

Electronic Supplementary Material

Coordination Molecular Hats Binding an Acetonitrile via C–H··· π Interactions

Li-Xia Liu,^a Hai-Ping Huang,^a Xin Li,^a Qing-Fu Sun,^a Cui-Rong Sun,^b Yi-Zhi Li^c and
Shu-Yan Yu^{*a}

^aLaboratory for Self-Assembly Chemistry, Department of Chemistry, Renmin University of China, Beijing 100872, P. R. China. Fax: (+86)10-6251-6614; Tel: (+86)10-6251-6614; E-mail: yusy@chem.ruc.edu.cn

^bDepartment of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China.

^cState Key Laboratory of Coordination Chemistry, Institute of Coordination Chemistry, Nanjing University, Nanjing, 210093, P. R. China.

*To whom correspondence should be addressed. E-mail: yusy@chem.ruc.edu.cn

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Experimental Section

Materials and Instruments: 1,10-phenanthroline (phen) and potassium hexafluorophosphate (99%) were purchased from ACROS ORGANICS and used without further purification. All other chemicals and solvents were of reagent grade and were purified according to conventional methods. ^1H and ^{13}C NMR experiments were performed on a Bruker Avance DMX400 spectrometer using TMS as internal standard. ESI-MS measurements were recorded with HP5989B mass spectrometer.

X-ray Structural Determinations: X-ray diffraction measurements were carried out at 291 K on a Bruker Smart Apex CCD area detector equipped with a graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The absorption correction for all complexes was performed using SADABS. All the structures were solved by direct methods and refined employing full-matrix least-squares on F2 by using SHELXTL (Bruker, 2000) program and expanded using Fourier techniques. All non-H atoms of the complexes were refined with anisotropic thermal parameters. The hydrogen atoms were included in idealized positions.

Synthesis:

[Pd₃(C5-phen)₃L₃](NO₃)₃ (1): [Pd(phen-crown-5)](NO₃)₂ (60.1 mg, 0.1 mmol) was added to a suspension of naphthanoimidazole (Nz) (16.8 mg, 0.1 mmol) in H₂O (5 mL), and the mixture was stirred for 2 h at room temperature. The resulting clear yellow solution was evaporated to dryness to give a yellow solid. Pure **1** as a microcrystalline yellow solid was obtained by the vapor diffusion of diethyl ether into a 2 mM solution of **1** in methanol at room temperature. Yield: 69.9 mg (99%). ^1H NMR (400 MHz, D₂O/[D₆]acetone = 1:2, 25 °C, TMS, ppm): $\delta = 9.72$ (s, 3 H, Nz-H₂), 9.21 (d, $J = 8.4$ Hz, 6 H; phen-H_{2,9}), 8.75 (s, 6 H, Nz-H_{4,9}), 8.50 (d, $J = 4.8$ Hz, 6 H; phen-H_{4,7}), 8.00 (m, 6H; phen-H_{3,8}), 7.72 (m, 6 H, Nz-H_{5,8}), 7.19 (m, 6 H, Nz-H_{6,7}), 4.70 (m, 12H;OCH₂), 4.19 (m, 12H; CH₂O), 3.88 (m, 12H;OCH₂), 3.83 (m, 12H; CH₂O). ESI-MS (methanol): m/z 996.7 [**1** - 2NO₃⁻]²⁺, 643.8 [**1** - 3NO₃⁻]³⁺. The PF₆⁻ salt of **1** (**1a**) was obtained by adding a ten-fold excess of KPF₆ to its aqueous solution at 333 K, which resulted in the immediate deposition of **1a** as yellow microcrystals in quantitative yield. The crystals were filtered, washed with minimum amount of cold water and dried under vacuum. ^1H NMR (400 MHz, CD₃CN, 25 °C, TMS, ppm): $\delta = 9.06$ (d, $J = 8.4$ Hz, 6 H; phen-H_{2,9}), 9.05 (s, 3 H, Nz-H₂), 8.59 (s, 6 H, Nz-H_{4,9}), 8.27 (d, $J = 5.2$ Hz, 6 H;

