Supplementary material for

Factors influencing mononuclear versus multinuclear coordination in a series of potentially hexadentate acyclic N_6 ligands: the roles of flexibility and chelate ring size.

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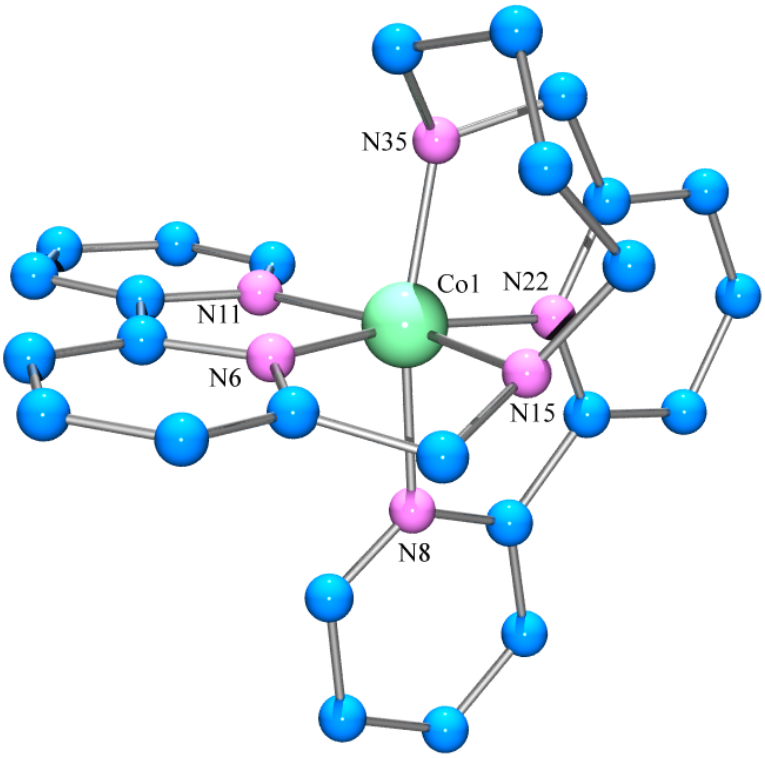

Figure S1: X-ray structure of the $[Co(bmbu)]^{3+}$ cation.

The above structure showed extensive disorder in both the cation and perchlorate anions. The disorder was resolved to a certain extent but, despite this, an acceptable R1 value could not be obtained (R1 = 11.45 %). All atoms were refined isotropically as attempts to refine the structure anisotropically gave numerous atoms which exhibited non-positive-definite temperature factors. In the $[Co(bmbu)]^{3+}$ cation, the entire bmbu ligand was found to be disordered over two sites, with approximately 54:46 occupancy. The conformation of the 7-membered chelate ring was found to be the same in both, attesting to a significant amount of rigidity and consistent with the ^{1}H NMR data for the complex (see main paper). The above diagram shows one of the two disordered components of the $[Co(bmbu)]^{3+}$ cation.

Mass spectra of complexes.

All spectra were recorded in MeCN in the presence of formate as calibrant. The peak in each spectrum at highest m/z generally corresponds to $\{[ML]ClO_4\}^+$ while that at lowest m/z generally corresponds to $[ML]^{2+}$. The presence of dimeric and trimeric species is indicated by the complex isotope pattern about the high m/z peak as discussed in the paper.

