

# Acenaphthenequinone based simple colorimetric anion sensor with only one binding site

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**Abstract** Quinonehydrazone compound **1** was designed to be a simple chromogenic anion sensor with one anion binding site. The sensor **1** was easily obtained in 83% yield by the condensation of acenaphthenequinone with 4-nitrophenylhydrazine in ethanol solution. In DMSO, sensor **1** could high selectively and visually detect anions with strong basicity (e.g.,  $\text{AcO}^-$ ,  $\text{F}^-$  and  $\text{H}_2\text{PO}_4^-$ ) from chloride, bromide, and iodide ions with weak basicity.

**Keywords** Anion sensor · “Naked-eye” · Quinonehydrazone · Acenaphthenequinone · Tautomerization

## Introduction

It has been well documented that anions such as  $\text{F}^-$ ,  $\text{CH}_3\text{COO}^-$ , and  $\text{H}_2\text{PO}_4^-$  are important in many biological processes and are known to be present in many commonly used agricultural fertilizers as well as in food additives [1]. For example, fluoride is associated with dental health and has a potential in treatment of osteoporosis [2, 3]. The chronic poisoning can be induced owing to the fact that fluoride is easily absorbed but is excreted slowly from the body. Overexposure to fluoride can lead to acute gastric and kidney problems [4]. Phosphates are biologically relevant anions that commonly occur; phosphorylated species play critical roles in a variety of fundamental processes such as genetic information storage, energy transduction,

signal processing, and membrane transport [5]. But over use of agricultural fertilizers causes eutrophication of lakes and inland waterways. As a result, the search for efficient chemosensors that can recognize and detect these anionic analytes would continue to be a major research area in current times [6–9].

Generally, a sensor molecule is composed of a receptor component that is responsible for binding the analyte and a signaling unit that is capable of translating the analyte-binding induced changes into an output signal [10, 11]. In the case of binding modes of the receptor with anions, those are classified basically into electrostatic interactions [12], hydrogen bond interactions [13], electron-deficient Lewis acid coordination via orbital overlap [14] and interactions with metal centers [15] etc. The hydrogen binding is widely used in anion recognition due its directionality, a feature which allows the design of receptors having ability to differentiate between anions with different geometries and hydrogen-bonding requirements [16–18]. The output signals are commonly probed either by spectroscopic techniques (e.g., fluorescence [19], absorption [20] and NMR [21] spectroscopy), a color change [22] or by evaluating the change in redox potential values [23]. Among these, a colorimetric response has a distinct advantage as they allow for “naked-eye” detection of the targeted analyte through a change in color. Accordingly, an increasing amount of research effort has been devoted to the design and development of novel colorimetric anion sensors. Such sensors require complicated preparation process [24–26] and hence, there is an urgent need for the development of simple colorimetric anion sensors.

In this study, a simple novel colorimetric sensor is designed and synthesized following the binding site-signaling subunit approach. Sensor **1** could be easily prepared

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by conjugating 4-nitrophenylhydrazine and acenaphthenequinone in a high yield. In the compound 1, the nitro and acenaphthenequinone groups acted as signalling unit, and the hydrazone moiety ( $-\text{NH}$ ) was an anion binding site. The sensor 1 exhibited a significant colorimetric response to anions with strong basicity in dry DMSO.

## Experimental section

### Apparatus

$^1\text{H}$  NMR spectra were obtained on a Varian UNITY Plus-400 MHz Spectrometer. ESI-MS was performed with a MARINER apparatus. C, H, N elemental analyses were made on an elemental vario EL. UV-vis spectra were recorded on a Shimadzu UV2450 Spectrophotometer at  $298.2 \pm 0.1$  K.

### Materials

All reagents for synthesis obtained commercially were used without further purification. In the titration experiments, all the anions were added in the form of tetrabutylammonium (TBA) salts, which were purchased from Sigma-Aldrich Chemical, stored in a vacuum desiccator containing self-indicating silica and dried fully before using. DMSO was dried with  $\text{CaH}_2$  and then distilled in reduced pressure.

