Bonding in tetrahedral Cu4(?3-X)4L 4 Copper(I) clusters: A DFT investigation

Vega, Andrés

Saillard, Jean Yves

DFT calculations on Cu4(?3-X)4L 4 (X = H, CH3, CCH, F, Cl, Br, I; L = NH3, PH3) indicate that, regardless of its nature, X- acts essentially as a two-electron ?-type ligand and that the covalent part of the Cu?Cu bonding depends mainly upon the a1 component of the orbital interaction between the L4Cu44+ and X44- fragments. The first excited state corresponds to the occupation of a Cu?Cu bonding LUMO of a1 symmetry, which is of dominant Cu(4s/4p) character when X- is an electronegative ligand, such as a halide. Consequently, this excited state is computed to exhibit Cu?Cu distances shorter than those in the ground state, in agreement with the luminescence properties of this type of compound.