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A new optical and electrochemical sensor for fluoride ion based on the functionalized boron–dipyrromethene dye with tetrathiafulvalene moiety

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ABSTRACT

A new tetrathiafulvalene (TTF) derivative with the boron–dipyrromethene (BODIPY) moiety shows selectively optical and electrochemical sensing for fluoride ion. The mechanism of anion recognition has been investigated by ^{1}H NMR titration and DFT calculations. The results show that the receptor with redox active TTF moiety and fluorescent BODIPY subunits may be useful as sensors for detecting and sensing fluoride ion.

Considerable attention has been focused on the recognition and sensing of anions, since anions play important roles in biological, industrial, and environmental processes.[1] In particular, the sensing of a fluoride anion has attracted growing attention because of its unique properties for biological and industrial applications.[2] However, systems that permit fluoride anion detection via dual means (such as optical and electrochemical) are rare.[3]

By either chemical or electrochemical oxidation, tetrathiafulvalene (TTF) moiety can be reversibly transformed to the corresponding cationic radical (TTF^+) and dication (TTF^{2+}). Based on the unique properties, a number of TTF derivatives have been employed in the development of electrochemical switches and sensors.[4] On the other hand, boron–dipyrromethene (BODIPY) is a very attractive functional group due to its excellent photochemical and photophysical properties, such as narrow and intense absorption and fluorescence bands, high fluorescence quantum yields and good solubility in most organic solvents,[5] which has been developed as fluorescent probes.[6] To develop a new molecular sensor featuring both photophysical property of BODIPY and electrochemical property of TTF, in this Letter, the title compound **1** is prepared by the reaction of **2** with **3** (Scheme 1).

The structure of compound **1** was determined by single-crystal X-ray diffraction.[7] Data collection parameters, selected bond lengths and angles are listed in SI. TTF moiety and amido group are nearly planar, forming a dihedral angle of 22° with the phenyl ring. Two pyrrole rings and the central six-member ring containing boron atom are essentially planar. The dihedral angle between para-phenyl ring and the BODIPY moiety is 53°, less than the related values in similar compounds.[8] The intermolecular hydrogen bond is observed between N3 and O1 from the neighboring molecule (2.235 Å, Fig. 1), and there are no π–π stacking interactions (Fig. S2).

The absorption spectra of compound **1** at different amount of F^- are shown in Figure 2. The narrow and intense absorption at 502 nm is characteristic of BODIPY framework in general.[5a,9]

Addition of a stoichiometric mole ratio of F^- causes a dramatic change in color from orange to amaranth, which is accompanied by the formation of a new broad absorption band centered at about 580 nm as well as decrease of BODIPY-characteristic peak. Meanwhile, no significant color change is observed after the addition of other anions such as $H_2PO_4^-$, BF_4^-, CH_3COO^-, ClO_4^-, HSO_4^-, NO_3^-, Cl^-, Br^-, and I^- (all as tetra-*n*-butylammonium salts, TBA salts) (Fig. 2), showing naked-eye detection of fluoride ion.[10] With a proposed 1:1 host-guest binding stoichiometry, association constants (K_a) of receptor **1** with various anions were also determined via standard UV-vis titrations (Fig. S4, Table S2). As expected, the new TTF-functionalized system **1** was found to display good selectivity and affinity for F^- ($K_a = 1.2 \times 10^3$, $K_a(F^-)/K_a(H_2PO_4^-) = 9.5$). It is noteworthy that this TTF-based system displays anion selectivity under water-containing conditions, which has been rarely reported so far as we know.

Furthermore, on excitation at 450 nm, compound **1** shows fluorescence with a wavelength maximum at 527 nm and the luminescence quantum efficiency is 6.7×10^{-3}. The significant decrease in fluorescence intensity is observed with the increasing amount of

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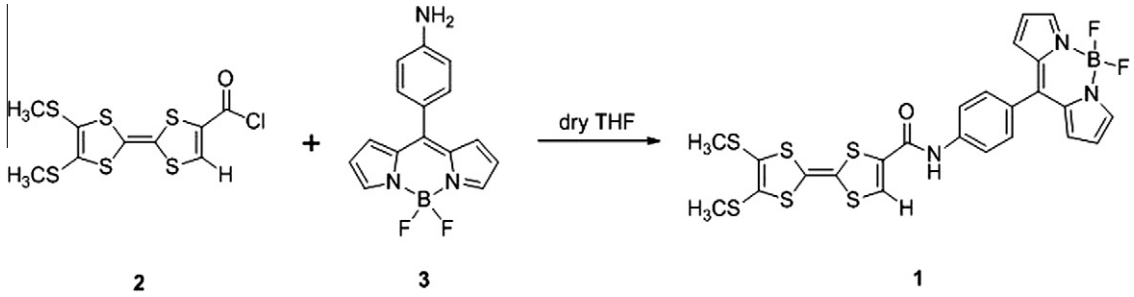

Scheme 1. Synthetic route to compound **1**.

