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Synthesis and characterization of novel tetra cyclo[4]pyrrole ether as an anion recognition element for nanocomposite nitrate ion selective carbon paste electrode

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ABSTRACT

Novel tetra cyclo[4]pyrrole ether cation (C4PE) was synthesized and characterized by different spectroscopy methods. Cyclo[4]pyrrole ether was synthesized by oxidation reaction of pyrrole with Cu(II) nitrate in acetonitrile. Conductometric data in acetonitrile shows C4PE behaves as a divalent cation salt with two nitrate ions undergoing primary and secondary dissociations. C4PE was used as a recognition element in the form of a composite with carbon paste as a selective electrode for the potentiometry sensing of nitrate in water samples. The electrode has a linear response to nitrate with a detection limit of 1×10^{-5} mol L^{-1} and exhibit a Nernstian slope (57.5 ± 0.6 mV/decade) between pH 3.6 and 9.6 with a fast response time less than 10 s. The selectivity coefficient values indicate high selectivity for nitrate ions over various anions ($NO_3 > NO_2^- > Cl^- > Br^- > I^- > F^- > CH_3COO^- > SO_4^{2-} > IO_3^- > ClO_4^-$). The electrodes were used over a period of 60 days with good reproducibility. The analytical usefulness of the proposed electrode has been evaluated by its application in the determination of nitrate ions in mineral and drinking water samples.

1. Introduction

Oligopyrrolic species have grown in popularity since they became recognized targets for synthesis early in the 20th century [1–9]. This diverse class of molecules includes polypyrrole (PPy) [10–12] as well as macrocycles such as porphyrins [13–15], expanded porphyrins (*i.e.* larger analogues of porphyrins) [16,17] and calixpyrroles (stabilized porphyrinogen analogues) [18,19]. Among conducting polymers, PPy is one of the most promising for commercial applications because of its good environmental stability, simple synthesis, and higher conductivity than many other conducting polymers. Its possible applications include (but are not limited to) various sensors, functional membranes, selective coatings, polymeric batteries and capacitors, electrochromic windows and displays, *etc.* [20–25]. Recently porphyrins and related tetrapyrrolic macrocycles and other oligopyrroles, particularly expanded porphyrins and calixpyrroles, have received attention as complexation reagent. In the porphyrin systems, centers around the initially unexpected finding that expanded porphyrins can act as anion receptors. This result has made these systems potentially interesting for using in a variety of applications, including anion sensing and transportation (for example, drug delivery), as well as chromatography-based purification of anions. Whereas cation coordination generally relies on the donor ability of the pyrrolic nitrogen, neutral substrate and anion recognition is typically achieved through hydrogen bonding through the pyrrolic N–H moiety. The selectivity of the pyrrolic macrocycle in question can be readily tuned by altering the shape and/or size of the binding cavity. Cyclo[8]pyrroles, cyclo[6]pyrrole and cyclo[7]pyrrole the first members of cyclo[n]pyrroles family, were synthesized using Fe(III)-based oxidative coupling procedure from bipyrrolic subunits [26,27]. One big challenge that remains is the synthesis of cyclo[n]pyrroles using simple pyrroles as starting materials. On the other hand by research on PPy applications, especially in the field of anion-selective sensors, it has been known that different dopant anions have a special effect on the morphology and selectivity of PPy [28–30]. The special and selective structures may be formed in addition to the linear polymer network and they are probably responsible for selective responses to specific analyts. The selectivity of PPys with different doping anions probably depends on specific and selective templated oligomers which form during polymerization. Polymerization rate can be reduced with increasing the stability of pyrrole radical cations in aprotic solvent such as acetonitile and using a mild oxidizing agent, so the oligomers could be

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achieved before the polymerization is complete. In the presence of copper cation as a mild oxidizing agent, template oligomeric pyrrole can be formed. Cu(II) has been used in the synthesis of polypyrroles [31,32].

Anions play fundamental roles in a wide number of environmental and biological processes and due to their importance the development of anion sensors and chemosensors have grown in recent years and has become an important sub-area within the field of anion chemistry [33–39]. Nitrates are widely used in explosives, fertilizers, drugs and many industrial products and hence their effluents may contain appreciable concentrations of nitrates and related ions [40]. The current WHO drinking water guideline is 50 mg L^{-1} of nitrate. Nitrate in drinking water is a major health concern because of its toxicity; especially to young children. The average human daily intake of nitrate/nitrite is 95 mg day^{-1} in adults [41]. In recent decades a great interest has been applied to development of new methods based on removal and determination of nitrate in water and waste water samples including kinetic methods [42], chromatography [43], and potentiometric detection based on ion-selective electrodes (ISEs). ISEs as a simple method have several advantages, for example speed, ease of preparation and procedures, simple instrumentation, short response time, no contamination, nondestructive, unaffected by color or turbidity, wide dynamic range, and reasonable selectivity [44]. Over the past five decades, carbon paste (a mixture of graphite powder and a binder pasting liquid) has become one of the most popular electrode materials used for the laboratory preparation of nitrate electrodes, and various sensors [45–51]. Chemically modified carbon paste electrodes (CMCPEs) are prepared by addition of a suitable modifier to carbon paste. The operation mechanism of such CMCPEs depends on the properties of the modifier materials used to import selectivity and sensitivity towards the target species. In recent years, pyrrole-containing entities have emerged as among the most versatile and useful of all known anion-binding agents [52]. To the best of our knowledge, this is the first time to synthesize cyclo[4]pyrrole ether and explore some of its structural properties. Herein we report the synthesis and characterization of tetra cyclopyrrole ether and a CMCPE as proposed for the determination of nitrate in the presence of each other without any prior separation step.

