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# Abstract

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The anion sensing properties of N-(4-nitrophenylazo)-N'-propyl thiourea chromoionophores have been investigated as free agents in bulk solution and following immobilization on a sol-gel silica film. In addition, the effect of a variety of organic spacers on the immobilized chromoionophores was examined. The binding constants of free chromoionophores with anions were greater than those of the corresponding immobilized chromoionophores in acetonitrile solution and their binding constants revealed a trend were  $CH_3CO_2^- > H_2PO_4^- > CI^-$ . However, the use of an organic spacer with an immobilized chromoionophore can change the binding constants of anions. An octadecyl group spacer, for example, led to an increase in the difference between the binding constants of the acetate ion and other anions and also enhanced selectivity for the acetate ion. Key Words

Chromophore, Silica film, Thiourea

#### Introduction

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The development of a sensing system for biologically and/or environmentally important anions has gained significant interest in recent years. <sup>1</sup> Anion sensing reagent, which can recognize target anions and sense us by optical or electrochemical signals, is a useful method for sensing these anions. Until now, many reagents which have much good affinity and selectivity have been developed. <sup>2</sup>

Moreover, in recent years, the research on the elucidation of the anion recognition behavior at the interface has also attracted attention. Specific reactions which cannot occur in bulk solution can feasibly occur at the interface, because the physicochemical properties of the interface are very different from those of the bulk solution. Nucleic acid bases and other biologically important molecules can be recognized by using multiple hydrogen bonds at the air/water interface.<sup>3</sup> Inorganic anions have been recognized by the thiourea and thiourea-isothiouronium type receptors at the oil/water interface.<sup>4</sup> It has been reported that the anions dissolved in aquerous media can be recognized through hydrogen bonding by self-assembled mono-layers on gold<sup>5</sup> or by LB film on HOPG.<sup>6</sup> The reports mentioned above indicate that hydrogen bonding can be useful in the recognition of hydrophilic anions at the interface in water. Anion sensing properties at the silica/water interface have also been studied. Sessler and co-workers immobilized calix[4]pyrroles onto silica gel and separated anions by HPLC.<sup>7</sup> Furthermore, some groups have immobilized anion recognition chromophores onto the surface of silica gel or mesoporous silica and measured fluoride,<sup>8</sup>

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hydrophobic carboxylates<sup>9</sup> and phosphate anions.<sup>10</sup>

Herein the fabrication of a new anion sensing silica film on a glass substrate is reported. Anion sensing silica film was fabricated by sol-gel method using sol solution containing tetraethoxysilane and a chromogenic anion receptor. Previously, we reported a selectively for the acetate ion in acetonitrile-water solution using a sensor molecule combining 4-nitrophenyl and thiourea functionality.<sup>11</sup> The substrate that we used as the foundation, which carried out the coat of the anion sensing silica film in this research, was glass which does not penetrate ultraviolet light. Therefore, N-(4-(4-nitrophenylazo)phenyl)-N'-propyl thiourea 1, which has an absorption band in a visible wavelength region, was used as the chromogenic anion receptor of the anion sensing silica film. This receptor associates with anions by hydrogen bonding with observable changes to the absorption spectra. The absorption spectra of this film therefore changes with the concentration of anions. To immobilize 1 on silica films, N-(4-(4-nitrophenylazo)phenyl)-N'-(3-(triethoxysylil)propyl) thiourea 2 was added into sol solution. The structure of 1 and 2 are depicted in scheme 1. The receptor 2 was created immediately and almost quantitatively by mixing 3-aminopropyl triethoxysilane and 4-nitro-4'-isothiocyanate azobenzene (ITC-AB). This substrate can be fabricated with ease from commercially inexpensive reagents, easily analyzed and used repeatedly. Three other silica films with the receptor bound were also produced containing sequentially hydrocarbons (alkyl or phenyl group), as shown in figure 1. By mixing short chain hydrocarbons sequentially (figures 1b and 1c), a

space is produced between the anion receptors. The introduction of a long alkyl chain lowered the polarity near the thiourea (figure 1d). Therefore, compared with the film of only a receptor molecule (figure 1a), a change in the selectivity and response was expected. Although these anion sensing films were too thin to measure the transmittance absorption spectrum, the anion sensing ability of the film was investigated instead by multiple internal reflectance absorption spectra with an optical waveguide system. Anion chromoionophore-bound silica films were fabricated on glass substrates and their anion-sensing abilities were evaluated.

