

Supporting Information

Monitoring Self-Sorting by Electrospray Ionization Mass Spectrometry: Formation Intermediates and Error-Correction during the Self-Assembly of Multiply Threaded Pseudorotaxanes

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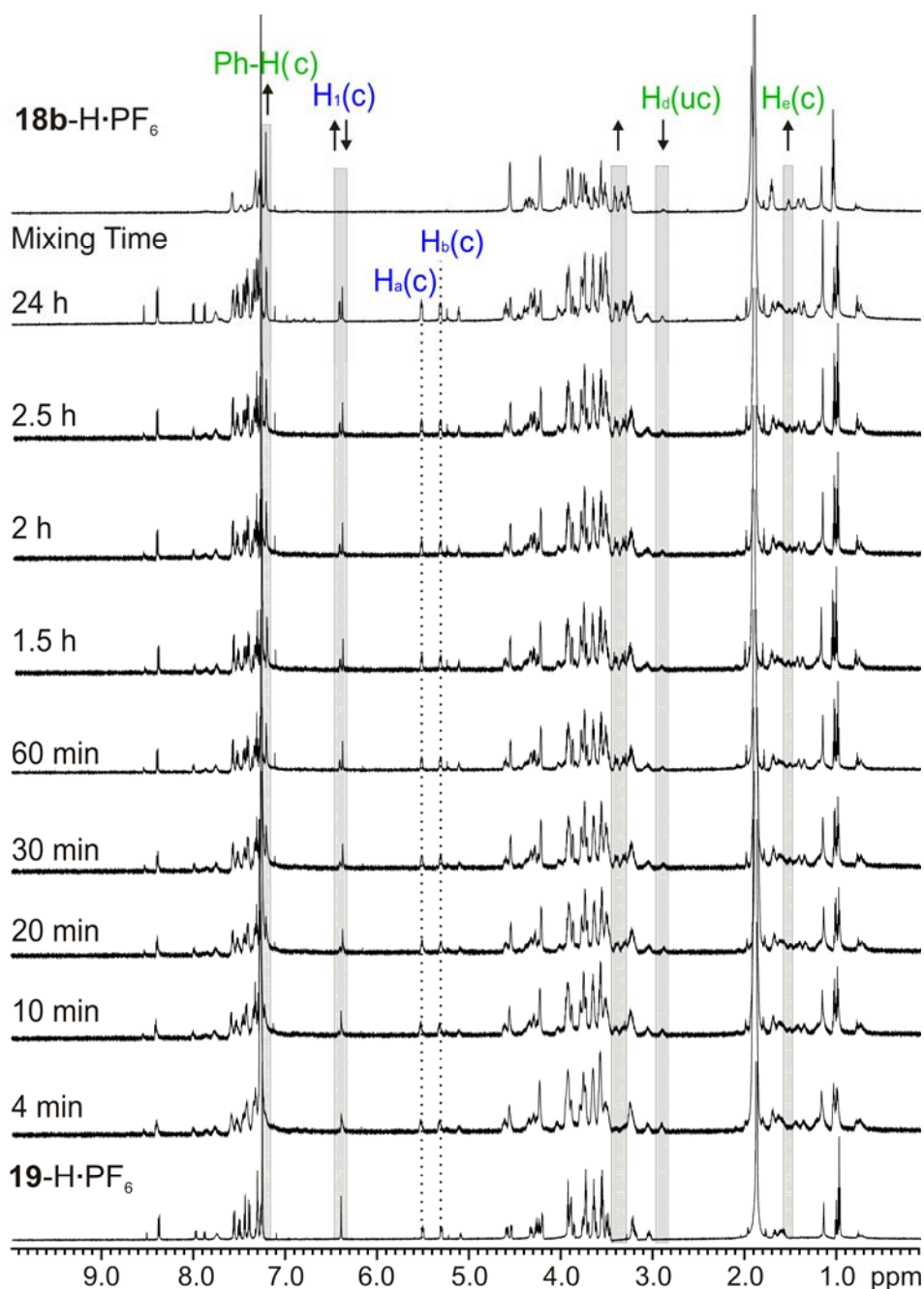


Figure S1. Changes of ^1H NMR spectra (700 MHz, 298 K, $\text{CDCl}_3:\text{CD}_3\text{CN} = 5:1$, 1.0 mM) with increasing reaction time after mixing $\mathbf{1}\text{-H}\cdot\text{PF}_6$ and $\mathbf{2}\text{-H}\cdot\text{PF}_6$ with $\mathbf{4}$ in a 1:1:1 ratio, and ^1H NMR spectra of independently generated $\mathbf{18b}\text{-H}\cdot\text{PF}_6$ and $\mathbf{19}\text{-H}\cdot\text{PF}_6$. Complexed and uncomplexed species are denoted by “c” and “uc” in parentheses, respectively. Fast processes occurring at a timescale less than 4 min are not observable with these NMR experiments. The signals for $\mathbf{18}\text{-H}\cdot\text{PF}_6$ were not identifiable due to significant signal overlapping and broadening and its low concentration. The complexation of $\mathbf{1}\text{-H}\cdot\text{PF}_6$ to the 24-crown-4 unit of $\mathbf{4}$ has almost finished within 4 min, while most of $\mathbf{2}\text{-H}\cdot\text{PF}_6$ is still free. It is then gradually consumed to afford $\mathbf{11}\text{-2H}\cdot\text{2PF}_6$ over time.