### General method

All titration experiments were carried out at 298.2 K, unless otherwise mentioned. UV-vis spectra and fluorescent spectra were measured using a Shimadzu UV2450 Spectrophotometer and a Shimadzu RF-5301PC Spectrophotometer, respectively. A  $5.0 \times 10^{-5}$  M solution of the compound 1 in dried DMSO and solutions of 0.10 M tetrabutylammonium (TBA) salts of the respective anions were prepared in dried DMSO and were stored under a dry atmosphere. These solutions were used for all spectroscopic studies after appropriate dilution. Then, given amount of the solution of 1 was added to the quartz cuvette and the increased amount of anions tested (0.1 M in  $\text{DMSO}-d_6$ ) was added to the solution above-mentioned, whose absorbance spectra was tested immediately.

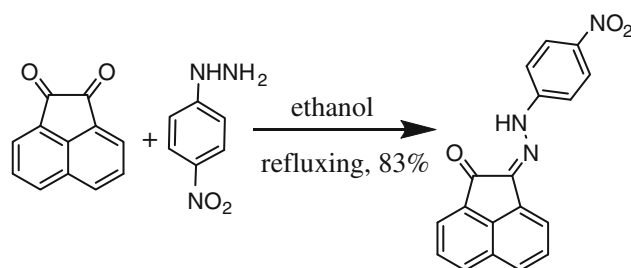
$^1\text{H}$ NMR titration experiments were carried out in the  $\text{DMSO}-d_6$  solution (TMS as an internal standard). A  $1.0 \times 10^{-2}$  M solution of the compound 1 in  $\text{DMSO}-d_6$  was prepared. Then, the increased amount of acetate anion (1.0 M in  $\text{DMSO}-d_6$ ) was added to the solution above-mentioned and  $^1\text{H}$  NMR of the host-guest system was tested.

### Synthesis of 5-(4'-Nitrophenylhydrazone) acenaphthenequinone-2-one (1)

The sensor 1 was synthesized according to Scheme 1. Acenaphthenequinone (0.18 g, 1.0 mmol) with a catalytic amount of acetic acid in ethanol was added dropwise a solution of 4-nitrophenylhydrazine (0.15 g, 1.0 mmol) in ethanol. Then the mixture was heated to reflux under magnetic stirring for 2 h. During the reaction a yellow precipitate appeared which was collected by filtration, washed with ethanol and dried in vacuo. Yield = 83%.  $^1\text{H}$  NMR (400 MHz;  $\text{DMSO}-d_6$ ;  $\text{Me}_4\text{Si}$ ):  $\delta_{\text{H}}$  13.029 (s,  $-\text{NH}$ , 1H), 8.379 (d,  $J = 8.0$  Hz, Ar-H, 1H), 8.282 (d,  $J = 9.2$  Hz, Ar-H, 2H), 8.108 (t, Ar-H, 2H), 7.952 (d,  $J = 6.8$  Hz, Ar-H, 1H), 7.906 (t, Ar-H, 1H), 7.831 (t, Ar-H, 1H), 7.759 (d,  $J = 8.8$  Hz, Ar-H, 2H); ESI-mass:  $m/z$  calcd. for  $\text{C}_{18}\text{H}_{11}\text{N}_3\text{O}_3$  [M] 317.08, found: 316.22 ([M-H] $^-$ ); Elemental analysis calcd for  $\text{C}_{18}\text{H}_{11}\text{N}_3\text{O}_3$ : C 68.14%, H 3.49%, N 13.24%, found: C 68.21%, H 3.62%, N 13.56%.

## Results and discussion

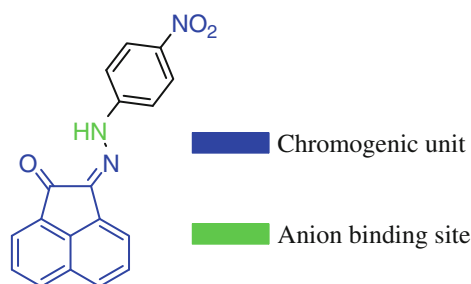
The quinonehydrazone derivatives were proven to be excellent colorimetric sensors for anions in dry DMSO or acetonitrile-water medium. In particular, such sensors ordinarily exhibit anion-induced tautomeric equilibria between azophenol and quinone-hydrazone, being responsible for "Naked-eye" detection of anions. For example, we [27] and S. J. Shao's group [28] prepared some anion sensors by the reaction of isatin with the corresponding hydrazine, respectively, which showed high selectivity for acetate. C. Y. Duan and co-workers [29] reported a chromo- and fluorogenic hybrid chemosensor based quinonehydrazone, which could detect fluoride ion in natural aqueous environments without any spectroscopic instrumentation. However, they only investigated the spectral responses of the chemosensor to fluoride with strong basicity and did not show spectral changes resulting from other anions ( $\text{AcO}^-$  and  $\text{H}_2\text{PO}_4^-$ ) with similar basicity with fluoride. Usually, detection and sensing of fluoride



