**Efficient Syntheses of π-Electron Deficient Macrocycles**

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**Supporting Information**

1. **General Methods**

All reagents and solvents were purchased from commercial sources and used without further purification. Compound **1**2+•2PF6─,S1 **3**,S2 **4**,S3 **5**,S4 **6**2+•2PF6-,S5 **7**2+•2PF6-,S6 **8**,S7 **9**,S8 **10**S9 were prepared according to literature procedures. Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature using Bruker AVANCE III 400/500 spectrometers, with working frequencies of 400/500 and 100/125 MHz for 1H and 13C, respectively. Chemical shifts are reported in ppm relative to the residual internal non-deuterated solvent signals (CD3CN: *δ =* 1.94 ppm; CDCl3: *δ =* 7.26 ppm). High-resolution mass spectra (HRMS) were recorded on an Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). UV/Vis/NIR absorption spectra were taken on a Cary Series UV-Vis-NIR spectrophotometer. X-ray crystallographic data were collected on a Bruker D8 Venture diffractometer. Isothermal titration calorimetry (ITC) experiments were performed on a MicroCal system, VP-ITC model.

1. **Synthetic Procedures**



**Scheme S1. Synthesis of 2**2+•2PF6─

**2**2+•2PF6─: A mixture of 4,4'-bipyridine (260.0 mg, 1.67 mmol) and 2-azidoethyl 4-methylbenzenesulfonate (1.612g, 6.69mmol) in DMF (10 mL) was stirred at 100 °C for 4d. The reaction mixture was then cooled to room temperature and the solvent was removed under vacuum. The solid was purified by means of flash column chromatography (1M NH4Cl in H2O/methanol/nitromethane (12:7:1); silica gel, 200-300 mesh). The organic components of solvent was removed, followed by adding NH4PF6 into the aqueous solution, which led to precipitation of white solid.. The solid-state sample was collected by filtration, yielding pure **2**2+•2PF6─ (880mg, 90%). **1H NMR** (400 MHz, CD3CN): δ = 8.91 (d, J = 6.0 Hz 4H), 8.41 (d, J = 6.0 Hz, 4H), 4.74 (t, J = 4.8 Hz, 4H), 4.00 (t, J = 4.8 Hz, 4H). **13C NMR** (100 MHz, CD3CN): δ = 150.1, 145.7, 126.8, 60.3, 49.8. HRMS-ESI for**2**2+•2PF6─, Calcd for C14H16F6N8P: *m/z* = 441.1129 [*M* – PF6]+; Found: 441.1143 [*M* – PF6]+.



**Scheme S2. Synthesis of M1**4+•4PF6─

**M1**4+•4PF6─: A mixture of **1**2+•2PF6─ (55 mg, 0.1 mmol) , **2**2+•2PF6─ (58 mg, 0.1mmol), Cu(CN)4PF6 (2mg,0.05mmol) and TBTA in acetone (100 mL) was stirred at room temperature under an N2 atmosphere for 8h. The solvent was then removed under vacuum. The resulting solid was purified by flash column chromatography (1M NH4Cl in H2O/methanol/nitromethane (12:7:1); silica gel, 200-300 mesh). After counteranion exchange, pure **M1**4+•4PF6─(46mg, 42%) was obtained as a white solid. **1H NMR** (400 MHz, CD3CN): δ = 8.81 (d, J = 6.0 Hz, 4H), 8.67 (d, J = 6.4 Hz, 4H), 8.26 (d, J = 6.0 Hz, 4H), 8.24 (d, J = 6.4 Hz, 4H), 7.84 (s, 2H), 5.13 (t, J = 7.2 Hz, 4H), 4.97 (t, J = 7.2 Hz, 4H), 4.94 (t, J = 6.4 Hz, 4H), 3.45 (t, J = 6.4 Hz, 4H). **13C NMR** (100 MHz, CD3CN): δ = 151.3, 151.0, 146.8, 146.3, 143.3, 128.1, 127.6, 125.5, 61.9, 61.8, 50.5, 27.0. HRMS-ESI for **M1**4+•4PF6─, Calcd for C32H32F12N10P2: *m/z* = 424.1128 [*M* – 2PF6]2+; Found: 424.1121 [*M* – 2PF6]2+.



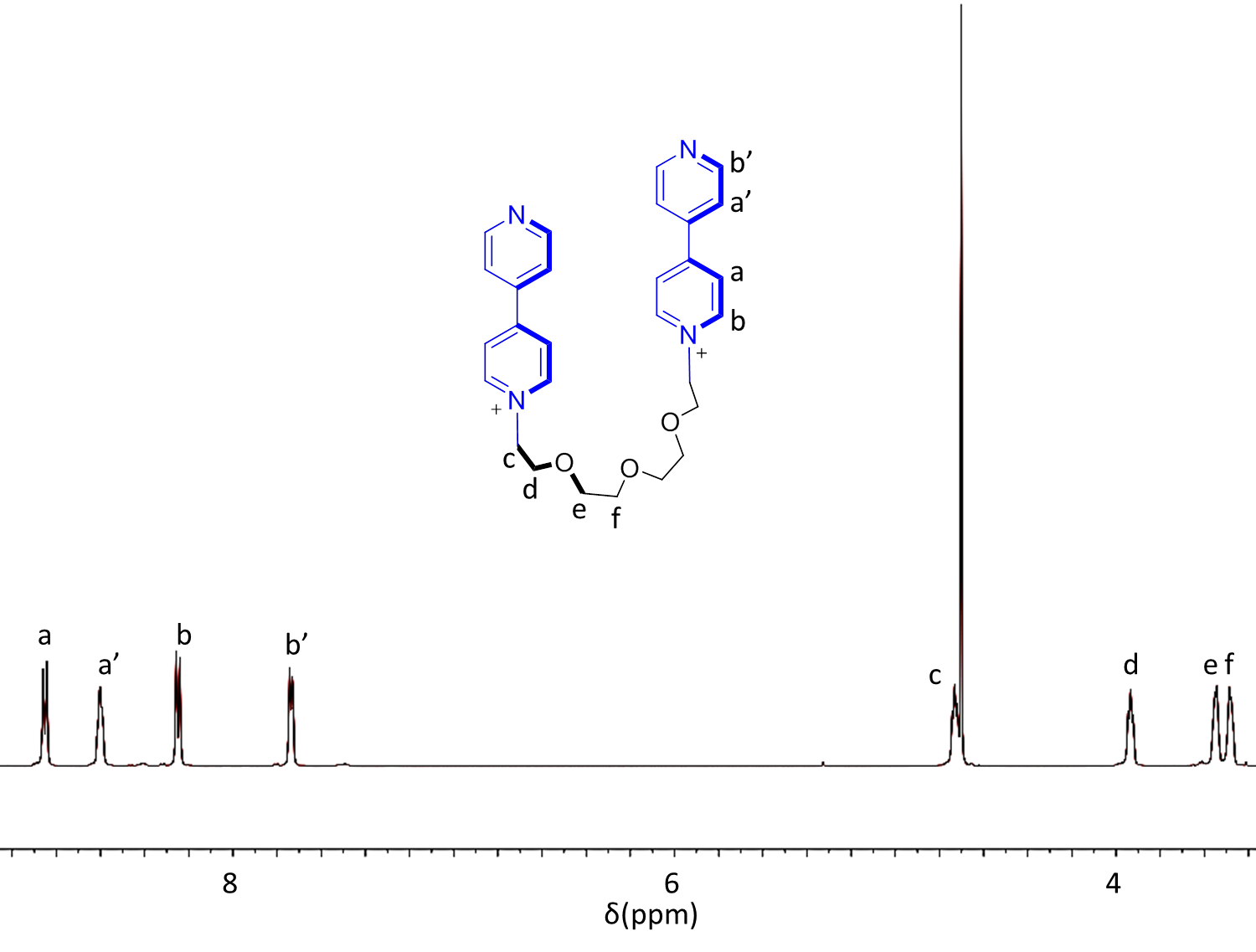
**Scheme S3.** Synthesis of **6**2+•2PF6-and **7**2+•2PF6-

**6**2+•2PF6-: To a solution of **8** (3.13 g, 8 mmol) in 100mL MeCN, 4,4'-bipyridine (5.0 g, 32 mmol) was added. The mixture was heated and reflux for 72 h. After cooling to room temporature, 150 mL ethyl ether was added into reaction mixture to give a yellow precipitation, which was collected by filtration and washed with ethyl ether and CH2Cl2. The solid was dissolved in water, and then NH4PF6 was added, which yielded white precipitates. The resulting precipitates was collected and washed with water. The crude product was purified by silica gel chromatography (eluent: aqueous NH4Cl solution/MeOH/MeNO2 = 12/7/1, v/v). After counteranion exchange, **6**2+•2PF6 (3.96g, 65%) was obtained as a pure white solid. 1H NMR(400MHz, CD3CN) δ 8.84 (d, *J* = 4.8Hz, 4H), 8.74 (d , *J* = 6.0Hz, 4H), 8.29 (d, *J* = 6.0 Hz, 4H), 7.77 (d, J = 4.8 Hz, 4H), 4.67 (t, *J* = 4.8 Hz, 4H), 3.90 (t, *J* = 4.8Hz, 4H), 3.56 (s，4H).



