Supporting Information

A New [3]Rotaxane Molecular Machine Based on a Dibenzylammonium and a Triazolium Station

Yi Jiang,\textsuperscript{ab} Jia-Bin Guo\textsuperscript{ab} and Chuan-Feng Chen*\textsuperscript{a}

\textsuperscript{a}Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. \textsuperscript{b}Graduate School, Chinese Academy of Sciences, Beijing 100049, China.

cchen@iccas.ac.cn

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1. Experimental section

General methods. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker DMX300 NMR. MALDI-TOF MS were obtained on a Bruker BIFLEXIII mass spectrometer. Elemental analyses were performed by the Analytical Laboratory of Institute of Chemistry, CAS. Materials obtained commercially were used without further purification.

**Synthesis of compound 4.** To the solution of compound $^5$ (1.1 g, 4 mmol) in dry DMF (20 mL) was added solid NaH (623 mg, 26 mmol). The resulting suspension was stirred at room temperature until the evolution of gas ceased (~25 min). To the above mixture was then added a solution of propargyl bromide in xylene (3.7 g, 31.4 mmol). After being stirred for 2 d, the reaction mixture was quenched by the addition of MeOH, and the solvents were removed in vacuo. The brown residue was then subjected to chromatography on silica (hexane/EtOAc = 2/1, v/v) to provide 4 as a yellow oil (0.79 g, 63%). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 7.57 (d, $J = 9.0$ Hz, 2H), 6.93 (d, $J = 9.0$ Hz, 2H), 4.14 (d, $J = 2.4$ Hz, 2H), 3.99 (t, $J = 6.6$ Hz, 2H), 3.51 (t, $J = 6.6$ Hz, 2H), 2.42 (t, $J = 2.4$ Hz, 4H), 1.84-1.75 (m, 2H), 1.64-1.57 (m, 2H), 1.47-1.31 (m, 12H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 162.5, 140.0, 119.4, 115.2, 103.6, 80.1, 74.1, 70.3, 68.4, 58.0, 29.51, 29.45, 29.4, 29.3, 29.0, 26.1, 25.9. EI-MS: m/z = 313 [M$^+$]. Anal. Calcd. for C$_{20}$H$_{27}$NO$_2$: C, 76.64; H, 8.68; N, 4.47. Found: C, 76.51; H, 8.49; N, 4.35.

**Synthesis of compound 3.** To a solution of compound 4 (0.80 g, 2.52 mmol) in anhydrous THF (40 mL) at 0 °C was slowly added lithium aluminum hydride (0.50 g, 13
mmol). The reaction mixture was warmed to 60 °C, refluxed under an argon atmosphere for 12 h, and then quenched by the addition of H2O (5.5 mL), 15% aqueous NaOH (5.5 mL) and H2O (5 mL), respectively. The organic layer was diluted with ethyl ether, and washed with water for three times to yield compound 3 as a yellow oil (0.70 g, 87% yield), which was used for the next step reaction without further purification. 1H NMR (300 MHz, CDCl3): δ = 7.22 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 4.14 (d, J = 2.4 Hz, 2H), 3.94 (t, J = 6.6 Hz, 2H), 3.81 (s, 2H), 3.51 (t, J = 6.6 Hz, 2H), 2.42 (t, J = 2.4 Hz, 4H), 1.94 (brs, 2H), 1.81-1.72 (m, 2H), 1.62-1.55 (m, 2H), 1.44-1.31 (m, 12H). 13C NMR (75 MHz, CDCl3): δ = 158.2, 134.6, 128.4, 114.6, 80.1, 74.0, 70.3, 68.0, 58.0, 45.8, 29.5, 29.40, 29.37, 29.30, 26.1, 26.0. EI-MS: m/z = 317 [M+]. Anal. Calcd. for C20H31NO2: C, 75.67; H, 9.84; N, 4.41. Found: C, 75.57; H, 9.72; N, 4.34.

