Few atom clusters at the origin of luminescence in Ag-LTA zeolites unraveled by a combination of XEOL and transmission-detected EXAFS assisted by DFT modeling

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Oligoatomic silver (Ag_n, n<10) nanoclusters featuring molecule-like optical transitions with absorption bands and bright luminescence emission offer great potential as ultrabright fluorescent and Raman-active labels.[1] We have showed that series of very luminescent with quantum yields close to unity[2] and highly homogeneous emissive species fingerprinted by their specific 2D excitation-emission plots could be generated in silver exchanged zeolites by heat treatment[3] and more recently by X-ray irradiation.[4] However, to date, no clear and definitive structure of the emitting species has been proposed.

We have used for the first time X-ray excited optical luminescence (XEOL) detected EXAFS at the Ag K-edge measured simultaneously with the conventional transmission detected EXAFS to unravel the exact structure of the silver oligomeric clusters at the origin of the bright green luminescence observed in partially Ag-exchanged LTA zeolites. The obtained structural and optical information has been used as a guide to perform a full (TD)DFT modeling of the clusters. They consist of a mixture of tetrahedral $Ag_4(H_2O)_x$ (x=2 & 4) species occupying the sodalite cages. The calculated frontier orbitals consist of a mixture of Ag s and d orbitals with a significant contribution from the cluster oxygen ligands states.

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