Supporting Information

Synthesis of a [2]Rotaxane Operated in basic Environment

Wenlong Yang, Yongjun Li, * Jianhong Zhang, Yanwen Yu, Taifeng Liu, 
Huibiao Liu, Yuliang Li *

* Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R. China,

b Graduate University of Chinese Academy of Sciences, Beijing 100080, P.R. China

E-mail: liyj@iccas.ac.cn, ylli@iccas.ac.cn
§1. Materials
Unless stated otherwise, all reagents and anhydrous solvents were purchased from Aldrich Chemicals and used without further purification.

§2. Instruments
Column chromatography: SiO₂ (200 – 300 mesh). TLC glass plates coated with SiO₂ F254 were visualized by UV light. ¹H and ¹³C NMR spectra were recorded on a Bruker AV 400 or 600 MHz instrument at a constant temperature of 298 K. Chemical
shifts are reported in parts per million from low to high field and referenced to TMS. MALDI-TOF mass spectra were recorded on a Bruker Biflex III MALDI-TOF spectrometer. UV/Vis spectra were measured on a Hitachi U-3010 spectrometer. Fluorescence excitation and emission spectra were recorded using a Hitachi F-4500 FL fluorimeter at a constant temperature of 298 K.
§3. Synthetic route
§4. Synthesis and characterization data of all compounds

![Chemical structure](image)

**Compound 1**: compound 1 was synthesized according to reference S1. M.p. = 174-175 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.65$ (m, 2 H), 7.51 (m, 2 H), 7.25-7.50 (m, 7H), 7.23 (m, 1H), 7.08 (m, 3H), 6.50 (m, 1H), 6.43 ppm (m, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta = 158.36$, 144.86, 141.16, 136.09, 133.53, 132.65, 131.34, 130.54, 130.09, 129.70, 129.23, 129.08, 128.94, 128.81, 128.46, 127.98, 127.44, 126.99, 126.13, 118.28, 118.07, 117.64, 113.23, 112.43 ppm; EI-MS: m/z 413.4; elemental analysis (%) calcd for C$_{28}$H$_{19}$N$_3$O: C 81.34, H 4.63, N 10.16; found: C 81.66, H 4.64, N 10.12.

**Compound 2**: LiAlH$_4$ (0.74 g, 20 mmol) was added slowly to a solution of the compound 1 (2 g, 4.8 mmol) in anhydrous THF at 0 °C. After being at room temperature overnight, the mixture was quenched with aqueous Na$_2$SO$_4$. After filtration, the solvent was evaporated off, and the residue was extracted with CH$_2$Cl$_2$. The combined organic layers were dried over Na$_2$SO$_4$. After concentrated in vacuo, the crude product was purified by chromatography (SiO$_2$: CH$_2$Cl$_2$/MeOH, 20:1) to afford compound 2 as slightly yellow oil in 58% yield. M.p. = 141-142 °C. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 7.54$ (m, 2 H), 7.06-7.36 (m, 14 H), 6.57 (m, 1 H), 6.46 (m, 1 H), 3.92 ppm (s, 2 H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta = 158.55$, 145.08, 144.23, 141.81, 135.80, 135.73, 135.26, 133.23, 131.46, 130.64, 129.98, 129.18, 128.75, 128.60, 128.39, 128.25, 128.17, 127.10, 127.01, 126.13, 118.02, 117.77, 113.16, 45.78 ppm; EI-MS: m/z 417; elemental analysis (%) calcd for C$_{28}$H$_{23}$N$_3$O: C 80.55, H 5.55, N 10.06; found: C 80.79, H 5.52, N 10.10.
Compound 5: A solution of the compound 2 (0.418 g, 1 mmol) and 3 (0.16 g, 1 mmol) in toluene (50 mL) was heated under reflux overnight by using a Dean-Stark apparatus. The solvent was removed under reduced pressure after the reaction was cooled to room temperature. The residue was dissolved in THF (50 mL), then NaBH₄ (0.4 g, 10.5 mmol) was added cautiously at 0 °C. The mixture was stirred at room temperature for a further 4 h. Water was added to quench the excess NaBH₄. The solvent was evaporated off, and the residue was extracted with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄. After concentrated in vacuo, the crude product compound 4 (300 mg, 0.53 mmol) was dissolved in acetone and a few drops of trifluoroacetic acid were added. After 0.5 hour, the solvent was removed under vacuo. The residue was dissolved in a mixture of acetone and water. Then the aqueous of NH₄PF₆ (122 mg, 0.75 mmol) was added. The mixture was stirred for 1 h and then the acetone was evaporated off. The aqueous solution was extracted with CH₂Cl₂ several times. The collected organic layers were dried over Na₂SO₄, filtered, and concentrated in vacuo to yield 5 as a yellow solid (600 mg, 85%). M.p. = 115-116 °C. ¹H NMR (CDCl₃, 400 MHz): δ = 7.53 (m, 2 H), 7.46 (m, 2 H), 7.16-7.38 (m, 10 H), 6.95-6.99 (m, 4 H), 6.65 (m, 1 H), 6.45 (m, 1 H), 4.78 (s, 2 H), 3.81 (s, 2 H), 3.67 ppm (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ = 158.49, 157.03, 144.22, 136.5, 132.89, 132.22, 131.96, 131.62, 131.19, 130.69, 129.69, 128.75, 127.56, 122.7, 119.22, 117.89, 115.47, 114.98, 111.17, 78.06, 76.15, 55.77 ppm; MS (MALDI-TOF): m/z 562.3; elemental analysis (%) calcd for C₃₈H₃₁N₃O₂: C 81.26, H 5.56, N 7.48; found: C 81.59, H 5.53, N 7.51.
Rotaxane **R-1-a**: A mixture of compound 5 (354 mg, 0.50 mmol), compound 6 (117 mg, 0.50 mmol), macrocycle DB24C8 (211 mg, 0.48 mmol), and [Cu(MeCN)₄]PF₆ (175 mg, 0.47 mmol) was stirred in dry CH₂Cl₂ at room temperature under nitrogen for 24 h. After removal of the solvent, the crude product was purified by column chromatography (SiO₂: CH₂Cl₂/MeOH 60:1) to afford rotaxane R-1-a (845 mg, 68%).

