Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Materials for

Synthesis and Structural Characterization of Inverse-Coordination Clusters from a Two-Electron Superatomic Copper Nanocluster

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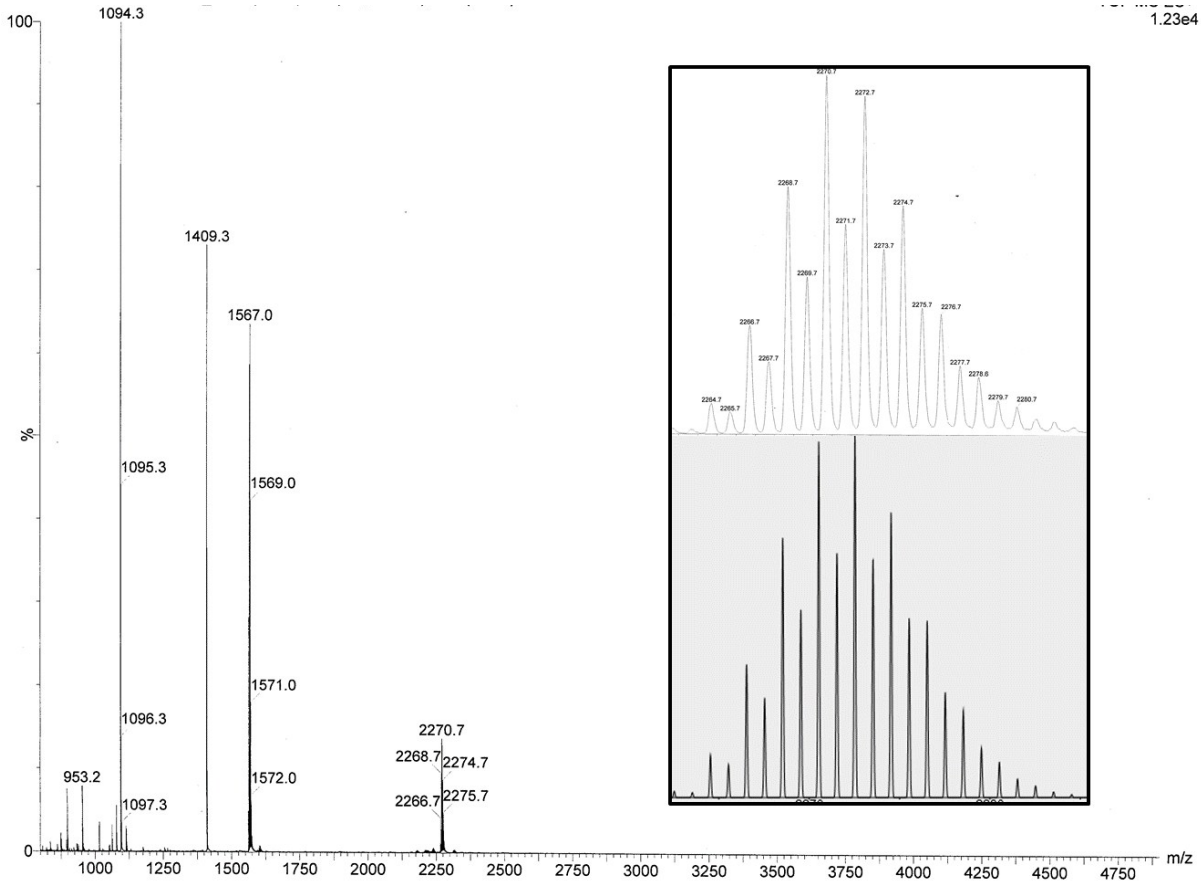

Figure S1. ESI-MS spectrum of **1c**, the inset shows experimental one in top and theoretical one in bottom.

