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A Novel Multisignaling Optical-electrochemical Chemosensor for Anions Based on Tetrathiafulvalene

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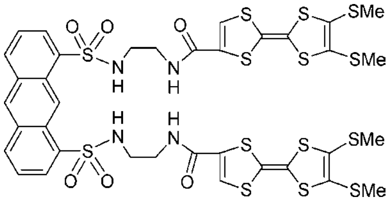
ABSTRACT



A multisignaling optical-electrochemical receptor for anions based on a triad with anthracene and TTF units was prepared. It showed a unique selectivity for fluoride ion over various anions with dramatic fluorescence enhancement in neutral condition and displayed a special recognition of $H_2PO_4^-$ in electrochemical studies with remarkable cathodic displacement of the first oxidation potential (E^1_{ox}) of the TTF unit.

In recent years, as a result of the realization of the many roles that anions play in biology, medicine, catalysis, and the environment, rather explosive progress in anion recognition chemistry has been seen.[1] Although the tetrathiafulvalene (TTF) unit has many attractive properties such as being a strong π-electron donor and an ideal redox-active unit and its oxidation to the radical cation ($TTF^{+\bullet}$) and dication (TTF^{2+}) occurring sequentially and reversibly in a desirable range, anion receptors incorporating a TTF unit are still uncommon.[2] Especially, no anion receptors incorporating a TTF unit that are capable of both optical and electrochemical sensing have been exploited so far.

It is well-known that the redox character of the TTF unit can induce quenching of the emission intensity of signaling subunits such as anthracene, naphthalene, and pyrene via a photoinduced electron transfer (PET) process.[3] Taking advantage of such a PET effect, we proposed that if a TTF unit and a photoactive unit were combined with linkages capable of anion recognition, the emission quenching degree would be modulated through the binding process. According to the Marcus theory,[4] the electron transfer rate exponentially decreases with the donor−acceptor (D/A) distance, so it can be deduced that upon anion complexation the distance between TTF units and fluorophore would be adjusted by the conformational changes. As a result, an ideal signaling output would be achieved by the designed receptor. It is known that the signal generation strategy based on binding-modulated D/A distance has successfully been employed in the development of biosensors.[5] However, it is not usually employed in the design of chemosensors.

Here, we report a new receptor (**1**) based on an anthracene disulfonamide derivative incorporating two TTF units. Through binding-modulated D/A distance, the receptor exhibits not only a high selectivity for fluoride ion over other

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[1] (a) Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419. (b) Gale, P. A. *Coord. Chem. Rev.* **2003**, *240*, 191. (c) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609. (d) Bondy, C. R.; Loeb, S. J. *Coord. Chem. Rev.* **2003**, *240*, 77.

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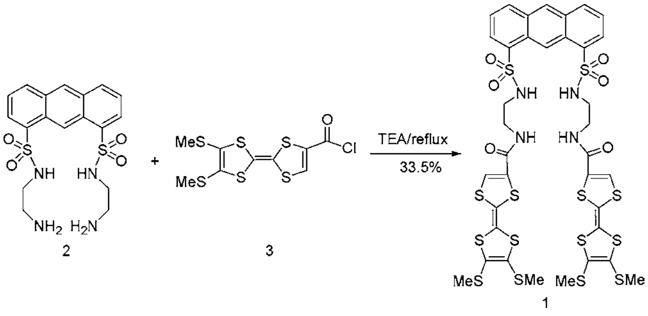
anions with dramatic fluorescence enhancement in neutral condition but also a special electrochemical recognition of $H_2PO_4^-$ with remarkable cathodic displacement of the first oxidation potential (E^{1}_{ox}) of the TTF unit.