M.p. = 139-140 °C. ¹H NMR (CD₃CN, 400 MHz, 298 K): δ = 8.56 (s, 1 H), 8.36 (m, 2H), 8.06 (m, 2H), 7.52 (m, 2H), 7.19-7.46 (m, 17H), 7.15 (m, 1H), 7.01 (m, 1H), 6.98 (m, 2H), 6.88 (m, 4H), 6.72 (m, 4H), 6.68 (m, 2H), 6.42 (m, 1H), 6.27 (m, 1H), 4.92 (s, 2H), 4.61 (s, 2H), 4.20 (s, 2H), 4.08 (m, 4H), 3.99 (m, 4H), 3.59 (m, 8H), 3.33 ppm (m, 4H); ¹³C NMR (CD₃CN, 100 MHz, 298 K) δ = 160.22, 159.75, 150.04, 148.83, 146.26, 144.78, 138.93, 136.22, 135.87, 134.58, 133.23, 132.94, 132.61, 132.5, 132.13, 131.85, 131.72, 131.35, 131.02, 130.81, 130.64, 130.43, 130.19, 129.92, 128.91, 127.82, 127.44, 126.96, 126.61, 124.94, 124.87, 124.75, 122.83, 116.56, 115.78, 114.43, 114.12, 71.94, 71.39, 69.46, 62.51, 53.67, 52.59, 47.49 ppm; MS (MALDI-TOF): m/z: 1243.5 [M]+, 1275.5 [M+O₂]+; elemental analysis (%) calcd for C₇₇H₇₅N₆F₆O₁₀P: C 66.56, H 5.44, N 6.05; found: C 66.78, H 5.42, N 6.09.
Thread T-1-a: A mixture of compound 5 (354 mg, 0.50 mmol), compound 6 (117 mg, 0.47 mmol), and [Cu(MeCN)₄]PF₆ (175 mg, 0.47 mmol) was stirred in dry CH₂Cl₂ at room temperature under nitrogen for 24 h. After removal of the solvent, the crude product was purified by column chromatography (SiO₂: CH₂Cl₂/MeOH 30:1) to afford Thread T-1-a (700 mg, 88%). M.p. = 132-133 °C. ¹H NMR (CD₃CN, 400 MHz, 298 K): δ = 8.69 (s, 1 H), 8.49 (d, 2H, J = 8.87 Hz), 8.15 (d, 2H, J = 8.38 Hz), 7.64-7.68 (m, 3H), 7.58-7.60 (m, 2H), 7.25-7.55 (m, 17H), 7.20 (t, 1H, J = 9.72, 7.22 Hz), 7.03 (d, 1H, J = 8.12 Hz), 6.98 (d, 2H, J = 7.52 Hz), 6.77-6.80 (m, 8H), 6.61 (s, 2H), 6.53-6.55 (m, 3H), 6.42 (t, 1H, J = 7.10 Hz), 4.99 (s, 2H), 3.88 (s, 2H), 3.77 ppm (s, 2H); ¹³C NMR (CDCl₃, 100 MHz, 298 K) δ = 159.71, 144.88, 143.55, 137.72, 135.36, 132.93, 131.39, 131.20, 131.05, 130.73, 130.34, 129.62, 129.55, 129.20, 128.54, 128.35, 127.77, 127.15, 126.86, 125.93, 125.44, 123.56, 122.87, 118.01, 117.79, 115.05, 112.85, 61.24, 50.25, 50.03, 46.57 ppm; MS (MALDI-TOF): m/z: 795.3 [M]⁺; elemental analysis (%) calcd for C₅₃H₄₂N₆F₆O₂P : C 67.65, H 4.61, N 8.93; found: C 67.93, H 4.58, N 8.97.
