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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 Fe³⁺ in non-buffered aqueous solution without interference with the background metal ions (Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Al³⁺, Cr³⁺, Mn²⁺, Fe²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Hg²⁺, Pb²⁺ and Ga³⁺). 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⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Al³⁺, Cr³⁺, Mn²⁺, Fe²⁺, Fe³⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Hg²⁺, Pb²⁺, Ga³⁺) 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. ^1H and ^{13}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 his 1:1 complex with 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 CH_2Cl_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 MgSO_4 and concentrated in vacuum. Compound **3** was isolated as a brown solid. Yield: 98%. ^1H NMR (250 MHz, CDCl_3): δ (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%. ^1H NMR (Fig. S1, Supplementary data) (250 MHz, CD_3CN): δ (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}C NMR (62.5 MHz, CD_3CN) (Fig. S2, Supplementary data): δ (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 (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 $\text{BH}_3\text{--THF}$ (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 $\text{MeOH--H}_2\text{O}$ –conc. HCl (4:1:1) 60 mL for 2 h. The aqueous layer was basified with 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%. ^1H NMR (250 MHz, CD_3CN) (Fig. S3, Supplementary data): δ (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}C NMR (62.5 MHz, CD_3CN) (Fig. S4, Supplementary data): δ (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 (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 $\text{BH}_3\text{--THF}$

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

	ϵ ($M^{-1} \text{ cm}^{-1}$)	λ_{exc} (nm)	λ_{em} (nm)	Φ_F^a
Compound 1	1.5×10^4	292	330–440	0.31
Compound 4	1.2×10^4	294	330–470	0.20

^a Quantum yields were estimated by using anthracene as a standard in ethanol.

Fig. 1 K^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+} , Ga^{3+} , Na^+ .

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. 3. Fluorescence emission spectrum of **1** (0.5 μM , λ_{exc} = 292 nm) vs. addition of Fe^{3+} (0–300 μM) 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^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+} and Ga^{3+} as perchlorate salts [33]. As shown in Fig. 1, the addition of 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 μM) of metal cations to a solution of **1** and **4** ($5.10^{-7} M$) in aqueous solution at room temperature and with an incubation time of 1 min. As expected from UV absorption of **1** (Fig. 2A), only 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 Fe^{3+} , Fe^{2+} and Cu^{2+} species and shows a loss of selectivity toward Fe^{3+} .

In order to calculate the association constants, compounds **1** and **4** were titrated with Fe^{3+} and Fe^{3+} , Fe^{2+} and Cu^{2+} perchlorate salts respectively (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.

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

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

	Fe^{3+}	Fe^{2+}	Cu^{2+}
Compound 1	7.0 ± 0.3 (2.5 μM)	—	—
Compound 4	4.2 ± 0.15 (2.6 μM)	4.8 ± 0.2 (2.4 μM)	3.7 ± 0.13 (3.1 μM)

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

The association constant of **1** vs. 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 Fe^{3+} and an equal amount of each previously mentioned metal cations (Fig. S7, Supplementary data) to evaluate their individual influence toward Fe^{3+} associated with

1. It reveals that cations did not individually impact the decrease of fluorescence of **1** toward Fe^{3+} . Furthermore, the presence of all Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Ni^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+} and 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 ^1H NMR experiment were carried out to get further information on the nature of complex formation between **1** and Fe^{3+} . The IR spectrum of **1** was characterized by the ether-crown (C-O-C) stretching band at 1121 cm^{-1} and the amide carbonyl (C=O) regions at 1645 cm^{-1} respectively (Fig. 5). Upon the addition of Fe^{3+} , both carbonyl and ether absorption bands were shifted to lower frequency (1605 and 1095 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 Fe^{3+} , we have performed a ^1H NMR experiment in CD_3CN (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 Fe^{3+} .

To complete binding pattern of 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 Fe^{3+} (bottom).

Fig. 6. ^1H NMR spectra of **1** in CD_3CN : **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 Fe^{3+} . This additional bond was, in the one hand, the aromatic part of carbazole unit in order to form cation- π interaction and, on the other hand, the oxygen of the carbonyl group. The complexation by cation- π 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 Cu^{2+} and 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. 8. CV showing the electrochemical polymerization of **1** from a 10^{-3} M solution in acetonitrile/water (2:8) with 1 M HClO_4 . The CV shows 10 cycles between +0.4 and +1.0 V. Scan rate = 0.1 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 V s^{-1} in acetonitrile/water mixture (2:8) with 1 M 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 Γ 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 ($\varnothing 1.3 \text{ cm}$). The electrochemical results show that the surface coverage is $6.92 \cdot 10^{+15}$ molecules per 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. 7. Optimized geometry of free **1** (A); **1**· Fe^{3+} (B) by 6.31G*/RHF ab initio method.

