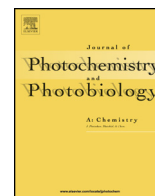




Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Syntheses and stimuli-responsive rocking motions of a rotaxane bearing different stoppers

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ARTICLE INFO

Article history:

Received 4 September 2015
Received in revised form 13 November 2015
Accepted 15 November 2015
Available online xxx

This paper was dedicated to Prof. Yoshihisa Inoue on the occasion of his retirement for his pronounced contribution to the field of photochemistry.

Keywords:

Photocycloaddition
Molecular switch
Rocking dynamics
Molecular machines
Rotaxanes
Crown compounds

ABSTRACT

A rotaxane composed of a ring molecule having a metaphenylene unit, which swings as a pendulum, and a dianthrylethane unit, which undergoes isomerization in response to external stimuli, and an axle molecule with two different stopper units was synthesized. The rates of the rocking motion, which were switched reversibly, changed substantially by changing the size of the ring component in response to photo- and thermal-stimuli.

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1. Introduction

The potential of mechanically interlocked molecules for nanoscale devices has involved intensive researches [1–5]. These devices exploit the unique relative motions of molecular components such as shuttling, circumrotation, and rocking [6–9]. Among them, control of shuttling motion has been studied most intensively, with the ultimate goal of implementing such systems in molecular electronic devices. Previously, we reported a rotaxane whose rate of shuttling motion was reduced to less than 1% by contracting the size of the ring component by photoirradiation [10]. In addition, the size of the ring component was transformed back to the original size by thermal ring opening, thus establishing a reversible and effective brake function that works in response to photochemical and thermal stimuli without producing chemical wastes. Moreover, we showed that a rocking rotaxane possessing a meta-phenylene unit in the ring component as a pendulum moiety exhibited fast rocking motion in its open form (Scheme 1, **A2@Ro**), whereas in its closed form (**A2@Rc**) generated by photochemical cycloaddition the rocking rate was reduced considerably (<0.1%)

[11]. In line with our previous findings, we report here the syntheses of a pair of rotaxanes **A3@Ro** /**A3@Rc** having different stopper groups at each end of the axle [12,13] and effective switching of the rocking rates by closing/opening of the ring unit in response to photo- and thermal-stimuli. In rotaxanes **A3@Ro** /**A3@Rc**, with a prospect for immobilization of the rotaxane on a gold surface [12], one of the stopper groups is a bulky triaryl-methane-based substituent with three thioacetate group.

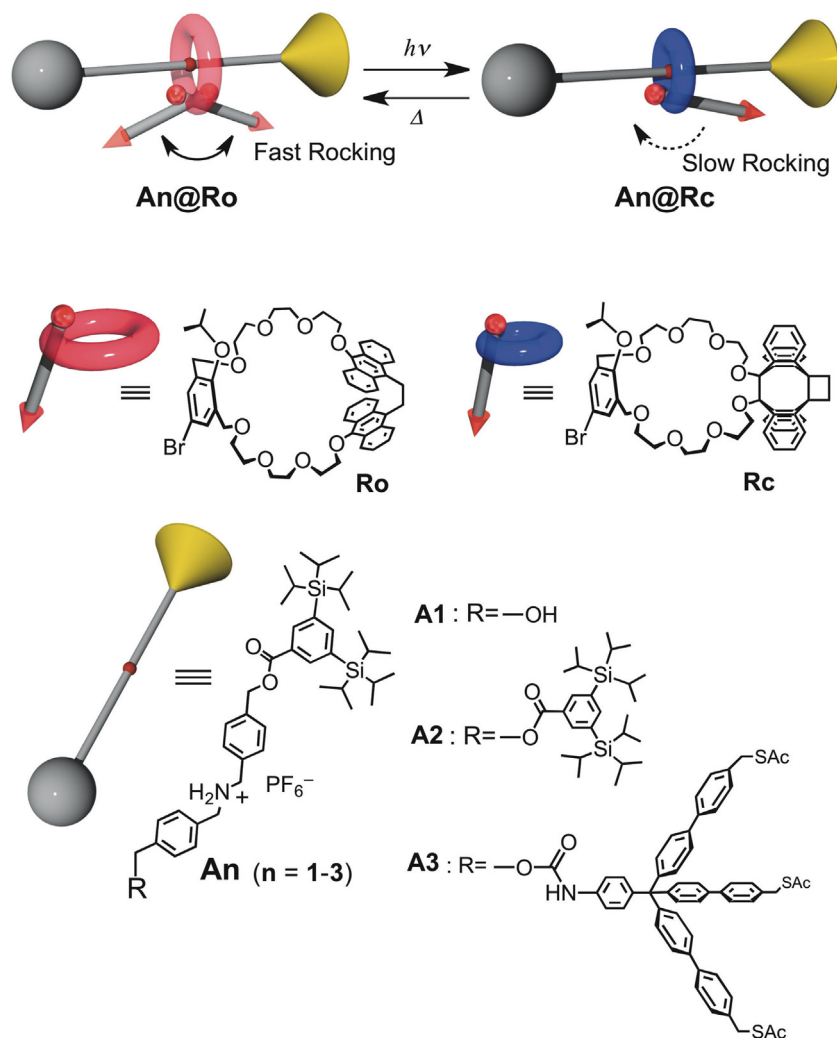
2. Experimental

2.1. Materials and measurements

For synthetic runs, dichloromethane, tetrahydrofuran, and diethyl ether were dried by a Glass Contour solvent purification system. Acetonitrile was distilled prior to use. For analytical runs, spectrophotomeric-grade acetonitrile, dichloromethane, diethyl ether, and tetrahydrofuran were used as received without further purification.

