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Supporting Information

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Reversible switching between macrocyclic and polymeric states by morphological control in a constitutional dynamic system

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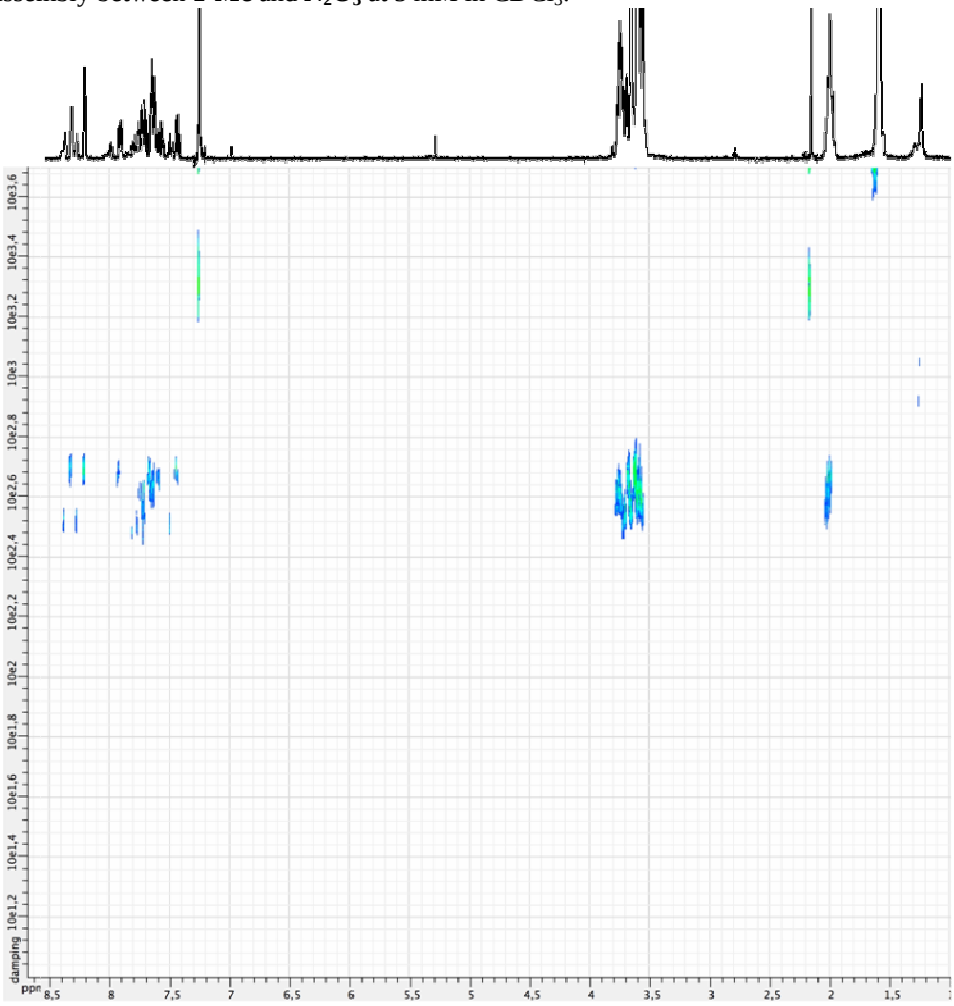
X-ray crystallographic data for **1-Me** : $[C_{14}H_{12}N_4O_2]$ (**1-Me**); 268.27 g·mol^{-1}; Orthorhombic; space group P212121; a = 3.8912(4), b = 17.965(2), c = 18.182(2) Å; V = 1271.0(2) Å^3; density : 1.402 g·cm^{-3}; λ (MoK_α 0.71073 Å; T = 173 K; Z = 4; F(000): 560; number of data measured : 2877; number of data with I > 2σ(*I*) : 1308; number of variables : 182; R = 0.0716; R_w = 0.1382; goodness-of-fit = 0.983.

X-ray crystallographic data for **M1'** : $[C_{20}H_{22}F_6N_6O_7S_2Zn]$ (**M1'**); 701.93 g·mol^{-1}; Orthorhombic; space group P21cn; a = 9.1175(3), b = 11.8639(5), c = 25.2536(10) Å; V = 2731.66(18) Å^3; density : 1.707 g·cm^{-3}; λ (MoK_α): 0.71073 Å; T = 173 K; Z = 4; F(000): 1424; number of data measured : 5773; number of data with I > 2σ(*I*) : 4455; number of variables : 389; R = 0.0482; R_w = 0.1063; goodness-of-fit = 1.042.

