Tetrahedron Letters 50 (2009) 1146–1150

Contents lists available at ScienceDirect

Tetrahedron Letters

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

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 [a], Jun Terao [b,*], Yuji Tanaka [a], Tomoka Maekawa [a], Nobuaki Kambe [a,*]

[a] Department of Applied Chemisry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
[b] Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

ARTICLE INFO

Article history:
Received 24 November 2008
Revised 17 December 2008
Accepted 18 December 2008
Available online 25 December 2008

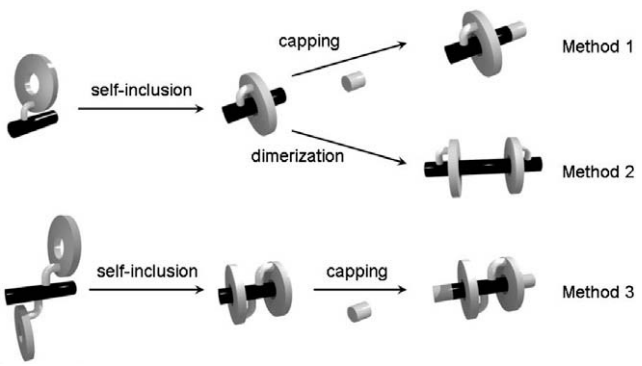
ABSTRACT

Linked symmetrical [3] and [5]rotaxanes consisting of an oligomeric phenylene ethynylene (OPE) framework as a π-conjugated guest moiety and lipophilic permethylated α-cyclodextrins (PM α-CDs), as macrocyclic hosts have been prepared by double intramolecular self-inclusion of an OPE guest unit carrying two PM α-CDs followed by capping with bulky stopper groups using click azide–alkyne Huisgen cycloaddition or Sonogashira coupling. The structures of these linked rotaxanes were determined by MALDI-TOF mass spectrum and two-dimensional NMR spectroscopy.

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] We are 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. Recently we have reported two new synthetic routes to linked rotaxanes bearing a π-conjugated system as a guest and permethylated α-cyclodextrin (PM α-CD) as a host (Scheme 1).[5,6] Our strategies employed for the syntheses of these linked rotaxanes were based on intramolecular self-inclusion of a π-conjugated linear guest unit through lipophilic PM α-CD linking to the guest moiety to form a pseudo [1]rotaxane which then gave rise to a [1]rotaxane[5] also called linked [2]rotaxane by end-capping (Method 1) or a linked [3]rotaxane[6] by dimerization (Method 2). Herein, we report 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).

Scheme 2 shows the synthetic route of our OPE-based linked [3]rotaxane. According to this process, modified PM α-CD diiodide **1** was prepared by the reaction of 6-*O*-monotosyl PM α-CD with 2,5-diiodo-1,4-benzenediol in 93% yield.[7] Sonogashira coupling reaction of **1** with 1-ethynyl-4-[2-(trimethylsilyl)ethynyl]-benzene, followed by deprotection of the trimethylsilyl group gave modified OPE having two PM α-CDs **3** in 75% yield over two steps.[8,9]

