Contents lists available at SciVerse ScienceDirect







journal homepage: www.elsevier.com/locate/inoche

# Colorimetric and fluorescence turn-on sensor for biologically important anions based on carbazole derivative

Xuefang Shang <sup>a,\*</sup>, Xinjuan Li <sup>b</sup>, Jie Han <sup>a</sup>, Shenyu Jia <sup>a</sup>, Jinlian Zhang <sup>c</sup>, Xiufang Xu <sup>d</sup>

<sup>a</sup> Department of Chemistry, Xinxiang Medical University, East of Jinsui Road, Xinxiang, Henan, 453003, China

<sup>b</sup> Department of Chemistry, Henan Normal University, East of Construction Road, Xinxiang, Henan, 453007, China

<sup>c</sup> School of Pharmacy, Xinxiang Medical University, East of Jinsui Road, Xinxiang, Henan, 453003, China

<sup>d</sup> Department of Chemistry, Nankai University, Tianjin, 300071, China

#### ARTICLE INFO

Article history: Received 13 September 2011 Accepted 22 November 2011 Available online 3 December 2011

Keywords: Colorimetric sensor Fluorescence PET Naked-eye Carbazole Determination limit

#### ABSTRACT

A colorimetric and fluorescent anion chemosensor containing carbazole group has been designed and synthesized based on photoinduced electron transfer (PET). The strong basic anions such as  $F^-$ ,  $AcO^-$  and  $H_2PO_4^$ resulted in significant red-shift in absorption band and enhancement in fluorescent emission intensity of the compound **1**, synchronously accompanied by a "naked eye" color change from light yellow to orangeyellow in organic medium. The determination limit of sensor **1** toward  $H_2PO_4^-$  is  $1.0 \times 10^{-6}$  mol·L<sup>-1</sup>. <sup>1</sup>H NMR titration experiments shed light on the nature of the interaction between **1** and the anions. Theoretical investigation further illustrated the possible binding mode of host–guest and the roles of molecular frontier orbitals in anion binding.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

The research field of chemosensors continues to expand with new synthetic molecules capable of recognizing anions which play an important role in a wide range of chemical and biological processes [1–5]. Among various biologically important anions, phosphates anion has received growing attention for its established role in a variety of fundamental processes such as energy transduction, signal processing, genetic information storage, and membrane transport [6]. Phosphates can also be found in many chemotherapeutic and antiviral drugs [7–9]. It is for sure that phosphate originating from the over use of agricultural fertilizers can also lead to eutrophication in inland waterways [10]. Hence, to recognize and sense phosphate ions and phosphorylated biomolecules is to be more and more important than other biologically functional anions [11–13].

Nowadays, a colorimetric receptor for special anionic species is increasing interest due to its simplicity and high sensitivity [14–17]. Colorimetric sensing is especially attractive, as it may allow "naked-eye" detection of the analyte without resorting to any expensive equipment [18,19]. In general, these chemosensors are constructed according to the receptor–chromophore general binomial, which involves the binding site and a chromophore or fluorophore which can translate the receptor–anion association into an optical signal

[20,21]. The mechanisms, which control the response of the chromophore or fluorophore to substrate binding, include photoinduced electron transfer (PET) [22], fluorescence (Förster) resonance energy transfer (FRET) [23], excimer/exciplex formation [24] or extinction, and photoinduced charge transfer (PCT) [25]. Among these signaling mechanisms, the PET mechanism is often exploited for the sensors showing the fluorescence response to the guest binding owing to that such fluorescent host molecules based on PET is mostly structurally simple [26].

Various types of artificial receptors have been developed that employ hydrogen bonds offered by specific binding sites as in amides [27], thioamide [28], azamacrocycles [29], urea or thiourea [30], and pyrroles [31,32] to bind anions with size and shape selectivity in various media. Phenol group is among the most frequently used fragments to design neutral receptors for the selective recognition of anions as it is able to strongly bind anions using directional hydrogen bonding interactions even in the aqueous solution [33,34]. Although anion receptors containing phenol group as a binding site have been researched, recognition mechanism based on the synergism of phenol and carbazole-NH is rarely reported in "naked-eye" detection of anions [35,36].

