LUMINESCENT SILVER CLUSTERS STABILIZED BY DNA OLIGOMER (5'-CCTCCTTCCTCC-3'): INVESTIGATIONS BY USE OF QM/MM APPROACH

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Fluorescent metal clusters have been extensively studied during the past years. For example, DNA-stabilized Ag clusters, exhibiting excellent brightness and photostability, are considered as a new promising type of emitters for various applications in photonic devices, bioassays, chemical sensors, biosensors. Despite the huge progress made over the past years in synthetic development of silver-based fluorescent clusters, an understanding of the structural origins of their emission properties tuning by modifications in DNA sequences remains elusive. Combined with quantum chemical (QM)/molecular mechanical (MM) calculations seem to be an unambiguous tool for identification of the structure of the fluorescent sites in Ag-DNA complexes.

In present work a palindrome 12-mer DNA sequence 5'-CCTCCTTCCTCC-3' was used as a template for Ag cluster formation and theoretical investigations. Comparison of experimental luminescent excitation spectra and preliminary calculated excitation spectra of different QM optimized isolated clusters and cytosine-cluster complexes consisting up to 3 silver atoms showed that fluorescent silver clusters included two silver atoms. On the basis of available experimental data and preliminary QM calculations we obtained an equilibrium structure of DNA-cluster complexes consisting of two silver atoms in fluorescent site and two DNA strands bound via cytosine-Ag^{+}-cytosine bonds by utilizing QM/MM approach realized in CP2K program. A reasonable agreement of the calculated electronic spectrum of the complex by the second order algebraic-diagrammatic construction scheme (ADC(2)) with the experimental fluorescence excitation spectrum supports the model of the fluorescent DNA-cluster complex. The proposed approach can be further used for determining the structure of other ligand-stabilized fluorescent metal clusters.