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A Fluoride-Selective PCT Chemosensor Based on Formation of a Static Pyrene Excimer

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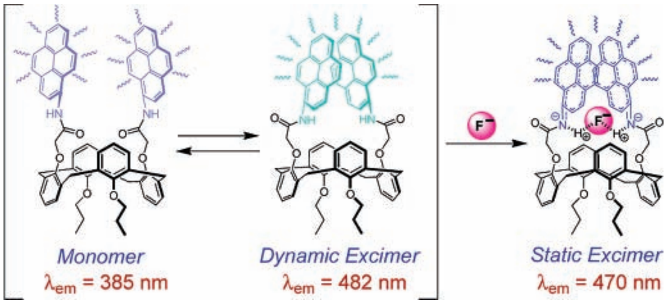
ABSTRACT



Calixarene-based fluorescent chemosensor 1 with two fluorogenic pyrene units conjugated to amide groups as guest recognition sites is synthesized. Complexation of F^- by 1 causes a red shift of its absorption band to 400 nm ($\Delta\lambda = 54$ nm) and a blue shift of the excimer emission to 470 nm ($\Delta\lambda = 12$ nm) together with enhanced fluorescence intensity. The blue-shifted excimer emission is attributed to a pyrene dimer formed in the ground state, a so-called static excimer.

Since anions are ubiquitous and play important roles in many biological and chemical systems, there is an increasing interest in the design and development of receptors that selectively recognize specific anions.[1] For instance, considerable effort has been devoted to studies of F^- receptors because of the serious effects of F^- in the human body.[2] Among anion receptors, colorimetric and/or fluorescent chemosensors are important because they provide high sensitivity and convenience for monitoring the anion recognition.[2,3]

Calix[4]arenes have been found to provide high selectivity and binding efficiency for both specific cations and anions.[4] As the signaling mechanism, most anion chemosensors developed to date utilize internal charge transfer in the ground

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state for a colorimetric chemosensor[3e,f] and photoinduced electron transfer (PET),[2d,e,3d,5] metal-to-ligand charge transfer (MLCT),[4c,6] or excimer/exciplex formation[7] for fluorescent chemosensors. Although photoinduced charge transfer (PCT) has been widely exploited for cation sensing,[8] it has been applied only rarely for anion sensing.[2b,c,4b] Here, we report a novel calix[4]arene-based PCT chemosensor (**1**) with a specific optical response to F^- and delineation of the complexation mode by comparison of the static excimer with the dynamic excimer.

The fluorescent ligand **1** was prepared by coupling 25,27-bis(chlorocarbonylmethoxy)-26,28-dipropyloxycalix[4]arene[9] with 1-aminopyrene and triethylamine in THF (Scheme S1). Compound **1** with a pyrene signaling subunit conjugated to an amide group as the recognition site can act as a PCT chemosensor. Free **1** displays a strong absorption band centered at 346 nm. Among the anions tested, F^-, Cl^-, Br^-, I^-, $CH_3CO_2^-$, HSO_4^-, and $H_2PO_4^-$ as their tetrabutylammonium salts in MeCN, only F^- interacts with **1** causing a red shift in its absorption band by 54 nm (Figure 1). The interaction of the amide hydrogen atoms with F^- promotes the delocalization of π electrons from the anionic nitrogen atoms to the pyrene moieties and a change of the $\pi-\pi^*$ transition from colorless to yellow, as shown in Figure 2.

