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Monovalent Anion Indicator Based on Fluorescence Quenching of Helical Fluorinated Poly(dialkylsilanes)

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ABSTRACT: This paper reports that fluorinated PSis with 3,3,3-trifluoropropyl and linear alkyl side chains (F-PSi)s demonstrated monovalent anion size dependent fluorescence quenching, which has potential as a novel type of chemosensor, "monovalent anion indicator". The extent of the fluorescent quenching was linearly increased by a decrease in the surface charge density of the monovalent anions. In addition, sensitivity toward monovalent anions was modulated by choosing an adequate length of linear alkyl chains, which efficiently served as a soft but strict molecular sieve for the monovalent anions. In contrast, nonfluorinated PSi did not show such an ability to discriminate monovalent anions, suggesting that the positively charged Si main chain stimulated the electrostatic interaction with monovalent anions.

Introduction

In the past few decades, fluorescent conjugated polymers (FCP)s have received a great deal of attention as chemosensory materials, because of their ability to provide signal amplification for the highly sensitive and selective fluorimeric detection.[1] In general, molecular designs of the FCP-based chemosensors are mainly divided into two categories based on the relationship between receptors for the analytes and fluorescent main chains: (i) analytes directly interact with the fluorescent main chain, resulting in changing the fluorescent properties, and (ii) receptor moieties connected to the side chains form the exterior surface of the polymer chains, in which the noncovalent/covalent binding process reports to the fluorescent main chain, following transduction into fluorescent signaling events.[1b] In both cases, tailored backbones or side chains have to be fitted to the intended purpose by the attachment of suitable analytes, which often requires further sophisticated molecular designs and skilful synthetic techniques. Thus, these strict specificities for the certain analytes may limit the broad range of use in applications of FCP-based chemosensors.

Although various FCP-based chemosensors for cationic or neutral species have been developed with relatively simple molecular designs utilizing electrostatic interaction or molecular size, those for anions have not been achieved with a limited number of cases because of their smaller charge to size ratio, a wide range of geometries, high solvation energies, and sensitivity to pH.[1f,h] Therefore, a key challenge of the FCP-based chemosensors is to establish priori designs toward a variety of anion species.[2]

In this paper, we first report that monovalent anions can be fluorometrically identified by the extent of quenching of σ-conjugated fluorescent polysilanes bearing 3,3,3-trifluoropropyl and an adequate length of linear alkyl chains as side chains. Here the ordinary linear alkyl chains, which have not been regarded as interactive receptors due to their less reactivity,[3] efficiently served as soft but strict molecular sieves for anion-size-dependent fluorescent quenching when the alkyl side chains surrounding the Si main chains formed the helical molecular grooves along the main chains.

PSis can be regarded as quasi-one-dimensional materials with delocalized σ-conjugated electrons along the Si main chain.[4] Their unique optical/electric properties have been rationalized by quantum confinement effects of these σ-conjugated electrons both theoretically[5] and experimentally.[6] Because of their 1-D direct band gap nature, PSis exhibit UV absorption around 300−380 nm, following fluorescence with relatively high quantum yield up to ca. 0.8 even at room temperature in solutions.[7] Their conformation-dependent-absorption/fluorescence properties have been extensively studied in terms of a chromophoric segmental model, where the individual segments are loosely electronically coupled, but which communicate through rapid energy migration.[6c] Therefore, a key advantage of PSi-based chemosensors is the potential of the PSis to exhibit collective and cooperative properties that are sensitive to significantly minor perturbations.

To demonstrate the fluorometric detection of monovalent anions, poly(3,3,3-trifluoropropyl *n*-alkylsilane)(F-PSi)s with methyl (F-PSi**1**), hexyl (F-PSi**2**), and decyl (F-PSi**3**) groups were specifically employed (Scheme 1a).[8] Aiming to enhance the ability of fluorescent quenching of F-PSis toward monovalent anions, we introduced the strong electron-withdrawing 3,3,3-trifluoropropyl group as an another side chain to generate the positively charged Si main chains.[9] According to the HSAB (hard and soft acids and bases) concept,[10] the delocalized polymeric anions can be regarded as a soft cation. Therefore, we originally expected that the fluorinated PSis stimulate electrostatic interactions with relatively soft anionic species.[11] Here it is noteworthy that optically inactive dialkyl PSis adopt helical conformations with equal amounts of both right- and left-handed helicities in solutions.[12] The surrounded alkyl side chains form helical grooves along the Si main chain, which efficiently acted as molecular sieves for monovalent anions during anion-size-dependent fluorescent quenching events.

