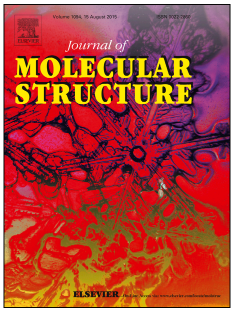

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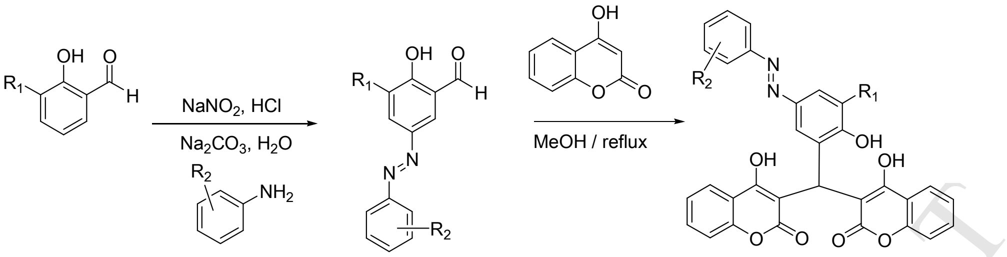
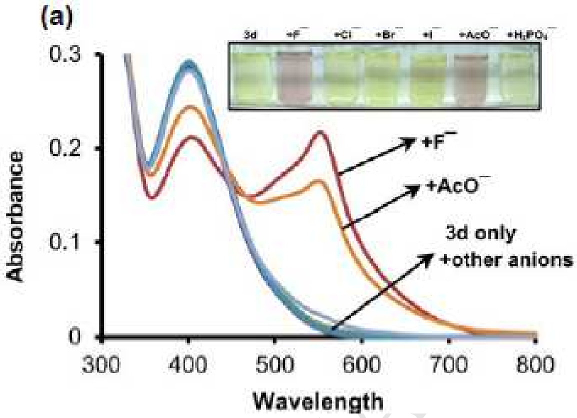
Graphical abstract





Synthesis and anion recognition studies of novel bis (4-hydroxycoumarin) methane azo dyes

Amorn Panitsiri, Sukanya Tongkhan, Widchaya Radchatawedchakoon and Uthai Sakee*

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Abstract

Four new bis (4-hydroxycoumarin) methane azo dyes were synthesized by the condensation of 4-hydroxycoumarin with four different azo salicylaldehydes and their structures were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, HRMS. Anion binding ability in dimethyl sulfoxide (DMSO) solutions with tetrabutylammonium (TBA) salts (F^-, Cl^-, Br^-, I^-, AcO^- and $H_2PO_4^-$) was investigated by the naked eye, as well as UV-visible spectroscopy. The sensor shows selective recognition towards fluoride and acetate. The binding affinity of the sensors with fluoride and acetate was calculated using UV–visible spectroscopic technique.

Keywords: anion, sensor, azo, coumarin, synthesis

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1. Introduction

Azo compounds are widely used as colorants in the textile, printing, cosmetics, drugs, foods coloring, and other consumer goods. There are about 3000 azo dyes currently in use all over the world. In general, they can be classified into monoazo-, diazo-, triazo- and polyazodyes, but the great majority of them are monoazo compounds, which have the common structure unit of the azo chromophore linking two aromatic systems [1-2]. Another application is analytical chemistry [3]. On the other hand azo compounds shown biological activities containing antimicrobial [4-5].

4-Hydroxycoumarin is an important component of numerous synthetic and natural products with wide-ranging biological activities [6] including anticoagulant [7], spasmolytic [8], and anti-HIV activities [9, 10]. They are also extensively used as analytical reagents [11, 12].

Anions play a major role in our daily life; being crucial to physiological function as well as various industrial process [13]. The development of new receptors, sensors and transporters for anionic species continues to be a rich area of research [14]. Most chemosensors developed so far are chromogenic and fluorescent sensors, which efficiently change their photophysical properties in the presence of anions [15]. One of particular interest in this regard involves the construction of colorimetric anion sensors [16]. Such sensors allow naked-eye detection of anions without the use of any spectroscopic instrumentation [17].

In the past few years, some chromogenic sensors based on coumarin have been developed for cations [18-20] and anions [21]. To date a number of azo-based colorimetric sensors for anions have been reported [22-25]. Generally, colorimetric chemosensor is made up of two main fragments, which involve the binding sites that interact with anions either electrostatically or through hydrogen bonding and the signal parts that connect to the binding sites either directly or intramolecularly linked which show the color changes in the anion recognition procession. The anion sensing, simplicity and high selectivity are still challenges for investigators and they attract much interest. In particular, to develop the naked-eye detection technique for the analysts without using any expensive equipment is of great interest in recent years.

