Supporting Information

Self-Assembly of Metallomacrocycles with Dipyrazole Ligands and Anion Sensing of [Pd_4Fe_2] Macrocycle with Ferrocene-Based Dipyrazole ligand

Liao-Yuan Yao,[a] Zheng-Su Yu,[b] Lin Qin,[a] Yi-Zhi Li,[b] Yu Qin,[b] and Shu-Yan Yu[a*]*

[a]Laboratory for Self-Assembly Chemistry, Department of Chemistry, Renmin University of China, Beijing 100872, People's Republic of China; [b]Department of Chemistry, State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute and State Key Laboratory of Analytical Chemistry for Life Science, Nanjing University, Nanjing 210093, People's Republic of China.

* To whom correspondence should be addressed. E-mail: yusy@ruc.edu.cn; qinyu75@nju.edu.cn.

Contents:

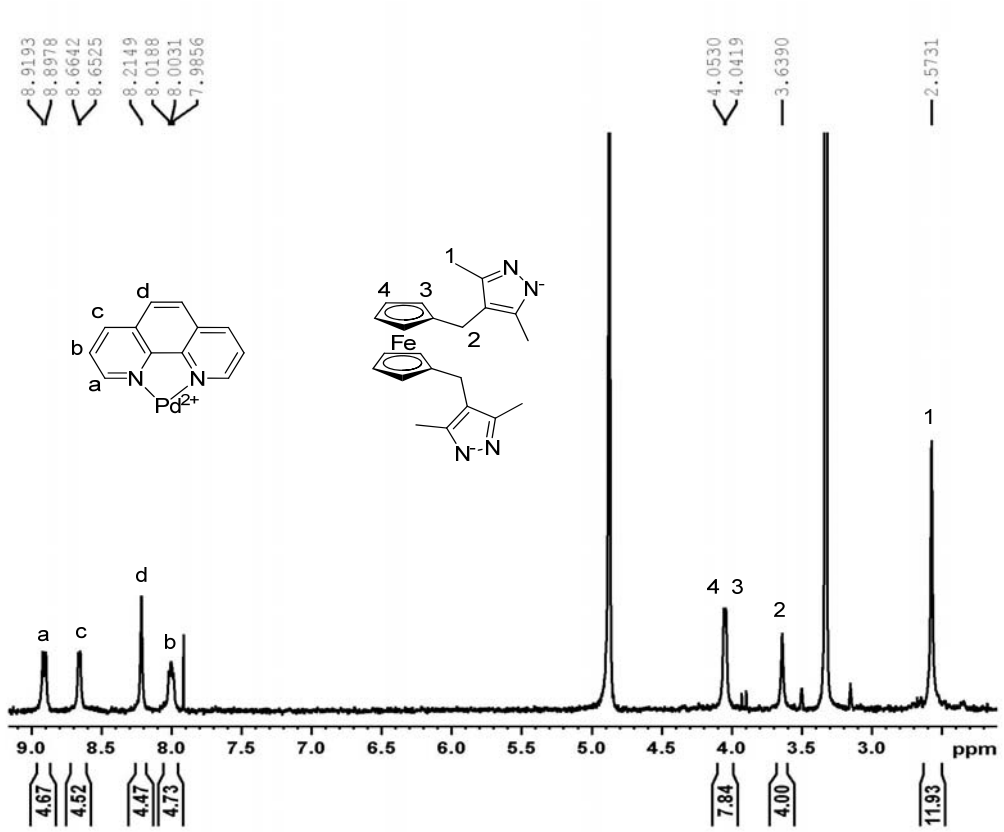

Fig. S1 ^{1}H NMR spectrum of **2**·4NO_3 in D_2O

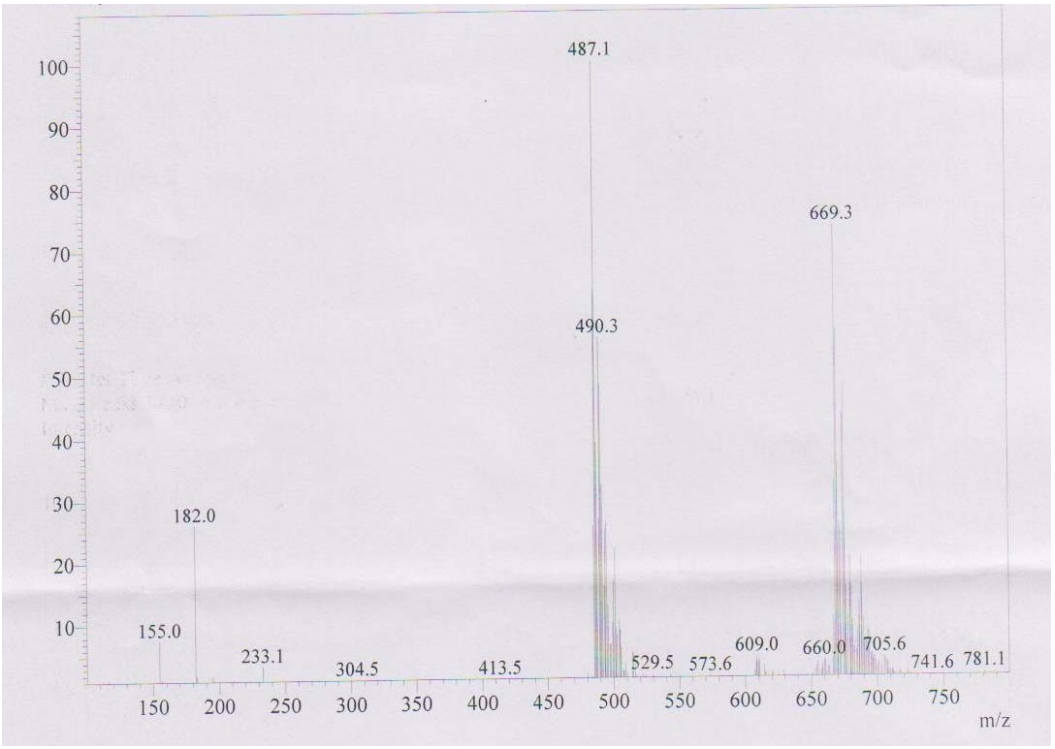

Fig. S2 ESI mass spectrum of **2**·4NO_3 in methanol.

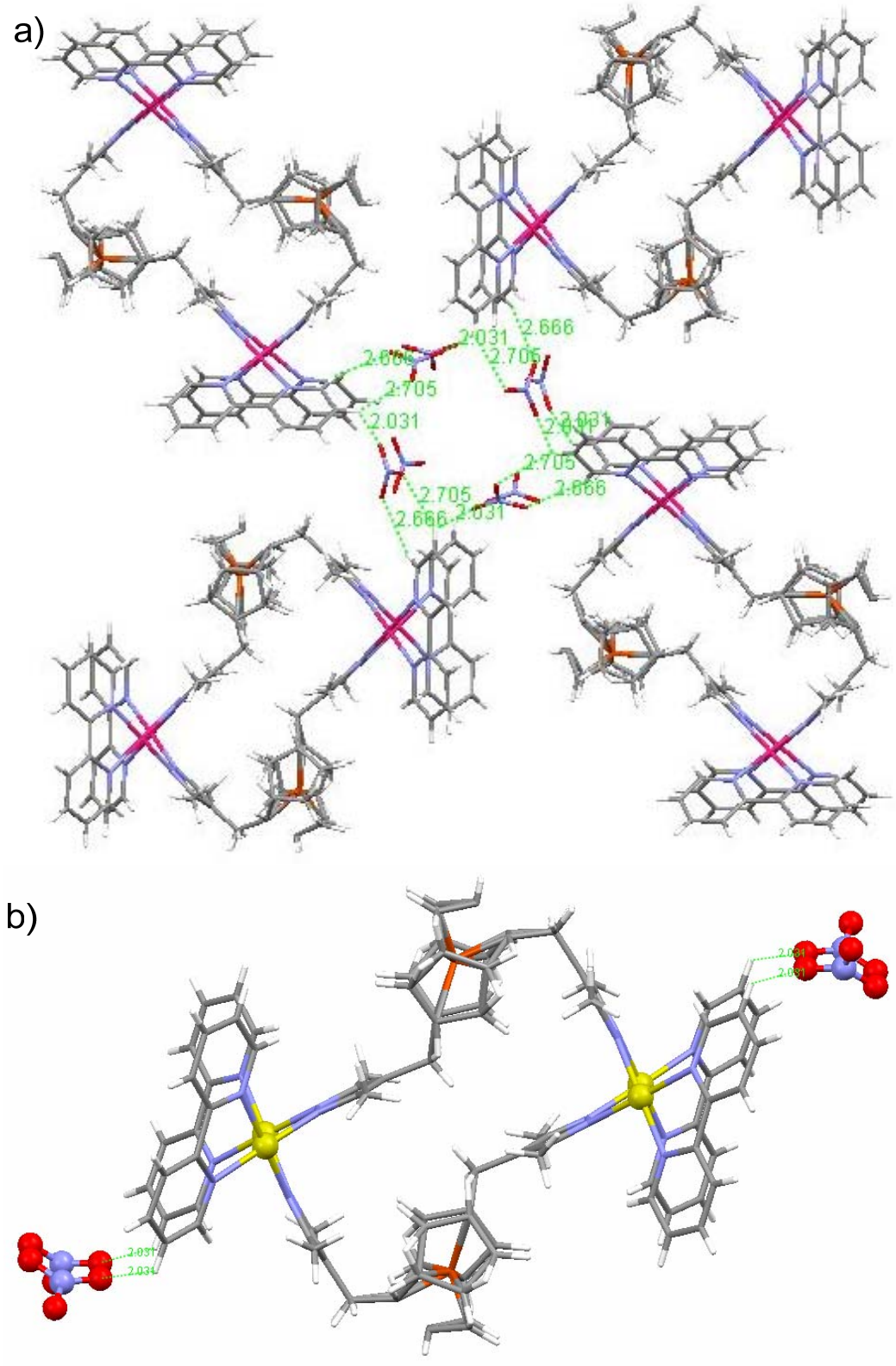

Fig. S3 a) The crystal packing diagram of complex **1**·4NO_3. b) Four NO_3^- trapped on **1** through C-H···O hydrogen bonds.

