

Supplementary information for

## **Cyclic poly(methyl acrylate) derived from [1]rotaxane terminated linear polymer via topological transformation**

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## Experimental section

### 1. General methods

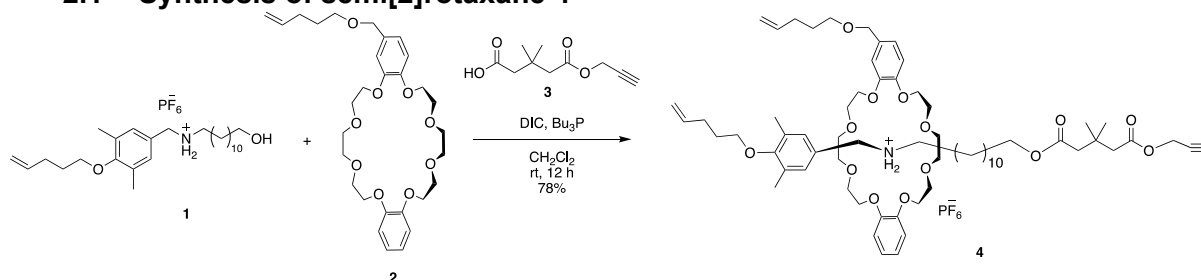
$^1\text{H}$  (300 MHz) NMR spectra were recorded on a Bruker Biospin AVANCE DPX-300 spectrometer using  $\text{CDCl}_3$  as the solvent, and tetramethylsilane was used as the internal standard. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. The size exclusion chromatography (SEC) in  $\text{CHCl}_3$  ( $0.85 \text{ mL} / \text{min}^{-1}$ ) was performed using a JASCO HSS-1500 system equipped with consecutive linear polystyrene gel columns (Shodex GPC K-804 and GPC K-805) at  $30^\circ\text{C}$ . The number of average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and polydispersity ( $M_w/M_n$ ) of the polymers were calculated on the basis of a polystyrene calibration. MALDI-TOF MS spectra were measured by a Shimadzu AXIMA-CFR mass spectrometer.

### Materials

All solvents were distilled or dried before use according to the general purification procedure.[1] Commercially available reagents were used without further purification unless otherwise noted. All reactions were carried out under inert atmosphere of argon. Silica gel column chromatography was performed using silica gel N 60 (grain size  $40\text{--}50 \mu\text{m}$ ) (Kanto Chemical Co. Inc., Tokyo, Japan). GPC (Gel permeation liquid column chromatography) was performed by LC-9204 system with JAIGEL 1H-40 (Japan Analytical Industry) with  $\text{CHCl}_3$  eluent.

## 2. Chemical synthesis

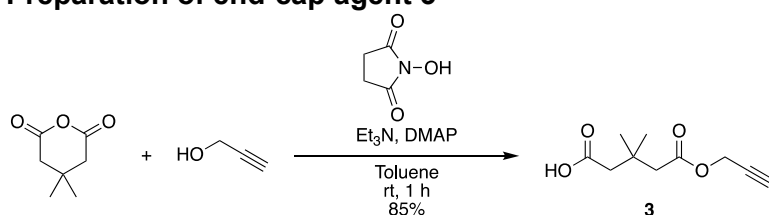
### 2.1 Synthesis of semi[2]rotaxane 4



### Synthesis of axle component 1 and ring component 2

Axle 1 and ring 2 were synthesized by using previously reported methods.[1, 2]

### Preparation of end-cap agent 3



To a mixture of 3,3-dimethylglutaric anhydride (5.0 g, 0.035 mol),  $N$ -hydroxysuccinimide (1.2 g, 0.011 mol) and DMAP (0.43 g, 0.0035 mol) in toluene (36 mL) were added propargyl alcohol (2.6 g, 0.046 mol) and triethylamine (1.1 g, 0.011 mol). The suspension was stirred for 1 h at room temperature and then diluted with EtOAc, washed with cold dil. HCl, dried over  $\text{Na}_2\text{SO}_4$ , and concentrated. The end cap 3 (5.9 g, 0.030 mol) was obtained in 85% yield as a colorless oil.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  4.70 (d,  $J = 2 \text{ Hz}$ , 2H), 2.52 (s, 2H), 2.51 (s, 2H), 2.49 (t,  $J = 2 \text{ Hz}$ , 1H), 1.18 (s, 6H) ppm.

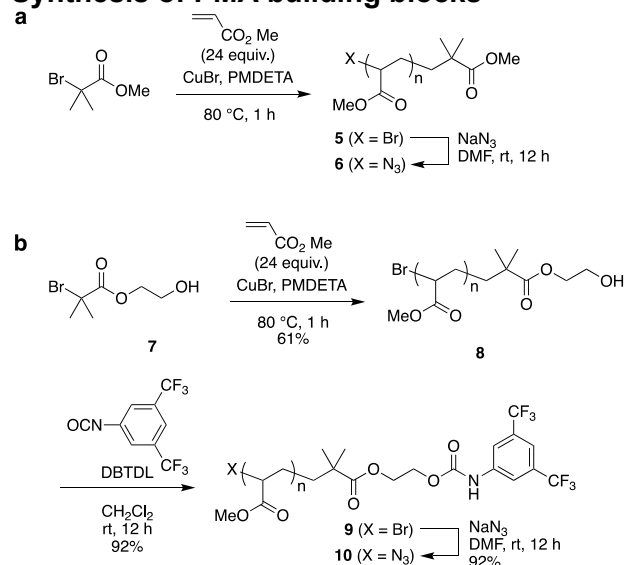
### Preparation of semi[2]rotaxane 4

To a solution of *sec*-ammonium salt 1 (0.50 g, 0.91 mmol), crown ether 2 (0.65 g, 1.2 mmol), and end cap 3 (0.72 g, 3.6 mmol) in  $\text{CH}_2\text{Cl}_2$  (3.8 mL) was added  $\text{PBU}_3$  (0.18 g, 0.91 mmol) and  $N,N'$ -diisopropylcarbodiimide (0.57 g, 4.6 mmol) at room temperature, and the solution was

stirred for 12 h. The reaction mixture was then poured into *n*-hexane (200 mL), and the precipitate was collected by decantation. The residue was purified by silica gel column chromatography (eluent: CHCl<sub>3</sub> / EtOAc = 1 / 1) and recycling preparative GPC to give semi[2]rotaxane **4** (0.87 g, 75 %) as a yellow foam.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 298 K) δ 7.10 (br, 2H), 7.00 (s, 2H), 6.97 - 6.80 (m, 7H), 5.96 - 5.76 (m, 2H), 5.14 - 4.95 (m, 4H), 4.67 (d, *J* = 2 Hz, 2H), 4.50 - 4.45 (m, 2H), 4.43 (s, 2H), 4.30 - 4.04 (m, 10H), 3.96 - 3.75 (m, 8H), 3.73 - 3.41 (m, 12H), 3.10 (br, 2H), 2.47 (s, 2H), 2.46 (t, *J* = 2 Hz, 1H), 2.42 (s, 2H), 2.30 (q, 2H, *J* = 6 Hz), 2.19 - 2.10 (m, 8H), 1.90 (quint., 2H, *J* = 6 Hz), 1.77 - 1.57 (m, 4H), 1.49 - 0.96 (m, 26H) ppm.