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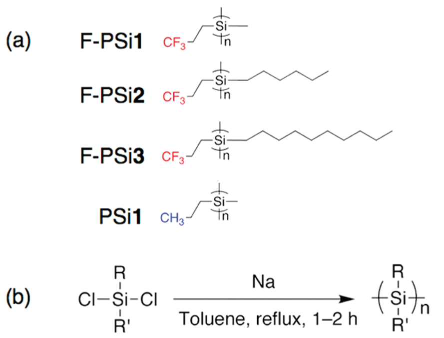
Experimental Section

PSis used in this study were prepared as described in previous papers.[4,13] Briefly, dichloro-*n*-alkyl(3,3,3-trifluoroprolyl)silane was polymerized by a sodium-mediated Wurtz reductive coupling reaction in refluxing toluene (Scheme 1b). The resulting samples were precipitated with careful successive additions of 2-propanol, ethanol, and methanol, which provided the PSis with relatively narrow molecular weight distribution (polydispersity index, PDI: 1.1−1.4) (Table 1). Molecular properties of the PSis, such as weight-averaged molecular weight (M_w), PDI, and viscosity index (α) were evaluated by a size exclusion chromatography (SEC) with a universal calibration. Both refractive and viscosity indexes were recorded on a Viscotek chromatograph using a Triple Detector Array 302 in series (Viscotek, Houston, TX). The obtained viscosity data were analyzed in terms of the touched-bead wormlike-chain model with excluded volume[14] to estimate roughly the Kuhn segment length λ^{-1} and the bead diameter d_B assuming the contour length (h = 0.2 nm) per residue and the excluded volume strength (B = 1.7 nm) for a previously investigated dialkyl polysilane, that is, poly{*n*-hexyl-[(*S*)-3-methylpentyl]silane}[15] (see ref 14 for the viscosity-radius expansion factor). To clarify the uncertainty in λ^{-1}'s, we also estimate them when B = 0.5 nm. Tetra-*n*-butylammonium (TBA) salts with F^-, Cl^-, Br^-, NO_3^-, HSO_4^-, PF_6^-, and I_3^- were employed as the corresponding monovalent anions. The values of monovalent anion volume were referred to a previous paper.[16] The surface charge densities (σ') of the monovalent anions were calculated by the following equation. $\sigma' = e/4\pi r^2$, where e and r indicate elementary electric charge and radius, respectively (Scheme 1c).[17]

Scheme 1. (a) Chemical Structures and (b) Synthesis of Polysilanes Used in This Study [F-PSi1, Poly(methyl-3,3,3-trifluoropropylsilane); F-PSi2, Poly(*n*-hexyl-3,3,3-trifluoropropylsilane); F-PSi3, Poly(*n*-decyl-3,3,3-trifluoropropylsilane); PSi1, Poly(methyl-*n*-propylsilane)] and (c) Volumes and Surface Charge Density of the Monovalent Anions[a]



(c)

Monovalent anion (X−)	F−	Cl−	Br−	NO3−	HSO4−	PF6−	I3−
Volume (nm3)	0.025	0.047	0.056	0.064	0.089	0.109	0.171
Surface charge density (mCm-3)	-389	-254	-227	-207	-166	-146	-108

[a] Data were taken from refs 15 and 16.

Table 1. Sample Data for PSis[a]

sample	$M_w/10^4$[b]	PDI(M_w/M_n)[c]	α[d]	λ^{-1}/nm[e]	d_B/nm[f]
F-PSi**1**	2.2	1.1	0.6	0.7 (2.0)	0.65 (0.8)
F-PSi**2**	4.0	1.4	0.8	0.8 (2.2)	0.4 (0.35)
F-PSi**3**	2.4	1.3	0.7	3.0 (4.5)	1.4 (1.3)
PSi**1**	4.0	1.3	0.7	0.8 (2.0)	0.75 (0.9)

[a] SEC conditions: temperature, 40 °C; solvent, tetrahydrofuran (THF). [b] M_w: weight-averaged molecular weight. [c] PDI: polydispersity index (M_w/M_n). [d] α: viscosity index. [e] λ^{-1}: Kuhn segment length. [f] d_B: path length. Parentheses: parameters when assuming B = 0.5 nm.