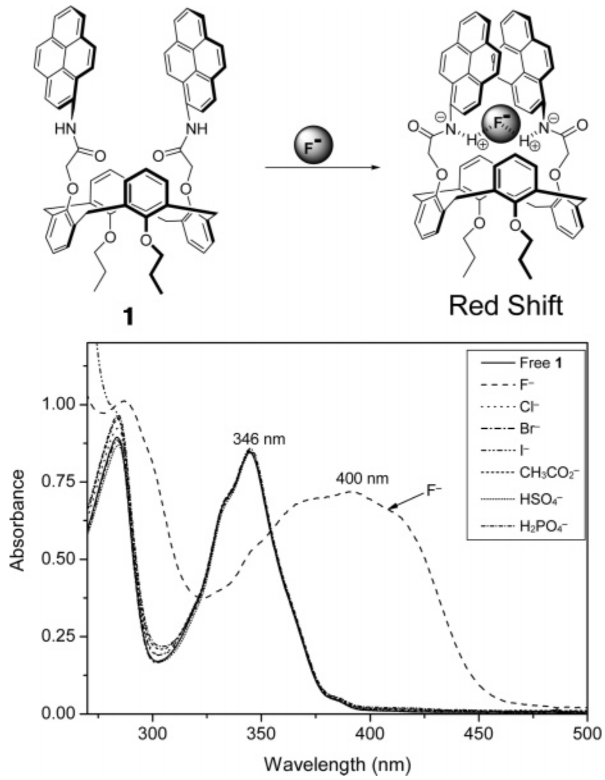

Figure 1. UV/vis spectra of **1** (0.20 mM) upon addition of tetrabutylammonium salts of F^-, Cl^-, Br^-, I^-, $CH_3CO_2^-$, HSO_4^-, and $H_2PO_4^-$ (60 mM) in MeCN.

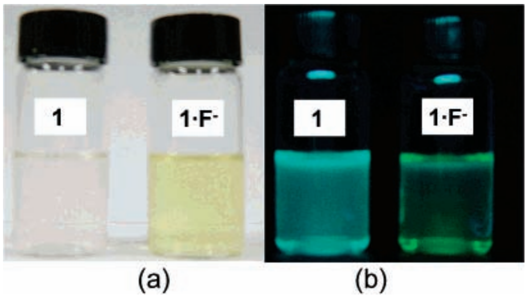

Figure 2. Visual changes for **1** in the presence of F^-: (a) color change; and (b) fluorescence change.

The absorption band at 346 nm of **1** gradually decreases with concomitant increase of a new band at 400 nm (Figure S1). From this titration experiment, the association constant (K_a) of **1** with F^- was calculated to be 2.5×10^2 M^{-1}.[10]

In the ^1H NMR spectrum (Figure S2), upon the addition of F^-, the NH peak disappeared and the aromatic proton peaks of the pyrenes changed, implicating induced charge transfer, which is also supported by the other set of ^1H NMR spectral changes for a monomeric pyreneamide (Figure S3). This phenomenon is similar to that reported by Choi and Hamilton.[3b]

With excitation at 346 nm, **1** exhibits monomer and excimer emissions at 385 and 482 nm, respectively. Addition of F^- to **1** induces a drastic change in its fluorescence spectrum, in which the monomer emission is strongly quenched and the excimer emission is blue-shifted by 12

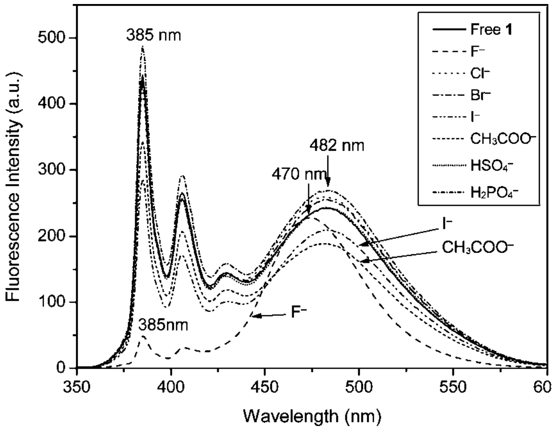

Figure 3. Fluorescence spectra of **1** (6.0 μM, excitation at 346 nm) upon addition of tetrabutylammonium salts of F^-, Cl^-, Br^-, I^-, $CH_3CO_2^-$, HSO_4^-, and $H_2PO_4^-$ (6.0 mM) in MeCN.

