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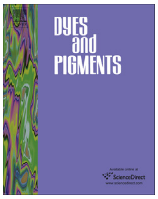

Binding porphyrins gated dithienylethene bridge

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ABSTRACT

Novel porphyrins strapped with photochromic dithienylethene have been developed for photochemical double-throw gated switch. Result shows the strapped porphyrins performed totally different but reversible binding capacity and fluorescence intensity when irradiated by different lights. On the one hand, the photochromism of the dithienylethene bridge is effectively gated by porphyrin ring through binding or unbinding Zn^{2+}. The central Zn^{2+} in the porphyrin ring is employed as a lock, external H^+ as a key, which can alternately turn on/off the photochromic switch of the dithienylethene bridge. On the other hand, the porphyrin's gate for binding/unbinding Zn^{2+} is reversibly regulated by dithienylethene switch with different irradiation lights. These distinctive properties might be utilized to multi-controlled molecular switches or logic gates.

1. Introduction

Photochromic dithienylethene derivatives (DTE) are known for the durable thermal stability and remarkable fatigue resistance derived from the low aromatic stabilization energy of the thiophene framework. Their versatile characteristics provide more desirable choices for various photocontrollable molecular switches and optical memory systems [1]. In view of this, plenty of multi-component systems, such as gated photochromic system, based dithienylethenes have been engineered in recent years. Gated photochromism is the property that the on/off photoactivity of a molecule is dependent on diverse external stimuli such as heat, coordination, chemical reactions, acidity or host–guest interaction [2]. Especially notable is the dithienylethene–porphyrin combination [3]. As we know, porphyrins are multi-responsive materials to multiple stimuli such as electricity, light, heat and chemicals [4]. They are convenient building blocks for various designs of functional molecules possessing novel architectures. Nowadays, porphyrin derivatives have been extensively used in a large number of photoinduced electron transfer system, molecular energy storage devices and optoelectronic switches including multicomponent molecules [5,6]. Recently, several examples of dithienylethene containing porphyrins have been reported for photoisomerization, complexing, nondestructive readout, long-distance mechanical communication, and so on [7,8]. These connection modes of the dithienylethenes and porphyrins involve mainly two types: one is coplanar or conjugated linkage to the periphery of porphyrin ring by covalent bonds [7]; the other is axial connection to the central metal ions of the porphyrin macrocycle via coordinate bonds [8]. These combinations showed appealing performances, but the π–π stack of the coplanar structure and relatively weak coordinate bonds between the metal and nonmetal might pose challenges for technological application. Given these factors, we now advance our understanding of the photo-chemical gated switch and present a kind of novel porphyrins strapped with photochromic dithienylethenes bridge, in which the photochromic dithienylethene unit was axially attached to meso-carbon of the porphyrin ring by covalent bonds, as shown in Chart 1. The synthetic procedures of the hybrid DTE-1, DTE-2 and their zinc complexes are shown in experimental section. Their structures were clearly confirmed by ^{1}H NMR, ^{13}C NMR, ^{1}H–^{1}H COSY, NOESY, HR-MS and MALDI-TOF. Their gated photochromic reactivity was investigated. Results show that the central Zn^{2+} in porphyrin ring alternately turned on/off the photochromic switch of the dithienylethene bridge through the gate of the porphyrin ring. Meanwhile, the porphyrin's gate for binding/unbinding Zn^{2+} was reversibly regulated by photochromic dithienylethene bridge through different irradiation lights.

2. Results and discussion

We first designed only one benzene as linker between the porphyrin ring and the dithienylethene bridge based on atom

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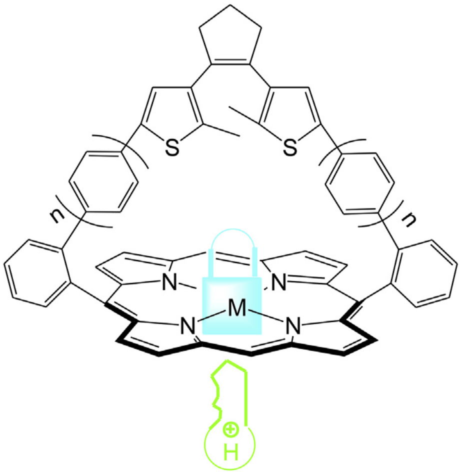


