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Synthesis, enhanced spectroscopic characterization and electrochemical grafting of N-(4-aminophenyl)aza-18-crown-6: Application of DEPT, HETCOR, HMBC-NMR and X-ray photoelectron spectroscopy

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ABSTRACT

This work describes the synthesis, characterization and electrochemical grafting of N-(4-aminophenyl)aza-18-crown-6 (4APA18C6). The key step in the synthesis is the reaction of N-phenylaza-18-crown-6 (PA18C6) with sodium nitrite. The compound, N-(4-nitrosophenyl)aza-18-crown-6 (NOPA18C6) could not be isolated purely from the reaction mixture, but a reduction of the residue with SnCl₂ gave the desired azacrown ether, N-(4-aminophenyl)aza-18-crown-6 (4APA18C6). To confirm its proposed structure detailed characterization techniques such as elemental analysis, FT-IR, ¹H NMR, ¹³C NMR, DEPT, HETCOR, HMBC and ESI mass-spectrometry were used. Due to the importance of azacrown compounds in the field of analytical chemistry, in the derivatization of dyes, chemical sensors and ionic extraction, as molecular receptors, grafting of 4APA18C6 on the glassy carbon (GC) surface has been investigated by amine oxidation to gain new insight into the modification area. The oxidation mechanism has been established, and the results are in accordance with the attachment of amines to a glassy carbon surface by cyclic voltammetry. The modification of 4APA18C6 molecules onto the glassy carbon surface was verified by cyclic voltammetry (CV), X-ray photoelectron spectroscopy (XPS) reflection–absorption infrared spectroscopy (RAIRS) and ellipsometry. The film on the GC surface was formed according to the layer-by-layer mechanism and the ellipsometric thickness was obtained around 11.5 ± 1.1 nm.

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1. Introduction

Crown ethers remain among the most important building blocks in supramolecular chemistry since their discovery in 1967 by Pedersen [1]. Numerous crown ethers have been prepared and several detailed reviews have been published giving an overview of the syntheses and properties of these compounds [2,3]. Aza crown ethers occupy a specific place among the macrocyclic crown ether ligands because of both their fascinating structures and high abilities of ligation with both alkali and alkaline earth as well as heavy-metal guest cations [4]. Because of their remarkably complex properties, the study of azacrown ethers has largely contributed to the development of host–guest interactions by improving selective fluorescent sensors for cation detection [5,6]. Several workers have reported azacrown ether derivatives with chromogenic groups [7,8] and it is known that varying the size of the azacrown ether ring or the chromophoric side arm can modify the properties of these compounds. Such changes produce agents with different sensitivities and selectivities for metal ions, including azacrown ether based dyes possessing a potential anionic site attached to the chromophore [9]. In addition, azacrown ethers are an important class of organic compounds that have found application in such diverse areas as synthetic receptors in molecular recognition processes [10] and, in some cases, anion complexation properties that are similar to those in certain biological systems [11,12]. They have an enhanced ligating ability for alkyl (or aryl) ammonium salts [13,14] and for transition metal cations [15,16] over the conventional crown ethers. The study of the electrochemical properties of organic compounds on GC widely attracts the interest of electrochemists and surface scientists because this kind of study can be essential for the development of new electronic devices and electrosynthesis [17]. In modification areas, GC electrodes are often used owing to their good electrochemical conductivity, and chemical and electrochemical inactivity [18]. Although the application of macrocyclic crown ether ligands, especially azacrown ethers as low molecular weight receptors used in assessing noncovalent bondings important in chemistry and biochemistry attracts intense attention, electrochemical grafting of crown ether



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derivatives and their binding properties on the glassy carbon surfaces have not been throughly investigated [19–21]. For that reason, we think that immobilization of azacrown ethers on glassy carbon surfaces can generate new materials with interesting properties due to their above mentioned specific complexation abilities with different alkaline, alkaline earths, and alkyl (or aryl) ammonium cations.