**Figure S1.** 1H NMR spectrum (400 MHz, CD3CN, 298 K) of **6**2+•2PF6-.

**7**2+•2PF6 was obtained in 61% yield, using a similar procedure as **7**2+•2PF6, except that **9** was used in the reaction. 1H NMR (400 MHz, CD3CN) δ 8.85 (d, *J* = 6.8Hz, 4H), 8.60 (br, 4H), 8.25(d, *J* = 6.8Hz, 4H), 7.74 (d, *J* = 4.8Hz, 4H), 4.73 (t, *J* = 4.8Hz, 4H), 3.93 (t, *J* = 4.8Hz, 4H), 3.55 (t, *J* = 2.0Hz, 4H), 3.48 (t, *J* = 2.0Hz, 4H)

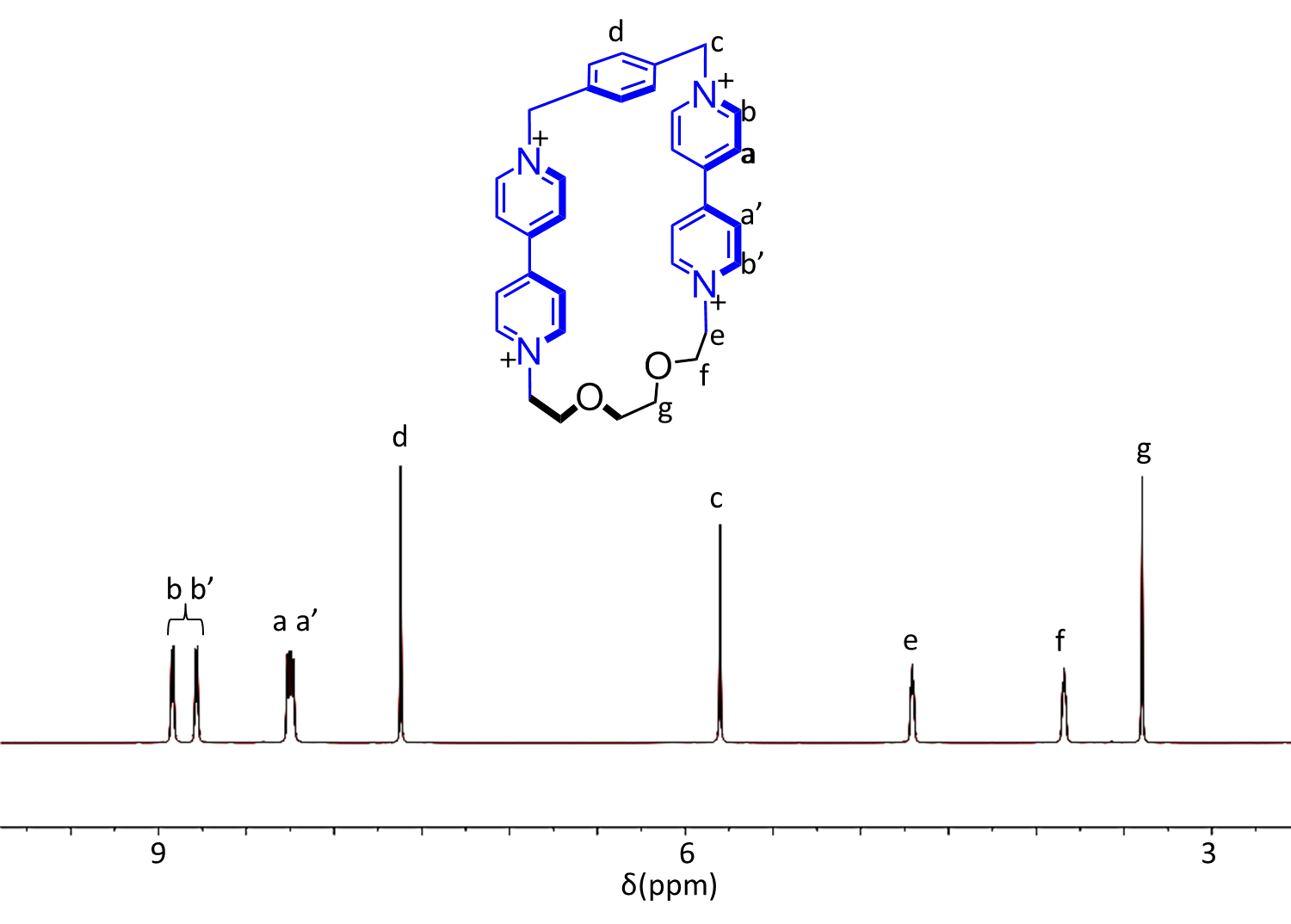


**Figure S2.** 1H NMR spectrum (400 MHz, CD3CN, 298 K) of **7**2+•2PF6-.

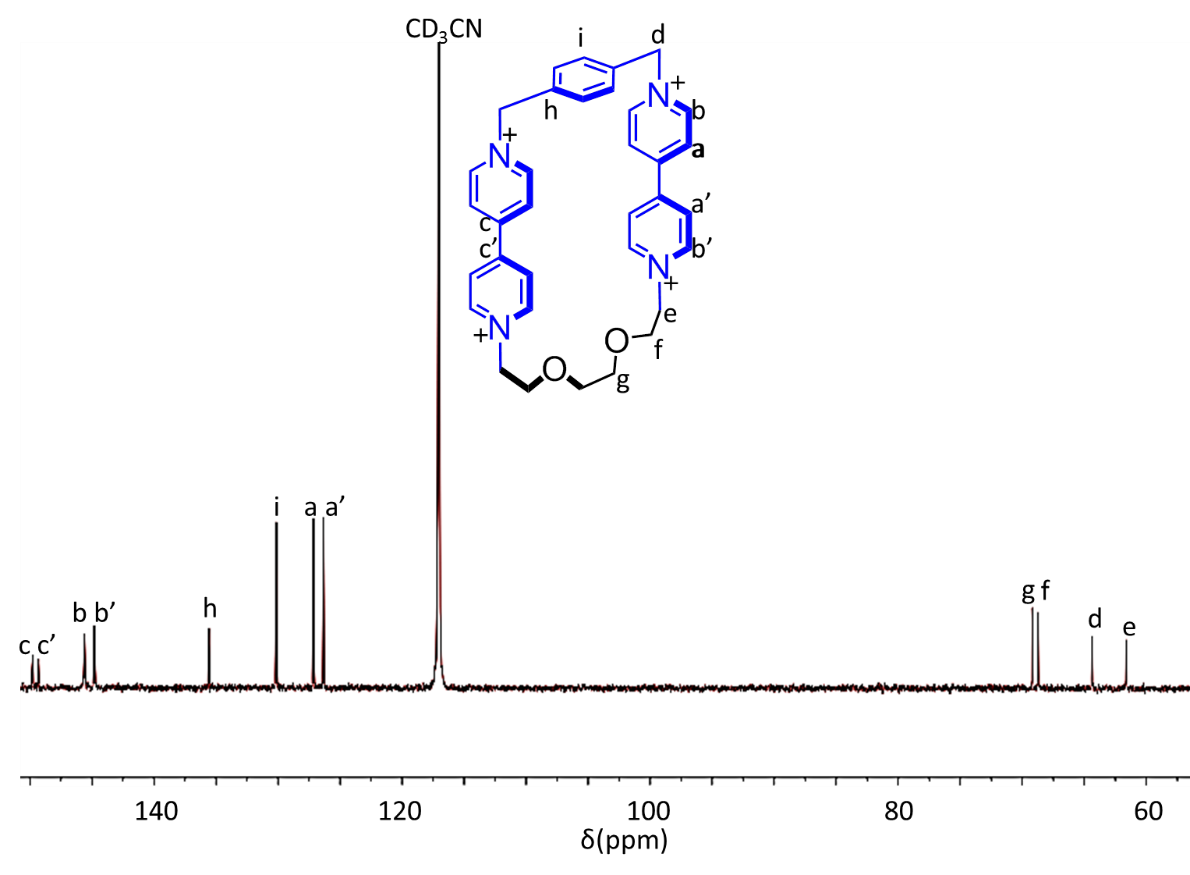


**Scheme S4.** Synthesis of **M2**4+•4PF6- **and M3**4+•4PF6-

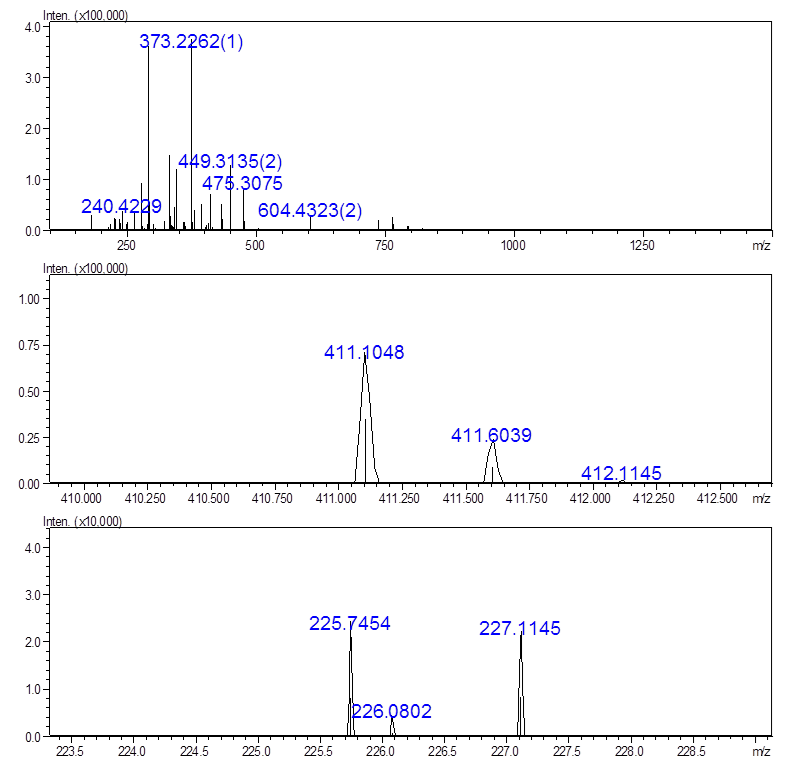
**M2**4+•4PF6-:Compound **6**2+•2PF6-(402 mg, 0.56 mmol) and 1,4-bis(bromomethyl)benzene (170 mg, 0.65 mmol) were stirred in MeCN (150 ml) at room temperature for 7 days. Excess amount of tetrabutylammonium chloride was added to the reaction mixture, yielding yellow precipitates. These solids were collected and purified by column chromatography. After counteranion exchange, pure **6**2+•2PF6- was obtained (36 mg, 8.4%). 1H NMR (400 MHz, CD3CN) δ 8.92(d, 4H, *J* = 6.5 Hz), 8.78 (d, 4H, *J* = 6.5 Hz), 8.25 (m, 8H), 7.62 (s, 4H), 5.80 (s, 4H), 4.71 (t, 4H, *J* = 4.5 Hz), 3.84 (t, 4H, *J* = 4.5 Hz). 