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Ratiometric Fluorescence Detection of Anions by Silanediol-based Receptors Bearing Anthryl and Pyrenyl Groups

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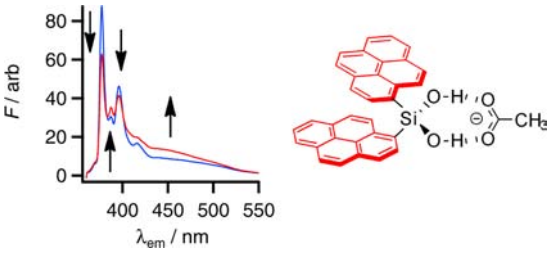
ABSTRACT



Two silanediol derivatives bearing 9-anthryl (2) and 1-pyrenyl (3) groups have been developed for fluorescence detection of anions. Receptor 3 showed favorable ratiometric response by fluorescence spectroscopy upon the addition of biologically relevant anions, such as acetate and dihydrogen phosphate in acetonitrile.

Anionic species play significant roles in a range of chemical, biological, and environmental processes; therefore, recognition of anions is a crucial topic in host−guest chemistry.[1] In this regard, the design and synthesis of artificial anion receptors have been developed in the last two decades. Neutral receptors bearing N−H groups[2] of amide, sulfonamide, urea, thiourea, and pyrrole have been well established; however, there are only a limited number of examples of receptors possessing O−H groups as an anion recognition site that have been studied. We and other groups have reported anion receptors bearing alcoholic[3] and phenolic[4] hydroxy groups. We have recently shown that a silanol hydroxy group can also be used as a recognition site for anions as a hydrogen bond donor. Anion recognition abilities of several receptors bearing silanol groups have been explored by our group by means of NMR spectroscopy.[5] In particular, silanediol **1** bearing

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two 1-naphthyl groups can recognize anions such as acetate and chloride in $CDCl_3$.[5a] More recently, silanediol derivatives, such as **1**, were applied to organocatalysts.[6,7] The receptor that can detect target species by fluorescence spectral change is widely accepted as a useful sensor due to convenience, low cost, and high sensitivity in diluted condition.[8] Silanediol **1** indeed shows fluorescence emission at 331 nm excited at 270 nm in chloroform; however, only small changes were observed upon the addition of such anions, suggesting that the electronic perturbation of the naphthyl group of **1** during the complexation with anions is unfortunately limited. We sought to modify the chromo/fluorophore from the naphthyl groups to more π-extended aryl groups to construct an effective fluorescence anion receptor based on the silanediol skeleton. In this regard, we report here the design and synthesis of silanediols **2** and **3** bearing 9-anthryl groups and 1-pyrenyl groups,[9] respectively (Figure 1). Silanediol **3** bearing two 1-pyrenyl moieties responds ratiometric fluorescence changes upon the addition of anions, in particular biologically relevant oxoanions. To the best of our knowledge, this is the first example of fluorescence anion sensor bearing silanol groups as recognition sites.

Synthesis of receptors **2** and **3** is illustrated in Scheme 1. 9-Bromoanthracene was lithiated by BuLi in ether at −78 °C, followed by reaction with tetrachlorosilane to give di(9-anthryl)silanedichloride.[10] The dichlorosilane was hydrolyzed with water in the presence of aniline and the crude mixture was purified by recrystallization from ether/hexane to give receptor **2** as an ethereal complex in 52% in two steps. 1-Bromopyrene was also lithiated by BuLi in THF at −60 °C and reacted with tetrachlorosilane giving di(1-pyrenyl)silanedichloride, which was immediately hydrolyzed with water without purification to give **3** in 16% yield. It should be noted that **3** was easily purified by column chromatography on deactivated silica gel by water (30% w/w). The products were identified by ^{1}H NMR, ^{13}C NMR, elemental analysis, and HRMS. The single crystals of **2** were fortunately obtained by recrystallization from ether/hexane. The overall crystal structure of **2** closely resembled that of **1**.[7] A dimer structure was formed by two molecules of **2** with two sets of intermolecular hydrogen bonds of Si−O−H···O−Si as shown in Figure 2. The residual Si−OH group was hydrogen bonded with ether oxygen incorporated from the solvent.