In this paper, we reported a colorimetric and fluorescent anion sensor **1** (N, N'-di(methylimino-1'-2'-hydroxyl-3',5'-dibromidobenzene)-3, 6-dichloro-1,8-diami-nocarbazole) providing phenol group and carbazole-NH as binding sites and conducting the PET signaling mechanism. We reasoned that the OH group and NH group were incorporated to the conjugated system with the carbazole moiety

<sup>\*</sup> Corresponding author: Tel.: +86 373 3029128; fax: +86 373 3029959. E-mail address: xuefangshang@126.com (X. Shang).

<sup>1387-7003/\$ –</sup> see front matter 0 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.inoche.2011.11.025

(fluorophore) which made the sensor **1** capable of sensing anions optically in organic medium possible. Just as expected, the sensor **1** showed "naked-eye" color changes from light yellow to orange and the fluorescence turn-on changes upon the addition of anions in organic solvent. Although several PET sensors for anions are known, such carbazole-NH and phenol group conjugated systems, employing neutral anion receptors and exhibiting an ideal PET behavior and color changes as signaling events, detectable by the "naked eye" upon anion binding, have been rarely reported.

# 2. Experimental

Most of the starting materials were obtained commercially and all reagents and solvents were of analytical grade. All anions, in the form of tetrabutylammonium salts [such as  $(n-C_4H_9)_4NF$ ,  $(n-C_4H_9)_4NCI$ ,  $(n-C_4H_9)_4NBr$ ,  $(n-C_4H_9)_4NI$ ,  $(n-C_4H_9)_4NACO$ ,  $(n-C_4H_9)_4NH_2PO_4$ ], were purchased from Sigma-Aldrich Chemical Co., and stored in a desiccator under vacuum containing self-indicating silica, and used without any further purification. Tetra-n-butylammonium salts were dried for 24 h in vacuum with  $P_2O_5$  at 333 K. Dimethyl sulfoxide (DMSO) was distilled in vacuum after dried with CaH<sub>2</sub>. C, H, N elemental analyses were made on Vanio-EL. <sup>1</sup>H NMR spectra were recorded on a Varian UNITY Plus-400 MHz Spectrometer. ESI-MS was performed with a MARINER apparatus. UV-vis titration experiments were made on a Shimadzu UV2550 Spectrophotometer at 298 K. The affinity constant,  $K_s$ , was obtained by non-linear least square calculation method for data fitting.

Compound **1** was synthesized according to the route shown in Scheme 1.

#### 2.1. 3,6-Dichlorocarbazole (2) [37]

To a three-neck, 250 ml round-bottomed flask, carbazole (10 g, 0.06 mol) and  $CH_2Cl_2$  (100 ml) were added and the flask was equipped with a mechanical stirrer and a thermometer. The resulting mixture was cooled to 0 °C and then  $SO_2Cl_2$  (9.6 ml, 0.12 mol) was added dropwise while the solution was being vigorously stirred (*note*: the temperature did not exceed 2 °C). After the addition, the cooling bath was removed and the reaction mixture was stirred for another 4 h at room temperature. Then, the solid precipitate was filtered, washed with  $CH_2Cl_2$  and dried to give raw product. The raw 3,6-dichlorocarbazole was suspended in 250 ml of hexane and boiled



**Fig. 1.** Changes in the absorption spectra of compound 1  $(2.6 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1})$  in absence and presence of H<sub>2</sub>PO<sub>4</sub> in DMSO.

for 0.5 h. The suspension was filtered, giving pure product. Yield: 72%; mp: 202–204  $^{\circ}$ C (lit. 205  $^{\circ}$ C).

#### 2.2. 3, 6-Dichloro-1, 8-dinitrocarbazole (3) [37]

To a three-neck, 250 ml round-bottomed flask, 3, 6dichlorocarbazole (8.35 g, 35 mmol), acetic acid (28 ml) and acetic anhydride (21 ml) were added and then, the flask was equipped with a magnetic stirrer, a dropping funnel and a thermometer. The solution was cooled to 1 °C and 100% HNO<sub>3</sub> (4.5 ml, 0.11 mol) began to be added dropwise while stirring and the temperature did not exceed 1 °C. Following the addition of 1/8 of the whole volume of HNO<sub>3</sub>, the cooling bath was replaced with an oil bath. The mixture was heated to 60 °C and half of HNO3 was added at this temperature. During the addition of the remaining HNO<sub>3</sub>, the reaction mixture was further heated, until it reached to 75 °C. After the addition was completed, the temperature of the solution was elevated to 110 °C for next 10 min. Afterward, the suspension was filtered while hot and the product was washed with boiling acetic acid (10 ml) and diethyl ether. Yield: 86%; mp: 282–283 °C (lit. 284 °C); <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>): δ 11.30 (s, 1H, NH), 8.98 (s, 2H), 8.49 (d, 2H); elemental analysis calcd. for C<sub>12</sub>H<sub>5</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>4</sub>: C, 44.20; H, 1.55; N, 12.89; found: C, 44.36; H, 1.61; N, 12.85. ESI-MS (*m*/*z*): 324.30 (*M*-H)<sup>-</sup>.