The target compound **1** was synthesized by reaction of **2** with 2 equiv of **3**, as described in Scheme 1. Compounds **2** and **3** were prepared according to protocols.[6]

Scheme 1. Synthesis of **1**



The fluorescent behavior of free receptor **1** was studied in CH_2Cl_2 solution. Compared with its precursor **2**, the emission of its anthracene unit was completely quenched by TTF units via an intramolecular PET mechanism, which provided an ideal platform for the excellent signaling output. Excitation wavelenth, λ_{ex}, of 325 nm was chosen on the basis of the fluorescence excitation spectrum of the **1**−F⁻ complex (Supporting Information). First of all, we investigated the effects of various anions on the fluorescence emission spectrum of receptor **1**. As shown in Figure 1, a remarkable emission intensity enhancement was observed for the receptor **1** in the presence of 10 equiv of F^-. In the same conditions, weak enhancements were found only in the presence of AcO^-, Cl^-, or $H_2PO_4^-$ and no obvious changes were found in the presence of Br^-, I^-, NO_3^-, or HSO_4^-. These results suggest that receptor **1** has a high selectivity for F^- over other anions. The stoichiometry of the **1**−F⁻ complex was determined by the method of continuous variations (Job's method). The result obtained indicates the formation of a 1:2 **1**−F⁻ complex. According to fluorescence titration experiments (Figure 2), the association constant[7] between **1** and fluoride was calculated to be 1.51×10^8 M^{-2} ($R > 0.999$). Similarly, the association constants for 1:1 complexes between **1** and acetate, chloride and dihydrogen phosphate were calculated to be 2.22×10^3 M^{-1} ($R > 0.999$), 5.67×10^2 M^{-1} ($R > 0.997$), and 4.77×10^2 M^{-1} ($R > 0.999$), respectively (errors were less than ±10%).

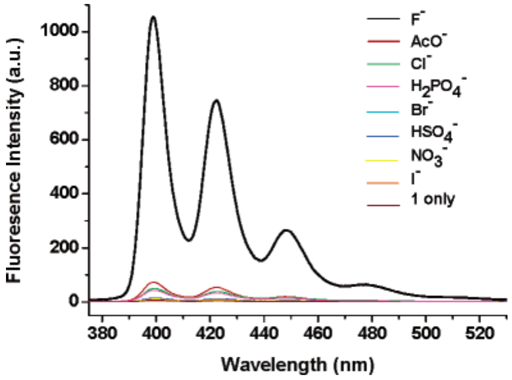


Figure 1. Fluorescent emission spectra of **1** (1.25×10^{-5} M) upon addition of 10 equiv of tetrabutylammonium anion salts in CH_2Cl_2 ($\lambda_{\mathrm{ex}} = 325$ nm).

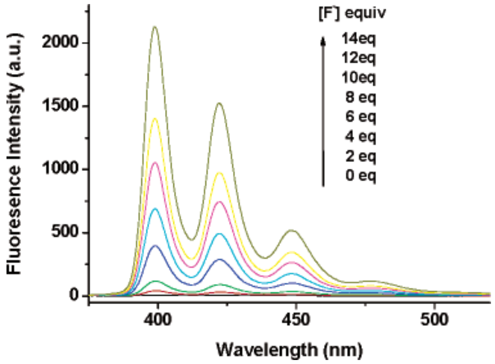


Figure 2. Changes in fluorescence emission for receptor **1** (1.25×10^{-5} M) upon addition of F^- in CH_2Cl_2 ($\lambda_{\mathrm{ex}} = 325$ nm).

The electrochemical detection of anionic species is a particular challenge. To explore further the utility of **1** as an electrochemical anion sensor, cyclic voltammetry (CV) studies were conducted in CH_2Cl_2. The progressive addition of F^- to the solution of **1** caused clear modifications in the cyclic voltammetry (Figure 3), from which a significant

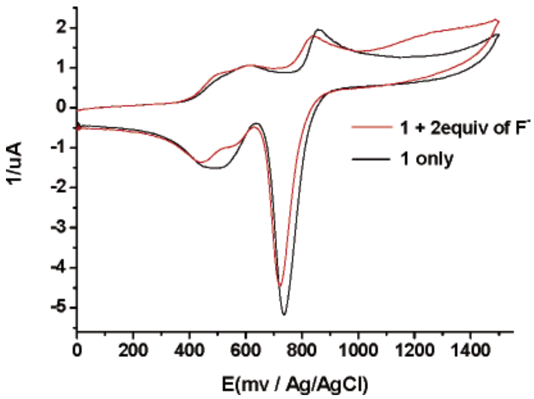


Figure 3. Cyclic voltammograms of the receptor **1** (1.25×10^{-4} M) recorded in CH_2Cl_2 at 298 K with n-Bu_4NClO_4 (0.1 M) as the supporting electrolyte in the presence of 2 equiv of n-Bu_4NF.