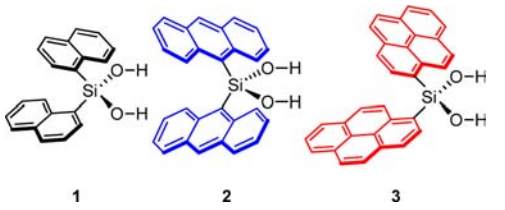
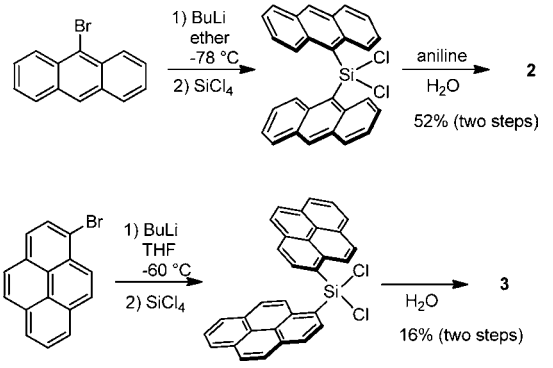


Figure 1. Silanediol derivatives.

Scheme 1. Synthesis of Receptors **2** and **3**



During the course of fluorescence study of **2**, we have found that **2** is easily decomposed by irradiation of UV light, even in fluorescence spectroscopy. Figure 3 shows photodegradation through irradiation of UV light at 365 nm by a handy UV lamp. Fluorescence intensity of **2** at around 400 nm was increased through an isoemissive point at 513 nm due to the dissociation Si−C bond by UV light to form anthracene in MeCN (Figure S5, Supporting Information). The produced anthracene was confirmed by the ^{1}H NMR spectrum of the reaction mixture. The half lifetime ($\tau_{1/2}$) of **2** was calculated to be 171 s. In the same condition, receptor **3** is more stable than **2**. Structured fluorescence peaks around 370−430 nm arising from pyrenyl monomer emission was slowly decreased by irradiating UV light (Figure S5) and $\tau_{1/2}$ of **3** was estimated to be 5890 s as shown in Figure 3. Therefore, the instability of **2** may be due to the steric hindrance of the C−H groups at 1- and 8-positions of the anthryl groups and/or the intramolecular proton transfer from the silanol hydroxy group to the *ipso*-position of the anthryl group. It should be pointed out that **2** is also unstable in $CDCl_3$ and fully decomposed overnight as determined by ^{1}H NMR spectroscopy. The photostability of **3** is sufficient for fluorescence titrations with anions, so that UV−vis and fluorescence responses of **3** upon the addition of anions were studied.

In order to evaluate the binding affinity of receptor **3**, we initially carried out UV−vis titrations with various anions as their tetrabutylammonium salts in MeCN. The UV−vis spectrum of **3** in MeCN showed well-resolved peaks at 348.0, 330.0, 316.0, 278.0, and 266.5 nm as frequently observed for pyrenyl derivatives as depicted in Figure 4A.

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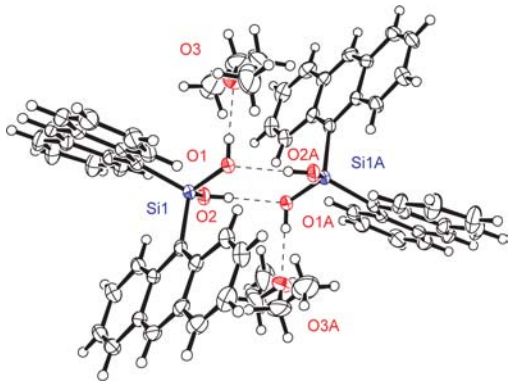

Figure 2. ORTEP view of the molecular structure of **2**·Et_2O. Displacement ellipsoids are scaled to the 50% probability level. Selected bond lengths for **2**·Et_2O: O2···O1A 2.776(2), O1···O3 2.669(3) Å.

