Electronic supplementary information:

Sterics and metal-ion radius control the self-assembly of $[M_2L_3]$ helicates

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1. Experimental

$[Co_2L_3](ClO_4)_4$

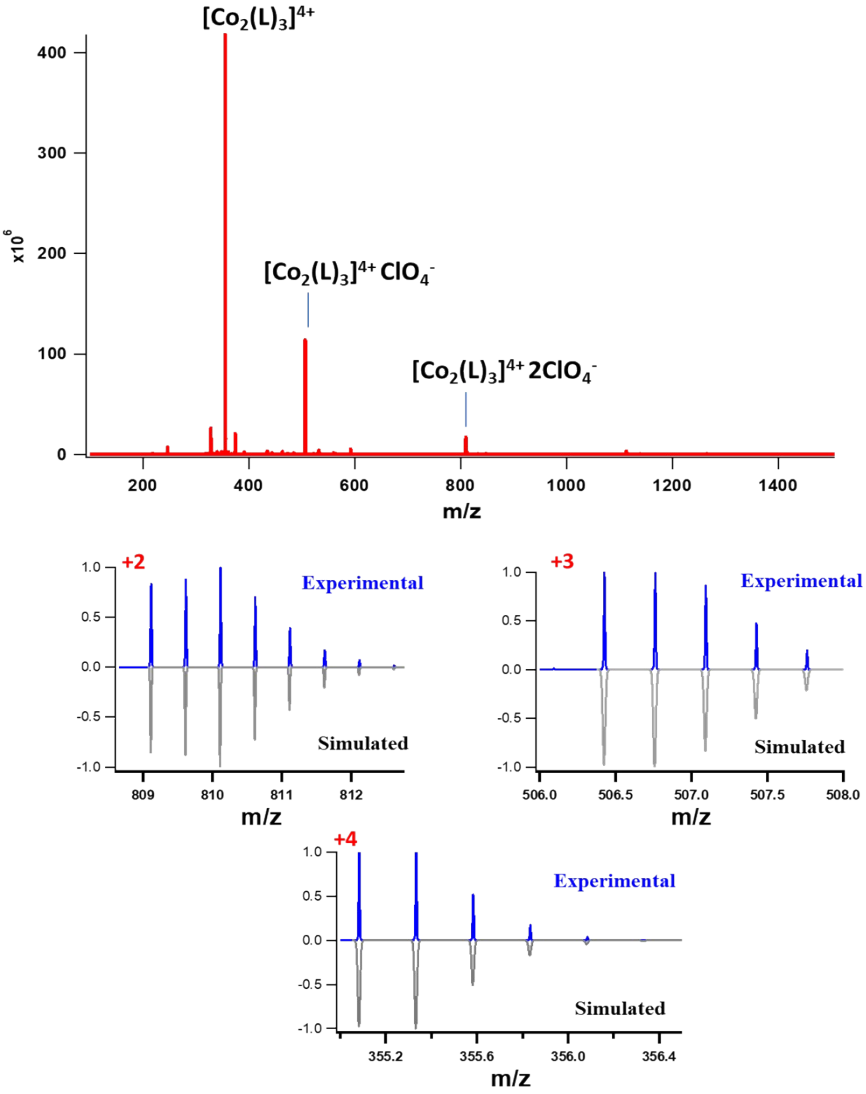

Figure S1 ESI-MS in CH_3CN of the product shows +2, +3 and +4 ions that correspond to 2, 3 and 4 losses of ClO_4^- ions from $[Co_2L_3]^{4+}$.

