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불소 이온 감지용 형광 센서의 개발

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Development of Highly Selective Fluorescent Chemosensors for Fluoride Ion

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요 약. 새로운 불소 이온 감지용 화학 센서를 합성하였다. 탈실리콘화 과정에서 만들어지는 페녹사이드를 친핵체로 사용하여 형광 물질로 락톤화되는 기존의 방법에 대한 추가적인 설명과 함께 탈실리콘화에 의한 방향족 화합물의 평면화를 통한 형광의 변화 방법이 새로이 제시되었다. 개발된 센서들은 불소에 대해 선택적인 친화력을 갖는 실리콘을 이용하므로 불소 이온에 대해 높은 선택성을 보였다. 또한, 합성된 센서에 공액 고분자를 연결하여 그 감도를 성공적으로 증대시켰다.

주제어: 불소 이온, 화학적 센서, 형광, 고리화 반응, 공액 고분자

ABSTRACT. Novel fluoride sensory systems have been successfully developed. Previously developed method of the fluoride-induced lactonization to fluorescent molecules was detailed, and newly developed fluoride-induced aromatic cyclization scheme was introduced. Based on the strategies using the specific affinity of fluoride to silicon, our systems are highly selective for fluoride ion. Incorporation of the developed sensor to a conjugated polymer has successfully enhanced its sensitivity to fluoride ion.

Keywords: Fluoride Ion, Chemical Sensor, Fluorescence, Cyclization Reaction, Conjugated Polymer

INTRODUCTION

Fluoride ion sensing has drawn growing attention over the last decades[1] due to its great potential for industrial and biological applications.[1f,1h] While conventional methods of fluoride sensing such as ion selective electrodes hold their ground, novel approaches are being introduced and hence progresses made in terms of selectivity and sensitivity.[2-5] There are, however, few receptors which "truly" differentiate fluoride over other anions, such as chloride, phosphate or nitrate. These anions can, in principle, compete with fluoride ion under the most synthetic receptor schemes based on the specific Lewis acid-base interaction, or the designed hydrogen-bonding. The binding events have, then, been converted into an electrochemical or optical response. These efforts have enjoyed successes and, in some cases, have resulted in the ability to visually detect fluoride ions.[4,5]

On the other hand, fluorescence remains as an important detection method due to its high detec-

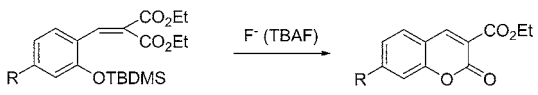
tion limit. The fluorescence response can be further amplified by utilizing the facile and efficient exciton-transporting properties of conjugated polymers (so-called the 'molecular wire approach').[6] These methods were originally demonstrated using electron-transfer quenching and variations on this scheme have been used to create a number of chemical and biological sensory methods, most of which involve changes in the emission intensities. In spite of these successes, it is generally preferable for a fluorescence signal to involve a new emission at a different wavelength rather than a modulation of an existing signal. The advantage of the latter approach is that a new signal is inherently easier to detect than an intensity change. Furthermore, new analyte-triggered emissions may offer high specificity and low background.

In a previous communication, we have demonstrated the fluoride-induced lactonization scheme to coumarin and its application to fluoride-sensing. Herein, we present in detail the development of this methodology and further extensions. Our strategy is based on the specific affinity of fluoride ion to silicon, and hence highly selective for fluoride ion.[7]

RESULT AND DISCUSSION

We have previously developed a fluoride-sensing system in which the fluoride triggered Si-O bond cleavage resulted in the formation of highly fluorescent coumarin derivatives (*Scheme* 1).[8]

Coumarin and its derivatives constitute an important class of organic laser dyes due to their large absorption cross-section and high radiative quantum yields.[9] Another important feature of coumarin is the tunability of its photophysical properties over a wide wavelength range through substituent effects.



