Electronic Supplementary Information

Complexation between triptycene-based macrotricyclic host and π-extended viologens: formation of supramolecular poly[3]pseudorotaxanes

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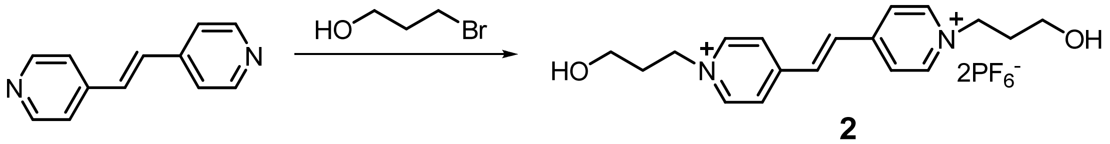
Contents

1. Synthetic procedure for π-extended viologens 2 and 3

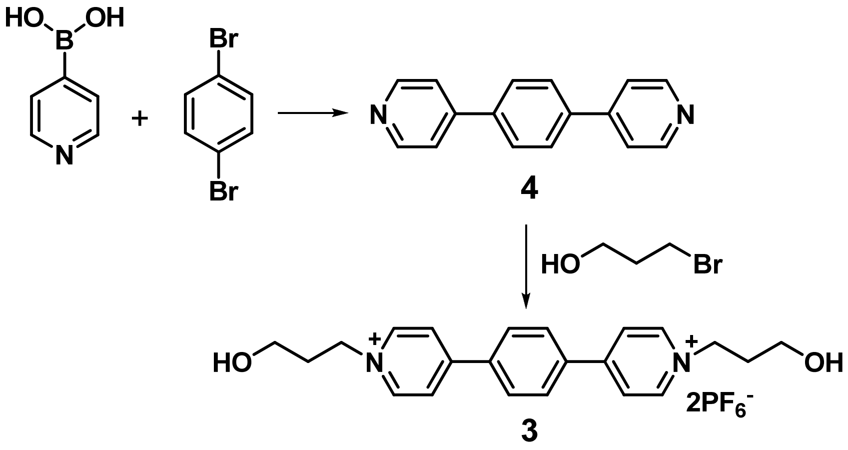
Melting points, taken on an electrothermal melting point apparatus, are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a DMX300 NMR. MALDI-TOF mass spectra were obtained on a BIFLEXIII mass spectrometer. Materials obtained commercially were used without further purification. Compounds **2** and **3** were prepared according to the same method as literature procedure.[S1]



2

Scheme 1. Synthesis of compound **2**.

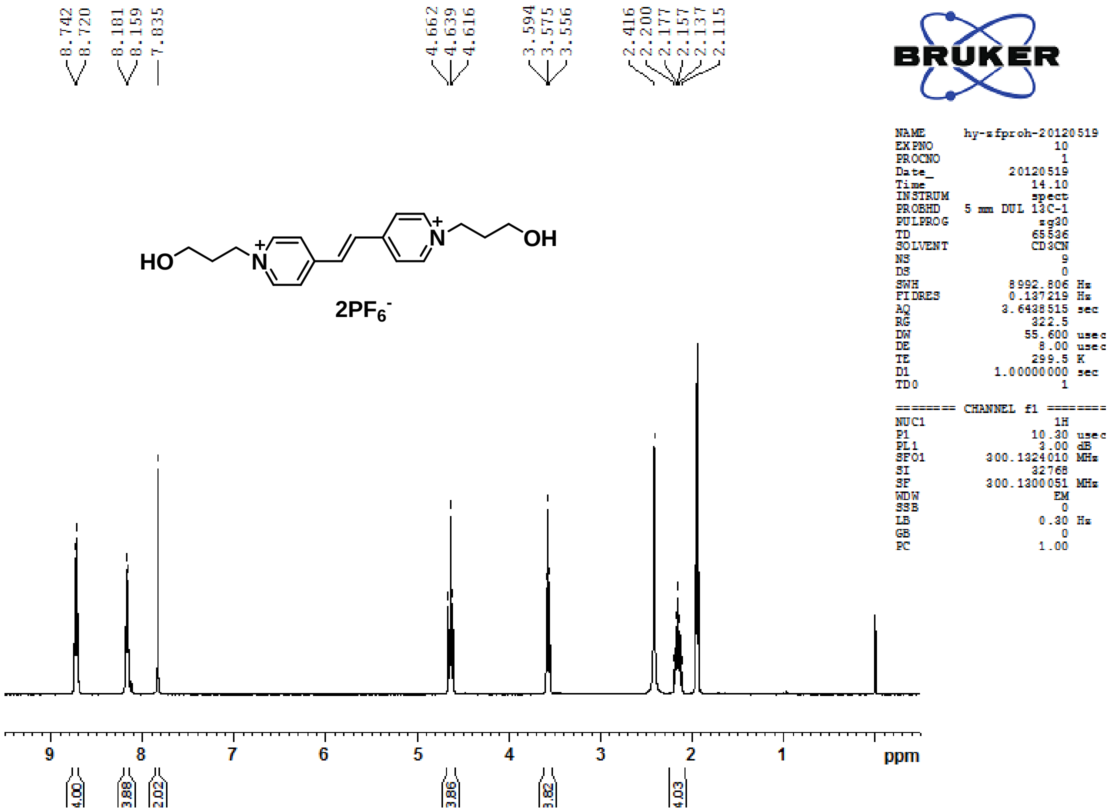
Synthesis of π-extended viologen 2. A mixture of (*E*)-1,2-di(pyridin-4-yl)ethene (0.45 g, 2.5 mmol) and 3-bromopropan-1-ol (1.04 g, 7.5 mmol) in CH_3CN (150 mL) was refluxed for 48 h. The resulting mixture was concentrated under reduced pressure, and yellow oil was obtained, which was dissolved in acetone and treated with NH_4PF_6, the solution was stirred at ambient temperature until clear. Then acetone was removed, the solid precipitate was collected by filtration, washed with water, and dried under vacuum to yield 32.3% of compound **2** as a white solid. Mp: 257-259 °C. ^{1}H NMR (300 MHz, CD_3CN): δ 2.16-2.20 (m, 4H), 3.57 (t, J = 5.4 Hz, 4H), 4.64 (t, J = 6.9 Hz, 4H), 7.84 (s, 2H), 8.17 (d, J = 6.8, 4H), 8.73 (d, J = 6.8 Hz, 4H). ^{13}C NMR (75 MHz, CD_3CN): δ 32.5, 57.1, 58.7, 125.5, 133.5, 144.8, 150.8. ESI-MS: *m/z* 150.2 $[M-2PF_6^-]^{2+}$. Anal. Calcd for $C_{18}H_{24}F_{12}N_2O_2P_2\cdot0.5H_2O$: C, 36.07; H, 4.20; N, 4.67. Found: C, 36.37; H, 4.34; N, 4.77.



