ORGANIC
LETTERS

2008
Vol. 10, No. 14
3065−3068

A Novel Redox-Fluorescence Switch Based on a Triad Containing Ferrocene and Perylene Diimide Units

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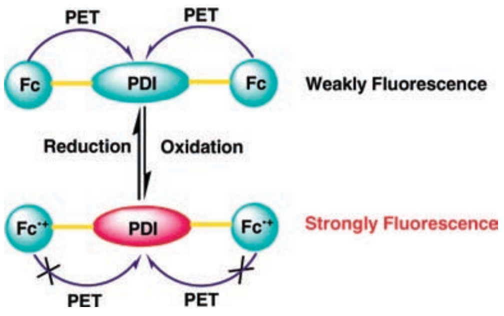
Received May 7, 2008

ABSTRACT



By taking advantage of the features of ferrocene as a redox-active electron donor unit and perylene diimide as a fluorescence unit, a new redox fluorescence switch can be constructed on the basis of this triad.

Molecular devices have received considerable attention in the past decades with the ever-increasing interest for molecular electronics and information storage system, as well as the continuous miniaturization of optoelectronic devices.[1] As an important component of molecular devices, molecular switches have been extensively explored due to their potential application as molecular valves,[2] molecular memories,[3] and chemical or biological sensors.[4] Molecular switches refer to molecules whose electronic and optical properties can change reversibly in response to various environmental stimuli.[5] Among the various switching materials available, using fluorescent components is one of the most attractive owing to its high sensitivity and the easy monitoring of the luminescence signals.[6] One general mechanism in fluorescence switches is photoinduced electron transfer (PET)[7]—in the off state of the switch, PET either to or from the fluorophore quenches the fluorescence.

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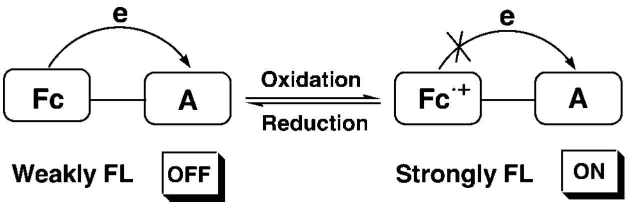
10.1021/ol801053t CCC: $40.75

Although fluorescent switches have been extensively explored,[8] fluorescence switches based on a redox reaction center ferrocene (Fc) are still rare and much less well-studied.[9] Our interest is the possibility to modulate the emission of fluorophore reversibly by redox reaction of the Fc group.

Herein, we designed a new fluorescence switch based on donor−acceptor (D−A) molecules, which incorporated a redox center Fc because of its excellent reversible redox properties and high stability.[10] More importantly, the electron-donating abilities of the Fc unit can be reversibly modulated by the chemical or electrochemical redox reaction. For this study, perylenetetracarboxylic diimide (PDI) was chosen as the fluorophore and electron acceptor. Besides its high fluorescence quantum yields which are near unity and its good photo and thermal stability,[11] the following considerations were taken into account. First, the fluorescence spectrum of PDI (500 ∼ 650 nm) is not significantly overlapped with the absorption spectrum of the oxidized cation radical of the Fc moiety (∼ 460 nm). Otherwise, intramolecular energy transfer would occur efficiently, and thus the expected fluorescence recovery of $Fc^{\bullet+}$−PDI would not be observed.[12] Second, the lowest excited singlet state of the Fc unit is higher in energy than that of the PDI subunit.[13] Thus, the reverse electron transfer from PDI* to $Fc^{\bullet+}$ cannot take place. If such electron transfer occurs, the fluorescence of the D−A molecules cannot be reversibly modulated by redox reaction.[14]

Thus, the working mechanism for such a redox fluorescence switch is proposed as follows in Scheme 1. First, the photoinduced electron transfer (PET) from the Fc unit to the excited electron acceptor would result in the fluorescence quenching of the PDI, with the D−A molecule showing weak fluorescence. Second, after oxidation, the electron-donating abilities of the Fc unit are reduced, and the PET reaction would be arrested, leading to fluorescence enhancement. Third, the reduction of the cation of Fc to neutral Fc would result in another fluorescence decrease.