## Synthesis of PMA building blocks



## Preparation of PMA **6**

A dry flask, charged with CuBr (0.020 g, 0.14 mmol), methyl 2-bromo-2-methylpropionate (0.11 g, 0.62 mmol), PMDETA (0.025 g, 0.14 mmol) and MA (1.3 g, 15 mmol) was sealed with a rubber septum and cycled three times between vacuum and argon to remove oxygen. The mixture was heated at 80 °C and reacted for 1h. After heating stopped, the reaction mixture was cooled to room temperature and diluted with THF. The solution was passed through a short alumina column and the solvent was evaporated. The product was purified by reprecipitation into *n*-hexane, **5** (1.23 g, 55 %) as a sticky solid.

To a solution of **5** (0.74 g, 0.21 mmol) in DMF (5 mL), NaN<sub>3</sub> (0.069 g, 1.1 mmol) was added and stirred at r.t. for 12 h. The reaction mixture was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The polymer was isolated by reprecipitation from CH<sub>2</sub>Cl<sub>2</sub> into *n*-hexane to obtain polymer **6** quantitatively.

## Preparation of PMA **10**

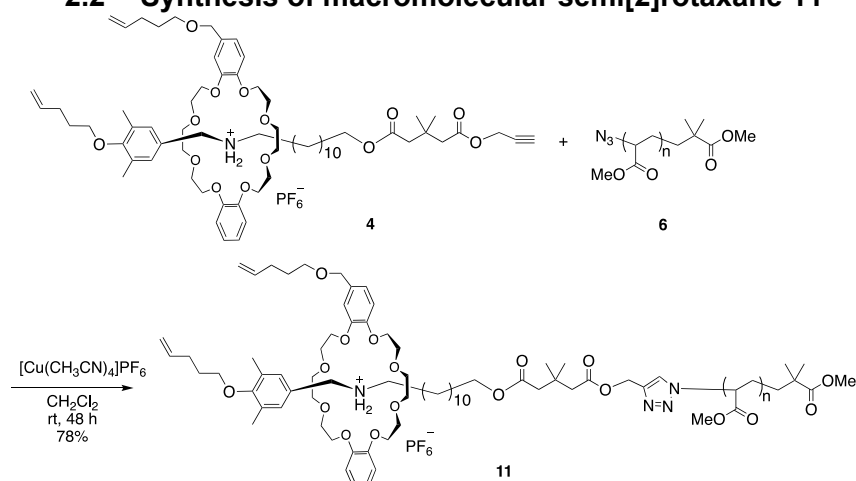
A dry flask, charged with CuBr (0.020 g, 0.14 mmol), 2-hydroxyethyl 2-bromoisobutyrate **7** (0.060 g, 0.62 mmol), PMDETA (0.025 g, 0.14 mmol) and MA (1.3 g, 15 mmol) was sealed with a rubber septum and cycled three times between vacuum and argon to remove oxygen. The mixture was heated at 80 °C and reacted for 1h. After heating stopped, the reaction mixture was cooled to room temperature and diluted with THF. The solution was passed through a short alumina column and the solvent was evaporated. The product was purified by reprecipitation into *n*-hexane, **8** (1.21 g, 61 %) as a sticky solid.

The polymer **8** (0.73 g, 0.23 mmol), 3,5-bistrifluoromethylphenylisocyanate (0.087 g, 3.5 mmol) and cat. DBTDL (1 drop) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and reacted 12 h at r.t. The

polymer was isolated by reprecipitation from CH<sub>2</sub>Cl<sub>2</sub> in *n*-hexane to obtain polymer **9** (0.74 g, yielded 92%).

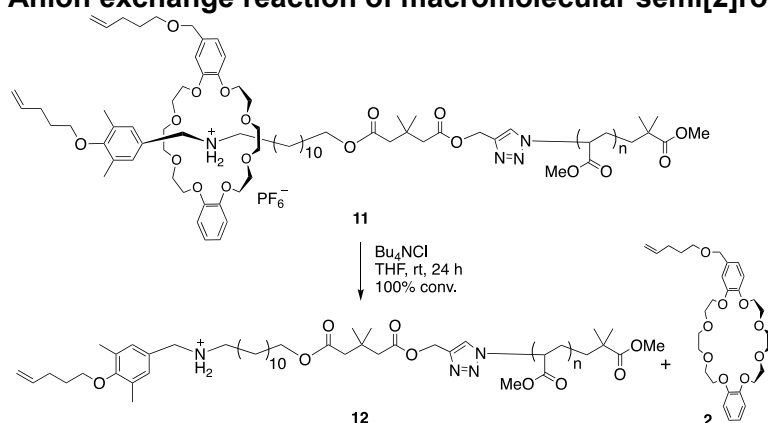
To a solution of **9** (0.74 g, 0.21 mmol) in DMF (5 mL), NaN<sub>3</sub> (0.069 g, 1.1 mmol) was added and stirred at r.t. for 12 h. The reaction mixture was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The polymer was isolated by reprecipitation from CH<sub>2</sub>Cl<sub>2</sub> into *n*-hexane to obtain polymer **10** quantitatively.