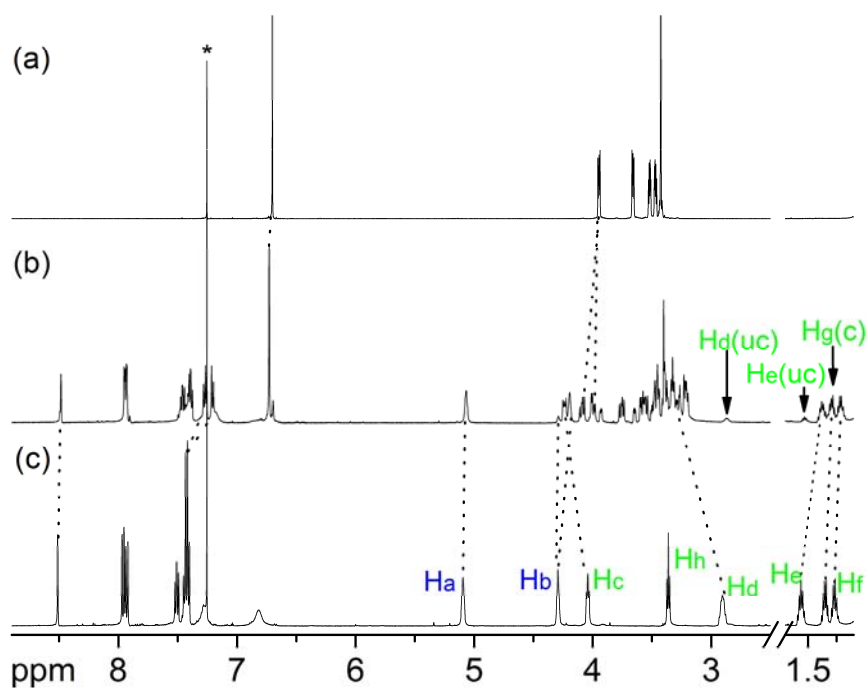


Figure S2. ^1H NMR spectra (500 MHz, 298 K, $\text{CDCl}_3:\text{CD}_3\text{CN} = 2:1$, 10.0 mM) of (a) **C7**, (c) **3-2H·2PF₆**, and (b) an equimolar mixture of **3-2H·2PF₆** and **C7**. Complexed and uncomplexed species are denoted by “c” and “uc” in the parentheses, respectively. Asterisk = solvent. The NMR results suggest **15-2H·2PF₆** to be the dominating species in a 1:1 mixture of **3-2H·2PF₆** and **C7** as indicated by the significant complexation-induced shifts of H_c , H_d , and H_e while H_a and H_b remain almost unaffected with respect to the free axle. This should be even more so, when the binding constants increase upon changing the solvent to a less polar one ($\text{CH}_2\text{Cl}_2 : \text{CH}_3\text{CN} = 8:1$, as used in the MS experiments).

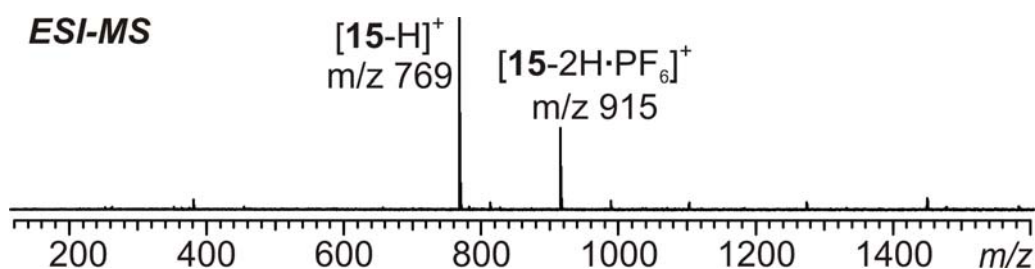


Figure S3. ESI-FTICR mass spectrum of 1:1 mixture (295 K, $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{CN} = 8:1$, 250 μM) of **3-2H·2PF₆** and **C7**. The result supports the conclusion from the NMR experiments.