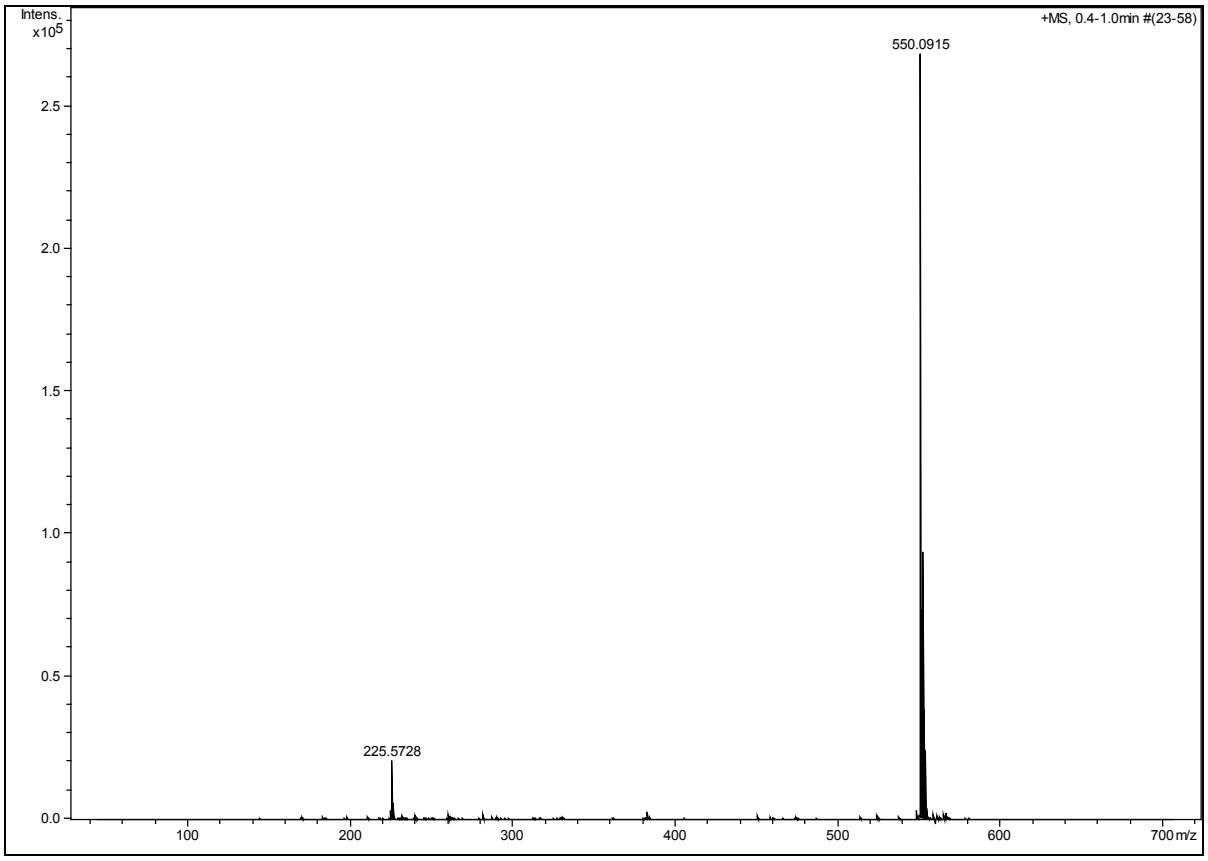

Figure S2: Mass spectrum of $[Mn(bmet)](ClO_4)_2$

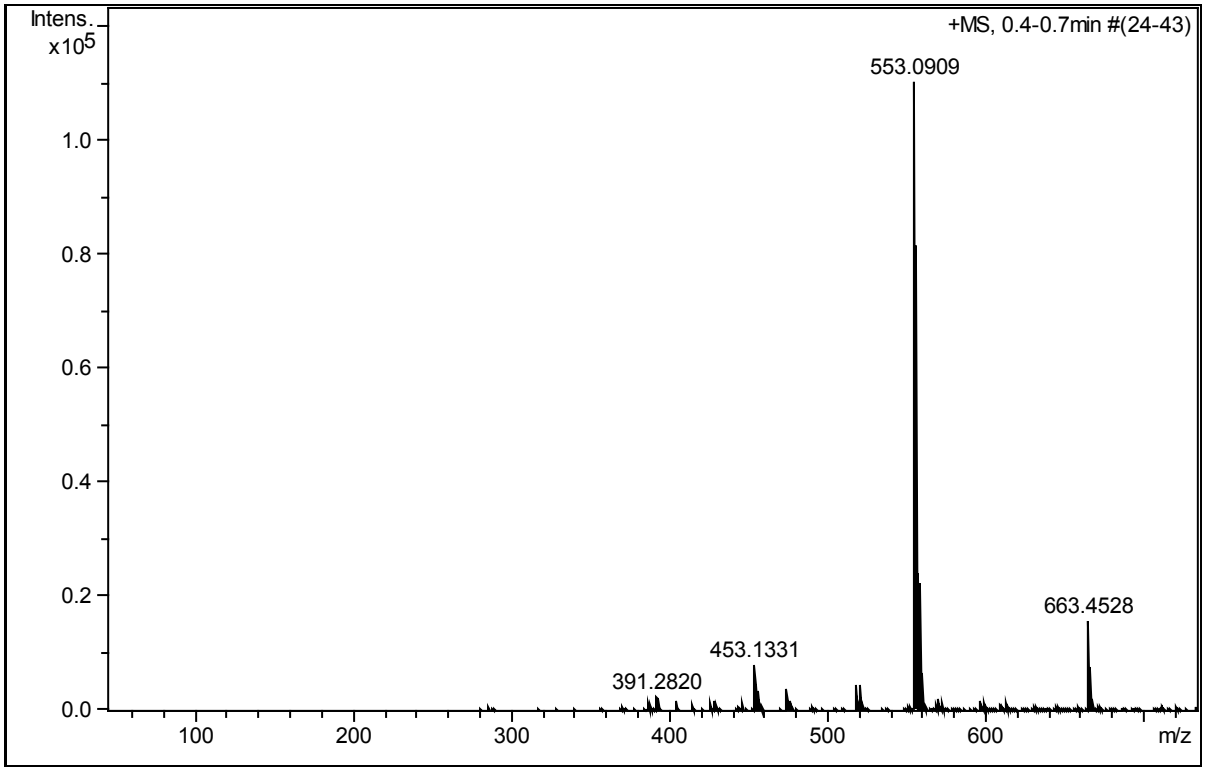