## 2.2 Synthesis of macromolecular semi[2]rotaxane **11**



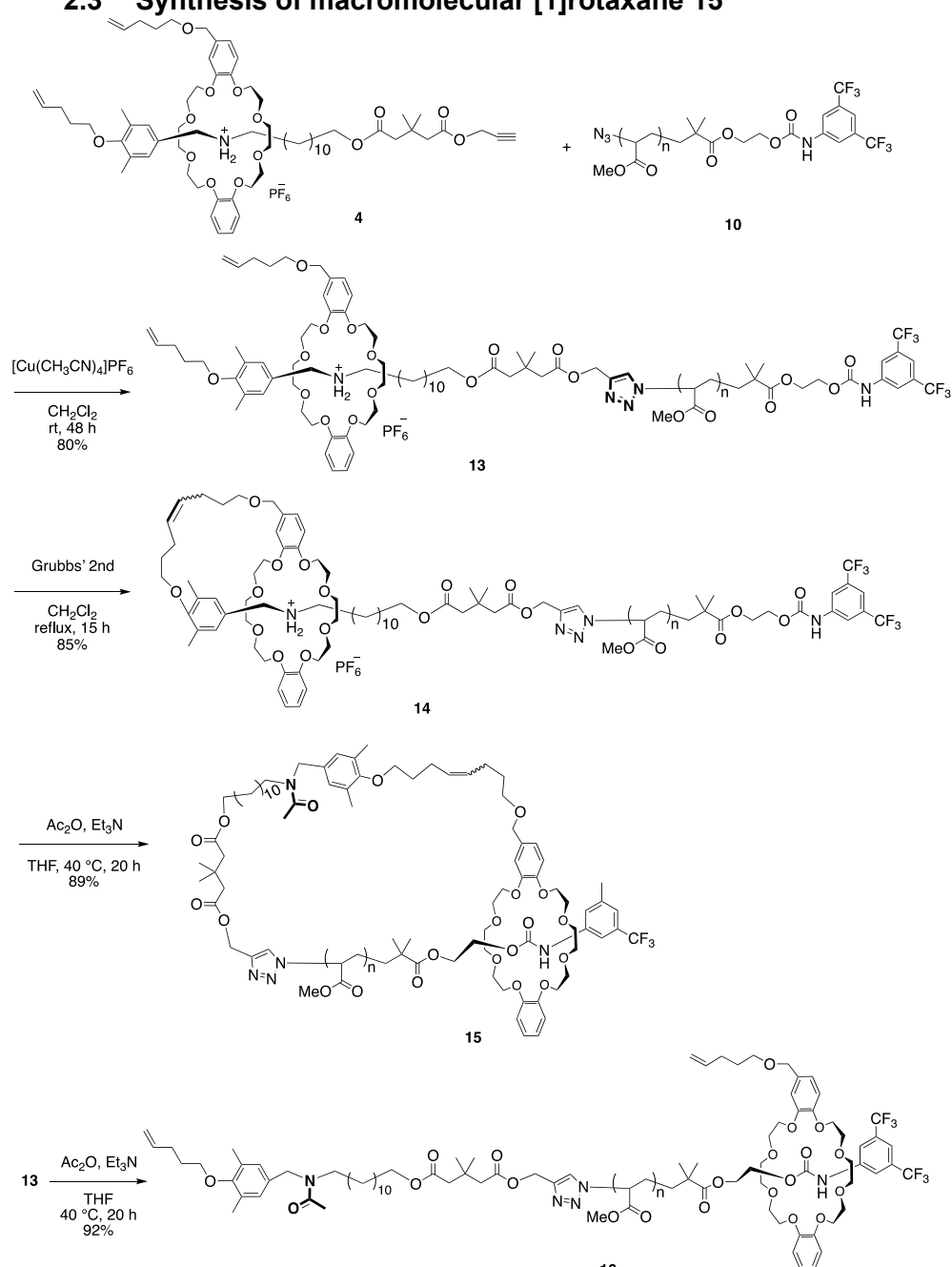
To a solution of rotaxane **4** (0.45 g, 0.35 mmol) and PMA **6** (0.74 g, 0.21 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL), [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> (0.086 g, 0.23 mmol) was added and evacuated three times and filled with argon. Then the mixture was stirred at r.t. for 48 h. After dilution of the reaction mixture with CH<sub>2</sub>Cl<sub>2</sub>, it was passed through a short aluminum column and the solvent was evaporated. The crude product was purified by recycling preparative GPC to remove the residual **4** to give **11** (0.82 g) in 78 % yield.

## Anion exchange reaction of macromolecular semi[2]rotaxane **11**



To a solution of **11** (50 mg, 10 μmol) in THF (2 mL), an excess of tetrabutylammonium chloride (28 mg, 0.10 mmol) was added and reacted at r.t. for 24 h. The solvent was removed by evaporation, and then the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>. The solution was washed with water and dried over MgSO<sub>4</sub>, filtered, and concentrated. Purification was performed by preparative GPC, and the high molecular weight region was collected to give **12** (41 mg, 92%).

### 2.3 Synthesis of macromolecular [1]rotaxane **15**



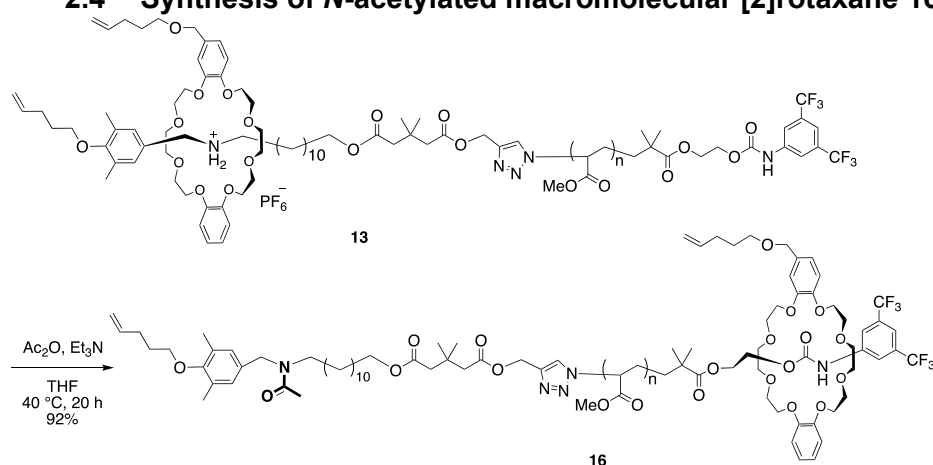
To a solution of semi[2]rotaxane **4** (0.45 g, 0.35 mmol) and PMA **8** (0.74 g, 0.23 mmol) in  $\text{CH}_2\text{Cl}_2$  (1.0 mL),  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (0.094 g, 0.25 mmol) was added and evacuated three times and filled with argon. The mixture was stirred at r.t. for 48 h. The solvent was removed by evaporation, and the residue was dissolved into  $\text{CH}_2\text{Cl}_2$ . The solution was passed through a short aluminum column and the solvent was evaporated. The product was purified by recycling preparative GPC to give macromolecular [2]rotaxane **13** (0.86 g) in 80 % yield.

