Synthesis of Benzothiazole Bearing Calixarene as a Chemical Sensor with Triggered Fluorescence Property for Chlorite Ion

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Abstract

A fluorescence probe based on calix[4]arene-benzothiazole platform was rationally designed and synthesized for the detection of chlorite ion in aqueous solution. The sensor candidate was characterized by such spectroscopic techniques as FTIR, fluorescence, ^{1}H- and ^{13}C-NMR along with HRMS analysis. During the photophysical characterization experiments, it was observed that the synthesized sensor candidate exhibited weak fluorescence while its chlorite detection created a strong blue fluorescence facilitating sensitive detection. Besides, the related chlorite probe possessed a large Stokes shift (158 nm) with large pseudo Stoke's shift within the value of 242 nm that enables more accurate detection among other tested ions. Considering that chlorite anion is formed from chlorine dioxide as a result of reduction, and the importance of on-site monitoring of the concentration range regulated by many countries, it is obvious that our sensor has presented a convenient detection option as an alternative method to fulfil the daily monitoring requirements.

Keywords: Water treatment, Chlorite detection, Fluorescent probe, Chemical sensor, Disinfection by-product.

Klorit İyonu İçin Tetiklenmiş Floresans Özelliğe Sahip Bir Kimyasal Sensör Olarak Benzotiyazol Grubu Taşıyan Kaliksaren Sentezi

Öz

Klorit anyonunun sulu çözeltilerdeki tespitine yönelik olarak, kaliks[4]aren-benzotiyazol platformuna dayalı bir floresans probu rasyonel bir şekilde tasarlandı ve sentezlendi. Bu sensör adayı, HRMS analizi ile birlikte FTIR, floresans, ^{1}H- ve ^{13}C-NMR gibi çeşitli spektroskopik teknikler aracılığıyla karakterize edildi. Fotofiziksel karakterizasyon deneyleri sırasında, sentezlenen sensör adayının zayıf bir floresans sergilediği, klorit tespiti sonucu ise hassas tespiti kolaylaştıran güçlü bir mavi floresans oluşturduğu görüldü. Bunun yanı sıra, ilgili klorit probu, test edilen diğer iyonlar arasında daha doğru tespiti mümkün kılan büyük bir Stokes kayması (158 nm) ile 242 nm değerinde büyük bir yalancı Stokes kaymasına sahiptir. Klorit anyonunun klor dioksitten indirgeme sonucu oluştuğu ve birçok ülke tarafından düzenlenen klorit iyonu konsantrasyon aralığının yerinde izlenmesinin önemi göz önünde bulundurulduğunda, sensörümüzün günlük izleme gereksinimlerini karşılamak için alternatif bir yöntem olarak uygun bir algılama seçeneği sunduğu apaçık ortadadır.

Anahtar Kelimeler: Su arıtımı, Klorit tespiti, Floresans algılayıcı, Kimyasal sensör, Dezenfeksiyon yan ürünü.

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1. Introduction

The disinfection process of water sources by treatment with chlorine dioxide (ClO_2) has brought a disadvantage along with many advantages [1-4]. The related process has been reviewed and all disinfection by-products (DBPs) have been identified in line with the studies in the literature [5-7]. In this sense, the formation of chlorite ion (ClO_2^-) has been an undesirable situation because of its potential of causing hemolytic anemia and adverse nervous system effects (lowered auditory startle amplitude, decreased exploratory activity) along with decreased absolute brain weight and altered liver weights [8,9]. However, disinfection has been essential for water sources safeguard, the health risks from disinfectants and disinfection by-products have been much less than the risks from consuming water that has not been disinfected [10]. Concordantly, when ClO_2 is used for the disinfection of drinking water, about 70% converts to ClO_2^- through a selective one-electron transfer mechanism leading to the reduction process [11, 12]. Many countries' regulations about maximum contaminant level for chlorite anion including the U.S. Environmental Protection Agency (EPA) and the World Health Organization (WHO) vary between the value of 0.2 and 1.0 ppm [13]. Hence, consistent with these restrictions, this unavoidable by-product has to be monitored daily by reliable, simple and inexpensive methodology in drinking water, particularly.

