Electronic Supplementary Information

Complexation between pentiptycene-based mono(crown ether)s and tetracationic cyclobis(paraquat-*p*-phenylene): who is the host or the guest?

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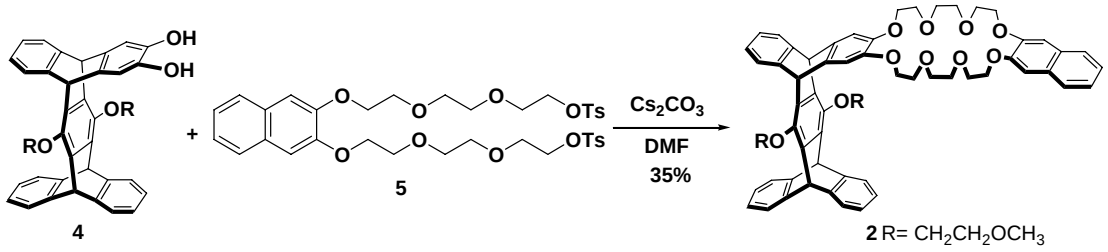
Contents

1. Synthetic procedure for compound 2

General methods. Melting points, taken on an electrothermal melting point apparatus, are uncorrected. ^{1}H NMR, ^{13}C NMR and ^{1}H-^{1}H COSY spectra were recorded on a DMX300 NMR, while ^{1}H-^{1}H ROESY spectra were recorded on an AVANCE 600 NMR. MALDI-TOF mass spectra were obtained on a BIFLEXIII mass spectrometer. Elemental analyses were performed by the Analytical Laboratory of Institute of Chemistry, CAS. Materials obtained commercially were used without further purification. Compounds **1**,[S1] bistosylate **5**,[S2] and cyclobis(paraquat-*p*-phenylene) tetra(hexafluorophosphate) **3**[S3] were prepared according to literature procedures. The association constant for the complexes **1**·**3** and **2**·**3** were determined according to the literature method.[S4]



Compound **2**. A suspension of cesium carbonate (1.33 g, 4.06 mmol) in anhydrous DMF (70 mL) under argon atmosphere was stirred vigorously for 10 min and then heated to 100 °C. To the mixture was added dropwise a solution of **4** (0.60 g, 0.98 mmol) and bistosylate **5** (0.72 g, 0.98 mmol) in anhydrous DMF (70 mL) over 12h. The reaction mixture was stirred at 100 °C for another 3d. After cooling down to ambient temperature, the mixture was filtered and washed with CH_2Cl_2 (60 mL). The filtrate was concentrated under reduced pressure to give a gray solid, which was

dissolved in CH_2Cl_2 (250 mL) and washed with diluted HCl. The organic layer was dried over anhydrous sodium sulfate. Removal of the solvent, the resulting oil was subjected to successive column chromatography over silica gel (eluent: 150:1 CH_2Cl_2/CH_3OH and then 100:1 CH_2Cl_2/CH_3OH) 0.35 g (35 %) of **2** as an off-white solid was obtained. Mp: 82-83 °C. ^{1}H NMR (300 MHz, 1:1 $CD_3CN/CDCl_3$): $\delta\delta$ 3.67 (s, 6H), 3.74-3.76 (m, 4H), 3.78-3.82 (m, 8H), 3.85-3.92 (m, 8H), 4.01-4.06 (m, 8H), 4.17-4.19 (m, 8H), 5.63 (s, 2H), 5.74 (s, 2H), 6.89-6.93 (m, 8H), 7.06 (s, 2H), 7.27-7.34 (m, 8H), 7.62-7.65 (m, 2H). ^{13}C NMR (75 MHz, CD_3CN): δ 47.7,48.1, 59.4, 69.2, 69.7, 69.9, 70.0, 71.1, 71.4, 71.9, 74.9, 108.0, 111.7, 123.3, 123.5, 123.6, 124.1, 125.0, 125.1, 126.3, 129.3, 136.4, 136.8, 138.8, 145.4, 145.5, 145.8, 145.9, 146.0, 149.1. MALDI-TOF MS: *m/z* 998.9 $[M]^+$, 1021.9 $[M+Na]^+$, 1037.9 $[M+K]^+$. Anal. Calcd for $C_{62}H_{62}O_{12}\cdot H_2O$: C, 73.21; H, 6.34. Found: C, 73.38; H, 6.33.

2. ^{1}H NMR and ^{13}C NMR spectra of compound 2

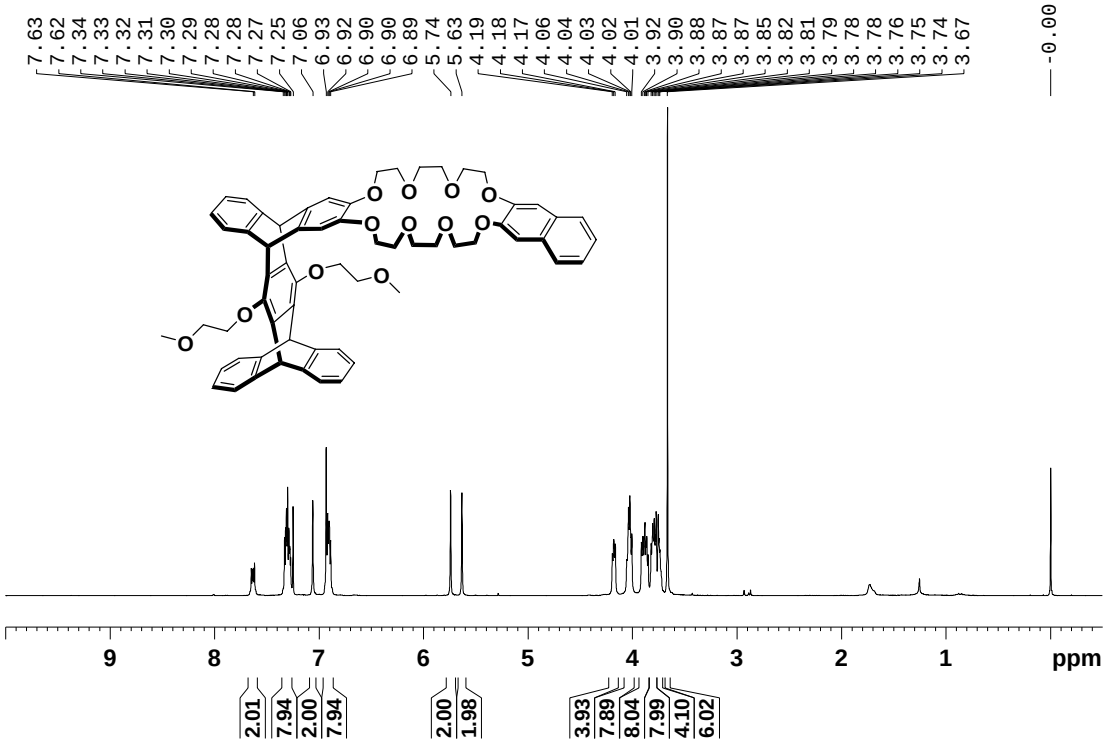


Fig. S1 ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **2**.

