SUPPLEMENTARY INFORMATION

A circular tris[2]catenane from molecular 'figure-of-eight'

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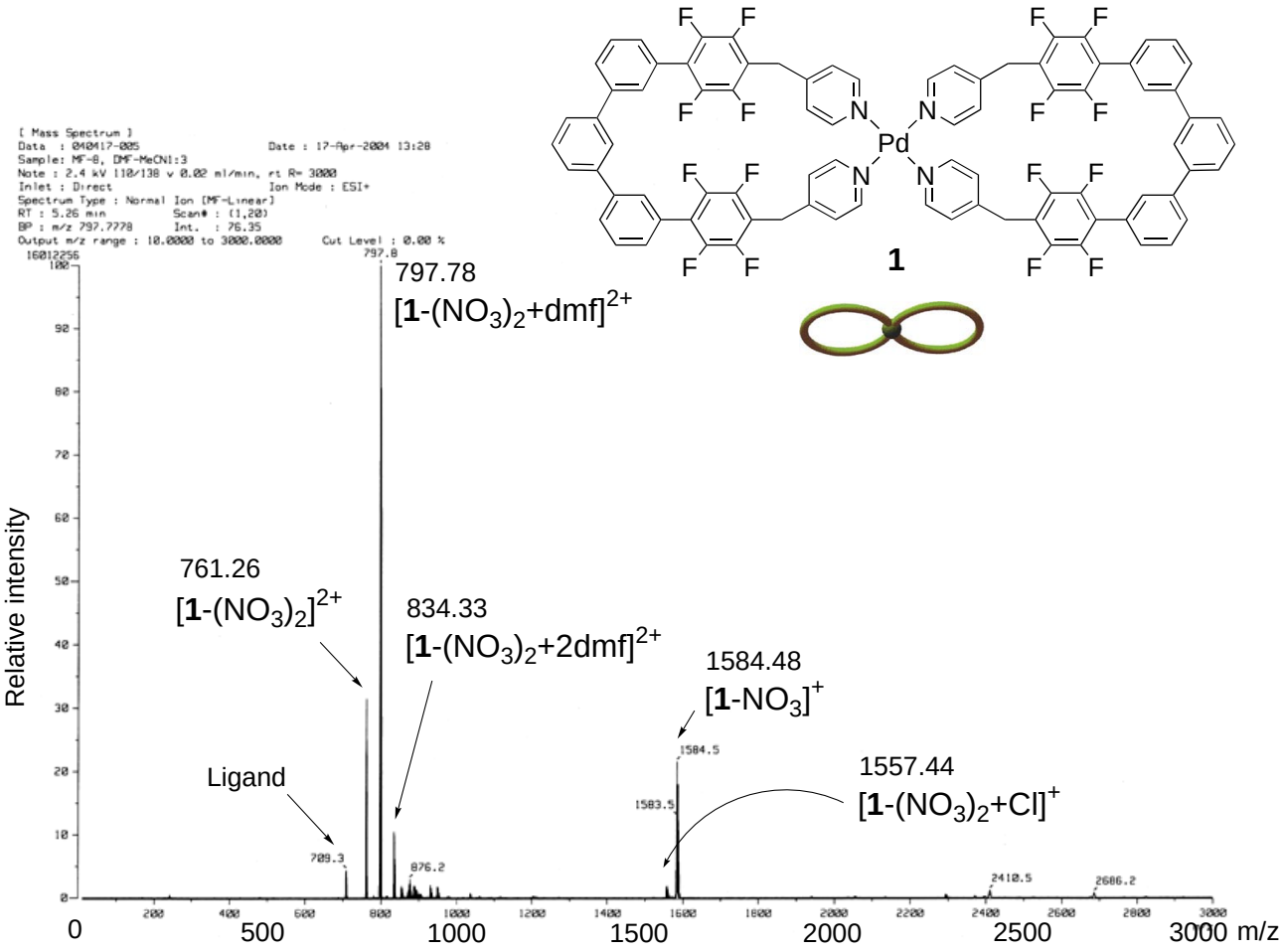
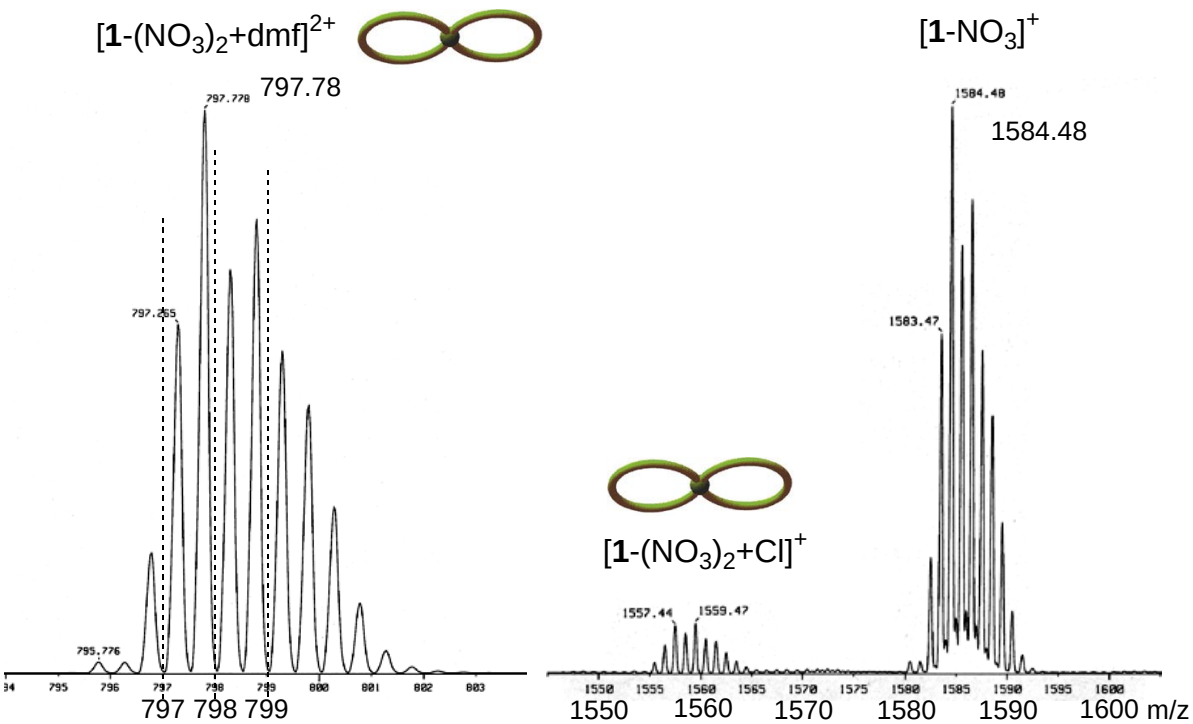
Complex 1: To a solution of the ligand (14.2 mg, 0.02 mmol) in DMSO (1 mL), $Pd(NO_3)_2$ (2.3 mg, 0.01 mmol) was added and the mixture was stirred for 15 min at 60 ℃ to give a pale yellow solution. Complex **1** was isolated as a white powder by adding a large amount of diethyl ether and it was crystallized from a DMF-MeOH-diethyl ether solution as colorless crystals. Yield 95%. mp 200 ℃ dec. ^{1}H NMR (500 MHz, DMSO-d_6, TMS) δ 9.64 (d, J = 5.8 Hz, 8H, PyH_α), 8.53 (s, 4H, ArH_d), 8.38 (d, J = 7.8 Hz, 4H, ArH_e), 8.32 (s, 2H, ArH_a), 8.30 (d, J = 7.8 Hz, 4H, ArH_c), 8.22-8.17 (m, 14H, PyH_β and Ar$H_{f\ and\ b}$), 8.05 (d, J = 8.2 Hz, 2H, ArH_g), 4.74 (s, 