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# New fluorescent and electropolymerizable *N*-azacrown carbazole as a selective probe for iron (III) in aqueous media

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## Abstract

A new *N*-azacrown carbazole fluoroionophore **1** was synthesized by microwave path and its sensing behavior toward metal ions was investigated by spectroscopic methods. This new structure proved to be an excellent selective fluorescent probe toward Fe<sup>3+</sup> in non-buffered aqueous solution without interference with the background metal ions (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Al<sup>3+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup> and Ga<sup>3+</sup>). Additionally, the immobilization of this new selective iron probe was successfully achieved on gold electrode by electro-polymerization and monitored by EQCM.

## Introduction

In the past decade the research of highly selective and sensitive organic fluorescent probes for metal ions recognition has gained extreme importance in environmental and biological area [1–3]. This is due to the fact that, among the numerous analytical methods, the fluorescence one is a great tool owing to its high sensitivity, and relatively simple instrumentation [4,5]. It also allows a real-time, nondestructive detection and/or quantification of chemical species. Besides the development of fluoroionophores for metal ions of groups I and II, significant exploration of fluorescent molecular sensors and switches for heavy transition metal (HTM) ions are actually involved [6–8]. Concerning HTM ions detection, fluorimetric analysis of iron [9–17] has nowadays attracted a great deal of attention due to its important role in the fields of environmental monitoring and biological science [18]. It could be noticed that literature gives only few examples of iron chemosensors operating in water and in most cases, these operate in buffered solutions due to the pH dependence of their fluorescence properties [19–22]. Among fluorescent chemosensors, those incorporating a carbazole core appear to be highly promising derivatives due to their attractive fluorescent properties and their ability to be electropolymerized in order to

form a thin film onto metal surfaces [23]. The polymer-coated electrodes then obtained may be used for electrocatalysis, electronics,

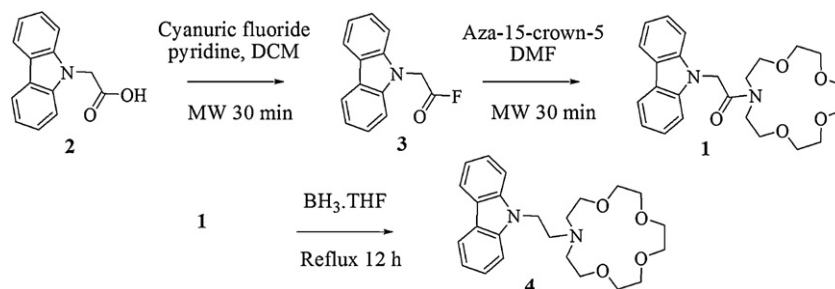
photoelectronics and photo-electrochemistry. Recently, polycarbazole derivatives were used to develop copper (II) ion-selective microelectrochemical transistors [24].

Consequently, in our continuing program on the design and synthesis of new chemosensors for recognition of environmental molecular species [25,26] and more particularly HTM [27], we report here an easy and rapid microwave assisted organic synthesis (MAOS) of a new selective iron (III) water soluble fluoroionophore **1**. This new iron molecular sensor was designed with typical fluorophore-spacer-receptor format comprising a fluorescent carbazole moiety linked to an aza-15-crown-5 with or without *N*-carbonyl methylene arm (compounds **1** and **4** respectively, Scheme 1). The photoluminescent properties of the complexation phenomenon of this new fluorescent probe were investigated in the presence of HTM and alkali metal ions. Finally, the redox properties of the carbazole unit were exploited to electropolymerize the aza-15-crown-5 receptor onto a gold surface with an EQCM monitoring.

## 1. Experimental

### 1.1. Materials and instrumentations

Perchlorate salts (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Al<sup>3+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Ga<sup>3+</sup>) were used as the



Scheme 1. Synthesis of chemosensors **1** and **4**.

metal cations source for fluorescence spectroscopy. Iron chloride salt was used as the metal cation source for infrared spectroscopy. All the chemicals used were purchased from Acros Organic or Sigma Aldrich and were used as received without further purification. Microwave-assisted reactions were performed on a monomode reactor Synthwave Prolabo402 (300 W) equipped with infrared pyrometer control and stirring mechanically.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker Avance 250 MHz spectrometer. Mass spectra were measured using a Platform II Micromass Apparatus. IR spectra were recorded using a Perkin–Elmer instrument. Fluorescence spectra were recorded using a Perkin–Elmer LS50B spectrometer. Electrochemical experiments were performed using an Autolab PGSTAT 30 workstation. A three electrode configuration was used with a platinum or gold disk as the working electrode and platinum wire as a counter electrode. An Ag/AgCl electrode was used as a reference. EQCM measurements were performed using a Maxtek RQCM apparatus with 5 MHz AT-cut gold crystal (Maxtek P/N 149211-1 Model SC-501-1).

