Supporting Information for

Reversible polyphenylacetylene helix conversion driven by a thermoresponsive rotaxane switch in the solid state

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1. Materials and Methods

All solvents were distilled or dried before use according to the general purification procedure. Commercially available reagents including NaBH(OAc)$_3$ (Tokyo Chemical Industry Co., Ltd.), paraformaldehyde (Nakalai Tesque, Ltd.), [Rh(nbd)Cl]$_2$ (Tokyo Chemical Industry Co., Ltd.), N-methylpyrrolidone (NMP, Wako Pure Chemical Industries, Ltd.), triethylamine (Wako Pure Chemical Industries, Ltd.), and trichloroacetic acid (Kanto Chemical Co., Inc.) were used without further purification unless otherwise noted. All reactions were carried out under inert atmosphere of argon. Alumina column chromatography was performed using MERCK Aluminium oxide 90 Standardized. Silica gel column chromatography was performed using silica gel 60 (spherical, grain size 40–50 µm) (Kanto Chemical Co. Inc., Tokyo, Japan). Compound 4, Rotaxanes TIPS·M1, M1 were synthesized according to literature$^1$ (Scheme 1). Axle precursor 6 was prepared according to literature$^2$. All prepared polymers could not be detected by NMR, so polymerization and the successible protonation and thermal deprotonation of polymers were confirmed by IR.

$^1$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra were recorded on a JEOL AL-400 spectrometer (JEOL, Tokyo, Japan) using CDCl$_3$ as the solvent, calibrated using tetramethyldisilane as the internal standard. Recycling preparative GPC was performed by JAI Co., Ltd. LC-9210NEXT system with CHCl$_3$ eluent. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer (JASCO, Tokyo, Japan). Thermogravimetric analyses were carried out with a Shimadzu DTG-60 (Shimadzu, Japan) (heating rate of 10 °C·min$^{-1}$) and Shimadzu DSC-60 (Shimadzu, Japan) (heating rate of 10 °C·min$^{-1}$) instrument under nitrogen. UV-vis spectra were taken on a JASCO V-550 UV-vis spectrophotometer (JASCO, Japan). FAB HR-MS and
ESI-TOF MS data were taken by the National University Corporation, Tokyo Institute of Technology, Center for Advanced Materials Analysis, on request. Raman spectra data were taken by JASCO Corporation.

2. Experiments

Scheme S1

Synthesis of rotaxane TIPS·M1

To a solution of sec-ammonium salt 6 (2.0 g, 7.8 mmol), dibenzo-24-crown-8-ether 5 (4.2 g, 9.4 mmol), and 3-bromo-5-(triisopropylsilyl)ethynylbenzoic acid 4 (3.6 g, 9.4 mmol) in CHCl₃ (20 mL) was added N, N'-diisopropylcarbodiimide (DIC) (3.4 mL, 22 mmol) and tributylphosphane (PBu₃) (0.11 mL, 1.2 mmol) at room temperature and the reaction mixture was stirred for 12 h. The reaction mixture was poured into hexane (70 mL), and the formed precipitates were collected by decantation. The precipitates were purified by silica gel column chromatography (CHCl₃ / EtOAc = 1 / 1, Rf = 0.4) and recycle preparative GPC to give monomer TIPS·M1 (4.7 g, 3.9 mmol) in 50% yield as a white solid.

¹H NMR (400 MHz, CDCl₃, 298 K) δ 8.08 (s, 1H), 8.04 (s, 1H), 7.78 (s, 1H), 7.59 (br, 2H), 7.35
Ammonium salt-type rotaxane monomer M1

To a solution of TIPS·M1 (0.50 g, 0.40 mmol) in THF (70 mL) was added tetra-n-butylammonium fluoride (1.1 mL, 1.0 mmol, 1.0 M THF solution) at room temperature, and stirred for 2 h. After the half amount of the THF was evaporated, the solution was extracted with CH₂Cl₂. The organic layer was washed with sat. NaHCO₃ solution and brine, dried over MgSO₄, and concentrated in vacuo. A white solid monomer M1 (0.29 g, 0.26 mmol) was obtained in 65% yield.