Scheme 1. General synthetic route to the target compound 1.



**Fig. 2.** Color changes of  $1 (2.6 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1})$  in DMSO in absence and presence of different anions (A: 1 only; B: 1 + 10 equiv. F<sup>-</sup>; C: 1 + 10 equiv. Cl<sup>-</sup>; D: 1 + 10 equiv. Br<sup>-</sup>; E: 1 + 10 equiv. I<sup>-</sup>; F: 1 + 10 equiv. AcO<sup>-</sup>; G: 1 + 10 equiv. H<sub>2</sub>PO<sub>4</sub><sup>-</sup>).

### 2.3. 3, 6-Dichloro-1, 8-diaminocarbazole (4)

To a three-neck, 250 ml round-bottomed flask, 3, 6-Dichloro-1,8-dinitrocarbazole (1.62 g, 5 mmol) and Pd/C were suspended in C<sub>2</sub>H<sub>5</sub>OH (100 ml). The solution was refluxing and NH<sub>2</sub>NH<sub>2</sub>·H<sub>2</sub>O (10 ml) resolved in C<sub>2</sub>H<sub>5</sub>OH (30 ml) was added dropwise. After the addition was completed, the mixture was refluxing for 12 h until the solution was changed to colorless. Then, the hot suspension was filtered and washed with ethanol. The solvent in filtrate was removed by rotary evaporator and the gray-white compound was obtained and recrystallized from ethanol. Yield: 59%; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  10.67 (s, 1H, NH), 8.91 (s, 2H), 8.36 (s, 2H); 5.42 (s, 4H, NH<sub>2</sub>) elemental analysis calcd. for C<sub>12</sub>H<sub>9</sub>Cl<sub>2</sub>N<sub>3</sub>: C, 54.16; H, 3.41; N, 15.79; found: C, 54.28; H, 3.66; N, 15.65.

# 2.4. N,N'-Di(methylimino-1'-2'-hydroxyl-3',5'-dibromidobenzene)-3, 6-dichloro-1,8-diaminocarbazole (1)

3, 6-Dichloro-1,8-diaminocarbazole (265 mg, 1 mmol) and 3,5-dibromo-salicylaldehyde (556 mg, 2 mmol) were suspended in 35 ml ethanol. The mixture was heated under refluxing for 4 h. The yellow precipitate was separated by filtration. The solid was washed with diethyl ether and dried under vacuum. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  13.24 (s, 2H, OH), 12.04 (s, 1H, NH), 9.06 (s, 2H), 8.29 (s, 2H), 7.98 (s, 4H), 7.53 (s, 2H). Elemental analysis: Calc. for C<sub>26</sub>H<sub>13</sub>Br<sub>4</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>2</sub>: C, 39.53; H, 1.66; N, 5.32; Found: C, 39.31; H, 1.74; N, 5.69. ESI-MS (*m/z*): 783.56 (*M*-H)<sup>-</sup>.

#### 3. Results and discussion

#### 3.1. UV-vis titration and "naked-eye" observation

The anion sensing ability of compound **1** with halide anions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup>), AcO<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> in dry DMSO was investigated in



**Fig. 3.** The spectral changes of compound 1  $(2.6 \times 10^{-5} \text{ mol} \cdot L^{-1})$  induced by the addition of 10 equiv of anions tested, respectively.

