SYNTHESIS OF MONOMERS AND POLYMERS BASED ON METAL [Pd(II), Pt(II), Ru(II), Ni(II) AND Cu(II)] FUNCTIONALISED 3,4–ETHYLENEDIOXYTHIOPHENE COMPLEXES AND THEIR CHARACTERIZATION

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SYNTHESIS OF MONOMERS AND POLYMERS BASED ON METAL [Pd(II), Pt(II), Ru(II), Ni(II) AND Cu(II)] FUNCTIONALISED 3,4–ETHYLENEDIOXYTHIOPHENE COMPLEXES AND THEIR CHARACTERIZATION

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Ruthenium, palladium and platinum metals with phosphine ligands are known to have applications in various fields of catalysis, including hydrogenation, isomerization and hydroformylation reactions. The application of metal phosphine and metal-cyclam functionalised EDOT complexes in some exciting new areas currently opening up to inorganic chemists, for example modified electrodes and conducting polymers. Functionalisations of electrodes with the redox–active and catalytically active metal complexes are of particular interest, since these have potential applications in sensing, electrocatalysis and especially in electrochromics.

More recently, a range of new EDOT derivatives functionalised with phosphine ligands, either pendant from the ethylene bridge (**59** and **63**) or attached directly to the thiophene 2-position (**50**) were investigated. Stable Pd(II), Pt(II) and Ru(II) complexes with these ligands were prepared. Normally tetraazamacrocycle complexes of 3d metals are electrocatalytically active. As such the synthesis and characterization of EDOT derivatives functionalised with 1,4,8,11-tetraazacyclo tetradecane (cyclam) ligand pendant to the ethylene bridge and prepared stable Cu(II) and Ni(II) complexes with these ligands were investigated.

Further stable Pt(II), Pd(II) and Ru(II) bis-EDOT derivatives functionalized with phosphines (**69**) were prepared. Interestingly these complexes succeed in making copolymers containing intact complexes, whereas the corresponding EDOT complexes failed to give the polymer.

Using the co-polymerization technique, all the complexes of copolymers were prepared. The functionalised PEDOT copolymer films were formed using electrolyte solutions containing functionalised EDOT complexes and EDOT (1:5 mole ratio; 0.01 M total monomer concentration), using repetitive scan cyclic voltammetry, on Pt, G.C, Au and ITO coated glass electrodes.

The copolymer was characterized by using electrochemical methods such as cyclic voltammetry, electrochemical impedance spectroscopy, X-Ray photoelectron spectroscopy, X-Ray fluorescence spectroscopy, and Electron dispersive spectroscopy. These characterization techniques established that the polymers made in the presence of $[MCl_2(\mathbf{50})_2]$ consisted only of poly-(3,4-ethylenedioxythiophene), whereas polymers made in the presence of other metal complexes were genuine co-polymers containing Ru(II), Pd(II), Pt(II) complexes.

This represents a new technique for depositing catalytically-active metal complexes of functionalised PEDOT-phosphine and PEDOT-cyclam matrices, for instance, on array supports for high-throughput synthetic devices or microfluidic systems. The successful polymerization of metal-cyclam functionalised EDOT further opens up the possibility of using the electrogenerated polymers as electrocatalysts in the reduction of alkyl halides. Also it was found that this method affords a better control of the metals concentration in the polymer matrix.