

## Photo-controlled Electrochemical Switch Based on Photochromic Tetraazaporphyrin Containing Ferrocene Units

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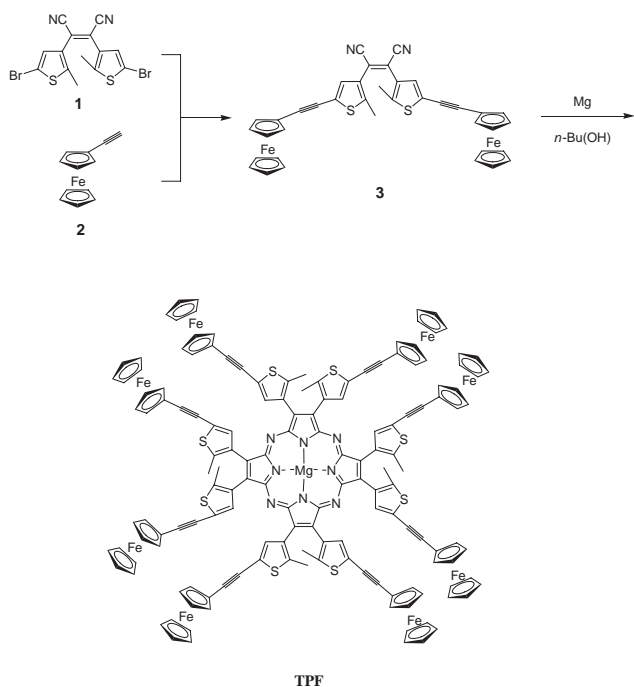
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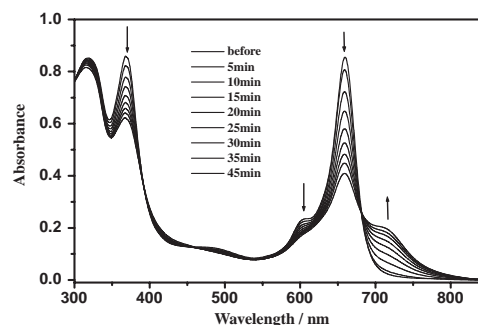
A new photochromic compound of tetraazaporphyrin magnesium(II) appended with eight ferrocene units by ethynyl **TPF** was synthesized. Its photochromic properties and electrochemical properties were studied. As its redox potential was reversibly changed accompanying the open- and closed-ring photoisomerization of **TPF** with UV-vis light irradiation, **TPF** may be used as electrochemical switch controlled by light.

Photochromism is the reversible transformation by photoirradiation, of a chemical species between two isomers having different absorption spectra.<sup>1</sup> The physical and chemical properties of photochromic compounds can be controlled by light, such as fluorescence emission,<sup>2</sup> infrared absorption,<sup>3</sup> optical rotation,<sup>4</sup> redox potential,<sup>5</sup> and magnetism.<sup>6</sup> Thereby, photochromic molecules have been attracting a great deal of attention for their potential technological application in optical memories and optical switching devices.<sup>1,7</sup> Recently, the electrochemical properties of photochromic diarylethenes had been studied.<sup>6,8</sup>

Herein, we report a new photochromic compound **TPF**, tetraazaporphyrin magnesium(II) appended with eight ferrocene units through ethynyl. The synthesis route was shown in Scheme 1. The center of the structure of **TPF** is tetraazaporphyrin magnesium(II) moiety, and the interspace is dithienylethene



**Scheme 1.** Synthetic routes of compound **TPF**.



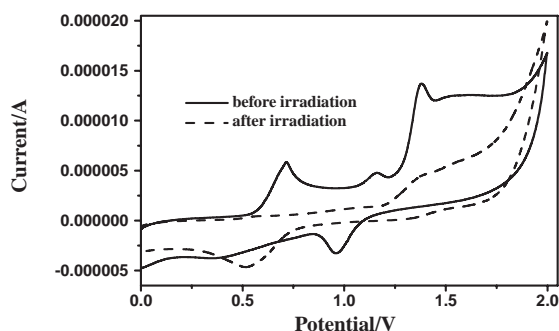
**Figure 1.** Absorption spectra of **TPF** in  $\text{CHCl}_3$  ( $2 \times 10^{-5}$  M) and the changes in absorption under different irradiation times by 365 nm.

moiety with the periphery of ferrocene moieties linked by ethynyl. The redox-active units (ferrocene) may be regulated by photochromic dithienylethene moieties. The electrochemical property of **TPF** was investigated.

The absorption spectra of compound **TPF** are shown in Figure 1. **TPF** exhibits a strong low-energy absorption band (Q-band) at 658 nm, accompanying by a slightly higher energy shoulder at 600 nm. Also present is a less intense, broad band (P-band) in the region between 450 and 550 nm, and another intense peak (B-band) at about 367 nm, known as the Soret-band.

Compound **TPF** exhibits photochromism in  $\text{CHCl}_3$ . Before irradiation with UV light, **TPF** has absorption peaks at 650, 365, and 318 nm. Upon irradiation of the solution of **TPF** with 365-nm light, the absorption band with a maximum of 658 nm gradually decreased and a new absorption band with a maximum at around 716 nm. As a result of photocyclization of photochromic dithienylethene moieties, an isosbestic point at 680 nm was observed. And the absorption spectra of closed-ring form did not obviously change at room temperature for a week. Upon irradiation with 710-nm light, the open-ring form of **TPF** regenerated, accompanying with the decreasing of the band at 716 nm. Thus the open-ring and the closed-ring form of **TPF** can be reversibly converted. However, the photochromism depended on the solvent. The photochromism of **TPF** in THF was not observed. Work on the explanation of this phenomenon is still ongoing.

