Studies on Synthesis of Encapsulated π-Conjugated Polymers Composed of Organic-soluble Linked Rotaxanes

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(有機溶媒に可溶な連結型ロタキサンからなる被覆π共役ポリマーの合成に関する研究)

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Preface

The study presented in this thesis has been carried out under the supervision of Professor Nobuaki Kambe at the Department of Applied Chemistry, Graduate School of Engineering, Osaka University and Associate Professor Jun Terao at the Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University.

The thesis is concerned with the synthesis of encapsulated π-conjugated polymer composed of linked rotaxanes as monomer units, which were prepared from π-conjugated-guest-linked permethylated cyclodextrins as key compounds. The objective of the thesis is to develop a methodology for encapsulating π-conjugated polymer at molecular level using advantage of organic synthetic chemistry and supramolecular chemistry and also to demonstrate usability of permethylated cyclodextrin (PMCD) in organic synthesis. The author hopes that the results and conclusions presented in this thesis will contribute to bottom-up construction of molecular devices in the future.

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List of Publications

1) Synthesis of an Organic-soluble π-Conjugated [1]Rotaxane

Susumu Tsuda, Jun Terao and Nobuaki Kambe

Chem. Lett. **2009**, *38*, 76-77.

2) Synthesis of a Linked [1]-[1]Rotaxane

Susumu Tsuda, Jun Terao, Keisuke Tsurui and Nobuaki Kambe

Chem. Lett. **2009**, *38*, 190-191.

3) Synthesis of Linked Symmetrical [3] and [5]Rotaxanes Having an Oligomeric Phenylene Ethynylene (OPE) Core Skeleton as a π-Conjugated Guest via Double Intramolecular Self-inclusion

Susumu Tsuda, Jun Terao, Yuji Tanaka, Tomoka Maekawa, and Nobuaki Kambe

Tetrahedron Lett. **2009**, *50*, 1146-1150.

4) Synthesis of Encapsulated π-Conjugated Polymers Composed of Linked Rotaxanes as Monomer Units

Susumu Tsuda, Jun Terao, Keisuke Tsurui and Nobuaki Kambe

in preparation.

5) Transition-Metal Catalyzed Synthesss of Rotaxane-type Encapsulated π-Conjugated Molecules via Intramolecular Self-inclusion of π-Conjugated Molecules bearing Permethylated α-Cyclodextrins

Susumu Tsuda, Jun Terao, Yuji Tanaka, Tomoka Maekawa, Kazuhiro Ikai, Yuko Okumoto, Keisuke Tsurui and Nobuaki Kambe

in preparation.

Supplementary Publications

1) Linear Oligomers Composed of a Photochromically Contractible and Extendable Janus [2]Rotaxane
Susumu Tsuda, Yoshio Aso and Takahiro Kaneda
Chem. Commun. **2006**, 3072-3074.

2) Polymerization of Pseudo Linked Rotaxane as a Monomer Unit
Yuji Tanaka, Jun Terao, Susumu Tsuda and Nobuaki Kambe
in preparation.

3) Intrinsic Mobility of Charge Carriers along Isolated (Phenylene Ethynylene) Chains in the Solid State by Electrodeless Measurement
Jun Terao, Susumu Tsuda, Yuji Tanaka, Tomoka Maekawa, Akinori Saeki, Shu Seki and Nobuaki Kambe
in preparation.

4) Organic Molecular Conducting Wire Formation on TiO_2 Nanocrystalline Structure: Towards Long-lived Charge Separated Systems
Yasuhiro Tachibana, Satoshi Makuta, Yasuhide Otsuka, Jun Terao, Susumu Tsuda, Nobuaki Kambe, and Susumu Kuwabata
in preparation

Table of Contents

General Introduction

π-Conjugated polymers[1] constitute one of the most important categories of materials used in the so-called "plastic electronics" or "organic electronics"[2] such as organic light emitting diodes (OLEDs),[3] organic field-effect transistors (OFETs),[4] and organic photovoltaic cells[5], since Shirakawa, Heeger, MacDiarmid and co-workers reported the synthesis and properties of polyacetylene[6] as conducting polymer.[7] Because the organic materials have several advantages such as low-cost, light weight, flexbility, processibility and tunable properties for application to the devices.[8] They are often loosely described as "molecular wires" because of the high charge-mobility along individual polymer chains.[9] However, inter-chain charge-mobilities can be fairly high, and π-π stacking interactions between polymer chains can dramatically affect the optical properties.[10] Furthermore, π-conjugated polymers are generally unstable by exposure to external stimuli such as light, heat and air.

These make it interesting to investigate a synthetic methodology for preparing encapsulated π-conjugated polymers in which the π-conjugated polymers are covered at the molecular level by a protective sheath (Figure 1).[11] Encapsulation can enhance the chemical stability, solubility, and optical properties of the π-conjugated core. When exploiting the electronic functionality of single molecules it is important to prevent cross-talk between polymer chains.

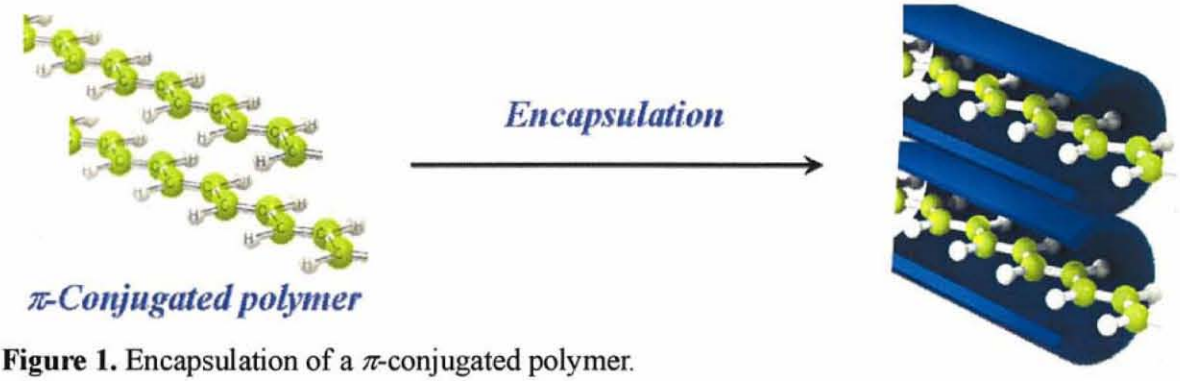

Figure 1. Encapsulation of a π-conjugated polymer.

Especially, dendrimer-based synthetic method[12] and polyrotaxane-based synthetic method[13,14] are the two major approaches to desirable encapsulated π-conjugated polymers for application to the devices. The synthetic strategy of dendronized π-conjugated polymers is to decorate π-conjugated

backbone with dendrons or sterically hindered side-chains (Figure 2 a). Their features are stereoregularity and high solubility in organic solvents. On the other hand, the synthetic strategy of polyrotaxane is to thread π-conjugated polymer through a series of encapsulating macrocycles such as cyclodextrins,[11] cyclophanes[12] and cucurbiturils (Figure 2 b). The primary structural feature of polyrotaxane is effective encapsulation of π-conjugated backbone.

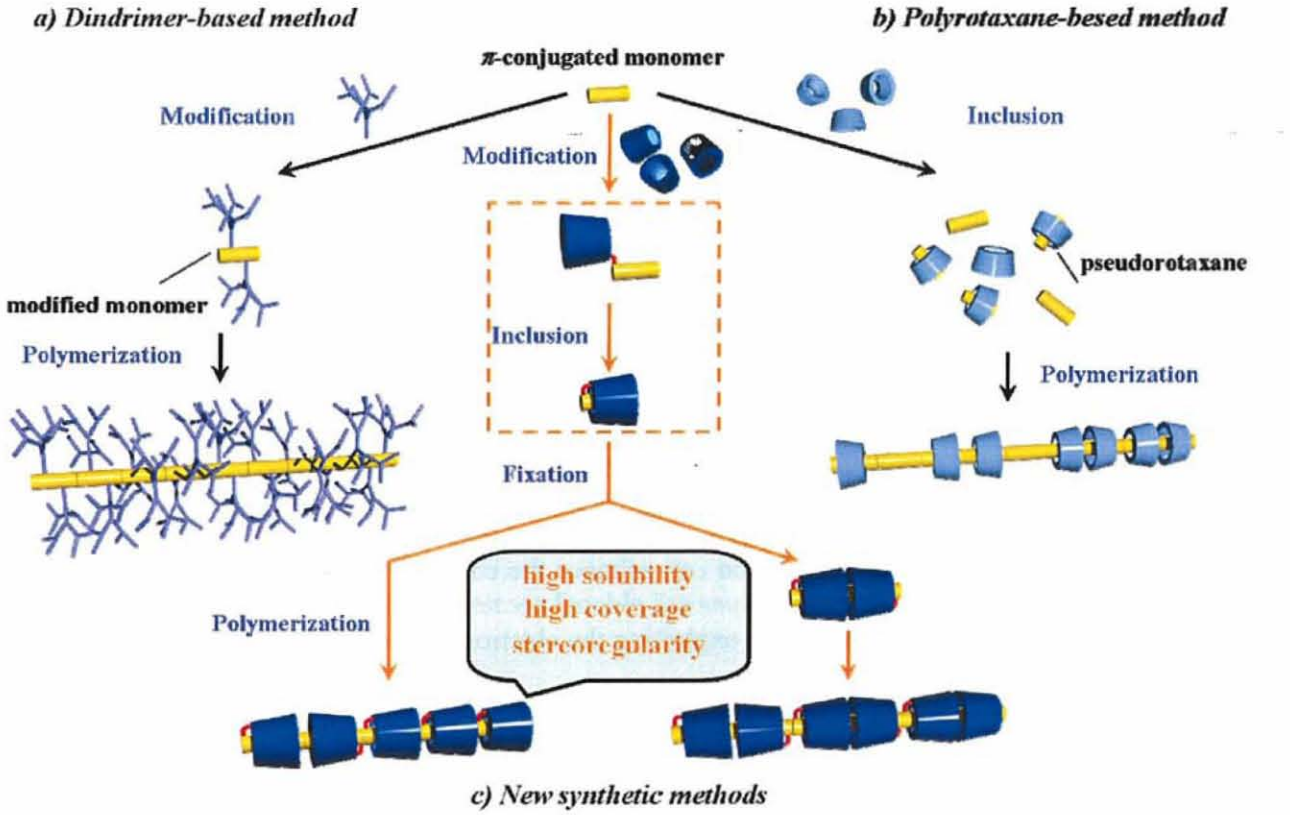

Figure 2. Synthetic methodologies of insulated molecular wires.

With wide interest in the development of encapsulated π-conjugated polymers toward organic advanced materials, the primary object of this thesis is to develop new methodologies for constructing encapsulated π-conjugated polymers by polymerization of "rotaxane unit" prepared via "self-inclusion" of π-conjugated monomer bearing permethylated α-cyclodextrin (PMα-CD). The new synthetic methods gave encapsulated π-conjugated polymers having high solubility, high coverage, and stereoregularity by the combined use of both advantages of polyrotaxane-based and dendrimer-based synthetic methodologies (Figure 2 c). This thesis consists of the following four chapters.

Chapter 1 deals with the synthesis of a linked [2]rotaxane via intramolecular self-inclusion of lipophilic PMα-CD bearing a diphenylacetylene derivative as a rigid π-conjugated system in aqueous medium and the subsequent end-capping of thus-obtained linked pseudo[2]rotaxane with a nonbulky π-conjugated molecule.

Chapter 2 describes the synthesis of a linked [3]rotaxane via intramolecular self-inclusion of a π-conjugated guest-linked PMα-CD and dimerization of thus-obtained linked pseudo[2]rotaxanes without any another bulky stopper molecule.

Chapter 3 describes the result of synthesis of oligo(phenylene ethynylene)-based linked [3] and [5]rotaxanes via double intramolecular self-inclusion and capping with two end-groups.

Chapter 4 describes the synthesis of encapsulated π-conjugated polymers by polymerization of linked [2]rotaxane or linked [3]rotaxane as monomer units.

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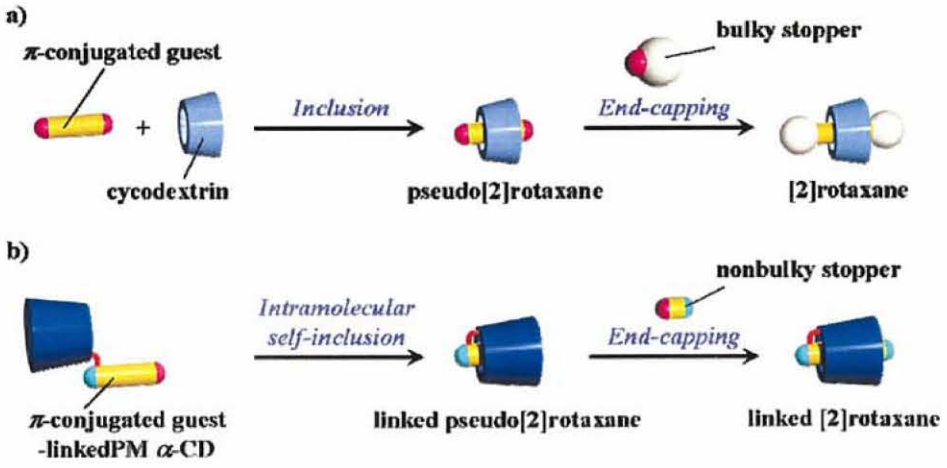
Chapter 1.

Synthesis of an Organic-soluble Linked [2]Rotaxane via Intramolecular Self-inclusion of a Guest-linked Permethylated α-Cyclodextrin

1.1 Introduction

π-Conjugated systems constitute a core technology for next-generation electronic materials such as organic light-emitting diodes (OLEDs), organic thin-film field-effect transistors, and fluorescent probes. Recently, particular attention has been paid to insulated π-conjugated systems with high stability, high solubility, and high fluorescence quantum yield arising from the decreased π-π interaction among the π-conjugated systemss and/or their separation from the external environment.[1]

Various water-soluble rotaxanes[2] having encapsulated π-conjugated systems have been prepared using cyclodextrins (CDs) as a protective cylindrical sheath.[3] For example, [2]rotaxanes as water-soluble encapsulated π-conjugated systems have been achieved by the inclusion of a π-conjugated system into a CD in aqueous medium followed by the end-capping of the inclusion complex with two water-soluble bulky stopper molecules at the both end of a π-conjugated system (Scheme 1. a).



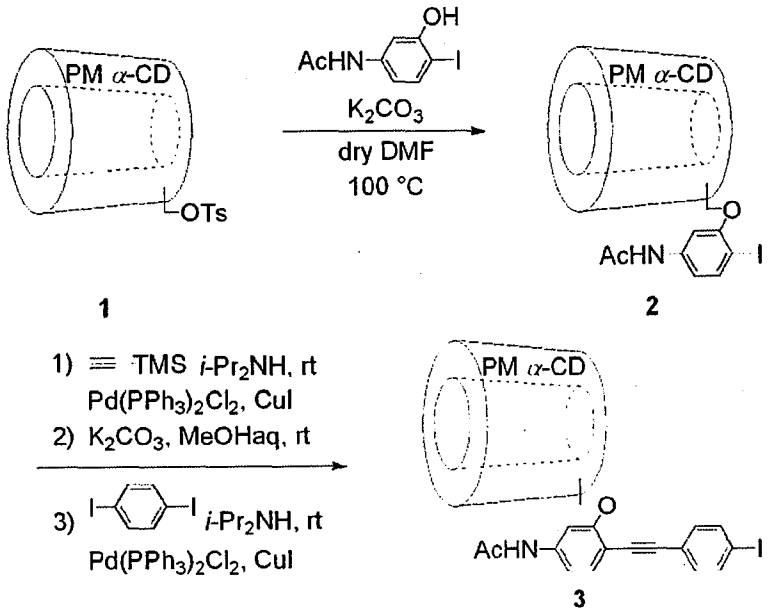
Scheme 1. Synthetic routes of rotaxanes. a) conventional [2]rotaxane, b) my linked [2]rotaxane.

Tian *et al.* synthesized a water-soluble linked [2]rotaxane[4,5] (also called [1]rotaxane[2]) by forming an intramolecular self-inclusion complex of an azobenzene-linked β-CD and subsequent end-capping with a water-soluble bulky stopper molecule for a light-driven molecular machine.

In this chapter, I describe a new synthetic method of a rotaxane having high organic solubility and high coverage of a π-conjugated system (axial guest) with a macrocyclic host. My strategy to fabricate a linked [2]rotaxane is based on intramolecular self-inclusion of lipophilic permethylated α-cyclodextrin (PMα-CD) bearing a diphenylacetylene derivative as a rigid π-conjugated system in aqueous medium and a subsequent end-capping of the formed linked pseudo[2]rotaxane with a nonbulky π-conjugated molecule by Suzuki-Miyaura coupling (Scheme 1. b).

1.2 Synthesis (*via Intramolecular Self-inclusion and End-capping*)

The π-conjugated guest-linked PMα-CD **3** as a rotaxane precursor was synthesized according to Scheme 2. The sysnthesis of 6-*O*-monotosyl PMα-CD **1**[6] and 2-iodo-5-acetamidophenol[7] was previously reported. Substitution reaction of 6-*O*-monotosyl PMα-CD **1** with 2-iodo-5-acetamidophenol gave a modified PMα-CD iodide **2** in 98% yield. The desired modified PMα-CD **3** was synthesized by sequential Sonogashira coupling of **2** with trimethylsilylacetylene and 1,4-diiodobenzene in 67% yield over three steps.



Scheme 2. Synthesis of a π-conjugated guest-linked PMα-CD **3**.

The intramolecular self-inclusion phenomenon of **3** has been confirmed by CPK model and been examined by ^{1}H NMR employing different solvents and concentrations. As shown in Figure 1, the NMR spectrum of **3** in $CDCl_3$ at room temperature, reveals the exclusion of the diphenylacetylene moiety from the cavity of the PMα-CD. The spectrum in CD_3OD at room temperature indicateds the presence of a mixture of **3** and its supramolecular complex (linked pseudo[2]rotaxane) **3'**. The intensity of new peaks (**a'-e'**) increased on standing at room temperature overnight or by warming up to 60 °C and then cooling to room temperature indicating the slow equilibrium process at room temperature. **3** was converted to the supramolecular complex **3'** in more high-polar solvent D_2O : CD_3OD = 1 : 1 and disappeared completely. The evidence that the NMR spectra of **3'** at different concentrations in CD_3OD or D_2O:CD_3OD = 1:1 showed no new peaks ascribable to oligomeric and/or polymeric supramolecular complexs may support intramolecular self-inclusion complex (linked pseudo[2]rotaxane) **3'**.

The formation of **3'** resulted in the following up- or down-field shift of aromatic protons in **3'**, $H_{a\text{-}a'}$ (-0.25), $H_{b\text{-}b'}$ (+0.56), $H_{c\text{-}c'}$ (+0.13), $H_{d\text{-}d'}$ (+0.49), $H_{e\text{-}e'}$ (+0.09 ppm). The remarkable down-field shift of $H_{d'}$ suggested that the protons are located very close to the α-1,4-glucosidic oxygen atoms of PMα-CD.[8]

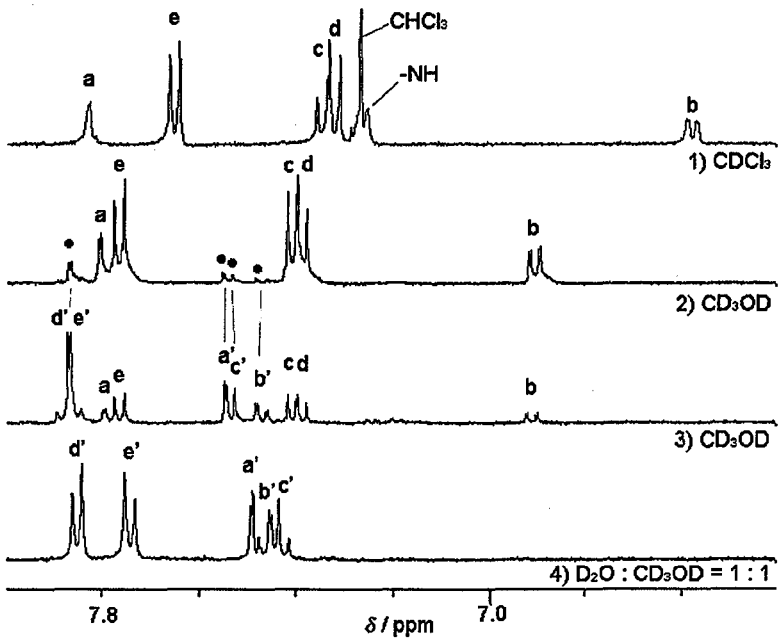
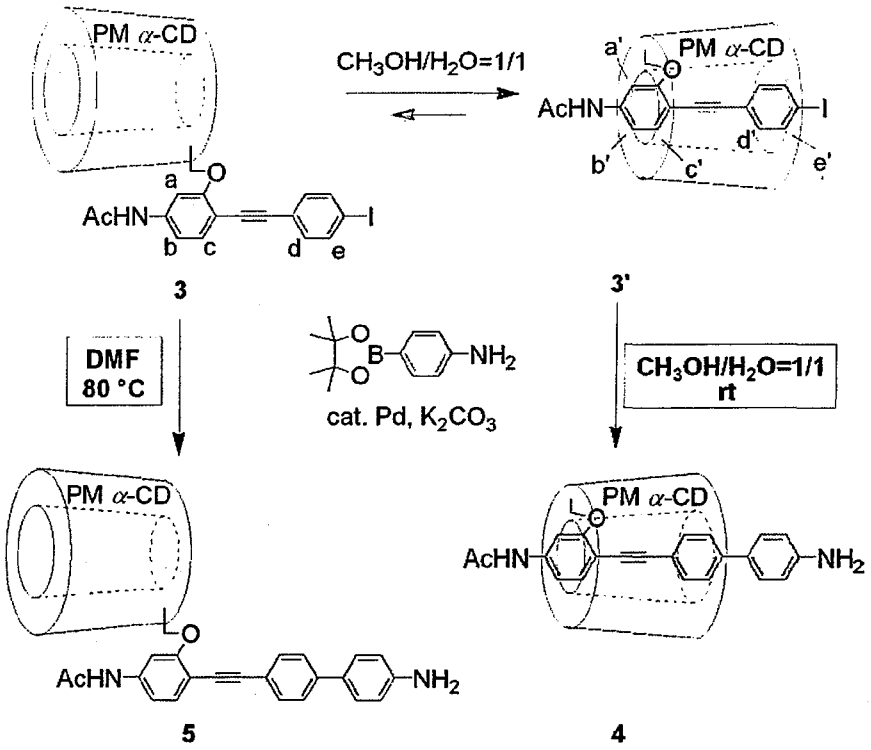


Figure 1. The aromatic region of 400 MHz ^{1}H NMR spectra of **3** in several solvents at rt. 1) $CDCl_3$; 2) CD_3OD (soon after dissolved); 3) CD_3OD after heating at 60 °C for 1 h and cooling to rt.