Among various analytical methods for ClO_2^- anion detection such as chromatographic [14, 15], spectrophotometric [16, 17], voltammetric [18], amperometric [19], capillary electrophoresis [20] and flow injection [21], the most promising one has been spectrofluorometric method with great superiorities in terms of extreme sensitivity and selectivity [22]. Thanks to the fluorescence sensors/probes to be produced in this context, measurements/imaging of ClO_2^- can be performed readily in the area where the samples have to be collected. Besides, ClO_2^- can be determined together with other important anions in the same conditions selectively based on their interactions with the host sensor molecules and the attainable detection limit is very low via these fluorogenic sensors. To the best of our knowledge, to date, although some reports have been listed in the literature on fluorescent detecting of different reactive oxygen species like hypochlorite and perchlorate [23-28], no accomplished study has been reported in fluorescent detection of chlorite anion.

Developing an ideal fluorescent sensor is the keystone for the fluorimetry-based anion recognition applications. As fluorophores, which have an important place in sensor design, benzothiazoles and its derivatives have showed several outstanding advantages such as large Stokes shift, high fluorescence quantum yield, excellent stability and chemically modifiability. More importantly, these attractive molecules have the opportunity to follow a recognition processes called excited state intramolecular proton transfer (ESIPT) thanks to the combination of both hydrogen donor and acceptor groups together in their structures [29-31]. The other important component for the anion sensor designing is the receptor with anion binding capability. While numerous types of binding sites/receptors for anions are developed, a scaffold that presents binding sites has been found to be necessary to impart a sufficient anion binding affinity to the sensor molecule [32]. At this point, derivatives and/or analogs of calix[4]arene macrocycle have taken their indispensable place in the literature thanks to capability of hosting molecules or ions in their favorably adopted cone-shaped hydrophobic cavities. Besides, OH functions, as chelating groups on the lower rim have been frequently chosen for the regioselective derivatization due to their affinity towards a molecule or ion. These all have been manifested by the applications in the field of host-guest chemistry, ion/molecular recognition, ion extraction and interaction with biomolecules [33-37]. However, while calixarene skeleton darivatization effort and introducing new host molecules to the literature is still increasing day by day, the fluorescence recognition studies of ClO_2^- ion based on this macrocycle are still unavailable. This encouraged us to steer fluorescent detection works with developing more efficient chemosensors with high sensitivity and selectivity through ClO_2^- ion.

Considering the chlorite ion detection topic from many aspects mentioned above, in this work, a fluorescent chlorite anion sensor has been recently designed and fabricated as a leading candidate that may fulfil the demand / fill the void in the most attractive areas such as supramolecular chemistry and environmental monitoring. We strongly believe that our conveniently synthesized chlorite sensor, as being first of its kind with its applicability in an aqueous environment and its distinct color changing sensitivity against chlorite anion, will be directive for the scientists who works or will work in the field of fluorescent detection of chlorite.

2. Material and Method

2.1. General

FTIR spectrum was recorded in ATR apparatus with a PerkinElmer Spectrum Two spectrophotometer. ^{1}H- and ^{13}C-NMR measurements were performed on an Agilent 400 MHz NMR spectrometer. The NMR data (chemical shifts, δ) were reported in ppm units with tetramethylsilane (TMS) as internal standard and deuterated chloroform ($CDCl_3$) as solvent. High resolution mass spectrum (HRMS) was acquired on an Agilent 6230 TOF-MS system with a positive ion mode electrospray ionization (ESI) technique. UV-Vis spectrum was obtained on a PerkinElmer Lambda 35 spectrophotometer with quartz cuvettes having 1 cm path lengthy. Fluorescence spectra measurements were recorded on an Agilent Cary Eclipse fluorescence spectrophotometer using excitation and emission slit widths, both 5 nm, and a quartz cell with 1 cm path length. All the solvents, reagents and aqueous anion solutions received from commercial suppliers were directly used without further purification. Thin layer chromatography (TLC) analyses with aluminum silica gel 60 F254 plates were performed for the reaction monitoring and flash column chromatography with 230 × 400 mesh silica gel 60 were applied for the compound purification.

