



# Exploring amide linkage in a polyviologen derivative towards simultaneous voltammetric determination of Pb(II), Cu(II) and Hg(II) ions



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## ABSTRACT

In this study, we report reductive electro-synthesis of a polyviologen derivative bearing amide linkage in its side chain, derived from a cyanopyridinium based monomer with amide functionality. The as grown film was characterized by cyclic voltammetry which displays a well-defined and reversible two step redox response characteristic of viologen. FTIR analysis show evidence of amide linkage and successful reduction of cyanopyridinium moieties to polyviologen. In situ multi ESR/UV-Vis-NIR spectroelectrochemistry show a single line in ESR signal, thereby suggesting polarons as the only charge carrier involved during charging/discharging process. Furthermore, a characteristic UV-Vis absorption spectra confirms viologen formation. Finally, the polyviologen film is subjected to simultaneous voltammetric determination of heavy metal ions, Pb(II), Cu(II) and Hg(II). The amide linkage in the polyviologen derivative is supposedly complexing these divalent metal ions, enabling their sensitive and simultaneous determination with low detection limits.

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## 1. Introduction

Simultaneous determination of trace metal ions in environmental samples is of great importance from environmental and biological point of view. The electrochemical voltammetric analysis is a widely used method for this purpose, due to its high sensitivity, low detection limits and the selectivity in detecting different metal ions at different potentials [1]. Moreover, the portability of the instrumentation and inexpensive operating costs allow the real-time analysis of trace metals in environmental samples. Chemically modified electrodes consisting of a recognition layer with selectivity for a target metal ion are widely used for the detection of hazardous metals [2]. Peptides/amides are an

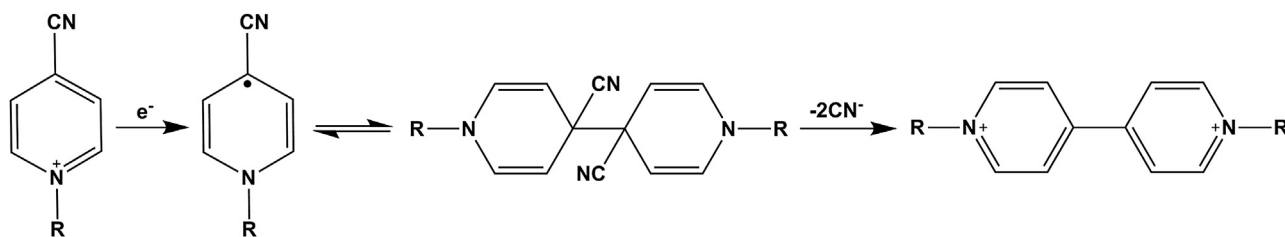
example of such recognition element because of their ability to bind or complex divalent metal ions [3].

Electroactive polymers with redox properties have gained considerable interest recently in the scientific research [4]. Especially polymers that can be electropolymerized directly on the electrode surface would be more appropriate for practical electroanalytical applications. For example, electropolymerized PEDOT/PSS modified glassy carbon electrode has been utilized for simultaneous determination of cadmium and lead [5]. Among the redox polymers, the polyviologens are of particular interest owing to their fast electron transfer reactions, electron accepting ability and porosity [6]. Polyviologen modified electrodes have been proposed for catalytic/electrocatalytic applications, electrochromic displays, organic electronics and photovoltaics [7–10]. However, such electropolymerizable polyviologens have been barely employed for electroanalysis; only few reports can be found [11]. There are several ways to obtain viologen oligomers. Our group has been working for a while on cyanopyridine based monomers which can be electrochemically reduced to viologen and subsequently electropolymerized to polyviologen [12,13]. This reductive coupling mechanism is illustrated in Scheme 1,

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**Scheme 1.** Reductive coupling reactions of 1-alkyl-4-cyanopyridinium ions to viologen.

where 4-cyanopyridyl radicals couple together to form a viologen skeleton with the elimination of two cyano groups.

Such polyviologen films are very stable showing a two-step redox voltammetric behavior characteristic of viologen [12]. Depending on the application, these polymers can be directly employed or the modification of the polymer/monomer is made for specific application [14].

In recent years, the in situ multi-spectroelectrochemical techniques have been employed for the thorough characterization of numerous electrochemical systems [15,16]. Unlike electrochemical techniques, the in situ ESR and UV-Vis-NIR spectroscopy methods provide detailed analysis of electronic, optical and paramagnetic features of the molecule under study. The spectroelectrochemical data thus not only provide information about the nature of charge carriers but also the doping mechanism and structural conformations of electrochemical system.

In this work, a cyanopyridine based monomer is synthesized where two cyanopyridines are separated by amide linker chain. The monomer is easily electropolymerized to polyviologen deposited as a film at the electrode/substrate. The voltammetric response of as grown film show two redox processes related to the viologen cation radicals and neutral states. The structural changes between monomer radicals and neutral states. The structural changes between monomer radicals and neutral states are realized by FTIR spectroscopy. A single line ESR signal and a typical viologen absorption spectra is acquired from multi ESR/UV-Vis-NIR spectroelectrochemical measurements. The polyviologen film with amide linkage in the side chain is further exploited to simultaneously determine heavy metal ions, Pb(II), Cu(II) and Hg(II) using differential pulse

voltammetry. The amide linkage in the polyviologen structure was expected to coordinate with the divalent metal ions, allowing their sensitive electrochemical detection.

