



A novel EIS field effect structures coated with TESUD-PPy-PVC-dibromoaza[7]helicene matrix for potassium ions detection

Moncef Tounsi^{a,c,*}, Mourad Ben Braiek^b, Houcine Barhoumi^a, Abdoullatif Baraket^c, Michael Lee^c, Nadia Zine^c, Abderrazak Maaref^a, Abdelhamid Errachid^{c,**}

^a Laboratoire des Interfaces et des Matériaux Avancés (LIMA), Faculté des Sciences de Monastir, Université de Monastir, Tunisia

^b Laboratoire de Synthèse Organique Asymétrique et Catalyse Homogène, Faculté des Sciences, Université de Monastir, Avenue de l'environnement, 5019, Monastir, Tunisia

^c Université de Lyon, Institut de Sciences Analytiques (ISA) – UMR 5280, 5 rue de la Doua, 69100 Villeurbanne, France

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ABSTRACT

In this work, we describe the development of new Aza[7]helicene-containing PVC-based membranes for the K⁺ ions quantification. Here, silicon nitride-based structures (Si-p/SiO₂/Si₃N₄) were developed and the surface was activated, functionalized with an aldehyde–silane (11-(Triethoxysilyl)undecanal (TESUD)), functionalized with polypyrrole (PPy), and coated with the polyvinylchloride (PVC)-membrane containing the Aza[7]helicene as ionophore. All stages of functionalization process have been thoroughly studied by contact angle measurements (CAMs) and atomic force microscopy (AFM). The developed ion-selective electrode (ISE) was then applied using electrochemical impedance spectroscopy (EIS) for the detection of potassium ions. A linear range was observed between 1.0×10^{-8} M to 1.0×10^{-3} M and a detection limit of 1.0×10^{-8} M was observed. The EIS results have showed a good sensitivity to potassium ion using this novel technique. The target helicene exhibited good solubility and excellent thermal stability with a high decomposition temperature (Td > 300 °C) and it indicates that helicene may be a promising material as ionophore for ion-selective electrodes (ISEs) elaboration.

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1. Introduction

Potassium ion (K⁺) is a mineral play key roles in biological systems and necessary for the proper function of the human body system, such as nerve transmission, regulation of blood pressure, maintenance of muscular strength and extracellular osmolarity [1,2]. Abnormal K⁺ concentration is a symptom of several diseases, including heart disease, diabetes, kidney diseases, and cancer [3]. Therefore, selective and sensitive K⁺ sensors are quite crucial for the detection of physiological potassium level to facilitate clinical diagnosis and treatment.

The determination of potassium ions has been carried out directly or indirectly by a variety of classical and instrumental methods, including

electrochemical method [4–7], fluorescence [8–15], atomic absorption spectrophotometry [16], colorimetry [17], atomic emission spectrometry [18], and ion chromatography [19]. Most of these methods require expensive, sophisticated and complicated instruments and also well-controlled experimental conditions, which limit the opportunity of their practical application. Electrochemical impedance spectroscopy (EIS) is a sensitive and suitable technique used to describe and investigate kinetics of the electrochemical interface for any modified electrodes [20]. This rapidly developing electrochemical technique has recently received attention in the field of analytical sciences and can be used as an analytical tool for the measurement of electric property changes of the biosensor in the presence of increasing concentrations of the analyte.

Helicenes are polycyclic aromatic compounds consisting of ortho-fused benzene rings with nonplanar topology with C₂-symmetric axis perpendicular to the axis of helicity as a result of the steric repulsive interaction between terminal aromatic rings [21]. Their specific backbone, which combines electron delocalization and non-planarity of the π -electron network, makes them very stable towards acids and bases and relatively high temperatures [22]. These helically-shaped molecules have found applications as potentially useful components in many fields of research, including supramolecular chemistry [23], molecular recognition [24] and asymmetric synthesis [25].

Abbreviations: PPy, Polypyrrole; TESUD, 11-(Triethoxysilyl)undecanal; CAMs, Contact angle measurements; EIS, Electrochemical impedance spectroscopy; Py, Pyrrole; AFM, Atomic force microscopy; KTpClPB, Potassium tetrakis(4-chlorophenyl)borate; DOS, Dioctyl sebacate; NBS, N-bromosuccinimide; DCM, Dichloromethane.

* Correspondence to: M. Tounsi, Laboratoire des Interfaces et des Matériaux Avancés (LIMA), Faculté des Sciences de Monastir, Université de Monastir, Tunisia.

