17 and 2.86 (6H, two singlets, SOMe); ^{13}C NMR (d, $CDCl_3$): 157.84, 157.72; (C2) 155.71, 155.68 (C4); 150.85 and 150.35 (C3); 118.67, 118.34 (C6); 115.71 (C5) and 43.35 (SOMe). Anal. Calcd. for $C_{12}H_{12}N_2S_2O_2$: C 51.41; H 4.31; N 9.99. Found: C 51.33; H 4.37; N 9.90 .

4,4′-Di(chloromethylthio)-2,2′-bipyridine: To a solution of 0.10g (0.36 mmol) of 4,4′-dimethylsulfinyl-2,2′-bipyridine in dichloromethane (2 cm^3), in a bottomed flask equipped with magnetic stirring and reflux condenser, was slowly added 0.15 cm^3 (2.00 mmol) of thionyl chloride. The mixture was stirred at room temperature for 24 h and after filtration and crystallization, 0.18 g (83%) of a yellowish solid (m.p. = 125–129 ^{o}C) was obtained; IR (KBr,cm^{-1}): 1080 (ν_{C-Cl}); ^{1}H NMR (d, $CDCl_3$): 8.49 (2H, d, H6H6′ *J* = 5.2 Hz), 8.37 (2H, d, H3H3′ *J* = 1.9 Hz); 7.22 (2H, dd, J = 5.3 and 1.7 Hz, H5H5″) and 5.10 (2H, s, SCH_2); ^{13}C NMR (d, $CDCl_3$): 160.87 (C2); 149.71 (C4); 148.91 (C3); 121.67 (C6); 119.37 (C5) and 48.85 (SCH_2). Anal. Calcd. for $C_{12}H_{10}N_2S_2Cl_2$: C 45.43; H 3.16; N 8.83. Found: C 45.39; H 3.21; N 8.80.

4,4′-Di(mercaptomethylthio)-2,2′-bipyridine: To a hot solution of 0.24 g (3.1 mmol) of thiourea in ethanol (2 cm^3), 0.49 g (1.55 mmol) of 4,4′-di(chloromethylthio)-2,2′-bipyridine in ethanol (3 cm^3) was added in small portions. After an exothermic reaction and cooling, the bis-isothiuronium salt was precipitated and dried. A mixture of this salt and 1.10 g of KOH, in 2 cm^3 of water, was kept under reflux for 5 hours. After acidation with dilute sulfuric acid (0.85 cm^3 in 2 cm^3 of water) and crystallization, 0.40 g (83%) of a yellowish solid (m.p. = 150^{o}C with decomposition) was obtained: IR (KBr, cm^{-1}): 2550 (ν_{S-H}), 870 (δ_{S-H}); ^{1}H NMR (d, DMSO-d_6): 8.49–8.53 (2H,dd, H6H6’ *J* = 4.8 Hz), 8.67–8.64 and 8.23–8.12 (2H, m, H3H3′ *J* = 1.9 Hz); 7.16–7.03 (2H, m, H5H5″) and 4.01 (4H, $2CH_2$). Anal. Calcd for $C_{12}H_{12}N_2S_4$: C 46.13; H, 3.87; N, 8.96; Found: 46.13; H 3.83; N, 8.90.

Cyclic voltammetry was carried out on a Princeton Applied Research model 283 potentiostat, using a quartz electrochemical cell containing the $Ag/AgNO_3$ (0.1 mol/dm^3) reference electrode in a Luggin compartment; the platinum wire auxiliary electrode and a removable gold disc working electrode. The potentials were converted to SHE, by adding 0.503 V.[15] The electrochemical experiments were carried out in acetonitrile solutions containing $LiClO_4$ (0.1 mol/dm^3), under an argon atmosphere. Optical measurements were carried out *in situ* using a fibre optics Wand probe attached to a Guided-Wave, model 260 spectrophotometer. FTIR spectra were recorded on a Shimadzu model 8300 spectrophotometer attached to a model AIM 8800 IR microscope, equipped with Ge-ATR probes.

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References

1 J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier and D. Moras, *Proc. Natl. Acad. Sci. USA*, 1987, **84,** 2565.
2 J.-M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995, Chap. 9.
3 R. Stiller and J.-M. Lehn, *Eur. J. Inorg. Chem.*, 1998, 977.
4 S. Cosnier, A. Deronzier and J.-C. Moutet, *J. Electroanal. Chem.*, 1985, **193,** 193.
5 S. Cosnier, A. Deronzier and J.-F. Roland, *J. Electroanal. Chem.*, 1990, **285**, 133.
6 C. Caix-Cecillon, S. Chardon-Noblat, A. Deronzier, M. Haukka, T.A. Pakkanen, R. Ziessel and D. Zsoldos, *J. Electroanal. Chem.*, 1999, **466,** 187.
7 P.R. Teasdale and G.G. Wallace, *Analyst*, 1993, **118,** 329**.**
8 C.L. Donnici, D.H. Máximo, L.L.C. Moreira, G.T. dos Reis, E.S. Cordeiro, I.M. F. de Oliveira, S. Carvalho and E. B. Paniago, *J. Braz. Chem. Soc.*, 1998, **9,** 455.
9 J.A. Connor and C. Overton, *J. Organometall. Chem.*, 1983, **249,** 165,
10 S. Anderson, E.C. Constable, K.R. Seddon, J.E. Turp, J.E. Baggott and M. Pilling, *J. Chem. Soc. Dalton Trans*., 1985, 2247.
11 H. Lund and M.M. Baizer (eds), *Organic Electrochemistry,* Dekker, New York, 1991, p 659.
12 P.K. Mallick, G.D. Danzer, D.P. Strommen and J.R. Kincaid, *J. Phys. Chem*., 1988, **92,** 5628.
13 N.B. Colthup, L.H. Daly and S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, New York, Academic Press, 1964.
14 A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. von Zelewsky, *Coord. Chem. Rev.*, 1988, **84,** 85.
15 B. Kratochvil, E. Lorah and C. Garber, *Anal. Chem.*, 1969, **41,** 1793.