The goal of this research is to characterize of the structure of 4APA18C6 in detail for the first time by using elemental analysis, FT-IR, ¹H NMR, ¹³C NMR, DEPT, HETCOR, HMBC and ESI mass-spectrometry, and to perform a modified GC surface using this unique compound to gain new insight into the modification area by the amine oxidation. In addition, this study also reports the characterization of the modified surface by using CV, XPS and RAIRS. Ellipsometry was used as a means of determining the thicknesses of the 4APA18C6 nanofilm at GC.

2. Experimental

2.1. Chemicals

Tetraethylene glycol (Merck), sodium hydroxide (Merck), p-toluenesulphonyl chloride (Merck), calcium chloride (Merck), sodium hydride (60% suspension in paraffin oil) (Merck), N-phenyldiethanolamine (Merck), sodium perchlorate monohydrate (Merck), sodium nitrite (Merck), sodium carbonate (Merck), anhydrous magnesium sulfate (Merck), tin(II) chloride (Fluka), silver nitrate (Fluka), activated carbon (Sigma-Aldrich), tetrabutylamonium-tetrafluoroborate (TBATFB) (Fluka), potassium ferricyanide (Sigma-Aldrich), potassium ferrocyanide (Merck), potassium chloride (Merck), ferrocene (Sigma), acetonitrile (MeCN) (Sigma), isopropyl alcohol (IPA) (Sigma), tetrahydrofuran (THF) (Merck), dichloromethane (Merck), methanol (Merck), ethylacetate (Sigma-Aldrich), hydrochloric acid (Merck), ethanol (Merck) were reagent grade quality and used as received from the supplier. All of the processes were performed in aqueous media, and the preparation of the aqueous solutions was carried out using an ultra pure quality of water with a resistance of \sim 18.3 M Ω cm (Human Power 1⁺ Scholar purification system). Before electrochemical experiments, solutions were purged with pure argon gas (99.999%) for at least ten minutes and an argon atmosphere was maintained over the solution during experiments. Tetraethyleneglycol ditosylate was prepared according to the published method [22]. NaPA18C6 and PA18C6 were prepared according to the modified methods reported in the literature [23,24]. The new compounds NOPA18C6 and 4APA18C6 were synthesized according to the modification of the reported procedure [24].

2.2. Apparatus

Elemental analyses (C, H, N) were determined using a LECO-932 CHNSO model analyzer. The ¹H and ¹³C NMR spectra were recorded on a Varian 400 MHz spectrometer in CDCl₃ with trimethylsilane as an internal standard. Infrared spectra were recorded directly as KBr pellets and directly from the film deposited on GC electrode in a FTIR spectrometer Bruker-Tensor 27 (Bruker Optics Inc., Ettlingen, Germany). Melting points were determined using an electrothermal apparatus and were uncorrected. All the electrochemical experiments were performed using a Gamry Reference 300 workstation (Gamry, USA). The working electrode was a bare or modified glassy carbon (GC) disk (BAS) with a geometric area of 0.027 cm². The reference electrode was either an Ag/AgCl/ KCl_(sat.) used in aqueous media or an Ag/Ag⁺ (0.01 M) used in MeCN. The auxiliary electrode was a Pt wire. The surface of the sample was analyzed using a SPECS X-ray photoelectron spectrometer (Berlin, Germany) system with unmonochromatized Al Ka radiation (1486.6 eV) as an X-ray anode. Ellipsometric thickness measurement of 4APA18C6 film was made with an ELX-02C/01R Model (Germany) high precision discrete wavelength ellipsometer. The wavelength was 532 nm for all experiments. The thickness values of the films at the GC-20 (Tokai, Japan) surface were determined from the average of the measurements using an incidence angle of 70°.