m.p. 127-130 °C; ¹H NMR (400 MHz, CDCl₃, 298 K) δ 8.14–8.13 (m, 1H), 8.06 (m, 1H), 7.80 (m, 1H), 7.59 (br, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 6.89–6.87 (m, 5H), 6.84 (br, 2H), 6.80–6.77 (m, 4H), 5.26 (s, 2H), 4.68–4.65 (m, 2H), 4.49–4.46 (m, 2H), 4.10–4.09 (m, 8H), 3.79–3.77 (m, 8H), 3.49 (s, 8H), 3.21 (s, 1H), 2.16 (s, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 164.1, 147.4, 139.0, 138.9, 138.4, 138.3, 136.6, 132.9, 132.8, 131.9, 131.8, 131.7, 131.3, 130.7, 129.7, 129.6, 128.2, 126.6, 126.5, 124.5, 122.2, 121.7, 112.6, 112.5, 80.9, 79.9, 70.6, 70.5, 70.2, 70.1, 68.1, 68.0, 66.6, 66.5, 52.9, 52.7, 52.6, 52.2, 52.1, 30.3, 29.4, 23.7, 21.2, 19.9, 19.5, 17.7, 13.5, 12.2 ppm; IR (KBr) ν 3442, 3275, 3152, 2923, 1726, 1595, 1566, 1505, 1455, 1355,
1279, 1253, 1191, 1124, 1057, 955, 843, 745, 669, 557 cm$^{-1}$, adapted from Ref. 1.

Lit$^1$ data: m.p. 129-131 °C; $^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ 8.14–8.13 (m, 1H), 8.06 (m, 1H), 7.80–7.79 (m, 1H), 7.59 (br, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 6.89–6.84 (m, 7H), 6.80–6.77 (m, 4H), 5.25 (s, 2H), 4.68–4.65 (m, 2H), 4.49–4.46 (m, 2H), 4.10–4.09 (m, 8H), 3.79 (m, 8H), 3.49 (s, 8H), 3.21 (s, 1H), 2.16 (s, 6H) ppm.

**N-Methylated amine-type rotaxane monomer A1**

A solution of M1 (0.22 g, 0.20 mmol), paraformaldehyde (0.15 g, 4.0 mmol), NaBH(OAc)$_3$ (0.27 g, 1.3 mmol), and triethylamine (0.50 mL) in NMP (3.0 mL) was stirred for 12 h at 70 °C under Ar atmosphere. The cooled reaction mixture was poured into water (0.50 L), and the precipitates were collected by filtration. The products were dissolved in ethyl acetate, washed with sat. NaHCO$_3$ solution and brine, dried over MgSO$_4$, and concentrated in vacuo. The residue was purified by Al$_2$O$_3$ column chromatography (EtOAc, $R_f = 0.4$) to give A1 (0.15 g, 0.16 mmol) in 80% yield as a white solid.

m.p. 52-53 °C. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ 8.69 (s, 1H), 8.58 (s, 1H), 7.88 (d, $J = 7.6$ Hz, 2H), 7.60 (s, 1H), 7.16 (d, $J = 7.6$ Hz, 2H), 6.93 (s, 2H), 6.87 (s, 1H), 6.83–6.80 (m, 4H), 6.75–6.73 (m, 4H), 5.30 (s, 2H), 4.08–4.04 (m, 8 H), 3.71–3.63 (m, 8H), 3.44 (s, 2H), 3.37 (s, 2H), 3.16 (m, 4H), 3.02 (m, 4H), 2.80 (s, 1H), 2.28 (s, 6H), 2.15 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$, 298K) δ 164.1, 147.3, 147.1, 138.9, 138.5, 136.6, 132.8, 132.1, 132.0, 131.8, 131.1, 130.9, 129.8, 129.1, 127.9, 124.5, 122.3, 121.5, 121.3, 111.9, 111.8, 81.0, 79.9, 71.8, 71.5, 70.5, 70.3, 68.2, 68.0, 66.7, 61.1, 60.3, 39.4, 21.2 ppm; IR (KBr) ν 3280, 2920, 1716, 1593, 1563, 1505, 1453, 1377, 1324, 1284, 1253, 1218, 1126, 1055, 952, 870, 840, 770, 740, 669 cm$^{-1}$; FAB HR-MS Calc’d for C$_{51}$H$_{59}$NO$_{10}$ [M+H]$^+$: $m/z = 924.3322$. Found: $m/z = 924.3336$. 

