含氧化还原活性基团的荧光分子开关构建与门

房晨婕*,1　李春钰1　傅晓飞1　岳衍峰2　严纯华*,2

(1 首都医科大学化学生物学与药学院,北京　100069)

(2 北京分子科学国家实验室,北京大学稀土材料化学与应用国家重点实验室,

北京大学-香港大学稀土材料和生物无机化学联合实验室,北京　100871)

摘要:报道了一个基于光致电子转移(PET)机理的双稳态荧光分子开关,其中具有氧化还原活性的二茂铁基团作为荧光团蒽 PET 过程的氧化还原控制单元,通过双 Schiff 碱 C=N 键与蒽相连。研究了不同条件下蒽的荧光发射行为。以不同的化学试剂作为体系的输入信号,以不同的荧光发射强度作为输出信号,利用荧光分子开关的质子化反应和氧化反应实现了一个分子水平的逻辑功能。输入信号及其相应的输出结果在分子水平上符合数字逻辑与门的真值表。

关键词:二茂铁;荧光;与门;氧化还原;光致电子转移过程
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Redox-Active Fluorescent Molecular Switch to Realize AND Logic Function

FANG Chen-Jie*,1　LI Chun-Yu1　FU Xiao-Fei1　YUE Yan-Feng2　YAN Chun-Hua*,2

(1College of Chemical Biology and Pharmaceutical Sciences, Capital Medical University, Beijing 100069)

(2Beijing National Laboratory for Molecular Sciences, State Key Lab of Rare Earth Materials Chemistry and Applications &

PKU-HKU Joint Lab in Rare Earth Materials and Bioinorganic Chemistry, College of Chemistry and Molecular Engineering,

Peking University, Beijing 100871)

Abstract:Based on the photo-induced electron transfer (PET) mechanism, a redox-active fluorescent molecular bistable switch was obtained with ferrocene as a reversible redox-control of PET and fluorophore anthracene as signaling unit. The fluorophore emission behaviors were studied under different conditions. With various chemicals as input signals and emission intensity under different conditions as output signals, the protonation and oxidation were used to realize the molecular logic function. The inputs and corresponding outputs give an excellent correlation with the truth table for a digital AND logic gate at molecular level.

Key words: ferrocene; fluorescence; AND logic gate; redox-active; PET process

In the increasing interests in the miniaturization of information technology, a promising strategy is afforded by the bottom-up approach to mimic computation at the (supra) molecular level [1 ~3]. Various molecular logic gates, combinational logic functions and molecular arithmetic devices have been designed to apply to any type of signals, including chemical and optical ones[4~8]. Among all the detectable signals, fluorescence emission is one of the most widely employed owing to its high sensitivity, feasibility in detection, and low cost in operation[9]. In addition, designing fluorescent redox-(or photo-) switchable materials is essential to provide a

non-destructive readout capability.

The signal-controlling functionalities in molecular systems have attracted considerable attention with the aim of designing and developing information storage and processing systems. However, the studies on molecular logic functionalities are still in the infant stage. The switchable bistable molecules with fluorescent quenching/enhancement controlled through redox process are of particular interest. Changes in the redox potential upon addition of certain guest could be of application in the control of the output fluorescent emission with a photo-induced electron transfer (PET) mechanism which offers the rational design of binary logic function. Towards this goal, we build a switchable bistable molecule(FcA, Scheme 1) with both ferrocenyl and anthryl groups in the present work. In our previous work, renowned electron donor and reversible redox-active tetrathiafulvalene(TTF) was employed to switch the fluorescent emission with a PET process and to construct the logic gate functions [10]. However, the poor solubility of the previous TTF system prevented us from further studies on the behaviors of the compound in different valence state in solution. A ferrocenyl group can be incorporated as a signal-controlling redox moiety due to its reversible oxidation-reduction characteristics. It also offers several additional advantages, such as good solubility, easy modulation, and low cost [11,12]. This approach allows one to utilize the fluorescence quenching of an anthracene moiety based on the PET from a ferrocenyl unit to an anthracene moiety. In the present system, it is also expected that the fluorescence can be reversibly "switched on and off" based on the reversible redox conversion between the ferrocene and the ferrocenium ion.
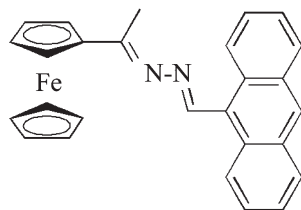
Scheme 1　Molecule FcA

