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ARTICLE

Excimer-monomer Switch: A Reaction-Based Approach for Selective Detection of Fluoride

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A N-aryl-1,8-naphthalimide based sensor (ES-1) bearing a trimethylsilyl ether has been synthesized by a two-step reaction for quantitative detection of fluoride (F^-). ES-1 exhibited monomer/excimer emissions at 410 and 524 nm respectively in CH_2Cl_2. In the presence of F^-, the desilylation of trimethylsilyl ether caused decay of the excimer emission as well as enhancement of the monomer emission to give a ratiometric signal. The fluoride-triggered desilylation showed a high reaction rate and high affinity to F^- over nine other interfering anions. ES-1 provided a novel fluorescence assay based on an excimer-monomer switch of N-aryl-1,8-naphthalimide to quantitatively measure F^- with a detection limit to be 0.133 ppm.

Introduction

In nature, fluoride (F^-) is an essential anion wildly existing in the soil, ocean and ground water with the abundance in the range of 10-100 μM.[1] As a ubiquitous anion, F^- plays important roles in many aspects of chemical, clinical, biological, environmental, and health sciences.[2] Many functions of F^- have been reported to completely rely on its concentration.[3] Therefore, developing a robust approach for quantitative detection of F^- in various samples, particularly by using fluorescence chemosensors, has attracted great interest in many research fields.[4] Due to the advantages of high sensitivity, low cost and non-destruction of samples, numerous fluorogenic sensors based on different sensing mechanisms have been reported for quantitative analysis of F^-.[5] However, development of a sensing approach to selectively recognize F^- but with a minimum interference from other anions in various sensing scenarios is always a challenge.[6] Recently, silyl ether has been employed as a sensing unit through fluoride-triggered desilylation to design reaction-based fluorescence chemosensors for F^- analysis, which showed significant improvement of selectivity to F^-.[7] However, these reaction-based F^- sensors usually required long responding time that significantly limited the applications, particularly for real-time detection.[8]

As a fluorescent molecule with many unique photophysical properties, 1,8-naphthalimides (NIs) have been intensively used as fluorophores to design fluorescence chemosensors on the basis of various mechanisms such as internal charge transfer (ICT), photoinduced electron transfer (PET), and föster resonance energy transfer (FRET) for different analysts.[9] Moreover, a stable excimer that showed a red-shifted emission but without corresponding absorption spectrum was also observed for a few NIs.[10] Although excimer-monomer emissions provided an excellent ratiometric signal for molecular recognition, the investigation of NI excimer and ratiometric sensors based on NI excimer-monomer switch were rarely reported.[11]

Based on the above consideration, we report a sensor (ES-1) designed on the basis of NI bearing a trimethylsilyl ether that was cleaved in the presence of F^- to give a ratiometric fluorescence signal between the excimer-monomer switch. The quantitative correlation between the amount of F^- and ratiometric signal had ES-1 performed as a sensitive sensor for detection of F^-. Compared to other F^- sensors, ES-1 displayed extremely high affinity to F^- over other anions based on the fluoride-triggered cleavage reaction, which showed a short responding time to F^-. Moreover, the excimer-monomer switch, which was rarely reported for NI, provided a novel mechanism with a ratiometric signal for sensor design on the basis of NI.

Results and discussion

ES-1, ES-2 and ES-3 were conveniently synthesized by a two-step reaction (Scheme 1). As the intermediate, compound 1 was prepared by using commercially available 1,8-naphthalic anhydride and 4-aminophenol in 2-methoxyethanol at 130 °C for 4 hr (97% yield). Compound 1 was mixed with three

chloroalkylsilane in pyridine at 50 °C for 12 hr to yield ES-1 (88%), ES-2 (85%) and ES-3 (80%) respectively. ES-1, ES-2 and ES-3 were characterized by ^{1}H NMR, ^{13}C NMR, and HRMS. The detailed synthetic procedures and structure characterization are available in the Experimental section and in the ESI.[†]
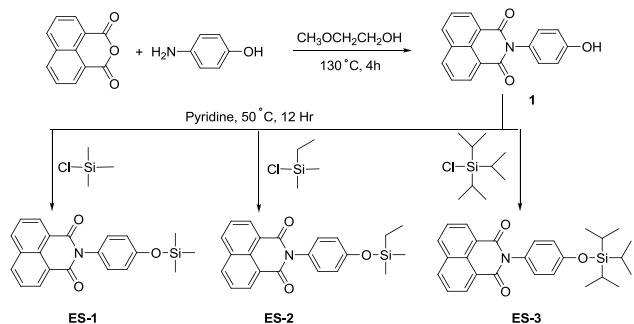
Scheme 1 The synthetic route to prepare reaction-based fluoride sensors (ES-1, ES-2 and ES-3)