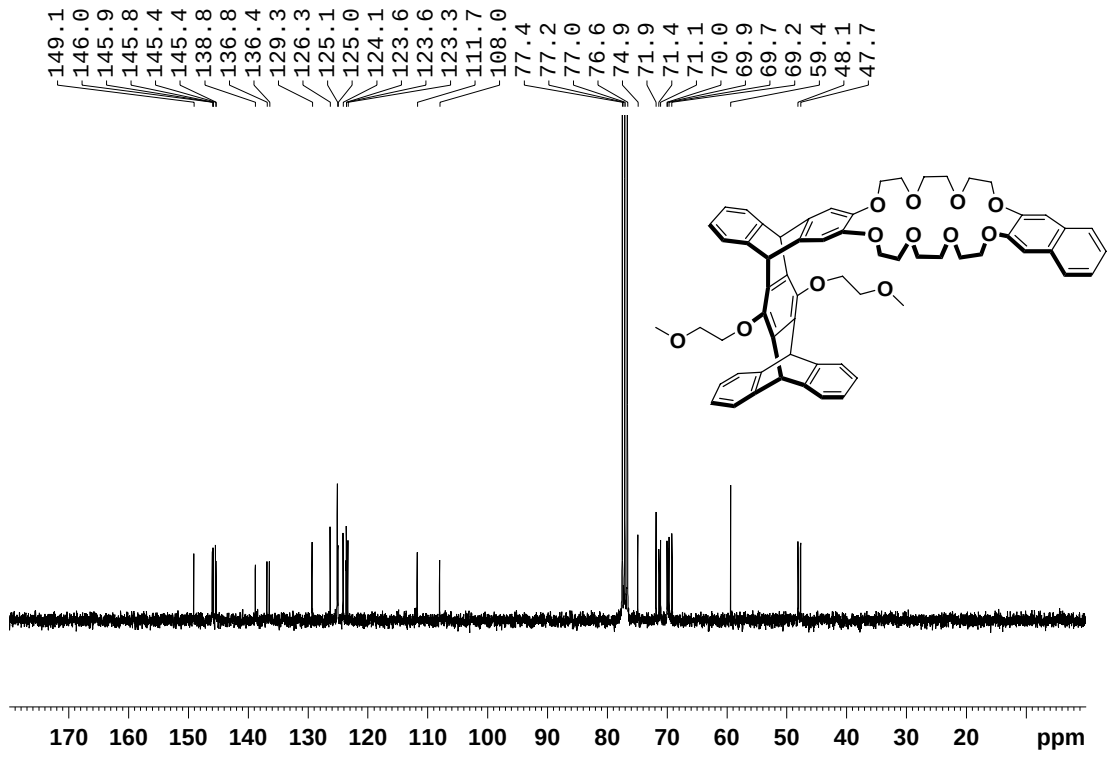


Fig. S2 ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **2**.

3. The comparison of ^{1}H NMR spectra between 2 and 3

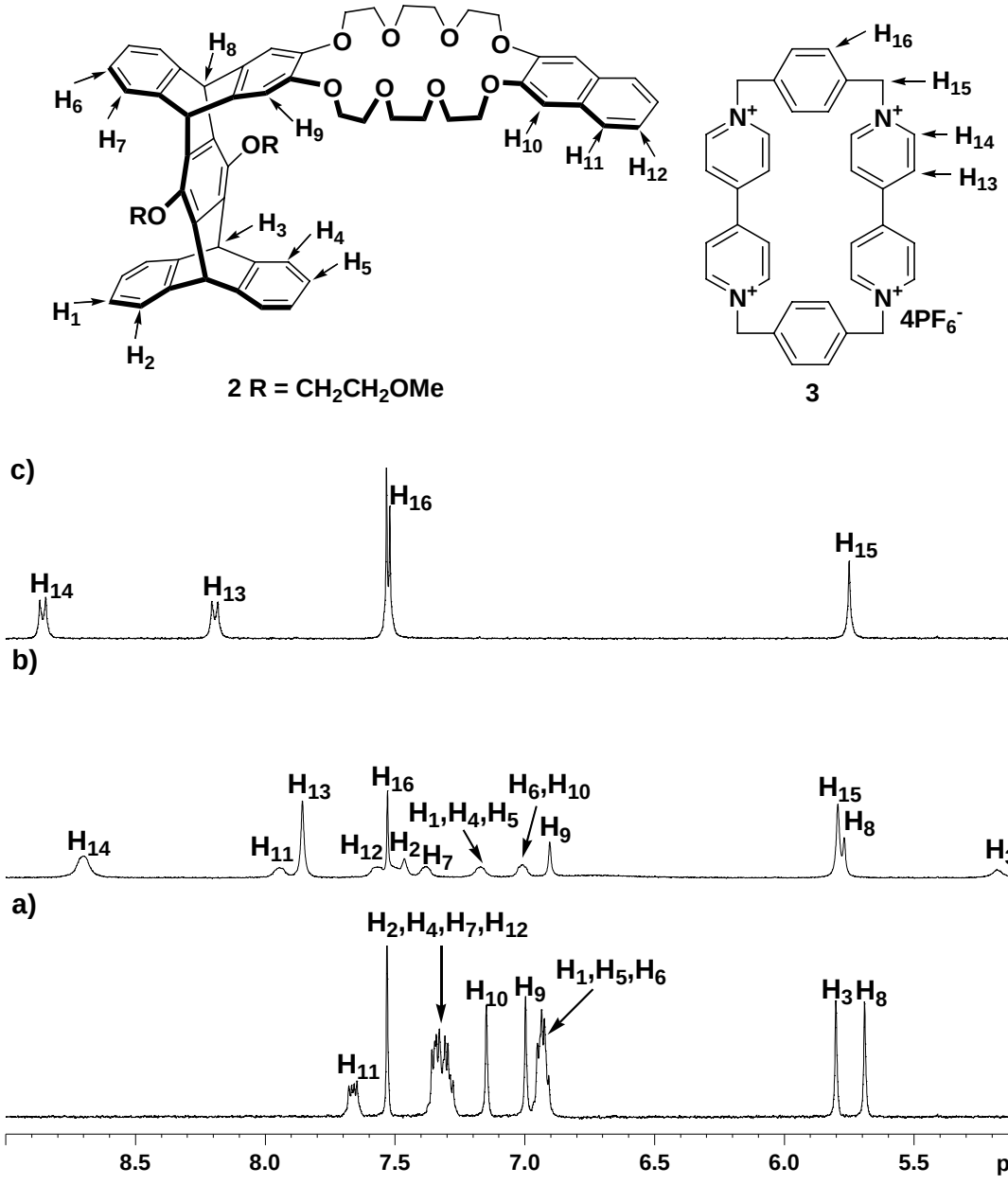


Fig. S3 Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$=2, 298 K) of (a) free **2**, (b) **2** and 1.0 equiv of **3**, (c) free **3**. [**2**] =2.0 mM.