detail through UV-vis spectroscopy and fluorescence emission. Fig. 1 shows the changes in UV-vis spectra of  $1 (2.6 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1})$  upon titration with the  $H_2PO_4$  solution. Obviously seen from Fig. 1, the UV-vis spectrum of free 1 exhibited two broad absorption bands centered at 340 nm and 410 nm. The first band (340 nm) could be assigned to the excitation of the  $\pi$  electrons in the carbazole system and the latter band was due to intramolecular charge-transfer (ICT) transitions within the whole structure of compound **1** [25]. With the stepwise addition of  $H_2PO_4^-$  ions to the DMSO solution of 1 (2.6×10<sup>-5</sup> mol·L<sup>-1</sup>), the absorbance values at 340 nm and 410 nm were reduced in intensity and simultaneously a new absorbance band at 470 nm was developed gradually. The red-shift phenomenon that occurred was induced by  $H_2PO_4^-$  ion in the absorption spectrum of compound **1**. Noticeably, the color of the solution changed from light-yellow to orange-yellow which was attributed to the significant development of absorption peak at 470 nm (Fig. 2). Interestingly, the addition of protic solvent (such as H<sub>2</sub>O or MeOH) to the solution of compound 1 bound to  $H_2PO_4^-$  made orange yellow solution change back to light yellow, which suggested hydrogen bonding donor solvent destroyed the binding between compound **1** and  $H_2PO_4^-$ . The above observations also demonstrated that the interactions between compound 1 and  $H_2PO_4^$ were hydrogen bonding interaction in essence [38,39]. In addition, there were two well-defined isosbestic points at 320 and 423 nm, respectively, indicating the stable complex having a certain stoichiometric ratio between compound **1** and  $H_2PO_4^-$  anion formed [40]. Particularly, the presence of AcO<sup>-</sup> and F<sup>-</sup> induced similar changes in UV-vis spectrum of compound **1** with those originating from the addition of H<sub>2</sub>PO<sub>4</sub>, but addition of excess equiv of Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> ions resulted in slight changes in the UV-vis spectrum of compound 1 (Fig. 3).

#### 3.2. Fluorescence titration

The photophysical response of compound **1** toward the addition of anions tested was also investigated in DMSO. Just as Fig. 4 shows, the



Fig. 4. Changes in the emission spectra of compound 1  $(2.6 \times 10^{-5} \text{ mol} \cdot L^{-1})$  in absence and presence of F<sup>-</sup> in DMSO.



Scheme 2. Proposed host-guest binding mode.

fluorescence spectrum of compound **1** exhibited emission band centered at 500 nm when excitated at 444 nm. Upon the addition of F<sup>-</sup> ions (0-10 equiv) to the solution of compound **1**, the fluorescence got enhanced. There were similar changes in the fluorescence emission of **1** induced by the addition of  $AcO^-$  and  $H_2PO_4^-$  ions with those of F<sup>-</sup>. To account for such fluorescence enhancement, the PET mechanism was exploited. As we all knew, the fluorescence of the anion PET chemosensor generally was 'turn off' rather than 'turn on' upon ion sensing unlike most PET sensors for cations. In the case of compound 1, the excited state of the fluorophore was not, or only to a minor extent, enhanced by electron transfer (ET) from the receptor to the fluorophore and the receptor-anion interaction. Upon the further addition of  $F^-$ , it appeared that the deprotonated species  $LH^{-}/L^{2-}$ , being more electron rich compared to the hydrogenbonded complex with fluoride, activated the PET process more efficiently and showed up a greater enhancing (Scheme 2). Nevertheless, fluorescence emission of sensor 1 was insensitive to addition of excess equiv of  $Cl^-$ ,  $Br^-$  and  $I^-$  ions (Fig. 5).

#### 3.3. Affinity constant

The job-plot analysis indicated that the spectral change could be ascribed to the formation of 1:1 host-guest complexation. The obtained affinity constants were listed in Table 1 using the method of non-linear least squares calculation according to the UV-vis data [41–43]. The selectivity trend of binding ability of compound **1** to anions followed the order of:  $H_2PO_4^- > AcO^- > F^- > > Cl^- ~Br^- ~I^-$ . It is apparent that the selectivity for specific anions can be rationalized on the basis of the anion's basicity and the interactions between the host and the anionic guests. However, multiple hydrogen-bond interactions are also necessary in high-affinity anion binding sites [44]. As



Fig. 5. Changes in intensity of the emission band at 480 nm in presence of 10 equiv of anions tested.

expected from their basicity,  $H_2PO_4^-$ ,  $AcO^-$  and  $F^-$  will bind more strongly than the other anions studied; in addition, the tetrahedral configuration of  $H_2PO_4^-$  ion may well match **1** in terms of shape and could form multiple hydrogen bonding interaction with compound **1**. Consequently,  $H_2PO_4^-$  ion can be selectively recognized from other anions based on its affinity constant. In addition, the affinity constants obtained by UV-vis data are in the same order of magnitude with it obtained by fluorescence data.