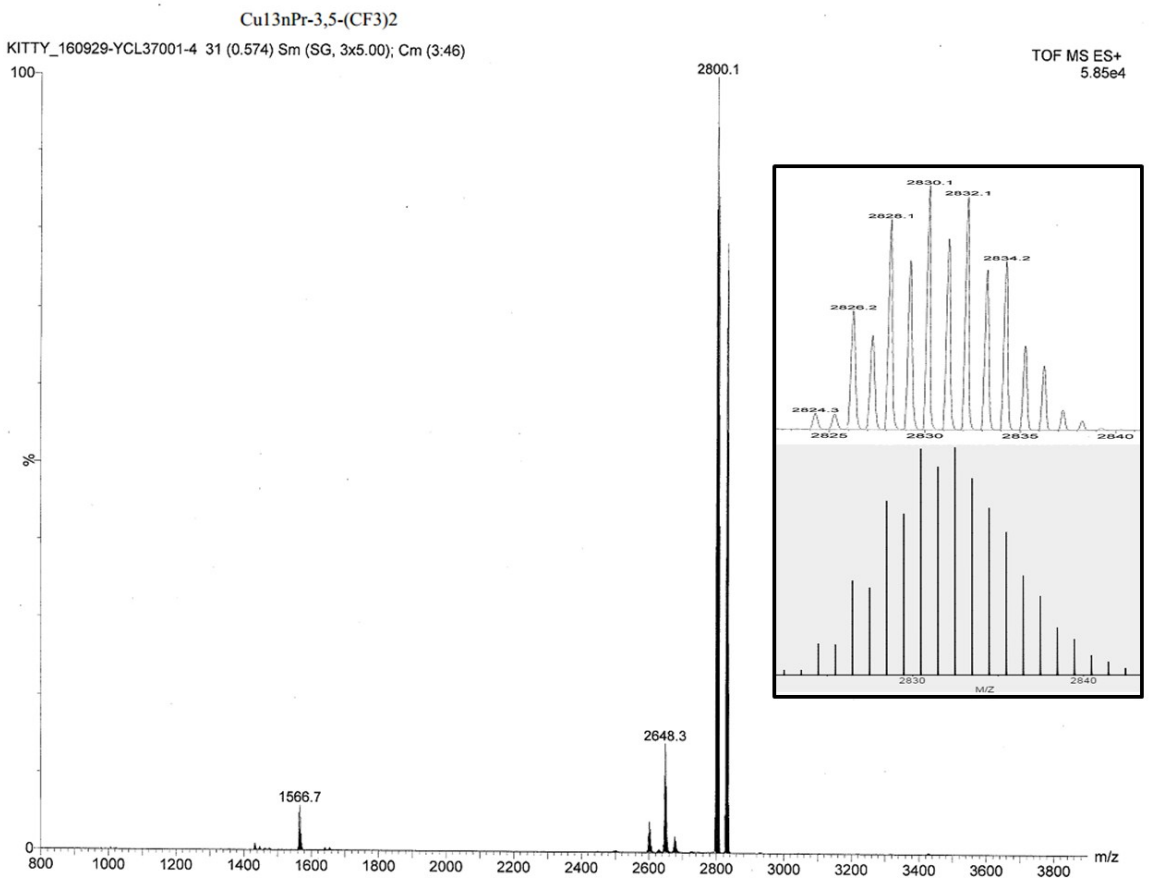

Figure S2. ESI-MS spectrum of **1d**, the inset shows experimental one in top and theoretical one in bottom.

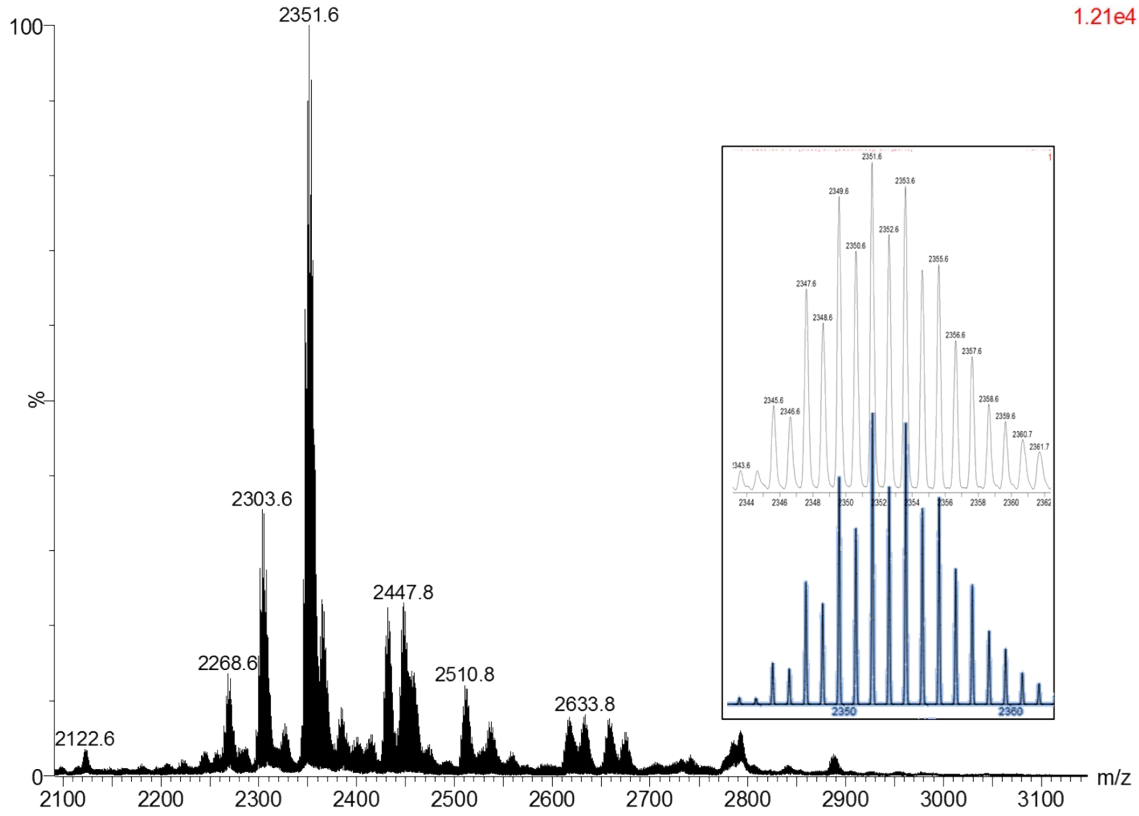

Figure S3. ESI-MS spectrum of **2a**, the inset shows experimental one in top and theoretical one in bottom.