13C NMR (100 MHz, CD3CN) δ 149.8, 149.3, 145.6, 145.8, 135.7, 130.1, 127.1, 126.3, 117.0, 69.2, 36.7, 64.4, 61.6. MS (ESI-HRMS) calcd for C34H36N4O24+•2PF6-: *m/z* = 411.1055 [*M* + 2 PF6] 2+, found *m/z* = 411.1048; calcd for C34H36N4O24+•PF6-: *m/z* = 225.7488 [*M* + PF6] 3+, found *m/z* = 225.7454.



**Figure S3.** 1H NMR spectrum (400 MHz, CD3CN, 298 K) of **M2**4+•4PF6-.

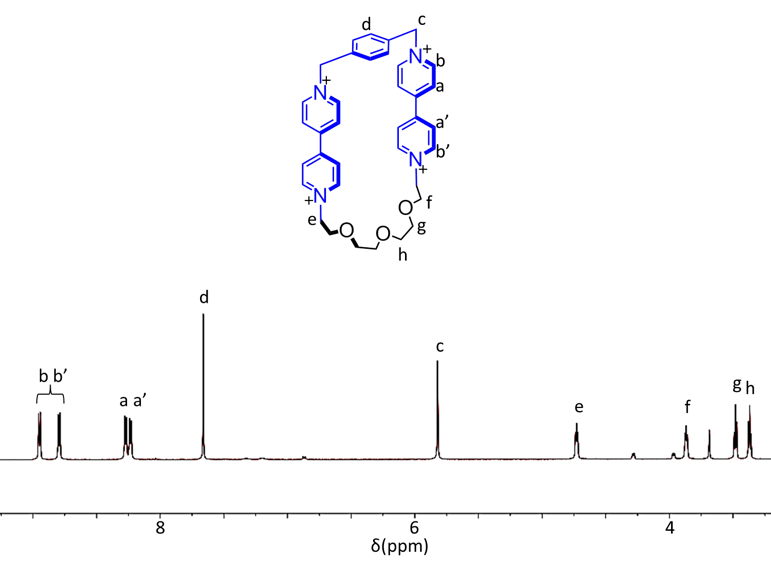


**Figure S4.** 13C NMR spectrum (100 MHz, CD3CN, 298 K) of **M2**4+•4PF6-.

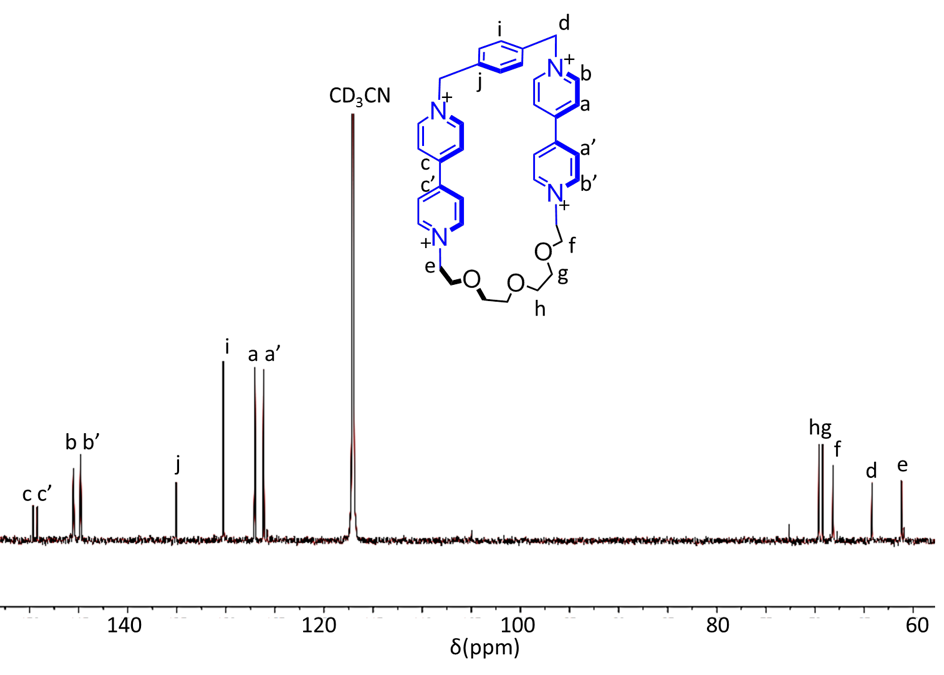


**Figure S5.** ESI-HRMS of **M2**4+•4PF6-.

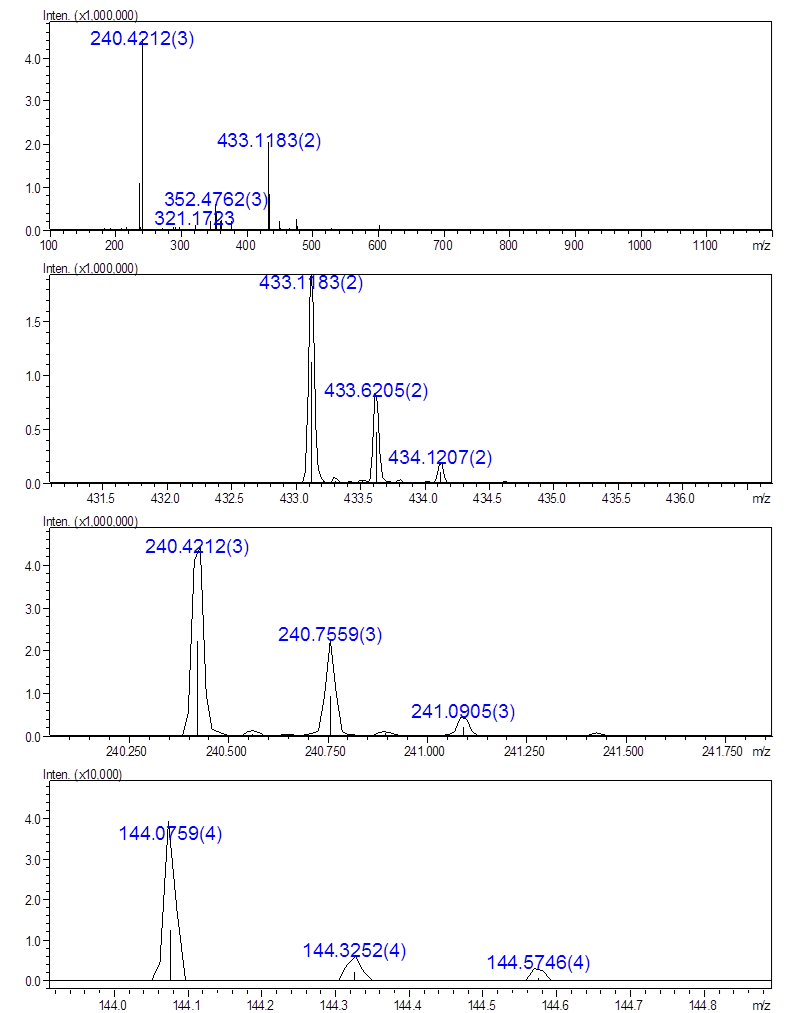
**M3**4+•4PF6- was prepared in 14 % yield in a similar procedure as that of **M3**4+•4PF6-,expect that **7**2+•2PF6- was used in the reaction. 1H NMR (400 MHz, CD3CN) 8.94 (s, 4H), 8.78 (d, *J* = 4.3Hz ,4H), 8.25 (d, *J* = 10.3Hz, 8H), 7.65 (s, 4H), 5.81 (s, 4H), 4.72 (t, 4H), 3.86 (s, 4H), 3.47 (s, 4H), 3.37 (s, 4H). 13C NMR(100MHz, CD3CN) δ 169.7, 169.2, 145.5, 144.8, 135.1, 130.3, 127.1, 126.2, 117.1, 69.6, 69.2, 68.2, 64.2, 61.2. MS (ESI-HRMS) calcd for : *m/z* = 433.12 [*M* + 2 PF6] 2+, found *m/z* = 433.1183; calcd for *m/z* = 240.42 [*M* + PF6] 3+, found *m/z* = 240.4212; calcd for *m/z* = 144.08 [*M*] 4+, found *m/z* = 144.0759.