Results and Discussion

Sample data for the PSis are summarized in Table 1. It is known that fluorescent quenching behavior of conjugated polymers is significantly affected by the molecular weight.[18] Especially, F-PSi**1** exhibits unique molecular weight-dependent optical properties.[8] In order to simplify the analyses of fluorescence quenching mechanism of F-PSis toward monovalent anions, we carefully chose the PSi's fractions with the similar ranges of M_w between 2.0 to 4.0 × 10^4 and with relatively narrow PDI (1.1−1.4) (Table 1).

Owing to their relatively shorter λ^{-1} and lower α values, the PSis used in this study are typically categorized as a flexible chain whereas bulky side groups sometimes stiffen significantly the main chain of poly(dialkylsilanes).[19] Thus, slight but gradual increase in λ^{-1} with elongation of PSi's simple linear alkyl side chains involves the steric repulsions among the neighboring linear alkyl chains, leading to elongation of the effective conjugation length of the Si main chain. F-PSis showed UV absorption at ca. 310 nm, suggesting that F-PSis adopted 7_3-helix structure in THF solution (Figure 1a). It is known that poly(dialkylsilane)s exhibit the clear relationship among the main-chain peak intensities per silicon repeat unit, ε (Si repeat unit)$^{-1}$ dm^{3}cm^{-1}, α, and the full width at half-maximum (fwhm) in THF at 30 °C.[18a] Thus, the value of ε increases exponentially as a function of the value of α. This relationship could be applicable for the fluorinated

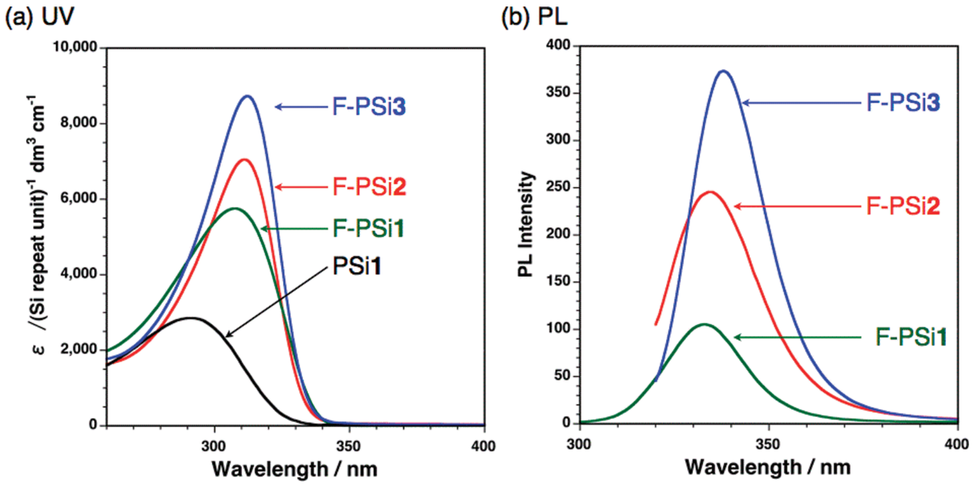


Figure 1. (a) UV and (b) PL spectra of PSis in THF at 25 °C. For UV and PL measurements, concentrations of PSis were adjusted to 3.0 × 10^{-5} M and 3.0 × 10^{-5} M, respectively. For PL spectra, all samples were excited at 300 nm at 25 °C.

