



A novel electrochemical and chromogenic guest-responsive anisidine-based chemosensor for transition metallic cations



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ABSTRACT

A new family of *N,N*-disubstituted *p*-anisidine-based electroactive ligands bearing dipyridinylamino- (**1**), difuranylamino- (**2**) and dithiophenylamino- (**3**) binding sites has been prepared by reductive alkylation of anisidine. The electrochemical investigations, in 0.1 mol/dm⁻³ LiClO₄ acetonitrile solution, showed that upon the addition of metallic cations, the redox features of **1** underwent drastic changes due to the cation chelation. The chemosensor complexation with Ni(II), Zn(II), Cd(II) and Pb(II) led to large anodic shifts of the oxidation potential peaks up to 700 mV depending on the metal cation. A particularly high sensitivity toward nickel(II) with a higher selectivity to zinc(II) were observed. However, in the same conditions, thiophenyl- and furfuryl- derivatives showed no sensitivity for any of the investigated cations. Moreover, UV-visible spectroscopy studies of **1** showed that the compound can act as a chromogenic guest-responsive and in presence of metallic cations, the absorption bands of compound **1** shifted due to a participation of the nitrogen lone pairs in the cation complexation. UV-visible spectroscopy did also allow to distinguish between the Ni(II) and Zn(II) complexes. Electrochemical and UV-visible spectroscopic investigations showed that the complexes have 1:2 stoichiometry [M(**1**)₂]²⁺ (M: Zn, Ni, Cd and Pb).

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1. Introduction

The design of molecular probes for the detection of cationic species can reveal all its importance if one considers the pivotal role played by metallic cations in the biological [1–3] and environmental field [4,5]. Indeed, almost all cations are present in live beings at different levels of concentrations and many of them are cofactors to enzymes [6], involved in biological processes [7,8] and act as neurotransmitters in the central nervous system [9]. Meanwhile, some others such as cadmium and lead are toxic and provoke serious health damages [10,11].

Finding new organic compounds useful as transducers for the design of new chemosensors is a continuous and actual field of research [12]. Either organometallic compounds or organic compounds can be used for this purpose [13,14], although the first class of compounds seemed to have receive more attention. Purely organic compounds gained a new revival with the work pioneered by Pearson and coworkers and Sibert and coworkers. They prepared many redox-active probes for cations based *N,N'*-tetraalkylated phenylenediamines (TAPD) [12,15–20]. It has been shown

that crown-ether, crown-thioether or dipodal chelating sites linked to TAPD-based transducers represent a suitable class of probes for a variety of alkaline [16], alkaline earth [13,17,18] and transition metallic ions [18,19]. Host-guest complexes are formed and their formation is monitored through the variation of the probe spectroscopic and electrochemical features [16–19]. Moreover, they can be used for the release of picomolar amounts of Ca²⁺ with high temporal and spatial resolution if they are properly linked to a gold electrode surface [20]. *p*-Aminophenol and *p*-dihydroxybenzene redox compounds, although structurally related to TAPD group, have not received the same attention as TAPD derivatives and have not been well explored for use as transducers in cations detection [21].

In this work, the synthesis of a series of new electroactive compounds based on *p*-anisidine (a *p*-aminophenol derivative) is reported (Fig. 1). Electrochemical investigations by means of cyclic voltammetry (CV) were undertaken to examine their potential usefulness as electroactive probes for the chelation of some transition metal cations. Changes induced by the chelation process especially in the electrochemical features of the probe were found to be a useful mean to monitor the complexation reaction of the cations with larger potential shifts in comparison with results obtained by Pearson et al. [15]. Moreover, UV-visible spectroscopic studies showed that changes induced in the probe absorption bands can

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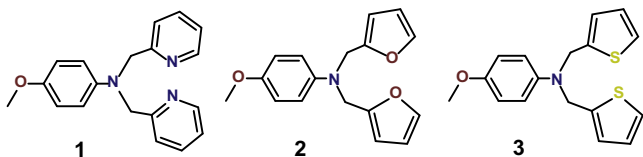


Fig. 1. Structures of *p*-anisidine-based electrochemical and chromogenic-guest responsive ligands.

used to monitor and to assess the phenomenon. The probe selectivity toward cations was also examined by studying the competition between them (see Fig. 4).

2. Material and methods

2.1. Reagents and chemicals

p-Anisidine, furfural, 2-thiophene carboxaldehyde, 2-pyridine carboxaldehyde, sodium borohydride, sodium bicarbonate, acetonitrile, methanol, ethyl acetate, cyclohexane, cadmium perchlorate ($\text{Cd}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$), nickel perchlorate ($\text{Ni}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$) and zinc perchlorate ($\text{Zn}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$) were purchased from Sigma–Aldrich (Germany) used as received except furfural was distilled prior to use. Lead perchlorate ($\text{Pb}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$) was prepared according to literature [22]. Thin layer chromatography (TLC) was performed on Fluka pre-coated aluminum sheets with F_{254} fluorescent silica gel. Preparative column chromatography was performed on Fluka silica gel 60 (0.040–0.063). Stock solutions of nickel, zinc, cadmium and lead 0.1 mol/dm^{-3} were prepared by dissolving the corresponding amounts of the metal perchlorate hydrate in acetonitrile.