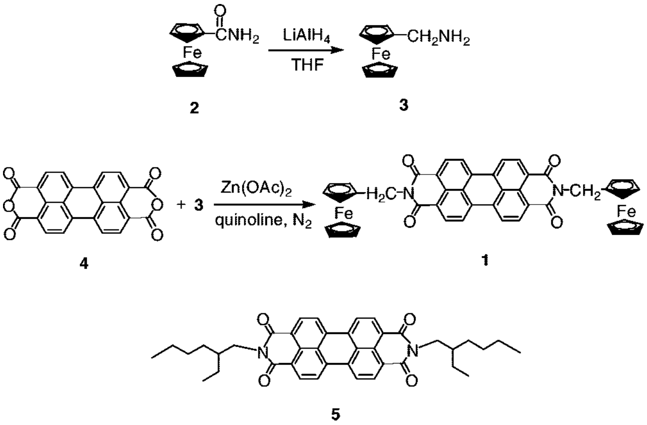
Scheme 1. Illustration of a Redox Fluorescence Switch Based on an Fc-Type Electron Donor



The synthesis and electrochemical and spectral studies of a new triad **1** consisting of one PDI unit and two Fc units were presented, demonstrating that such new redox fluorescence switches based on the triad **1** can be constructed.

Synthesis of triad **1** is depicted in Scheme 2. Starting from compound **3** (Scheme 2), which was prepared by reduction of Ferrocenecarboxamide,[15] direct condensation of **3** with **4** in the presence of $Zn(OAc)_2$ led to the novel compound **1** in an overall yield of 43% after purification with column chromatography.

Scheme 2. Synthesis of Triad **1** and the Chemical Structures of Reference Compound **5**



The solution phase electrochemical properties of the triad **1** were investigated by cyclic voltammetry (CV). As shown in Figure 1, only a one-electron reversible oxidation wave with $E_{1/2}(\mathrm{Ox}) = +\ 0.12$ V (vs Fc/Fc^+) was observed in the anodic direction, corresponding to the $Fc^{\bullet+}$−PDI. As expected, the oxidation of the PDI moiety was not observed. In the cathodic direction, triad **1** showed two reversible reduction waves at $E^1_{1/2}(\mathrm{Red}) = -0.96$ V and $E^2_{1/2}(\mathrm{Red}) = -1.13$ V (vs Fc/Fc^+), which were attributed to the successive

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(17) This was calculated with the Rehm−Weller equation: $\Delta G_{\mathrm{PET}} = E(\mathrm{ox}) - E(\mathrm{red}) - E(\mathrm{ex}) - e^2/\varepsilon r$, with $E(\mathrm{ox}) = 0.12$ V, $E(\mathrm{red}) = -0.96$ V, $\lambda(\mathrm{ex}) = 490$ nm, and $e^2/\varepsilon r = -0.1$ eV. See:(a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (b) Grabowski, Z. R.; Dobkowski, J. *Pure Appl. Chem.* **1983**, *55*, 245.

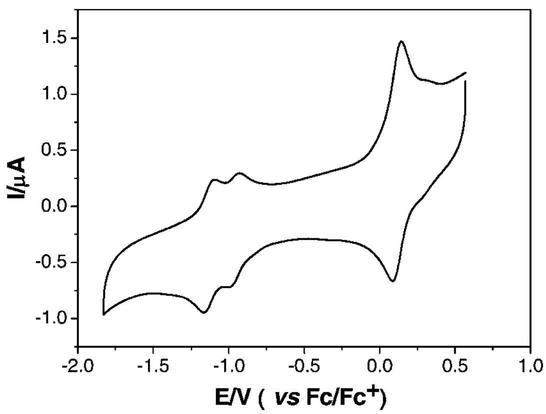

Figure 1. Cyclovoltammogram of triad **1** in CH_2Cl_2 (scanning rate 50 mV/s) with thin-plate of platinum as the working electrode, platinum wire as the counter electrode, Ag wire as the reference electrode (−0.430 V vs Fc/Fc^+), and *n*-Bu_4NPF_6 (0.1 M) as the supporting electrolyte.

formation of the anion radical Fc−PDI^- and the dianion Fc−PDI^{2-}, respectively.

