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Dual-controlled dithienylmaleimide switch containing ferrocene units

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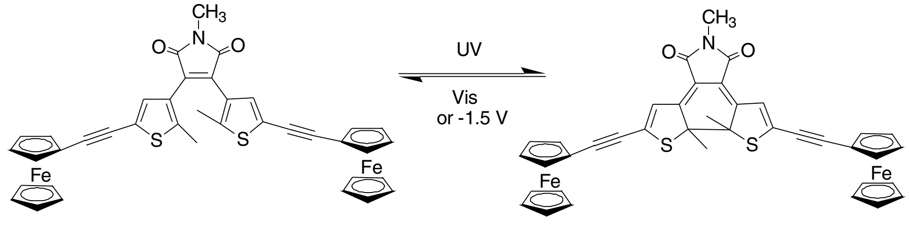
Abstract—A novel photochromic dithienylmaleimide (**TMF**) appended with two ferrocene units was synthesized from 2,3-bis(5-bromo-2-methylthiophen-3-yl)fumaronitrile. Its photochromic properties, electrochemical properties and magnetism were studied. Both fluorescence emission and redox potential were reversibly changed accompanying the open and closed-ring photoisomerization of **TMF** with UV/vis light irradiation and electrochemical redox. **TMF** may be used for fluorescent switch and electrochemical switch controlled by both light and electrochemical redox.

Photochromism is the term used for a reversible photo-induced transformation of a molecule between two isomers whose absorption spectra are distinguishably different. Thereby, photochromic molecules have attracted much attention because of the potential application to optical memories and switching devices.[1,2] Among various types of photochromic compounds, diarylethenes with heterocyclic aryl groups belonging to a new class of photochromic switches can be created for use in optoelectronic and photo-optical devices,[1,3,4] because of their high fatigue resistance and thermal stability.[5,6] Diarylethenes exhibit reversible variations in their physical and chemical characteristics such as fluorescence emission,[7–9] infrared absorption,[10,11] optical rotation,[12] redox potential[13,14] and magnetism[15] when stimulated by distinct light. Irie and his co-workers have described that the intramolecular magnetism was reversibly photoswitched by incorporating two radical moieties into a photochromic diarylethene spin coupler.[15] Furthermore, Branda and co-workers have demonstrated that several dithienylethene derivatives were chemically or electrochemically oxidized undergoing the same ring-closing and ring-opening reactions that are induced by light.[13,16,17]

We report herein a new photochromic compound of dithienylmaleimide **TMF** appended with two ferrocene units through a new synthetic strategy from 2,3-bis(5-bromo-2-methylthiophen-3-yl)fumaronitrile (compound **2**) (Scheme 1). We also describe the photochromic properties, electrochemical properties and magnetism of compound **TMF**. Finally, we find that there are not only



TMF (O)

TMF (C)

Keywords: Photochromism; Dithienylmaleimide; Redox potential; Magnetism.

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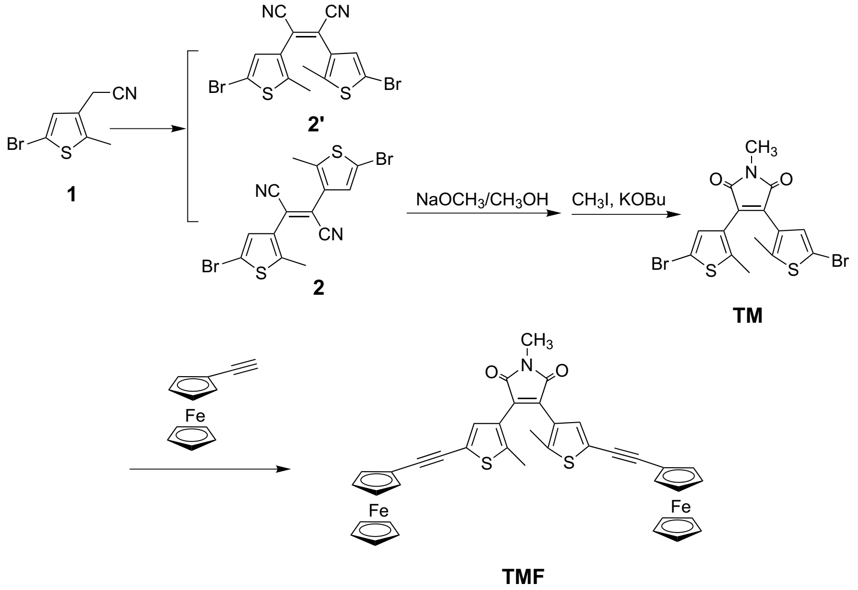