Herein, as a part of our ongoing research on analyst recognition, we designed and synthesized new and simple anion sensors **3a-d** containing both hydrogen-bond-donor group (4-hydroxycoumarin) and chromogenic unit (azophenyl) and studied their anion recognition behaviors toward biologically important fluoride and acetate ions over other anions with high selectivity. In addition, the sensing processes can be realized by the ‘naked-eye’ determination as it has a remarkable color response.

Scheme 1.

2. Experimental

2.1. General

All solvents and reagents were purchased from commercial sources and used as received. IR spectra were recorded on Perkin Elmer SPECTRUM GX, FT-IR spectrophotometer. Spectra were recorded as pressed KBr disc. The ^{1}H and ^{13}C NMR spectra were measured with a Bruker AVANCE 400 spectrometer operating at 400 and 100 MHz, respectively. The chemical shifts (δ) are reported in ppm, and coupling constants (J) are given in Hz. The spectra were taken in CD_3SOCD_3 and the residual solvent signal of CH_3SOCH_3 at δ 2.50 and 39.5 was used as reference for ^{1}H and ^{13}C NMR spectra, respectively. The HRMS mass spectra were recorded on micrOTOF spectrometer.

2.2. Synthesis

*2.2.1 General procedure for **3a-d** synthesis*

*2.2.1.1 Synthesis derivatives of azo aromatic aldehyde (**2a-d**)*

The structures of synthesized azo aromatic aldehyde are shown in Scheme 1. A 0 °C solution **I** of aniline derivatives (10 mmol) in deionized water (10 mL) and HCl (2 mL) was prepared. A 0 °C solution **II** of $NaNO_2$ (15 mmol) in deionized water (5 mL) was dropwised into the solution I. The mixture was stirred for 10 min. A solution of Na_2CO_3 (30 mmol) in deionized water (30 mL) at 0 °C was added aldehyde derivatives **1a** or **1b** (10 mmol). The solution of aldehyde derivatives and Na_2CO_3 was dropwised into the mixture solution of I and II and then the solution was stirred 2 h in cool bath. The reaction was adjusted the pH to 7 by adding the solution of HCl. The precipitated products **2a-d** were filtered and heated in the oven.

2.2.1.2 Representative procedure for the synthesis of sensors **3a-d**

4-Hydroxycoumarin (2 mmol) was added into the solution of azo aromatic aldehydes **2a–d** (1 mmol) in methanol (10 mL). The reaction was stirred and refluxed for 12 h. After heating, the precipitated products **3a–d** were filtered and recrystallized from ethanol to afford a pure product.

*Sensor **3a***; Orange solid, Yield: 86%; FT-IR (KBr, cm^{-1})3416,2835 1608, 1535, 1413; ^1H NMR (400 MHz, d_6-DMSO): δ 6.36 (s, 1H, CH), 6.81 (d, 1H, *J* = 8.4 Hz, ArH), 7.18-7.28 (m, 4H, ArH), 7.34-7.50 (m, 5H, ArH), 7.6 (d, 1H, *J* = 8.4 Hz, ArH), 7.72 (d, 2H, *J* = 8.0 Hz, ArH), 7.95-7.96 (m, 3H, ArH). ^{13}C NMR (100 MHz, d_6-DMSO): 33.08, 103.61, 115.46, 115.52, 119.36, 120.15, 122.52, 122.45, 123.02, 124.39, 127.52, 128.86, 129.05, 129.71, 130.69, 145.23, 152.45, 158.84, 165.95, 168.62; HRMS (*m/z*): found 533.1398 (calculated: 533.1349) for $C_{31}H_{21}N_2O_7^+$, $[MH]^+$

*Sensor **3b***; Orange solid, Yield: 81%; FT-IR (KBr, cm^{-1}) 3415, 2836, 1609, 1537, 1420;^1H NMR (400 MHz, d_6-DMSO): δ 2.37 (s, 3H, CH_3), 6.40 (s, 1H, CH), 6.83 (d, 1H, *J* = 7.2 Hz, ArH), 6.91-7.00 (m, 2H, ArH), 7.14-7.18 (m, 4H, ArH), 7.30-7.40 (m, 3H, ArH), 7.52 (d, 1H, *J* = 8.0 Hz, ArH), 7.59 (d, 1H, *J* = 8.0 Hz, ArH), 7.99 (d, 2H, *J* = 8.0 Hz, ArH), 8.07

(s, 1H, ArH); ^{13}C NMR (100 MHz, d_6-DMSO): 21.30, 33.24, 103.74, 115.74, 116.19, 119.40, 120.05, 120.32, 122.43, 123.50, 124.96, 128.06, 128.68, 130.66, 131.11, 138.68, 146.14, 152.45, 152.86, 158.00, 168.06, 170.89; HRMS (*m/z*): found 547.1545 (calculated: 547.1505) for $C_{32}H_{23}N_2O_7^+$, $[MH]^+$