The photophysical properties of ES-1, ES-2 and ES-3 were investigated in different solvents including hexane, dichloromethane (DCM), ethyl acetate (EtOAc), acetonitrile (MeCN), methanol (MeOH), and acetonitrile-water (MeCN-H_2O = 9:1). As shown in Table 1, all of three compounds showed the maximum absorption wavelength around 330 nm in various solvents, but the maximum emission wavelength was varied between 361 nm and 426 nm because of the strong solvation effect. In the less polar solvents, an excimer emission with a longer wavelength was observed for ES-1, ES-2 and ES-3 (Fig. S1 and S2). In particular, ES-1 exhibited a strong excimer emission at 524 nm in DCM. However, none of three molecules showed an excimer emission in the polar media (i.e., MeOH and MeCN-H_2O). Compared to ES-1 and ES-2, ES-3 displayed much weaker excimer emission because of the isopropyl groups from silyl ether, which might prevent the formation of excimer at excited state.

Table 1. Photophysical properties of ES-1, ES-2 and ES-3 in different solvents at 25 °C.

Media	ES-1			ES-2			ES-3		
	λ_{ab} (nm)	λ_{em} (nm)	λ_{em} (Excimer) (nm)	λ_{ab} (nm)	λ_{em} (nm)	λ_{em} (Excimer) (nm)	λ_{ab} (nm)	λ_{em} (nm)	λ_{em} (Excimer) (nm)
Hexane	325	426	454	326	401	451	326	402	449
DCM	334	410	524	334	376	531	334	376	524
EtOAc	330	365	525	330	370	527	329	405	—
MeCN	332	368	558	332	375	549	332	376	—
MEOH	334	371	—	334	382	—	334	401	—
MeCN/H_2O (9:1)	333	370	—	333	381	—	333	378	—

As shown in Scheme 2, ES-1 was designed on the fluoride-triggered desilylation reaction, which is a widely used reaction for the protection of hydroxyl group. In the presence of F^-, the

Si-O bond in the silyl ether was cleaved to yield a phenoxide, which changed photophysical properties of entire molecule. Based on recent results obtained from our group, the trimethylsilyl ether showed an extremely high sensitivity and selectivity to the fluoride-triggered desilylation, functioning as a recognition unit for the detection of F^- over other anions.[12] Thus, ES-1 was designed on the basis of trimethylsilyl ether for specific detection of F^-. Moreover, an ethyldimethylsilyl ether and a triisopropylsilyl ether were employed for ES-2 and ES-3 as the recognition units for comparison.
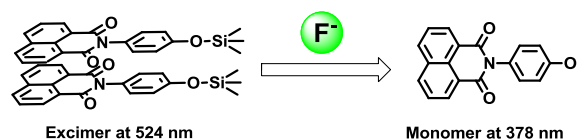
Scheme 2 ES-1 displayed a strong excimer emission at 524 nm in DCM. Upon addition of F^-, the fluoride-triggered desilylation completely disrupted the excimer emission and significantly enhanced the monomer emission at 378 nm.

Fluorescence titrations were conducted to investigate the sensing properties of ES-1 for detection of F^-. After incubating ES-1 (5.0×10^{-5}M) with 0-10 equiv F^- in DCM at 25 °C for 5 min, fluorescence spectra were collected with a excitation wavelength at 334 nm. ES-1 displayed the maximum emission at 410 nm, representing the regular emission of NI, as well as a strong excimer emission at 524 nm. The ratio of $I_{monomer}/I_{excimer}$ was observed to be 1.27. With addition up to 10 equiv F^- to ES-1 solution, substantial spectral changes were observed (Fig. 1).