Before irradiation with UV light, both the B-band (367 nm) and the Q-band (658 nm) of **TPF** were red-shifted comparing with those of tetraazaporphyrin magnesium(II) with bis(dithienylethene) moieties (B-band: 365 nm; Q-band: 650 nm) as we reported before.<sup>9</sup> The red-shifting arisen from that the ferrocene moieties linking to tetraazaporphyrin magnesium(II) moiety by ethynyl could extend the conjugation of the whole molecule system. The Q-band (715 nm) of **TPF** after irradiation with 365-nm light was also red-shifted comparing with that of tetraazapor-



**Figure 2.** Cyclic voltammograms of **TPF** in  $\text{CH}_2\text{Cl}_2$  ( $1 \times 10^{-3}$  M) before (solid line) and after (dashed line) irradiation with 365-nm light at a scan rate of 50 mV/s.

phyrin magnesium(II) with bisthiénylene moieties (Q-band: 711 nm).

Tetraazaporphyrin magnesium(II) with bisthiénylene moieties has strong fluorescence emission, while no fluorescence emission was observed for **TPF** accompanying its photoisomerization by irradiation with UV light. This could be rationalized by the efficient quenching via intramolecular electron transfer from the ferrocene to tetraazaporphyrin magnesium(II) moiety.<sup>10</sup>

The electrochemical studies of **TPF** were performed on a VersaStar II electrochemical analyzer. The cyclic voltammograms of **TPF** in dichloromethane containing tetrabutylammonium perchlorate (0.1 M) was shown in Figure 2.<sup>11</sup> Before irradiation with UV light, the open-ring form of **TPF** shows oxidation waves at 0.71, 1.16, and 1.38 V, and reduction waves at 0.36 and 0.96 V. Comparing with the cyclic voltammogram of compound **3** accompanying its photoisomerization by irradiation with 365-nm light, we can conclude that the first couple wave (0.71 and 0.36 V) belongs to ferrocene moiety, the second couple wave (1.16 and 0.96 V) belongs to tetraazaporphyrin magnesium(II), and that the third wave 1.38 V is an irreversible oxidation wave belonging to dithienylene.<sup>12</sup> After irradiation with 365-nm light to reach the photostationary state, there were only one oxidation wave at 1.38 V and one reduction wave at 0.51 V. The waves at 1.38 and 0.51 V were considered as one couple wave assignable to the whole conjugative molecule **TPF** after irradiation with 365-nm light. Before irradiation with UV light, the redox-active centers of tetraazaporphyrin magnesium(II) and ferrocene moieties were independent,<sup>10</sup> the characteristic redox waves of ferrocene moieties, tetraazaporphyrin magnesium(II) and dithienylene appeared distinguishingly. After irradiation with 365-nm light, the conjugation effect of **TPF** increased owing to the cyclization of the dithienylene units.<sup>9</sup> Thus, the redox-active centers of the tetraazaporphyrin magnesium(II) and ferrocene moieties affected each other resulting in one couple redox wave for whole molecule. Work on the above assumption is still ongoing.

As there was obvious difference on the cyclic voltammograms between the open-ring form and closed-ring form of **TPF**, **TPF**<sup>13</sup> could be used as photo-controlled electrochemical switch. Before irradiation with UV light, the oxidation waves of open-ring form of **TPF** appeared at 0.71 and 1.16 V. After irradiation with 365-nm light, the open-ring form of **TPF** converted to the closed-ring form accompanied with the disappearance of the oxidation waves at 0.71 and 1.16 V. Subsequent irradiation

with 710-nm light, the open-ring form of **TPF** regenerated and the cyclic voltammogram returned to the characteristic of the open-ring form of **TPF**. Thus, the oxidation waves at 0.71 or 1.16 V could be used as the detecting signal for application of electrochemical switch.

In summary, a new photochromic compound **TPF** had been synthesized. Due to the obvious difference on electrochemical property between the open-ring form and closed-ring form, **TPF** could be used as photo-controlled electrochemical switch.

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- Cyclic voltammetry measurements were performed using a platinum disk working electrode, a platinum wire counter electrode, an Ag/AgCl (in a saturated NaCl solution) reference electrode, and tetrabutylammonium perchlorate (0.1 M) as the electrolyte. All results were referenced against ferrocene (0.50 V vs SCE).
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- Synthesis of **TPF**: Magnesium powder 0.12 g (5 mmol) was added to 50 mL dry *n*-Bu(OH) and heated to boil under argon atmosphere. At the same time, a small chip of iodine was added to initiate the formation of  $\text{Mg}(\text{BuO})_2$ , heating was continued for 24 h. Over the time a gray suspension of  $\text{Mg}(\text{BuO})_2$  was formed. The solution then was cooled to room temperature. 2,3-Bis(5-ferrocenylethynyl-2-methylthiophen-3-yl)maleonitrile (**3**) 0.34 g (0.5 mmol) was added, and the reaction mixture was further heated under reflux for 48 h. The solvent was removed by distillation and the green-black crude product was purified by column chromatography on silica gel (hexane/dichloromethane, 2:1). Yield: 69 mg (20%). <sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.41 (s, 24H), 4.33 (m, 56H), 4.66 (s, 16H), 7.77 (s, 8H); MALDI-TOF-MS (*m/z*): calcd for  $(\text{C}_{152}\text{H}_{104}\text{Fe}_8\text{MgN}_8\text{S}_8)$  2770.09, found: 2770.14.