*Sensor **3c***; Red solid, Yield: 80%; FT-IR (KBr, cm^{-1}) 3450, 2936, 1610, 1543, 1421;^{1}H NMR (400 MHz, d_6-DMSO): δ 2.40 (s, 3H, CH_3), δ 3.84 (s, 3H, OCH_3), 6.42 (s, 1H, CH), 7.18-7.23 (m, 5H, ArH), 7.28-7.35 (m, 4H, ArH), 7.43-7.74 (m, 3H, ArH), 7.98 (d, 2H, *J* = 7.6 Hz, ArH); ^{13}C NMR (100 MHz, d_6-DMSO):21.20, 33.00, 55.79, 97.72, 103.72, 109.86, 115.46, 119.73, 120.32, 122.36, 122.98, 124.37, 124.58, 128.66, 130.52, 130.65, 138.53, 144.68, 147.53, 147.78, 152.51, 166.49, 169.21; HRMS (*m/z*): found 577.1656 (calculated: 577.1611) for $C_{33}H_{25}N_2O_8^+$, $[MH]^+$

*Sensor **3d***; Red solid, Yield: 86%; FT-IR (KBr, cm^{-1}) 3451, 2948, 1610, 1540, 1409;^{1}H NMR (400 MHz, d_6-DMSO): δ 3.76 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.48 (s, 1H, CH), 6.93 (d, 1H, *J* = 7.6 Hz, ArH), 7.14-7.22 (m, 6H, ArH), 7.30-7.40 (m, 4H, ArH), 7.82 (s, 1H, ArH), 7.99(d, 2H, *J* = 8.0 Hz, ArH); ^{13}C NMR (100 MHz, d_6-DMSO): 32.90, 55.40, 55.78, 97.85, 103.72, 105.85, 115.58, 116.19, 116.34, 120.34, 123.22, 124.49, 124.83, 127.90, 129.54, 130.85, 144.99, 147.27, 147.34, 152.48, 153.91, 160.14, 167.59, 170.29; HRMS (*m/z*): found 593.1623 (calculated: 593.1560) for $C_{33}H_{25}N_2O_9^+$, $[MH]^+$

2.3. UV–vis experiments

Deionized water was used throughout all experiments. All UV–vis spectroscopy was carried out just after the addition of anions in DMSO or a DMSO/H_2O binary solution,while keeping the sensor concentration constant (2.0×10^{-5} M) on a Perkin Elmer Lambda25 UV-vis spectrometer. All anions (AcO^-, F^-, Cl^-, Br^-, I^- and $H_2PO_4^-$) were used as tetra-*n*-butylammonium salts

3. Result and discussion

3.1. Synthesis of novel sensors

New four azo dyes having bis-4-hydroxycoumarin, 3a-d have been synthesized via condensation reaction of 4-hydroxycoumarin with four different azo salicylaldehydes (**2a-d**) in methanol in good yield (Scheme 1). General synthetic method for 2a-d was reported in our previous paper [25]. The resultant products were characterized using standard spectroscopic techniques. The characteristic IR absorption bands of 3a-d were determined in KBr disk. The functional groups of these compounds have been identified from the infrared spectrum. The bands in the region 3415–3451 cm^{-1} attributed to the (O–H) vibrations. The aliphatic (C–H) vibration bands were observed in the range of 2835-2948 cm^{-1}.The bands in the region 1608-1610 cm^{-1} were assigned to (C=O) lactone carbonyl function of coumarin. Two bands in the range of 1409-1421 and 1535-1543 cm^{-1} were assigned to the azo group –N=N–and –C=C–) (aromatic) stretching, respectively. ^1H and ^{13}C NMR spectra of the synthesized azo dyes having bis-4-hydroxycoumarin were recorded. The formation of **3a-d** was confirmed by the disappearance of aldehyde protons and the appearance of aliphatic methine protons at δ 6.36, δ 6.40, δ 6.42 and δ 6.48 ppm for **3a**, **3b**, **3c** and **3d**, in ^1H NMR spectra, respectively. The ^{13}C NMR spectra of these compounds exhibited the signals due to the presence of aromatic, carbonyl, methine and methyl carbons. The carbonyl carbon shifts were observed in the range of δ 165.59-170.89 ppm. The appearance of aliphatic methine carbons was observed at δ 33.08, δ 33.24, δ 33.00 and δ 32.90 ppm for **3a**, **3b**, **3c** and **3d**, respectively. All the aromatic carbon atoms were observed in the range of 97.71-160.14 ppm. Two aliphatic signals (δ 21.30 and δ 21.20 ppm for **3b** and **3c**, respectively) were assigned to the methyl group carbon atoms. The carbon atom of CH_3O- groups was observed at δ 55.79 ppm for **3c** and δ 55.40 and 55.78 ppm for **3d.**