phen-H_{4,7}), 7.83 (dd, $J = 5.2$ Hz, $J = 8.4$, 6H; phen-H_{3,8}), 7.73 (dd, $J = 3.2$ Hz, $J = 6.4$ Hz, 6 H, Nz-H_{5,8}), 7.19 (dd, $J = 3.1$ Hz, $J = 6.5$ Hz, 6 H, Nz-H_{6,7}), 4.61 (m, 12H;OCH₂), 4.08 (m, 12H; CH₂O), 3.78 (m, 12H;OCH₂), 3.71 (m, 12H; CH₂O). ¹³C NMR (400 MHz, CD₃CN, 25 °C, TMS, ppm): δ 153.9, 150.6, 145.1, 143.8, 140.6, 136.1, 130.4, 128.3, 127.5, 125.8, 124.5, 113.7, 74.9, 70.6, 70.0. ESI-MS (acetonitrile): m/z 1038.2 [**1a** – 2 PF₆⁻]²⁺, 643.8 [**1a** – 3 PF₆⁻]³⁺.

[Pd₃(C6-phen)₃L₃](NO₃)₃ (2): The same procedure as employed for **1** was followed except that [Pd(phen-crown-6)](NO₃)₂ (64.5 mg, 0.1 mmol) and Nz (16.8 mg, 0.1 mmol) was used as the starting material. Pure **2** as a microcrystalline yellow solid was obtained by the vapor diffusion of diethyl ether into a 2 mM solution of **2** in methanol at room temperature. Yield: 74.3 mg (99%). ¹H NMR (400 MHz, [D₆]Acetone/D₂O=2:1, 25 °C, TMS, ppm): δ = 9.74 (s, 3 H, Nz-H₂), 9.22 (d, $J = 8.4$ Hz, 6 H; phen-H_{2,9}), 8.75 (s, 6 H, Nz-H_{4,9}), 8.50 (d, $J = 4.8$ Hz, 6 H; phen-H_{4,7}), 8.00 (m, 6H; phen-H_{3,8}), 7.73 (m, 6 H, Nz-H_{5,8}), 7.18 (m, 6 H, Nz-H_{6,7}), 4.71 (m, 12H;OCH₂), 4.15 (m, 12H; CH₂O), 3.86 (m, 12H; CH₂O), 3.83 (m, 12H;OCH₂), 3.77 (m, 12H; CH₂O). ¹³C NMR (400 MHz, CD₃CN, 25 °C, TMS, ppm): δ 154.3, 150.7, 144.9, 143.4, 140.2, 136.0, 130.4, 127.9, 127.6, 126.0, 124.2, 113.0, 74.4, 70.2, 70.0, 69.8. ESI-MS (methanol): m/z 1062.7 [**2** – 2NO₃⁻]²⁺, 687.8 [**2** – 3NO₃⁻]³⁺.

Figure S1. ^1H NMR spectra of **1** (400M, $[\text{D}_6]$ Acetone/ D_2O =2:1, 25 °C, TMS)

