LANTMOD: Quantum Chemical modeling of photophysical properties of Ln(III)-complexes with organic chromophores

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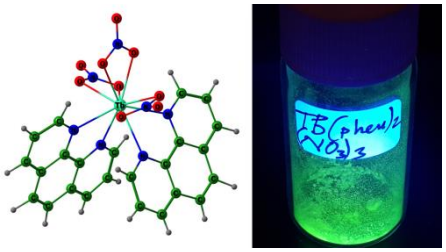

Figure 1: Tb(III) complex – molecular model (left) and luminescence (right).

❖ Description of the problem

The design of lanthanide complexes with antenna-chromophores, with application for luminescent devices, includes selection of new photo-organic systems that have a high molar absorption coefficient and efficient energy transfer in the excited state on the central lanthanide ion. With the help of a theoretical approach, combining quantum chemical calculations, empirical and Judd-Ofelt and Malta models, efficient Ln(III)-based optical materials are developed with a view to achieving a stable structure with high luminescent quantum yield. The geometry optimization and simulation of the absorption and emission spectra are performed with DFT/TDDFT methods, and to assess the strength of spin-orbit coupling in the complexes, multi-reference ab initio methods are applied. The theoretical study is carried out in close relation with experimental measurements. The software packages Gaussian16-RevC.01 [1] and ORCA4.1.2 [2] are used for the calculation protocol. The tasks have been elaborated by a team from the Laboratory of Theoretical and Computational Chemistry at IGIC-BAS, in cooperation with a team from the Faculty of Chemistry and Pharmacy at Sofia University 'St. Kliment Ohridski'.

Use of HPC Infrastructure

The calculations were performed on the Avitohol supercomputer. It is located in the HPC center of IICT-BAS [3] and it is maintained by the National Center for High-Performance and Distributed Computing (NCHDC), subject to the National Roadmap for Research Infrastructures (NRRI) [4].The results were obtained using up to 10 HP Cluster Platform SL250S GEN8 servers, each with 2 Intel Xeon E2650 v2 CPUs and 2 Intel Xeon Phi 7120P coprocessors.

❖ Results and Future Work

The average time needed for the computations is 5-7 days. Unfortunately, Gaussian and ORCA do not allow parallelization on more than 1 computing node. The following results were obtained:

- A prediction of the energy diagrams and the paths of electronic relaxation after excitation by UV-light.
- A qualitative description of the energy transfer process in the examined systems. An establishment of the factors responsible for achieving high luminescent quantum yield.

The obtained results have been reported in 2 publications [5,6].

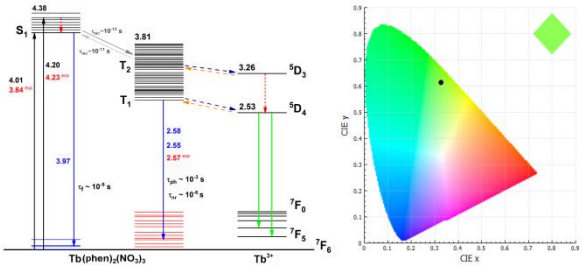

Figure 2: Jablonski diagram (left) and chromaticity diagram(right).

The described computational strategy is currently expanded towards complexes of Ln(III) with phosphine-oxide and dithiocarbamate-based chromophores.

1. http://gaussian.com/
2. https://orcaforum.kofo.mpg.de/app.php/portal
3. http://www.iict.bas.bg/avitohol/
4. http://nchdc.acad.bg/
5. Georgieva et. al. *Spectrochimica Acta A* 2020, 240, 118591.
6. Zahariev et.al. *Dyes and Pigments* 2021, 185, 108890.