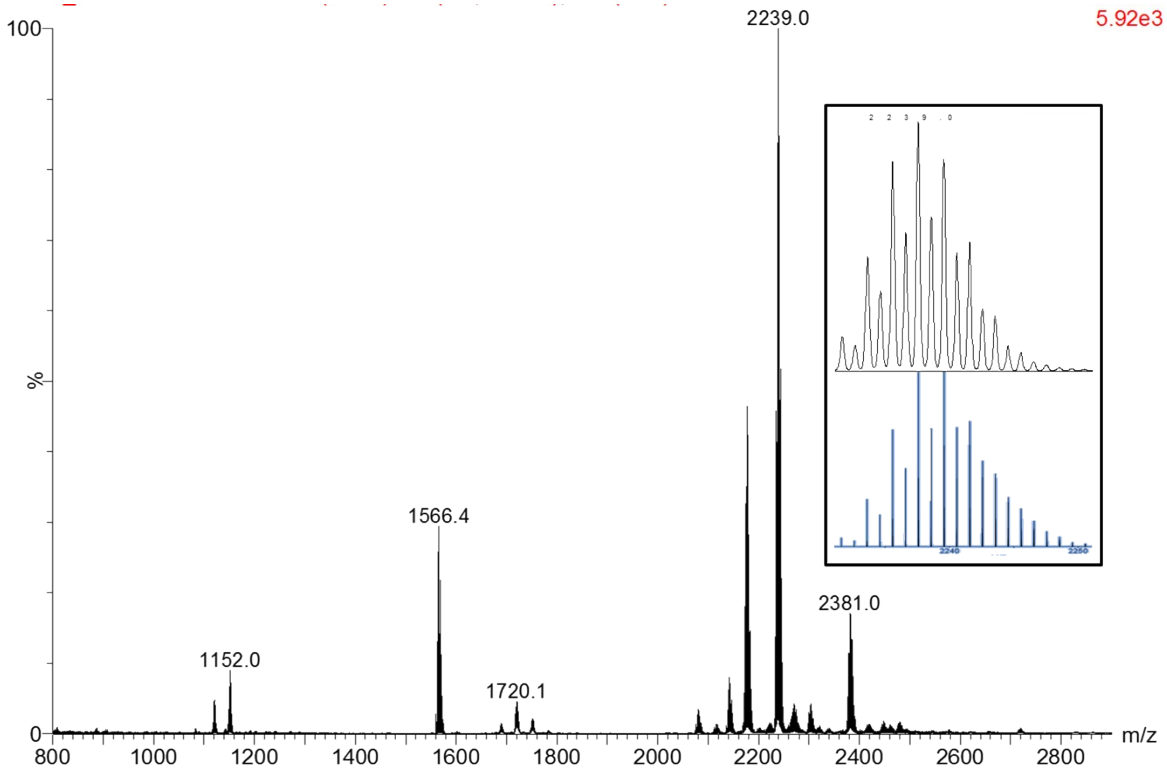

Figure S4. ESI-MS spectrum of **2c**, the inset shows experimental one in top and theoretical one in bottom.

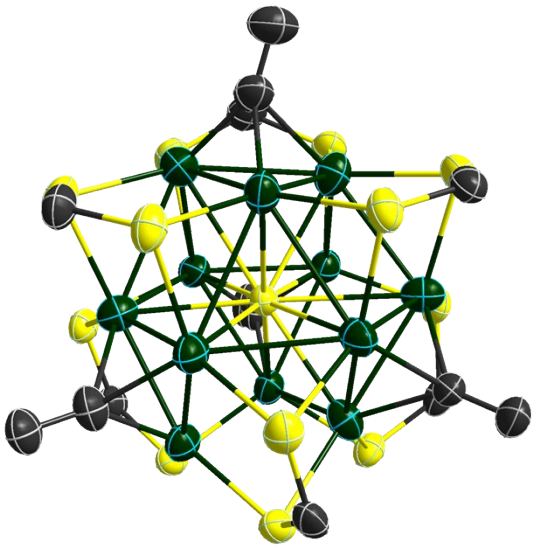

Figure S5. Molecular structure of **2b** with 30% thermal probability ellipsoids. All N^nBu_2 and $C(O)OCH_2CH_3$ moieties are omitted for clarity.; Carbon gray, copper green, sulfur yellow.