Scheme 2. Synthesis of linked [2]rotaxane **4** and unencapsulated compound **5** by Suzuki-Miyaura cross-coupling in different solvents.

In order to fix linked pseudo[2]rotaxane **3'** by capping the end of guest moiety with a π-conjugated molecule, **3'** was treated with aniline boronic ester under Suzuki-Miyaura coupling conditions in H_2O:CH_3OH = 1:1 solusion (Scheme 2). The desired fixed linked [2]rotaxane **4** was handily purified by silica gel column chromatography and was obtained in pure form in high yield (80%). This linked [2]rotaxane is soluble in various organic solvents such as methanol, diethyl ether, chloroform, toluene, and DMF (Table 1).

It is known that the decomplexation of linked [2]rotaxane "*flipping*" mechanism is often observed owing to large flexibility of a PMα-CD in comparison to that of native α-CD.[9] However, linked [2]rotaxane **4** was stable in $CDCl_3$ for more than seven days without decomplexation. The corresponding un encapsulated compound **5** was intentionally synthesized by the reaction of **3** with aniline boronic ester in DMF instead of 1:1 solution of H_2O and CH_3OH (Scheme 2).

Table 1. Solubility test of linked [2]rotaxane **4**.[a]

Solvent	Solubility (mg / mL)
Hexane	2.56×10^{-4}
Diethyl ether	16
Toluene	38
Chloroform	177
DMF	143
Methanol	128
Ethanol	192

[a]The solubility was determined by UV-vis spectroscopy using a calibrated curve.

Kaneda et al. succeeded in synthesizing dimeric cyclic [2]rotaxane via end capping of dimeric cyclic inclusion compound of a para substituted azophenol-linked PMα-CD by azo coupling using sterically hindered naphthol derivative.[8] In my linked [2]rotaxane synthesis, however, MALDI-TOF mass spectrum exhibited only the signal at *m/z* 1558 corresponding to $[\mathbf{4} + Na]^+$. No evidence for the formation of dimeric cyclic [2]rotaxane was detected by MALDI TOF MS and GPC analysis. It is quite

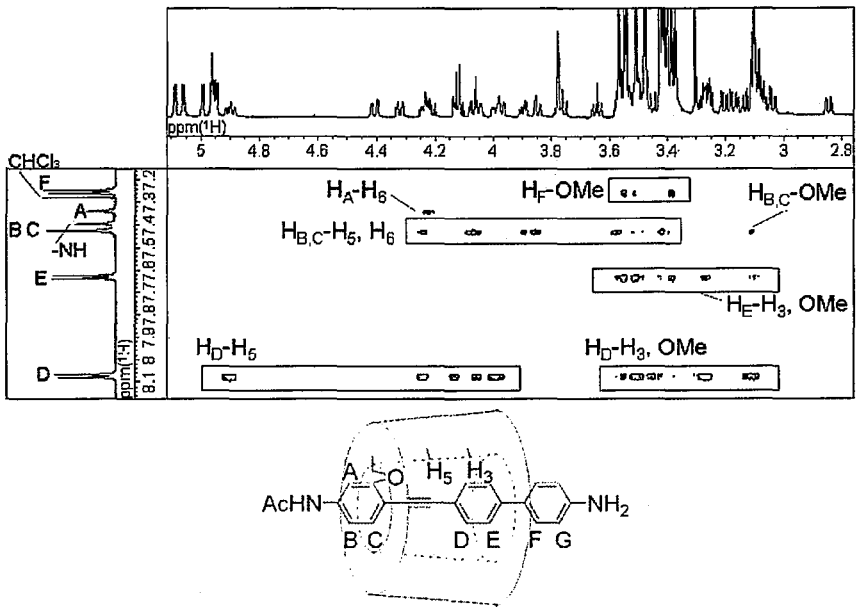


Figure 2. A section of the ROESY NMR spectrum of [1]rotaxane **4** recorded in $CDCl_3$.

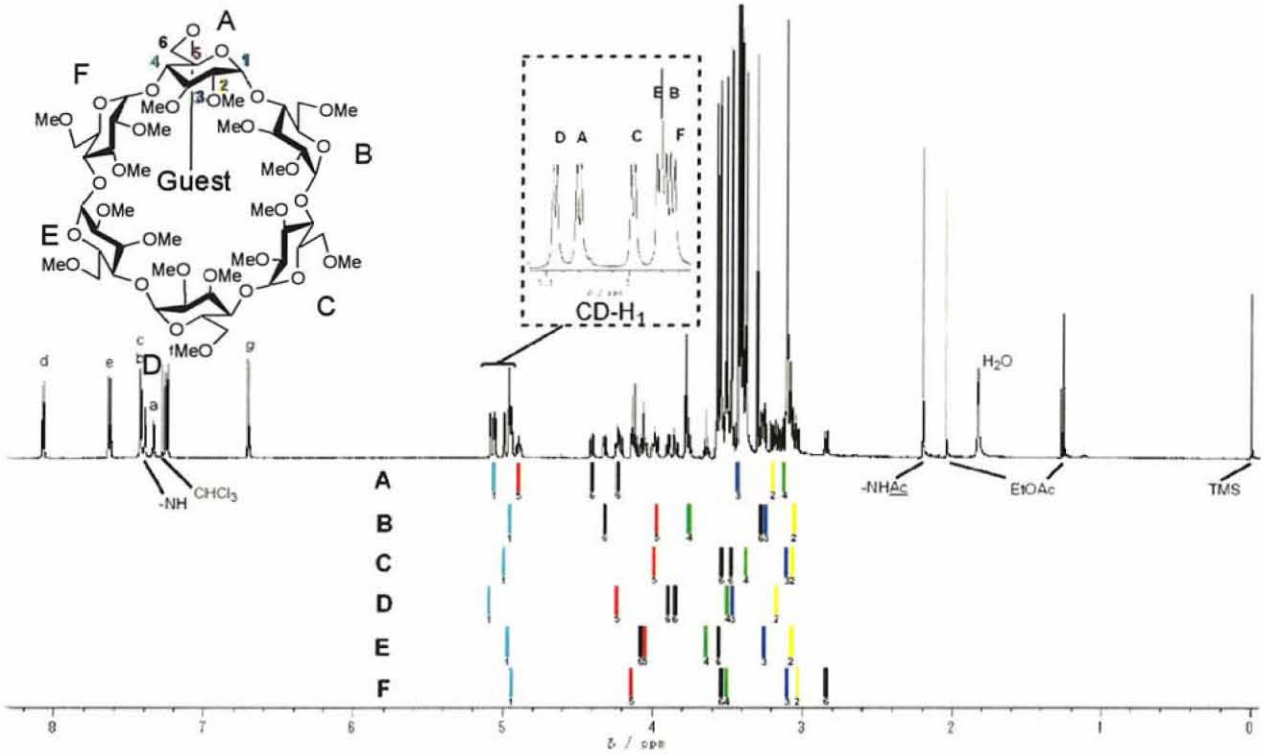


Figure 3. Assignments for the PMα-CD protons of [1]rotaxane **4**, as determined using TOCSY, COSY, ROESY NMR spectrometry, and ^{1}H NMR spectrum recorded in $CDCl_3$ at 600 MHz.

interesting that a linked pseudo[2]rotaxane was selectively generated from ortho substituted diphenylacetylene-linked PMα-CD via intramolecular self- inclusion. In order to confirm the structure of this linked [2]rotaxane the protons of PMα-CD were assignment by 2D TOCSY, COSY and ROESY NMR (Figure 3). The NOEs between protons on the diphenylacetylene moiety (H_D, H_E) and the internal protons (H_3, H_5) of the PMα-CD were observed by 2D ROESY NMR (Figure 2).

A crystal of a linked [2]rotaxane **4** was grown from a mixture of DMSO and H_2O. Figure 4 shows the structure of this linked [2]rotaxane. To the best of my knowledge, this is the first observation of a linked [2]rotaxane structure by X-ray crystallography and the first crystal structure of rotaxanes using PMCD derivatives as a macrocycle.

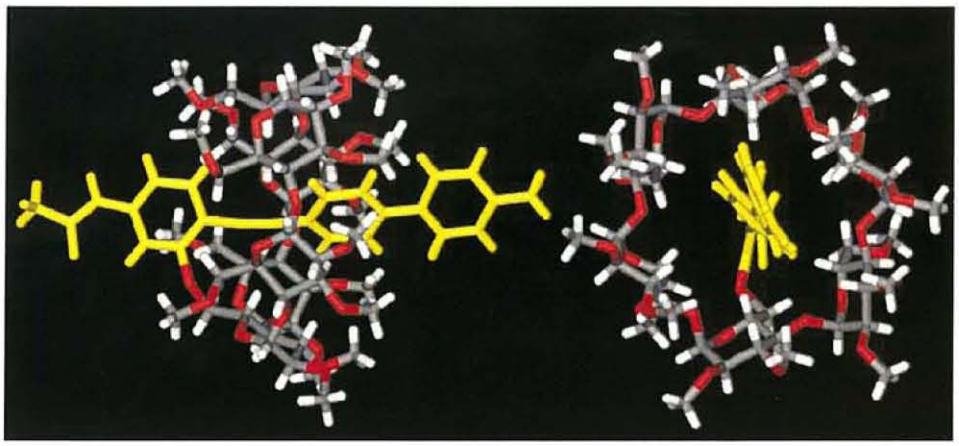


Figure 4. Molecular structure of linked [2]rotaxane **4**. Space group $P2_12_12_1$ (#19) with a = 14.485(3) Å, b = 19.552(4) Å, c = 29.126(6) Å, Z = 4, ρ = 1.249 g/cm^3, R = 0.105, Rw = 0.172 T = 153 K.

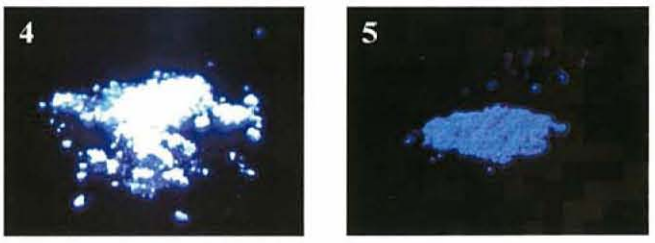
1.3 Fluorescence Properties

In order to examine the shielding effect of PMα-CD, we compared the fluorescence quantum yield of **4** with that of the corresponding uninsulated compound **5**. As expected, there is a significant fluorescence enhancement in **4** especially in solid state suggesting that encapsulation of the chromophore by PMα-CD is essential to attain efficient fluorescence properties.

Table 2. Optical properties and fluorescence quantum yields.[a]

Sample	Absorption (λ_{max}/nm)	Emission (λ_{max}/nm)	$\Phi_{solution}$	Φ_{solid}
4	328	398	0.89	0.68
5	338	396	0.71	0.06

[a]Spectra were recorded in $CHCl_3$. Absolute quantum yields were determined by a calibrated integrating sphere system.



UV lamp (365 nm)

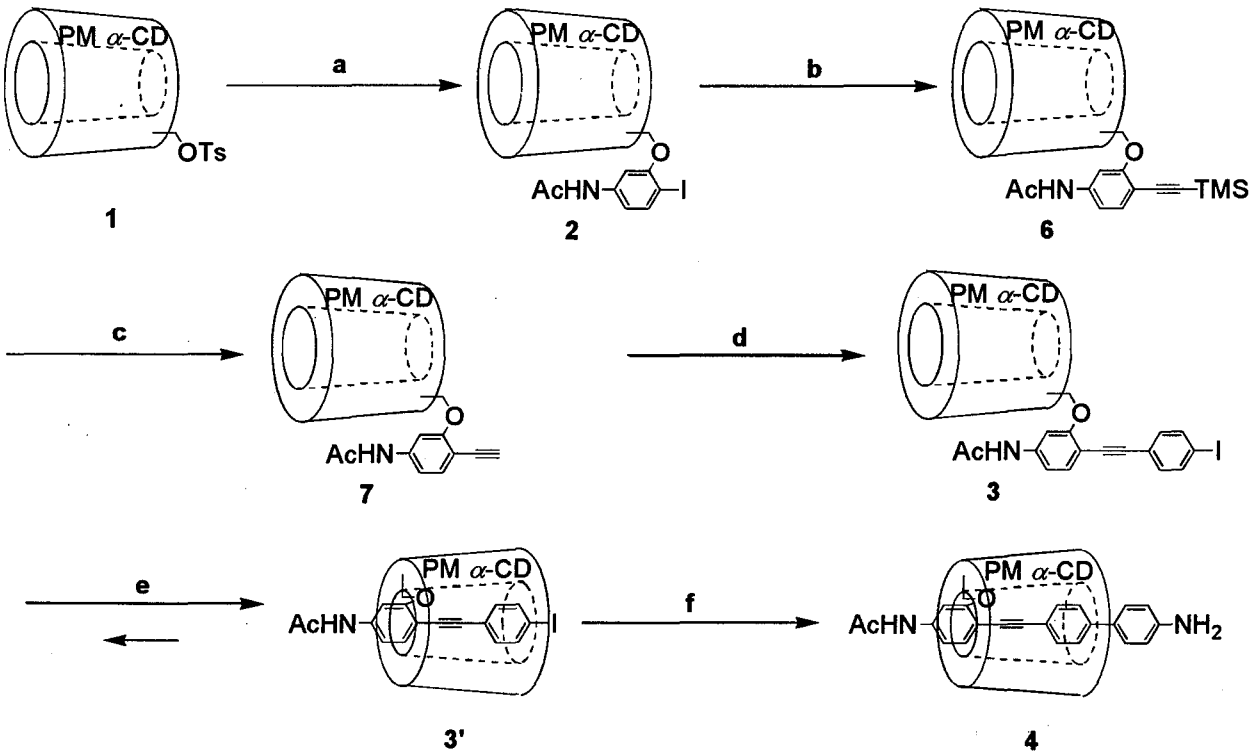
1.4 Conclusion

In conclusion, an organic-soluble linked [2]rotaxane was prepared via intramolecular self-inclusion of PMα-CD bearing a diphenylacetylene moiety and subsequent end-capping with an aniline unit by the Suzuki-Miyaura coupling. The structure of this linked [2]rotaxane in solusion and solid was determined by 2D NMR and X-ray crystallography, respectively. The present study revealed that bulky stoppers are not necessary when linked [2]rotaxane consist of PMα-CD as a macrocyclic host and a rigid π-conjugated system as the guest moiety are linked each other.

1.5 Experimental Section

General Comments: 6-*O*-monotosyl PMα-CD **1** was prepared by the procedure reported previously by Kaneda *et al.* 2-Iodo-5-acetamidophenol was also prepared by the procedure similar to those reported previously. Other reagents were purchased from commercial sources and used without further purification. Commercially available dehydrated DMF was used without further distillation. Melting points were measured with a Stanford Research Systems MPA100 apparatus. GC Mass spectra (EI) were obtained on a SATURN GCMS-2000 operating in the electron impact mode (70eV) equipped with a RTX-5 30MX.25MMX.25U column. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra was obtained with α-cyano-4-hydroxycinnamic acid as a matrix and NaTFA as a cationization reagent on a SHIMADZU KRATOS TOF MASS spectrometer AXIMA-CFR Plus. ^{1}H NMR for 400 MHz and ^{13}C NMR for 100 MHz spectra were recorded by a JEOL JNM-Alice 400 spectrometer. 2D-COSY, ROESY, and TOCSY for 600MHz were recorded by a Varian INOVA-600. Elemental analyses were performed on Perkin Elmer 240C apparatus in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University.

Synthetic Scheme of [1]rotaxane 4



Reagents and Conditions: (a) 2-iodo-5-acetamidophenol, K_2CO_3, dry DMF, 100 °C; (b) trimethylsilyl acetylene, $Pd(PPh_3)_2Cl_2$, CuI, *i*-Pr_2NH, rt; (c) K_2CO_3, MeOHaq., rt; (d) 1,4-diiodobenzene, $Pd(PPh_3)_2Cl_2$, CuI, *i*-Pr_2NH, rt; (e) MeOH/H_2O (1/1), 60 °C ~ rt; (f) 4-(4,4,5,5-tetramethyle-1,3,2-dioxaborolan-2-yl)aniline, $Pd(OAc)_2$, K_2CO_3, MeOH/H_2O (1/1), rt.

Synthesis of 2: 2-Iodo-5-acetamidophenol (12.2 g, 44.0 mmol), 6-*O*-monotosyl PMα-CD (50.0 g, 36.6 mmol) and dry K_2CO_3 (10.1 g, 73.1 mmol) were dissolved in dry DMF (200 mL). The reaction mixture was stirred under nitrogen at 100 °C for 1 day and cooled to room temperature. The mixture was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was separated and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel (1:1, toluene:EtOAc and 9:1, EtOAc:EtOH) to yield **2** as a white solid (52.5 g, 98%). m.p.: 120-123 °C; MALDI-TOF MS: (*m/z*) 1494 ($[M+Na]^+$, $C_{61}H_{100}INO_{31}Na$, calcd. 1493); ^1H NMR (400MHz, $CDCl_3$, 23.7 °C): δ_H = 7.64 (d, J = 8.4 Hz, 1H, ArH), 7.51 (d, J = 2.1 Hz, 1H, ArH), 7.14 (s, 1H, NH), 6.67 (dd, J = 2.1, 8.4 Hz, 1H, ArH), 5.12-5.00 (m, 6H, CD-H_1), 4.44-3.10 (m, 87H, CD-H, OCH_3), 2.15 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$, 21.5 °C): δ_C =

168.16, 157.84, 139.74, 138.8-138.7 (several peaks overlapped), 113.37, 113.30, 104.56, 104.46, 100.6-99.7 (several peaks overlapped), 82.8-82.0 (several peaks overlapped), 79.42, 71.4-71.1 (several peaks overlapped), 70.42, 69.72, 61.84, 59.2-59.0 (several peaks overlapped), 58.69, 58.62, 57.9-57.8 (several peaks overlapped), 24.85, 24.74; Anal. Calcd for $C_{61}H_{100}INO_{31}\cdot H_2O$: C, 49.23; H, 6.91; N, 0.94%; Found: C, 48.99; H, 6.53; N, 1.06%.