Herein, we report the logic function system employing ferrocene as a signal-controlling unit. This simple molecule FcA acts as a fluorescence switchable molecular system whose fluorescence emission intensity depends on the oxidation state of the ferrocene moiety. In this study, we demonstrate that this molecule can be used to construct an AND logic gate.

FcA was prepared with a modified facile route [13] starting with acetylated ferrocene and hydrated hydrazine and then reacting with anthracene-10-carbaldehyde.

The steady-state fluorescent spectra indicate that the presence of the electron-donating ferrocene in the molecule quenches the excited states of the anthryl unit (Fig.1). The emission bands centered at 432 nm of the anthracene is significantly reduced through a PET mechanism, with the electron-transfer from electron-donor ferrocene moiety to electron-receptor anthracene group[14~17]. It is attributed to the existence of electron-transfer paths from the electron-donor ferrocene to the photo-excited state of the anthracene. The electron-transfer paths are not operative remarkably upon oxidation of the ferrocene to the ferrocenium ion, due to the reduction of the electron density in the ferrocenium ion. Thus, oxidation of the ferrocenyl moiety eliminates the possibility of electron-transfer quenching of the anthracene excited state. Following oxidation of Fe(II) to Fe(III), a strong emission with characteristic fine structure, in which the emission peak of anthracene is centered at 438 nm, is restored through suppress of the electron-transfer process(Fig.1).

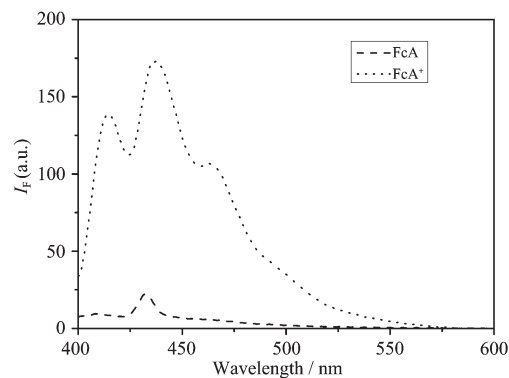Based on the distinct fluorescence properties of

Fig.1　Fluorescence spectra of neutral and oxidized FcA(1.0×10^{-5} mol·L^{-1}) with one equivalent CuSO$_4$ in water(1.0×10^{-3} mol·L^{-1}) as oxidative agent(λ_{ex}=382 nm)

FcA and FcA$^+$, FcA can be operated within the molecule as a controllable fluorescent "off-on" switch, which can be applied to construct the basic logic gate. In the present work, the logic gate AND is realized with the fluorescence at 438 nm as the output signal and the threshold of normalized intensity 0.42. The experimental emission intensities and the truth table for the AND gate are shown in Fig.2 and Table 1, respectively. The neutral molecule FcA is designed to have a PET process to the anthryl group which is linked to ferrocene by Schiff-base C=N bonds. Therefore, the emission band centered at 432 nm from anthracene moiety is very weak, due to the quenching effect of the ferrocene. This is the "off" state of fluorescence. It is well known that ferrocene is an efficient fluorescence quencher via both energy transfer and reductive quenching processes. The occurrence of an electron-transfer mechanism is thermodynamically favorable as it can be demonstrated from electrochemical and photophysical data.
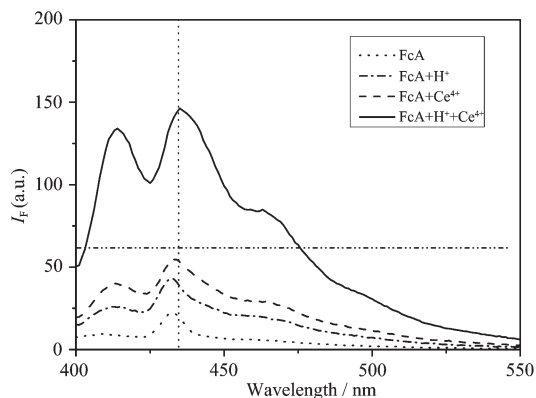