In cation recognition, determination limit was reported by many literatures. While, determination limit of anion is almost not reported. Thus, the determination limit of sensor **1** to  $H_2PO_4^-$  was studied (Fig. 6). The interaction of sensor **1** with  $H_2PO_4^-$  could be detected down to at least a concentration of  $1.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ , at this time the concentration of  $H_2PO_4^-$  ion is  $2.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ . And the corresponding absorption intensity increase to 1.3 times, which showed that sensor **1** could potentially be used as a sensor for monitoring  $H_2PO_4^-$  levels in physiological and environmental systems.

#### 3.4. <sup>1</sup>H NMR titration

To further shed light on the nature of the interaction between compound **1** and the anions, as an example, <sup>1</sup>H NMR spectral changes upon the addition of  $F^-$  as their tetrabutylammonium salts to the DMSO- $d_6$  solution of **1** (1×10<sup>-2</sup> mol·L<sup>-1</sup>) were investigated. Obviously observed from Fig. 7, the peak at 12.04 ppm, which was assigned to ---NH, broadened and exhibited a downfield shift to 12.28 ppm upon the addition of different equiv of F<sup>-</sup> indicating the strong hydrogen-bonding interactions occurred between compound **1** and F<sup>-</sup> ion [45]. The hydroxyl proton peak at 13.24 ppm, exhibited an upfield shift to 12.75 ppm and then thoroughly disappeared with the increase of F<sup>-</sup> ion. Such a significant upfield was rarely seen in the ever-reported PET anion sensors. The reason may be as following: In compound 1, hydroxyl group formed intramolecular hydrogen bond with the near Br atom, which can be proved by theoretical investigation. With the addition of 0.5 equiv of F<sup>-</sup> ion, intramolecular hydrogen bond was broken which induced deshielding effect and the proton peak of hydroxyl group shifted to the upfield direction.

 Table 1

 Affinity constants of compound 1 with various anions.

Anions <sup>a</sup>	$K_{\rm s}$ (UV)	$K_{\rm s}$ (fluorescence)
H <sub>2</sub> PO <sub>4</sub>	$(2.13\pm 0.19)\!\times\! 10^4$	$(2.02\pm0.11)\! imes\!10^4$
AcO	$(1.79 \pm 0.26) \times 10^4$	$(1.98 \pm 0.24)  imes 10^4$
F	$(1.08 \pm 0.18) \times 10^4$	$(0.98 \pm 0.17)  imes 10^4$
Cl	ND <sup>b</sup>	ND
Br	ND	ND
Ι	ND	ND

<sup>a</sup> All anions were added in the form of tetra-n-butylammonium (TBA) salts. <sup>b</sup> The affinity constant could not be determined.



Fig. 6. The change of absorption intensity of sensor 1 in 475 nm with the increase of  $\rm H_2PO_4^-$  concentration.

With the further addition of  $F^-$  ion, one hydroxyl moiety was deprotonated due to the formation of FHF<sup>-</sup>. The proton peak of FHF<sup>-</sup> did not appear which may be related with the small quantity water in DMSO-*d*<sub>6</sub> [46]. The carbazole protons (Ha: 8.19 ppm; Hb: 7.53 ppm) exhibited a slight upfield shift which indicated the increase of the electron density on them owing to the through-bond effects. The proton peaks of phenyl (Hc and Hd, 7.98 ppm) were overlapped and then splitted when the anion was absence and presence, respectively. With the increase of  $F^-$  ion, the proton peaks of phenyl splitted to two peaks which shifted to the downfield and upfield direction, respectively.

#### 3.5. Theoretical investigation

The geometry of compound **1** was optimized (Fig. 8) using density functional theory at B3LYP/3-21G level with Gaussian03 program [47]. From Fig. 8, the intramolecular hydrogen bonds indeed exist in compound **1** between carbozale-NH and hydroxyl group in benzene ring or hydroxyl group and the bromide atom. This result can explain the <sup>1</sup>HNMR titration phenomena in the interacted process of host-guest.

In addition, selected frontier orbitals for compound **1** are shown in Fig. 9. We introduced molecular frontier orbital in order to explain UV–vis absorption spectra in the interacted process of host–guest



**Fig. 7.** <sup>1</sup>H NMR spectra of compound **1** in DMSO- $d_6$  (1×10<sup>-2</sup> mol·L<sup>-1</sup>) upon addition of molar equiv of F<sup>-</sup>.