Synthesis of 6: **2** (20.0 g, 13.6 mmol) was dissolved in *i*-Pr_2NH (100 mL). Under a nitrogen, trimethylsilylacetylene (2.70 g, 27.2 mmol), $Pd(PPh_3)_2Cl_2$ (190 mg, 0.27 mmol) and CuI (104 mg, 0.55 mmol) were added to the solution, and then the reaction mixture was stirred at room temperature for 1 day. The mixture was dried *in vacuo*, and the residue was purified by column chromatography on silica gel (9:1, EtOAc:EtOH) to yield **6** as a pale yellow solid (15.6 g, 79%). m.p.: 131-134 °C; MALDI-TOF MS: (*m/z*) 1464 ($[M+Na]^+$, $C_{66}H_{109}NO_{31}SiNa$, calcd. 1464); ^1H NMR (400MHz, $CDCl_3$, 23.2 °C): δ_H = 7.78 (d, J = 1.2 Hz, 1H, ArH), 7.29 (d, J = 8.2 Hz, 1H, ArH), 7.17 (s, 1H, NH), 6.50 (dd, J = 1.2, 8.2 Hz, 1H, ArH), 5.10-5.01 (m, 6H, CD-H_1), 4.56-3.07 (m, 87H, CD-H, OCH_3), 2.16 (s, 3H, CH_3CO), 0.24 (s, 9H, $(CH_3)_3Si$); ^{13}C NMR (100 MHz, $CDCl_3$, 22.1 °C): δ_C = 167.91, 160.10, 139.35, 133.70, 110.23, 108.12, 103.12, 102.99, 101.09, 100.54, 100.2-100.1 (several peaks overlapped), 99.81, 99.69, 99.42, 97.42, 82.3-81.9(several peaks overlapped), 81.68, 81.08, 71.5-70.4 (several peaks overlapped), 67.30, 67.06, 62.33, 61.69, 61.62, 60.95, 59.2-57.2 (several peaks overlapped), 24.77, 24.66, 0.03; Anal. Calcd for $C_{66}H_{109}NO_{31}Si\cdot 2H_2O$: C, 53.68; H, 7.71; N, 0.95%; Found: C, 53.92; H, 7.41; N, 0.88%.

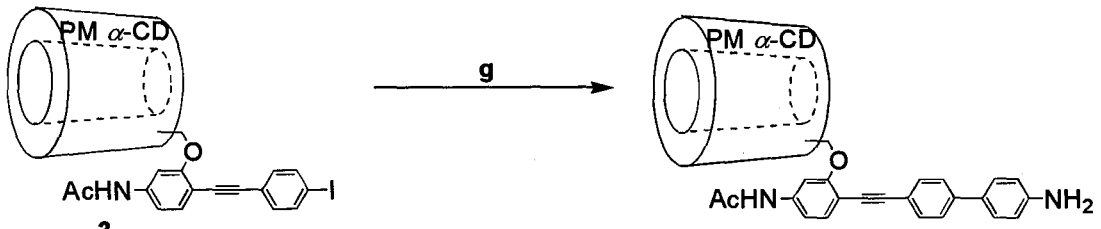
Synthesis of 7: **6** (15.6 g, 10.8 mmol) and K_2CO_3 (14.9 g, 108 mmol) were dissolved in MeOH (260 mL) and H_2O (30 mL). The reaction mixture was stirred under nitrogen at room temperature for 1 day. The mixture was diluted with EtOAc and washed with brine. The organic layer was separated and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel (9:1, EtOAc:EtOH) to yield **7** as a pale yellow solid (14.1 g, 95%). m.p.: 117-120 °C; MALDI-TOF MS: (*m/z*) 1392 ($[M+Na]^+$, $C_{63}H_{101}NO_{31}Na$, calcd. 1391); ^1H NMR

(400MHz, $CDCl_3$, 22.9 °C): δ_H = 7.59 (d, J = 1.7 Hz, 1H, ArH), 7.35 (d, J = 8.3 Hz, 1H, ArH), 7.17 (s, 1H, NH), 6.73 (dd, J = 1.7, 8.3 Hz, 1H, ArH), 5.12-5.00 (m, 6H, CD-H_1), 4.44-3.10 (m, 88H, CD-H, OCH_3, CCH), 2.16 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$, 21.9 °C): δ_C = 168.13, 160.51, 139.73, 133.95, 110.80, 107.22, 103.71, 103.60, 100.4-99.5 (several peaks overlapped), 82.7-81.8 (several peaks overlapped), 80.22, 81.14, 80.73, 80.59, 80.13, 71.4-70.1 (several peaks overlapped), 70.49, 61.79, 61.73, 59.1-57.4 (several peaks overlapped), 24.77; Anal. Calcd for $C_{63}H_{101}NO_{31}\cdot 2H_2O$: C, 53.88; H, 7.54; N, 1.00%; Found: C, 53.76; H, 7.22; N, 0.99%.

Synthesis of 3: 7 (14.1 g, 10.3 mmol) was dissolved in *i*-Pr_2NH (100 mL). Under a nitrogen atmosphere, 1,4-diiodopenzene (13.6 g, 41.2 mmol), $Pd(PPh_3)_2Cl_2$ (723 mg, 1.03 mmol) and CuI (19.6 mg, 0.103 mmol) were added to the solution, and then the reaction mixture was stirred at room temperature for 1 day. The mixture was dried *in vacuo*, and the residue was purified by column chromatography on silica gel (9:1, EtOAc:EtOH) to yield **3** as a pale yellow solid (10.8 g, 67%). m.p.: 143-147 °C; MALDI-TOF MS: (*m/z*) 1590 ($[M+Na]^+$, $C_{69}H_{104}INO_{31}Na$, calcd. 1593); ^1H NMR (400MHz, $CDCl_3$, 23.7 °C): δ_H = 7.82 (d, J = 1.6 Hz, 1H, ArH), 7.65 (d, J = 8.2 Hz, 2H, ArH), 7.35 (d, J = 8.3 Hz, 1H, ArH), 7.32 (d, J = 8.2 Hz, 2H, ArH), 7.19 (s, 1H, NH), 6.57 (dd, J = 1.6, 8.3 Hz, 1H, ArH), 5.15-5.00 (m, 6H, CD-H_1), 4.62-3.01 (m, 87H, CD-H, OCH_3), 2.17 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$, 20.5 °C): δ_C = 168.15, 159.88, 139.65, 137.41, 137.32, 133.1-132.9 (several peaks overlapped), 123.08, 110.71, 108.06, 103.53, 100.5-99.5 (several peaks overlapped), 93.55, 92.14, 87.51, 82.4-81.8 (several peaks overlapped), 81.58, 81.14, 81.03, 71.60, 71.21, 70.58, 61.8-61.6 (several peaks overlapped), 59.2-57.2 (several peaks overlapped), 24.77; Anal. Calcd for $C_{69}H_{104}INO_{31}\cdot H_2O$: C, 52.17; H, 6.73; N, 0.88%; Found: C, 52.02; H, 6.41; N, 0.81%.

Synthesis of 4: 3 (5.0 g, 3.2 mmol) was dissolved in MeOH (500 mL), and then the solution was heated at 60 °C. H_2O (500 mL) was added dropwise to the solution. The solution was stirred at 60 °C for 1 h and cooled to room temperature. Under a nitrogen atmosphere,

4-(4,4,5,5-tetramethyle-1,3,2-dioxaborolan-2-yl)aniline (1.75 g, 8.0 mmol), $Pd(OAc)_2$ (140 mg, 0.64 mmol) and K_2CO_3 (4.4 g, 32 mmol) were added to the solution, and then the reaction mixture was stirred at room temperature for 1 week. During the mixture was stirred, $Pd(OAc)_2$ (140 mg, 0.64 mmol) was further added to the mixture twice. The mixture was diluted with EtOAc and washed with brine. The organic layer was separated and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel(9:1, EtOAc:EtOH, with Et_3N (2%v/v)) to yield **4** as a light brown solid (3.9 g, 80%). m.p.: 246-247 °C; MALDI-TOF MS: (*m/z*) 1558 ($[M+Na]^+$, $C_{75}H_{110}N_2O_{31}Na$, calcd. 1559); ^1H NMR (400MHz, $CDCl_3$, 22.3 °C): δ_H = 8.08 (d, J = 8.3 Hz, 2H, ArH), 7.63 (d, J = 8.3 Hz, 2H, ArH), 7.42 (s, 2H, ArH), 7.34 (s, 1H, ArH), 7.25 (d, J = 8.3 Hz, 2H, ArH), 7.23 (s, 1H, NH), 6.70 (d, J = 8.3 Hz, 2H, ArH), 5.10-4.94 (m, 6H, CD-H_1), 4.93-2.83 (m, 89H, CD-H, NH_2, OCH_3), 2.21 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$, 21.1 °C): δ_C = 168.24, 162.40, 146.19, 141.65, 139.40, 133.56, 132.83, 130.77, 127.55, 127.45, 126.0-125.9 (several peaks overlapped), 120.19, 115.45, 114.20, 112.93, 112.79, 112.38, 100.9-99.8 (several peaks overlapped), 93.86, 86.72, 83.88, 82.8-81.21 (several peaks overlapped), 72.3-70.22 (several peaks overlapped), 62.0-61.6 (several peaks overlapped), 59.1-57.5 (several peaks overlapped), 24.85; Anal. Calcd for $C_{75}H_{110}N_2O_{31} \cdot 2H_2O$: C, 57.31; H, 7.31; N, 1.78%; Found: C, 57.14; H, 6.91; N, 1.72%.



Reagents and Conditions: (g) 4-(4,4,5,5-tetramethyle-1,3,2-dioxaborolan-2-yl)aniline, $Pd(PPh_3)_4$, K_2CO_3, DMF, 80 °C.

Synthesis of 5. Under a nitrogen atmosphere, **3** (2.9 g, 1.8 mmol), 4-(4,4,5,5-tetramethyle-1,3,2-dioxaborolan-2-yl)aniline (610 mg, 2.8 mmol), $Pd(PPh_3)_4$ (110 mg, 0.09 mmol) and K_2CO_3 (1.5 g, 11 mmol) was dissolved in DMF (50 mL), and then the reaction mixture was

stirred at 80 °C for 1 day. The mixture was diluted with EtOAc and washed with brine. The organic layer was separated and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel (9:1, EtOAc:EtOH) to yield **5** as a pale pink solid (2.5 g, 87%). m.p.: 150-153 °C; MALDI-TOF MS: (*m/z*) 1558 ($[M+Na]^+$, $C_{75}H_{110}N_2O_{31}Na$, calcd. 1559); ^1H NMR (400MHz, $CDCl_3$, 18.6 °C): δ_H = 7.84 (s, 1H, ArH), 7.60 (d, J = 8.2 Hz, 2H, ArH), 7.49 (d, J = 8.2 Hz, 2H, ArH), 7.42 (d, J = 8.4 Hz, 2H, ArH), 7.37 (d, J = 8.4 Hz, 1H, ArH), 7.24 (s, 1H, NH), 6.77 (d, J = 8.4 Hz, 2H, ArH), 6.58 (d, J = 8.4 Hz, 1H, ArH),5.21-5.01 (m, 6H, CD-H_1), 4.62-3.03 (m, 89H, CD-H, NH_2, OCH_3), 2.18 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$, 21.1 °C): δ_C = 168.06, 159.77, 146.11, 140.53, 139.19, 133.04, 131.86, 130.61, 127.83, 125.99, 121.28, 115.35, 110.75, 108.80, 103.66, 100.46, 100.17-100.03 (several peaks overlapped), 99.63, 93.36, 86.22, 82.37-82.10 (several peaks overlapped), 81.84, 81.63, 81.17, 81.03, 71.60, 71.29-71.17 (several peaks overlapped), 70.70, 67.51, 61.82-61.70 (several peaks overlapped), 59.24, 59.05-59.00 (several peaks overlapped), 58.69, 58.15, 57.83, 57.76, 57.18, 24.86 Anal. Calcd for $C_{75}H_{110}N_2O_{31}\cdot 3H_2O$: C, 56.66; H, 7.35; N, 1.76%; Found: C, 56.51; H, 7.20; N, 1.66%.

1.6 References and Notes

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2) For nomenclature of rotaxanes, see: Yerin, A.; Wilks, E. S.; Moss, G P.; Harada, A. *Pure Appl. Chem.* **2008**, *80*, 2041-2068.

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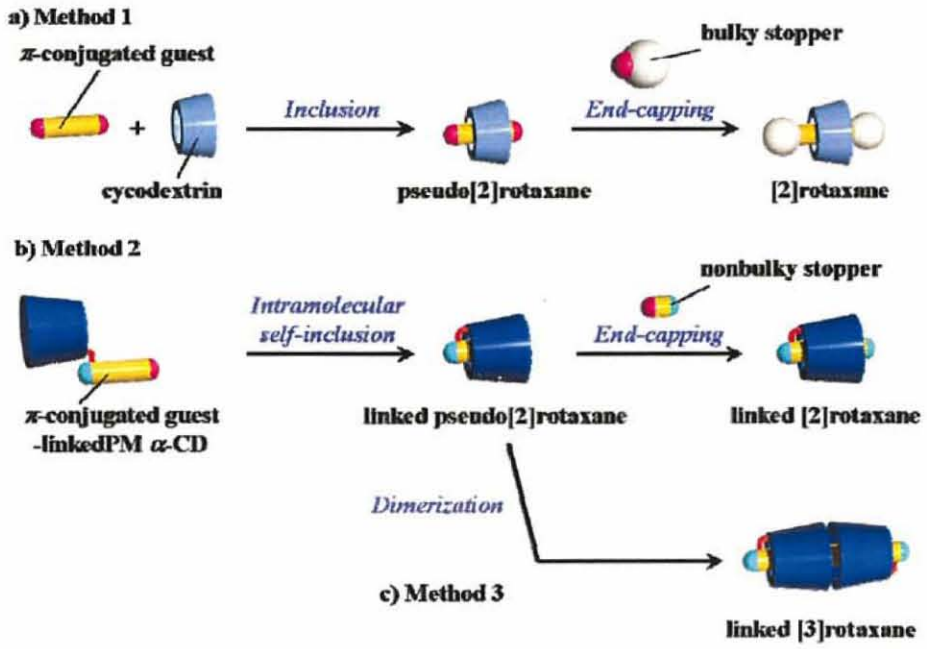
Chapter 2.

Synthesis of a Linked [3]Rotaxane via Dimerization of Intramolecular Self-inclusion Complexes

2.1 Introduction

Rotaxanes have attracted considerable attention because of their unique physical properties and potential applications in molecular devices.[1] It is known that the encapsulation of π-conjugated systems can lead to an enhancement in their chemical stability and fluorescence efficiency.[2] Rotaxanes have usually been synthesized by threading an axle molecule through a macrocycle followed by capping with two bulky stoppers (Scheme 1, Method 1).[3] We have revealed in the chapter 1 that an organic-soluble linked [2]rotaxane (also called [1]rotaxane) can be synthesized in good yield by the intramolecular self-inclusion of a lipophilic PMα-CD carrying a rigid π-conjugated axle moiety followed by capping with a small aniline unit as a stopper (Scheme 1, Method 2).[4]

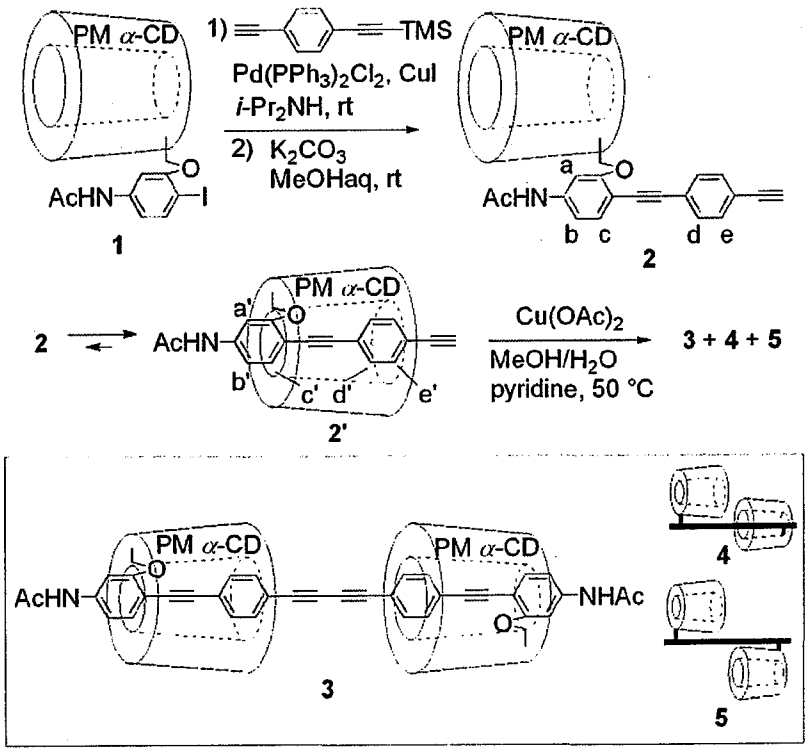


Scheme 1. Synthetic routes of rotaxanes. a) a conventional [2]rotaxane, b) a linked [2]rotaxane in chapter 1, c) a linked [3]rotaxane in this chapter.

In this chapter, I describe the synthesis of a linked [3]rotaxane[5] as a highly encapsulated π-conjugated system via intramolecular self-inclusion of a π-conjugated guest-linked PMα-CD and dimerization of thus-formed linked pseudo[2]rotaxanes without any another bulky stopper molecules (Scheme 1, Method 3).

2.2 Synthesis (*via Intramolecular Self-inclusion and Dimerization*)

Scheme 2 shows my strategy for the synthesis of linked [3]rotaxane. The reaction of 6-*O*-monotosyl PMα-CD with 2-iodo-5-acetamidophenol result in a modified PMα-CD iodide **1**[4] in 98% yield. Sonogashira coupling reaction of **1** with (4-ethynylphenylethynyl)-trimethylsilane[6] followed by the deprotection of the trimethylsiliyl group gave an ethynyltolan-linked PMα-CD **2** in 71% yield over two steps.



Scheme 2. Synthesis of a linked [3]rotaxane **3**.

The intramolecular self-inclusion phenomenon on **2** has been confirmed by using solvent- and

concentration- dependent ^{1}H NMR methods.[4] As shown in Figure 1, the NMR spectrum of **2** in $CDCl_3$ reveals the exclusion of the diphenylacetylene moiety from the cavity of the PMα-CD. A spectrum in CD_3OD showed an equilibrium mixture of two species, **2** and its supramolecular complex (linked pseudo[2]rotaxane) **2'**. When a more hydrophilic medium, D_2O/CD_3OD/pyridine-d_5 (10/5/1) has been used at 50 °C, this complex **2'** formed quantitatively. The fact that there was no change in the ^{1}H NMR spectra at different concentrations in the hydrophilic medium (Eglinton coupling conditions) indicated that the intramolecular self-inclusion complex (linked pseudo[2]rotaxane) **2'** was selectively generated from **2**.

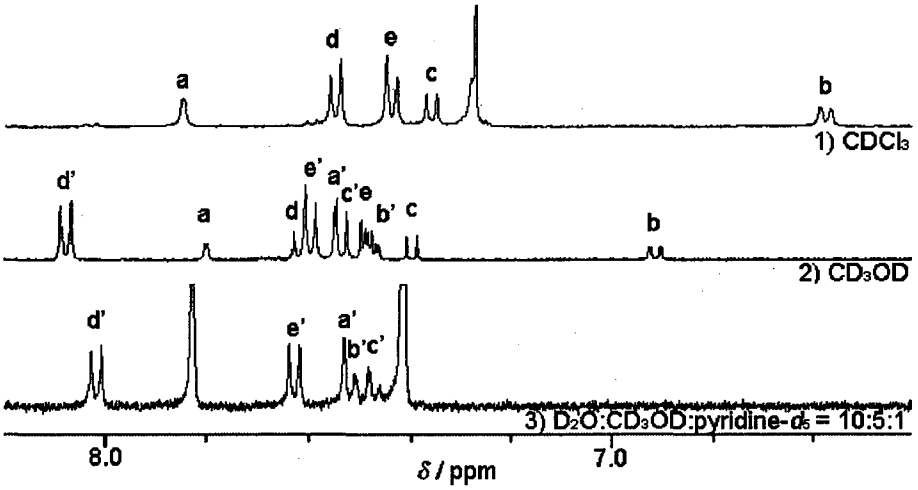


Figure 1. The aromatic region of 400 MHz ^{1}H NMR Spectra of **2** in several solvents. 1) $CDCl_3$ at rt; 2) CD_3OD at rt; 3) D_2O:CD_3OD:pyridine = 10:5:1 at 50 °C.

We then carried out the dimerization of **2'** by using Eglinton coupling in D_2O/CD_3OD/pyridine-d_5 (10/5/1) at 50 °C for 10 days. The formation of the desired dimer **3** was inferred from the MALDI-TOF mass spectrum, which displayed a strong signal at *m/z* 2959 for the corresponding $[\mathbf{3} + Na]^+$ ion. The NMR analysis of the crude product indicated the formation of the desired linked [3]rotaxane **3** in 81% yield along with linked [2]rotaxane **4** and unencapsulated dimer **5** as byproducts. The formation of byproducts indicates an ethynyl group of the excluded complex **2** is higher reactive than that of linked psuedo[2]rotaxane **2'**. These dimers were successfully separated in pure form by using silica gel column chromatography. The isolated yields of **3**, **4** and **5** were 52%, 18% and 2% yield, respectively.

Compounds **3**, **4**, and **5** had the same parent peak (*m/z*) in the MALDI-TOF mass spectrum but exhibited considerably different ^{1}H NMR spectra (Figure 2).