Fig.2　Fluorescence spectra of FcA in THF($1.0×10^{-5}$ mol·L^{-1}) under different input conditions($1.0×10^{-5}$ mol·L^{-1} $(NH_4)_2Ce(NO_3)_6$ and $2.2×10^{-4}$ mol·L^{-1} CF_3COOH) (λ_{ex}=382 nm)

Table 1　Truth table for AND logic gate

H$^+$	Ce^{4+}	FL^a
0	0	0(0.15)
0	1	0(0.29)
1	0	0(0.37)
1	1	1(1.0)

^{a}Normalized fluorescence intensities (FL) are shown in the brackets

The electrochemical study of FcA was carried out in THF solution containing n-Bu$_4$NPF$_6$ as supporting electrolyte(Figs.3~5). The reversible oxidation wave at +0.645 V corresponds to the oxidation of the ferrocenyl
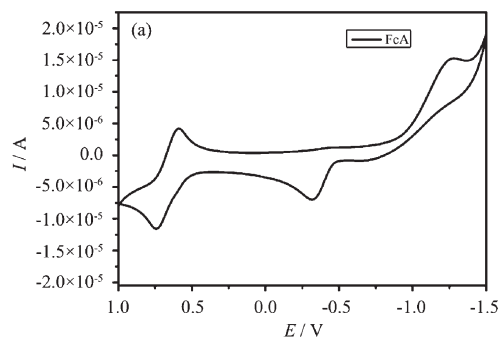

Fig.3　Cyclic voltammogram of FcA in THF ($1.0×10^{-5}$ mol·L^{-1}) containing n-Bu$_4$NPF$_6$ with a Pt disk used as working electrode, a Pt wire as the counter electrode, a Ag/AgCl electrode as the reference electrode, and ferrocene as the external standard
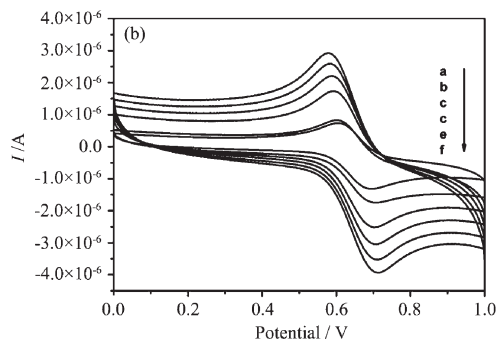

Fig.4　Cyclic voltammogram of FcA in THF at various scan rates of 0.05(a), 0.1(b), 0.2(c), 0.3(d), 0.4(e), and 0.5(f) V·s^{-1} with a Pt disk used as working electrode, a Pt wire as the counter electrode, a Ag/AgCl electrode as the reference electrode, and ferrocene as the external standard
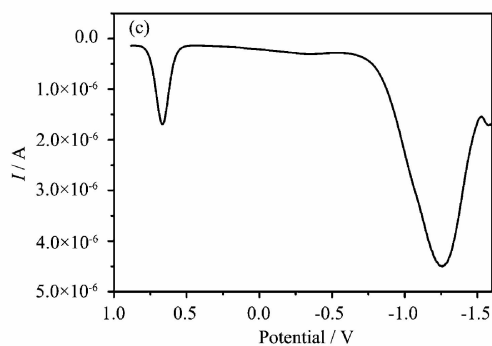

