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### ACCEPTED MANUSCRIPT

<AT>Novel hybrid based on a poly[Ni(*salen*)] film and WO<sub>3</sub> nanoparticles with electrochromic properties

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#### <ABS-HEAD>ABSTRACT

<ABS-P>The strategy of combining electroactive polymers and inorganic nanomaterials has been widely explored in recent years in order to improve some of their properties, namely electrocatalysis and electrochromism. This report focuses on a new composite prepared through the electropolymerization of the transition metal complex [Ni(3-Mesalen)], designated as [1], in the presence of WO<sub>3</sub> nanoparticles (NPs) and its electrochromic (EC) performance. The WO<sub>3</sub> NPs were prepared using tungsten metal powder; their characterization indicated quasi-spherical morphology, high crystallinity and particle sizes in the range 30 - 40 nm. The nanocomposite WO<sub>3</sub>@poly[1] films displayed similar electrochemical responses to those of pristine poly[1] films in LiClO<sub>4</sub>/CH<sub>3</sub>CN, but higher electroactive surface coverages, an advantage of NPs incorporation in the nanocomposite. The presence of the WO<sub>3</sub> NPs in the poly[1] matrix was assessed by X-ray photoelectron spectroscopy and scanning electronic microscopy. The nanocomposite presented similar electronic spectra to those of poly[1], indicating that the electronic structure of the pristine film is maintained in the nanocomposite, but exhibited lower  $\varepsilon$ -values for bands associated with charge transfer transitions for high oxidised states, revealing an enhanced stability towards ligand over-oxidation.

<ABS-P>The WO<sub>3</sub>@poly[1] nanocomposite showed more favourable EC properties in LiClO<sub>4</sub>/CH<sub>3</sub>CN than the pristine film. For typical coverages ( $\Gamma$  = 0.06-0.10 µmol cm<sup>-2</sup>) the composite showed lower switching times ( $\tau$  = 1.3 - 3.6 s), higher optical contrast ( $\Delta T \approx 31$  %, an improvement of ca. 40 %) and better colouration efficiencies (in the range  $\eta$  = 104 - 115 cm<sup>2</sup> C<sup>-1</sup>, improvement of ca. 13 - 22 %).

<KWD>Keywords: Electrochromism; Electroactive polymers; Metal salen complexes;

Tungsten trioxide; Polymeric nanocomposites.

#### <H1>1. INTRODUCTION

The science and technology of conducting polymers (CPs, also called conjugated polymers or synthetic metals) have travelled a long way since the discovery of polyacetylene in 1970 [1,2]. These materials are characterized by a backbone based on alternating single/double bonds, typically formed from aromatic monomers (e.g. thiophenes, pyrroles and anilines), and have the ability to undergo reversible oxidation (p-doping) and reduction (undoping), which allow them to switch between neutral (insulating) and oxidised (conducting) forms [3].

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