Scheme 2. Synthesis of compound **3**.

Synthesis of π-extended viologen 3. A mixture of **4**[S2] (0.284 g, 1.2 mmol) and 3-bromopropan-1-ol (1.69 g, 12.2 mmol) in DMF (30 mL) was refluxed for 48 h. The resulting mixture was concentrated under reduced pressure, and yellow oil was washed with CH_3CN, the crude product was dissolved in acetone and treated with NH_4PF_6, the solution was stirred at ambient temperature until clear. Then acetone was removed, the solid precipitate was collected by filtration, washed with water, and dried under vacuum to yield 53.4% of compound **3** as a white solid. Mp: 252-254 °C. ^{1}H NMR (300 MHz, CD_3CN): δ 2.15-2.20 (m, 4H), 3.59 (t, J = 5.4 Hz, 4H), 4.67 (t, J = 7.2 Hz, 4H), 8.14 (s, 2H), 8.33 (d, J = 7.0, 4H), 8.79 (d, J = 7.0 Hz, 4H). ^{13}C NMR (75 MHz, CD_3CN): δ 32.6, 57.2, 58.5, 125.2, 129.0, 136.8, 144.6, 154.6. ESI-MS: *m/z* 175.2 $[M-2PF_6^-]^{2+}$. Anal. Calcd for $C_{22}H_{26}F_{12}N_2O_2P_2\cdot0.25NH_4PF_6$: C, 38.79; H, 4.00; N, 4.63. Found: C, 38.60; H, 3.89; N, 4.36.

2. ^{1}H NMR and ^{13}C NMR spectra of π-extended viologens 2 and 3



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PROCNO                       1
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PULPROG                   zg30
TD                       65536
SOLVENT                  CD3CN
NS                           9
DS                           0
SWH                   8992.806 Hz
FIDRES                0.137219 Hz
AQ                   3.6438515 sec
RG                       322.5
DW                      55.600 usec
DE                        8.00 usec
TE                       299.5 K
D1                  1.00000000 sec
TD0                          1

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P1                       10.30 usec
PL1                       3.00 dB
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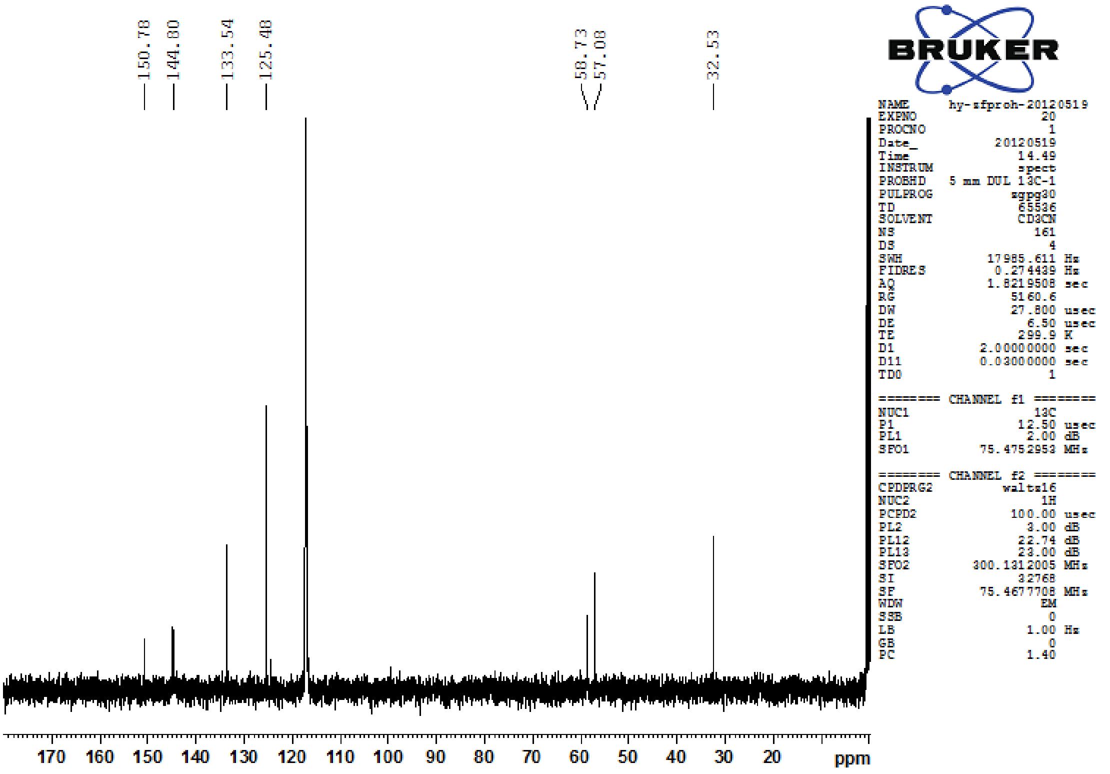
Fig. S1 ^{1}H NMR spectrum (300 MHz, CD_3CN) of **2**.



