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Electrochemical polymerization and characterization of a functional dicarbazole conducting polymer

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Abstract

The electropolymerization of the unique dicarbazole monomer, 2,6-bis-carbazole-9-yl-hexanoic acid pentafluorophenyl ester, is reported. This chiral monomer possesses two carbazole units and a chiral grafting center, activated ester for covalent amine-coupling. Contrary to monocarbazole monomers unable of internal cross-linking, its specifically designed dicarbazole skeleton allowed us to obtain highly reticulated polydicarbazole films functionalized for probe coupling. Full analysis of its electrochemical polymerization revealed different oxidation potentials for the two structurally different carbazole units. The electrochemical activity of the polydicarbazole-coated electrode has been characterized in different redox electrolytes. Contacted by a model protein (BSA), this film has been easily passivated at the $\text{Ru}(\text{bpy})_3(\text{PF}_6)_3$ electrochemical window.

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1. Introduction

Conducting polymers (CPs), that can be grown electrochemically or chemically from suitable oxidizable monomers, have recently attracted much attention in the field of microfabricated biosensing devices (biosensors, immunosensors) [1–7]. Besides this specific field, functional CPs boosted the successful development of electrochromic windows and light-emitting diodes [8–10], of non linear optics-based instrumentation [11,12], of solid-state batteries [13–15], and of photovoltaic cells [16,17].

CPs-based microdevices can immobilize capture probes by physical non-covalent entrapment (entrapment during the polymer growth) or by covalent bonding to a polymeric network that contains unique grafting chemical groups (post-polymerization functionalization) [1,18,19]. Since most of the electrochemically

grown CPs are conducting, sensing of film-analyte interactions can be monitored electrochemically in a sensitive and reproducible way onto patterned functional conductive areas (micro-/nanoelectrodes, arrays of micro-/nanoelectrodes) [20]. Therefore, looking for improved novel CPs in terms of intrinsic matrix performances such as functionality's variety, permeation rate to analytes, cross-linking, and porosity should be investigated systematically for optimization.

A new class of polycarbazole-CPs has been developed recently. The polycarbazole-CPs found rather limited applications, except poly-vinylcarbazole presenting unique optical and electrochemical properties [21,22]. It is known that, during poly-*N*-carbazole growth, *N*-alkylated monomers electropolymerized at the 3-3' and 6-6' heterocyclic positions, affording mainly tetramers soluble in the electrochemical medium [23–27]. Because of this solubility issue forbidding film production, interest in this CPs class for sensing applications was rather limited calling for newly designed electropolymerizable carbazole monomers overcoming this limitation. Moreover, if successfully grown, such polycarbazole-CPs films should include an appropriate grafting surface chemistry to link covalently capture probes of interest

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(post-polymerization functionalization) resulting in innovative polycarbazole-CPs based transducing surfaces.

The present communication reports that our newly designed dicarbazole monomer [28], 2,6-bis-carbazole-9-yl-hexanoic acid pentafluorophenyl ester, could be electropolymerized onto a Pt electrode toward a chemically stable functional polydicarbazole-film (Fig. 1). The presence of two carbazole units enables the generation of insoluble highly reticulated polymeric chains (Fig. 5) and explained the successful generation of this polydicarbazole film [23]. Moreover, its electrochemical polymerization process has been compared to the mono-carbazole analogue, 9-*N*-ethyl carbazole (Fig. 1), enabling its entire description. Clearly, different oxidation potentials could be used to oxidize selectively the two carbazole heterocycles. Likely related to their distance from the electron-withdrawing ester of the monomer, this selectivity effect is even preserved at lower current intensities after the polymerization due to dangling chains of the polymer. A Pt electrode (\varnothing 1.0 mm) was covered by this polydicarbazole film containing pentafluorophenol esters that are able to attach covalently bovine serum albumin (BSA, model protein) through its lysine residues. An electrochemical sensing of this post-polymerization reagentless covalent grafting of BSA has been performed in the presence of the $\text{Rupy}_3(\text{PF}_6)$ redox couple.