Synthesis of $[Co_2L_3](PF_6)_6$

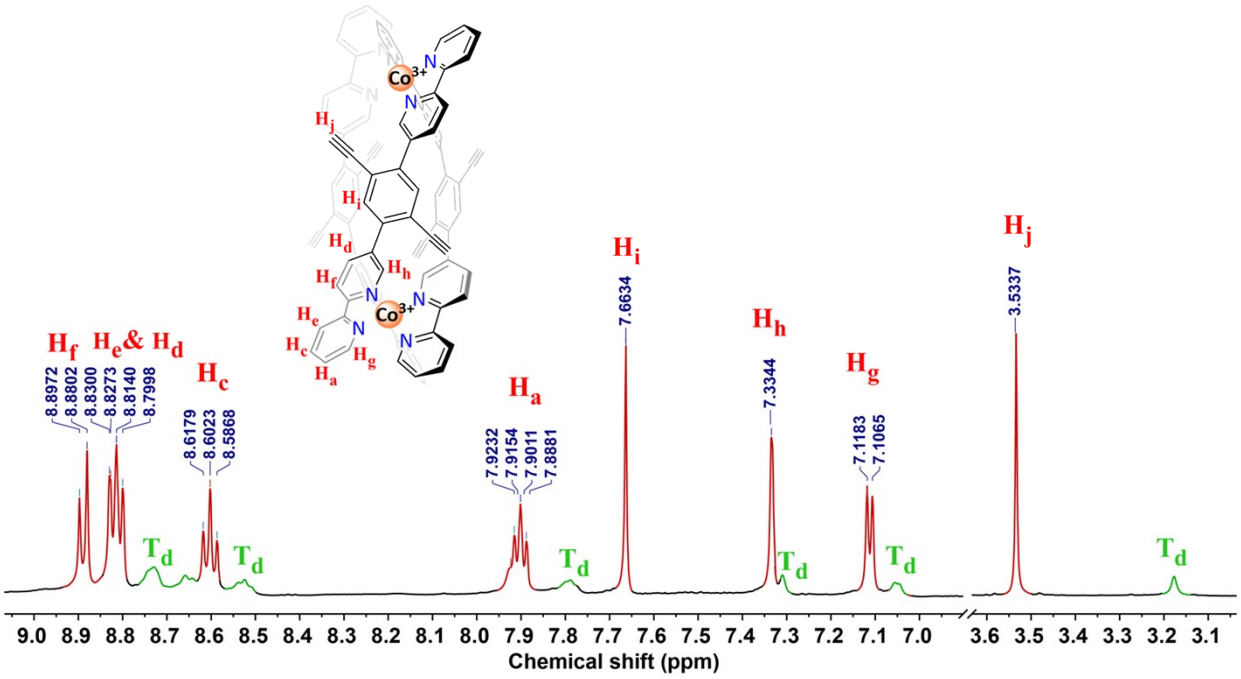

Figure S2 The ^{1}H NMR spectrum (500 MHz, CD_3CN, 298K) of Co(III) $[Co_2(\mathbf{L})_3](PF_6)_6$ with peak assignments. ^{1}H NMR peaks of small amount of tetrahedral (Td) assembly are shown in green colour.