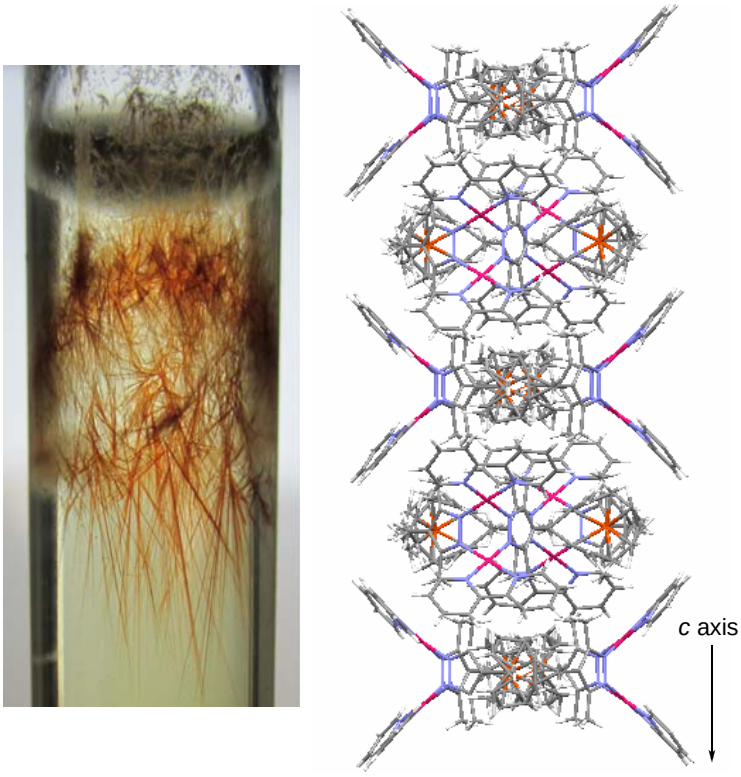

Fig. S4 Left: the needle crystals of **1**·4NO_3. Right: the molecules of **1**·4NO_3 packing along c axis.