2. Experimental

2.1. Synthesis of the dicarbazole monocarboxy-monomer (Fig. 1)

The (*S*)-dicarbazole monomer (Fig. 1) has been synthesized homochirally at *C*(2) (enantiomeric enrichment better than 98%) from commercially available methyl (*L*)-lysinate in three defined steps: (a) a modified Clauson–Kaas reaction (2,5-dimethoxytetrahydrofuran, AcOH/dioxan, 1 h at 110 °C and overnight at 20 °C), (b) an ester saponification (2/1 $\text{ClCH}_2\text{CH}_2/\text{EtOH}$, 0.5 M NaOH, overnight reflux), and (c) a

pentafluorophenyl ester preparation (DCC, CH_2Cl_2 , pentafluorophenol, 2 h, 20 °C; overall synthetic yield: 23.3%) [28]. It has been characterized spectroscopically (FT-IR, $^1\text{H}/^{13}\text{C}$ -NMR, CI-MS) and its homogeneity checked by TLC and analytical HPLC. Yellow solid: ^1H -NMR (CDCl_3 , 200 MHz) δ (ppm) 8.13 (d, $J = 7.7$ Hz, 2H), 8.06 (d, $J = 7.7$ Hz, 2H), 7.50–7.15 (m, 12H), 5.46 (dd, $J = 5.0$ Hz, 10.6 Hz, 1H), 4.10 (m, 2H), 2.71–1.25 (m, 6H); ^{13}C -NMR (CDCl_3 , 50 MHz) δ (ppm) 166.9 (C=O), 143.1, 140.2, 126.2, 125.7, 123.6, 122.8, 120.6, 120.4, 120.1, 118.9, 109.2, 108.5, 56.2 (CH), 42.4 (CH₂), 29.3 (CH₂), 28.3 (CH₂), 24.0 (CH₂); MS (CI, CH_4^+): 612 (100%) $[\text{M}]^+$; FT-IR (KBr, ν cm^{-1}): 1784 (s, C=O). $[\alpha]_{\text{D}}^{20} = -9$ ($c = 10$ g l^{-1} , acetonitrile).

2.2. Electrochemical apparatus and procedures

The electrochemical polymerization and characterization of the above (*S*)-dicarbazole monomer were done under a dry nitrogen atmosphere (< 1 ppm H_2O and O_2), using an Eco Chemie Autolab 20 potentiostat. The experiments were carried out in a three-electrode cell configuration. A Pt disk (\varnothing 1.0 mm) and wire were used respectively as the working and the counter electrodes. Potentials are reported versus Ag/AgNO₃, the reference electrode. All the above experiments were performed using cyclic voltammetry at a scan rate of 100 mV s^{-1} . The basic electrolyte composition consisted of 0.2 M battery grade TBAClO₄ (tetrabutylammonium perchlorate) in dry acetonitrile. For the polymerization process, 10 mM dicarbazole-monomer were added to the electrolyte. In the case of the coverage investigation, two redox couples were employed: (i) 15 mM of Ferrocene/Ferrocenium ($\text{Fe}^{+2}/\text{Fe}^{+3}$); and (ii) 10 mM I₂, LiI, both in acetonitrile. The immobilization was studied using the $\text{Rupy}_3(\text{PF}_6)$ redox couple which fits the electrochemical window of the observed polydicarbazole film in the conducting region. The fabrication and analysis of the polydicarbazole biosensor were done in the following steps. First, electropolymerization of the dicarbazole monocarboxylate monomer by cyclic voltammetry varying between 0 and 1.2 V. Second, the typical electro-

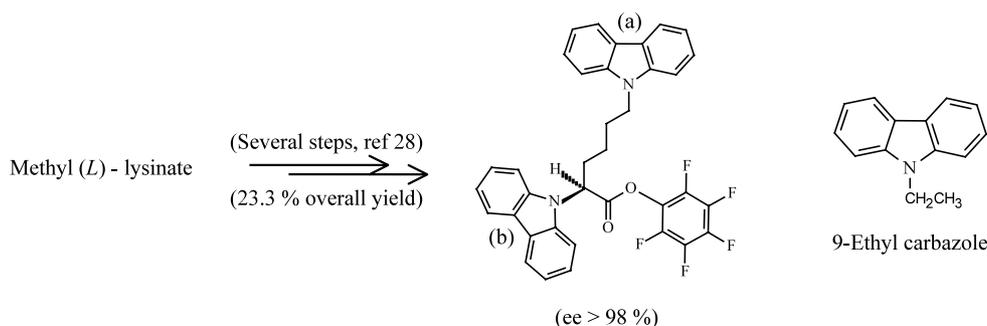


Fig. 1. Chemical structures of the dicarbazole and monocarbazole monomers used in this study.

chemical behavior of the polydicarbazole polymer was measured in the basic electrolyte with and without the $\text{Rupy}_3(\text{PF}_6)$ redox couple. Finally, after 3 h soaking in an aqueous solution of the sensed element (0.5 mg/ml BSA, bovine serum albumin), the electrode was rinsed with water, dried and measured again in the presence of the $\text{Rupy}_3(\text{PF}_6)$ redox couple.

