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Preparation and characterization of Pt^{2+}, Pd^{2+} and Ru^{2+} functionalised 3, 4-ethylenedioxythiophene

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Efforts to incorporate covalently-bound metal complexes into electrogenerated conjugated polymer films have been stimulated by the possible applications of the resulting films in electrocatalysis, electrochromic devices and sensing. Most work to date has been performed using derivatives of thiophene or pyrrole. The former have very positive oxidation potentials, limiting the range of metal complexes that can be employed. The latter have the advantage of lower monomer oxidation potentials, but often form conjugated polymers that are not stable to redox cycling. Derivatives of 3,4-ethylenedioxythiophene (EDOT) combine the best features of thiophenes (robust conjugated materials, relatively straightforward synthetic chemistry) and pyrroles (lower oxidation potentials; polymers often stable to redox cycling in water). We have used PEDOT derivatives to develop electrochemical sensors for proteins and for oligonucleotides.

More recently, we have investigated a range of new EDOT derivatives functionalised with phosphine ligands, either pendant from the ethylene bridge, or attached directly to the thiophene 2-position. We have made stable Pd(II), Pt(II) and Ru(II) complexes with these ligands, and we have investigated the electrogeneration of polymer films containing the complexes by copolymerisation with EDOT. This could represent a new technique for depositing catalytically-active metal complexes, for instance on array supports for high-throughput synthesis devices, or microfluidic systems. The films have been characterised using electrochemical methods and X-Ray photoelectron spectroscopy. Results suggest that it is necessary to include a 'spacer' between the EDOT unit and the phosphine complex in order to succeed in making copolymers containing intact complexes.

Keywords: Electrochemical methods, X-Ray photoelectron spectroscopy, Metal-phosphine complexes.

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