Figure S3: Mass spectrum of $[Ni(bmet)](ClO_4)_2$

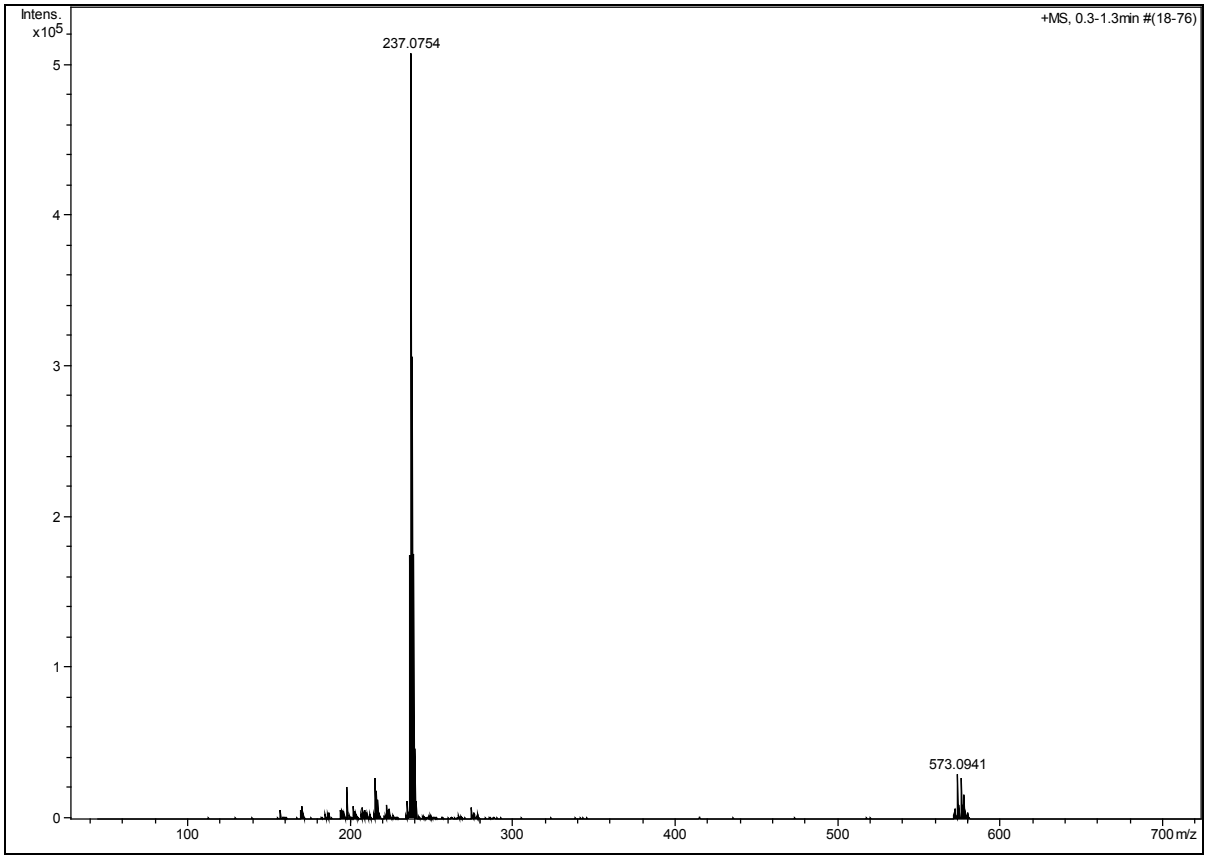

Figure S4: Mass spectrum