



A new thermo- and photo-driven [2]rotaxane

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ARTICLE INFO

Article history:

Received 17 October 2008

Revised 20 November 2008

Accepted 21 November 2008

Available online 27 November 2008

ABSTRACT

A new rotaxane with functional chromophores porphyrin and fluorene as stoppers has been synthesized. It displays dual fluorescent character. The macrocycle ring can shuttle between the fumaramide part and the succinimide part on the dumbbell. Heating and UV light irradiating on the rotaxane lead to the reversible *E/Z* conversion, driving the ring to shuttle between the two stations. The optical properties of porphyrin and fluorene stoppers of the thread do not change so much while the ring shuttles because the macrocycle does not interact with the two stoppers. However, the active group, propargyloxy, is introduced onto the two sides of the ring so that the rotaxane has the potential to be functionalized by further decoration.

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Switchable rotaxanes^{1,2} have attracted more attention because of their ability to experience the relative movements of their ring and dumbbell components in response to external stimuli, such as pH, redox change, and light. After several years of development, there are many different rotaxane systems nowadays.³ As technology and methodology of synthesizing and characterizing of rotaxane develop, it becomes convenient to achieve our goal to obtain controllable and functional rotaxanes, leading to the possible use of rotaxanes as new type of materials.⁴ To control the shuttling of the ring, the rod of rotaxane needs to have the ability to converse the structure of the station reversibly, such as isomerization of the double bond or gaining and losing of an electron.⁵ On the other hand, functional groups with extraordinary properties should be contained on either thread or macrocycle of the rotaxane to get the functional rotaxanes.⁶ The ring is an ideal carrier because it is movable and can be easily decorated.⁷ If the ring of rotaxane is appended with fragments that can apparently affect the optical or electrical characteristics of the thread, its controllable shuttling will lead to reversible changes of the property of rotaxane. This process has the potential use in areas such as molecular switch and the device for logical gate.^{8,9} On the basis of this purpose, we designed the structure as follows; Two fluorescent groups, porphyrin and fluorene were used as stoppers at the two sides of the dumbbell. There are two stations, fumaramide and succinimide on the thread, while the double bond of fumaramide station can undergo the process of photo-isomerization; Two symmetrical reactive points, like alkyne, are sited on the ring of the rotaxane, waiting for further decoration. Such molecular design has the potential characters as follows: Firstly, it is able to shuttle. The isomerization of the double bond of fumaramide station