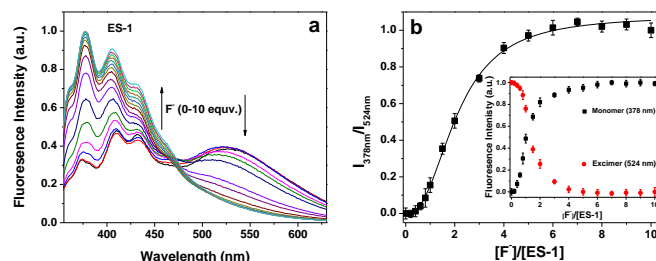**Fig. 1** (a) The emission spectra of ES-1 (5.0×10^{-5}M) with addition of 0-10 equiv F^- in DCM (λ_{ex}=334 nm). (b) In the presence of F^-, the monomer emission of ES-1 (at 378 nm) increased with the decline of the excimer emission (at 524 nm) at 25 °C.

A decline of emission at 524 nm with a concomitant increase in the region of 365-430 nm was recorded, indicating the excimer of ES-1 was interrupted by F^-. The excimer of ES-1 was extremely sensitive to the F^- that 5 equiv F^- completely quenched excimer fluorescence. In the presence of F^-, the maximum emission wavelength of ES-1 was shifted from 410 nm to 378 nm, revealing the desilylation yielded a phenoxide, which showed a structure change from ES-1. To verify the formation of excimer for ES-1, the absorption spectra were collected during the titration process. As shown in Fig. S3, no

significant change was observed for absorption spectra with addition of F⁻ that strongly suggested the emission at 524 nm represented the excimer emission of ES-1. Moreover, fluoride titrations were also carried out for ES-2 and ES-3 under the same conditions used for ES-1 (Fig. 2). Compared to ES-1, both of ES-2 and ES-3 exhibited a weaker excimer emission with a ratio of $I_{monomer}/I_{excimer}$ as 2.17 and 3.70 respectively. In the presence of F⁻, although the ratiometric signal was observed for both of ES-2 and ES-3, the scale of fluorescence change was much less than ES-1.
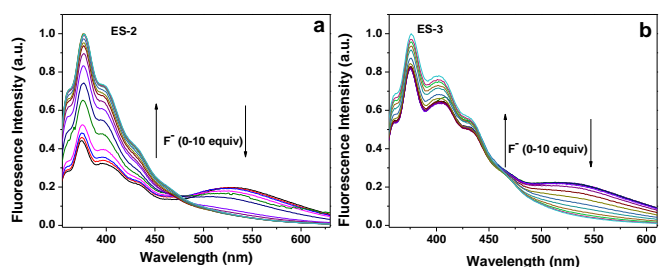

Fig. 2 The emission spectra of (a) ES-2 (5.0×10^{-5}M) and (b) ES-3 (5.0×10^{-5}M) with addition of 0-10 equiv F⁻ in DCM (λ_{ex}=334 nm).

To investigate the interaction between ES-1 and F⁻, ¹H NMR spectra of ES-1 (1.0×10^{-4} M) were collected in the presence of 0-5 equiv F⁻ in the CDCl₃ solution (Fig. 3). The free ES-1 gave two doublet peaks in the region of δ 7.0-7.3 ppm corresponding to four hydrogens on the phenyl ring. With addition of F⁻, theses protons on phenyl ring moved to up-field due to the shielding effect, indicating a species with high electron density (i.e., phenolate) has been formed from the desilylation. On the contrary, protons on naphthalene moiety did not show any significant change during the titration. The ¹H NMR titration data clearly revealed that fluoride induced a desilylation of the
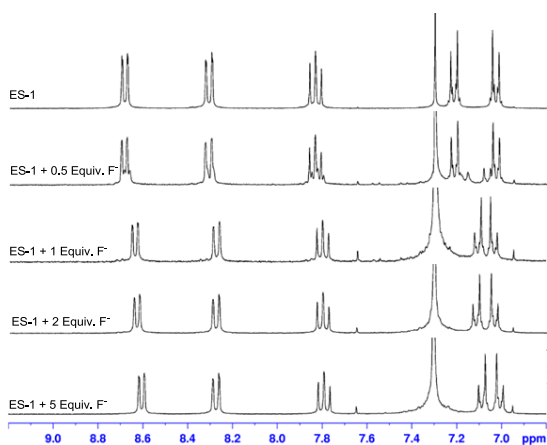

Fig. 3 ¹H NMR spectra of ES-1 with addition of F⁻ (0-5 equiv) in CDCl₃.

trimethylsilyl ether on the phenyl ring of ES-1 through cleavage of Si-O bond to form a phenolate anion. Also, the invariable ¹H NMR spectra of naphthalene part during the titration confirmed that fluoride triggered an excimer-monomer switch.