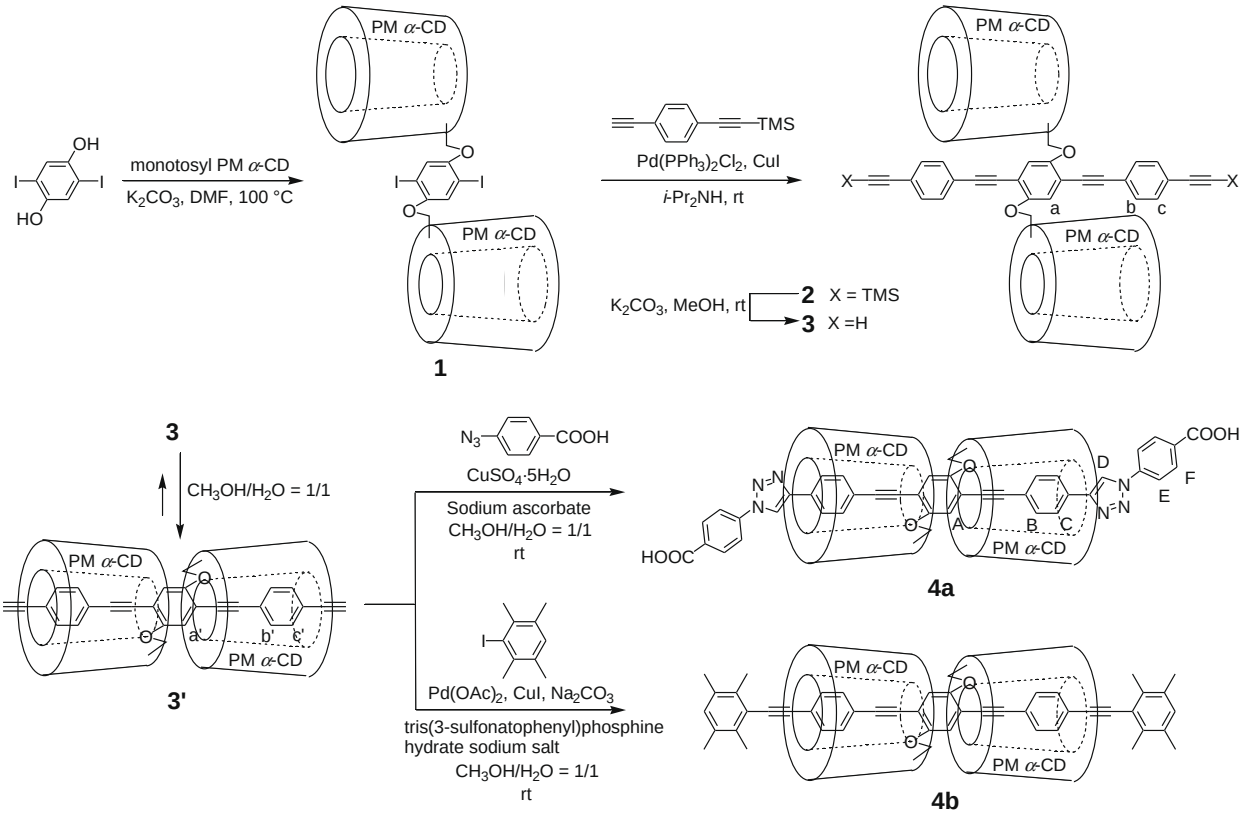
The double intramolecular self-inclusion phenomenon of **3** has been confirmed by ^{1}H NMR employing different solvents and concentrations. The NMR spectrum of aromatic protons of **3** in CD_2Cl_2 reveals the exclusion of the OPE moiety from the cavity of the PM α-CDs (Fig. 1a). A spectrum in CD_3OD at room temperature showed an equilibrium mixture of two species, **3** and its supramolecular complex (pseudo linked [3]rotaxane) **3′** (Fig. 1b). The intensity of **3′** decreased and peaks of **3** increased by warming up to 55 °C (Fig. 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 (Fig. 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-inclu-



Scheme 1. Our synthetic routes to linked rotaxanes.

* Corresponding authors. Tel.: +81 75 383 2516; fax: +81 75 383 2514 (J.T.).
E-mail address: terao@scl.kyoto-u.ac.jp (J. Terao).

0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.12.087



Scheme 2. Synthesis of linked symmetrical [3]rotaxanes **4** via double intramolecular self-inclusion of **3**.

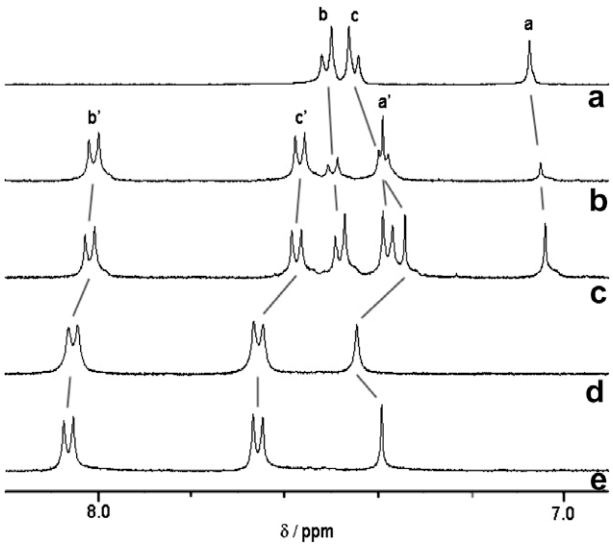


Figure 1. The aromatic region of 400 MHz ^{1}H NMR spectra of a two PM α-CD-linked OPE **3** in several solvents. (a) CD_2Cl_2 at rt; (b) CD_3OD at rt; (c) CD_3OD at 55 °C; (d) CD_3OD–D_2O = 3: 1 at rt; (e) CD_3OD–D_2O = 3: 1 at 55 °C.

sion complex **3′**. In addition, **3′** was stable even at 55 °C in the same hydrophilic medium (Fig. 1e).