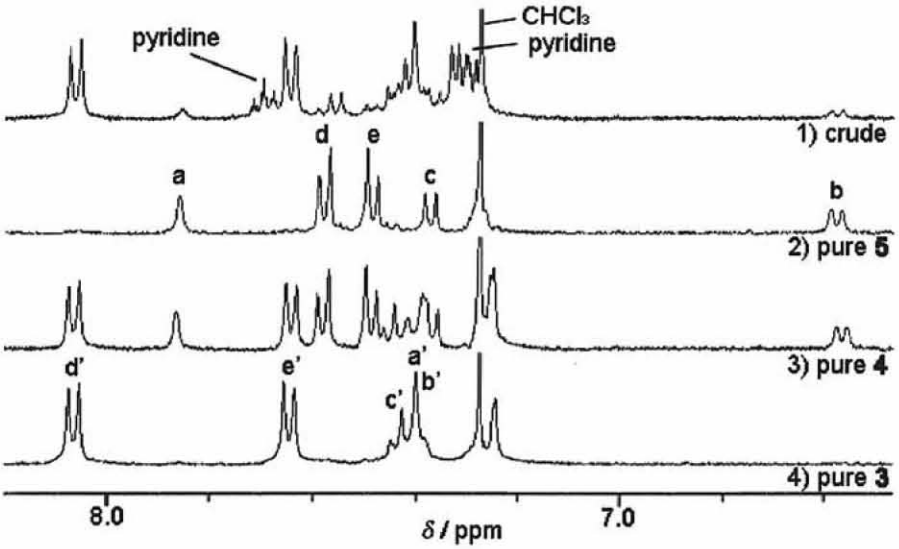


Figure 2. The aromatic region of 400 MHz ^{1}H NMR spectra in $CDCl_3$ at rt. 1) Eglinton reaction mixture; 2) unencapsulated dimer **5**; 3) linked [2]rotaxane **4**; 4) linked [3]rotaxane **3**.

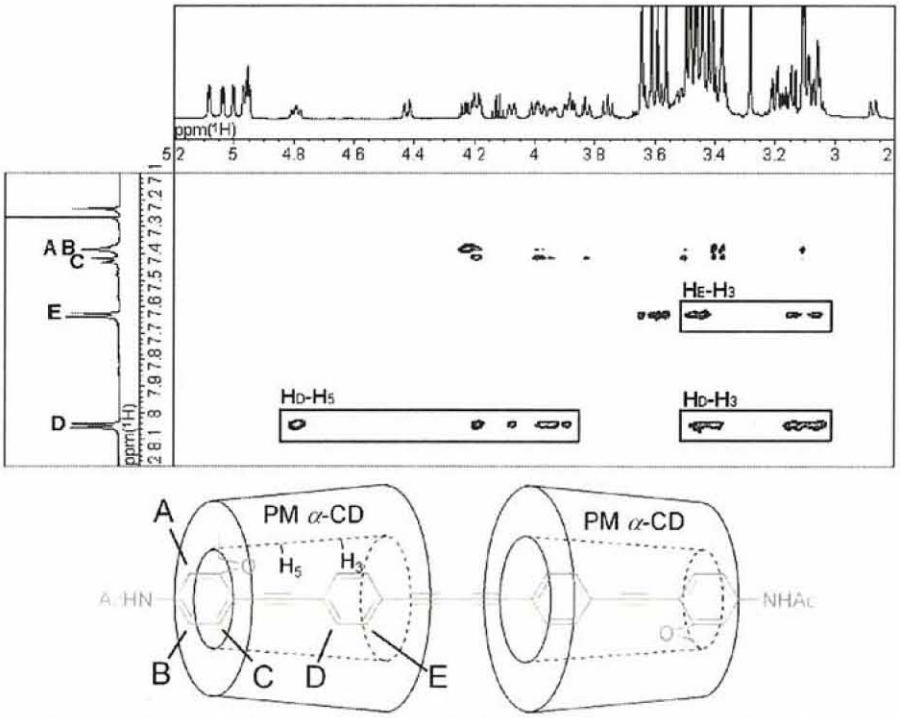


Figure 3. The section of the 600 MHz ROESY NMR spectrum of linked [3]rotaxane **3** in $CDCl_3$ at 25 °C with a mixing time of 300 ms and the proposed conformation.

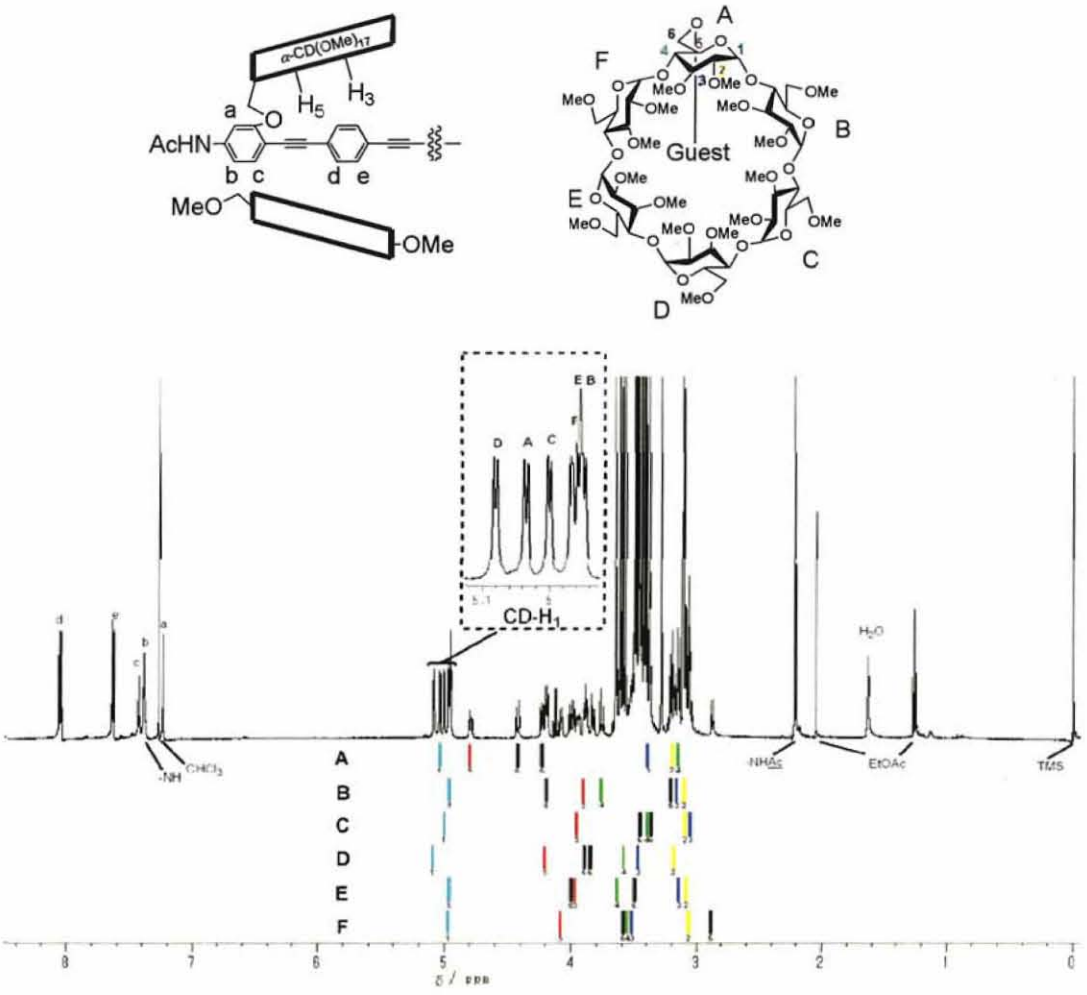


Figure 4. Assignments for the CD protons of linked[3]rotaxane **3** as determined using TOCSY, COSY, ROESY NMR spectrometry, and ^{1}H NMR spectrum recorded in $CDCl_3$ at 600 MHz.

In order to confirm the inclusion structure of this linked [3]rotaxane the protons of PMα-CD were assignment by 2D TOCSY, COSY and ROESY NMR (Figure 4). The NOEs between the axial tolan proton H_D and CD protons (H_3 and H_5) and between H_E and H_3 indicated that the axial π- conjugated system was embedded in the PMα-CD cavity to form linked [3]rotaxane (Figure 3).

2.3 Optical Properties

In order to examine the shielding effect of PMα-CD, we compared the fluorescence quantum yield of **3** with that of the corresponding partially encapsulated linked [2]rotaxane **4** and unencapsulated

compound **5**. As expected, there is an increasing fluorescence enhancement with coverage ratio of the whole π-conjugated axle molecule especially in solid state suggesting that high coverage ratio is essential to attain efficient fluorescence properties.

Table 1. Optical properties and fluorescence quantum yields.[a]

Sample	Absorption (λ_{max}/nm)	Emission (λ_{max}/nm)	$\Phi_{solution}$	Φ_{solid}
3	361	403	0.62	0.47
4	366	410	0.68	0.33
5	370	413	0.70	0.14

[a]Spectra were recorded in $CHCl_3$. Absolute quantum yields were determined by a calibrated integrating sphere system.

UV lamp (365 nm)

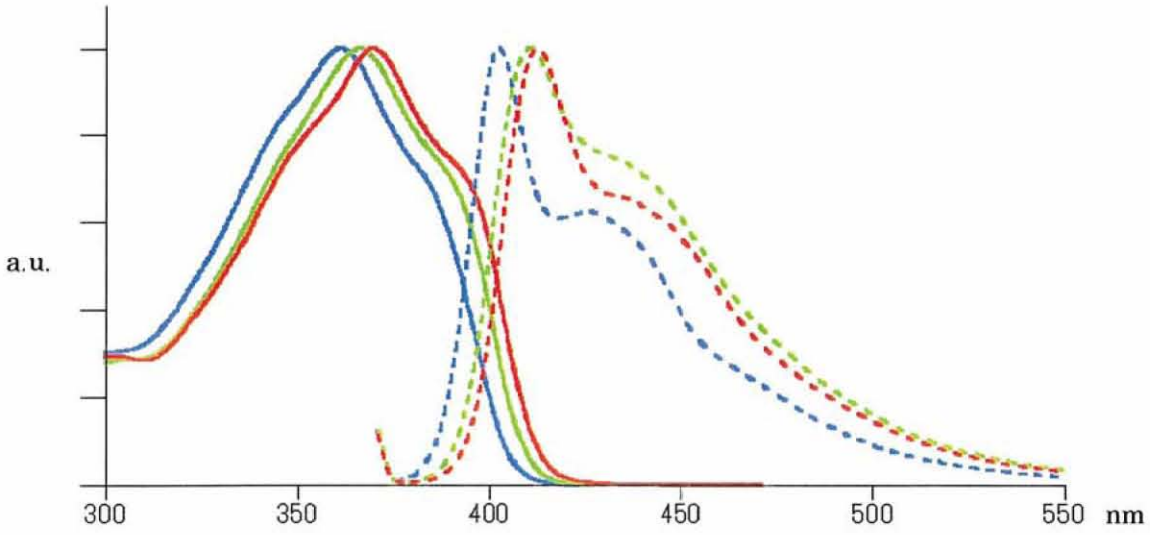


Figure 5. UV-vis spectra (solid lines) and emission spectra (dotted lines) of linked [3]rotaxane **3** (blue), linked [2]rotaxane **4** (green) and unencapsulated compound **5** (red).

In order to examine the shielding effect of PMα-CD, we investigated the fluorescence quenching of **3**, **4** and **5** with an electron acceptor.[8] As shown by the Stern-Volmer plots in Figure 6, the viologen analog (1,1'-di-*n*-hepthyl-4,4'- bipyridinium dibromide) quenched the fluorescence of the linked [3]rotaxane **3** considerably less than those of linked [2]rotaxane **4** and unencapsulated π-conjugated molecule **5**. It is noteworthy that fluorescence of partially encapsulated linked [2]rotaxane **4** was quenched at the same level as **5** suggesting that high coverage ratio of the whole conjugated axle is essential to attain efficient fluorescence properties. Further experiments will be required to determine the fluorescence quenching mechanisms in these systems.

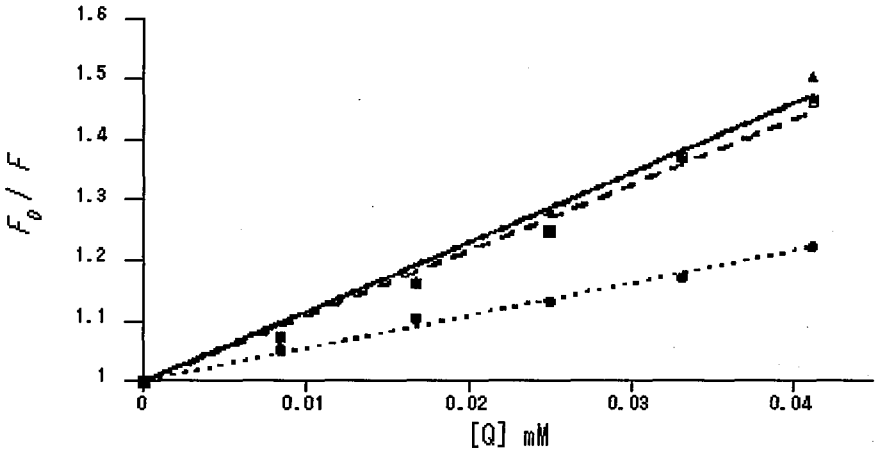


Figure 6. Stern-Volmer plots for titration of **3** (dotted line, circle), **4** (dashed line, square) and **5** (solid line, triangle) with 1,1'-di-*n*-hepthyl-4,4'-bipyridinium dibromide in $CHCl_3$. The concentration of **3**, **4** and **5** was 5.3×10^{-8} M

2.4 Conclusion

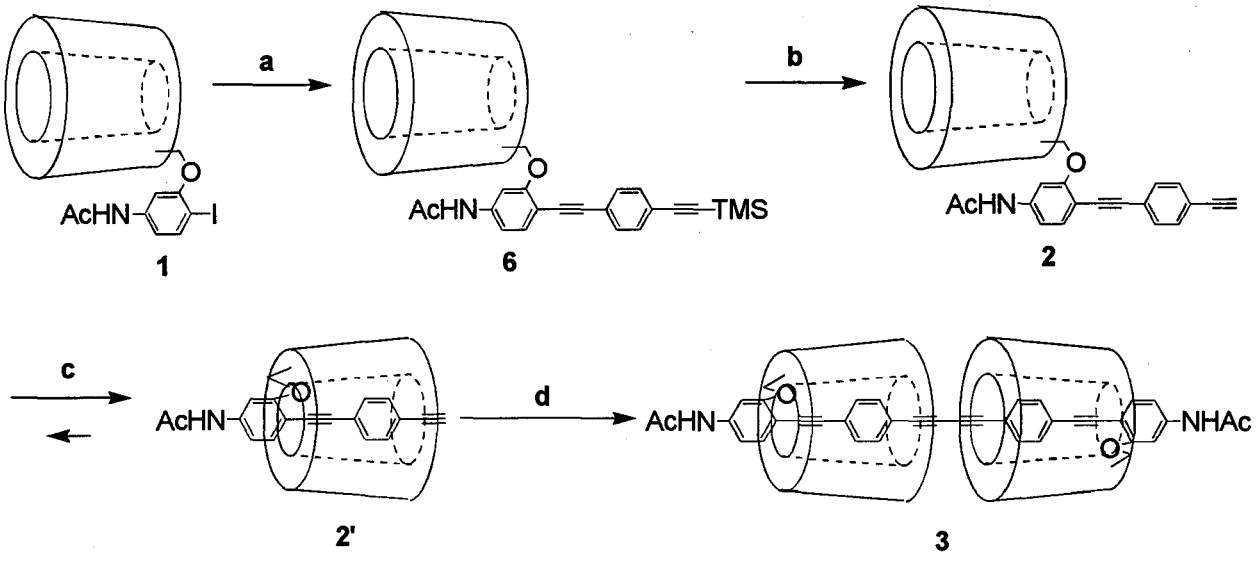
In conclusion, a highly organic soluble and highly encapsulated π-conjugated system was synthesized without any another bulky stopper molecules. This supramolecular structure of symmetric linked [3]rotaxane was determined by 2D NMR measurement. The Stern-Volmer plots of titration experiments indicated that the present linked [3]rotaxane exhibits strong insulation effect in prohibiting the approach of a quencher to the π-conjugated system.

2.5 Experimental Section

General Comments: A modified PMα-CD **1** was prepared by the previous reported procedure.[4]

(4-ethynylphenylethynyl)-trimethylsilane[6] were also prepared by the procedures similar to those reported previously. Other reagents were purchased from commercial sources and used without further purification. Commercially available dehydrated DMF was used without further distillation. Melting points were measured with a Stanford Research Systems MPA100 apparatus. GC Mass spectra (EI) were obtained on a SATURN GCMS-2000 operating in the electron impact mode (70eV) equipped with a RTX-5 30MX.25MMX.25U column. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra was obtained with α-cyano-4-hydroxycinnamic acid as a matrix and NaTFA as a cationization reagent on a SHIMADZU KRATOS TOF MASS spectrometer AXIMA-CFR Plus. ^{1}H NMR for 400 MHz and ^{13}C NMR for 100 MHz spectra were recorded by a JEOL JNM-Alice 400 spectrometer. 2D-COSY, ROESY, and TOCSY for 600MHz were recorded by a Varian INOVA-600. Elemental analyses were performed on Perkin Elmer 240C apparatus in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University.

Synthetic Scheme of linked [3]rotaxane 3



Reagents and Conditions: (a) 4-(trimethylsilylethynyl)phenylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, *i*-Pr_2NH, 40 °C; (b) K_2CO_3, MeOHaq., rt; (c) $MeOH/H_2O$ (1/1), 60 °C ~ rt; (d) $Cu(OAc)_2$, $MeOH/H_2O$ (1/2), pyridine, 50 °C.

Synthesis of 6: **1** (26.0 g, 17.7 mmol) was dissolved in *i*-Pr_2NH (200 mL). Under a nitrogen, 1-ethynyl-4-(trimethylsilylethynyl)benzene (5.30 g, 26.6 mmol), $Pd(PPh_3)_2Cl_2$ (248 mg, 0.35 mmol) and CuI (135 mg, 0.71 mmol) were added to the solution, and then the reaction mixture was stirred at room temperature for 9 h. The mixture was dried *in vacuo*, and the residue was purified by column chromatography on silica gel (9:1, EtOAc:EtOH) to yield **6** as a pale yellow solid (23.3 g, 85%). m.p.: 158-160 °C; MALDI-TOF MS: (*m/z*) 1564 ($[M+Na]^+$, $C_{74}H_{113}NO_{31}SiNa$, calcd. 1564); ^1H NMR (400MHz, $CDCl_3$, 20.2 °C): δ_H = 7.83 (d, J = 1.4 Hz, 1H, ArH), 7.52 (d, J = 8.3 Hz, 2H, ArH), 7.41 (d, J = 8.3 Hz, 2H, ArH), 7.35 (d, J = 8.3 Hz, 1H, ArH), 7.34 (s, 1H, NH), 6.59 (dd, J = 1.4, 8.3 Hz, 1H, ArH), 5.17-5.00 (m, 6H, CD-H_1), 4.60-3.04 (m, 87H, CD-H, OCH_3), 2.18 (s, 3H, CH_3CO), 0.26 (s, 9H, $(CH_3)_3Si$); ^{13}C NMR (100 MHz, $CDCl_3$, 20.6 °C): δ_C = 168.15, 160.02, 139.64, 133.27, 131.89, 131.35, 123.80, 122.50, 110.85, 108.39, 104.85, 103.71, 100.57, 100.19, 99.74, 96.07, 92.93, 88.12, 82.5-82.0 (several peaks overlapped), 81.72, 81.27, 81.14, 71.7-71.1 (several peaks overlapped), 70.74, 67.65, 62.0-61.8 (several peaks overlapped), 59.3-59.0 (several peaks overlapped), 58.78, 58.32, 58.0-57.8 (several peaks overlapped), 57.33, 24.97, 0.00; Anal. Calcd for $C_{74}H_{113}NO_{31}Si \cdot H_2O$: C, 57.02; H, 7.44; N, 0.90%; Found: C, 56.62; H, 7.15; N, 0.99%.