3. Results and discussion

3.1. Electrochemical polymerization

The electrochemical oxidation of the dicarbazole monocarboxy monomer in solution generates a reactive radical cation that can react either with neighboring radical cation or neutral monomers to produce the polymer [29]. Fig. 2 presents the potentiodynamic growth of the polymer during successive cyclic voltammetry. The cyclic voltammetry, which was scanned between 0 and 1.2 V, shows three oxidation peaks denoted P, A and B. We assign peak P to the oxidation of the polymer to its conductive state, and peaks A and B to the monomer. This discrimination is based on two observations. First, peak P appears only from the second scan while A and B are present in all scans. In other words, the oxidation of peak P is associated with the existence of a polymer. The second observation relates to the different percentage growth of the peaks. The average increment of peak P during each voltammetry cycle was 22% versus an increment of only 3% for both peaks A and B. In other words, peaks A and B represent a different process than peak P. The different growth percentages seem to indicate that the monomer cannot penetrate the polymer film. Thus, despite the significant thickening of the polymer film associated with the increase of peak P, the polymer surface area related to peaks A and B hardly changes. Peaks A and B can be related to the monomer in two ways: (1) peak A

indicates the generation of a radical cation in the two carbazole units while peak B indicates the formation of a di-cation. (2) Both peak A and peak B relate to a radical cation-mediated oxidation, each peak belonging to a different carbazole unit. In order to resolve the electrochemical processes related to these peaks, we polymerized the monomer, 9-ethyl carbazole (Fig. 1), which has only one *N*-ethyl substituted carbazole unit. The electropolymerization is shown in Fig. 3 and the peaks are denoted as P' and A'. Like the dicarbazole polymerization, peak P' of the mono-carbazole process is assigned to the polymer transformation to the conductive state. In this case, the average percentage growth per cycle is 4% (compared with 22% in the dicarbazole case). The low percentage growth results from the high solubility of the polymer, which limits the polymer layer thickness. In the same manner, peak A' which is attributed to the oxidation of a mono-carbazole to its corresponding radical cation increased only by 0.3% per cycle, because the electrode surface area did not increase. If peaks A and B of the dicarbazole ester polymerization are related to the generation of a radical cation and a di-cation, then, peak B should also appear in the electropolymerization of the monoethyl carbazole. The absence of a third peak (B) in the monoethyl carbazole process shows therefore, that peak B belongs to the polymerization of the second carbazole unit in the dicarbazole ester. The two carbazole units labeled (a) and (b) in Fig. 1 differ by the distance to the chiral center and to the electron-attracting group pentafluorophenyl ester. Thus, it seems that the oxidation of the carbazole (b) closer to the chiral center, requires more positive potential than carbazole (a). By the same sense, the oxidation of the mono-carbazole should occur at a less positive potential than of carbazole (a). Indeed, the oxidation onset potentials of the mono-carbazole, carbazole (a) and carbazole (b) of the dicarbazole ester are quite well ordered 0.68, 0.70 and 0.94 V. This same trend holds for the peak potentials, $A' < A < B$. Consequently, we assign peaks A and B to the carbazole units

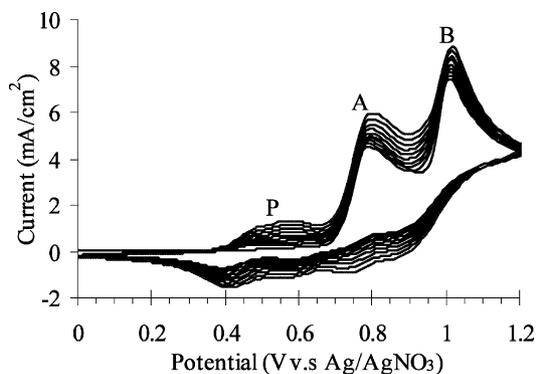


Fig. 2. Potentiodynamic growth of the polydicarbazole film in 0.2 M TBAClO_4 and 10 mM dicarbazole solution. The potential was scanned 10 cycles between 0 to 1.2 V at a scan rate of 100 mV s^{-1} . Peak P is the characteristic peak of the polymer and A and B relate to the monomer.