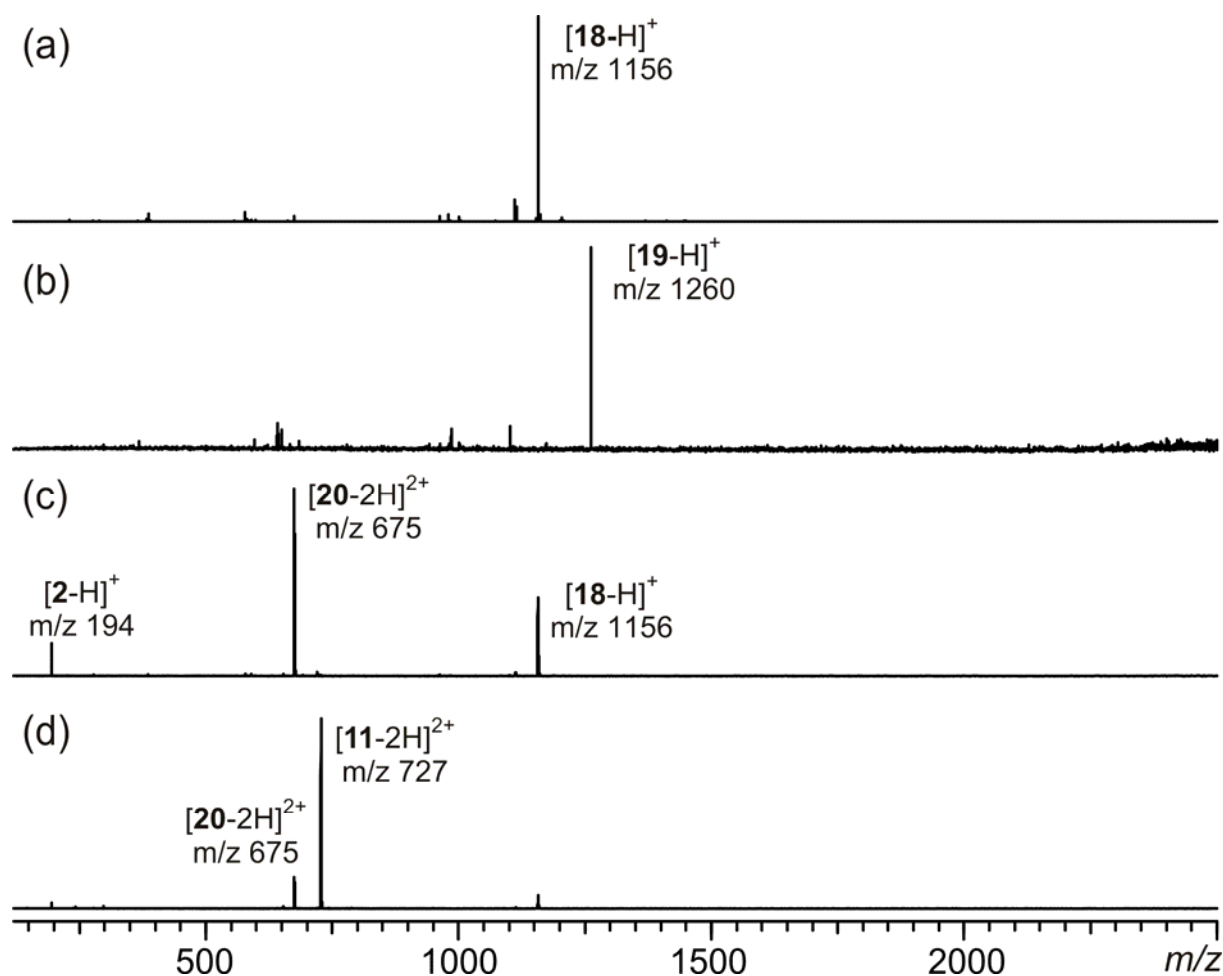


Figure S4. ESI-FTICR mass spectra (295 K, $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{CN} = 8:1$, 250 μM) of (a) 1:1 mixture of **2-H** $\cdot\text{PF}_6$ and **4**, (b) 1:1 mixture of **1-H** $\cdot\text{PF}_6$ and **4**, (c) 2:1 mixture of **2-H** $\cdot\text{PF}_6$ and **4** ($[\mathbf{4}] = 250 \mu\text{M}$), and (d) 1:2:1 mixture of **1-H** $\cdot\text{PF}_6$, **2-H** $\cdot\text{PF}_6$, and **4** ($[\mathbf{4}] = 250 \mu\text{M}$). These results indicate: (i) **19-H** $\cdot\text{PF}_6$ and **18b-H** $\cdot\text{PF}_6$ are the by far major species in the 1:1 mixtures of **4** with **1-H** $\cdot\text{PF}_6$ and **2-H** $\cdot\text{PF}_6$, respectively; (ii) **20-2H** $\cdot 2\text{PF}_6$ is dominant in the 2:1 mixture of **2-H** $\cdot\text{PF}_6$ and **4**, and **18-H** $\cdot\text{PF}_6$ may exist as minor species even when considering the fragmentation of $[\mathbf{20-2H}]^{2+}$ into $[\mathbf{2-H}]^+$ and $[\mathbf{18-H}]^+$ during ionization process since the intensity of $[\mathbf{18-H}]^+$ is much higher than that of $[\mathbf{2-H}]^+$; (iii) self-sorted pseudorotaxane **11-2H** $\cdot 2\text{PF}_6$ is thermodynamically favored over mismatched structure **20-2H** $\cdot 2\text{PF}_6$ in a 1:2:1 mixture of **1-H** $\cdot\text{PF}_6$, **2-H** $\cdot\text{PF}_6$, and **4**.