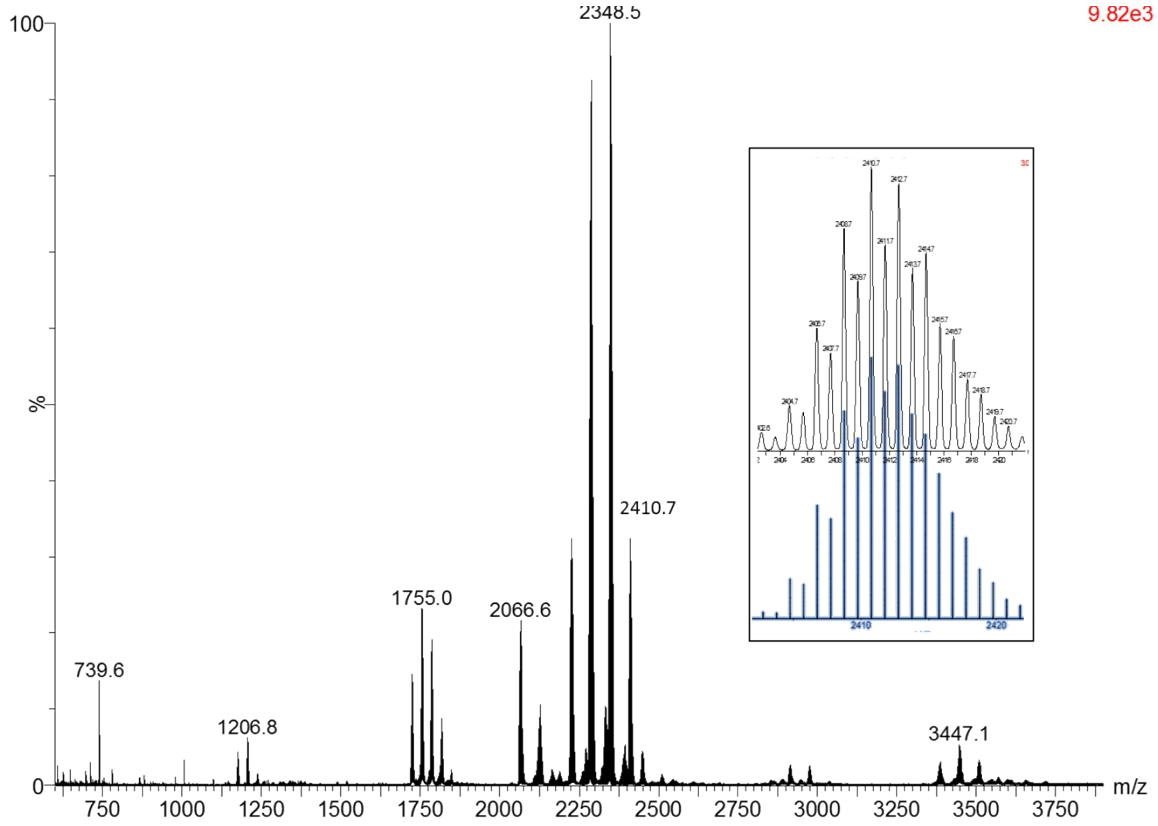

Figure S6. ESI-MS spectrum of **3b**, the inset shows experimental one in top and theoretical one in bottom.

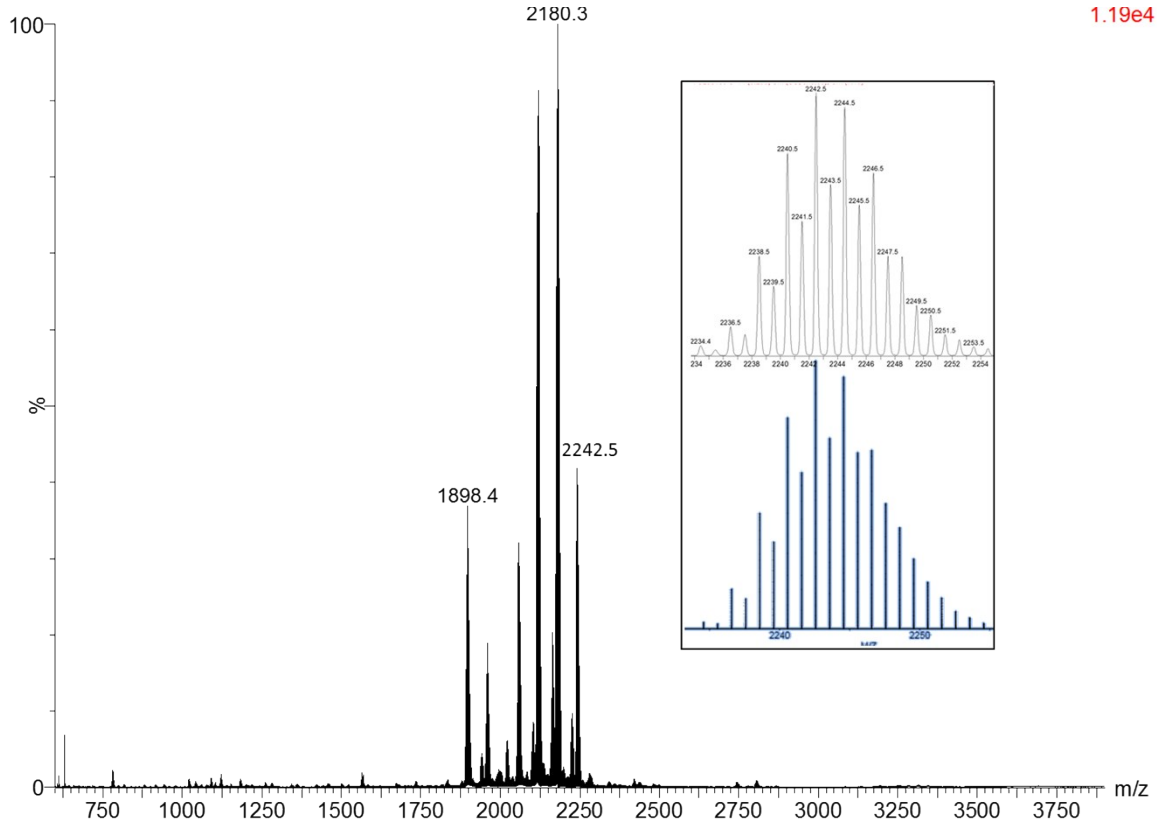

Figure S7. ESI-MS spectrum of **3c**, the inset shows experimental one in top and theoretical one in bottom.