2.2. Synthesis of Chemosensor V

An intermediate chloroacetamide compound (**III**) was synthesized according to a previous report [38]. Following, the target sensor candidate, compound **V** was obtained via a similar method from our previous work [39]. Concordantly, the solution of chloroacetamide **III** (1.51 g, 5.0 mmol) and KI (1.0 g, 6.0 mmol) in acetone was added dropwise to the solution of calix[4]arene **IV** (849 mg, 2.0 mmol) with K_2CO_3 (691 mg, 5.0 mmol) in toluene. After this reaction mixture was stirred at room temperature for an hour, it was continued under reflux with TLC monitoring. When the reaction was complete, it was allowed to

cool to room temperature and the solvent was evaporated under reduced pressure. The obtained residue was purified by silica gel flash column chromatography using CH_2Cl_2:Hexane (10:1, v/v) solvent system to obtain the pure compound **V**, namely 25,27-bis(N-(benzothiazole-4-yl)-acetamide)-26,28-dihydroxy-calix[4]arene in 52% yield. FTIR (ATR) v cm^{-1} 1214 (C-O-C), 1301 (C-N), 1589 (C=C), 1616 (C=N), 1688 (C=O); ^{1}H NMR (400 MHz) δ 11.75 (s, 2H, NH), 8.20 (d, J = 8.2 Hz, 2H, ArH), 7.85 (d, J = 8.2 Hz, 2H, ArH), 7.82 – 7.71 (m, 2H, ArOH), 7.35 – 7.23 (m, 16H, ArH), 6.91 (d, J = 7.5 Hz, 4H, ArH), 6.81 – 6.72 (m, 2H, ArH), 6.67 (t, J = 7.5 Hz, 2H, ArH), 4.71 (s, 4H, OCH$_2$), 4.51 (d, J = 13.3 Hz, 4H, ArCH$_2$Ar), 3.44 (d, J = 13.3 Hz, 4H, ArCH$_2$Ar); ^{13}C NMR (100 MHz) δ 173.2, 169.2, 157.1, 152.5, 149.7, 143.2, 142.7, 138.3, 137.3, 135.3, 132.9, 132.1, 131.1, 129.8, 128.0, 127.4, 127.4, 127.1, 126.2, 125.8, 125.7, 120.3, 71.6, 31.3, 30.2. HRMS (ESI-TOF) calcd for $C_{58}H_{44}N_4O_6S_2K$ [M+K]$^+$ 995.2205, found 995.2231.

2.3. Fluorescence Experiments

All solutions of anions; chromate (CrO_4^{2-}), chloride (Cl^-), chlorite (ClO_2^-), chlorate (ClO_3^-), perchlorate (ClO_4^-), fluoride (F^-), bromate (BrO_3^-), nitrate (NO_3^-), phosphate (PO_4^{3-}) and sulphate (SO_4^{2-}) were used directly from their readily available sodium salts at a concentration of 1000 ppm. The sensor compound **V** was also dissolved in THF:H$_2$O (70:30, v/v) with a concentration value of 9.38 × 10^{-5} M. Lastly, diluted sensor **V** solution (1 equiv) and anion solutions (10 equiv) were stirred vigorously and the resulting complex solutions were measured initially with the fluorescence spectrophotometry for their fluorometric response.

3. Results and Discussion

3.1. Design, Synthesis, Characterization and Photophysical Properties of Sensor V

The sensor **V** was prepared by following the synthetic route with two-step shown in Scheme 1. As is seen, firstly, benzothiazole compound (**I**) was reacted with chloroacetyl chloride (**II**) in the presence of Et$_3$N in CH$_2$Cl$_2$ to furnish chloroacetamide compound **III** which is a more synthetically versatile intermediate. Followingly, another substitution reaction between calix[4]arene (**IV**) and the intermediate **III** in the presence of K$_2$CO$_3$ / KI in acetone/toluene solvent system was selectively carried out in order to obtain the target sensor **V**. The purity of conveniently synthesized **V** was confirmed with its characterization data of such spectroscopic techniques as FTIR, ^{1}H- and ^{13}C-NMR along with HRMS analysis.

