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Synthesis of new [2]rotaxane including a macrocyclic receptor and a photochromic unit

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Abstract

The novel photochromic [2]rotaxane based on chromene molecule introduced into a crown-containing macrocyclic receptor was synthesized. The photochemical properties of rotaxane could be modified by the complexation of the crown ether moiety.

Keywords: [2]Rotaxane; Chromene; Naphthopyran; Crown ether

The design and the synthesis of organic molecular materials in which structure and macroscopic properties can be controlled by external triggers, are of major importance in emerging optoelectronic and nanotechnologies.[1] In this context, the photochromic crown compounds which combine properties of ion-selective binding and photo-induced switching are of particular interest.[2] Furthermore, a number of crown-containing [2]rotaxanes with salt-binding properties were developed.[3] The incorporation of a photochromic unit into such molecule can allow control of its dynamics by color changing because of metal cations and anions binding. In the present work, we report a convenient synthetic approach to introduce chromene molecules into crown-containing macrocyclic receptor with a formation of [2]rotaxane possessing photochromic metal-ion sensitive properties.

The aim of the present study is a rotaxane including chromene and crown units: the motions of such system have good perspectives to be controlled by metallocomplexation between crown ether and the merocyanine form of a chromene under the light irradiation (Fig. 1). The

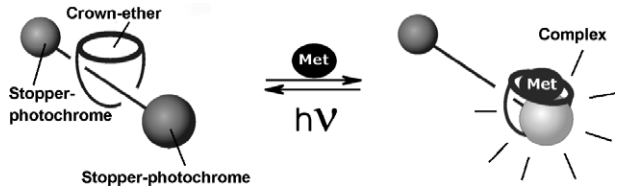

Fig. 1. New rotaxane which can be controlled by metallocomplexation.

new targeted [2]rotaxane system consists of a binaphthopyran light-sensitive axle **1** and the macrocyclic receptor **2**[3] (Scheme 1), the last one was synthesized by Smith and co-workers. The constituents of both units are rather convenient starting materials for the synthesis. 18-Dibenzo-crown-6 ether is a reasonable price compound; hydroxynaphthopyrans can be easily obtained[4] through the condensation of commercially available 1,1-diphenyl-propyn-1-ol with hydroxynaphthalene.

Computer modeling was used to predict the conformation of the receptor-wheels and the chromene-axles. It demonstrated that the dimensions of the stoppers efficiently prevent the axles to escape from the wheels and at the same time they are suitable to allow a complexation. Modeling study was realized with Ampac 8.15 using semi-empirical AM1 force field[5] (Fig. 2).

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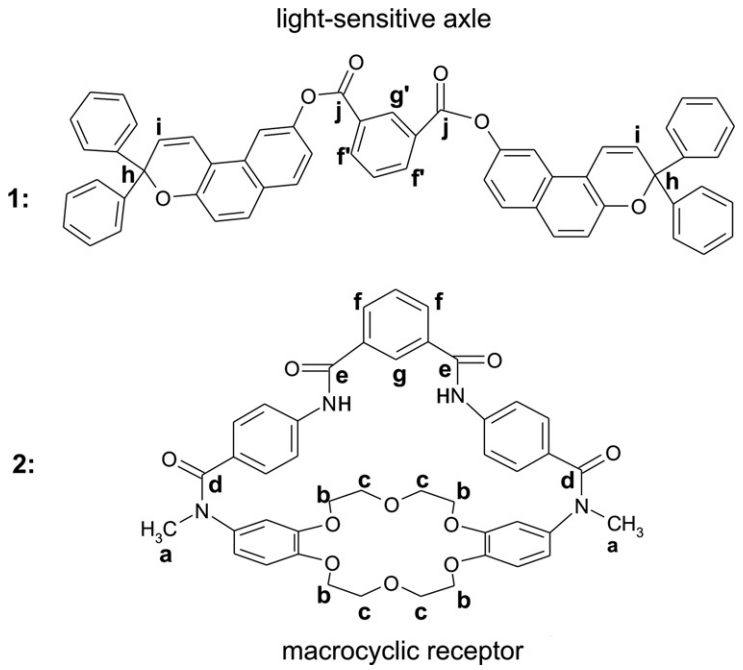


Scheme 1. Structures of the light-sensitive axle **1** and the macrocyclic receptor **2**.