¹H NMR (400 MHz) and ¹³C NMR (100 MHz) measurements were performed in CDCl₃ at 30 °C unless otherwise stated. The chemical shifts of ¹H NMR and ¹³C NMR signals are quoted relative to internal CHCl₃ (δ = 7.26 and 77.0) or tetramethylsilane. IR spectra

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Scheme 1. Switching of rocking rates of rotaxanes based on change in size of the ring components.

were recorded as a KBr disk or a neat film. UV-vis spectra were recorded in acetonitrile. Preparative HPLC separation was undertaken with a JAI LC-908 chromatograph by using 600 mm \times 20 mm JAIGEL-1H and 2H GPC columns with CHCl_3 as an eluent.

2.2. Synthetic procedures and characterizations

2.2.1. Bis(4-hydroxymethylbenzyl)amine (**1**)

This compound was obtained from bis(4-carbomethoxybenzyl)amine according to the literature procedure [11,13,14].

2.2.2. N-(tert-Butoxycarbonyl) bis(4-hydroxymethylbenzyl)amine (**2**)

This compound was obtained from **1** according to the literature procedure [13].

2.2.3. Syntheses of axle **A1**: method (a)

2.2.3.1. Synthesis of 3. **2** (44.5 mg, 125 μmol), 3,5-bis(triisopropylsilyl)benzoic anhydride [14]. (104 mg, 122 μmol), DMAP (2.50 mg, 20.5 μmol), Et_3N (26.0 μL , 18.9 mg, 187 μmol), and CH_2Cl_2 (3 mL) were placed in a 20 mL two-necked flask under nitrogen. The mixture was stirred for 16 h after which time the solvent was removed under reduced pressure. The resulting crude product was subjected to column chromatography (silica gel;

hexane/EtOAc (4:1)) and then preparative HPLC to give **3** as a colorless oil (62.8 mg, 66%) which solidified upon standing. ^1H NMR (400 MHz, CDCl_3 , 30 $^\circ\text{C}$) δ 8.20 (d, $J = 1.1$ Hz, 2H), 7.83 (t, $J = 1.1$ Hz, 1H), 7.83 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 8.2$ Hz, 2H), 7.21 (br s, 4H), 5.38 (s, 2H), 4.68 (d, $J = 5.4$ Hz, 2H), 4.47–4.23 (br m, 4H), 1.72 (t, $J = 5.4$ Hz, 1H), 1.49 (s, 9H), 1.43 (sept, $J = 7.4$ Hz, 6H), 1.08 (d, $J = 7.4$ Hz, 36H); ^{13}C NMR (100 MHz, CDCl_3 , 30 $^\circ\text{C}$) δ 167.2, 156.0, 147.0, 140.0, 137.9, 137.4, 136.5, 135.6, 134.1, 128.2, 127.9, 127.65, 127.24, 80.2, 66.04, 65.1, 49.0, 28.4, 18.5, 10.8; IR(KBr) 3439, 2944, 2890, 2866, 1723, 1697, 1462, 1411, 1365, 1269, 1164, 1131, 882, 677, 645 cm^{-1} ; MS (ESI) m/z 797 ($\text{M} + \text{Na}^+$). Anal. Calcd. for $\text{C}_{46}\text{H}_{71}\text{NO}_5\text{Si}_2$: C, 71.36; H, 9.24; N, 1.81. Found: C, 71.30; H, 9.25; N, 1.87.

2.2.3.2. Synthesis of 4. Under an atmosphere of nitrogen, trifluoroacetic acid (11.5 mL, 17.7 g, 155 mmol) was added to a solution of **3** (1.00 g, 1.29 mmol) in CH_2Cl_2 (40 mL). After the reaction mixture was stirred at ambient temperature for 14 h, it was diluted with CH_2Cl_2 (200 mL), washed with 1 M aqueous NaHCO_3 (20 mL) twice and then with brine. The organic layer was dried (MgSO_4) and concentrated under reduced pressure. The crude product was subjected to column chromatography (silica gel; $\text{CHCl}_3/\text{EtOH}$ (95:5–3:1)) to give **4** as a colorless oil (777 mg, 90%) which solidified upon standing. ^1H NMR (300 MHz, CDCl_3 ,

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