In FTIR spectrum of sensor **V**, as an evidence of intermolecular bonding through chloroacetyl moiety, characteristic stretching peaks for C=N and C=O groups were observed at 1616 and 1688 cm^{-1}, respectively. In ^{1}H NMR spectrum, while methylene bridge protons (ArCH$_2$Ar) of calix[4]arene cone were detected at 3.44 and 4.51 ppm as doublets, methylene of chloroacetyl linking group (OCH$_2$CO) were displayed at 4.71 ppm. Besides, NH protons at 11.75 ppm as singlet and the sufficient number of aromatic protons distributed between 8.20 and 6.67 indicated that the desired sensor candidate compound was successfully synthesized. The characteristic peaks of methylene carbons belonging to calix cone and chloroacetyl moiety at 71.6, 31.3 and 30.2 ppm, respectively in the ^{13}C NMR also support this consideration. Additionally, HRMS spectrum of **V** displayed a molecular ion peak [M+K]$^+$ at 995.2231 as the most conclusive evidence that fits the expectations for the structural elucidation.
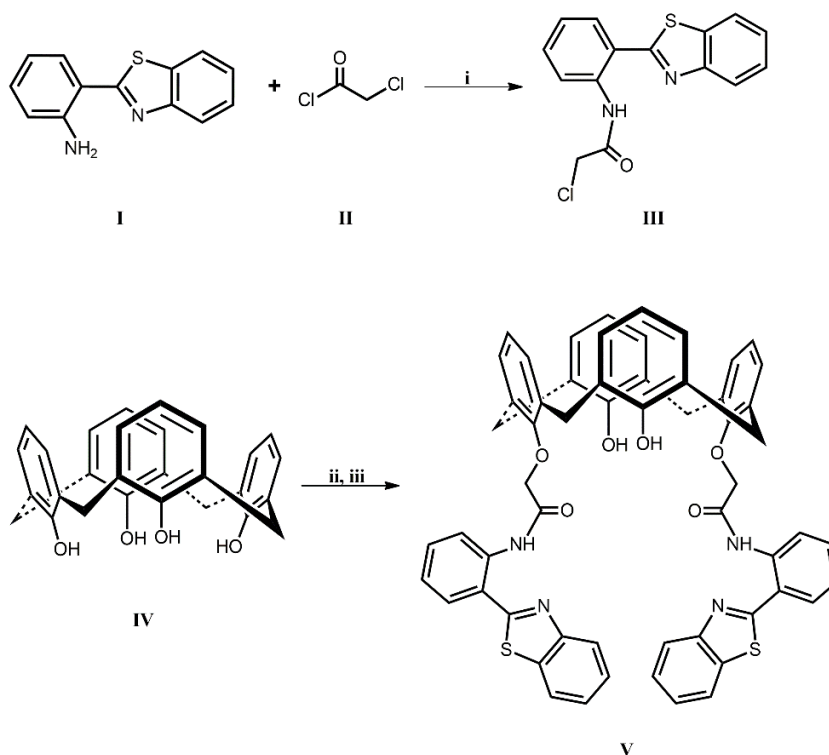
Scheme 1. Synthetic route of the sensor, benzothiazole bearing calix[4]arene V; Reagents and conditions: (i) Et$_3$N, CH$_2$Cl$_2$, r.t.; (ii) K$_2$CO$_3$, toluene, r.t.; (iii) III, KI, acetone, reflux

The photophysical properties of sensor candidate were investigated by UV-Vis and fluorescence spectra along with selectivity/sensitivity studies. The sensor candidate **V** is soluble in common organic solvents such as DMSO, THF, CHCl$_3$ and in aqueous solution with organic solvents such as THF. Figure 1 shows the fluorescence viewing of THF solutions within the increasing water amount containing the same concentrations of compound **V**. Due to the best fluorescent response that would allow us to see the photophysical changes most clearly [40, 41], the ratio of 70:30 (v/v) THF-H$_2$O mixture was selected for further fluorescence experiments such as selectivity and sensitivity. The maximum absorption band of compound **V** (9.38×10^{-5} M) in the relevant ratio of THF-H$_2$O lied at 310 nm, and upon excitation, the maximum emission wavelength was observed at 552 nm (Fig. 2) showing a significant pseudo Stokes shift ($\Delta\lambda = 242$ nm).

3.2. Selectivity Studies

As shown in Figure 2, the sensor candidate **V** shows weak fluorescence at 552 nm itself. By the addition of various anions such as CrO$_4^{2-}$, Cl$^-$, ClO$_3^-$, ClO$_4^-$, F$^-$, BrO$_3^-$, NO$_3^-$, PO$_4^{3-}$ and SO$_4^{2-}$ to the solutions containing compound **V**, the fluorescence

spectra were scarcely changed. In contrast, addition of ClO$_2^-$ anion to **V** created a strong blue fluorescence at 468 nm while the main emission band at 552 nm disappeared along with a large Stokes shift with the value of 158 nm (Fig. 2). As can be seen from the photo taken under fluorescent lamp as Figure 3, this observation indicated that chlorite anion selectively triggered fluorescence enhancement of compound **V** over other competitive anions.