2.3. Synthesis of the azacrown ethers

2.3.1. N-(Phenylaza-18-crown-6) sodium perchlorate monohydrate, [NaPA18C6] ClO₄·H₂O

This compound was prepared using a modification of the procedure reported in the literature [23,24]. A two-necked flask equipped with a dropping funnel was evacuated and refilled with argon, and then 300 mL dry THF and NaH (60% suspension in paraffin oil) (6.40 g, 16.1×10^{-2} mol) were added and refluxed. N-phenyldiethanolamine (14.5 g, 8.11×10^{-2} mol) and tetraethylenergycol ditosylate (40.2 g, 8.11×10^{-2} mol) were dissolved in 300 mL dry THF and then slowly added dropwise to the reaction mixture. The addition was completed in 3 h, and refluxing was continued for another 5 h. After cooling, the solid was filtered and washed with THF. and the filtrate was concentrated under reduced pressure. The residue dissolved in 10 mL methanol. To this solution, a solution of sodium perchlorate monohydrate (11.3 g, 8.11×10^{-2} mol) in 15 mL methanol was added. The mixture was refluxed for 10 min after which the mixture was concentrated to a small volume followed by the addition of ethylacetate. The mixture was evaporated and the residue was recrystallized from ethylacetate, to give 19.2 g (50%) of the sodium perchlorate complex, mp.: 148 °C.

IR (cm⁻¹): 3339, 3062, 3038, 2962, 2915, 2878, 1649, 1626, 1597, 1494, 1251, 1110, 882, 735, 623 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ = 1.56 (s, 2H, H₂O), 3.59–3.78 (m, 24H, NCH₂, OCH₂), 6.80–6.85 (m, 3H, ArH), 7.21–7.27 (m, 2H, ArH), ¹³C NMR: δ = 51.35, 69.08, 69.12, 69.32, 69.62, 71.13, 116.37, 119.39, 129.55, 149.58, C₁₈H₃₁NO₁₀NaCI: calcd. C 45.05, H 6.51, N 2.92; found C 45.15, H 6.48, N 2.90.

2.3.2. N-Phenylaza-18-crown-6, [PA18C6]

This compound was prepared using a modification of the procedure reported in the literature [23]. N-phenylaza-18-crown-6 sodium perchlorate monohydrate (19.2 g) was decomposed by treatment with a mixture of $CH_2Cl_2:H_2O$ (1:1); the organic layer was separated, dried and evaporated to give N-phenylaza-18-crown-6, 10.1 g of (50%), mp.:35 °C.

IR (cm⁻¹): 3059, 3024,2950, 2900, 2869, 2800, 1599, 1573, 1465, 1250, 1115, 839, 749. ¹H NMR (CDCl₃, 400 MHz, 25 °C): δ = 3.60–3.77 (m, 24H, NCH₂, OCH₂), 6.64–6.69(m, 3H, ArH), 7.17–7.21(m, 2H, ArH).¹³C NMR: δ = 51.52, 68.94, 70.90, 70.98, 71.03, 71.06, 111.85, 116.10, 129.51, 147.99, C₁₈H₂₉NO₅: calcd. C 63.69, H 8.61, N 4.13; found C 63.50, H 8.63, N 4.11.

2.3.3. N-(4-Nitrosophenyl)aza-18-crown-6, [NOPA18C6]

This compound was prepared by modifying the procedure reported in the literature [24]. N-Phenylaza-18-crown-6 (3.39 g, 10.1 mmol) was dissolved in 5 mL warmed hydrochloric acid (37%). Ice was then added and the mixture was stirred at a temperature below 5 °C. An aqueous solution of NaNO₂ (0.71 g, 10.1 mmol) in 2 mL H₂O was slowly added. After this addition, the mixture was stirred for 20 min. The mixture separated into two layers upon the addition of ice water (30 mL) and dichloromethane (20 mL). The mixture was adjusted to basic conditions upon vigorous stirring using saturated Na₂CO₃. The aqueous layer was extracted with dichloromethane several times. The dichloromethane extracts that were green in color were combined, and

dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated to dryness, leaving behind a green residue. The green residue was used in the synthesis of N-(4-aminophe-nyl)aza-18-crown-6 directly without purification.