2.2. Apparatus

The electrochemical experiments were conducted in 0.1 mol/dm^{-3} lithium perchlorate acetonitrile solution in a three-electrode glass cell using a PC-controlled Metrohm PGSTAT101 potentiostat. Nova software (version 1.8) was used for experiment design and data acquisition. A platinum wire, a silver/silver chloride ($\text{Ag}/\text{AgCl}/\text{Cl}^- 3 \text{ M KCl}$) and a glassy carbon disk electrode were used respectively as counter electrode, reference electrode and working electrode. Cyclic voltammograms were recorded at RT at a potential scan rate of 0.10 V s^{-1} . Metal transition ions were added as a solution of the corresponding perchlorate salts in acetonitrile. ^1H and ^{13}C spectra were recorded on a Bruker Advance 300 MHz apparatus in CDCl_3 . Chemical shifts are given in ppm according to tetramethylsilane (TMS) signals as an internal reference. IR

(ATR) spectra were measured on a PerkinElmer Alpha ATR spectrophotometer. UV–visible spectra were measured in acetonitrile using a PC-controlled UNICO 3802 double beam spectrophotometer in 1 cm-length quartz cell.

2.3. Synthesis of compound 1

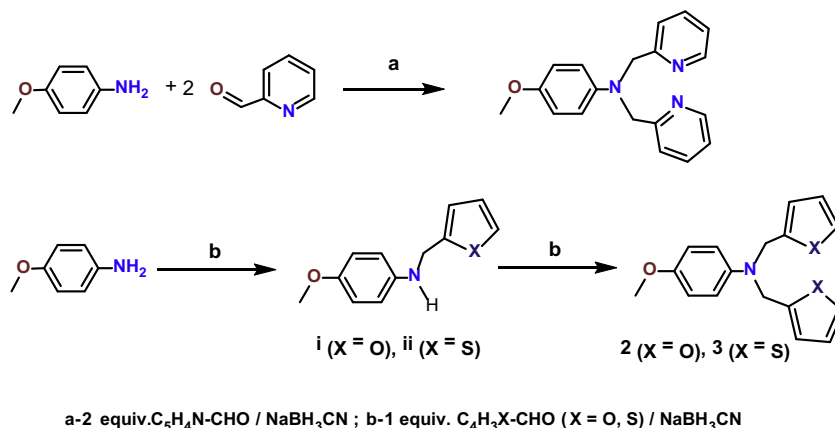
The target molecule **1** was prepared according to previously published procedures [18,19]. Briefly, to a solution of *p*-anisidine (5.0 mmol, 1.0 equiv.) dissolved in methanol, were added a pyridine carboxaldehyde (10.0 mmol, 2.0 equiv.) and acetic acid (40.0 mmol, 8.0 equiv.), the mixture was stirred for 12 h at RT. Sodium cyanoborohydride (5.0 mmol, 1.0 equiv.) were added and stirred or further 6 h. At the end, the methanol was removed under vacuum; the residue was neutralized by sodium bicarbonate solution and extracted with ethyl acetate ($3 \times 15 \text{ mL}$). The organic layer was washed with distilled water, and then dried over anhydrous sodium sulfate. The filtrate was concentrated and the residue was purified by recrystallization in diethyl ether. The details of the compounds **2** and **3** synthesis are given in Electronic Supporting Material file (ESM file).

N,N-bis(pyridin-2-ylmethyl)-4-methoxyaniline (**1**): yield: 45%; mp: $104\text{--}106^\circ\text{C}$; ^1H RMN (CDCl_3 , 300 MHz): δ/ppm : 3.70 (s, 3H, CH_3), 4.75 (s, 4H, CH_2), 6.55 (d, 2H, $\text{CH}_{\text{arom.}}$), 6.76 (d, 2H, $\text{CH}_{\text{arom.}}$), 7.19–8.72 (10H, $\text{CH}_{\text{arom.}}$); ^{13}C RMN (CDCl_3 , 75.5 MHz): δ/ppm : 159.2 (C=N), 151.8, 149.6, 142.7, 136.7, 122.0, 121.1, 114.8, 114.2, 77.2 (CH_2), 55.7 (CH_3O); IR (cm^{-1}): $\nu_{\text{C-H}}$: 2988, $\nu_{\text{C-H}}$: 2901, $\nu_{\text{C=C}}$: 1510, $\nu_{\text{C-N}}$: 1227, $\nu_{\text{C-O}}$: 1067; GC–MS ($t = 12.03 \text{ min}$): $m/z = 305.07$ (M^+), 212.97 ($\text{M}-\text{C}_5\text{H}_4\text{N}-\text{CH}_2^+$), 119.87 ($\text{H}_3\text{CO}-\text{PhNH}$), 92.95 ($\text{C}_5\text{H}_4\text{N}-\text{CH}_3^+$).

3. Results and discussion

3.1. Synthesis

Reductive alkylation of anisidine was used to prepare the corresponding *N,N*-disubstituted anilines **1**, **2** and **3** in a one-step or two separated steps reaction, respectively (Scheme 1). Only, pyridine carboxaldehyde gave the desired product (**1**) in one step, for compounds **2** and **3**, the intermediates **i** and **ii** were instead isolated. After, optimization of the reaction conditions, products **2** and **3** were obtained after a second alkylation in satisfactory yields (50% and 70%), respectively. The structures of compounds **1–3** were confirmed from their spectroscopic data and in case of compound **1** by GC–MS analysis. In each case, the aldehydes were used in excess in order to ensure the complete transformation of the starting amine.



Scheme 1. Synthetic route of compounds **1**, **2** and **3**.

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