In order to fix pseudo linked [3]rotaxane structure by end-capping the OPE moiety by click reaction, **3′** was treated with 4-azidobenzoic acid having a bulky group in the presence of $CuSO_4·5H_2O$ 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 by 2D TOCSY, COSY, and ROESY NMR spectra. The NOEs between protons on the OPE moiety and the internal protons of the PM α-CDs were observed. The NOE between H_A of the OPE moiety and H_6 located on the narrow rim of the PM α-CD indicates that two PM α-CDs were located in tail-to-tail arrangement (Fig. 2).

In order to elongate the OPE units, we treated **3′** with 2,3,5,6-tetramethyliodobenzene in CH_3OH–H_2O = 1:1 in the presence of $Pd(OAc)_2$, CuI, Na_2CO_3, and tris(3-sulfonatophenyl)phosphine hydrate sodium salt and obtained the desired linked [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

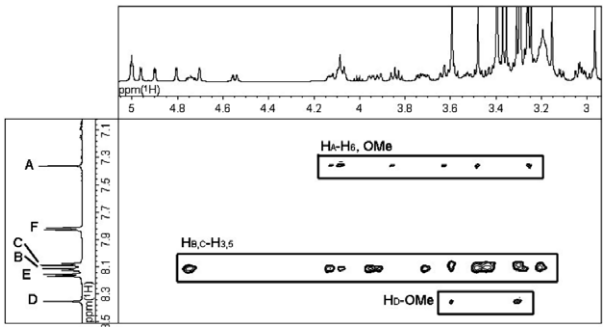
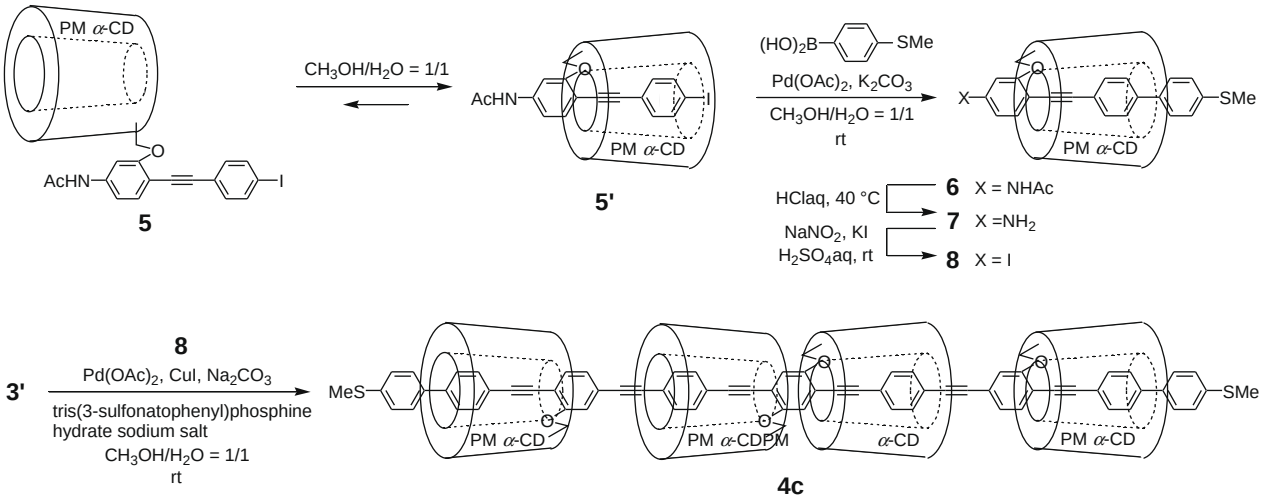


Figure 2. ROESY NMR spectrum of linked [3]rotaxane **4a** in CD_2Cl_2 at 25 °C.



