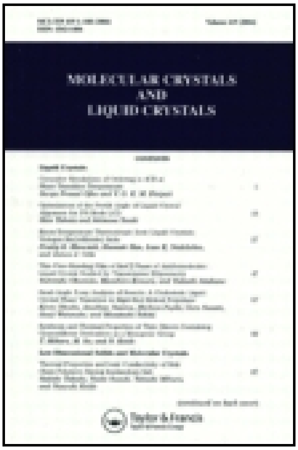

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Novel Photochromic Tetraazaporphyrin Mg (II) Containing Bisthienylethene

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Novel Photochromic Tetraazaporphyrin Mg (II) Containing Bisthienylethene

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A novel π- conjugated photochromic tetraazaporphyrin Mg(II) *based on dithienylethene was synthesized by a concise route. All compounds were characterized by ^{1}H NMR spectra and mass spectra etc. The spectroscopic properties including fluorescence and photochromic quantum yields of the compound were also measured.*

Keywords: dithienylethene; luminescence; photochromic; synthesis

INTRODUCTION

Various types of photochromic compounds have been so far synthesized in an attempt to apply the compounds to optoelectronic devices [1]. Among of them, bisthienylethene (BTE) derivatives are the most promising compounds because of their excellent fatigue resistance and thermal stability in both isomeric forms [2,3]. The property changes of BTE during the photochromic process, such as the refractive index, dielectric constant, oxidation/reduction potential, photoluminescence, can be applied to various optoelectronic devices, such as optical memory, photooptical switching, display, and photodriven actuators [2–5]. From the viewpoint of practical application, it is

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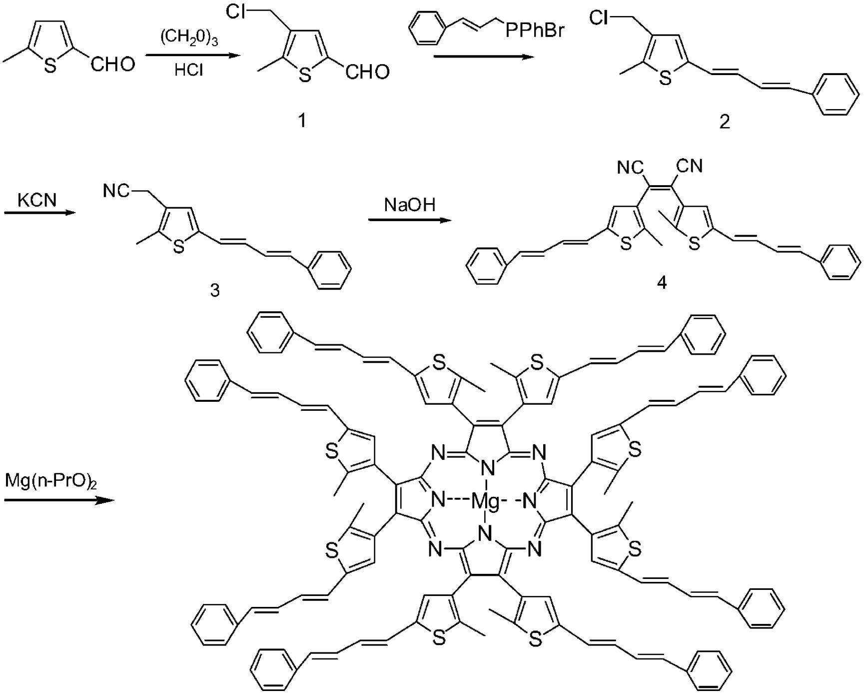
desired to develop photochromic compounds that have high sensitivity in the longer wavelength. Introduction of a large π- conjugated system is effective to increase coefficient of the closed-ring isomer and shift the absorption band to a longer wavelength [2]. Our group [6–9] has reported a series of novel bisthienylethene- based photochromic tetraazaporphyrin and unsymmetrical- phthalocyanine, which exhibit excellent photochromic property such as excellent fatigue resistance and thermal stability in both isomeric forms, especially their high maximum extinction coefficient and the changes of near infrared fluorescence of them along with photochromism. The attractive properties of BTE-based phthalocyanine and tetraazaporphyrin hybrids encourage us to design and synthesize a novel photochromic tetraazaporphyrin Mg(II)(BTE-TAP, Scheme 1) based on bisthienylethene.

EXPERIMENTAL

Instruments. Absorption spectra and fluorescence spectra were measured on a Varian Cary500 UV-Vis and a Varian Cary Eclipse



SCHEME 1 Synthetic route of the compound (BTE-TAP).