4. ^{1}H-^{1}H COSY spectra of the complexes 1·3 and 2·3

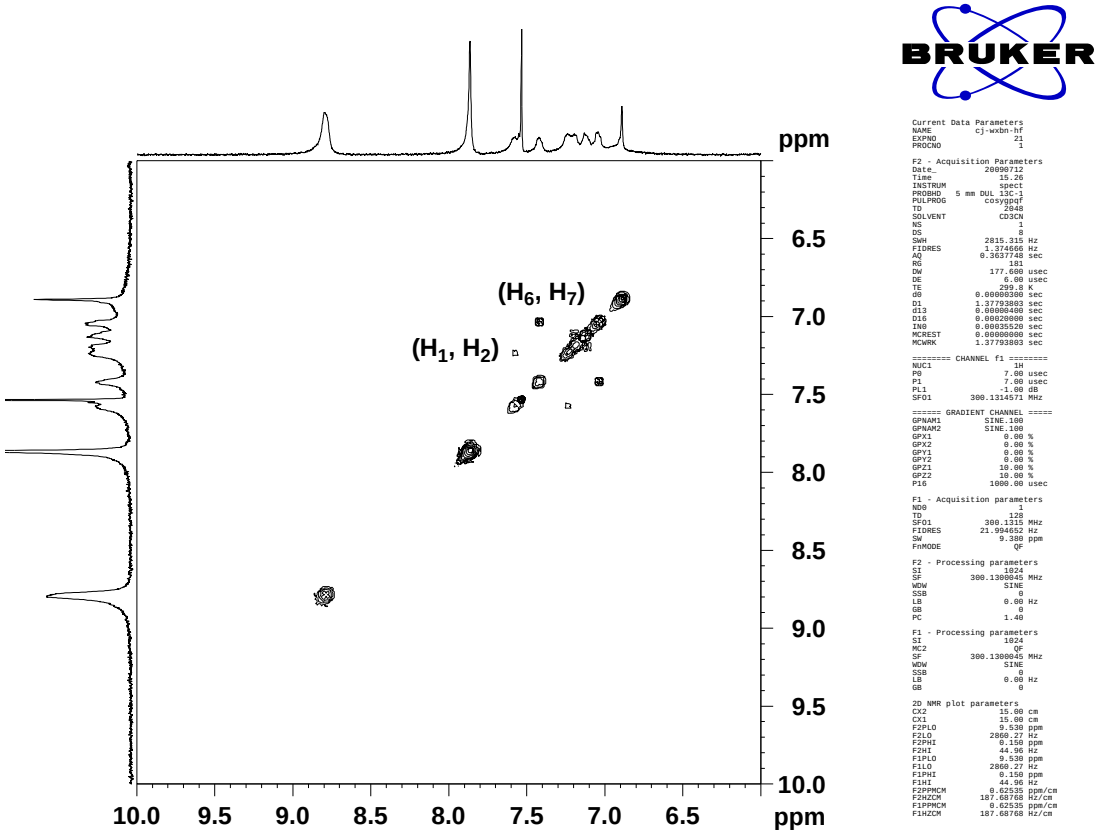


Fig. S4 ^{1}H-^{1}H COSY spectrum (300 MHz, $CD_3CN/CDCl_3$=2) of **1** and 1 equiv of **3**. $[\mathbf{1}]_0$ = 2 mM.