Scheme 1. Synthetic route of the compound **TMF**.

marked changes in emission, redox potential and magnetism between the open-ring and closed-ring forms of **TMF** but also that the ring-opening reaction could be induced by electrochemical redox. Especially, the fluorescence was observed in the closed-ring form of **TMF**, on the contrary, the fluorescence normally exhibits in the open-ring form of diarylethenes. Thereby, dithienylmaleimide **TMF** can be used for fluorescent switch, electrochemical switch and magnetism switch integrating into one molecule. And the switch can be controlled by both light and electrochemical redox.

Dithienylmaleimides have been prepared from the base hydrolysis of 2,3-bis(2,5-dimethylthiophen-3-yl)-maleonitrile and further imidization with alkylamine,[18] while dithienylmaleimide 2,3-bis(2-bromo-5-methylthio-phen-3-yl)-*N*-methyl maleic imide **TM** was prepared via 2,3-bis(5-bromo-2-methylthiophen-3-yl)fumaronitrile **2** in a two-step synthesis procedure.[19] 2,3-Bis(5-bromo-2-methyl-thiophen-3-yl)fumaronitrile **2** was hydrolyzed with sodium methoxide–methanol solution, followed by N-methylation with potassium *tert*-butoxide and iodomethane, to give the target compound 2,3-bis(2-bromo-5-methylthiophen-3-yl)-*N*-methyl maleic imide **TM**. In this procedure, the isolation of the pure 2,3-bis(2-bromo-5-methylthiophen-3-yl)-maleimide product from the previous reaction was ignored and the overall yield of the N-methylated maleimide compound was high enough (46%). However, what is most recommendable is that 2,3-bis(5-bromo-2-methyl-thiophen-3-yl)-fumaronitrile **2** was utilized as the starting material in the synthesis procedure, which was previously considered as a byproduct having no photochromic properties of the coupling of 2-(2-bromo-5-methylthiophen-3-yl)-acetonitrile. 2,3-Bis(5-bromo-2-methylthiophen-3-yl)-maleonitrile **2′**, which was the only useful product in the coupling reaction, is not only essentially a photochromic material,[5] but also can be used as an intermediate for further preparation of other photochromic tetraazaporphyrin compounds.[20,21] The synthesis method reported here can be performed on a large scale from cheap starting materials, and can be used as a novel