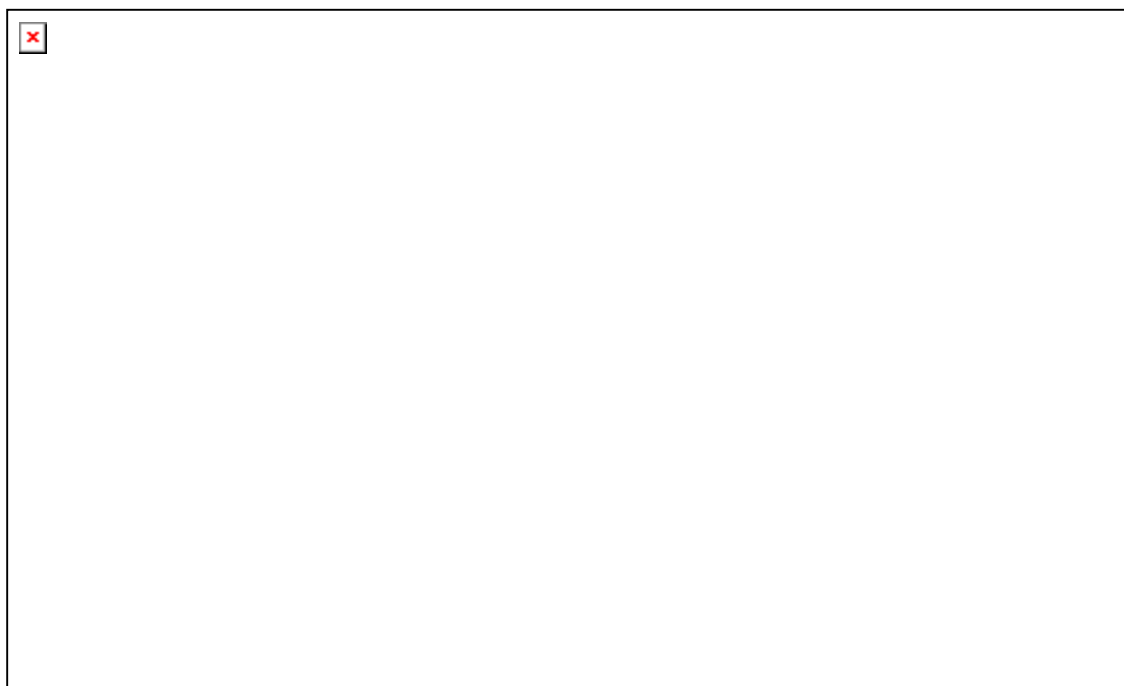


Figure S2. ^{13}C NMR spectra of **1a** (400M, $[\text{D}_6]$ Acetone/ D_2O =2:1, 25 °C, TMS)

