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

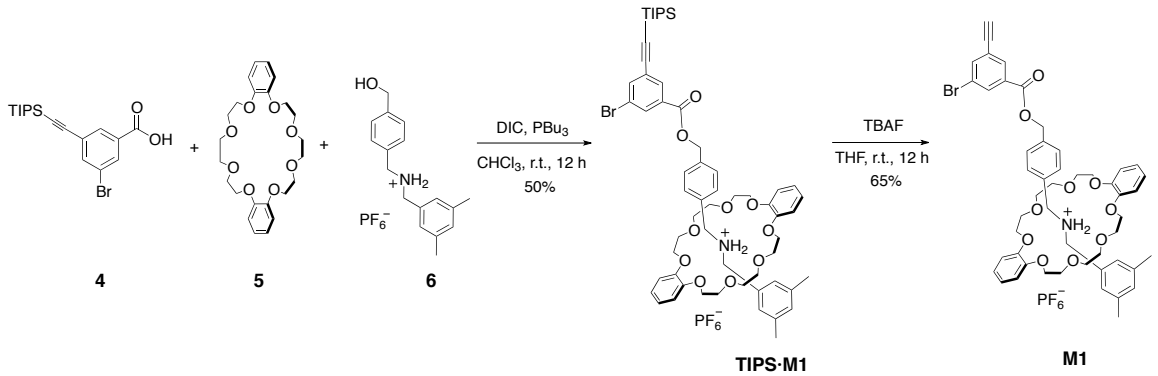
All solvents were distilled or dried before use according to the general purification procedure. Commercially available reagents including $NaBH(OAc)_3$ (Tokyo Chemical Industry Co., Ltd.), paraformaldehyde (Nakalai Tesque, Ltd.), $[Rh(nbd)Cl]_2$ (Tokyo Chemical Industry Co., Ltd.), *N*-methylpyrrolidone (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 tetramethylsilane 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 $°C \cdot min^{-1}$) and Shimadzu DSC-60 (Shimadzu, Japan) (heating rate of 10 $°C \cdot min^{-1}$) 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 $CHCl_3$ (20 mL) was added *N*, *N'*-diisopropylcarbodiimide (DIC) (3.4 mL, 22 mmol) and tributylphosphane (PBu_3) (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 ($CHCl_3$ / EtOAc = 1 / 1, R_f = 0.4) and recycle preparative GPC to give monomer **TIPS·M1** (4.7 g, 3.9 mmol) in 50% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.08 (s, 1H), 8.04 (s, 1H), 7.78 (s, 1H), 7.59 (br, 2H), 7.35

(d, J = 7.8 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H), 6.89–6.86 (m, 5H), 6.85 (s, 2H), 6.79–6.76 (m, 4H) 5.27 (s, 2H), 4.65–4.64 (m, 2H), 4.48–4.45 (m, 2H), 4.10–4.09 (m, 8H), 3.78–3.77 (m, 8H), 3.49 (s, 8H), 2.16 (s, 6H), 1.12 (s, 21H) ppm, adapted from Ref. 1;

Lit[1]. data: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.09 (s, 1H), 8.04 (s, 1H), 7.79 (s, 1H), 7.59 (br, 2H), 7.36 (d, J = 7.8 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H), 6.89–6.86 (m, 5H), 6.84 (s, 2H), 6.79–6.77 (m, 4H), 5.27 (s, 2H), 4.67–4.64 (m, 2H), 4.49–4.45 (m, 2H), 4.10–4.09 (m, 8H), 3.79–3.77 (m, 8H), 3.48 (s, 8H), 2.16 (s, 6H), 1.12 (s, 21H) ppm.

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 CH_2Cl_2. The organic layer was washed with sat. $NaHCO_3$ solution and brine, dried over $MgSO_4$, and concentrated *in vacuo*. A white solid momomer **M1** (0.29 g, 0.26 mmol) was obtained in 65% yield.

m.p. 127-130 °C; 1H NMR (400 MHz, $CDCl_3$, 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; ^{13}C NMR (100 MHz, $CDCl_3$, 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_2O_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.

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 $CHCl_3$ (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.) ^{1}H NMR (400 MHz, $CDCl_3$, 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), 3.83–3.74 (m, 8H), 3.57–3.52 (s, 8H), 3.15 (s, 1H), 2.85 (s, 3H), 2.25 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 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 $C_{53}H_{59}BrCl_3NO_{12}$ $[M\text{-}Cl_3CCOO]^+$: m/z = 926.3297. Found: m/z = 926.3296. $[Cl_3CCOO]^-$: 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 $CHCl_3$ (0.48 mL) was added a solution consisted of $[RhCl(nbd)]_2$ (4.0 mg, 8.7 μL), and Et_3N (10 μL) in $CHCl_3$ (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.

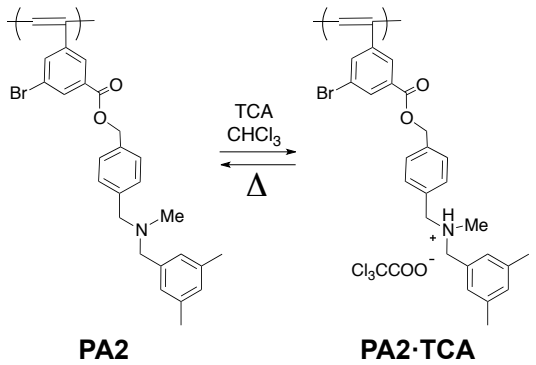
IR (KBr) ν 2872, 1717, 1593, 1504, 1452, 1325, 1252, 1215, 1052, 950, 739 cm^{-1}.

Ammonium-type polyphenylacetylene PA1·TCA

To a solution of **PA1** (20 mg, 21 μmol) in $CHCl_3$ (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) ν 2924, 1734, 1505, 1250, 1125, 952, 845, 680 cm^{-1}.

Scheme S2



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.

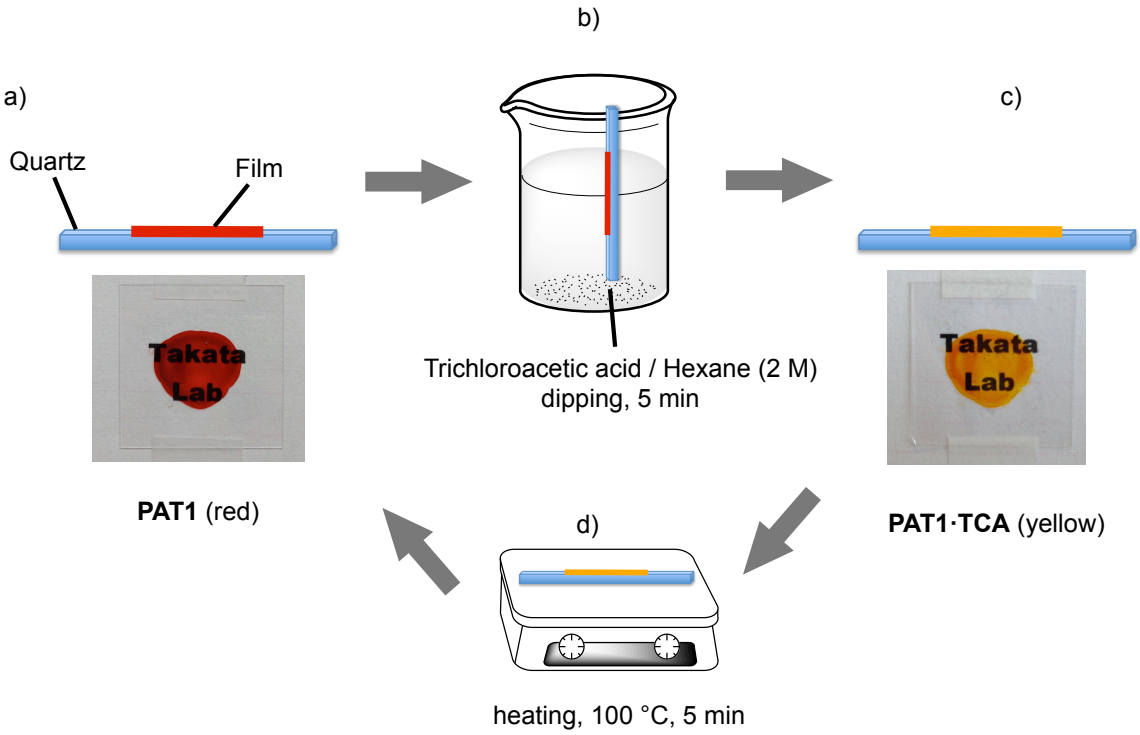
IR (KBr) ν 3447, 1560, 1419, 1094, 937 cm^{-1}.

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 $CHCl_3$ (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.)

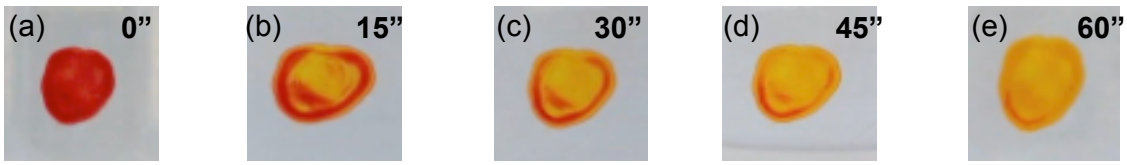


Fig. S1. Photos of **PA1** dipping into the Cl_3CCOOH/hexane solution (2.0 M) at (a) 0 sec, (b) 15 sec, (c) 30 sec, (d) 45 sec, and (e) 60 sec, respectively, to obtain **PA1·TCA** as an orange film (Original concentration of **PA1** chloroform solution: 0.022 M).

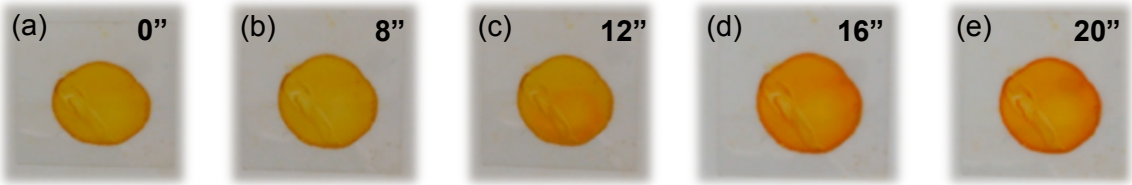


Fig. S2. Photos of **PA1·TCA** heating at 100 °C on a hotplate at (a) 0 sec, (b) 8 sec, (c) 12 sec, (d) 16 sec, and (e) 20 sec, respectively, to obtain **PA1** as a red film (Original concentration of **PA1** chloroform solution: 0.011 M).