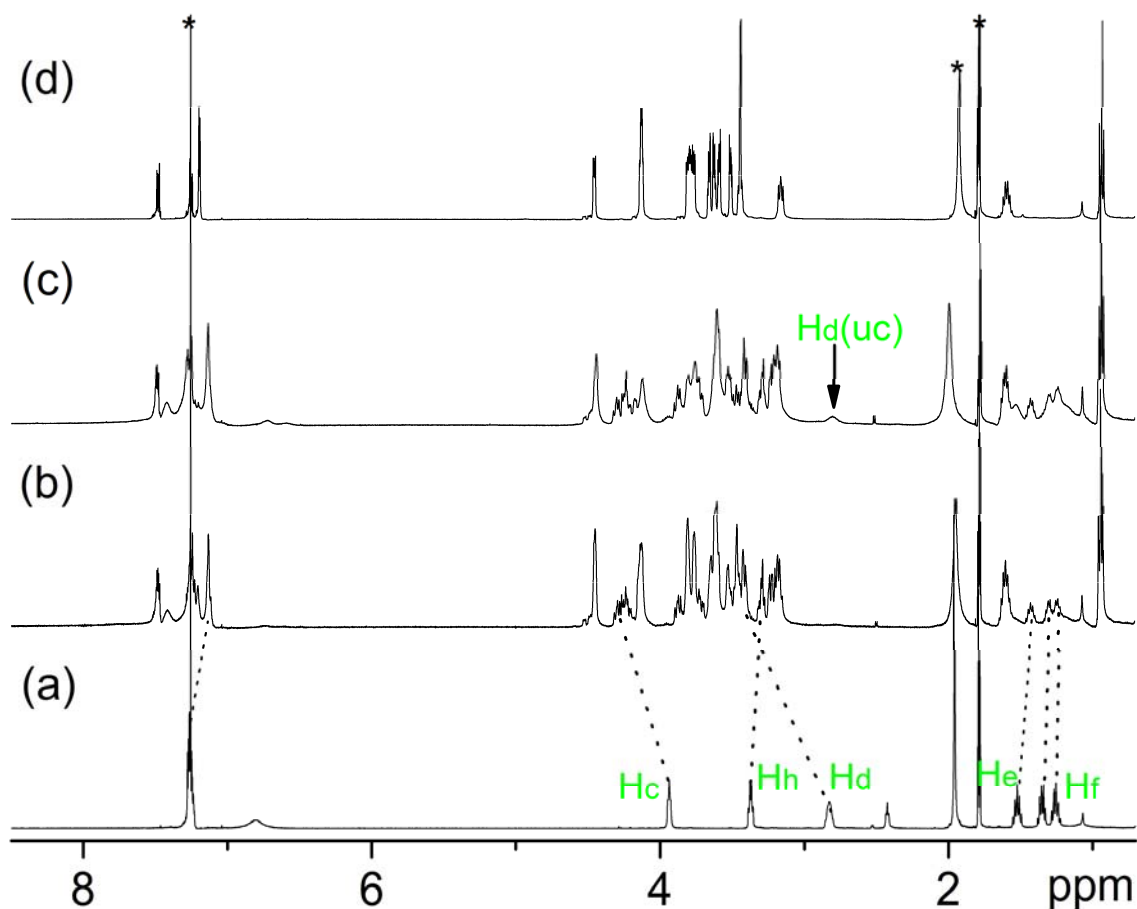


Figure S5. ^1H NMR spectra (500 MHz, 298 K, $\text{CDCl}_3:\text{CD}_3\text{CN} = 2:1$, 10.0 mM) of (a) $2\text{-H}\cdot\text{PF}_6$, (d) **4**, (b) 1:1 mixture of $2\text{-H}\cdot\text{PF}_6$ and **4**, and (c) 2:1 mixture of $2\text{-H}\cdot\text{PF}_6$ and **4**. The “uc” in the parentheses denotes the signal from uncomplexed species. Asterisk = solvent. The similar shifting of H_c , H_d , H_e , and H_f as observed for $[2\text{-H@C7}]\cdot\text{PF}_6$ (Figure 1) and the absence of free H_d in (b) indicate that $18\text{b}\text{-H}\cdot\text{PF}_6$ is dominant in this solution. The assignment of $20\text{-2H}\cdot 2\text{PF}_6$ in the 2:1 mixture of $2\text{-H}\cdot\text{PF}_6$ and **4** is inconclusive due to serious signal overlapping and broadening. But considering the MS result in Figure S4, $20\text{-2H}\cdot 2\text{PF}_6$ is believed to be the major species as indirectly suggested by the low peak intensity of free H_d in Figure S5d.

