Chemistry
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Accepted Article

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To be cited as: *Chem. Eur. J.* 10.1002/chem.202004505

Link to VoR: https://doi.org/10.1002/chem.202004505

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10.1002/chem.202004505

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Cyclodextrin-Based [c2]Daisy Chain Rotaxane Insulating Two Diarylacetylene Cores

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Abstract: A [c2]daisy chain rotaxane with two diarylacetylene cores was efficiently synthesized in 53% yield by capping a C2-symmetric pseudo[2]rotaxane composed of two diarylacetylene-substituted permethylated α-cyclodextrins (PM α-CDs) with aniline stoppers. The maximum absorption wavelength of the [c2]daisy chain rotaxane remained almost unchanged in various solvents, unlike that of the stoppered monomer, indicating that the two independent diarylacetylene cores were insulated from the external environment by the PM α-CDs. Furthermore, the [c2]daisy chain rotaxane exhibited fluorescence emission derived from both diarylacetylene monomers and the excimer, which implies that the [c2]daisy chain structure can undergo contraction and extension. This is the first demonstration of a system in which excimer formation between two π-conjugated molecules within an isolated space can be controlled by the unique motion of a [c2]daisy chain rotaxane.

π-Conjugated hydrocarbons have attractive optical and electronic properties that can be exploited for the development of light-emitting and electronic devices.[1] Several π-conjugated hydrocarbons (e.g., pyrene, perylene, and diarylacetylene derivatives) form excimers in solution and in the solid state.[2–4] The emission of such excimers is often shifted to a longer wavelength than the intrinsic monomer emission owing to the *H*- and *J*-aggregation of multiple π-conjugated hydrocarbon molecules. Insulating the two identical molecules involved in excimer formation from other molecules and/or the external environment allows the essential properties of the excimer to be investigated in detail, which will lead to the development of new functional molecules.

In pioneering studies by Inouye and colleagues, two perylene (or pyrene) cores were successfully insulated in the cavities of two γ-cyclodextrins (γ-CDs), cyclic oligosaccharides consisting of eight α-D-glucopyranoses, using a simple rotaxane strategy (Figure 1a). The resulting spatially restricted excimers were found to emit strong circularly polarized luminescence.[5] However, the desired [4]rotaxane was obtained in very low yield. Therefore, a new strategy is required for the efficient production of functional molecules that can generate spatially restricted excimers.

Several research groups have previously developed synthetic methods for [c2]daisy chain rotaxanes,[6–8] wherein two subunits bearing both axle and ring components are associated by threading each axle through the other ring to form a pseudo[2]rotaxane that is mechanically interlocked by capping with bulky terminal groups (Figure 1b). This strategy is efficient for symmetric pseudo[2]rotaxane formation because the host–guest interactions between the two subunits are doubled, as each unit includes both host (ring) and guest (axle) moieties. Kaneda's group synthesized a C2-symmetric [2]rotaxane (which they called a Janus [2]rotaxane) in high yield using lipophilic azobenzene-substituted permethylated α-cyclodextrin (PM α-CD) derivatives that were also soluble in aqueous solutions.[6a] Therefore, this strategy is suitable for creating a supramolecular architecture that can insulate two identical π-conjugated hydrocarbon cores.[9] Herein, we prepared a [c2]daisy chain rotaxane insulating two diarylacetylene cores using a PM α-CD bearing a diarylacetylene moiety. Furthermore, the physical properties of the obtained rotaxane were investigated using UV-Vis absorption and fluorescence measurements.

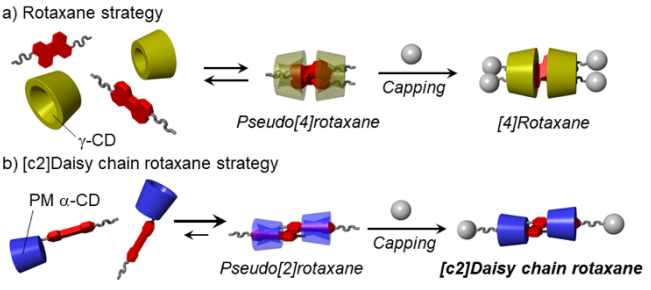
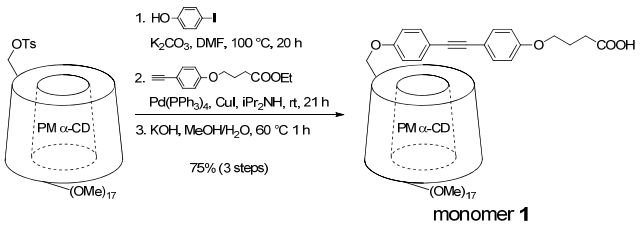


Figure 1. Synthetic strategies for rotaxanes insulating two π-conjugated molecular cores.