The fluorescence spectrum of triad **1** was taken in CH_2Cl_2 using an excitation at 490 nm, which resulted in the excitation of the PDI unit. For comparison, the emission spectrum of the reference compound **5**[16] was also recorded in Figure 2.

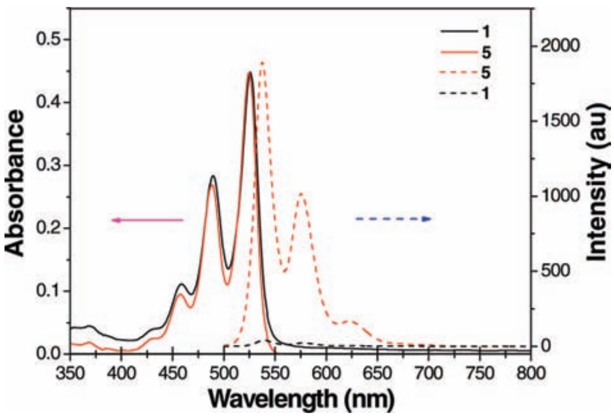

Figure 2. Fluorescence (dash line) and UV/vis absorption (solid line) spectra of triad **1** and **5** in CH_2Cl_2 ($A = 0.45$). Excitation wavelength was 490 nm.

Their fluorescence spectra revealed three emission bands located around 533, 577, and 625 nm, which were indeed the mirror images of the UV/vis absorption spectra, implying that the fluorescence of **1** is due to the PDI unit. It is noteworthy that the emission intensity of **1** was dramatically reduced compared to that of **5** under the same conditions.

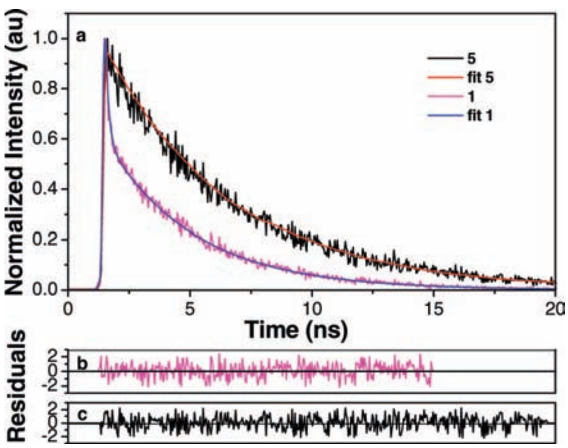

Figure 3. (a) Time profiles of fluorescence lifetime measurement of **5** and triad **1** (3.2×10^{-5} M) in CH_2Cl_2. (b) Residuals for biexponential fit of **1**. (c) Residuals for single exponential fit of 5.

The fluorescence decay of compounds **5** and **1** in CH_2Cl_2 was recorded at 530 nm upon excitation at 490 nm. Time profiles of fluorescence intensities of both compounds were shown in Figure 3. In the case of **5**, the decay obeyed single exponential function giving a single fluorescence lifetime ($\tau_0 = 4.77$ ns). On the other hand, the decay of triad **1** consisted of a fast decay component ($\tau_1 = 0.14$ ns, 59%) and slow component ($\tau_2 = 3.66$ ns, 41%). From the shorter lifetime compared with **5**, an appreciable increase in the decay rate of triad **1** was observed. It indicates that there may be electron transfer or energy transfer when Fc was linked to PDI.