4. Spectra

4.1. ^{1}H NMR spectra

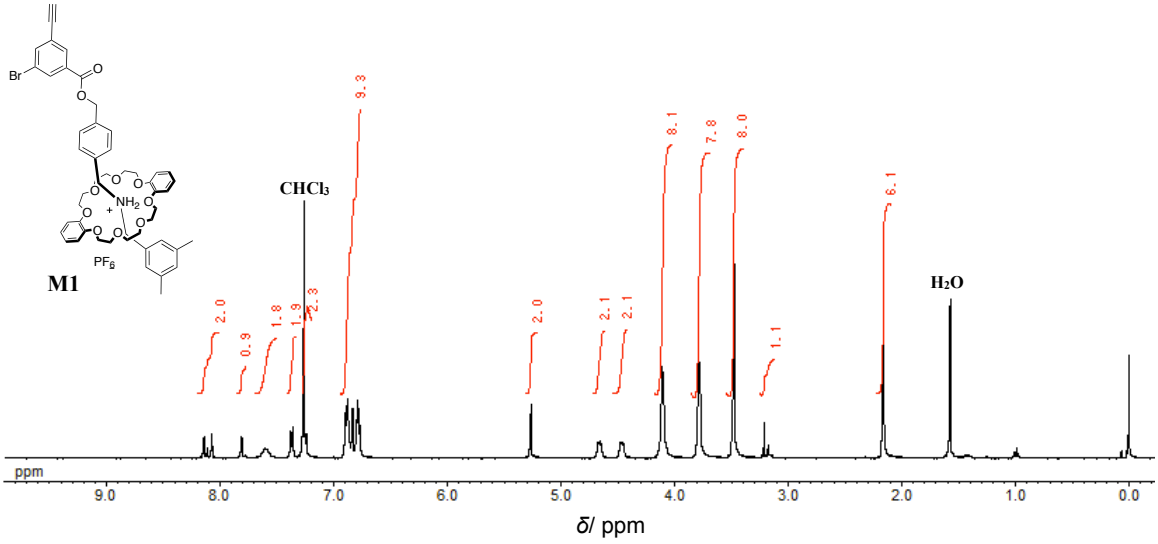


Fig. S3. ^{1}H NMR spectrum of monomer **M1** (400 MHz, $CDCl_3$, 298 K).

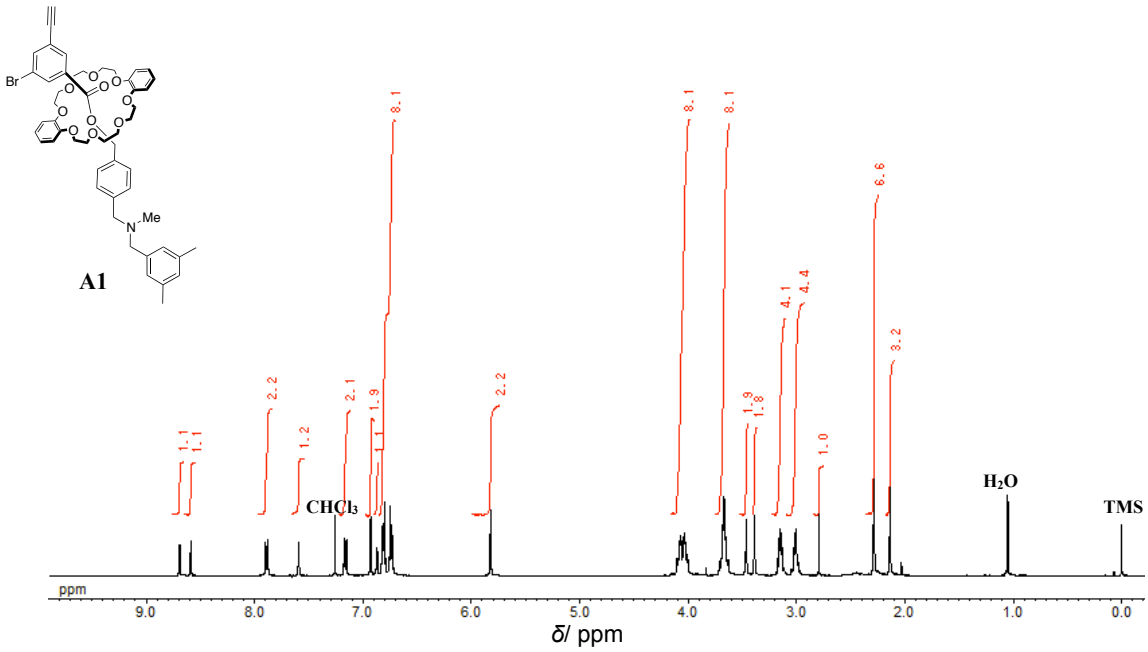


Fig. S4. ^{1}H NMR spectrum of monomer **A1** (400 MHz, $CDCl_3$, 298 K).

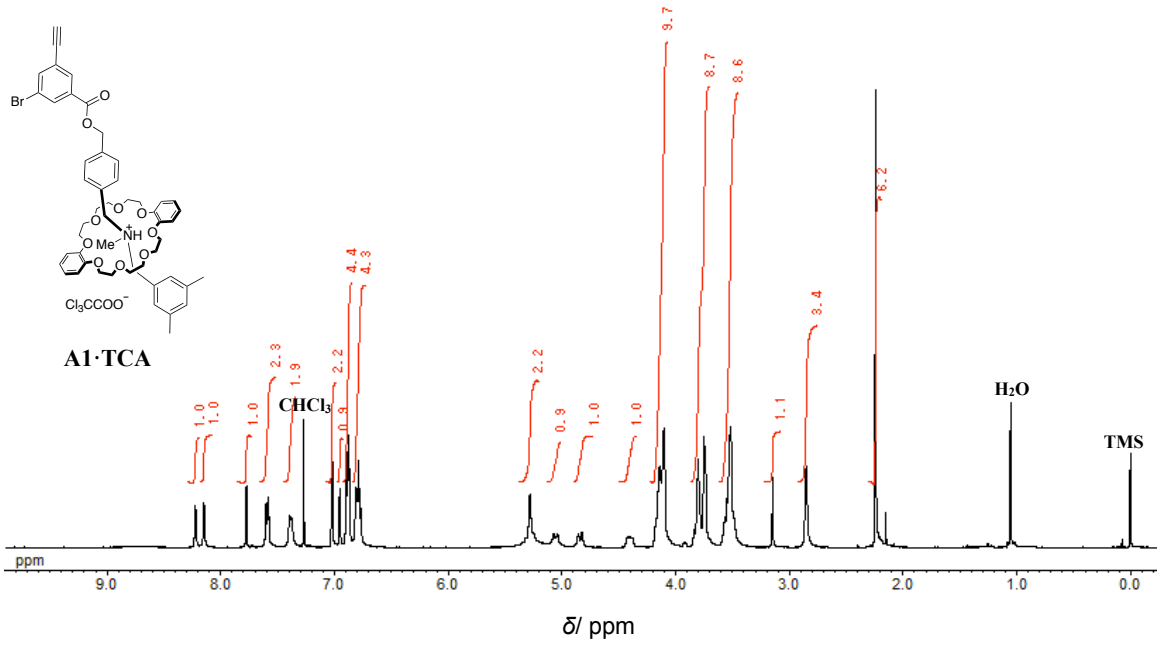


Fig. S5. ^{1}H NMR spectrum of monomer **A1·TCA** (400 MHz, $CDCl_3$, 298 K).

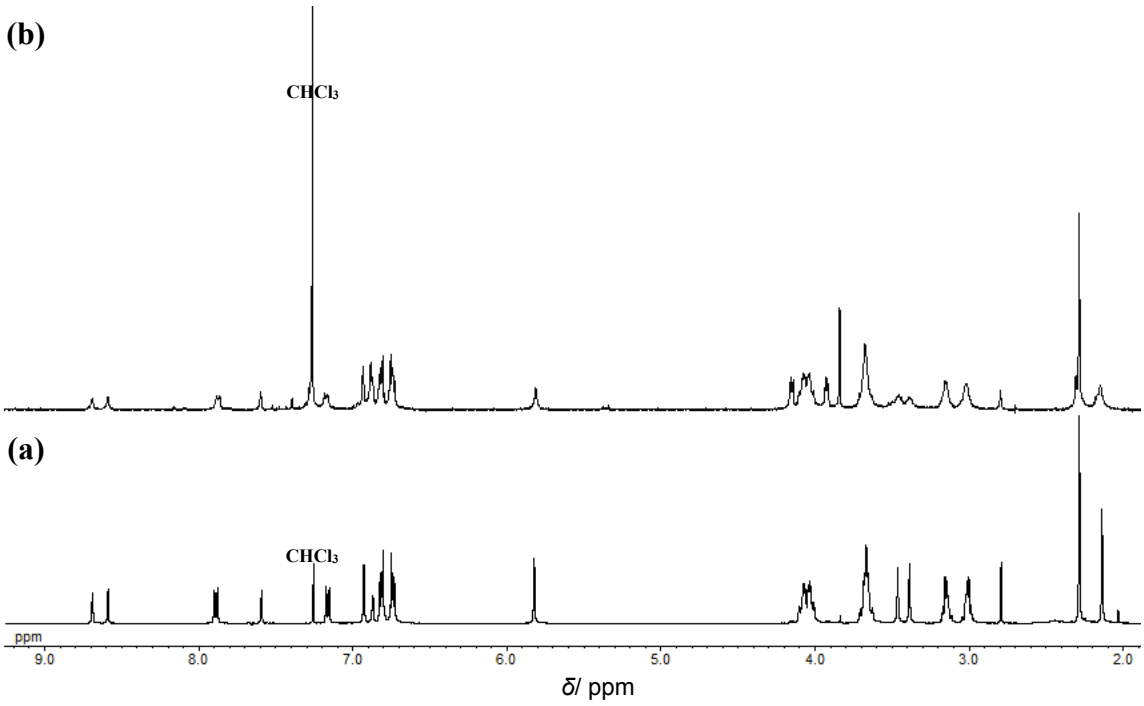


Fig. S6. ^{1}H NMR spectra of (a) **A1** and (b) residue of **A1·TCA** heating until 200 °C (400 MHz, 298 K, $CDCl_3$).