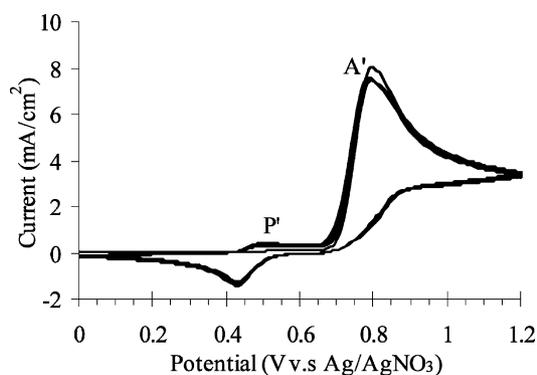


Fig. 3. Electropolymerization of the mono-carbazole. Same conditions like the dicarbazole (Fig. 2). Peak P' is the characteristic peak of the polymer and A' relates to the monomer.

(a) and (b), respectively. We note that polymerization of the dicarbazole monomer at a potential range that can only oxidize the carbazole unit labeled (a) (up to 0.85 V, not shown) showed similar behavior to the monocarbazole case. That is, a stable polymer film was not produced on the electrode since the carbazole unit labeled (b) remained neutral thus prohibiting the cross-linking.

3.2. Electrochemical behavior of the polymer

The polydicarbazole polymer was electrochemically characterized in its basic electrolyte (free of monomer). Fig. 4 presents a typical cyclic voltammetry of the polydicarbazole, showing three reversible peaks with some overlap between two of the oxidation peaks. The typical voltammetry resembles the polymerization process (Fig. 2). The first oxidation peak, which occurs at the potential of peak P in the polymerization process, results from the polymer transition. The onset potential of the second peak, 0.7 V, is also similar to the oxidation peak (A) of the polymerization. The third oxidation peak overlaps the second one and, thus, its onset is not well defined. However, it is clearly shifted negatively with respect to peak B of the polymerization process. Here, also, we attributed the two latter peaks to the oxidation of carbazole units, only that in this case these carbazoles are connected to the polymer. Fig. 5 shows the three possible polymerization paths for the dicarbazole ester monomer. Due to the monomer lack of symmetry, the polymer chains can grow through a–a, b–b or a–b bonds. Most of the monomers are cross linked by both carbazole units. However, one can expect a small fraction mainly in chain terminals in which only one carbazole is polymerized. This structure leads to sided dandling carbazole units of both type a and b with approximately the same oxidation potentials as the free monomer in solution. A small potential shift is however

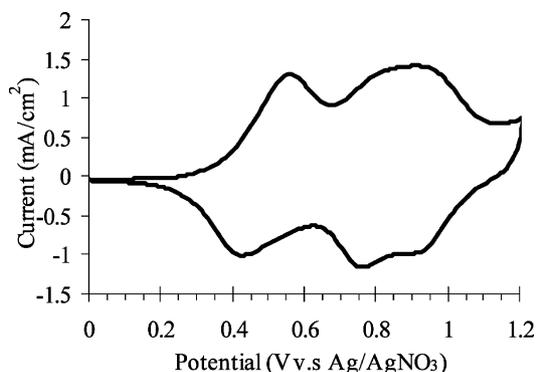


Fig. 4. Typical cyclic voltammetry of the polydicarbazole film in a solution free of monomer. Showing narrow peak, which is related to the polymer and spread peak, which is actually two peaks that belong to dandling carbazole units.

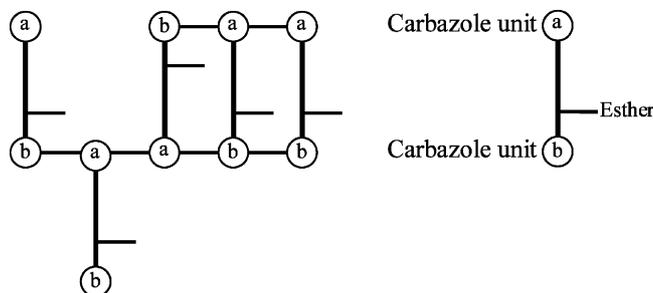


Fig. 5. Schematic view of the possibilities for coupling between two dicarbazole monomers. The carbazole unit which is away from the ester is denoted as a and the other unit as b. Therefore, the polymer chains can grow through a–a, b–b or a–b bonds.