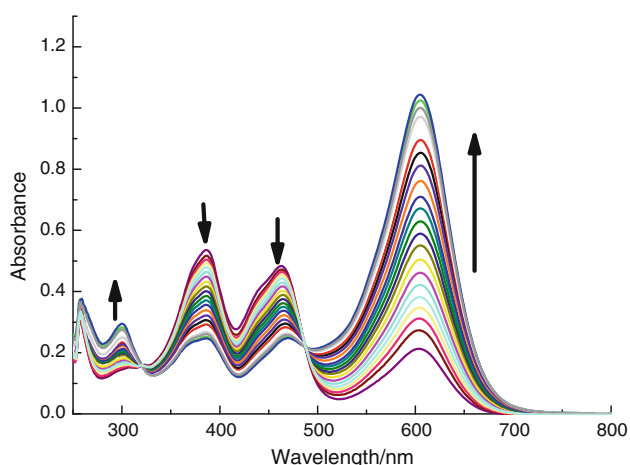
**Scheme 1** The synthesis route of the receptor 1

extremely suffers from interference from such anions. As part of our ongoing research programme into the development of quinonehydrazone based colorimetric anion sensor, a new sensor based on 5-(4'-nitrophenylhydrazine) acenaphthenequinone-2-one (**1**) was designed and synthesized. In compound **1**, the nitro group (an electron withdrawing group) not only acts as a chromogenic unit but also can increase the acidity of the anion binding site (the hydrazone moiety:  $-\text{NH}$ ) [30]. Importantly, the sensor **1** is easily prepared through only one step from starting materials. Next, the interactions between **1** and anions with different configuration (e.g.,  $\text{F}^-$ ,  $\text{AcO}^-$ , and  $\text{H}_2\text{PO}_4^-$ ) were investigated using the spectral titrations Fig. 1.

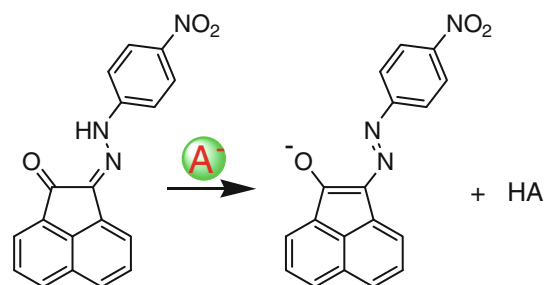
The changes in absorption spectra of the sensor **1** ( $2 \times 10^{-5}$  M, DMSO) during the acetate titration are shown in Fig. 2. Free sensor **1** exhibited three absorption peaks centered at 384, 461, and 603 nm, respectively. On addition of  $\text{AcO}^-$  to the solution of **1**, the absorption band at 384 and 461 nm decreased, and the other bands at 603 nm increased prominently with isosbestic points at 319 and 488 nm. The possible explanation for the spectral changes could be given as follow (see Scheme 2). Before



**Fig. 1** The structure of the sensor **1**



**Fig. 2** Spectral changes of the sensor **1** ( $2 \times 10^{-5}$  M) with increasing concentrations of  $\text{AcO}^-$  in DMSO