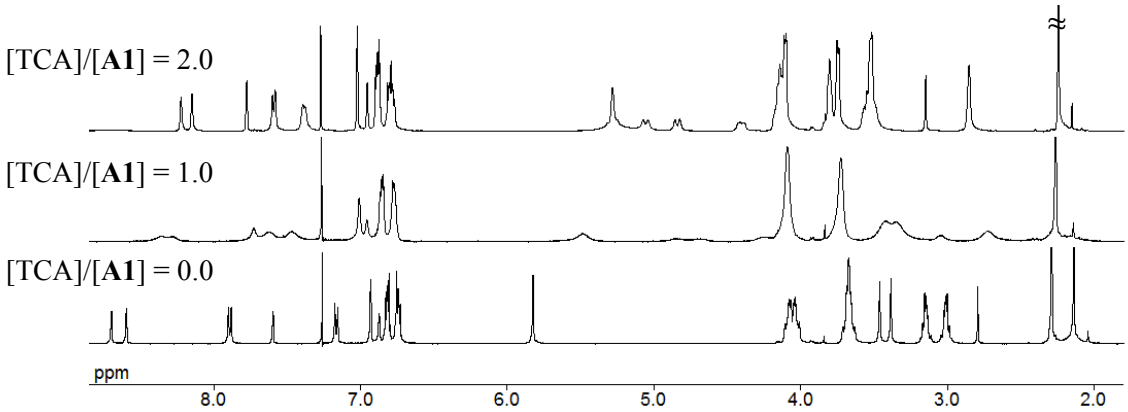


Fig. S7. ^{1}H NMR spectra of titration of TCA into **A1** in $CDCl_3$ (400 MHz, 298 K, $CDCl_3$).

4.2. HH COSY correlations spectra

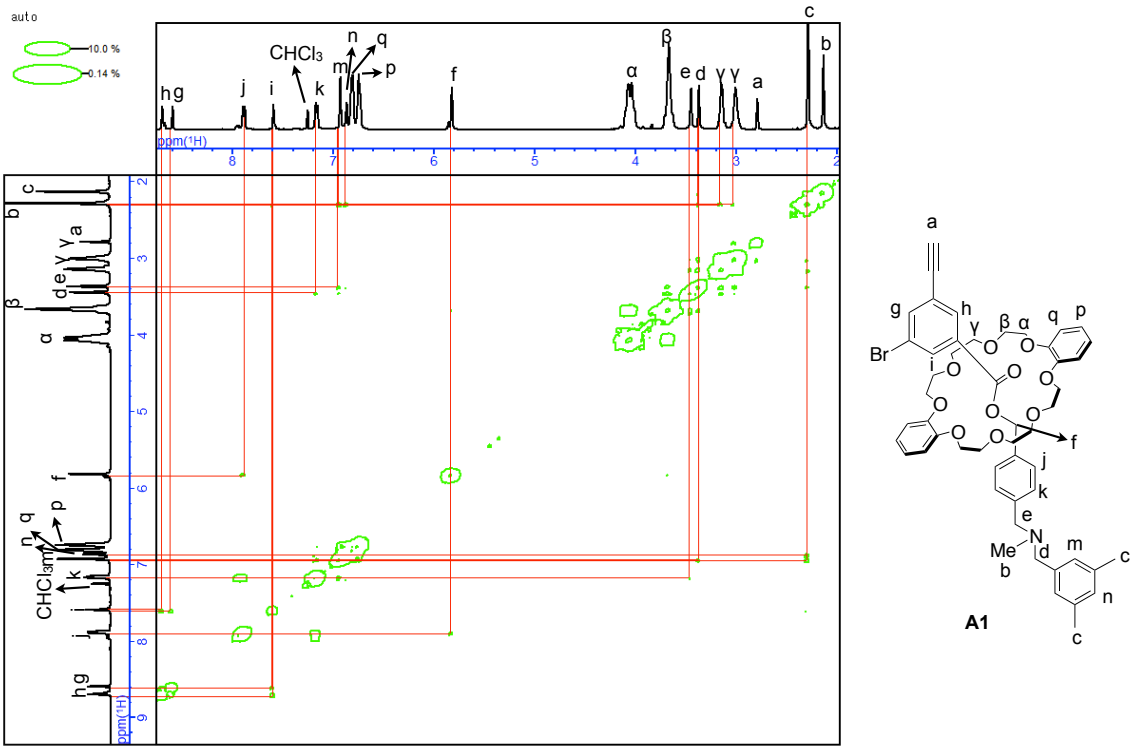


Fig. S8. HH COSY correlations of **A1** (400 MHz, $CDCl_3$, 298 K)

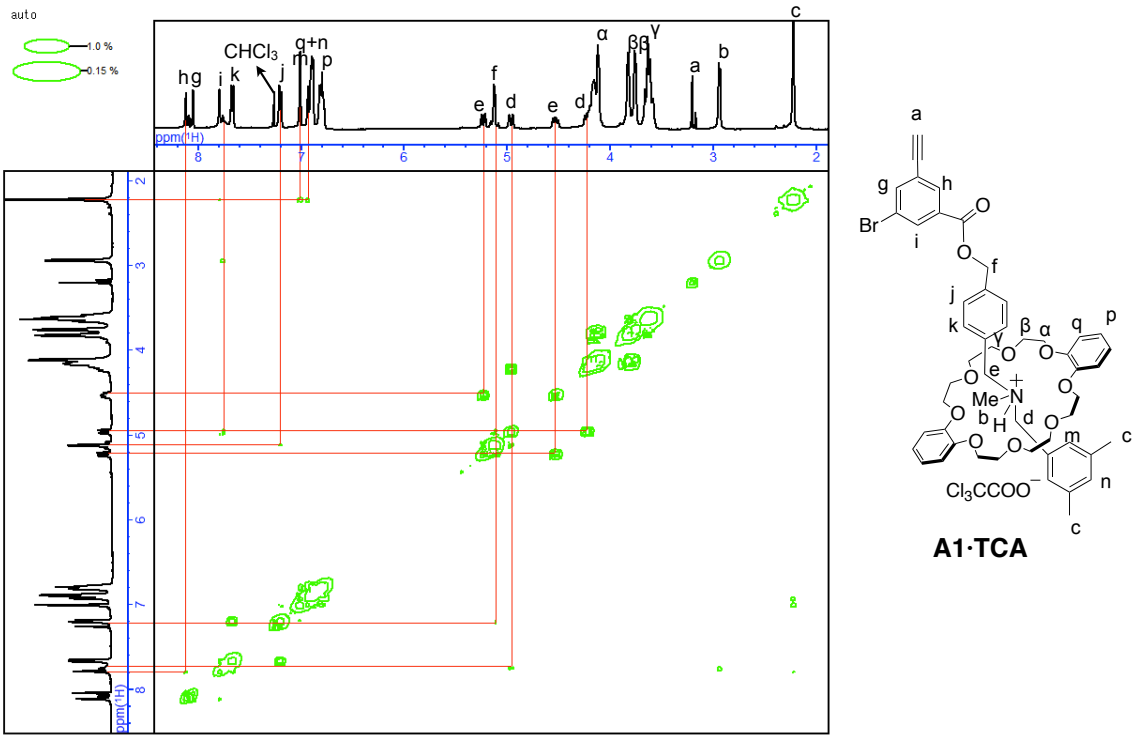


Fig. S9. HH COSY correlations of **A1·TCA** (400 MHz, $CDCl_3$, 298 K)

4.3. ^{13}C NMR spectra

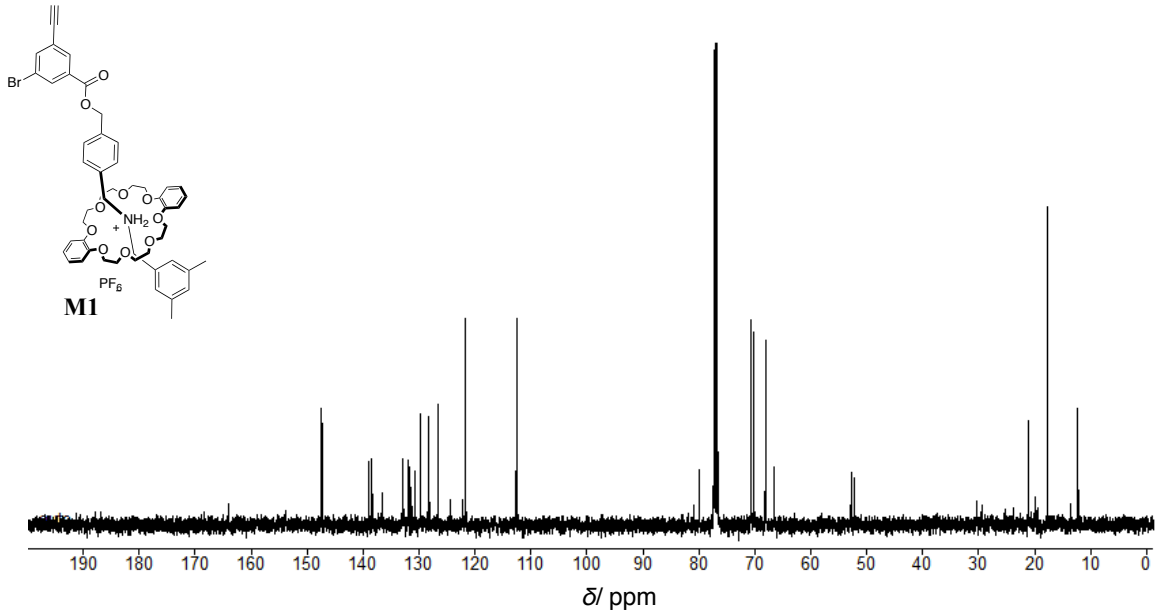


Fig. S10. ^{13}C NMR spectrum of monomer **M1** (100 MHz, $CDCl_3$, 298 K).