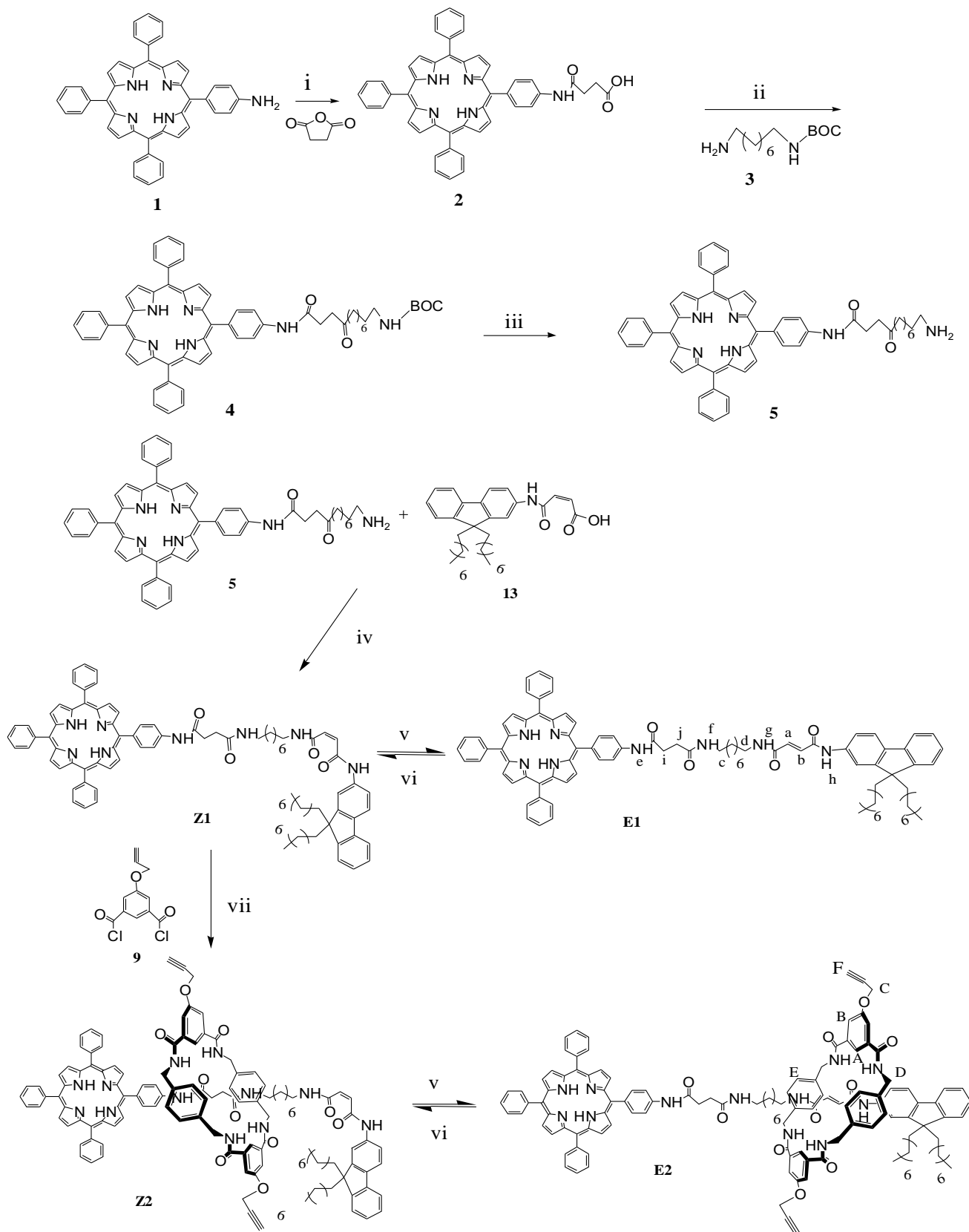
can drive the ring shuttling on the thread. Secondly, it is functional. It displayed the fluorescent output of porphyrin and fluorene. Moreover, we can introduce different kinds of compounds by reactions, such as 'Click' and 'Sonogashira coupling', with the active alkyne groups appended on the ring, so as to affect the optical properties of porphyrin and fluorene on the thread. Lastly, the symmetrical two alkyne groups on the ring can undergo polymerization.

The synthesis of the thread is shown as Scheme 1. 5-(4-Aminophenyl)-10,15,20-triphenyl-porphyrin **1** reacts with succinic anhydride to obtain the succinic derivative **2**. The derivative **2** could be coupled with (8-amine-oxal)-carbamic acid *tert*-butyl ester **3**, using EDCI/DMAP. After deprotection, the *tert*-butyl ester is transformed to a free amine which then couples with fluorene appended fumaric acid **13** using EDCI/DMAP couple to yield the target thread. The double bond of the fumaramide part is now at its *Z* form,¹⁰ so it is marked as **Z1**.

The rotaxane was assembled by slow addition of isophthaloyl-chloride and *p*-xylylenediamine in the presence of NEt₃ (Scheme 1). After the reaction, the target rotaxane **Z2** was obtained by flash chromatography, and the unreacted thread was also recycled. As the double bond of fumarimide part was at its *Z* form, this structure was not profitable to form hydrogen bond with the ring.^{11,12} So the ring of the rotaxane **Z2** overrides on the succinimide part, and is near the porphyrin part while far away from the fluorene part. The HRMS spectra show the peaks at 1983 and 1341, referring to rotaxane **Z2** and the decomposed thread (Fig. S3).¹³

The driven process of the rotaxane was shown in Scheme 1. First of all, after heating to 400 K, the thread **Z1** converts to its *E* form, which is marked as **E1**. HPLC analysis shows that there is about 50% of **Z1** converted to **E1** (Fig. S1a),¹³ and pure **E1** can be obtained easily by flash chromatography. After irradiation of **E1** at 254 nm, it will convert back to **Z1** partially.¹⁵ So the process of