of $[Zn(bmpp)](ClO_4)_2$

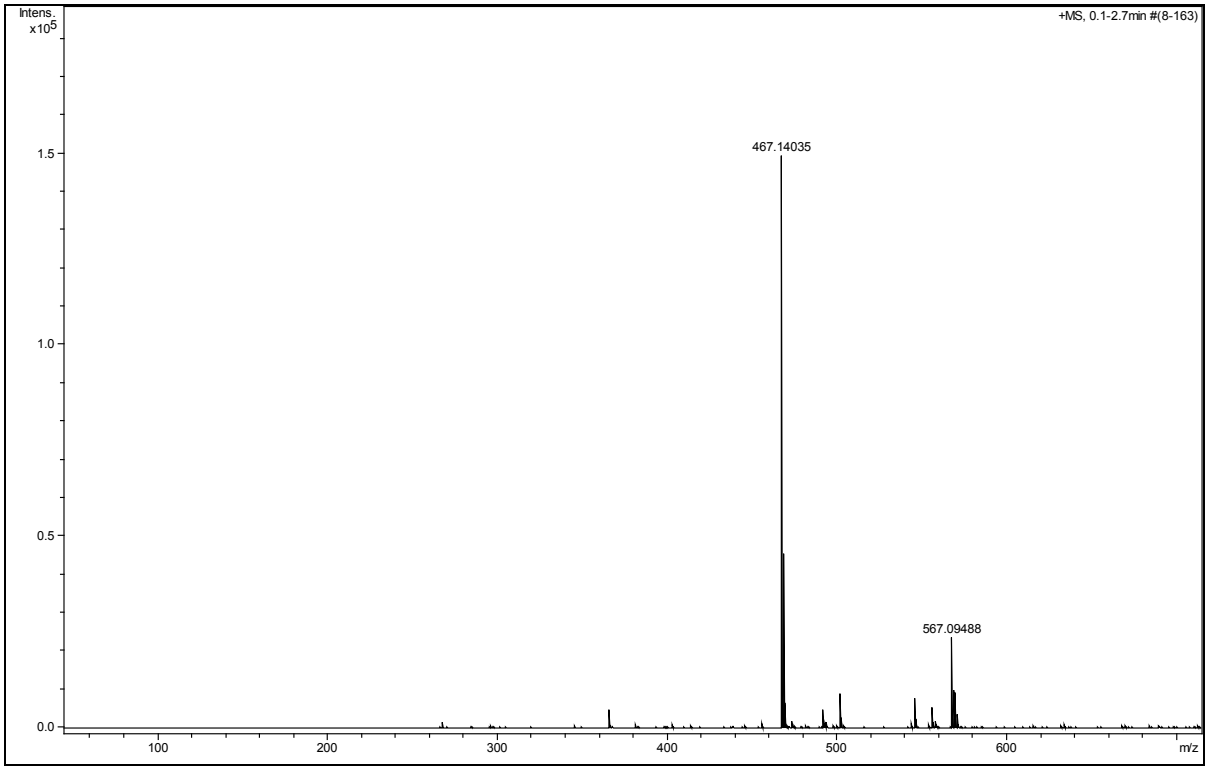

Figure S5: Mass spectrum of $[Co(bmpp)](ClO_4)_3$