## 2. Experimental

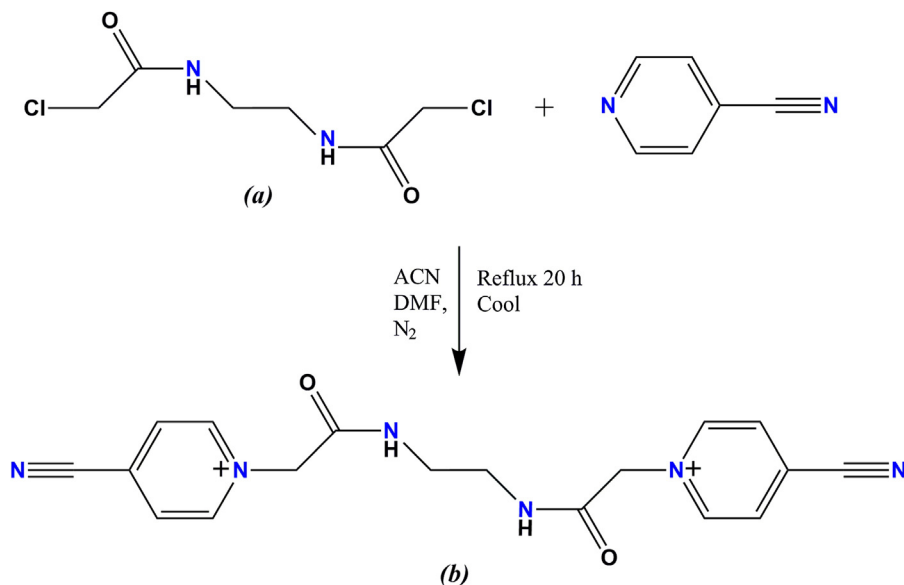
### 2.1. Synthesis of monomer

#### 2.1.1. Synthesis of *N,N'*-1,2-ethanedylbis[2-chloroacetamide] (*a*)

2.64 mL (39.5 mmol) of ethylene diamine was dissolved in 50 mL of diethyl ether and 8.5 g (61.5 mmol) of potassium carbonate was added. The mixture was cooled down to 0°C. Then 5 mL (62.8 mmol) of chloroacetyl chloride dissolved in 100 mL of diethyl ether was added dropwise while keeping the mixture at 0°C. The solution was then allowed to warm to RT and the stirring was continued overnight. After filtration, the solution was washed with water and the organic phase was collected and evaporated to dryness under reduced pressure. Additional purification with column chromatography (Hex/CH<sub>2</sub>Cl<sub>2</sub> 1:1 as eluent) yielded 2.9 g (13.61 mmol) of the product (**a**). <sup>1</sup>H NMR (DMSO): 8.28 (2H, t), 4.04 (4H, s), 3.16 (4H, dd). <sup>13</sup>C NMR: 166 (2), 163 (2), 43 (2)

#### 2.1.2. Synthesis of 1,1'-[1,2-ethanedylbis(imino(2-oxo-2,1-ethanedyl))]bis-(4-cyanopyridin-1-ium) dibromide (*b*)

2.5 g (11.75 mmol) of product (**a**) and 9.75 g (93.65 mmol) of *p*-cyanopyridine were dissolved in 150 mL of acetonitrile and 20 mL of DMF under nitrogen atmosphere. The solution was then refluxed for 20 h. After cooling down, the mixture was further



**Scheme 2.** Synthesis of cyanopyridine based monomer containing amide groups.

cooled in freezer to precipitate all the product. After filtration and drying under vacuum, 1.6 g (4.5 mmol) of pure product (**b**) was obtained (Scheme 2).  $^1\text{H}$  NMR (DMSO): 9.06 (4H, d), 8.49 (4H, d), 5.6 (4H, s), 4.00 (4H, s).  $^{13}\text{C}$  NMR: 165(2), 147(4), 131(4), 129(2), 114(2), 62(2), 39(2)

## 2.2. Electrochemistry

Polyviologen (PV) films were electropolymerized from 0.1 M NaCl aqueous electrolyte solution containing 0.2 M monomer. The electrochemical polymerization and all other electrochemical measurements were carried out in a three-electrode cell performing cyclic voltammetry (CV) measurements using Autolab (PGSTAT101) potentiostat. Glassy carbon (GC,  $d=3$  mm) substrate was used as working electrode while a platinum wire and a Ag/AgCl electrode served as counter electrode and reference electrode, respectively. The Ag/AgCl electrode was calibrated vs. ferrocene ( $\text{Fe}/\text{Fe}^+$ ) ( $E_{1/2}(\text{Fe}/\text{Fe}^+)=0.45$  V) before the experiments. All electrochemical tests and CV experiments were performed using deionized water and 0.1 M NaCl as supporting electrolyte. The solutions were deaerated by a dry nitrogen ( $\text{N}_2$ ) stream before each experiment and blanketed with it during the electropolymerization. The PV film was electrosynthesized by potential cycling between 0 V and  $-1.2$  V using 25 cycles at a scan rate of  $50$   $\text{mVs}^{-1}$ . After electropolymerization, the polymer films were washed with copious amount of deionized water in order to remove the electrolyte or monomer residues. The electrochemical response of previously cleaned as-deposited films was studied in 0.1 M NaCl aqueous electrolyte by CV technique using a potential window of 0 to  $-1.2$  V.