Fig. 8. Optimized geometry of compound 1.

induced electron transition of frontier orbital. The highest HOMO density in compound **1** is mainly localized on the carbazole moiety. While the highest LUMO density is mainly localized on one phenyl ring moiety and carbazole moiety, this demonstrates that it is the electron transition of the highest HOMO that arouse the red-shift phenomenon in UV-vis spectra of **1**-anion.

According to the results from UV–vis spectral, fluorescent and <sup>1</sup>H NMR titrations, the proposed host–guest binding mode in the solution was depicted in Scheme 2. In the complex structure, an anion interacted with compound **1** via N—H and O—H hydrogen bonds. With the further addition of anion, hydroxyl group deprotonated and the hydrogen bond still existed in carbozale–NH and anion.



Fig. 9. Molecular orbital level of compound 1, a) HOMO; b) LUMO.

# 4. Conclusion

In conclusion, a colorimetric and fluorescent anion sensor, which allows so-called naked-eye detection in a straightforward and inexpensive manner, offering qualitative and quantitative information without using expensive equipment, has been developed. And what is more attractive is that the sensor is based on photoinduced electron transfer (PET) fluorescence enhancement (turn-on), which offers the potential for high sensitivity. In addition, the determination limit of sensor 1 toward  $H_2PO_4^-$  is  $1.0 \times 10^{-6}$  mol·L<sup>-1</sup> which indicates that this sensor could potentially be useful as a probe for monitoring  $H_2PO_4^-$  levels in physiological and environmental systems. What is more, the sensor is expected to have many opportunities in detection of  $H_2PO_4^-$  ion in real life owing to the simplicity and sensitivity of the analysis.

#### Acknowledgments

This work was supported by the Nature Science Fund of Henan Province (2010B150024), Young Teacher Fund of Henan Province and Doctorial Starting Fund of Xinxiang Medical University.

#### References

- C. Caltagirone, P.A. Gale, Anion receptor chemistry: highlights from 2007, Chem. Soc. Rev. 38 (2009) 520–563.
- [2] K. Bowman-James, Alfred Werner revisited: the coordination chemistry of anions, Acc. Chem. Res. 38 (2005) 671–678.
- [3] P.A. Gale, Structural and molecular recognition studies with acyclic anion receptors, Acc. Chem. Res. 39 (2006) 465–475.
- [4] C.R. Bondy, S.J. Loeb, Amide based receptors for anions, Coord. Chem. Rev. 240 (2003) 77-99.
- [5] P.A. Gale, Anion and ion-pair receptor chemistry: highlights from 2000 and 2001, Coord. Chem. Rev. 240 (2003) 191–221.
- [6] J.L. Sessler, D.G. Cho, V. Lynch, Diindolylquinoxalines: effective indole-based receptors for phosphate anion, J. Am. Chem. Soc. 128 (2006) 16518–16519.
- [7] P.A. Furman, J.A. Fyfe, M.H. Clair St, K. Weinhold, J.L. Rideout, G.A. Freeman, et al., Phosphorylation of 3'-azido-3'-deoxythymidine and selective interaction of the 5'-triphosphate with human immunodeficiency virus reverse transcriptase, Proc. Natl. Acad. Sci. U. S. A. 83 (1986) 8333–8337.
- [8] V. Král, J.L. Sessler, Molecular recognition via base-pairing and phosphate chelation. Ditopic and tritopic sapphyrin-based receptors for the recognition and transport of nucleotide monophosphates, Tetrahedron 51 (1995) 539–554.
- [9] A. Ojida, Y. Mito-oka, K. Sada, I. Hamachi, Molecular recognition and fluorescence sensing of monophosphorylated peptides in aqueous solution by bis (zinc (II)dipicolylamine)-based artificial receptors, J. Am. Chem. Soc. 126 (2004) 2454–2463.
- [10] P.A. Gale, A phenylhydrazone-based indole receptor for sensing acetate, Chem. Commun. 30 (2005) 3761–3772.
- [11] G.W. Lee, N. Singh, D.O. Jang, Benzimidazole and thiourea conjugated fluorescent hybrid receptor for selective recognition of PO<sub>4</sub><sup>3-</sup>, Tetrahedron Lett. 49 (2008) 1952–1956.
- [12] J.L. Jimenez Blanco, P. Bootello, J.M. Benito, C. Ortiz Mellet, J.M. Garcia Fernandez, Urea-, thiourea-, and guanidine-linked glycooligomers as phosphate binders in water, J. Org. Chem. 71 (2006) 5136–5143.
- [13] D.A. Jose, S. Mishra, A. Ghosh, A. Shrivastav, S.K. Mishra, A. Das, Colorimetric sensor for ATP in aqueous solution, Org. Lett. 9 (2007) 1979–1982.
- [14] T. Gunnlaugsson, M. Glynn, G.M. Tocci, P.E. Kruger, F.M. Pfeffer, Anion recognition and sensing in organic and aqueous media using luminescent and colorimetric sensors, Coord. Chem. Rev. 250 (2006) 3094–3117.
- [15] M. Zhang, M.Y. Li, F.Y. Li, Y.F. Cheng, J.P. Zhang, T. Yi, C. Huang, A novel Y-type, two-photon active fluorophore: synthesis and application in ratiometric fluorescent sensor for fluoride anion, Dyes Pigments 76 (2008) 408–414.
- [16] D.A. Jose, P. Kar, D. Koley, B. Ganguly, Phenol-and catechol-based ruthenium (II) polypyridyl complexes as colorimetric sensors for fluoride ions, Inorg. Chem. 46 (2007) 5576–5584.
- [17] J. Shao, X. Yu, X. Xu, H. Lin, Z. Cai, H.K. Lin, Colorimetric and fluorescent sensing of biologically important fluoride in physiological pH condition based on a positive homotropic allosteric system, Talanta 79 (2009) 547–551.
- [18] V. Amendola, D. Esteban-Gomez, L. Fabbrizzi, M. Licchelli, What anions do to NHcontaining receptors, Acc. Chem. Res. 39 (2006) 343–353.
- [19] Z. Yang, K. Zhang, F. Gong, S. Li, J. Chen, J.S. Ma, L.N. Sobenina, A.I. Mikhaleva, B.A. Trofimov, G. Yang, A highly selective fluorescent sensor for fluoride anion based