## Experimental

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## **Reagents and apparatus**

NMR spectra were obtained on a Bruker Avance III-400 instrument using the residual solvent signal of DMSO or CHCl<sub>3</sub> as a reference. Transmittance UV-Vis spectra were recorded at room temperature with a JASCO V-550-DS spectrophotometer (Japan Spectroscopic Co. Ltd., Tokyo, Japan) using a quartz cell of 1.0 cm path length. All of the reagents used for the synthesis were special or first grade and used as received. Note that the stabilizer (ethanol, contains about 0.3% -1.0%) in CHCl<sub>3</sub> was not removed. All of the guest anions were commercially available as tetrabutylammonium salts. HPLC-grade 1,2-dichloroethane (1,2-DCE) and ethanol were purchased from Wako Pure Chemical Industries (Tokyo, Japan). Spectrometric-grade acetonitrile (MeCN) was purchased from Nacalai Tesque, Inc. (Kyoto, Japan). 3-aminopropyl triethoxysilane (APTES),

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dimethyldiethoxysilane (DMDES), diphenyldiethoxysilane (DPDES) and octadecyldimethylmethoxysilane (ODDMMS) were purchased from Tokyo Kasei Co. Ltd., (Kyoto, Japan).

# **Synthesis**

Synthesis of 4-nitro-4'-isothicyanatoazobenzene (ITC-AB)

*4-nitro-4'-isothiocyanatoazobenzene* was synthesized according to an improved version of a literature method.<sup>12</sup> Thiophosgene (0.17 g, 1.48 mmol), triethylamine (0.18 g, 1.78 mmol) and 4-(4-nitrophenylazo)aniline (0.35 g, 1.44 mmol) were dissolved in tetrahydrofuran (THF) and the solution was refluxed for 3 h. After cooling to room temperature, THF of the reaction mixture was reduced to about 1/3 by evaporation and the residue was dissolved in CHCl<sub>3</sub>. This CHCl<sub>3</sub> solution was washed twice with water and then with brine and dried (Na<sub>2</sub>SO<sub>4</sub>). The solvent was removed by evaporation and the residue purified by silica gel column chromatography (hexane/CHCl<sub>3</sub> 1:1). Orange solid, 0.135 g. (48%). <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>,):  $\delta$  8.42 (d, 2H, *J* = 9.0 Hz), 8.09 (d, 2H, *J* = 9.0 Hz), 8.03 (d, 2H, *J* = 8.7 Hz), 7.68 (d, 2H, *J* = 8.7 Hz), <sup>13</sup>C-NMR(100 MHz, DMSO-d<sub>6</sub>,):  $\delta$  154.4, 149.6, 148.1, 135.3, 133.2, 126.7, 124.4, 124.0, 123.0. IR (KBr): 2101 cm<sup>-1</sup> (-N=C=S). ESI-HRMS m/z: [M+H]+ Calcd for C13H8O2N4S 284.0373; Found: 284.0376.

4-nitro-4'-isothicyanatoazobenzene (0.142 g, 0.50 mmol) was dissolved in CHCl<sub>3</sub>. Propylamine (1.0

mL, 12 mmol) was added to the solution and the mixture was stirred at room temperature for 24 h. The solvent was removed by evaporation and the residue was purified by silica gel column chromatography (CHCl<sub>3</sub>). Red solid, 0.166 g (96%).

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>,): δ9.91 (s, 1H), 8.42 (d, 2H, *J* = 10.0 Hz), 8.15 (s, 1H), 8.04 (d, 2H, *J* = 10.0 Hz), 7.93 (d, 2H, *J* = 9.0 Hz), 7.80 (d, 2H, *J* = 9.0 Hz), 3.44 (s, 2H), 1.58 (q, 2H, *J* = 7.0 Hz), 0.91 (t, 3H, *J* = 7.4 Hz). <sup>13</sup>C-NMR(100 MHz, DMSO-d<sub>6</sub>,): δ179.5, 154.9, 147.5, 146.9, 143.7, 124.4, 123.4, 122.5, 120.8, 45.0, 20.9, 10.7. ESI-HRMS m/z: [M-H]- Calcd for C16H17O2N5S 342.1030; Found 342.1033.