Fluorescence spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AM 500 spectrometer with tetramethyl silane as internal reference. Mass spectra were obtained on a HP5989 mass spectrometer. Optical experiments were carried out at room temperature using a photochemical apparatus (British Applied Photophysics, Limited) with a 200 W Hg lamp. The synthetic route of the compound (BTE-TAP) is illustrated in Scheme 1.

4-chloromethyl-5-methyl-thiophene-2-carbaldehyde 1

79% yield.^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.38 (s, 6H, CH_3), 4.38 (s, 2H, Cl$-CH_2-$), 7.50 (s, 1H, thiophene), 9.62(s, 1H, $-$CHO). m/z: 174.0(M^+)

3-chloromethyl-2-methyl-5-(4-phenyl-buta-1,3-dienyl)-thiophene 2

56% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.43 (s, 3H, CH_3), 4.54 (s, 2H, Cl$-CH_2-$), 6.89 (s, 1H, thiophene), 6.64–6.86 (m, 4H, olefinic) 7.24–7.44(m, 5H, benzene). m/z: 274 .0(M^+)

2-methyl-5- (4-phenyl-buta-1,3-dienyl)-thiophen-3-yl)-acetonitrile 3

81% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.36 (s, 3H, CH_3), 4.06 (s, 2H, CN$-CH_2-$), 6.87 (s, 1H, thiophene), 6.56–6.84(m, 4H, olefinic) 7.22–7.42(m, 5H, benzene). m/z: 265.1(M^+)

2,3-bis [2-methyl-5- (4-pheny-buta-1,3-dienyl)-thiophene-3-yl]- but-2-enedinitrile 4

To 12 ml 50% NaOH aqueous solution containing tetrabutylammonium bromine salt (0.1 g) was added a mixture of 2-methyl-5- (4-phenyl-buta-1,3-dienyl)-thiophen-3-yl)-acetonitrile 3(1.325 g, 5 mmol) in component solvent (benzene:CCl_4:CH_2Cl_2 = 3:2:1 (v/v/v)) at 40°C. The solution was stirred for 2 h at 45°C. The reaction mixture was poured into water and the product was extracted with CH_2Cl_2 (3×10 ml), washed with brine. The combined organic extracts are dried over anhydrous magnesium sulfate ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica gel (petroleum ether/dichloromethane = 2:1(v/v)) to give cis-form product 4 in 20% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 2.25 (s, 6H), 6.86 (s, 2H, thiophene), 6.56–6.67 (s, 4H, olefinic), 7.26–7.41(m, 10H, benzene) m/z: 526.2(M^+)

Synthesis of 2,3,7,8,12,13,17,18-Octakis (2′-methyl-3′-thienyl-5′- (4″-phenyl-buta-1″,3″-dienyl))tetraazaporphyrin)Mg (II) (BTE-TAP)

Magnesium power (0.125 g, 5.2 mmol) were stirred in anhydrous n-propanol (25 ml) and heated to reflux under argon for 24 h; Compound 4 (0.75 g, 1.42 mmol) was added to the resulting magnesium n-propanol suspension. The reaction mixture was stirred at reflux under nitrogen for 48 h and allowed to cool to room temperature. The solvent was evaporated by distillation and the blue-black residue was dissolved in $CHCl_3$ and filtered. The solids were further washed with $CHCl_3$ until the washings were colorless. The chromatography (hexane/$CHCl_3$/THF = 4:1:1(v/v/v)) gave pure BTE-TAP in yield 20%. ^1H NMR (500 MHz $CDCl_3$): δ (ppm): 2.31 (s, 24H, CH_3), 6.92 (s, 8H, thiophene), 6.56–6.76(m, 32H, olefinic), 7.26–7.46 (m, 40H, benzene). MALDI-TOF-MS: calculated: 2130.6: found 2129.6($M^+ - 1$), 2130.6(M^+), 2131.6($M^+ + 1$)

RESULTS AND DISCUSSION

Figure 1 shows absorption spectral change of bisthienylethene derivative 4 in CH_2Cl_2. The absorption peak of the open-ring form was