## 1.2. Computational methodology

To obtain more information about the conformational changes of the crown ethers used upon complexation with iron ion, the molecular structures of the free ligands and their 1:1 complex with  $\text{Fe}^{3+}$  were carried out using the Spartan software of Wavefunction Inc. The preliminary conformational distribution search has been performed by using the MMFF94s molecular mechanics force field. The structures were then optimized based on the 6.31G\* basic set at the restricted Hartree–Fock (RHF) level of theory.

## 1.3. Synthesis

### 1.3.1. 2-(9H-carbazol-9-yl)acetyl fluoride (3)

To an ice-cold solution of 2-(9H-carbazol-9-yl)acetic acid **2** (1.00 g; 4.44 mmol) in  $\text{CH}_2\text{Cl}_2$  under nitrogen atmosphere, pyridine (0.69 g; 8.88 mmol) and cyanuric fluoride (1.19 g; 8.88 mmol) were successively added. The resulting solution was irradiated in a focused microwave oven at 40 °C for 30 min and then washed several times with water, dried over anhydrous  $\text{MgSO}_4$  and concentrated in vacuum. Compound **3** was isolated as a brown solid. Yield: 98%.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 5.22 (s, 2H), 7.27–7.35 (m, 4H), 7.52 (t,  $J = 7.50$  Hz, 2H), 8.14 (d,  $J = 7.75$  Hz, 2H).

### 2.3.2. 2-(9H-carbazol-9-yl)-1-(1,4,10,13-tetraoxa-7-azacyclopentadecan-7-yl)ethanone (1)

To a cold solution of aza-15-crown-5 (0.50 g; 2.28 mmol) in DMF (10 mL) was added 2-(9H-carbazol-9-yl)acetyl fluoride **3** (0.57 g; 2.51 mmol). The resulting solution was irradiated in a focused microwave oven at 40 °C for 30 min and then concentrated under reduced pressure to give yellow oil which was purified by column chromatography (EtOAc/MeOH 8:2). Crystallization from EtOAc

gave the desired amide as a white solid. Yield: 81%.  $^1\text{H}$  NMR (Fig. S1, Supplementary data) (250 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) 3.45–3.78 (m, 18H), 3.90 (t,  $J = 5.40$  Hz, 2H), 5.31 (s, 2H), 7.22 (t,  $J = 7.00$  Hz, 2H), 7.39–7.48 (m, 4H), 8.12 (d,  $J = 7.75$  Hz, 2H) (Fig. S1).  $^{13}\text{C}$  NMR (62.5 MHz,  $\text{CD}_3\text{CN}$ ) (Fig. S2, Supplementary data):  $\delta$  (ppm) 44.0, 48.9, 49.3, 68.1, 69.2, 69.3, 69.4, 69.7, 70.0, 70.4, 108.79, 118.5, 119.7, 122.2, 125.3, 140.9, 167.28 (Fig. S2). Mass ( $\text{ES}^+$ )  $m/z$  (%): 427 [ $\text{M}+1$ ] $^+$  (10%), 449 [ $\text{M}+23$ ] $^+$  (100%).

