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Short Communication

Terpyridine-based metallopolymer thin films as active layer in ammonia sensor device

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ABSTRACT

A metal-containing polymer has been prepared by electropolymerization of an homoleptic Ru(II)-terpyridine complex bearing pyrrole heterocycles. The polymer is obtained as a thin film at the surface of electrodes, and has been characterized by electrochemical measurements, XPS and microscopy. It has been shown that this polymer acts as an active gas sensitive layer since it enables the detection of an ammonia gas flow through layer's resistivity measurements.

1. Introduction

Chemical sensors are widely used nowadays for the detection of various analytes such as explosives [1], heavy metals [2] or Volatile Organic Compounds [3] to name a few. Detection is possible through the measurement of the variation of a physical property of an active layer (*e.g.* fluorescence, resistivity) in the presence of the analyte to be detected. Many materials are available to act as active layers. Examples include conjugated polymers [4], Metal-Organic-Frameworks (MOFs) [5], nanoparticules [6] or Molecularly Imprinted Polymers (MIPs) [7,8]. Polythiophenes bearing pendant terpyridine moieties have been already used as active layers in electrochemical sensors for metallic cations [9,10]. But to the best of our knowledge, metal-containing polythiophenes, polyselenophene or polypyrroles with in-chain terpyridines have not been evaluated as potential materials for gas sensing devices. Since these materials are easily prepared and polymerized onto electrodes surfaces [11–15], they could be a valuable option for the fabrication of this kind of sensors devices. This paper describes first the synthesis and the characterization of a thin film of metallopolymer **1** (Fig. 1) onto electrodes surfaces and second its assessment as an active layer for ammonia sensing.

Detection of ammonia in the air is a key issue to protect the environment and people's health. High concentrations are easy to detect with human nose because the gas has a very penetrating odor. The lower limit of human ammonia perception by smell is tabulated to be around 50 ppm. However, even below this limit, ammonia is irritating to the respiratory system, skin and eyes. Thus, it is necessary to detect such substance with high sensitive devices.

2. Experimental

2.1. Synthesis

All reagents were purchased from commercial suppliers and used as received. 2-acetylpyridine and pyrrole-2-carboxaldéhyde are commercially available. All compounds are controlled by NMR ^{1}H and ^{13}C. Spectra were recorded on a Brucker AC 300 at 300 MHz. Melting points were measured with a Stuart SMP 3 melting point apparatus and are uncorrected. All these analysis are not presented in this paper.

2.2. Electrochemistry and surface characterization

Electrochemical measurements were carried out using a PGSTAT30 AUTOLAB potentiostat and a classical three-electrode setup consisting of a Ag/AgCl/KCl (3 M) reference electrode (205 mV/SHE), a platinum wire counter-electrode and a working

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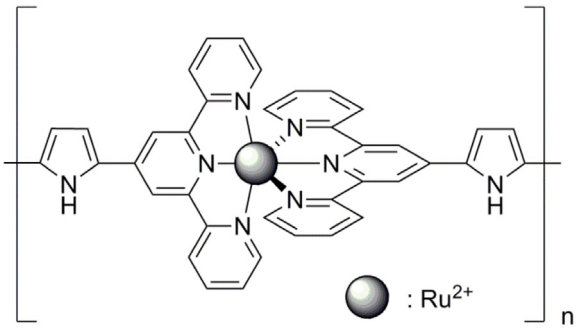


Fig. 1. Chemical structure of metallopolymer **1** (counter-anions omitted).

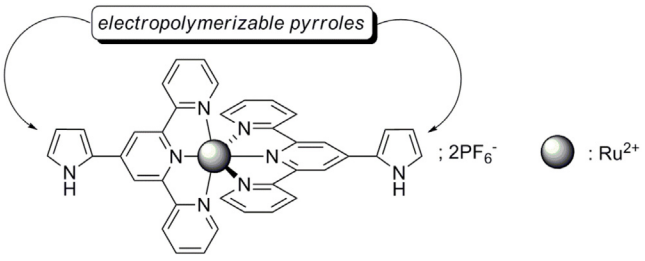


Fig. 2. Molecular structure of monomer **2**.

electrode on which the deposit was realized. X-ray Photoelectron Spectroscopy (XPS, Thermo VG spectrometer) was used to control elemental composition and oxidation state of elements at the surface. All spectra were recorded at a 45° take-off angle, relative to the substrate with a spectrometer using monochromatized Al Kα radiation (1486.6 eV). The binding energies of the core-levels were calibrated against the C1s binding energy set at 285.0 eV, an energy characteristic of alkyl moieties. The peaks were analysed using mixed Gaussian–Lorentzian curves (80% of Gaussian character).