Scheme 1. Synthesis of monomer **1**.

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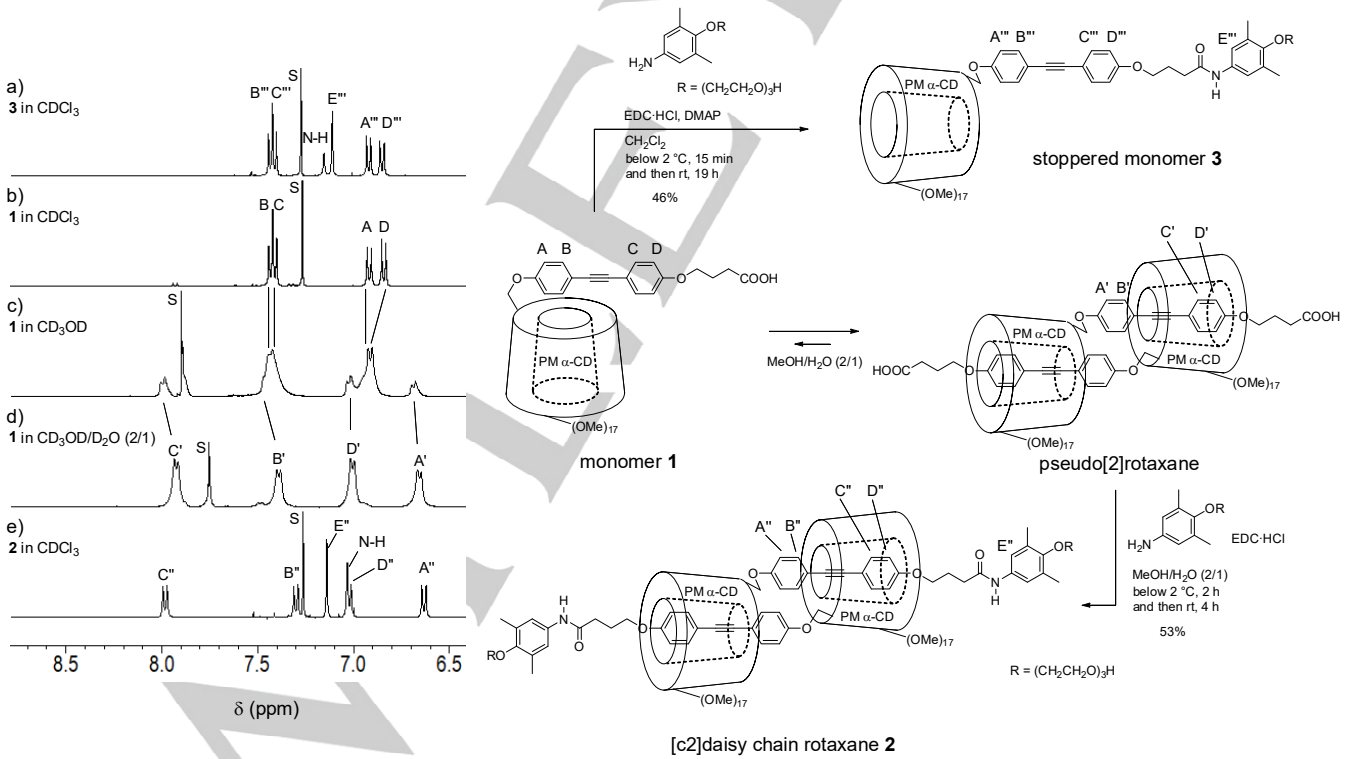
Monomer **1** with a PM α-CD moiety as a ring component and a diarylacetylene moiety as an axle component was prepared from PM α-CD monotosylate[10] in 75% yield (3 steps), as shown in Scheme 1. Using monomer **1**, the formation of pseudorotaxanes was investigated using solvent-dependent ^{1}H NMR measurements. As shown in Scheme 2b, four doublets derived from the diarylacetylene moiety of monomer **1** were observed in the aromatic region of the ^{1}H NMR spectrum in $CDCl_3$. Host–guest interactions between monomer units are generally weakened in chloroform. Therefore, the doublets were attributed to nonassociated monomer **1**,[11] which is assumed to be the only species in chloroform. The doublets were assigned to aromatic protons A–D of nonassociated monomer **1** by 2D NMR measurements. In CD_3OD, in addition to the peaks of the nonassociated species, small broad peaks corresponding to an associated species appeared at 8.00, 7.45, 7.02, and 6.69 ppm (Scheme 2c). Furthermore, in CD_3OD/D_2O (2/1), the peaks of nonassociated monomer **1** almost disappeared while four new broad doublets were clearly observed (Scheme 2d). These broad doublets were attributed to protons A′–D′ of diarylacetylene insulated in a pseudo[2]rotaxane by comparison with the NMR data for previously reported [c2]daisy chain rotaxanes.[6a,b]