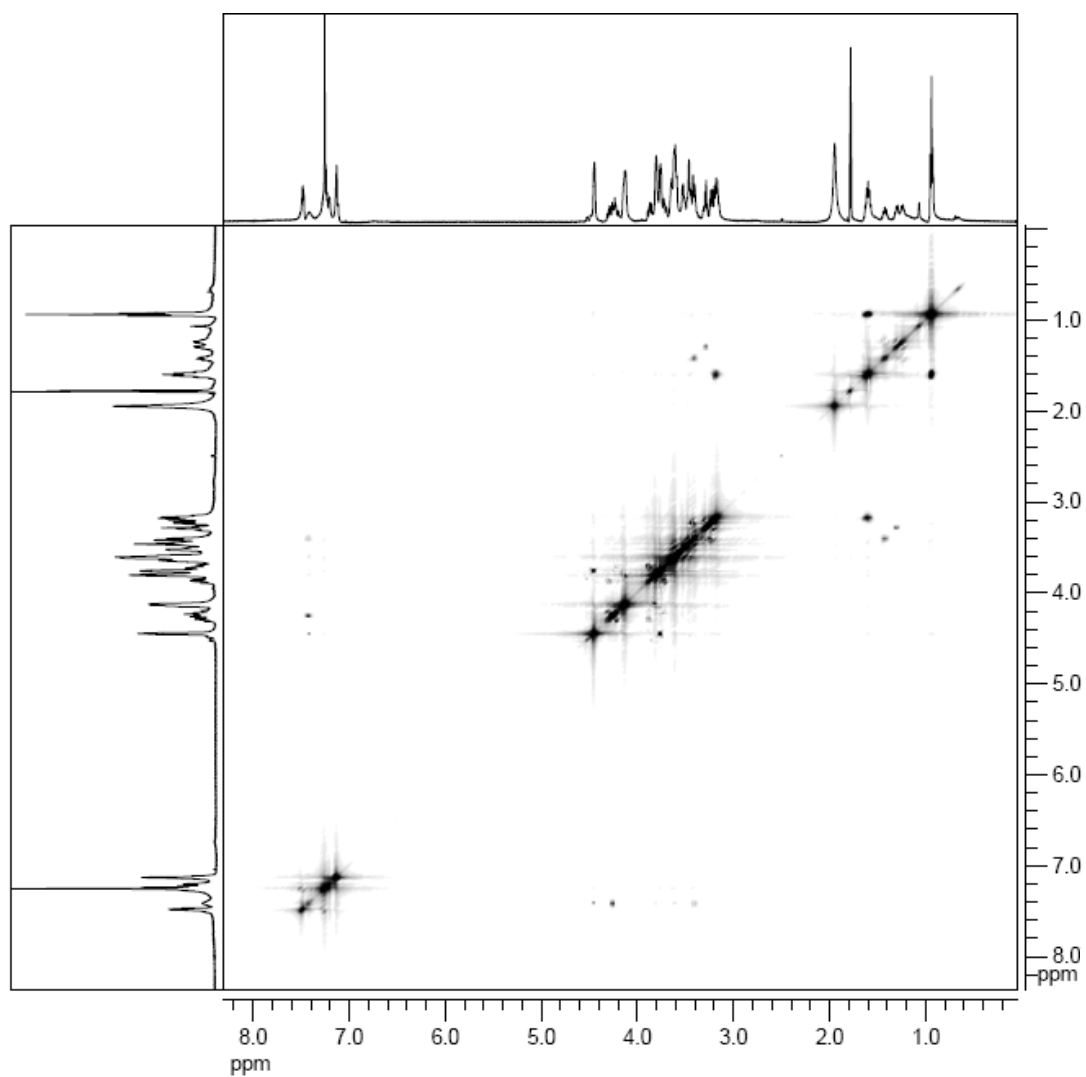


Figure S6. ¹H-¹H COSY NMR spectrum (500 MHz, 298 K, CDCl₃:CD₃CN = 2:1, 10.0 mM) of 1:1 mixture of **2**-H•PF₆ and **4**. The COSY spectrum supports the assignments for the peaks in Figure S5b.