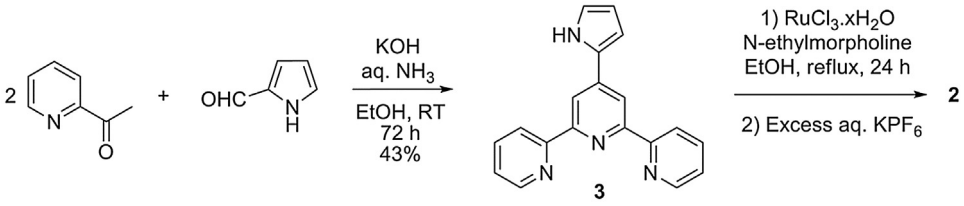
Scanning electron microscopy (SEM) characterization was carried out using FEI 450 apparatus.

2.3. Sensor technology – gas sensitive layer deposition

Sensitive layers were elaborated onto commercial sensor platform (Hearaeus® MSP 632) made with interdigitated electrodes (platinium) deposited on a ceramic substrate. This platform enabled both the layer's temperature to be controlled and the layer's electrical properties to be measured.

2.4. NH_3 procedure detection

To perform the gas tests, the NH_3 flow was obtained from a certified commercial cylinder (100 ppm NH_3 diluted in dry air). The electrical response of the sensor was obtained by computing the electrical resistance versus exposition time. The sensor was exposed to a constant dry air flow (100 mL min^{-1}) for 24 h before conducting each experiment under pollutant (conditioning



Scheme 1. Synthetic pathway towards monomer **2** from commercially available reagents.

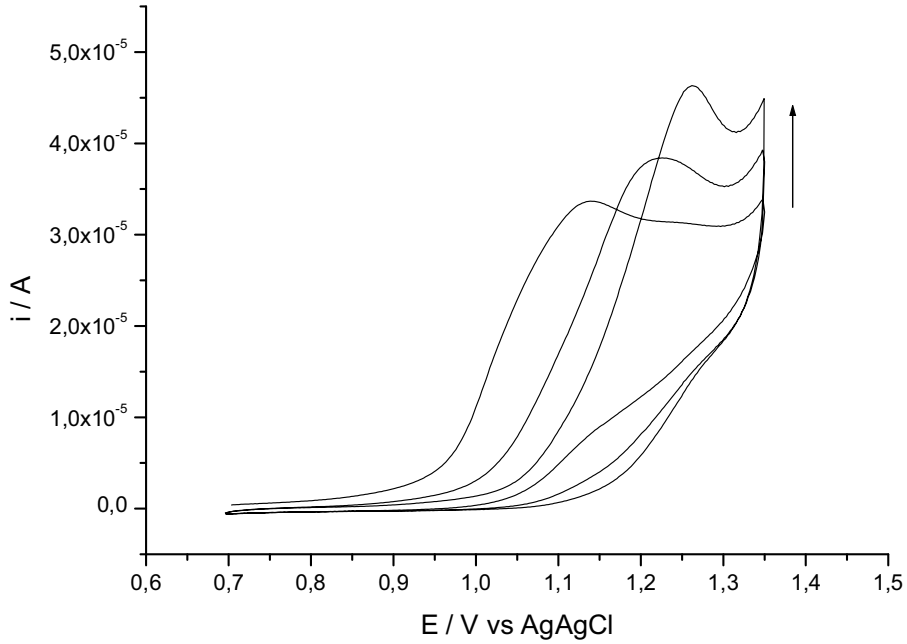


Fig. 3. Cyclic voltammogram (50 mV/s) of 2 mM of complex **2** in 0.1 M tetraethylammonium tetrafluoroborate acetonitrile solution on platinum disk (0.038 cm^2). The arrow indicates current evolution with cycle number increase.