2.3.4. N-(4-aminophenyl)aza-18-crown-6. [4APA18C6]

This was prepared by a modification of a literature procedure [24]. The crude N-(4-nitrosophenyl)aza-18-crown-6 was dissolved in 3 mL hydrochloric acid (37%) and 1.6 mL water. SnCl₂ (1.85 g, 10.1 mmol) was then added in portions while stirring at 40 °C. Water (20 mL) was added to dilute the solution after 20 min and the mixture was allowed to continue stirring for another 30 min. After the addition of NaOH (40%), the crude product appeared as a brown oil. The mixture was extracted with dichloromethane several times and the combined dichloromethane extracts were dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated to dryness leaving brown oils. Subsequent recrystallization from acetonitrile gave the product as brown crystals at quantitative yield, mp.: 37 °C.

IR (cm⁻¹): 3438, 3370, 3057, 3024, 2904, 2890, 2700, 1631, 1597, 1507, 1472, 1279, 1194, 1101, 836, 751.¹H NMR (CDCl₃, 400 MHz, 25 °C): 3.51 (s, 2H, NH₂), 3.60–3.73 (m, 24H, CH₂O and CH₂N) 6.68 (dd, 2H, ArH), 7.20 (dd, 2H, ArH).¹³C NMR: δ = 51.50, 68.95, 70.93, 71.01, 71.06, 71.09, 111.77, 116.03, 129.51, 148.02. EI MS: *m*/*z* 355.2517 [MH]⁺. C₁₈H₃₀N₂O₅: calcd. C 61.00, H 8.53, N 7.90; found C 60.98, H 8.57, N 7.98.

2.4. Electrochemical studies

2.4.1. Cleaning and preparing the GC electrode for modification

Glassy carbon electrodes were prepared by first polishing them with fine wet emery papers with grain size of 4000 (Buehler, Lake Bluff, IL, USA) followed by 0.1 μ m and 0.05 μ m alumina slurry on a polishing pad (Buehler, Lake Bluff, IL, USA) to gain a mirror-like appearance. The electrodes were sonicated for 15 min in water and in 50:50 (v/v) isopropyl alcohol and acetonitrile (IPA + MeCN) solution purified over activated carbon. Before derivatization, the electrodes were dried with an argon gas stream.

2.4.2. Preparation of 4APA18C6 nanofilm on GC

A modification of GC electrodes was performed in a solution of 1 mM 4APA18C6 in 0.1 M TBATFB in acetonitrile vs. Ag^+/Ag (0.01 M) reference electrode using CV with a scan rate of 100 mV s⁻¹ for 10 cycles between 0 V and 2.6 V. The 4APA18C6 solution was deaerated with argon for at least 10 min prior to grafting. A fresh sample of 4APA18C6 was used for each modification process. Following the modification, electrodes were rinsed with acetonitrile and kept in a dust free argon atmosphere until use.

3. Results and discussion

The synthetic strategy for the formation of the aza crown ethers involves a reaction between tetraethyleneglycol ditosylate and Nphenylenediethanolamine with excess NaH refluxing in THF (Scheme 1).

Azacrown derivatives were unambiguously characterized by elemental analyses, FT-IR, ¹H and ¹³C NMR spectroscopies as well as 4APA18C6 compound was characterized by DEPT and 2D-NMR spectroscopies (HETCOR and HMBC) and ESI high resolution mass spectrometry. Azacrown derivatives (NaPA18C6 and PA18C6) were obtained in good yields, while the amino compound 4APA18C6 was obtained in quantitative yield.

3.1. Spectroscopic characterizations of azacrown ethers

In the FTIR spectra of NaPA18C6, 4APA18C6 and PA18C6 compounds, characteristic asymmetric and symmetric medium intensity stretching vibrations of v_{Ar-H} are observed at 3070– 3057 cm⁻¹ and 3038–3024 cm⁻¹. Asymmetric and symmetric C—O—C stretching vibration bands are observed at 1110 and 882 cm⁻¹ for NaPA18C6; at 1101 and 836 cm⁻¹ for 4APA18C6 and at 1115 and 839 cm⁻¹ for PA18C6 compounds, respectively.