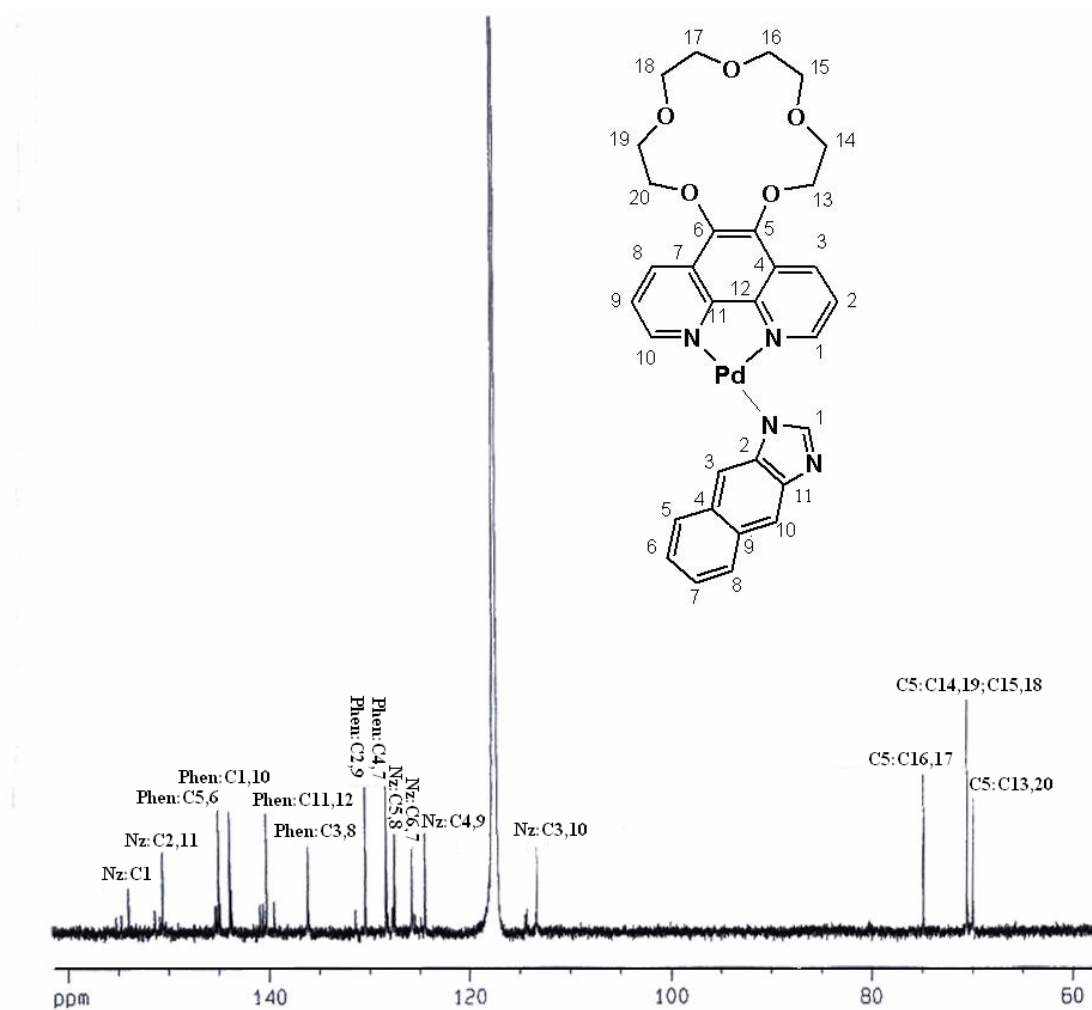


Figure S3. ^1H NMR spectra of **2** (400M, $[\text{D}_6]$ Acetone/ D_2O =2:1, 25 °C, TMS)

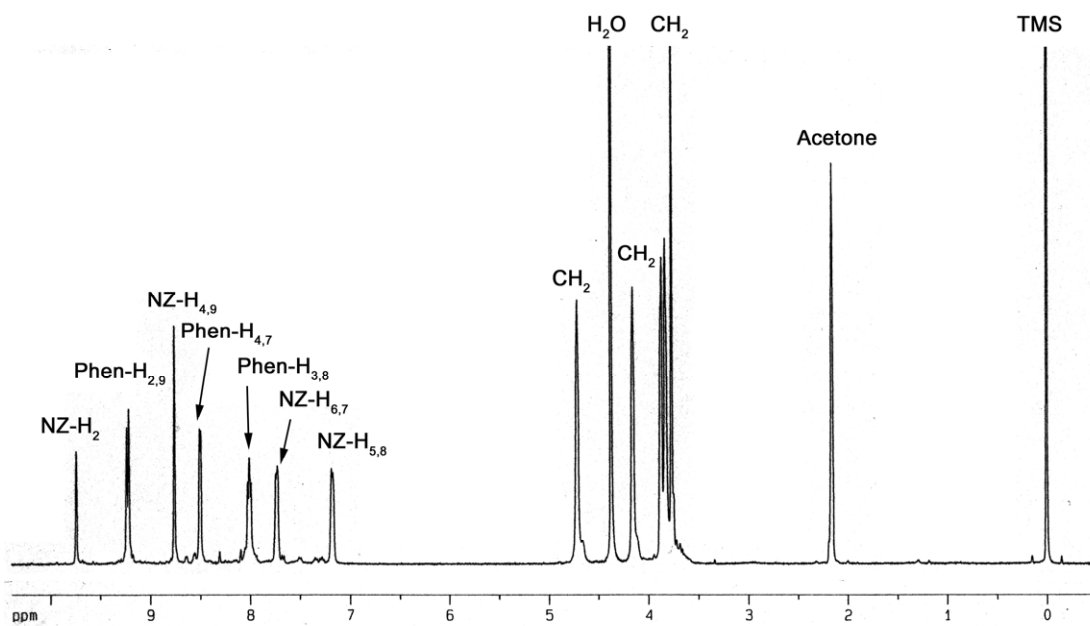


Figure S4. ^{13}C NMR spectra of **2** (400M, $[\text{D}_6]$ Acetone/ D_2O =2:1, 25 °C, TMS)