4H, -CH_2-). ^{13}C NMR (125 MHz, DMSO-d_6, $CHCl_3$) δ 152.5 (Cq), 152.2 (CH_α), 145.5 (d, J = 247 Hz, CF_i), 144.4 (d, J = 247 Hz, CF_j), 141.6 (Cq), 141.0 (Cq), 131.0 (CH_f), 130.5 (CH_g), 130.4 (CH_b), 129.3 (CH_d), 129.1 (CH_e), 128.3 (Cq), 128.2 (CH_β), 127.6 (CH_c), 125.9 (CH_a), 120.3 (t, J = 17.0 Hz, CF_h), 116.7 (t, J = 18.6 Hz, CF_k), 28.2 (-CH$_2$-). ^{19}F NMR (300 MHz, DMSO-d_6, CF_3COOH) δ -64.56 (m, 4F, ArF), -64.98 (m, 4F, ArF). IR (KBr, cm^{-1}) 1475, 1280, 1330, 1176, 994, 788. CSI-MS m/z 761 $[\mathbf{1}\text{-}(NO_3)_2]^{2+}$, 798 $[\mathbf{1}\text{-}(NO_3)_2+dmf]^{2+}$, 1559 $[\mathbf{1}\text{-}(NO_3)_2+Cl]^{+}$. Elemental Analysis: Calcd for $C_{84}H_{48}N_6F_{16}PdO_6\cdot DMF\cdot H_2O$: C, 60.10; H, 3.30; N, 5.64%; Found: C, 60.38; H, 3.21; N, 5.69%. $\mathbf{1}\cdot 4Et_2O$ was obtained as colorless crystals suitable for X-ray crystallographic studies.

Catenation: Complex **1** was transformed into catenated dimmer $(\mathbf{1})_2$ and trimer $(\mathbf{1})_3$ in a polar media. Water was added into a DMSO solution of **1** at low concentration(0.5 mM). The reaction mixture was stirred for 30 min at 60 ℃. In a control experiment using D_2O-DMSO-d_6, the formation of catenated compounds was monitored by ^{1}H NMR.

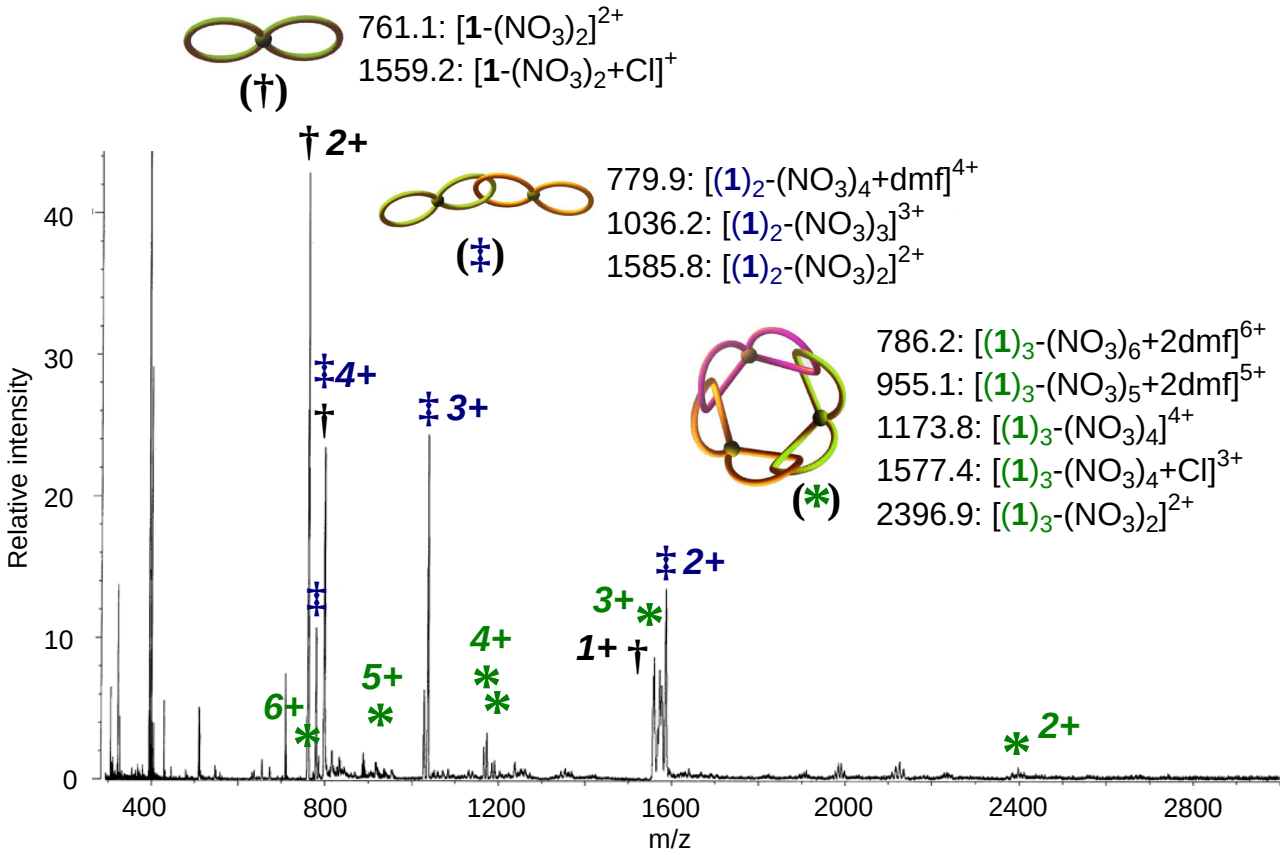
CSI-MS of **1** (DMF-MeCN 1:3 solution)