1: R = H — **1a**

2: R = $N(CH_2CH_3)_2$ — **2a**

Scheme 1. Fluoride-induced cyclization of the indicators (**1** and **2**) led to the fluorescent coumarin derivatives (**1a** and **2a**).

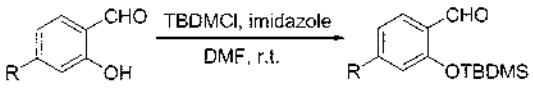
Table 1. Photophysical data in dichloromethane.

Compound	Abs.max.[a] (log ε)	Emission max.[a]	Φ [%][b]
1	322 (3.66)	-	<0.01
2	386 (4.31)	450	0.2
3	255 (5.66)	-	<0.01
8	378 (4.76)[c]	482	12
1a	334 (3.71)	415	12
2a	417 (4.39)	450	81
3a	256 (6.68)	336	46[d]
8a	396 (4.80)[c]	517	30

[a]Given in nanometers. [b]Determined with quinine sulfate as a standard.
[c]Per monomer unit. [d]Determined with 2-aminopyridine as a standard.

The absorption spectra of the 7-amino substituted indicator **2** (abs. max. 386 nm) and its cyclized product **2a** (abs. max. 417 nm) were, indeed, red shifted significantly compared to those of the unsubstituted analogues **1** (abs. max. 322 nm) and **1a** (abs. max. 334 nm). The originally non-fluorescent compounds **1** and **2** displayed strong fluorescence upon cyclization to coumarin derivatives **1a** (emission max. 415 nm; Φ= 12%) and **2a** (emission max. 450 nm; Φ= 81%), respectively (*Table* 1).

Synthesis of the indicators involves a two-step sequence, namely, silylation of the corresponding 2-hydroxy benzaldehyde, followed by a condensation reaction under the titanium-mediated Knoevenagel conditions (*Scheme* 2).[8,10] To avoid a possible *trans-cis* isomerization of the double bond, we used diethyl malonate to introduce the compounds with the symmetrically substituted double bond, **1** and **2**. This strategy allowed us to keep the ester group close to the reactive phenoxide, which is a key requisite for lactonization to occur before it is converted into a phenol.

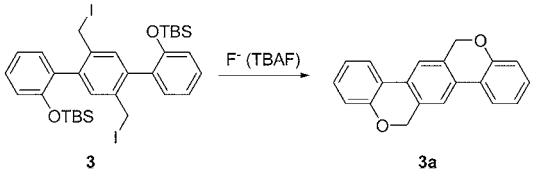


i. $TiCl_4$ in CCl_4 to THF, 0 °C
ii. diethylmalonate in THF, pyridine

1: R = H

2: R = $N(CH_2CH_3)_2$

Scheme 2. Synthesis of the indicators **1** and **2**.

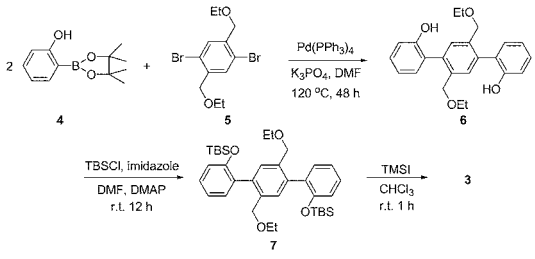


Scheme 3. Fluoride-induced cyclization of the indicator **3** led to the fluorescent molecule **3a** with a planar structure.