In the ¹H NMR spectra characteristics of NaPA18C6 and 4APA18C6, both aza crown ether functionalities and the benzene ring are easily identified. The signals in all the ¹H NMR spectra of the azacrown ether-functionalized compounds can be grouped into two regions. The first region includes signals with chemical shifts between 7.17–7.27 ppm and 6.64–6.85 ppm, which are assigned



Scheme 1. Synthetic scheme for 4APA18C6.

to the aromatic protons. The second region shows the peaks with chemical shifts at 3.59–3.78 ppm as multiplets for the protons of ethylenic chains.

The ¹³C NMR spectra of the compounds NaPA18C6 and PA18C6 confirmed the proposed structures (Scheme 1). In the ¹³C NMR spectra of both compounds, ten expected different carbon atoms are observed that are consistent with the structures of the compounds on the basis of molecular symmetry (Scheme 2).

The structure of the new compound, 4APA18C6, is characterized in detail using elemental analysis, FT-IR, ¹H-, ¹³C NMR, DEPT, HET-COR, HMBC and ESI mass-spectrometry. In the ¹H NMR spectrum of this compound, aromatic protons are observed at 7.20 ppm for H₉ and 6.68 ppm for H₈ as two doublets of doublets (³J_{HH} = 7.2 Hz and ⁴J_{HH} = 1.7) (Fig. 1).The protons of the ethylenic chains moieties shows peaks with chemical shifts at 3.59–3.78 ppm as multiplets.

In the ¹³C NMR spectrum of 4APA18C6 (Fig. 2), ten different carbon atoms are observed which are consistent with the proposed structure of the compound on the basis of molecular symmetry (Scheme 2). Distortionless enhancement of NMR signals by polarization transfer (DEPT) is used to better discriminate the different types of carbons present in 4APA18C6 (Fig. 2).

The DEPT spectrum of 4APA18C6 gives the CH₂ peaks at 51.50, 68.95, 70.93, 71.01, 71.06, and 71.09 ppm, and CH peaks at 111.77 and 129.51 ppm. It can be seen that there is no CH₃ peak in the DEPT spectrum. The other peaks of 13 C NMR except for the peaks in DEPT spectrum are non-protonated carbons. The chemical shifts of different carbons and the assignments of the protons are made using the correlation experiments and written on the spectra in Figs. 3 and 4.

Assignments of the protons and carbons are also made by two dimensional heteronuclear-correlated experiments, HETCOR, (Fig. 3) using delay values that correspond to ${}^{1}J(CH)$, and HMBC (Fig. 4) using delay values that correspond to ${}^{2}J(CH)$ or ${}^{3}J(CH)$ and even ${}^{4}J(CH)$ between the carbons and protons.



Scheme 2. The numbering of azacrown ethers for ¹H- and ¹³C NMR.





Fig. 2. The ¹³C NMR and DEPT spectra of 4APA18C6.







Fig. 4. HMBC spectrum of 4APA18C6.

The mass spectrum and the elemental analysis of 4APA18C6 support the reduction reaction of NOPA18C6 with SnCl₂. The mass spectrum of 4APA18C6 (Fig. 5) contains peak at m/z = 355.2517 which corresponds to [MH]⁺.

In addition, further characterization of 4APA18C6 was also performed at the solid surface by the covalent grafting of this molecule onto the GC substrate using CV, XPS, RAIRS and ellipsometry as described in the following sections.

3.2. Characterization of 4APA18C6 modified glassy carbon surface

Although the synthesis and fascinating behavior of azacrown derivatives have been exploited in a wide range of applications,



including organic synthesis, catalysts [25], fluoroionophores [26,27], receptors [28], and membrane sensors [29], there is no reported literature including grafting of this compound to carbon surfaces by amine oxidation. These molecules can serve as sensitive and selective sensors of cations by binding them through the azacrown ether moiety at solid surfaces [30–32]. Therefore immobilization of these compounds onto the GC surface can be advantageous in the field of cation sensor applications. For these reasons we electrochemically immobilized the 4APA18C6 (Scheme 3) onto the GC surface.