We prefer to attribute the origin of the fluorescence quenching in triad **1** to the photoinduced electron transfer between the ferrocene unit and the PDI unit because of the following facts. First, ΔG for the photoinduced electron transfer from the Fc to the PDI moiety is estimated to be −1.35 eV,[17] and this negative value of ΔG indicates that this reaction is thermodynamically favorable. Second, there is no spectral overlap between the absorption spectrum of the ferrocene moiety and the fluorescence spectrum of the PDI unit. Hence, the possibility of energy transfer can be ruled out. In addition, quenching via aggregation of the PDI chromophore is excluded because the UV/vis spectra do not show any signs of aggregation (Figure 2). Accordingly, the shorter τ_1 value (0.14 ns) of triad **1** can be attributed predominantly to charge separation between the Fc and PDI moieties, while the longer τ_2 value (3.66 ns) is similar to the intrinsic fluorescence lifetime of the PDI chromophore.[18]

The fluorescence efficiency of triad **1** was estimated by measuring the fluorescence quantum yields (Φ_F) (see Supporting Information) on the basis of the absorption and fluorescence spectra taken in CH_2Cl_2. The fluorescence of **1** was considerably quenched ($\Phi_F = 3.9 \times 10^{-3}$, comparable with the value of $\Phi_{F,Cal}$) with respect to that of **5** ($\Phi_F = 0.85$).[19] This great difference in the quantum yields confirmed that PET from the Fc unit to the PDI moiety may quench the fluorescence of PDI in triad **1**.

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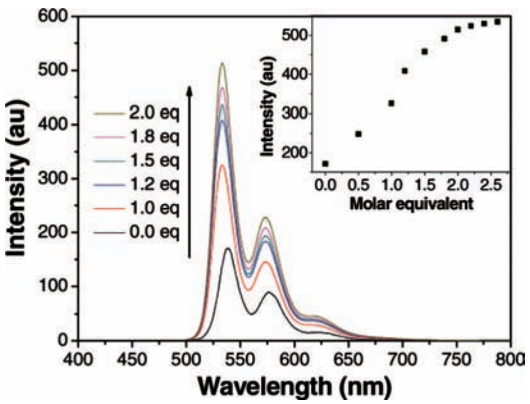

Figure 4. Fluorescence spectra of triad **1** (4.3×10^{-5} M) in THF in the presence of different amounts of $Fe(ClO_4)_3$. Inset: the fluorescence intensity at 533 nm vs the molar equivalent of $Fe(ClO_4)_3$.

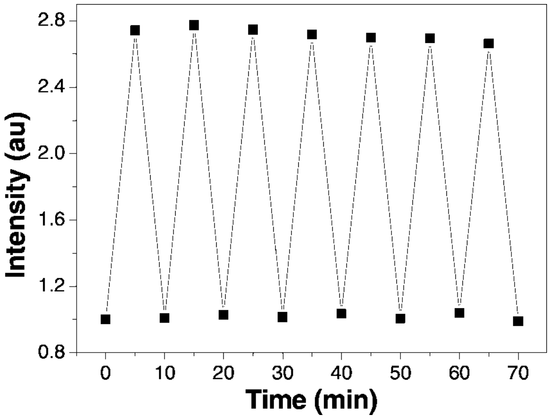

Figure 5. Stepwise oxidation and reduction cycles carried out in CH_2Cl_2 with triad **1** (3.2×10^{-4} M) by chronoamperometric analysis, which uses fixed potentials at + 0.17 V (for oxidation) and − 0.30 V (for reduction) changed every 300 s, following the changes by the evolution of the fluorescence intensity at 533 nm ($\lambda_{ex} = 490$ nm).