## **Anion Sensing Substrate Preparation**

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The substrate was the slide glass plate (Matsunami,  $98 \times 26 \times 1.0$  mm) with the refractive index of 1.524 at 1.06 µm. The substrate was cut into  $26 \times 10$  mm sections and etched with 0.1 M NaOH solution for 30 second and then washed with 0.1 M HNO<sub>3</sub> solution and water.

Anion sensing silica film was made on this substrate by sol-gel method. ITC-AB (12 mg, 0.042 mmol), APTES (0.01 ml, 0.043 mmol) and either DMDES, DPDES or ODDMMS (0.042 mmol in either case) were agitated in a 2:1 mixture of ethanol/1,2-DCE at room temperature for 24 h. The

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contents of sol solutions are summarized in table 1. The solution was casted on the substrate with a spin coater (4000 rpm, 30 second) and heat-treated at 150 °C for 2 h in air on a hot plate.

#### **Total-Internal-Reflection Absorption Spectrum Measurement**

The total-internal-reflection absorption spectrum of anion sensing silica film was measured over the wavelength range of 360–800 nm using a bespoke optical waveguide spectrophotometer which has previously been described.<sup>13</sup> The 10  $\mu$ l of sample solution (anion-contained acetonitrile) was dropped onto the film coated glass substrate and a cover glass (Matsunami, 18 × 18 × 0.1 mm) was placed over the sample solution to prevent evaporation of acetonitrile. All measurements were repeated three times.

#### **Result and Discussion**

The anion recognition behavior of non-immobilized anion receptor **1** in acetonitrile solution was examined by UV-Vis and NMR spectroscopy. Figure 2 shows the changes in the absorption spectra of **1** on addition of acetate in acetonitrile. Receptor **1** has an absorption peak at 389 nm assigned to a charge transfer between the nitrogen atom of the thiourea moiety and nitrophenylazo group. When acetate was added, the absorption peak was shifted to 425 nm with the isosbestic point at 401 nm. Such a bathochromic shift was also observed for dihydrogenphosphate and chloride anions. Solution color changed from yellow to orange. From the binding constants, the anion selectivity of receptor 1 was acetate > dihydrogenphosphate > chloride, following the anion basicity and the binding constants ( $K_{11}$ ) themselves were  $1.4 \times 10^5 \text{ M}^{-1}$ ,  $5.3 \times 10^4 \text{ M}^{-1}$  and  $2.1 \times 10^3 \text{ M}^{-1}$  respectively. The binding ability of 1 was found to be superior to other structurally simpler amide,<sup>14</sup> urea and thiourea<sup>15</sup> anion recognition molecules. This greater affinity is derived from the enhanced acidity of the thiourea which was affected by the electron withdrawing effect of the neighboring nitro group. However, the binding ability of 1 was inferior to well-structured receptors,<sup>16</sup> thiourea combined with nitro phenyl group<sup>11</sup> and positively charged receptors such as isothioureas<sup>17</sup> and guanidines.<sup>18</sup> The electron withdrawing effect was buffered by the azobenzene group and the acidity of the thiourea didn't increase as much. Both spectral and solution color changes were in agreement with those reported in the literature.<sup>19</sup> The process of the hydrogen-bond formation was investigated by <sup>1</sup>H-NMR titration. Figure 3 shows the changes in the <sup>1</sup>H-NMR spectra of 1 in the absence and the presence of acetate in CD<sub>3</sub>CN. Two NH proton peaks were appeared at 8.54 ppm and 7.05 ppm. Upon addition of acetate anion, significant downfield shifts (up to 3.1 ppm) of the peaks were observed, indicating that the **1** and acetate form the complex *via* hydrogen bonding.

