

Synthesis and photochromism of a new binuclear porphyrazinato magnesium(II)

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Abstract—The synthesis, characterization and photochromism of a new coplanar binuclear porphyrazine bearing six bis-(trimethylthiophenyl) photochromic functionalities at the periphery are described. The synthetic route is concise and the near-infrared luminescence changes of this binuclear porphyrazine can be regulated in a reversible manner by the photoisomerization of the bithienylethene moiety.

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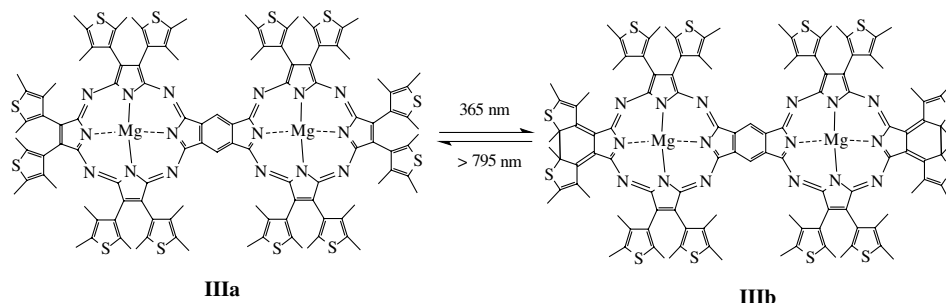
The design, synthesis and applications of organic photochromic molecules have recently been the subject of great interest because of their potential ability for information storage, imaging devices and switches.^{1–5} When irradiated by a light with appropriate wavelength, photochromic molecule can be interconverted between its two isomeric states photochemically. Each isomer state can represent ‘0’ or ‘1’ for a binary digital code.⁶ The difference of two photoisomers can be identified and readout by their spectroscopic and other physical properties. Among photochromic molecules, bithienylethenes (BTEs) with heterocyclic aryl groups have become the promising candidates for the applications due to their good thermal stability of the both isomers, high resistant fatigue and easily monitored property by UV–vis spectroscopy.^{7–14}

While the BTEs molecules have a number of useful properties, considerable effort has been made to synthesize novel photochromic materials, both with the view to design new structures, which may improve the photochromic characteristics (or show unusual properties) and to meet the requirements for practical applications.^{15–17} Many scientists (e.g., Irie’s, Feringa’s and Branda’s groups) have done a lot of excellent works about this topic in recent years.^{15–21} Because the metal complexes of porphyrazines exhibit high fluorescence

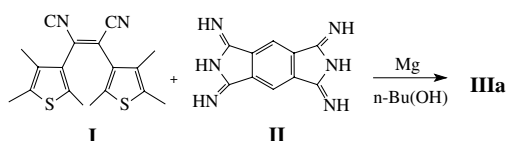
yield in the infrared (IR) region, their fluorescent changes in the photochromic process could be used as a sensitive binary optical readout. Fused photochromic dithiophenes functional groups directly to the β -position of the pyrrole units of porphyrazines (tetraazaporphyrines), we synthesized a series of novel photochromic porphyrazines containing 2, 4, 6 and 8 thiophenyl groups.²² It was well known that porphyrazines show tailorable and varied solubility and electronic optical, magnetic and redox properties, which are in practical use as catalysts, deodorants, write-once disc and so forth.²³ To further increase the number of adjustable photochromic parameters of the subunit, we now report a new binuclear porphyrazine (compound **IIIa** shown in Scheme 1) bearing six photochromic bis-(trimethylthiophenyl) units at the periphery. The binuclear porphyrazine structure is rigidly constrained in a coplanar arrangement with extended π -conjugated subunits. To the best of our knowledge, it is the first family of photochromic binuclear porphyrazines with six bis-(trimethylthiophenyl) moieties (totally 12 trimethylthiophenyl groups) with obvious photochromic characteristics in IR region. The synthetic route is concise and convenient. In fact, there were some other reports about multi-photochromic systems.²⁴ It is interesting to link or couple photochromes, because then the possibility exists that each photochrome can exist in an open (O) or closed (C) state, and so, if two identical photochromes are coupled, three states, closed–closed (C–C), closed–open (C–O) and open–open (O–O), might exist. With more than a simple on–off switch, higher logic operations become possible.^{24a,25}

Keywords: Photochromism; Binuclear porphyrazine; Luminescence.

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Scheme 1. The photochromic process of the two isomers.



Scheme 2. The synthesis route of compound **IIIa**.

The synthesis of compound **IIIa** was illustrated in **Scheme 2**. It was the cyclization of bis(1,3-diimino isoindoline) (**II**),^{23b} and 1,2-dicyano-bis(trimethyl-3-thiophenyl)ethane (**I**) under a nitrogen atmosphere at the reflux temperature for 48 h with a yield of 6.6%.[†] The molecular ion peak of **IIIa** ($M = 2185.57$, very strong) was observed as well as the following fragmentations: 2163.59 ($M - Mg + 2H^+$), 2141.64 ($M - 2Mg + 4H^+$).[†]Compound **IIIa**: ¹H NMR (500 MHz, $CDCl_3$, ppm): 10.55 (s, 2H), 2.24 (s, 36H), 2.07 (s, 36H), 1.74 (s, 36H). Anal. Calcd for $C_{118}H_{110}Mg_2N_{16}S_{12}$: C: 64.85; H: 5.07; N: 10.25%. Found: C, 64.61; H, 5.17; N, 10.11.