The reaction rate of desilylation was also investigated by using the fluorescence titration. After addition of 5 equiv F⁻ into ES-1 (5.0×10^{-5}M) solution, the excimer emission at 524 nm that reflected the process of desilylation, was measured in 5 min. As shown in the Fig. 4, the excimer emission was rapidly
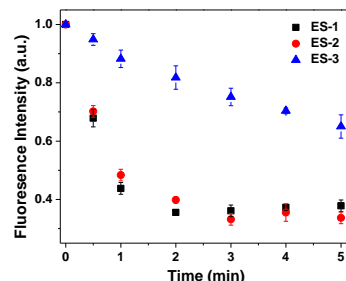

Fig. 4 The intensity change of excimer emission for ES-1, ES-2 and ES-3 (5.0×10^{-5}M) with addition of 5 equiv F⁻ in DCM at 25 °C (λ_{ex}=334 nm).

quenched within 2 min, indicating the high reaction rate for fluoride-triggered desilylation. For comparison, the desilylation rates for ES-2 and ES-3 were also measured under same conditions. ES-2 showed a very similar desilylation rate as ES-1, whereas ES-3 gave a relatively low rate that could be caused by steric hindrance from isopropyl groups on ES-3. The overall rate constants of ES-1 ES-2 and ES-3 (5.0×10^{-5} M) based on Pseudo-first-order reaction were calculated to be 2.7×10^{-2} S⁻¹, 2.0×10^{-2} S⁻¹, 6.8×10^{-3} S⁻¹ respectively in the presence of F⁻

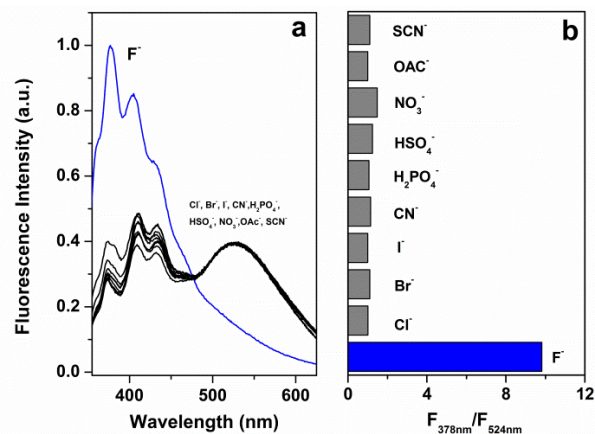**Fig. 5** (a) Fluorescence emission spectra of ES-1 (5.0×10^{-5}M) in the presence of 10 equiv various anions (F⁻, Cl⁻, Br⁻, I⁻, CN⁻, H₂PO₄⁻, HSO₄⁻, NO₃⁻, OAc⁻, SCN⁻) in DCM. (b) ES-1 displayed high affinity to react with F⁻ over other anions, showing a ratiometric signal with a decrease of excimer emission at 524 nm and an increase of monomer emission at 378nm.

$(2.5 \times 10^{-4}$ M). Moreover, the detection limit of ES-1 was determined to be 0.133 ppm for F$^-$. All of data clearly supported that ES-1 performed as a highly sensitive approach with a ratiometric signal for recognition of F$^-$.

The anion recognition ability of ES-1 was investigated by using fluorescence titration for F$^-$, Cl$^-$, Br$^-$, I$^-$, CN$^-$, H$_2$PO$_4^-$, HSO$_4^-$, NO$_3^-$, OAc$^-$ and SCN$^-$ in DCM. After incubating ES-1 $(5.0 \times 10^{-5}$ M) with each of anions (10 equiv) for 5 min, the fluorescence spectra were collected. As shown in Fig. 5, upon addition of F$^-$, the excimer emission of ES-1 was completely quenched while monomer emission was enhanced up to 2.7 fold. The intensity ratio of monomer to excimer ($I_{monomer}/I_{excimer}$) was changed from 1.27 to 9.82. However, no remarkable fluorescence change was observed for ES-1 in the presence of any other anions, suggesting the high affinity to F$^-$. These results clearly indicated that ES-1 could be used as robust approach to quantitatively detect F$^-$ in the complicated environment.