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C8H17O

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Synthesis of compound 2. 4-Hydroxy-3,5-dimethoxybenzaldehyde (2 g, 11 mmol), 1-bromooctane (8.50 g, 44 mmol), and potassium carbonate (4.50 g, 33 mmol) were suspended in anhydrous CH3CN (50 mL). The mixture was heated to 80 °C and stirred for 1 d. The reaction mixture was then diluted with water and washed with ethyl acetate for three times to give a crude product, which was purified by column chromatography (SiO2: hexanes:ethyl acetate 6:1) to yield the alkylated product as a pale oil (2.55 g, 79% yield). 1H NMR (300 MHz, CDCl3): δ = 9.86 (s, 1H), 7.12 (s, 2H), 4.07 (t, J = 6.6 Hz, 2H), 3.91 (s, 6H), 3.81 (s, 2H), 1.79-1.71 (m, 2H), 1.48-1.43 (m, 8H), 0.88 (t, J = 6.6 Hz, 3H). 13C NMR (75 MHz, CDCl3): δ = 191.0, 153.9, 143.1, 131.5, 106.7, 73.7, 56.2, 31.8, 30.1, 29.3, 29.2, 25.7, 22.6, 14.1. EI-MS: m/z = 294 [M+]. Anal. Calcd. for C17H26O4: C, 69.36; H, 8.90. Found: C, 69.29; H, 8.79.
Synthesis of compound 2-H·PF₆. A mixture of 2 (317 mg, 2.31 mmol) and 3 (679 mg, 2.31 mmol) in dry toluene (70 mL) was refluxed overnight in a Dean-Stark apparatus under nitrogen atmosphere. The solvent was removed under vacuum, and the residue was dissolved in MeOH (50 mL). To the solution was then added NaBH₄ (1 g, 26.3 mmol) in portion. After the mixture was stirred for overnight, the solvent was removed under vacuum, and the residue was extracted by dichloromethane. The organic layer was washed by brine till clear, dried over anhydrous sodium sulfate, and then concentrated to give the free amine compound. To a solution of the amine in dry DCM (20 mL) was added HCl (10.0 mL) at room temperature. After the mixture was stirred for 2 h under nitrogen atmosphere, the solvent was removed under vacuum. The residue was dissolved in MeOH (2 mL), and then added saturated NH₄PF₆ (8 mL) to yield a white precipitate. After being filtered, washed with H₂O, and dried under vacuum, the title compound 2-H·PF₆ as a pale yellow oil was obtained in 65% yield. ¹H NMR (300 MHz, CD₃CN): δ = 7.39 (d, J = 8.7 Hz, 2 H), 6.99 (d, J = 8.7 Hz, 2 H), 6.73 (s, 2 H), 4.19-4.15 (m, 4 H), 4.11 (d, J = 2.4 Hz, 2 H), 4.02 (t, J = 6.6 Hz, 2 H), 3.92 (t, J = 6.6 Hz, 2 H), 3.83 (s, 6 H), 3.48 (t, J = 5.4 Hz, 2 H), 2.68 (t, J = 2.4 Hz, 4 H), 1.82-1.72 (m, 2 H), 1.69-1.62 (m, 2 H), 1.58-1.33 (m, 24 H), 0.94 (t, J = 6.6 Hz, 3 H). ¹³C NMR (75 MHz, CD₃CN): δ = 159.9, 153.5, 137.7, 131.5, 125.2, 121.7, 114.5, 107.1, 80.0, 73.9, 72.6, 69.4, 67.7, 57.1, 55.5, 51.0, 50.5, 31.3, 29.6, 28.9, 28.8, 28.74, 28.70, 28.6, 25.3, 22.1, 13.1. MALDI-TOF MS: m/z = 596.5 [M-PF₆]⁺. Anal. Calcd. for C₃₇H₅₈NO₅PF₆: C, 59.91; H, 7.88; N, 1.89. Found: C, 59.78; H, 7.73; N, 1.76.
Synthesis of compound 6. 3,5-Dimethylphenol (2.44 g, 2 mmol), 1-bromooc-tane (7.32 g, 3 mmol), and potassium carbonate (5.52 g, 4 mmol) were suspended in anhydrous CH₃CN (50 mL). After being heated to 80 °C, and stirred for 1 d, the reaction mixture was diluted with water, and washed with ethyl acetate for three times to give a crude product, which was purified by column chromatography (SiO₂, hexanes:ethyl acetate 5:1) to yield the alkylated product 6 as a pale oil (3.60 g, 68% yield). ¹H NMR (300 MHz, CDCl₃): δ = 6.59 (s, 1H), 6.53 (s, 2H), 3.93 (t, J = 5.7 Hz, 2H), 3.43 (t, J = 6.6 Hz, 2H), 2.28 (s, 6H), 1.92-1.85 (m, 2H), 1.80-1.75 (m, 2H), 1.51-1.49 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ = 159.1, 139.2, 122.3, 112.2, 67.5, 33.9, 32.7, 29.2, 28.0, 25.4, 21.5. EI-MS: m/z = 284 [M⁺]. Anal. Calcd. for C₁₄H₂₁BrO: C, 58.95; H, 7.42. Found: C, 58.76; H, 7.54.