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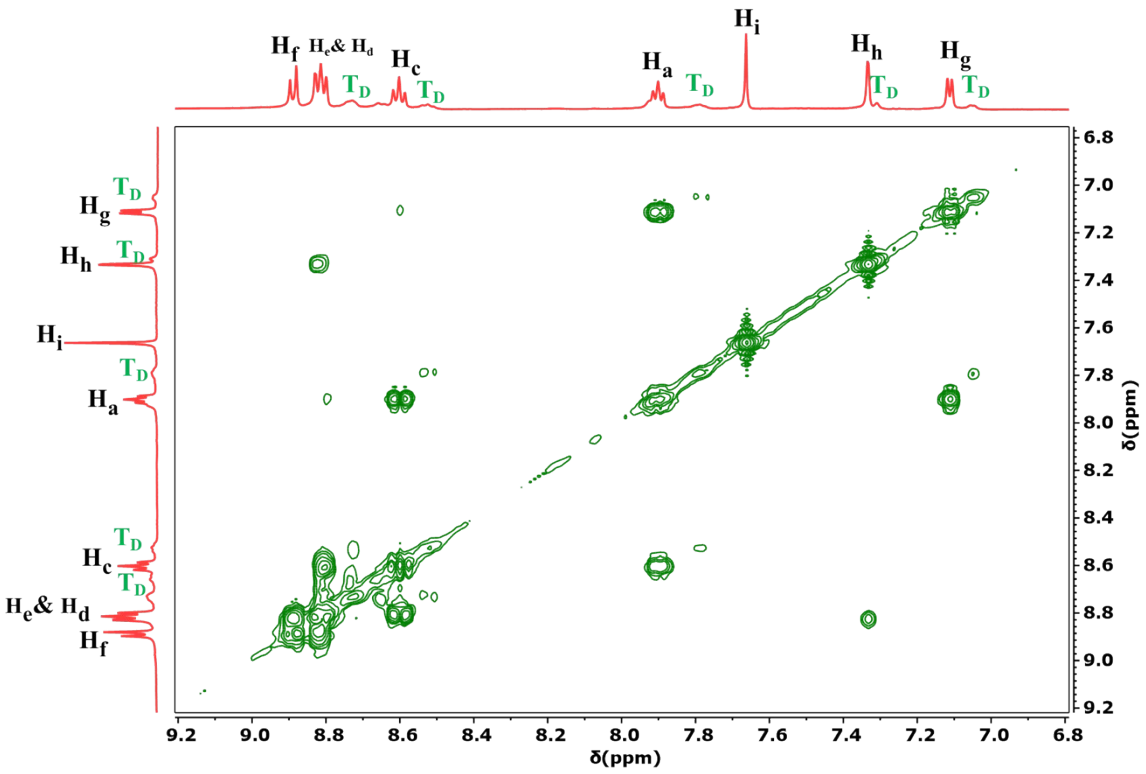
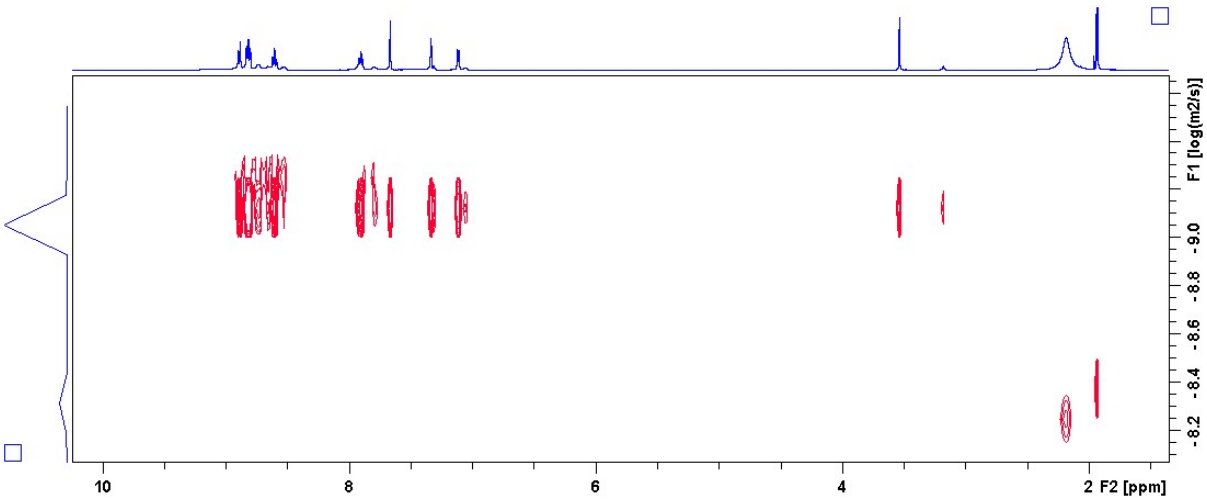


Figure S3 ^{1}H-^{1}H COSY NMR (500 MHz, CD3CN, 298K) of the Co(III) complex with ligand-**L**.