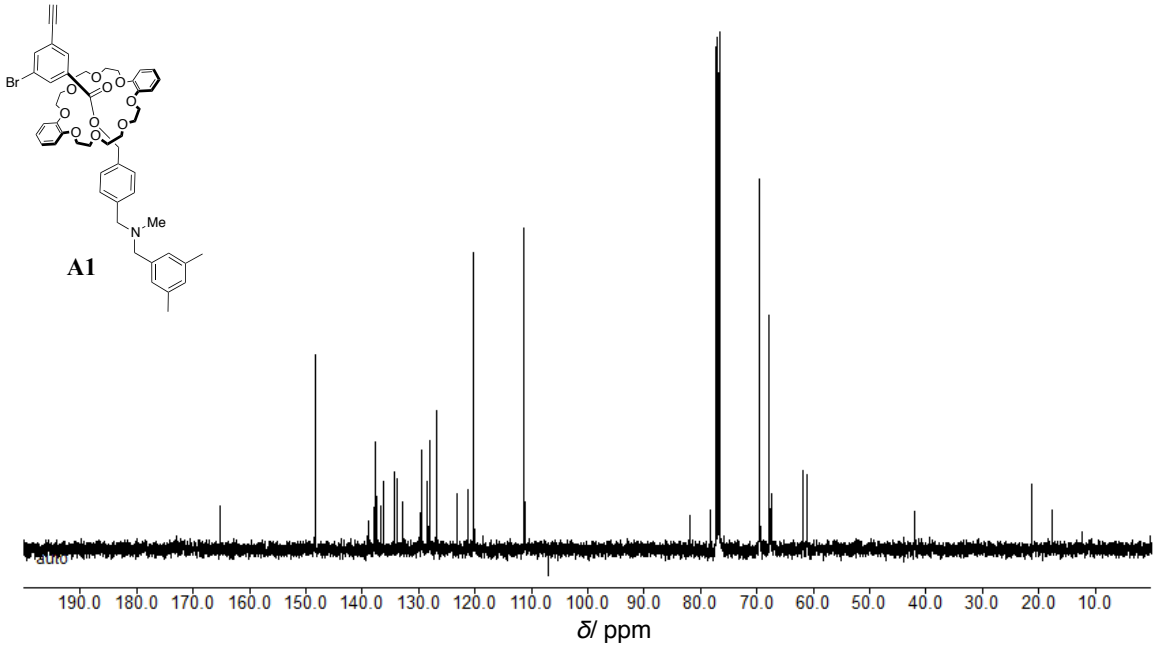


Fig. S11. ^{13}C NMR spectrum of monomer **A1** (100 MHz, $CDCl_3$, 298 K).

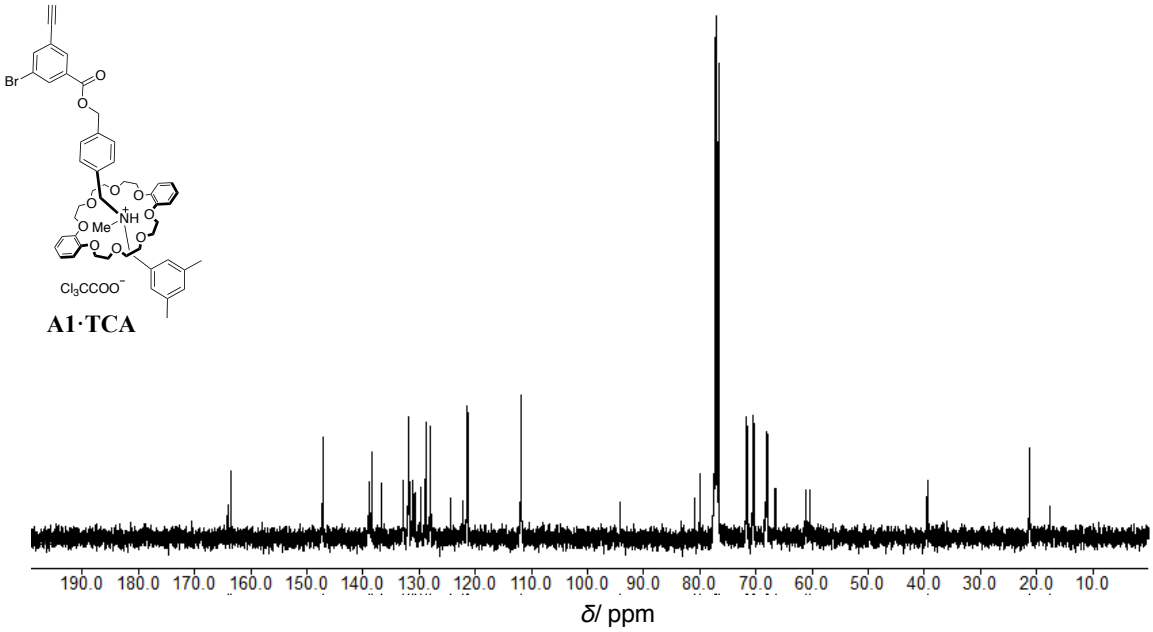


Fig. S12. ^{13}C NMR spectrum of monomer **A1·TCA** (100 MHz, $CDCl_3$, 298 K).

4.4. IR spectra

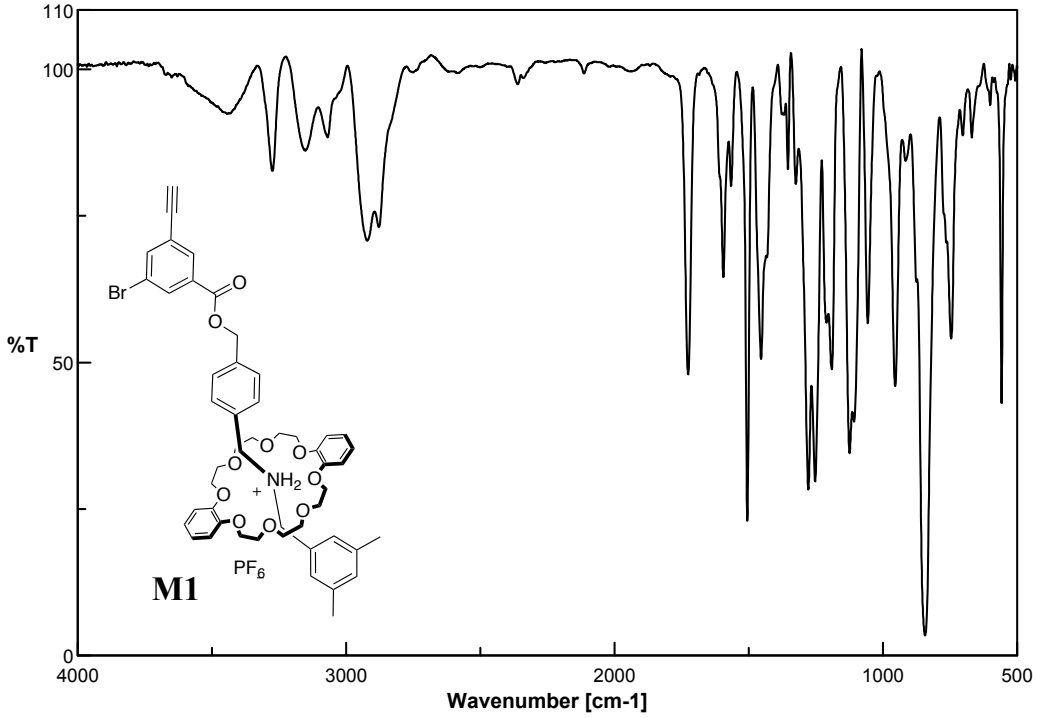


Fig. S13. IR spectrum of monomer **M1** (KBr).

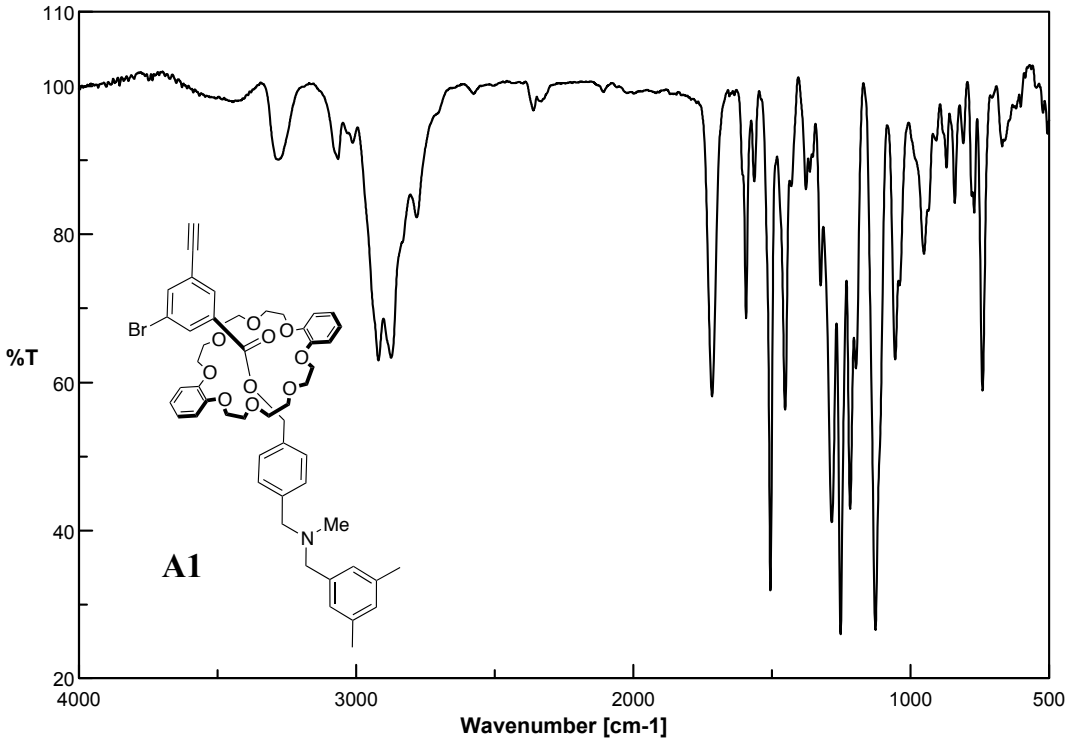


Fig. S14. IR spectrum of monomer **A1** (KBr).

