One-pot Syntheses of Donor-Acceptor [2]Rotaxanes Based on Cryptand/Paraquat Recognition Motif

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Supporting Information

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1. Benesi-Hildebrand plots for the association constants of 1a·3 and 1b·3 in CD$_3$CN

**Figure S1** Benesi-Hildebrand plots for the formation of [2]pseudorotaxanes cryptand 1a with paraquat derivative 3 based on the data for proton H$_{11}$ at 22°C in CD$_3$CN. [3]$_0$ = 0.50 mM.

**Figure S2** Benesi-Hildebrand plots for the formation of [2]pseudorotaxanes cryptand 1b with paraquat derivative 3 based on the data for proton H$_{11}$ at 22°C in CD$_3$CN. [3]$_0$ = 0.50 mM.
2. Mole ratio plots for determination of stoichiometry of complexation between cryptand 1a/1b and paraquat derivative 3

![Figure S3](image)

**Figure S3** Mole ratio plots for determination of stoichiometry of complexation between (a) cryptand 1a and paraquat derivative 3, and (b) cryptand 1b and paraquat derivative 3 in [D₆]acetone. [3]₀ = 2.00mM

3. Electrospray ionization mass spectra of host 1a/1b with guest 3 in acetonitrile

![Figure S4](image)

**Figure S4** Low-resolution ESI-MS of [2]pseudorotaxane 1a·3 in acetonitrile
Figure S5 Low-resolution ESI-MS of [2]pseudorotaxane 1b·3 in acetonitrile

4. $^1$H NMR and Low-resolution ESI-MS spectra of dumbbell-shaped compound 6

Figure S6 $^1$H NMR spectrum (400MHz, CD$_3$COCD$_3$, 22°C) of dumbbell-shaped compound 6
5. $^1$H NMR and $^{13}$C NMR spectra of [2]rotaxane 7

![Figure S7](image)

**Figure S7** Low-resolution ESI-MS of dumbbell-shaped compound 6

![Figure S8](image)

**Figure S8** $^1$H NMR spectrum (400MHz, CD$_3$COCD$_3$, 22°C) of [2]rotaxane 7
Figure S9 $^{13}$C NMR spectrum (100MHz, CD$_3$COCD$_3$, 22°C) of [2]rotaxane 7


Figure S10 Low-resolution ESI-MS of [2]rotaxane 7
Figure S11 High-resolution ESI-MS of [2]rotaxane 7

7. $^1$H NMR and $^{13}$C NMR spectra of [2]rotaxane 8

Figure S12 $^1$H NMR spectrum (400MHz, CD$_3$COCD$_3$, 22°C) of [2]rotaxane 8
Figure S13 $^{13}$C NMR spectrum (100MHz, CD$_3$COCD$_3$, 22°C) of [2]rotaxane 8

8. Low- and high-resolution electrospray ionization mass spectra of [2]rotaxane 8

Figure S14 Low-resolution ESI-MS of [2]rotaxane 8
Figure S15 High-resolution ESI-MS of [2]rotaxane 8

9. $^1$H-$^1$H COSY and $^{13}$C-$^1$H COSY spectra of [2]rotaxane 7

Figure S16 $^1$H-$^1$H COSY spectrum (400MHz, CD$_3$COCD$_3$, 22°C) of [2]rotaxane 7
Figure S17 $^{13}$C-$^1$H COSY spectrum (400MHz, CD$_3$COCD$_3$, 22°C) of [2]rotaxane 7

10. $^1$H-$^1$H NOESY and $^{13}$C-$^1$H HMQC spectra of [2]rotaxane 7
Figure S18 ¹H-¹H NOESY spectrum (400MHz, CD$_3$COCD$_3$, 22°C) of [2]rotaxane 7

Figure S18 ¹³C-¹H HMQC spectrum (400MHz, CD$_3$COCD$_3$, 22°C) of [2]rotaxane 7
11. $^1\text{H}-^1\text{H}$ COSY and $^{13}\text{C}-^1\text{H}$ COSY spectra of [2]rotaxane 8

**Figure S20** $^1\text{H}-^1\text{H}$ COSY spectrum (400MHz, CD$_3$COCD$_3$, 22°C) of [2]rotaxane 8

**Figure S21** $^{13}\text{C}-^1\text{H}$ COSY spectrum (400MHz, CD$_3$COCD$_3$, 22°C) of [2]rotaxane 8

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12. $^1$H-$^1$H NOESY and $^{13}$C-$^1$H HMQC spectra of [2]rotaxane 8

