



Construction and optical properties of dithienylethene-based photoswitchable [n]rotaxane (n = 2, 3)



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ABSTRACT

Mechanically interlocked structures such as rotaxanes and catenanes provide a novel backbone for constructing functional materials with unique structural characteristics. In this study, the novel photo-switchable [n]rotaxanes **11** and **12** based on dithienylethene unit were efficiently synthesized by the classical template-directed clipping approach. And their structures were well-confirmed by NMR, MS and elemental analysis. Investigation on photochromic properties indicated that dithienylethene-based [n]rotaxanes had good reversibility and excellent fatigue resistance upon irradiation with UV or visible light. And they displayed also excellent fluorescence switchable behavior. Interestingly, It was found that [2]rotaxane **11** had better photoisomerization properties in comparison to its corresponding macrocycle **4**, which indicated that the non-covalent components on the [2]rotaxane **11** could influence the photo-switching properties. Furthermore, the mechanically interlocked molecules containing two dithienylethene backbones displayed around a 2-fold increase in the molar absorption coefficient compared with that of the mono dithienylethene derivative, which was consistent with the reported [n]rotaxane **9** and **10**.

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1. Introduction

In recent years, research on the mechanically interlocked molecules (MIMs), such as rotaxanes and catenanes, have been widely developed due to not only their topological importance but also potential applications in molecular devices and as components of molecular machinery [1–9]. Rotaxanes, topologically unique structures consisting of a dumbbell shaped molecule which is threaded through a macrocycle, have captured the increasing attention since it was reported in 1967 [10]. Recently, there have been a large number of rotaxanes synthesized by multifarious approaches such as capping, clipping, slipping, active templates, and others [11–13]. In the clipping method, a dumbbell shaped component recognizes and binds the macrocyclic precursors and

simultaneously templates the formation of the macrocycles around recognition sites. In 2001, Stoddart's group firstly reported efficient synthesis of [2]rotaxanes by clipping two components of a 24-crown-8 heterocrown ether, the 2, 6-pyridinedicarboxaldehyde **1** and the tetraethylene glycol bis(2-aminophenyl)ether **2**, onto dumbbell-shaped molecules containing dialkylammonium **5** [14], as shown in Scheme 1. Subsequently, the same clipping approach was also adopted by Yin and coworkers, the dumbbell-shaped molecules **6** with two ammonium moieties was utilized to construct [3]rotaxane [15]. However, the rapid development of rotaxanes has promoted the understanding of design strategies and functionalization of synthetic supramolecular systems.

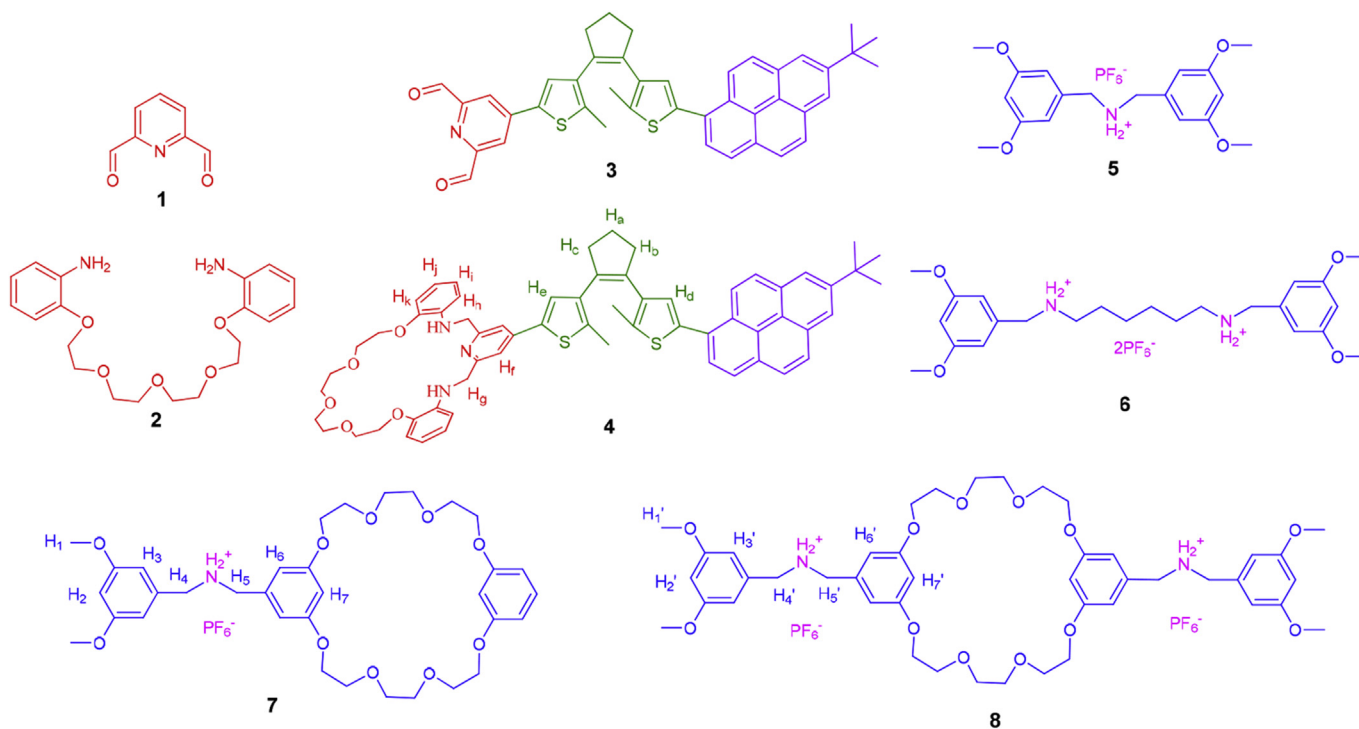
Photochromic dithienylethene compounds have attracted significant attention due to their potential application for photonics devices, such as optical memory media and photo-optical switches by virtue of their excellent thermally irreversible properties, high photoisomerization quantum yields, and remarkable fatigue resistance [16–23]. At present, synthetic MIMs based on the dithienylethene unit have attracted some attention [24]. For example, Tian et al. reported a multi-state [2]rotaxane based on dithienylethene unit which could alter intercomponent interactions in a