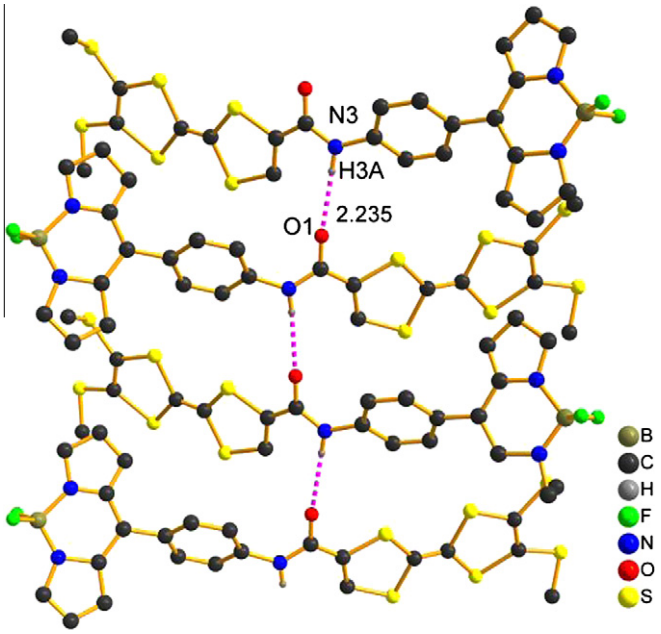

Figure 1. Hydrogen bonds in the crystal structure of **1** (the dotted lines represent hydrogen bonds and hydrogen atoms with no hydrogen bonds are omitted for clarity).

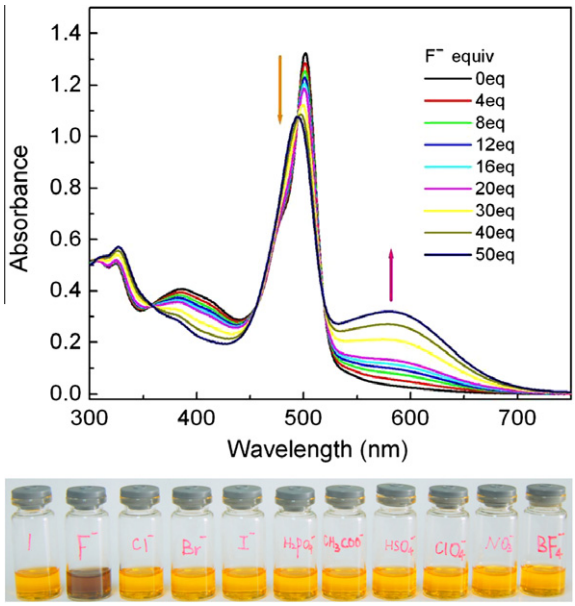

Figure 2. Top: UV-vis absorption spectra of compound **1** (2.5×10^{-5} M) in the presence of F^-, measured in DMSO: H_2O = 95:5; Bottom: Color changes observed for **1** upon addition of 50 equiv of anions as TBA salt.

fluoride anion, indicating the quenching effect from F^- (Fig. 3a). In the same conditions, very weak quenching is found only in the presence of CH_3COO^- and $H_2PO_4^-$, while no obvious decrease in intensity is observed with the addition of 50 equiv of other anions (Fig. 3b). As a result, compound **1** exhibits highly selective fluorescent response for F^- ion over other anions.

Oxidation–reduction processes were determined by cyclic voltammetry (CV) in CH_2Cl_2. As shown in Figure 4, compound **1** exhibits two reversible single-electron redox couples at 0.402 and 0.787 V, corresponding to the successive reversible oxidation of neutral TTF (TTF^0) to the radical cation (TTF^+) and then to the dication (TTF^{2+}). Shifts of $E^1_{1/2}$ and $E^2_{1/2}$ were observed upon addition of fluoride ion (Fig. 4). Specifically, the addition of fluoride ion yielded an additional redox couple at 0.858 V and a cathodic shift of 17 mV of the first redox wave value. When 4 equiv of F^- was added, the original second redox couple disappeared, experiencing an anodic shift of 71 mV. Similar shifts were reported by adding dihydrogen phosphate to TTF based system.[11] In general, when anions are added to TTF-based redox-responsive receptors, cathodic shifts for redox potentials can be observed. The reason is that the bound anion serves to stabilize the positively charged TTF moiety produced upon oxidation.[12] Other anions were also added to detect oxidation-reduction processes (Fig. S5). However, no new peaks appeared and only slight shifts of the first redox couple were observed.

In order to investigate the anion binding interactions between **1** and fluoride ion, titration ^1H NMR experiments in DMSO-d_6 were performed (Fig. 5). It is noteworthy that not only –N*H* ($\Delta\delta$ = 1.05 ppm at 4.0 equiv) but also –C≡C–*H* of the TTF unit ($\Delta\delta$ = 0.14 ppm at 4.0 equiv) are downfield shifted with the addition of fluoride ion. The results suggest that there are significant hydrogen bonding interactions between fluoride ion and the N*H* or/and TTF moiety. Furthermore, the considerably larger shift of –N*H* indicates its stronger hydrogen bonding interaction with fluoride ion. The overall effect from fluoride ion can stabilize radical cation (TTF^+) and makes **1** easier to be oxidized, which is in agreement with the decreasing of the first redox potential of **1**.

Theoretical calculations of **1** and model compound **1**+F^- were carried out by density functional theory (DFT). It is noteworthy to mention that fluoride ion is surrounded by three hydrogen atoms (hydrogen atoms on amido unit, TTF and phenyl ring) after its interaction with **1** (Fig. 6). As shown in Table S4, for N–H···F hydrogen bond, the bond length of N–H considerably increases due to strong attraction between hydrogen atom and fluoride ion. The bond length of H···F and bond angle of N–H···F are characteristic of strong hydrogen bond. On the other hand, optimized geometry of **1**+F^- also indicates that there is weak hydrogen bonding interaction between TTF (–C≡C–*H*) and fluoride ion, and almost no interaction between phenyl ring and fluoride ion. Therefore, it is