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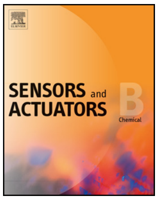

Colorimetric detection and determination of Fe(III), Co(II), Cu(II) and Sn(II) in aqueous media by acrylic polymers with pendant terpyridine motifs

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ABSTRACT

Colorimetric cation responsive water soluble polymers and manageable films or membranes have been designed. The sensory materials respond with a colour change to the presence in water of Fe(III), Co(II), Cu(II), and Sn(II). The colour change is specific of each metal cation, and enables its identification (purple for iron, orange for cobalt, green for copper, and yellow for tin). The design of the materials relies on an addition monomer having a terpyridine moiety, which behaves as a dye in presence of transition metal cations due to its proven chelating capability towards these species and the colour development that always accompany the metallic complex formation. Water solutions of the sensory linear polymers allow for the UV/vis titration of Fe(III), Co(II), Cu(II), and Sn(II) with a limit of detection of 1.3×10^{-7}, 6.4×10^{-8}, 1.3×10^{-5} and 1.4×10^{-5} M, respectively. On the other hand, sensory kits, cut from sensory membranes, permitted the visual quantification of the cations in a dynamic range of five decades (1×10^{-7} to 5×10^{-3} M) for Fe(III) and Co(II) and of two decades (9×10^{-5} to 9×10^{-3} M) for Cu(II) and Sn(II). Titration curves can also be drawn from a picture taken to the sensory kits with a smartphone, by using the digital colour definition of the materials as analytical signal. Also, after entering into contact with hands, shapes of metallic objects (iron and cobalt containing tools) can be colour revealed by pressing the hands on paper or cotton fabrics wetted with water solutions of the linear sensory polymer.

1. Introduction

The costless, in situ, and fast detection and quantification of transition metal cations in pure water are of the utmost environmental, industrial, and health importance. Traditional techniques, such as atomic absorption spectroscopy (AAS) or inductively coupled plasma mass spectrometry (ICP-MS), enable the selective and precise detection and quantification of the mentioned chemical species. However, they are heavy, bulky, extremely expensive techniques and require trained personnel. On the other hand, chemical sensors have become a simple species detection method for non-trained personnel, especially if the transduction is chromogenic (i.e., by a colour change) and the detection can be carried out visually.

Chemical sensors are an emerging technology with expanding applicability to a number of fields, such as civil security, environmental control and remediation, medicine, and industrial control. Moreover, sensory polymers, which are macromolecules that have receptor motifs (or binding sites) in their structure, represent a step further and show significant advances over discrete (or low molecular mass) chemosensors. Thus, polymers can be prepared or transformed into films, coatings or finished sensory materials with different shapes. Distinct polymer geometries are achievable (linear, spherical, and tridimensional crosslinked network). They can be easily designed to work in hydrophobic or hydrophilic environments and can be used to sense both vapours and liquids. Also, they exhibit collective properties sensitive to minor perturbations. Finally, their sensory moieties cannot migrate with the concomitant increase in the performance stability along time, improve in the thermal and chemical resistance, and can be easily reused.

Chemosensory polymers following a research methodology based on a guaranteed of success strategy have been prepared.

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That is to say, once chemical species to be detected are selected, the so-called targets, fully confident receptors for such targets are looked in scientific literature to find, usually, discrete organic molecules that are insoluble in water; then, their chemical structure is slightly modified by including a polymerizable group; and finally it is copolymerized with commercial hydrophilic and hydrophobic monomers to have water soluble linear polymers and crosslinked membranes with gel structures that allow for the detection in 100% water. The target species for this work are transition metal cations (Fe(III), Co(II), Cu(II) and Sn(II)), and the receptor core is based on a terpyridine (2,2′:6′,2′′-terpyridine, tpy) motif.

Morgan and Burstal isolated tpy and described its purple complex with iron(II) in the 1930s [1]. Since then tpy has become one of the most used ligands with multiple applications in different research and technological areas, such as coordination polymers [2–4]; sensors for anion [5–8], cations [9–17], both [18,19], and biomolecules [20,21]; gelation and solvochromic sensors [22]; luminescent converters [23–25]; photon harvesting [26] and catalysis [27]. Terpyridine derivatives are multivalent pyridine ligands that exhibit strong binding affinity towards a broad set of transition metal cations. This extremely strong interactions come both from the dπ-dπ* back bonding of the cations to the *N*-heterocycle rings and from the chelate effect [28,29].

Here, the tpy structure has been modified with a polymerizable methacrylamide group and two kind of chromogenic sensory materials have been prepared: linear polymers and solid film-shaped dense membranes comprised of crosslinked polymer networks. The tpy-monomer (~1% mol) was copolymerized with a balance of hydrophilic and hydrophobic commercial co-monomers (~99% mol) to give linear copolymers and networks (membranes). The linear polymers are water soluble. The membranes are solid, exhibit gel behaviour, and can be used to prepare manageable solid sensory kits. Both type of materials respond with development of different colour depending on the presence of Fe(III), Co(II), Cu(II) and Sn(II) in 100% water under controlled acidic conditions. The detection in 100% water is relevant for real-life environmental applications, whereas the acidic conditions avoid the analytical complexity of dealing with presence of different species of each cation (for instance, for iron at pH 2 only Fe^{3+} species are present, while at pH > 2 there are different equilibria of Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2{}^{+}$, and $Fe(OH)_3$). Also, the usual presence in most research studies of organic solvents, due to the insolubility in water of conventional probes, influence the selectivity of the tpy core [30].