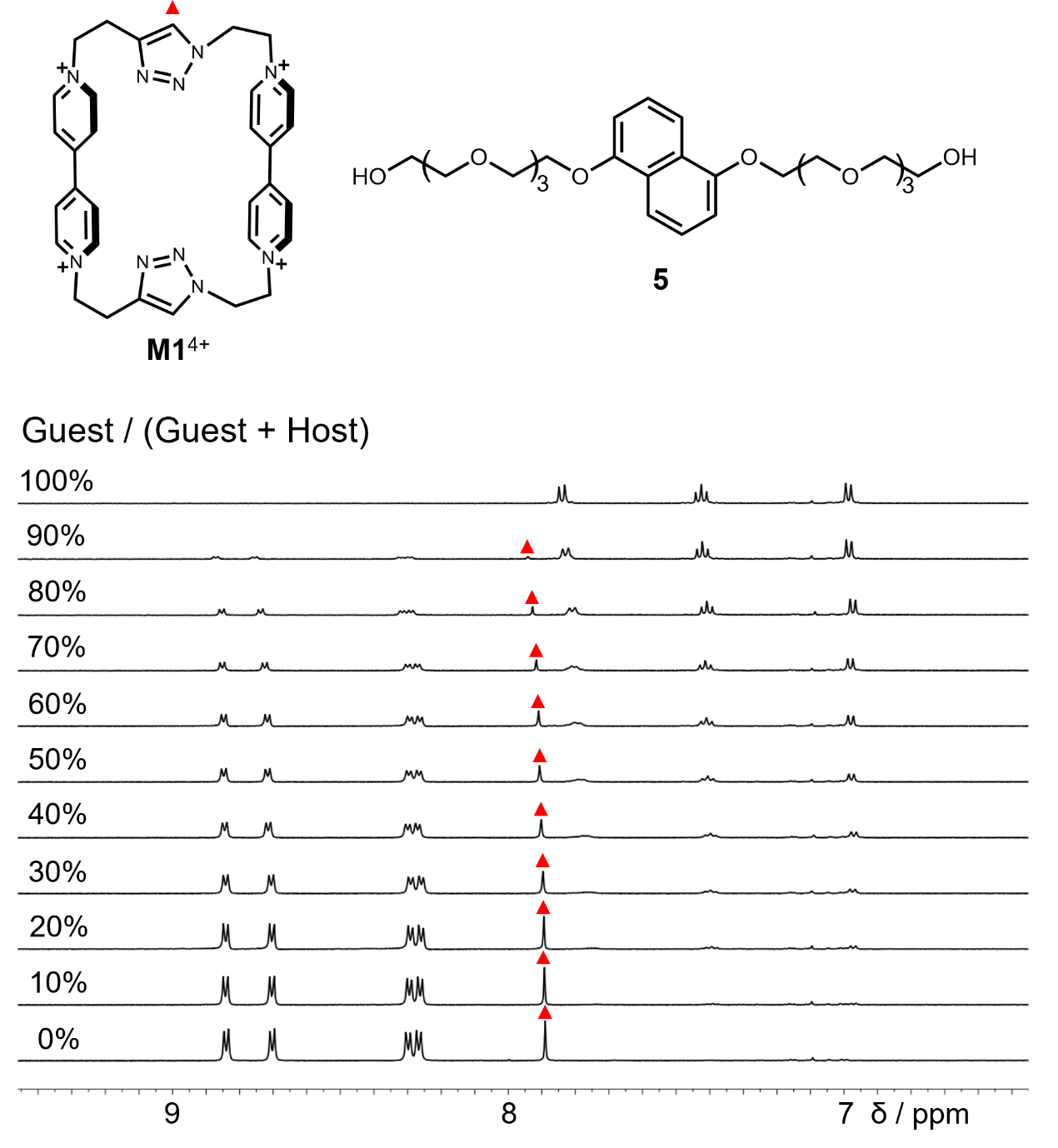
**Figure S6.** 1H NMR spectrum (400 MHz, CD3CN, 298 K) of **M3**4+•4PF6-.



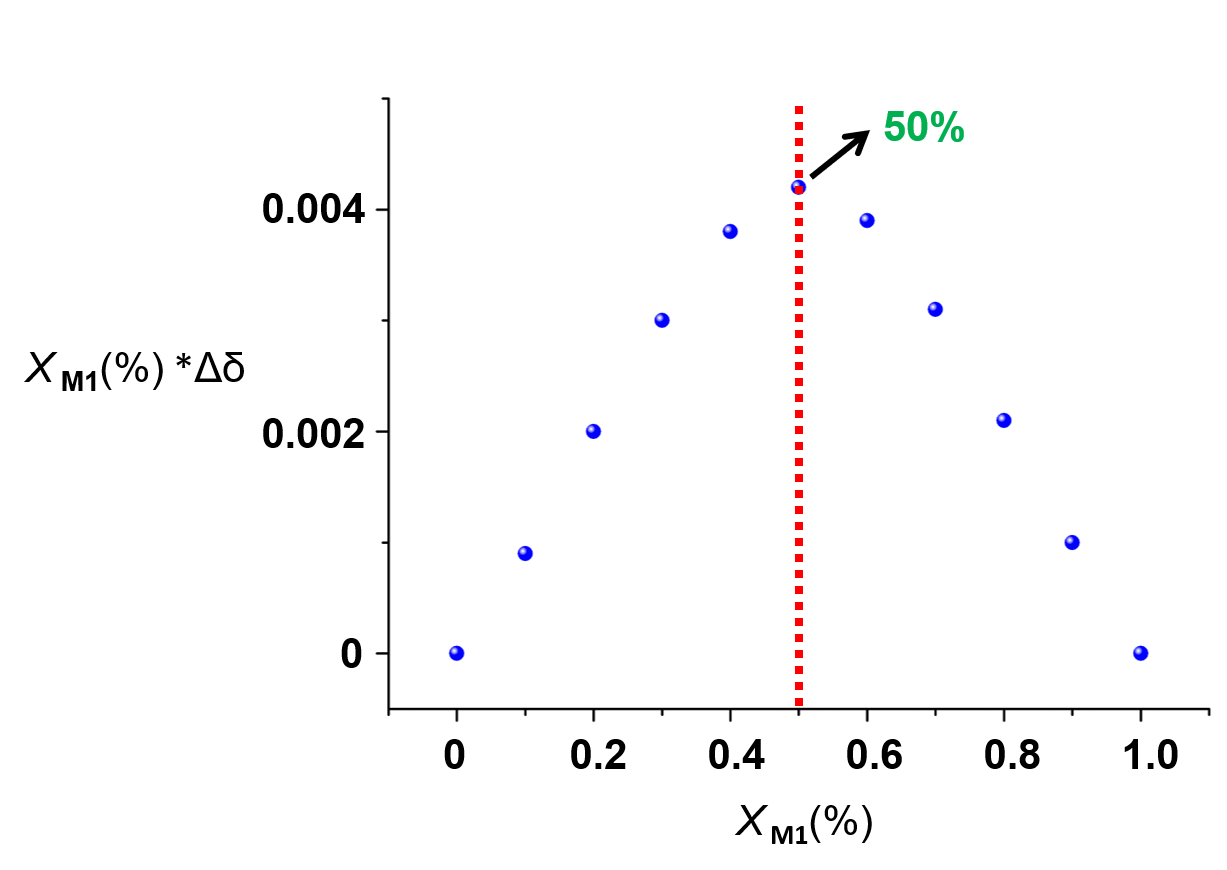
**Figure S7.** 13C NMR spectrum (100 MHz, CD3CN, 298 K) of **M3**4+•4PF6-.