The absorption spectra of anion receptor **2** based on silica film on a glass substrate was measured by the optical waveguide system. Figure 4 shows the changes in the absorption spectra of receptor molecule only film (substrate AR) on addition of acetate. The absorption peak observed at 389 nm was shifted to 412 nm with an isosbestic point at 400 nm. The absorption peak position in the absence of acetate and the isosbestic point were approximately consisted with the bulk behavior. However, the absorption spectra were shifted in the  $10^{-6}$  M –  $10^{-2}$  M region for acetate, whereas the absorption spectra of **1** were shifted in the  $10^{-6}$  M –  $10^{-5}$  M region in the acetonitrile solution. Similar reductions in anion response ability were also observed for dihydrogenphosphate and chloride anions. The results showed that immobilization on substrate led to a reduction in the anion response ability. The possibility that an anion sensing reagent arranged densely with enough space for an anion to enter is not securable, as a result of producing a film only using an anion sensing reagent, is worthy of mention. Furthermore, intermolecular hydrogen bonds may have formed between the adjoining thiocarbonyl and NH moiety of a thiourea group, as a result of having arranged the anion recognizing reagent densely (figure 1a).

To improve the anion response ability and selectivity, alkyl chains (CH<sub>3</sub> or C<sub>18</sub>H<sub>37</sub>) or phenyl groups were introduced to the anion sensing silica film. The introduction of the methyl group (substrate AR-Me, Fig. 1b) created some space near anion receptor **2**, allowing anion and solvent molecule to reach deep inside the film. A Phenyl group can provide cover close to the thiourea moiety of **2** (substrate AR-Ph, Fig. 1c), whereas the long alkyl chain of the octadecyl group covers all of **2** (substrate AR-Od, Fig. 1d). It was expected that these differences would affect the anion response and selectivity.

Downloaded by University of Arizona on 11 December 2012 Published on 10 December 2012 on http://pubs.rsc.org | doi:10.1039/C2NJ40714K All substrates observed the bathochromic shift with anion containing acetonitrile solution. Figure 5 shows the absorption changes of AR, AR-Od and anion receptor 1 at various concentrations of acetate in acetonitrile solution. Responses for anions were improved in three substrates (AR-Me, AR-Ph and AR-Od) compared with the substrate AR. However, the response from a substrate did not reach to the level of strength observed in the acetonitrile. Nonlinear fitting was performed on the assumption that anion receptor 2 reacts with anions with a 1:1 stoichiometry. The stability constants are summarized in table 2. The trend in anion selectivity for substrates AR, AR-Me and AR-Ph was acetate  $\approx$  dihydrogenphosphate > chloride. These results differed from the selectivity observed in acetonitrile. In contrast, the anion selectivity of substrate AR-Od showed the same tendency as the result in an acetonitrile. The acetate ion has a methyl group with a high affinity for alkyl groups and was able to approach the thiourea group between the octadecyl groups with greater ease than the other anions.

To investigate the anion recognizing behavior mentioned above, the measurement was repeated at least 20 times in all the substrates, but neither the unfolding of a spectrum nor the decrease of the absorbance was observed. Therefore, we concluded that the endurance of the anion sensing silica film fabricated by the present study is high.

Finally, we attempted to use these substrates for anion sensing in water and acetonitrile-water mixed solution. However, no response was observed in any of the substrate-anion combinations. Other

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groups have achieved anion recognition in water at self-assembled monolayers on a gold electrode<sup>5</sup> and with LB film on the HOPG<sup>6</sup> using the hydrogen bond-forming receptor. This result showed that as for the film made from the sol-gel process, a hydrogen bond does not function in the water/silica film interface.

## Conclusion

An anion sensing silica film was fabricated on a glass substrate. The anion sensing silica film consisted of a N-(4-(4-nitrophenylazo)phenyl)-N'-propyl thiourea which was used as the chromoionophore for anions and an alkyl or phenyl spacer group set in a silica matrix. The anion sensing abilities of the films were evaluated by changes in the total-internal-reflection absorption spectra at various concentrations of anion. As a result, the response from the anion sensing film decreased to a 1/100 of its value when compared with the response from the anion receptor in bulk solution. Response was improved by the addition of each functional group spacer, including methyl, phenyl and octadecyl and the selectivity was also changed by adding these alkyl groups. These results show that response and selectivity for anions can be controlled by varying the type and the quantity of a spacer. With this in mind, we are currently trying to improve the response of such films by investigating the type and the quantity of the spacer molecules involved.

# References

1 a) T. R. Crompton, Determination of Anions: A Guide for the Analytical Chemist, Springer,

Berlin, 1996. b) Fundamentals and Apprications of Anion Separations, Eds: B. A. Moyer, R. P.

Singh, Kluwer Academic/Plenum, New York, 2004.