2. Experimental part

2.1. Materials

All materials and solvents were commercially available and used as received, unless otherwise indicated: 2-acetylpyridine (98%, Alfa Aesar), iodine (≥99.8%, Sigma–Aldrich), 4-nitrobenzaldehyde (99%, Alfa Aesar), ammonium acetate (97%, Alfa Aesar), tin chloride anhydrous (98%, Alfa Aesar), methacryloyl chloride (97%, Alfa Aesar), triethylamine (TEA) (≥99%, Aldrich), pyridine (≥99%, Probus), sodium hydroxide (99.9%, VWR-Prolabo), hydrochloric acid (37%, VWR-Prolabo), *N*-methyl-2-pyrrolidone (NMP) (99%, Aldrich), ethanol (99.97%, VWR-Prolabo), diethyl ether (≥99,5%, Aldrich), $SnCl_2$ anhydrous (98%, Alfa Aesar), $Fe(NO_3)_3{\cdot}9H_2O$ (VWR-Prolabo), $Cu(NO_3)_2{\cdot}3H_2O$ (98%, Sigma–Aldrich), $Co(NO_3)_2{\cdot}6H_2O$ (≥99%, Labkem), NaCl (≥99%, Sigma–Aldrich), KCl (99.5%, Scharlau), $Al(NO_3)_2{\cdot}9H_2O$ (≥989%, Sigma–Aldrich), $Pb(NO_3)_2$ (≥99%, Fluka), LiCl (≥99%, Sigma–Aldrich), $Zn(NO_3)_2{\cdot}6H_2O$ (98%, Aldrich), $Mg(NO_3)_2{\cdot}6H_2O$ (≥99%, Labkem), $Cd(NO_3)_2$ (98.5%, Alfa Aesar), $Ni(NO_3)_2{\cdot}6H_2O$ (98.5%, Sigma–Aldrich), methyl methacrylate (**MMA**) (99%, Aldrich), 1-vinyl-2-pyrrolidone (**VP**) (≥99%, Sigma–Aldrich), ethylene glycol dimethacrylate (**EGDMMA**) (98%, Sigma–Aldrich), Azo-bis-isobutyronitrile (AIBN, ≥98%, Aldrich) was recrystallised twice from methanol.

2.2. Instrumentation and measurements

^{1}H and ^{13}C NMR spectra were recorded with a Varian Inova 400 spectrometer operating at 399.92 and 100.57 MHz, respectively, with deuterated chloroform ($CDCl_3$) as the solvent.

UV/vis spectra were recorded using a Hitachi U-3900 UV/vis spectrophotometer.

Infrared spectra (FTIR) were recorded with a FT/IR-4200 FT-IR Jasco spectrometer with an ATR-PRO410-S single reflection accessory. Low-resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV on an Agilent 6890 N mass spectrometer. Thermogravimetric analysis (TGA) data were recorded for a 5-mg sample under a nitrogen or oxygen atmosphere on a TA Instrument Q50 TGA analyser at a scan rate of $10\,^{\circ}C\,min^{-1}$. The limiting oxygen index (LOI) was estimated using the following experimental Van Krevelen equation: LOI = 17.5 + 0.4 CR, where CR is the char yield weight percentage at 800 °C, which was obtained from the TGA measurements under a nitrogen atmosphere.

The water-swelling percentage (WSP) of the membrane was obtained from the weights of a dry sample membrane (ω_d) and a water-swelled sample membrane (ω_s) as follows: $100 \times [(\omega_s - \omega_d)/\omega_d]$ (the membrane was immersed in pure water at 20 °C until the swelled equilibrium was achieved).

To determine the tensile properties of the polymer films (membranes), strips (5 mm in width and 30 mm in length) were cut from polymer films of 112 and 115 μm thickness for **Mem1** and **Mem2**, respectively, on a SHIMADZU EZ Test Compact Table-Top Universal Tester at 20 °C. Mechanical clamps were used and an extension rate of $5\,mm\,min^{-1}$ was applied using a gauge length of 9.44 mm. At least 6 samples were tested for each polymer, and the data was then averaged.

The limit of detection (LOD) and limit of quantification were estimated by the following equations: $LOD = 3.3 \times SD/s$ and $LOQ = 10 \times SD/s$, where SD is the standard deviation of a blank sample and s is the slope of the calibration curve in a region of low concentration of target species.

The qualitative and quantitative chromogenic responses of sensory squares (~5 mm × 5 mm) cut from membranes (**Mem1** and **Mem2**) towards Fe(III), Co(II), Cu(II) and Sn(II) in water solution were studied by immersing the squares in a number of sealed vials with 1 mL of buffered water, containing each vial a known concentration of one of the target cations (pH = 2, buffer: KCl–HCl). The resident time was 24 h and the temperature 25 °C. The qualitative evaluation of the sensing performance of the materials was carried out visually. On the other hand, the quantitative study was performed using a digital picture of the sensory squares taken with a smartphone by treatment of the colour definition data of each disc (RGB parameters, R = purple, G = green, B = blue). These parameters were obtained for each square directly after taking the photograph of the set squares through using the app called ColourMeter of a conventional Android smartphone (for each square 121 (11 × 11) pixels were averaged). The three RGB parameters were reduced to one variable (PC1, principal component 1), using principal component analysis (PCA), which provided an account of >78% of the information on the three RGB parameters, thus allowing for the elaboration of simple 2D titration curves ([cation] vs. PC1) with concomitant noise reduction, without a significant loss of information, and with independence of the type of camera, lighting, quality of the image and so on [31,32].