Compound **IIIb** was gained by irradiating of the CH_2Cl_2 solution of **IIIa** with 365 nm light. Its ¹H NMR spectrum was got by the subtraction for the integration of **IIIa** from the integration of photo-stationary state.²⁶ Three new methyl protons (assigned to the methyl protons of the closed-ring diarylethenes of **IIIb**) NMR peaks appeared at 2.13, 1.97 and 1.84 ppm, respectively. The ¹H NMR spectra and the integration ratios of the proton peaks all agreed with the structure of **IIIb** shown in **Scheme 1**.[†]Likewise, the cyclization of the BTE units occurring at the contrapositions is relative stable to the preliminary calculations.^{22b,23d}

Due to the large π -conjugate system, the absorption of the closed isomer is red-shifted to about 800 nm, and the emission spectra show interesting photoregulated fluorescence changes in near-IR region. This system has sensitive binary optical readout capability benefiting for the optical memory media. The compound has good solubilities in many common organic solvents such as CH_2Cl_2 , $CHCl_3$, EtOH or THF because of the peripheral substitutes and its uniform thin solid film can be obtained by the spin-coating technique. It has very large

absorption coefficient in CH_2Cl_2 ($\epsilon = 1.3 \times 10^5 M^{-1} cm^{-1}$ at 745 nm), which is also an important characteristic required to be improved for high sensitivity of the photochromic media at present.

Figure 1 shows a typical absorption changes for the photochromic reaction between **IIIa** and **IIIb**. Compared with the absorption spectra of the mononuclear porphyrazine bearing bis-(trimethylthiophenyl) units,^{22c} it is broader and extended into the near-IR region. In addition, although the intensity of the main Q band of the mononuclear porphyrazines was generally larger than that of the Soret band, the intensities of Q band and Soret band for the binuclear complex **IIIa** are almost comparable. The band at lower energy appears to be corresponding Q_{0-0} band, while that at higher energy may be the Q_{0-1} vibration band. The cyclic voltammetric behavior of compound **III** did not change after 100 electrochemical cycles,[†] which indicates that this binuclear photochromic porphyrazine possesses adequate stability to meet the performance conditions required for erasable data memory, especially for the electrochromic applications.

Upon irradiation with 365 nm light, a new absorption peak at 795 nm was observed in CH_2Cl_2

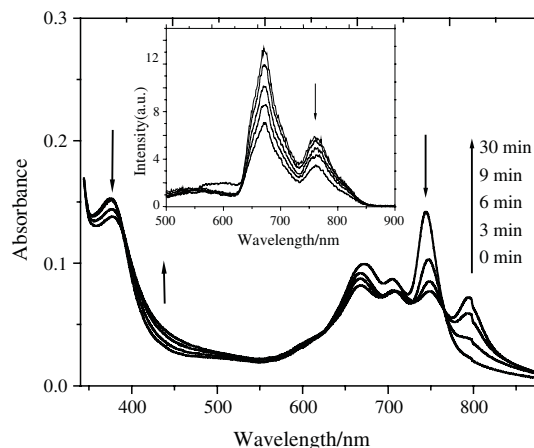


Figure 1. Absorption spectra of compound **IIIa** in CH_2Cl_2 ($\sim 2.0 \times 10^{-5} M$) and the spectral changes under different irradiation time by light of 365 nm. Insert figure: the emission spectral changes of **IIIa** in CH_2Cl_2 (excited at 480 nm) with different irradiation time by 365 nm.

[†]The experimental details, synthetic and spectroscopic data were available in supplementary information.

Table 1. The data of selective band absorption ($\lambda_{\max}^{\text{Ab}}/\text{nm}$) and photochromic quantum yields Φ of **III** in CH_2Cl_2 and in PC film

Compound	III (in CH_2Cl_2)	III (in PC film)
$\lambda_{\max}^{\text{Ab}}$ (open)	745, 705, 673	753, 711, 669
$\lambda_{\max}^{\text{Ab}}$ (closed)	795, 715	810, 741, 679
Φ for O→C	0.37	0.06
Φ for C→O	0.16	0.02

($\epsilon = 1.1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$). Irradiation with 365 nm light for 30 min, the system reached the photostationary state, and clear isobestic points were observed at 766, 626 and 389 nm, respectively. The blue solution label of the opening form turned to a green one of the closed form **IIIb**. The green solution changed back to the blue one easily by the irradiation with the light of 795 nm. The quantum yields of the photo-cyclization reaction of this compound were summarized in Table 1. It was also found that compound **III** exhibited an obvious photochromism in the polycarbonate (PC) film,[†] although the quantum yields were relatively low (less than 0.1). Compound **IIIa** in PC film has two Q absorption bands at 753 and 669 nm (red shifted than those in CH_2Cl_2). Upon irradiation with 365 nm light, the absorption of the two Q bands gradually decreased, and a new absorption band with a maximum at 810 nm appeared (shown in Table 1 and Supplementary Information).[†] The back conversion occurs on the irradiation of **IIIb** by light of 810 nm.