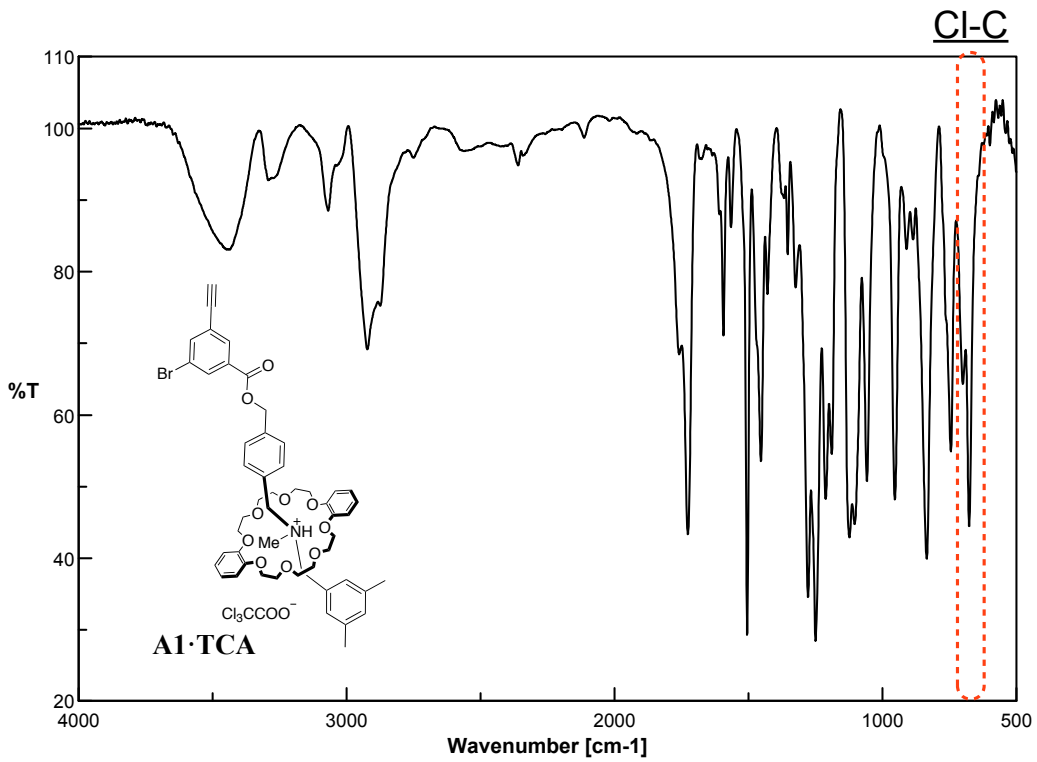


Fig. S15. IR spectrum of monomer **A1·TCA** (KBr).

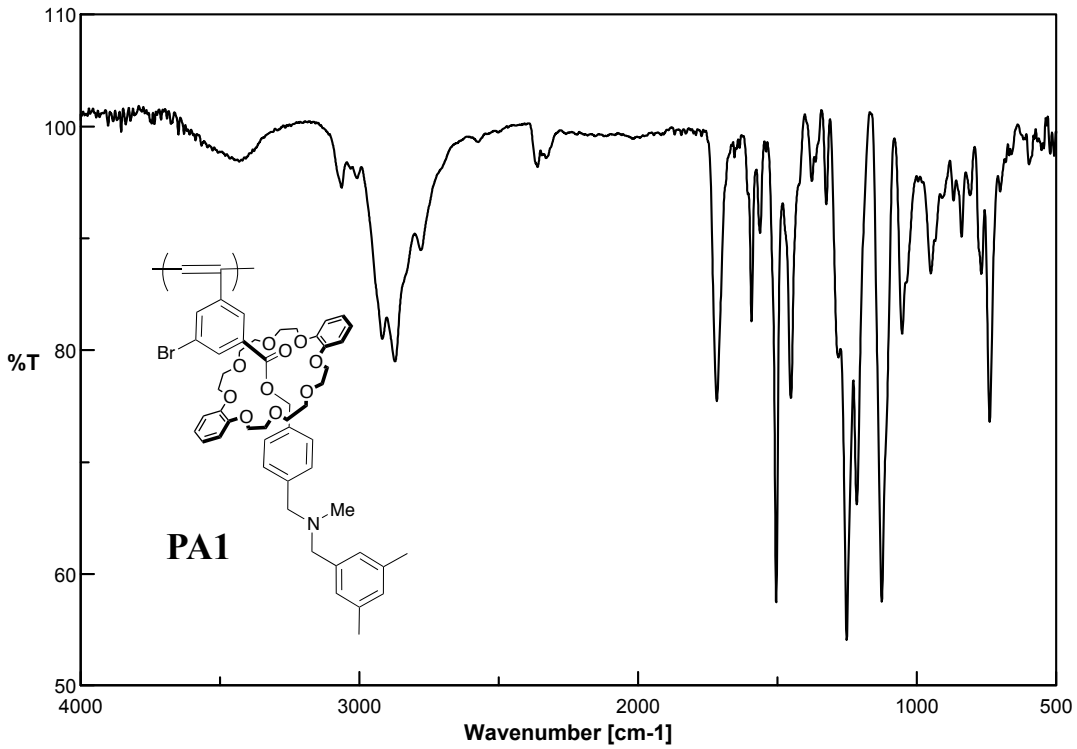


Fig. S16. IR spectrum of polyphenylacetylene **PA1** (KBr).

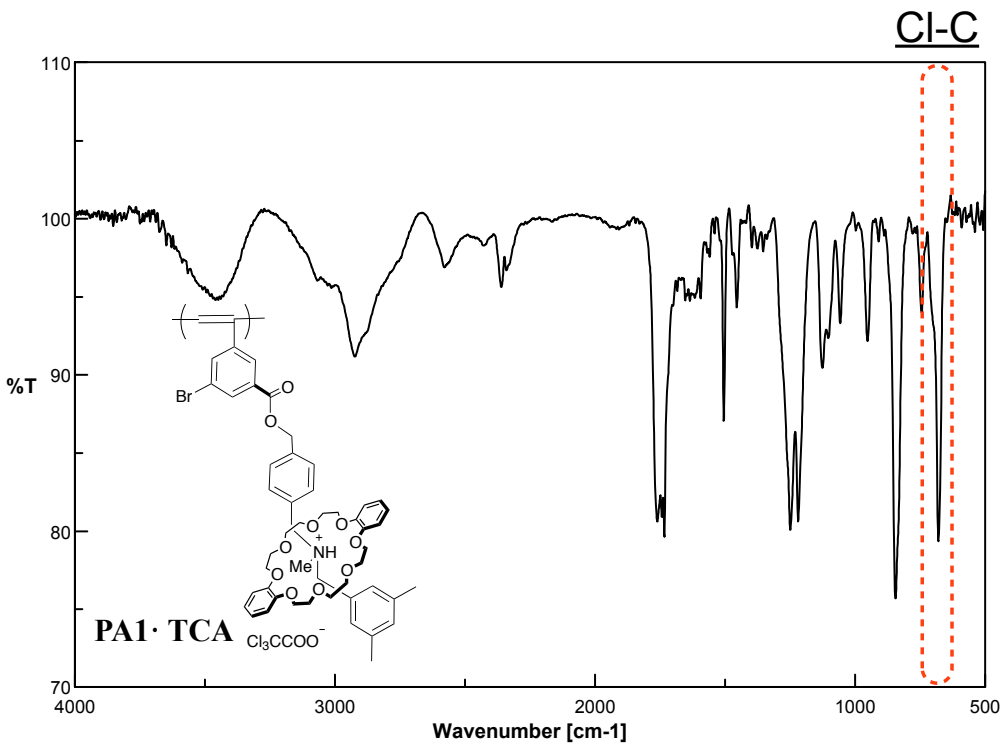


Fig. S17. IR spectrum of polyphenylacetylene **PA1·TCA** (KBr).

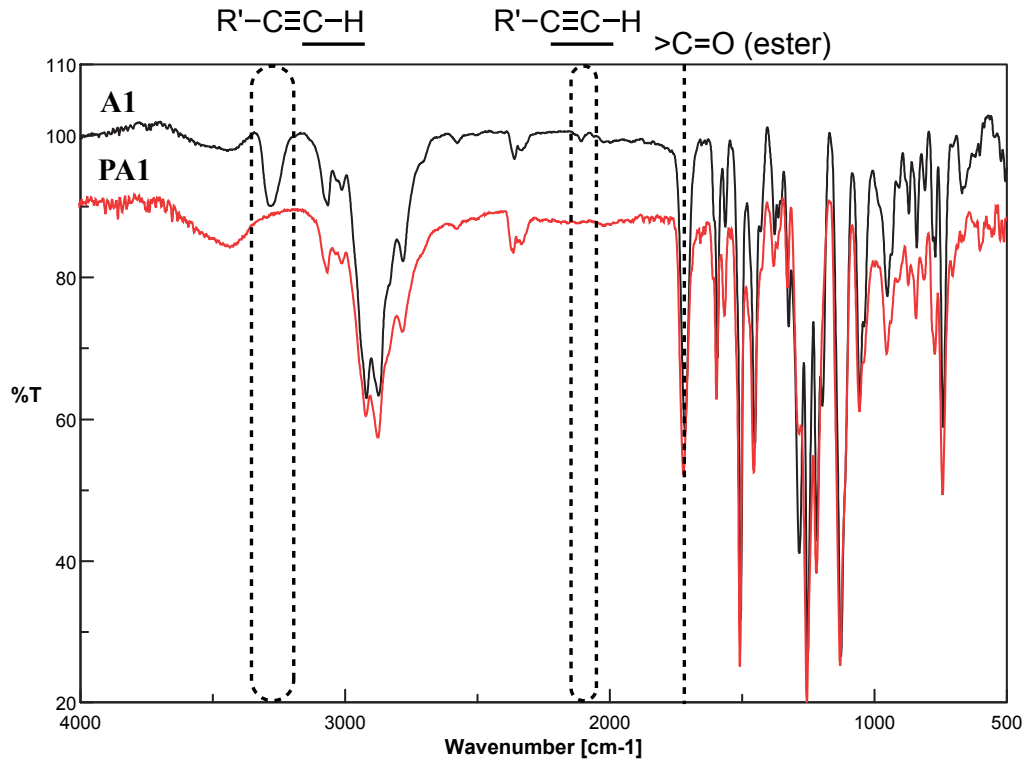


Fig. S18. IR spectra of **A1** and **PA1** (KBr).