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TD                       65536
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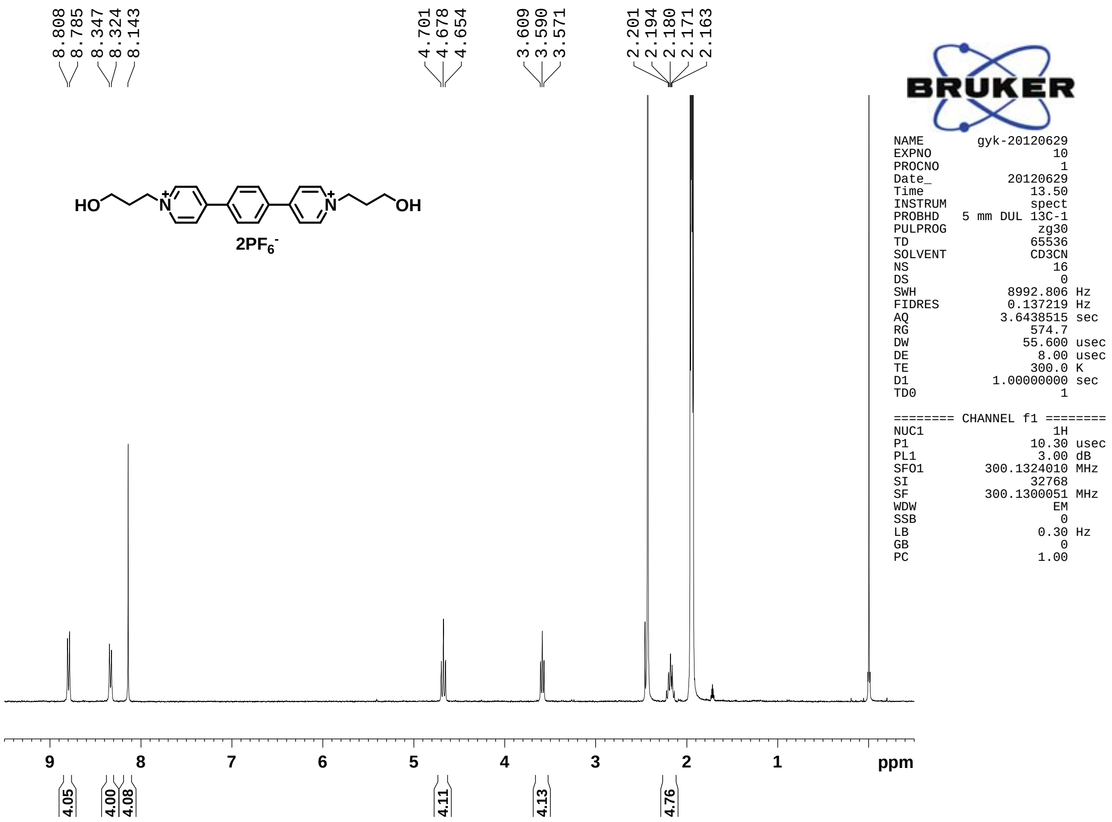
Fig. S2 ^{13}C NMR spectrum (75 MHz, CD_3CN) of **2**.