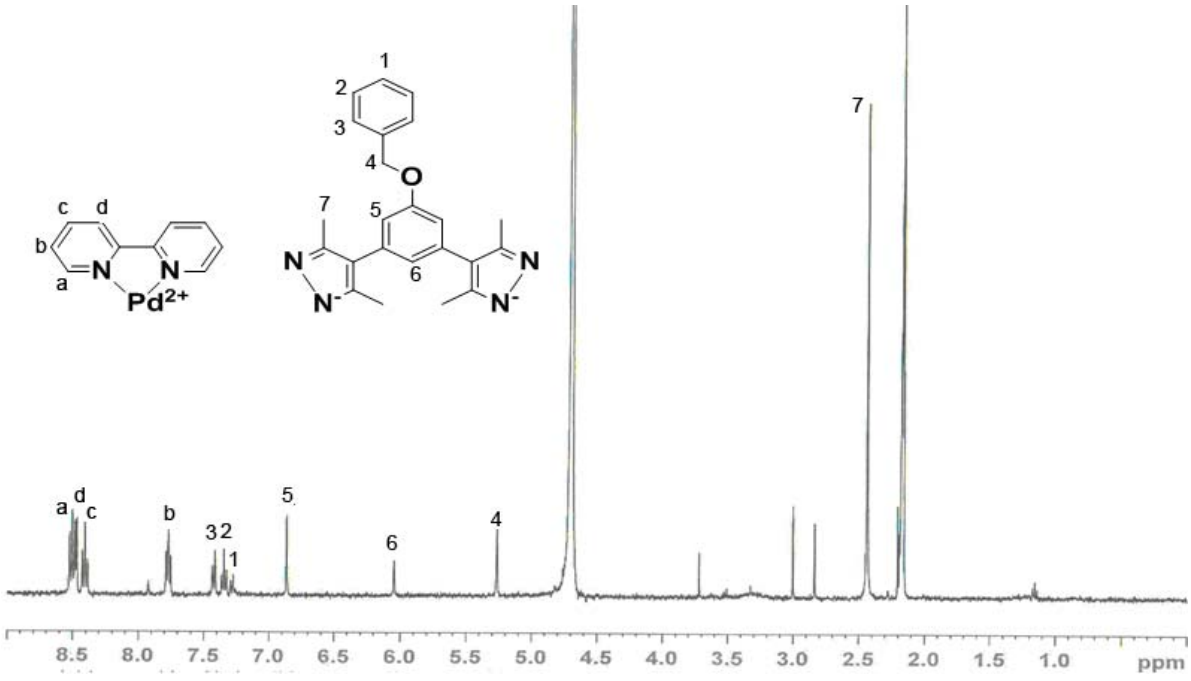

Fig. S5 ^{1}H NMR spectrum of **3**·4NO_3 in D_2O

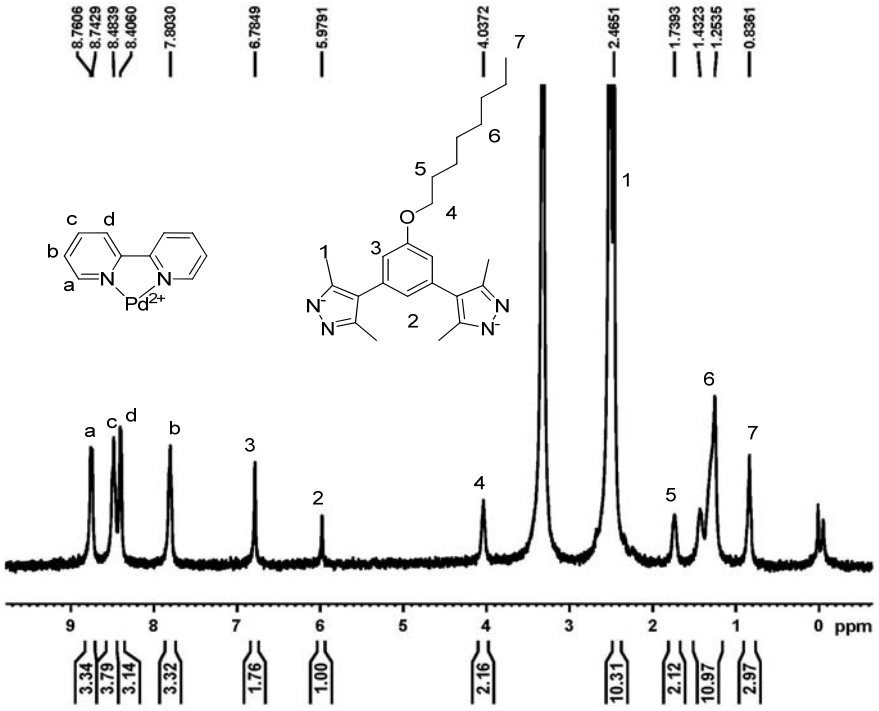

Fig. S6 ^{1}H NMR spectrum of **5**·4NO_3 in DMSO-d_6

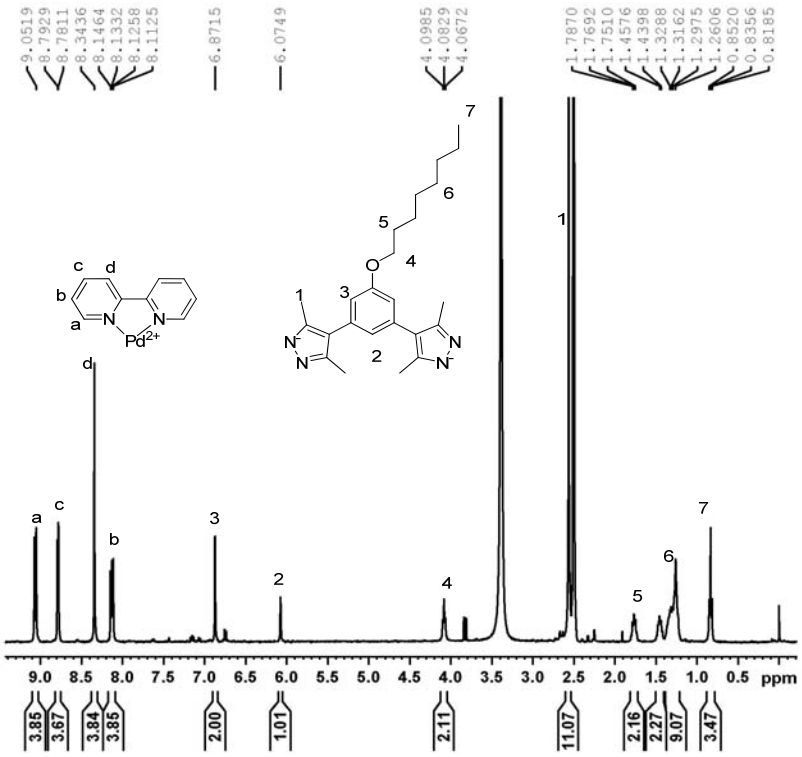