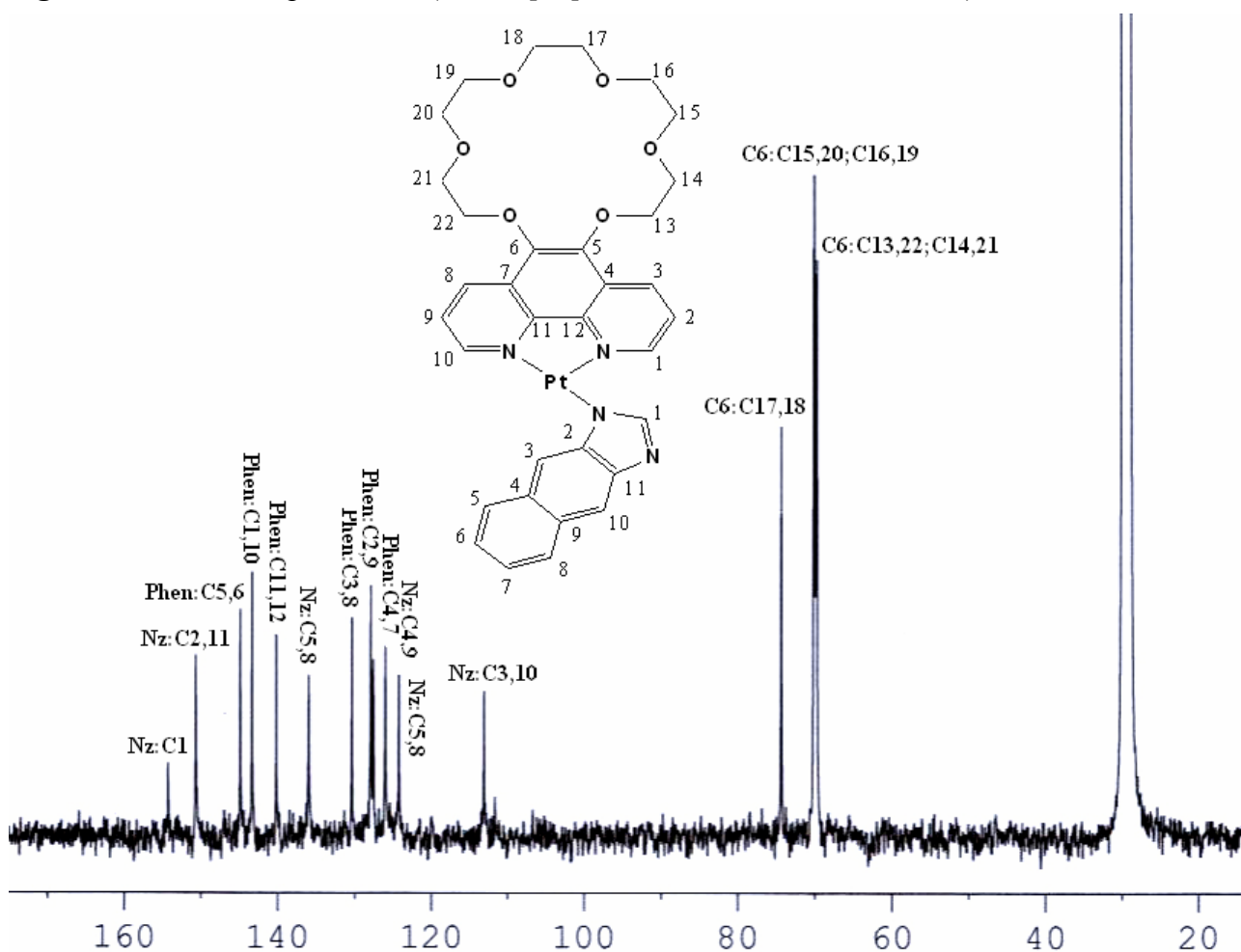


Figure S5. ESI-MS spectra of **1** in methanol; the inset shows the isotopic distribution of the species $[1-3\text{NO}_3^-]^{3+}$.