3.3. Titration Studies

The results of fluorescence titration of compound **V** with chlorite anion is shown in Figure 4 in order to get insight into the sensitivity of **V** to ClO$_2^-$. To investigate the detection limit of the sensor **V** for ClO$_2^-$, compound **V** (9.38×10^{-5} M) was treated with various concentrations of ClO$_2^-$ (0–20 equivalents). Incremental addition of chlorite increases the fluorescence intensity remarkably at 468 nm. Also shown as an inset in Figure 4, the linear relationship between the fluorescence intensity and chlorite concentrations was clearly observed.
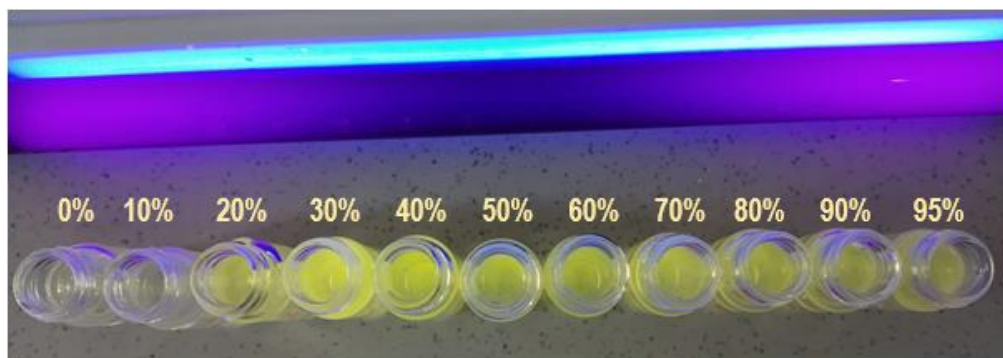

*Figure 1. Fluorescence viewing of sensor **V** in THF-H$_2$O solutions with increasing water fractions*
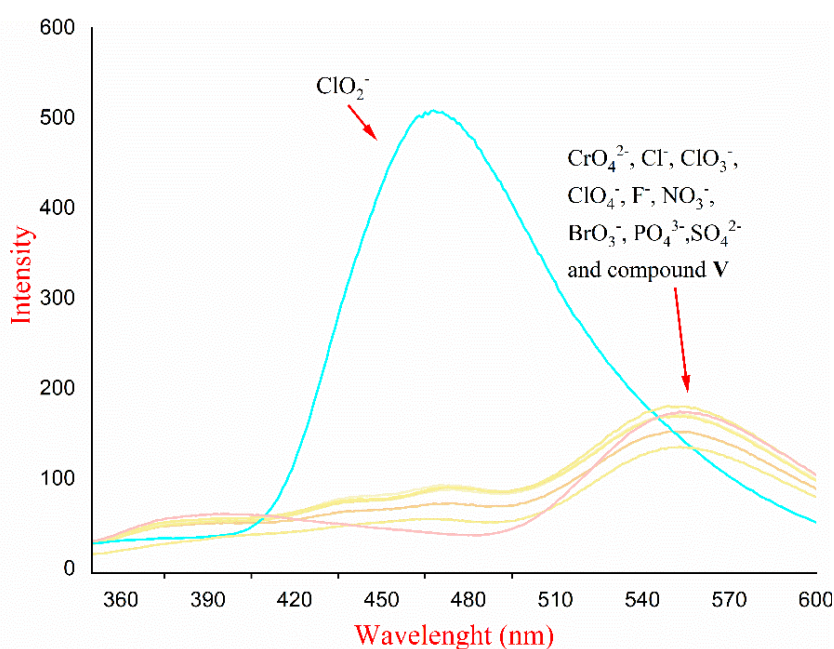