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TD                   65536
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FIDRES           0.137219 Hz
AQ              3.6438515 sec
RG                   574.7
DW                  55.600 usec
DE                    8.00 usec
TE                   300.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
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PL1                   3.00 dB
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SI                   32768
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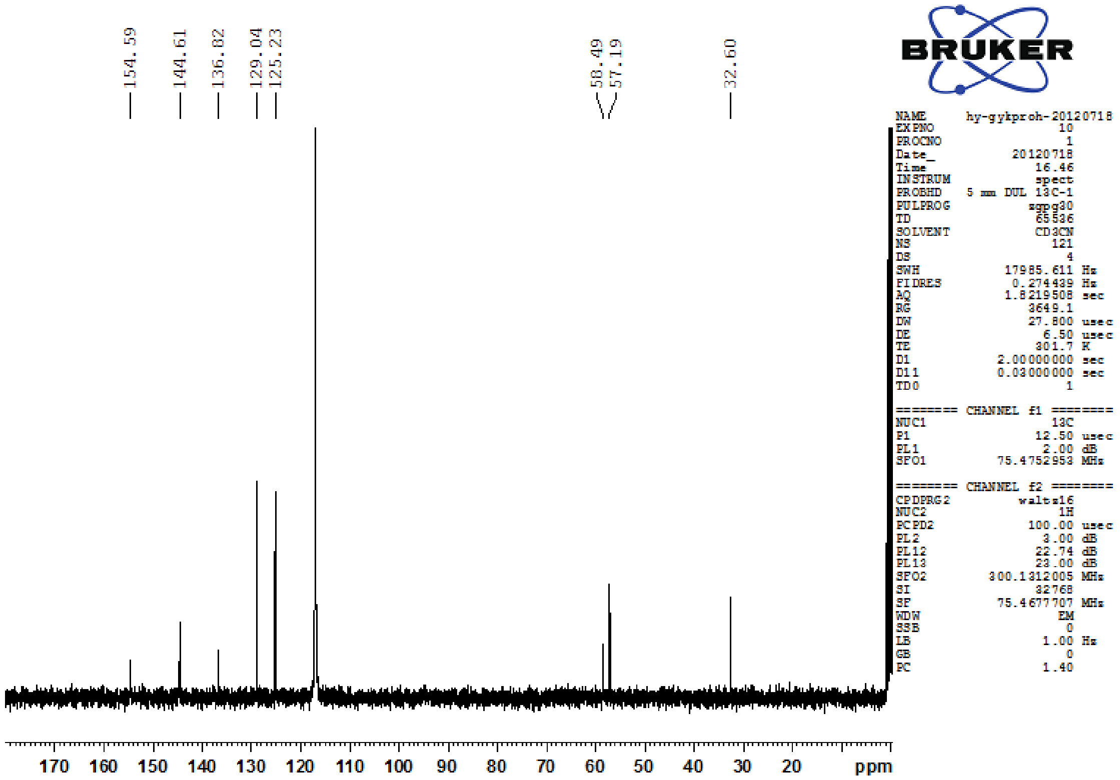
Fig. S3 ^{1}H NMR spectrum (300 MHz, CD_3CN) of **3**.



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NS                     121
DS                       4
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FIDRES            0.274439 Hz
AQ               1.8219508 sec
RG                  3649.1
DW                  27.800 usec
DE                    6.50 usec
TE                   301.7 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
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PL1                   2.00 dB
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
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PCPD2               100.00 usec
PL2                   3.00 dB
PL12                 22.74 dB
PL13                 23.00 dB
SFO2           300.1312005 MHz
SI                   32768
SF              75.4677707 MHz
WDW                     EM
SSB                      0
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PC                    1.40
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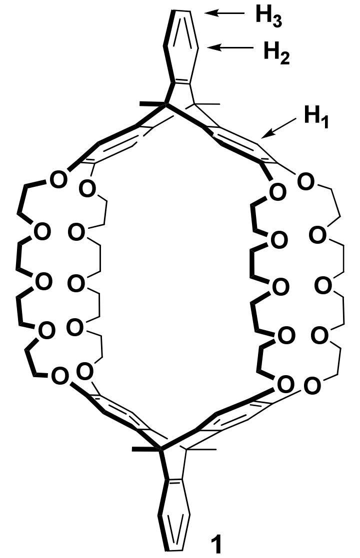
Fig. S4 ^{13}C NMR spectrum (75 MHz, CD_3CN) of **3**.

3. ^{1}H NMR spectroscopic titrations of complexes



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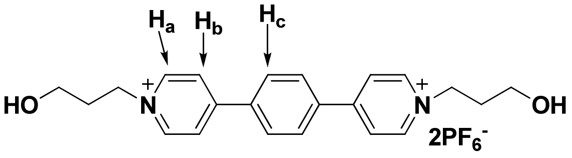

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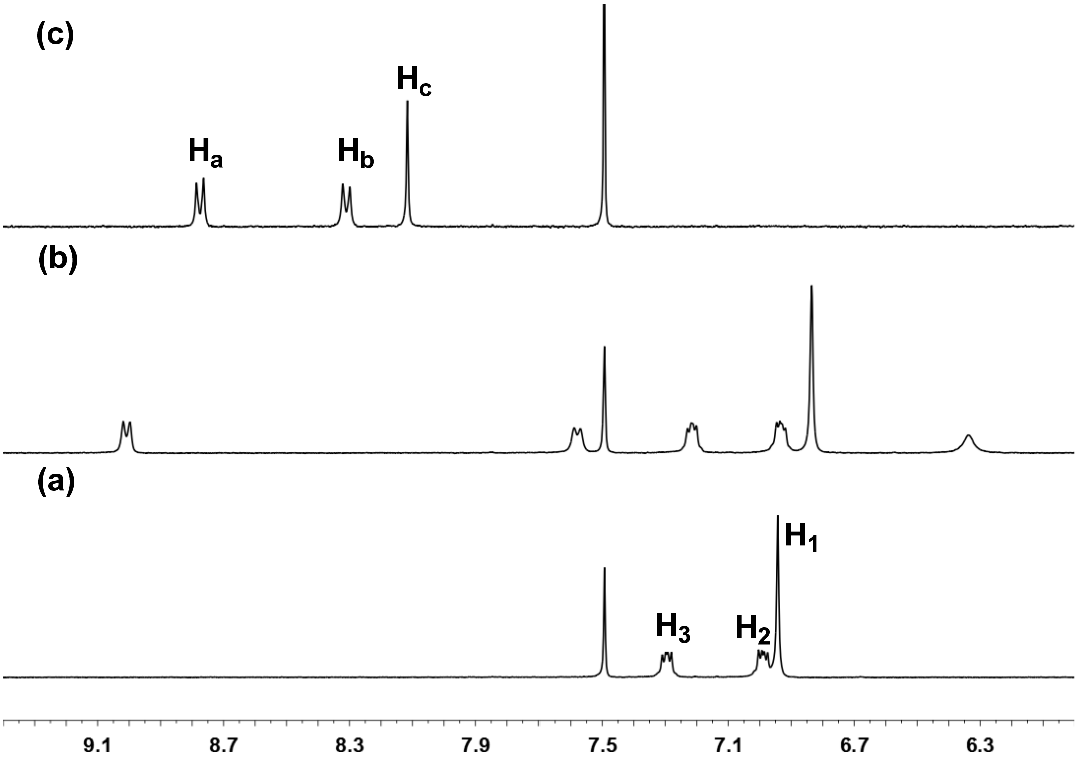