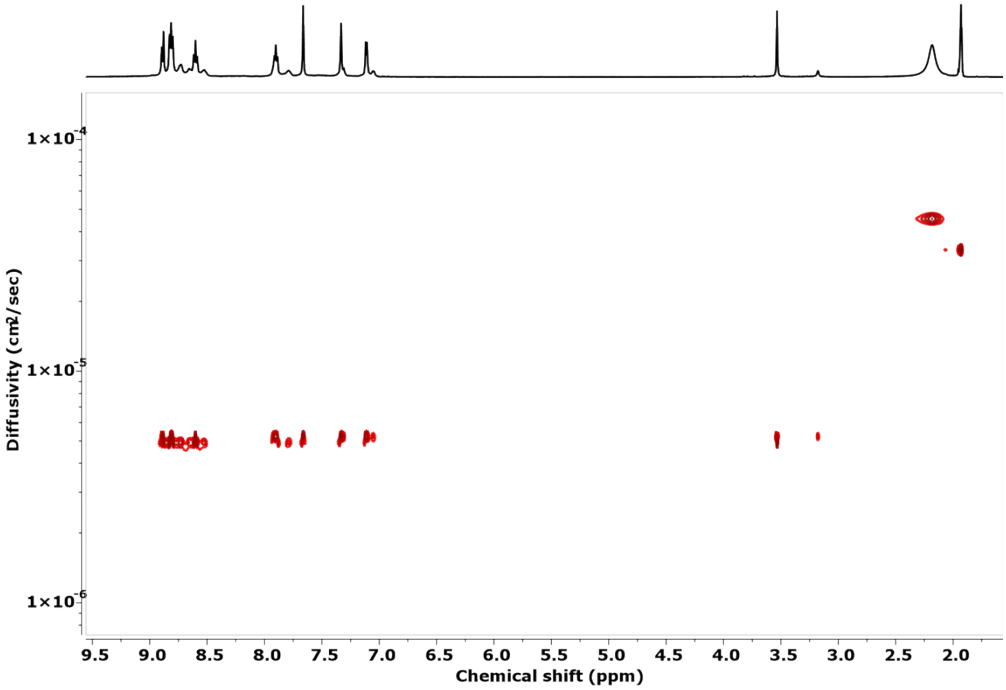


Figure S4 ^{1}H 2D DOSY NMR (500 MHz, CD_3CN, 298K) of the Co(III) complex with ligand-**L.**