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

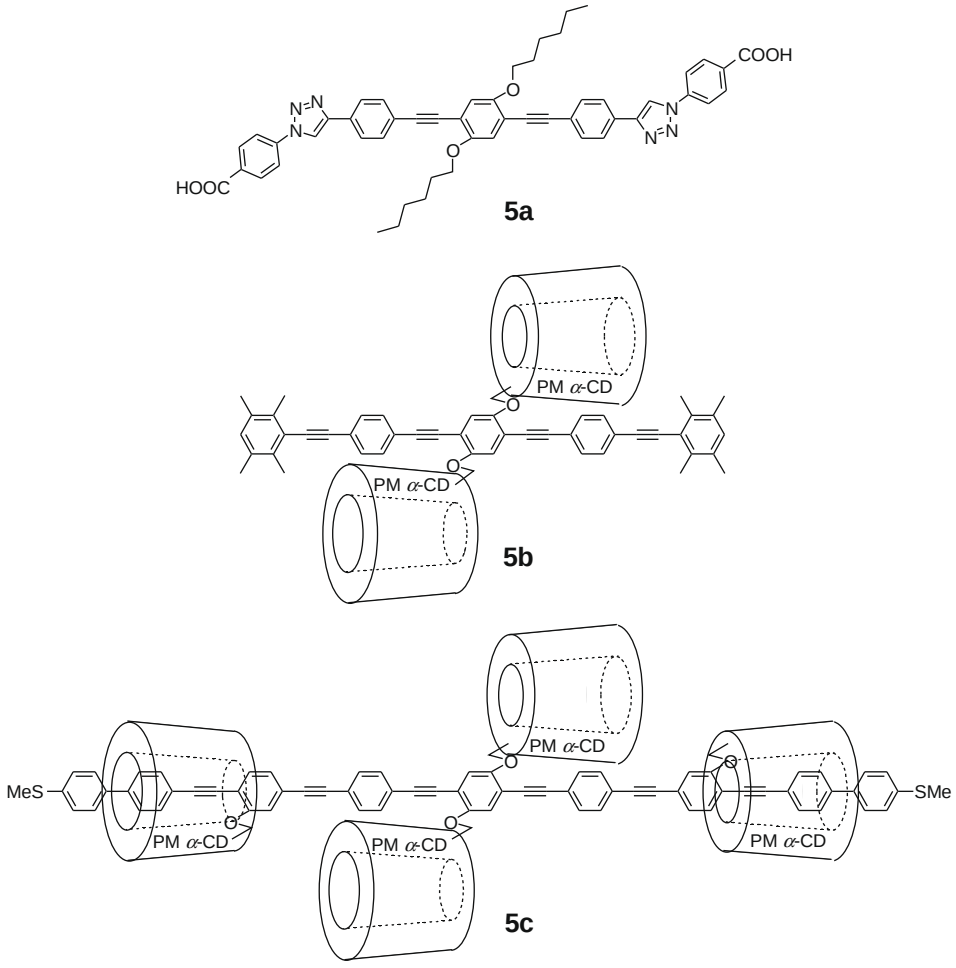


Figure 3. The structure of reference compounds **5a–c**.

unit in the solvent system. As shown in Scheme 3, **8** was prepared via self-inclusion of tolan moiety bearing a PM α-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 PM α-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 PM α-CDs according to the space-filling model.

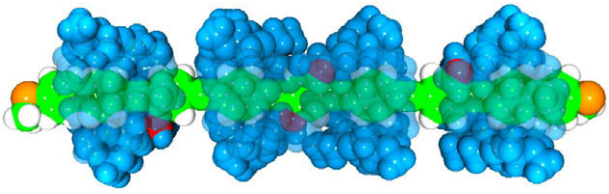


Figure 4. A space-filling model of the linked symmetrical [5]rotaxane.

Table 1
Wavelengths of the absorption and emission maxima and photoluminescence quantum yields[a]

Sample	$\lambda_{max,\ abs}$ (nm) [log ε]	$\lambda_{max,\ em}$ (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
5a	384 [4.70][b]	423[b]	0.82[b]	0.003
5b	392 [4.28]	444	0.84	0.01
5c	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.