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Scheme 1. Synthesis of bistable rotaxanes **Z2** and **E2**. Reagents and conditions: (i) $\text{CHCl}_3/\text{Et}_3\text{N}$, room temperature, 95%; (ii) DMAP, EDCl, CHCl_3 , 0°C , 65%; (iii) trifluoroacetic acid, CH_2Cl_2 , room temperature, 99%; (iv) DMAP, EDCl, CHCl_3 , 0°C , 35%; (v) 1,1,2,2-tetra-chloride ethylene, 400 K, 50%; (vi) CH_2Cl_2 , 254 nm, 30%; (vii) *para*-xylenediamine, $\text{Et}_3\text{N}/\text{CHCl}_3$, 0°C , 8%; DMAP = 4-dimethylaminopyridine, EDCl = 1-(3-dimethylaminopropyl)-3-ethyl-carbodiimide hydrochloride, Boc = *tert*-butoxycarbonyl.

the reversible control of the thread has been achieved. Then we studied the same procedure of rotaxane. HPLC showed that the

converting ratio from **Z2** to **E2** after heating to 400 K was about 51% (Fig. S1b).¹³ After purification, the structure of **E2** was con-

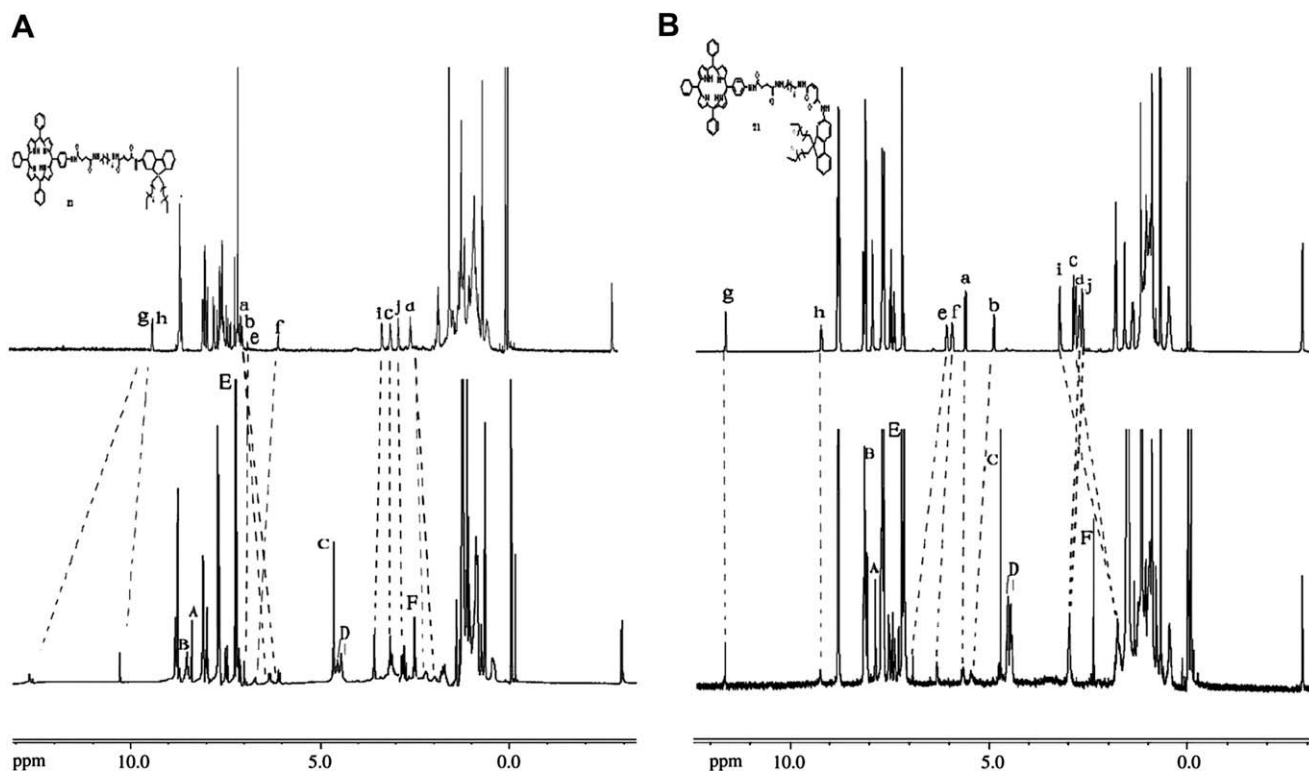


Figure 1. ^1H NMR (400 MHz) of (A), thread **E1** (up), rotaxane **E2** (bottom) in CDCl_3 , (B), thread **Z1** (up), rotaxane **Z2** (bottom) in CDCl_3 .

firmed by ^1H NMR. The *E* form of fumarimide part of the thread is more suitable to form the hydrogen bonds with the ring,^{11,12} so the ring shuttles from the porphyrin side to the fluorene side.