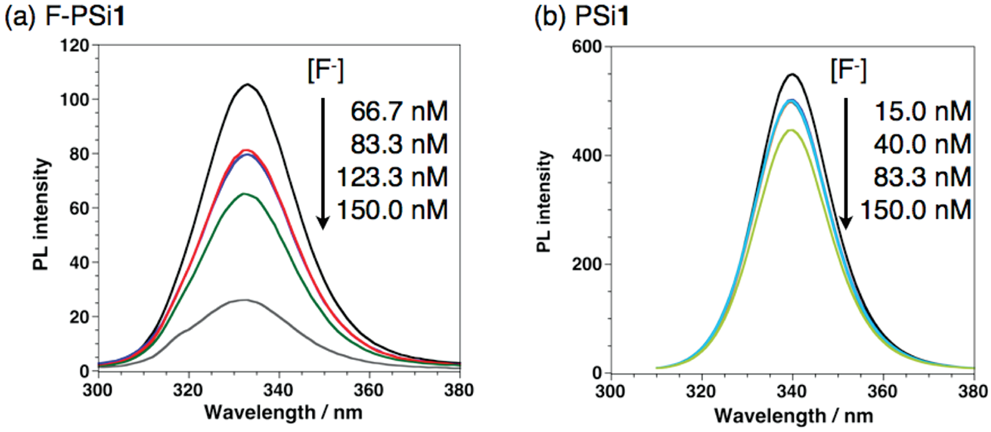


Figure 2. Changes in fluorescence spectra of (a) F-PSi**1** and (b) PSi**1** by successive addition of *n*-tetrabutylammonium fluoride (TBAF). Concentrations of F-PSi**1** and PSi**1** were adjusted to be 3.0×10^{-5} M in THF. Final stoiciometric ratio was set at [Si repeat unit]/[F^-] = 200 ([F^-] = 150.0 nM). All spectra were taken with excitation at 300 nm at 25 °C.

polysilanes used in this work. Furthermore, subtle change in persistence length of the F-PSi drastically affected their fluorescence behavior. Thus, the fluorescence intensity of F-PSi**3** with decyl group exhibited approximately three times greater value than that of F-PSi**1** with methyl group (Figure 1b). This global-conformation-related fluorometric property of the F-PSis played an essential role in the enhancement of the sensitivity for fluorometric detection toward the monovalent anions.

To evaluate potential ability of F-PSis as a fluorometric anion indicator, we first observed changes in fluorescent intensity of the F-PSi**1** and nonfluorinated PSi**1** by successive addition of fluoride (TBAF). Here nonfluorinated PSi**1** was used as an analogue of F-PSi**1** with *n*-propyl group, instead of 3,3,3-trifluoropropyl group. From the values of M_w and PDI, the degree of polymerizations (DP_n) of F-PSi**1** and PSi**1** were calculated to be 143 and 358, respectively. Final concentration of fluoride in the PSi/THF solution was adjusted to be [F^-] = 150 nM, which corresponded to the stoichiometric ratio between Si repeating unit and fluoride [Si]/[F^-] = ca. 200. The characteristic monomodal fluorescent signals of the PSis with maximum peak at ca. 330−340 nm by excitation at 300 nm were monitored (Figure 2).

Upon addition of 150 nM fluoride, F-PSi**1** immediately quenched by ca. 80%, compared to the original fluorescent intensity of F-PSi**1** (Figure 2a), whereas PSi**1** did not show such significant fluorescent quenching even through the same titration condition was applied (Figure 2b). Here it is noteworthy that the stoichiometric ratio between Si repeating unit and fluoride is nearly identical to the degree of polymerization of F-PSi**1** (DP_n = 143). Thus, entire fluorescence chromospheres in a F-PSi**1** single chain were highly efficiently quenched by a sole fluoride through an electrostatic interaction with a positively charged Si atom in the main chain. On the other hand, PSi**1** did not show such fluorescence quenching by fluoride because nonionic Si main chains of PSi**1** could not electrostatically interact with fluoride.

To realize advantages of F-PSi as a fluorimetric indicator of monovalent anions, fluorescent quenching was examined with a variety of sizes of monovalent anions (Figure 3). Upon addition of the monovalent anions into the PSi solution, fluorescence of F-PSi**1** was successively quenched, in which the extents of fluorescence quenching was increased nearly in proportion to the surface charge density of the monovalent anions, F^- > NO_3^-, Br^- > Cl^- > HSO_4^- > PF_6^- > I_3^- (Scheme 1c). According to the HSAB concept, the delocalized polymeric cation along the Si main chain could be regarded as a soft base,[11] therefore it should preferentially interact with relatively soft acids. However, the present systematic study on monovalent anion size for fluorescence quenching revealed that F-PSi**1** preferred to interact with relatively hard acids, rather than soft acids.