Rotaxane R-2-a: Rotaxane R-1-a (100 mg, 0.08 mmol) was dissolved in iodomethane (2 mL) and the mixture was stirred for 24 h at 40 °C. Then iodomethane was evaporated and the solid was washed with Et₂O to give an orange solid. Then, to a suspension of the previous solid in H₂O (10 mL) were added NH₄PF₆ (16.3 mg, 0.1 mmol) and CH₂Cl₂ (15 mL). Then the resulted bilayer solution was vigorously stirred for 1h. After separation, the aqueous layer was extracted with CH₂Cl₂ (x3). The organic layers were combined, dried over Na₂SO₄, and concentrated to obtain quantitatively the rotaxane R-2-a (123 mg) as a yellow solid. M.p. = 128-129 °C. ¹H NMR (CD₃CN, 400 MHz, 298 K): δ = 8.85 (s, 1 H), 8.36 (d, 2H, J = 9.14 Hz), 8.24 (m, 3H), 7.74 (t, 2H, J = 6.81, 7.62 Hz), 7.65 (t, 2H, J = 7.84, 6.81 Hz), 7.52-7.55 (m, 4H), 7.49 (m, 2H), 7.38 (d, 1H, J = 8.33 Hz), 7.27-7.32 (m, 7H), 7.19 (m, 1H), 7.09 (d, 2H, J = 8.65 Hz), 7.03 (m, 1H), 6.78-6.84 (m, 10H), 6.57 (m, 1H), 6.54 (d, 2H, J = 8.62 Hz), 6.44 (m, 1H), 4.95 (s, 2H), 4.75 (m, 2H), 4.42 (m, 2H), 4.16 (s, 3H), 4.05-4.09 (m, 4H), 3.93-3.96 (m 4H), 3.65-3.68 (m, 8H), 3.51-3.55 (m, 4H), 3.31-3.35 ppm (m, 4H); ¹³C NMR (CD₃CN, 100 MHz, 298 K) δ = 159.20, 158.30, 149.52, 148.28, 148.15, 145.67, 140.53, 139.54, 132.64, 132.36, 132.18, 132.15, 131.21, 130.49, 130.17, 129.97, 129.58, 129.35, 129.07, 127.20, 126.68, 115.44, 115.25, 113.83, 113.63, 71.46, 71.29, 70.92, 70.74, 69.85, 69.52, 68.88, 58.77, 52.96, 52.19, 50.98, 39.60 ppm; MS (MALDI-TOF): m/z: 1257.6 [M-H]⁺; elemental analysis (% calcd for C₇₈H₇₈N₆F₁₂O₁₀P₂: C 60.46, H 5.07, N 5.42; found: C 60.69, H 5.04, N
Thread **T-2-a**: Thread **T-2-a** was synthesized by using the same procedure as described for the preparation of rotaxane **R-2-a**. M.p. = 121-122 °C. $^1$H NMR (CD$_3$CN, 400 MHz, 298 K): $\delta = 8.81$ (s, 1 H), 8.33 (d, 2H, $J = 8.88$ Hz), 8.24 (m, 3H), 7.71 (m, 2H), 7.63 (m, 2H), 7.62 (m, 3H), 7.18-7.52 (m, 16H), 6.93-7.01 (m, 4H), 6.75 (s, 2H), 6.57 (m, 1H), 6.45 (m, 1H), 5.16 (s, 2H), 4.17 (s, 3H), 3.93 (s, 2H), 3.84 ppm (s, 2H); $^{13}$C NMR (CD$_3$CN, 100 MHz, 298 K) $\delta = 159.21$, 145.75, 135.74, 135.22, 132.47, 132.37, 132.16, 132.06, 130.73, 130.51, 130.20, 129.48, 129.38, 129.06, 126.65, 118.38, 116.37, 115.92, 115.80, 59.04, 55.26, 51.01, 39.57 ppm; MS (MALDI-TOF): m/z: 812.4 [M+H]$^+$; elemental analysis (%) calcd for C$_{54}$H$_{46}$N$_6$F$_{12}$O$_2$P$_2$: C 58.91, H 4.21, N 7.63; found: C 59.12, H 4.19, N 7.65.