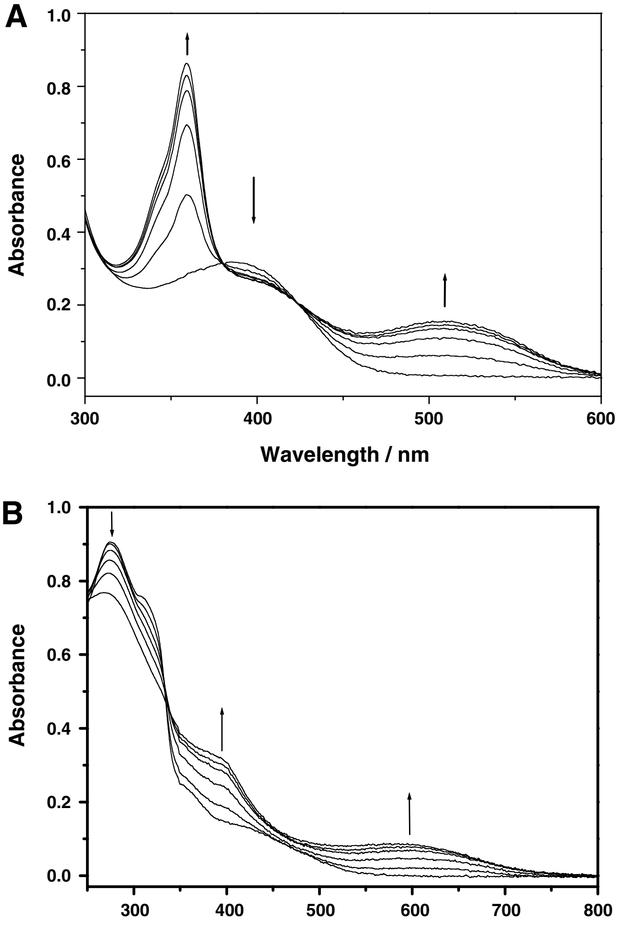

Figure 1. Absorption spectra of **TM** (A) and **TMF** (B) in $CHCl_3$ (2×10^{-5} M) and the changes under different irradiation times by 365 nm.

synthesis route to prepare another species of diarylethene photochromic compounds.

The absorption spectra of compound **TM** and **TMF** are shown in Figure 1. Upon irradiation with UV light of 365 nm, new absorption bands at 358 nm and 510 nm for **TM**, 400 nm and 600 nm for **TMF** appeared, originating from photocyclization and the formation of their closed-ring forms. At the same time, the colorless $CHCl_3$ solution of **TM** gradually turned red, while the yellow $CHCl_3$ solution of **TMF** turned green. The open-ring form of **TM** and **TMF** can be recovered by irradiation with visible light >510 nm and >600 nm, respectively. The maximal absorption band of the closed-ring form of **TMF** was red-shifted compared with that of the closed-ring form of **TM**, as the ferrocene moieties linking to photochromic moiety by ethynyl could extend the conjugation of the whole molecular system.

The emission spectra through photo-excitation at 380 nm for **TM** and 340 nm for **TMF** are shown in Figure 2. The open-ring form of **TM** exhibited fluorescence at 530 nm in $CHCl_3$ solution when excited at 380 nm. The fluorescence intensity decreased along with the open-ring form of **TM** converting to the closed-ring form of **TM** upon irradiation with 365 nm light. On the contrary, the open-ring form of **TMF** exhibited no or very weak fluorescence, but an increased intensity of fluorescence at 530 nm was observed when excited at 340 nm upon irradiation with 365 nm light due to the formation of the closed-ring form of **TMF**. The decreasing emission of compound **TM** resulting from the emission of the dithienylmaleimide unit at 530 nm matches the absorption spectrum of the closed-ring form of the dithienylmaleimide unit, then the fluorescence is efficiently quenched by the intramolecular energy transfer when the photochromic unit converts from the open-ring form to the closed-ring form upon irradiation with 365 nm light.

Since ferrocene is an effective triplet quencher, the fluorescence of the open-ring form of **TMF** was quenched by ferrocene units via intramolecular electron transfer from ferrocene to dithienylmaleimide. However, the recovered emission of the closed-ring form of **TMF** may be due to the weakened intramolecular electron transfer and the very small spectral overlap between the emission of dithienylmaleimide and the absorption of the closed-ring form of **TMF**.[22] The fluorescence signal changes were much more pronounced in **TMF** than that in **TM**. The ratio of the fluorescence signal change was 12:1 for **TMF**. The fact that the fluorescence intensity of **TMF** can be modulated in this way indicated that **TMF** could be functioned as a reversible photoswitch fluorescence device using the sensitivity fluorescence detection method.