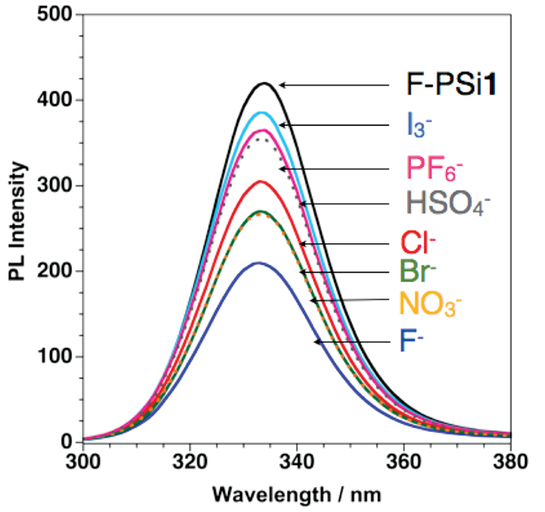


Figure 3. Changes in fluorescence spectra of F-PSi**1** (3.0×10^{-5} M/THF) by adding a series of monovalent anions (4.5×10^{-5} M/THF). All spectra were monitored after 30 min of addition of monovalent anions at 25 °C. All samples were taken with excitation at 310 nm.

To clarify this unexpected electrostatic interaction between delocalized polymeric cation and monovalent anions along with fluorescence quenching, we hypothesized that alkyl side chains may act as a molecular sieve for size-discrimination of the monovalent anions, by the following rationale. When ordinal small organic and/or inorganic salts dissolve in solvents, electric charges in both cations and anions are located on their surfaces and solvates by the solvent molecules. However, in the case of F-PSis, positively charged Si main chains were surrounded by both 3,3,3-trifluoropropyl and linear alkyl groups due to their helical conformations with an equal amount of right- and left-handed helicities in solutions. Therefore, the monovalent anions have to pass through the alkyl side chain's clad layers to reach the positively charged Si main chain. Thus, the more compact the steric sizes of the monovalent anions are, the easier the monovalent anions access to the positively charged Si main chain through the electrostatic interaction.

To quantify the size-dependent fluorescence quenching of the monovalent anion species, Stern−Volmer constants (K_{SV}) for each monovalent anion were plotted as a function of their surface charge densities (Figure 4). Here K_{SV} was obtained by the

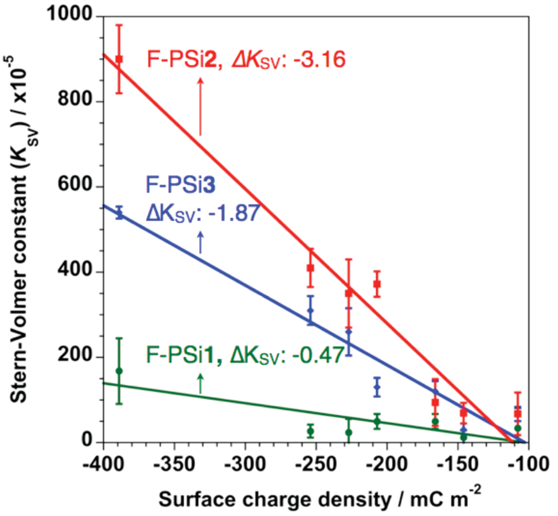


Figure 4. Correlation between Stern−Volmer constant for fluorescence quenching of fluorinated polysilanes and surface charge density of the monovalent anions. Red, blue, and green solid lines correspond to F-PSi**2**, F-PSi**3**, and F-PSi**1**, respectively.

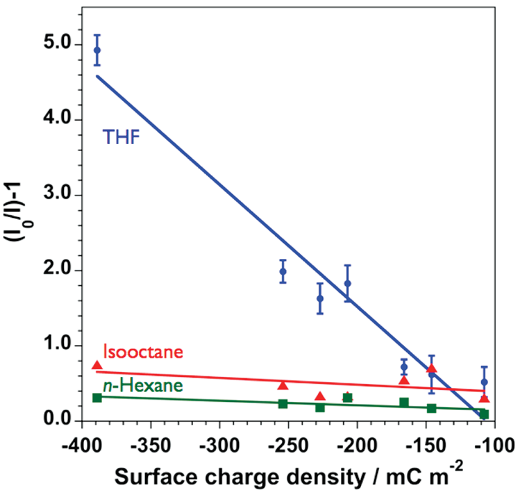


Figure 5. Solvent polarlity effect on fluorescence quenching of F-PSi3 (3.0×10^{-5} M) as a function of surface charge density of the monovalent anions. [F^-]/[Si] per monomer unit] = 5.0×10^{-3}. Dielectric constants (ε) for THF (polar solvent), isooctane (nonpolar solvent), and *n*-hexane (nonpolar solvent) are 7.58, 3.50, and 1.88, respectively.