expected due to the physical connection of the carbazole unit to the polymer network. The overall potential difference between the free carbazole in solution and the dandling carbazole in the polymer network is analogous to the difference between the oxidation of dissolved ions and ions that adsorb the electrode. Another fact that supports this polymer description is related to the ratio between the three oxidation peaks currents. In the typical cyclic voltammetry of the polymer, the three peaks have almost similar currents, while in the polymerization process (Fig. 2), peaks A and B are three times higher than peak P. Taking peak P as a common reference, the high currents observed during the polymerization results from the excess of monomer in solution while in the typical cyclic voltammetry only the dandling carbazole units are available.

3.3. Electrode coverage by the polydicarbazole polymer

Electro-sensing properties of the above polydicarbazole polymer will be based on electron transfer through the polymer to electroactive species in solution before and after linkage of any probe onto the polymer [23]. Therefore, it is necessary to determine whether a full polymer coverage has been obtained since pinholes in the polymer film can alter the expected results and reduce the overall sensitivity of the electrochemical sensor. Conducting polymers can be switched between the neutral insulating and the oxidized conducting states [30]. The coverage measurements were done using the ferrocene/ferrocenium ($\text{Fe}^{+2}/\text{Fe}^{+3}$) and I^-/I_3^- redox couples, which have redox potentials in the insulating region of the polymer. Fig. 6 presents a cyclic voltammetry of the coated Pt electrode in a ferrocene/ferrocenium solution and a cyclic voltammetry of a bare platinum as a reference. Fig. 6 clearly shows that, at potentials more negative than 0.35 V, the polymer coating attenuates the current by 90%, almost to the background level. Fig. 7 shows the same trend of current attenuation by the polymer, 97%, but in the presence of

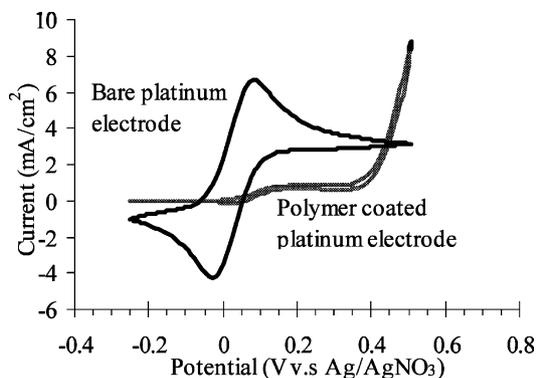


Fig. 6. Cyclic voltammetry of a polydicarbazole coated Pt electrode and, for comparison, of a bare platinum electrode in the presence of ferrocene/ferrocenium ($\text{Fe}^{+2}/\text{Fe}^{+3}$) as a redox couple. The polymer is insulating at the redox potential of ferrocene/ferrocenium and, thus, the current attenuation indicates that a thin layer of polymer was formed.

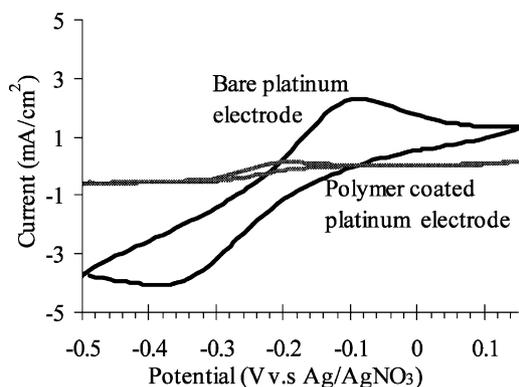


Fig. 7. Cyclic voltammetry of a polydicarbazole coated Pt electrode and, for comparison, of a bare platinum electrode in the presence of I^-/I_3^- as a redox couple. The same trend of current attenuation as in Fig. 6 indicates a passivation of the surface by the polymer rather than a repulsion of the ions by the charged polymer.