deprotonation procedure:
To a solution of the rotaxane **R-1(2)-a** or thread **T-1(2)-a** (1 equiv) in acetone was added a large excess of DIEA (100 equiv) and the mixture was stirred for 1h. After evaporation, and in order to remove the diisopropylethylammonium hexafluorophosphate, the crude was diluted with CH$_2$Cl$_2$ and water was added. The aqueous layer was extracted with CH$_2$Cl$_2$ (x3) then the organic layers were combined, dried over Na$_2$SO$_4$ and concentrated. Et$_2$O was added to dissolve the excess of DIEA then removed to obtain the rotaxane **R-1(2)-b** or thread **T-1(2)-b**.
§5. NMR and MS spectra

$^1$H NMR (CDCl$_3$, 400 MHz) of Compound 2

![NMR spectrum of Compound 2 with peak assignments]

$^{13}$C NMR (CDCl$_3$, 100 MHz) of compound 2

![C NMR spectrum of Compound 2 with peak assignments]
\[^1\text{H} \text{NMR (CDCl}_3, \text{400 MHz}) \text{ of compound 5}\]

\[^{13}\text{C} \text{NMR (CDCl}_3, \text{100 MHz}) \text{ of compound 5}\]
$^1$H NMR (CDCl₃, 400 MHz) of R-1-a

$^{13}$C NMR (CDCl₃, 100 MHz) of R-1-a
$^1$H NMR (CDCl$_3$, 400 MHz) of T-1-a

$^{13}$C NMR (CDCl$_3$, 100 MHz) of T-1-a
$^1$H NMR (CDCl$_3$, 400 MHz) of T-2-a

$^{13}$C NMR (CDCl$_3$, 100 MHz) of T-2-a
$^1$H NMR (CD$_3$CN, 400 MHz) of **R-2-b**

MS of compound 2
MALDI-TOF of compound 5

MALDI-TOF, CCA, A, 2010, 11, 12

MALDI-TOF of T-1-a

MALDI-TOF, CCA, A, 2010, 11, 16
MALDI-TOF of R-1-a

MALDI-TOF, CCA, YWL-100825, 2010, 08, 25

MALDI-TOF of T-2-a

MALDI-TOF, CCA, C, 2010, 11, 16
MALDI-TOF of R-2-a

MALDI-TOF, CCA, B, 2010, 11, 16
§6. COSY-NMR spectra of R-2-a

Figure S0. The COSY-NMR spectra (600 MHz, CD$_3$CN, 298 K) of R-2-a.
§7. UV/Vis and FL spectra and titrational 1H NMR spectra of R-2-b

Fig. S1. Absorption spectra of compound 6, 5, T-1-a, T-2-a, R-1-a and R-2-a (1 × 10^{-5} M, 298 K) in CH$_3$CN.

Fig. S2. Fluorescence spectra of R-2-b (λ$_{exc}$ = 370 nm, 1 × 10^{-5} M) in CH$_3$CN (addition and removal of DIEA).
Fig. S3. Fluorescence spectra of R-2-b ($\lambda_{exc} = 310$ nm, $1 \times 10^{-5}$ M) in CH$_3$CN with various equivalents of DIEA (0 equiv to 50 equiv).

Fig. S4. Fluorescence spectra of T-2-b ($\lambda_{exc} = 370$ nm, $1 \times 10^{-5}$ M) in CH$_3$CN with various equivalents of DIEA (0 equiv to 50 equiv).
Fig. S5 $^1$H NMR spectra of R-2-b in CD$_3$CN at 298 K upon titrational addition of DIEA

Reference: