Describing the Antenna-Effect in Eu Complexes with TD-DFT

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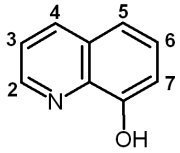
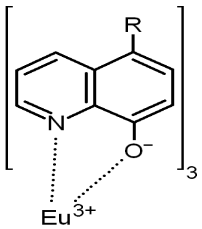
The special interest on finding stable emitting compounds which cover the whole region of the electromagnetic spectrum focuses on lanthanide complexes, e.g. composed of central Eu(III) ion and organic quinolinate-ligands, $Eu(Q)_3$.
Energy transfer occurs via the so called "antenna-effect", where the ligand system is excited and transfers the energy via ISC to the triplet state of the ligand followed by an energy transfer to the 4f electrons of the Eu ion [1]. Emission occurs only via 4f electron transition from the $^5D_0$ state of Eu(III) to the $^7F_2$ state with an energy of ~2.023eV.

The main goal of the present study is the tuning of the singlet-triplet energy transfer in $Eu(Q)_3$ complexes by using different electron donating and accepting substituents in different positions at the ligand.



A series of 8-hydroxyquinolinoline molecules with different substituents in 5-position (-OMe, -H, -CHO, $-HSO_3$, -Py, -CN, $-NH_2$, $-NO_2$, -Ph) and with the substituents $–NH_2$, $-NO_2$, -Ph, $-SO_3$ and –Py in the remaining positions were calculated (Fig. 1).



For three substituents ($-HSO_3$, $-NH_2$ as electron donor and $-NO_2$ as electron acceptor) and the unsubstituted quinoline ligand, the Eu complexes were calculated and the different absorption energies were compared (Fig.2). Solvent studies with a continuum model and with explicit solvent molecules were done for EtOH and CH_2Cl_2, respectively. The photophysics of the singlet and triplet states is discussed and all results were compared with available experimental data [2-4].

Density Functional Theory (TD-B3LYP) was used for the investigation of the photophysics and the singlet and triplet state of both, the ligands and the complexes. Based on the knowledge, that the 4 f electrons do not participate in the ligand to Eu bonding, Eu is described by ECP's including the 4f electrons in the core [5]. The triple-zeta-basis set TZVP was used for the ligand system. Relativistic effects are accounted for via the relativistic ECP's and by ZORA calculations.

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