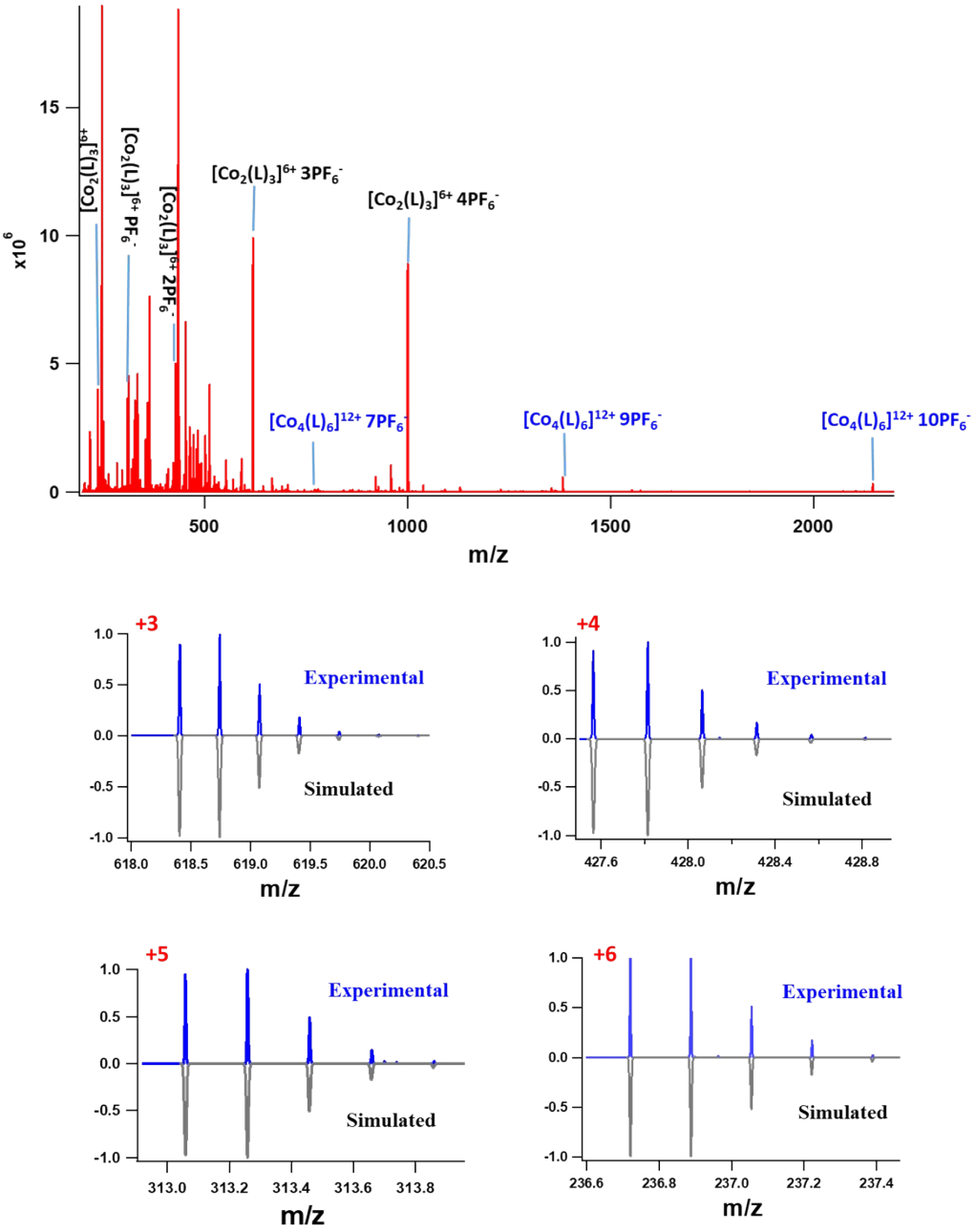


Figure S5 ESI-MS in CH_3CN of the product shows +2, to +6 ions that correspond to successive losses of PF_6^- ions from $[Co_2\mathbf{L}_3]^{6+}$ and small peaks for +2 to +5 ions that corresponds to successive losses of PF_6^- ions from $[Co_4\mathbf{L}_6]^{12+}$.