## 2.3. Characterizations

The FTIR spectra of monomer and polymer samples were recorded by a Bruker VERTEX 70 FTIR spectrometer equipped with a Harrick VideoMVP™ diamond ATR accessory using liquid nitrogen cooled MCT (broad-band) detector. For each spectrum, 128 interferograms were recorded at spectral resolution of  $4$   $\text{cm}^{-1}$ . The polymer sample was recovered from the GC surface after electropolymerization.

The surface morphology of the film was imaged by a Leo (Zeiss) 1530 Gemini FEG scanning electron microscope (SEM). PV film was electrodeposited on the ITO electrode (specific surface conductivity  $100 \Omega \square^{-1}$ , Delta-technology Inc., active diameter of 10 mm) before SEM imaging.

## 2.4. In situ ESR/UV–Vis–NIR spectroelectrochemistry

In situ ESR/UV–vis–NIR spectroelectrochemical experiments were performed in the optical ESR cavity (ER 4104OR, Bruker Germany) using a specially designed flat cell. ESR spectra were recorded by the EMX Micro X-band CW spectrometer (Bruker, Germany). UV–vis–NIR spectra were measured by Avantes spectrometer AvaSpec-2048  $\times$  14-USB2 equipped with a CCD detector and AvaSpec-NIR256-2.2 with the InGaAs detector applying the AvaSoft 7.5 software. Both the ESR and the UV–vis–NIR spectrometer were connected to a HEKA potentiostat PG 390. Triggering was performed by the software package PotMaster v2  $\times$  40 (HEKA Electronic, Germany). The spectroelectrochemical flat cell with a three-electrode arrangement consisted of a laminated working electrode with a ITO plate, a platinum wire as a counter electrode and a silver wire as pseudoreference electrode. ITO electrode with an area of  $0.096$   $\text{cm}^2$  was positioned between two pieces of chemically resistant polyester based lamination foils (DocuSeal, USA) to obtain the small well defined electrochemically active surface with an insulated electrical

contact, with circular holes giving  $0.1$   $\text{cm}^2$  of free active electrode surface. Due to the poor adhesion of the electrodeposited film on the Au or Pt microgrid, ITO electrode was selected for the in situ measurements.

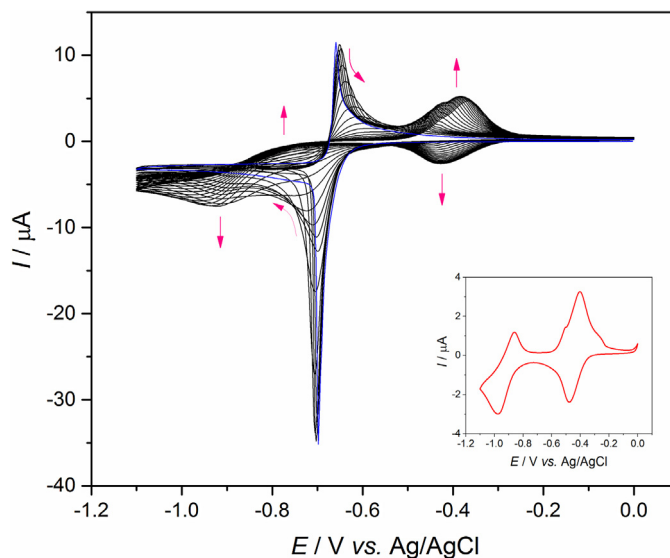
## 2.5. Analytical procedure for simultaneous determination of heavy metals

A PV coated GC electrode was used as a working electrode for the heavy metal ions determination. The complete analysis was carried out using Autolab (PGSTAT101) potentiostat performing differential pulse voltammetry (DPV). Stock solution of 0.01 M Pb (II), Cu(II) and Hg(II) was prepared in aqueous 0.1 M NaCl ( $\text{pH}=7$ ) solution and diluted to various concentrations for the ion sensing measurements. The parameters for DPV measurements: Step potential, 0.005 V; modulation amplitude, 0.025 V; modulation time, 0.05 s and interval time, 0.2 s.

