



Bis-pyrene carbocations for chromogenic and fluorogenic dual-detection of fluoride anion in situ

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ABSTRACT

We have designed and synthesized a new carbocation precursor (carbinol) based on bis-pyrene derivative. The carbinol can be transformed to stable carbocations with quenched fluorescence and long wavelength absorption. The stable carbocations can be further used as fluoride anion detection in acidic environment, which show both chromogenic and fluorogenic responses in the presence of fluoride anion. UV–vis and fluorescence spectroscopy were utilized to monitor the changes during detection process. The responsive mechanism was studied by quantum chemical calculations and the results indicate that the carbocation mediated formation of C–F covalent bond leads to this dual responsive phenomenon. The bis-pyrene carbocations and corresponding F adduct was confirmed MALDI-TOF mass spectrum. The successful elucidation of this new mechanism opens a new avenue for carbocation-based sensor or biological labeling in the future.

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1. Introduction

Fluoride anion (F^-) detection has attracted growing attentions because of its pivotal importance in the fields of environmental science and food industry.¹ Appropriate amount of fluoride is often added to drinking water and toothpaste for its beneficial effects in dental and skeletal health.² However, chronic exposure to high levels of the fluoride leads to organ disorders, dental or even skeletal fluorosis.³ To solve this problem, various receptor molecules responded to F^- have been reported.^{2e,g,4–6} Different from other anions, fluoride anion shows small anionic diameter and strong electronegativity, and it still remains challenge for design and synthesis of the selective receptor for F^- .¹

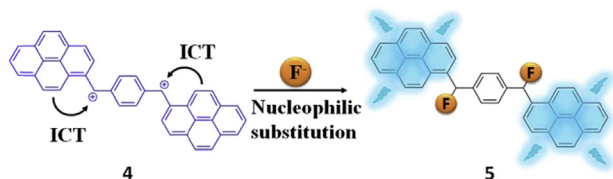
Over the past decades, extensive efforts have been devoted to develop new methods for selective detection of fluoride anions.^{2e,g,4–6} Accordingly, various optically responsive molecules for fluoride have been explored mainly based on three molecular mechanisms, i.e., (i) hydrogen bonding formation between fluoride and NH hydrogen (amide, pyrrole, indole, urea, and thiourea).^{2e,4} An optical-responsive chromophore covalently conjugate to a skeleton containing H-bond donor sites, and the resulting receptor can selectively bind with fluoride to give $H \cdots F^-$ type complex; (ii) fluoroborate complexation mechanism. For example, due

to the intrinsic Lewis acidity, boron-centered receptors couple with fluorides to afford fluoroborate complex via donation of an electron pair of the fluoride anion into the p_z -orbital of the boron center;^{2g,5} and (iii) fluoride mediated desilylation, i.e., Swager et al. developed a fluoride-triggered Si–O bond cleavage reaction for highly sensitive detection fluoride by fluorescence spectroscopy.⁶

Carbocations have been intensively investigated owing to its unique reaction selectivity and optically responsive properties.⁷ Carbocations are able to synthesize and stabilize in the presence of acid. Many organic synthesis,⁸ biosynthesis,⁹ and pathogenic mechanism¹⁰ involve carbocations as an intermediate of nucleophilic substitution reactions, such as *N*-heterocycles pharmaceuticals, terpenes, and DNA alkylation according to reports. Recently, carbocation has been utilized as a reaction-based probes and/or labelers,¹¹ in which the obviously colorimetric response of carbocation was observed by coupling the labeler with active amine or thiol residues of proteins.

Herein, we reported a new strategy for fluoride anion detection in acidic environment based on bis-pyrene carbocations, which exhibit both chromogenic and fluorogenic responses in the presence of fluoride. As depicted in Scheme 1, the solution of bis-pyrene carbocations **4** shows negligible fluorescence intensity due to intramolecular charge transfer (ICT).^{7b,12} Upon the bis-pyrene carbocations are substituted by fluoride anion in acid environment, the color of the solution change from blue to transparent with remarkably enhanced fluorescence emission.

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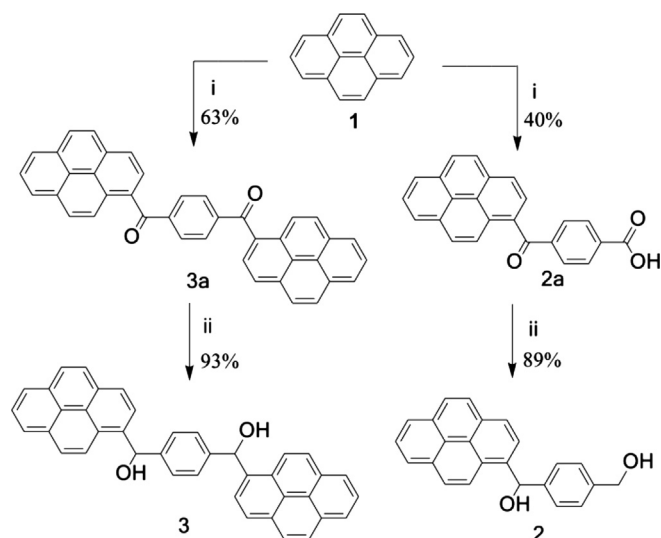


Scheme 1. A plausible mechanism of the detection of F^- by using stable bis-pyrene carbocations. The bis-pyrene carbocations **4** with quenched fluorescence due to intramolecular charge transfer (ICT) recovers its fluorescence upon coupling with fluoride through nucleophilic substitution.