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Trichloroacetate-type rotaxane A1·TCA

Trichloroacetic acid (98 mg, 0.60 mmol) was added to a solution of A1 (0.20 g, 0.20 mmol) in CHCl₃ (2.0 mL) at room temperature, and stirred for 10 min. After the solvent was removed under the reduced pressure, the residue was washed with hexane to remove the excess amount of trichloroacetic acid and dried in vacuo to give A1·TCA (0.26 g, 0.20 mmol) in 100% yield as a white solid.

m.p. 95 °C (decomp.) ¹H NMR (400 MHz, CDCl₃, 298 K) δ 8.22 (s, 1H), 8.15 (s, 1H), 7.78 (s, 1H), 7.59 (br, 2H), 7.38 (br, 2H), 7.27 (s, 1H), 7.02 (s, 2H), 6.95 (s, 1H), 6.89–6.96 (m, 4H), 6.81–6.76 (m, 4H), 5.28 (s, 2H), 5.05 (d, J = 13.2 Hz, 1H), 4.83 (d, J = 13.2 Hz, 1H), 4.40 (d, J = 7.8 Hz, 1H), 4.13 (d, J = 7.8 Hz, 1H), 4.11–4.09 (m, 8H), 3.81–3.74 (m, 8H), 3.57–3.52 (s, 8H), 3.15 (s, 1H), 2.85 (s, 3H), 2.25 (s, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 164.1, 163.5, 147.2, 147.1, 138.9, 138.5, 136.6, 132.8, 131.9, 131.8, 131.2, 130.8, 129.8, 128.8, 127.9, 124.4, 122.2, 121.4, 121.3, 111.9, 111.8, 94.1, 80.9, 79.9, 71.7, 71.5, 70.5, 70.3, 68.2, 68.0, 66.5, 64.4, 61.0, 60.3, 39.5, 21.2, 17.6 ppm; IR (KBr) ν 3438, 3068, 2923, 1727, 1593, 1565, 1505, 1454, 1429, 1354, 1279, 1250, 1212, 1190, 1123, 1058, 954, 834, 744, 676 cm⁻¹; ESI-TOF Calc’d for C₅₃H₅₉BrCl₃NO₁₂ [M-Cl₃CCOO]⁺: m/z = 926.3297. Found: m/z = 926.3296. [Cl₃CCOO]⁻: m/z = 160.8964. Found: m/z = 160.8971.

Synthesis of amine-type polyphenylacetylene PA1

To a solution of monomer A1 (0.20 g, 14 µmol) in CHCl₃ (0.48 mL) was added a solution consisted of [RhCl(nbd)]₂ (4.0 mg, 8.7 µL), and Et₃N (10 µL) in CHCl₃ (1.0 mL), and the mixture was stirred for 4 h at room temperature. The solution was poured into MeOH (20 mL). The
precipitates were collected by filtration to give polyphenylacetylene PA1 (0.15 g, 0.10 mmol, as a red solid in 90% yield.

IR (KBr) v 2872, 1717, 1593, 1504, 1452, 1325, 1252, 1215, 1052, 950, 739 cm⁻¹.

**Ammonium-type polyphenylacetylene PA1·TCA**

To a solution of PA1 (20 mg, 21 µmol) in CHCl₃ (5.0 mL) was added trichloroacetic acid (9.8 mg, 60 µmol) at room temperature, and stirred for 10 min. The reaction solution was concentrated in vacuo. The residue was washed with hexane to remove the excess amount of trichloroacetic acid and dried in vacuo to give PA1·TCA (26 mg, 21 µmol) as a red solid in 100% yield.

IR (KBr) v 2924, 1734, 1505, 1250, 1125, 952, 845, 680 cm⁻¹.

**Scheme S2**

![Scheme S2](image)

**Synthesis of polyphenylacetylene PA2**

The tert-amine-type dumbbell polyphenylacetylene PA2 was synthesized using the same methods with the PA1 as a yellow solid in 80% yield.

IR (KBr) v 3447, 1560, 1419, 1094, 937 cm⁻¹.

**Ammonium-type polyphenylacetylene PA2·TCA**
The tert-ammonium-type dumbbell polyphenylacetylene PA2·TCA was synthesized using the same methods with PA1·TCA as a yellow solid in 100% yield.

IR (KBr) ν 3418, 1751, 1623, 1265, 849, 833, 679 cm⁻¹.

3. Film preparation method and switching process

Scheme S3. Schematic illustration of switching process at the film state.

**Preparation of Films (high concentration):**

a) 2.0 mg amine-type polyphenylacetylene PA1 was dissolved in 100 µL CHCl₃ (0.022 M). Casting this solution onto the surface of quarts and then dried overnight to remove the solvent to obtain PA1 film.

b) Dipping this PA1 film into the trichloroacetic acid hexane solution (2.0 M) for 5 min.

c) Dried overnight to removed the solvent, ammonium-type film PA1·TCA was obtained as a yellow one.

d) Heating the PA1·TCA film on a hotplate at 100 °C for 5 min, the film color changed from yellow to red, indicated amine-type film PA1 was achieved. (The heating time of ammonium-type film is dependent on the thickness of film and concentration of
polymer chloroform solution.)