The absorption and emission spectra and photoluminescence quantum yields of linked rotaxanes **4a–c** are summarized in Table 1. The elongation of phenylene ethynylene units from two to six resulted in bathochromic shift by about 16 nm. In order to examine the shielding effect of PM α-CD, we compared the fluorescence quantum yields of **4** with that of the corresponding uninsulated compounds **5a–c** (Fig. 3). The uninsulated compounds **5b–c** as references were intentionally synthesized by the reaction of **3** with the corresponding iodobenzene derivatives in *i*-Pr_2NH instead of 1:1 solution of H_2O and CH_3OH. As expected, there are significant fluorescence enhancements in **4** especially in solid state suggesting that encapsulation of OPEs by PM α-CD is essential to attain efficient fluorescence properties.

In conclusion, a highly organic-soluble linked [3] and [5]rotaxanes were prepared via double intramolecular self-inclusion of an OPE moiety bearing two PM α-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.

Acknowledgments

The authors thank instrumental Analysis Center, Faculty of Engineering, Osaka University, for 2D NMR experiments. One of the authors S.T. express his special thanks for The Global COE (center of excellence) Program 'Global Education and Research Center for Bio-Environmental Chemistry' of Osaka University.

References and notes

1. (a) Wautelet, P.; Moroni, M.; Oswald, L.; Moigne, J. L.; Pham, A.; Bigot, J.-Y. *Macromolecules* **1996**, *29*, 446–455; (b) Mcllroy, S. P.; Clo, E.; Nikolajsen, L.; Frederiksen, P. K.; Nielsen, C. B.; Mikkelsen, K. V.; Gothelf, K. V.; Ogilby, P. R. *J. Org. Chem.* **2005**, *70*, 1134–1146; (c) Zhao, Y.; Shirai, Y.; Slepkov, A. D.; Cheng, L.; Alemany, L. B.; Sasaki, T.; Hegmann, F. A.; Tour, J. M. *Chem. Eur. J.* **2005**, *11*, 3643–3658; (d) Robey, S. W.; Ciszek, J. W.; Tour, J. M. *J. Phys. Chem. C* **2007**, *111*, 17206–17212; (e) Mongin, O.; Porrès, L.; Charlot, M.; Katan, C.; Blanchard-Desce, M. *Chem. Eur. J.* **2007**, *13*, 1481–1498.
2. (a) Holzer, W.; Pichlmaier, M.; Drotleff, E.; Penzkofer, A.; Bradley, D. D. C.; Blau, W. J. *Opt. Commun.* **1999**, 24–28; (b) Hong, J. M.; Cho, H. N.; Kim, D. Y.; Kim, C. Y. *Synth. Met.* **1999**, 933–934; (c) Pschirer, N. G.; Vaughn, M. E.; Dong, Y. B.; zur Loye, H.-C.; Bunz, U. H. F. *Chem. Commun.* **2000**, 85–86; (d) Huber, C.; Bangerter, F.; Caseri, W. R.; Weder, C. *J. Am. Chem. Soc.* **2001**, *123*, 3857–3863; (e) Chen, W.; Joly, A. G.; Malm, J.-O.; Bovin, J.-O.; Wang, S. *J. Phys. Chem. B* **2003**, *107*, 6544–6551; (f) Clark, A. P.-Z.; Shen, K.-F.; Rubin, Y. F.; Tolbert, S. H. *Nano Lett.* **2005**, *5*, 1647–1652; (g) Zhi, Y.-G.; Lai, S.-W.; Chan, Q. K.-W.; Law, Y.-C.; Tong, G. S.-M.; Che, C.-M. *Eur. J. Org. Chem.* **2006**, 3125–3139; (h) Ding, C.; Babu, G.; Orita, A.; Hirate, T.; Otera, J. *Synlett* **2007**, 2559–2563; (i) Satrijo, A.; Kooi, S. E.; Swager, T. M. *Macromolecules* **2007**, *40*, 8833–8841; (j) Zhao, X.; Jiang, H.; Schanze, K. S. *Macromolecules* **2008**, *41*, 3422–3428; (k) Kokado, K.; Chujo, Y. *J. Poly. Sci. Part A: Poly. Chem.* **2008**, *46*, 3749–3755.
3. (a) Hirohata, M.; Tada, K.; Kawai, T.; Onoda, M.; Yoshino, K. *Synth. Met.* **1997**, *85*, 1273–1274; (b) Montali, A.; Smith, P.; Weder, C. *Synth. Met.* **1998**, *97*, 123–126; (c) Arias-Marin, E.; Amault, J. C.; Guillon, D.; Maillou, T.; Moigne, J. L.; Geffroy, B.; Nunzi, J. M. *Langmuir* **2000**, *16*, 4309–4318; (d) Anderson, S. *Chem. Eur. J.* **2001**, *7*, 4706–4714; (e) Lu, S.; Yang, M.; Luo, J.; Cao, Y. *Synth. Met.* **2004**, *140*, 199–202; (f) Breen, C. A.; Rifai, S.; Bulovic, V.; Swager, T. M. *Nano Lett.* **2005**, *5*, 1597–1601; (g) Fenenko, L.; Shao, G.; Orita, A.; Yahiro, M.; Otera, J.; Svechnikov, S.; Adachi, C. *Chem. Commun.* **2007**, 2278–2280.
4. Frampton, M. J.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 1028–1064.
5. Tsuda, S.; Terao, J.; Kambe, N. *Chem. Lett.* **2009**, *38*, 76–77.
6. Tsuda, S.; Terao, J.; Tsurui, K.; Kambe, N., in press.
7. *Synthesis of* **1**: 2,5-dihydroxy-1,4-diiodobenzene (1.20 g, 3.33 mmol), 6-*O*-monotosyl PM α-CD (10.0 g, 7.32 mmol), and dry K_2CO_3 (9.20 g, 66.6 mmol) were placed in a round-bottomed 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 (8.43 g, 93%). Mp: 138–141 °C; MALDI-TOF MS: (*m*/*z*) 2767 ($[M+Na]^+$, $C_{112}H_{188}I_2O_{60}Na$, calcd 2770); ^1H 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.
8. *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 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%). Mp: 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.
9. *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%). Mp: >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.
10. *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 cooling 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 24 h. 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%). Mp: 247–250 °C; MALDI-TOF MS: (*m*/*z*) 3093 ($[M+Na]^+$, $C_{146}H_{208}N_6O_{64}Na$, calcd 3092); ^1H NMR (400 MHz, 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.
11. *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 to the solution. This suspended solution was stirred at 70 °C for 1 h. After cooling to ambient temperature were added 2,3,5,6-tetramethyliodobenzene (24 mg, 91 μmol) and 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 24 h. 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%). Mp: >200 °C (decomposed); MALDI-TOF MS: (*m*/*z*) 3036 ($[M+Na]^+$, $C_{152}H_{222}O_{60}Na$, calcd 3030); ^1H NMR (400 MHz, 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.