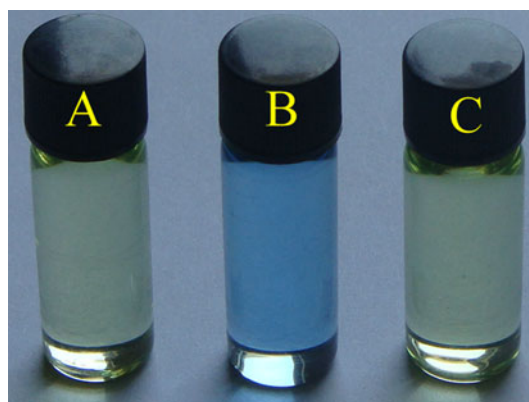


**Scheme 2** Anion-induced tautomerism of the sensor **1** in solution

interaction with  $\text{AcO}^-$ , the quinonehydrazone isomer of the compound **1** dominates in solution, and thus the weak absorption centered at 603 nm ( $\epsilon = 10500 \text{ M}^{-1} \text{ cm}^{-1}$ ) is observed. Upon interaction with  $\text{AcO}^-$ , the quinonehydrazone tautomer of **1** is promoted to the azophenol tautomer, resulting in that the absorption at 603 nm ( $\epsilon = 52500 \text{ M}^{-1} \text{ cm}^{-1}$ ) of the azophenol tautomer increases, which is consistent with the reported results [29]. Synchronously, addition of  $\text{AcO}^-$  to the solution of **1** induced a visual change in color from light green to blue, possibly resulting from deprotonation of **1** (see Fig. 3).

In addition, the sensor **1** has similar spectral responses towards  $\text{H}_2\text{PO}_4^-$  and  $\text{F}^-$  with similar basicity with  $\text{AcO}^-$  and is insensitive to addition of a large excess of chloride, bromide and iodide ions (see Fig. 4). The results indicate that the sensor **1** can high selectively recognize anions with strong basicity (e.g.,  $\text{AcO}^-$ ,  $\text{F}^-$ , and  $\text{H}_2\text{PO}_4^-$ ) from chloride, bromide, and iodide ions with weak basicity.

The association constants of the compound **1** for anionic species were determined by nonlinear fitting analyses of the titration curves according to the eq. (1), 1:1 host-guest complexation [31].



**Fig. 3** Color changes of the receptor **1** ( $2 \times 10^{-5}$  M) in absence and presence of different anions (a the free **1**; b **1** + 5 equiv  $\text{AcO}^-$ ,  $\text{H}_2\text{PO}_4^-$ , or  $\text{F}^-$ ; c **1** + excessive equiv  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ ) in DMSO

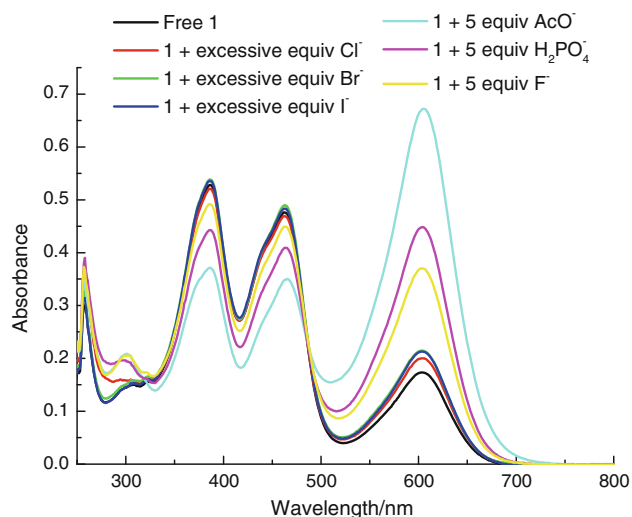
$$A = A_0 + \frac{(A_{\text{lim}} - A) \left\{ c_{\text{H}} + c_{\text{G}} + 1/k_{\text{ass}} - \left[ (c_{\text{H}} + c_{\text{G}} + 1/k_{\text{ass}})^2 - 4c_{\text{H}}c_{\text{G}} \right]^{1/2} \right\}}{2c_{\text{H}}} \quad (1)$$

Where,  $c_{\text{G}}$  and  $c_{\text{H}}$  are the concentration of guest and host, respectively, and  $A$  is the intensity of absorbance at certain concentration of host and guest.  $A_0$  is the intensity of absorbance of host only and  $A_{\text{lim}}$  is the maximum intensity of absorbance of host when guest is added.  $K_{\text{ass}}$  is the equilibrium constant. The association constants displayed in Table 1 were obtained by fitting the profiles of absorbances measured at the fixed wavelength (603 nm) versus [Anion] to Eq. 1 for a 1:1 binding isotherm.