3.2. Colorimetric and UV–vis spectroscopic studies

The interaction of the synthesized sensors **3a-d** with anions was firstly investigated at room temperature in DMSO solution by naked eye analysis and UV–vis absorption method and the anions added as their tetrabutylammonium salts. Visual inspection of the sensors **3a-d** with various anions such as AcO^-, F^-, Cl^-, Br^-, I^- and $H_2PO_4^-$ was carried out through colorimetric analysis (Fig 1 (a-d)). The color or spectra of 3a-d solution did not change upon addition of 5 equiv. of Cl^-, Br^- and I^-. Noticeable and appreciable color changes were observed when the sensors **3c** and **3d** were treated with fluoride and acetate anions, which induce an immediate color change from yellow to orange yellow for **3c** and purple for **3d** (Fig 1 (a) and (b)). During the addition of $H_2PO_4^-$ showed the color change from yellow to light orange yellow for only **3d** (Fig 1 (d)). This selectivity of **3c** and **3d** toward to F^- and AcO^- may be due to both the strong basicity of anions and a steric hindrance effect of CH_3O- group from the host [30].

Fig.1.

Different from **3c**, **3d** contains two methoxy groups, resulting in significant absorption spectrum and color changes (Fig. 1(c and d)) not only for F^- and AcO^-, but also for $H_2PO_4^-$, bearing OH groups. Consequently, addition of fluorides into the solution of **3c** gave significant bathochromic shift from 382 to 531nm (Δλ = 149 nm), as shown in Table 1 and Fig 1. (c). Meanwhile, AcO^- induced a similar but smaller wavelength change in **3c** (Δλ = 103 nm). Although azophenol chromophore and two methoxy groups with a structure in **3d** contributed to its selective sensing of F^{-}, AcO^{-}, and $H_2PO_4^{-}$, **3d** can not allow for calorimetric differentiation of F^{-}, AcO^{-}, and $H_2PO_4^{-}$, in which almost the same wavelength changes for **3a-d** are listed in Table 1. Evidently, the changes in the absorption spectral profile of 3d is better than other. The most remarkable color based changes were observed with azophenol-sensor, **3d** appended with o-methoxyphenol and p-methoxyazophenyl groups. The results indicated the methoxy on the azobenzene unit could improve visible sensing ability.

Table 1.

As the second experiment, to examine the possibility of application of the sensor **3d** to analytical chemistry, the anion recognition ability of receptor **3d** was tested in mixed water/DMSO medium. In general, hydration will terminate the anion sensing behavior, water the strong competitive solvent in the hydrogen bonding. On addition of different anions, the receptor able to show visually detectable color changes when the water content was not more than 10% (v/v) in DMSO (Fig. 2b). In 5%(v/v) aqueous DMSO (Fig. 2a), the presence of AcO^{-} and F^{-} induced similar changes in UV–vis spectrum of **3d** to that observed in pure DMSO (Fig. 1d) which clearly demonstrate that anions are acting here as a base and giving rise to the deprotonation upon interaction with the receptor **3d**. No remarkable spectral changes of **3d** were observed in presence of $H_2PO_4^{-}$,which suggested hydrogen bonding donor solvent destroyed the binding between **3d** and $H_2PO_4^{-}$.

Fig.2.

The further binding properties of **3d** toward F^{-} and AcO^{-} were studied by UV–vis titration experiments. The stoichiometry between **3d** with anions (F^{-} and AcO^{-}) was determined by Job’s plot that indicates formation of host–guest complex in 1:1 stoichiometry (Fig. 3).

Fig.3.

The association constant of **3d** with F^{-} and AcO^{-} were calculated based on the UV–vis titration through the Benesi–Hildebrand equation [26](Fig. 4), which inferred that the selectivity trends of binding affinities of anions for **3d** were determined to be AcO^{-} ($1.49 \times 10^{2}\ M^{-1}$) > F^{-} ($0.26 \times 10^{2}\ M^{-1}$). The sensor **3d** had a higher binding affinity for acetate anion, which could be rationalized on basis of shape complementarity between the host and the anionic guests, and higher basicity in compared to F^{-}.

Fig.4.

4. Conclusion

In summary, four new bis (4-hydroxycoumarin) methane azo dyes have been synthesized and their spectral behaviors and anion recognition properties were fully investigated. The results indicated that the sensors **3c** and **3d** can selectively detected F^{-} or AcO^{-} anions. Especially, compound **3d** is capable of naked-eye detecting of F^{-} and AcO^{-} in a straightforward and inexpensive manner. Further the anion recognition was easily monitored by anion-complexation induced changes in UV-vis spectroscopic studies. Naked-eyes detectable color changes for acetate and fluoride were realized successfully in aqueous solution, which made it possible to detect acetate and fluoride for practical analysis and application.

Acknowledgements

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References

[1] H.S. Freeman, A.T. Peters, Colorants for non-textile applications, Elsevier London, 2000.