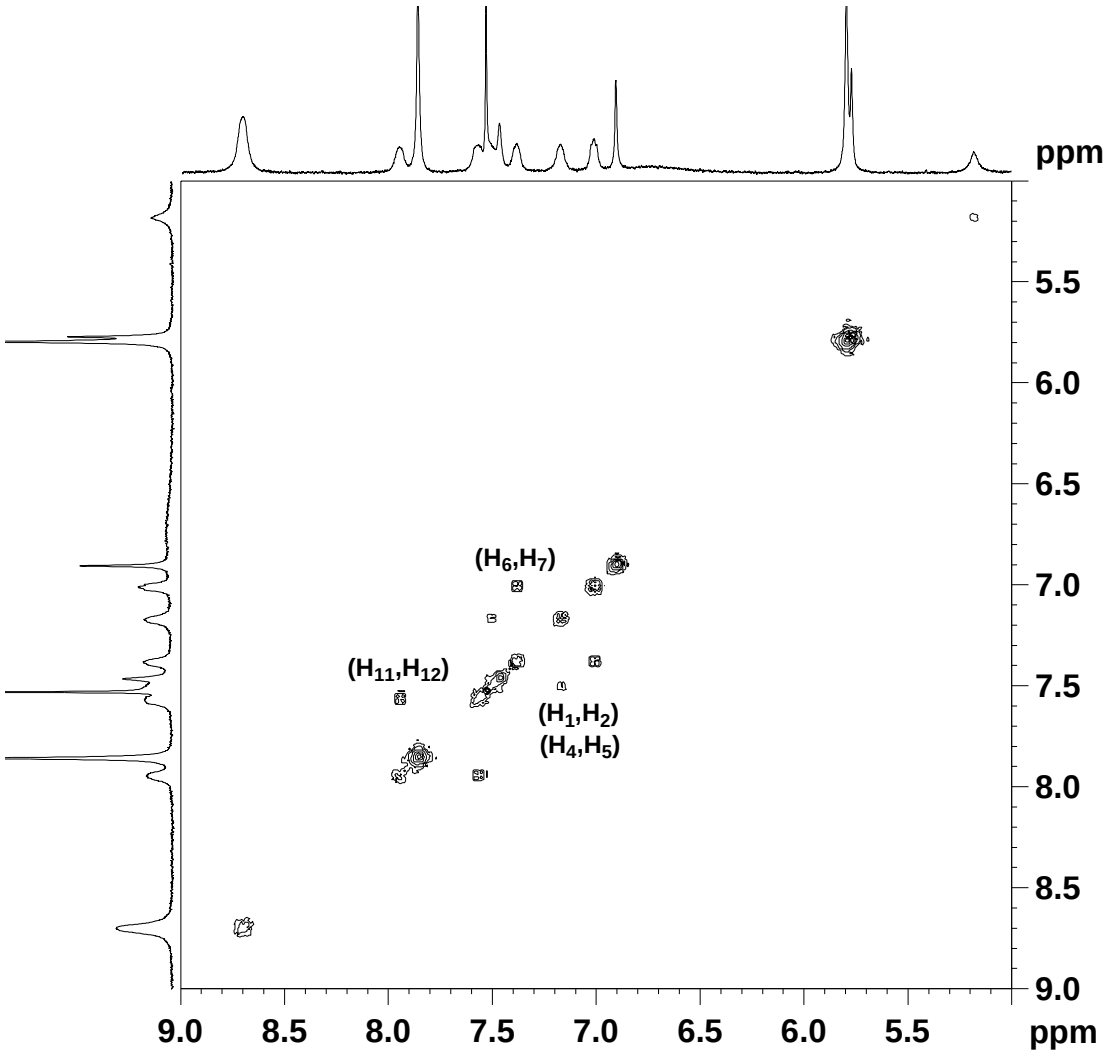


Fig. S5 ^{1}H-^{1}H COSY spectrum (300 MHz, $CD_3CN/CDCl_3$=2) of **2** and 1 equiv of **3**. $[\mathbf{2}]_0$ = 2 mM.

5. ROESY spectra of the complexes 1·3 and 2·3

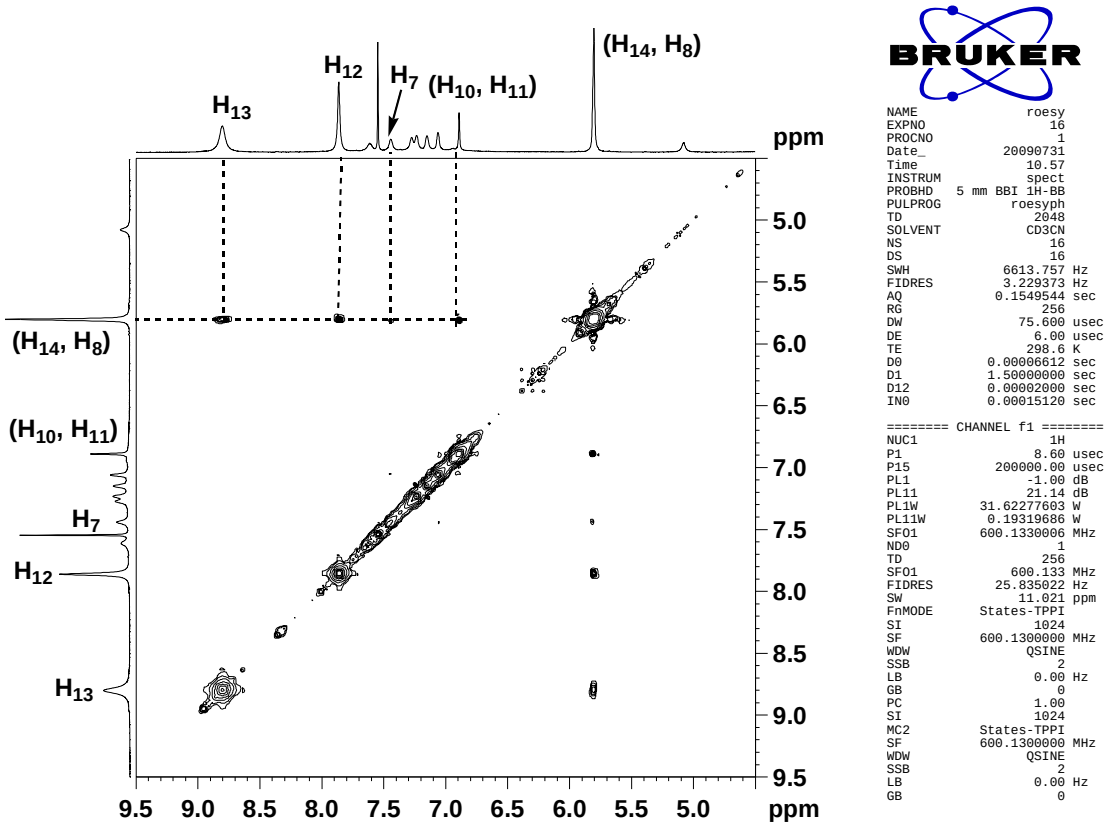


Fig. S6 ^{1}H-^{1}H ROESY spectrum (600 MHz, $CD_3CN/CDCl_3$=2) of **1** and 1 equiv of **3**. $[\mathbf{1}]_0$ = 2 mM.