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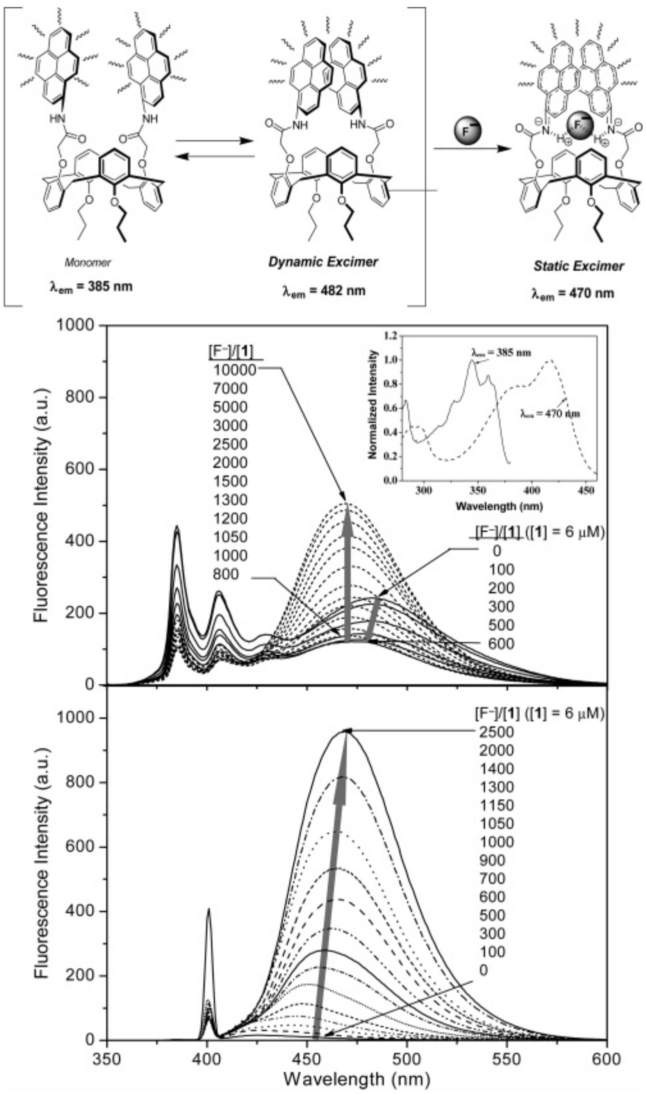

Figure 4. Fluorescence spectra of **1** (6.0 μM) upon titration with $Bu_4N^+F^-$ in MeCN. Excitation wavelengths were (a) 346 and (b) 400 nm, respectively. Inset: excitation spectra (normalized) monitored at 385 (solid line) and 470 nm (dashed line) in the presence of 1000 equiv of $Bu_4N^+F^-$.

nm (Figures 3 and 4). In contrast, other anions gave only a slight change in fluorescence intensities with no wavelength changes (Figure 3). When F^- is added up to 600 equiv, both excimer and monomer emissions of **1** are gradually quenched. This is due to photoinduced electron transfer (PET) from F^- to the pyrene units, as well as to the wavelength shift for the UV absorption band (Figures 1 and S1). On the other hand, addition of more than 600 equiv of F^- developed a new band at 470 nm with a steady decrease of the monomer emission at 385 nm. Noticeably, upon excitation of **1** at 400 nm, the peak at 470 nm is remarkably enhanced with increasing F^- concentration (Figure 4b). These observations suggest that the chemical species absorbing the energy at 400 nm are such that their pyrene pendants form a static dimer in the ground state, caused by hydrogen bonding between F^- and amide protons. This proposal can be clarified by characterizing the nature of the blue-shifted emission to 470 nm and the original emission at 482 nm.

Depending on the origin of the pyrene dimer, there are two kinds of excimers: a dynamic excimer and a static excimer.[11] The former is emitted from a pyrene dimer formed in the excited state, whereas the latter is emitted from a pyrene dimer formed in the ground state.[11] In **1**, the excitation spectrum monitored at the monomer wavelength (385 nm) is almost identical to that recorded at the excimer wavelength (482 nm), indicating that the emission at 482 nm arises from the dynamic excimer (Figure S4).[11,12] On the other hand, the excitation spectrum of **1**·F^- monitored at 470 nm is remarkably red-shifted ($\Delta\lambda = 73$ nm) in comparison with that measured at 385 nm, which establishes that the 470 nm emission comes from the static excimer (Figure 4a, inset).[11,12] Thus, the chemical species corresponding to 470 and 385 nm emissions are different.