Stern−Volmer equation; $(F_0/F) - 1 = K_{SV}[\text{analyte}]$, where F_0 and F are fluorescence intensity without and with analyte, respectively.[20] Consequently, the values of K_{SV} were linearly decreased with increase in the surface charge density of the monovalent anions. Furthermore, by introducing relatively longer alkyl side chains, the slopes of the K_{SV} against surface charge density became steeper, indicating that sensitivity of F-PSi toward the monovalent anions can be modulated by simply adjusting the alkyl lengths. Indeed, the slope of F-PSi**2** with hexyl group ($\Delta K_{SV} = -3.16$) became approximately seven times greater than that of F-PSi**1** with methyl group ($\Delta K_{SV} = -0.47$), whereas the slope of F-PSi**3** with decyl group ($\Delta K_{SV} = -1.87$) remained four times greater than that of F-PSi**1**. This linear relationship between K_{SV} and surface charge density is advantageous for potential use of F-PSis as a fluorometric indicator toward monovalent anions. Furthermore, alkyl-length-dependent moderation of sensitivity suggests the fluorometric sensitivity toward monovalent anions can be optimized by simple molecular design with an adequate alkyl length only.

To further elucidate the fluorescence quenching mechanism, we attempted combinational analyses with ^{1}H, ^{13}C, and ^{29}Si NMR measurements. Unfortunately, significant evidence on interaction between monovalent anions and F-PSis could not be obtained from ^{1}H, ^{13}C, and ^{29}Si NMR measurements. However, on further reflection, we concluded that it would be reasonable that significant chemical shifts were undetectable in conventional NMR measurements. Because stoichiometric ratio among fluoride and Si repeating unit were adjusted to be 200, indicating that only a sole fluoride could interact with a PSi single chain, followed by efficient fluorescent quenching the whole chromophores in the main chain. Such subtle changes in chemical conditions could not be detected by conventional NMR technique.

Here a key question has arisen whether the F-PSis recognized steric sizes of only monovalent anions or those as tetra-*n*-butyl ammonium salts. To address the question, effects of solvent's polarity on the fluorescence quenching were carried out. Because the polar solvents have ability to ionize organic solvents through the solvation, whereas nonpolar solvents do not. Here THF (dielectric constant, ε: 7.58), isooctane (ε: 3.00), and *n*-hexane (ε: 1.88) were used as polar, intermediate, and nonpolar solvent, respectively.[21] The values of fluorescence quenching efficiency $[(I_0/I) - 1]$ of F-PSi**3** (3.0×10^{-5} M, [monovalent anion]/[Si per monomer unit] = 5.0×10^{-3}) were plotted as a function of the surface charge density. Consequently, fluorescence quenching of F-PSi**3** hardly occurred in isooctane and *n*-hexane although in THF, showed a clear linear relationship between fluorescence quenching efficiency and surface charge density of the monovalent anions (Figure 5). Therefore, we concluded that F-PSis could recognize the steric sizes of the monovalent anions, rather than those of the tetra-*n*-butylammonium salts.

To further clarify the nature of the alkyl-length-dependent fluorescence quenching behavior of F-PSis toward monovalent anions, computational studies with molecular mechanics calculations were performed using PCFF force fields (Materials Studio 4.0, Accelrys Inc., San Diego, CA). To simplify the calculations, F-PSi oligomers with 20-Si repeating units were employed as models of F-PSis. The dihedral angles of F-PSis were set at 154° based on evidence that F-PSis adopted a 7_3 helix in THF (Figure 1a).