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 Fe³⁺ 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 Fe³⁺. By contrast, the addition of other metals cations such as Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Al³⁺, Cr³⁺, Mn²⁺, Fe²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Hg²⁺, Pb²⁺ and Ga³⁺ 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 Fe³⁺ 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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References

- [1] B. Valeur, I. Leray, Design principles of fluorescent molecular sensors for cation recognition, *Coordination Chemistry Reviews* 205 (2000) 3–40.
- [2] J.F. Callan, A.P. de Silva, D.C. Magri, Luminescent sensors and switches in the early 21st century, *Tetrahedron* 61 (2005) 8551–8588.
- [3] L. Basabe-Desmonts, D.N. Reinhoudt, M. Crego-Calama, Design of fluorescent materials for chemical sensing, *Chemical Society Reviews* 36 (2007) 993–1017.
- [4] J.R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 2nd ed., Kluwer, New York, NY, 1999.
- [5] B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim, Germany, 2002.
- [6] I. Móczár, P. Huszthy, A. Mezei, M. Kádár, J. Nyitrai, K. Tóth, Synthesis and optical characterization of novel azacrown ethers containing an acridinone or an *N*-methylacridinone unit as potential fluorescent chemosensors, *Tetrahedron* 66 (2010) 350–358.
- [7] L. Wang, W. Qin, W. Liu, A sensitive Schiff-base fluorescent indicator for the detection of Zn²⁺, *Inorganic Chemistry Communications* 13 (2010) 1122–1125.
- [8] P. Dinake, P.E. Prokhorova, V.S. Talanov, R.J. Butcher, G.G. Talanova, A new fluorogenic calix[4]arene *N*-dansylcarboxamide in the cone conformation for selective optical recognition of mercury(II), *Tetrahedron Letters* 51 (2010) 5016–5019.
- [9] X.B. Zhang, G. Cheng, W.J. Zhang, G.L. Shen, R.Q. Yu, A fluorescent chemical sensor for Fe³⁺ based on blocking of intramolecular proton transfer of a quinoxaline derivative, *Talanta* 71 (2007) 171–177.
- [10] M. Kumar, R. Kumar, V. Bhalla, On–Off reversible switch for Fe³⁺ and F[–] mimicking XNOR logic function, *Tetrahedron Letters* 51 (2010) 5559–5562.
- [11] R. Peng, F. Wang, Y. Sha, Synthesis of 5-dialkyl(aryl)aminomethyl-8-hydroxyquinoline dansylates as selective fluorescent sensors for Fe³⁺, *Molecules* 12 (2007) 1191–1201.
- [12] D. Kennedy, D. Brown, S. Burdette, Probing nitrobenzhydryl uncaging mechanisms using ferriccast, *Organic Letters* 12 (2010) 4486–4489.
- [13] Y. Xiang, A. Tong, New rhodamine-based chemosensor exhibiting selective Fe³⁺ amplified fluorescence, *Organic Letters* 8 (2006) 1549–1552.
- [14] Z. Hu, Y. Feng, H. Huang, L. Ding, X. Wang, C. Lin, M. Li, C. Ma, Fe³⁺ selective fluorescence probe based on rhodamine B and its application in bioimaging, *Sensors and Actuators B: Chemical* 156 (2011) 428–432.
- [15] W. Yin, H. Cui, Z. Yang, C. Li, M. She, B. Yin, J. Li, G. Zhao, Z. Shi, Facile synthesis and characterization of rhodamine-based colorimetric and off-on fluorescent chemosensor for Fe³⁺, *Sensors and Actuators B: Chemical* 157 (2011) 675–680.
- [16] S. Dalapati, S. Jana, Md.A. Alam, N. Guchhait, Multifunctional fluorescent probe selective for Cu(II) and Fe(III) with dual-mode of binding approach, *Sensors and Actuators B: Chemical* 160 (2011) 1106–1111.
- [17] N. Narayanaswamy, T. Govindaraju, Aldazine-based colorimetric sensors for Cu²⁺ and Fe³⁺, *Sensors and Actuators B: Chemical* 161 (2012) 304–310.
- [18] B.P. Esposito, S. Epsztejn, W. Breuer, Z.I. Cabantchik, A review of fluorescence methods for assessing labile iron in cells and biological fluids, *Analytical Biochemistry* 304 (2002) 1–18.
- [19] J. Hua, Y.G. Wang, A highly selective and sensitive fluorescent chemosensor for Fe³⁺ in physiological aqueous solution, *Chemistry Letters* 34 (2005) 98–99.
- [20] J. Yao, W. Dou, W. Qin, W. Liu, A new coumarin-based chemosensor for Fe³⁺ in water, *Inorganic Chemistry Communications* 12 (2009) 116–118.
- [21] N. Singh, N. Kaur, J. Dunn, M. MacKay, J.F. Callan, A new fluorescent chemosensor for iron(III) based on the *p*-aminobisulfonate receptor, *Tetrahedron Letters* 50 (2009) 953–956.
- [22] K.S. Moon, Y.K. Yang, S. Ji, J. Tae, Aminoxy-linked rhodamine hydroxamate as fluorescent chemosensor for Fe³⁺ in aqueous media, *Tetrahedron Letters* 51 (2010) 3290–3293.
- [23] E. Sezer, J. Heinze, Voltammetric, EQCM and in situ conductivity studies of 3,6-bis(2-thienyl)-*N*-ethyl carbazole, *Electrochimica Acta* 51 (2006) 3668–3673.
- [24] V. Saxena, V. Shirodkar, R. Prakash, Copper(II) ion-selective microelectrochemical transistor, *Journal of Solid State Electrochemistry* 4 (2000) 234–236.
- [25] F. Delattre, P. Woisel, G. Surpateanu, F. Cazier, P. Blach, 1-(4-Nitrophenoxycarbonyl)-7-pyridin-4-yl indolizine: a new versatile fluorescent building block. Application to the synthesis of a series of fluorescent beta-cyclodextrins, *Tetrahedron* 61 (2005) 3939–3945.
- [26] I. Mallard Favier, P. Blach, F. Cazier, F. Delattre, Efficient synthesis of a fluorescent tripod detection system for pesticides by microwave-assisted click chemistry, *Carbohydrate Research* 344 (2009) 161–166.
- [27] A.V. Tsukanov, A.D. Dubonosov, V.A. Bren, V.I. Minkin, Organic chemosensors with crown-ether groups, *Chemistry of Heterocyclic Compounds* 44 (2008) 899–922.