Table 1 demonstrated binding abilities of the sensor 1 with different anions with disparate shapes and basicity. Obviously, the selectivity trends of binding affinities of anions for 1 were determined to be  $\text{AcO}^- > \text{H}_2\text{PO}_4^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ . In general, such selectivity of sensors with only a single binding site could be rationalized on the basis of the guest basicity, which had been proven in the literatures [32]. It seemed that the selectivity of 1 for  $\text{AcO}^-$  could be ascribed to the basicity of the anions (the  $\text{p}K_{\text{b}}$

values of  $\text{AcO}^-$ ,  $\text{F}^-$ , and  $\text{H}_2\text{PO}_4^-$  in water are 9.24, 10.83, and 11.88 [33], respectively). The selectivity of 1 for  $\text{AcO}^-$  agrees well with that reported by us [27] and S. J. Shao [28] previously.

To further investigate the nature of host–guest interactions,  $^1\text{H}$  NMR titration experiments were conducted in  $\text{DMSO-}d_6$ . Figure 5 depicts changes in chemical shifts of 1 in absence and presence of  $\text{AcO}^-$ . Clearly, the peak at 13.04 ppm, which is assigned to  $-\text{NH}$ , disappeared when 2 equiv  $\text{AcO}^-$  ions are added. The result implies the hydrazone moiety acts as an anion binding site and exhibits deprotonation upon exposure to  $\text{AcO}^-$ . Also, the color response to  $\text{AcO}^-$  of 1 is well supported by this finding. In addition, the phenyl protons shifted upfield significantly, indicating that the increase of the electron density on the phenyl ring owing to the through-bond effects [34]. Therefore, the proposed anion binding mode is demonstrated in Scheme 2.



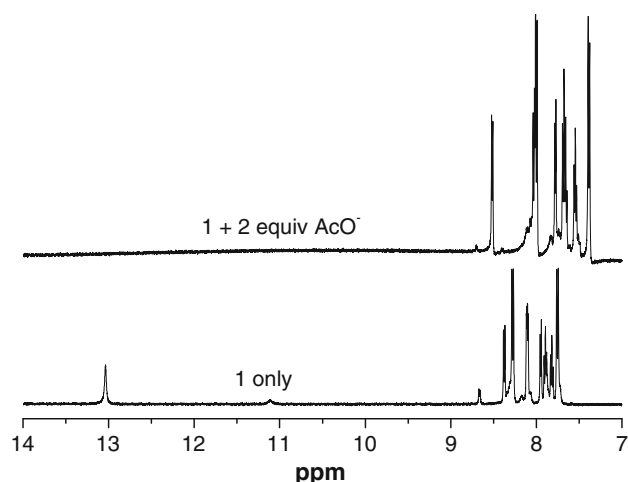
**Fig. 4** The spectral changes of the sensor 1 ( $2 \times 10^{-5}$  M) induced by the different anions tested in MMSO

**Table 1** Association constants ( $K_{\text{ass}} \times 10^4 \text{ mol}^{-1} \text{ L}$ ) of the sensor 1 with anions in  $\text{DMSO}$  at  $298.2 \pm 0.1$  K

Anion	$\text{AcO}^-$	$\text{H}_2\text{PO}_4^-$	$\text{F}^-$	$\text{Cl}^-$	$\text{Br}^-$	$\text{I}^-$
$K_{\text{ass}} \times 10^4$ ( $\text{M}^{-1}$ )	$6.30 \pm 0.35$	$2.00 \pm 0.22$	$1.76 \pm 0.24$	ND	ND	ND
$R^2$	0.999	0.997	0.995	–	–	–

## Conclusion

In conclusion, a new and simple colorimetric anion sensor based on a quinonehydrazone derivative was successfully designed and prepared. The sensor 1 showed a tautomeric equilibrium between azophenol form and quinonehydrazone form in solution. Upon interaction with anions with



**Fig. 5**  $^1\text{H}$  NMR titration of 1 ( $1 \times 10^{-2}$  M,  $\text{DMSO-}d_6$ ) with  $[\text{Bu}_4\text{N}]\text{AcO}$

strong basicity (e.g.,  $\text{AcO}^-$ ,  $\text{F}^-$ , and  $\text{H}_2\text{PO}_4^-$ ), the quinonehydrazone form was promoted to the azophenol form and thus the “naked-eye” determination of anions could be achieved (color changes from light green to blue).