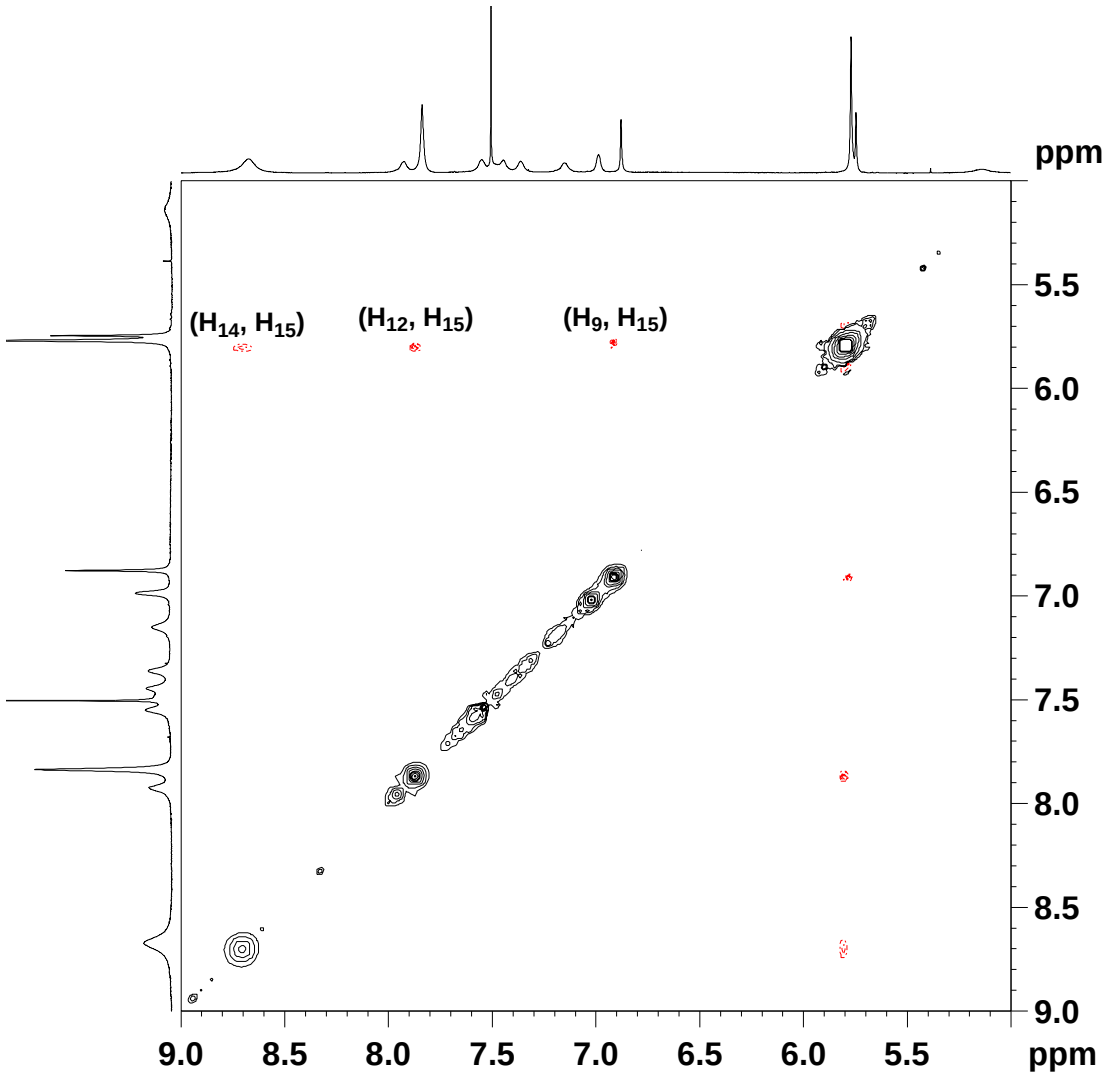


Fig. S7 ^{1}H-^{1}H ROESY spectrum (600 MHz, $CD_3CN/CDCl_3$=2) of **2** and 1 equiv of **3**. $[\mathbf{2}]_0$ = 2 mM.

6. Determination of the association constants

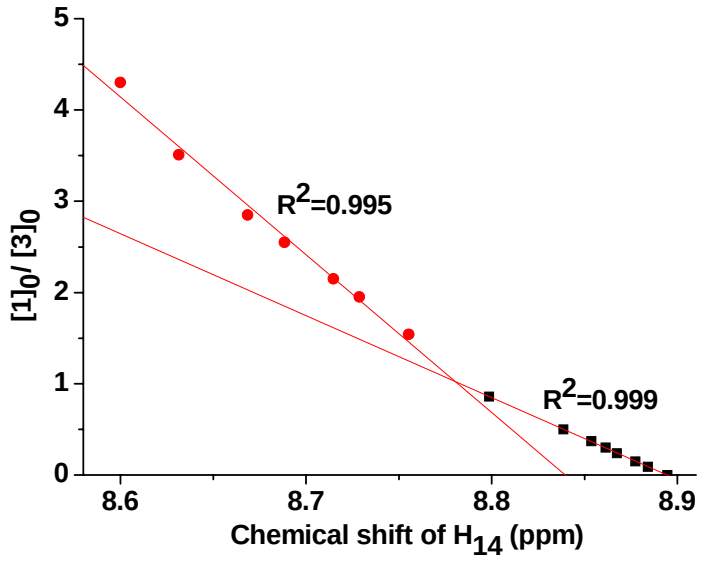


Fig. S8 Mole ratio plot for the complexation of **1** and **3** in $CD_3CN/CDCl_3$ (2:1 v/v) at 298 K.

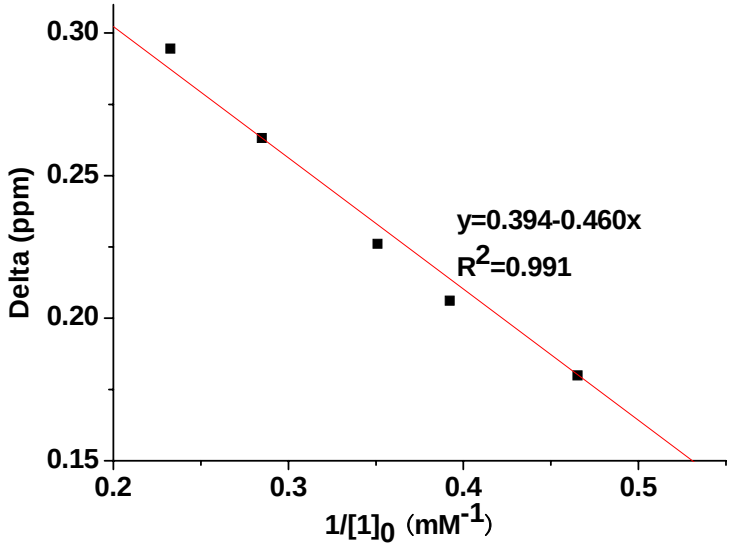


Fig. S9 Determination of Δ_0 of H_{14} for the complexation of **1** and **3** in $CD_3CN/CDCl_3$ (2:1 v/v) at 298 K.

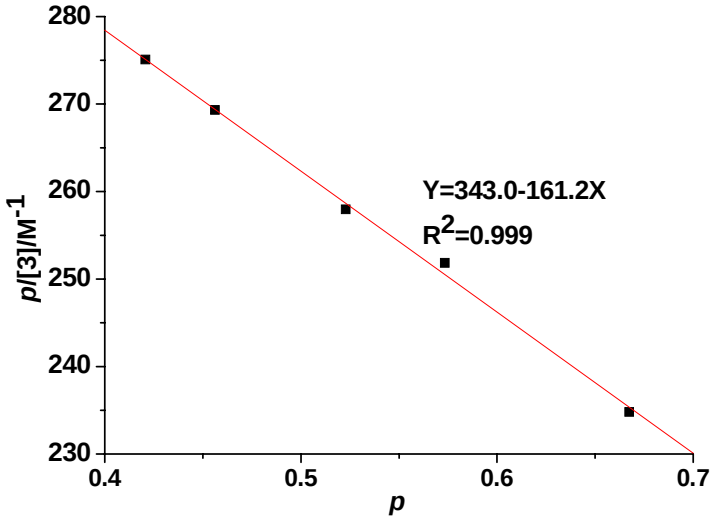


Fig. S10 Scatchard plot for the complexation of **1** and **3** in $CD_3CN/CDCl_3$ (2:1 v/v) at 298 K.

