



Electrochemically synthesised xanthone-cored conjugated polymers as materials for electrochromic windows

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ABSTRACT

In this work, we present the electrochemical polymerisation process of triarylamine-xanthone derivatives and behaviour of the formed polymers using various potentiodynamic techniques. The formed electropolymers have limited conjugation but show very promising electrochromic behaviour. Furthermore, by coupling the electrochemical analysis with each polymer's spectroscopic output, we were able to evaluate doping processes and the type of charge carriers formed. Through careful analysis, we were able to describe the electropolymerisation process and formed triarylamine-based polyxanthone derivatives. The polymers were found to exhibit good stability and good colouration efficiency to suggesting that they have potential application in electrochromic devices.

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1. Introduction

All-organic electroactive materials have seen rapid growth in publication output and commercial development for use in optoelectronic applications [1,2] such as in organic light-emitting diodes (LEDs), photovoltaic cells, field-effect transistors [3,4] and lasers [5]. The current interest in these materials can be attributed to their surmounting practical benefits over heavy metal materials, including lower production cost, flexibility, and reduced environmental footprint.

For newly developed optoelectronic materials to be competitive with commercial counterparts they must contain properties that allow for the amelioration of device efficiency, lifetime and running or mass-production costs. This requires the production of new materials with good electrical conductivity, defined charge carrier balance and tuned transitional ground and excited states. Polymers

have been flagged as materials amenable to extend the potential of organic optoelectronics [6] due to the fact that they are easy to deposit [7,8] from spin-coated/solution processing techniques, creating layers that are less costly (when compared to vacuum deposition methods) and are known to form amorphous device layers [9,10] with fewer crystalline domains, resulting in improved reproducibility and transport characteristics [8]. Furthermore, polymeric materials display significant synthetic flexibility allowing for variable physical and electronic properties such as HOMO/LUMO band gaps [11] and emissive properties [6,12] as well as significant changes in carrier mobility and chemical stability [13,14].

Electropolymerisation has a long history [15], spanning back to the 1970s-1980s of polymerisation of aromatic heterocyclic materials such as anilines [16], fluorenes, thiophenes [17], carbazoles, pyrenes and indoles [18,19]. This technique has already been acknowledged as a unique method in order to create new electroactive materials with improved transport, thermal, and mechanical properties required for useful optoelectronic constituents [20], leading to cost-effective printing initiatives [21]. Electropolymerised conjugated compounds could also be used as unique materials for electrochromic windows in which electrochemical

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doping causes changes in absorptivity due to the formation of polaronic/bipolaronic moieties in the polymer structure [22–26]. Such electrochromic windows could absorb in a broad range of the visible light spectrum [25–29], potentially creating black electrochromic materials [29–31].

Here we present an electrochemical investigation of three electroactive donor-acceptor-donor (D-A-D) materials, with triarylamines and xanthone to be used as electropolymerised materials for potential electroactive applications. While triarylamines such as diphenylamines (DPA) have already been shown to electropolymerise well [20,32–35], the mechanism of polymerisation, including polymerisation site, and extent of branching have been pinpointed using a combination of complimentary potentiodynamic techniques not previously highlighted in the literature. Furthermore, both DPA [36–39] and xanthenes [40,41] have been shown to be useful electroactive materials for applications such as Organic Light Emitting Diodes (OLEDs) and so it was considered that merging these properties would obtain excellent materials for our investigation (Scheme 1) and has thus been proven to be useful materials for electrochromic windows, with comparable colour efficiency to the few literature examples [42–44].

2. Experimental section

2.1. Materials

All commercially available compounds were used as received. All solvents for the synthesis were dried and then distilled before use. Electrochemical measurements were performed in 10^{-3} M concentrations of the monomers. Electrochemical studies were conducted in 0.1 M argon purged solutions of Bu_4NBF_4 (dried), 99% (Sigma-Aldrich) in dichloromethane (DCM), CHROMASOLV[®], 99.9% (Sigma-Aldrich) and acetonitrile, 99.9%, Extra Dry, AcroSeal[™] (ACROS Organics) solvents at room temperature. UV–Vis–NIR spectroelectrochemical measurements were performed on an Indium Tin Oxide (ITO) coated quartz working electrode. Polymeric layers were synthesised on an ITO electrode in conditions similar to that of cyclic voltammetric measurements.