Synthesis of compound 7. Compound 6 (908 mg, 3.20 mmol) and NaN₃ (623 mg, 9.58 mmol) were mixed in anhydrous DMF (10 mL), and the reaction mixture under an atmosphere of N₂ was stirred at room temperature for 2 d. DMF was then removed under reduced pressure, and the residue was dissolved in EtOAc and then washed with H₂O (3 × 10 mL). The organic layer was dried, and subjected to column chromatography (SiO₂: 1:1 CH₂Cl₂/hexane) to afford the azide 7 as an off-white oil (727 mg, 92%). ¹H NMR (300 MHz, CDCl₃): δ = 6.57 (s, 1H), 6.51 (s, 2H), 3.90 (t, J = 6.6 Hz, 2H), 3.24 (t, J = 6.9 Hz, 2H), 2.27 (s, 6H), 1.78-1.71 (m, 2H), 1.65-1.56 (m, 2H), 1.50-1.40 (m, 4H). ¹³C NMR (75 MHz, CDCl₃): δ = 159.2, 139.2, 122.4, 112.3, 67.5, 51.4, 29.3, 28.9, 26.9, 25.8, 21.5. EI-MS: m/z = 247 [M⁺]. Anal. Calcd. for C₁₄H₂₁N₃O: C, 67.98; H, 8.56; N, 16.99.
Found: C, 67.88; H, 8.42; N, 16.89.

Synthesis of compound 3-\(\text{H·PF}_6\). To the mixture of compound 7 (54 mg, 0.2 mmol) and 2-\(\text{H·PF}_6\) (76 mg 0.1 mmol) in CHCl₃ (2 mL) was added \([\text{Cu(CH}_3\text{CN})_4]\text{PF}_6\) (35 mg, 0.1 mmol). The reaction mixture was stirred for 24 h. After evaporation, the residue was subjected to silica gel column chromatography (SiO₂: MeOH:CH₂Cl₂ = 1:30, v/v) to give 3-\(\text{H·PF}_6\) (80.8 mg, 82%) as a yellow oil. ¹H NMR (300 MHz, 1:1 CDCl₃:CD₃CN): \(\delta = 7.63 (s, 1H), 7.29 (d, \text{ } J = 8.2 \text{ Hz, } 2H), 6.83 (d, \text{ } J = 8.2 \text{ Hz, } 2H), 6.67 (s, 2H), 6.56 (s, 1H), 6.49 (s, 2H), 4.52 (s, 2H), 4.33 (t, \text{ } J = 7.1 \text{ Hz, } 2H), 3.93-3.75 (m, 18H), 3.46 (t, \text{ } J = 6.5 \text{ Hz, } 2H), 2.25 (s, 6H), 1.87-1.67 (m, 6H), 1.65-1.26 (m, 38H), 0.86 (t, \text{ } J = 7.0 \text{ Hz, } 3H). ¹³C NMR (75 MHz, 1:1 CDCl₃:CD₃CN): \(\delta = 158.3, 157.9, 152.6, 144.1, 138.2, 135.6, 131.7, 129.4, 128.0, 121.9, 121.3, 113.6, 111.3, 105.1, 72.2, 69.5, 67.0, 66.5, 63.1, 55.1, 51.2, 50.5, 49.1, 30.9, 29.2, 28.7, 28.5, 28.41, 28.35, 28.3, 28.1, 25.2, 25.0, 24.5, 21.7.\)

MALDI-TOF MS: \(m/z = 866.4 \text{ [M-PF}_6^+\text{+Na}^+]\). Anal. Calcd. for C₅₁H₇ₙF₆N₄O₆P: C, 61.93; H, 8.05; N, 5.66. Found: C, 61.72; H, 7.93; N, 5.76.
Synthesis of [3]rotaxane 4-2H·2PF₆. To the mixture of host 1 (20 mg, 0.0174 mmol) and 2-H·PF₆ (38.8 mg 0.052 mmol) in CHCl₃ (2 mL) was added [Cu(CH₃CN)₄]PF₆ (17.8 mg, 0.048 mmol) and compound 7 (27.4 mg, 0.11 mmol). The reaction mixture was stirred for 24 h. After evaporation, the residue was subjected to silica gel column chromatography (SiO₂: MeOH:CH₂Cl₂ = 1:100) to give the 4-2H·2PF₆ (22.3 mg, 41%).