To test the possibility of **1** to act as a fluorescence switch, the chemical oxidation of the Fc unit was performed using $Fe(ClO_4)_3$ as an oxidant. As shown in Figure 4, the emission intensity of **1** was enhanced dramatically upon the addition of $Fe(ClO_4)_3$ to the solution of triad **1**, and the fluorescence intensity grew with an increasing amount of $Fe(ClO_4)_3$. This result demonstrates the possibility of establishing a new redox-fluorescence switch based on triad **1**, as the $Fc \rightarrow Fc^{\bullet +}$ transformation can be operated reversibly.

Electrochemical oxidation of triad **1** was performed by applying an oxidation potential of + 0.17 V (vs Fc/Fc^+) to the solution of **1** in CH_2Cl_2 (3.2×10^{-4} M) containing $n\text{-}Bu_4NPF_6$ (0.1 M) as the supporting electrolyte. As shown in Figure S2A, the fluorescence intensity of **1** was gradually enhanced with the increasing time of electrochemical oxidation. After applying the oxidation potential for 300 s, no obvious changes were observed in the emission spectrum. Interestingly, a subsequent application of a reduction potential of −0.30 V (vs Fc/Fc^+) to the oxidized solution resulted in the decrease of fluorescence, and the initial low fluorescence intensity of the solution (before applying an oxidation potential) was almost completely recovered after the reduction potential was applied for 300 s (Figure S2B). Oxidation of triad **1** and its subsequent reduction were carried out for several cycles without any fatigue, as shown in Figure 5.

This fluorescence change can be understood by reference to the cyclic voltammogram of **1** (Figure 1), where the cation radical of the Fc unit was generated during the oxidation since the oxidation potential (+ 0.17 V vs Fc/Fc^+) applied was higher than that of the oxidation potential of the Fc unit in triad **1**. When a reduction potential was explored, the cation radical of the Fc unit would be reduced to the neutral state. So the PET from the Fc subunit to the PDI unit can be modulated off and on sequentially, because of the different electron-donating ability of the neutral Fc unit and the Fc radical cation. As a result, a new reversible redox-fluorescence switch can be constructed on the basis of triad **1** by taking advantage of the peculiar features of the Fc-type donor, i.e., the reversible modulation of the electron-donating abilities of the Fc unit and the PDI as a fluorescent read-out unit.

In summary, the synthesis and spectra as well as the spectroelectrochemical studies of a new and fast redox-fluorescent molecular switch based on a ferrocene−perylene diimide are presented. Chemical oxidation can lead to the fluorescence enhancement for the solution triad **1**. Most importantly, the fluorescence intensity of the solution of **1** can be reversibly modulated by the electrochemical oxidation and reduction sequentially. Therefore, a new redox fluorescence switch can be established on the basis of triad **1**. Such behavior of triad **1** can be attributed to the special spectral and redox properties of the Fc and PDI units. The synthesis and investigations of new Fc-type triads with other linking groups between the donor and acceptor are underway. These new triads might find potential applications in designing molecular devices such as probes and sensors for redox processes.

Acknowledgment. National Natural Science Foundation of China (Nos. 50221201, 90301010, 50502033), the Chinese Academy of Sciences, the National Research Fund for Fundamental Key Project No. 973 (2006CB806200).

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

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(19) The quantum yields of charge separation (Φ_{CS}) and fluorescence quantum yield ($\Phi_{F,Cal}$) were calculated: $\Phi_{CS} = [(1/\tau_1) - (1/\tau_0)]/(1/\tau_1) = 0.97$ and $\Phi_{F,Cal} = 1 - \Phi_{CS} = 0.03$. Note that the τ_1 value is near to the limit of our instrument, the actual value might be even shorter. See: (a) Watanabe, N.; Kihara, N.; Furusho, Y.; Takata, T.; Araki, Y.; Ito, O. *Angew. Chem., Int. Ed.* **2003**, *42*, 681. (b) Araki, Y.; Luo, H. X.; Nakamura, T.; Fujitsuka, M.; Ito, O.; Kanato, H.; Aso, Y.; Otsubo, T. *J. Phys. Chem. A* **2004**, *108*, 10649.