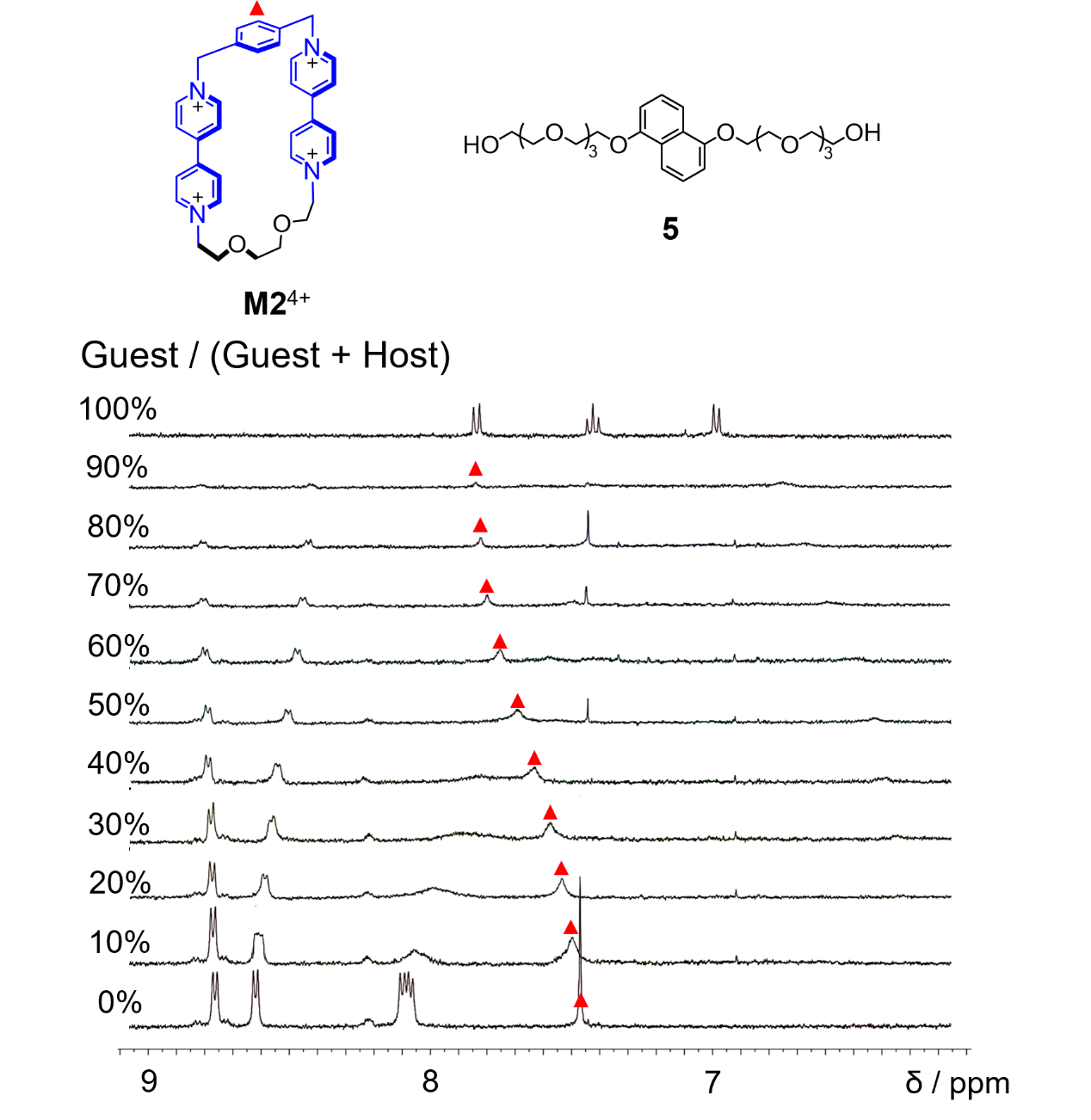
**Figure S8.** ESI-HRMS of **M3**4+•4PF6-.



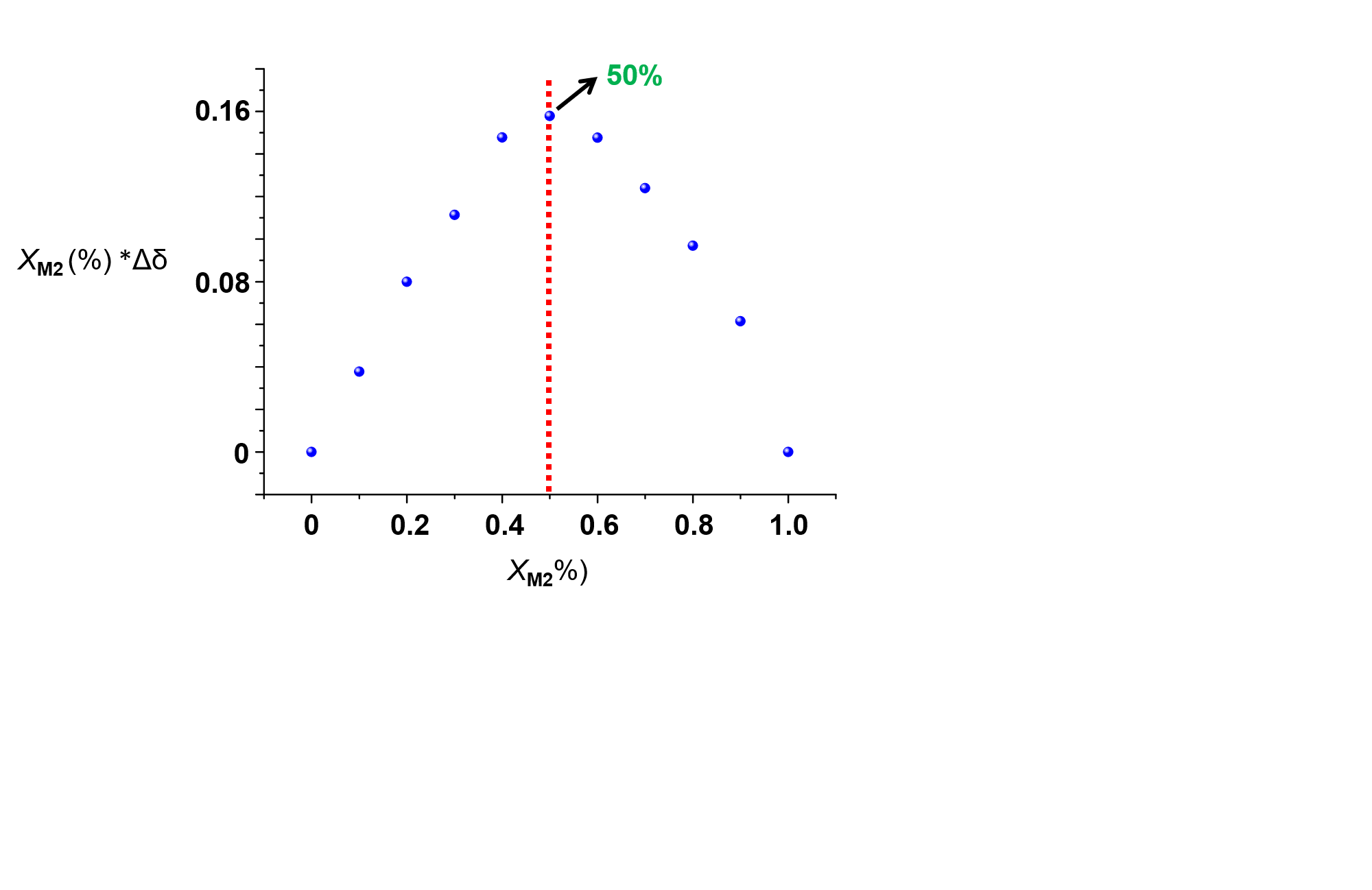
**Figure S9.** 1H NMR spectra (400 MHz, CD3CN, 298 K) of a mixture of **M1**4+•4PF6- and **5** with different ratios of [**5**]/([**5**]+[**M1**4+]). The chemical shifts of the resonances, which are labeled with red triangles, are used to make the job plot. [**5**]+[**M1**4+] is kept constant, which is 1 mM.