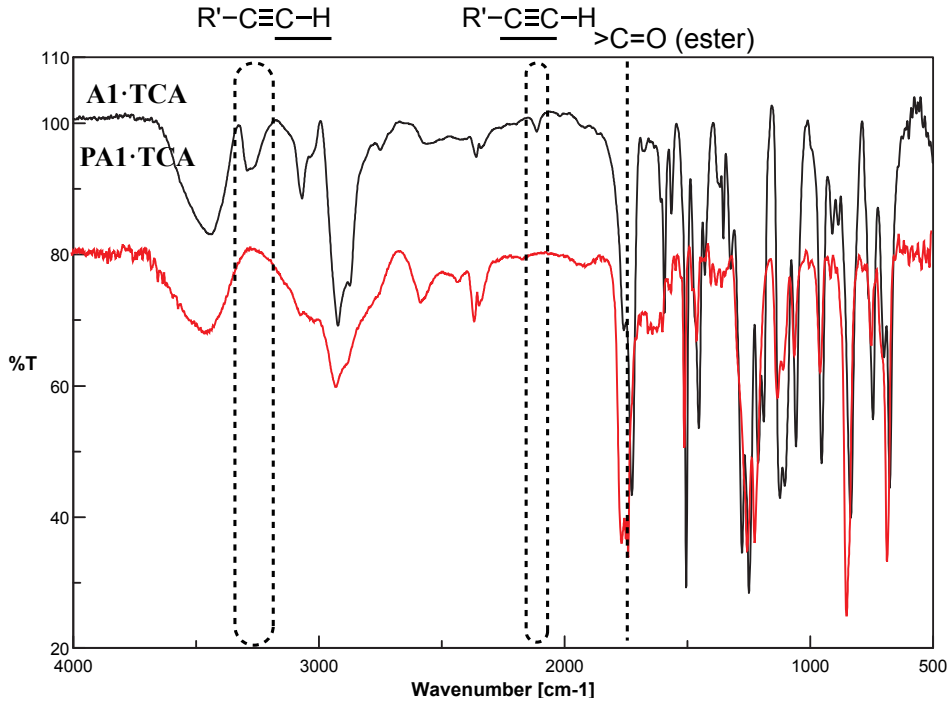


Fig. S19. IR spectra of **A1·TCA** and **PA1·TCA** (KBr).

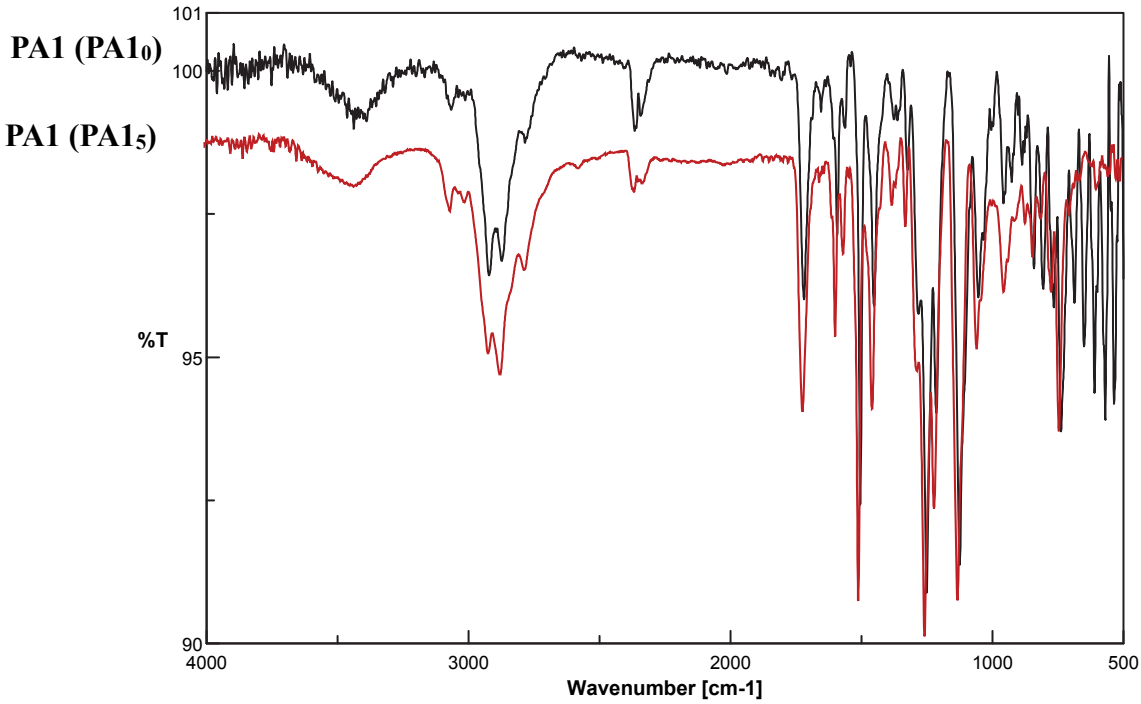


Fig. S20. IR spectra of polyphenylacetylene **PA1$_0$** and **PA1$_5$** (KBr).

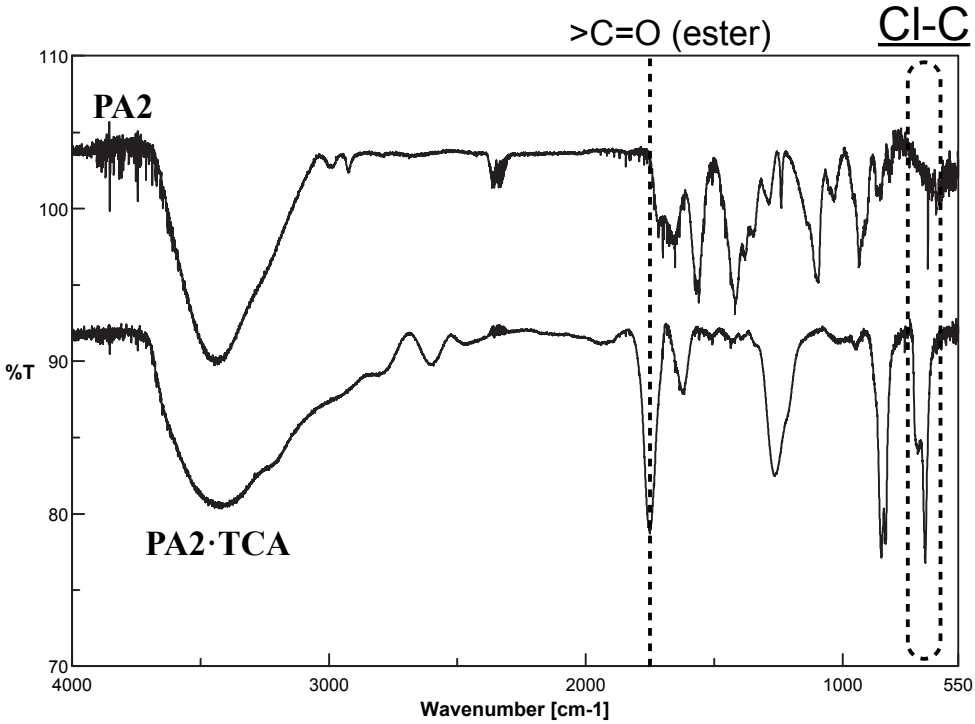
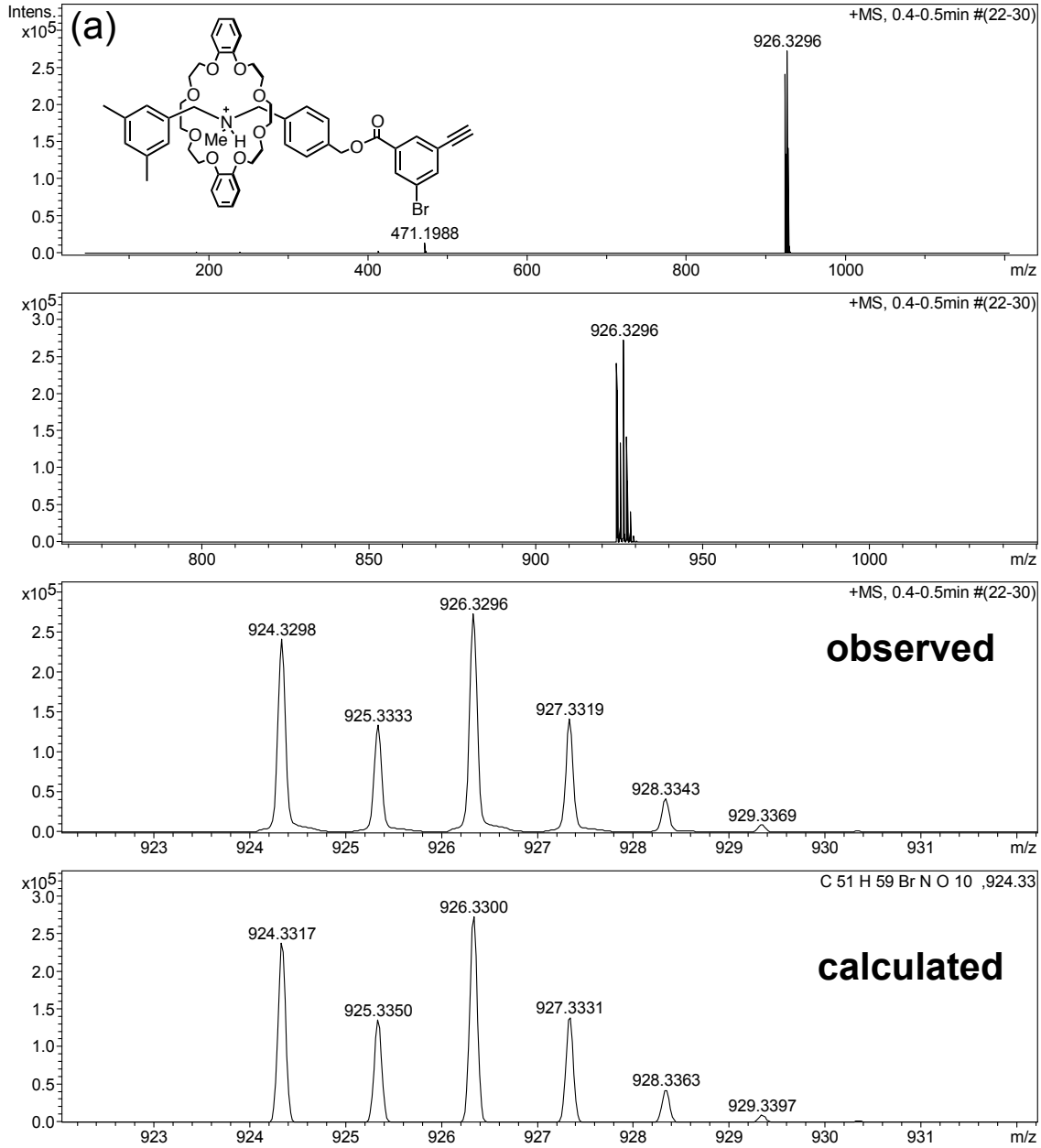


Fig. S21. IR spectra of polyphenylacetylene **PA2** and **PA2·TCA** (KBr).