on pyrazole derivative: naked eye "no-yes" detection, J. Photochem. Photobiol. A: Chem. 217 (2011) 29-34.

- [20] R. Nishiyabu, P. Anzenbacher Jr., 1, 3-Indane-based chromogenic calixpyrroles with push-pull chromophores: synthesis and anion sensing, Org. Lett. 8 (2006) 359–362.
- [21] Y.H. Wang, H. Lin, J. Shao, Z.S. Cai, H.K. Lin, A phenylhydrazone-based indole receptor for sensing acetate, Talanta 74 (2008) 1122–1125.
- [22] J. Shao, Y.H. Qiao, H. Lin, H.K. Lin, A turn-on fluorescent anion receptor based on N, N'-di-b-naphthyl-1, 10-phenanthroline-2, 9-diamide, J. Lumin. 128 (2008) 1985–1988.
- [23] M.A. Hossain, H. Mihara, A. Ueno, Novel peptides bearing pyrene and coumarin units with or without b-cyclodextrin in their side chains exhibit intramolecular fluorescence resonance energy transfer, J. Am. Chem. Soc. 125 (2003) 11178–11179.
- [24] J.S. Kim, D.T. Quang, Calixarene-derived fluorescent probes, Chem. Rev. 107 (2007) 3780–3799.
- [25] J. Shao, H. Lin, H.K. Lin, Rational design of a colorimetric and ratiometric fluorescent chemosensor based on intramolecular charge transfer (ICT), Talanta 77 (2008) 273–277.
- [26] J.R. Lakowicz (Ed.), Principles of Fluorescence Spectroscopy, Plenum Publishers Corp, New York, 1999.
- [27] M. Jesús Seguí, J. Lizondo-Sabater, A. Benito, A new ion-selective electrode for anionic surfactants, Talanta 71 (2007) 333–338.
- [28] Shin-ichi Kondo, Masanori Nagamine, Satoshi Karasawa, Masaya Ishihara, Masafumi Unno, Yumihiko Yano, Anion recognition by 2,2'-binaphthalene derivatives bearing urea and thiourea groups at 8- and 8'-positions by UV-vis and fluorescence spectroscopies, Tetrahedron 67 (2011) 943–950.
- [29] John S. Mendy, Musabbir A. Saeed, Frank R. Fronczek, Douglas R. Powell, Md. Alamgir Hossain, Anion recognition and sensing by a new macrocyclic dinuclear copper(II) complex: a selective receptor for iodide, Inorg. Chem. 49 (2010) 7223–7225.
- [30] R. Velu, V.T. Ramakrishnan, P. Ramamurthy, Selective fluoride ion recognition by a thiourea based receptor linked acridinedione functionalized gold nanoparticles, J. Photoch. Photobiol. A: Chem. 217 (2011) 313–320.
- [31] R. Custelcean, L.H. Delmau, B.A. Moyer, J.L. Sessler, W.-S. Cho, D. Gross, G.W. Bates, S.J. Brooks, M.E. Light, P.A. Gale, Angew. Chem. Int. Ed. 44 (2005) 2537–2542.
- [32] J.L. Sessler, D.-G. Cho, M. Stepien, V. Lynch, J. Waluk, Z.S. Yoon, D.J. Kim, Am. Chem. Soc. 128 (2006) 12640–12641.