Synthesis of 2: **6** (17.0 g, 11.0 mmol) and K_2CO_3 (7.6 g, 55.0 mmol) were dissolved in MeOH (300 mL) and H_2O (60 mL). The reaction mixture was stirred under nitrogen at room temperature for 18 h. The mixture was diluted with EtOAc and washed with brine. The organic layer was separated and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel (9:1, EtOAc:EtOH) to yield **2** as a pale yellow solid (13.4 g, 83%). m.p.: 146-148 °C; MALDI-TOF MS: (*m/z*) 1491 ($[M+Na]^+$, $C_{71}H_{105}NO_{31}Na$, calcd. 1492); ^1H NMR (400MHz, $CDCl_3$, 20.3 °C): δ_H = 7.84 (d, J = 1.3 Hz, 1H, ArH), 7.55 (d, J = 8.3 Hz, 2H, ArH), 7.44 (d, J = 8.3 Hz, 2H, ArH), 7.36 (d, J = 8.3 Hz, 1H, ArH), 7.28 (s, 1H, NH), 6.58 (dd, J = 1.3, 8.3 Hz, 1H, ArH), 5.17-5.00 (m, 6H, CD-H_1), 4.63-3.02 (m, 88H, CD-H, OCH_3, CCH), 2.18 (s, 3H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$, 20.1 °C): δ_C = 168.06, 160.02, 139.62, 133.21, 132.00, 131.39, 124.18,

121.41, 110.74, 108.26, 103.59, 100.54, 100.13, 99.74, 92.68, 88.18, 83.43, 82.5-81.9 (several peaks overlapped), 81.68, 81.25, 81.10, 78.70, 71.7-71.1 (several peaks overlapped), 70.68, 67.56, 61.9-61.7 (several peaks overlapped), 59.29, 59.06, 58.73, 58.26, 57.9-57.8 (several peaks overlapped), 57.26, 24.94; Anal. Calcd for $C_{71}H_{105}NO_{31}\cdot 2H_2O$: C, 56.68; H, 7.30; N, 0.93%; Found: C, 56.65; H, 6.98; N, 0.89%.

Synthesis of 3: 2 (6.0 g, 4.1 mmol) was dissolved in MeOH (60 mL) and pyridine (12mL), and then the solution was heated at 60 °C. H_2O (120 mL) was added dropwise to the solution. The solution was stirred at 60 °C for 1 h and cooled to room temperature. $Cu(OAc)_2$ (4.5 g, 24.6 mmol) were added to the solution, and then the reaction mixture was stirred at 50 °C for 10 day. The mixture was diluted with EtOAc and washed with brine. The organic layer was separated and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel(4:1, EtOAc:EtOH, and 4:1, EtOAc:EtOH, with Et_3N (2%v/v)) to yield **3** as a pale yellow solid (3.1 g, 52%). m.p.: 215-217 °C; MALDI-TOF MS: (*m/z*) 2959 ($[M+Na]^+$, $C_{142}H_{208}N_2O_{62}Na$, calcd. 2958); ^1H NMR (400MHz, $CDCl_3$, 20.4 °C): $\delta_H = 8.05$ (d, $J = 8.3$ Hz, 4H, ArH), 7.64 (d, $J = 8.3$ Hz, 4H, ArH), 7.40 (m, 6H, ArH), 7.32 (s, 2H, NH), 5.09-4.96 (m, 12H, CD-H_1), 4.81-2.86 (m, 174H, CD-H, OCH_3), 2.21 (s, 6H, CH_3CO); ^{13}C NMR (100 MHz, $CDCl_3$, 20.3 °C): δ_C = 168.28, 162.59, 140.02, 133.69, 132.45, 132.16, 123.72, 121.86, 114.11, 112.64, 111.57, 100.72, 100.39, 100.12, 99.86, 98.04, 92.83, 89.44, 83.84, 82.8-82.0 (several peaks overlapped), 81.7-81.0 (several peaks overlapped), 75.46, 72.32, 71.9-71.1 (several peaks overlapped), 70.66, 70.20, 62.05, 62.00, 61.83, 61.77, 59.2-59.0 (several peaks overlapped), 58.75, 58.40, 58.08, 57.9-57.5 (several peaks overlapped), 24.83; Anal. Calcd for $C_{142}H_{208}N_2O_{62}\cdot 4H_2O$: C, 56.71; H, 7.24; N, 0.93%; Found: C, 56.71; H, 6.86; N, 0.97%.

2.6 References and Notes

1) For interlocked compounds, see: a) *Molecular catenanes, Rotaxanes and Knots*, ed. by Sauvate, J.-P.; Dietrich-Buchecker, C. Wiley-VCH, Weinhiem, **1999**; b) Amabilino, D. B.; Stoddart, J. F.

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2) Frampton, M. J.; Anderson, H. L. *Angew. Chem. Int. Ed.* **2007**, *46*, 1028-1046.

3) a) Vögtle, F.; Dünnwald, T.; Schmidt, T. *Acc. Chem. Res.* **1996**, *29*, 451-460; b) Jäger, R.; Vögtle, F. *Angew. Chem. Int. Ed.* **1997**, *36*, 930-944; c) Nepogodiev, S. A.; Stoddart, J. F. *Chem. Rev.* **1998**, *98*, 1959-1976; d) Sauvage, J.-P. *Acc. Chem. Res.* **1998**, *31*, 611-619; e) Wenz, G; Han, B.-H.; Müller, A. *Chem. Rev.* **2006**, 782-817; f) Vickers, M. S.; Beer, P. D. *Chem. Soc. Rev.* **2007**, *36*, 211-225; g) Champin, B.; Mobian, P.; Sauvage, J.-P. *Chem. Soc. Rev.* **2007**, *36*, 358-366.

4) Tsuda, S.; Terao, J.; Kambe, N. *Chem. Lett.* **2009**, *38*, 76-77.

5) For nomenclature of interlocked compounds, see: Safarowsky, O.; Windisch, B.; Mohry, A.; Vögtle, F. *J. Prakt. Chem.* **2000**, *342*, 437-444.

6) For synthetic details, see: Rodríguez, J. G; Tejedor, J. L.; Parra, T. L.; Díaz, C. *Tetrahedron* **2006**, *62*, 3355-3361.

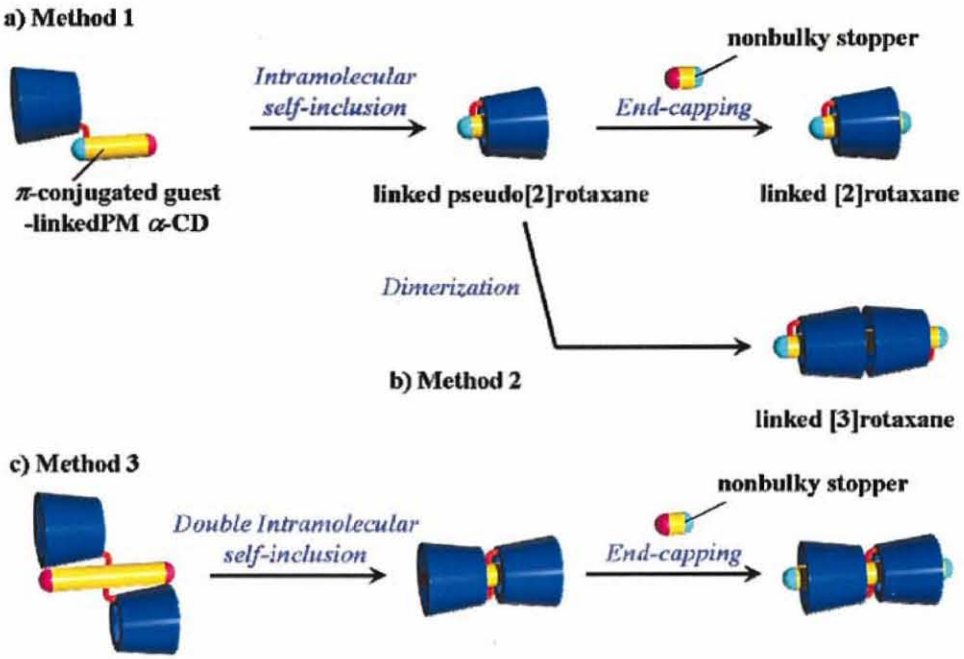
7) a) Taylor, P. N.; Hagan, A. J.; Anderson, H. L. *Org. Biomol. Chem.* **2003**, *1*, 3851-3856; b) Park, J. S.; Wilson, J. N.; Hardcastle, K. I.; Bunz, U. H. F.; Srinivasarao, M. *J. Am. Chem. Soc.* **2006**, *128*, 7714-7715.

Chapter 3.

Synthesis of Linked Symmetrical [3] and [5]Rotaxanes Having an Oligomeric Phenylene Ethynylene (OPE) Core Skeleton as a π-Conjugated Guest via Double Intramolecular Self-inclusion

3.1 Introduction

Oligomeric phenylene ethynylenes (OPEs) are among the most extensively studied families of molecular electronics materials due to their interesting photophysical properties including nonlinear optical (NLO) response,[1] luminescence,[2,3] and electroluminescence.[3] I am interested in developing new methods for encapsulation[4] of π-conjugated compounds in order to realize higher solubility, fluorescence quantum yields, electroluminescence efficiencies, and chemical stabilities of the π-conjugated systems. In chapter 1 and 2, I have described two new synthetic routes of linked rotaxanes

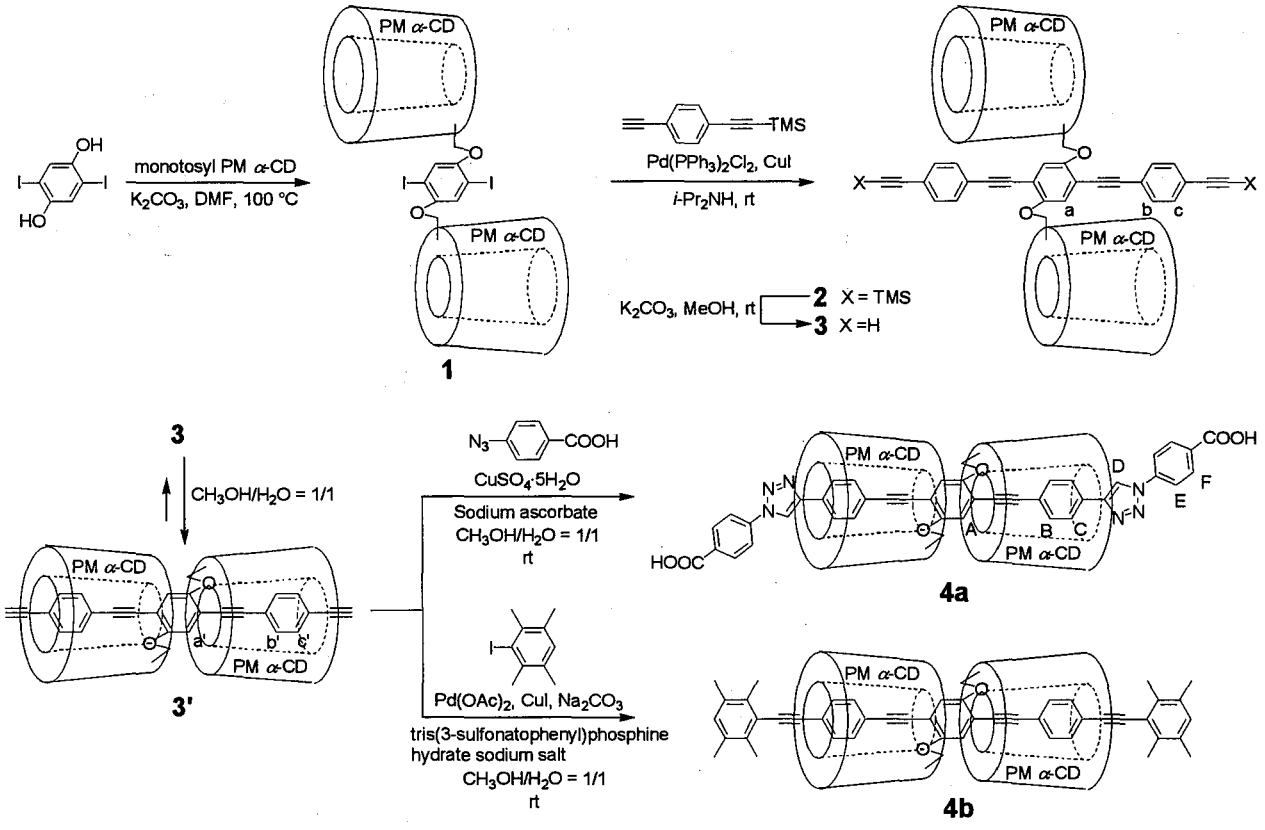


Scheme 1. Synthetic routes of linked rotaxanes. a) a linked [2]rotaxane in chapter 1; b) a linked [3]rotaxane in chapter 2; c) a linked rotaxane in this chapter 3.

bearing a π-conjugated system as a guest and permethylated α-cyclodextrin (PMα-CD) as a host (Scheme 1).[5,6] My strategies employed for the syntheses of these linked rotaxanes were based on intramolecular self-inclusion of a π-conjugated linear guest unit through lipophilic PMα-CD linking to the guest moiety to form a linked pseudo[2]rotaxane which then gave rise to a linked [2]rotaxane[5] also called [1]rotaxane by end-capping (Method 1) or a linked [3]rotaxane[6] by dimerization (Method 2).

In chapter 3, I describe the synthesis of OPE-based linked [3] and [5]rotaxanes via double intramolecular self-inclusion and capping with two end-groups (Scheme 1, Method 3).

3.2 Synthesis (*via Double Intramolecular Self-inclusion*)



Scheme 2. Synthesis of π-conjugated guest bearing two PMα-CDs.

Scheme 2 shows the synthetic route of our OPE-based linked [3]rotaxane. According to this process, modified PMα-CD diiodide **1** was prepared by the reaction of 6-*O*-monotosyl PMα-CD with 2,5-diiodo-1,4-benzenediol in 93% yield. Sonogashira coupling reaction of **1** with

1-ethynyl-4-[2-(trimethylsilyl)ethynyl]-benzene, followed by deprotection of the trimethylsiliyl group gave modified OPE having two PMα-CDs **3** in 75% yield over two steps.

The double intramolecular self-inclusion phenomenon of **3** has been confirmed by ^{1}H NMR employing different solvents and concentrations. The NMR spectrum of aromatic protons of **3** in CD_2Cl_2 reveals the exclusion of the OPE moiety from the cavity of the PMα-CDs (Figure 1a). A spectrum in CD_3OD at room temperature showed an equilibrium mixture of two species, **3** and its supramolecular complex (linked pseudo[3]rotaxane) **3'** (Figure 1b). The intensity of **3'** decreased and peaks of **3** increased by warming up to 55 °C (Figure 1c). When a more hydrophilic medium (CD_3OD:D_2O =3:1) has been used, **3** was completely converted to the supramolecular complex **3'** at room temperature (Figure 1d). The evidence that the NMR spectra of **3'** at different concentrations in CD_3OD showed no new peaks ascribable to oligomeric and/or polymeric supramolecular complexes may support double intramolecular self-inclusion complex **3'**. In addition, **3'** was stable even at 55 °C in the same hydrophilic medium (Figure 1e).

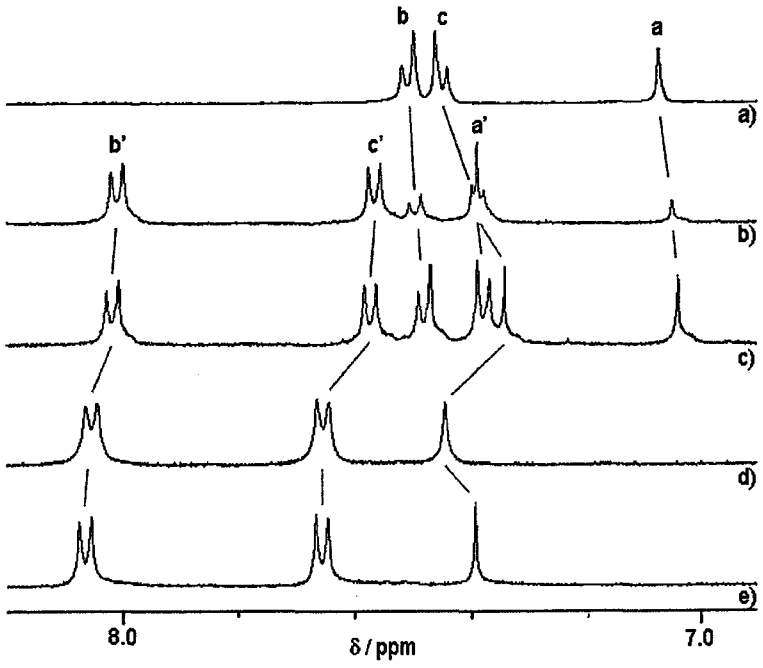


Figure 1. The aromatic region of 400 MHz ^{1}H NMR spectra of a two PMα-CD-linked OPE **3** in several solvents. a) CD_2Cl_2 at rt; b) CD_3OD at rt; c) CD_3OD at 55 °C; d) CD_3OD : D_2O = 3 : 1 at rt; e) CD_3OD : D_2O = 3 : 1 at 55 °C.

In order to fix pseudo linked [3]rotaxane structure by end-capping the OPE moiety by click reaction, **3'** was treated with 4-azido-benzoic acid having a bulky group in the presence of $CuSO_4 \cdot 5H_2O$ and sodium ascorbate at room temperature. After purification by silica gel column chromatography, the desired linked symmetrical [3]rotaxane having two phenylene ethynylene units **4a** was obtained in 89% yield.[10] This evidence suggests that pseudo [1]rotaxane **3'** was formed efficiently in CH_3OH:H_2O = 1:1. The structure of this linked [3]rotaxane **4a** was confirmed by MALDI-TOF mass spectrum, GPC analysis and 2D TOCSY, COSY and ROESY NMR spectra. The NOEs between protons on the OPE moiety and the internal protons of the PMα-CDs were observed. The NOE between H_A of the OPE moiety and H_6 located on the narrow rim of the PMα-CD indicates that two PMα-CDs formed in tail-to-tail arrangement (Figure 2).

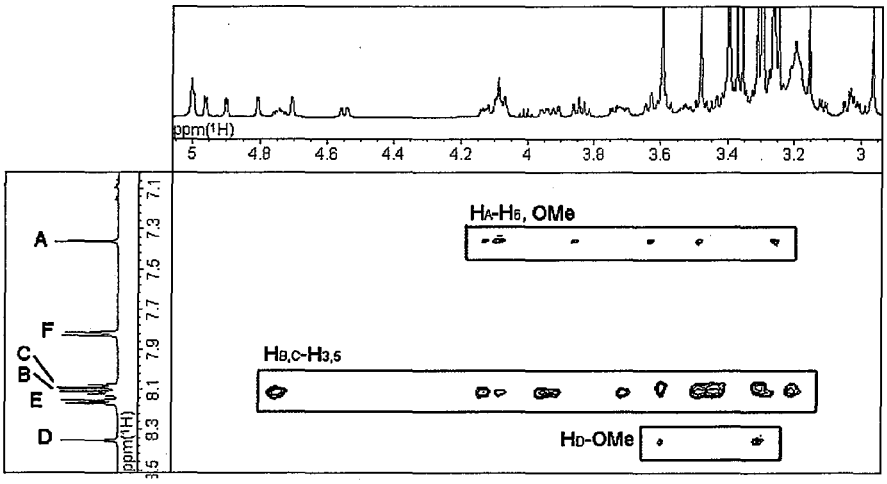
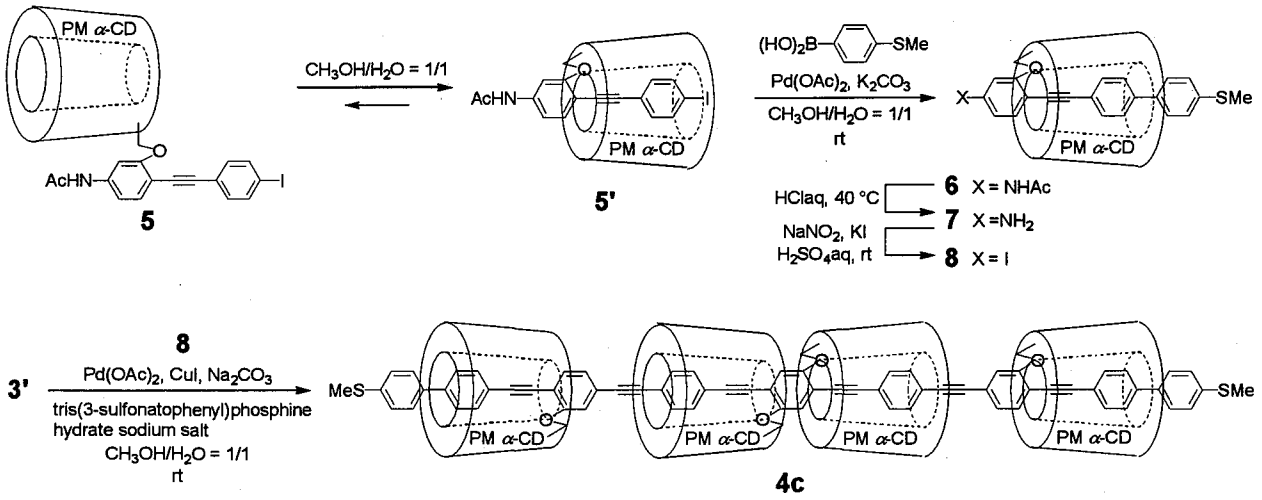


Figure 2. ROESY NMR spectrum of linked [3]rotaxane **4a** in CD_2Cl_2 at 25 °C.