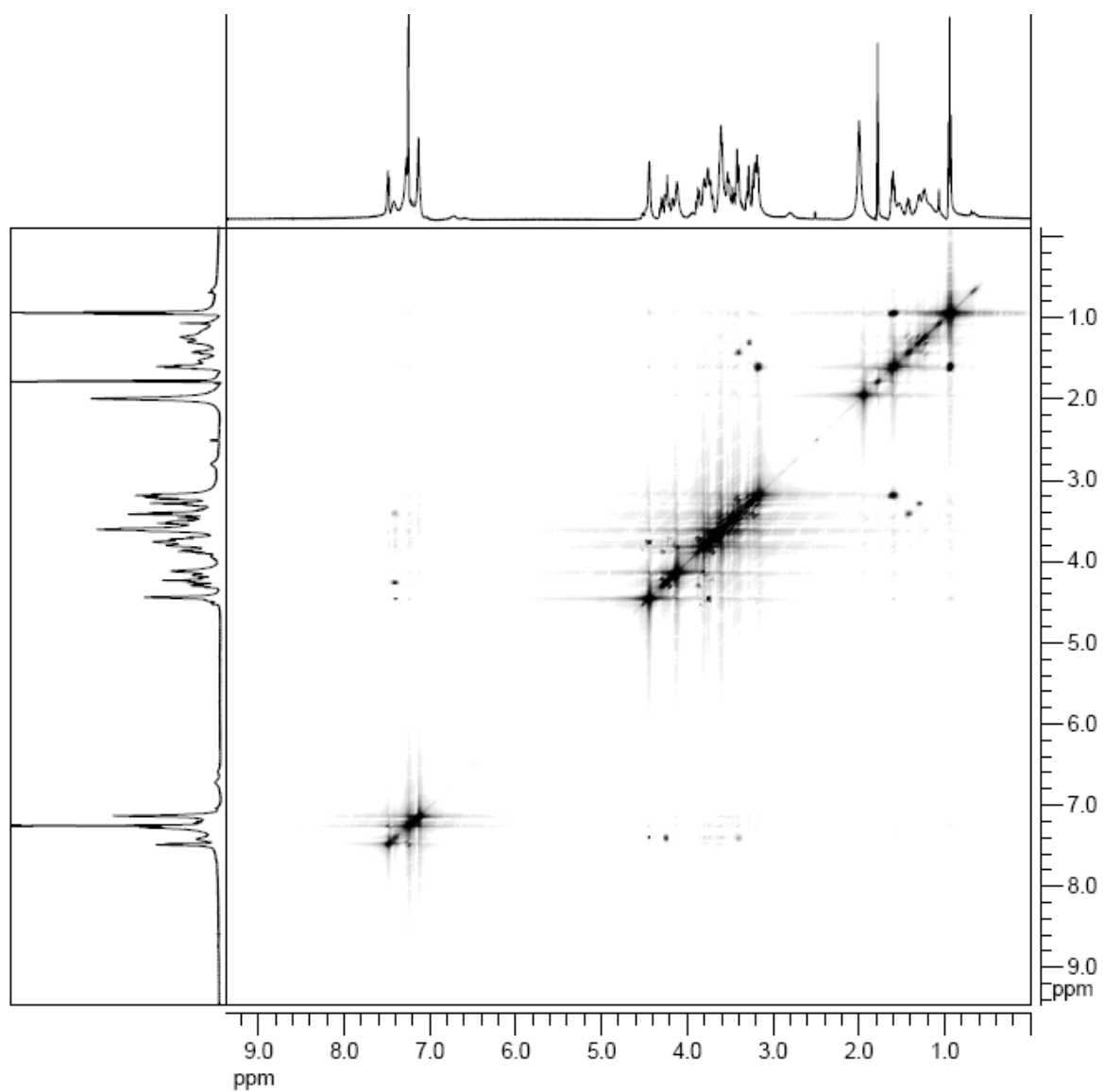


Figure S7. ^1H - ^1H COSY NMR spectrum (500 MHz, 298 K, $\text{CDCl}_3:\text{CD}_3\text{CN} = 2:1$, 10.0 mM) of 2:1 mixture of $\mathbf{2}\text{-H}\cdot\text{PF}_6$ and $\mathbf{4}$. Due to significant signal overlapping and broadening, the COSY spectrum still could not contribute to the identification of $\mathbf{20}\text{-2H}\cdot\text{2PF}_6$ in the 2:1 mixture of $\mathbf{2}\text{-H}\cdot\text{PF}_6$ and $\mathbf{4}$.