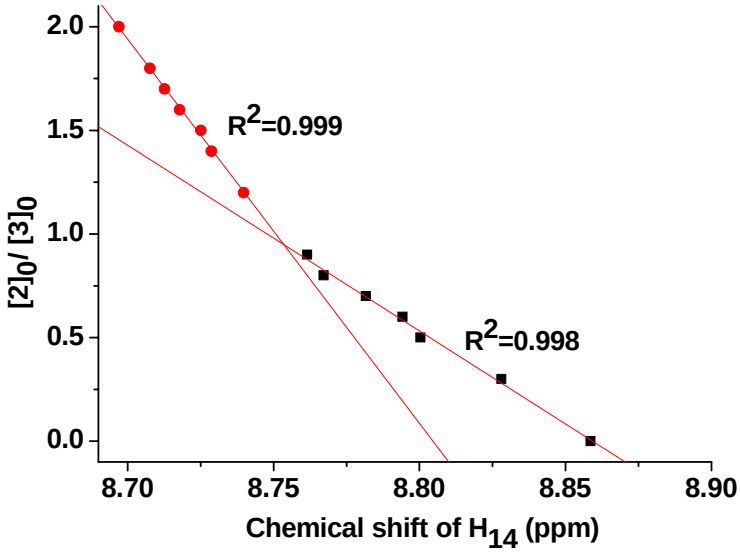


Fig. S11 Mole ratio plot for the complexation of **2** and **3** in $CD_3CN/CDCl_3$ (2:1 v/v) at 298 K.

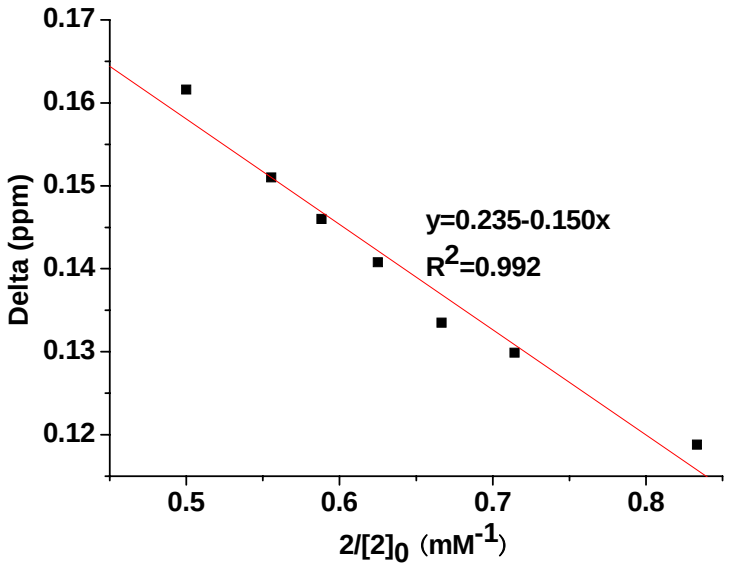


Fig. S12 Determination of Δ_0 of H_{14} for the complexation of **2** and **3** in $CD_3CN/CDCl_3$ (2:1 v/v) at 298 K.

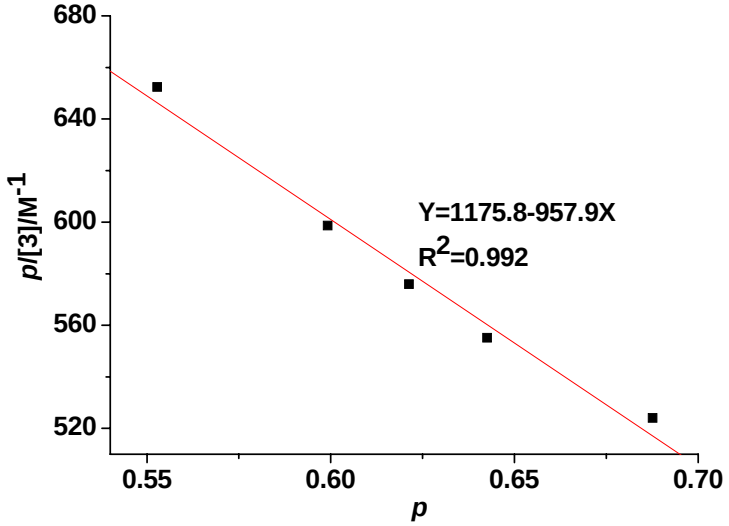


Fig. S13 Scatchard plot for the complexation of **2** and **3** in $CD_3CN/CDCl_3$ (2:1 v/v) at 298 K.