In order to elongated the OPE units, we treated **3'** with 2,3,5,6-tetramethyliodobenzene in CH_3OH:H_2O = 3:1 in the presence of $Pd(OAc)_2$, CuI, Na_2CO_3, and tris(3-sulfonatophenyl)phosphine hydrate sodium salt and obtained the desired fixed [3]rotaxane having four phenylene ethynylene units **4b** in pure form but in only a 21% yield, probably because of the insolubility of 2,3,5,6-tetramethyliodobenzene in the mixed solvent of H_2O and CH_3OH.[11] This problem was solved by using [1]rotaxane **8** as a soluble stopper unit in the solvent system. As shown in Scheme 3, **8** was prepared via self-inclusion of tolan moiety bearing a PMα-CD following our method reported

previously (Method 1).[5,12] The reaction of **3'** with the [1]rotaxane as a stopper unit under Sonogashira coupling reaction conditions gave the desired linked symmetrical [5]rotaxane having six phenylene ethynylene units **4c** in 72% yield after purification with silica gel column chromatography.[13] High solubility of these PMα-CD derivatives **1-8** in various organic solvents is advantageous for their isolation compared with water soluble CD derivatives. The structure of **4c** was also confirmed by MALDI-TOF mass, 2D NMR. As shown in Figure 4, OPE guest was highly insulated with four PMα-CDs according to the space-filling model.



Scheme 3. Synthesis of linked [5]rotaxane **4c** via double intramolecular self-inclusion of **3**.

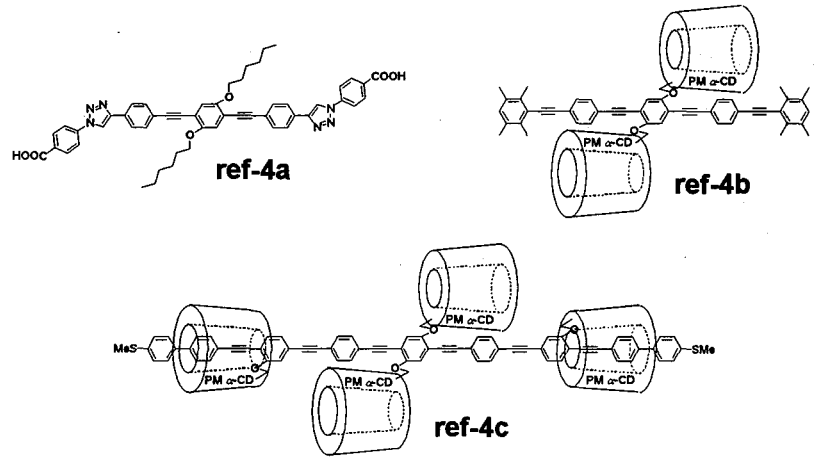
3.3 Luminescent Properties

The absorption and emission spectra and photoluminescence quantum yields of linked rotaxanes 4a-c and the corresponding reference compounds ref-4a-4c (Figure 3) are summarized in Table 1. The elongation of phenylene ethynylene units from two to six resulted in bathochromic shift by about 16 nm. Furthermore, shielding effect of PMα-CDs for these OPEs led to the efficient fluorescence enhancement especially in solid state.

Table 1. Optical properties and fluorescence quantum yields.[a]

sample	Absorption (λ_{max}/nm)[log ε]	Emission (λ_{max}/nm)	$\Phi_{solution}$	Φ_{solid}
4a	356 [3.82]	390, 411	0.82	0.14
4b	364 [3.75]	402, 423	0.92	0.14
4c	372 [4.08]	413, 436	0.87	0.37
ref-4a	384 [4.70][b]	423	0.82	0.003
ref-4b	392 [4.28]	444	0.84	0.01
ref-4c	392 [4.66]	438, 466	0.91	0.19

[a]Spectra were recorded in $CHCl_3$. Absolute quantum yields were determined by a calibrated integrating sphere system.[b]in $CHCl_3$:DMSO = 1:1



3.4 Conclusion

In conclusion, a highly organic-soluble linked [3] and [5]rotaxanes were prepared via double intramolecular self-inclusion of an OPE moiety bearing two PMα-CDs and subsequent end-capping by click reaction or Sonogashira coupling reaction. These linked rotaxanes are highly soluble in various organic solvents such as methanol, ethyl acetate, chloroform, toluene, and DMF. The remarkable fluorescence enhancement was observed in these linked rotaxanes both in solution and in solid state. This is the first successful example of rotaxane synthesis via selective double self-inclusion process.

3.5 Experimental Section

General Comments: 2,5-diiodo-1,4-benzenediol and 1-ethynyl-4-[2-(trimethylsilyl)ethynyl]-benzene were prepared by the previous reported procedure. Other reagents were purchased from commercial sources and used without further purification. Commercially available dehydrated DMF was used without further distillation. Melting points were measured with a Stanford Research Systems MPA100 apparatus. GC Mass spectra (EI) were obtained on a SATURN GCMS-2000 operating in the electron impact mode (70eV) equipped with a RTX-5 30MX.25MMX.25U column. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra was obtained with α-cyano-4-hydroxycinnamic acid as a matrix and NaTFA as a cationization reagent on a SHIMADZU KRATOS TOF MASS spectrometer AXIMA-CFR Plus. ^{1}H NMR for 400 MHz and ^{13}C NMR for 100 MHz spectra were recorded by a JEOL JNM-Alice 400 spectrometer. 2D-COSY, ROESY, and TOCSY for 600MHz were recorded by a Varian INOVA-600. Elemental analyses were performed on Perkin Elmer 240C apparatus in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University.

synthesis of 1: 2,5-dihydroxy-1,4-diiodobenene (1.20 g, 3.33 mmol), 6-*O*-monotosyl PMα-CD (10.0 g, 7.32 mmol) and dry K_2CO_3 (9.20 g, 66.6 mmol) were placed in a round-bottom flask and dried at 100 °C in vacuo. The mixture was dissolved in DMF (70 mL). The reaction mixture was stirred at 100 °C overnight. The mixture was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was separated and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel with EtOAc-EtOH (9:1) as eluent to yield **1** as an orange solid (8.43g, 93%). m.p.:138-141 °C; MALDI-TOF MS: (m/z) 2767 ($[M+Na]^+$, $C_{112}H_{188}I_2O_{60}Na$, calcd. 2770); ^{1}H NMR (400 MHz, $CDCl_3$, 22.3 °C): δ_H = 7.20 (s, 2H, ArH), 5.13-5.00 (m, 12H, CD-H_1), 4.50-3.10 (m, 174H, CD-H, OCH_3); Anal. Calcd for $C_{112}H_{188}I_2O_{60}\cdot H_2O$: C, 48.94; H, 6.89%; Found: C, 48.62; H, 6.92%.

synthesis of 2: **1** (5.49 g, 2.0 mmol) was dissolved in *i*-Pr_2NH (50 mL). Under a nitrogen atmosphere, $Pd(PPh_3)_2Cl_2$ (70 mg, 0.10 mmol), CuI (14 mg, 0.10 mmol) and (4-ethynylphenylethynyl)-silane (1.19 g, 6.0 mmol) were added into the solution, and then the reaction mixture was stirred under at room temperature. The mixture was filtered through a celite pad and concentrated, followed by a chromatographic purification on silica gel with EtOAc-EtOH (9:1) as eluent to yield **2** as orange solid (4.64 g, 80%). m.p.:138-141 °C; MALDI-TOF MS: (m/z) 2909 ($[M+Na]^+$, $C_{138}H_{214}O_{60}Si_2Na$, calcd. 2910); ^1H NMR (400 MHz, CD_2Cl_2, 21.4 °C): δ_H = 7.49 (d, J = 8.4 Hz, 4H, ArH), 7.41 (d, J = 8.4 Hz, 4H, ArH), 7.07 (s, 2H, ArH), 5.08-4.92 (m, 12H, CD-H_1), 4.83-2.99 (m, 174H, CD-H, OCH_3), 0.23 (s, 18H, $(CH_3)_3Si$); Anal. Calcd for $C_{138}H_{214}O_{60}Si_2 \cdot H_2O$: C, 57.01; H,7.49%; Found: C, 56.90 ; H, 7.18%.

synthesis of 3: **2** (644 mg, 0.223 mmol) was dissolved in MeOH (8 mL) and K_2CO_3 (1.1 g, 7.96 mmol) was added to the solution. Under a nitrogen atmosphere, the reaction mixture was stirred at room temperature for 30 min. The mixture was diluted with EtOAc and washed with brine. The organic layer was separated and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel with EtOAc-EtOH (9:1) as eluent to yield **3** as a brilliant yellow solid (573 mg, 94%). m.p.: >201 °C (decomposed); MALDI-TOF MS: (m/z) 2768 ($[M+Na]^+$, $C_{132}H_{198}O_{60}Na$, calcd. 2766); ^1H NMR (400 MHz, CD_2Cl_2, 14.2 °C): δ_H = 7.53 (d, J = 8.4 Hz, 4H, ArH), 7.47 (d, J = 8.4 Hz, 4H, ArH), 7.09 (s, 2H, ArH), 5.09-4.93 (m, 12H, CD-H_1), 4.86-3.01 (m, 176H, CD-H, CCH, OCH_3); Anal. Calcd for $C_{132}H_{198}O_{60} \cdot 2H_2O$: C, 57.01; H, 7.32%; Found: C, 56.62; H, 6.97 %.

synthesis of 4a: **3** (116 mg, 42 μmol) was dissolved in MeOH (12 mL) and water (12 mL) was added in the solution. This suspended solution was stirred at 70 °C for 1 h. After cooled to ambient temperature, were added 4-azido-benzoic acid (41 mg, 0.25 mmol), $CuSO_4 \cdot 5H_2O$ (21 mg, 170 μmol) and sodium ascorbate (33 mg, 0.34 mmol) into the solution. The mixture was stirred at room

temperature for 24h. The reaction mixture was treated with HClaq (0.1 N) and extracted with CH_2Cl_2. The combined organic layer was washed with saturated aqueous NaCl solution and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (9:1, CH_2Cl_2:MeOH (1% v/v TFA(trifluoroacetic acid)), 9:1, CH_2Cl_2:MeOH (5% v/v TFA), MeOH) to yield **4a** as a pale yellow solid (116 mg, 89%). m.p.: 247-250 °C; MALDI-TOF MS: (m/z) 3093 ($[M+Na]^+$, $C_{146}H_{208}N_6O_{64}Na$, calcd. 3092); ^1H NMR (400MHz, CD_2Cl_2, 21.5 °C): δ_H = 8.35 (s, 2H, ArH), 8.16 (d, J = 8.7 Hz, 4H, ArH), 8.12 (d, J = 8.2 Hz, 4H, ArH), 8.09 (d, J = 8.2 Hz, 4H, ArH), 7.83 (d, J = 8.7 Hz, 4H, ArH), 7.36 (s, 2H, ArH), 5.01-4.70 (m, 12H, CD-H_1), 4.56-2.71 (m, 176H, CD-H, CCH, OCH_3); Anal. Calcd for $C_{146}H_{208}N_6O_{64}\cdot 3H_2O$: C, 56.11; H, 6.90; N, 2.69%; Found: C, 55.91; H, 6.51; N, 2.66%.

synthesis of 4b: 3 (100 mg, 36 μmol) was dissolved in MeOH (10 mL) under a nitrogen atmosphere and degassed water (10 mL) was added in the solution. This suspended solution was stirred at 70 °C for 1 h. After cooled to ambient temperature, were added 2,3,5,6-tetramethyliodobenzene (24 mg, 91 μmol), Na_2CO_3 (23 mg, 0.22 mmol) into the solution. Then the catalyst solution of $Pd(OAc)_2$ (0.33 mg, 1.5 μmol), tris(3-sulfonatophenyl)phosphine hydrate sodium salt (1.7 mg, 2.9 μmol) and CuI (0.035 mg, 0.18 μmol) in water(0.10 mL), and triethylamine (100 μL) were added. The mixture was stirred at room temperature for 24h. The reaction mixture was treated with dilute aqueous HCl (0.1 N) and extracted with CH_2Cl_2. The combined organic layer was washed with saturated aqueous NaCl solution and dried over anhydrous Na_2SO_4, and filtered to remove insoluble fractions. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (9:1, EtOAc:EtOH, 8:2, EtOAc:EtOH) to yield **4b** as a pale yellow solid (23 mg, 21%). m.p.: > 200 °C (decomposed); MALDI-TOF MS: (m/z) 3036 ($[M+Na]^+$, $C_{152}H_{222}O_{60}Na$, calcd. 3030); ^1H NMR (400MHz, CD_2Cl_2, 21.5 °C): δ_H = 8.07 (d, J = 8.3 Hz, 4H, ArH), 7.71 (d, J = 8.3 Hz, 4H, ArH), 7.40 (s, 2H, ArH), 6.92 (s, 2H, ArH), 5.05-4.73 (m, 12H, CD-H_1), 4.58-2.74 (m, 174H, CD-H, OCH_3), 2.30 (s, 12H, $ArCH_3$), 2.20 (s, 12H, $ArCH_3$); Anal. Calcd for $C_{152}H_{222}O_{60}\cdot 3H_2O$: C, 59.59; H, 7.50%; Found: C,

59.51; H, 7.31%.

syntheses of 5-8: 5-8 were prepared by the procedures similar to those of a [1]rotaxane described in chapter 1. **data for 6:** A white solid; m.p.: 242-245 °C; MALDI-TOF-MS: (m/z) 1587 ($[M+Na]^+$, $C_{76}H_{111}NO_{31}SNa$, calcd. 1589); ^1H NMR (400MHz, $CDCl_3$, 24.0 °C): δ_H = 8.12 (d, J = 8.3 Hz, 2H, ArH), 7.67 (d, J = 8.3 Hz, 2H, ArH), 7.44 (m, 2H, ArH), 7.35 (m, 4H, NH, ArH), 7.28 (d, J = 8.3 Hz, 2H, ArH), 5.09-4.96 (m, 6H, CD-H_1), 4.91-2.85 (m, 87H, CD-H, OCH_3), 2.51 (s, 3H, SCH_3), 2.21 (s, 3H, CH_3CO); Anal. Calcd for $C_{76}H_{111}NO_{31}S{\cdot}2H_2O$: C, 56.95; H, 7.23; N, 0.87%; Found: C, 57.13; H, 6.87; N, 0.86%; **data for 7:** A pale yellow solid (2.76 g, 92% yield); m.p.: 221-225 °C; MALDI-TOF-MS: (m/z) 1546 ($[M+Na]^+$, $C_{74}H_{109}NO_{30}SNa$, calcd. 1547); ^1H NMR (400MHz, $CDCl_3$, 23.6 °C): δ_H = 8.08 (d, J = 8.3 Hz, 2H, ArH), 7.65 (d, J = 8.3 Hz, 2H, ArH), 7.36 (d, J = 8.3 Hz, 2H, ArH), 7.28 (d, J = 8.3 Hz, 2H, ArH), 7.23 (d, J = 8.8 Hz, 1H, ArH), 6.44 (m, 2H, ArH), 5.10-4.96 (m, 6H, CD-H_1), 4.92-2.86 (m, 89H, NH, CD-H, OCH_3), 2.51 (s, 3H, SCH_3); Anal. Calcd for $C_{74}H_{109}NO_{30}S{\cdot}H_2O$: C, 57.61; H, 7.25; N, 0.91%; Found: C, 57.54; H, 6.93; N, 0.89%; **data for 8:** A pale yellow solid (1.9 g, 54% yield); m.p.: 243-246 °C; MALDI-TOF-MS: (m/z) 1657 ($[M+Na]^+$, $C_{74}H_{107}IO_{30}SNa$, calcd. 1658); ^1H NMR (400MHz, $CDCl_3$, 23.2 °C): δ_H = 8.14 (d, J = 8.3 Hz, 2H, ArH), 7.68 (d, J = 8.3 Hz, 2H, ArH), 7.53 (d, J = 1.5 Hz, 1H, ArH), 7.49 (dd, J = 1.5, 8.3 Hz, 1H, ArH), 7.36 (d, J = 8.5 Hz, 2H, ArH), 7.29 (d, J = 8.5 Hz, 2H, ArH), 7.25 (d, J = 8.3 Hz, 1H, ArH), 5.09-4.95 (m, 6H, CD-H_1), 4.87-2.90 (m, 87H, CD-H, OCH_3), 2.52 (s, 3H, SCH_3); Anal. Calcd for $C_{74}H_{107}IO_{30}S$: C, 54.34; H, 6.59%; Found: C, 54.07; H, 6.37%.

synthesis of 4c: 4c was prepared by the procedure similar to that of **4b**. The residue was purified by preparative HPLC to yield **4c** as a pale yellow solid (74 mg, 72%). m.p.: > 260 °C (decomposed); MALDI-TOF-MS: (m/z) 5783 ($[M+Na]^+$, $C_{280}H_{410}O_{120}S_2Na$, calcd. 5780); ^1H NMR (400MHz, CD_2Cl_2, 20.4 °C): δ_H = 8.10 (d, J = 8.6 Hz, 4H, ArH), 8.07 (d, J = 8.3 Hz, 4H, ArH), 7.69 (d, J = 8.3 Hz, 4H, ArH), 7.66 (d, J = 8.6 Hz, 4H, ArH), 7.46 (d, J = 7.8 Hz, 2H, ArH), 7.42 (s, 2H, ArH), 7.37 (d, J = 8.7

Hz, 4H, ArH), 7.25 (d, J = 8.7 Hz, 4H, ArH), 7.21-7.18 (m, 4H, ArH), 5.05-4.82 (m, 24H, CD-H_1), 4.76-2.70 (m, 348H, CD-H, OCH_3), 2.48 (s, 6H, SCH_3); Anal. Calcd for $C_{280}H_{410}O_{120}S_2 \cdot 4H_2O$: C, 57.66; H, 7.22%; Found: C, 57.45; H, 6.84%.

3.6 References and Notes

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Chapter 4.

Encapsulated π-Conjugated Polymer Composed of Linked Rotaxane as Monomer Units

4.1 Introduction

π-Conjugated polymers[1] constitute the most important categories of materials used in the so-called "plastic electronics" or "organic electronics"[2] such as organic light emitting diodes (OLEDs),[3] organic field-effect transistors (OFETs),[4] and organic photovoltaic cells[5] and even "molecular wires" in molecular electronics due to their electrical and optical properties. Furthermore, the organic materials have several advantage such as low-cost, lightweight, low-power, flexbility, processibility and tunable properties for application to the devices.[6] However, π-conjugated polymer are generally unstable by

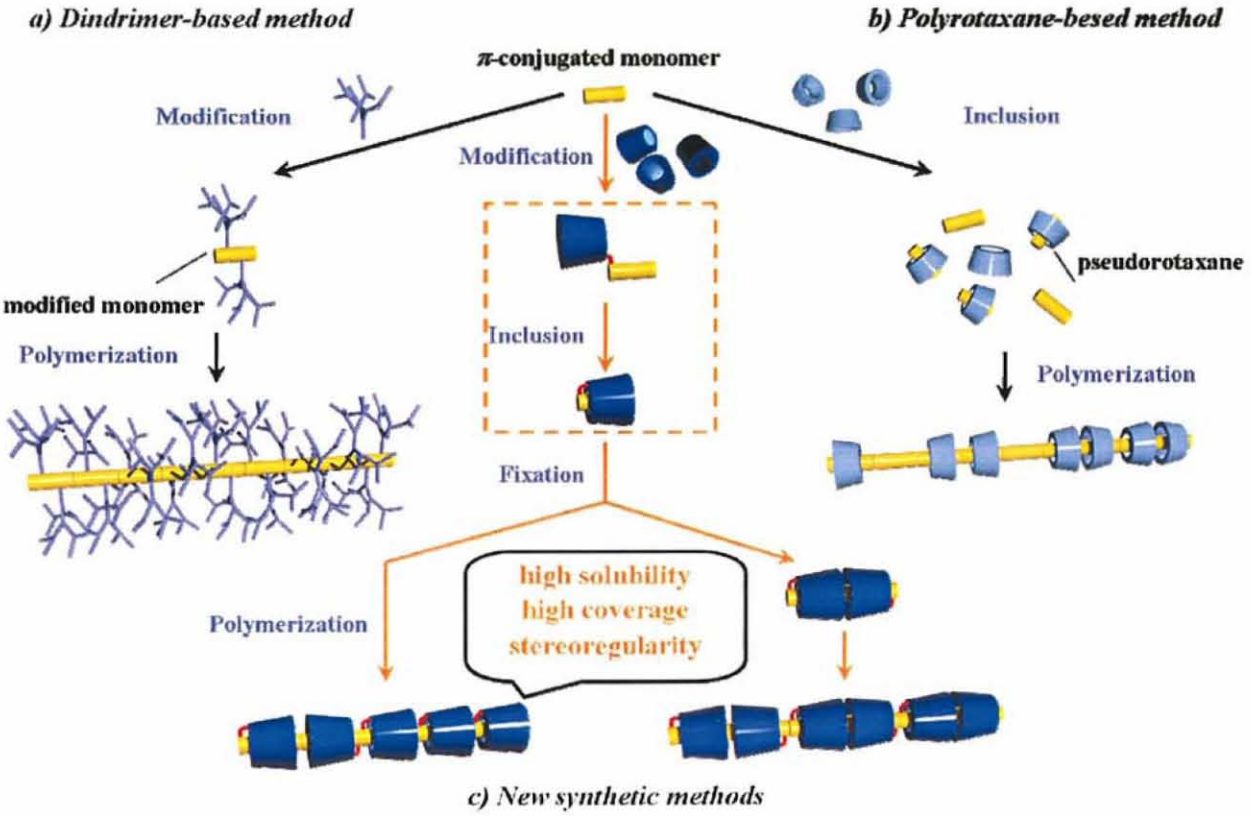


Figure 1. Synthetic methodologies of insulated molecular wires.