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## References

- Cammann, K., Ross, B., Katerkamp, A., Reinbold, J., Gründig, B., Renneberg, R.: “Chemical and biochemical sensors” in Ullman’s encyclopedia of industrial chemistry, 6th edn. Wiley-VCH, New York (1998)
- Kirk, L.K.: Biochemistry of the halogens and inorganic halides. Plenum Press, New York (1991)
- Kleerekoper, M.: The role of fluoride in the prevention of osteoporosis. *Endocrinol. Metabol. Clin. North Amer* **27**, 441–452 (1998)
- Michigami, Y., Kuroda, Y., Ueda, K., Yamamoto, Y.: Determination of urinary fluoride by ion chromatography. *Anal. Chim. Acta* **274**, 299–302 (1993)
- Sessler, J.L., Cho, D., Lynch, V.: Diindolylquinoxalines: effective indole-based receptors for phosphate anion. *J. Am. Chem. Soc.* **128**, 16518–16519 (2006)
- Ghosh, A., Verma, S., Ganguly, B., Ghosh, H.N., Das, A.: Influence of Urea N-H acidity on receptor-anionic and neutral analyte binding in a ruthenium(ii)-polypyridyl-based colorimetric sensor. *Eur. J. Inorg. Chem* **17**, 2496–2507 (2009)
- Kim, G., Kim, H.: Doubly activated coumarin as a colorimetric and fluorescent chemodosimeter for cyanide. *Tetrahedron Lett.* **51**, 185–187 (2010)
- Luxami, V., Kumar, A., Hundal, M.S., Kumar, S.: Internal electric field driven chromofluorescent chemodosimeter for fluoride ions. *Sensor. Actuat. B* **145**, 1–6 (2010)
- Farinha, A.S.F., Tomé, A.C., Cavaleiro, J.A.S.: (*E*)-3-(*meso*-Octamethylcalix[4]pyrrol-2-yl)propenal: a versatile precursor for calix[4]pyrrole-based chromogenic anion sensors. *Tetrahedron Lett.* **51**, 2184–2187 (2010). doi:10.1016/j.tetlet.2010.02.091
- Kim, S.K., Lee, D.H., Hong, J., Yoon, J.: Chemosensors for Pyrophosphate. *Acc. Chem. Res.* **42**, 23–31 (2009)
- Martínez-Máñez, R., Sancenón, F.: Fluorogenic and chromogenic chemosensors and reagents for anions. *Chem. Rev.* **103**, 4419–4476 (2003)
- Xu, Z., Kim, S.K., Yoon, J.: Revisit to imidazolium receptors for the recognition of anions: highlighted research during 2006–2009. *Chem. Soc. Rev.* **39**, 1457–1466 (2010). doi:10.1039/b918937h
- Dydio, P., Zieliński, T., Jurczak, J.: 7, 7'-Diureido-2, 2'-diindolylmethanes: anion receptors effective in a highly competitive solvent, methanol. *Org. Lett.* **12**, 1076–1078 (2010). doi:10.1021/ol1000395
- Hudson, Z.M., Zhao, S., Wang, R., Wang, S.: Switchable ambient-temperature singlet-triplet dual emission in triarylboron-pt(II) complexes. *Chem. Eur. J* **15**, 6131–6137 (2009)
- Park, C., Hong, J.: A new fluorescent sensor for the detection of pyrophosphate based on a tetraphenylethylene moiety. *Tetrahedron Lett.* **51**, 1960–1962 (2010). doi:10.1016/j.tetlet.2010.02.009
- Shao, J., Qiao, Y., Lin, H., Lin, H.: A C3-symmetric colorimetric anion sensor bearing hydrazone groups as binding sites. *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **71**, 1736–1740 (2009)
- Arunachalam, M., Ghosh, P.: Bistripodand amide host for compartmental recognition of multiple oxyanions. *Org. Lett* **12**, 328–331 (2010)
- Shao, J., Lin, H., Lin, H.: A simple and efficient colorimetric anion sensor based on a thiourea group in DMSO and DMSO-water and its real-life application. *Talanta* **75**, 1015–1020 (2008)