Fig. S7 ^{1}H NMR spectrum of **6**·4NO_3 in DMSO-d_6

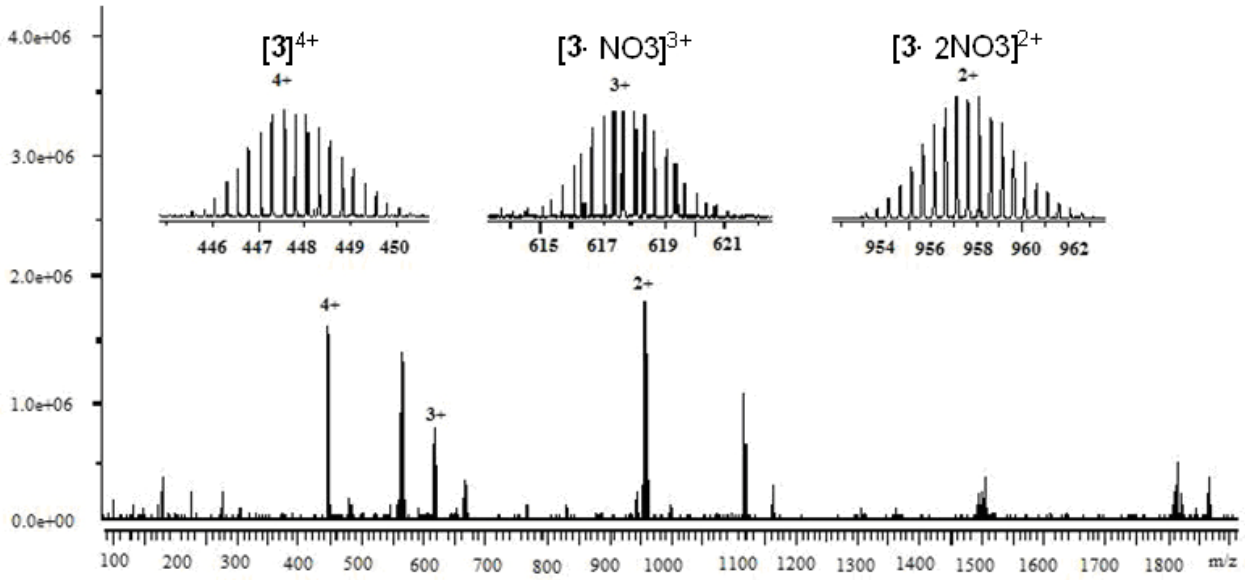

Fig. S8 ESI mass spectrum of **3**·4NO_3 in methanol. The inset shows the isotopic distribution of the species [**3**]$^{4+}$, [**3**·NO_3]$^{3+}$, and [**3**·2NO_3]$^{2+}$.