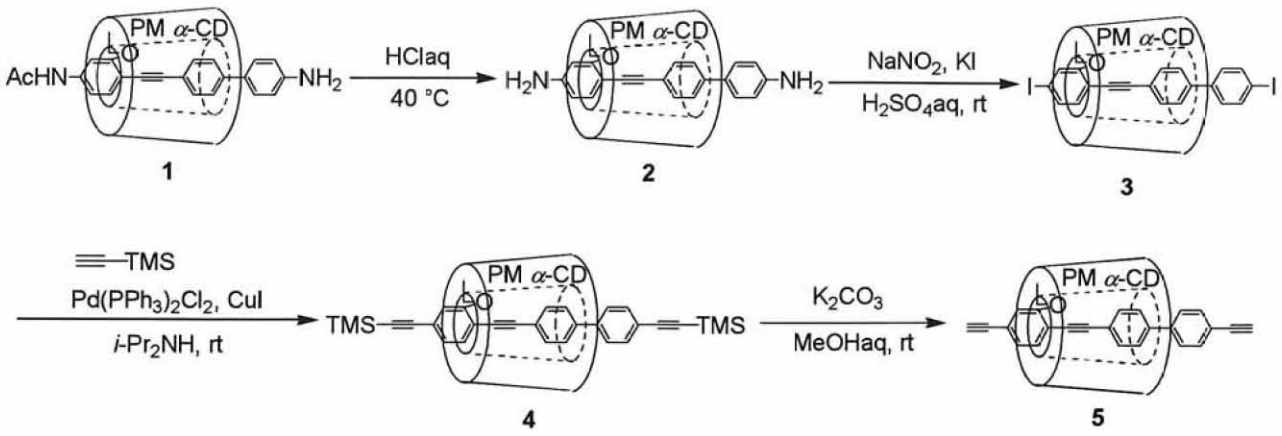
exposition to external stimulus such as light, heat and air. Furthoermore, cross-talk or short-circuit by interchain interaction between π-conjugated polymers can dramatically decrease their electrical and optical behavior. These make it interesting to study "insulated" or "encapsulated" molecular wires in which the π-conjugated polymers are encapsulated at the molecular level by a protective sheath, controlling the interchain interaction and then enhancing conductivity, fluorescence, stability and solubility compared with corresponding π-conjugated polymers.

The synthetic methodologies of insulated molecular wires have been researched and developed.[7] Especially, dendrimer-based synthetic method[8] and polyrotaxane-based synthetic method[9] are strong candidates as the methodology of desirable insulated molecular wires for application to the devices. The synthetic strategy of dendronized π-conjugated polymers is to decorate π-conjugated backbone with dendrons or steric hindered side-chains (Figure 1 a). Their features are stereoregularity and high solubility in organic solvents. On the other hand, the synthetic strategy of polyrotaxane is to thread π-conjugated polymer through cyclodextrins as encapsulating macrocycles (Figure 1 b). The primary structural feature of polyrotaxane is effective encapsulation of π-conjugated backbone.

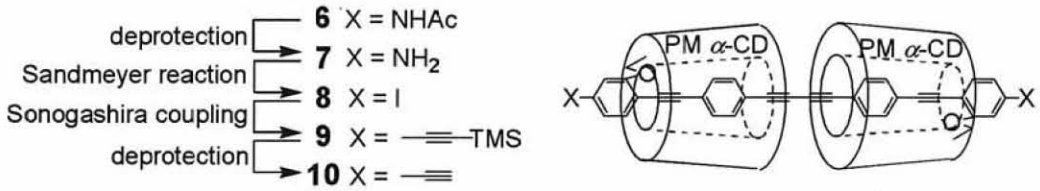
In this chapter, I describe new methodologies of insulated molecular wire by polymerization of linked rotaxanes (described in chapter 1 and 2) as monomer units to form encapsulated π-conjugated polymers having high solubility, high coverage, and stereoregularity (Figure 1 c).

4.2 Synthesis of Linked Rotaxane Monomers

Scheme 1 shows the synthetic route of a linked [2]rotaxane having two polymerization sites. According to this process, firstly, deprotection of the acetamide group on linked [2]rotaxane **1** gave linked [2]rotaxane diamine **2** in 98% yield. Secondly, **2** was treated with $NaNO_2$ and KI to give linked [2]rotaxane diiodide **3** in 67% yield. Finally, Sonogashira coupling of **3** with trimethylsilyl acethylene, followed by deprotection of the trimethylsiliyl group gave linked [2]rotaxane **5** having two terminal ethynyl groups as monomer unit of encapsulated π-conjugated polymer in 88% yield over two steps. Linked [3]rotaxane **10** was also dirived form **6** in 37% yield over four steps by similar procedure. The



Scheme 1. Synthesis of linked [2]rotaxane **5** having polymerization sites.



Scheme 2. Synthesis of linked [3]rotaxane **10** having polymerization sites.

structure of these linked rotaxanes **5** and **10** were confirmed by ^{1}H NMR and ROESY NMR spectra. According to space-filling models shown in Figure 2, encapsulating ratios of macrocycle ageinst π-conjugated backbone of linked [2] and [3]rotaxane was about 60% and 77%, respectively.

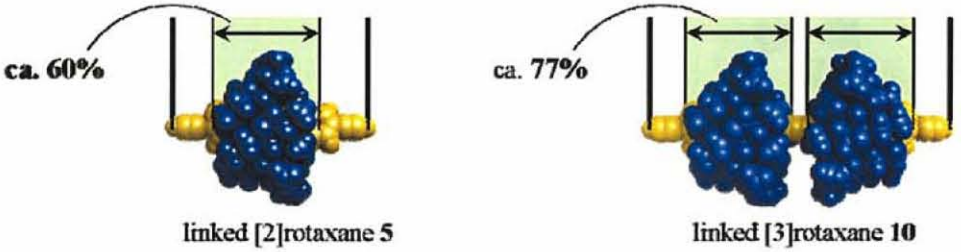


Figure 2. Space-filling model of linked rotaxanes.

4.3 Polymerization of Linked Rotaxanes

In order to give encapsulated π-conjugated polymer, Eglinton polymerization of linked [2]rotaxane **5** (6.6mM) as monomer unit was carried out in the presence of $Cu(OAc)_2$ (50mM) in pyridine at room

temperature. According to the GPC analysis, linked rotaxane oligomers (2 ~ 13-mer) were formed after 30 min and then linked rotaxane monomer was completely disappeared after 64 hours. Number- and weight-Average molecular weights(Mn and Mw) and the polydisperse index (PDI) of thus formed linked [2]rotaxane polymer **poly-5** were estimated at 1.93×10^4, 3.88×10^4 and 2.01, respectively, with polystylene standards as calibration standards. Therefore, the repeating number is obtained as ca. 26, which indicates that the length of encapsulated π-conjugated polymer is ca. 50 nm.

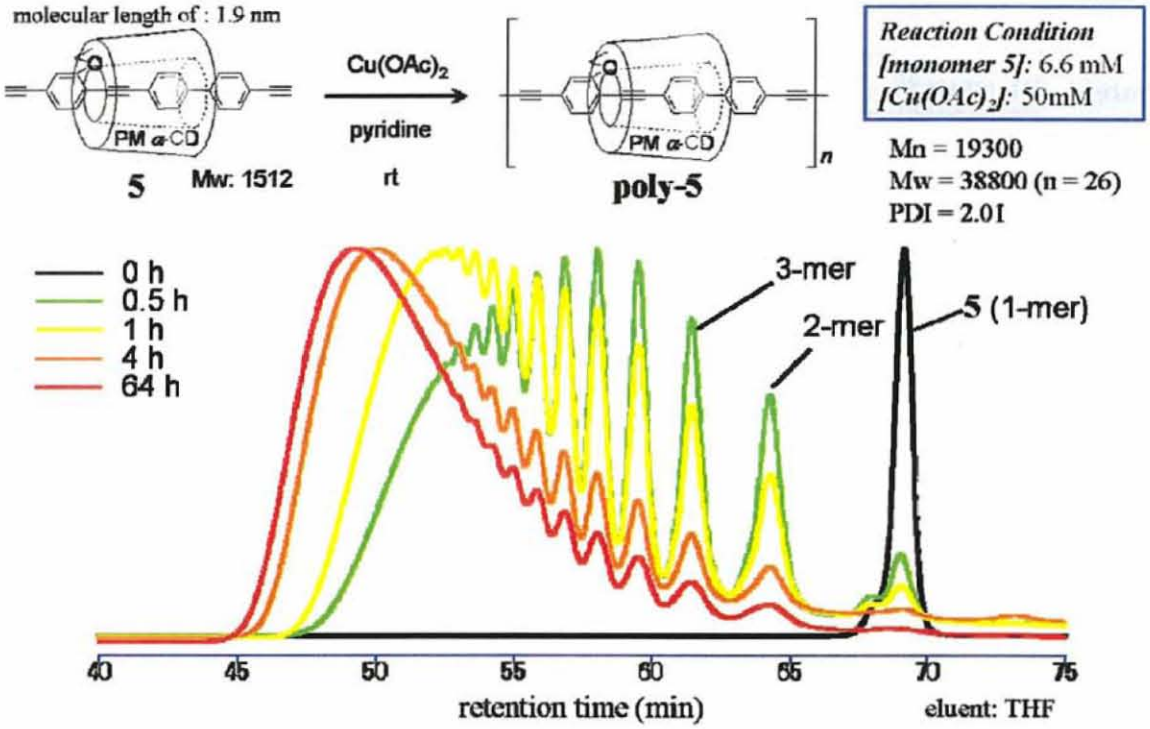


Figure 3. Polymerization of linked [2]rotaxane **5** and the GPC analysis.

As shown in Figure 4, the matrix-assisted laser desorption time-of-flight (MALDI-TOF) mass spectrum of **poly-5** provides excelent evidence for its structural authenticity. All the observed peaks correspond to expected singly charged molecular ions, with more than 20 repeat units. Furthermore, a broading NMR spectrum of **poly-5** similar to that of the linked [2]rotaxane monomer **5** indicated that encapsulated π-conjugated polymer repeating **5** as a unit was formed without structural deficit.

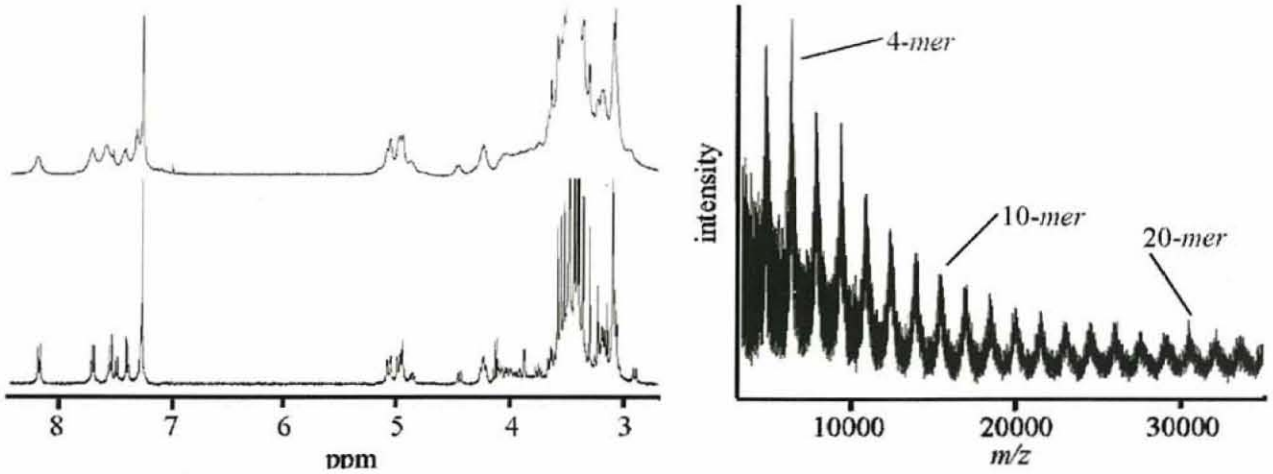
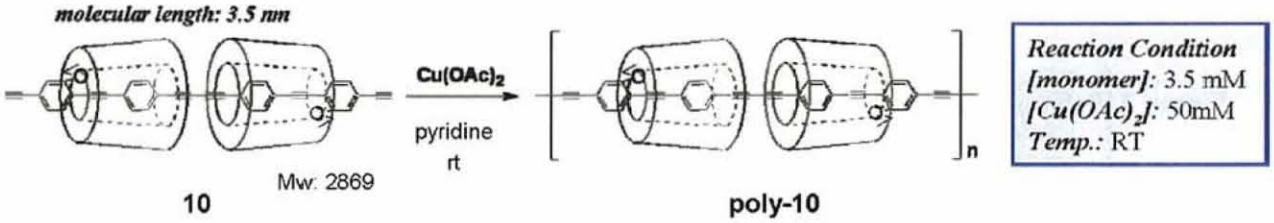


Figure 4. ^{1}H NMR spectra (left) of **5** (under) and **poly-5** (upper) and MALDI-TOF mass spectrum (right) of **poly-5**.

Eglinton polymerization of linked [3]rotaxane **10** (3.5 mM) as monomer unit was also carried out in the presence of $Cu(OAc)_2$ (50mM) in pyridine at room temperature (Scheme 3). GPC analysis, MALDI-TOF mass spectrum and ^{1}H NMR spectrum shown comparable result to polymerization of **5**. Mn, Mw and PDI of thus formed linked [3]rotaxane polymer **poly-10** were estimated at 1.55×10^4, 9.74×10^4 and 6.28, respectively. Therefore, the repeating number is obtained as ca. 34, which indicates that the length of encapsulated π-conjugated polymer is ca. 120 nm.



Scheme 3. Polymerization of linked [3]rotaxane **10**.

In order to calculate the solubility of these linked rotaxane polymers, high-molecular weight polymers (**poly-5**: Mn = 2.07×10^5, Mw = 2.42×10^5, PDI= 1.2; **poly-10**: Mn = 2.38×10^5, Mw = 2.82×10^5, PDI = 1.2) were separeted in pure form by gel permeation chromatography (GPC). The solubility test of thus separated linked rotaxane polymers shown that each polymers were soluble in various organic solvents such as ethyl acetate chloroform, toluene, and dimethylformamide (DMF)

except hexane, diethyl ether, methanol (Table 1). The solubility of **poly-10** is more higher than that of **poly-5** in ethyl acetate and DMF, which indicates that **poly-10** is more highly encapsulated with PMα-CDs (having high solubility in these solvent) compared with **poly-5**. This corresponds with the result of estimation of encapsulating ratios using spece filling models.

Table 1. Solubility test of linked rotaxane polymers **poly-5** and **poly-10**.[a]

Solvent	Solubility of **poly-5** (mg / mL)	Solubility of **poly-10** (mg / mL)
Hexane	insoluble	insoluble
Diethyl ether	insoluble	insoluble
Methanol	hardly soluble	hardly soluble
Ethyl acetate	0.51	26
Chloroform	54	34
Toluene	5.2	3.3
DMF	2.5	52

[a]The solubility was determined by UV-vis spectroscopy using a calibrated curve.

4.4 Polymerization of Linked Rotaxane in Poor Solvents

With the aim of controlling degree of polymerization to obtain encapsulated π-conjugated polymers having various molecular lengths, Eglinton polymerization of linked [2]rotaxane **5** (6.6mM) as monomer unit was carried out in the presence of $Cu(OAc)_2$ (50mM) in pyridine solusion including methanol as poor solvent at room temperature (Figure 5). According to the GPC analysis, in methanol:pyridine = 9:1, linked rotaxane oligomers (< 9-mer) were only formed after 64 hours. On the other hand, in methanol:pyridine = 1:1, medium molecular weight polymers was formed. In these solvent systems, the fluorescent precipitate was observed soon after starting polymerization. This indicates that oligomers or polymers having low solubility in the poor solvent were precipitated.

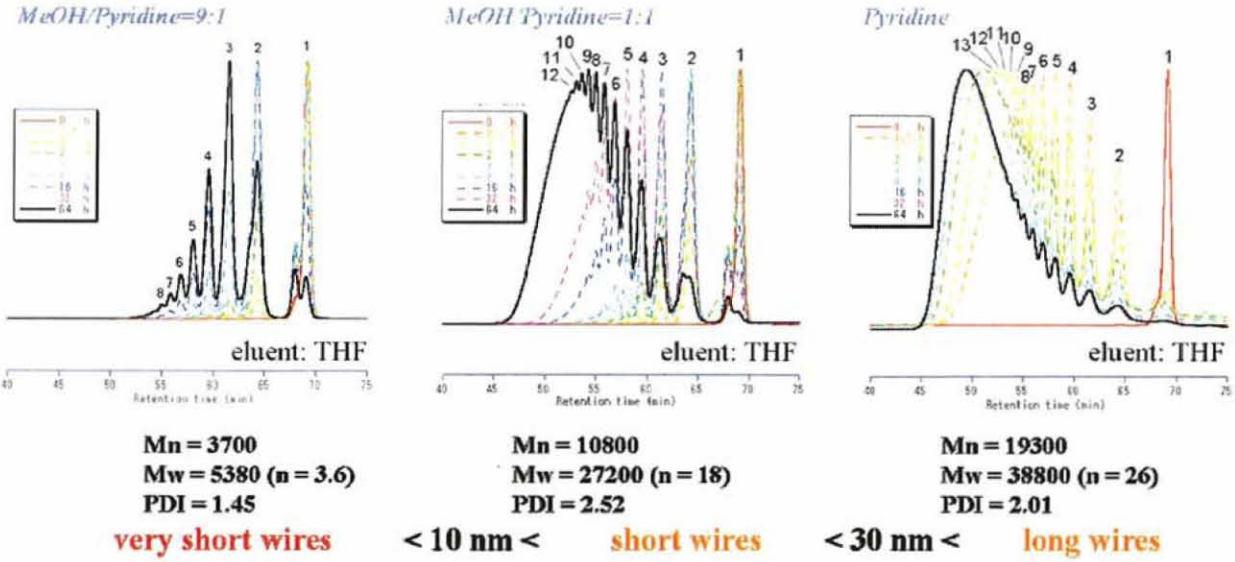


Figure 5. Polymerization of linked [2]rotaxane **5** in poor solvents.

In this section, I demonstrated controlling degree of polymerization of linked [2]rotaxane **5** using methanol as poor solvent.

4.5 Luminescent Properties

The absorption and emission spectra and photoluminescence quantum yields of linked rotaxanes (**5** and **10**),linked rotaxane polymer (**poly-5** and **poly-10**) and the corresponding reference compounds (**11**, **12**, **poly-11** and **poly-12**) are summarized in Table 2.

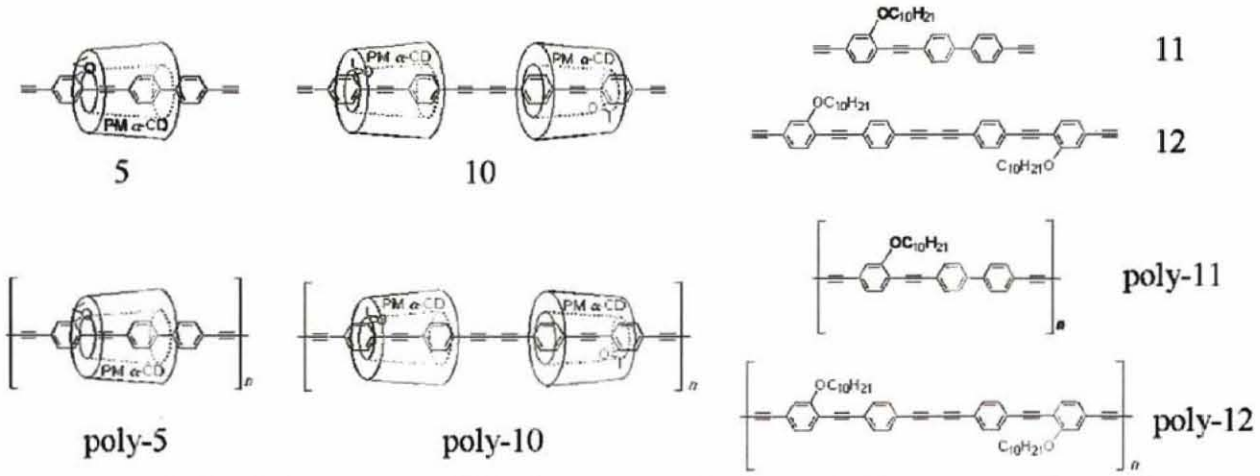
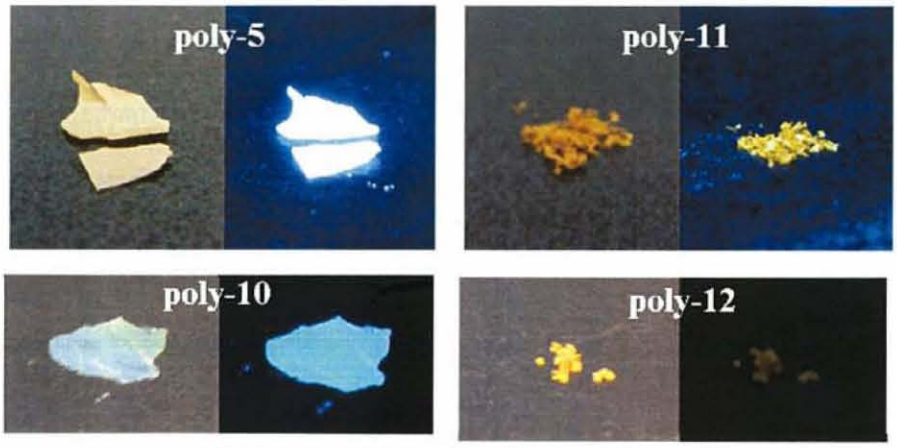


Figure 6. Linked rotaxanes, linked rotaxane polymers and the corresponding reference compounds.