1H NMR (300 MHz, 1:1 CDCl₃:CD₃CN): δ = 7.66 (s, 2H), 7.33-7.30 (m, 4H), 7.03-7.01 (m, 16H), 6.71 (s, 4H), 6.56 (s, 2H), 6.49 (s, 4H), 5.57 (d, J = 8.3 Hz, 2H), 5.36 (d, J = 8.3 Hz, 2H), 4.69 (br, 4H), 4.55 (s, 2H), 4.41-4.30 (m, 8H), 4.11-4.08 (m, 4H), 3.96-3.87 (m, 24H), 3.82 (s, 12H), 3.72-3.61 (m, 10H), 3.56-3.43 (m, 12H), 3.31-3.18 (m, 14H), 2.88-2.82 (m, 4H), 2.28 (s, 12H), 2.25 (s, 12H), 1.74-1.67 (m, 10H), 1.59-1.26 (m, 78H), 0.86 (t, J = 7.0 Hz, 12H). 13C NMR (75 MHz, CDCl₃): δ = 159.0, 158.6, 153.4, 148.3, 144.1, 143.7, 142.7, 142.4, 139.2, 138.0, 129.2, 128.4, 124.8, 122.4, 121.2, 120.2, 113.8, 112.3, 108.0, 107.1, 106.7, 70.7, 70.6, 70.3, 70.2, 69.0, 67.4, 64.2, 56.3, 48.0, 31.8, 30.1, 29.7, 29.5, 29.4, 29.3, 29.1, 26.24, 26.15, 25.9, 25.6, 22.7, 21.4, 14.1. MALDI-TOF MS: m/z = 2834.7 [M-2PF₆-H⁺]⁺. HRMS cald for [M-2PF₆]⁺: 1417.8560. Found: 1417.8513.
Synthesis of [3]rotaxane 5-4H·4PF₆. [3]Rotaxane 4-2H·2PF₆ (22.3 mg, 0.0065 mmol) was dissolved in iodomethane (6 mL), and the mixture was stirred for 4 d at room temperature. The excess iodomethane was evaporated, and the solid was washed with Et₂O to give a yellow solid. To a suspension of the solid in H₂O (4 mL) was added NH₄PF₆ (41 mg, 0.2 mmol) and CH₂Cl₂ (4 mL), respectively. The resulted mixture was vigorously stirred for 1 hour. The aqueous layer was extracted with CH₂Cl₂ (4 mL × 3). The combined organic layer was dried over Na₂SO₄, and then concentrated to give the [3]rotaxane 5-4H·4PF₆ (20.5 mg, 92%) as a pale yellow solid. ¹H NMR (300 MHz, 1:1 CDCl₃:CD₃CN): δ = 8.27 (s, 2H), 7.33-7.30 (m, 4H), 7.05-7.01 (m, 16H), 6.72 (s, 4H), 6.57 (s, 2H), 6.50 (s, 4H), 6.59 (d, J = 8.7 Hz, 2H), 5.37 (d, J = 8.7 Hz, 2H), 4.68 (br, 4H), 4.53 (t, J = 7.3 Hz, 4H), 4.38 (t, J = 9.6 Hz, 4H), 4.20 (s, 6H), 4.11-4.08 (m, 4H), 4.00-3.89 (m, 24H), 3.83-3.66 (m, 24H), 3.64-3.43 (m, 18H), 3.33-3.16 (m, 10H), 2.88-2.82 (m, 4H), 2.29 (s, 12H), 2.25 (s, 12H), 1.74-1.26 (m, 88H), 0.88 (t, J = 7.0 Hz, 12H). ¹³C NMR (75 MHz, CDCl₃): δ = 159.1, 158.6, 153.5, 148.2, 144.3, 143.7, 142.8, 142.4, 141.1, 139.1, 129.1, 128.2, 124.9, 122.3, 121.4, 120.2, 113.5, 112.3, 108.1, 106.8, 73.7, 71.7, 70.6, 70.4, 70.3, 70.1, 69.1, 67.9, 59.9, 56.3, 54.0, 48.0, 38.3, 31.8, 30.2, 29.7, 29.4, 29.3, 29.1, 29.04, 28.97, 25.93, 25.87, 25.7, 25.6, 25.3, 227.7, 21.4, 14.1. MALDI-TOF MS: m/z = 3009.6 [M-H⁺-3PF₆]⁺. HRMS cald for [M-2PF₆]⁺: 1003.5743. Found: 1003.5758.