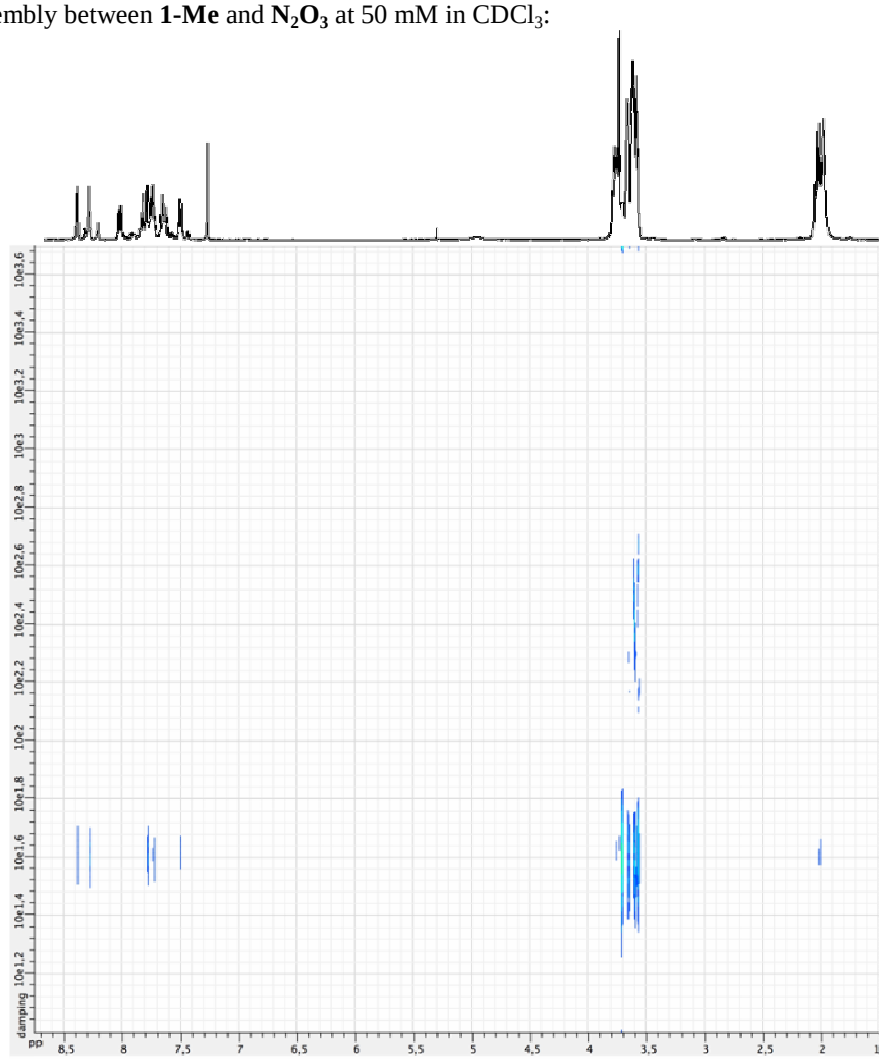
(E)-6-((2-(6-formylpyridin-2-yl)-2-methylhydrazono)methyl)picolinaldehyde **1-Me**:
^{1}H NMR (400 MHz, $CDCl_3$ filtered on basic alumina) δ (ppm) 10.09 (s, 1H), 9.99 (s, 1H), 8.24 (dd, J = 7.3 Hz, J = 1.5 Hz, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.90 (m, 3H), 7.80 (t, J = 8.3 Hz, 1H), 7.53 (d, J = 7.8 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR ($CDCl_3$ filtered on basic alumina) δ (ppm) 193.4, 193.1, 157.4, 155.7, 152.4, 150.5, 138.4, 137.3, 134.7, 123.5, 121.0, 114.8, 114.7, 29.8; HR-ESI-MS (m/z) calculated for $[C_{14}H_{12}N_4O_2+Li]^+$ 275.1120, found 275.1126, $[C_{14}H_{12}N_4O_2+Na]^+$ 291.0858, found 291.0863, $[C_{14}H_{12}N_4O_2+K]^+$ 307.0597, found 307.0617

(E)-6-((2-(6-formylpyridin-2-yl)-2-octylhydrazono)methyl)picolinaldehyde **1-Oct**:
^{1}H NMR (400 MHz, $CDCl_3$ filtered on basic alumina) δ (ppm) 10.08 (s, 1H), 9.95 (s, 1H), 8.21 (dd, J = 7.6 Hz, J = 1.6 Hz, 1H), 7.88 (m, 4H), 7.76 (t, J = 8 Hz, 1H), 7.50 (dd, J = 7.2 Hz, J = 0.8 Hz, 1H), 4.42 (t, J = 7.2 Hz, 2H), 1.72 (m, 2H), 1.35 (m, 10H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ filtered on basic alumina) δ (ppm) 193.5, 193.0, 157.2, 155.9, 152.3, 150.5, 138.2, 137.1, 133.8, 123.4, 121.0, 114.5, 114.3, 42.1, 31.7, 29.2, 29.1, 26.9, 24.7, 22.6, 14.0; HR-ESI-MS (m/z) calculated for $[C_{21}H_{26}N_4O_2+Li]^+$ 373.2216 (100.0%), 374.2249 (22.7%), found 373.2229, 374.2260, $[C_{21}H_{26}N_4O_2+Na]^+$ 389.1953 (100.0%), 390.1987 (22.7%), 391.2021 (2.5%), found 389.1970, 390.2002, 391.2060

