



Highly efficient and selective probes based on polycyclic aromatic hydrocarbons with trimethylsilylethynyl groups for fluoride anion detection



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ABSTRACT

Two polycyclic aromatic hydrocarbons bearing trimethylsilylethynyl groups were designed and synthesized as new colorimetric and ratiometric fluorescent probes for fluoride anion. Both probes exhibit high specific selectivity and sensitivity for F^- compared to other anions. When F^- is added to the solution of the probe, the trimethylsilyl substituents can be removed immediately, and the color of the solution changes from yellow to colorless under ambient light. Moreover, test papers based on the probes are prepared, which could be applied to detect F^- in organic phase.

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1. Introduction

The development of chemosensors to recognize and sense biologically and environmentally important anions has attracted considerable attention in recent years due to their importance in chemistry and biotechnology.^{1,2} Among these anions, fluoride, having the smallest ionic radius and highest charge density, has arisen as an intriguing target because fluoride plays an essential role in a broad range of biological, medical, and technological processes.³ As is well known, fluoride has been used in preventing dental caries, and treatment of osteoporosis.⁴ Nevertheless, excess F^- released from a variety of sources can lead to human pathologies, such as osteoporosis, fluorosis and other diseases.^{5–7} Therefore, research on sensitive and selective probes for F^- detection becomes more and more crucial.

Although considerable progress has been made in sensing of F^- by using various chemosensors based on hydrogen bonding^{8,9} or Lewis acid coordination.^{10,11} The chemodosimeter method,^{12,13} which utilizes target anions to induce specific chemical reactions, received much less attention comparatively. This approach often displays high selectivity when proper fluorophores and reactive groups are introduced into the probes.¹⁴ To date, several

fluorophore-based probes attached trimethylsilylethynyl groups has been developed to detect F^- , such as boron-dipyromethene (BODIPY) derivatives,^{15,16} naphthalene diimide derivatives,¹⁷ and pyrene derivatives.¹⁸ The research results all prove that the fluoride-triggered cleavage of C–Si is a very promising method for F^- detection.

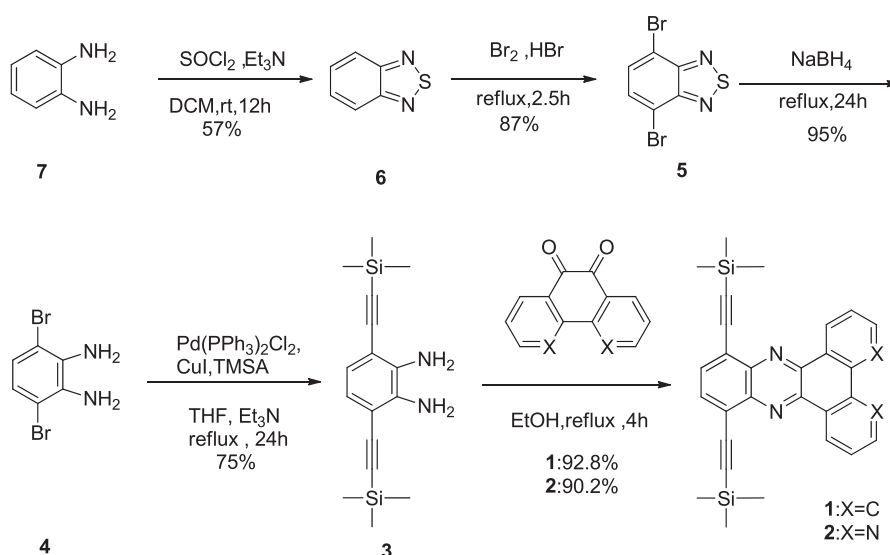
In the past few decades, great attention has been devoted into large polycyclic aromatic hydrocarbons (PAHs), because they have been widely employed as active layers inorganic electronics and optoelectronics.^{19–21} However, the chemosensors based on PAHs as core structure are very limited, particularly in detecting F^- . Only in 2013, Zhang group²² reported two novel larger azaacenes, which act as an efficient anion probe for the naked-eye detection of F^- and $H_2PO_4^-$ through anion- π interactions. To the best of our knowledge, no PAHs based probes have been used for the F^- detection via the fluoride-triggered cleavage of C–Si. We envision that new probes containing PAHs core and trimethylsilylethynyl groups can recognize F^- efficiently and selectively. In this work, we report the design, synthesis and characterization of two novel PAHs based probes, which exhibits high sensitivity, rapid response and naked-eye recognition for F^- . The detection limits for two probes towards F^- are 48 nM and 50 nM in THF, respectively, which are lower than the F^- probes reported previously.^{10,11,16,23–34}