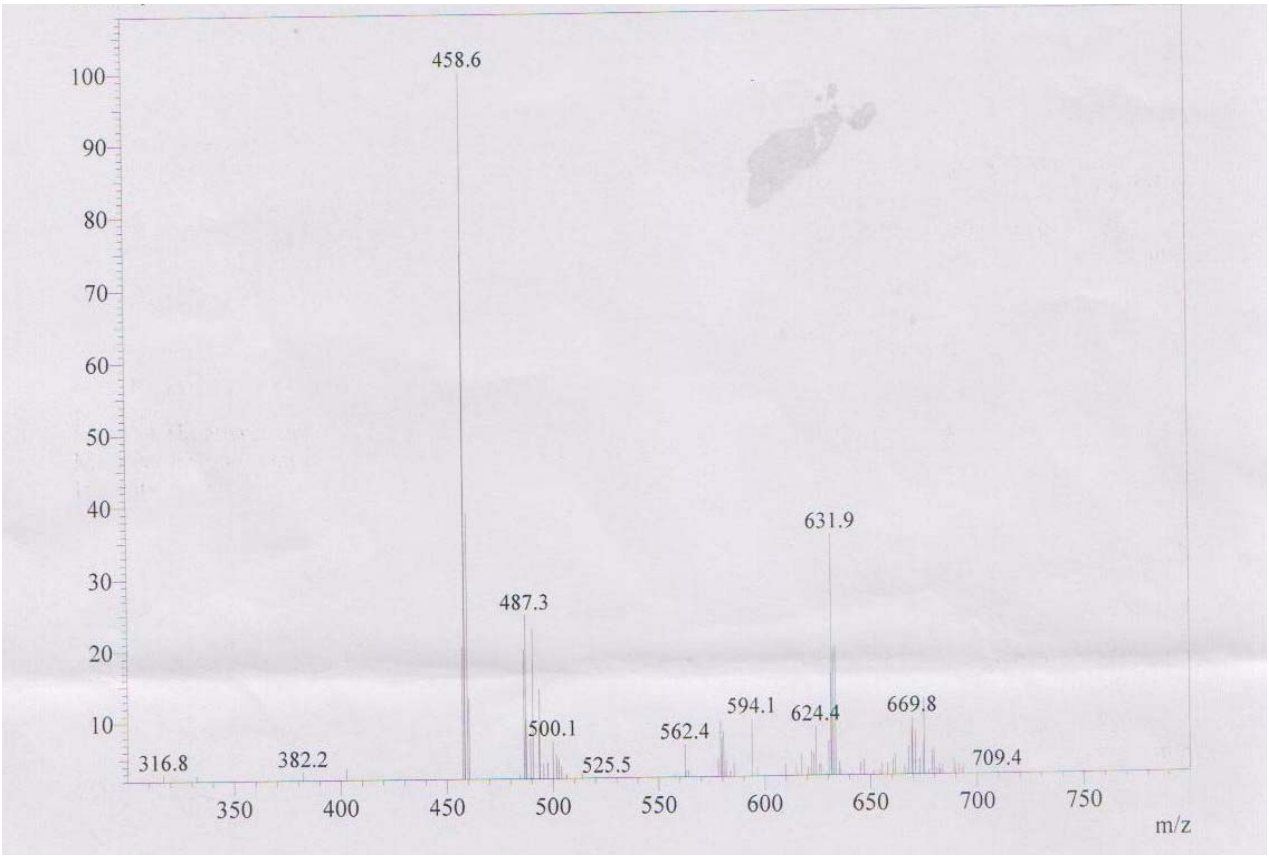

Fig. S9 ESI mass spectrum of **5**·4NO_3 in methanol.

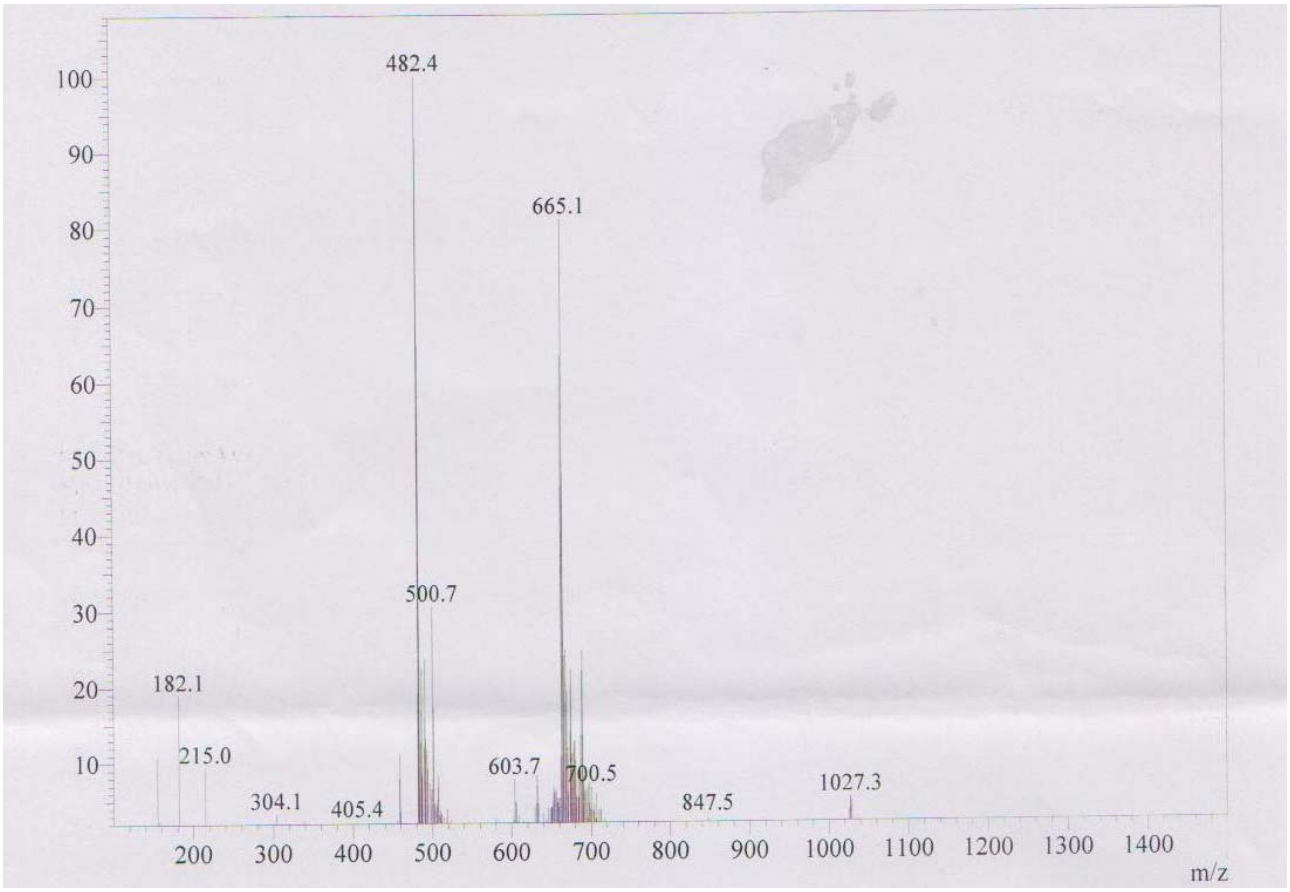

Fig. S10 ESI mass spectrum of **6**·4NO_3 in methanol.