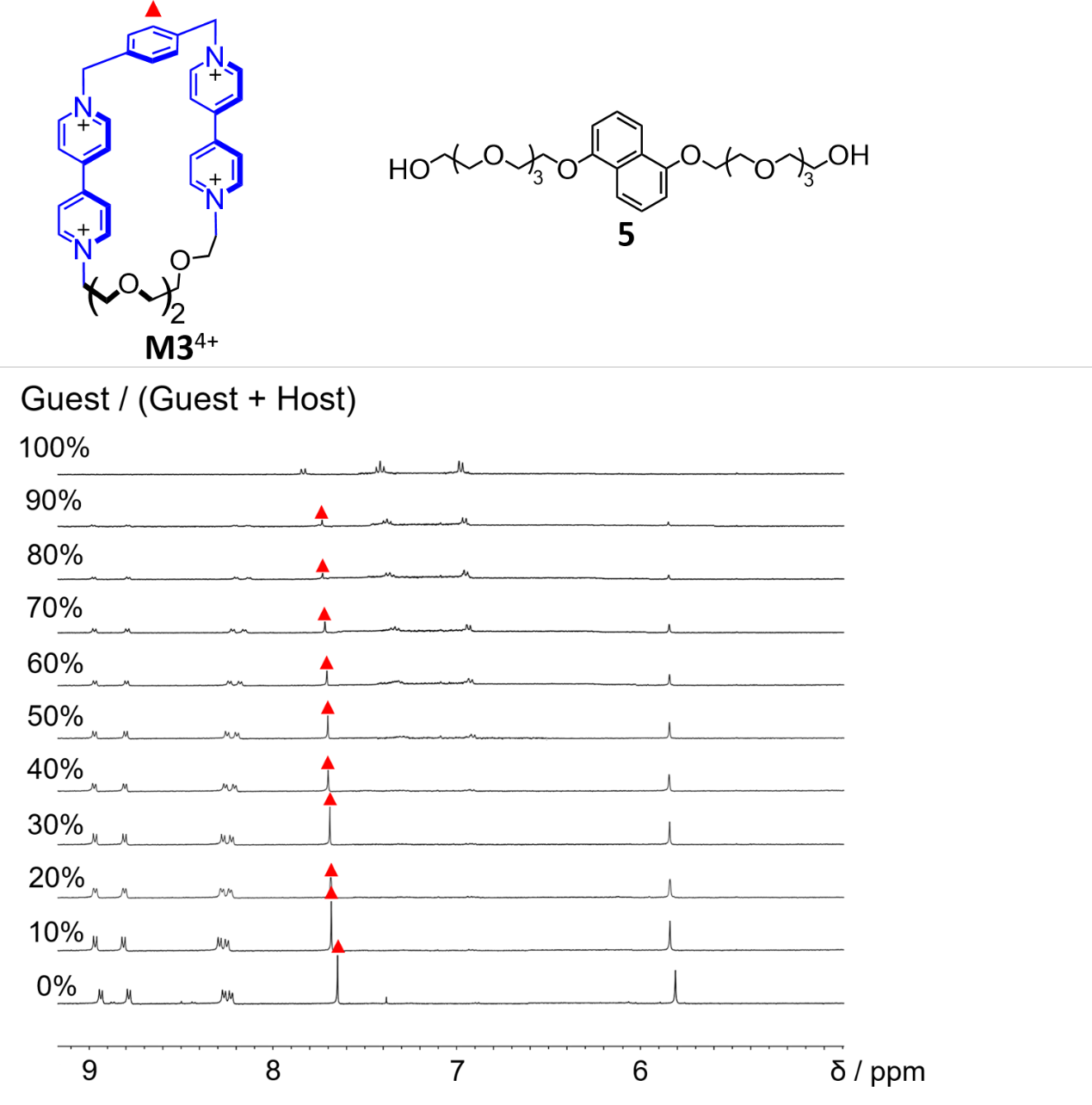
**Figure S10.** Job plot of **5** ⊂**M1**4+•4PF6-, indicating a 1:1 binding model, which is obtained from the data in Figure S9.



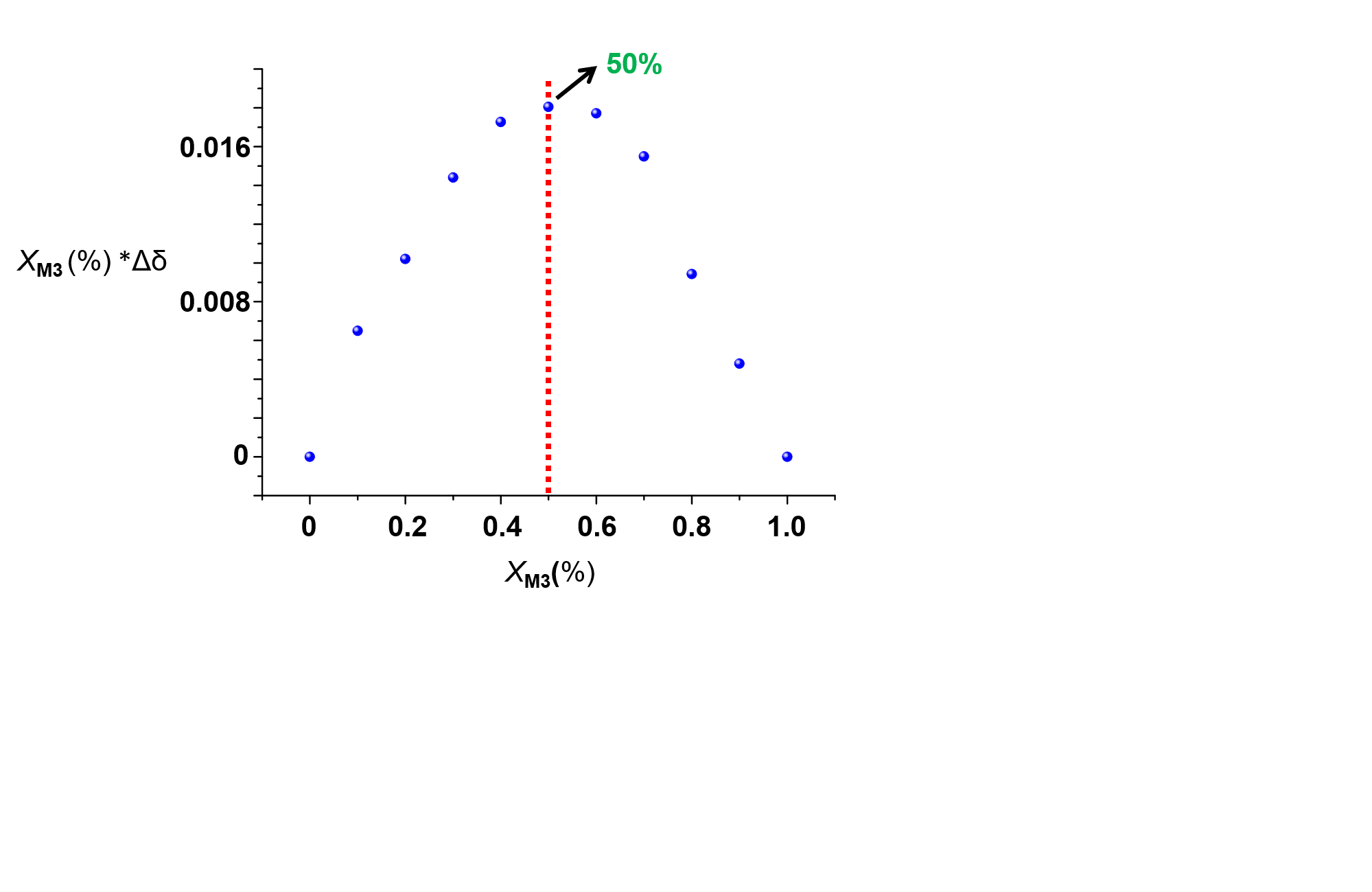
**Figure S11.** 1H NMR spectra (400 MHz, CD3CN, 298 K) of a mixture of **M2**4+•4PF6- and **5** with different ratios of [**5**]/([**5**]+[**M2**4+]). The chemical shifts of the resonances, which are labeled with red triangles, are used to make the job plot. [**5**]+[**M2**4+] is kept constant, which is 1 mM.



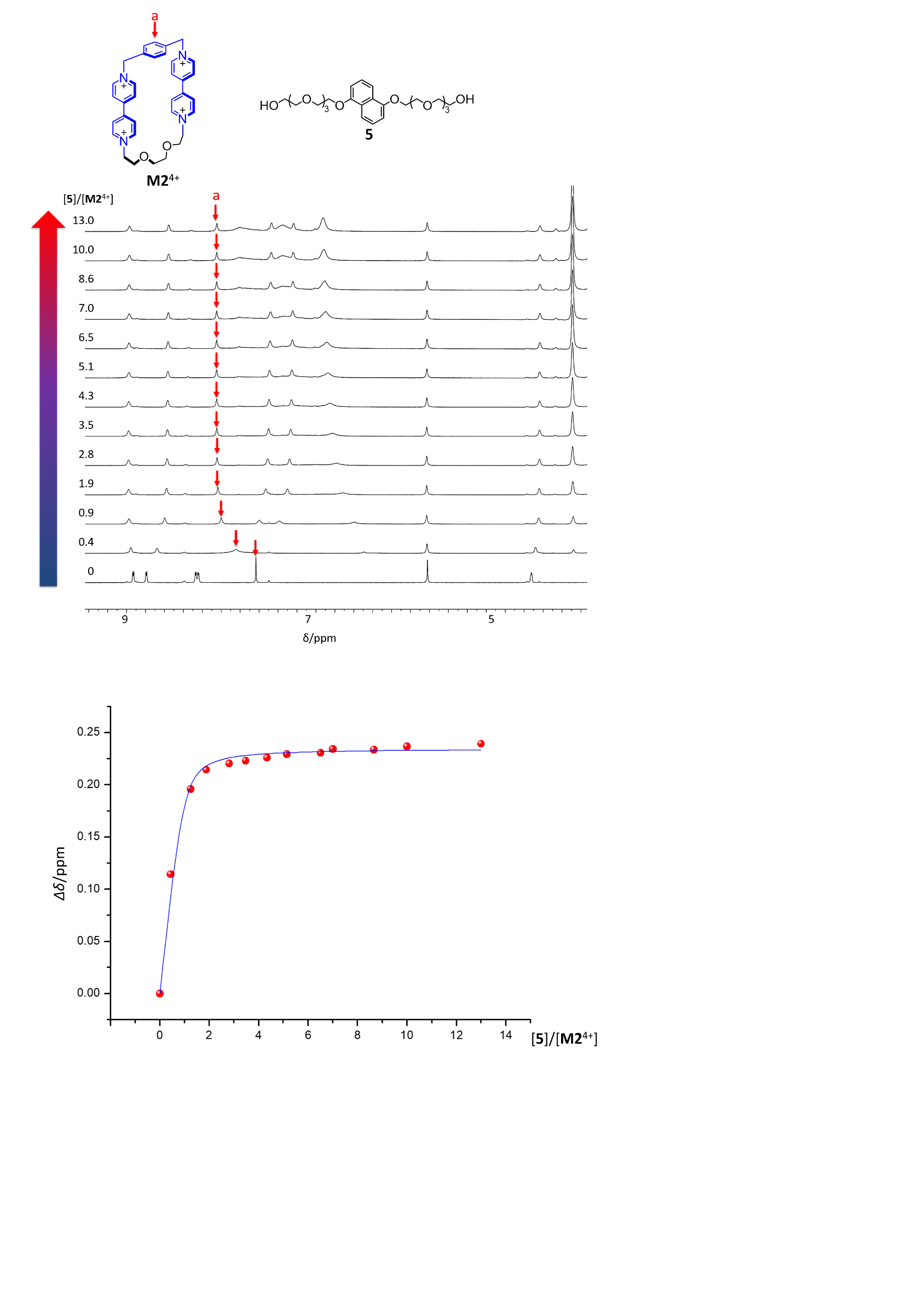
**Figure S12.** Job plot of **5** ⊂**M2**4+•4PF6-, indicating a 1:1 binding model, which is obtained from the data in Figure S11.