** Corresponding author.

E-mail addresses: tounsi1981@live.fr (M. Tounsi), abdelhamid.errachid-el-salhi@univ-lyon1.fr (A. Errachid).

For instance, heptahelicene is a particularly interesting [n]helicene containing one complete turn of the helix and high optical stability (racemization barrier $40.5 \text{ kcal mol}^{-1}$) [21,22]. Such heptacyclic structures have seen interest for their ability to act as a chiral “molecular tweezer” [26]. Many theoretical calculations during the last ten years show the strong interaction that may exist between carbohelicenes and a number of ions. As the interaction between the two terminal benzene rings of carbo[7]helicene and alkali cations [27], the trapping of metallic ions (Cr, Mo, and W) into carbo[7]helicene [28,29], or as the formation of ferrocene from a helicene, by the study of the stability of Fe^{2+} complexation with a polycyclic hydrocarbon composed of 10 fused cyclopentadiene rings has been investigated [30–32].

The synthetic approach makes use of 3,6-dibromo-9-methylcarbazole as suitable building block for the synthesis of appropriately substituted 1,2-diarylethene which can then be easily converted into helically chiral heptacyclic system under UV irradiation (Scheme 1) [33]. Moreover, carbazole was selected as the starting material because it has excellent fluorescence features [34] and carbazole derivatives are commonly used as fluorescence probes/sensors [35]. Despite this interesting property, we will be limited in this work in study the electrochemical behavior of the ISE- K^+ by the method of impedance spectroscopy. And we will address to the property of the fluorescence of Aza[n]helicene in a subsequent a novel PVC-membrane optical sensor [10–12] for K^+ detection.

In this work, we report the preparation of carbazole-based Aza[7]helicene **4** as organic sensing ionophores and its application for ion sensor. The sensitivity of the developed material towards K^+ ions was characterized by electrochemical impedance spectroscopy (EIS). The membrane surface was characterized by contact angle measurements (CAMs), atomic force microscopy (AFM) and Scanning Electron Microscopy (SEM).

2. Materials and methods

2.1. Reagents

All reagents used were of analytical grade. 11-(Triethoxysilyl) undecanal (TESUD) was purchased from Gelest, USA. Sulfuric acid (H_2SO_4) (30%), sodium dodecyl sulfate (SDS), iron (III) chloride, and pyrrole were purchased from Sigma Aldrich, France. Hydrogen peroxide (H_2O_2) (35% wt.), dioctyl sebacate (DOS), potassium tetrakis(4-chlorophenyl)borate (KTpClPB), polyvinylchloride (PVC), and tetrahydrofuran (THF) were obtained from Fluka, France. The chloride salts of all cations were of the highest purity available and used without further purification (all from Fluka). The ligand dibromoaza[7]helicene was used as the neutral carrier in the ISE potassium selective devices

(Fig. 1) and prepared at the Asymmetric Organic Synthesis and Homogeneous Catalysis Laboratory, Monastir, Tunisia. The analyte ions studied were K^+ . All solutions were prepared with deionized water purified by a Milli-Q Element System (resistance $18.2 \text{ M}\Omega\text{cm}$).