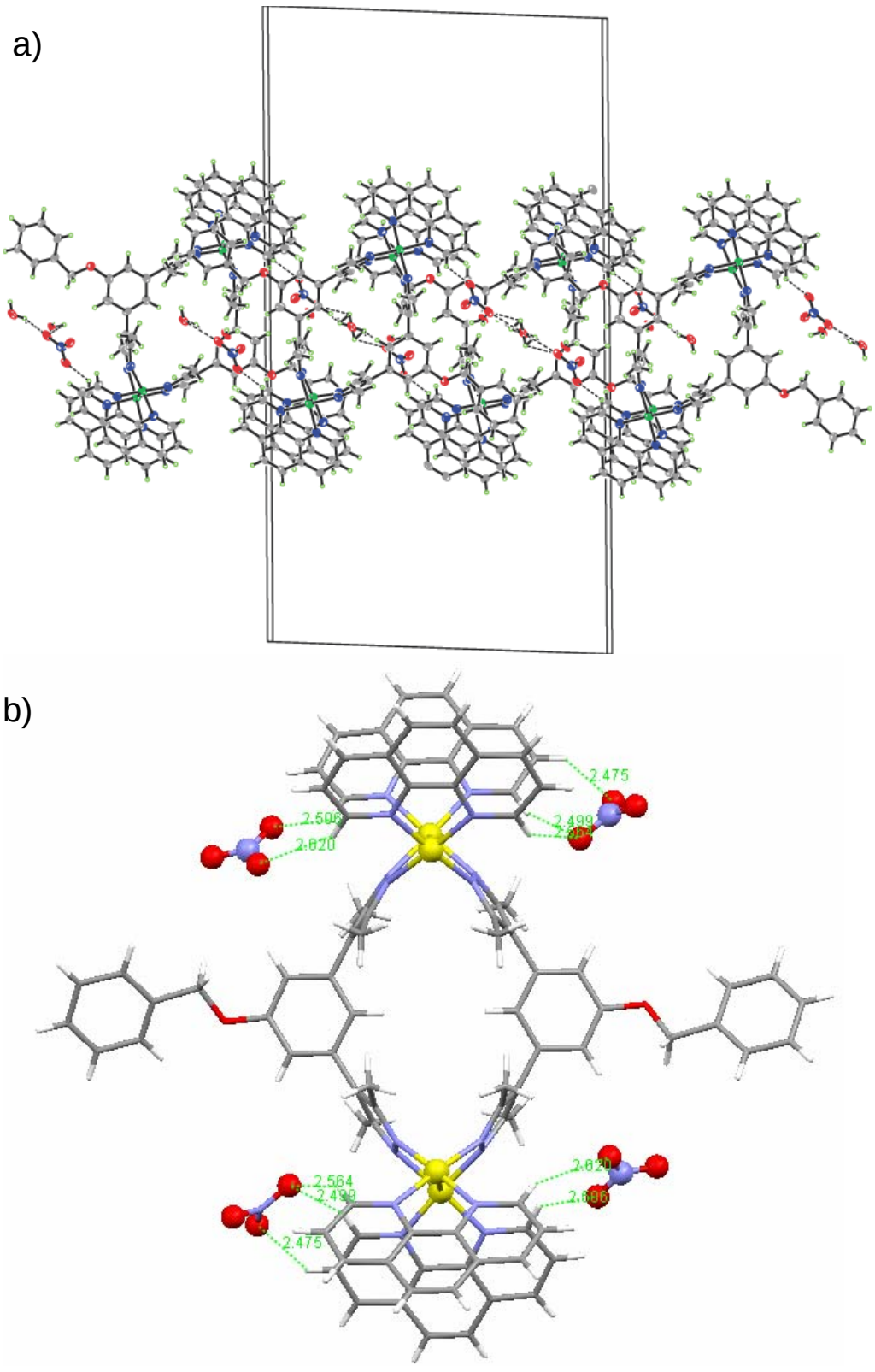

Fig. S11 a) The crystal packing diagram of complex **4**·4NO_3. b) Four NO_3^- trapped on **4** through C-H···O hydrogen bonds.