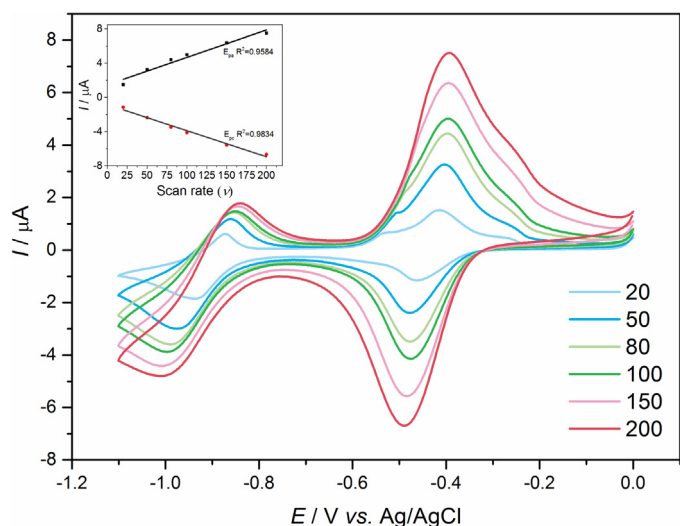
## 3. Results and Discussions

Fig. 1 shows continuous cyclic voltammograms of 0.2 M monomer in 0.1 M NaCl aqueous electrolyte using GC electrode. In the first scan, a very steep reduction peak is observed at  $-0.7$  V, together with an oxidation peak at  $-0.65$  V, which showed minor tailing. These peaks are assigned to the voltammetric response of  $-\text{C}=\text{N}$  group. With repetition of the scans, these reduction and oxidation peaks were decreased successively, while new reduction peaks at  $-0.42$  and  $-0.91$  V and oxidation peaks at  $-0.37$  and  $-0.76$  V appeared and then increased. Upon continuous cycling, an obscure purple layer was observed near the vicinity of the electrode surface.

After electropolymerization, the PV modified electrode is repeatedly rinsed with deionized water. Since the film is at the neutral electronic state, the purple color of the film changed to yellow. The CV of the PV modified electrode in 0.1 M NaCl aqueous electrolyte showed two pairs of redox waves most commonly observed for viologens (Inset of Fig. 1). While the first redox couple is assigned to the viologen radical cation formation ( $\text{V}^{2+}/\text{V}^{•+}$ ), the second broad and less intense peak is due to the viologens in the neutral state ( $\text{V}^{•+}/\text{V}^0$ ). Similar voltammetric behavior has been



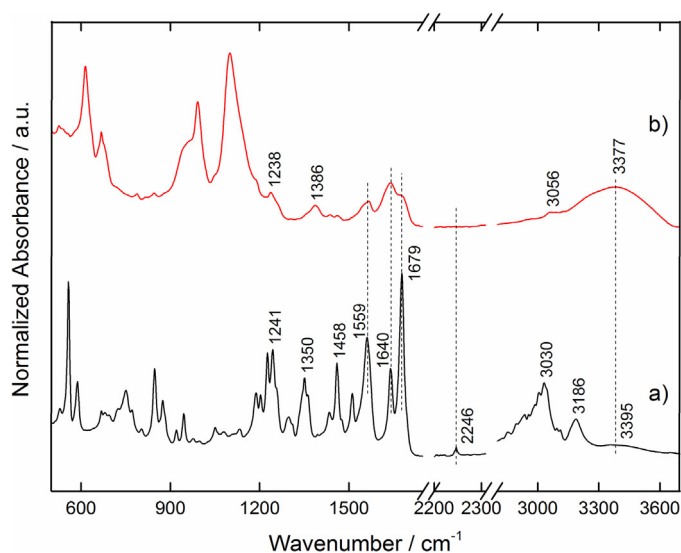
**Fig. 1.** CVs for the reductive electropolymerization of polyviologen (PV) derivative on a GC electrode in 0.1 M NaCl aqueous electrolyte. Scan rate:  $50$   $\text{mVs}^{-1}$ . **Inset:** CV response of PV deposited GC electrode in 0.1 M NaCl aqueous electrolyte at a scan rate of  $50$   $\text{mVs}^{-1}$ .



**Fig. 2.** CVs of the PV modified GC electrode in 0.1 M NaCl aqueous electrolyte at different scan rates viz. 20, 50, 80, 100, 150, 200 mVs<sup>-1</sup>. **Inset:** Scan rate dependence of PV on GC electrode.

previously reported for viologen/polyviologen films electropolymerized in identical manner [12]. When characterized at different scan rates (20, 50, 80, 100, 150, 200 mV/s), the PV modified electrode exhibits well defined two step redox response, as illustrated in Fig. 2. As the scan rate increases, the current increases linearly (Inset of Fig. 2), suggesting the adequate reversibility of such redox active polymeric systems.

In order to realize the structural changes in polyviologen derived from cyanopyridine based monomer, the samples were subjected to FTIR analysis. Fig. 3 represents infrared spectra of monomer and polymer in solid state. As a general observation, one can see that monomer spectrum contains several peaks due to the different functional groups involved in its structure. After electropolymerization, the polymer spectrum contains few broad peaks. A broad band at  $\sim 3400$  cm<sup>-1</sup> due to  $-\text{NH}$  stretching can be observed in both monomer and polymer spectrum. The ring/alkyl stretching vibrations (C–H, C–C, C=C) are mainly observed in monomer spectrum between 2800–3200 cm<sup>-1</sup>. A tiny peak at 2246 cm<sup>-1</sup> due to  $-\text{C}\equiv\text{N}$  stretching can be noticeable in monomer spectrum,