The fluorescence emission spectra of compound **III** were shown as the insert figure in Figure 1. The changes of the fluorescent intensity of **III** in CH_2Cl_2 can be observed when irradiation with 365 nm light. Compound **IIIa** displays significant fluorescence intensity at around 680 and 760 nm. Upon irradiation with 365 nm light, the closed-ring form **IIIb** was produced and the fluorescence intensity was reduced by nearly 50%. It is because that the nonfluorescent closed-ring forms were produced and the intramolecular energy transfer from the binuclear porphyrazine core to the ring-closed form of the BTE units quenches effectively the fluorescence of the porphyrazine.^{22b}

The photostationary state with the isobestic points was assigned the closed-ring form shown in Scheme 1, in which the cyclization of the bisthienylethene units occurs at the contrapositions of the binuclear porphyrazine (i.e., the crossing opposite of the binuclear porphyrazine). No any new deviation of isobestic points can be observed when we prolonged UV irradiation until the complete photodamage of compound **IIIa**. The very similar phenomena had been reported in Mitchell's bis-photochrome,^{24b} where two dihydropyrenes fused to a chrysene spacer, both the photochromes opened and closed. However, many bis- (or multi-) photochromes linked via a linear spacer or no spacer group reported previously by Branda^{24c} and Irie and co-workers^{24d,e} showed the stepwise cyclization reactions with multi-color photochromism or only one closed form intermediate O→C isomer generally. Prolonged irradiation resulted in irreversible destruction of the system by way of a rearranged side product. So they stated that it is possible that on irradiation of the O→C form with UV light,

the excited energy transfers within the molecule and this transfer prevents further cyclization. This explanation could be used for the binuclear porphyrazine synthesized here: the excitation energy transferring from the excited open-ring units to the closed-ring forms through the macrocycle is considered to suppress the further photo-cyclization of the isomer **IIIb**.

In fact, the results detected in this experiment for the photostationary state that the cyclization of the BTE units occurs at the contrapositions of this binuclear porphyrazine (i.e., the crossing opposite of the binuclear porphyrazine shown in Scheme 1) did not exclude the possibility of the stepwise cyclization reactions. This suggests that during the UV irradiation, the C→O intermediate with only one closed form of the bisthienylethene unit was formed first. Before UV irradiation, we firstly got the ¹H NMR spectrum of **IIIa** in CDCl_3 . Then irradiated the solution with 365 nm light for about 3 min, the three new methyl and one aromatic proton NMR peaks appeared at 2.13, 1.97, 1.84 and 10.63 ppm (aromatic proton), respectively. The new signals can be detected with the decreasing of the original peaks at 2.24, 2.07, 1.74 and 10.55 ppm. The three new singlet signals at 2.13, 1.97 and 1.84 ppm were assigned to the methyl protons of the closed-ring form of BTE. After subtracted for the integration of **IIIa** from the integration of the photo-stationary state, we got the ¹H NMR ratio between the peaks at 2.13 and 2.24 ppm, likewise the other two corresponding methyl proton peaks, is nearly 1:5. This is the evidence for the intermediate with only one BTE closed form in the NMR spectra, although there is insufficient large difference in the chemical shifts and experimental error. Irradiation more than 9 min on the system, the integrations of the three singlet signals at 2.13, 1.97 and 1.84 ppm increased and the ratio between the peaks at 2.13 and 2.24 ppm reached to 1:2. This NMR ratio maintained for a prolonged UV irradiation. By these evidences, we think that the closed-ring photostationary structure should be **IIIb** with the two BTE closed-ring forms shown in Scheme 1. Currently, we have not been able to separate the isomers by chromatography; however, we will pursue the search for good intermediate spectra in the future.

In conclusion, a new photochromic binuclear porphyrazine bearing six bis-(trimethylthiophenyl) units at the periphery has been prepared with a concise and simple way. This binuclear porphyrazine undergoes open-to-closed ring or closed-to-open ring photoisomerization in different quantum yields by the irradiation with 365 or 795 nm light. The near-IR luminescence changes of this binuclear porphyrazine can be regulated in a reversible manner by the photoisomerization of the bisthienylethene moiety, which would be useful for fluorescent probes and optical readout for erasable memory media.

Acknowledgements

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Supplementary data

The experimental details, synthetic and spectroscopic data are available in the Supplementary data with this article, in the online version, at [doi:10.1016/j.tetlet.2004.08.111](https://doi.org/10.1016/j.tetlet.2004.08.111).

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