Experimental section

Apparatus

Absorbance spectra were collected by 8453 UV-Visible Spectrophotometer (Agilent Technologies). Fluorescence measurements were all performed by using a FluoroMax-4 Spectrofluorometer (Horiba Jobin Yvon, USA). All of fluorescence spectra were recorded in a 1 cm quartz cuvette at 25 °C. The excitation and emission slits were set at 3 nm. ^{1}H and ^{13}C NMR spectra were recorded on (^{1}H 300MHz, ^{13}C 75MHz) Bruker 300 Ultra-Shield spectrometer at room temperature.

Reagents

All reagents used for synthesis and measurements were purchased from Sigma-Aldrich (MO, USA), Fisher Scientific (USA) and Acros Organics (USA) in analytical grade and used as received, unless otherwise stated. All of anions (F$^-$, Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, HSO$_4^-$, CN$^-$, SCN$^-$, OAc$^-$, and H$_2$PO$_4^-$) used for measurements were tetrabutylammonium (TBA) salts.

Synthesis and characterization

2-(4-hydroxyphenyl)-1H-benzo[de]isoquinoline-1,3(2H) dione (1): 1,8-naphthalimic anhydride (991 mg, 5.0 mmol) was mixed with 4-aminophenol (636 mg, 6.0 mmol) in 10 mL 2-methoxyethanol at 130 °C for 4 hours under refluxing. The reaction mixture was poured into 30 mL 6% HCl in ice bath to

collect a grey precipitate as compound 1 by filtration without further purification (1.40g, 97%). ^{1}H NMR (300 MHz, DMSO) δ: 6.87 (d, $J=$ 8.04 Hz, 2H), 7.15 (d, $J=$ 7.86 Hz, 2H), 7.90 (t, $J=$ 7.77 Hz, 2H), 8.49 (d, $J=$ 7.29 Hz, 4H), 9.66 (s, 1H); ^{13}C NMR (75 MHz, DMSO) δ: 115.9, 123.1, 127.4, 127.7, 128.2, 130.4, 131.2, 131.9, 134.8, 157.6, 164.3.

2-(4-(trimethylsilyloxy)phenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (ES-1): Compound 1 (200 mg, 0.69 mmol) and chlorotrimethylsilane (230 mg, 2.1 mmol) were dissolved in 10 mL pyridine at 50 °C for 12 hours. The reaction mixture was poured into 30 mL 6% HCl in the ice bath to collect a brown precipitate as the crude product by filtration. Then the crude product was purified by the silica gel (200-400 mesh, 60 Å) column chromatography (CH$_2$Cl$_2$) to yield a white solid as ES-1 (219 mg, 88%). Melting point (m.p.): 199.3 °C. ^{1}H NMR (300 MHz, DMSO) δ: 0.32 (s, 9H), 6.98 (d, $J=$ 8.64 Hz, 2H), 7.26 (d, $J=$ 8.64 Hz, 2H), 7.91 (t, $J=$ 7.68 Hz, 2H), 8.49-8.52 (m, 4H); ^{13}C NMR (75MHz, DMSO) δ: 0.7, 120.2, 123.1, 127.8, 128.3, 129.7, 130.7, 131.2, 132.0, 134.9, 154.9, 164.4. TOF MS EI$^+$: M$^+$ m/z 361.1134 (calcd.), 361.1132 (found).

2-(4-(ethyldimethylsilyloxy)phenyl)-1H benzo[de]isoquinoline-1,3(2H)-dione (ES-2): Compound 1 (200 mg, 0.69 mmol) and chloroethyldimethylsilane (260 mg, 2.1 mmol) were dissolved in 10 mL pyridine at 50 °C for 12 hours. The reaction mixture was poured into 30 mL 6% HCl in ice bath to collect a white precipitate as crude product by filtration. Then the crude product was purified by the silica gel (200-400 mesh, 60 Å) column chromatography (CH$_2$Cl$_2$:EtOAc = 4:1) to yield a white solid ES-2 (220 mg, 85%). Melting point (m.p.): 171.2 °C. ^{1}H NMR (300 MHz, DMSO) δ: 0.29 (s, 6H), 0.71-0.79 (m, 2H), 1.00 (t, $J=$ 8.10 Hz, 3H), 6.98 (d, $J=$ 8.73 Hz, 2H), 7.26 (d, $J=$ 8.67 Hz, 2H), 7.90 (t, $J=$ 7.68 Hz, 2H), 8.48-8.52 (m, 4H); ^{13}C NMR (75 MHz, DMSO) δ: 2.4, 10.8, 12.1, 124.0, 126.8, 131.4, 132.0, 133.5, 134.5, 134.9, 135.6, 138.6, 158.8, 168.0. TOF MS EI$^+$: M$^+$ m/z 375.1291 (calcd.), 375.1293 (found).