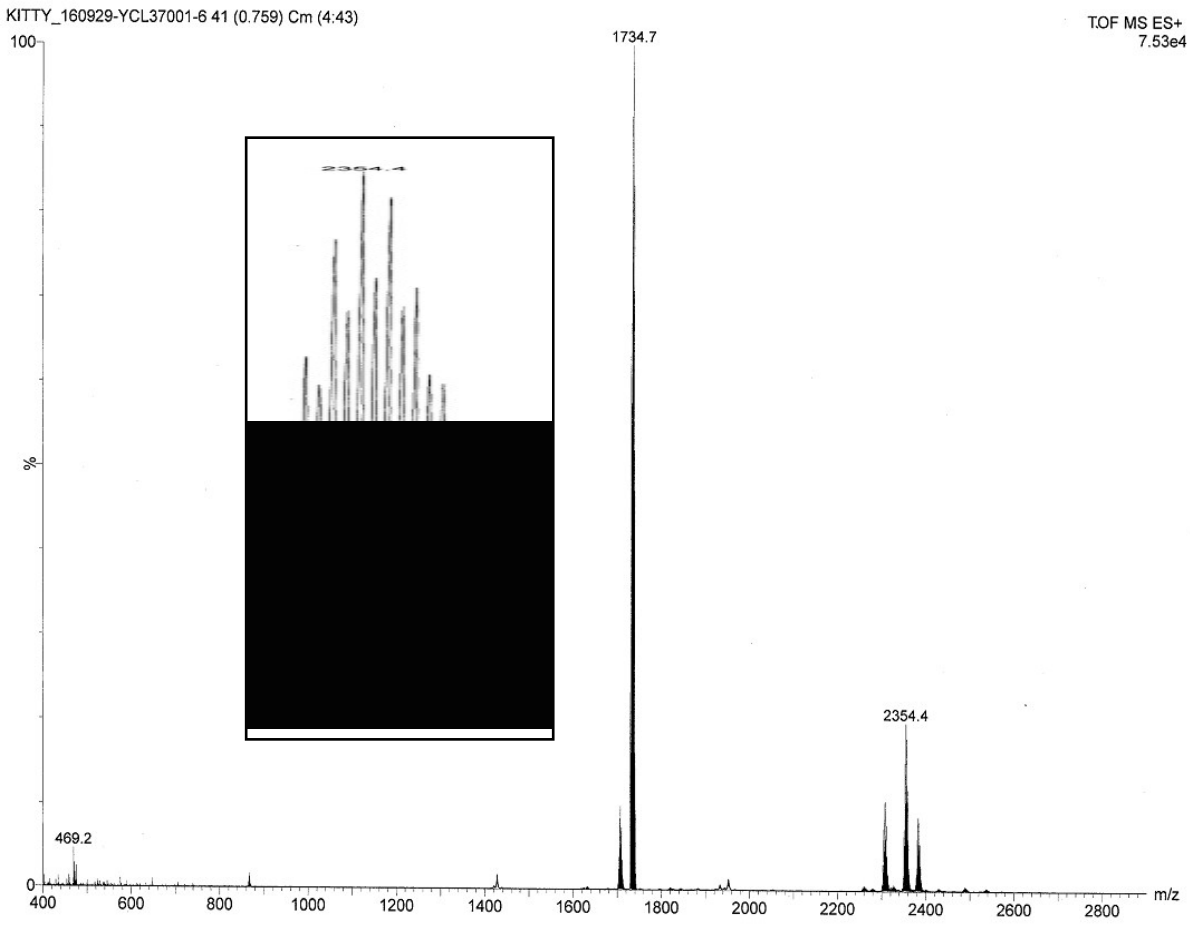

Figure S8. ESI-MS spectrum of **3a**, the inset shows experimental one in top and theoretical one in bottom.