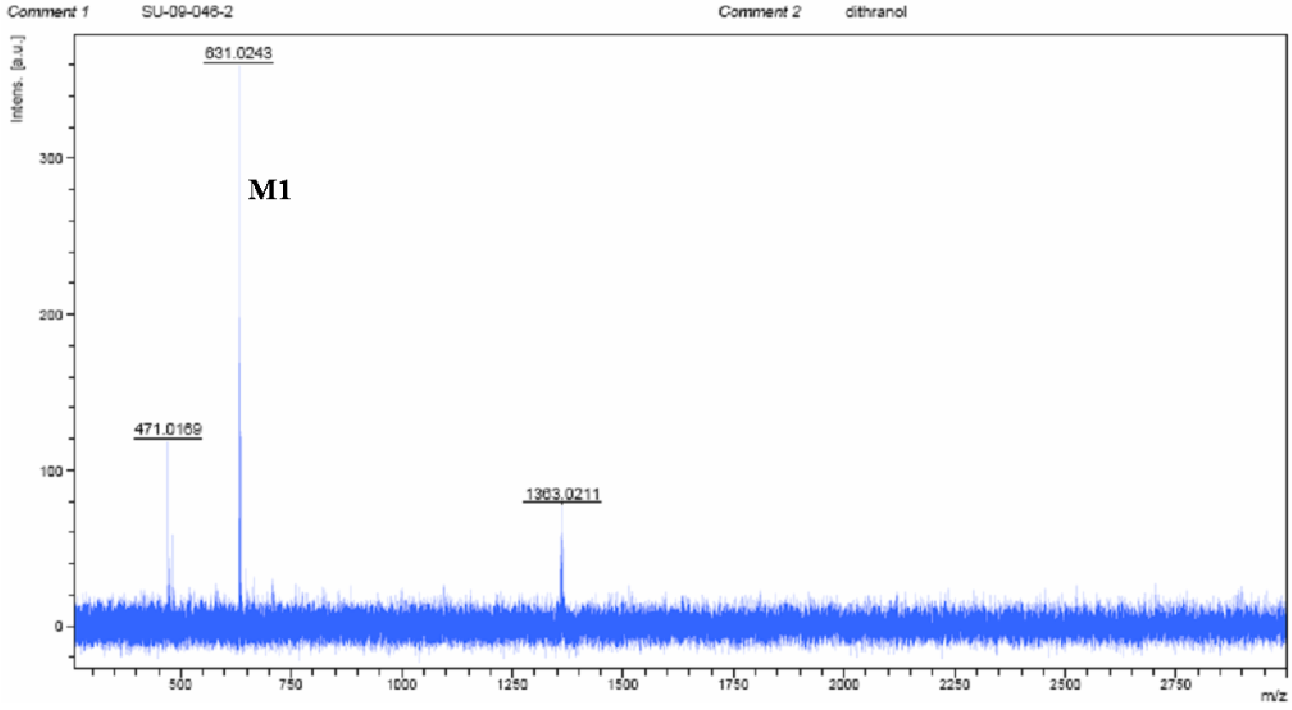
DOSY of the self-assembly between **1-Me** and **N_2O_3** at 5 mM in $CDCl_3$:

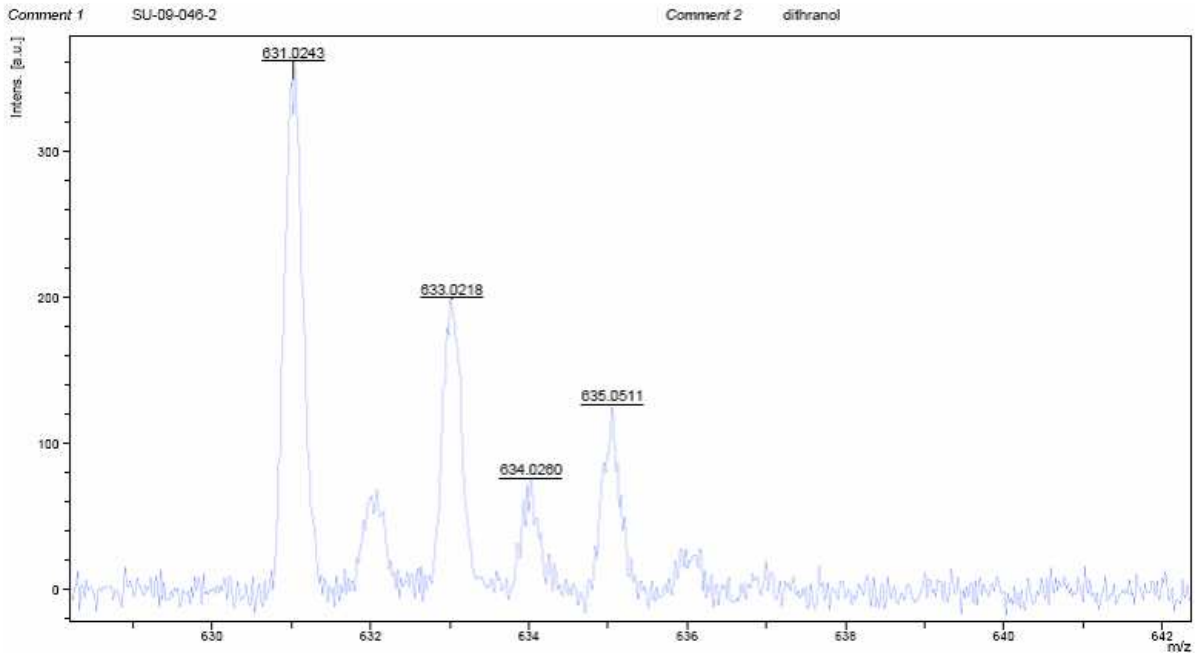


DOSY of the self-assembly between **1-Me** and $\mathbf{N_2O_3}$ at 50 mM in $CDCl_3$:



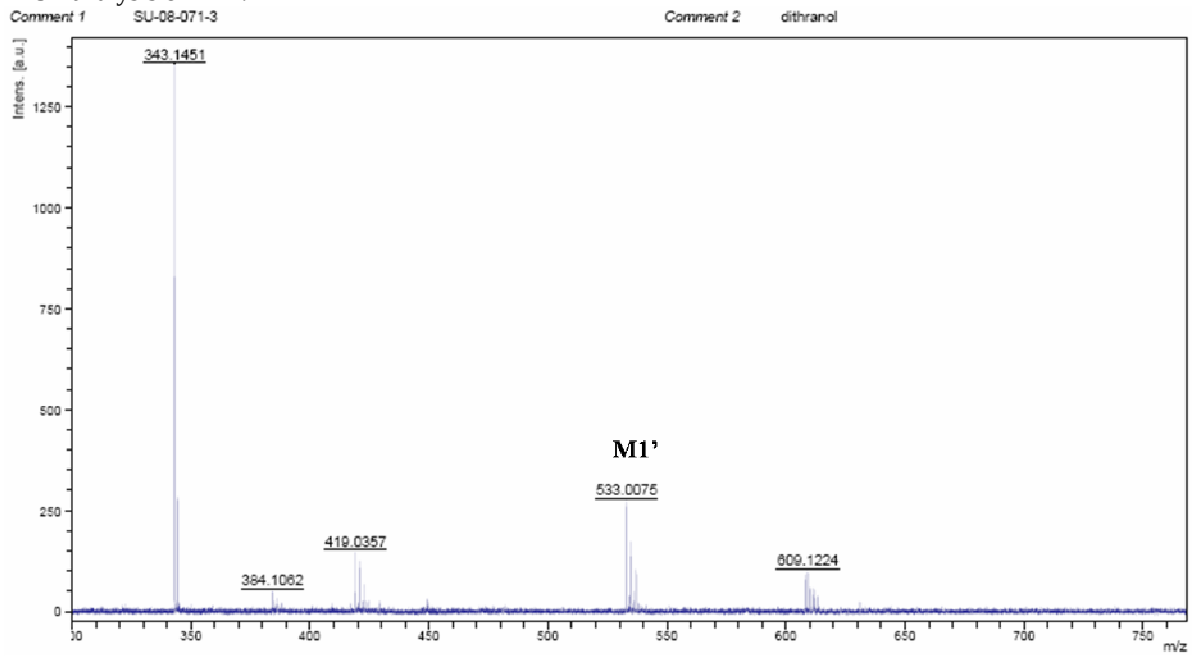
MALDI-TOF analysis of **M1** after 2 macrocycle/polymer switching cycles:

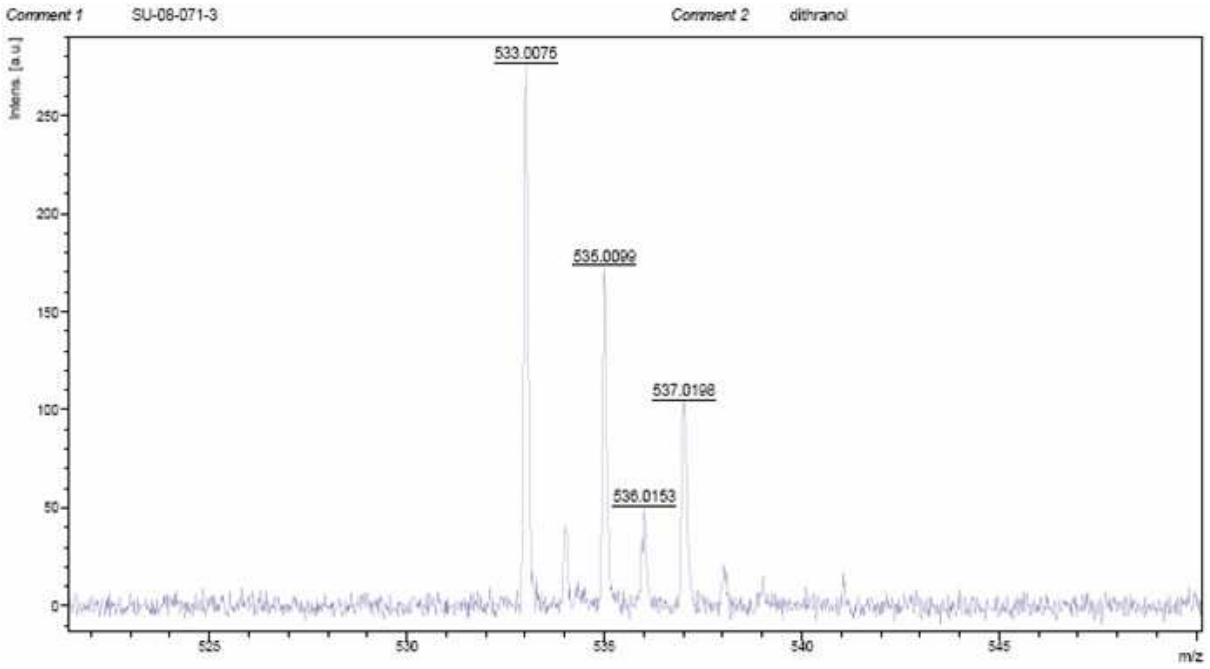




Calculated for $[C_{26}H_{34}F_3N_6O_3SZn]^+$ (m/z): 631.1657 (100.0%), 633.1626 (57.4%), 635.1614 (38.6%), 632.1690 (28.1%), 634.1659 (16.1%), 636.1647 (10.8%)

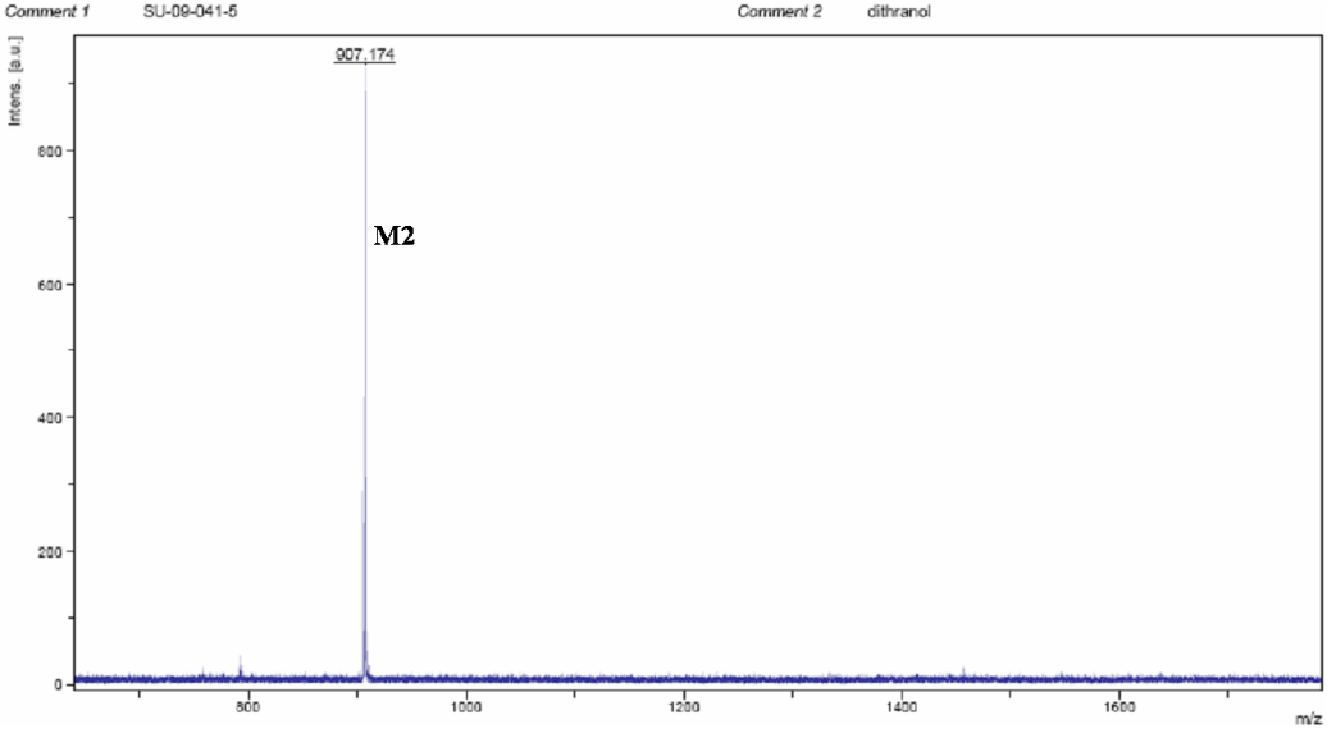
MALDI-TOF analysis of **M1'**:

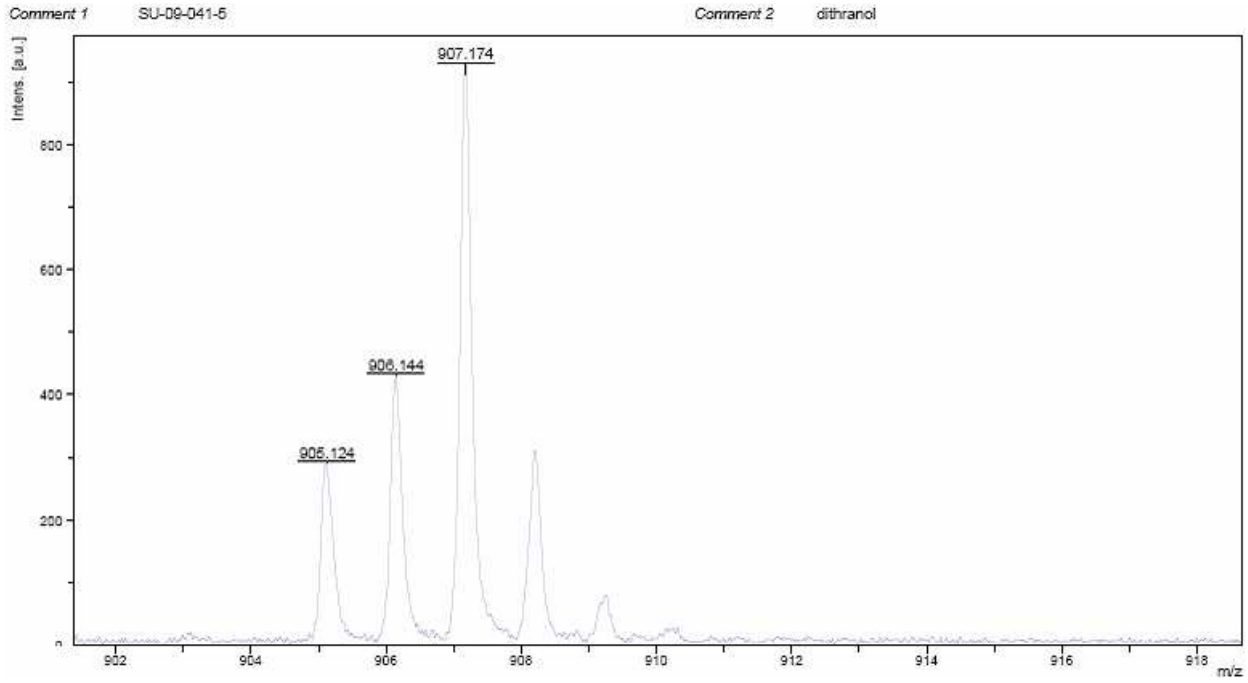




Calculated for $[C_{19}H_{20}F_3N_6O_3SZn]^+$ (m/z): 533.0561 (100.0%), 535.0530 (57.4%), 537.0518 (38.6%), 534.0595 (20.5%), 536.0564 (11.8%), 536.0541 (8.4%), 538.0552 (7.9%), 535.0519 (4.5%), 537.0488 (2.6%), 534.0532 (2.2%), 535.0628 (2.0%), 539.0476 (1.7%), 537.0575 (1.7%), 539.0523 (1.3%), 536.0500 (1.3%), 537.0597 (1.1%)