*Figure 2. Fluorescence spectrum of sensor **V** in the absence and presence of various anions in THF-H$_2$O (70:30, v/v)*
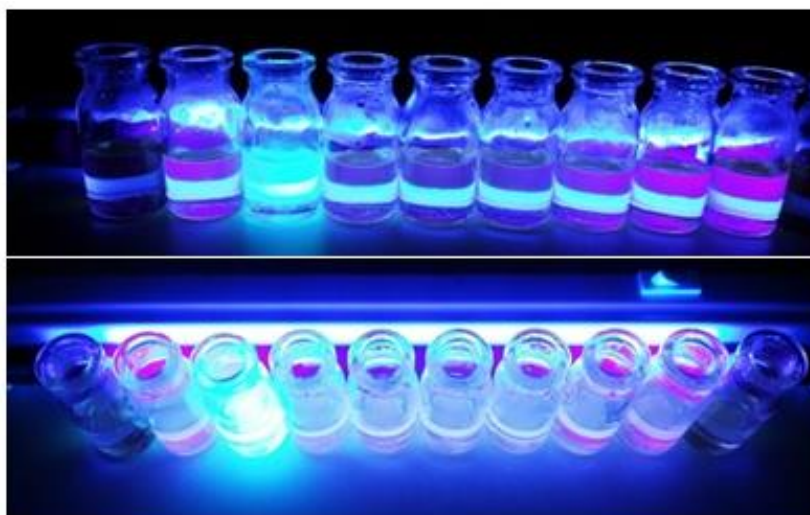
*Figure 3. Photograph of the fluorometric responses of sensor **V** toward various anions in THF-H$_2$O (70:30, v/v)*
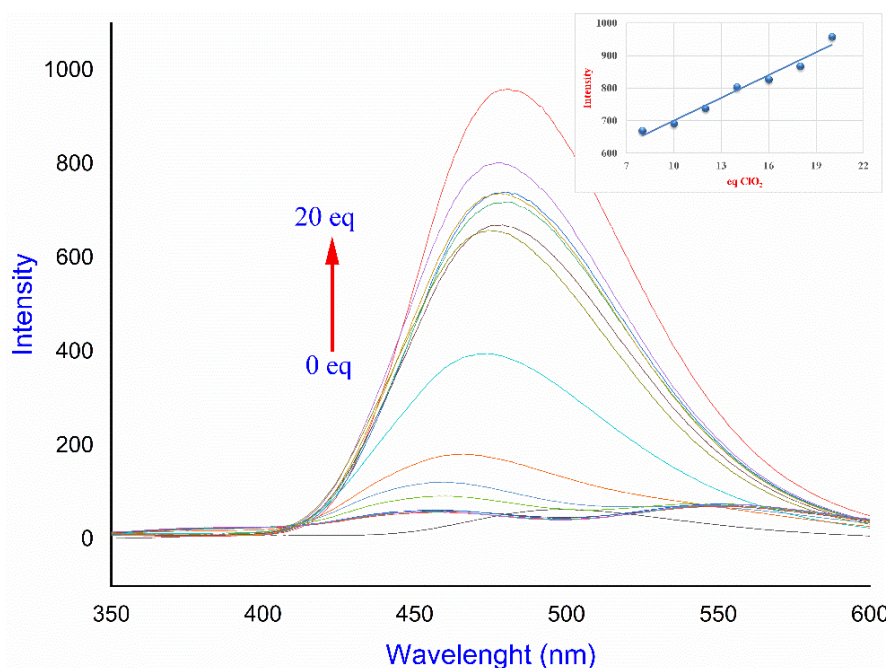

Figure 4. Changes in the fluorescence emission spectrum of sensor **V** with various equivalents of ClO$_2^-$ ion; inset: fluorescence intensity versus chlorite concentration

4. Conclusions and Recommendations

A recently synthesized fluorogenic chemosensor compound (**V**) for the determination of chlorite ion is reported. Fluorescent measurements were performed in aqueous medium that enables the water analysis method to be applied on site. In that medium, the chemosensor exhibits remarkably enhanced fluorescence accompanied with a colour change from yellow to blue for chlorite anion. These results obtained in the study show that the sensor compound **V** can provide excellent performance with the production of fluorometric responses selectively and sensitively for chlorite anions in aqueous systems without affecting from other competing ions. Therefore, we can proudly say that the related method is suitable for controlling of chlorite anion in water sources, which has a great importance for the human health and the sensor would find a great deal of practical applications in chlorite monitoring. In addition, a clear understanding of the response style of chlorite anion is of great value in terms of significance for the gaining insight about reactive oxygen species-calixarene interactions in sensor design. In this way, new ideas for the design of especially, new 1,3-disubstituted calixarene based analogues/derivatives will come to the light. Within this context, our simultaneous studies based on calix[4]arene scaffold with regard to its selective/sensitive recognition ability towards various anions is currently under progress.

5. Acknowledge

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