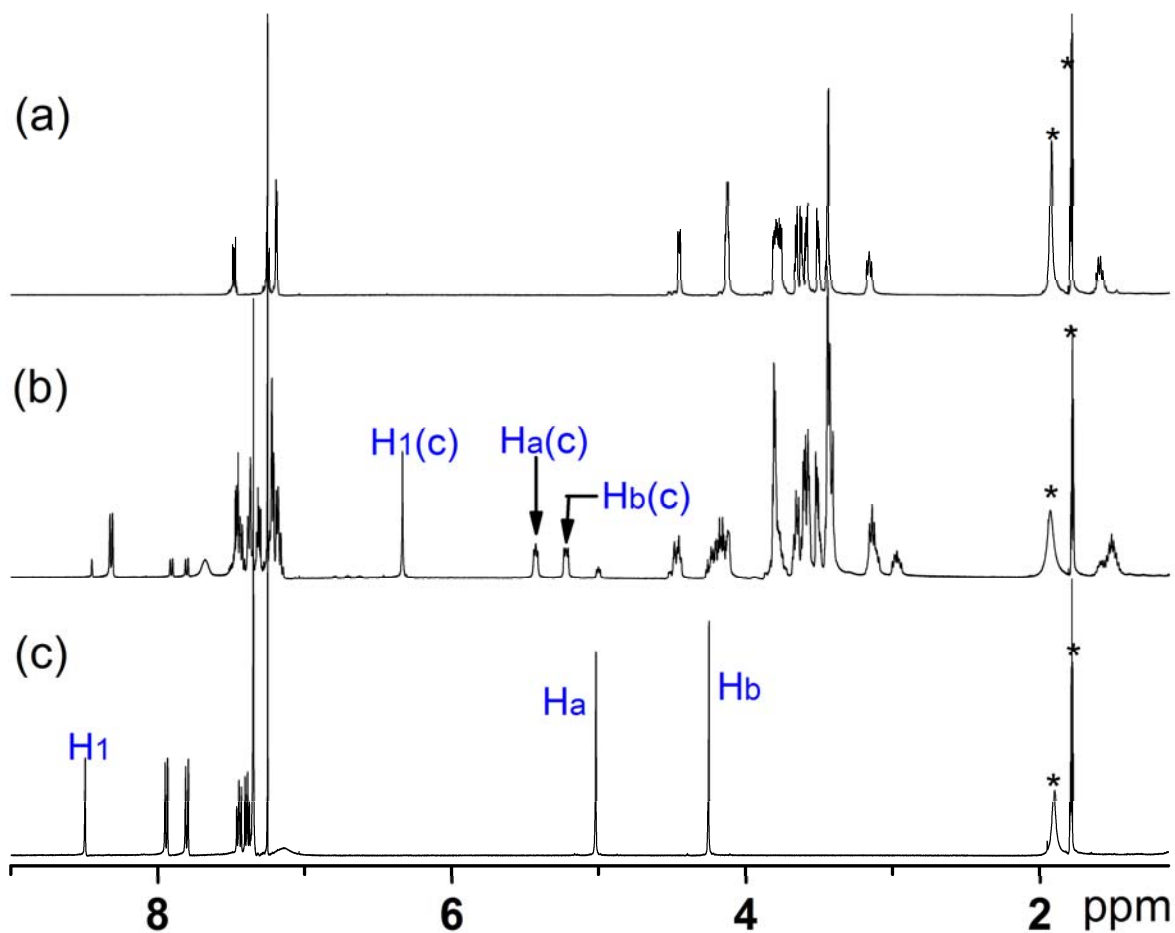


Figure S8. ¹H NMR spectra (500 MHz, 298 K, CDCl₃:CD₃CN = 2:1, 10.0 mM) of (a) **4**, (c) **1-H·PF₆**, and (b) 1:1 mixture of **1-H·PF₆** and **4**. The “c” in the parentheses denotes the signal from complexed species. Asterisk = solvent. The obvious complexation-induced shift of H₁, H_a, and H_b indicate **19-H·PF₆** to be the predominant complex in this solution, which is in line with the MS results.

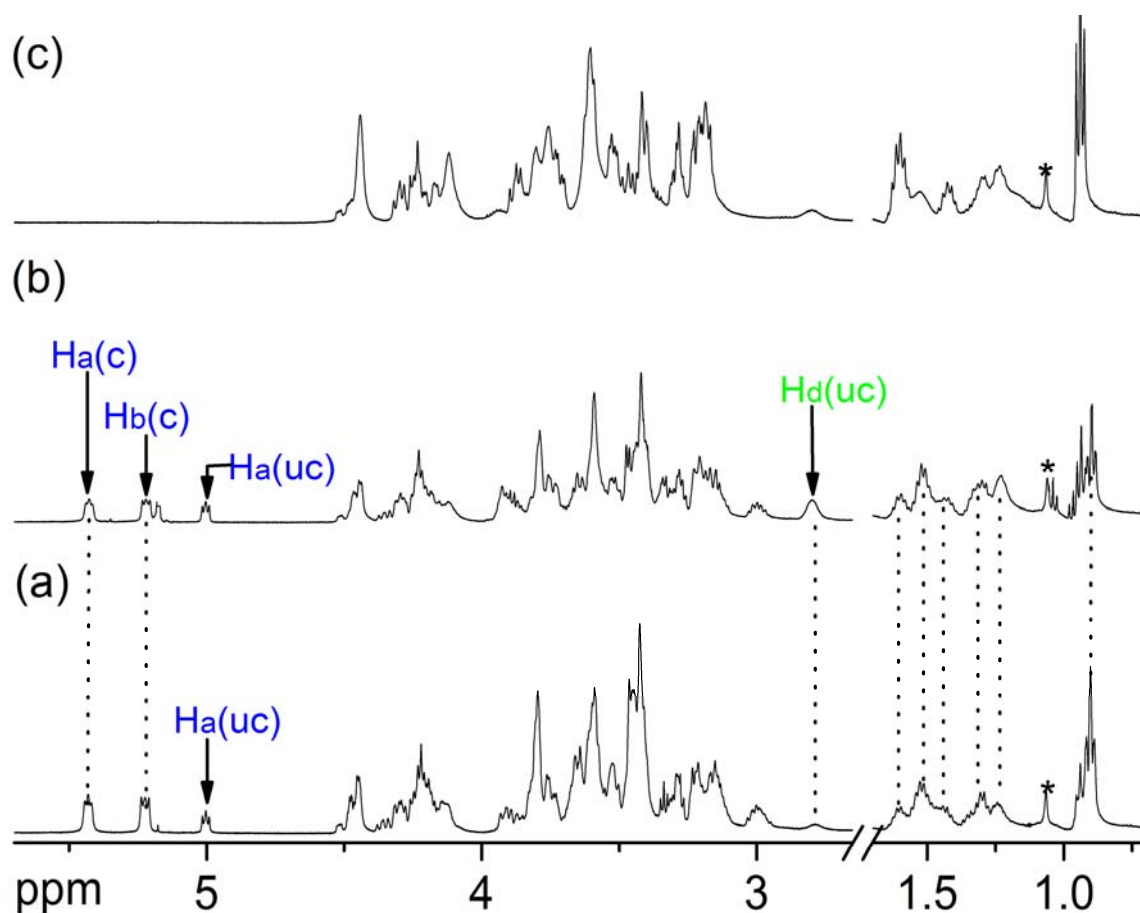


Figure S9. ¹H NMR spectra (500 MHz, 298 K, CDCl₃:CD₃CN = 2:1, 10.0 mM) of (a) 1:1:1 mixture of **1**-H·PF₆, **2**-H·PF₆, and **4**, (b) 1:2:1 mixture of **1**-H·PF₆, **2**-H·PF₆, and **4**, and (c) 2:1 mixture of **2**-H·PF₆ and **4**. Complexed and uncomplexed species are denoted by “c” and “uc” in the parentheses, respectively. Asterisk = solvent impurity. The significant signal overlapping and broadening hamper the unambiguous assignment of all species in 1:2:1 mixture of **1**-H·PF₆, **2**-H·PF₆, and **4**. But with the previous knowledge about the related systems in mind, complexed H_a and H_b and uncomplexed H_d and their peak integrations suggest **11**-2H·2PF₆ to be the primary species. With respect to **20**-2H·2PF₆, the NMR result is inconclusive but MS results indicate that it coexist with **11**-2H·2PF₆ in this solution as a minor species (Figure S4d).