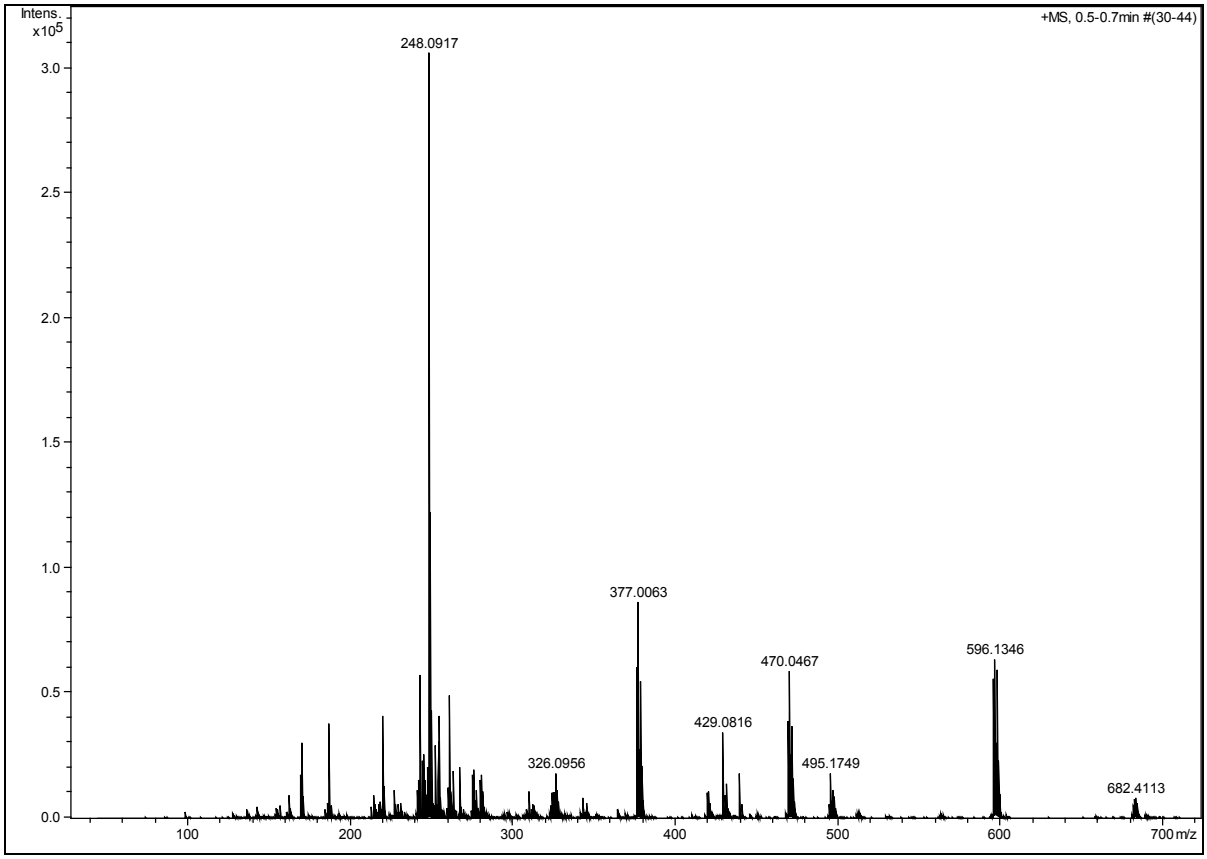

Figure S6: Mass spectrum of a 1:1 MeCN solution of $[Ni(H_2O)_6](ClO_4)_2$ and bmpt