Fig. S5 Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of (a) free **1**, (b) **1** and 1.0 equiv of **3**, and (c) free **3**. $[\mathbf{1}]_0$ =3.0 mM.

4. Determination of the association constants

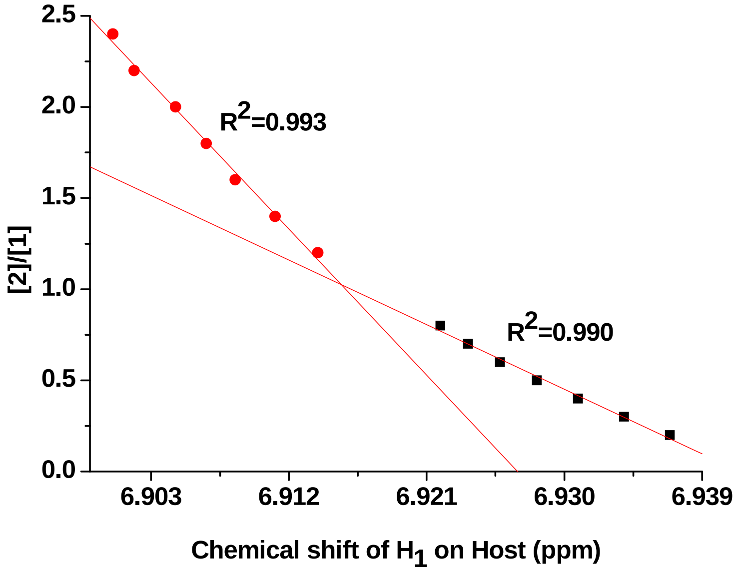

Fig. S6 Mole ratio plot for the complexation of **1** and **2** in $CD_3CN/CDCl_3$ = 1:1 at 298 K.

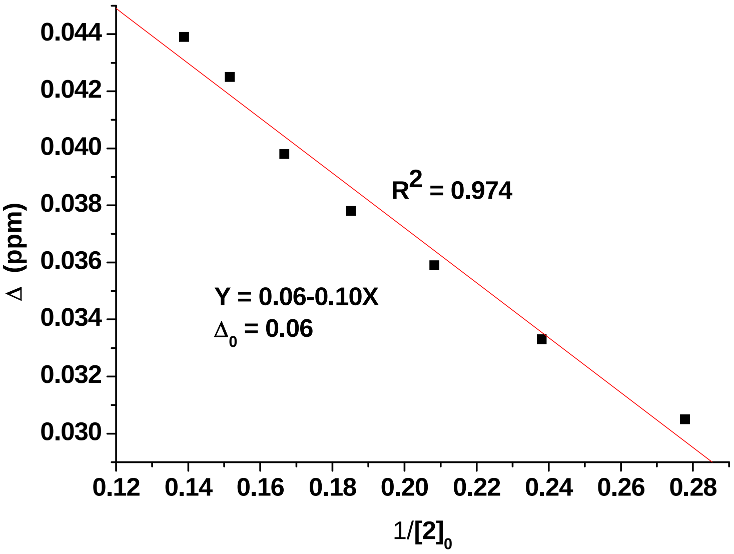

Fig. S7 Determination of Δ_0 of H_1 for the complexation of **1** and **2** in $CD_3CN/CDCl_3$ = 1:1 at 298 K.

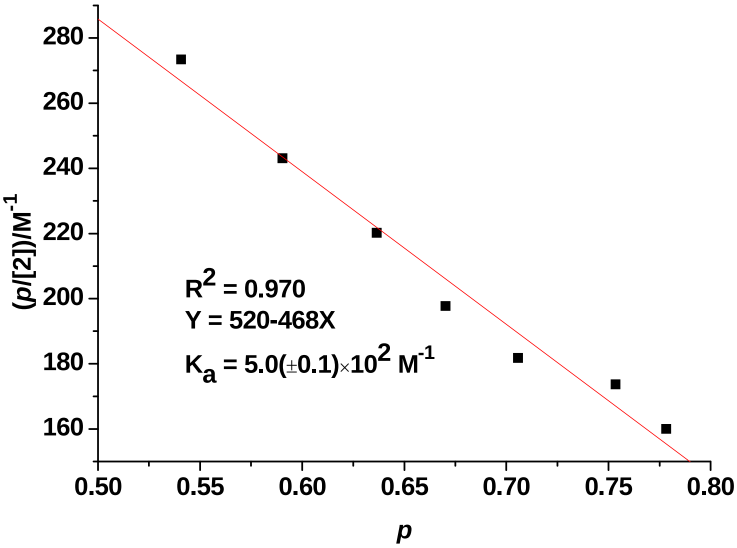

Fig. S8 Scatchard plot for the complexation of **1** and **2** in $CD_3CN/CDCl_3 = 1:1$ at 298 K.