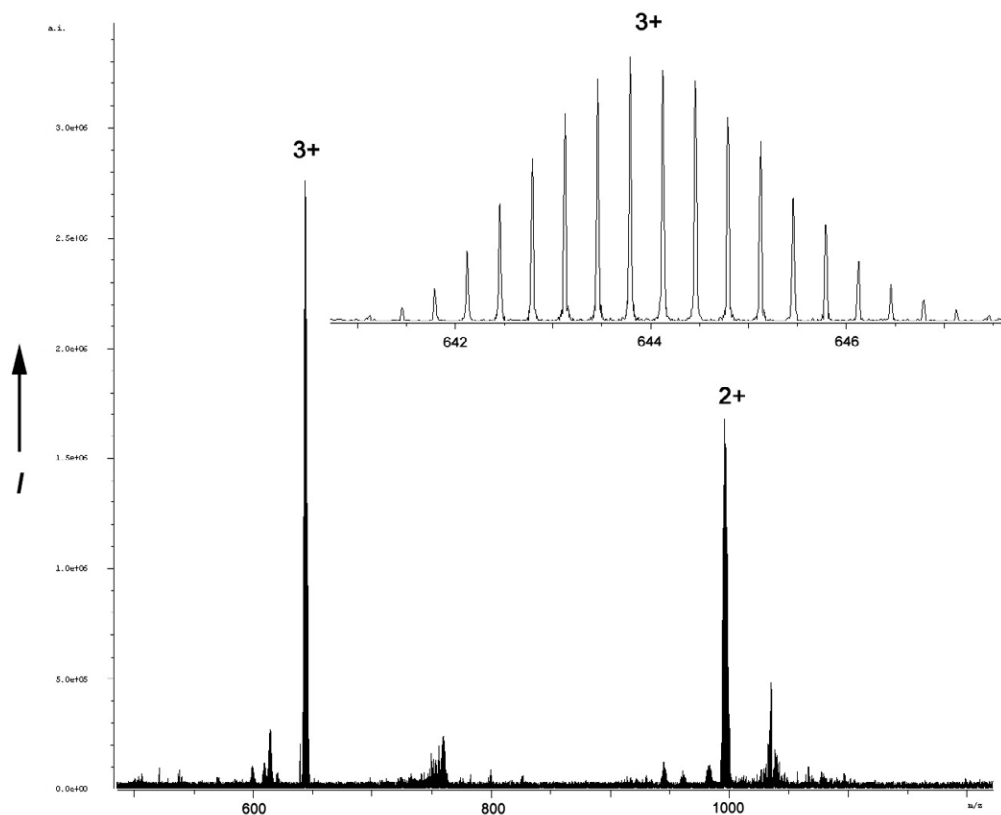


Figure S6. ESI-MS spectra of **1a** in acetonitrile; the inset shows the isotopic distribution of the species $[1a-3\text{NO}_3^-]^{3+}$.

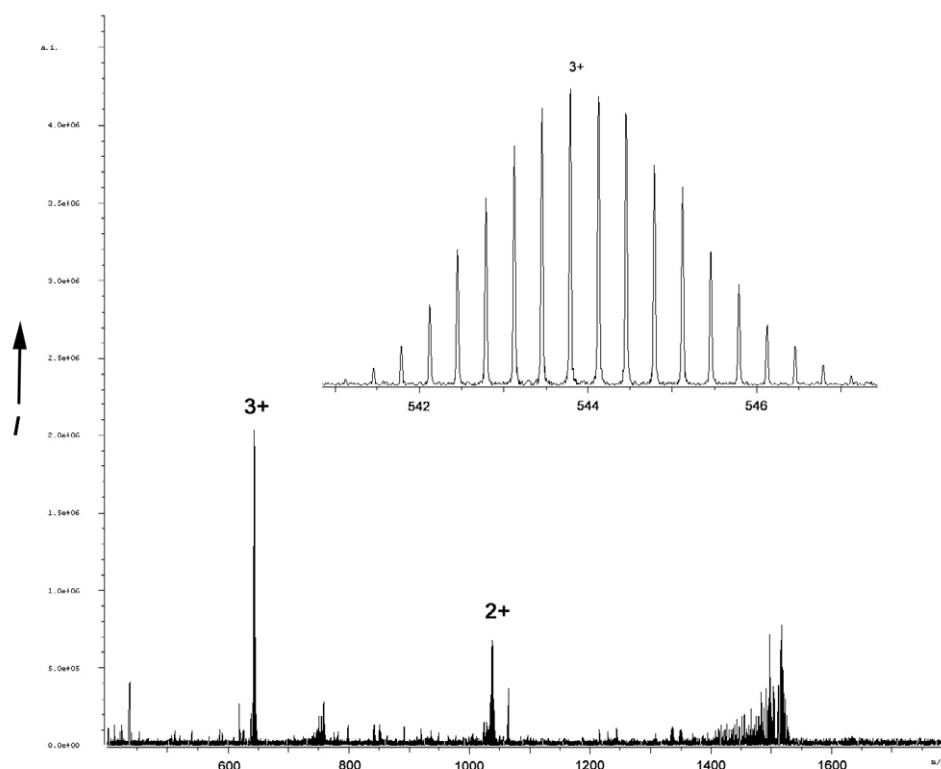


Figure S7. ESI-MS spectra of **2** in methanol; the inset shows the isotopic distribution of the species $[2-3\text{NO}_3^-]^{3+}$.