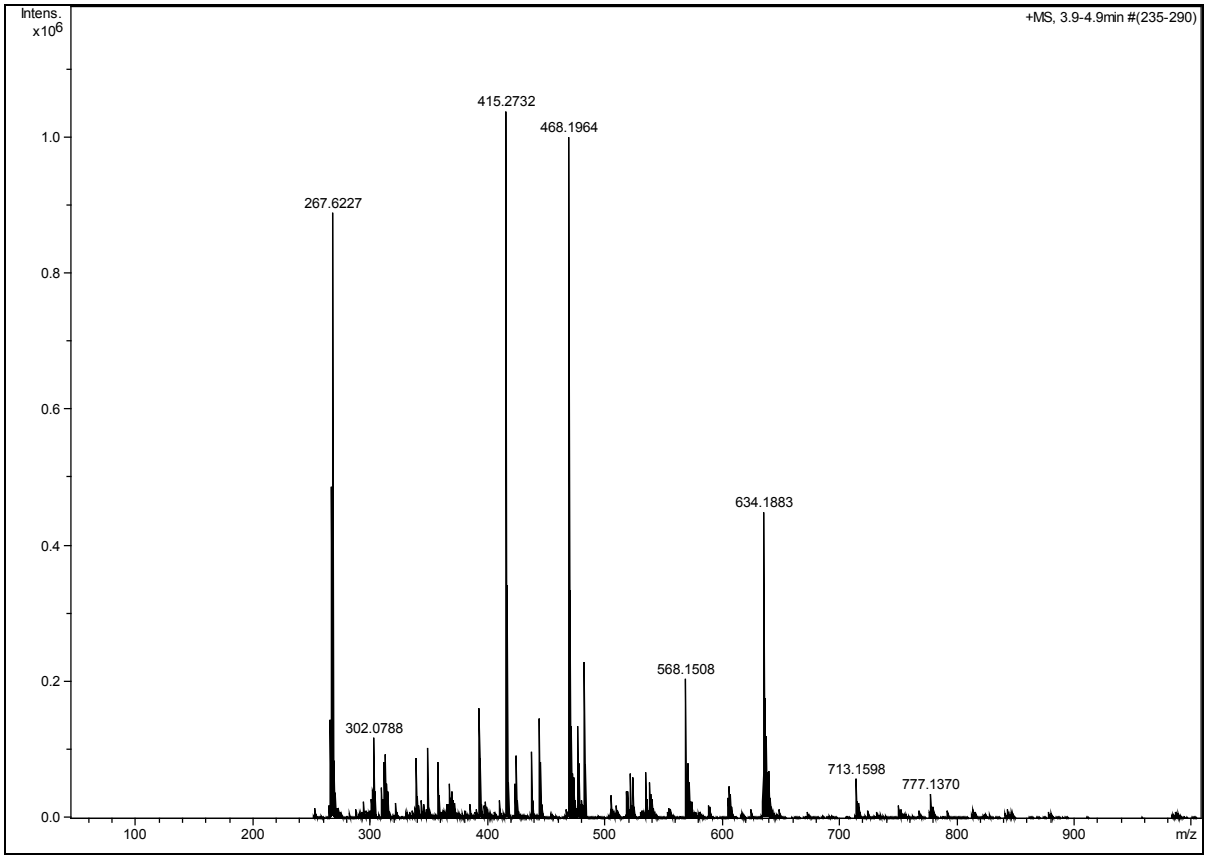

Figure S7: Mass spectrum of a 1:1 MeCN solution of $[Mn(H_2O)_6](ClO_4)_2$ and bmot