### 2.3.3. 2-(9H-carbazol-9-yl)-1-(1,4,10,13-tetraoxa-7-azacyclopentadecan-7-yl)ethane (4)

**1** (500 mg, 1.17 mmol) was dissolved in anhydrous THF (50 mL) and then was slowly added to  $\text{BH}_3$ –THF (47 mL, 1.0 M, 46.94 mmol) at room temperature. The resulting solution was refluxed for 12 h, and the excess borane was eliminated with methanol. Solvents were removed under vacuum and the residue was hydrolyzed in refluxing MeOH– $\text{H}_2\text{O}$ –conc. HCl (4:1:1) 60 mL for 2 h. The aqueous layer was basified with  $\text{NaHCO}_3$  and then extracted by DCM. The resulting oily product was purified by column chromatography on silica gel (EtOAc/MeOH 1:1). Compound **4** was isolated as brown oil. Yield: 74%.  $^1\text{H}$  NMR (250 MHz,  $\text{CD}_3\text{CN}$ ) (Fig. S3, Supplementary data):  $\delta$  (ppm) 2.72 (t,  $J = 5.81$  Hz, 4H), 2.92 (t,  $J = 7.00$  Hz, 2H), 3.40–3.50 (m, 16H), 4.42 (t,  $J = 7.00$  Hz, 2H), 7.21 (t,  $J = 7.00$  Hz, 2H), 7.43–7.56 (m, 4H), 8.11 (d,  $J = 7.62$  Hz, 2H).  $^{13}\text{C}$  NMR (62.5 MHz,  $\text{CD}_3\text{CN}$ ) (Fig. S4, Supplementary data):  $\delta$  (ppm) 42.5, 55.1, 55.9, 70.6, 70.7, 70.8, 71.2, 110.1, 119.7, 121.0, 123.4, 126.5, 141.3. Mass ( $\text{ES}^+$ )  $m/z$  (%): 435 [ $\text{M}+23$ ] $^+$  (100%).

## 2. Results and discussion

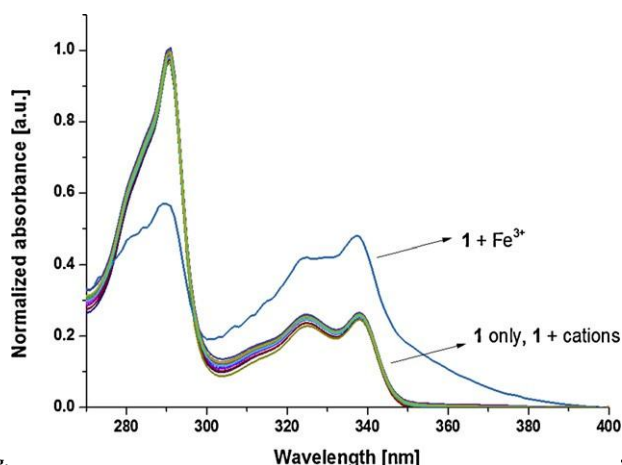
### 2.1. Synthesis

Firstly, aza-15-crown-5 was synthesized according to the procedure of Okahara and coworkers [28] from diethanolamine and triethylene glycol ditosylate [29] and 2-(9H-carbazol-9-yl)acetic acid **2** was produced following the procedure of Zhang and al. [30]. Initially the coupling reaction between aza-15-crown-5 and **2** was performed by the well-known DCC/DMAP approach [31] at room temperature for three days as well as MAOS procedure to give **1** in moderate yields (50% and 65% respectively). Consequently to increase yields, we reacted **2** with an excess of cyanuric fluoride [32] by MAOS path to provide in quasi quantitative yield the more reactive 2-(9H-carbazol-9-yl)acetyl fluoride **3**. The *N*-acylation of aza-15-crown-5 with the *N*-carbazole acyl fluoride derivative **3** was then undertaken under microwave irradiation. As predicted, microwave irradiation provided a faster and more efficient synthesis of **1** with an improved yield of 81%. Furthermore in order to understand the contribution of spacer in the recognition phenomenon, the carbonyl group of the chemosensor **1** was then reduced in anhydrous THF under soft addition of  $\text{BH}_3$ –THF

**Table 1**  
Photophysical parameters of fluorescent crown derivatives **1** and **4**.

	$\epsilon$ ( $M^{-1} \text{ cm}^{-1}$ )	$\lambda_{\text{exc}}$ (nm)	$\lambda_{\text{em}}$ (nm)	$\Phi_F^a$
Compound <b>1</b>	$1.5 \times 10^4$	292	330–440	0.31
Compound <b>4</b>	$1.2 \times 10^4$	294	330–470	0.20

<sup>a</sup> Quantum yields were estimated by using anthracene as a standard in ethanol.