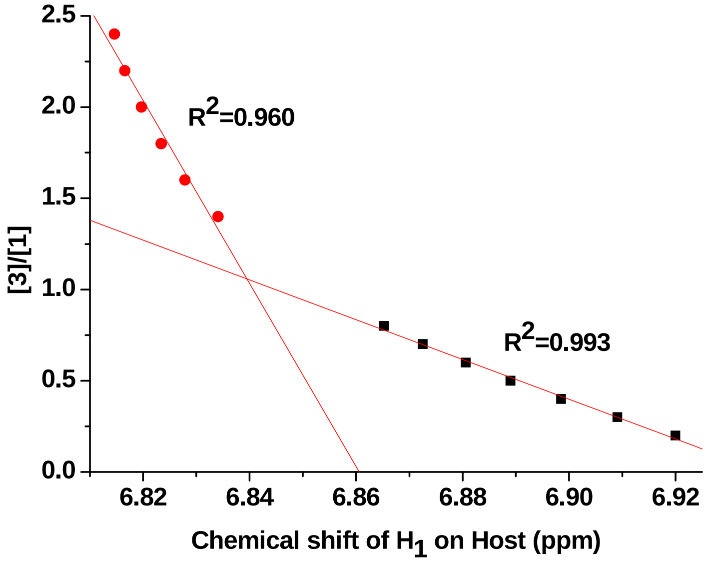

Fig. S9 Mole ratio plot for the complexation of **1** and **3** in $CD_3CN/CDCl_3 = 1:1$ at 298 K.

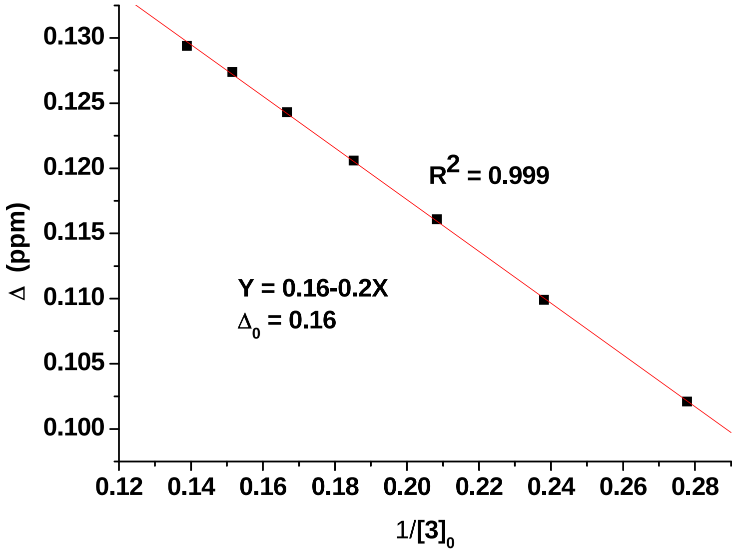

Fig. S10 Determination of Δ_0 of H_1 for the complexation of **1** and **3** in $CD_3CN/CDCl_3$ = 1:1 at 298 K.

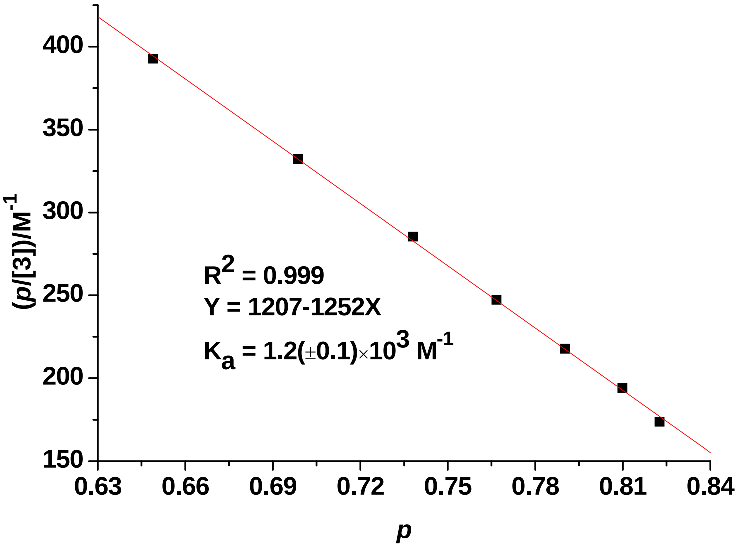

Fig. S11 Scatchard plot for the complexation of **1** and **3** in $CD_3CN/CDCl_3$ = 1:1 at 298 K.