To further exploit the fluoride-induced cyclization scheme, we have also developed a fluoride sensory system where the fluoride-induced cyclization caused planarization of the aromatic units, resulting in the increase of fluorescence. The phenoxide, generated from the fluoride-induced desilylation, reacted with the neighboring benzyl iodide by nucleophilic substitution, leading to cyclize to form a ladder-type planar structure (*Scheme* 3).[11]

Although the absorption spectra of the cyclized product **3a** did not show a bathochromic shift, compared to that of its precursor **3**, the transformation from a flexible chromophore to a rigid extended one caused a dramatic increase in the emission efficiency by reducing the nonradiative rate (Φ= <0.01% for **3** and 46% for **3a**; *Table* 1). In fact, the indicator **3** was non-fluorescent as the aromatic rings in **3** undergo geometrical (vibrational-rotational) changes in the excited state that facilitate nonradiative processes. A strong fluorescence was observed only after the cyclization, induced by fluoride ion, which eliminates rotation about the phenyl-phenyl bond.

Synthesis of the sensory molecule **3** is shown in *Scheme* 4. The diethoxy terphenyl **6** was obtained by the Pd-catalyzed cross coupling reaction of the corresponding borate **4** with the dibromide **5**. Silylation of the phenol in **6** using TBDMSCl afforded **7**.[12] Finally, the ethoxy benzyl group in **7** was transformed into the corresponding iodo benzyl group as in **3** using TMSI.[13]



Scheme 4. Synthetic route to the sensory molecule **3**.

Both fluoride-induced coumarin formation (*Scheme* 1) and aromatic planarization (*Scheme* 3) schemes were quantitative and irreversible. Monitoring the reaction *in situ* by measuring the fluorescence intensity revealed that the rate of both cyclization reactions (**2** to **2a** and **3** to **3a**) was found to be first order in **2** and **3**, respectively, and independent of fluoride. This result indicates that the silyl cleavage (or fluoride association with the silyl group) is fast and that the cyclization is the slow step for both reactions. There was, however, a significant increase in the rate for the aromatic planarization scheme ($k = 2 \times 10^{-4}$ s^{-1} for **2** to **2a** and 2×10^{-2} s^{-1} for **3** to **3a**). Much faster nucleophilic substitution of the phenoxide with highly reactive benzyl iodide in **3**, compared to the nucleophilic acyl substitution in **2**, was ascribed to this result. Indeed, the cyclization of **3** to **3a** effected by fluoride ion (in the form of its tetrabutylammonium salt) in THF solution reached a complete conversion in just 2 min with only two equimolar of fluoride ion relative to the indicator **3** (*Fig.* 1). In contrast, cyclization of **2** to **2a** was too slow to reach a complete conversion under similar conditions as for **3**. The fluorescence emission

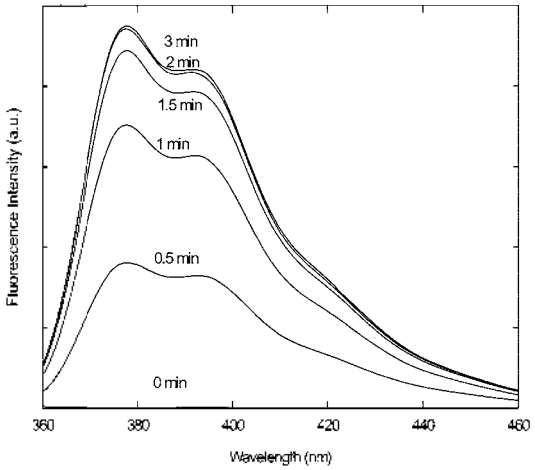
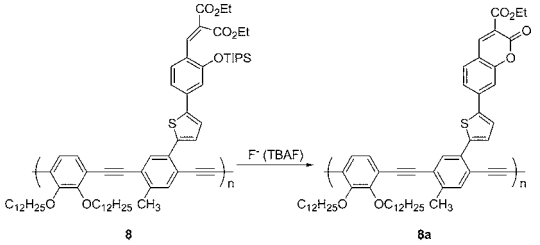


Fig. 1. Emission spectral changes upon addition of TBAF to **3** in THF: **3**, 3.5×10^{-6} M and TBAF, 7×10^{-6} M.