The structure of the pseudo[2]rotaxane was then fixed by capping with a water-soluble dimethylaniline derivative via a condensation reaction with 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) in CH_3OH/H_2O (2/1). Desired [c2]daisy chain rotaxane **2** was obtained in 53% yield after purification by silica gel column chromatography. The symmetrical and dimeric structure of rotaxane **2** was confirmed based on its ^{1}H NMR spectrum (Scheme 2e) and its ESI-HRMS spectrum, in which the peaks at *m/z* 1182.8757 and 1762.8195 corresponded to sodium adducts[12] (calculated *m/z* of $[M\cdot3Na]^{3+}$: 1182.8755; calculated *m/z* of $[M\cdot2Na]^{2+}$: 1762.8186) (Figure S1). The peaks in the aromatic region of the ^{1}H NMR spectrum of rotaxane **2** were assigned to protons A″–E″ and the N–H proton by ^{1}H NMR and 2D NMR measurements. Notably, these assignments correspond reasonably well with those estimated for the protons of the pseudo[2]rotaxane.

Stoppered monomer **3** was also prepared via the condensation reaction in dichloromethane. The assignments of the peaks in the aromatic region of the ^{1}H NMR spectrum of stoppered monomer **3** are shown in Scheme 2a. Protons C″ and D″ in rotaxane **2** are shifted downfield ($\Delta\delta_{C''-C'''}$ +0.57 ppm and $\Delta\delta_{D''-D'''}$ +0.17 ppm) relative to protons C‴ and D‴ in stoppered monomer **3** owing to the deshielding effect of the glycosidic oxygens located inside the CD cavity. In contrast, protons A″ and B″ in rotaxane **2** are shifted upfield relative to protons A‴ and B‴ in stoppered monomer **3** ($\Delta\delta_{A''-A'''}$ −0.29 ppm and $\Delta\delta_{B''-B'''}$ −0.13 ppm) by the paracyclophane-like proximity of the benzene rings bound directly to the PM α-CDs. These shifts indicate that the two diarylacetylene cores in rotaxane **2** face each other in a symmetric manner, as depicted in Scheme 2. The benzene rings connected directly to the PM α-CDs partially overlap, whereas the other benzene rings are located within the PM α-CD cavities.



Scheme 2. Partial ^{1}H NMR spectra[a] of a) stoppered monomer **3** in $CDCl_3$ at rt, b) monomer **1** in $CDCl_3$ at rt, c) monomer **1** in CD_3OD at rt, d) monomer **1** in CD_3OD/D_2O (2/1) at rt, and e) rotaxane **2** in $CDCl_3$ at rt, and syntheses of [c2]daisy chain rotaxane **2** and stoppered monomer **3**. [a] The chloroform peak is denoted by S in the ^{1}H NMR spectra.

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Table 1. Maximum absorption peaks (λ_{max}) of rotaxane **2** and stoppered monomer **3**.[a]

Solvent	Rotaxane **2** [nm]	Stoppered monomer **3** [nm]
Chloroform	297, 316	296, 315
Tetrahydrofuran	296, 315	295, 314
Methanol	296, 315	293, 311
Acetonitrile	296, 315	294, 313
Dimethyl sulfoxide	297, 316	297, 316

[a] Conditions: [**2**] = 1.7 × 10^{-5} M, [**3**] = 3.4 × 10^{-5} M.