Small but reproducible bathochromic shifts of the UV−vis spectra of **3** were observed (Figure 4B) upon the addition of AcO^- through isosbestic points at 348.0, 338.5, and 332.0 nm. A similar result was found upon the addition of $H_2PO_4^-$. However, virtually no spectral changes were observed upon the addition of HSO_4^-, NO_3^-, Cl^-, and Br^- reflecting weak association with these anions. The association constants of **3** for AcO^- and $H_2PO_4^-$ were calculated to be $1.52 \pm 0.12 \times 10^4$ and $8.32 \pm 0.44 \times 10^3$ mol^{-1} dm^3, respectively, by nonlinear curve fitting analysis with the UV−vis spectral titrations.

Figure 5A shows the fluorescence spectrum of receptor **3** excited at 348 nm in MeCN. The structured monomer emission at 377.0, 387.5, 396.0, and 416.0 nm and weak excimer emission at around 450 nm were observed.

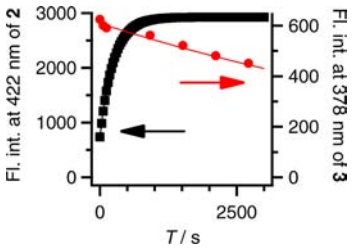

Figure 3. Time course of fluorescence intensities of **2** (■) and **3** (red ●) irradiating UV light at 365 nm.

The fluorescence intensities ratios at 377.0 and 450.0 nm were constant in 1.67×10^{-7}–2.0×10^{-6} mol dm^{-3} indicating that the excimer emission can be attributed to the intramolecular excimer formation of two pyrenyl groups of **3** rather than intermolecular one at least in this concentration range.[11] Upon the gradual addition of

(11) For excimer emission by di(1-pyrenyl)oligosilanes, see: Delercq, D.; Delbeke, P.; Schryver, F. C. D.; Meervelt, L. V.; Miller, R. D. *J. Am. Chem. Soc.* **1993**, *115*, 5702.

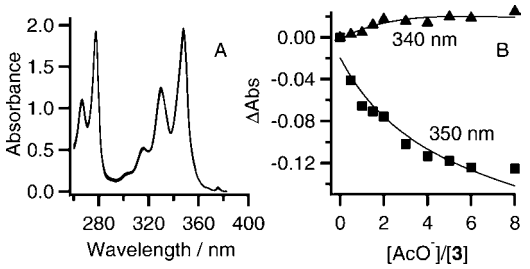

Figure 4. (A) UV−vis spectra of **3** upon the addition of AcO^- in MeCN at 298 K. [**3**] = 2.5×10^{-5} mol dm^{-3} and [AcO^-] = 0–2.0×10^{-4} mol dm^{-3}. (B) Absorbance changes of **3** upon the addition of AcO^- at 340 and 350 nm.

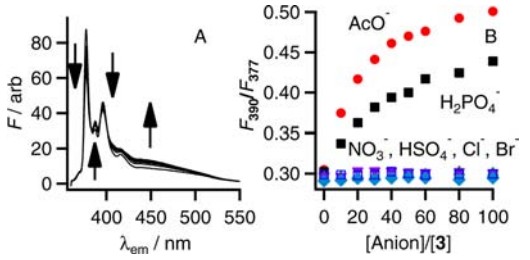

Figure 5. (A) Fluorescence spectra of **3** upon the addition of AcO^- in MeCN at 298 K. [**3**] = 2.0×10^{-6} mol dm^{-3}, [AcO^-] = 0–2.0×10^{-4} mol dm^{-3}, and λ_{ex} = 348 nm. (B) Ratio of fluorescence intensities at 390 and 377 nm of **3** upon the addition of AcO^- (red ●), $H_2PO_4^-$ (■), HSO_4^- (blue ◆), NO_3^- (blue □), Cl^- (green ▲), and Br^- (purple ▼).