The electrochemical studies of **TMF** were performed on a VersaStar II electrochemical analyzer. The cyclic voltammograms of **TMF** in dichloromethane containing tetrabutylammonium perchloride (0.1 M) are shown in Figure 3. The open-ring form of **TMF** showed oxidation waves at 0.65 and 1.35 V and reduction waves at 0.30 and 0.71 V. The first couple wave (0.65 and 0.3 V) belongs to ferrocene moiety. After irradiation with 365 nm light to reach the photostationary state, there was only one couple wave which appeared at 0.61 and 0.35 V and was attributed to ferrocene moiety. Upon subsequent irradiation with visible light (>600 nm), the cyclic voltammogram changed back to the characteristic

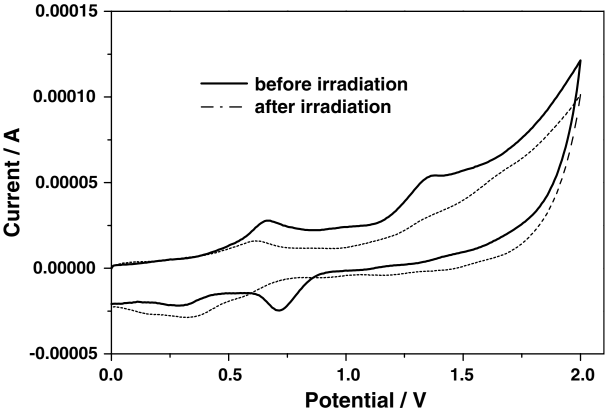

Figure 3. Cyclic voltammograms of **TMF** in CH_2Cl_2 solution (1×10^{-3} M) before (solid line) and after (dashed line) irradiation with 365 nm light at a scan rate of 200 mV/s.

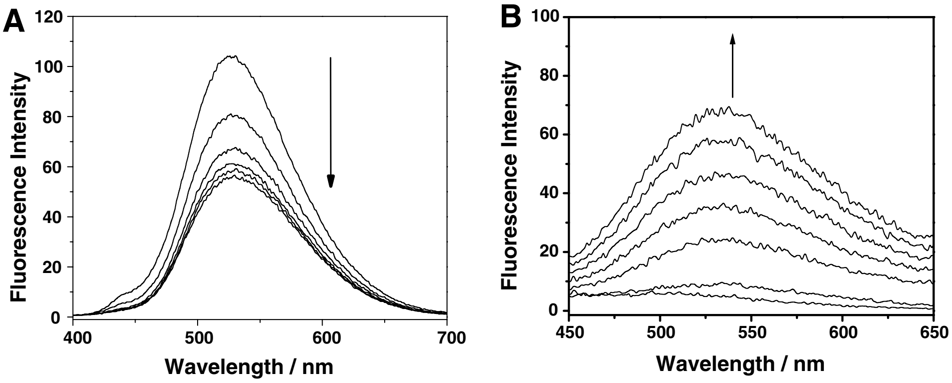

Figure 2. Emission spectra of **TM** (A) and **TMF** (B) excited at 380 nm for **TM** and 340 nm for **TMF** in $CHCl_3$ (2×10^{-5} M) under different UV irradiation times.

of the ring-open form of **TMF**. Hereby, the clear difference and the reversible changes of the redox potentials of **TMF** (open-ring form) and **TMF** (closed-ring form) suggested that compound **TMF** could be used as electrochemical switch controlled with UV/vis irradiation.

During the electrochemical studies, we found that the oxidation wave at 1.35 V reappeared after the photostationary state of **TMF** in CH_2Cl_2 solution was swept through 500 redox cycles (shown in Fig. 4). The phenomenon suggested that the ring-open reaction was also triggered by the redox process. When the photostationary state of **TMF** in CH_2Cl_2 (3×10^{-5} M) containing tetra-butylammonium perchloride (0.1 M) was electrolyzed at −1.5 V, the green solution turned yellow and the intensity of the absorption at 600 nm decreased accompanying the decreased intensity of emission at 530 nm (the absorption spectra are shown in Supplementary data Fig. S1). Irradiating with 365 nm light, the yellow solution converted to green again corresponding to the closed-ring form of **TMF**. Consequently, **TMF** exhibited redox-driven ring-opening. The switch of **TMF** can be controlled with both light and electrochemical redox. The open-ring form of **TMF** converted to the closed-ring form by irradiation with 365 nm light, then irradiation with visible light (>600 nm) or electrolysis at −1.5 V, the open-ring form of **TMF** was generated again.