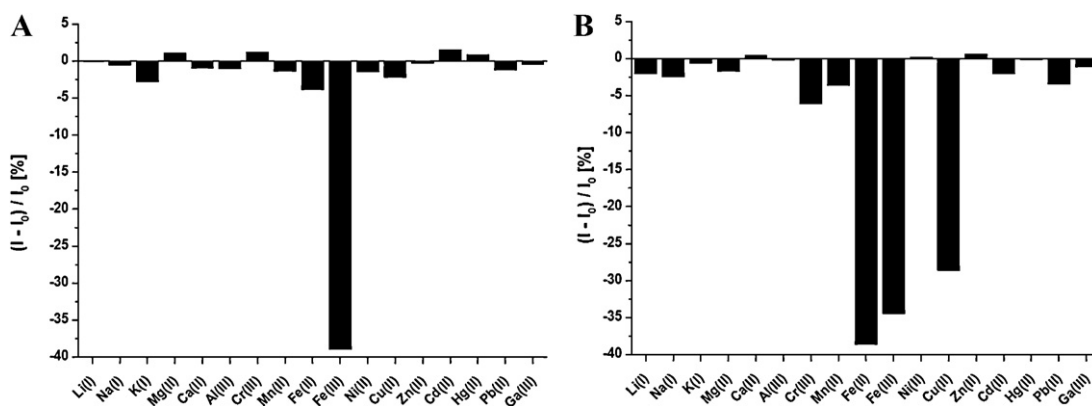
**Fig. 1.** Normalized absorbance vs. Wavelength [nm] for compound **1** and **1 + Fe<sup>3+</sup>** and **1 + cations** (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Al<sup>3+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Ga<sup>3+</sup>).

to afford an *N*-azacrown-carbazole derivative **4** without carbonyl entity between fluorophore and crown-ether.

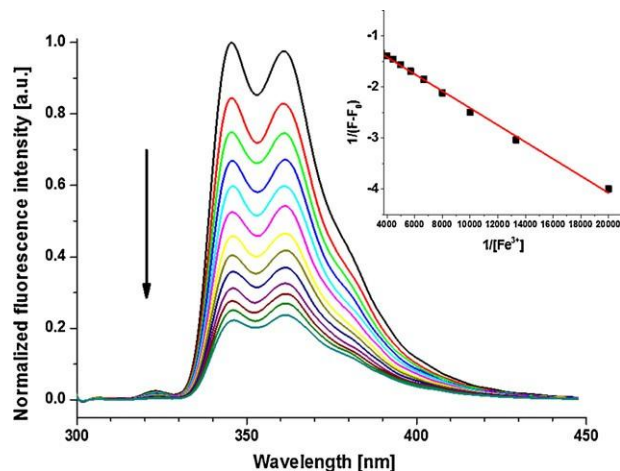
## 2.2. UV-vis absorption and fluorescence properties

The absorption and emission spectral properties of crown derivatives **1** and **4** were studied in water (Table 1). Absorption spectrum of **1** (Fig. 1) showed absorption bands in range of 270–350 nm along with a maximum centered at 292 nm while compound **4** have an absorption bands around 275–355 nm with a maximum absorption slightly shifted at 294 nm (Fig. S5, Supplementary data). As shown in Table 1, the fluorescence quantum yield is higher for the crown derivative **1** than for compound **4**.

In order to study the influence of pH on the spectrometric properties, the new fluorescent crown derivatives were first investigated over a pH range of 2–12. The results show no significant change of absorption spectra for compound **1** indicating no pH dependence (Fig. 6A, Supplementary data). Contrary to **1**, compound **4** shows strong pH dependence (Fig. S6B, Supplementary data). Therefore its  $pK_a$  of 7.8 require to work in buffered



**Fig. 2.** Change in fluorescence emission of compound **1** (A) and **4** (B) (0.5  $\mu\text{M}$ ,  $\lambda_{\text{exc}} = 292 \text{ nm}$ , water) upon addition of 200 equivalents of various metal cations as perchlorate salts.



**Fig. 3.** Fluorescence emission spectrum of **1** (0.5  $\mu\text{M}$ ,  $\lambda_{\text{exc}} = 292 \text{ nm}$ ) vs. addition of  $\text{Fe}^{3+}$  (0–300  $\mu\text{M}$ ) in water. Inset: Benesi–Hildebrand plot.

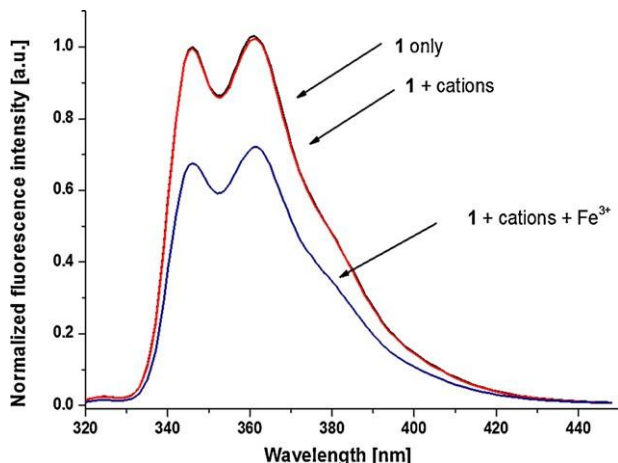
solution at pH 9. Unfortunately, in these conditions and at this level of concentration, all metals precipitate and it was not possible to carry out UV-vis absorption experiments with compound **4**. The absorption spectra of new crown ether **1** were then performed upon addition of various metal ions such as Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Al<sup>3+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup> and Ga<sup>3+</sup> as perchlorate salts [33]. As shown in Fig. 1, the addition of  $\text{Fe}^{3+}$  causes an increase of the absorption band between 330 and 350 nm while the G–G\* transition at 292 nm progressively decrease. In our experiments, the presence of other metal cations doesn't cause any significant alterations of the UV-vis spectra (Fig. 1).