[2] D.M. Marmion, Handbook of U.S. Colorants, third ed., Wiley, New York, 1991.

[3] R. G. Anderson, G. Nickless, Analyst. 92 (1967) 207.

[4] H.G. Garg, R.A. Sharma, J. Med. Chem. 12 (1996) 1122.

[5] E.J. Modest, H.N. Schlein, G.E. Foley, J. Pharmacol. 9 (1957) 68.

[6] M. Li, J. Li, B. Liu, Y. Zhou, X. Li, X. Xue, Z. Hou, X. Luo, Eur. J. Pharmacol. 721 (2013) 151.

[7] R. O'Reilly, J. Ohms, C. Motley, J. Biol. Chem. 244 (1969) 1303.

[8] C. Stacchino, R. Spano, A. Pettiti, Bull. Chim. Farm. 122 (1983) 158.

[9] H. Zhao, N. Neamati, H. Hong, A. Mazumder, S. Wang, S. Sunder, G.W.A. Milne, Y. Pommier, T.R. Burke Jr., J. Med. Chem. 40 (1997) 242.

[10] Marcal de Queiroz P Italy PCT Int Appl WO 98 25,608 (Cl. A61K31/37), 18 Jun 1998.

[11] K. Sen, P. Bagchi, J. Org. Chem. 24 (1959) 316.

[12] R.F. Chen, Anal. Lett. 1 (1968) 423.

[13] R. M. Duke, E. B. Veale, F. M. Pfeffer, P. E. Kruger, T Gunnlaugsson, Chem. Soc. Rev. 39 (2010) 3936.

[14] C. Caltagirone, P. A. Gale, Chem. Soc. Rev. 38 (2009) 520.

[15] S. Hu, Y. Guo, J. Xu, S. Shao, Org. Biomol. Chem. 6 (2008) 2071.

[16] C-F. Chen, Q-Y. Chen, New J. Chem. 30 (2006) 143.

[17] P. Piatek, J. Jurczak, Chem. Commun. (2002) 2450.

[18] D. Sarkar, A. Pramanik, S. Biswas, P. Karmakar, T. K. Mondal, RSC Adv. 4 (2014) 30666.

[19] D. Sarkar, A. K. Pramanik, T. K. Mondal, RSC Adv. 4 (2014) 25341.

[20] L. Wang, D. Ye, D. Cao, Spectrochim. Acta A 90 (2012) 40.

[21] Y. H. Kim, M. G. Choi, H. G. Im, S. Ahn, W. Shim, S-K. Chang, Dyes and Pigments 92 (2012) 1199.

[22] K. Rezaeian, H. Khanmohammadi, Spectrochim. Acta A 133 (2014) 31.

[23] H. Khanmohammadi, K. Rezaeian, A. Abdollahi, Spectrochim. Acta A 139 (2015) 405.

[24] V. Reena, S. Suganya, S. Velmathi, J. Fluorine Chem, 153 (2013) 89.

[25] W. Radchatawedchakoon, W. Sangsuwan, S. Kruanetr, U. Sakee, Spectrochim.

Acta A 121 (2014) 306.

[26] Q. Li, Y. Guo, J. Xu, S. Shao, J. Photochem. Photobiol., B 103 (2011) 140.

Table 1. The optical response of 3a-d (2×10^{-5} M) to different anion in DMSO

Compound	λ_{max}/nm	ε/cm^{-1}M^{-1}	Anion-induced wavelength changes (λ_{max}/nm)					
			AcO^-	F^-	Cl^-	Br^-	I^-	$H_2PO_4^-$
3a	366	2.01×10^4	109	134	n	n	n	n
3b	367	2.02×10^4	108	158	n	n	n	n
3c	382	1.98×10^4	103	149	n	n	n	n
3d	401	1.47×10^4	152	154	n	n	n	152
3d[a]	401	1.45×10^4	149	151	n	n	n	n
3d[b]	400	1.41×10^4	150	152	n	n	n	n