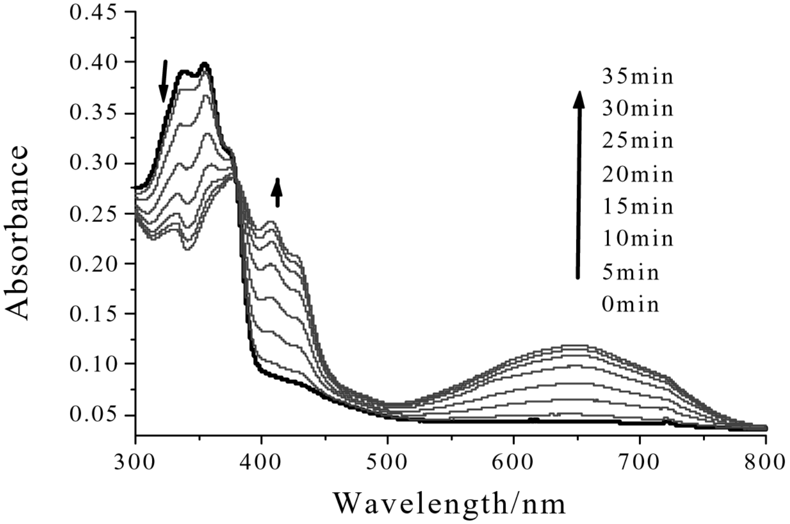


FIGURE 1 Absorption spectra of compound 4 in CH_2Cl_2 (1.0×10^{-5} mol/L) and the changes in absorption of the compounds under different irradiation time by light of 365 nm.

observed at 353 nm. Upon irradiation with UV light (365 nm), the colorless solution of bisthienylethene 4 in CH_2Cl_2 turned to green and an absorption band appeared at 654 nm and shoulder peak 415 nm. The red-shift of the absorption maximum in the bisthienylethene 4 from its open-ring form to its closed-ring form is attributed to larger π-conjugation in the whole molecule. In the open-ring form, an effective conjugation interruption at 3-thiophene existed in the bisthienylethene 4 in CH_2Cl_2 and π-electrons are localized in the two thiophene units, while in the closed-ring π-electrons delocalize along in the whole molecule to form a large π- conjugated system.

Figure 2 shows absorption spectral changes of BTE-TAP in $CHCl_3$ (1.0×10^{-5} mol/L) with irradiation 365 nm light. Before the irradiation of UV light, the solution of BTE-TAP in $CHCl_3$ shows two typical absorption peaks at 366 nm (B-band) and 666 nm (Q-band), and weak absorption band from 400 nm–600 nm. It can be readily interpreted using Gouterman's four orbital model [10]. Upon irradiation with UV light (365 nm), The absorption peak of 366 nm and 666 nm were gradually weakened. The new absorption peak appeared at 725 nm and strengthen with the irradiation time. When the solution of BTE-TAP reached the photostationary state, isosbestic points were observed at 416 nm and 697 nm. The initial cyan solution

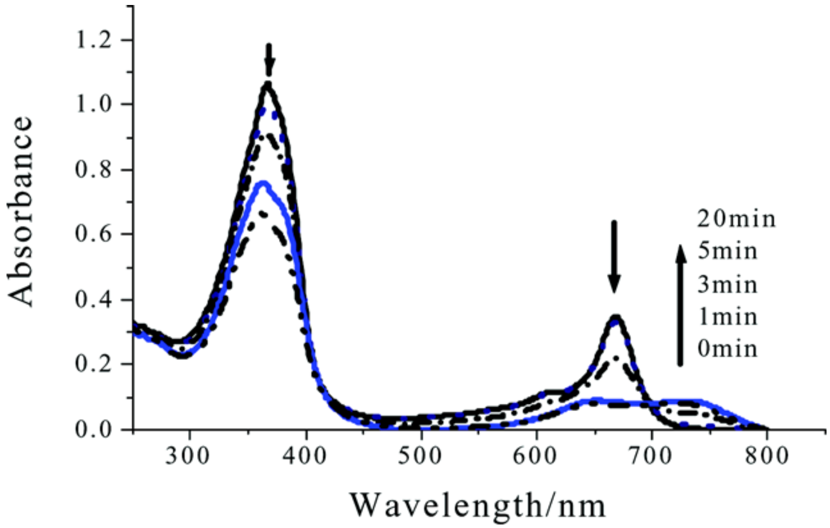


FIGURE 2 Absorption spectra of BTE-TAP in $CHCl_3$ (1.0×10^{-5} mol/L) and the changes in absorption of the compounds under different irradiation time by light of 365 nm.

of BTE-TAP turned to green, which is probably ascribed to the closed isomerization of BTE-TAP. After photochromic reaction, the part conjugated system of tetraazaporphyrin Mg (II) stretch to the π-conjugated bisthienylethene unit, but because of the steric hindrance of the π-conjugated bisthienylethene unit, which is lead to the whole molecular noncoplanar, the π-electrons only delocalized the part of BTE-TAP. In addition, although the BTE-TAP has four bisthienylethene derivate units, there are perhaps only part bisthienylethenes can happen to photocyclization [6].