The grafting of primary amines to carbon surfaces by electrooxidation in anhydrous conditions has been widely investigated [33– 35]. Fig. 6 shows cyclic voltammograms of 1 mM 4APA18C6 solution in acetonitrile containing 0.1 M TBATFB recorded at GC electrode. The voltammograms are consistent with the grafting of a blocking film to the GC electrode. The first cycle displays a quasireversible (in appearance) and irreversible oxidation peaks. The first one is observed at approximately 0.5 V and the second one at 1.9 V. The less positive peak can be attributed to the oxidation of redox active N atom in the azacrown ring and given the resonance stabilized radical cation. This behavior is also observed for N-phenylaza-15 crown-5 compound on a Pt surface, which is structurally similar to 4APA18C6 but without amine substituent [19–21]. There is an irreversible redox process at Epa = 1.9 V,



Scheme 3. Possible grafting mechanism for 4APA18C6 on GC surface.



Fig. 6. CV voltammogram for electrografting of 4APA18C6 on GC vs. Ag/Ag⁴ (0.01 M) in 0.1 M TBATFB in acetonitrile. Scan rate is 100 mV s⁻¹.

which is assigned to amine oxidation, and when the potential is repeatedly scanned over the same range, the peak rapidly diminishes in size. These observations are indicative of a formation of a film on the electrode surface which blocks further oxidation of the amine group of 4APA18C6. Scheme 3 shows the proposed overall reaction which results in formation of a surface C—N covalent bond. Mechanistic studies have demonstrated that the initiallyformed radical cation deprotonates giving a C-centered radical, followed by isomerisation to an amino radical which covalently couples to the surface [33–37] and is consistent with the results described here.

The characteristics of the electrode coating with 4APA18C6 could be conveniently monitored by examining the various redox probes response such as potassium ferricyanide and ferrocene by CV technique. Fig. 7 shows cyclic voltammograms of approximately 1 mM K₃[Fe(CN)₆] (in 0.1 M KCl) and 1 mM ferrocene (in 0.1 M TBATFB in MeCN) recorded at a polished GC electrode and a GC electrode modified with 4APA18C6. In comparison to the cyclic voltammograms obtained at the bare and modified GC electrode, the reversible wave for the ferricyanide and ferrocene at the bare GC was almost completely precluded at the modified surfaces.

To further characterize 4APA18C6 grafted to the GC surface, modified samples were then analyzed using XPS, which is a strong tool to examine the elemental distribution on the solid electrode



Fig. 7. Cyclic voltammograms of (a) 1 mM potassiumferricyanide (in 0.1 M KCl) vs. Ag/AgCl/KCl sat reference electrode (b) 1 mM ferrocene (in 0.1 M TBATFB in MeCN) vs. Ag/Ag⁺ reference electrode on bare GC (-) and on GC-4APA18C6 (- \bullet -) electrodes. Scan rate is 100 mV s⁻¹.



Fig. 8. XPS survey spectra for the (a) unmodified GC and (b) 4APA18C6 modified GC surface.

surfaces. Fig. 8 shows the XPS survey spectra for unmodified GC and 4APA18C6 modified GC surfaces. In Fig. 8, the C, N, O and F peaks are observed, providing evidence that 4APA18C6 has been immobilized onto the surface. The main difference between these two spectra is the appearance of N_{1s} and increase of O_{1s} signals after the modification of the carbon surface.