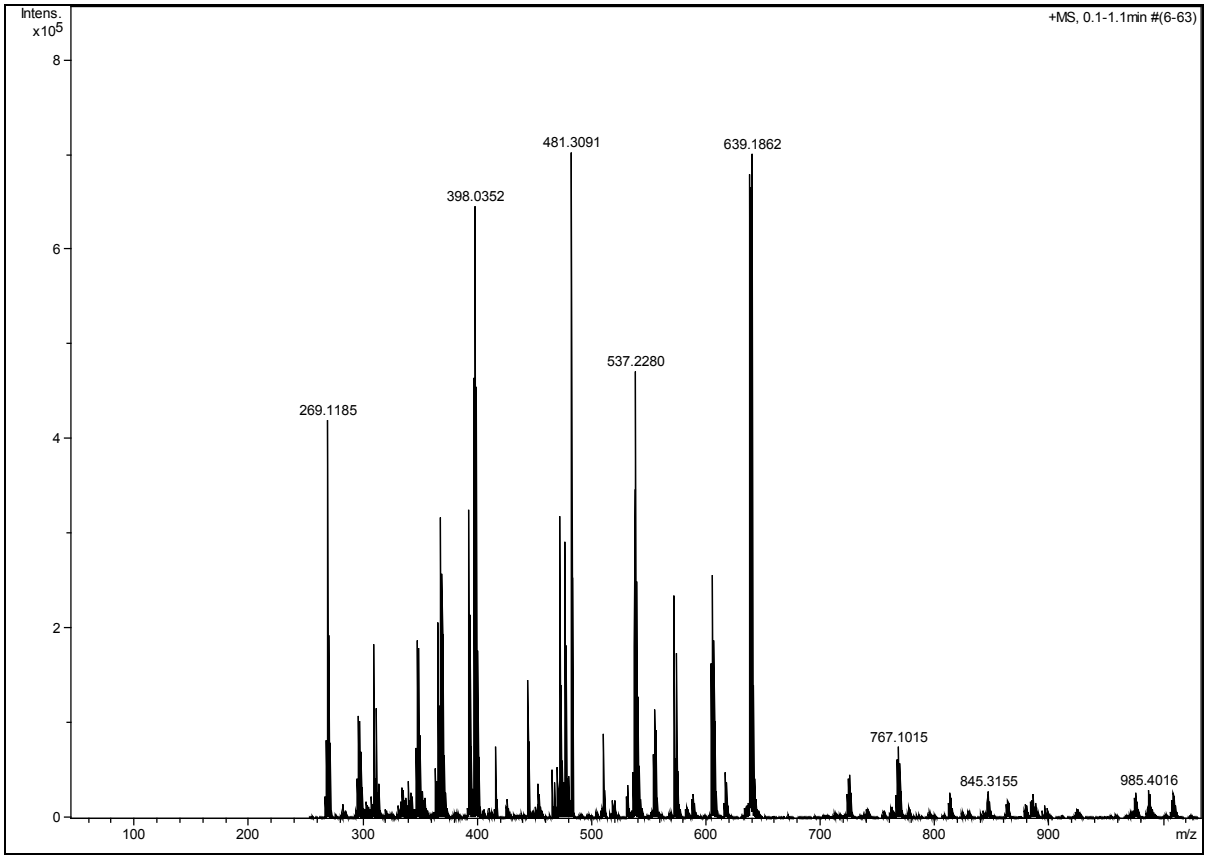

Figure S8: Mass spectrum of a 1:1 MeCN solution of $[Ni(H_2O)_6](ClO_4)_2$ and bmot