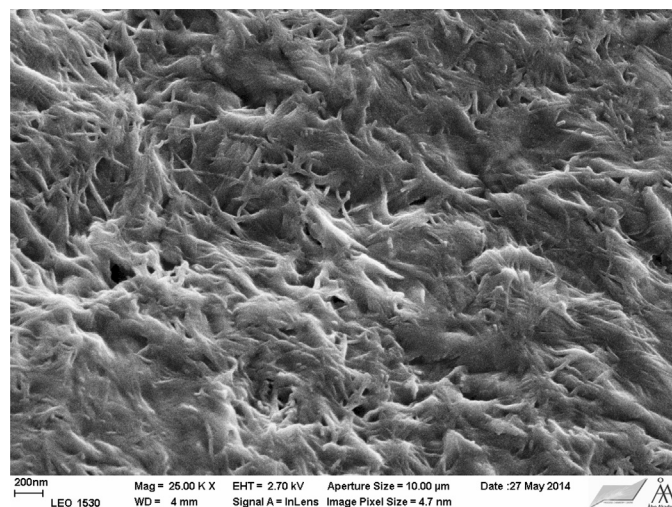
**Fig. 3.** FTIR spectra of (a) monomer and (b) polymer (PV).

however disappeared from PV spectrum, indicating successful electroreduction of cyanopyridinium ions towards polyviologen formation [12]. The band at 1679 cm<sup>-1</sup> assigned to carbonyl stretching can be seen in monomer spectrum with higher absorption intensity contrary to a shoulder found in polymer spectrum. This frequency is lower than the normal carbonyl frequency around 1700 cm<sup>-1</sup>, suggesting the interaction of carbonyl group with other surface groups [17]. A band due to pyridine ring  $-\text{C}=\text{N}$  stretching vibrations at 1640 cm<sup>-1</sup> is consistent in both monomer and polymer spectrum. Other bands at 1559, 1458, 1350 and 1241 cm<sup>-1</sup> are assigned to C–C/N–H stretch, CON stretch, C–C stretch and C–O/N–H bending [17]. All the infrared absorptions below 1200 cm<sup>-1</sup> have been attributed to the alkyl/aromatic ring stretch and bend vibrations and some due to the vibrational modes of amide functionality. There is a slight shift in the polymer bands compared to those of monomer, possibly due to the formation of long chain polymer consisting of viologen repeating units derived from reductive electropolymerization of cyanopyridine based monomer precursor.

For SEM imaging, the PV film is electrodeposited on ITO electrode. As shown in Fig. 4, the SEM image of PV consists of compact and fibrous/cotton like texture all over the surface of the electrode. Although various conjugated polymers show such morphology, it is interesting and exceptional for these kind of redox polymers.

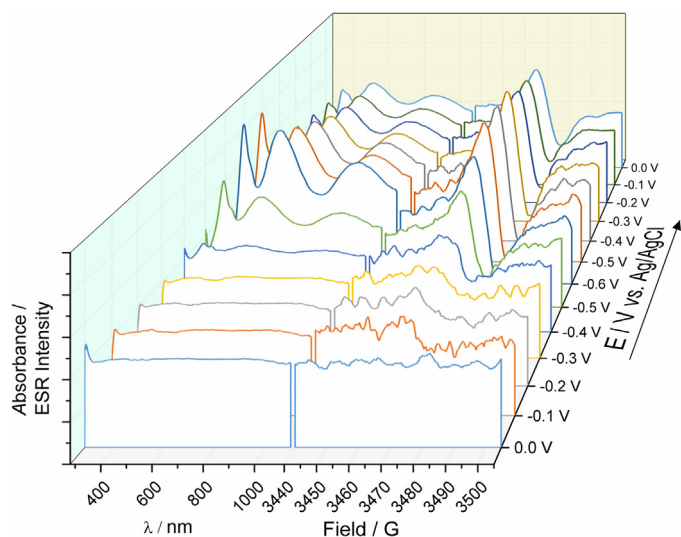
The in situ ESR/UV–Vis–NIR spectroelectrochemical study enables the information concerning the nature of charge carriers and their induced changes to the structure of the molecule under study. Fig. 5 shows potential dependence of the UV–Vis–NIR (left) and ESR spectra (right) obtained simultaneously during electrochemical reduction of a PV film in 0.1 M NaCl–aqueous electrolyte at 5 mV/s. Thirteen spectra were acquired during the potential charging/discharging course between 0 and  $-0.6$  V.

The ESR spectra consist of a single line centered at 3472 G and the shape of the signal does not change during the whole potential scan. At the beginning, the relative concentration of spins is constant. This is due to the spin-bearing species being trapped into the PV film, resulting in hardly any change in the ESR intensity. As the potential reaches  $-0.4$  V, the concentration of spins starts to grow and the intensity of ESR signal increases reaching its maximum at  $-0.6$  V. This sudden increase in the line intensity of ESR signal can be explained by the radical monocation formation in viologen species. The existence of the ESR signal during the

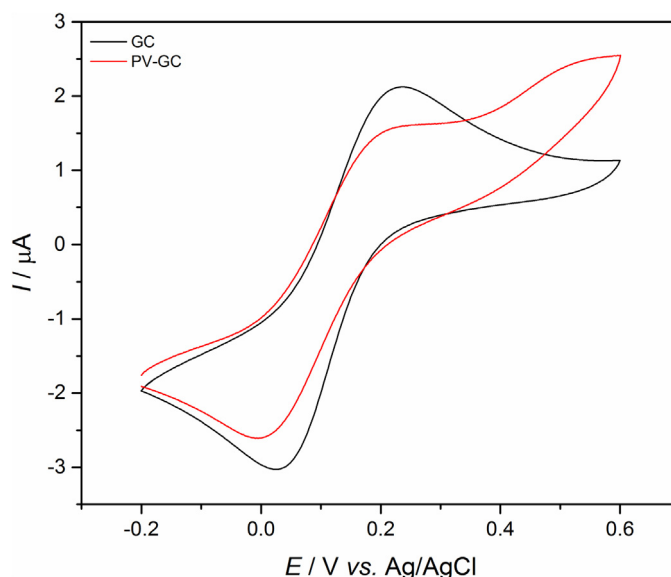


**Fig. 4.** SEM image of electropolymerized polyviologen derivative.





**Fig. 5.** Evolution of in situ UV-Vis-NIR (right side) and ESR (left side) spectra obtained during potential charging/discharging scan of PV modified ITO electrode in 0.1 M NaCl aqueous electrolyte.