12. *Syntheses of* **5–8**: **5–8** were prepared by the procedures similar to those of a [1]rotaxane reported previously. *Data for* **6**: A white solid; mp: 242–245 °C; MALDI-TOF-MS: (*m*/*z*) 1587 ($[M+Na]^+$, $C_{76}H_{111}NO_{31}SNa$, calcd 1589); ^1H NMR (400 MHz, $CDCl_3$, 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); mp: 221–225 °C; MALDI-TOF-MS: (*m*/*z*) 1546 ($[M+Na]^+$, $C_{74}H_{109}NO_{30}SNa$, calcd 1547); ^1H NMR (400 MHz, $CDCl_3$, 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); mp: 243–246 °C; MALDI-TOF-MS: (*m*/*z*) 1657 ($[M+Na]^+$, $C_{74}H_{107}IO_{30}SNa$, calcd 1658); ^1H NMR (400 MHz, $CDCl_3$, 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.

13. *Synthesis of* **4c**: **4c** was prepared by the procedure similar to that of **4b**. The residue was purified by column chromatography on silica gel (9:1, EtOAc–EtOH) to yield **4c** as a pale yellow solid (74 mg, 72%). Mp: >260 °C (decomposed); MALDI-TOF-MS: (*m*/*z*) 5783 ($[M+Na]^+$, $C_{280}H_{410}O_{120}S_2Na$, calcd 5780); ^1H NMR (400 MHz, 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.