2. Result and discussion

2.1. Synthesis of compounds **2** and **3**

In this proof-of-concept study, a relatively stable carbocation with optical activity is required to monitor the reaction process by spectroscopy. Pyrene was chosen as fluorogenic group and delocalized π system to stabilize the carbocation (Scheme 2). The carbocation precursor **3** was synthesized from pyrene by Friedel–Crafts acylation and followed reduction. For the purpose of comparison, the mono-substituted pyrene **2** as a reference compound was prepared in a similar synthetic method. The full synthetic details were shown in Experimental part (Figs. S1–S12).



Scheme 2. Synthetic route of compounds **2** and **3**. Compound **2** is a mono-pyrene reference molecule. i, terephthaloyl chloride (1 equiv for **3a**, 0.5 equiv for **2a**), $AlCl_3$, CH_2Cl_2 ; ii, $NaBH_4$, ethanol.

2.2. Preparation and stability of carbocation **4**

To obtain the carbocation **4**, compound **3** in chloroform was added with trifluoroacetic acid (TFA). This process could be monitored by UV–vis spectroscopy. Upon addition of TFA (from 100 to 600 μL , 6.5 M) into a solution of chloroform (2 mL) containing **3** ($c=5 \times 10^{-5}$ M), the absorption maxima of **3** at 330 and 347 nm decreased and two new peaks appeared at 440 and 645 nm, respectively. Accordingly, the color of the solution changed from colorless to deep blue as shown in Fig. 1(a). These results indicated the formation of bis-pyrene carbocations **4**.¹³ Meanwhile, the formation of **4** was monitored by fluorescence spectroscopy. With addition of TFA from 2 to 200 μL (6.5 M) into a solution of chloroform (1 mL) containing **3** ($c=2 \times 10^{-6}$ M), the fluorescence intensity of **3** with emission peaks at 378, 398, and 423 nm was quenched and a new peak formed at about 445 nm (Fig. 1(b)). The quenched fluorescence upon formation of bis-pyrene carbocations **4** was

directly visualized under the UV excitation ($\lambda_{ex}=365$ nm) (Fig. 1(b), inset). The corresponding NMR spectra are not available due to the low solubility of carbocations **4** in all tested solvents ($CHCl_3$ +TFA, DMSO+TFA, and etc.).

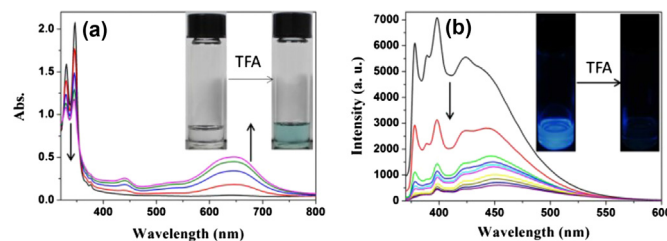


Fig. 1. Changes in UV–vis absorption (a) and fluorescence (b) of **3** upon gradual addition of TFA in chloroform. Inset: (a) photographs of **3** with visible color changes and (b) fluorescence changes (UV illumination) in chloroform.

To utilize the carbocations for fluoride detection, the carbocations should keep stable during employed. The large π -conjugated pyrene unit could effectively stabilize the carbocations.¹⁴ Hence, the bis-pyrene carbocation **4** are stable and the carbocations disappeared in 15 h, which was characterized by the UV–vis spectroscopy through monitoring the characteristic absorption change of **4** at 645 nm. As shown in Fig. 2(b), the interval of each line was 150 min for **3**. The next titration process with anions usually takes 5 min. Hence, we assure that the carbocations of **3** were stable during next titration process. However, the carbocation of a reference compound **2** can only stabilize less than 2 h under the same condition (Fig. 2(a)), which was not stable enough for next titration. The results identified that the bis-pyrene carbocations **4** with two pyrene units could be more benefit for delocalization and stabilization of the positive charges of carbocations than one pyrene unit¹⁴ (Fig. 2 and S13). The stable carbocations **4** were obtained by us for further experiments.

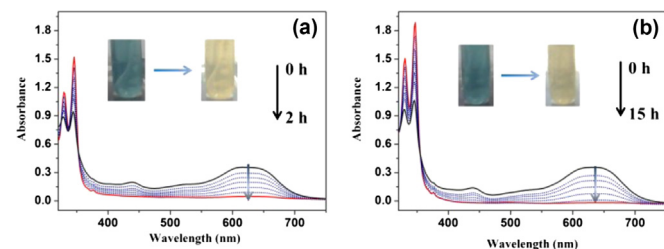


Fig. 2. Stability of compound **2** (a) and **3** (b) carbocations under ambient condition, indicating that the bis-pyrene can stabilize the carbocations.

2.3. Chromogenic and fluorogenic responses of carbocation **4**

The fluorescence responses of **4** toward a series of anions (F^- , Cl^- , Br^- , I^- , CO_3^{2-} , $H_2PO_4^-$, OAc^- , SO_4^{2-} , and CN^- from their tetrabutyl ammonium salts) were tested. Upon addition of variable anions (10^{-5} M) into a $CHCl_3$ solution containing **4** ($c=3.3 \times 10^{-5}$ M), the peaks at 440 and 645 nm of **4** became weak or disappeared and some new peaks at 360 and 420 nm formed (Fig. S14), indicating the formation of **4** and anion complexes.¹⁵ Furthermore, fluorescent titration experiments of **4** ($c=3.3 \times 10^{-5}$ M) with halide anions (from 0 to 10^{-4} M) in $CHCl_3$ were performed to observe the fluorescence intensity change. Upon addition of F^- into a solution of **4**, the fluorescence intensity of the **4**- F^- adduct was remarkably enhanced as the concentration of F^- was increased. The fluorescence emission maxima of the resulted **4**- F^- adduct formed at 380, 412, and

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