PREPARATION AND CHARACTERIZATION OF MONOMERIC AND POLYMERIC Ni-CYCLAM ETHYLENEDIOXYTHIOPHENE COMPLEX

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Introduction

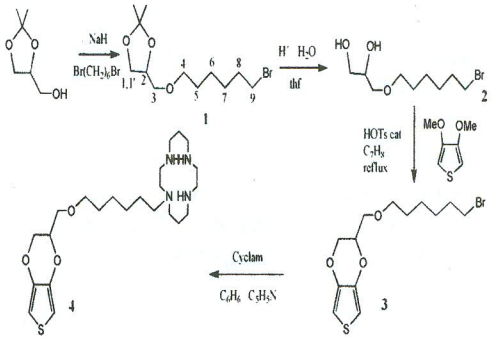
The chemistry of the monomer 3,4-ethylenedioxythiophene (EDOT), has been investigated thoroughly in recent years with the aim of developing synthetic routes to prepare tailor-made functionalised EDOT derivatives. Poly(3,4-ethylenedioxythiophene) (PEDOT) is a particularly stable polythiophene derivative. The electron rich oxygen-bridge in EDOT unit greatly lowers the redox potentials of both the monomer and the polymer compared to bare thiophene. In the present study, we have chosen cyclam, a square planar macrocyclic system, because it forms non-labile complexes of Ni(II) oxidation state while leaving coordination sites free for the formation of octahedral intermediates during reactions with electrophiles.

Materials and Methods

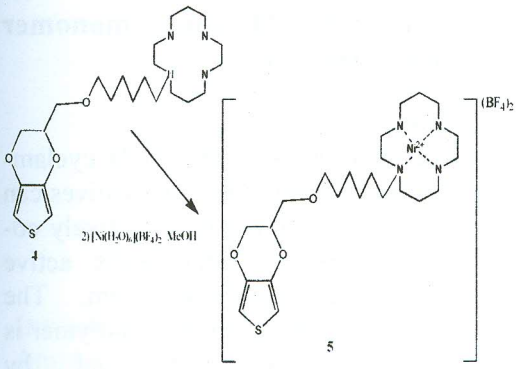
For the electrochemistry experiment, tetrabutylammonium tetrafluroborate (Bu_4NBF_4) and anhydrous CH_3CN (99.97 %, electrochemistry grade) were used. All the solvents and electrolytes were handled under Schlenk conditions. The three-electrode electrochemical cell was used with separate compartments of the working (glassy carbon, 0.1 mm diameter), the auxiliary (Pt gauze),and Quasi reference (Polypyrolle coated Pt wire) electrodes. The potentiostat was an Autolab PG-30 (EcoChimie, Netherlands). X-Ray Photoelectron Spectroscopy (XPS) was recorded in a Scienta ESCA 300 spectro meter (Daresbury laboratory, U.K). Thin film of copolymers were grown on the Au coated glass plate (11 mm x 11 mm) by repetive scan cyclic voltammetry for XPS analysis

Results and Discussion

3,4 Dimethoxythiophene and complex **3** were prepared as described previously (Velauthamurty and Higgins, 2009). Treatment of **3** with 1,4,8,11-tetraazacyclotetradecane (cyclam) in benzene/ pyridine in the presence of catalytic amount of 4-(dimethyl- amino)pyridine gave a brown coloured semisolid which has been identified to be functionalized EDOT-cyclam **4**.



Scheme 1. Syntheses of ligand 4



Scheme 2. Syntheses of Complex 5

Synthesis of EDOT–functionalized ligand and complexes

Spectroscopic and analytical data indicated that it was sufficiently pure to use as prepared. Reaction of **4** with $[Ni(H_2O)_6(BF_4)_2]$ in MeOH gave sparingly soluble complex **5**. The microanalytical and mass spectrometry data were consistent with the expected formula, $[M(BF_4)_2(\mathbf{4})_2]$ where $M = Ni^{2+}$.