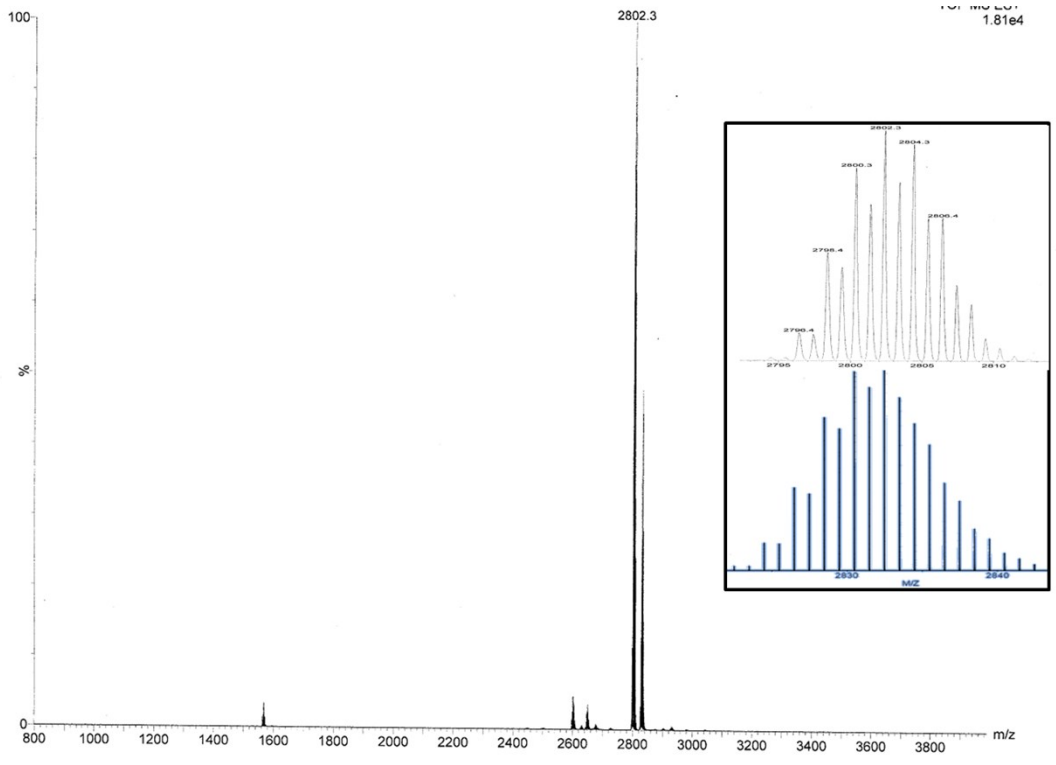

Figure S9. ESI-MS spectrum of **3d**, the inset shows experimental one in top and theoretical one in bottom.

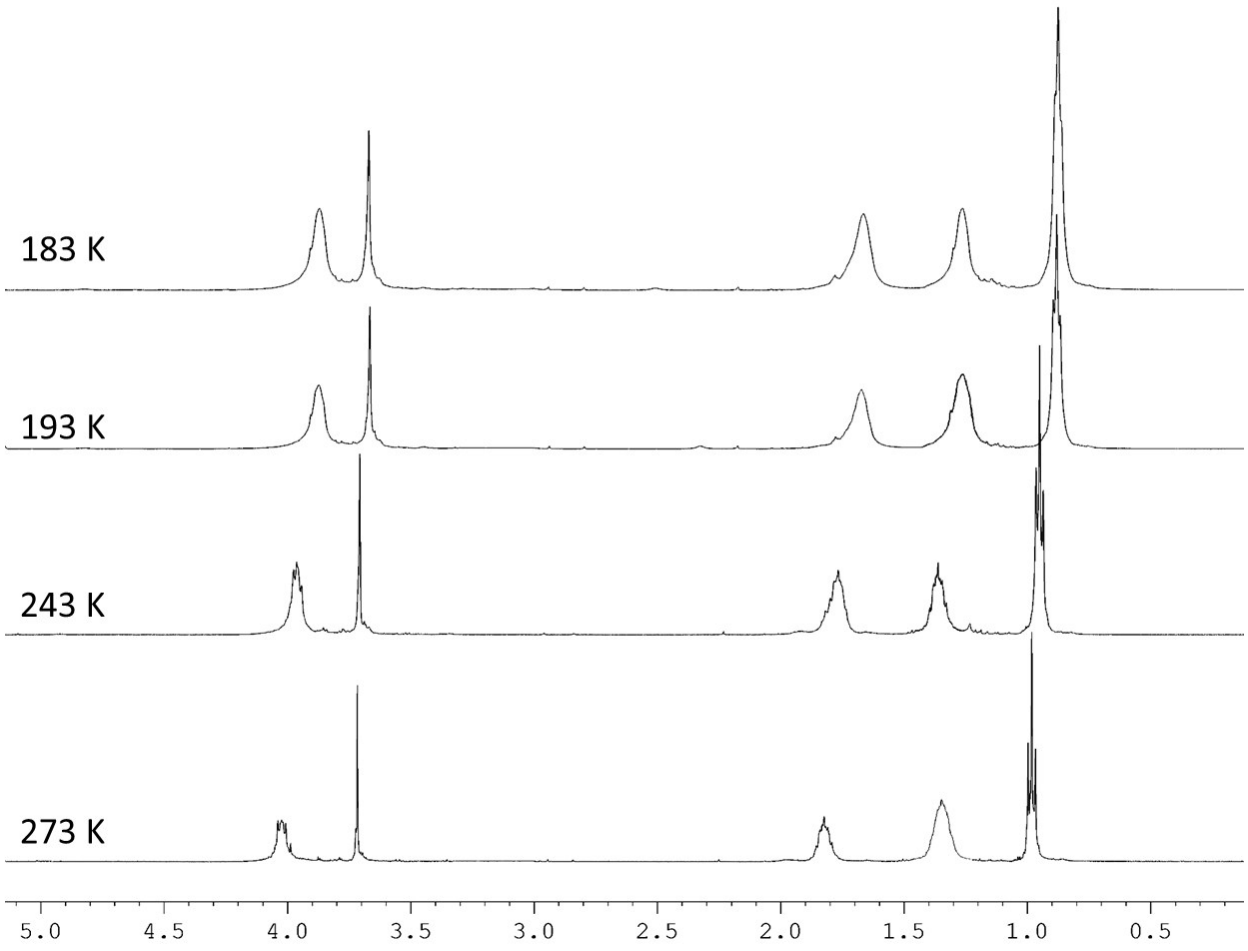

Figure S10. Variable temperature ^{1}H NMR spectrum of **2a** in CD_2Cl_2 solvent.