To a solution of macromolecular [2]rotaxane **13** (0.14 g, 0.029 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 mL), Grubbs' catalyst 2<sup>nd</sup> generation (7.3 mg, 0.0086 mmol) was added and degassed by three consecutive freeze pump-thaw cycles, then filled with argon. The solution was heated to reflux and stirred for 15 h. The reaction mixture was cooled to room temperature and the solvent was removed to about half under reduced pressure. The solution was poured into hexane to reprecipitate the polymer, and the formed polymer precipitate was collected by filtration.

Further purification was performed by preparative GPC with  $\text{CHCl}_3$  as the eluent to obtain macromolecular [1]rotaxane **14** (0.12 g) in 85% yield.

To a solution of **14** (0.10 g, 0.021 mmol), acetic anhydride (0.11 g, 1.1 mmol), and triethylamine (0.21 g, 2.2 mmol) in THF (0.50 mL) was stirred at 40 °C for 20 h. After the solvent was evaporated, the residue was purified by a preparative GPC with  $\text{CHCl}_3$  as the eluent to obtain *N*-acetylated macromolecular [1]rotaxane **15** (0.088 g) in 89% yield.

## 2.4 Synthesis of *N*-acetylated macromolecular [2]rotaxane **16**



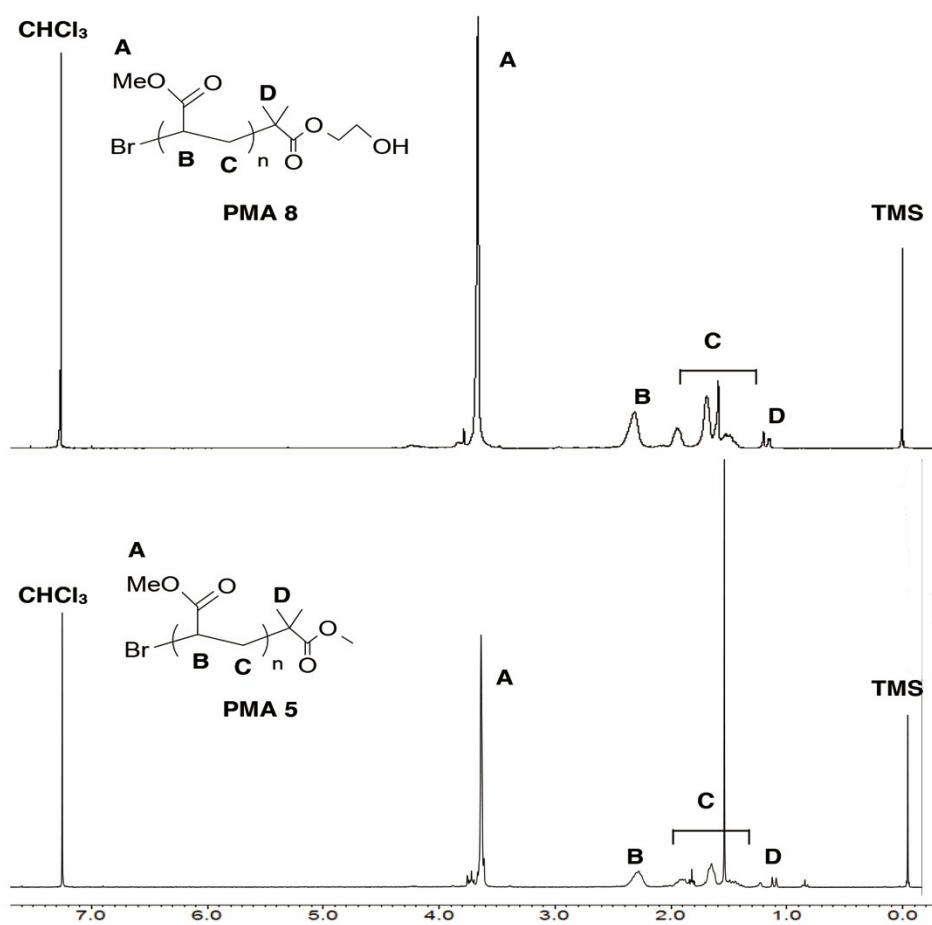
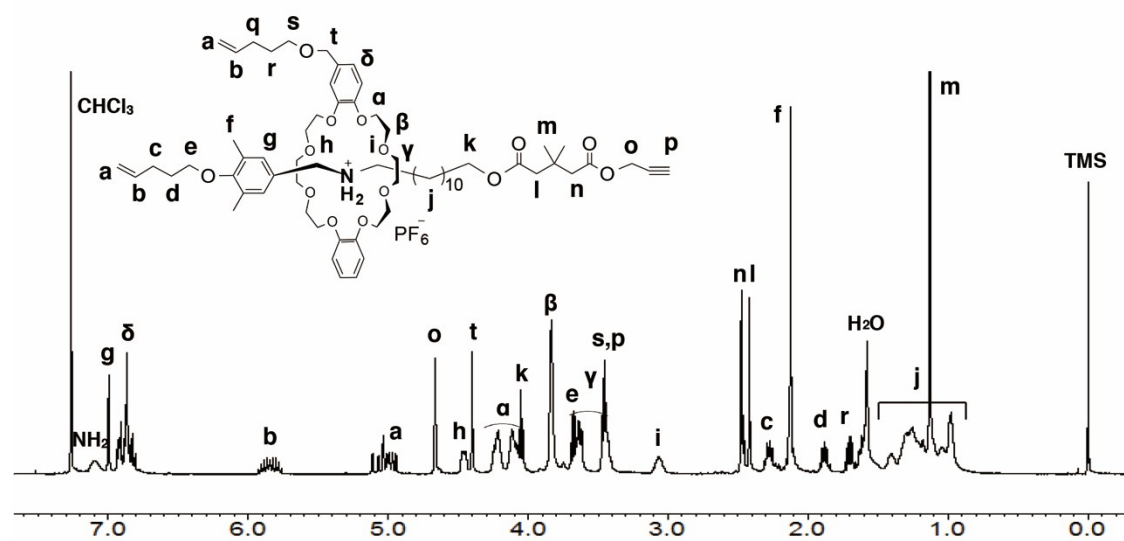
Scheme S1.