Scheme 5. A fluoride sensory polymer **8** and its cyclized form **8a**.

intensity continued to increase over a period of several hours.[8] It required more than 10-fold excess of fluoride ion to reach the saturation of the emission intensity within a reasonable period of time, i.e. 2-3 hours.

To enhance its sensitivity of the indicator **2**, we have incorporated our sensory system into a conjugated polymer (*Scheme* 5). The design feature of the sensory polymer **8** was to introduce a thiophene unit to bridge the sensory *o*-silyloxybenzylidene malonate moiety and the conjugated polymer.[14]

Although the reaction rate of the polymer **8** was expected to be somewhat lower than that of **2**,[15] the sensitivity of this sensory polymer to fluoride ion turned out to be sufficiently higher. Only 0.1 molar ratio of the fluoride ion (1.6×10^{-7} M of TBAF) relative to the sensory polymer **8** concentration (1.5×10^{-6} M in THF) was required to observe the fluorescence intensity maximum within a similar period of time (3 h) (*Fig.* 2). This result clearly indicated that the sensory polymer **8** was about 100 times more sensitive than its small molecule-based counterpart **2**.[16]

The signal amplification by the use of the conjugated polymer can be explained by the energy-transfer mechanism (known as Dexter energy transfer for small molecules) wherein activation of an indicator locally perturbs the band gap of the polymer. Hence in strongly electronically coupled conjugation schemes, only a few cyclization events induced by fluoride ion would produce local minima in the band gap that trap mobile excitons to give a new emission. The facile transport of excitons in conjugated polymers would allow to sample many transduction sites and therefore dramatically increase the

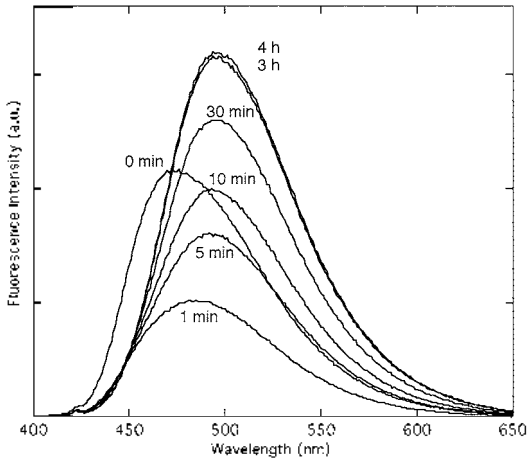


Fig. 2. Emission spectral changes upon addition of TBAF to **8** in THF: **8**, 1.5×10^{-6} M and TBAF, 1.6×10^{-7} M.

probability of emission change.

In addition, the effect of coumarin formation on the band gap of polymer **8** was readily monitored by inspecting the absorption and emission spectra before and after quantitative conversion to **8a** by treatment with an excess of TBAF (*Fig.* 3 and *Table* 1). In other words, the sensory polymer **8** afforded a change in fluorescence from blue to blue-green and

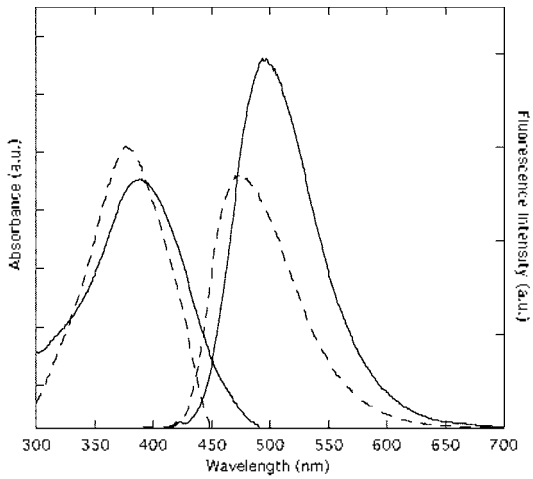


Fig. 3. Absorption and emission spectra of the sensory polymer **8** showing changes before addition (dashed line) and 3 h after (solid line) the addition of TBAF in THF solution: **8**, 1.5×10^{-6} M and TBAF, 1.6×0^{-7} M. For **8**, λ_{max} = 378 nm; ε = 57600 M^{-1} cm^{-1}; emission λ_{max} = 482 nm and **8a**, λ_{max} = 396 nm; ε = 63400 M^{-1} cm^{-1}; emission λ_{max} = 517 nm.