2 a) F. P. Schmidtchen, and M. Berger, *Chem. Rev.* 1997, **97**, 1609-1646. b) P. D. Beer, and P. A.

Gale, Angew. Chem. Int. Ed. 2001, 40, 486-516. c) R. Martínez-Máñez, and F. Sancenón, Chem. Rev.

2003, 103, 4419-4476. d) T. Gunnlaugsson, M. Glynn, G. M. Tocci, P. E. Kruger, and F. M. Pfeffer,

Coord. Chem. Rev. 2006, 250, 3094–3117. e) V. Amendola, D. Esteban-Gómez, L. Fabbrizzi, and M.

Licchelli, Acc. Chem. Res. 2006, 39, 343-353. f) C. Caltagirone, and P. A. Gale, Chem. Soc. Rev.

2009, 38, 520-563. g) D. T. Quang and J. S. Kim, Chem. Rev. 2010, 110, 6280-6301. h) H. J. Kim, J.

H. Lee, H. Lee, J. H. Lee, J. H. Lee, J. H. Jung and J. S. Kim, Adv. Func. Mater. 2011, 21,

4035-4040. i) M. E. Moragues, R. Martínez-Máñez, and F. Sancenón, *Chem. Soc. Rev.* 2011, **40**, 2593-2643.

3 a) K. Ariga, and T. Kunitake, *Acc. Chem. Res.* 1998, **31**, 371-378. b) U. Rädler, C. Heiz, P. L.
Luisi, and R. Tampé, *Langmuir*, 1998, **14**, 6620-6624. c) K. Ariga, A. Kamino, X. Cha, and T.
Kunitake, *Langmuir*, 1999, **15**, 3875-3885. d) Y. Ebara, K. Mizutani and Y. Okahata *Langmuir*, 2000, **16**, 2416-2418.

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# **New Journal of Chemistry**

- 4 a) K. Shigemori, S. Nishizawa, T. Yokobori, T. Shioya and N. Teramae *New J. Chem.* 2002, 26, 1102-1104. b) R. Kato, Cui-- S. Nishizawa, T. Yokobori, T. Shioya and N. Teramae *Tetrahedron Lett.* 2004, 45, 4273-4276.
- 5 Sheng Zhang, Amit Palkar, and Luis Echegoyen, Langmuir, 2006, 22, 10732-10738.

6 K. P. Xiao, P. Bühlmann, Y. Umezawa, Anal. Chem. 1999, 71, 1183-1187.

7 a) B. L. Iverson, R. E. Thomas, V. Kral, and J. L. Sessler, J. Am. Chem. Soc. 1994, 116,

2663-2664. b) J. L. Sessler, P. A. Gale, and J. W. Genge, Chem. Eur. J. 1998, 4, 1095-1099.

8 H. J. Kim, M. H. Lee, L. Mutihac, J. Vicens and J. S. Kim, Chem. Soc. Rev. 2012, 41, 1173-1190.

E. Kim, H. J. Kim, D. R. Bae, S. J. Lee, E. J. Cho, M. R. Seo, J. S. Kim, and J. H. Jung, New J.

Chem. 2008, 32, 1003-1007. b) S. M. Seo, E. J. Cho, S. J. Lee, K. C. Nam, S.-H. Park and J. H. Jung,

Microporous Mesoporous Mater. 2008, 114, 448-454.

9 A. B. Descalzo, K. Rurack, H. Weisshoff, R. Martínez-Máñez, M. D. Marcos, P. Amoros, K.
Hoffmann, and J. Soto, *J. Am. Chem. Soc.* 2005, **127**, 184-200. b) P. Calero, E. Aznar, J. M. Lloris,
M. D. Marcos, R. Martínez-Máñez, J. V. Ros-Lis, J. Soto, and F. Sancenón, *Chem. Commun.* 2008, 1668-1670.

10 M. Comes, M. D. Marcos, R. Martínez-Máñez, F. Sancenón, J. Soto, L. A. Villaescusa and P. Amorós, *Chem. Commun.* 2008, 3639-3641.