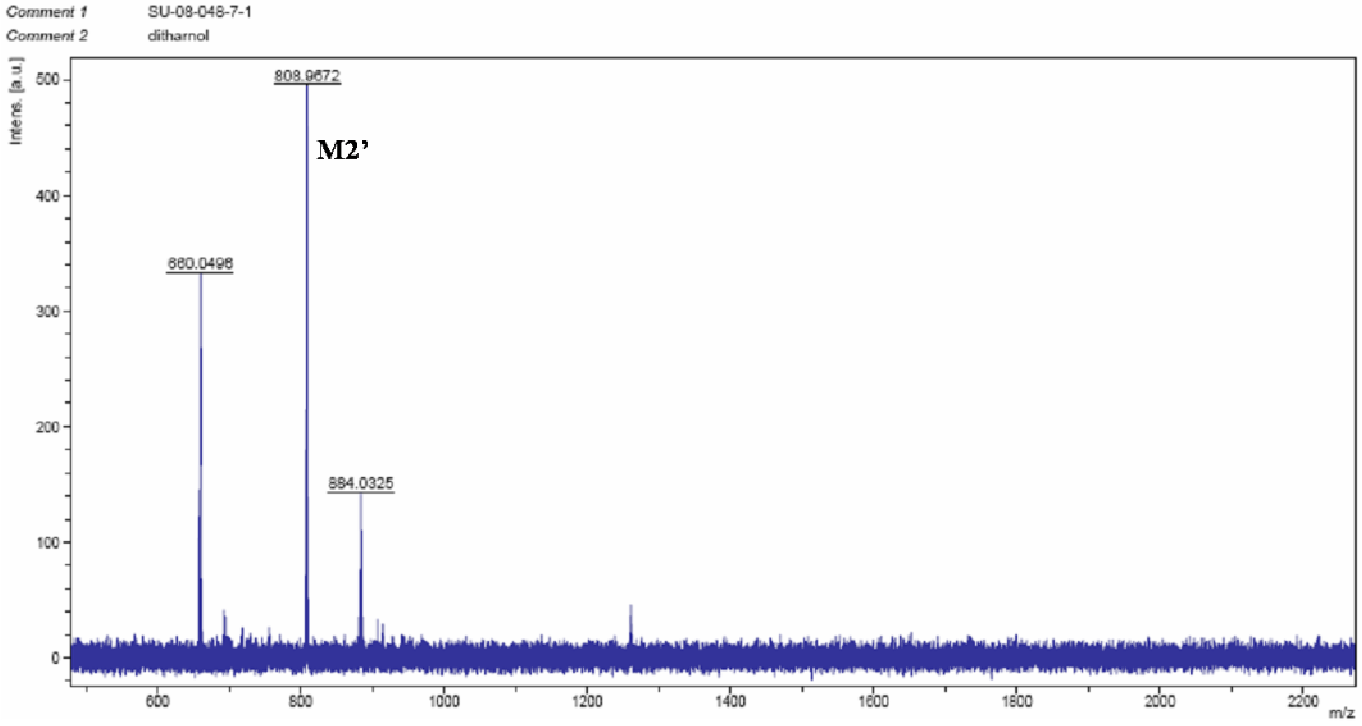
MALDI-TOF analysis of **M2**:

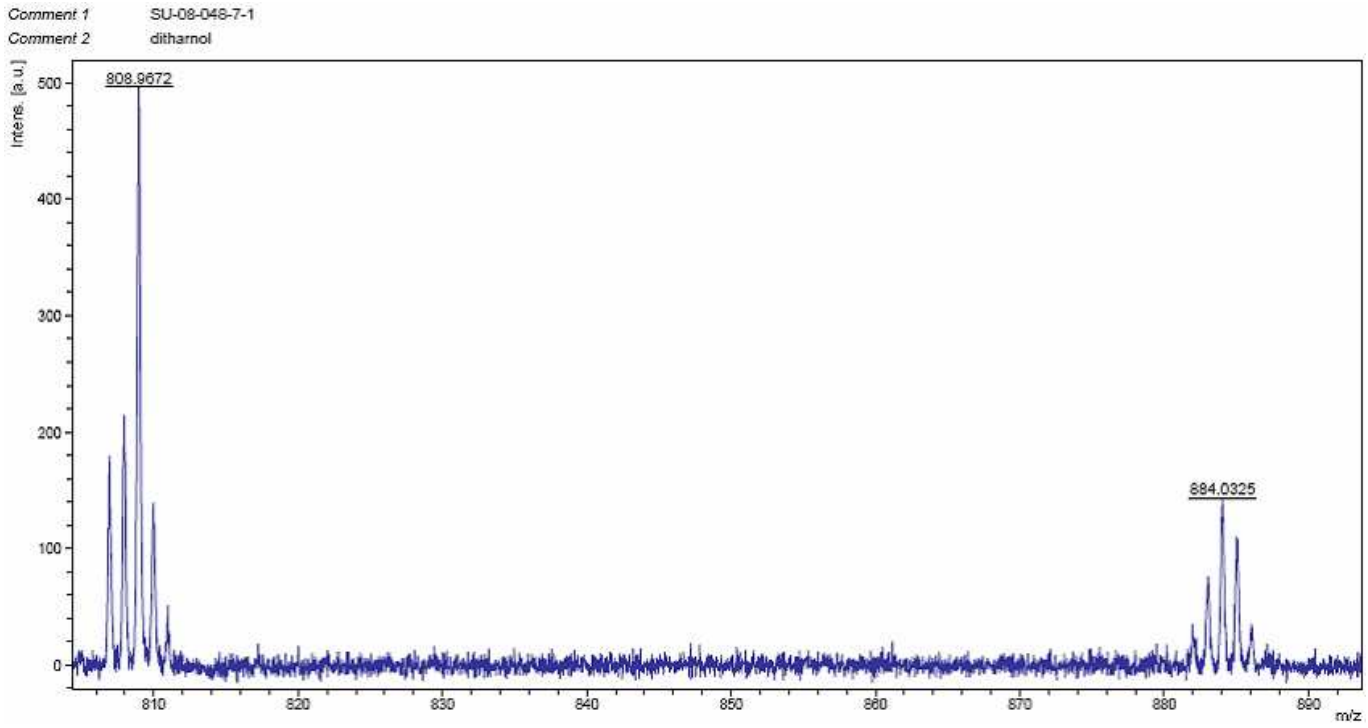




Calculated for $[C_{32}H_{46}F_3N_6O_6PbS]^+$ (m/z): 907.2918 (100.0%), 905.2896 (46.0%), 906.2910 (42.2%), 908.2952 (34.6%), 906.2930 (15.9%), 907.2944 (14.6%), 909.2985 (5.8%), 909.2876 (4.5%), 908.2888 (2.9%), 903.2882 (2.7%), 907.2963 (2.7%), 908.2978 (2.4%), 907.2854 (2.1%), 908.2868 (1.9%), 910.2910 (1.6%), 909.2960 (1.2%), 906.2866 (1.0%)

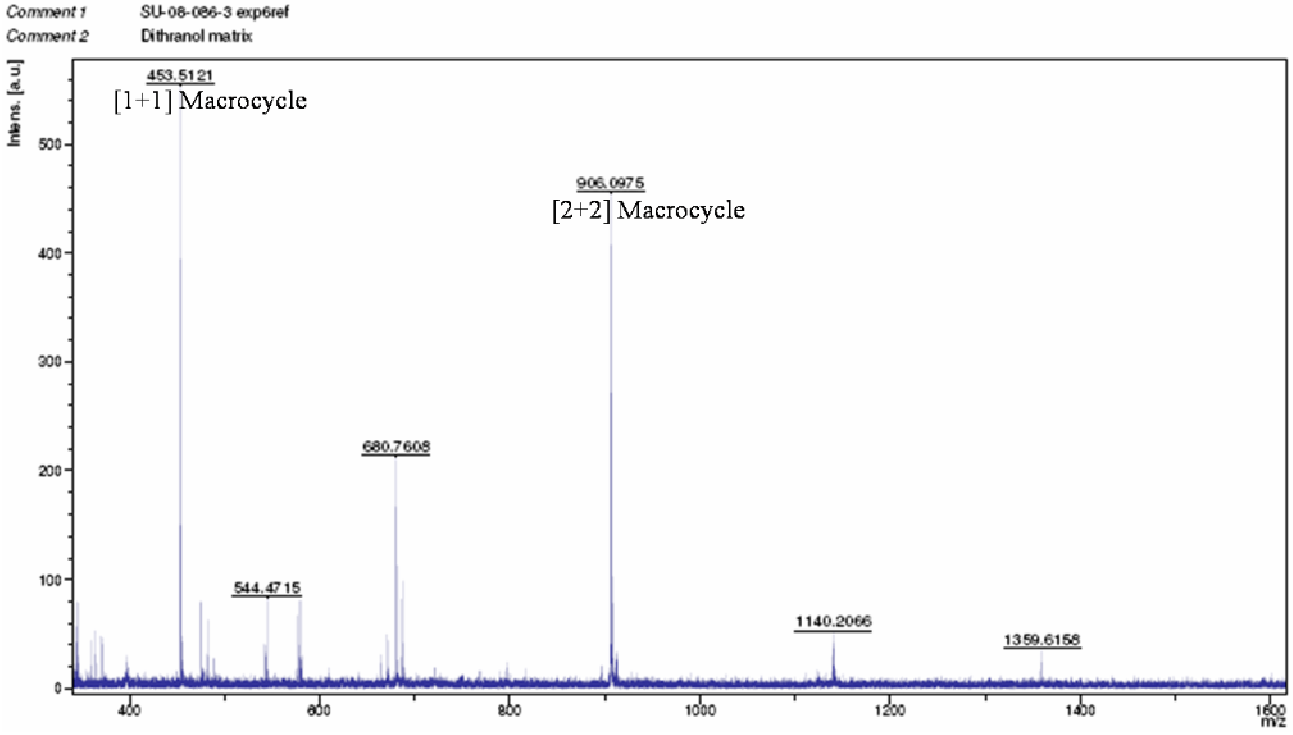
MALDI-TOF analysis of **M2'**:

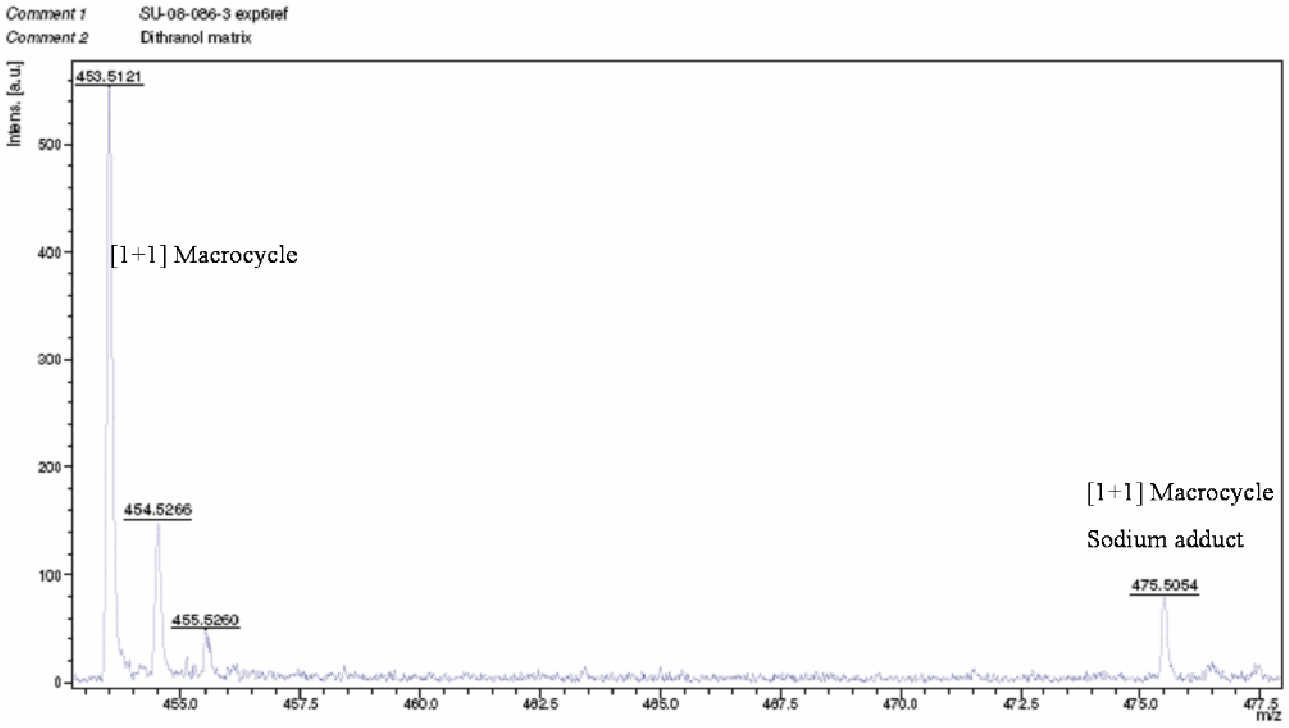




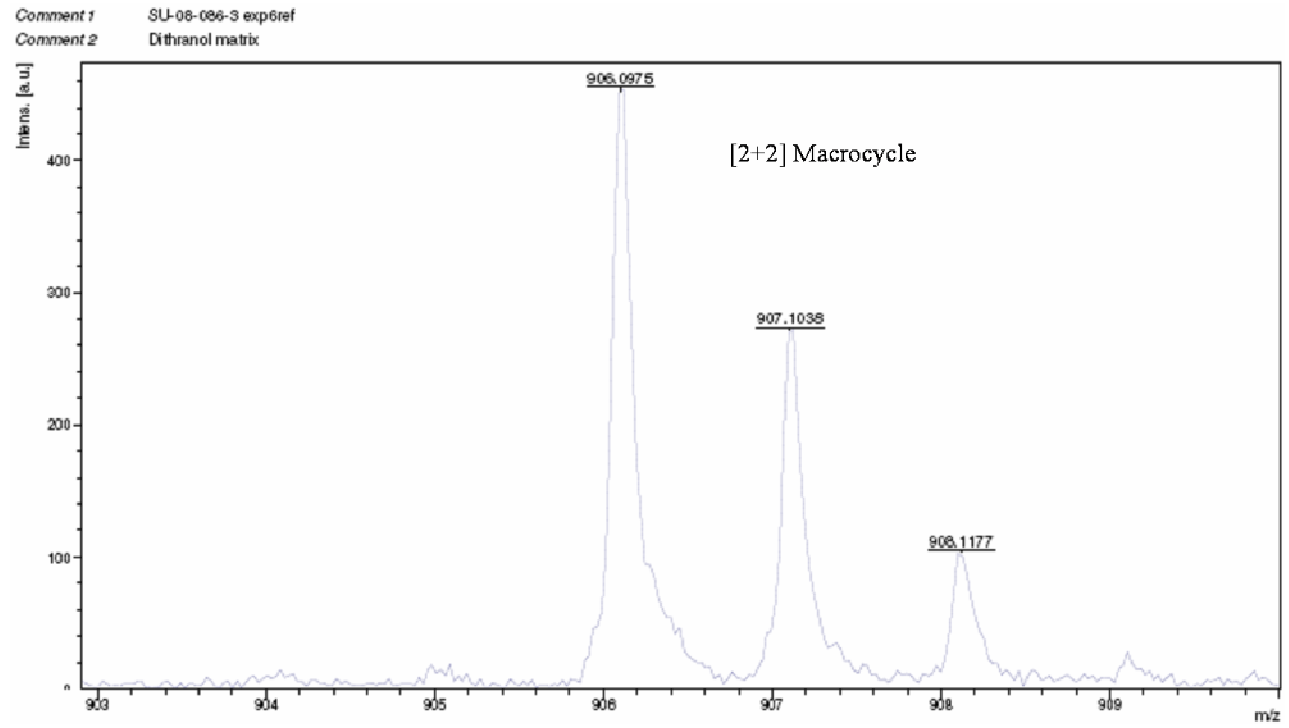
Calculated for $[C_{25}H_{32}F_3N_6O_6PbS]^+$ (m/z): 809.1822 (100.0%), 807.1801 (46.0%), 808.1815 (42.2%), 810.1856 (27.0%), 808.1834 (12.4%), 809.1848 (11.4%), 811.1780 (4.5%), 811.1890 (3.5%), 805.1786 (2.7%), 810.1793 (2.2%), 809.1759 (2.1%), 810.1773 (1.9%), 809.1868 (1.6%), 810.1882 (1.5%), 811.1865 (1.2%)

MALDI-TOF analysis of the self-assembly between **1-Me** and $\mathbf{N_2O_3}$ showing the macrocyclic species present at low concentration (marked with * in Fig. 5):





Calculated for $[C_{24}H_{32}N_6O_3+H]^+$ (m/z): 453.2614 (100.0%), 454.2648 (26.0%), 455.2681 (3.2%)



Calculated for $[C_{48}H_{64}N_{12}O_6+H]^+$ (m/z): 905.5150 (100.0%), 906.5184 (51.9%), 907.5217 (13.2%), 906.5120 (4.4%), 907.5154 (2.3%), 908.5251 (2.2%), 907.5192 (1.2%)