this change could be detected visually. This is because fluoride-induced cyclization events in the side-chains of the sensory polymer **8** produced local minima in the band gap of the conjugated polymer. The excitions were, then, recombined at these trapping sites, causing the new lower-energy emission, that is, fluoride-induced lactonization in the side chains produced a trapping site with a smaller band gap and recombination of excitons at that site resulted in a new emission.

EXPERIMENTAL

Melting points were determined using Büchi 510 melting point apparatus and uncorrected. IR spectra were recorded on a Nicolet MAGNA 560-FTIR spectrometer. ^{1}H NMR spectra were recorded on a Bruker Advance DPX-300 and DPX-500 instruments using deuterochloroform as reference or internal deuterium lock. The chemical shift data for each signal are given in units of δ (ppm) relative to tetramethylsilane (TMS) where δ (TMS) = 0, and referenced to the solvent residual. ^{13}C NMR spectra were recorded on a Bruker Advance-500 (125.7 MHz) instrument using internal deuterium lock and proton decoupling. Mass spectra were obtained on a JEOL JMS-AX505WA instrument. UV-visible absorption spectra and fluorescence spectra were measured with Hewlett Packard 8452A diode array spectrometer and SPEX Fluorolog-τ2 fluorometer (model FL 112, 450 W, xenon lamp), respectively, using spectral grade THF or CH_2Cl_2 as a solvent. The measurements were carried out at 25 °C using a quartz cell with a path length of 1 cm. The kinetic studies for the cyclization of the indicators **2** and **3** in dichloromethane were followed by measuring the fluorescence spectra after mixing **2** and **3**, respectively, with TBAF in a quartz cell. The reaction was carried out at room temperature under the excess amount of TBAF (initial concentration [indicators]<<[TBAF]) and the reaction was expected to reach 100% conversion of **2** to **2a** (and **3** to **3a**). Separate solutions of different concentrations of **2** (and **3**) with TBAF in THF were prepared and mixed to investigate the kinetics. In all cases, the concentration was low enough to maintain a UV absorption that was below 0.1. The rate of the cyclization was determined by fitting the fluorescence intensities of the samples to the Pseudo-First Order Equation (1): $Ln(F_{max} - F_t/F_{max}) = -kt$, where F_t and F_{max} are the fluorescence intensities at the monitoring wavelengths at times t and the maxima values which are the last fluorescence intensities when the cyclization of the indicators (**2** and **3**) reached the conversion of 100%. The k is the apparent rate constant.

Reagents were purified and dried by standard technique. All air and water-sensitive synthetic manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques.

Diethoxy terphenyl (6): A Schlenk tube containing a magnetic stirring bar was charged with $Pd(PPh_3)_4$ (88.3 mg, 0.057 mmol), compound **5** (0.40 g, 1.13 mmol) and K_3PO_4 (0.89 g, 4.20 mmol). The tube was evacuated and backfilled with nitrogen and then the pinacol ester of 2-hydroxyphenylboronic acid **4** (0.50 g, 2.27 mmol) in degassed DMF (6.2 mL) was added. The mixture was stirred at 120 °C for 48 h under nitrogen. The reaction mixture was allowed to cool to room temperature and then was concentrated under reduced pressure. The mixture was extracted with $CHCl_3$ (3×20 mL) and the combined organic layers were washed with HCl (1 M; 20 mL), water (20 mL), brine (20 mL), dried over $MgSO_4$ and evaporated. The crude product was purified by column chromatography (3:1 to 2:1 hexane: EtOAc) to give **6** as a white crystal (0.18 g, 42%); m.p. 157-159 °C; R_f 0.33 (2:1 hexane: EtOAc); ν_{max} (KBr)/cm^{-1} 3427, 2976, 2927, 2854, 1638, 1482, 1443, 1382, 1351, 1287, 1226 and 1095; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.36 (2H, s), 7.27 (2H, dd, *J*=7.5 and 7.5), 7.14 (2H, m), 7.01 (4H, dd, *J*=7.5 and 7.5), 6.66 (2H, br signal, 2×O*H*), 4.28 (4H, s), 3.47 (4H, q, *J*=6.5) and 1.17 (6H, t, *J*=6.5); m/z (FAB) 378 (M^+, 20%), 149 (85%) and 57 (100%).