2-(4-(triisopropylsilyloxy)phenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (ES-3): Compound 1 (200 mg, 0.69 mmol) and chlorotriisopropylsilane (405 mg, 2.1 mmol) were dissolved in 10 mL pyridine at 50 °C for 12 hours. The reaction mixture was poured into 30 mL 6% HCl in the ice bath to collect a brown precipitate as the crude product by filtration. Then the crude product was purified by the silica gel (200-400 mesh, 60 Å) column chromatography (CH$_2$Cl$_2$:EtOAc = 6:1) to yield a white solid ES-3 (246 mg, 80%). Melting point (m.p.): 170.3 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 1.18 (d, $J=$ 6.99 Hz, 18H), 1.28-1.40 (m, 3H), 7.06 (d, $J=$ 8.79 Hz, 2H), 7.19 (d, $J=$ 8.76 Hz, 2H), 7.83 (t, $J=$ 7.62 Hz, 2H), 8.31 (d, $J=$ 8.28 Hz, 2H),

8.68 (d, J= 7.29 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ: 12.7, 18.0, 120.6, 122.9, 127.2, 128.1, 128.6, 129.5, 131.7, 134.2, 156.3, 164.6. TOF MS EI$^+$: M$^+$ m/z 445.2072 (calcd.), 445.2060 (found).

Conclusions

In conclusion, we reported a facile fluoride sensor (ES-1) that used the fluoride-triggered desilylation of trimethylsilyl ether to specifically recognize fluoride over other interfering anions. Compared to current fluoride sensors using the same mechanism, ES-1 showed an extremely short responding time to F$^-$. Based on the simple synthetic route, excellent selectivity and low detection limit, ES-1 behaved as an applicable approach for quantitative detection of F$^-$. Moreover, ES-1 showed a ratiometric signal based excimer/monomer emission of NI responding to the presence of F$^-$. This result clearly addressed that a strong intermolecular interaction, between different NI molecules, led to an excimer at excited state, which was rarely reported for NI and could be used as a sensing mechanism to design fluorescence chemosensors with ratiometric signal in the future.

Acknowledgements

Notes and references

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† Electronic Supplementary Information (ESI) available: characterization data including ^{1}H NMR, ^{13}C NMR spectra, HRMS data, and absorption spectra.See DOI: 10.1039/b000000x/

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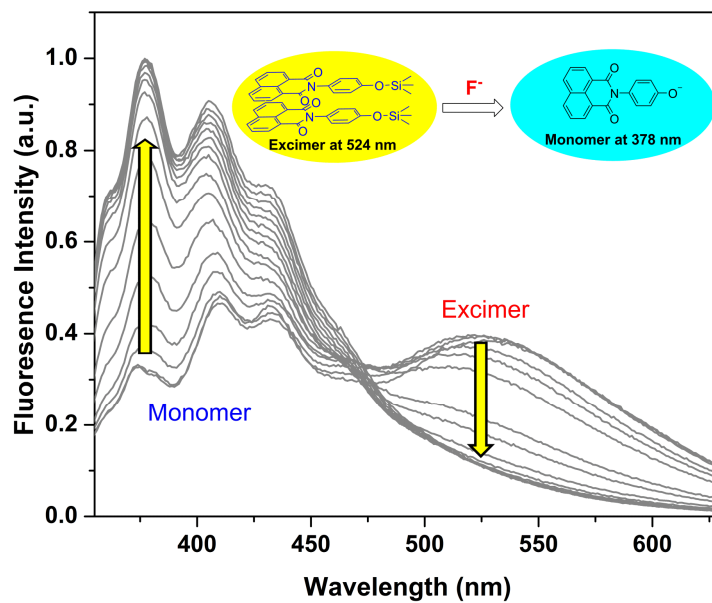
Desilylation triggered excimer-monomer switch based on 1,8-naphthalimide was used as a sensing strategy for detection of fluoride.