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Scheme 1. Chemical structures of intermediates 1–8.

photochromic multi-state [2]rotaxane [25]. Subsequently, Liu and co-workers reported a [2]pseudorotaxane formed from an unsymmetrical diarylperfluorocyclopentene and a Eu^{3+} complex of terpyridinyl-dibenzo-24-crown-8, which revealed dual-stimulus luminescent lanthanide molecular switching behavior modulated by host-guest interaction and optical stimuli [26]. Recently, we found that the mechanical interaction can adjust the photoisomerization behavior of photochromic dithienylethenes when crown ethers or cucurbituril were threaded into the dithienylethenes to form the corresponding rotaxanes or pseudorotaxanes [27,28]. However, we still know very little about these compounds, especially in the field of photoswitchable mechanically interlocked molecules. Recently, our group replaced 2, 6-pyridinedicarboxaldehyde **1** with the dithienylethene-functionalized 2, 6-pyridinedicarboxaldehyde **3** to realize self-assembly around the ammonium salts **5** and **6** by the clipping approach to construct two novel [2]rotaxane **9** and [3]rotaxane **10** [29], as shown in Scheme S1. And it was found that [3]rotaxane **10** containing two dithienylethene backbones display around a 2-fold increase in the molar absorption coefficient compared with that of the mono dithienylethene derivative **9**. This was an interesting finding that some photochromic signal could integrate well without any interrelationship among two components bridged by noncovalent hydrogen bond. So it will inspire us to investigate this system further. In 2013, our group reported two types of dual-functional molecules **7** and **8** which are composed of crown ether and ammonium building blocks [6]. Herein, we designed and synthesized the novel [n] rotaxanes **11** and **12** based on dithienylethene unit by the clipping reaction of the dithienylethene-functionalized 2, 6-pyridinedicarboxaldehyde **3**, the tetraethylene glycol bis(2-aminophenyl) ether **2** and dual-functional building blocks **7**, **8**, as shown in Scheme 2, and to investigate their photochromic properties in this photoswitchable rotaxane systems. Their structures have been characterized and their photoisomerization and emission behaviors are investigated.

2. Experimental section

2.1. Materials and general methods

All reactions and assembly processes were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. CH_3CN and CH_2Cl_2 was dried with calcium hydride and then distilled. Dithienylethene-functionalized 2, 6-pyridinedicarboxaldehyde **3** was synthesized following the previously reported method [29]. All other starting materials were obtained commercially as analytical grade and used without further purification. ^1H and ^{13}C NMR spectra were collected on American Varian Mercury Plus spectrometer (400 MHz). ^1H and ^{13}C NMR chemical shifts are relative to TMS. Mass spectra were measured in the MALDI mode. Mass spectra were recorded on the Bruker ultrafleXtreme (II) MALDI-TOF spectrometer. Elemental analyses (C, H, N) were performed by the Microanalytical Services, College of Chemistry, CCNU. UV-Vis spectra were obtained on U-3310 UV Spectrophotometer. And fluorescence spectra were obtained on a Hitachi Model F-4500 fluorescent spectrophotometer. In the photoisomerization reaction, UV light irradiation (254 nm) was carried out using a ZF5UV lamp, and visible light was irradiated using a LZG 220 V 500 W tungsten lamp ($\lambda > 402$ nm) with cut-off filters.

2.2. Synthesis of photoswitchable [2]rotaxane **11**

A solution of **3** (130 mg, 0.2 mmol), the dialkylammonium **7** (155 mg, 0.2 mmol) and tetraethyleneglycol bis(2-aminophenyl) ether **2** (75 mg, 0.2 mmol) in dry CH_3CN (20 mL) and dichloromethane (6 mL) was stirred for 5 days at room temperature under an argon atmosphere. Then $\text{BH}_3 \cdot \text{THF}$ (1.6 mL, 1.0 M) was added and the solution was further stirred overnight. The solvents were removed under vacuum and the residue was purified by column chromatography (silica gel, $\text{DCM}/\text{MeCN}/\text{MeOH} = 100:0:0-75:25:1$) to obtain photoswitchable [2]rotaxane **11** as a brown solid, yield

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