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2. Results and discussion

2.1. Synthesis

4,7-Dibromobenzo[*c*][1,2,5]-thiadiazole, 3,6-dibromobenzene-1,2-diamine, and 3,6-ditrimethyl-silylethynylbenzene-1,2-diamine were prepared from the starting material benzene-1,2-diamine according to the literature procedure.³⁵ Two synthetic routes were designed and employed to obtain the target compounds. First, PAHs were prepared through the cyclization of compound **4** with different ketones, and then reacted with trimethylsilylacetylene to afford the compound **1** and **2**. However, the target compounds were obtained in low yields due to the poor solubility of PAHs (33% for **1** and 21% for **2**). Secondly, as shown in Scheme 1, compound **3** was prepared by compound **4** and trimethylsilylacetylene via Sonogashira reaction (55% yield). Then probes **1** and **2** were synthesized by the cyclization of compound **3** and corresponding ketones in relative high yields (92.8% for **1** and 90.2% for **2**).³⁶ It is also noted that compound **3** was unstable in air and need to be used immediately for the next step synthesis. The synthesized target compounds were characterized by FTIR, ¹H NMR, ¹³C NMR, MS and elemental analyses.



Scheme 1. Synthesis of probes **1** and **2**.

2.2. Selectivity studies

The selectivity of probes **1** and **2** towards F⁻ was firstly evaluated by using tetrabutylammonium fluoride (TBAF) as fluoride source. Various anions including F⁻, Cl⁻, Br⁻, I⁻, OAc⁻, H₂PO₄⁻, HSO₄⁻ and ClO₄⁻ were investigated by UV–vis absorption and fluorescence spectra.^{37,38} As shown in Fig. 1, notable changes in the absorption and fluorescence spectra upon the addition of 5 equiv F⁻ were observed. When F⁻ was added to the solution of **1**, the absorption peak blue-shifted, leading to a color changing from yellow to colorless and could be easily recognized by the naked-eye. Meanwhile, the intensity of original emission at 447 nm decreased and a new emission centered at 427 nm appeared, which resulted in a significant color changing from cyan to blue under the 365 nm UV-lamp (Fig. 1(c)). In comparison, minor changes were observed in both absorption and fluorescence when other anions were introduced into the solutions of probes. Again, the

highly selective sensing ability of probe **1** for F⁻ could be demonstrated in the presence of Cl⁻, Br⁻, I⁻, OAc⁻, H₂PO₄⁻, HSO₄⁻ and ClO₄⁻ (Fig. 1(d)). Namely, the fluorescent response of probe **1** to F⁻ could be hardly interfered by other anions. Most results of probe **2** for recognizing F⁻ are similar with probe **1** except the absorption peak ($\lambda_{\text{abs}}=408$ nm), which exhibits 15 nm blue-shift compared to that of probe **1** (ESD, Fig. S9).

2.3. Response time

To evaluate response time of probe **1** (1×10^{-5} M) towards F⁻ (5 equiv) by fluorescence method,³³ fluorescence spectra were recorded in THF at 0–60 s after F⁻ was introduced to the probes. As shown in Fig. 2 a saturation of fluorescence intensity appeared after 10 s for probe **1**, which is consistent with the response time of the probes containing the C≡C–SiMe₃ groups.^{15–18} The interaction between probe **2** and F⁻ was also completed within 10 s (ESD, Fig. S10). Moreover, the response time of the probes attached C≡C–SiMe₃ substituent is much shorter than those probes with Si–O bonds, which usually exhibits response times in the minutes range.^{10,11,16,23–34}

2.4. Titration experiment

The results of the absorption and fluorescence titrations of probe **1** with F⁻ are shown in Fig. 3.³⁹ When the concentration of F⁻ increases, the original bands of absorption and fluorescence display obvious blue-shift. In absorption titration spectra of probe **1** (Fig. 3a), the absorption peaks at 393 and 374 nm gradually decreased and blue-shifted to 386 and 367 nm. The two well-defined isosbestic points appeared at 389 and 370 nm, indicating the formation of alkyne compound upon treatment of probe **1** with F⁻.^{15–18} The results of the fluorescence titrations of probe **1** with F⁻ are shown in Fig. 3b. With the concentration of F⁻ boosting, the original fluorescent peak at 448 nm decreased gradually while a new fluorescent band centered at 427 nm appeared. The results obtained were in good agreement with those of UV–vis absorption spectroscopy. In addition, the near-linear correlation curves of probe **1** at 448 and 427 nm (vs F⁻ concentration in THF)

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