To a solution of macromolecular [2]rotaxane **13** (0.10 g, 0.021 mmol), acetic anhydride (0.11 g, 1.1 mmol), and triethylamine (0.21 g, 2.2 mmol) in THF (0.50 mL) was stirred at 40 °C for 20 h. The solution was purified by a preparative GPC with  $\text{CHCl}_3$  as the eluent to obtain *N*-acetylated macromolecular [2]rotaxane **16** (0.094 g) in 92% yield.

## 3. References

- [1] D. Aoki, S. Uchida, K. Nakazono, Y. Koyama, T. Takata, *ACS Macro Lett.* **2013**, 2, 461.
- [2] T. Ogawa, N. Usuki, K. Nakazono, T. Takata, *Chem. Commun.* **2015**, 51, 5606.

#### 4. Spectra of synthesized chemicals



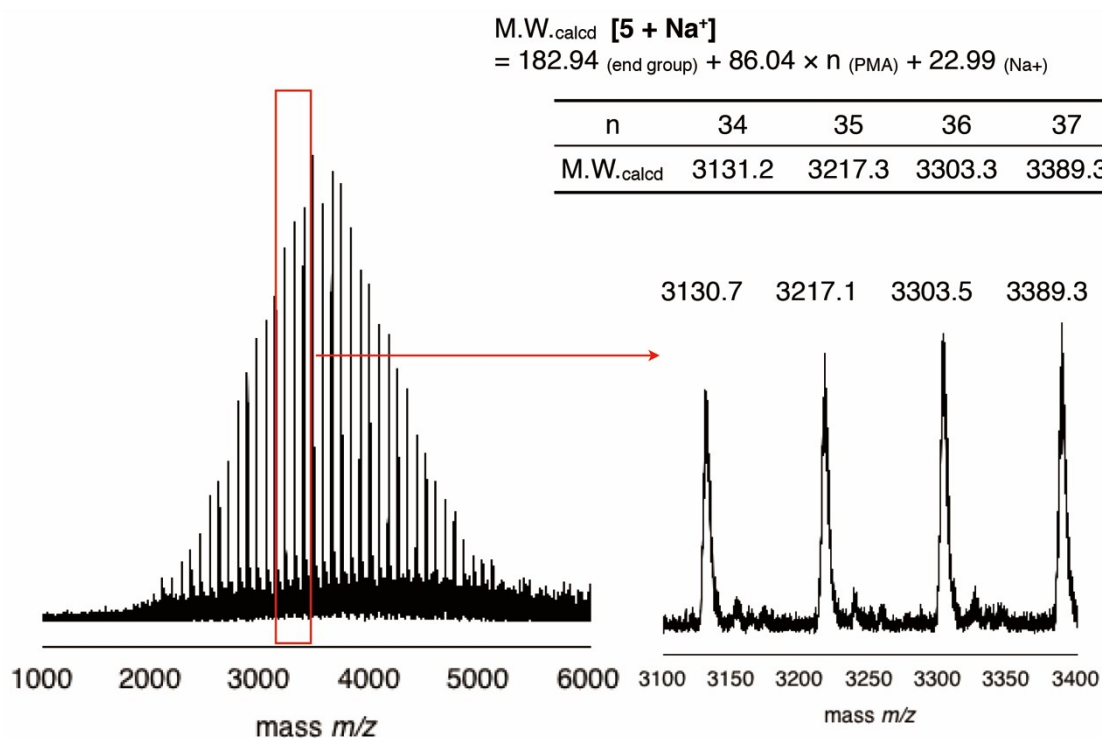


Figure S3. MALDI-TOF mass spectrum of 5

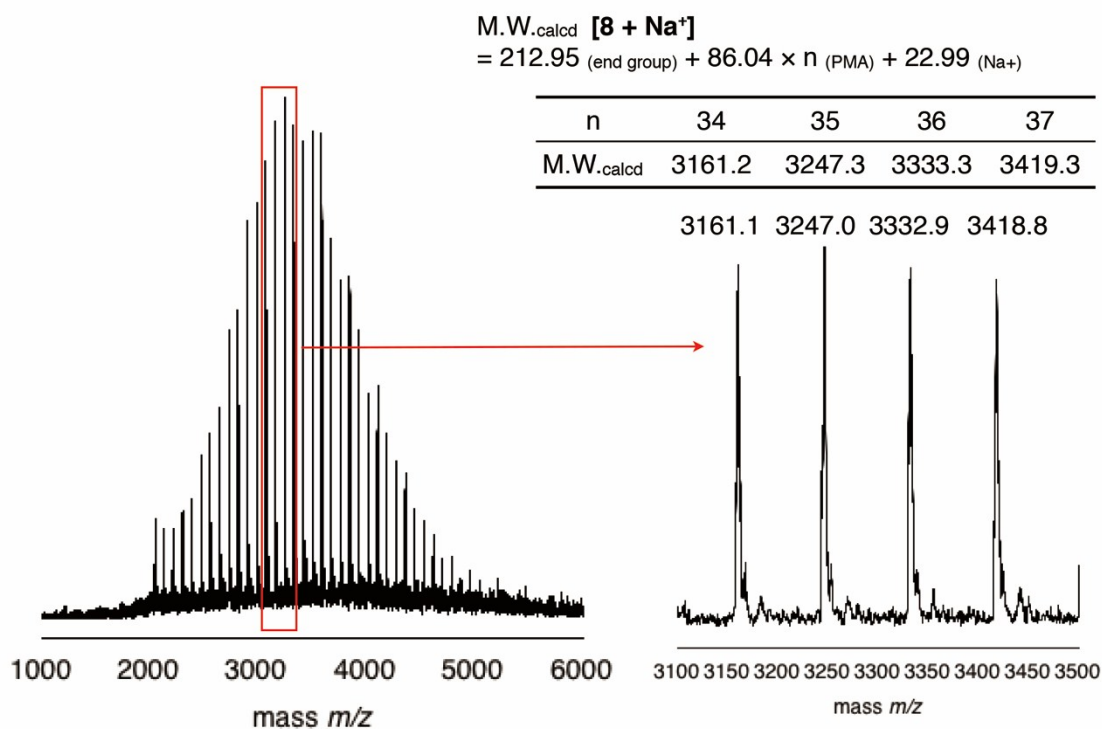
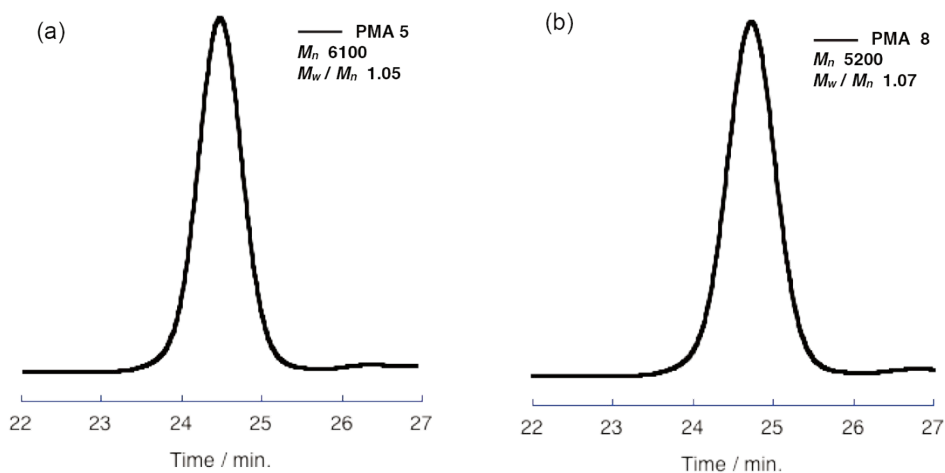
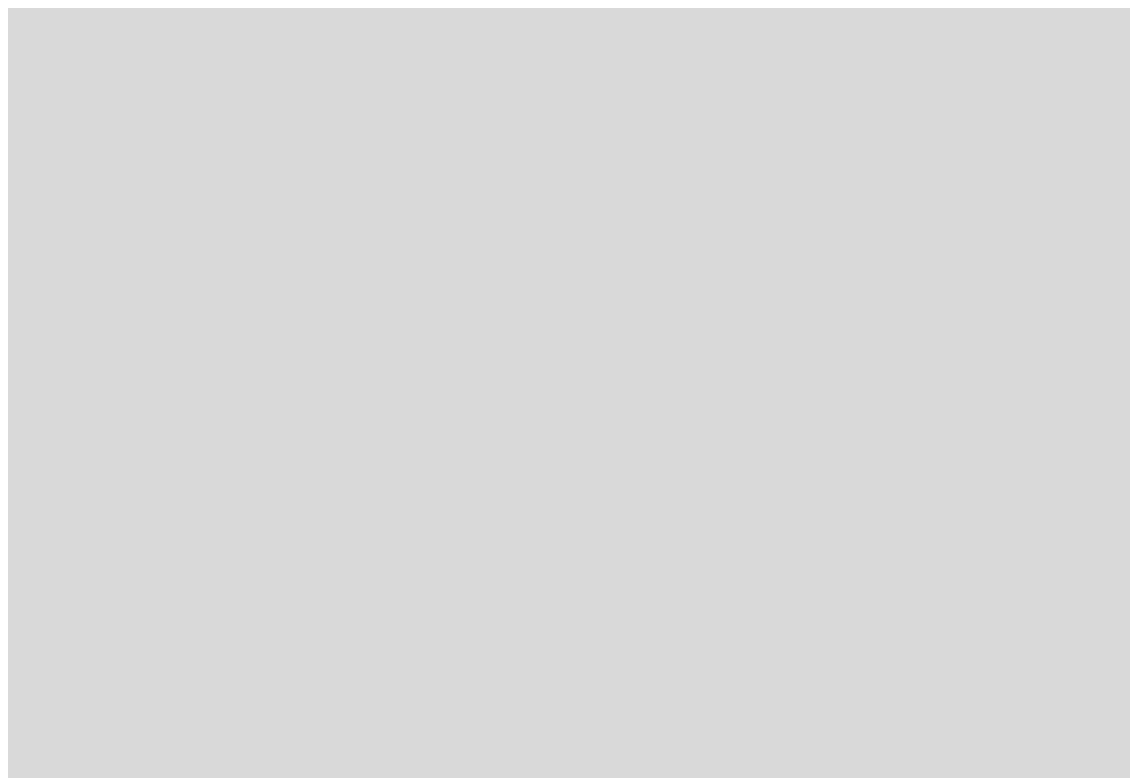


Figure S4. MALDI-TOF mass spectrum of 8

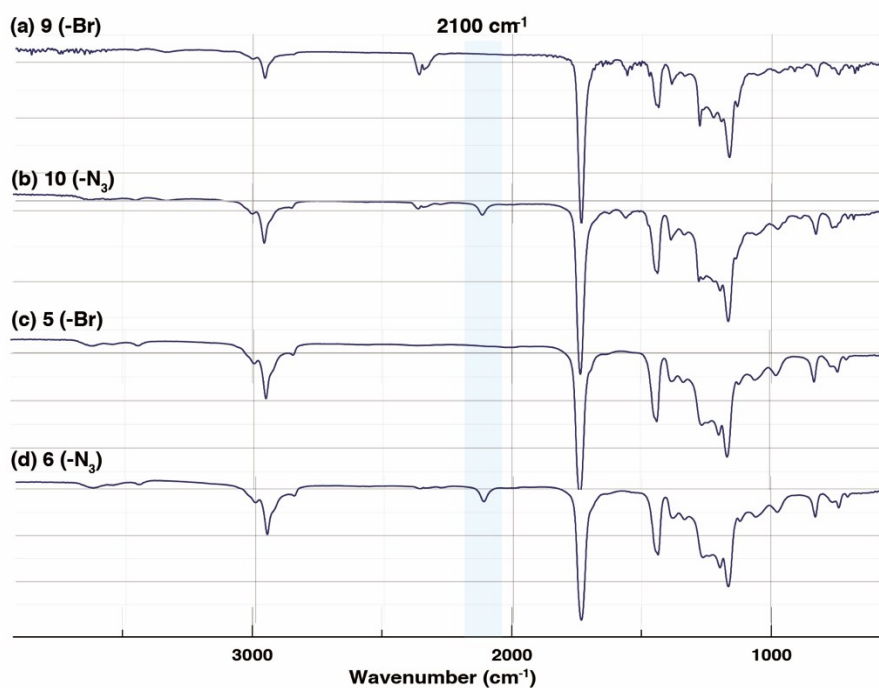




**Figure S5. SEC traces of PMA 5 (a) and PMA 8 (b)**  
(eluent:  $\text{CHCl}_3$ , flow rate 0.85 mL/min, detected by UV, PSt standards)