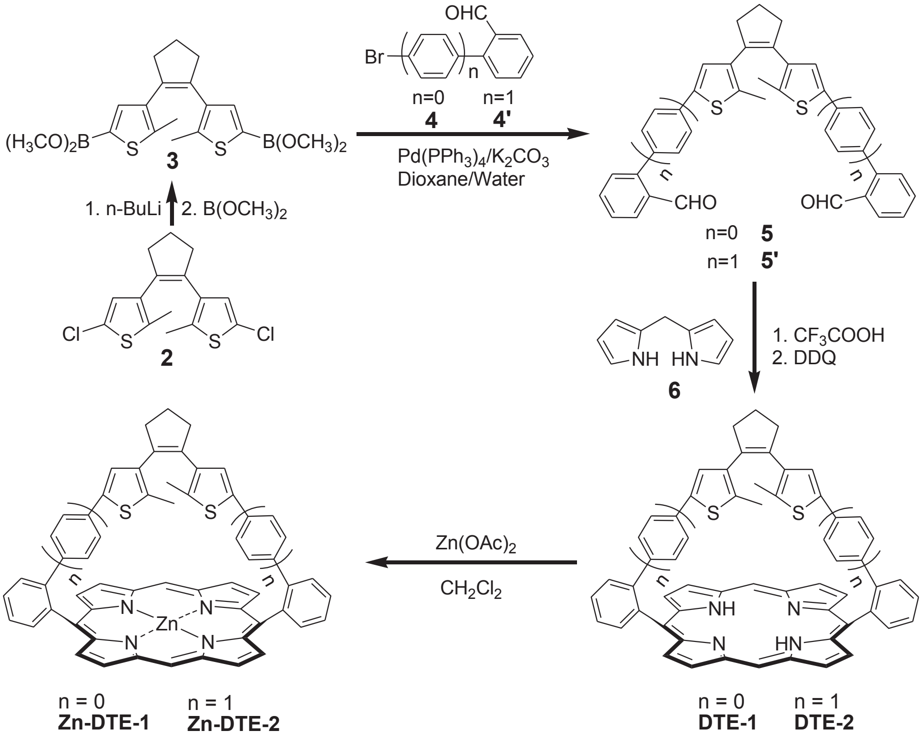
	n=0	n=1
M=2H	DTE-1	DTE-2
M=Zn	Zn-DTE-1	Zn-DTE-2

Chart 1. Structure schematic of the strapped porphyrins.

economy and successfully synthesized the hybrid *DTE-1* as the procedure shown in Scheme 1. However, when we tried to investigate the photochromic performance of *DTE-1*, we found it is hardly to detect any changes by ^{1}H NMR after photoirradiation, although there were some slightly differences in UV–vis spectroscopy. We think it might be because of the narrow space between the dithienylethene bridge and the porphyrin ring constraining the con-rotatory cyclization of the two thiophenes [7b]. Thus we increased the distance between the porphyrin and the dithienylehtene to two benzenes and further synthesized *DTE-2* by the similar method shown in Scheme 1.

The ^{1}H NMR spectra of the porphyrin-dithienylethene hybrid *DTE-2* contrasted with the precursor of dithienylethene **5′** are given in Fig. 1. It showed clearly the superposition of the dithienylethene and porphyrin as expected. Compared with the corresponding proton signals of dithienylethene **5′**, the four proton signals from *1-4* in hybrid *DTE-2* all dramatically moved to downfield owing to locating in the deshielding region of the porphyrin ring. However, chemical shifts of the proton *5–10* in *DTE-2* all underwent a remarkable upfield shift as a result of the shield effect of the macrocyclic porphyrin. These evidences clearly indicated that the dithienylethene bridge has been axially attached to the porphyrin ring as expected. Likewise, the proton signals of the hybrid *DTE-1* also displayed distinct downfield and upfield shifts due to the magnetic anisotropy of the porphyrin (Supporting Information, Fig. S1). The shifts of the proton signals in *DTE-1* were even more significant than those of *DTE-2*, because the distance between the dithienylethene bridge and the porphyrin in *DTE-1* was shorter than that of *DTE-2*, thus its corresponding protons in dithienylethene bridge suffered more strong shielding effect from the porphyrin ring.

Reversible photoisomerization between the open and closed form of *DTE-2* has been examined in CH_2Cl_2 (2.0×10^{-5} mol/L). Fig. 2 presented the changes in the absorption spectra of *DTE-2* upon photoirradiation. It featured the typical porphyrin Q-band in 450–650 nm and the Soret band at around 414 nm. When irradiated by 365 nm UV light, the band in the 250–300 nm region, which is mainly attributed to the open form of DTE unit [9], decreased gradually and the broad absorption band at about 550–650 nm increased due to the formation of closed form of DTE moiety. There was a clear isosbestic point at 422 nm, which indicated that the photoisomerization is a monomolecular procedure in which only two isomers generate [10]. While the absorbance of the DTE unit changed by irradiation, the Soret band at 414 nm of porphyrin unit decreased and slightly red-shifted, which is



Scheme 1. The synthetic procedures for the hybrid DTE-1, DTE-2 and their zinc complexes.