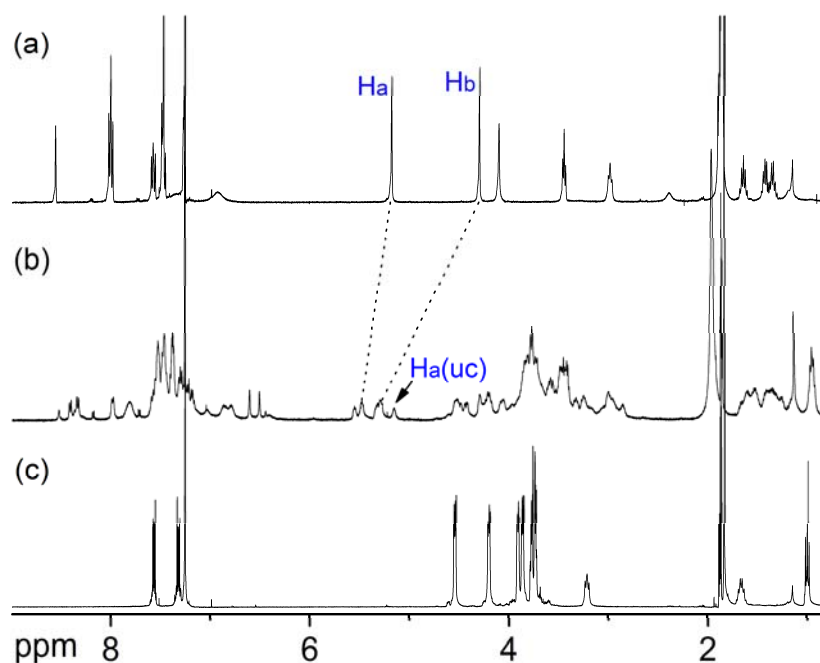


Figure S10. ^1H NMR spectra (500 MHz, 298 K, $\text{CDCl}_3:\text{CD}_3\text{CN} = 5:1$, 2.0 mM) of (a) $3\text{-}2\text{H}\cdot 2\text{PF}_6$, (c) **6**, and (b) 2:1 mixture of $3\text{-}2\text{H}\cdot 2\text{PF}_6$ and **6**. The “uc” in the parentheses denotes the signal from uncomplexed species. The NMR results suggest $25\text{-}4\text{H}\cdot 4\text{PF}_6$ is dominant in this solution since most of H_a on $3\text{-}2\text{H}\cdot 2\text{PF}_6$ experience complexation-induced shift after mixing with **6** in 2:1 ratio.

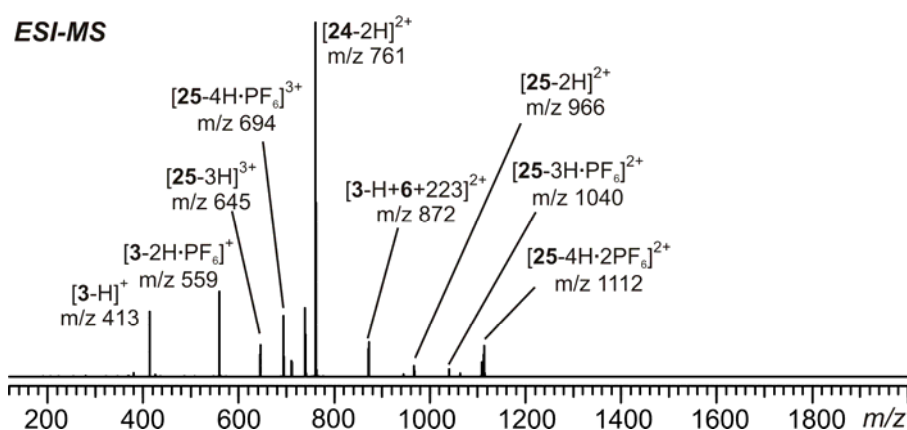


Figure S11. ESI-FTICR mass spectrum of 2:1 mixture of $3\text{-}2\text{H}\cdot 2\text{PF}_6$ and **6** (295 K, $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{CN} = 8:1$, 250 μM) under identical ionization condition as used for the kinetics study of $13\text{-}4\text{H}\cdot 4\text{PF}_6$. The mass spectrum shows a low intensity of $25\text{-}4\text{H}\cdot 4\text{PF}_6$ with a charge distribution from dication to tetracation. Some fragments (m/z 413, 559, and 872) are also observed. This is presumably derived from the instability (or metastability) of multiply charged ions of $25\text{-}4\text{H}\cdot 4\text{PF}_6$ in the gas phase, which fragment quickly after their generation in the ion source.