[a] Solvent as 5% H_2O/DMSO

[b] Solvent as 10% H_2O/DMSO

Figure Captions

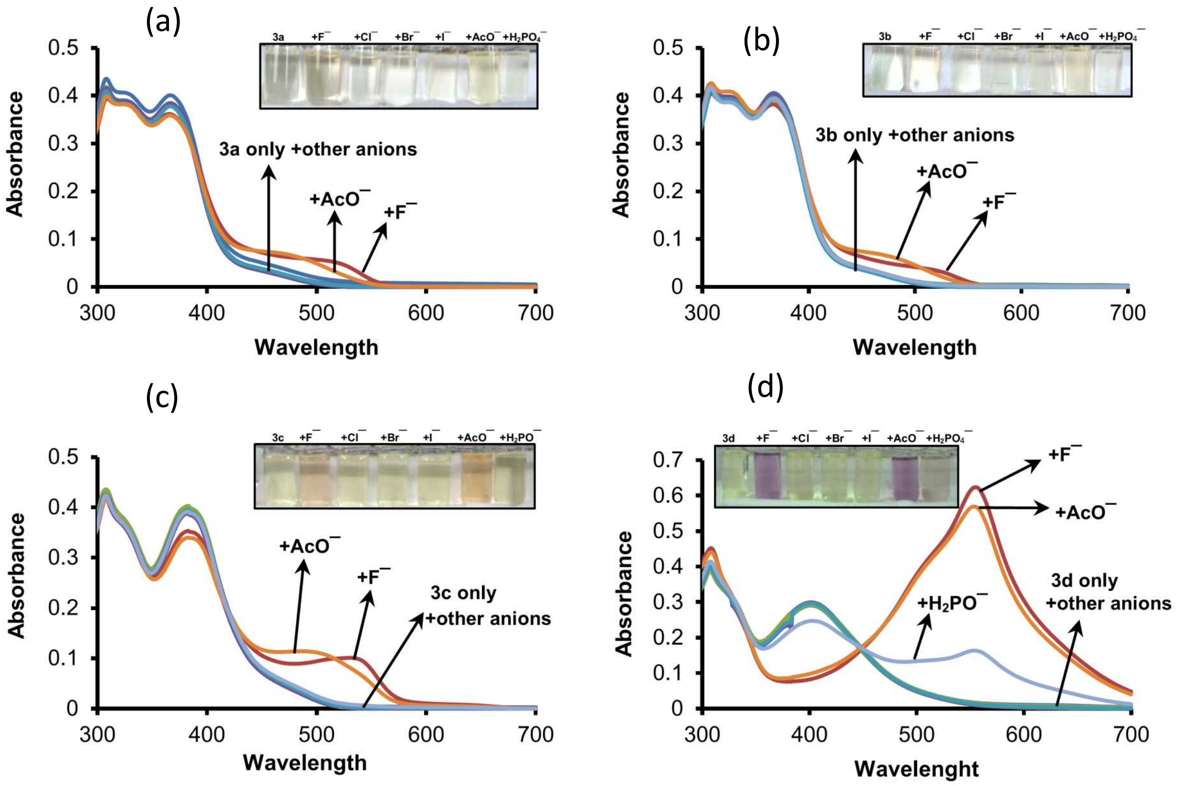
Fig.1. UV–vis absorption spectra of **3a–d** (2.0 × 10^{-5} M) in the presence of 10 equiv of various anions in DMSO; (a) **3a**, (b) **3b**, (c) **3c** and (d) **3d**

Fig.2. UV–vis absorption changes of **3d** with various anions (10 equiv); (a) **3d** = 2.0 × 10^{-5} M in 5% H_2O in DMSO and (b) **3d** = 2.0 × 10^{-5} M in 10% H_2O in DMSO.

Fig.3. . (a) UV–vis spectrum changes of **3d** (2.0 × 10^{-5} M) upon addition of fluoride anion (0–12 equiv.) in 5% H_2O in DMSO. (b) Job's plot analysis of **3d**-F^- complex in 5% H_2O in DMSO at 550 nm. (c) UV–vis spectrum changes of **3d** (2.0 × 10^{-5} M) upon addition of acetate anion (0–12 equiv.) in 5% H_2O in DMSO. (d) Job's plot analysis of **3d**-AcO^- complex in 5% H_2O in DMSO at 550 nm.

Fig.4. Benesi–Hildebrand plot assuming 1:1 stoichiometry for association between **3d** and (a) F^-, (b) AcO^- anion.

Fig.1.


(a)
3a
+F⁻
+Cl⁻
+Br⁻
+I⁻
+AcO⁻
+H2PO4⁻
Absorbance
Wavelength
3a only +other anions
+AcO⁻
+F⁻
(b)
3b
3b only +other anions
+AcO⁻
+F⁻
(c)
3c
+AcO⁻
+F⁻
3c only
+other anions
(d)
3d
+F⁻
+AcO⁻
+H2PO⁻
3d only
+other anions
Wavelenght
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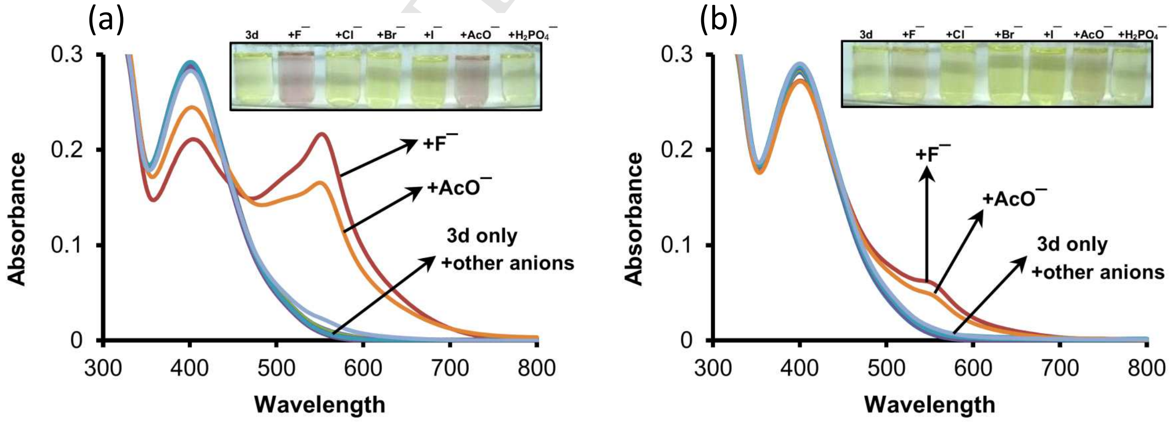
400
500
600
700