Comparison of the ^1H NMR of rotaxane **E2** (Fig. 1A, bottom) and **Z2** (Fig. 1B, bottom) with their thread **E1** and **Z1**, respectively, shows us the ring's location on the thread. The ^1H NMR spectra of rotaxane **Z2** in CDCl_3 shows an upfield shift of the protons on the succinimide part compared with the one of **Z1**, from 3.30 and 2.70 ppm to 1.90 and 1.88 ppm, respectively (Fig. 1B, Hi, and Hj). This effect was observed because of the shielding of the benzyl aromatic rings on the macrocycle over the thread.¹⁴ A shift of the amide protons near succinimide moiety to the aromatic region was observed on the spectrum of rotaxane **Z2** in CDCl_3 compared with **Z1**, from 6.10 and 5.95 ppm to 7.00 and 6.58 ppm correspondingly (Fig. 1B, He, and Hf). This is caused by hydrogen bond with ring.¹³ Meanwhile, signals of Ha, Hb, Hg, and Hh, which associated with fumaramide part did not change obviously. These effects proved that the macrocycle of rotaxane **Z2** is laid on the succinimide template. On the other hand, the ^1H NMR changing between **E1** and **E2** are just opposite to the one described above. The ^1H NMR spectrum of rotaxane **E2** in CDCl_3 shows an upfield shift of the protons on the fumaramide double bond, from 7.15 and 7.22 ppm to 6.08 and 6.35 ppm, respectively (Fig. 1A, Ha, and Hb); A downfield shifting of the amide protons near fumaramide part was observed, comparing ^1H NMR of **E2** with that of **E1**, from 9.58 and 9.60 ppm to 10.25 and 12.65 ppm (Fig. 1A, Hg, and Hh). The ^1H NMR signals referring to protons of succinimide part did not change remarkably. These effects confirm that the macrocycle of rotaxane **E2** overrides on the fumaramide template.¹³

It shows no difference among the absorption and fluorescent spectrums of rotaxane **Z2**, **E2** and their threads **Z1**, **E1** in CH_2Cl_2 . The absorption spectrum shows the superposition of fluorene and porphyrin spectra (Fig. S2a). The absorption band around 250 nm and 350 nm are attributed to fluorene moiety, and the

sharp absorption at 418 nm is attributed to the Soret-band absorption of porphyrin moiety. From 500 nm to 650 nm, there are four weak peaks which can be assigned to the Q-band absorptions of porphyrin. Excited at 250 nm in CH_2Cl_2 , both rotaxanes and their threads displayed the fluorescence of fluorene and porphyrin moieties, at 350 nm and 650 nm, respectively (Fig. S2b).

In summary, a new rotaxane with dual fluorescence contributed from porphyrin and fluorene stoppers was assembled by hydrogen bonding, utilizing succinimide and fumaramide as templates. Heat and UV-light can drive the ring to shuttle between two stations on the thread. The optical properties of porphyrin and fluorene stoppers of the thread do not change so much while the ring shuttles. However, the active propargyloxy on the ring makes the rotaxane have the potential to couple with groups that can impact the optical properties of porphyrin or fluorene moieties of the rotaxane, a crucial step to establish the functional rotaxane system with dual input and dual fluorescent output. This work is now on the way.

Acknowledgments

This work was supported by the NSFC/China, National Basic Research 973 Program (2006CB806200), and Scientific Committee of Shanghai.

Supplementary data

Supplementary data (experimental procedure and characterization for all intermediates and compounds, ^1H NMR spectra of all compounds, MALDI-TOF spectra of key intermediates and UV-vis absorption spectra of compounds **E2** and **Z2**, HPLC spectra of **E1**, **Z1**, **E2**, and **Z2**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.11.080.

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- See the [Supplementary data](#).
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- The general experiments of converting procedures of thread and rotaxane can be found in [Supplementary data](#).