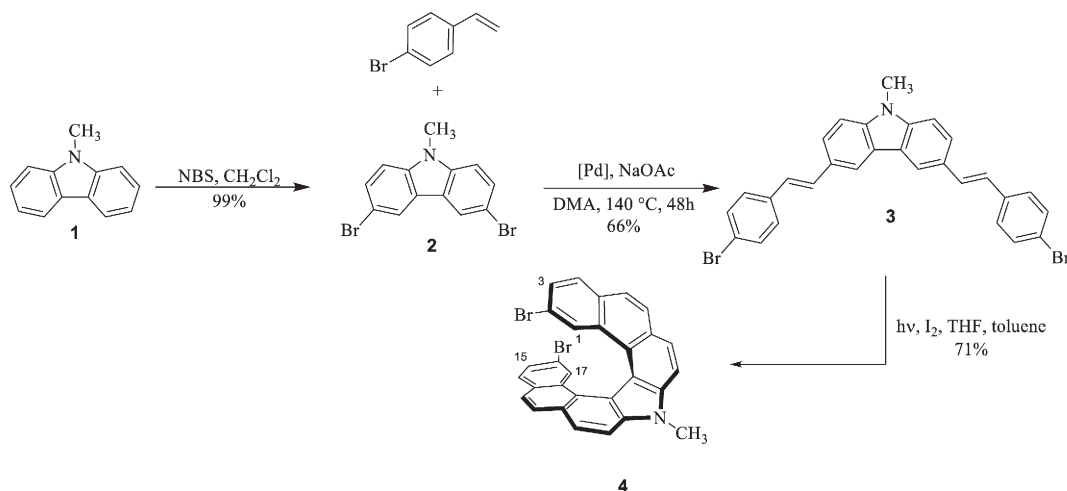
2.2. Ionophore synthesis

2.2.1. General procedure for the preparation of diarylethene **3**:

N-methylcarbazole **1** was stirred with two equivalents of N-bromosuccinimide (NBS) in dichloromethane (DCM). The quantitative yield (99%) of the resulting dibrominated derivative **2** was obtained after purification by flash chromatography. A solution of 3,6-dibromo-9-methylcarbazole **2** (1 g, 3 mmol) and dry NaOAc (532 mg, 6.6 mmol) in *N,N*-dimethylacetamide (8 mL) was placed in a two-necked flask, fitted with a septum, which is degassed and purged with argon three times. To this was added 4-bromostyrene (0.96 mL, 8.4 mmol) and the mixture was heated to 100°C . When this temperature was reached, a solution of Herrmann's catalyst (58 mg, 2%) in *N,N*-dimethylacetamide (2 mL) was added and the mixture was heated at 140°C for about 48 h. The reaction was quenched by the addition of 5% HCl solution, then stirred for 30 min at room temperature and extracted with CHCl_3 ($3 \times 50 \text{ mL}$). The combined organic layers were dried over Na_2SO_4 and evaporated to dryness. After column chromatography with cyclohexane/EtOAc (80:20), product **3** was obtained in 66% yield (1.05 g) as a light yellow solid (Scheme 1). mp = $197\text{--}199^\circ\text{C}$; ^1H NMR ($\text{DMSO-}d_6$, 300 MHz): δ (ppm) = 3.69 (s, 3H, CH_3), 6.87 (d, $J = 8.7 \text{ Hz}$, 4H), 7.12 (d, $J = 16.5 \text{ Hz}$, 2H, H_{vinyl}), 7.17 (d, $J = 16.5 \text{ Hz}$, 2H, H_{vinyl}), 7.37 (d, $J = 8.4 \text{ Hz}$, 2H), 7.47 (d, $J = 8.7 \text{ Hz}$, 4H), 7.56 (d, $J = 8.4 \text{ Hz}$, 2H), 8.27 (s, 2H); ^{13}C NMR ($\text{DMSO-}d_6$, 75 MHz): δ (ppm) = 29.86, 111.66, 114.54, 118.40, 121.04, 123.24, 124.89, 125.48, 127.66, 128.86, 130.66, 140.05; HRMS (MALDI-TOF) calcd for $\text{C}_{29}\text{H}_{21}\text{Br}_2\text{N}$ $[\text{M}]^+$: 541.00407; found: 541.00393.

2.2.2. General procedure for the preparation of dibromoaza[7]helicene **4**

To a solution of alkene **3** (150 mg, 0.27 mmol) in 1 L of toluene/THF (95:05) was added a stoichiometric amount of I_2 . The solution was irradiated using a falling-film photoreactor and a high-pressure Hg-vapor lamp (500 W, Hanovia). The reaction was monitored by TLC. Following completion, solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica gel with cyclohexane/EtOAc (80:20) to give helicene **4** as a pale yellow solid (105 mg, 71%) (Scheme 1); ^1H NMR (CDCl_3 , 300 MHz): δ (ppm) = 4.30 (s, 3 H, CH_3), 7.32 (dd, $J_1 = 8.7, J_2 = 2.1 \text{ Hz}$, 2 H), 7.43 (d, $J = 1.5 \text{ Hz}$, 2 H), 7.75 (d, $J = 8.4 \text{ Hz}$, 2 H), 7.89 (d, $J = 8.4 \text{ Hz}$, 2 H), 7.97 (d, $J = 8.4 \text{ Hz}$, 2 H), 8.08 (d, $J = 8.7 \text{ Hz}$, 2 H), 8.15 (d, $J = 8.4 \text{ Hz}$,



Scheme 1. The synthesis of the helically chiral heptacyclic system **4**.

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