Silylation of 6 to afford 7: To a stirred solution of compound **6** (0.17 g, 0.46 mmol) in dry DMF (5 mL) was added *tert*-butyldimethylsilyl chloride (0.15 g,

1.01 mmol) at room temperature under nitrogen, followed by the addition of imidazole (94.4 mg, 1.38 mmlo) and 4-di(methylamino)pyridine (2 mg, cat.). The mixture was stirred for 12 hour, and was extracted with EtOAc (3×20 mL), washed with brine (20 mL), dried over $MgSO_4$ and evaporated. The crude product was purified by column chromatography (20:1 hexane:EtOAc) to give the product **7** as a white solid (0.223 g, 79%); m.p. 114-116 °C; R_f 0.45 (10:1 hexane: EtOAc); ν_{max} (KBr)/cm^{-1} 3070, 3028, 2957, 2927, 2890, 2857, 1601, 1574, 1482, 1443 and 1092; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.34 (2H, s), 7.25 (2H, dd, *J*=7.5 and 7.5), 7.16 (2H, d, *J*=7.5), 7.02 (2H, dd, *J*=7.5 and 7.5), 6.90 (2H, d, *J*=7.5), 4.40 (4H, ABq, *J*=13.6, 2×ArCH_2), 3.30 (4H, q, *J*=7.0), 1.07 (6H, t, *J*=7.0), 0.75 (18H, br s) and 0.08 (12H, s); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 153.1, 137.3, 136.2, 133.1, 131.4, 129.2, 128.6, 121.4, 119.7, 70.1, 65.4, 25.6, 18.1, 15.4 and -4.0; m/z (FAB) 606 (M^-, 5%) and 73 (100%).

Iodo benzyl sensory molecule (3): To a stirred solution of compound **7** (0.18 g, 0.29 mmol) in dry $CHCl_3$ (3 mL) was added 0.5 M trimethylsilyl chloride in $CHCl_3$ (1.18 mL, 0.59 mmol) at room temperature under nitrogen. The mixture was stirred for 1 hour followed by the addition of methanol (5 mL) and water (5 mL), and was extracted with EtOAc (3×15 mL), washed with NaOH solution (1M; 15 mL), brine (15 mL), dried over $MgSO_4$ and evaporated. The crude product was purified by column chromatography (20:1 hexane: EtOAc) to give the product **3** as a white solid (0.184 g, 80%); m.p. 166-168 °C; R_f 0.55 (10:1 hexane: EtOAc); ν_{max} (KBr)/cm^{-1} 3064, 3025, 2951, 2924, 2957, 1601, 1574, 1482, 1443, 1263, 1226 and 912; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.32 (2H, dd, *J*=7.5 and 7.5), 7.19 (4H, br d, *J*=7.5), 7.08 (2H, dd, *J*=7.5 and 7.5), 6.92 (2H, d, *J*=7.5), 4.36 (4H, ABq, *J*=9.4, 2×ArCH_2), 0.75 (18H, br s, 2×SiC(CH_3)$_3$) and 0.13 (12H, s, 2×Si(CH_3)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 152.7, 138.8, 137.4, 132.6, 131.8, 131.0, 129.4, 121.8, 119.9, 25.7, 18.2, 4.9 and -3.7; m/z (FAB) 770 (M^-, 5%), 643 [(M-I)$^-$, 35%], 516 (M-I$_2$)$^-$, 35% and 73 (100%); [Found: (M-I)$^-$ 643.1925. $C_{32}H_{44}IO_2Si_2$ requires *M*, 634.1925.