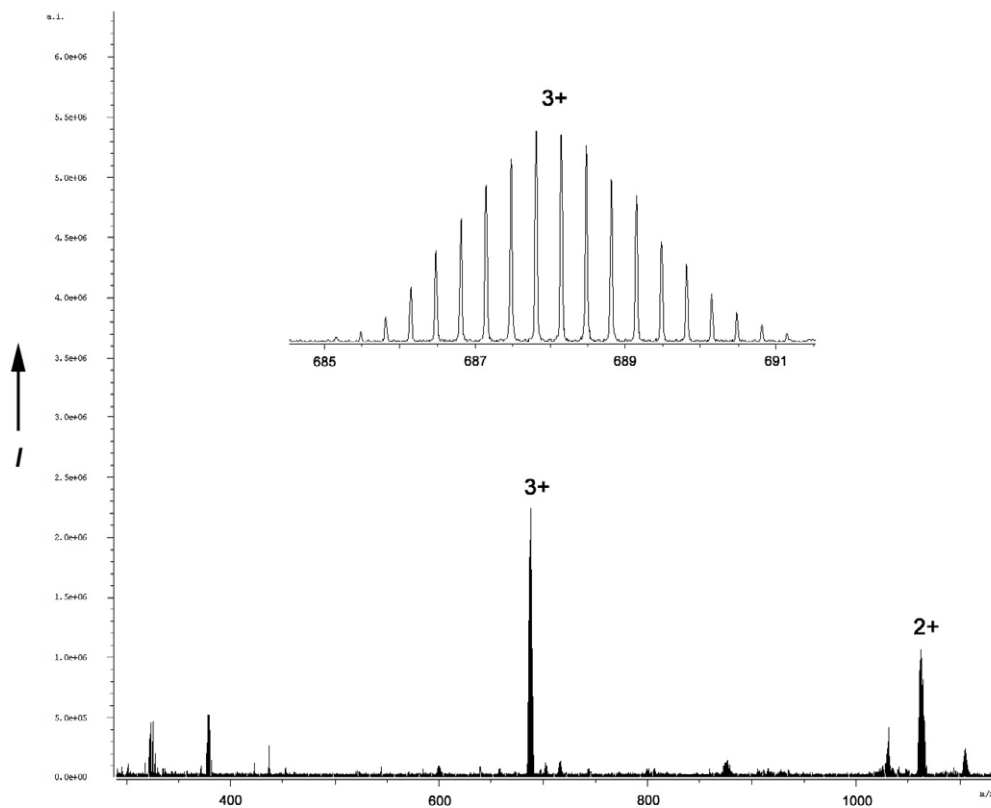


Table S1. Hydrogen bond lengths (Å) and angles (°) for **1a**

D–H···A	D(D–H)	D(H···A)	D(D···A)	∠(DHA)
C1–H1···N13	0.93	2.43	3.169(5)	136
C8–H8···F12 ^a	0.93	2.40	3.277(4)	157
C103–H10···F6	0.93	2.44	3.186(5)	135
C15–H15···F3 ^b	0.93	2.43	3.189(4)	139
C26–H26···F1	0.93	2.41	3.081(5)	129
C47–H47···O10 ^b	0.93	2.57	3.273(5)	133
C58–H58···O7 ^b	0.93	2.45	3.249(5)	145
C69–H69···O8 ^b	0.93	2.17	3.044(5)	156
C74–H74B···O2	0.93	2.20	2.558(5)	100
C79–H79A···O13 ^c	0.93	2.47	3.142(5)	126
C80–H80B···O12 ^c	0.93	2.42	3.317(5)	155
C83–H83A···F14 ^b	0.93	2.54	3.483(5)	165
C89–H89A···F4 ^d	0.93	2.41	3.226(5)	142
C95–H95C···N7	0.93	2.27	3.198(5)	163
C99–H99B···F6	0.93	2.46	3.209(5)	134

Symmetry codes: ^a x, -1+y, z; ^b 2-x, -y, 1-z; ^c 1+x, -1+y, z; ^d 1-x, 1-y, 1-z.

Figure S8. Packing diagram with channel formed by the cavity of complex **1a** viewed along the b axis.