The C_{1s} peak observed in the high resolution spectrum was deconvoluted into two Gaussian peaks at 284.81 eV (C-C and C-H), 286.60 eV (C-O and C-N) (Fig. 9a). Examination of the N_{1s} spectra (Fig. 9b) supports the analysis by C_{1s} spectra and provides the successful modification with 4APA18C6. By comparison of the N_{1s} photoemission peak with that of a reported spectrum of bare GC, we conclude that the peak at 399.67 eV corresponds to azacrown ether (-N-C-) nitrogen [38]. The residual high binding energy tail at 402.33 eV in the N_{1s} spectra is assigned to the quaternary nitrogen of Bu_4N^+ residue which is abundant in the medium during the modification process [39]. The peak at 400.47 eV is assigned to the amine nitrogen of compound 4APA18C6 covalently bonded to the GC surface. In addition, the high-resolution O_{1s} peak at 532.87 eV (Fig. 9c) indicates that a large amount of surface oxygen was present in the form of C-O bonds most likely of azacrown ether oxygen atoms. The observation of the F_{1s} peak at approximately 690 eV for 4APA18C6 modified GC surface is anticipated as some surface contamination by the BF_4^- ions of the supporting electrolyte during modification [40]. A small O_{1s} peak observed in the bare GC spectrum at about 530 eV is attributed to the surface oxides that form spontaneously on most carbon surfaces due to the atmospheric attacks, as has been reported in the literature [41,42].

In addition to the CV and XPS measurements, to confirm the covalent attachment of 4APA18C6 to the GC surface, RAIRS measurements were also performed. RAIRS spectra were acquired in a range of 4000–600 cm⁻¹ and shown in Fig. 10. Although, the peak at 3400 cm⁻¹ for N—H vibration [43] is not noticeable in the RAIRS spectra, the weak N—H in plane vibration mode at 1676 cm⁻¹ implies the existence of N—H bonds for the immobilized 4APA18C6 [38]. A possible reason for the absence of N—H bands may be the orientation of the molecules with respect to the surface. Since RAIRS offers a means of probing vibrations at the surface which have a dipole perpendicular to the surface [44], it is possible that some of the N—H bonds are parallel to the surface. Therefore, absence of the main vibration of N—H does not necessarily imply the lack of N—H bonds in the final structure. Saturated C—H stretching vibration modes and aromatic ring modes (C=C stretch)



Binding Energy (eV)

Fig. 9. Deconvoluted narrow region XPS spectra of 4APA18C6 modified GC surface for the (a) $C_{1s},$ (b) $N_{1s},$ and (c) $O_{1s}.$

appeared between 2956–2906 cm⁻¹ and 1513–1408 cm⁻¹ range, respectively. Additionally, observation of asymmetric and symmetric C—O—C signals at approximately 1044 cm⁻¹ and 932 cm⁻¹, respectively, indicates that the proposed grafting has occurred.

Ellipsometric thickness of the 4APA18C6 film at the GC surface was found as 11.5 ± 1.1 nm by modeling the system using the software of the instrument [45]. A four layer model was used as graphite/glassy carbon substrate/4APA18C6 film/air to fit experimental data. Refractive indices of 3.0841 for graphite, 1.9000 for GC, 1.0000 for organic layer, 1.0000 for air and extinction coefficients of -1.7820 for graphite, -0.8100 for GC, 0.0000 for organic layer, 0.0000 for air are assigned, supposing thickness, refractive indices



Fig. 10. RAIRS spectrum for 4APA18C6 modified GC surface.

and extinction coefficients are reasonably correlated for all films [46]. The thickness of the 4APA18C6 film is 11.5 ± 1.1 nm which corresponds approximately to a 10 layer when compared to the theoretical thickness of 12.8 Å.

4. Conclusion

In summary, a new aza crown derivative, 4APA18C6, was synthesized. Its structure was characterized extensively by using elemental analysis, FT-IR, ¹H NMR, ¹³C NMR, DEPT, HETCOR, HMBC, ESI mass-spectrometry. Due to the importance of azacrown compounds in the field of analytical chemistry, chemical sensors and ionic extraction, as molecular receptors, grafting of 4APA18C6 on GC surface has been performed to obtain new insight into the modification area and to generate new materials with interesting properties. The mechanism of modification, and the covalent attachment of 4APA18C6 on the GC surface, was confirmed by various characterization techniques including CV, XPS and RAIRS. The film on the GC surface was formed according to the layer-by-layer mechanism and the ellipsometric thickness was obtained around 11.5 ± 1.1 nm.

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