**Fig. 6.** CVs of GC electrode and PV modified GC electrode in 5 mM  $K_3[Fe(CN)_6]$  solution in 0.1 M NaCl (pH=7) at a scan rate of  $50 \text{ mVs}^{-1}$ .

whole n-doping process is an evidence of the formation of paramagnetic charge carriers, i.e. positive polarons. During discharging, a decrease in the ESR intensity can be observed. However, it is not totally reversible since the ESR intensity is slightly higher at the end of the scan compared to that at initial scan. This phenomenon is very common in several conjugated polymers [18]. This spectral behavior might be due to the charge carriers that might have remain trapped inside the film and partially because of the ITO electrode which is not a desired substrate for n-doping reactions.

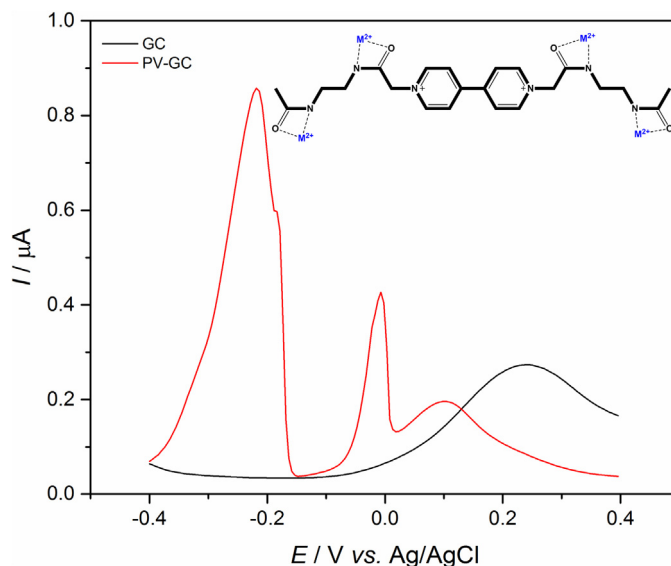
The UV-Vis-NIR spectra follows similar potential dependence as that of ESR during both charging and discharging. In the beginning of the potential scan, no substantial changes are observed until the potential reaches  $-0.4 \text{ V}$ , when three characteristic absorption bands at  $\sim 400$ ,  $550$  and  $900 \text{ nm}$  appear. The bands are assigned to the viologen cation radical formation [12]. From the ESR spectra, one can reveal that at the same potential, the paramagnetic species were detected, confirming that absorption profile is associated to the same charge carriers. With increasing potential, all three absorption bands increases. During the reverse scan, absorption intensity decreases gradually for all three bands. At the end of the charging/discharging course, absorbance is higher than at the beginning of the scan and does not reach to its initial value, similarly as for the ESR signal. The changes in ESR and absorption spectra occurs in parallel, suggesting identical voltage dependence during the entire potential scan.

The ESR and UV-Vis-NIR spectra confirms that there is only one paramagnetic charge carrier, which is polarons involved in the first reduction step of the PV. This is in contrast to the ESR spectra of viologen molecules which comprises a well resolved hyperfine splitting [19]. The spectroelectrochemical data thus suggests that reductive electropolymerization of cyanopyridine based monomer resulted in polymeric viologen formation, thereby showing a single line in the ESR spectra connected to polaronic charge carriers, and not hyperfine splitting.

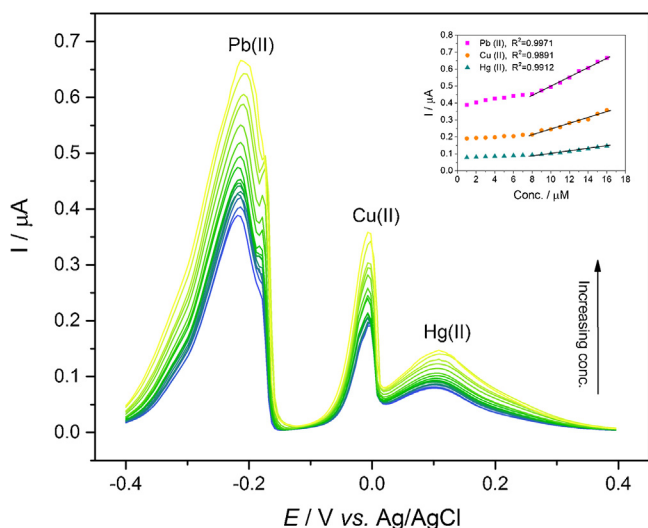
**Fig. 6** shows the voltammetric behavior of the GC and PV modified GC electrode for the ferrocyanide/ferricyanide redox couple in electrolyte. A well-defined redox response of the probe is observed for the GC electrode. When PV modified GC electrode is scanned, slightly different shape of the redox curve is obtained

with decrease in peak currents. This lowering in peak current might be due to the redox polymer PV which is not conducting enough and partly due to the covalently bound peptide side group of PV [20].