2.1.1. General synthesis

The detailed methodology for the synthesis of triarylamines based on xanthone is depicted in Scheme 2 and the molecular structures of the synthesised derivatives are illustrated in Scheme 1. The starting bromo derivative, 2,7-Dibromoxanthen-9-one required for the present study was synthesised according to the reported procedure [45] and the bromo precursor was conveniently converted to the triarylaminated derivatives by treating it with the corresponding diarylamine using a palladium catalysed Buchwald–Hartwig amination reaction [46,47], utilising palladium–bis(dibenzylideneacetone) [$\text{Pd}(\text{dba})_2$] as a catalyst, 2-dicyclohexylphosphino-2',6'-dimethylbiphenyl (SPhos) as a ligand and sodium-tert-butoxide as a base, under nitrogen atmosphere for 12–24 h at 100 °C, giving derivatives **XDPAOMe**, **XNAP** and **XDPA** with a yield of more than 50% (SI) [48].

2.2. Measurements

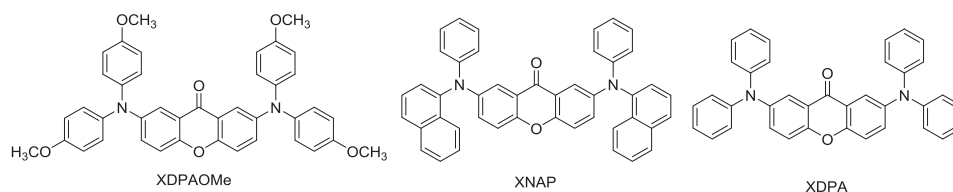
^1H NMR spectra and ^{13}C NMR spectra were recorded using CDCl_3 on a Bruker 300 Ultrashield spectrometer with Tetramethylsilane (TMS) as an internal reference at a working frequency of 300 MHz and 75 MHz, respectively. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Frontier 91579. High Resolution Mass spectrometric measurements were recorded on a TOF Micromass YA-105 H <superscript></superscript> R-MS system. The electrochemical investigation was carried out using Autolab PGSTAT20 and PGSTAT100 (Metrohm Autolab) potentiostats. The electrochemical cell comprised of a platinum disk with 1 mm diameter of working area as the working electrode, silver wire electrode as the reference electrode and a platinum wire as the auxiliary electrode. The reference electrode was calibrated against a ferrocene/ferrocenium (Fc/Fc^+) redox couple in the same conditions (solvent, salt) for all electrochemical measurements. Cyclic voltammetry measurements were conducted at room temperature with a scan rate of 100 mV s^{-1} . UV–Vis–NIR spectra in the spectroelectrochemical analysis were recorded on a HP 8453 spectrometer and Ocean Optics QE6500. In situ EPR spectroelectrochemical experiments were performed using a JES-FA 200 (JEOL) spectrometer. The g-factor value was determined with the aid of a JEOL internal standard, knowing that the third line of the Mn-standard spectrum has a g-factor of 2.03324. The width of the EPR signal has been calculated as a distance in mT between the minimum and the maximum of the spectrum.

3. Results and discussion

3.1. Electrochemical investigation of monomers and electropolymerisation

Electrochemical and spectroelectrochemical studies of the three materials show remarkably different responses and their electropolymerisation (or lack thereof) was analysed using various electrochemically driven techniques. CV of **XDPAOMe** shows a 3-step oxidation with no discernible reduction step in dichloromethane solvent (Fig. 1a and supplementary Fig. S1a). Within the oxidation window, there are two reversible redox couples close to each other at +0.32 V and +0.45 V and a single irreversible oxidation peak at +0.90 V. During consecutive positive potential sweeps of **XDPAOMe**, no side reactions are observed. The good reversibility of the redox process could be explained due to its molecular structure. As **XDPAOMe** contains methoxy units in the 4 position of the DPA donor benzenes, these moieties block the oxidative active site and subsequently remove the possibility of side reactions occurring on the working electrode.

CV of **XNAP**, on the other hand, displays shows two reversible redox couples at +0.55 and +0.70 V (Fig. 1b). As seen in **XDPAOMe**, no reduction of the xanthone moiety is observed (Supplementary Fig. S1c). Continual oxidative sweeps reveal the growth of an electropolymer, (**polyXNAP**), upon the working electrode, indicated by a sharp increase in peak current. The converging of oxidation peaks in subsequent scans to one value equal to +0.65 V



Scheme 1. Monomers studied in this work.

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