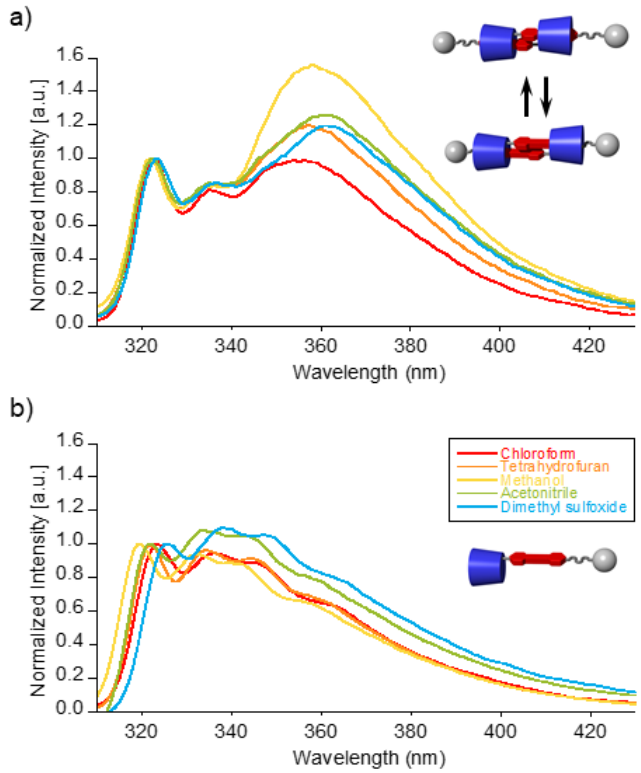

Figure 2. Fluorescence spectra of (a) rotaxane **2** and (b) stoppered monomer **3**. Conditions: [**2**] = 2.6 × 10^{-7} M, [**3**] = 1.9 × 10^{-6} M, excitation at the maximum absorption wavelength in the range of 311–316 nm.

The absorption peaks (λ_{max}) of rotaxane **2** and stoppered monomer **3** in various solvents are listed in Table 1. For rotaxane **2**, the absorption spectra in various solvents overlapped well (Figure S2a), and the absorption maximum did not shift significantly. In contrast, a shift of up to 5 nm was observed for the absorption maximum of stoppered monomer **3** (Figure S2b). Similar trends were also observed for the monomer emission of **2** and **3** (Figure 2). The shapes of the bands in the absorption spectra of rotaxane **2** and stoppered monomer **3** were similar, which suggests that the ground-state interaction between the two diarylacetylenes in rotaxane **2** is weak. These results confirmed that the two independent diarylacetylene cores of rotaxane **2** were insulated from the external environment by the PM α-CDs.

As shown in Figure 2, stoppered monomer **3** exhibited only monomer emission in various solvents at a concentration of 1.9 × 10^{-6} M. In contrast, rotaxane **2** showed both monomer and excimer emission at a much lower concentration (2.6 × 10^{-7} M). As there is an alkyl spacer between the diarylacetylene unit and the aniline stopper, the distance between the two diarylacetylene cores in rotaxane **2** can be varied by contraction or extension of the molecular length along the long axis (Figure 2a). This is a characteristic behavior of [c2]daisy chain rotaxane, also known as the molecular muscle.[6–8,13] When the two diarylacetylene cores are in close proximity, an excimer can form, resulting in excimer emission; otherwise, monomer emission occurs. These results imply that contraction and extension of the [c2]daisy chain structure of rotaxane **2** occurs in solution by shuttling the PM α-CDs along the axle components. Unfortunately, multiple chemical species with different conformations were not observed by ^{1}H NMR spectroscopy owing to the fast shuttling of the subunits in rotaxane **2** on the NMR time scale.

In summary, we efficiently synthesized a [c2]daisy chain rotaxane insulating two diarylacetylene cores using the Janus [2]rotaxane strategy. The obtained rotaxane showed both excimer and monomer emission in various solvents, which implied that fast shuttling of the rotaxane subunits occurred in solution. This work demonstrates for the first time that excimer generation can be controlled within an isolated space by the unique structural motion of the [c2]daisy chain rotaxane. Thus, the [c2]daisy chain rotaxane strategy is a powerful tool for developing optical and electronic materials based on spatially restricted excimers of π-conjugated hydrocarbons. It is expected that switchable optical and electronic materials will be developed based on [c2]daisy chain rotaxane units. In our future study, we will investigate the motion of rotaxane and its effect on the optical properties.

Acknowledgements

This work was supported by the Iketani Science and Technology Foundation (No. 0321005-A). The electrospray ionization mass spectrometry measurements were performed at the Analytical Instrument Facility, Graduate School of Science, Osaka University. We thank Prof. Dr. Rui Umeda (Faculty of Chemistry, Materials and Bioengineering, Kansai University) for discussions of the absorption and fluorescence data.

Conflict of interest

The authors declare no conflict of interest.

Keywords: [c2]daisy chain • cyclodextrins • diarylacetylene • excimer • rotaxanes

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10.1002/chem.202004505

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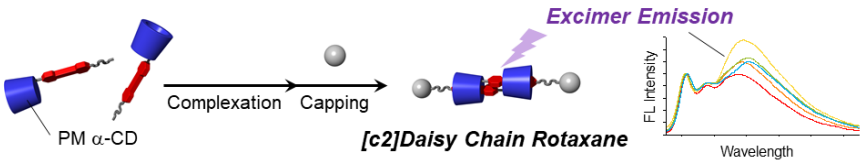

A [c2]daisy chain rotaxane, in which two independent diarylacetylene cores are insulated by two permethylated α-cyclodextrins (PM α-CDs), was efficiently synthesized using the Janus [2]rotaxane strategy. The observation of both monomer and excimer emission in various solvents revealed that frequent shuttling of the rotaxane subunits occurs in solution.