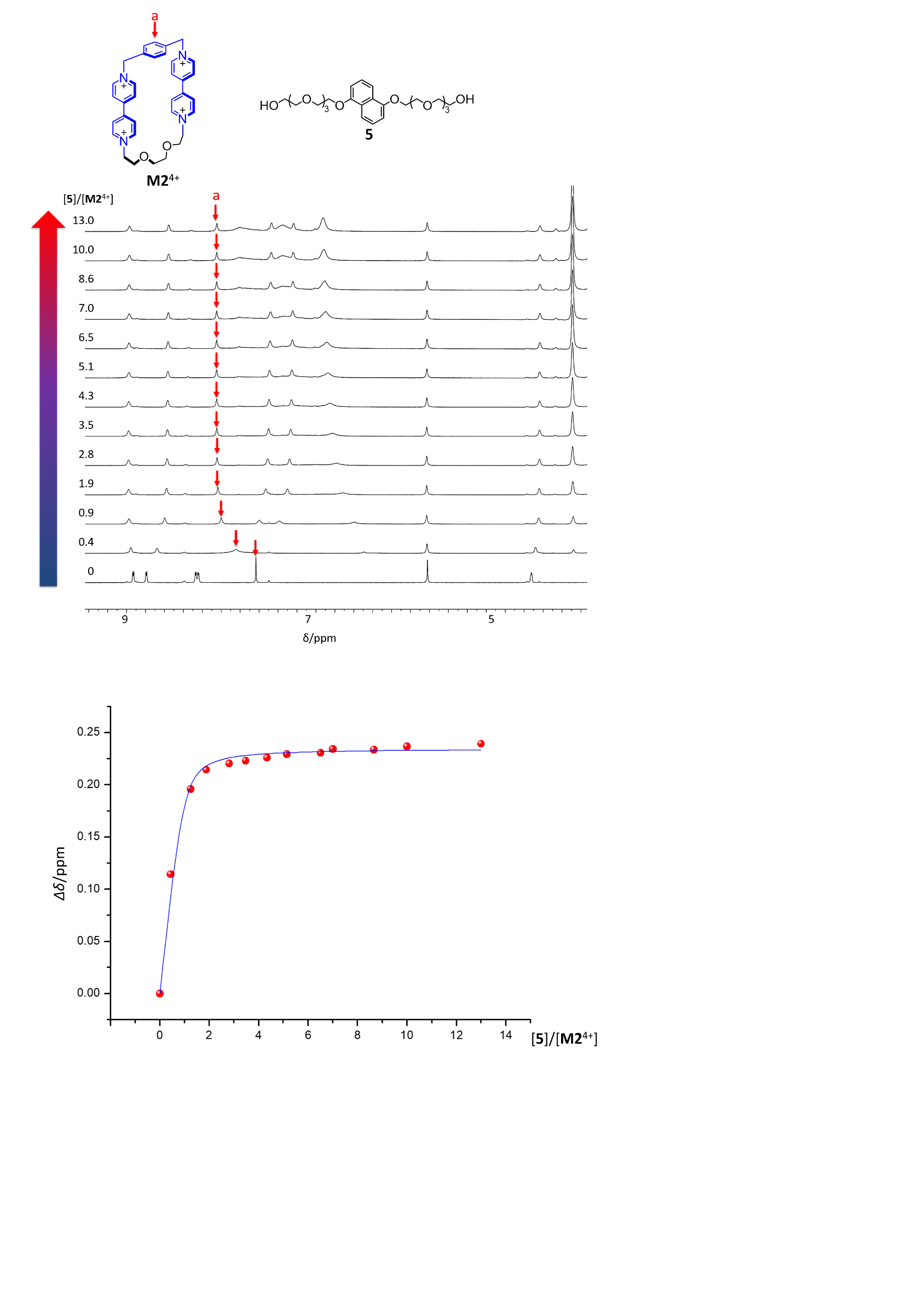
**Figure S13.** 1H NMR spectra (400 MHz, CD3CN, 298 K) of a mixture of **M3**4+•4PF6- and **5** with different ratios of [**5**]/([**5**]+[**M3**4+]). The chemical shifts of the resonances, which are labeled with red triangles, are used to make the job plot. [**5**]+[**M3**4+] is kept constant, which is 1 mM.



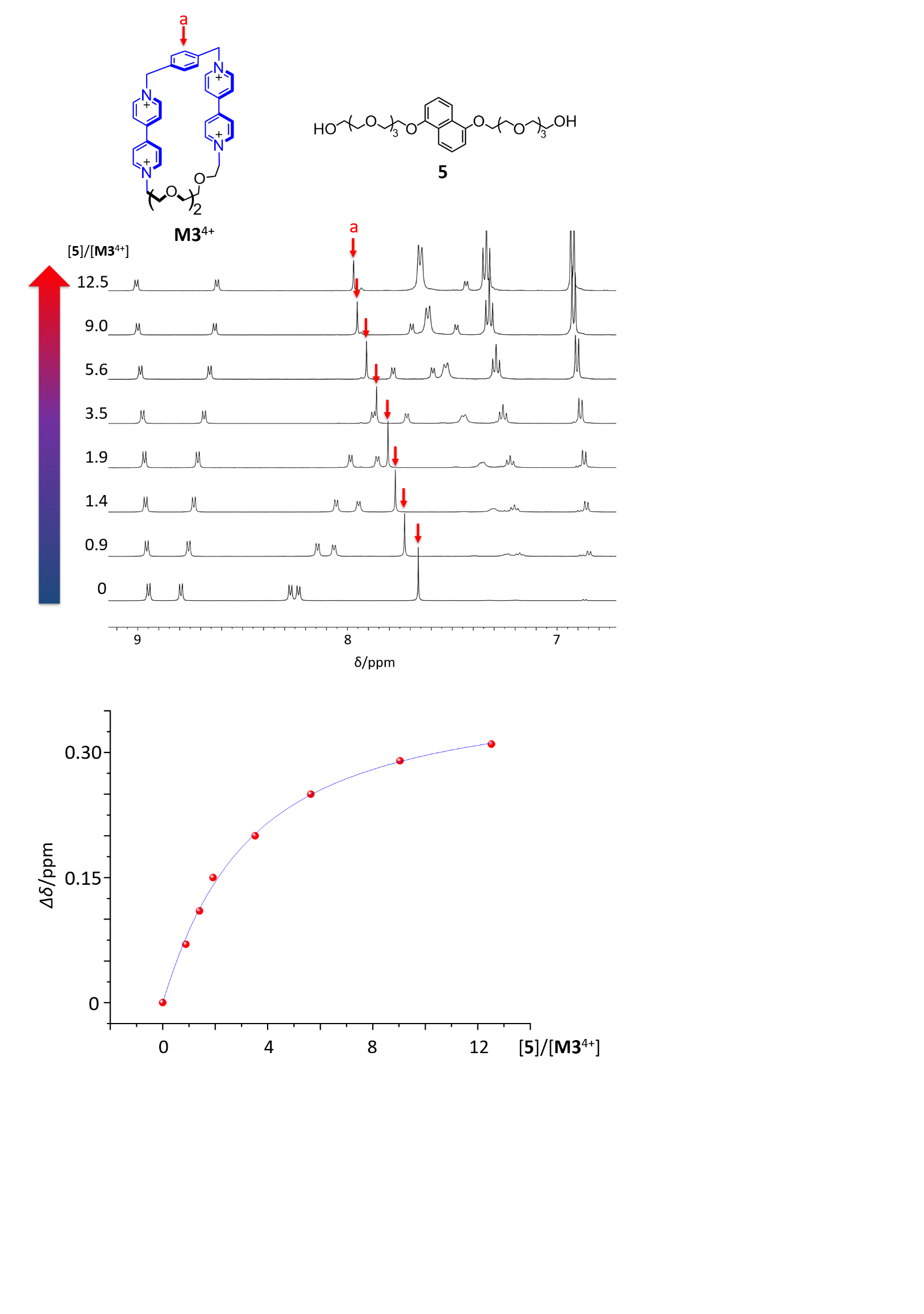
**Figure S14.** Job plot of **5** ⊂**M3**4+•4PF6-, indicating a 1:1 binding model, which is obtained from the data in Figure S13.