- [33] X. Bao, Y.H. Zhou, Synthesis and recognition properties of a class of simple colorimetric anion chemosensors containing OH and CONH groups, Sensor. Actuat. B: Chem. 147 (2010) 434-441.
- [34] S.-H. Kim, I.-J. Hwang, S.-Y. Gwon, S.M. Burkinshaw, Y.-A. Son, An anion sensor based on the displacement of 2,6-dichlorophenol-indo-o-cresol sodium salt from a water-soluble tetrasulfonated calix[4]arene, Dyes Pigments 88 (2011) 84-87.
- [35] Z.H. Lin, S.J. Ou, C.Y. Duan, B.G. Zhang, Z.P. Bai, Naked-eye detection of fluoride ion in water: a remarkably selective easy-to-prepare test paper, Chem. Commun. (2006) 624–626.
- [36] Y.-M. Zhang, Q. Lin, T.-B. Wei, D.-D. Wang, H. Yao, Y.-L. Wang, Simple colorimetric sensors with high selectivity for acetate and chloride in aqueous solution, Sensor. Actuat. B: Chem. 137 (2009) 447–455.
- [37] M.J. Chmielewski, M. Charon, J. Jurczak, 1,8-diamino-3,6-dichlorocarbazole: a promising building block for anion receptors, J. Org. Lett. 6 (2004) 3501–3504.
- [38] X. Zhang, L. Guo, F.-Y. Wu, Y.-B. Jiang, Development of fluorescent sensing of anions under excited-state intermolecular proton transfer signaling mechanism, Org. Lett. 5 (2003) 2667–2670.
- [39] S.Y. Liu, Y.B. He, J.L. Wu, L.H. Wei, H.J. Qin, L.Z. Meng, L. Hu, Calix[4]arenes containing thiourea and amide moieties: neutral receptors towards α, ω-dicarboxylate anions, Org. Biomol. Chem. 2 (2004) 1582–1586.
- [40] Y. Kubo, M. Kato, Y. Yoshihiro Misawa, S. Tokita, Tetrahedron Lett. 45 (2004) 3769–3773.
- [41] Y. Liu, B.H. Han, H.Y. Zhang, Spectroscopic studies on molecular recognition of modified cyclodextrins, Curr. Org. Chem. 8 (2004) 35–46.
- [42] Y. Liu, C.C. You, H.Y. Zhang, Supramolecular Chemistry, Nankai University Publication, Tian Jin, 2001.
- [43] J. Bourson, J. Pouget, B. Valeur, Ion-responsive fluorescent compounds. 4. Effect of cation binding on the photophysical properties of a coumarin linked to monoazaand diaza-crown ethers, J. Phys. Chem. 97 (1993) 4552–4557.
- [44] I.V. Korendovych, M. Cho, P.L. Butler, R.J. Staples, E.V. Rybak-Akimova, Anion binding to monotopic and ditopic macrocyclic amides, Org. Lett. 8 (2006) 3171–3174.
- [45] M. Bonizzoni, L. Fabbrizzi, A. Taglietti, F. Tiengo, Eur. J. Org. Chem. (2006) 3567–3574.
- [46] M. Boiocchi, L. Del Boca, D.E. Gomez, L. Fabbrizzi, M. Licchelli, E. Monzani, Nature of urea\_fluoride interaction: incipient and definitive proton transfer, J. Am. Chem. Soc. 126 (2004) 16507–16514.
- [47] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, et al., Gaussian 03, Revision A.1, Gaussian, Inc, Pittsburgh PA, 2003.