2. Experimental section

2.1. Chemicals and apparatus

Pyrrole received from Merck Company was distilled and stored in a refrigerator in dark prior to use. Copper nitrate, acetonitrile and other reagents and materials were of analytical grade purchased from Sigma–Aldrich Company. Thin layer chromatography was performed on pre-coated plates of silica gel 60 F254 from Merck using ethyl acetate with hexane mixtures as the developing system. CHN analysis was carried out on Perkin-Elmer 2400. Infrared spectra were obtained in the 4000–400 cm^{-1} range using a Nicolet 100 FT-IR spectrometer. ^{1}H NMR spectra were recorded using deuterated dimethyl sulfoxide with tetramethylsilane as internal standard on a Bruker DRX500 and FT NMR spectrometer. Composition was checked by X-ray photoelectron spectroscopy (XPS) with a VG Microtech, twin anode, XR3E2 X-ray source, using Al $K\alpha = 1486.6$ eV. The size and morphology of the nanoparticles were characterized by scanning electron microscope (SEM-EDX, XL30 and Philips Netherland). A Metrohm model 713 (Herisau, Switzerland) pH-meter with a combined glass electrode was used for pH measurements. The conductance measurements were performed using a Metrohm conductometer (Model 712), in a water-bath thermostated at a constant temperature which was maintained within ±0.1 °C. The potential was measured by using a standard two-probe method by an assembled computer interface for data processing and signal acquisition, which were automatically performed on a microcomputer.

2.2. Synthesis

Our synthetic strategy is based on the use of the Cu(II) as the mild oxidizing agent which is shown in Scheme 1, so the oligomers could be achieved before the polymerization is complete in aprotic solvent such as acetonitile. Copper nitrate (0.5 mmol dissolved in 50 mL of acetonitrile) was added to pyrrole (3 mmol dissolved in 30 mL of acetonitrile) and was maintained at room temperature. Completion of cyclization reaction time was checked by absorbance measurement. After 3 days blue solution was decanted away from its black polymeric and solvent was removed by rotary evaporation (80 °C for 30 min). Then, the dark product formed and washed by double distilled water. The result of thin layer chromatography tests with hexane/ethyl acetate (1:3) was showed only one band. The product was dried in vacuum for 16 h at 50 °C to obtain C4PE as a dark product (140 mg, 42%) with the m.p. > 270 °C and studied by different structural analysis instruments.

2.3. Spectroscopic characterization

To obtain information about the elemental composition of the product, CHNO analysis was employed. Microanalysis carried out for $C_{16}H_{10}O_{10}N_6$. Calculated: C, 43.05; H, 2.24; N, 18.83%; O, 35.87. Found: C, 42.77; H, 2.26; N, 18.62%; O, 36.35. FAB-MS (m/z): [M-2] found, 444.

The FT-IR spectrum of C4PE was identified. The bands at 3106, 1462 cm^{-1} correspond to the stretching vibrations of aromatic C—H and C═C bonds respectively. There are strong bands at 1045 and 1086 cm^{-1} which are assigned to the in-plane deformation vibration of pyrrole ring. A skeletal vibration of pyrrole ring appears at 1546 cm^{-1}. The band at 1249 cm^{-1} belongs to C—O bond in unsaturated ethers. Amine vibrational stretching mode was identified at 3408 cm^{-1}. The bands at 2854 and 2921 cm^{-1} are related to nitrate and amine salt respectively [53]. The product was characterized by its ^{1}H NMR spectra. The NMR spectrum is unusually high symmetry (not shown). The signal corresponding to the NH protons in the spectrum of C4PE was recorded in DMSO at room temperature. This experiment enables assignment of the two peaks 7.45 and 6.61 ppm (relative surface area = 2.2) to the ring nitrogens with an attached hydrogen. The only two remaining signals, two singlets at 1.22 and 0.84 ppm (relative surface area = 2.2) are assigned to the β C–H protons. There are two types of signals in the spectrum (with the same relative surface area = 2.2) could indicate the presence of two isomers of C4PE whose peak area are in agreement with the proposed *cis* and *trans* conformations. It is important to appreciate that no solid-state structural information is available for C4PE nitrate.

To obtain information about the species involved in C4PE, XPS analysis was employed. XPS spectra of C4PE in a low resolution survey scan are shown in Fig. 1a. The binding energies for C1s at 285 eV, N1s at 398.7 eV, O1s at 531.5 eV, were identified. The N1s spectrum, Fig. 1b shows two peak, one broad peak with a FWHM = 3.93 eV centered at 398.75 and other at 405.77 eV with a FWHM = 2.83 eV. These asymmetrical peaks can be fitted by three peaks. The lowest energy peak centered at 398.75 is associated with pyrrolic nitrogen. The other peaks centered at 401.45 and 405.77 eV is due to nitrogens of nitrate groups that later appears at higher energy probably due to hydrogen bonding with the hydrogens linked to pyrrolic nitrogens in C4PE ring. The C1s spectrum of C4PE (Fig. 1c) shows one broad peak centered at 285 eV with FWHM = 3.28 eV. The line shape of this peak reveals an asymmetrical peak that can be fitted by two peaks. The two lowest energy peaks centered at 286.01 and 284.6 eV are associated with α- and β-carbons respectively [54].