I^-/I_3^- as a redox couple. Since the significant current decrease is associated with both positive (Fig. 6) and negative (Fig. 7) ions, we conclude that the effect is associated with the passivation of the surface by the polymer film and not a repulsion of the ions by the charged polymer. This result is in accordance with the literature that deals with the morphology of conducting polymers [31–33]. Accordingly, a thin homogeneous film is deposited first before the main deposition of a porous non-compact polymer layer. Thus, in the insulating potential range, the thin layer prevents the electron transfer to the electrolyte almost entirely, leaving a negligible current due to a few pinholes in the film. When the polymer starts to conduct at potentials above 0.35 V (Fig. 4), a large increase of electron transfer through the conducting thin layer is observed.

3.4. Polydicarbazole-based electrosensor

A useful electroensing strategy using this system should necessitate the passivation of the polymer surface by covalently linking the NH_2 -containing molecular probe of interest to the pentafluorophenol ester present at the polymer surface. Such a passivation may be detected electrochemically [23]. In our case, following the covalent coupling of BSA onto the polymer film (2 h incubation at room temperature with a 0.5 mg ml^{-1} BSA aqueous solution), electrochemical measurements have been performed using a redox couple, whose redox potential is in the conducting region of the polymer beyond the three previous oxidation peaks. As presented in Fig. 8, $\text{Rupy}_3(\text{PF}_6)$, which oxidizes at 1.32 V, is suitable for this measurement. Before the BSA immobilization, the cyclic voltammetry of the polydicarbazole film is similar to the typical one with the addition of the $\text{Rupy}_3(\text{PF}_6)$ at 1.32 V. The latter, which belongs to the oxidation of $\text{Rupy}_3(\text{PF}_6)$, is reduced by 60% after the covalent grafting of the insulating BSA. Therefore, the loss of $\text{Rupy}_3(\text{PF}_6)$ activity demonstrates the sensing ability of this polydicarbazole coated electrode.

4. Conclusion

The electrochemical polymerization of a unique functional dicarbazole monomer has been performed. The first peak in the polymerization process was assigned to the oxidation of the conducting polydicarbazole film which grows onto the electrode. A comparison to the mono-carbazole polymerization indicated that the second and the third peaks in the dicarbazole process belonged to the selective oxidation of each of the two carbazole units to its radical cation. The observed difference in oxidation potentials of these two carbazole units resulted from the unequal distance to the active carboxyl center. The typical cyclic voltammetry of the

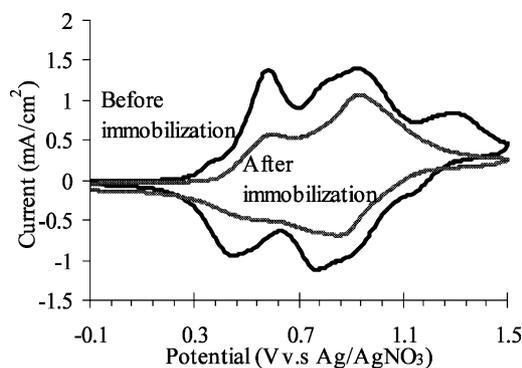


Fig. 8. Cyclic voltammetry of the polymer coated Pt electrode in the presence of $\text{Rupy}_3(\text{PF}_6)$ as a redox couple. The disappearance of the $\text{Rupy}_3(\text{PF}_6)$ oxidation peak (onset potential of 1.16 V) after immobilization of BSA demonstrates the sensing ability of this polydicarbazole coated electrode.

polydicarbazole film showed a similar three peaks system with some overlap between two of the oxidation peaks. Like the polymerization process, the first peak belonged to polymer oxidation, while the two other ones belonged to sided dandling carbazole units which were not cross-linked. A thin polydicarbazole film has been deposited as indicated by measurements of electron transfer through it to electroactive species which have redox potentials in the insulating region of the polymer. Therefore, this functional polydicarbazole film has been used to sense electrochemically the covalent attachment of BSA onto it in the presence of the redox couple $\text{Ru}(\text{bpy})_3(\text{PF}_6)$ which has a redox potential in the conducting region of the polydicarbazole polymer.