11 R. Kato, S. Nishizawa, T. Hayashita, and N. Teramae, *Tetrahedron Lett.* 2001, 42, 5053-5056.

- 12 A. Martvoň, K. Antoš, and T. Sticzay, Collect. Czech. Chem. Commun. 1969, 34, 3912-3920.
- 13 R. Kato, K. Kide, T. Hattori, A. Wakahara, and M. Yamaguchi, Anal. Lett. 2011, 44, 577-584.
- 14 P. D. Beer, A. R. Graydon, A. O. M. Johnson, and D. K. Smith, Inorg. Chem. 1997, 36,

2112-2118.

- 15 a) S. Kondo, M. Nagamine, S. Karasawa, M. Ishihara, M. Unno and Y. Yano, Tetrahedron
- 2011, 67, 943-950. b) T. R. Kerry, and M. H. Kim, J. Am. Chem. Soc. 1994, 116, 7072-7080.
- 16 Raymond C. Jagessar, Maoyu Shang, W. Robert Scheidt, and Dennis H. Burns, J. Am. Chem.

Soc. 1998, 120, 11684–11692.

17 Y. Kubo, S. Ishihara, M. Tsukahara, and S. Tokita, J. Chem. Soc. Perkin Trans. 2, 2002,

1455-1460.

18 R. P. Dixson, S. J. Geib and A. D. Hamilton, J. Am. Chem. Soc. 1992, 114, 365-366.

19 J. V. Ros-Lis, R. Martínez-Máñez, F. Sancenón, J. Soto, K. Rurack, and H. Weißhoff, Eur. J.

Org. Chem. 2007, 2449-2458.

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The anion sensing properties of N-(4-nitrophenylazo)-N'-propyl thiourea chromoionophores have been investigated as free agents in bulk solution and following immobilization on a sol-gel silica film. 41x21mm (300 x 300 DPI)



Scheme 1. Synthetic route to chromogenic anion receptors **1** and **2**. *Reagents and conditions:* (i): CSCl<sub>2</sub>, (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N, THF, reflux (ii): n-C<sub>3</sub>H<sub>7</sub>NH<sub>2</sub>, THF, r.t. (iii): NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, EtOH-1,2-DCE, r.t.



Figure 1. Surface structures and binding images of anion sensing film (a) AR, (b) AR-Me, (c) AR-Ph and (d) AR-Od.

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Changes in the absorption spectra of **1** on addition of the acetate anion.  $[\mathbf{1}] = 1.0 \times 10^{-5}$  M in MeCN. Counter cation : tetrabutylammonium cation.



Figure 3. <sup>1</sup>H-NMR spectra of **1** in the absence and the presence of 1 equiv. of acetate anion.  $[\mathbf{1}] = 1.0 \text{ mM}$  in CD<sub>3</sub>CN.



Figure 4. Changes in the absorption spectra of substrate AR at various concentrations of the acetate anion in acetonitrile.

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Figure 5. Absorbance at 425 nm of MeCN solution (open squares), at 409 nm of film AR-Od (solid squares) and at 409 nm of film AR (open circles) for various concentrations of acetate  $(0 - 2.0 \times 10^{-2} \text{ M})$  in acetonitrile.



Table 1. Contents of the silane coupling reagents (APTES, DMDES, DPDES and ODDMS) and isothiocyanate azobenzene (ITC-AB) of the sol solutions of the anion sensing silica film.

	K <sub>11</sub> M <sup>-1</sup>				
Anion	1 (in MeCN)	AR	AR-Me	AR-Ph	AR-Od
MeCO <sub>2</sub> -	(1.4±0.1) × 10⁵	(9.1±1.6) × 10 <sup>2</sup>	(1.9±0.3) × 10 <sup>3</sup>	(1.6±0.7) × 10 <sup>3</sup>	(1.7±0.3) × 10 <sup>4</sup>
H <sub>2</sub> PO <sub>4</sub> -	(5.3±1.1) × 10 <sup>4</sup>	(1.3±0.3) × 10 <sup>3</sup>	(1.7±0.3) × 10 <sup>3</sup>	(1.2±0.4) × 10 <sup>3</sup>	(1.0±0.8) × 10 <sup>3</sup>
Cl-	(2.1±0.5) × 10 <sup>3</sup>	< 100	(3.8±0.4) × 10 <sup>2</sup>	(7.2±2.1) × 10 <sup>2</sup>	< 100

Table 2. 1:1 Binding Constants for acetate, phosphate and chloride in MeCN (solution) with AR, AR-Me, AR-Ph and AR-Od (film).