Fig. 2.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+Br⁻
+I⁻
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Absorbance
Wavelength
+F⁻
+AcO⁻
3d only
+other anions
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700
800

Fig. 3.

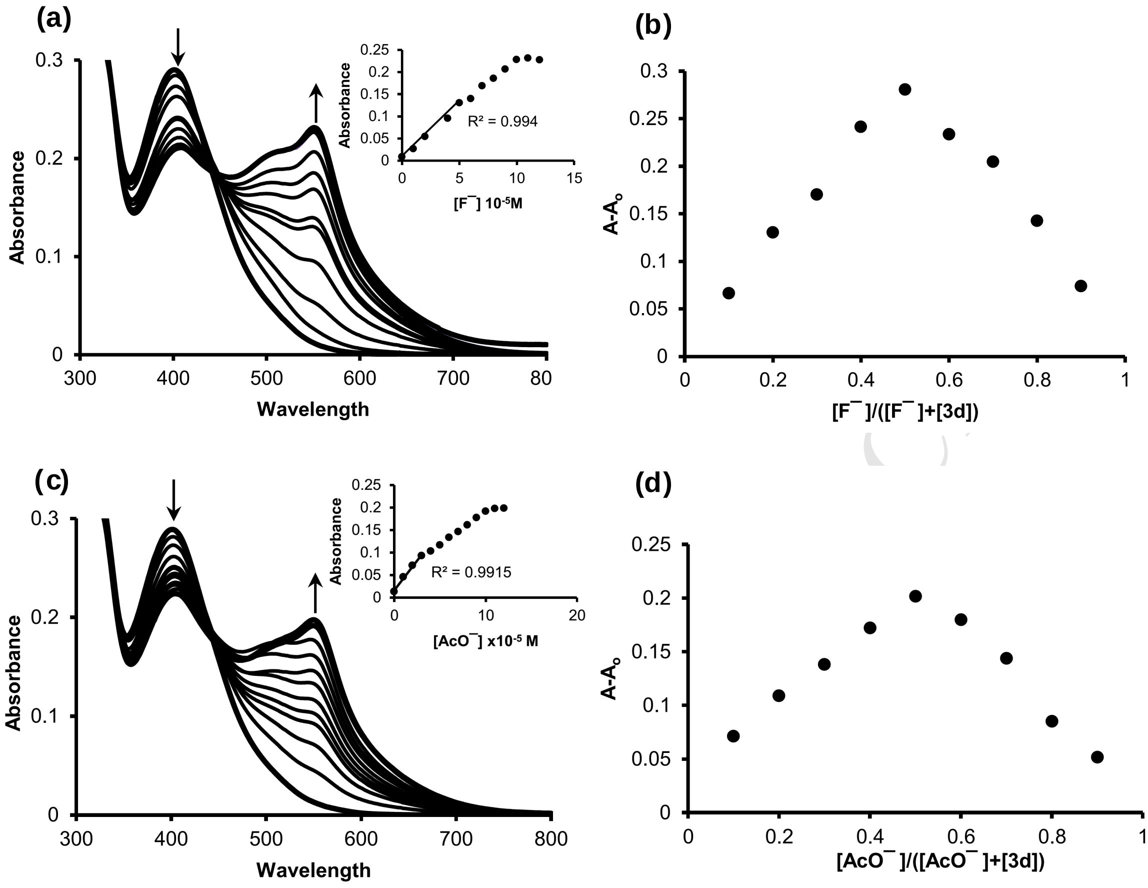
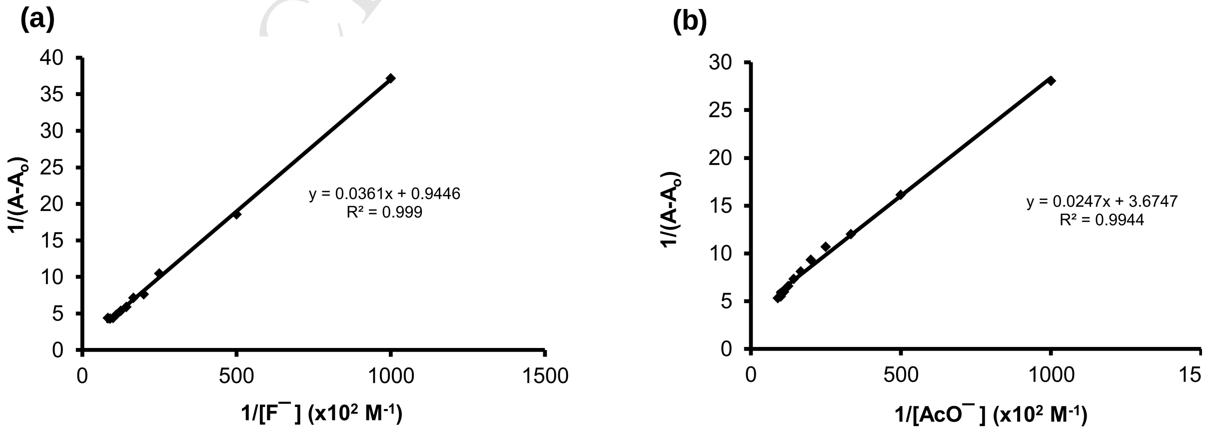
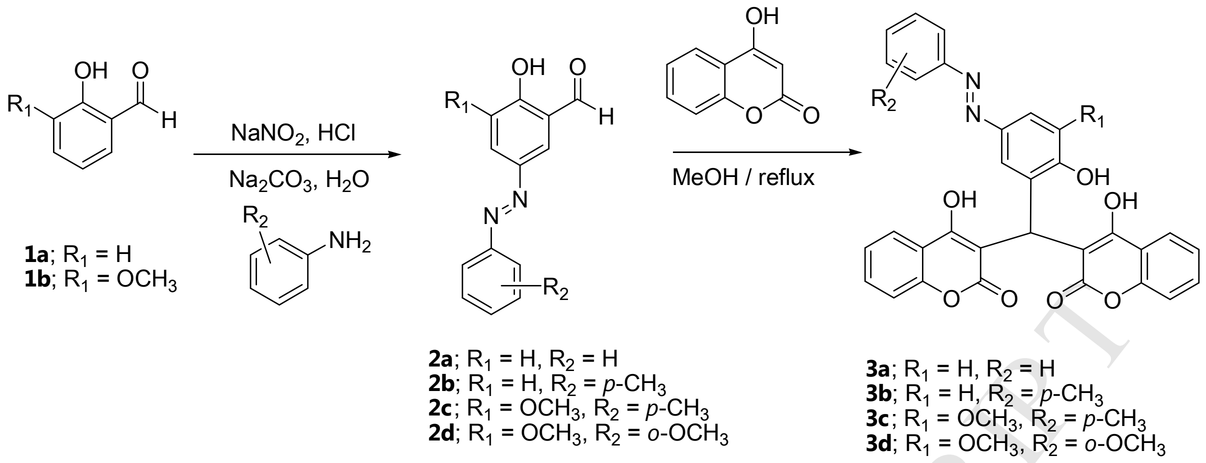