Fig. 2 shows the variation of fluorescence emission after addition of 200 equivalents (100  $\mu\text{M}$ ) of metal cations to a solution of **1** and **4** ( $5 \cdot 10^{-7} \text{ M}$ ) in aqueous solution at room temperature and with an incubation time of 1 min. As expected from UV absorption of **1** (Fig. 2A), only  $\text{Fe}^{3+}$  induced a significant fluorescence quenching of up to 39% suggesting a selectivity phenomenon. To prevent the amine protonation, the fluorescent emission experiments of **4** were carried out at pH = 9 with addition of the same series of cations (Fig. 2B). The examination of results reveals a decrease of the fluorescence intensity for  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  species and shows a loss of selectivity toward  $\text{Fe}^{3+}$ .

In order to calculate the association constants, compounds **1** and **4** were titrated with  $\text{Fe}^{3+}$  and  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  perchlorate salts respectively ( $\text{Fe}^{3+}$  vs. **1** as example in Fig. 3). The non-linear regression analysis of fluorescence flattening allowed to estimate the association constant [34] which was compiled in Table 2.

**Table 2**Complex formation constants  $K$  ( $10^3 \text{ M}^{-1}$ ) and limit of detections (LOD) of compound **1** and **4**.

	$\text{Fe}^{3+}$	$\text{Fe}^{2+}$	$\text{Cu}^{2+}$
Compound <b>1</b>	$7.0 \pm 0.3$ (2.5 $\mu\text{M}$ )	—	—
Compound <b>4</b>	$4.2 \pm 0.15$ (2.6 $\mu\text{M}$ )	$4.8 \pm 0.2$ (2.4 $\mu\text{M}$ )	$3.7 \pm 0.13$ (3.1 $\mu\text{M}$ )



**Fig. 4.** Fluorescence response of chemosensor **1** (0.5  $\mu\text{M}$ ,  $\lambda_{\text{ex}} = 292 \text{ nm}$ ) alone, with 200 equiv. of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Ga}^{3+}$  (top) and with addition of 200 equiv. of  $\text{Fe}^{3+}$  (bottom).

The association constant of **1** vs.  $\text{Fe}^{3+}$  is higher compared to the other values obtained for **4** and is consistent with a selectivity induced by a specific interaction between the metal ion and the ligand. Furthermore, the calculated limit of detections (LOD) are comparable with dedicated literature [16,17,35].

To confirm the selectivity of fluorescent crown derivative **1**, we have then performed fluorescence experiment in contaminated medium by various cations. Then, the fluorescence spectrum of **1** was recorded in the presence of  $\text{Fe}^{3+}$  and an equal amount of each previously mentioned metal cations (Fig. S7, Supplementary data) to evaluate their individual influence toward  $\text{Fe}^{3+}$  associated with