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References

- [1] S. Cosnier, *Biosens. Bioelectron.* 14 (1999) 443.
- [2] S. Cosnier, *Can. J. Chem. Eng.* 76 (1998) 1000.
- [3] A. Deronzier, J.C. Moutet, *Curr. Top. Electrochem.* 3 (1994) 159.
- [4] N.C. Foulds, C.R. Lowe, *J. Chem. Soc. Faraday Trans. I* 32 (1986) 1259.
- [5] M. Hiller, C. Kranz, J. Huber, P. Bauerle, W. Schuhmann, *Adv. Mater.* 8 (1996) 219.
- [6] M.D. Imisides, R. John, G.G. Wallace, *Chemtech* 26 (1996) 19.
- [7] T.M. Swager, M.J. Marsella, L. Bicknell, Q. Zhou, *J. Macromol. Sci. Pure Appl. Chem.* A31 (1994) 1893.
- [8] M.A. De Paoli, A.F. Nogueira, D.A. Machado, C. Longo, *Electrochim. Acta* 46 (2001) 4243.
- [9] Q. Pei, Y. Yang, G. Yu, Y. Cao, A.J. Heeger, *Synth. Met.* 85 (1997) 1229.
- [10] K. Tada, M. Onoda, H. Nakayama, *Jpn. J. Appl. Phys. Pt. 2* 38 (1999) L833.
- [11] T. Wada, H. Okawa, L. Wang, K. Nanjo, T. Masuda, M. Tabata, H. Sasabe, *Abstr. Pap. Am. Chem. Soc.* 212 (1996) 117.
- [12] Y.D. Zhang, L.M. Wang, T. Wada, H. Sasabe, *Macromol. Chem. Phys.* 197 (1996) 667.
- [13] S. Neves, C.P. Fonseca, *J. Power Sources* 107 (2002) 13.
- [14] N. Oyama, O. Hatozaki, *Macromol. Symp.* 156 (2000) 171.
- [15] H. Uemachi, Y. Iwasa, T. Mitani, *Electrochim. Acta* 46 (2001) 2305.
- [16] A. Fujii, A.A. Zakhidov, V.V. Borovkov, Y. Ohmori, K. Yoshino, *Jpn. J. Appl. Phys. Pt. 2* 35 (1996) L1438.
- [17] K. Tada, M. Onoda, H. Nakayama, K. Yoshino, *Synth. Met.* 102 (1999) 982.
- [18] G. Zotti, *Synth. Met.* 51 (1992) 373.
- [19] M. Tropanowicz, T. Krawczynsky vel Krawczyk, *Mikrochim. Acta* 121 (1995) 167.
- [20] C. Kranz, H. Wohlschlager, H.L. Schmidt, W. Schuhmann, *Electroanalysis* 10 (1998) 546.
- [21] S. Madhavan, K.S.V. Santhanam, *Mol. Cryst. Liq. Cryst.* 160 (1988) 111.
- [22] G. Mengoli, M.M. Musiani, B. Schreck, S. Zecchin, *J. Electroanal. Chem.* 246 (1988) 73.
- [23] S. Cosnier, S. Szunerits, R.S. Marks, J.P. Lellouche, K. Perie, *J. Biochem. Biophys. Methods* 50 (2001) 65.
- [24] A. Desbene-Monvernay, J.E. Dubois, P.C. Lacaze, *J. Chem. Soc. Chem. Commun.* 6 (1985) 370.
- [25] A. Desbene-Monvernay, J.E. Dubois, P.E. Lacaze, *J. Electroanal. Chem.* 189 (1985) 51.
- [26] A. Desbene-Monvernay, P.C. Lacaze, M. Delamar, *J. Electroanal. Chem.* 334 (1992) 241.
- [27] S. Cattarin, G. Mengoli, M.M. Musiani, B. Schreck, *J. Electroanal. Chem.* 246 (1988) 87.
- [28] K. Perie, R.S. Marks, S. Szunerits, S. Cosnier, J.-P. Lellouche, *Tetrahedron Lett.* 41 (2000) 3725.
- [29] A.S. Sarac, O. Yavuz, E. Sezer, *Polymer* 41 (2000) 839.
- [30] G. Garcia-Belmonte, J. Bisquert, E.C. Pereira, F. Fabregat-Santiago, *J. Electroanal. Chem.* 508 (2001) 48.
- [31] M.A. Vorotyntsev, M. Casalta, E. Pousson, L. Roullier, G. Boni, C. Moise, *Electrochim. Acta* 46 (2001) 4017.
- [32] M.D. Levi, N.M. Alpatova, E.V. Ovsyannikova, M.A. Vorotyntsev, *J. Electroanal. Chem.* 351 (1993) 271.
- [33] V.E. Kazarinov, M.D. Levi, A.M. Skundin, M.A. Vorotyntsev, *J. Electroanal. Chem.* 271 (1989) 193.