Linear alkyl and 3,3,3-trifluoropropyl groups helically surrounded the Si main chain to form the exterior surfaces, which can be regarded as a "core/clad" structure (Figure 6). Thus, the positively charged fluorescent Si main chains were protected by both 3,3,3-trifluoropropyl and linear alkyl chains, which acted as buffer phases to regulate the access of monovalent anions to the positively charged Si main chain. To understand the alkyl-length-dependency of sensitivity of monovalent anions, F-PSi**2** (hexyl) > F-PSi**3** (decyl) > F-PSi**1** (methyl), we focused on the relationship between molecular length between 3,3,3-trifluoropropyl and linear alkyl chain. (i) F-PSi**2** (3,3,3-trifluoropropyl ≈ hexyl): Hexyl group, which slightly longer than 3,3,3-trifluoropropyl group, formed helical groove with 1.3 nm width (Figure 6a, yellow line). Interestingly, molecular length of TBA was nearly identical to the width of the groove. Therefore, TBA was trapped at the exterior surface and only monovalent anions could access to the positively charged Si main chains (Figure 6a). (ii) F-PSi**1** (3,3,3-trifluoropropyl > methyl): The exterior surfaces were formed by electron-withdrawing 3,3,3-trifluoropropyl groups, therefore TBAs preferred to interact with the exterior surfaces rather than the Si main chain core. This led to weaken the positive polarity of the Si main chain (Figure 6b). (iii) F-PSi**3** (3,3,3-trifluoropropyl < decyl): Both 3,3,3-trifluoropropyl and Si main chains were covered by decyl groups. Because of steric crowdness of *n*-decyl layers, both TBA and its counteranions were thought to be repelled from the exterior surfaces (Figure 6c). For reasons described above, we concluded that alkyl-chain-length-dependency of fluorescence sensitivity essentially originated from the

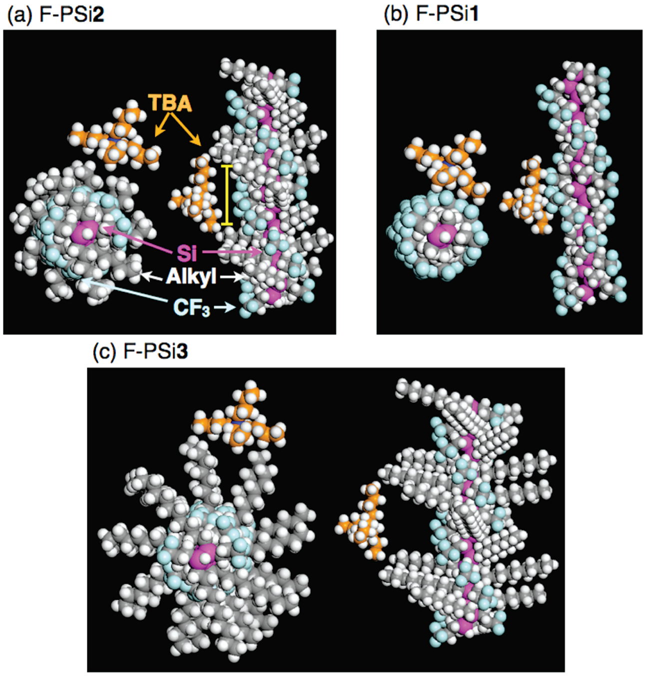


Figure 6. Proposed structures of fluorinated PSi with TBA cation. (a) F-PSi**2**/TBA, (b) F-PSi**1**/TBA, and (C) F-PSi**3**/TBA. To simplify the calculation, PSi oligomer with 20 monomers (with 20-Si repeating units) was employed as a model of fluorinated PSi. PCFF was used as a force field.

relationship between 3,3,3-trifrluoropropyl and linear alkyl chains, which regulated accessibility of monovalent anions to the positively charged Si main chain.

In conclusion, we have demonstrated that fluorescence of the fluorinated PSi with 3,3,3-trifluoropropyl and linear alkyl side chains was quenched by monovalent anions. The extent of the fluorescent quenching was linearly increased by a decrease in the surface charge density of the monovalent anions. This is because an inherent nature of the polysilanes to adopt helical conformation produce helical grooves made by alkyl side chains along to the Si main chain, which act as soft but strict monovalent anion recognition sites. The knowledge gained from this work will serve as a guide toward designing fluorimetric anion sensing by using the fluorescent conjugated polymers.

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