Synthesis of $[Zn_2L_3](ClO_4)_4$

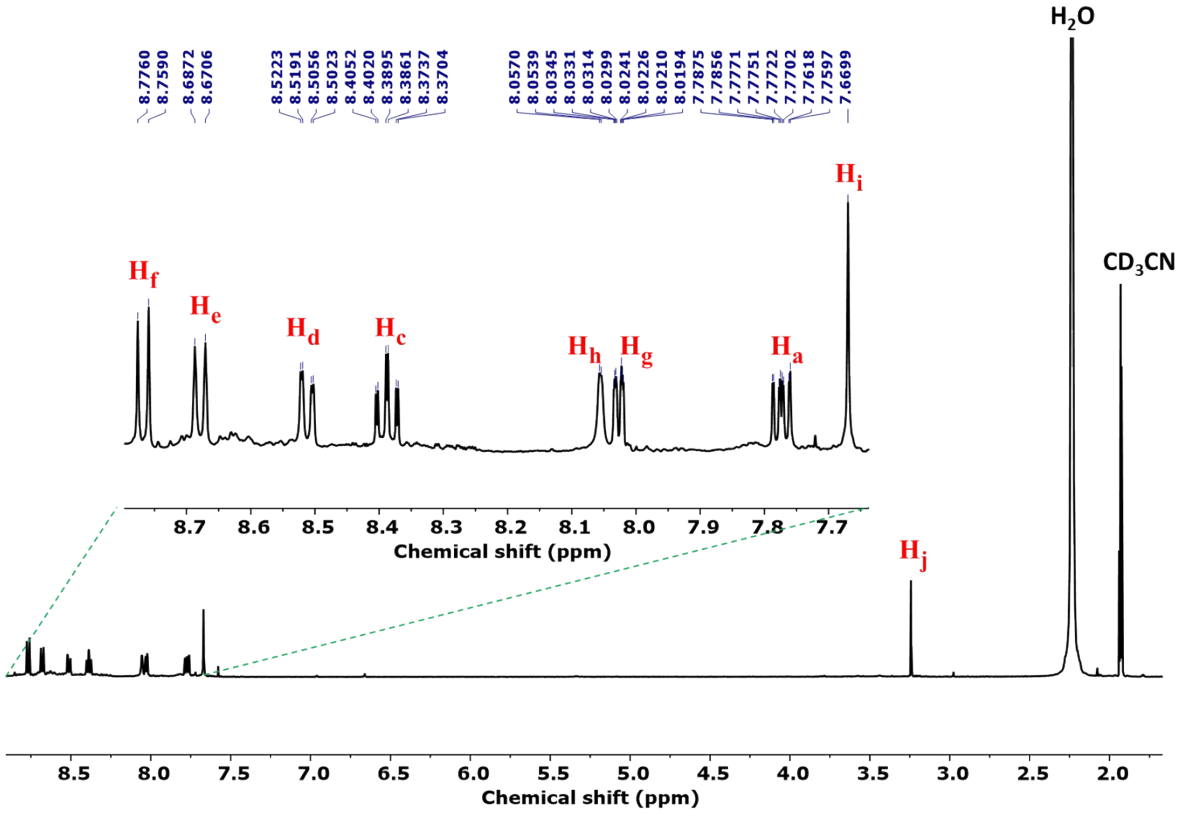


Figure S6 The ^{1}H NMR spectrum (500 MHz, CD_3CN, 298K) of Zn(II) complex with ligand **L.**

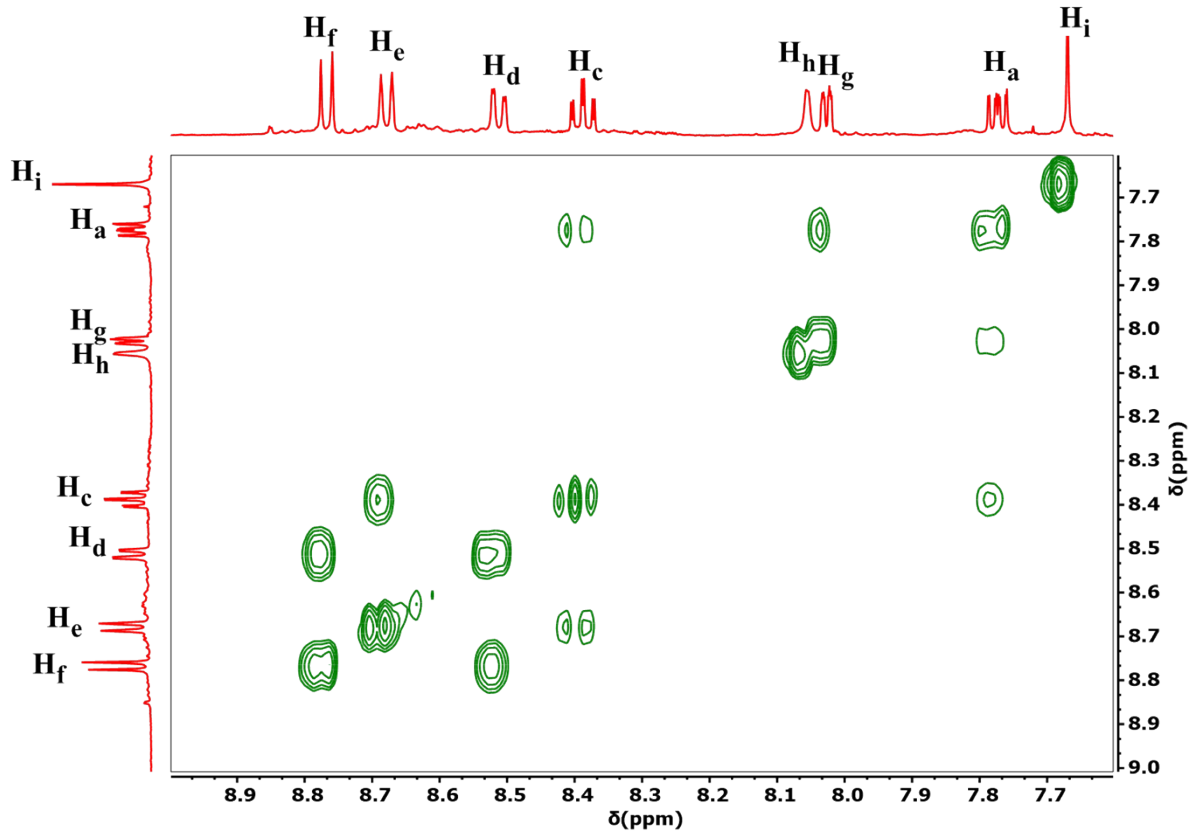


Figure S7 ^{1}H-^{1}H COSY NMR (500 MHz, CD3CN, 298K) of the Zn(II) complex with ligand-**L**.

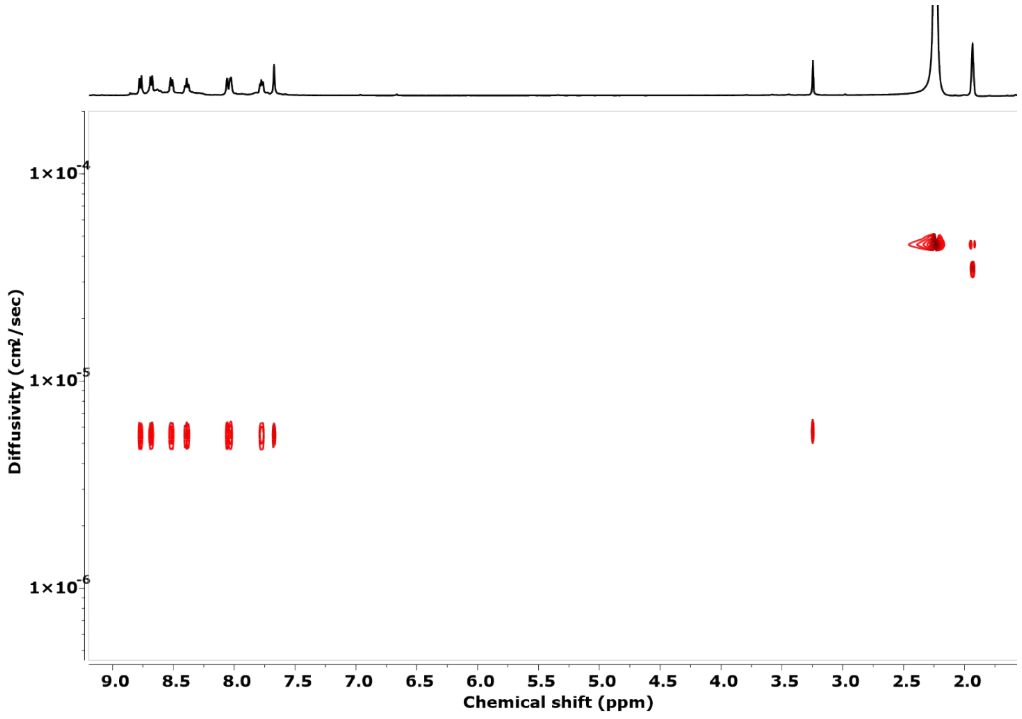


Figure S8 ^{1}H 2D DOSY NMR (500 MHz, CD_3CN, 298K) of the Zn(II) complex with ligand-**L.**