Table 1 summarizes the data of absorption maxima and the molar coefficients of the open- and closed-ring form in solution. As shown in Table 1, the wavelength of closed-ring isomers of 4 and BTE-TAP were 654 nm and 725 nm, respectively, which are attributed π-electrons delocalize along in the whole molecule to form a large π- conjugated system. The cycloreversion quantum yields of compound 4 and BTE-TAP were 0.25 and 0.09, respectively. In addition, these compounds exhibit the higher molar absorption coefficients.

Figure 3 shows the fluorescence emission spectrum of BTE-TAP in $CHCl_3$ (1.0×10^{-5}mol/L) and the changes under different irradiation time by light of 365 nm at room temperature. For the open-ring of BTE-TAP, the emission with λ_{max} at 675 nm was observed when excited at 480 nm. It is inferred that the fluorescence of BTE-TAP result from two sources (i.e. the open ring form of the bisthienylethene 4 units and the tetraazaporphyrin cycle) and greatly depend on the ratio between the open and the closed-ring states of bisthienylethene. When photo-cyclized by light of 365 nm, the fluorescence intensity gradually decreased under different irradiation time and almost disappeared for the photostationary state. The fluorescence intensity changes originated from two causes: One hand, the non-fluorescent closed forms are produced; On the other hand, the intramolecular energy transfer from the tetraazaporphyrin cycle to the closed-ring

TABLE 1 The Data of Absorption λ_{max} (nm), Quantum Yield of Cyclization (Φ_{O-C}) and Cycloreversion (Φ_{C-O}) of the Compounds

			Quantum yield	
Compound	λ_{max}/nm(open) $\varepsilon/10^4\,M^{-1}cm^{-1}$	λ_{max}/nm(closed) $\varepsilon/10^4\,M^{-1}cm^{-1}$	cyclization (Φ_{O-C})	cycloreversion (Φ_{C-O})
4^a	353 (4.0)	654 (1.1)	0.38	0.25
BTE-TAP^b	366 (10.6)	725 (0.8)	0.25	0.09

^{a}in CH_2Cl_2; ^{b}in $CHCl_3$.

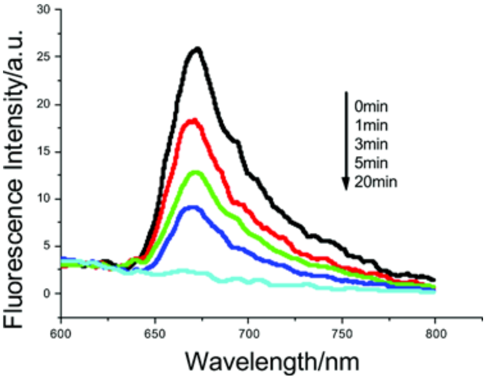


FIGURE 3 Emission spectra and the changes of BTE-TAP (λex = 480 nm) in $CHCl_3$ (1.0×10^{-5}mol/L) under different irradiation time by light of 365 nm at room temperature.

form of the hybrids would also quench the fluorescence of the tetraazaporphyrin. The irradiation by light of 725 nm regenerates the open ring form of BTE-TPA and restores the original emission. This system is a promising candidate for non-destructive read-out by method of photocontrolled luminescence. Because the fluorescence emission of the BTE-TPA is at 675 nm when excited at 480 nm, where the BTE unit has no absorption, both the open ring forms and the closed ring forms are non-active for photochemical reaction at these two wavelengths (675 nm and 480 nm). The open ring of BTE-TPA emits at 675 nm, where is an insensitive wavelength for photo-recyclization despite slight overlap with the UV-vis spectrum of BTE-TPA. The application experiments made with this system are done in progress.

CONCLUSION

We synthesized a novel photochromic tetraazaporphyrin Mg (II) containing bisthienylethene unit by a concise route. All compounds were characterized by ^{1}H NMR spectra and Mass spectra. We investigated photochromic properties of bisthienylethene derivative 4 and the photochromic tetraazaporphyrin Mg (II) (BTE-TAP). They exhibit good photochromic properties, especially, high molar absorption coefficient of BTE-TAP and the long-wavelength absorption band of the closed-ring isomers, which are promised to application in optical memory because of sensitivity in the long-wavelength and non-destructive readout by means of photoregulated luminescence.

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