Figure S22 $^1$H-$^1$H NOESY spectrum (400MHz, CD$_3$COCD$_3$, 22°C) of [2]rotaxane 8

Figure S23 $^{13}$C-$^1$H HMQC spectrum (400MHz, CD$_3$COCD$_3$, 22°C) of [2]rotaxane 8
13. UV-Vis absorption spectra of cryptand 1a, cryptand 1b, dumbbell-shaped component 6, [2]rotaxane 7 and [2]rotaxane 8

![UV-Vis absorption spectra](image)

**Figure S24** The UV-Vis absorption spectra of cryptand 1a, cryptand 1b, dumbbell-shaped component 6, [2]rotaxane 7 and [2]rotaxane 8 at room temperature in acetonitrile ([C]₀ = 5.0*10⁻⁵ M).


**X-ray analysis data of [2]pseudorotaxane 1a·3:** Crystallographic data: block, pale red, 0.35×0.21×0.11 mm³, C₅₆H₆₀F₁₂N₂O₁₀P₂, FW 1211.00, Monoclinic, space group P2₁/c, a = 12.789(3), b = 26.622(6), c = 20.717(4) Å, α = 90.00, β = 127.862(10), γ = 90.00°, V = 5569(2) Å³, Z = 4, D_c = 1.444 g·cm⁻³, T = 293(2) K, μ = 0.178 mm⁻¹, 28408 measured reflections, 10036 independent reflections, 739 parameters, 0 restraints, F(000) = 2512, R₁ = 0.2044, wR₂ = 0.3405 (all data), R₁ = 0.0974, wR₂ = 0.2718 [I > 2σ(I)], max. Residual density 0.612 e·Å⁻³, goodness-of-fit (F²) = 1.031.

15. X-ray analysis data of [2]pseudorotaxane 1b·3

**X-ray analysis data of [2]pseudorotaxane 1b·3:** Crystallographic data: block, pale red, 0.48×0.24×0.11 mm³, C₅₆H₆₈F₁₂N₂O₁₀P₂, FW 1219.06, Triclinic, space group P-1, a = 13.672(11), b = 14.541(11), c = 16.402(12) Å, α = 112.152(10), β = 92.063(12), γ = 104.285(12)°, V = 2897(4) Å³, Z = 2, D_c = 1.398 g·cm⁻³, T = 298(2) K, μ = 0.172 mm⁻¹, 15071 measured reflections, 10446 independent reflections, 739 parameters, 0 restraints, F(000) = 1272, R₁ = 0.3528, wR₂ = 0.3405 (all data).
data), $R_1 = 0.1022$, $wR_2 = 0.2318 \ [I > 2\sigma(I)]$, max. Residual density 0.486 $\text{e} \cdot \text{Å}^{-3}$, goodness-of-fit ($F^2$) = 0.949.

The level A alerts in [2]pseudorotaxane 1b-3 was due to small size of the crystal, which resulted in weak diffraction. We tried our best, including growing crystals in different solvent systems and performing data collection on different single crystals, but no better data set could be obtained.


**X-ray analysis data of [2]rotaxane 7:** Crystallographic data: block, yellow, 0.68×0.35×0.21 mm$^3$, C$_{72}$H$_{92}$F$_{12}$N$_2$O$_{11}$P$_2$, FW 1451.42, Monoclinic, space group P2$_1$/c, $a= 13.677(3)$, $b = 17.347(4)$, $c = 34.994(7)$ Å, $\alpha = 90.00$, $\beta = 106.807(7)$, $\gamma = 90.00^\circ$, $V = 7922(3)$ Å$^3$, $Z = 4$, $D_c = 1.217$ g·cm$^{-3}$, $T = 298(2)$K, $\mu = 0.137$ mm$^{-1}$, 73478 measured reflections, 13959 independent reflections, 955 parameters, 384 restraints, $F(000) = 3056$, $R_1 = 0.2379$, $wR_2 = 0.5147$ (all data), $R_1 = 0.1610$, $wR_2 = 0.4757 \ [I > 2\sigma(I)]$, max. Residual density 0.910 $\text{e} \cdot \text{Å}^{-3}$, goodness-of-fit ($F^2$) = 1.717.

The crystal data of [2]rotaxane 7 is not well. The relatively high $R_1$, $wR_2$ and $F^2$ was attributed to the disorder of tert-butyl group. All attempts to obtain better quality crystals failed. Although the present crystal data is not good, the framework can be clearly solved and the crystallographic data strongly supports the spectroscopic characterizations.