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splitting of the first wave was observed. In the cases of AcO^- and Cl^-, CV results were similar to that of fluoride (Supporting Information); such behavior was reminiscent of the formation of a mixed-valence complex that was first reported by Bechgaard and co-workers.[8] Indeed, a broadening or a splitting of the first oxidation wave was observed when two TTF units covalently linked with a short flexible linkage. It can be explained by a strong propensity to form MV complexes, which stabilize the monocationic species. In our case, upon binding with F^- or other small anions, the guest anion connected the two flexible arms by hydrogen bonding to bring the TTF units closer to each other, which would facilitate the formation of mixed-valance complexes.

Upon addition of $H_2PO_4^-$ and HSO_4^-, CV studies of **1** did not show a three-wave pattern. However, it was interestingly found that the increasing addition of $H_2PO_4^-$ to the solution of **1** not only resulted in a dramatic cathodic shift of the first oxidation potential of the TTF unit but also accompanied the appearance of a new redox system at +0.41 V (Figure 4). The peak current of this new wave increased gradually with increase in the amount of the $H_2PO_4^-$, while the peak current of the original wave decreased gradually and disappeared when 2 equiv of $H_2PO_4^-$ was added. It is noteworthy that the cathodic shift of the first oxidation potential is independent of the second oxidation process. This phenomenon revealed the advantage of the TTF unit over the widely studied ferrocene-based receptor in which the presence of only one redox system does not allow the expulsion of the anionic species to be controlled. Furthermore, a large magnitude of cathodic perturbations up to $\Delta E^{1}_{\mathrm{ox}} = 172$ mV was observed, which is the highest value observed so far for ligands based on TTF unit.[9]

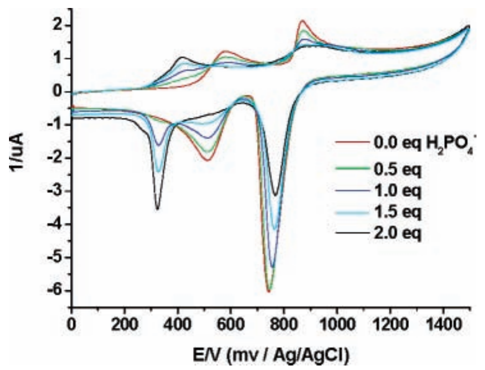

Figure 4. Cyclic voltammograms of the receptor **1** (1.25×10^{-4} M) recorded in CH_2Cl_2 at 298 K with n-Bu_4NClO_4 (0.1 M) as the supporting electrolyte in the presence of increasing amounts n-$Bu_4NH_2PO_4$.

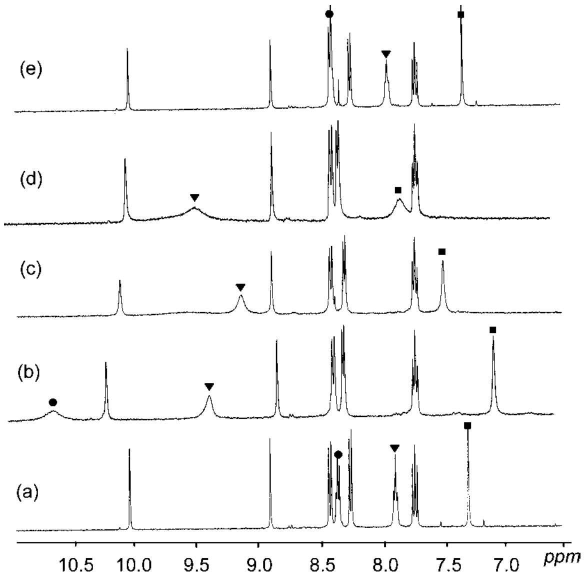

Figure 5. Partial ^1H NMR spectrum (400 MHz) of **1** (2.5×10^{-3} M) in DMSO-d_6 at 25 °C: (a) receptor **1** only; (b) **1** + 2 equiv of n-Bu_4NF; (c) **1** + 2 equiv of n-Bu_4NOAc; (d) **1** + 2 equiv of n-$Bu_4NH_2PO_4$; (e) **1** + 2 equiv of n-Bu_4NCl. (■) C═C−H of the TTF unit; (▼) NH; (●) NH