AcO^- to an MeCN solution of receptor **3**, the intensities at 377.0 and 396.0 nm were decreased along with increases of intensities the peak at 382.5 nm and broad excimer emission at around 450 nm. The fluorescence changes passed through isoemissive points at 372.5, 382.5, 393.0, and 400.5 nm suggesting 1:1 complex formation. A similar result was observed upon the addition of $H_2PO_4^-$, however, small or negligible spectral changes were observed upon the addition of HSO_4^-, NO_3^-, Cl^-, and Br^- as seen in the UV−vis spectral titrations described above. These results indicate that the useful dual-wavelength ratiometric fluorescence measurement can be conducted by the receptor **3** for AcO^- and $H_2PO_4^-$.[12] Ratiometric fluorescent sensors are attractive because the ratiometric measurement between two emission intensities can increase the dynamic

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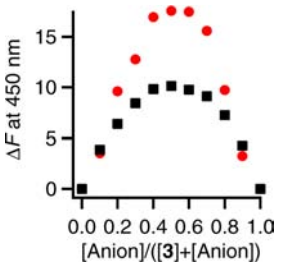
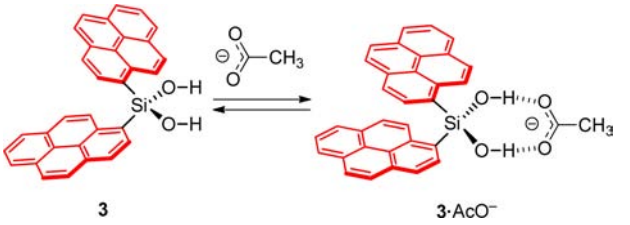


Figure 6. Job's plots of **3** with AcO^- (red ●) and $H_2PO_4^-$ (■) by fluorescence spectroscopy in MeCN. [**3**] + [anion] = 2.0×10^{-6} mol dm^{-3} and λ_{ex} = 348 nm.

range and provide built-in correction for partial decomposition of sensors and environmental effects around sensor molecule such as pH, polarity, and temperature. Figure 5B shows the ratio of fluorescence intensities at 390 and 377 nm upon the addition of anions. It is clear that selective recognition of biologically relevant anions, AcO^- and $H_2PO_4^-$ by receptor **3** was achieved. The stoichiometries of the complex for **3** with AcO^- and $H_2PO_4^-$ were confirmed by Job plot analysis depicted in Figure 6. The maxima at a mole fraction of 0.5 indicate 1:1 receptor–guest binding for both anions. The association constants of **3** for AcO^- and $H_2PO_4^-$ were calculated to be $3.16 \pm 0.17 \times 10^4$ and $1.26 \pm 0.13 \times 10^4$ mol^{-1} dm^3, respectively, by nonlinear curve fitting regression with the fluorescence spectral titrations. These values are in fairly good agreement with those from the UV–vis titrations. The association constant of **1** for AcO^- was determined to be $5.57 \pm 0.68 \times 10^3$ mol^{-1} dm^3 by ^1H NMR titrations[5a] and the value is comparable to that of **3** described above. On the contrary, the addition of other anions, HSO_4^-, NO_3^-, Cl^-, and Br^- cause no change on fluorescence intensity indicating weak association with these anions as observed for UV–vis spectral titrations.

A proposed equilibrium between receptor **3** and anions is shown in Scheme 2. Two hydroxy groups of **3** cooperatively bind oxoanions such as AcO^- and $H_2PO_4^-$ as

Scheme 2. Proposed Equilibrium of **3** with AcO^-



observed for **1**·Cl^- complex by X-ray crystallographic analysis.[5a] During the complexation with the oxoanions, the O–Si–O bond angle increases, concomitant with decrease of the bond angle of two pyrenyl groups, C–Si–C. Therefore, the small increase of the excimer emission of **3** was observed by a partial overlapping of the π-electrons of two pyrenyl groups at excite state upon the addition of oxoanions.

In conclusion, we have synthesized novel silanediol-based receptors **2** and **3** bearing 9-anthryl and 1-pyrenyl groups as fluorophores, respectively. Although receptor **2** is unstable by irradiation of UV light, receptor **3** is sufficiently stable to use fluorescence titrations. Receptor **3** shows favorable and effective ratiometric fluorescence changes upon the addition of biologically important oxoanions in MeCN.

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Supporting Information Available. Experimental details, compounds characterization, X-ray crystallographic study of **2**, UV–vis and fluorescence titrations of the receptors. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.