XPS Characterization of the copolymer 5

The Ni 2p spectrum shows two main peaks due to Ni $2p_{3/2}$ and Ni $2p_{1/2}$ at 832 eV and 858 eV, respectively. The peaks due to N 1s, O 1s and S 2p were observed at 402.5, 532.9 and 164.1 eV, respectively. XPS data confirms that the Ni (II) is coordinated through 4 N atoms of Cyclam and the unit containing this coordination complex attached to EDOT through the spacer group has been incorporated intact into the copolymer

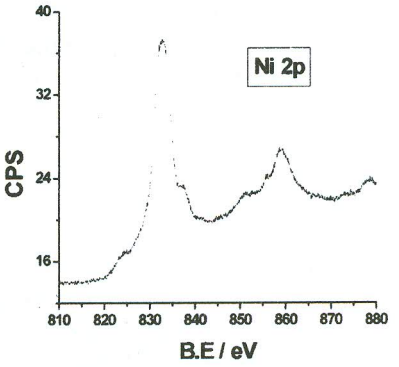


Figure 1. XPS data for the copolymer : Ni 2p region

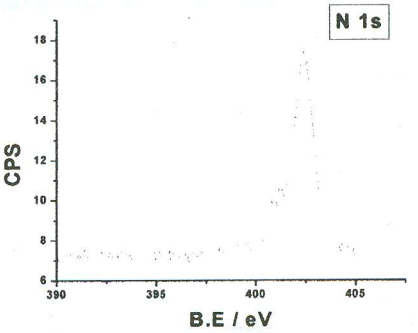


Figure 2. XPS data for the copolymer: N 1s region

Interestingly the ratio of Ni:N was found to be 1:4 indicating that the square planar coordination around Ni(II) has not been disturbed during polymeriz- ation.

Electrochemical synthesis of complex 5 The electrochemical oxidation of 5 alone did not result in the formation of polymer films on the electrode surface. We therefore attempted to grow polymer films from electrolyte solutions containing **5** and EDOT (5:1 mole ratio; 0.01 M total monomer concentration) using repetitive scan cyclic voltammetry as shown in Figure 3 and we were fortunate to get redox-active polymer

films deposited on the electrodes. The Figure 3B shows a chemically reversible oxidation peak at + 1.08 V due to the Ni(III)/Ni(II) couple.

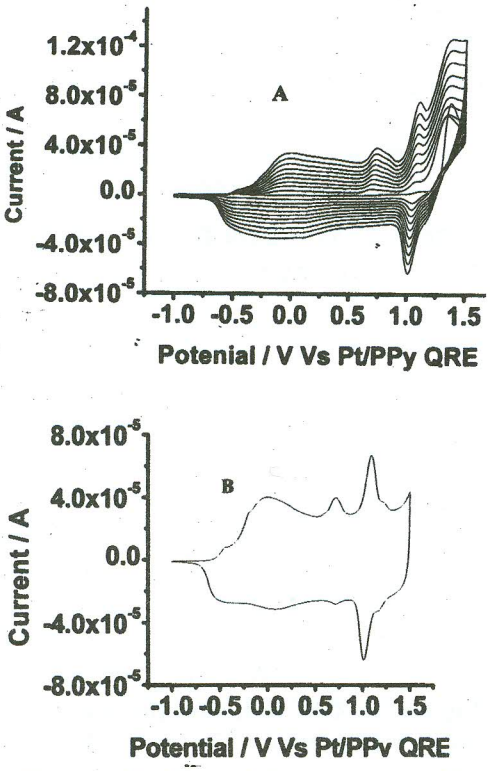


Figure 3. Repetitive scan cyclic voltammograms in the growth of copolymer EDOT:5 copolymer (A) and cyclic voltammogram of an EDOT:5 copolymer in the background electrolyte (B) Conditi -ons used were scan rate of 100 mV s^{-1} in 0.1 M Bu_4NBF_4/CH_3CN electrolyte with 0.01 M total monomer concentration.

Conclusion

We have shown that Ni(II) cyclam-funcationalised EDOT derivatives can be synthesized and be effectively co-polymerized to form redox active conjugated copolymer film. The presence of Ni(II) in the copolymer is confirmed by XPS and by electrochemical method. This successful co-polymerization opens up the possibility of using this copolymer as an electrocatalyst in the reduction of alkyl halides.

Acknowledgement

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References

Velauthamurty. K, Higgins. S. J, Rajapaksae. R. M. G., Bacsa. J, Zalinge. H, Nichols. R. J and Haiss. W. (2009). Synthesis and characterization of monomeric and polymeric Pd(II) and Pt(II) complexes of 3,4-ethylenedioxy thiophene functionalized phosphi- ne ligands. Journal of Materials Chemistry, 19: 1850-1858.