To look into the anion binding properties of receptor **1**, ^1H NMR experiments in DMSO-d_6 were performed (Figure 5). When 2 equiv of fluoride was added to the solution of **1**, its ^1H NMR spectrum displayed dramatic changes. Two amide N−H signals shifted significantly downfield ($\Delta\delta = +1.46$ and $+2.27$ ppm, respectively). Interestingly, downfield shift of the 9-H of anthracene moiety ($\Delta\delta = +0.12$ ppm) was also observed, which could be another example of hydrogen bonding between aromatic hydrogen and anion.[10] On the other hand, upfield shifts of 10-H of the anthracene moiety ($\Delta\delta = -0.12$ ppm) and C═C−H of the TTF unit ($\Delta\delta = -0.29$ ppm) were observed. These observations led us to the conclusion that two fluoride ions had more effective hydrogen bond interactions not only with the protons of the amide but also with the 9-H of anthracene. As a consequence, two-bond F^- anions rigidified the receptor, which led to the efficiency of the PET process to be reduced (Figure 5). Therefore, the remarkable enhancement of fluorescence intensity upon addition of fluoride ion was observed. It is noted that a similar result was reported by Bryce et al.[11] They demonstrated that in phthalocyanine−TTF hybrids the degree of fluorescence quenching was dependent on both the separation of the photoactive moiety and TTF units and the flexibility of the linking group. Especially, the degree of quenching was highly temperature-dependent; when the solution cooled to a transparent glass, a sharp increase in emission was shown. This suggested that the solvent solidi-

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fied the flexible arms and froze them into a configuration where quenching was not favorable. These results were consistent with the observations in our case.

In the case of the acetate, one of amide protons was induced to downfield shift smaller than those for F^-, and another one disappeared or broadened (Figure 5c). Meanwhile, a slight downfield shift of the 9-H of the anthracene moiety ($\Delta\delta = +0.08$ ppm) was observed. It was also noted that a downfield shift of C═C−H of the TTF unit ($\Delta\delta = +0.21$ ppm) was observed. Upon addition of 2 equiv of $H_2PO_4^-$, significant changes occurred (Figure 5d). Two amide protons shifted downfield, and a large downfield shift of the C═C−H of the TTF unit was observed ($\Delta\delta = +0.58$ ppm). These observations concerning the ^{1}H NMR spectra obtained with fluoride, acetate, and chloride led us to the conclusion that on complexation with $H_2PO_4^-$ the large size and tetrahedral shape of $H_2PO_4^-$ made this ion noncomplementary for the receptor's size, and the ring would be pushed apart to favor the hydrogen bonding with C═C−H of the TTF unit. As a result, the spacer became longer, the distance between the TTFs increased, and hence the effects of the MV complex become less pronounced. In addition, $C-H\cdots H_2PO_4^-$ hydrogen bonding interaction was attributed to the large magnitude of cathodic perturbations in the CV. The results can be explained by delocalization of the negative charge from the binding site $C{=}C-H\cdots H_2PO_4^-$ to the TTF core, which makes them either easier to oxidize or harder to reduce than the free redox-active receptor **1**. In the case of chloride ion, slight chemical shifts of amide protons ($\Delta\delta = +0.057$ and $+0.057$ ppm, respectively) were observed (Figure 5), which is also consistent with the results of optical and electrochemical experiments.

In summary, we have presented a highly sensitive and selective anion receptor with the dual capability of sensing anions by electrochemical and optical means. The mechanism based on binding-modulation D/A distance was responsible for the fluorescence recognition process. Meanwhile, the $C-H\cdots O$ hydrogen bonding between C═C−H of the TTF unit and $H_2PO_4^-$ played an important role in regulating the electrochemical selectivity. Consequently, we took advantage of the unique properties of the bis-TTF and fully displayed its good utility as a building block in the design of anion sensors.

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Supporting Information Available: Experimental procedure and characterization for compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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