**Fig. S1.** Photos of PA1 dipping into the Cl₃CCOOH/hexane solution (2.0 M) at (a) 0 sec, (b) 15 sec, (c) 30 sec, (d) 45 sec, and (e) 60 sec, respectively, to obtain PA1·TCA as an orange film (Original concentration of PA1 chloroform solution: 0.022 M).

**Fig. S2.** Photos of PA1·TCA heating at 100 °C on a hotplate at (a) 0 sec, (b) 8 sec, (c) 12 sec, (d) 16 sec, and (e) 20 sec, respectively, to obtain PA1 as a red film (Original concentration of PA1 chloroform solution: 0.011 M).
4. Spectra

4.1. $^1$H NMR spectra

**Fig. S3.** $^1$H NMR spectrum of monomer M1 (400 MHz, CDCl$_3$, 298 K).

**Fig. S4.** $^1$H NMR spectrum of monomer A1 (400 MHz, CDCl$_3$, 298 K).
Fig. S5. $^1$H NMR spectrum of monomer A1·TCA (400 MHz, CDCl$_3$, 298 K).

Fig. S6. $^1$H NMR spectra of (a) A1 and (b) residue of A1·TCA heating until 200 °C (400 MHz, 298 K, CDCl$_3$).
Fig. S7. $^1$H NMR spectra of titration of TCA into A1 in CDCl$_3$ (400 MHz, 298 K, CDCl$_3$).

4.2. HH COSY correlations spectra

Fig. S8. HH COSY correlations of A1 (400 MHz, CDCl$_3$, 298 K)
Fig. S9. HH COSY correlations of A1·TCA (400 MHz, CDCl₃, 298 K)

4.3. $^{13}$C NMR spectra

Fig. S10. $^{13}$C NMR spectrum of monomer M1 (100 MHz, CDCl₃, 298 K).
**Fig. S11.** $^{13}$C NMR spectrum of monomer A1 (100 MHz, CDCl$_3$, 298 K).

**Fig. S12.** $^{13}$C NMR spectrum of monomer A1·TCA (100 MHz, CDCl$_3$, 298 K).
4.4. IR spectra

**Fig. S13.** IR spectrum of monomer M1 (KBr).

**Fig. S14.** IR spectrum of monomer A1 (KBr).
**Fig. S15.** IR spectrum of monomer A1·TCA (KBr).

**Fig. S16.** IR spectrum of polyphenylacetylene PA1 (KBr).
Fig. S17. IR spectrum of polyphenylacetylene PA1·TCA (KBr).

Fig. S18. IR spectra of A1 and PA1 (KBr).
**Fig. S19.** IR spectra of A1·TCA and PA1·TCA (KBr).

**Fig. S20.** IR spectra of polyphenylacetylene PA1$_0$ and PA1$_5$ (KBr).
Fig. S21. IR spectra of polyphenylacetylene PA2 and PA2·TCA (KBr).
4.5. ESI-TOF spectra

(a)

![ESI-TOF spectra diagram]

- Observed
- Calculated
Fig. S22. ESI-TOF spectra of rotaxane A1·TCA: (a) rotaxane-type ammonium ion, and (b) trichloroacetate.
5. UV–vis spectra

Fig. S23. UV–vis spectra of PA1 film (298 K): (a) at room temperature; (b) after thermal annealing preprocessing: heating at 100 °C for 10 min.

Fig. S24. UV–vis spectra of films of PA1 (red lines) and PA1·TCA (blue line) by repeated heating and acidification progresses into the Cl₃CCOOH/hexane (2.0 M) in the consecutive 5 cycles.
Fig. S25. UV–vis spectra of PA1 film PA1₀ (before thermal annealing preproces), PA1₅ (in the fifth cycle) and PA1’₅ (dissolved PA1₅ into the CHCl₃).
Blank experiment:

Fig. S26. Synthesis of film $\text{PA1} \cdot \text{TFA}$ and UV–vis spectra of: (a) $\text{PA1}$ film ($\lambda_{\text{max}} = 502$ nm); (b) $\text{PA1} \cdot \text{TFA}$ film ($\lambda_{\text{max}} = 432$ nm, produced by dipping $\text{PA1}$ film into the trifluoroacetic acid hexane for 5 min); and (c) $\text{PA1} \cdot \text{TFA}$ film heated at 100 °C for 5 min ($\lambda_{\text{max}} = 432$ nm).
6. DSC

**Fig. S27.** DSC profiles of: (a) PA1 and (b) PA1·TCA (heating and cooling rate: 10 °C·min⁻¹; 2nd heating and cooling from 30 °C to 200 °C under N₂ atmosphere).
7. References