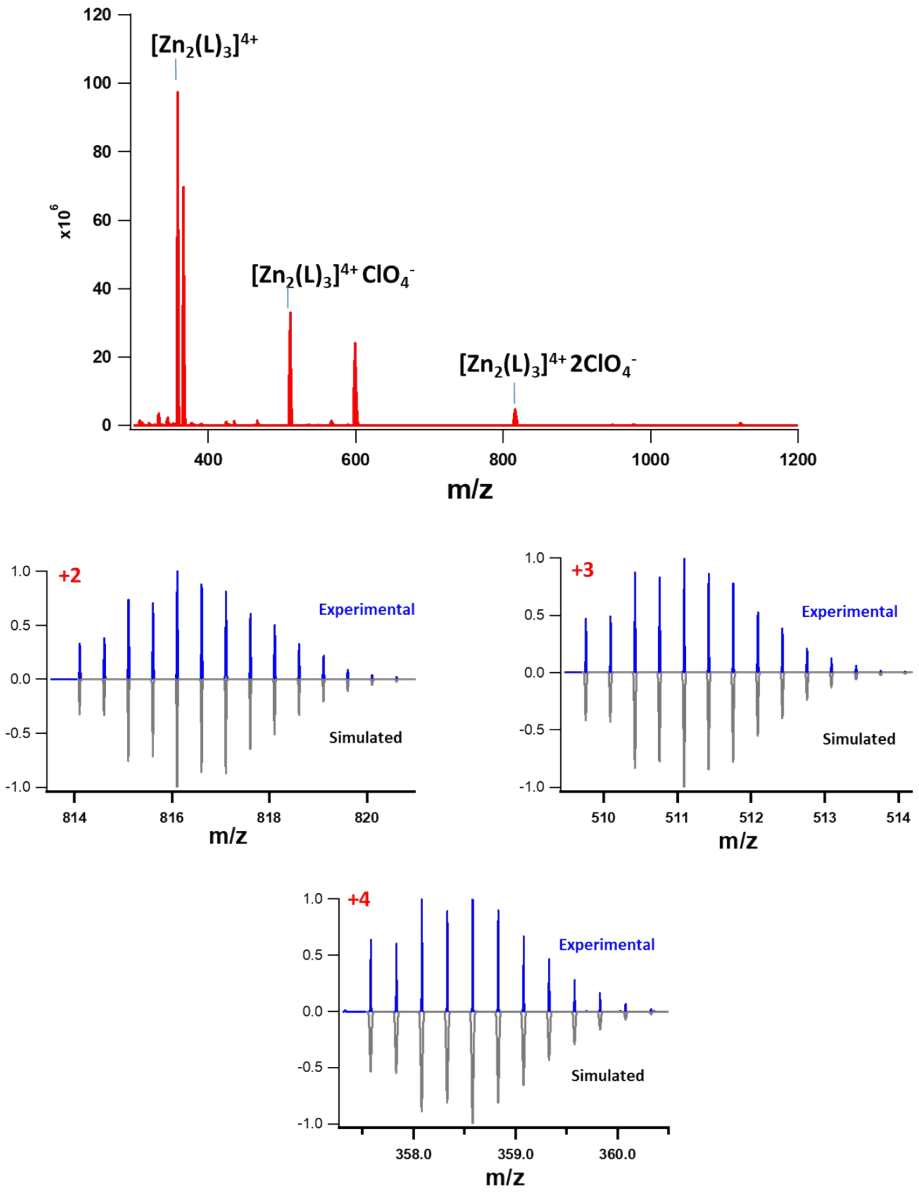


Figure S9 ESI-MS in CH_3CN of the product shows +2, +3 and +4 ions that correspond to 2, 3 and 4 losses of ClO_4^- ions from $[Zn_2\mathbf{L}_3]^{4+}$.