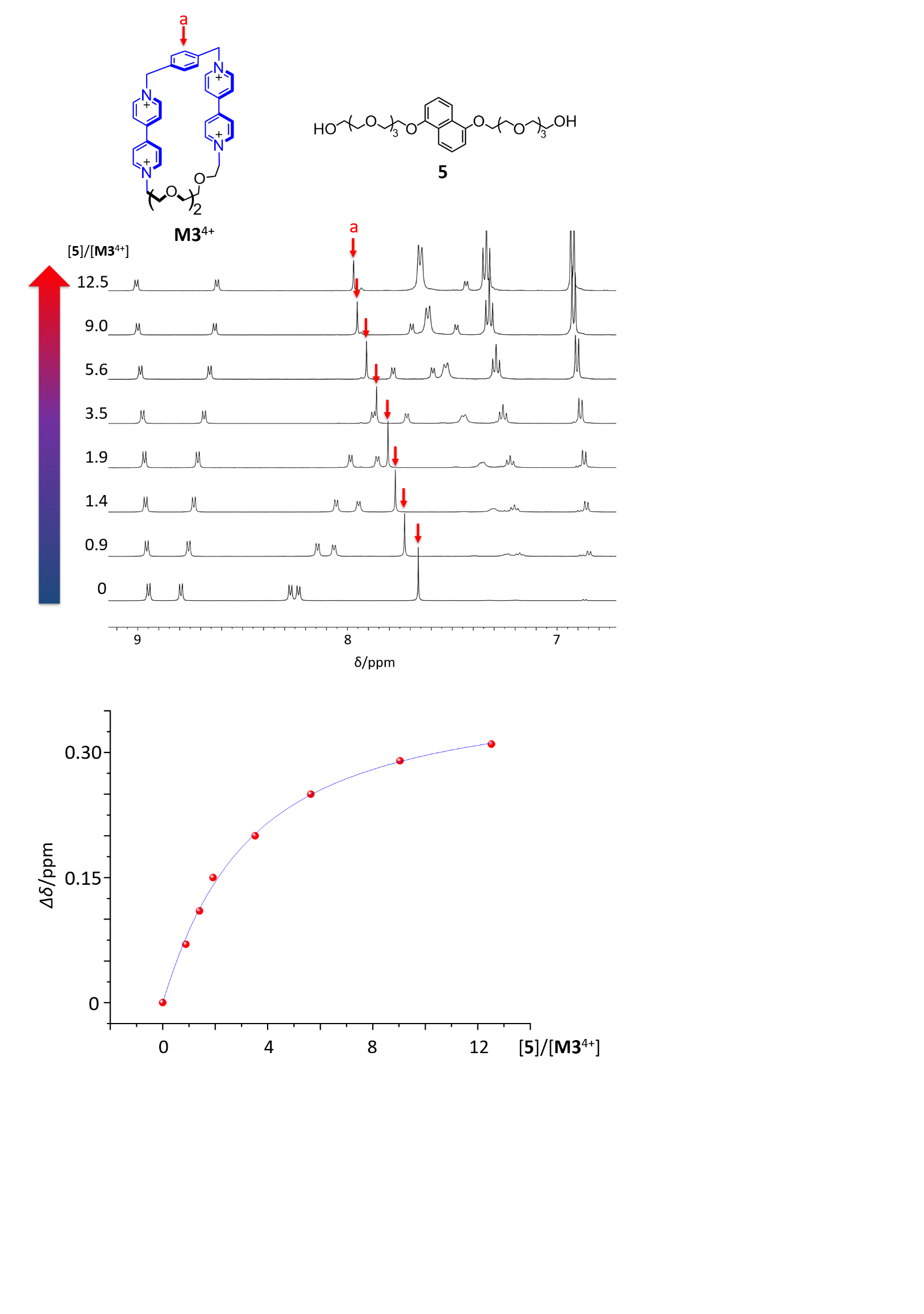
**Figure S15**. 1H NMR spectrum (500 MHz, CD3CN, 298 K) of **M2**4+•4PF6− (1.9 mM) when titrated with **5** at 25 oC. The shifts of the resonances labeled with red arrows are used to make the plot for calculating the binding constant of **5** ⊂**M2**4+.



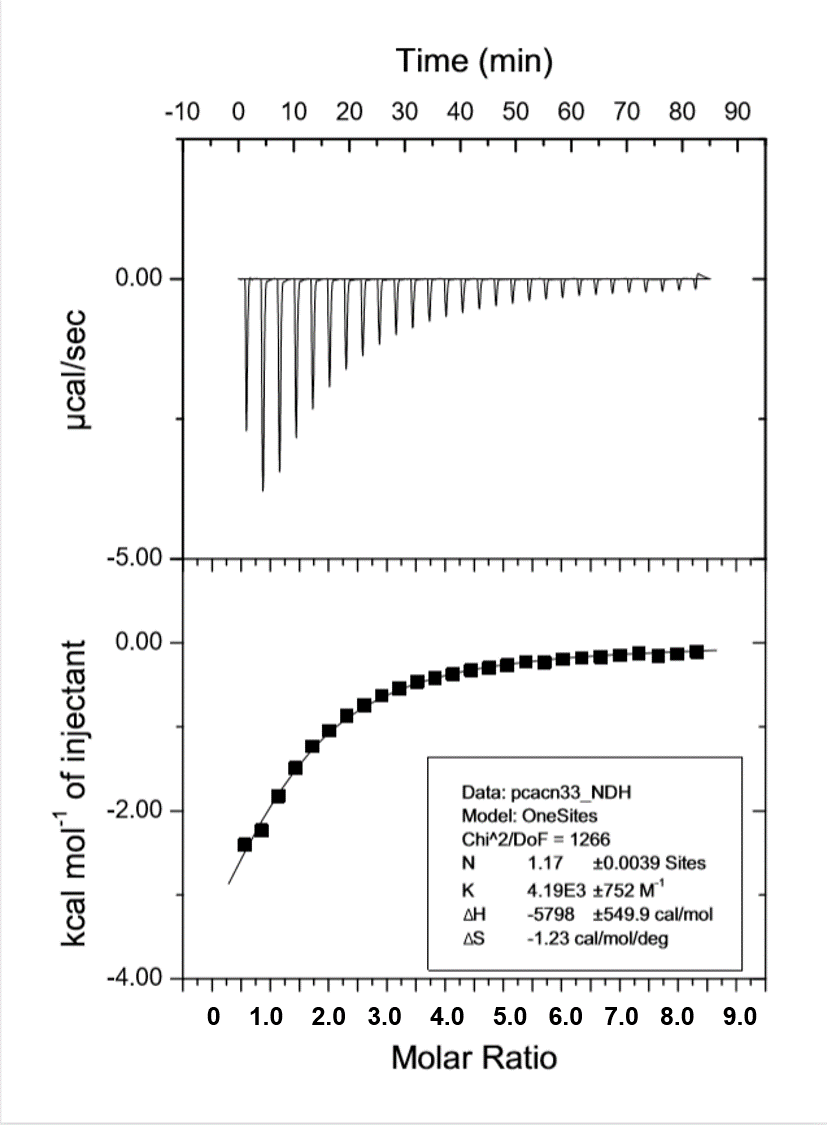
**Figure S16.** The plot of the resonance shifts based on the corresponding 1H NMR spectra in Figure S15. Binding constant is determined to be 7.14 ± 0.23 × 103 M-1.



**Figure S17**. 1H NMR spectrum (500 MHz, CD3CN, 298 K) of **M3**4+•4PF6− (1.7mM) when titrated with **5** at 25 oC. The shifts of the resonances labeled with red arrows are used to make the plot for calculating the binding constant of **5** ⊂**M3**4+.



**Figure S18.** 1H NMR spectra (500 MHz, CD3CN, 298 K) of **M3**4+•4PF6− (1.7mM) upon addition of different amount of **5**. Plot of the downfield shifts (Δδ) of the resonance of proton a (marked by red arrows in spectra). Binding constant is determined to be 5.90 ± 1.0 × 102 M-1.



**Figure S19**. ITC (Isothermal Titration Calorimetry) experiments to calculate the binding constant of the complex **5** ⊂ **M2**4+•4PF6. The Ka for the complex was determined to be 4.19 ± 0.75 × 103 M−1 in CH3CN, which was consistent with that determined by NMR titration experiment.ΔH and ΔS were determined to be −5.78 ± 0.55 × 103 cal·mol−1 and −1.23 cal·mol−1·K−1, respectively.

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