Fig.5　Differential pulse voltammetry diagram of FcA in THF($1.0×10^{-5}$ mol·L^{-1}) containing n-Bu$_4$NPF$_6$ with a Pt disk used as working electrode, a Pt wire as the counter electrode, a Ag/AgCl electrode as the reference electrode

group while the irreversible reduction peak around −1.26 V is attributed to the reduction of the anthryl group. The oxidation wave at 0.32 V is uncertain, which might arise from a new species following reduction of anthryl group [13]. Compared with the redox potential 0.557 V of parent ferrocene, the significant cathodic electrochemical shift of the ferrocenyl redox potential of ca. 90 mV indicates the electron transfer from the ferrocene to the anthracene. The cyclic voltammogram at different scanning rates demonstrates the electrochemical reversibility of the $Fe(II)/Fe(III)$ redox couple of FcA at potentials lower than +1.0 V.

With the potential data and the emission data, the free energy of the process(anthracene+Fc→anthracene⁻+Fc⁺) in which the ferrocene acts as a reductive quencher can be calculated with the equation of Rehm-Weller[14,15] and ΔG is −0.83 eV, which indicates that photo-induced electron transfer from the ferrocene to the anthryl fluorophore can occur spontaneously. Additionally, an energy transfer quenching mechanism also plays the role [16], since the overlap between the absorption and emission is not negligible(Fig.6).
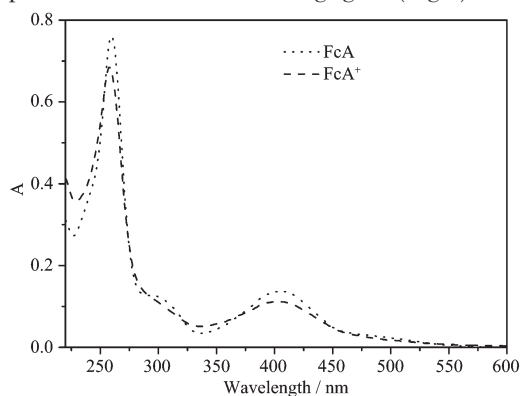

Fig.6　Absorption spectra of FcA and oxidized FcA⁺ in THF ($1.0×10^{-5}$ mol·L⁻¹)

Although PET from the ferrocene is significant, the PET from amine group of the Schiff-base is not negligible. When the amine group is proton-free, it serves also as an PET donor (ΔG_{PET} =−0.1 eV) [14,15,17]. When protons are present in sufficient concentration, the protonated aminomethylene moiety behaves as an electron-withdrawing group which disturbs and suppresses slightly the PET process from the ferrocene moiety, thus results in a slight enhancement of the fluorescent emission. However, the intensity of the emission at 438 nm is under the threshold, and this state is denoted as the logic-0 state. When Ce^{4+} in the neutral medium is introduced, the ferrocene moiety is slowly oxidized and thereby its electron donating character is slowly weakened. This disturbs and suppresses PET process, leading to a slight enhancement of the fluorophore emission. The emission intensity at 438 nm is also under the threshold, and the state is corresponding to the logic-0 state. If both proton and Ce^{4+} are applied simultaneously, a large fluorescence enhancement is observed in the present molecular system, corresponding to the logic-1 state. The fluorescence enhancement is mainly due to the strong oxidation of Ce^{4+} in the acid medium, which leads to the ferrocene to be oxidized to ferrocenium, weakening the electron donating ability of ferrocene, and thus makes PET process invalid. The fluorophore emission spectra behaviors under these different inputs give an excellent correlation with the truth table for a digital AND logic gate.

The fluorescent logic gates can be potentially operated at the single molecule level and in wireless mode, thus increase the interests in the mimicking of the computing functions at the molecular level and targeting the future molecular computer. Among the research of the molecular logic devices, a great challenge is the recyclable performance and reset capability of these logic gates with photonic and chemical inputs. In a recent communication [18], an elegant approach is achieved with photochromic compounds used, due to their intrinsic photo-induced configuration change and thereby photophysical property change.

In this work, we have realized logic function at molecular level in the solution state. The further work on immobilization of the logic gates on surfaces or using microfluidic devices is in progress.

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