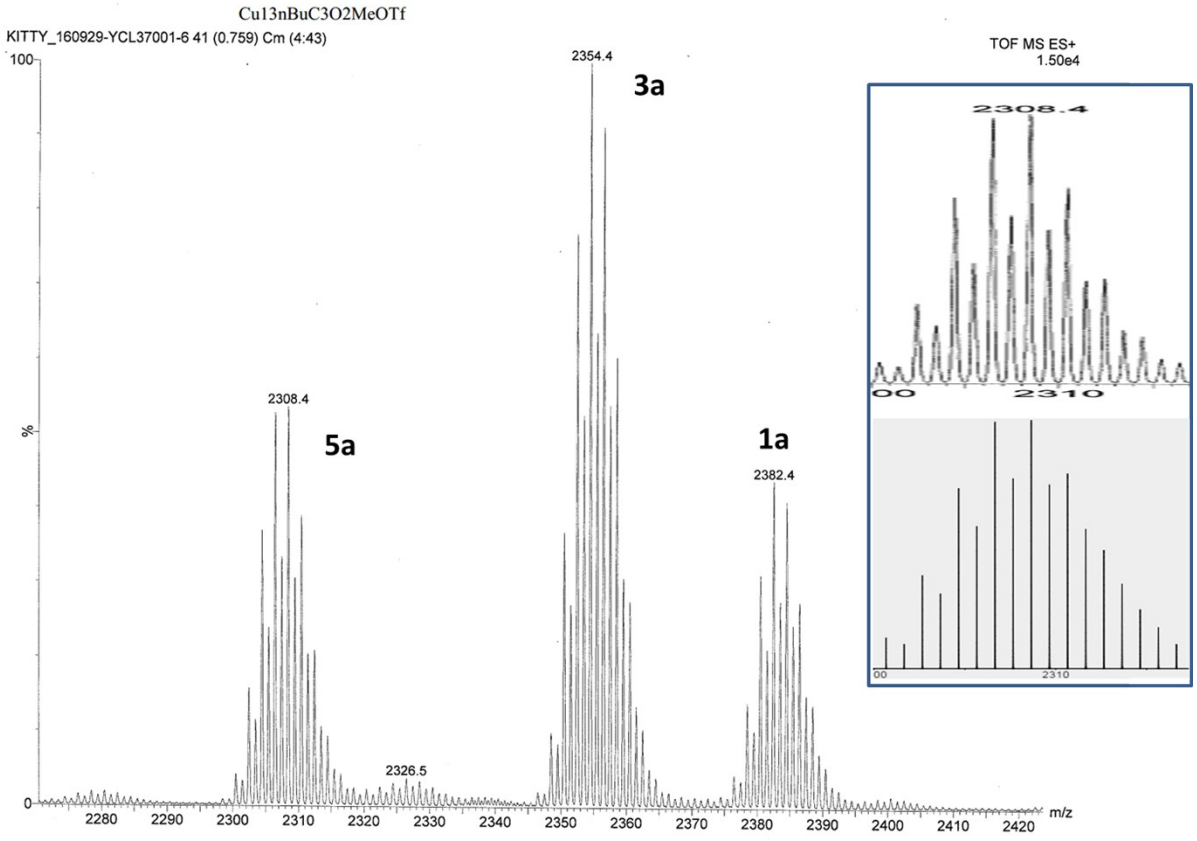

Figure S11. ESI-MS spectrum of **5a**, the inset shows experimental one in top and theoretical one in bottom.

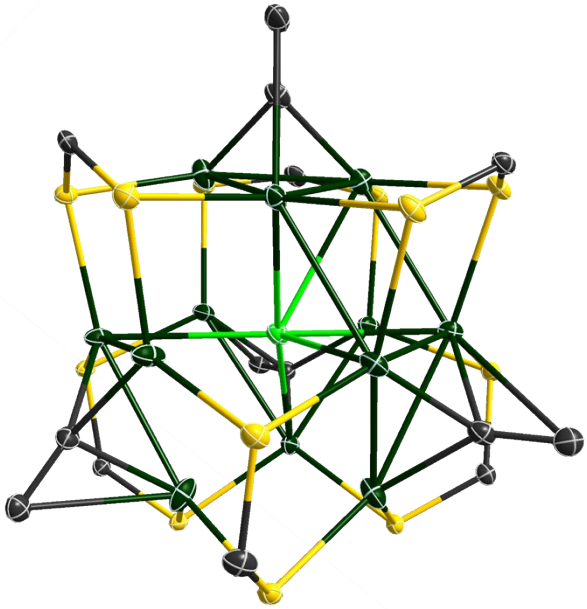

Figure S12. Structure of the cluster cation **3d** with 30% thermal probability ellipsoids. All N^nPr_2 and 3,5-$(CF_3)_2C_6H_3$ groups are omitted for clarity; Carbon gray, copper dark green, sulfur yellow, chlorine green.