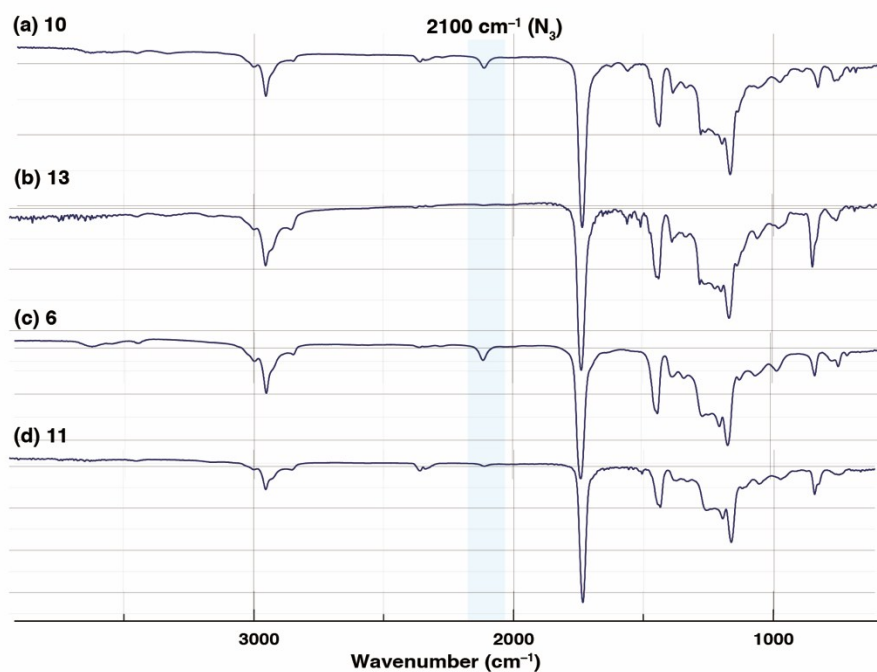


**Figure S6. MALDI-TOF mass spectrum of 9**



FT-IR spectra of 5, 6, 9, and 10 (NaCl).

Figure S7. FT-IR spectra of 5, 6, 9, 10



FT-IR spectra of 6, 11, 10, and 13 (NaCl).