- Xu, Z., Singh, N.J., Lim, J., Pan, J., Kim, H.N., Park, S., Kim, K.S., Yoon, J.: Unique sandwich stacking of pyrene-adenine-pyrene for selective and ratiometric fluorescent sensing of ATP at physiological pH. *J. Am. Chem. Soc.* **131**, 15528–15533 (2009)
- Shao, J., Yu, X., Xu, X., Lin, H., Cai, Z., Lin, H.: Colorimetric and fluorescent sensing of biologically important fluoride in physiological pH condition based on a positive homotropic allosteric system. *Talanta* **79**, 547–551 (2009)
- Caltagirone, C., Mulas, A., Isaia, F., Lippolis, V., Gale, P.A., Light, M.E.: Metal-induced pre-organisation for anion recognition in a neutral platinum-containing receptor. *Chem. Commun.* **41**, 6279–6281 (2009)
- Gimeno, N., Li, X., Durrant, J.R., Vilar, R.: Cyanide sensing with organic dyes: studies in solution and on nanostructured  $\text{Al}_2\text{O}_3$  surfaces. *Chem. Eur. J* **14**, 3006–3012 (2008)
- Saha, D., Das, S., Bhaumik, C., Dutta, S., Baitalik, S.: Monometallic and bimetallic ruthenium(II) complexes derived from 4, 5-Bis(benzimidazol-2-yl)imidazole (H3Imbzim) and 2, 2'-bipyridine as colorimetric sensors for anions: synthesis, characterization, and binding studies. *Inorg. Chem* **49**, 2334–2348 (2010)
- Bhosale, S.V., Bhosale, S.V., Kalyankar, M.B., Langford, S.J.: A core-substituted naphthalene diimide fluoride sensor. *Org. Lett* **11**, 5418–5421 (2009)
- Yoo, J., Kim, M., Hong, S., Sessler, J.L., Lee, C.: Selective sensing of anions with calix[4]pyrroles strapped with chromogenic dipyrrolylquinoxalines. *J. Org. Chem.* **74**, 1065–1069 (2009)
- Lou, X., Qiang, L., Qin, J., Li, Z.: A new rhodamine-based colorimetric cyanide chemosensor: convenient detecting procedure and high sensitivity and selectivity. *ACS Appl. Mater. Interfaces* **1**, 2529–2535 (2009)
- Shao, J., Wang, Y., Lin, H., Li, J., Lin, H.: A novel indole phenylhydrazone receptor: synthesis and recognition for acetate anion. *Sensor. Actuat. B* **134**, 849–853 (2008)
- Hu, S., Guo, Y., Xu, J., Shao, S.: A selective chromogenic molecular sensor for acetate anions in a mixed acetonitrile–water medium. *Org. Biomol. Chem* **6**, 2071–2075 (2008)
- Lin, Z., Ou, S., Duan, C., Zhang, B., Bai, Z.: Naked-eye detection of fluoride ion in water: a remarkably selective easy-to-prepare test paper. *Chem. Commun.* **16**, 624–626 (2006)
- Lee, G.W., Kim, N., Jeong, K.: Synthesis of Biindole–Diazo Conjugates as a Colorimetric Anion Receptor. *Org. Lett* **12**, 2634–2637 (2010)
- Bourson, J., Pouget, J., Valeur, B.: Ion-responsive fluorescent compounds. 4. Effect of cation binding on the photophysical properties of a coumarin linked to monoaza- and diaza-crown ethers. *J. Phys. Chem.* **97**, 4552–44570 (1993)
- Korendovych, I.V., Cho, M., Butler, P.L., Staples, R.J., Rybak-Akimova, E.V.: Anion binding to monotopic and ditopic macrocyclic amides. *Org. Lett* **8**, 3171–3174 (2006)
- Jencks in, W.P., March, J.: Advanced organic chemistry, 3rd edn. Wiley, New York (1985)
- Boiocchi, M., Boca, L.D., Gómez, D.E., Fabbrizzi, L., Licchelli, M., Monzani, E.: Nature of urea–fluoride interaction: incipient and definitive proton transfer. *J. Am. Chem. Soc.* **126**, 16507–16514 (2004)