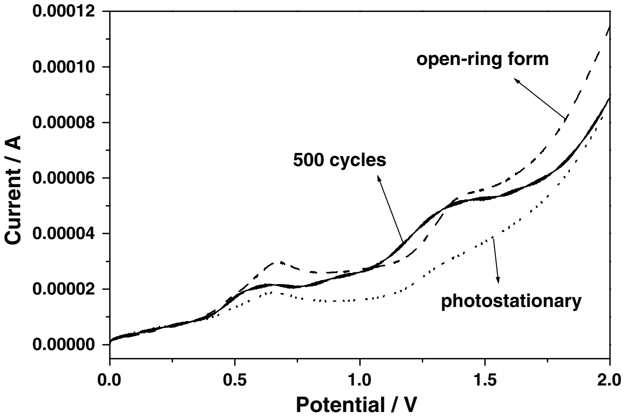

Figure 4. Linear scan of **TMF** in CH_2Cl_2 solution (1×10^{-3} M) before (dashed line), after (dot line) irradiation with 365 nm light and multiple sweeps of **TMF** (closed form) (500 cycles) at a scan rate of 200 mV/s.

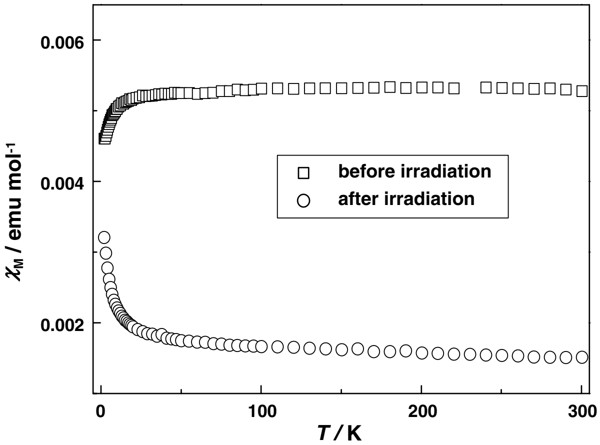

Figure 5. χ_M versus T plots of **TMF**. Two plots described the susceptibilities of **TMF** before and after irradiated by UV light, respectively.

The magnetic susceptibilities of **TMF** were measured in the 2–300 K temperature range and shown as χ_M versus T (temperature) plots in Figure 5. Two different lines described the susceptibilities of **TMF** before and after irradiated with UV light, respectively. **TMF** showed the diamagnetism before irradiation and susceptibility increased at low temperature. After irradiation with UV light, **TMF** turned to be paramagnetic and the susceptibility decreased at low temperature. There was a distinct difference between the open-ring and closed-ring form of **TMF**. With a considerable variance from the photoswitched magnetism of diarylethenes by incorporating radical moieties, the magnetic system of **TMF** was more stable, because that ferrocene was a robust unit. Thereby, the application of **TMF** would not be restricted by an environment like oxygen and temperature.

In conclusion, dithienylmaleimide appended with two ferrocene units has been synthesized via a novel strategy and its photochromic properties, electrochemical properties and magnetism have been studied. It is demonstrated that **TMF** exhibits special fluorescent switching properties and electrochemical switching properties on the basis of photoisomerization of dithienylmaleimide with UV/vis light irradiation and electrochemical redox. This may offer a new system by which a dual-controlled switching can be achieved within one molecule.

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Supplementary data

The experimental details, synthetic and spectroscopic data are available in Supplementary data. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.10.146.

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