The performance of the modified electrode towards simultaneous detection of heavy metal ions, Pb(II), Cu(II) and Hg(II), is evaluated by differential pulse voltammetry (DPV) (**Fig. 7**). Since the analytical signal with better resolution was desired, DPV method was preferred which enhances the sensitivity of the detection by eliminating the non-Faradaic current. Compared to the DPV response of GC electrode, all the heavy metal ions show well-defined oxidation peaks for the PV deposited GC electrode. While bare GC electrode shows only one peak at  $\sim 0.25 \text{ V}$ , the polyviologen coated GC electrode exhibit three characteristic anodic peaks well separated from each other with potential values



**Fig. 7.** DPV curves for  $25 \mu\text{M}$  of Pb(II), Cu(II) and Hg(II) ions in 0.1 M NaCl aqueous solution (pH=7) obtained at GC electrode and PV modified GC electrode. **Inset:** Schematic illustration of possible binding sites of metal ions.



**Fig. 8.** DPVs of the Pb(II), Cu(II) and Hg(II) ions in 0.1 M NaCl aqueous solution (pH = 7) at different concentrations ranging from 1–16  $\mu\text{M}$  recorded at PV modified GC electrode. **Inset:** Corresponding calibration plot of current ( $I$ ) as a function of concentrations of respective metal ions.

at  $-0.212$ ,  $-0.007$  and  $0.108$  V corresponding to Pb(II), Cu(II) and Hg(II) ions respectively. The relative peak potentials are identical to those reported for divalent Pb, Cu and Hg ions [21,22]. This electroanalytical performance of polyviologen towards trace metal ions might be attributed to the amide linkage in the polymeric backbone of PV. It is well known that amides/peptides have tendency to bind divalent metal ions [23]. Such complexation of metal ions through amide chain might have occurred in the PV bearing amide functionality and is therefore utilized for sensitive detection of heavy metal ions. The possible binding sites can be envisaged via two donor atoms that complexes the metal, the amide nitrogen or carbonyl oxygen, as illustrated in the inset of Fig. 7. Moreover, polyviologens are known for their anion exchange characteristics [24]. Therefore, in chloride rich environment, the  $\text{M}^{2+}$  forms negative complex ion  $\text{MCl}_n^{2-}$  which can be accumulated on PV modified electrode, assisting the sensitive determination of heavy metals.

Fig. 8 demonstrates the voltammetric response for the simultaneous determination of Pb(II), Cu(II) and Hg(II) ions at different concentrations. As the concentration increases from 1–16  $\mu\text{M}$ , the anodic peak current increases successively, allowing sensitive detection of all three ions, clearly separated from each other. The corresponding calibration plot for all three ions show linear dependence of current to concentration, particularly in the range of 8–16  $\mu\text{M}$  with correlation coefficient ( $R^2$ ) in between 0.98–0.99 (Inset of Fig. 8). The detection limit for the simultaneous determination of all three ions is close to 10  $\mu\text{M}$ . These results show the potential of PV film with amide linker towards determination of the heavy metal ions. Such hazardous metals coexist in the industrial effluents and the overlapping oxidation potentials makes their separation and detection difficult in real-time. The proposed method provide simple, fast, sensitive and simultaneous electroanalysis of such heavy metals in aqueous streams.

#### 4. Conclusions

In this work, a cyanopyridine based monomer with amide functionality at the side chain has been synthesized and

electropolymerized. The cyclic voltammetric data show two redox waves characteristic of viologen. The structural analysis is evident by FTIR spectroscopy showing complete utilization of cyanopyridinium monomer to viologen by disappearance of cyanide stretching vibration. From in situ spectroelectrochemical study, the ESR spectra depicts single line related to polaronic charge carriers and UV–Vis–NIR spectra show characteristic absorption bands typical of viologen. The polyviologen film was finally demonstrated for sensitive and simultaneous voltammetric determination of Pb(II), Cu(II) and Hg(II) ions, owing to the amide linkage in the polymeric chain and its possible binding to divalent ions.