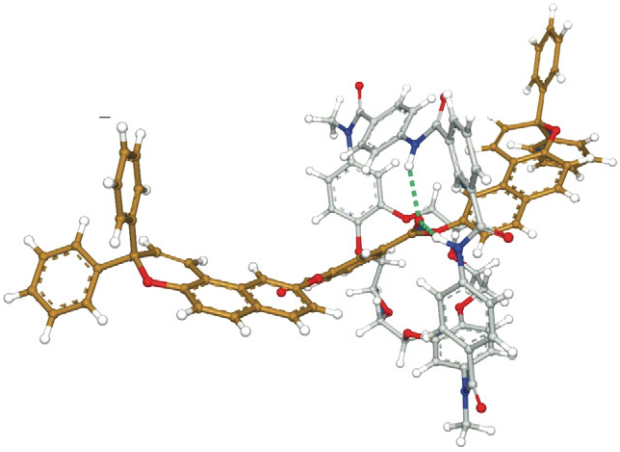
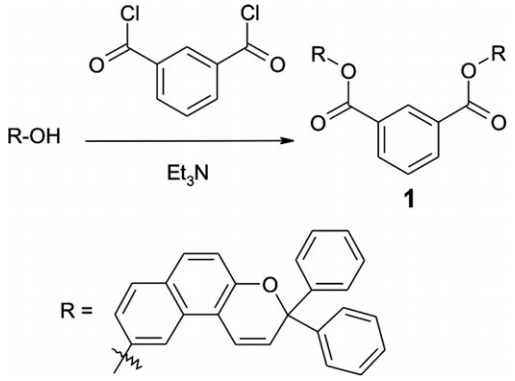


Fig. 2. Modeled conformation of rotaxane **3**.



Scheme 2. Synthesis of binaphthopyran unit **1**.

At the beginning of our study, the synthesis of free chromene-axle was accomplished to confirm its photochemical properties. Binaphthopyran unit **1** was obtained[6] by the condensation of 3,3-diphenyl-9-hydroxy-3*H*-naphtho[2,1-*b*]-pyran with isophthaloyl dichloride (Scheme 2) in 98% yield.

The novel compound showed absorbance in the UV spectra region but it was transparent in the visible spectra region (Fig. 3). After the irradiation of UV light[7] during

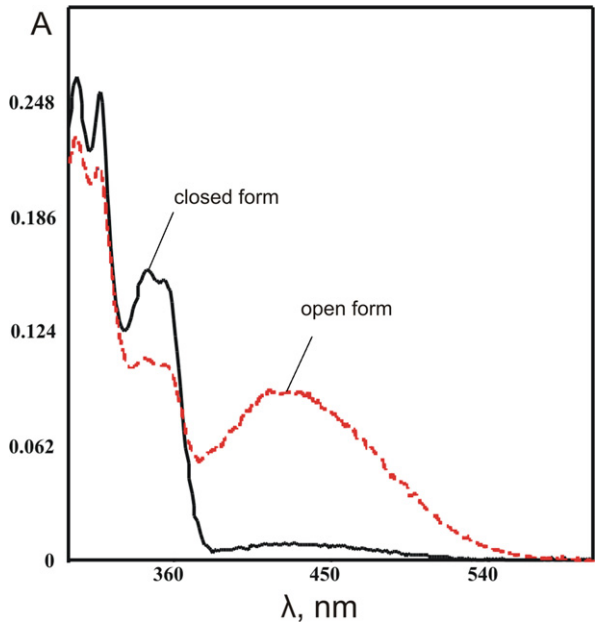


Fig. 3. Absorption spectra of **1** (acetonitrile solutions, $C = 0.84 \times 10^{-5}$ M) under dark condition (closed form) and after UV-irradiation during 1 min (open form.)