7. ^{1}H NMR spectra of complexes 1·3 and 2·3 at low temperatures

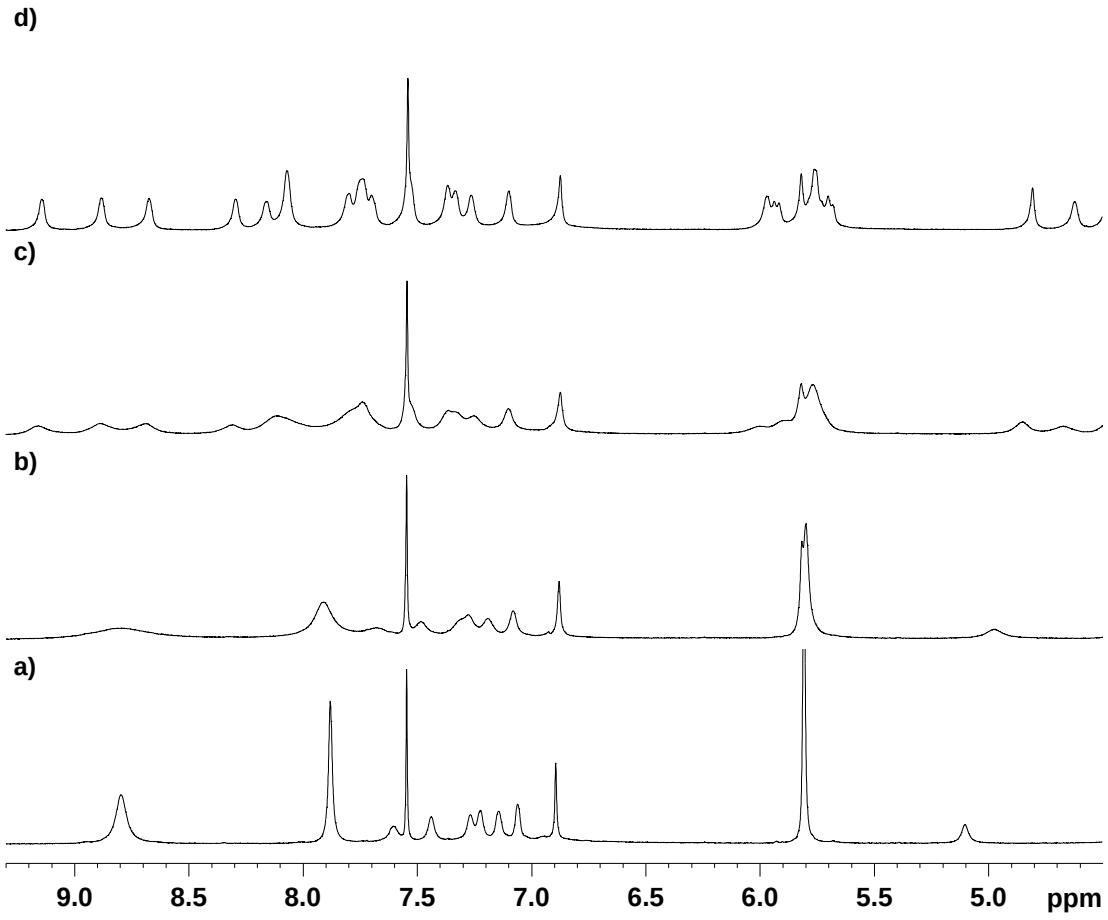


Fig. S14 Partial ^{1}H NMR spectra (600 MHz, $CD_3CN/CDCl_3$=2) of a solution of **1** and 1.0 equiv of **3** at (a) 298 K, (b) 278 K, (c) 258 K, (d) 238 K. $[\mathbf{1}]_0$ =2.0 mM.

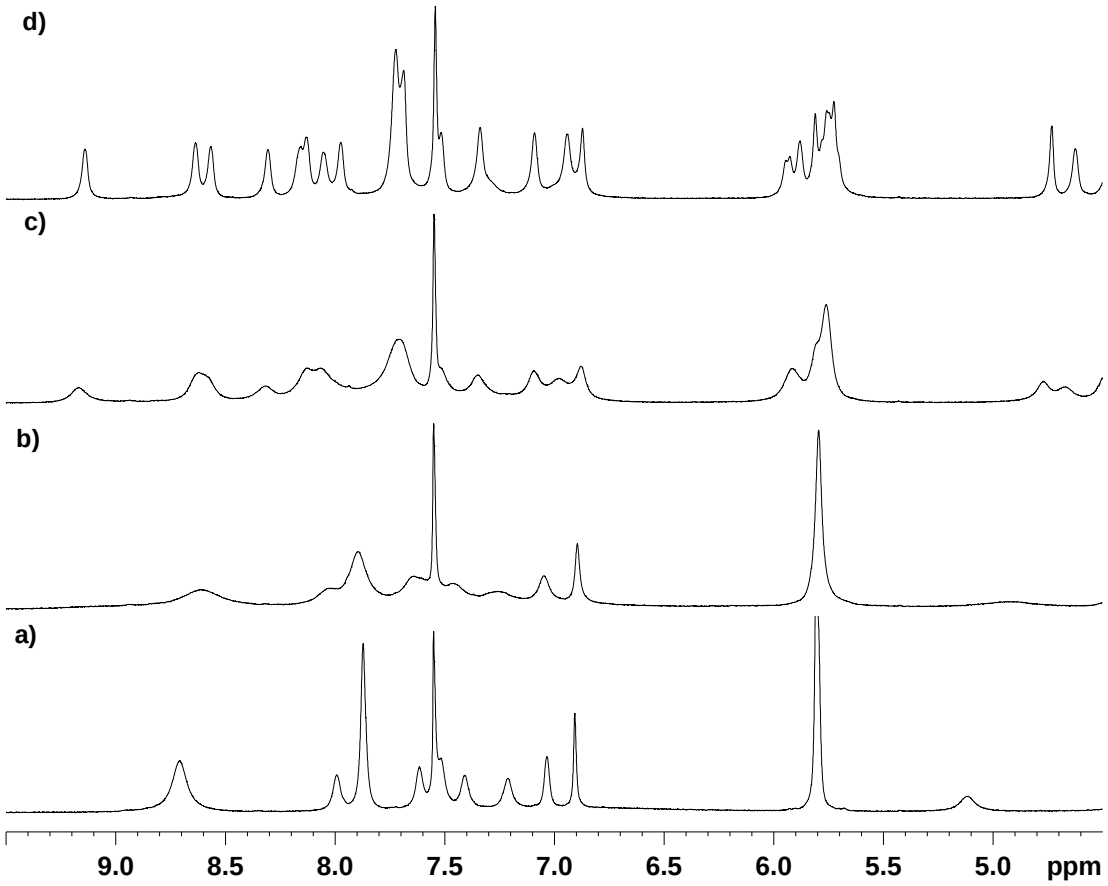


Fig. S15 Partial ^{1}H NMR spectra (600 MHz, $CD_3CN/CDCl_3$=2) of a solution of **2** and 1.0 equiv of **3** at (a) 298 K, (b) 278 K, (c) 258 K, (d) 238 K. $[\mathbf{2}]_0$ =2.0 mM.