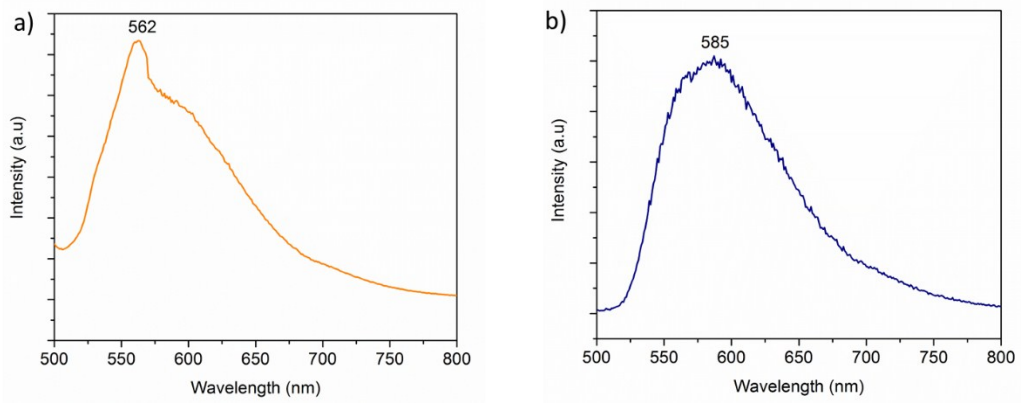

Figure S13. Emission spectra of sulphur-centred (a) and chlorine centred (b) **2a** and **3a** respectively in chloroform. (in SI)

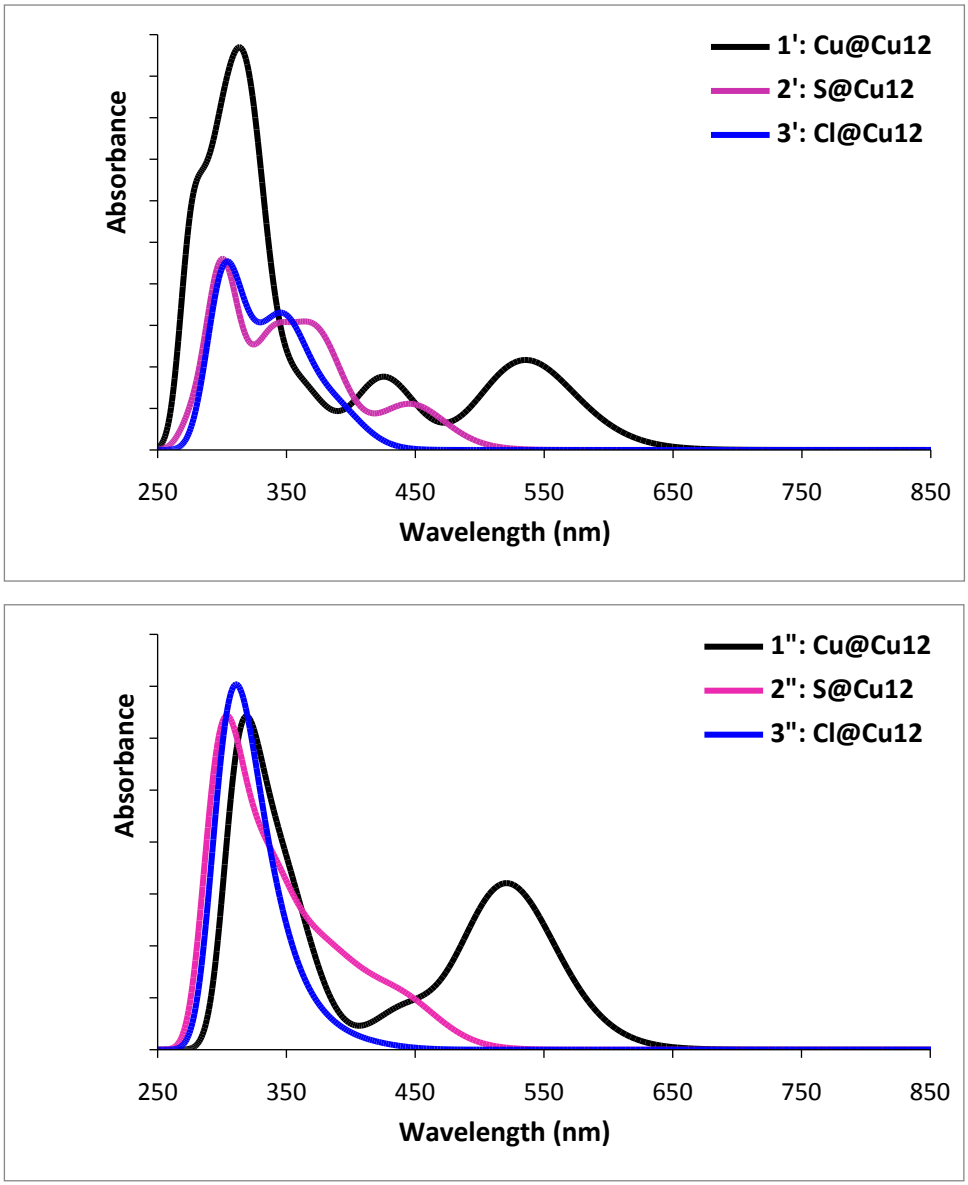

Figure S14. TDDFT-simulated spectra of **1'-3'** (top) and **1"-3"** (bottom).