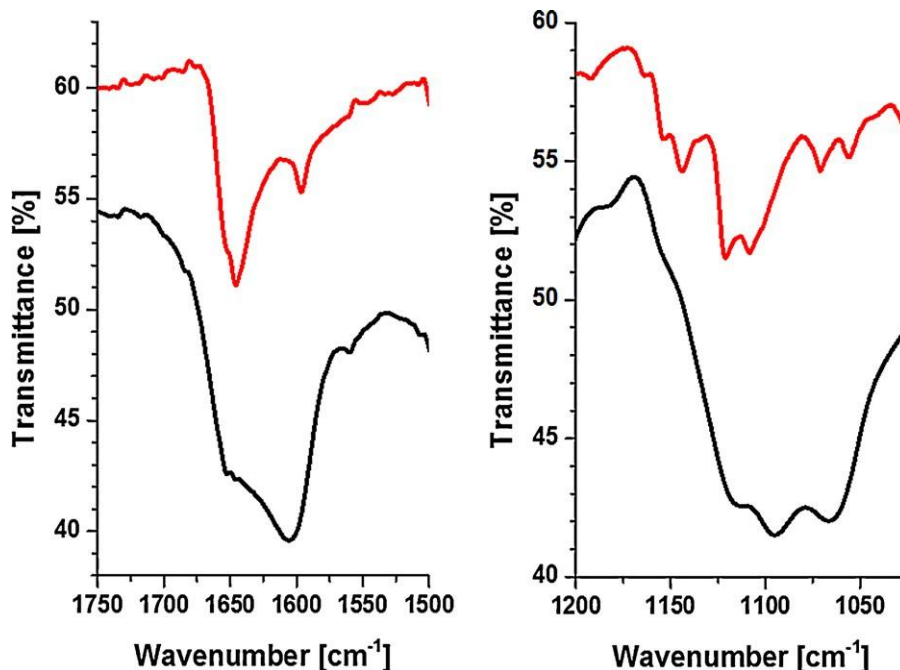
**1**. It reveals that cations did not individually impact the decrease of fluorescence of **1** toward  $\text{Fe}^{3+}$ . Furthermore, the presence of all  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Ga}^{3+}$  did not influence the fluorescence spectrum (Fig. 4) thereby confirming the highly iron (III) selectivity of this new probe. In addition, the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  quench ratio of 1:0.1 appears to be interesting for speciation study.

### 2.3. Binding pattern and molecular modeling

Since, it is reasonable to assume that *N*-carbonyl methylene arm of **1** is involved in the chelation phenomenon, infrared spectroscopy studies and  $^1\text{H}$  NMR experiment were carried out to get further information on the nature of complex formation between **1** and  $\text{Fe}^{3+}$ . The IR spectrum of **1** was characterized by the ether-crown (C-O-C) stretching band at  $1121 \text{ cm}^{-1}$  and the amide carbonyl (C=O) regions at  $1645 \text{ cm}^{-1}$  respectively (Fig. 5). Upon the addition of  $\text{Fe}^{3+}$ , both carbonyl and ether absorption bands were shifted to lower frequency ( $1605$  and  $1095 \text{ cm}^{-1}$ , respectively) which confirms that both carbonyl and azacrown ether moiety are involved in the recognition phenomenon [36].

To consolidate the coordination pattern between **1** and  $\text{Fe}^{3+}$ , we have performed a  $^1\text{H}$  NMR experiment in  $\text{CD}_3\text{CN}$  (Fig. 6). As shown, the addition of 1 equiv. of  $\text{Fe}(\text{ClO}_4)_3$  induces a shift of methylenic group to 5.31 ppm toward 5.71 ppm that is consistent with IR experiment where the carbonyl moiety was involved in the chelation of  $\text{Fe}^{3+}$ .

To complete binding pattern of  $\text{Fe}^{3+}$  with chemosensor **1**, molecular modeling was performed using 6.31G\*/RHF ab initio method based on 1:1 stoichiometry (Fig. 7) previously estimated by Benesi-Hildebrand plot (Fig. 3, inset) [37]. In our models, we have firstly chelated the iron ion with one molecule of water, oxygen's



**Fig. 5.** IR spectra of compound **1** (top) and chemosensor **1** in the presence of  $\text{Fe}^{3+}$  (bottom).

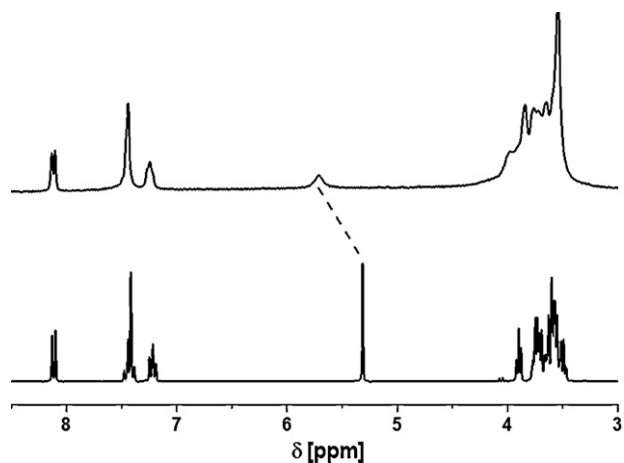


Fig. 6.  $^1\text{H}$  NMR spectra of **1** in  $\text{CD}_3\text{CN}$ : **1** alone (bottom), **1** + 1 equiv. of  $\text{Fe}(\text{ClO}_4)_3$  (top).

atoms from crown ether and an additional bond to satisfy the coordination number of  $\text{Fe}^{3+}$ . This additional bond was, in the one hand, the aromatic part of carbazole unit in order to form cation-G interaction and, on the other hand, the oxygen of the carbonyl group. The complexation by cation-G interaction was not energetically favored due to excessive proximity between carbazole moiety and crown ether. Thus, only the optimized structure of Fig. 7B revealed that a metal ion binds with the carbonyl as well as with oxygen atoms from the crown ether moiety.