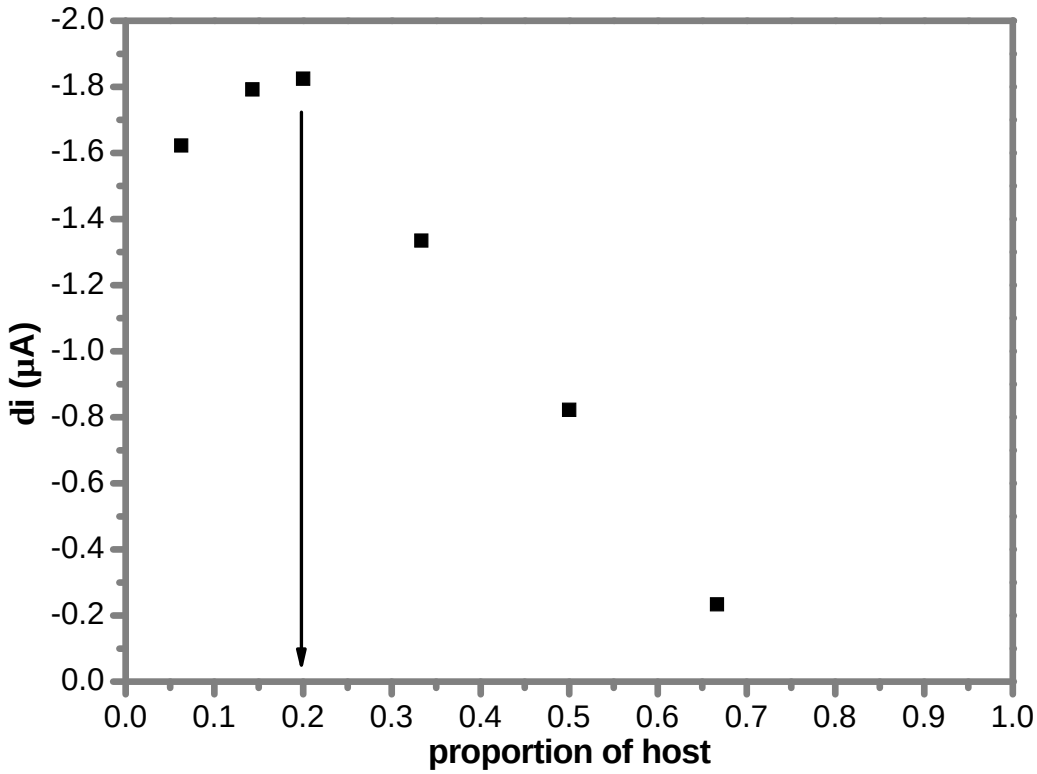

Fig. S12 Job's plot analysis.

Table S1 Selected Bond Lengths (Å) and Angles (°) for **1**·4NO_3

Pd1-N1	2.037(3)	Pd1-N2	2.072(3)
Pd1-N3	2.045(3)	Pd1-N4	2.016(3)
Fe1-C15	2.088(6)	Fe1-C16	2.023(8)
Fe1-C17	1.955(3)	Fe1-C18	1.928(3)
Fe1-C19	2.097(7)	Fe1-C20	1.877(6)
Fe1-C21	1.868(6)	Fe1-C22	1.937(8)
N1-Pd1-N2	84.13(11)	N1-Pd1-N3	96.57(11)
N1-Pd1-N4	179.93(13)	N2-Pd1-N3	178.31(11)
N2-Pd1-N4	95.80(11)	N3-Pd1-N4	83.51(11)

Table S2 Hydrogen bond lengths (Å) and angles (º) for the complex **1**·4NO_3

D−H···A	D(D-H)	D(H···A)	D(D···A)	∠(DHA)
C9−H9···O2	0.9300	2.0300	2.595(4)	118.00

Symmetry Code: y,1-x,z

Table S3 Selected Bond Lengths (Å) and Angles (°) for **4**·4NO_3

Pd1-N1	1.999(4)	Pd1-N2	2.022(4)
Pd1-N6	2.005(4)	Pd1-N8	2.005(4)
Pd2-N3	2.004(4)	Pd2-N4	1.984(5)
Pd2-N5	1.995(4)	Pd2-N7	1.993(4)
N5-N6	1.388(5)	N7-N8	1.347(5)
N1-Pd1-N2	81.91(18)	N6-Pd1-N8	86.33(16)
N3-Pd2-N4	80.86(17)	N5-Pd2-N7	84.96(17)
Pd1-N6-N5	117.3(3)	Pd1-N8-N7	119.8(3)
Pd2-N6-N5	121.2(3)	Pd2-N7-N8	116.8(3)

Table S4 Hydrogen bond lengths (Å) and angles (º) for the complex **4**·4NO_3

D−H···A	D(D-H)	D(H···A)	D(D···A)	∠(DHA)
O5W−H5X···O6^{y}	0.8500	1.9300	2.592(4)	134.00
O5W−H5Y···O6^{u}	0.8500	2.2200	2.592(4)	106.00
C1−H1···O3^{d}	0.9300	2.5000	3.361(7)	154.00
C2−H2···O4^{d}	0.9300	2.4700	3.148(6)	129.00
C3−H3···O2^{e}	0.9300	2.3900	3.201(6)	145.00

C10−H10···O7[i]	0.9300	2.5100	3.249(6)	137.00
C13−H13···O3[d]	0.9300	2.5600	3.347(7)	142.00
C15−H15···O4[j]	0.9300	2.3400	3.169(5)	149.00
C20−H20···O3[m]	0.9300	2.4700	3.351(6)	158.00
C25−H25B···O5[o]	0.9600	2.5800	3.185(6)	121.00
C43−H43···O1	0.9300	2.3800	2.719(6)	101.00

Symmetry Code: [y]-1+x,1-y,-1/2+z; [u]1-x,1-y,1-z; [d]x,1-y,-1/2+z; [e]3/2-x,3/2-y,1-z; [i]x,y,-1+z; [j]3/2-x,1/2-y,1-z; [m]x,-1+y,-1+z; [o]2-x,-y,1-z