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#### References

- [1] D.W. Arrigan, Tutorial review. Voltammetric determination of trace metals and organics after accumulation at modified electrodes, *Analyst* 119 (1994) 1953–1966.
- [2] H. Dong, H. Zheng, L. Lin, B. Ye, Determination of thallium and cadmium on a chemically modified electrode with Langmuir–Blodgett film of p-allylcalix [4] arene, *Sensors Actuators B: Chem.* 115 (2006) 303–308.
- [3] J.J. Gooding, D.B. Hibbert, W. Yang, Electrochemical metal ion sensors. Exploiting amino acids and peptides as recognition elements, *Sensors* 1 (2001) 75–90.
- [4] B. Gadgil, P. Damlin, T. Ääritalo, J. Kankare, C. Kvarnström, Electrosynthesis and characterization of viologen cross linked thiophene copolymer, *Electrochim. Acta* 97 (2013) 378–385.
- [5] S. Anandhakumar, J. Mathiyarasu, K.L.N. Phani, V. Yegnamaran, Simultaneous determination of cadmium and lead using PEDOT/PSS modified glassy carbon electrode, *American Journal of Analytical Chemistry* 2 (2011) 470.
- [6] B. Gadgil, P. Damlin, A. Viinikanoja, M. Heinonen, C. Kvarnström, One-pot synthesis of an Au/Au 2 S viologen hybrid nanocomposite for efficient catalytic applications, *Journal of Materials Chemistry A* 3 (2015) 9731–9737.
- [7] L. Yang, J. Frith, N. Garcia-Araez, J. Owen, A new method to prevent degradation of lithium–oxygen batteries: reduction of superoxide by viologen, *Chemical Communications* 51 (2015) 1705–1708.
- [8] B. Gadgil, P. Damlin, M. Heinonen, C. Kvarnström, A facile one step electrostatically driven electrocodeposition of polyviologen-reduced graphene oxide nanocomposite films for enhanced electrochromic performance, *Carbon* 89 (2015) 53–62.
- [9] C.S. Kim, S. Lee, L.L. Tinker, S. Bernhard, Y. Loo, Cobaltocene-Doped Viologen as Functional Components in Organic Electronics, *Chem. Mater.* 21 (2009) 4583–4588.
- [10] M. Young Jo, Y. Eun Ha, J. Hyun Kim, Polyviologen derivatives as an interfacial layer in polymer solar cells, *Sol. Energy Mater. Sol. Cells* 107 (2012) 1–8.
- [11] K. Cheng, P. Chen, Polyviologen modified glassy carbon electrode employed for anodic stripping voltammetric determination of mercury (II), *Electroanalysis* 20 (2008) 207–210.
- [12] B. Gadgil, E. Dmitrieva, P. Damlin, T. Ääritalo, C. Kvarnström, Redox reactions in a linear polyviologen derivative studied by in situ ESR/UV–vis–NIR spectroelectrochemistry, *Journal of Solid State Electrochemistry* 19 (2015) 77–83.
- [13] N. Wang, A. Kähkönen, P. Damlin, T. Ääritalo, J. Kankare, C. Kvarnström, Electrochemical synthesis and characterization of branched viologen derivatives, *Electrochim. Acta* 154 (2015) 361–369.
- [14] B. Gadgil, P. Damlin, T. Ääritalo, C. Kvarnström, Electrosynthesis of viologen cross-linked polythiophene in ionic liquid and its electrochromic properties, *Electrochim. Acta* 133 (2014) 268–274.
- [15] L. Dunsch, Recent Advances in in situ multi-spectroelectrochemistry, *Journal of Solid State Electrochemistry* 15 (2011) 1631–1646.
- [16] B. Gadgil, P. Damlin, E. Dmitrieva, T. Ääritalo, C. Kvarnström, ESR/UV–Vis–NIR spectroelectrochemical study and electrochromic contrast enhancement of a polythiophene derivative bearing a pendant viologen, *RSC Advances* 5 (2015) 42242–42249.
- [17] L. Liao, C. Lien, D. Shieh, F. Chen, J. Lin, FTIR study of adsorption and photochemistry of amide on powdered TiO<sub>2</sub>: Comparison of benzamide with acetamide, *Physical Chemistry Chemical Physics* 4 (2002) 4584–4589.
- [18] B. Meana-Esteban, A. Petr, C. Kvarnström, A. Ivaska, L. Dunsch, Poly(2-methoxynaphthalene): A spectroelectrochemical study on a fused ring conducting polymer, *Electrochim. Acta* 115 (2014) 10–15.

- [19] R.D. Webster, R.A.W. Dryfe, J.C. Eklund, C. Lee, R.G. Compton, In situ electrochemical ESR studies of reactive radicals: the reductions of bromo-anthraquinone and methyl viologen, *J. Electroanal. Chem.* 402 (1996) 167–174.
- [20] N. Serrano, B. Prieto-Simón, X. Cetó, M. del Valle, Array of peptide-modified electrodes for the simultaneous determination of Pb (II), Cd (II) and Zn (II), *Talanta* 125 (2014) 159–166.
- [21] R. Madhu, K.V. Sankar, S. Chen, R.K. Selvan, Eco-friendly synthesis of activated carbon from dead mango leaves for the ultrahigh sensitive detection of toxic heavy metal ions and energy storage applications, *RSC Advances* 4 (2014) 1225–1233.
- [22] A. Afkhami, H. Bagheri, H. Khoshsafar, M. Saber-Tehrani, M. Tabatabaee, A. Shirzadmehr, Simultaneous trace-levels determination of Hg(II) and Pb(II) ions in various samples using a modified carbon paste electrode based on multi-walled carbon nanotubes and a new synthesized Schiff base, *Anal. Chim. Acta* 746 (2012) 98–106.
- [23] H. Sigel, R.B. Martin, Coordinating properties of the amide bond. Stability and structure of metal ion complexes of peptides and related ligands, *Chem. Rev.* 82 (1982) 385–426.
- [24] P. Hsu, W. Ciou, P. Chen, Electrochemical Determination of Cu (II) Ions in Chloride-Rich Environment Using Polyviologen-Modified Glassy Carbon Electrodes, *J. Chin. Chem. Soc.* 57 (2010) 244–251.