Cyclization of the indicator 3 to give 3a: Tetrabutylammoniun fluoride (1 M in THF; 0.17 mL, 0.17 mmol) was added to a stirred solution of the silyoxy indicator **3** (60 mg, 0.078 mmol) in THF (1 mL) at room temperature under nitrogen. The mixture was allowed to stir for 5 min at this temperature. The reaction mixtures was concentrated *in vacuo* and the residue was passed through a short plug of silica to give the **3a** as a white solid (22 mg, 100%); m.p. 187-190 °C; R_f 0.38 (10:1 hexane:EtOAc); ν_{max} (KBr)/cm^{-1} 2957, 2923, 2853, 1731, 1603, 1490, 1451, 1234 and 1039; ^{1}H NMR (300 MHz, DMSO-d_6, δ) 7.88 (2H, d, *J*=7.5), 7.78 (2H, s), 7.30 (2H, dd, *J*=8.0 and 7.5), 7.11 (2H, dd, *J*=.8.0 and 7.5), 7.00 (2H, d, *J*=7.5) and 5.20 (4H, s); ^{13}C NMR (75 MHz, DMSO-d_6, δ) 154.3, 131.5, 129.7, 128.9, 123.5, 122.3, 122.1, 118.6, 117.1 and 67.5; m/z (FAB) 286 (M^-, 20%), 285 [(M-1)$^-$, 20%], 186 (75%) and 149 (100%); [Found: M^- 286.0994. $C_{20}H_{14}O_2$ requires *M*, 286.0994].

CONCLUSION

We have introduced novel fluoride sensory systems and showed the possibility to amplify the response using the receptor-semiconductor conjugate. To our knowledge, this is the first example to use the fluoride-induced chemical cyclization reactions as fluoride-sensing systems. In addition, while most fluoride sensors known rely on changes in emission intensity, our sensory systems belong to few indicators which utilize new fluorescence signal.

As our strategies are based on the specific affinity of fluoride to silicon, they are highly selective for fluoride ion. Indeed, all the indicators developed were stable to an excess of chloride or iodide ion.

Other advantages of our sensory systems include the possibility to tune their colors by synthetic manipulation. We intend to prepare more elaborate systems to explore this possibility and also apply our approaches to other analytes of interest.

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11. Other applications of the fluoride-induced planarization of the aromatic unit include organic transistors where the effective conjugation of π–orbitals are crucial, and this will be addressed in a full paper.
12. It was necessary to silylate the phenol in **6** after it was obtained, as the Pd-catalyzed cross coupling reaction of **5** with the silylated form of **4** gave the desired product **7** in a very low yield (<5%), probably due to the steric hindrance of the silyl group. Alteration of the silyl group to the less hindered TESCl gave the same result.
13. The sterically favored ethoxy group was selectively silylated by TMSI, which was then displaced by iodide. Jung, M. E.; Lyster, M. A. *J. Org. Chem.* **1977**, *42*, 3761.
14. Synthesis of the sensory molecules (**1**, **2** and **8**) was reported. See reference 8.
15. Kinetic studies for the polymer **8** were not possible in the same way as for the small molecule **2** (or **3**), as the fluorescence quantum yield of the polymer varies as a function of conversion and at low conversion we observe less efficient emission.
16. The signal amplification by the 'molecular wire approach' was not attempted for the fluoride-induced aromatic planarization scheme (*Scheme* 3) due to the difficulties in the synthesis of the corresponding sensory polymer.