(High Resolution R=3000)

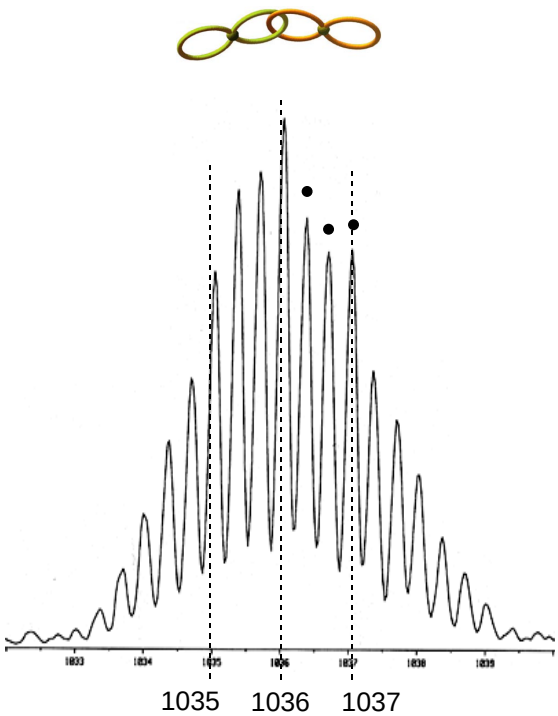


CSI-MS of the mixture $(\mathbf{1})_{1\text{-}3}$ (DMF-H_2O 1:1.2 solution)

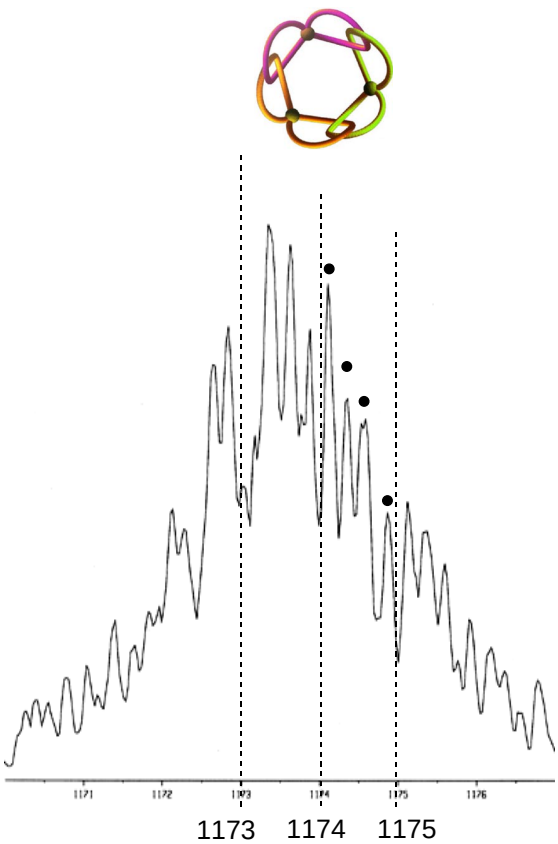


(High Resolution R=3000)

1036.2: $[(\mathbf{1})_2\text{-}(NO_3)_3]^{3+}$



1173.8: $[(\mathbf{1})_3\text{-}(NO_3)_4]^{4+}$



CSI-MS of the mixture (**1**)$_{1\text{-}3}$ (DMF-H_2O 1:1.2 solution)