5. ESI-MS spectra of poly[3]pseudorotaxanes

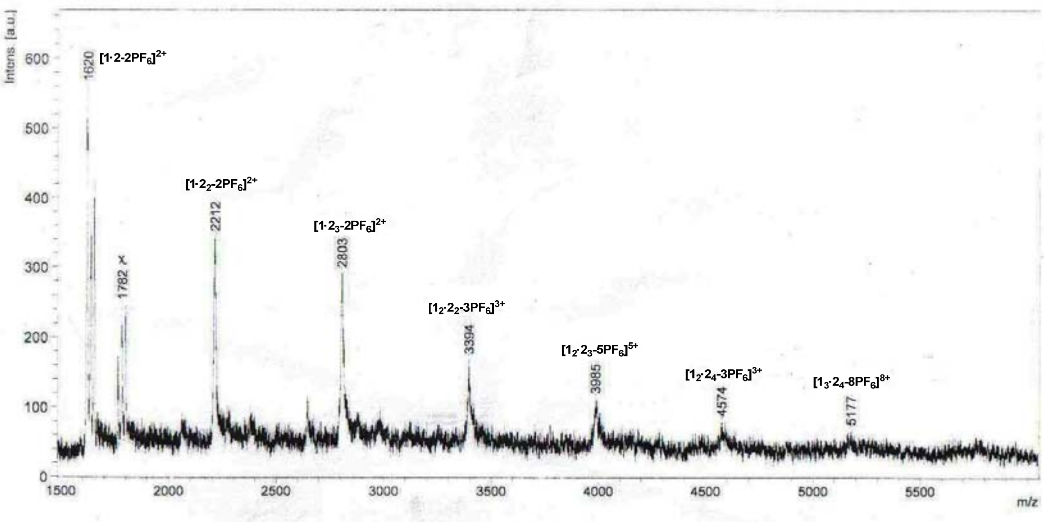

Fig. S12 MOLDI-TOF MS spectrum of poly[3]pseudorotaxane **(1·2)**$_n$.

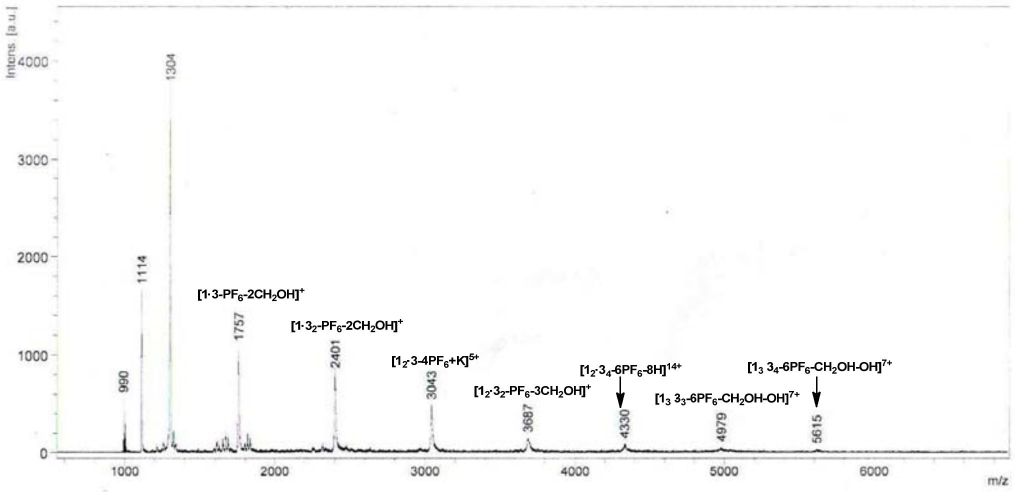

Fig. S13 MOLDI-TOF MS spectrum of poly[3]pseudorotaxane (**1·3**)$_n$.

6. Crystal structures and data of poly[3]pseudorotaxanes

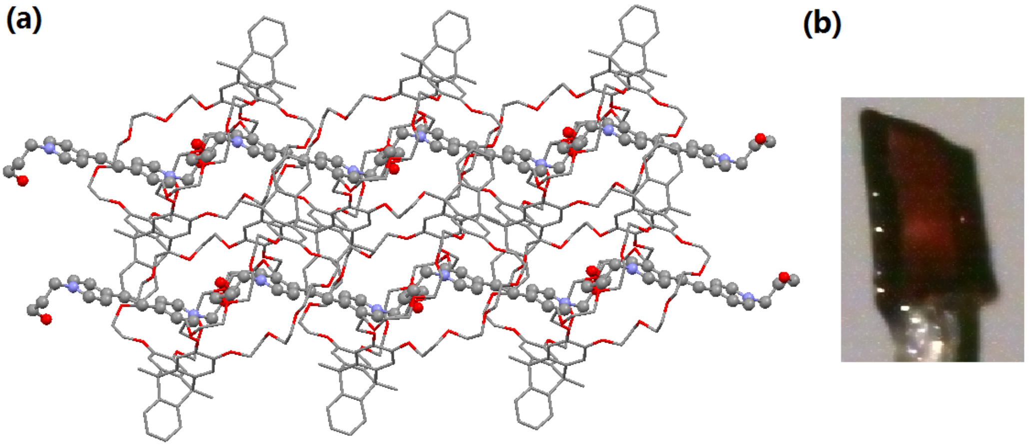

Fig. S14 (a) Packing of supramolecular poly[3]pseudorotaxane (**1·2**)$_n$. (b) Single crystal of complex **1·2**. PF_6^- counterions, and hydrogen atoms are omitted for clarity.

Because of the lack of heavy atoms in the complex and the presence of disordered PF_6^-, crown ether chains and solvent molecules, we need to restrain the bond length of O3−C27, O3'−C27', C27−C28, C27'−C28 by DFIX, and restrain the Uiso of O3, C27, O3' and C27' by SIMU and ISOR.