4.5. ESI-TOF spectra



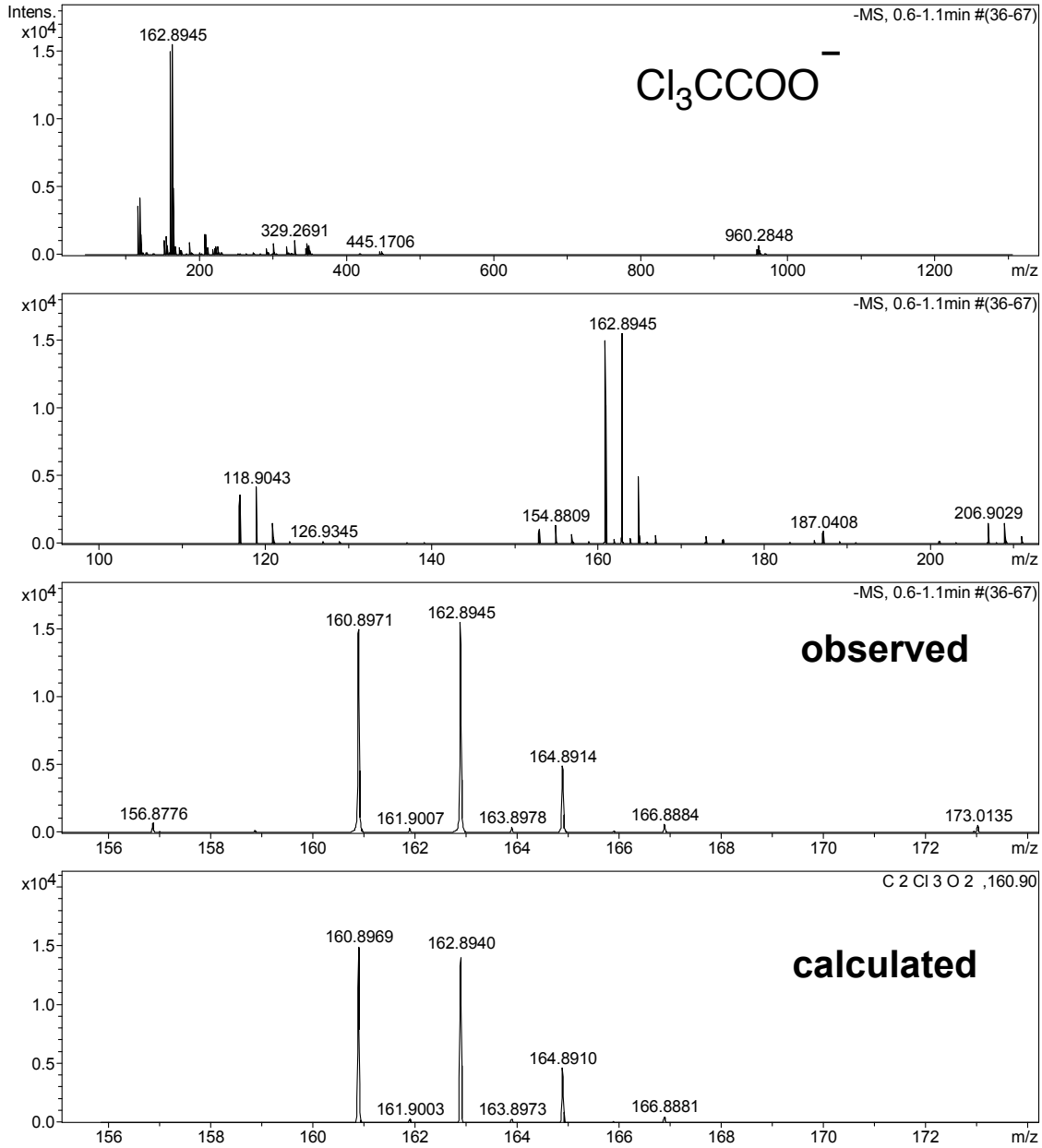


Fig. S22. ESI-TOF spectra of rotaxane **A1·TCA**: (a) rotaxane-type ammonium ion, and (b) trichloroacetate.

5. UV–vis spectra

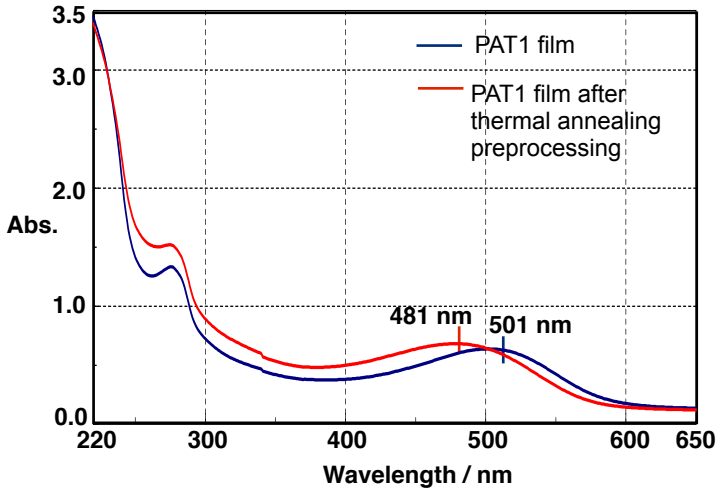


Fig. S23. UV–vis spectra of **PA1** film (298 K): (a) at room temperature; (b) after thermal annealing preprocessing: heating at 100 °C for 10 min.

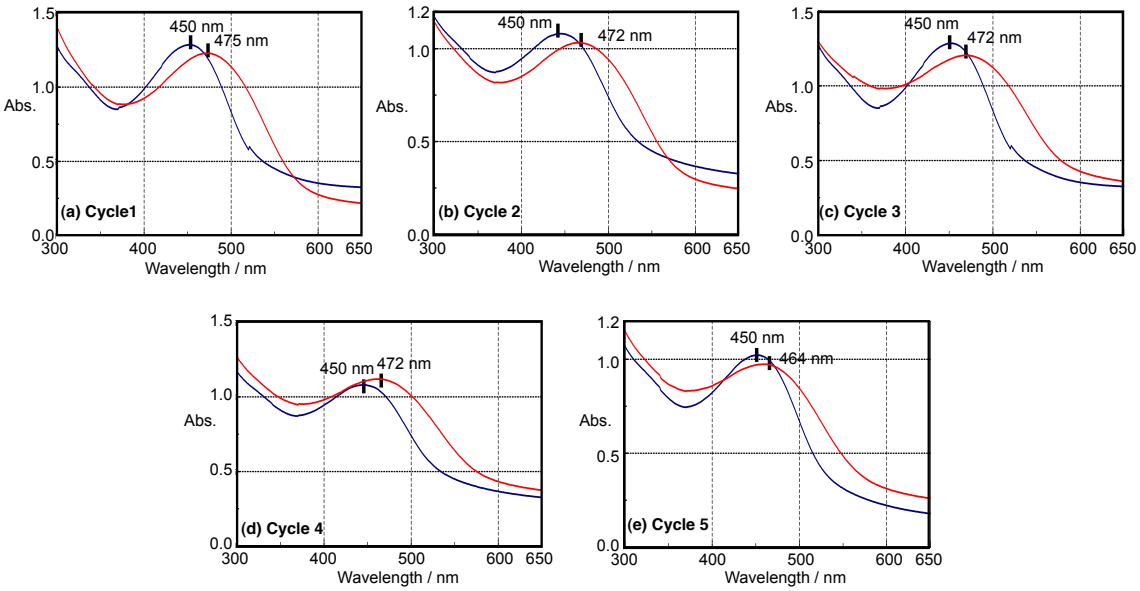


Fig. S24. UV–vis spectra of films of **PA1** (red lines) and **PA1·TCA** (blue line) by repeated heating and acidification progresses into the Cl_3CCOOH/hexane (2.0 M) in the consecutive 5 cycles.