Figure S8. FT-IR spectra of 6, 10, 11, 13

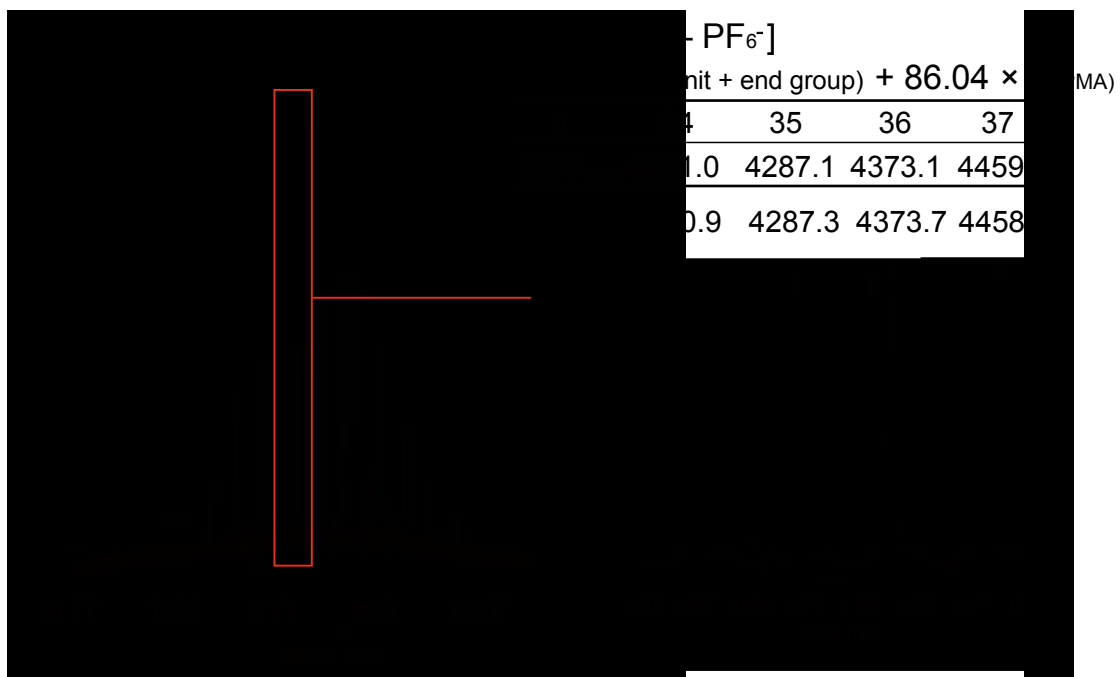


Figure S9. MALDI-TOF mass spectrum of 11

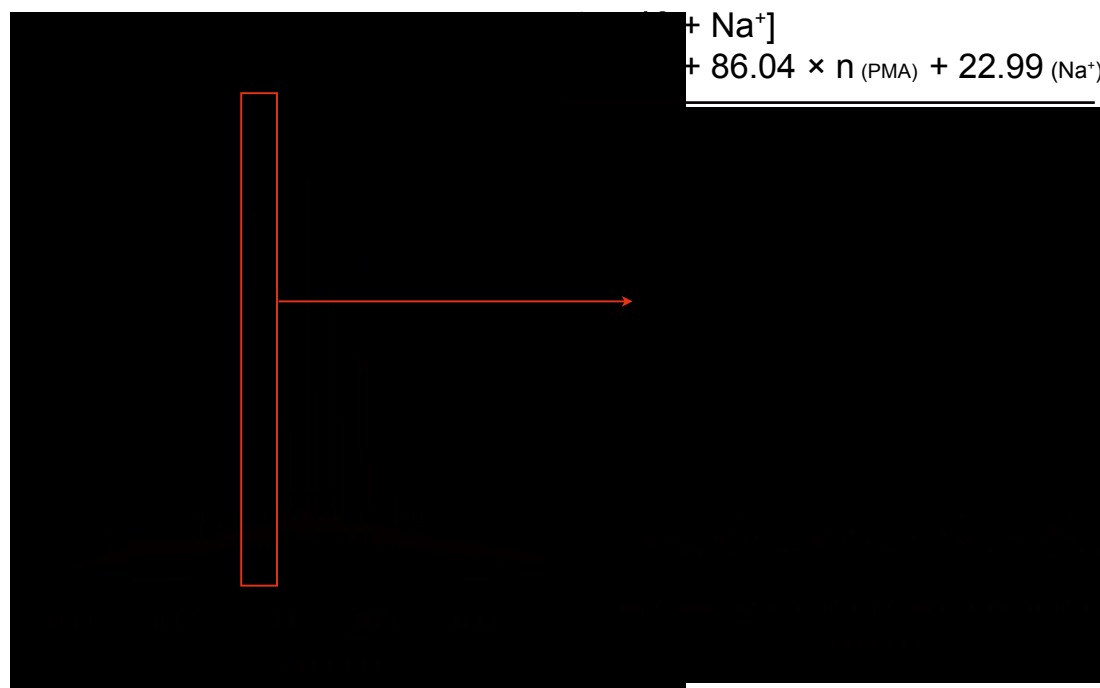


Figure S10. MALDI-TOF mass spectrum of 12

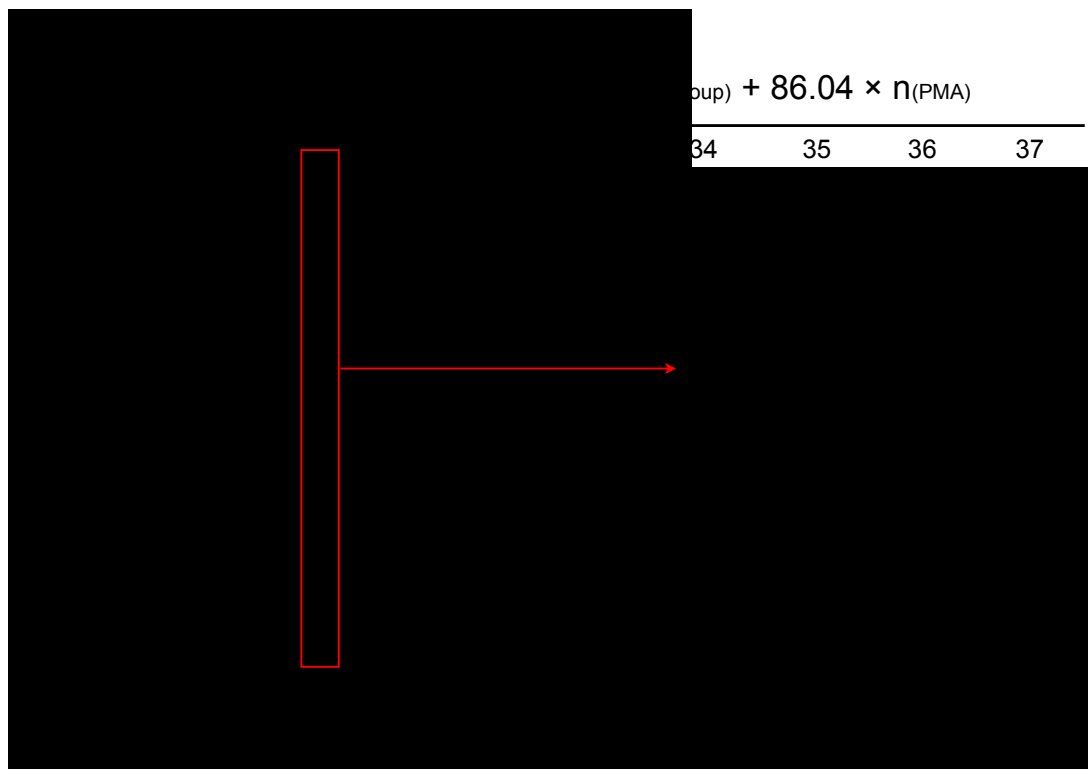


Figure S11. MALDI-TOF mass spectrum of 13

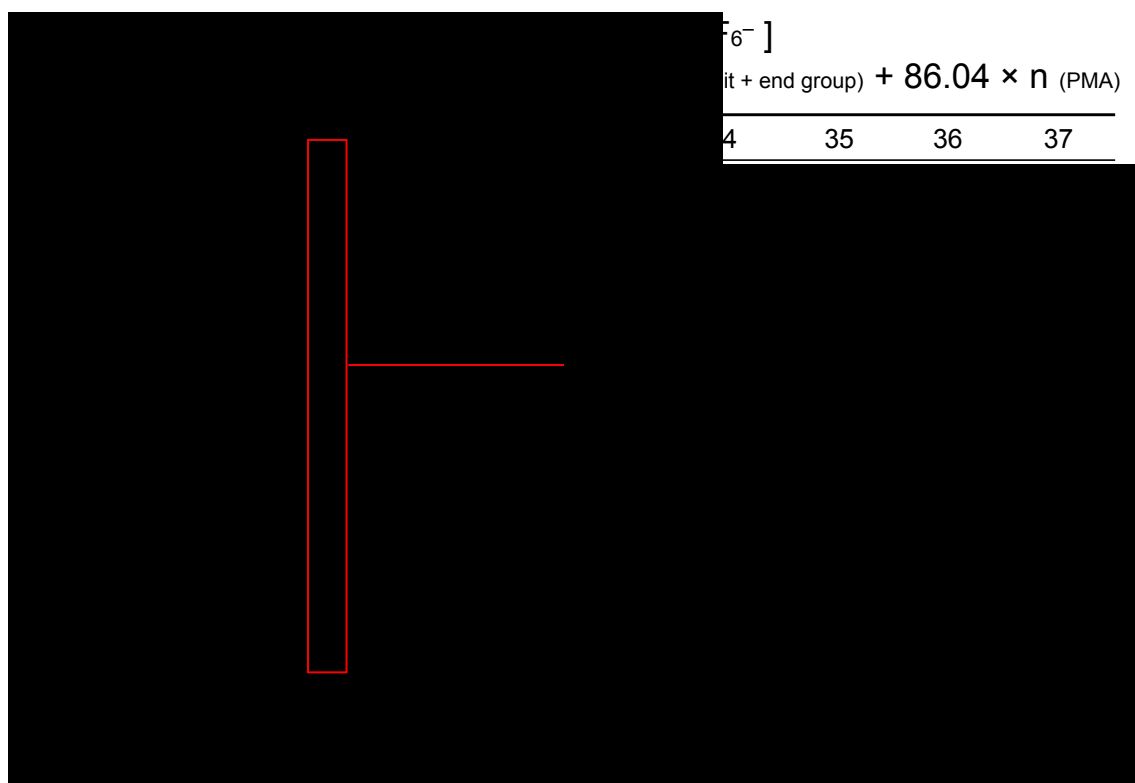


Figure S12. MALDI-TOF mass spectrum of 14