8. ESI-MS spectra of the complexes 1·3 and 2·3

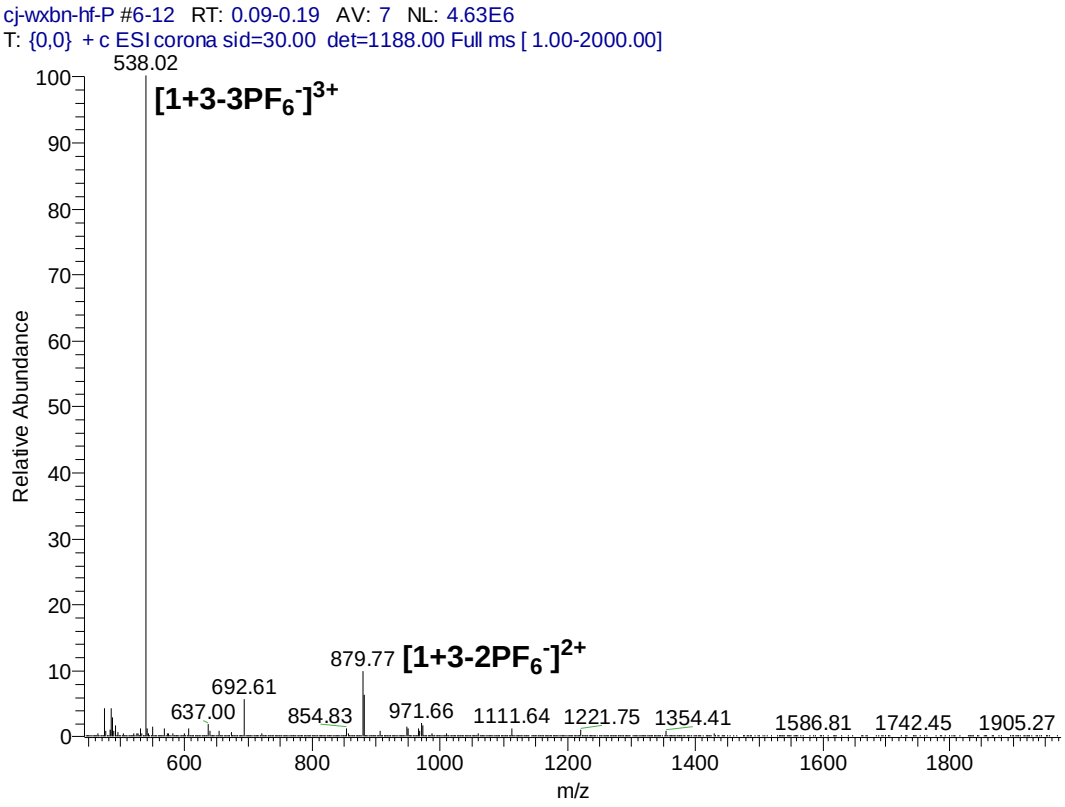


Fig. S16 ESI-MS spectrum of the complex **1·3**.

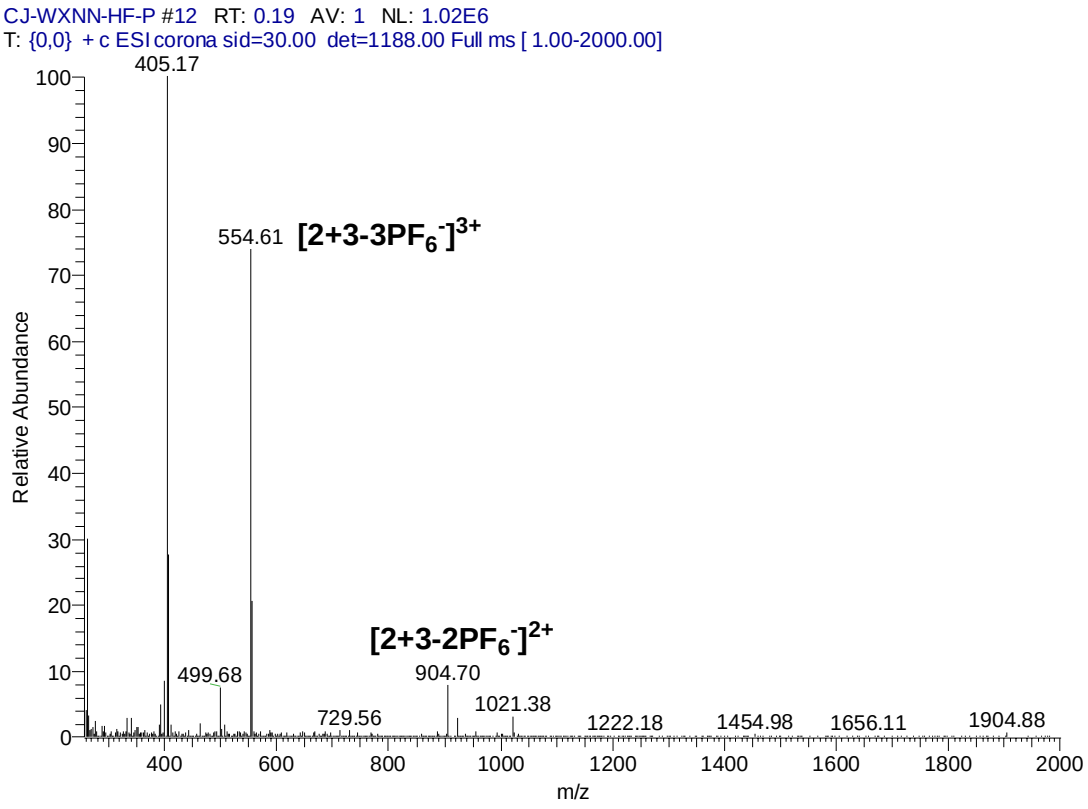


Fig. S17 ESI-MS spectrum of the complex **2·3**.

9. Cyclic voltammetry (CV) curves

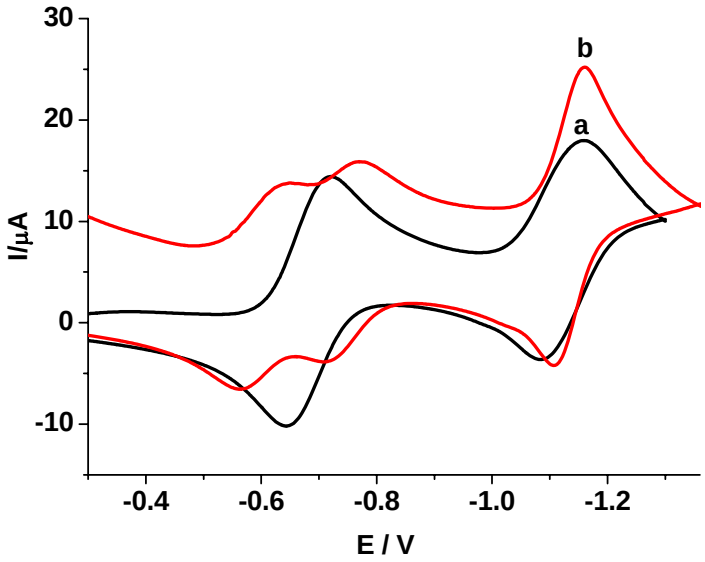


Fig. S18 CV curves for a solution of $\mathbf{3}^{4+}$ (1.0×10^{-3} M) in CH_3CN-$(NBu_4)PF_6$ (0.1 M) in the absence (black line) and the presence (red line) of **1** (3.0×10^{-3} M). Working electrode: Pt. Scan rate: $0.1Vs^{-1}$.

10. References

[S1] J. Cao, H.-Y. Lu, X.-J. You, Q.-Y. Zheng and C.-F. Chen, *Org. Lett.*, 2009, **11**, 4446-4449.

[S2] J. D. Badjic, C. M. Ronconi, J. F. Stoddart, V. Balzani, S. Silvi and A. Credi, *J. Am. Chem. Soc.*, 2006, **128**, 1489-1499.

[S3] B. Odell, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1547-1550.

[S4] (*a*) T. Han and C.-F. Chen, *Org. Lett.*, 2006, **8**, 1069-1072; (*b*) Connors, K. A. *Binding Constants*; J. Wiley and Sons: New York, 1987.