Reference:
2. $^1$H NMR and $^{13}$C NMR spectra of all new compounds

**Figure S1.** $^1$H NMR spectrum (300 MHz, CDCl$_3$) of 4.

**Figure S2.** $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of 4.
Figure S3. $^1$H NMR spectrum (300 MHz, CDCl$_3$) of 3.

Figure S4. $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of 3.
Figure S5. $^1$H NMR spectrum (300 MHz, CDCl$_3$) of 2.

Figure S6. $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of 2.
Figure S7. $^1$H NMR spectrum (300 MHz, CD$_3$CN) of 2-H·PF$_6$.

Figure S8. $^{13}$C NMR spectrum (75 MHz, CD$_3$CN) of 2-H·PF$_6$. 
Figure S9. $^1$H NMR spectrum (300 MHz, CDCl$_3$) of 6.

Figure S10. $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of 6.
Figure S11. ¹H NMR spectrum (300 MHz, CDCl₃) of 7.

Figure S12. ¹³C NMR spectrum (75 MHz, CDCl₃) of 7.
Figure S13. $^1$H NMR spectrum (300 MHz, CD$_3$CN) of 3-H·PF$_6$.

Figure S14. $^{13}$C NMR spectrum (75 MHz, CD$_3$CN) of 3-H·PF$_6$. 

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Figure S15. $^1$H NMR spectrum (300 MHz, 1:1 CDCl$_3$:CD$_3$CN) of 4-2H·2PF$_6$.

Figure S16. $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of 4-2H·2PF$_6$. 

S16
Figure S17. $^1$H NMR spectrum (300 MHz, 1:1 CDCl$_3$:CD$_3$CN) of 5-4H·4PF$_6$.

Figure S18. $^{13}$C NMR spectrum (75 MHz, CDCl$_3$) of 5-4H·4PF$_6$. 
3. Partial $^1$H NMR spectra of 1, 2-H·PF$_6$, and 1 and 2.0 equiv of 2-H·PF$_6$

![Diagram of molecular structures]

Figure S19. Partial $^1$H NMR spectra (300 MHz, CDCl$_3$:CD$_3$CN = 1:1, 298 K) of (a) 2-H·PF$_6$, (b) 1 and 2.0 equiv of 2-H·PF$_6$, and (c) host 1. [1]$_0$ = 1.0 mM.
4. Partial $^1$H-$^1$H COSY and NOESY spectra of 1 and 2.0 equiv of 2-H·PF$_6$

Figure S20. Partial $^1$H-$^1$H COSY spectrum (600 MHz, CDCl$_3$:CD$_3$CN = 1:1, 298 K) of 1 and 2.0 equiv of 2-H·PF$_6$. $[1]_0 = 1.0$ mM.
Figure S21. Partial $^1$H-$^1$H NOESY spectrum (600 MHz, CDCl$_3$:CD$_3$CN = 1:1, 298 K) of 1 and 2.0 equiv of 2-H·PF$_6$. [I]$_0$ = 1.0 mM.
5. ESI-MS spectrum of complex 1·(2-H·PF₆)₂

Figure S22. ESI-MS spectrum of complex 1·(2-H·PF₆)₂.
6. Partial $^1$H-$^1$H COSY and ROESY spectra of 4-2H·2PF$_6$

**Figure S23.** Partial $^1$H-$^1$H COSY spectrum (600 MHz, CDCl$_3$:CD$_3$CN = 1:1, 298 K) of 4-2H·2PF$_6$. 
Figure S24. Partial $^1$H-$^1$H ROESY spectrum (600 MHz, CDCl$_3$:CD$_3$CN = 1:1, 298 K) of 4-2H·2PF$_6$. 

S23
7. Partial $^1$H-$^1$H COSY spectra of 5-4H·4PF$_6$ before and after addition of 4 equiv DBU

Figure S25. Partial $^1$H-$^1$H COSY spectrum (600 MHz, CDCl$_3$:CD$_3$CN = 1:1, 298 K) of 5-4H·4PF$_6$.
Figure S26. Partial $^1$H-$^1$H COSY spectrum (600 MHz, CDCl$_3$:CD$_3$CN = 1:1, 298 K) of 5-4H·4PF$_6$ after the addition of 4 equiv DBU.
8. ESI-HRMS spectrum of [3]rotaxane 4-2H·2PF$_6$

Figure S27. Calculated (top) and experimental (bottom) ESI-HRMS spectrum of 4-2H·2PF$_6$.
9. ESI-HRMS spectrum of [3]rotaxane 5-4H·4PF₆

Figure S28. Calculated (top) and experimental (bottom) ESI-HRMS spectrum of 5-4H·4PF₆.