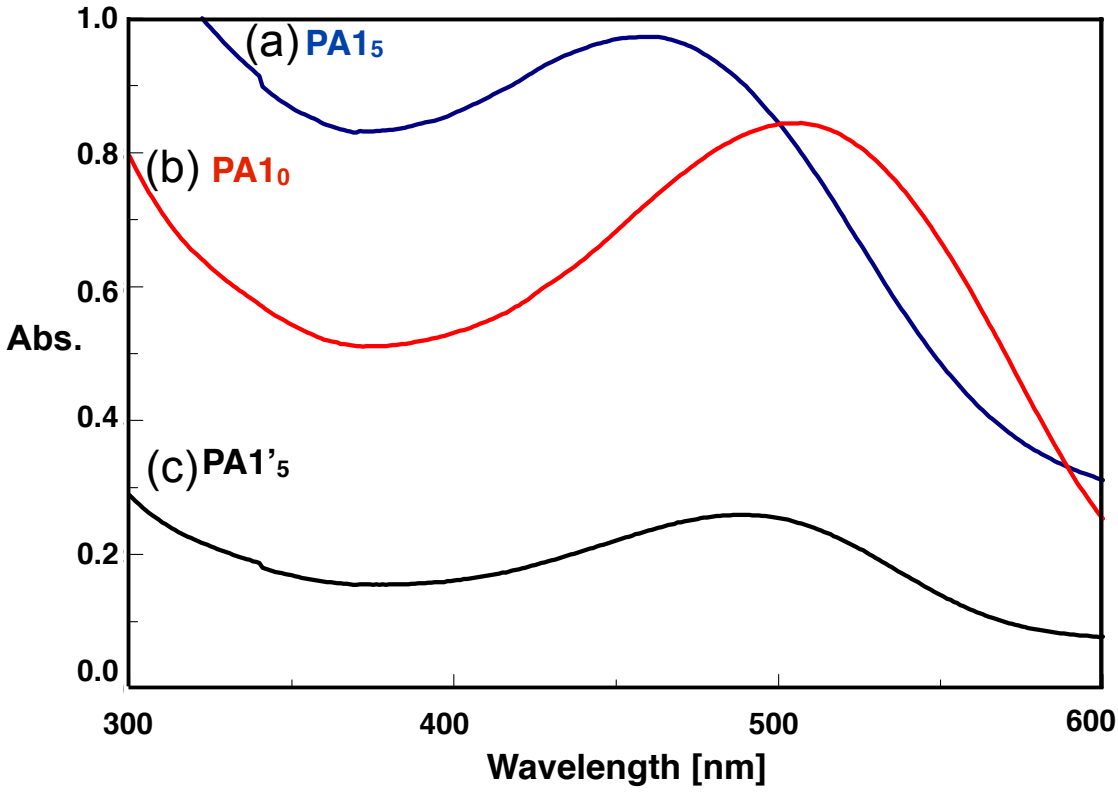


Fig. S25. UV–vis spectra of **PA1** film **PA1$_0$** (before thermal annealing preprocess), **PA1$_5$** (in the fifth cycle) and **PA1'$_5$** (dissolved **PA1$_5$** into the $CHCl_3$).

Blank experiment :

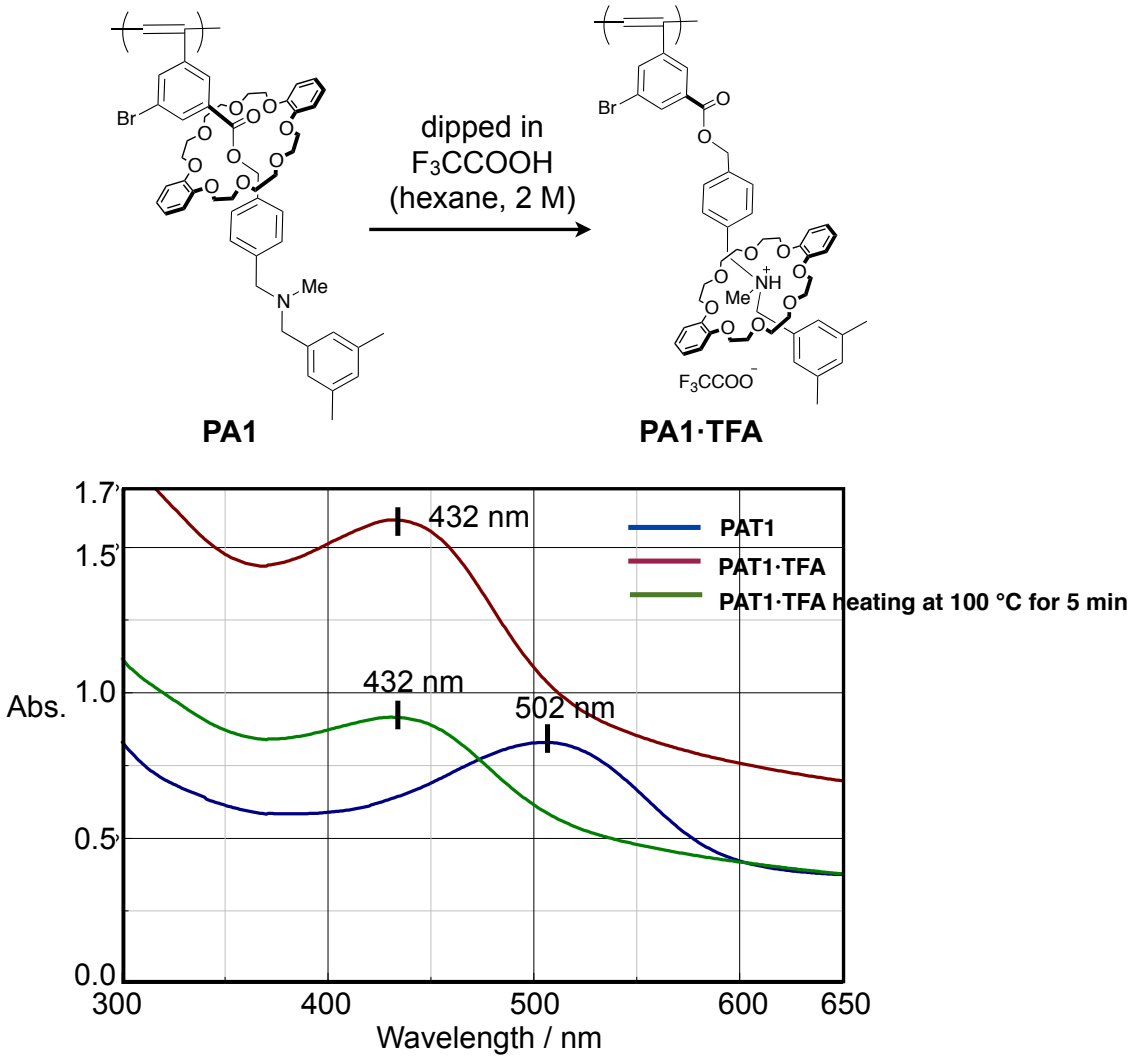


Fig. S26. Synthesis of film **PA1·TFA** and UV–vis spectra of: (a) **PA1** film (λ_{max} = 502 nm); (b) **PA1·TFA** film (λ_{max} = 432 nm, produced by dipping **PA1** film into the trifluoroacetic acid hexane for 5 min); and (c) **PA1·TFA** film heated at 100 °C for 5 min (λ_{max} = 432 nm).

6. DSC

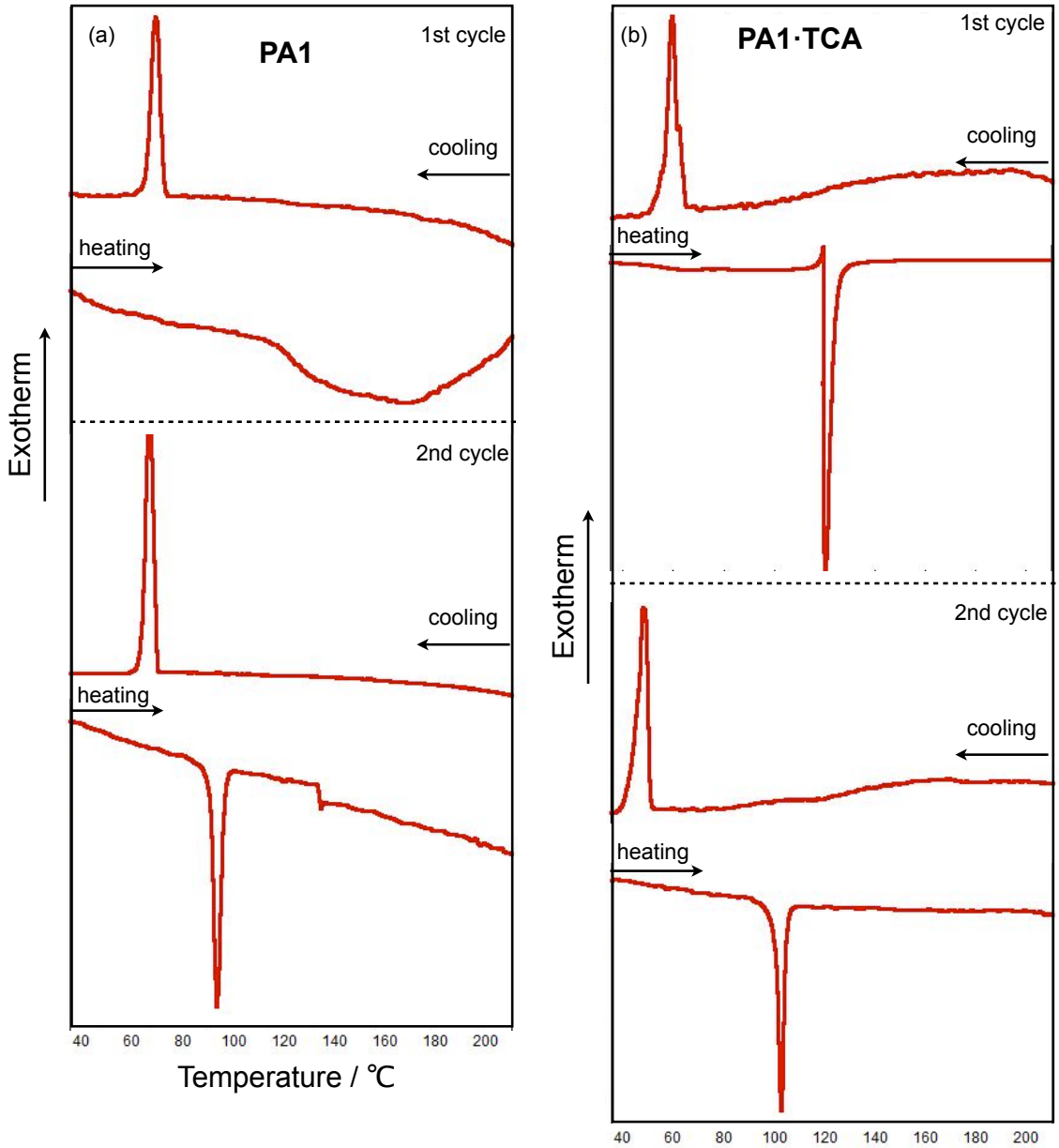


Fig. S27. DSC profiles of: (a) **PA1** and (b) **PA1·TCA** (heating and cooling rate: 10 °C·min^{-1}: 2nd heating and cooling from 30 °C to 200 °C under N_2 atmosphere).

7. References

1) K. Nakazono, K. Fukasawa, T. Sato, Y. Koyama, T. Takata, *Polym. J.* **2010**, *42*, 208-215.

2) N. Kihara, Y. Tachibana, H. Kawasaki, T. Takata, *Chem. Lett*. **2000**, *29*, 506-507.