In consequence, as for alkali metal complex with lariat ether amide described by Gokel and coworkers [38], we assume that the presence of an amide group in probe **1** affects the conformation and consequently the binding properties of the macrocyclic azacrown ether which induce the selectivity. Thus, this effective binding affinity of iron with the receptor coupled with the absence of quenching effect of other paramagnetic  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  cations tend to establish that the fluorescent quenching mechanism is due to a static quenching process for the best part but a dynamic quenching process may also occur at high concentration of iron.

#### 2.4. Electrochemical properties

As previously outlined in this paper, electropolymerization by cyclic voltammetry (CV) is an effective technique to create films onto surfaces [39]. Hence, we turned our attention to whether **1** could be electropolymerized onto an electrode surface using this technique. To test the ability to form network ultrathin films,

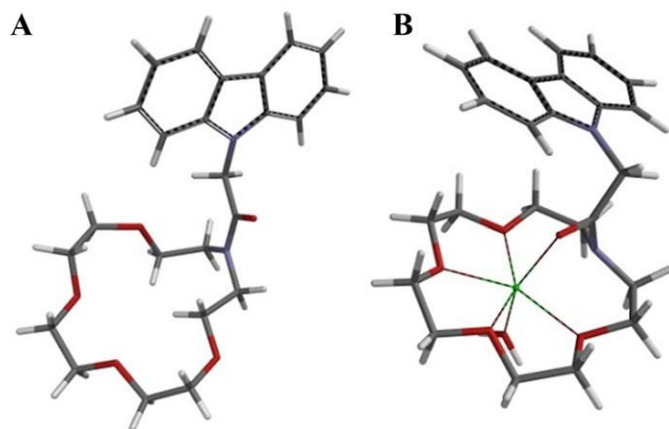


Fig. 7. Optimized geometry of free **1** (A); **1**· $\text{Fe}^{3+}$  (B) by 6.31G\*/RHF ab initio method.

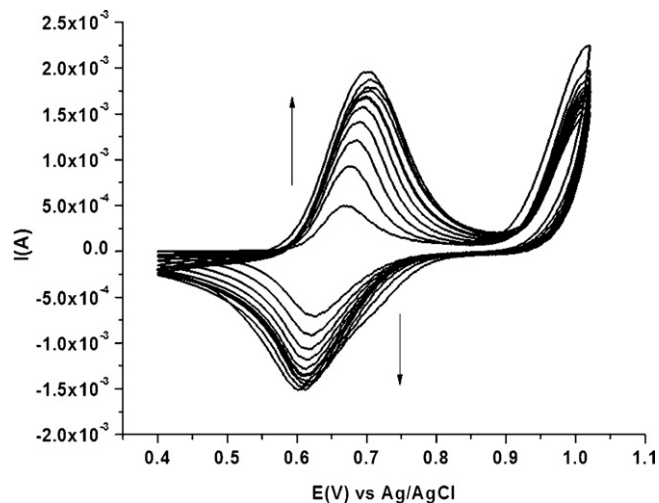


Fig. 8. CV showing the electrochemical polymerization of **1** from a  $10^{-3}$  M solution in acetonitrile/water (2:8) with 1 M  $\text{HClO}_4$ . The CV shows 10 cycles between +0.4 and +1.0 V. Scan rate =  $0.1 \text{ V s}^{-1}$ .

chemosensor **1** was electropolymerized for 10 cycles (Fig. 8) at a range of 0.4–1.0 V with a scan rate of  $0.1 \text{ V s}^{-1}$  in acetonitrile/water mixture (2:8) with 1 M  $\text{HClO}_4$  as electrolyte (WE, gold-coated slide; CE, Pt wire; RE, Ag/AgCl).