Table 2. Optical properties and fluorescence quantum yields.[a]

Sample	Absorption (λ_{max}/nm)	Emission (λ_{max}/nm)	$\Phi_{solution}$	Φ_{solid}
5	325	367, 383	0.62	0.19
10	357	397,420	0.49	0.17
11	338	373, 389	0.68	0.089
12	368	403, 427	0.61	0.073
poly-5[b]	386	420, 445	0.70	0.14
poly-10[b]	402	425, 450	0.52	0.14
poly-11	---	---	---	<0.001
poly-12	---	---	---	<0.002

[a]Spectra were recorded in THF. Absolute quantum yields were determined by a calibrated integrating sphere system.[b]using separated **poly-5** (Mn = 2.07× 10^5, Mw = 2.42×10^5, PDI = 1.2) and **poly-10** (Mn = 2.38×10^5, Mw = 2.82×10^5 , PDI = 1.2).



UV lamp (365 nm)

The elongation of π-conjugated backbone from linked rotaxanes (**5** and **6**) to the polymer (**poly-5** and **poly-6**) resulted in bathochromic shift by about 61 nm and 45 nm, respectively. Furthermore, in each linked rotaxanes, shielding effect of PMα-CDs for π-conjugated polymer led to the efficient fluorescence enhancement especially in solid state.

4.6 Surface Morphology of a Linked [2]Rotaxane Polymers

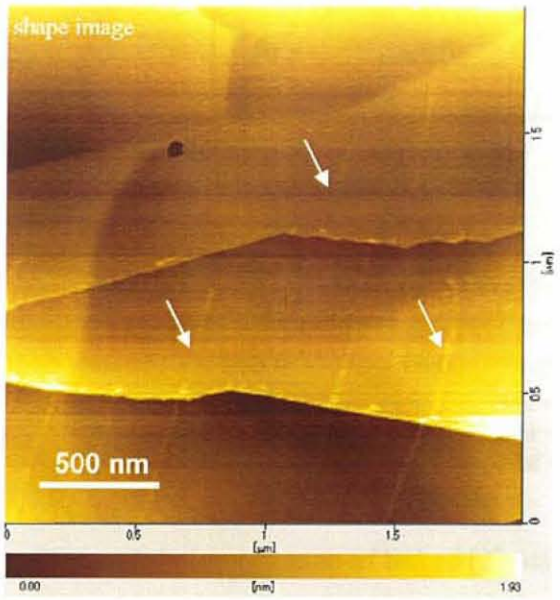


Figure 7. Tapping mode AFM images of a linked rotaxane polymer **poly-5** spin-coated from $CHCl_3$ solution on a HOPG substrate.

To observe the shape of linked [2]rotaxane polymer **poly-5** by AFM, the highly diluted solution of **poly-5** (Mn = 3.01×10^5, Mw = 3.31×10^5, PDI = 1.1) was dropped to HOPG substrate, and then the substrate was spun using rotational equipment and dried in air. Tapping mode AFM images look like good dispersion of the population of the polymers. **Poly-5** was observed as highly linear architecture (figure 7). The height of most linear architectures is 0.4-0.5 nm, which is remarkably smaller than the expected diameter PMα-CD (1.2 nm) and has to be corrected for imaging artifacts. The corrected width of the architecture was estimated at about 1.1 nm by talking into account a tip radius of 7 nm and the height determined above.

4.7 Conclusion

In conclusion, The synthesis of encapsulated π-conjugated polymers composed of linked rotaxanes as monomer units was succeeded. The linked rotaxane polymer are highly solble in various organic solvents. controlling degree of polymerization of linked [2]rotaxane **5** using methanol as poor solvent was demonstrated. The shielding effect of PMα-CDs for π-conjugated polymer led to the efficient fluorescence enhancement especially in solid state. **Poly-5** was observed as highly linear architecture.

4.8 Experimental Section

General Comments: Melting points were measured with a Stanford Research Systems MPA100 apparatus. GC Mass spectra (EI) were obtained on a SATURN GCMS-2000 operating in the electron impact mode (70eV) equipped with a RTX-5 30MX.25MMX.25U column. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra was obtained with α-cyano-4-hydroxycinnamic acid as a matrix and NaTFA as a cationization reagent on a SHIMADZU KRATOS TOF MASS spectrometer AXIMA-CFR Plus. ^{1}H NMR spectra for 400 MHz were recorded by a JEOL JNM-Alice 400 spectrometer. 2D-COSY, ROESY, and TOCSY for 600MHz were recorded by a Varian INOVA-600. Elemental analyses were performed on Perkin Elmer 240C apparatus in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University. The HPLC separation was performed on a Japan Analytical Industry Co. Ltd. LC-9204 recycling preparative HPLC equipped with JAIGEL-1H and -2H columns or LC-908 recycling preparative HPLC equipped with JAIGEL-2.5H and -3H columns using $CHCl_3$ as the eluent. Analytical size-exclusion chromatography (SEC) was carried out on a GL-Science GL-7400 HPLC System equipped with a GL-7410 HPLC pump, a GL-7400 UV detector, and GL-7454 RI detector through a column set consisting of Shodex KF-801, -802, -802.5, -803, -804 using THF as the eluent at a flow rate of 0.6 mL min^{-1}. Average molecular weights and the polydisperse index (PDI) of linked rotaxane polymers were estimated with polystylene standards as calibration standards.

Synthesis of 2: **1** (4.0 g, 2.6 mmol) was dissolved in 1M HCl (200 mL). The solution was stirred under nitrogen at 40 °C for 7 h. The mixture was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was separated and dried over Na_2SO_4 to yield **2** as a light brown solid (3.8 g, 98%). m.p.: 201-203 °C; MALDI-TOF-MS: (*m/z*) 1516 ($[M+Na]^+$, $C_{73}H_{108}N_2O_{30}Na$, calcd. 1517); ^{1}H NMR (400MHz, $CDCl_3$, 22.1 °C): δ_H = 8.04 (d, J = 8.3 Hz, 2H, ArH), 7.60 (d, J = 8.3 Hz, 2H, ArH), 7.24 (d, J = 8.3 Hz, 2H, ArH), 7.22 (d, J = 8.7 Hz, 1H, ArH), 6.70 (d, J = 8.3 Hz, 2H, ArH),

6.45-6.43 (m, 2H, ArH), 5.10-4.94 (m, 6H, CD-H_1), 4.93-2.85 (m, 87H, CD-H, OCH_3); Anal. Calcd for $C_{73}H_{108}N_2O_{30}\cdot 2H_2O$: C, 57.32; H, 7.38; N, 1.83%; Found: C, 57.43; H, 6.99; N, 1.72%.

Synthesis of 3: 2 (3.0 g, 2.0 mmol) was dissolved in 1M H_2SO_4 (60mL) and cooled to 0-5 °C. The solution was added dropwise a cold solution of $NaNO_2$ (300 mg, 4.4 mmol) in H_2O (40 mL). The reaction mixture was stirred at 0-5 °C for 1 h, and then the mixture was added to a solution of KI (3.3 g, 20 mmol). After the resulting mixture was stirred at room temperature for 1 h, the mixture was filtered. The brown solid was purified by column chromatography on silica gel(9:1, EtOAc:EtOH) to yield **3** as a pale yellow solid (2.3 g, 67%). m.p.: 238-241 °C; MALDI-TOF-MS: (*m/z*) 1738 ($[M+Na]^+$, $C_{73}H_{104}I_2O_{30}Na$, calcd. 1738); ^1H NMR (400MHz, $CDCl_3$, 22.4 °C): δ_H = 8.15 (d, J = 8.3 Hz, 2H, ArH), 7.76 (d, J = 8.3 Hz, 2H, ArH), 7.65 (d, J = 8.3 Hz, 2H, ArH), 7.53 (d, J = 1.5 Hz, 1H, ArH), 7.49 (dd, J = 1.5, 8.3 Hz, 1H, ArH), 7.25 (d, J = 8.3 Hz, 1H, ArH), 7.16 (d, J = 8.3 Hz, 2H, ArH), 5.08-4.95 (m, 6H, CD-H_1), 4.85-2.89 (m, 87H, CD-H, OCH_3); Anal. Calcd for $C_{73}H_{104}I_2O_{30}$: C, 51.11; H, 6.11%; Found: C, 51.17; H, 5.84%.

Synthesis of 4: 3 (2.9 g, 1.7 mmol) was dissolved in *i*-Pr_2NH (60 mL). Under a nitrogen atmosphere, trimethylsilylacethylene (1.0 g, 10 mmol), $Pd(PPh_3)_2Cl_2$ (24 mg, 0.034 mmol) and CuI (13 mg, 0.068 mol) were added to the solution, and then the reaction mixture was stirred at room temperature for 6 h. The mixture was dried *in vacuo*, and the residue was purified by column chromatography on silica gel (9:1, EtOAc:EtOH) to yield **4** as a pale yellow solid (2.8 g, quant). m.p.: 168-170 °C; MALDI-TOF-MS: (*m/z*) 1679 ($[M+Na]^+$, $C_{83}H_{122}O_{30}Si_2Na$, calcd. 1679); ^1H NMR (400MHz, $CDCl_3$, 22.0 °C): δ_H = 8.15 (d, J = 8.3 Hz, 2H, ArH), 7.69 (d, J = 8.3 Hz, 2H, ArH), 7.51 (d, J = 8.3 Hz, 2H, ArH), 7.45 (d, J = 7.8 Hz, 1H, ArH), 7.38 (d, J = 8.3 Hz, 2H, ArH), 7.25-7.23 (m, 2H, ArH), 5.09-4.94 (m, 6H, CD-H_1), 4.89-2.85 (m, 87H, CD-H, OCH_3), 0.27 (s, 9H, $(CH_3)_3Si$), 0.25 (s, 9H, $(CH_3)_3Si$); Anal. Calcd for $C_{83}H_{122}O_{30}Si_2\cdot H_2O$: C, 59.55; H, 7.47%; Found: C, 59.39; H, 7.17%.

Synthesis of 5: **4** (400 mg, 0.24 mmol) and K_2CO_3 (199 mg, 1.4 mmol) were dissolved in EtOH (20 mL) and H_2O (5 mL). The reaction mixture was stirred under nitrogen at room temperature for 5 h. The mixture was diluted with EtOAc and washed with brine. The organic layer was separated and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the residue was purified by preparative GPC (JAIGEL-1H/2H, eluent $CHCl_3$) to yield **5** as a pale yellow solid (310 mg, 88%). m.p.: 233-236 °C; MALDI-TOF-MS: (*m/z*) 1534 ($[M+Na]^+$, $C_{77}H_{106}O_{30}Na$, calcd. 1535); ^1H NMR (400MHz, $CDCl_3$, 18.2 °C): δ_H = 8.17 (d, J = 8.3 Hz, 2H, ArH), 7.69 (d, J = 8.3 Hz, 2H, ArH), 7.54 (d, J = 8.3 Hz, 2H, ArH), 7.49 (d, J = 7.8 Hz, 1H, ArH), 7.39 (d, J = 8.3 Hz, 2H, ArH), 7.28-7.25 (m, 2H, ArH), 5.09-4.95 (m, 6H, CD-H_1), 4.89-2.89 (m, 89H, CCH, CD-H, OCH_3); Anal. Calcd for $C_{77}H_{106}O_{30}\cdot H_2O$: C, 60.46; H, 7.12%; Found: C, 60.64; H, 6.86%.

Synthesis of 7: **6** (3.1 g, 1.1 mmol) was dissolved in THF (30 mL) and 1M HCl (150 mL). The solution was stirred under nitrogen at 50 °C for 21 h. The mixture was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was separated and dried over Na_2SO_4 to yield **7** as a light brown solid (2.9 g, 91%). m.p.: 209-211 °C; MALDI-TOF-MS: (*m/z*) 2875 ($[M+Na]^+$, $C_{138}H_{204}N_2O_{60}Na$, calcd. 2874); ^1H NMR (400MHz, $CDCl_3$, 23.7 °C): δ_H = 8.00 (d, J = 8.3 Hz, 4H, ArH), 7.61 (d, J = 8.3 Hz, 4H, ArH), 7.21 (d, J = 8.3 Hz, 2H, ArH), 6.44 (m, 4H, ArH), 5.10-4.97 (m, 12H, CD-H_1), 4.83-2.87 (m, 178H, NH, CD-H, OCH_3); Anal. Calcd for $C_{138}H_{204}N_2O_{60}\cdot 2H_2O$: C, 57.41; H, 7.26; N, 0.97%; Found: C, 57.24; H, 6.92; N, 0.92%.

Synthesis of 8: **7** (5.6 g, 1.9 mmol) was dissolved in 1M H_2SO_4 (120mL) and cooled to 0-5 °C. The solution was added dropwise a cold solution of $NaNO_2$ (290 mg, 4.2 mmol) in H_2O (80 mL). The reaction mixture was stirred at 0-5 °C for 1 h, and then the mixture was added to a solution of KI (3.2 g, 19 mmol) in H_2O (80 mL). After the resulting mixture was stirred at room temperature for 1 h, the mixture was filtered. The brown solid was purified by column chromatography on silica gel(4:1, EtOAc:EtOH) to yield **8** as a pale yellow solid (4.3 g, 73%). m.p.: 199-201 °C; MALDI-TOF-MS:

(*m/z*) 3098 ([M+Na]$^+$, $C_{138}H_{200}I_2O_{60}Na$, calcd. 3096); ^{1}H NMR (400MHz, $CDCl_3$, 22.4 °C): δ_H = 8.06 (d, J = 8.3 Hz, 4H, ArH), 7.64 (d, J = 8.3 Hz, 4H, ArH), 7.53 (d, J = 1.4 Hz, 2H, ArH), 7.49 (dd, J = 1.4, 8.0 Hz, 2H, ArH), 7.23 (d, J = 8.0 Hz, 2H, ArH), 5.08-4.95 (m, 12H, CD-H_1), 4.77-2.91 (m, 174H, CD-H, OCH_3); Anal. Calcd for $C_{138}H_{200}I_2O_{60}\cdot 3H_2O$: C, 53.01; H, 6.64%; Found: C, 52.91; H, 6.24%.

Synthesis of 9: **8** (4.3 g, 1.4 mmol) was dissolved in THF (30 mL) and *i*-Pr_2NH (80 mL). Under a nitrogen atmosphere, trimethylsilylacethylene (830 mg, 8.4 mmol), $Pd(PPh_3)_2Cl_2$ (40 mg, 0.057 mmol) and CuI (22 mg, 0.12 mol) were added to the solution, and then the reaction mixture was stirred at room temperature for 14 h. The mixture was dried *in vacuo*, and the residue was purified by column chromatography on silica gel (4:1, EtOAc:EtOH) to yield **9** as a pale yellow solid (2.7 g, 64%). m.p.: 201-205 °C; MALDI-TOF-MS: (*m/z*) 3038 ([M+Na]$^+$, $C_{148}H_{218}O_{60}Si_2Na$, calcd. 3036); ^{1}H NMR (400MHz, $CDCl_3$, 23.3 °C): δ_H = 8.07 (d, J = 8.3 Hz, 4H, ArH), 7.65 (d, J = 8.3 Hz, 4H, ArH), 7.43 (d, J = 8.0 Hz, 2H, ArH), 7.25 (d, J = 1.4 Hz, 2H, ArH), 7.23 (dd, J = 1.4, 8.0 Hz, 2H, ArH), 5.09-4.95 (m, 12H, CD-H_1), 4.79-2.87 (m, 174H, CD-H, OCH_3), 0.27 (s, 18H, $(CH_3)_3Si$); Anal. Calcd for $C_{148}H_{218}O_{60}Si_2\cdot H_2O$: C, 58.64; H, 7.31%; Found: C, 58.53; H, 7.05%.

Synthesis of 10: **9** (270 mg, 0.090 mmol) and K_2CO_3 (124 mg, 0.90 mmol) were dissolved in MeOH (5 mL) and H_2O (2.5 mL). The reaction mixture was stirred under nitrogen at room temperature for 5 h. The mixture was diluted with EtOAc and washed with brine. The organic layer was separated and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the residue was purified by preparative GPC (JAIGEL-1H/2H, eluent $CHCl_3$) to yield **10** as a pale yellow solid (230 mg, 88%). m.p.: 212-214 °C; MALDI-TOF-MS: (*m/z*) 2894 ([M+Na]$^+$, $C_{142}H_{202}O_{60}Na$, calcd. 2892); ^{1}H NMR (400MHz, $CDCl_3$, 24.5 °C): δ_H = 8.07 (d, J = 8.3 Hz, 4H, ArH), 7.65 (d, J = 8.3 Hz, 4H, ArH), 7.47 (d, J = 8.6 Hz, 2H, ArH), 7.26 (m, 4H, ArH), 5.08-4.95 (m, 12H, CD-H_1), 4.80-2.90 (m, 176H, CCH, CD-H, OCH_3); Anal. Calcd for $C_{142}H_{202}O_{60}\cdot 2H_2O$: C, 58.71; H, 7.15%; Found: C, 58.54; H, 6.90%.

4.9 References and Notes

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Conclusion

In this thesis, the synthesis of linked rotaxanes and the effects of encapsulation of π-conjugated backbone with PMα-CD were first discussed, which was followed by the discussion on the synthesis encapsulated π-conjugated polymer by polymerization of the linked rotaxanes. The major results and conclusion in each chapter of this thesis are summarized as follows.

In Chapter 1, linked [2]rotaxane, which is soluble in organic solvents, was prepared via intramolecular self-inclusion of PMα-CD bearing a diphenylacetylene moiety and the subsequent end-capping with an aniline unit by the Suzuki-Miyaura coupling. The structures of this linked [2]rotaxane in solusion as well as in the solid state were determined by 2D NMR and X-ray crystallography, respectively. The present study revealed that bulky stoppers are not necessary when linked [2]rotaxane consist of PMα-CD (as a macrocyclic host) and a rigid π-conjugated system (as the guest moiety) are linked to each other.

In Chapter 2, a highly organic-soluble and highly encapsulated π-conjugated system was synthesized without using bulky stopper molecule. The supramolecular structure of this symmetric linked [3]rotaxane was determined by 2D NMR measurement. The fluorescence Stern-Volmer plots indicated that the present [1]-[1]rotaxane exhibits strong insulation effect by prohibiting the approach of a quencher to the π-conjugated system.

In Chapter 3, highly organic-soluble linked [3] and [5]rotaxanes were prepared via double intramolecular self-inclusion of an OPE moiety bearing two PMα-CDs and the subsequent end-capping by click reaction or Sonogashira coupling reaction. These linked rotaxanes are highly soluble in various organic solvents such as methanol, ethyl acetate, chloroform, toluene, and DMF. The remarkable fluorescence enhancement was observed in these linked rotaxanes both in solution and in the solid state. This is the first successful example of rotaxane synthesis via a selective double self-inclusion process.

In Chapter 4, the successful synthesis of encapsulated π-conjugated polymers composed of linked rotaxanes as monomer units was achieved. The linked rotaxane polymers are highly soluble in various

organic solvents. The degree of polymerization of linked [2]rotaxane was shown to be effectively controlled by using methanol as a poor solvent. The shielding effect of PMα-CDs for π-conjugated polymer led to the efficient fluorescence enhancement especially in the solid state. A linked rotaxane polymer was observed as highly linear architecture by AFM measurement.

In this thesis, the development of methodology for encapsulating π-conjugated polymer at molecular level using advantage of organic synthetic chemistry and supramolecular chemistry was demonstrated. Usability of permethylated cyclodextrin (PMCD) in organic synthesis was also demonstrated. The results and conclusions presented in this thesis will contribute to bottom-up construction of molecular devices in the future.

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