To verify the F^- selectivity of **1**, we also conducted a competitive titration experiment. F^- was titrated into a MeCN solution of **1** containing six other anions. The results shown in Figure S5 clearly demonstrate a high F^- selectivity for compound **1**.

To obtain further insight on the static and dynamic excimer, we carried out ab initio density functional theory (DFT) calculations with B3LYP exchange functionals and a 6-31G* basis set using a suite of Gaussian 98 programs.[13] In **1**, the pyrene moieties do not have π-stacking structure in ground state; hence, no static excimer is present, as observed in our previous study.[9] However, the calculated structure of **1**·F^- clearly shows displaced π-stacking interactions between the pyrene moieties, in which the pyrene units are separated by about 5 Å, as is typical displaced π-stacking in benzene dimer. In **1**, the N−H bond length is 1.01 Å and the N···N interatomic distance is 8.09 Å. In **1**·F^-, the N−H bond length is 1.05 Å, the N···N distance is 5.30 Å; the N···F distance is 2.66 Å, and the hydrogen bonded H···F distance is 1.62 Å. It should be noted that the F^- does not completely abstract one of the amide protons. If F^- completely abstracts one of the amide protons, it will form F−H, then the arrangement will be N^-···H−F···H−N, with one

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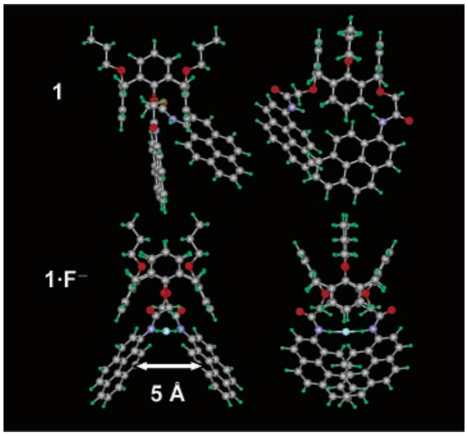

Figure 5. Front views (left column) and side views (right column) of B3LYP/6-31G* predicted structures of **1** and **1**·F⁻.

charged hydrogen bond and one normal hydrogen bond. However, in the calculated structure, there exist two charged hydrogen bonds with the arrangement of N−H···F⁻···H−N. Thus, in our system, the charged hydrogen bonding may be stronger than normal hydrogen bonding. The pyrene emits from its excimer by forming a dimer of a symmetrical sandwich-like structure, and its blue-shifted excimer emission is induced by partial overlap of the pyrene dimer.[11,12,14] Accordingly, the blue-shifted excimer emission upon addition of F⁻ to **1** is due to a formation of a partially overlapping static pyrene dimer, which is supported by the ab initio calculations. Despite the PET, in **1**·F⁻, a significant enhancement of the fluorescence intensity at 470 nm is probably due to a restriction of rotational motion of the *N*-pyrene that would otherwise lead to nonradiative decay.[3b,15] In summary, a novel calixarene-based fluorescent chemosensor **1** has been prepared. Effective strong charged hydrogen bonding gives rise to a red-shifted absorption. With excitation at 346 nm, the two facing pyrene units in free **1** form a *dynamic eximer* with emission at 482 nm and a monomer with emission at 385 nm. Complexation of F⁻ by **1** causes its absorption band to red-shift by 54 nm and excimer emission to blue-shift by 12 nm with enhanced fluorescence. The blue-shifted excimer emission is attributed to a *static excimer*.

Supporting Information Available: Preparative procedures and analytical data for compound **1** and additional ^{1}H NMR, UV−vis spectra, and additional excitation spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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