The first anodic scan (Fig. S8, Supplementary data) shows an oxidation potential at around 1 V for **1** ascribed to the formation of the carbazole cation radical. During the second scan, a new sharp oxidation wave appears at a lower potential intensities (0.7 V) indicating that the electrochemical-chemical reaction generates an oligomeric/polymeric material that is easier to oxidize than the monomer **1**. Upon repeated scans, an increase in the oxidation and reduction currents is observed, indicating the occurrence of the growth of a film onto the working electrode surface according to a radical mechanism [40,41]. Following deposition, the functionalized surface was successively washed with ultrapure water and its electrochemistry was then investigated in a fresh aqueous solution of 1 M perchloric acid using CV. Oxidative scans between +0.25 and

+0.90 V were recorded and clearly revealed the redox wave due to the oxidation of carbazole framework and thus provided clear evidence of deposition of carbazole moiety on the electrode surface. Moreover, the current increase of the redox process proved to be linear as a function of the scan rate as expected for surface bound electro-active material (Fig. 9a and b). The film proved to be reasonably stable, displaying a similar current/voltage response for more than 10 cycles.

Additionally, the electrodeposition was investigated using a combined electrochemistry and quartz crystal microbalance (EQCM) (Fig. S9, Supplementary data). It is seen that the frequency decreased monotonically with potential scans indicating the progressively deposition of a carbazole film onto the gold surface. The surface coverage  $\Gamma$  of the redox species can be calculated by integrating the anodic peak area [42] (charge  $Q$ ) according to  $\Gamma = Q/nFA$ , where  $F$  is the Faraday constant,  $n$  the number of electrons exchanged ( $n = 0.5$ , i.e. only half of carbazole units display a positive charge) [40], and  $A$  the surface area ( $\varnothing$  1.3 cm). The electrochemical results show that the surface coverage is  $6.92 \cdot 10^{15}$  molecules per  $\text{cm}^2$  which is in the same order of magnitude than those previously described for unsubstituted *N*-carbazole. From our literature knowledge, it is the first time that an *N*-azacrown carbazole derivative has been coated as a pendant unit onto a gold working electrode surface via carbazole electropolymerization. In addition, we attempt to realize similar electrodeposition with the reduced *N*-carbazole-azacrown **4**. No increasing in the oxidation

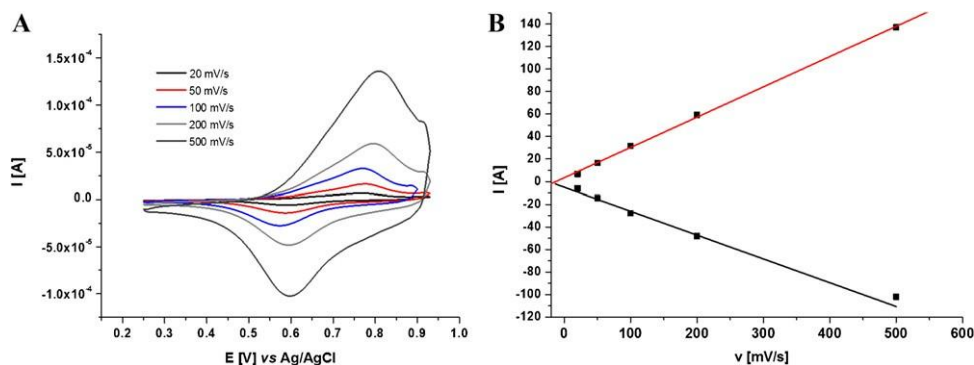


Fig. 9. Cyclic voltamograms at different scan rates of chemosensor **1** – grafted gold surface (left). Peak current as a function of scan rate for anodic and cathodic peaks (right).

and reduction currents could be observed (Fig. S10, Supplementary data). We presume that the protonation of the free tertiary amine is responsible for this lack of electro-deposition because of the high solubility of protonated form of **4** in water.

### 3. Conclusions

In conclusion, we have successfully designed a new *N*-azacrown carbazole chemosensor allowing the specific detection of  $\text{Fe}^{3+}$  ion. The synthesis was efficiently carried out with good yield and reduced reaction time using microwave-assisted synthesis. We measured a significant and quantifiable decrease of the fluorescence intensity of chemosensor **1** upon addition of  $\text{Fe}^{3+}$ . By contrast, the addition of other metals cations such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Ga}^{3+}$  do not significantly modify the fluorescence emission allowing the specificity quantification of iron concentration. The non-pH dependence of the fluorescence properties of **1** provides an effective means for  $\text{Fe}^{3+}$  sensing in water. Moreover chemosensor **1** was successfully electropolymerized on gold electrode and work is under way in our laboratory to investigate its recognition properties toward metal cations.

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