- [28] H. Maeda, S. Furuyoshi, Y. Nakatsuji, M. Okahara, Synthesis of monoaza crown ethers from N,N-di[oligo(oxyalkylene)]amines and oligoethylene glycol di(p-toluenesulfonates) or corresponding dichloride's, *Bulletin of the Chemical Society of Japan* 56 (1983) 212–218.
- [29] P.-E. Danjou, D. Wallyn, F. Cazier-Dennin, F. Delattre, Ultrasound-promoted tosylation of oligo(ethylene glycols), *Ultrasonics Sonochemistry* 19 (2012) 1201–1204.
- [30] X.J. Zhang, Y.P. Tian, S.L. Li, M.H. Jiang, A. Usman, S. Chantapromma, H.K. Fun, Zn(II) and Cd(II) N-carbazolyacetates with strong fluorescence, *Polyhedron* 22 (2003) 397–402.
- [31] E.S. Meadows, L.J. Barbour, R. Ferdani, G.W. Gokel, Dimer formation in alkali metal complexes of 15- and 18-membered indole-containing lariat ether amides, *Journal of Supramolecular Chemistry* 1 (2001) 111–115.
- [32] G. Cooke, V.M. Rotello, A. Radhi, Fluorocarbonyltetrathiafulvalene: an effective building block for the production of tetrathiafulvalene esters and amides, *Tetrahedron Letters* 40 (1999) 8611–8613.
- [33] CAUTION: Perchlorates salts are explosives materials it should be handle with care.
- [34] Y. Wang, T. Ikeda, H. Ikeda, A. Ueno, F. Toda, Dansyl- β -cyclodextrins as fluorescent sensors responsive to organic compounds, *Bulletin of the Chemical Society of Japan* 67 (1994) 1598–1607.
- [35] L. Zhang, B. Li, Z. Su, S. Yue, Novel rare-earth(III)-based water soluble emitters for Fe(III) detection, *Sensors and Actuators B: Chemical* 143 (2010) 595–599.
- [36] X. Zhang, Y. Shiraishi, T. Hirai, Fe(III)- and Hg(II)-selective dual channel fluorescence of a rhodamine–azacrown ether conjugate, *Tetrahedron Letters* 49 (2008) 4178–4181.
- [37] J.H. Hildebrand, H.A. Benesi, A spectroscopic investigation of the interaction of iodine with aromatic hydrocarbons, *Journal of the American Chemical Society* 71 (1949) 2703–2707.
- [38] J. Hu, L.J. Barbour, R. Ferdani, G.W. Gokel, Solid state network formation in arene-sidearmed lariat ether complexes: Contrasting behavior of sodium, potassium, and calcium cation complexes, *Journal of Supramolecular Chemistry* 1 (2001) 157–163.
- [39] G. Cooke, L.M. Daniels, F. Cazier, J.F. Garety, S.G. Hewage, A. Parkin, G. Rabani, V.M. Rotello, C.C. Wilson, P. Woisel, The synthesis of a pyrrole-functionalized cyclobis(paraquat-p-phenylene) derivative and its corresponding [2]rotaxane and [2]catenane and their subsequent deposition onto an electrode surface, *Tetrahedron* 63 (2007) 11114–11121.
- [40] I. György, Formation and redox behaviour of polycarbazole prepared by electropolymerization of solid carbazole crystals immobilized on an electrode surface, *Journal of Solid State Electrochemistry* 7 (2003) 503–510.
- [41] G. Jiang, R. Ponnappati, R. Pernites, C.D. Grande, M.J. Felipe, E. Foster, R. Advincula, Nanoparticle formation and ultrathin film electrodeposition of carbazole dendronized polynorbornenes prepared by ring-opening metathesis polymerization, *Langmuir* 26 (2010) 17629–17639.
- [42] M.A. Watson, J. Lyskawa, C. Zobrist, D. Fournier, M. Jimenez, M. Traisnel, L. Gengembre, P. Woisel, A. Clickable, Titanium surface platform, *Langmuir* 26 (2010) 15920–15924.

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