Table S1. Crystal data for complex **1·2**

Identification code	a
Empirical formula	$C_{94}H_{116}F_{12}N_2O_{22}P_2$
Formula weight	1915.83
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 13.650(3) Å alpha = 82.751(12)˚
	b = 18.189(4) Å beta = 72.674(7)˚
	c = 19.264(4) Å gamma = 80.096(10)˚
Volume	4483.5(15) $Å^3$
Z, Calculated density	2, 1.419 Mg/m^3
Absorption coefficient	0.149 mm^{-1}
F(000)	2016

Crystal size	0.46 x 0.29 x 0.18 mm
Theta range for data collection	1.11 to 25.00°
Limiting indices	-15<=h<=16, -21<=k<=21, -22<=l<=22
Reflections collected / unique	33579/15710 [R(int) = 0.0541]
Completeness to theta = 25.00	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.7929
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15710/42/1212
Goodness-of-fit on F^2	1.140
Final R indices [I>2sigma(I)]	R_1 = 0.1189, wR_2 = 0.2636
R indices (all data)	R_1 = 0.1529, wR_2 = 0.2869
Largest diff. peak and hole	1.000 and -0.671 e.Å^{-3}

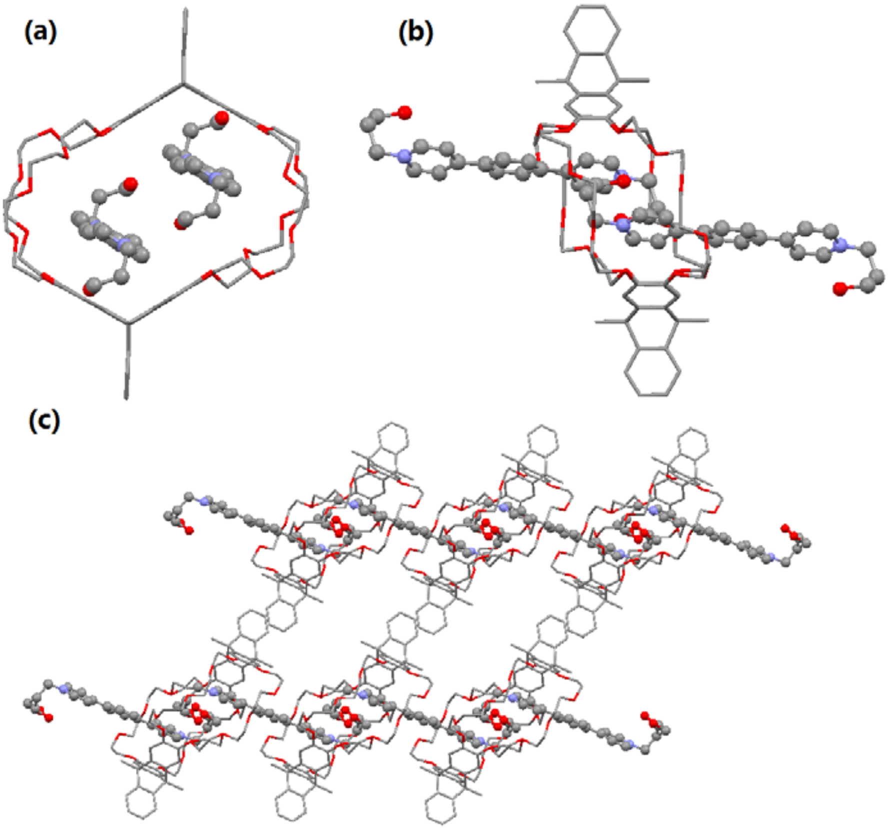

Fig. S15 Top view (a) and side view (b) of the crystal structure of complex **1·3**. (c) Packing of the supramolecular poly[3]pseudorotaxane (**1·3**)$_n$. PF_6^- counterions, and hydrogen atoms are omitted for clarity.

Table S2. Crystal data for complex **1·3**

Identification code	a
Empirical formula	$C_{98}H_{118}F_{12}N_2O_{22}P_2$
Formula weight	1965.88
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	*a* = 12.768(3) Å alpha = 72.17(3)°
	b = 13.623(3) Å beta = 88.99(3)°
	c = 14.010(3) Å gamma = 83.52(3)°
Volume	2304.6(8) $Å^3$
Z, Calculated density	1, 1.416 Mg/m^3
Absorption coefficient	0.147 mm^{-1}
F(000)	1034
Crystal size	0.45 x 0.35 x 0.13 mm
Theta range for data collection	1.53 to 27.49°
Limiting indices	-15<=h<=15, -16<=k<=16, -16<=l<=16
Reflections collected / unique	17391/8092 [R(int) = 0.0489]
Completeness to theta = 25.00	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0. 6796
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8092/262/719
Goodness-of-fit on F^2	1.116
Final R indices [I>2sigma(I)]	R_1 = 0.0969, wR_2 = 0.2247
R indices (all data)	R_1 = 0.1116, wR_2 = 0.2374
Largest diff. peak and hole	0.653 and -0.474 e.$Å^{-3}$

References

S1. J.-M. Zhao, Q.-S. Zong, T. Han, J.-F. Xiang and C.-F. Chen, *J. Org. Chem.*, 2008, **73**, 6800.

S2. K. Biradha, Y. Hongo and M. Fujita, *Angew. Chem. Int. Ed.*, 2000, **39**, 3843.