(a)
Absorbance
0.3
0.2
0.1
0
300
400
500
600
700
80
Wavelength
Absorbance
0.25
0.2
0.15
0.1
0.05
0
0
5
10
15
R² = 0.994
[F¯] 10⁻⁵M
(b)
A-Aₒ
0.3
0.25
0.2
0.15
0.1
0.05
0
0
0.2
0.4
0.6
0.8
1
[F¯]/([F¯]+[3d])
(c)
Absorbance
0.3
0.2
0.1
0
300
400
500
600
700
800
Wavelength
Absorbance
0.25
0.2
0.15
0.1
0.05
0
0
10
20
R² = 0.9915
[AcO¯] x10⁻⁵ M
(d)
A-Aₒ
0.25
0.2
0.15
0.1
0.05
0
0
0.2
0.4
0.6
0.8
1
[AcO¯]/([AcO¯]+[3d])

Fig. 4.


(a)
1/(A-Aₒ)
40
35
30
25
20
15
10
5
0
0
500
1000
1500
y = 0.0361x + 0.9446
R² = 0.999
1/[F¯] (x10² M⁻¹)
(b)
1/(A-Aₒ)
30
25
20
15
10
5
0
0
500
1000
15
y = 0.0247x + 3.6747
R² = 0.9944
1/[AcO¯] (x10² M⁻¹)



Scheme 1. Synthetic procedures for sensors **3a-3d**

Highlights

1) New azo dyes having bis-4-hydroxycoumarin were synthesized for anion sensor evaluation.
2) It is a very good naked eye detection sensor.